NRC·CNRC

NRC.CANADA.CA

PHASE IDENTIFICATION

The 15th Canadian Powder Diffraction Workshop

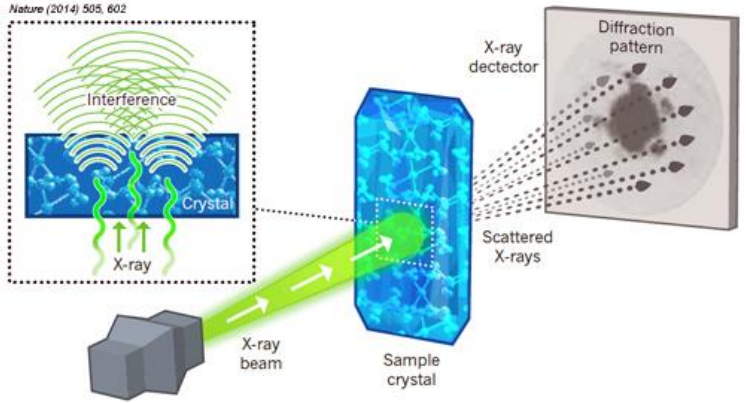
Bussaraporn Patarachao

National Research Council Canada

Phase Identification

Phase identification is the most important application of X-ray Diffraction

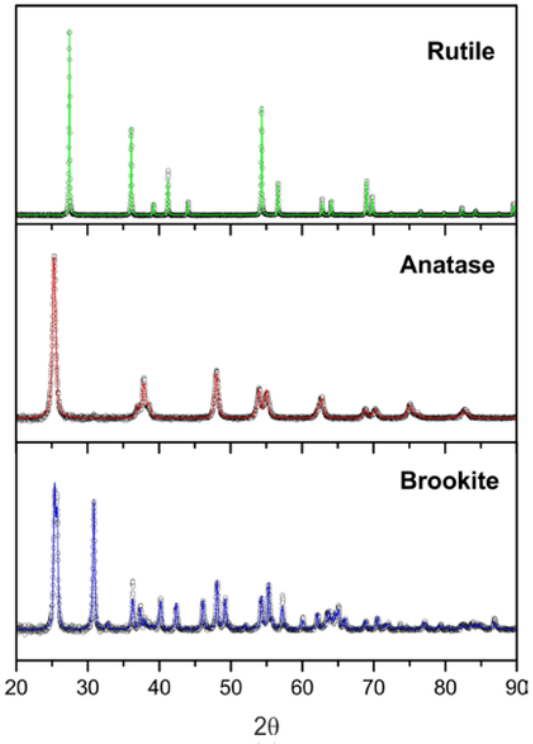
- XRD is mostly sensitive to structural differences
- It can quickly distinguish between crystalline phases of a variety of materials
- Each unique crystal structure generates a ‘fingerprint’ pattern of scattered X-ray beam (diffraction peak positions and intensities)
- The ‘fingerprint’ allows for identification of material



Phase identification must be done before Rietveld Refinement

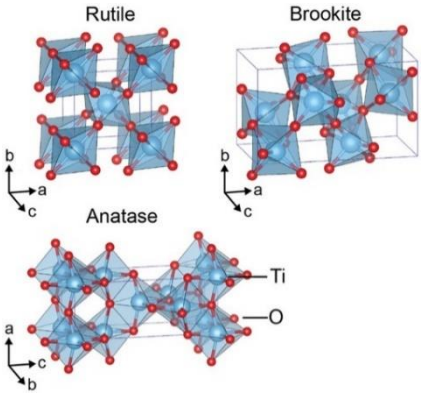
Polymorphs

- Polymorphs are phases with the same chemical composition but have different crystal structures
- XRD can easily distinguish and identify polymorphs
- Polymorphism identification is an important task for many applications, especially for pharmaceutical industry



Monai. M. et-al, (2017) Catalysts 7(10):304

Crystal structures of TiO_2

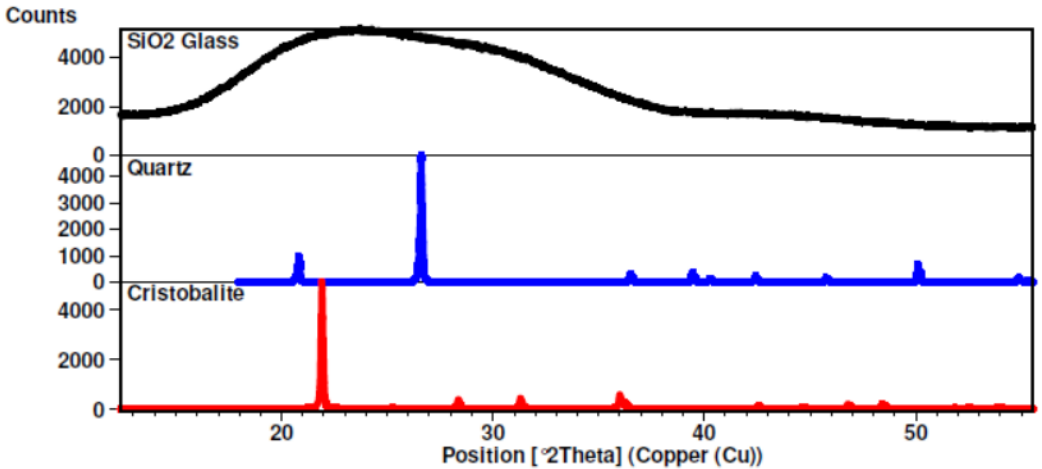


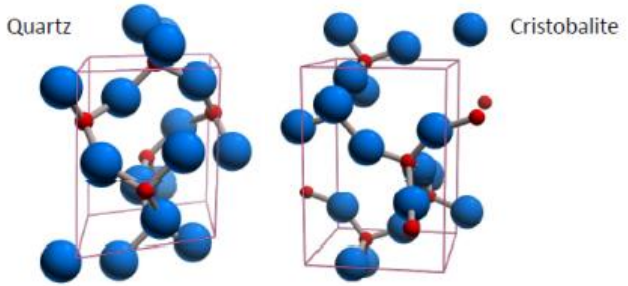
Rutile (tetragonal, P42/mmm)
Brookite (orthorhombic, Pbca)
Anatase (tetragonal, I41/amd)

Haggerty J. E. S. et-al, Scientific reports (2017):15232

Polymorphs

Three phases of SiO_2 are chemically equivalent



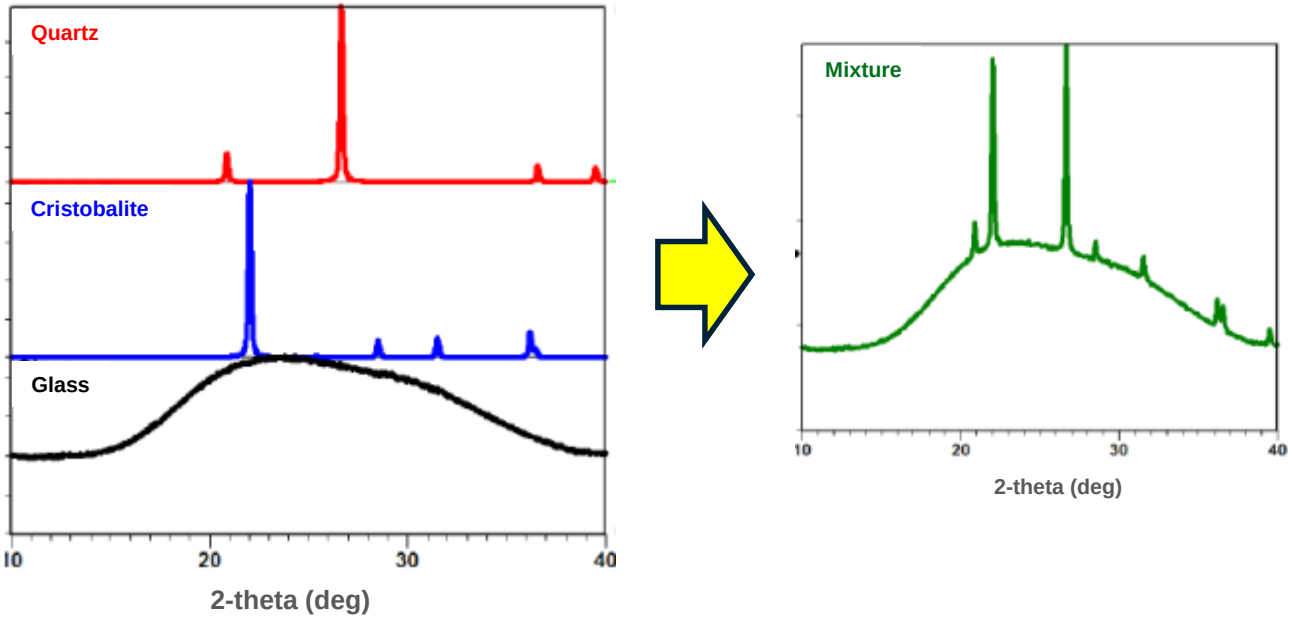


Quartz and Christobalite are crystalline and have long-range atomic structure but have different arrangement of Si and O atom. They produce sharp peaks with different XRD patterns

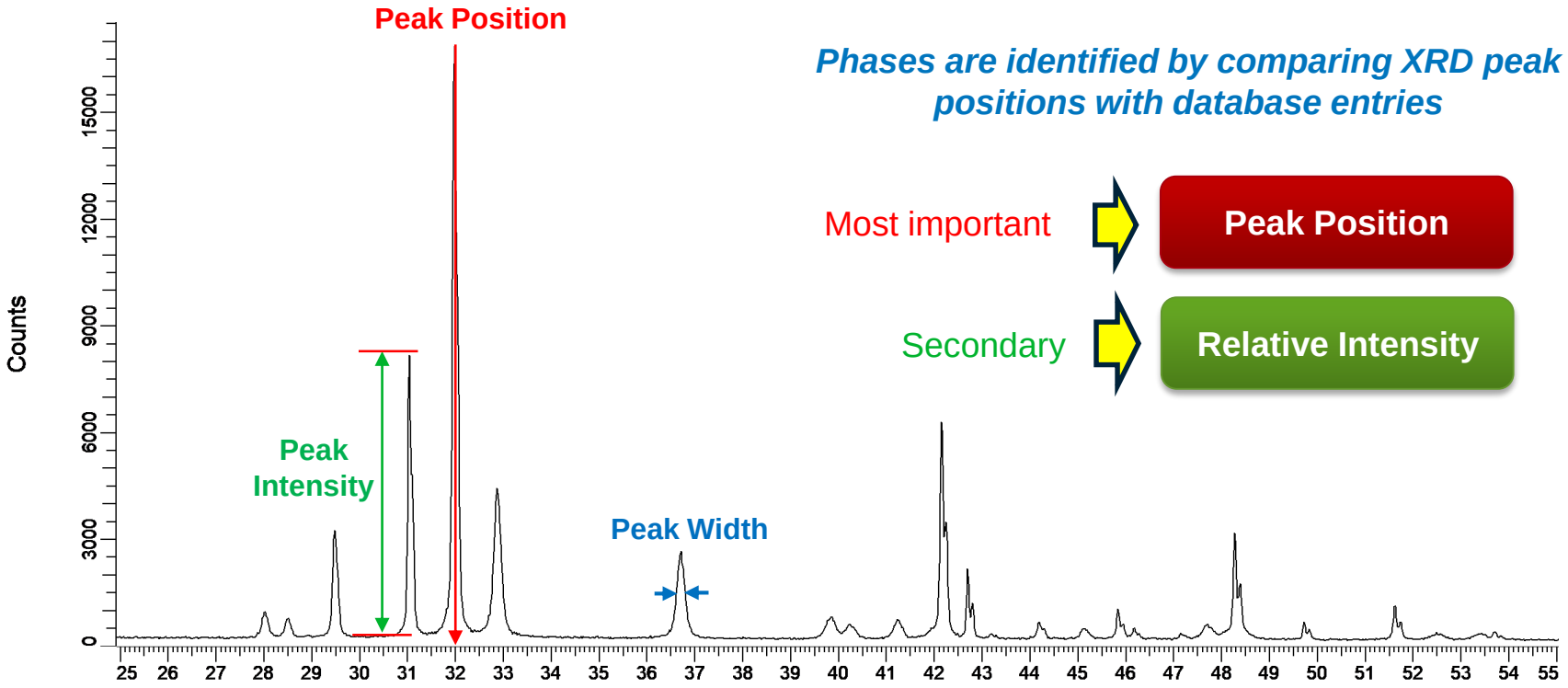
SiO_2 glass is amorphous → No long-range atomic order → Produces only broad peaks

Phase composition of a sample

The diffraction pattern of a mixture is the sum of the scattering from each component phase



What matters for phase identification?



Phases are identified by comparing XRD peak positions with database entries

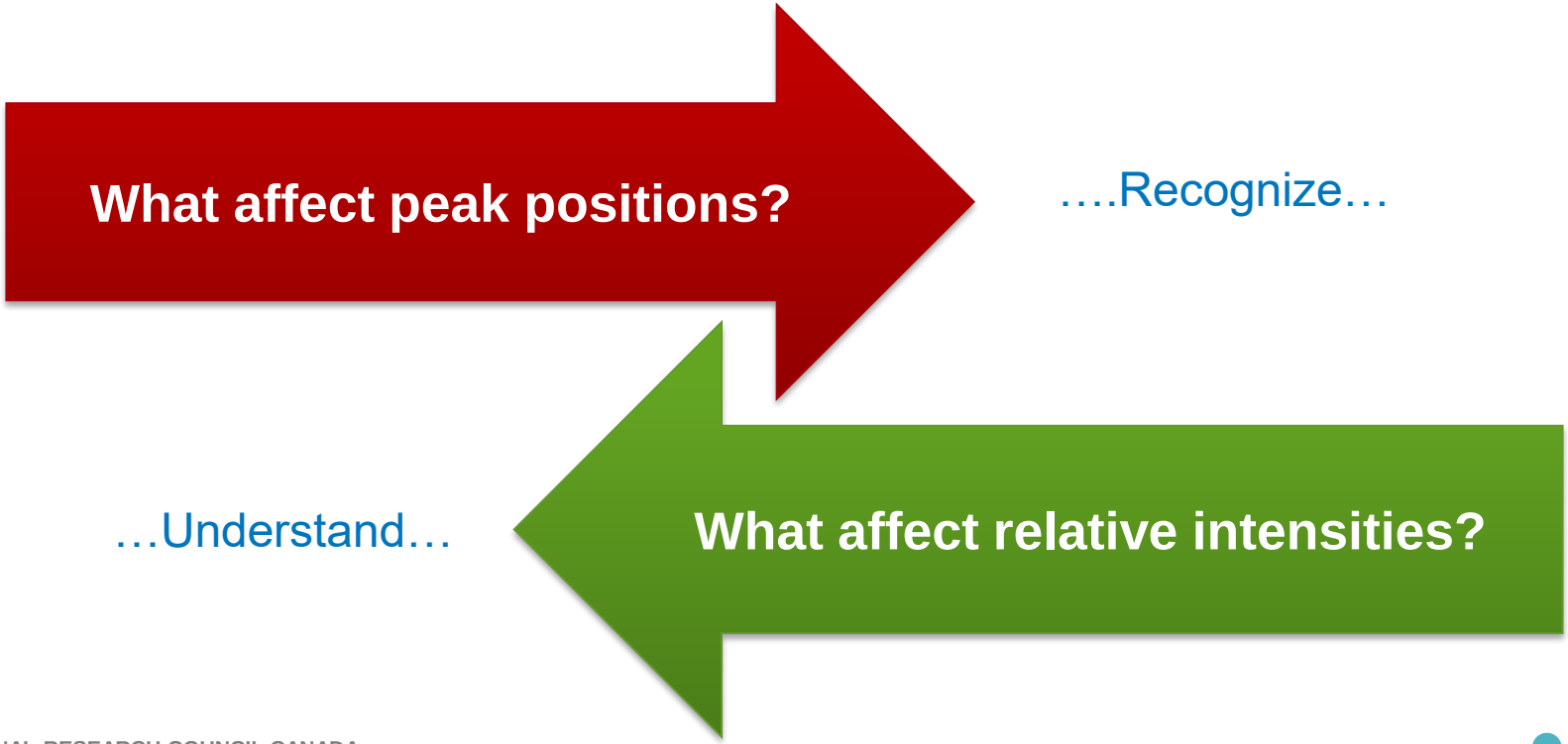
Most important → **Peak Position**

Secondary → **Relative Intensity**

SOURCES OF ERROR

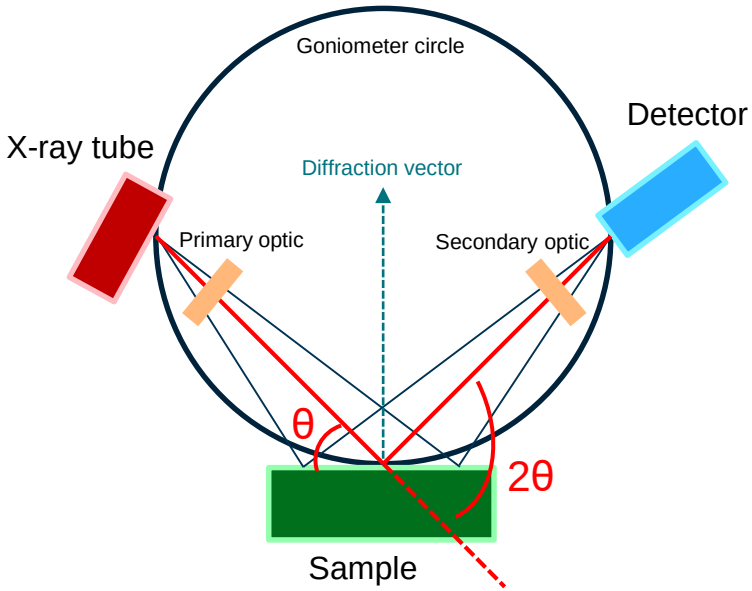
XRD Phase Identification

Sources of error



Focusing circle of Bragg-Brentano geometry

Bragg-Brentano geometry is used in most of powder x-ray diffractometers



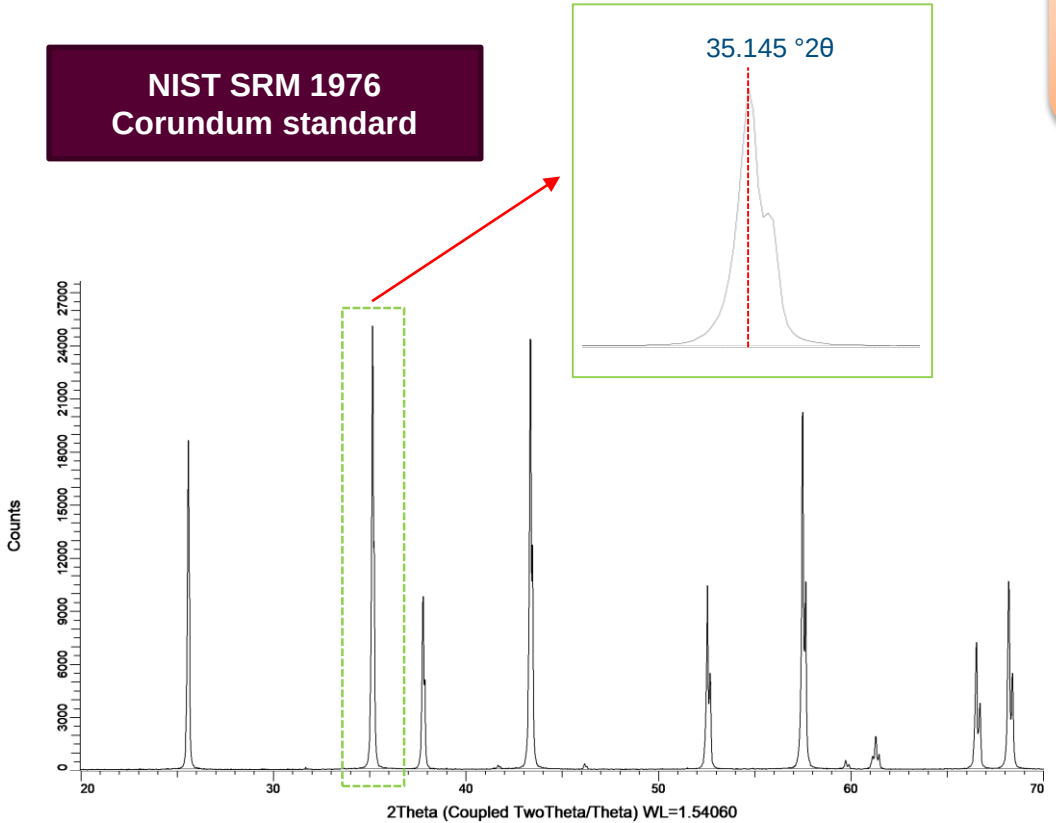
The diffracted x-ray beam converges at the focal point of the detector producing sharp, well-defined diffraction peaks

If the source (x-ray tube), sample and detector are not aligned on the focusing circle, the diffracted x-ray beam will not converge a the correct position of the detector causing error to appear in the data

Peak position error are often associated with focusing circle of Bragg-Brentano geometry

Zero point error

NIST SRM 1976
Corundum standard



System misalignment error

Check with NIST SRM 1976

Accuracy of each peak position ≤ ±0.01° 2θ

Reflection (hkl)	Peak Position (2θ)	Relative Intensity
(012)	25.575	23.62
(104)	**35.148**	**100.00**
(110)	37.776	
(006)	41.673	
(113)	43.352	37.16
(024)	52.549	20.68
(116)	57.495	87.83
(018)	61.297	
(214)	66.515	
(300)	68.207	12.43

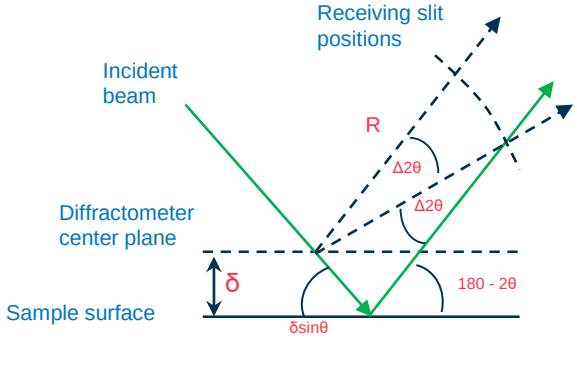
Certified Reference Values

Sample displacement error

Is the sample too high or too low compared to the diffractometer center plane?

Sample is too high (positive displacement) → **Peak shift to higher angles (right)**

Sample is too low (negative displacement) → **Peak shift to lower angles (left)**



$$\Delta 2\theta_{deg} = -\frac{2 \times \left(180/\pi\right) \times \cos(\theta) \times \delta}{R}$$

Can be minimized by using zero background holder

Not an issue with parallel beam system

0.1mm error will shift peaks approx. 0.045°

Sample transparency error

If the X-ray penetrate a long way into the sample can get a ‘sample displacement’ even if the height is perfect

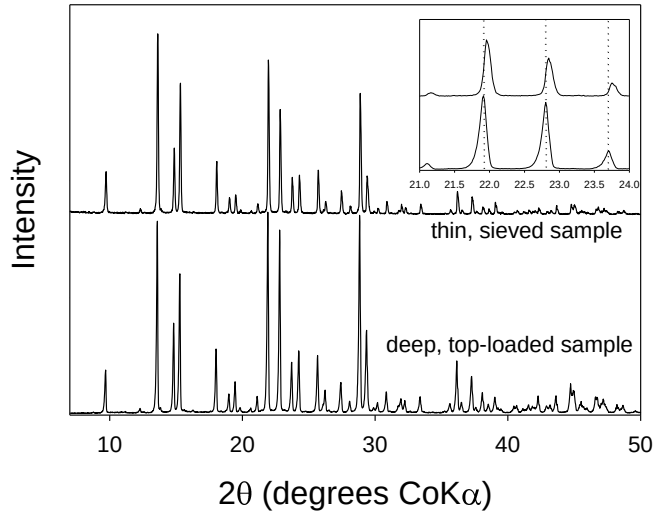
Depth of penetration depends on the mass absorption coefficient of the sample and the incident angle of the x-ray beam

Not all x-rays are diffracting from the same location in the sample causing peak position errors and peak asymmetry

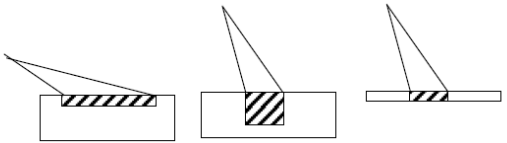
More problematic in organic and low absorbing (low atomic number) samples

Can be minimized by using a thin sample

Also not an issue with parallel beam system



Diffraction patterns from powdered sucrose as both deep and thin samples



Relative intensities - Sources of error

- Particle statistics (grain size)
- Preferential orientation
- Crystal structure
- Microabsorption (multiphase samples)

DATABASE AND SOFTWARE

XRD Phase Identification

Database

- Collection of powder diffraction data (Crystallographic Information Files)
- Provides insight into the structural and crystallographic properties of a material
- Allows for phase identification using powder diffraction techniques

Database

Commercial

Powder Diffraction file (PDF) Database

Produced and maintained by International Centre for Diffraction Data (ICDD)

Open access

Crystallography Open Database (COD)

All data have been placed in the public domain by the contributors

Powder Diffraction File (PDF) database

PDF is produced in several different formats in order to serve different groups of users

PDF-4+

480,300+ entries

Inorganic materials

Requires yearly renewal

PDF-4/Minerals

50,000+ entries

Minerals

Subset of PDF-4+

PDF-4/Organics

608,700+ entries

Organics

Commercial and regulatory fields

PDF-2

339,500+ entries

Inorganic materials

Licensed for 5 years

Common organic materials

PDF card

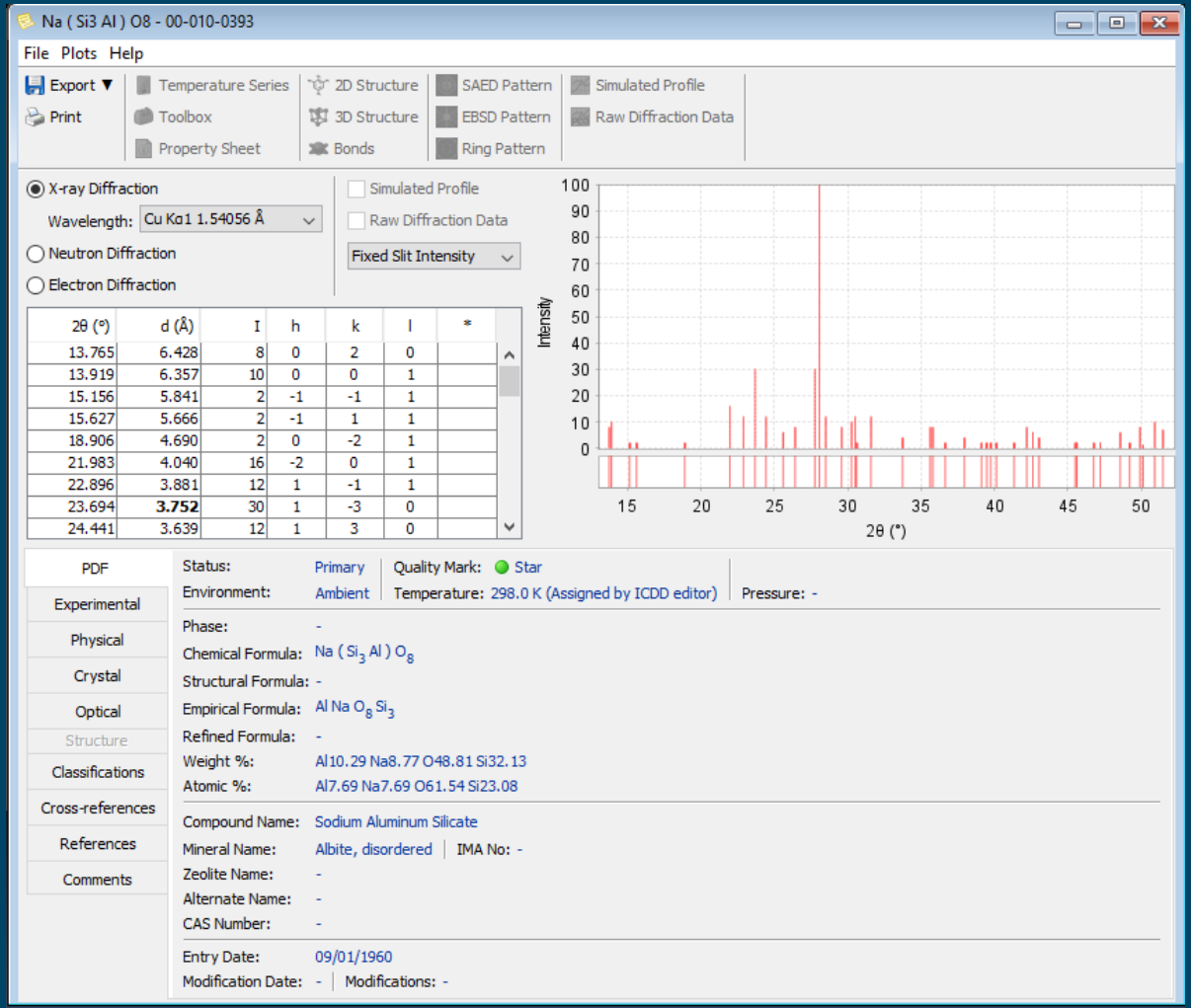
PDF card for an entry contains a lot of useful crystallographic information, including literature references

"The Powder Diffraction File: a quality materials characterization database"

Crystallography Education Article
Published online by Cambridge University Press

Stacy Gates-Rector and Thomas Blanton (ICDD)

Powder Diffraction, 34 (4), December 2019



Crystallography Open Database (COD)

Open-access collection of crystal structures of organic, inorganic, metal-organic compounds and minerals, excluding biopolymers

https://www.crystallography.net/cod.html

Registered users are able to contribute published and unpublished structures of small molecules and small to medium sized unit cell crystals to the database

Contains Crystallographic Information Files as defined by International Union of Crystallography (IUCr)

493183 entries as of 2022-10-01

Software

Software for XRD phase identification

HighScore	Diffrac.Eva	PDXL	Sleve	Match!	Jade	+
Malvern Panalytical	Bruker-Axs LLC	Rigaku	ICDD	Crystal Impact	MDI	Many
PDF-2/4 COD	PDF-2/4 COD	PDF-2 COD	PDF-2/4	PDF-2/4	PDF-2/4	More

SEARCH/MATCH

XRD Phase Identification

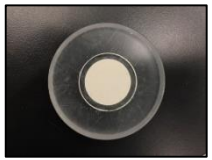
Search/Match – General process

- Search/Match function is available in all software
- Use the measured data directly
- If the background is high, background subtraction recommended before search-match
- Striping $K\alpha_2$ peaks and smooth raw data are optional
- Perform automatic and/or manual search for peaks using database
- Check the results by comparing them with your XRD pattern (best matches are listed first)
- Select one or several of top raking results that match your data

Search/Match – Example

Geological sample (Athabasca oil sands mine site)

Particle size reduction (Micronizing mill)



Random powder mount
Zero background holder

Bruker D8 Advance XRD set up in Bragg Brentano geometry (theta-theta), configured with a Cobalt (Co) X-ray tube and a Position Sensitive Detector (VÅNTEC-1)

2-theta: 10 – 70
Step size: 0.02
Scan speed: 1s/step

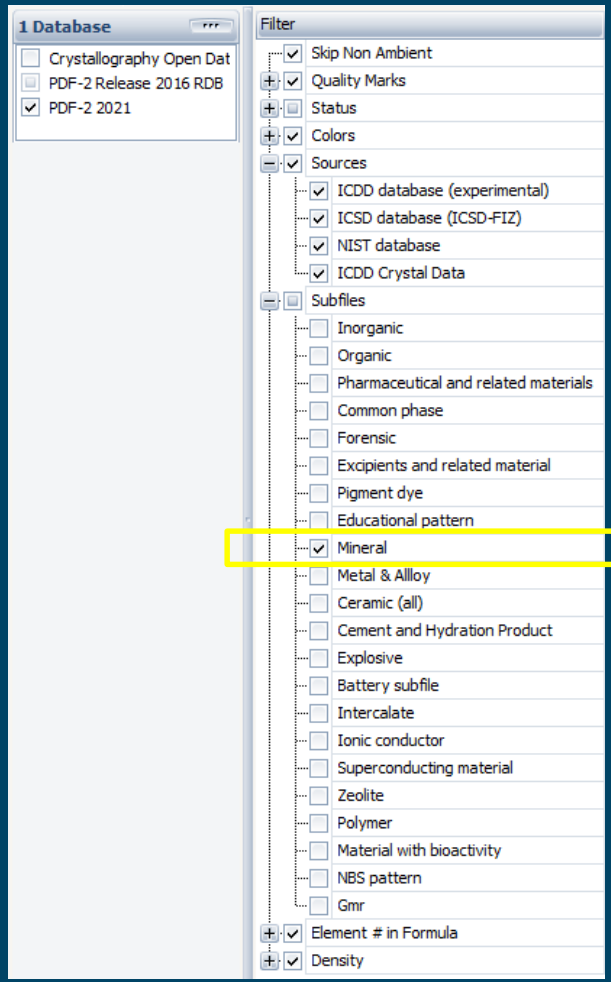
DIFFRAC.Eva V4.1.1 software
Bruker AXS LLC.

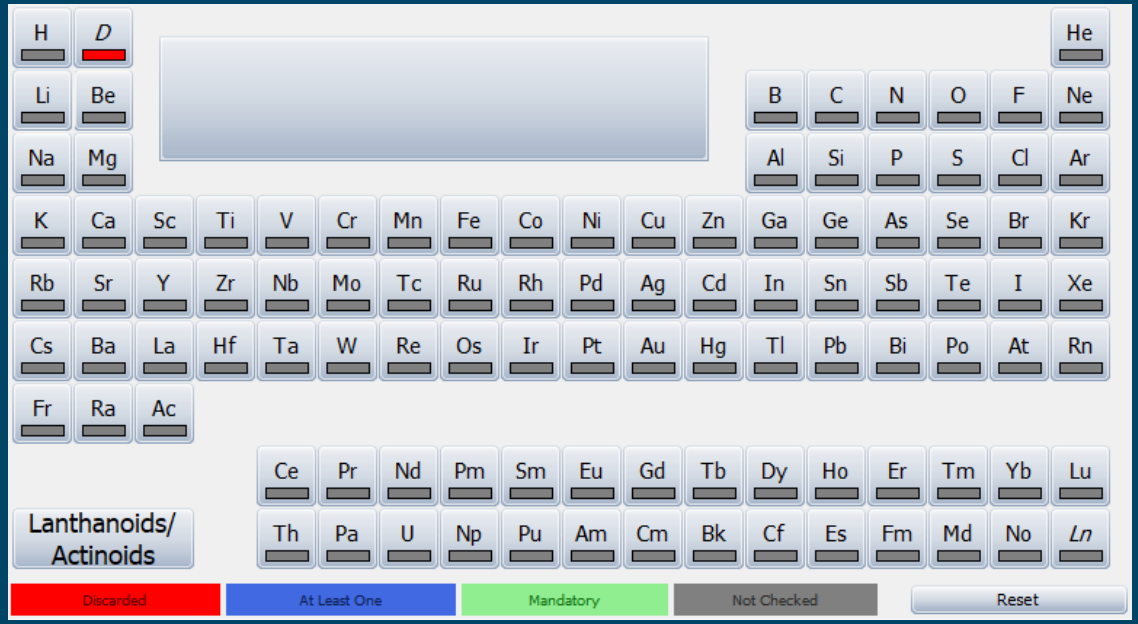
PDF-2 database

Search/Match - Limiting the results

Before perform a search, it's always a good idea to limit the results by filtering database categories and/or chemical information

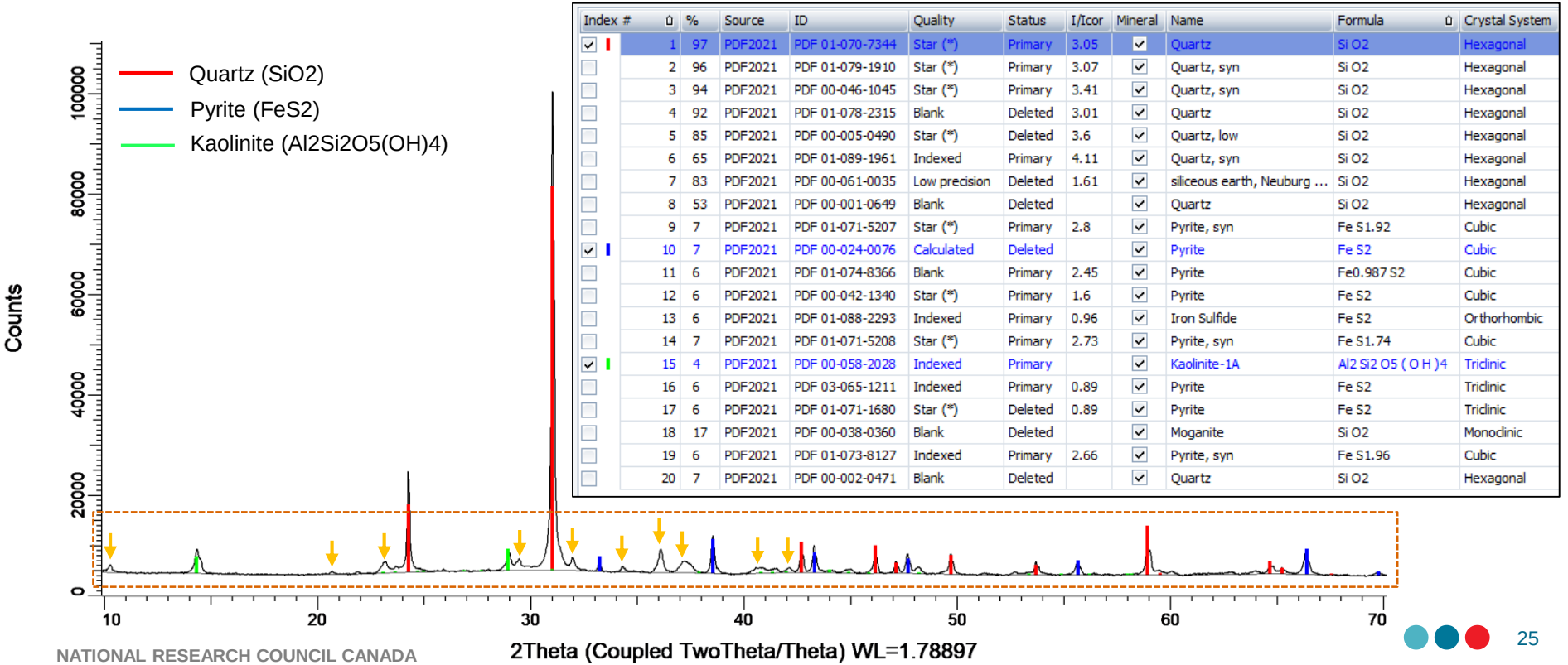
Note that there is no subfiles in COD database





Search/Match – Automatic

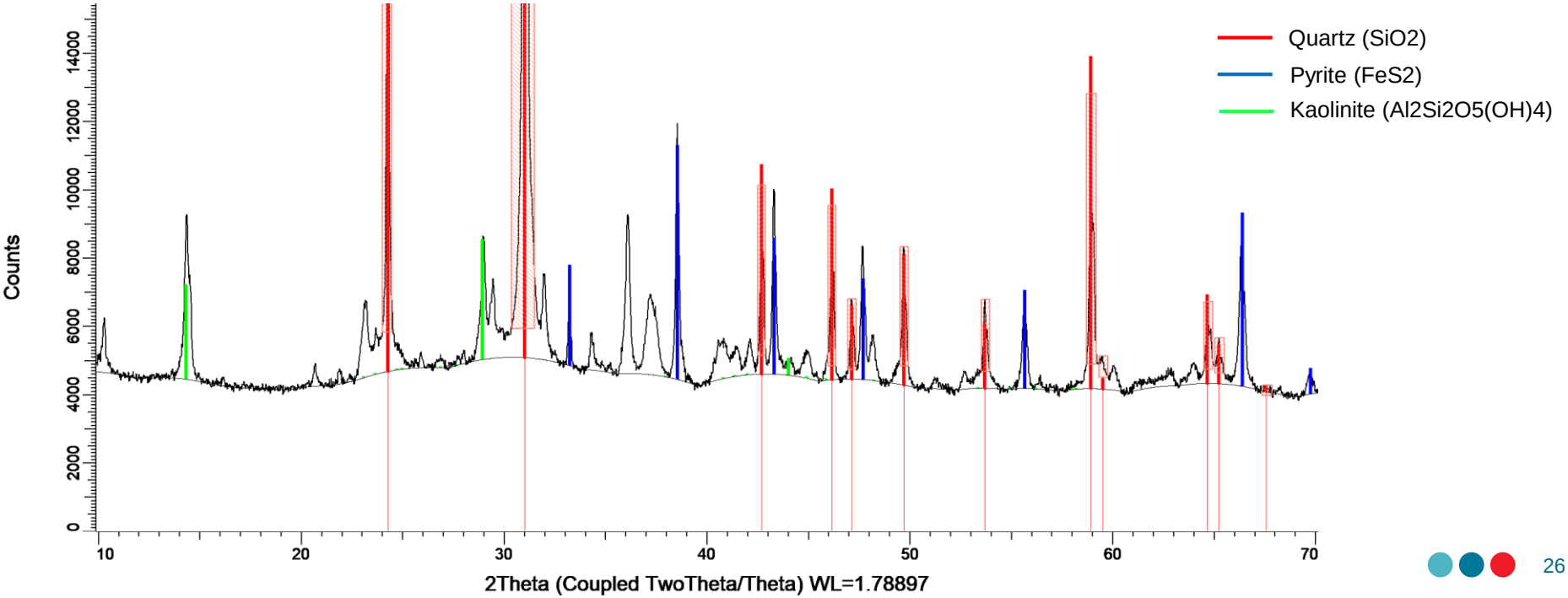
Matched 9332/25163 candidates in 7.7 seconds!



Index #	%	Source	ID	Quality	Status	I/Icor	Mineral	Name	Formula	Crystal System
1	97	PDF2021	PDF 01-070-7344	Star (*)	Primary	3.05	☑	Quartz	Si O2	Hexagonal
2	96	PDF2021	PDF 01-079-1910	Star (*)	Primary	3.07	☑	Quartz, syn	Si O2	Hexagonal
3	94	PDF2021	PDF 00-046-1045	Star (*)	Primary	3.41	☑	Quartz, syn	Si O2	Hexagonal
4	92	PDF2021	PDF 01-078-2315	Blank	Deleted	3.01	☑	Quartz	Si O2	Hexagonal
5	85	PDF2021	PDF 00-005-0490	Star (*)	Deleted	3.6	☑	Quartz, low	Si O2	Hexagonal
6	65	PDF2021	PDF 01-089-1961	Indexed	Primary	4.11	☑	Quartz, syn	Si O2	Hexagonal
7	83	PDF2021	PDF 00-061-0035	Low precision	Deleted	1.61	☑	siliceous earth, Neuburg ...	Si O2	Hexagonal
8	53	PDF2021	PDF 00-001-0649	Blank	Deleted		☑	Quartz	Si O2	Hexagonal
9	7	PDF2021	PDF 01-071-5207	Star (*)	Primary	2.8	☑	Pyrite, syn	Fe S1.92	Cubic
10	7	PDF2021	PDF 00-024-0076	Calculated	Deleted		☑	Pyrite	Fe S2	Cubic
11	6	PDF2021	PDF 01-074-8366	Blank	Primary	2.45	☑	Pyrite	Fe0.987 S2	Cubic
12	6	PDF2021	PDF 00-042-1340	Star (*)	Primary	1.6	☑	Pyrite	Fe S2	Cubic
13	6	PDF2021	PDF 01-088-2293	Indexed	Primary	0.96	☑	Iron Sulfide	Fe S2	Orthorhombic
14	7	PDF2021	PDF 01-071-5208	Star (*)	Primary	2.73	☑	Pyrite, syn	Fe S1.74	Cubic
15	4	PDF2021	PDF 00-058-2028	Indexed	Primary		☑	Kaolinite-1A	Al2 Si2 O5 (O H)4	Triclinic
16	6	PDF2021	PDF 03-065-1211	Indexed	Primary	0.89	☑	Pyrite	Fe S2	Triclinic
17	6	PDF2021	PDF 01-071-1680	Star (*)	Deleted	0.89	☑	Pyrite	Fe S2	Triclinic
18	17	PDF2021	PDF 00-038-0360	Blank	Deleted		☑	Moganite	Si O2	Monoclinic
19	6	PDF2021	PDF 01-073-8127	Indexed	Primary	2.66	☑	Pyrite, syn	Fe S1.96	Cubic
20	7	PDF2021	PDF 00-002-0471	Blank	Deleted		☑	Quartz	Si O2	Hexagonal

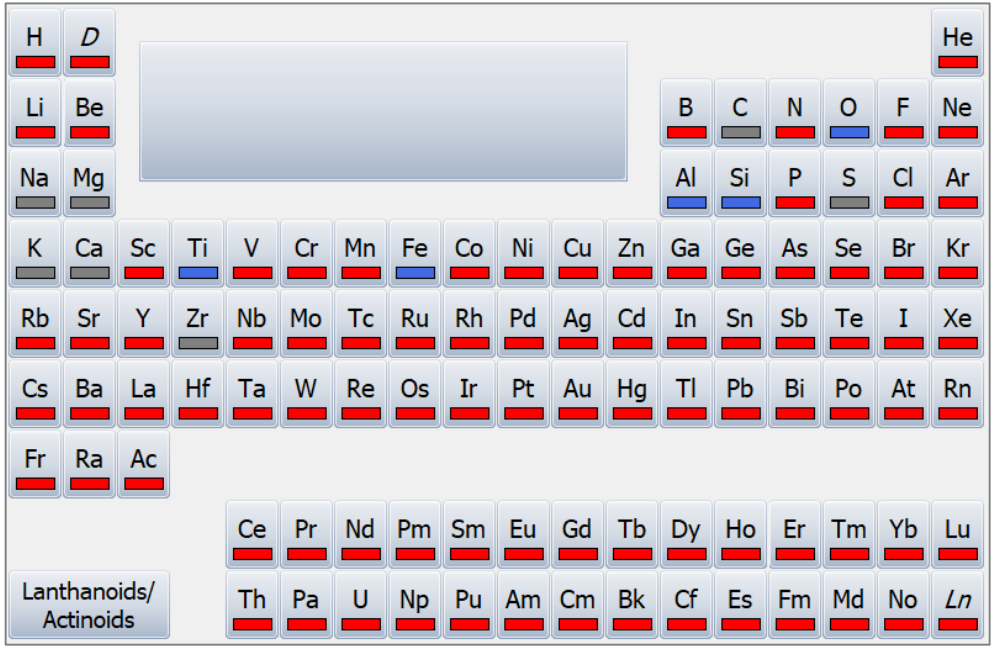
Search/Match – Residue

Residue searches can be helpful in identifying minor phases



Search/Match – Restrictions

Select elements that must / may / must not be present



Discarded

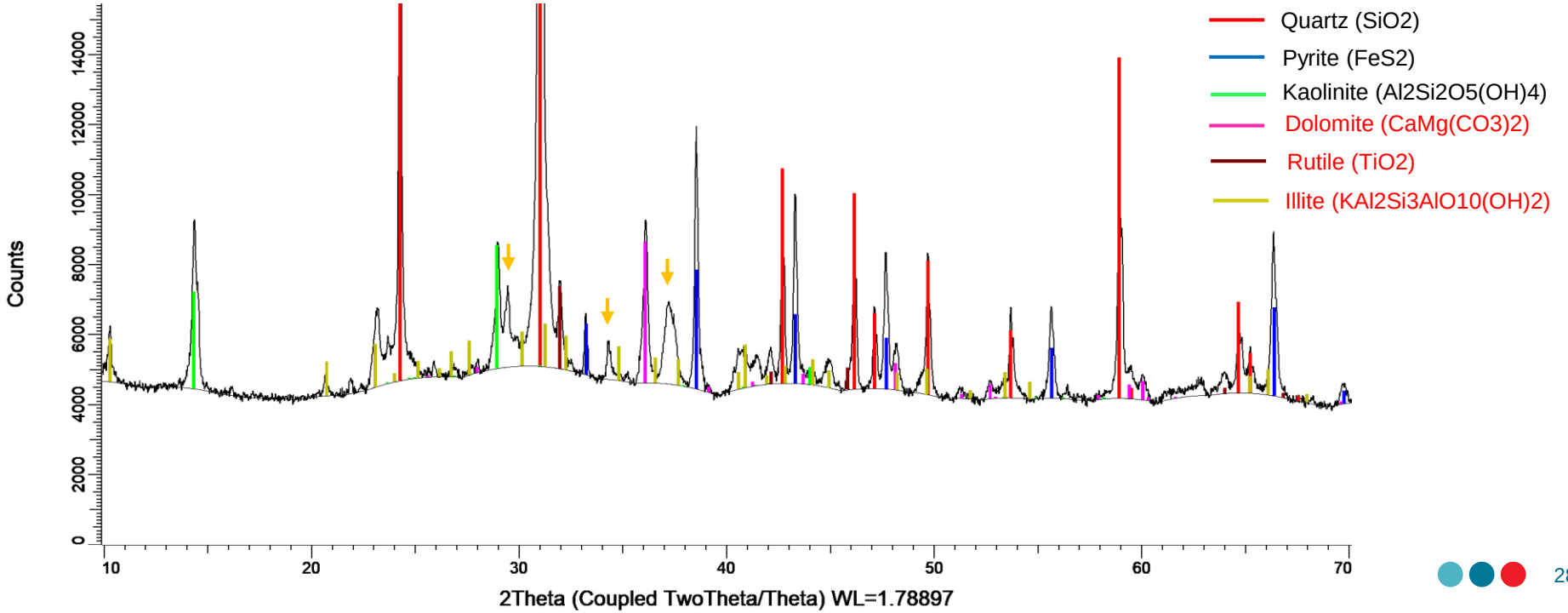
At Least One

Mandatory

Not Checked

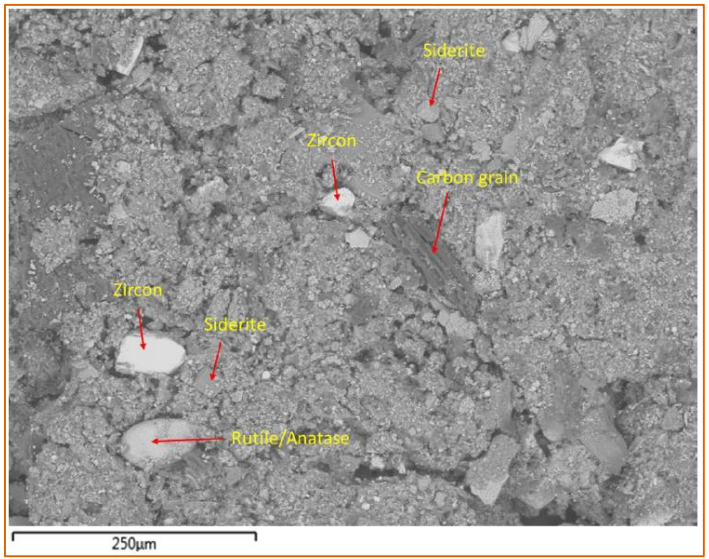
Search/Match – Restrictions

Able to identify 3 more phases but three more peaks that still could not be matched



Search/Match – Use Other Techniques

Revisit elemental compositions – check for what missing
Use information from other analytical techniques



SEM image of the Athabasca oil sands sample

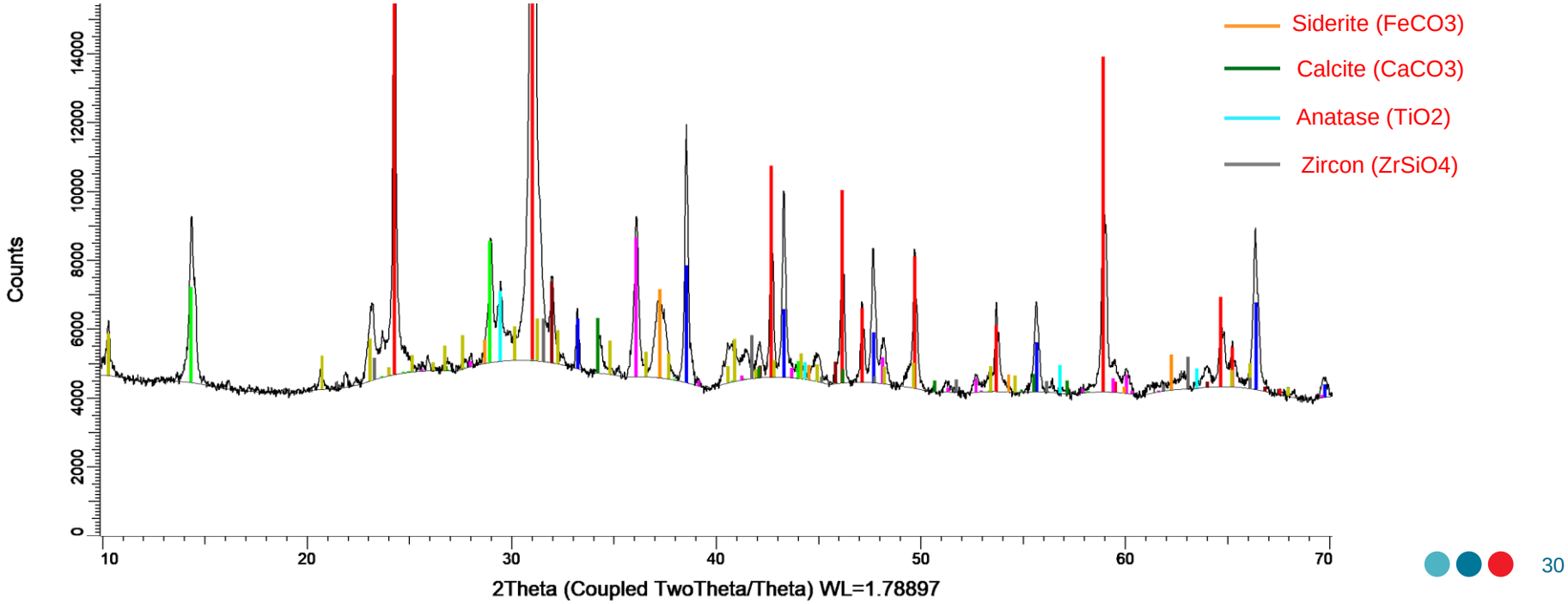
Element	Conc. (wt%)	S.D.
Na	0.25	±0.08
Mg	1.09	±0.07
K	0.81	±0.05
Ca	2.04	±0.27
Al	4.49	±0.16
Si	23.61	±0.24
Ti	1.90	±0.02
Fe	5.69	±0.18
Zr	0.41	±0.09
C	10.08	±0.36
S	3.71	±0.13

WD-XRF

Elemental Analyzer

Search/Match – Final Result

4 more phases were identified – Total of 10 minerals



Search/Match – No Luck?

What else can be done if there are still unidentified peaks remaining?

- **Look for spurious peaks (Kβ, Tungsten, etc.) – can be done using vendor software**
- **Look for possible contamination**
- **Try to separate the components if the material contains multiple phases**
- **Measure wider range of scan in order to collect more peaks (lower or higher angle)**
- **Obtain additional information about the sample from other analytical techniques**
- **Search for literatures and references**

Search/Match – No Luck?

At the end of the day…..

- **After doing everything you could and still couldn't find the match, the unidentified peaks can be reported as unknown**
- **It may be possible that the unknown phases were not categorized before and it might not be included in a database. Using a different database is another option.**

Search/Match – Things to keep in mind

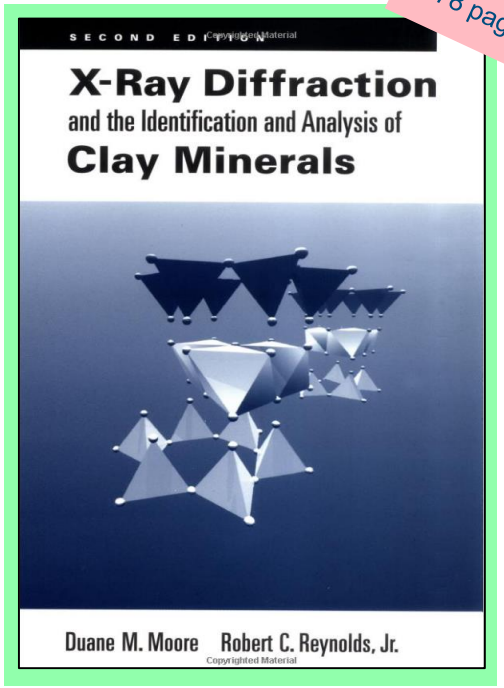
- Search/match results only give a list of suggestions.
- It is up to you to choose the correct ones.
- To identify a particular phase both peak positions and relative intensities must fit. In general this requirement should hold for at least three peaks.
- Sometimes even with the most sophisticated search-match software and the best database cannot provide a complete solution.

TYPE OF SAMPLES

XRD Phase Identification

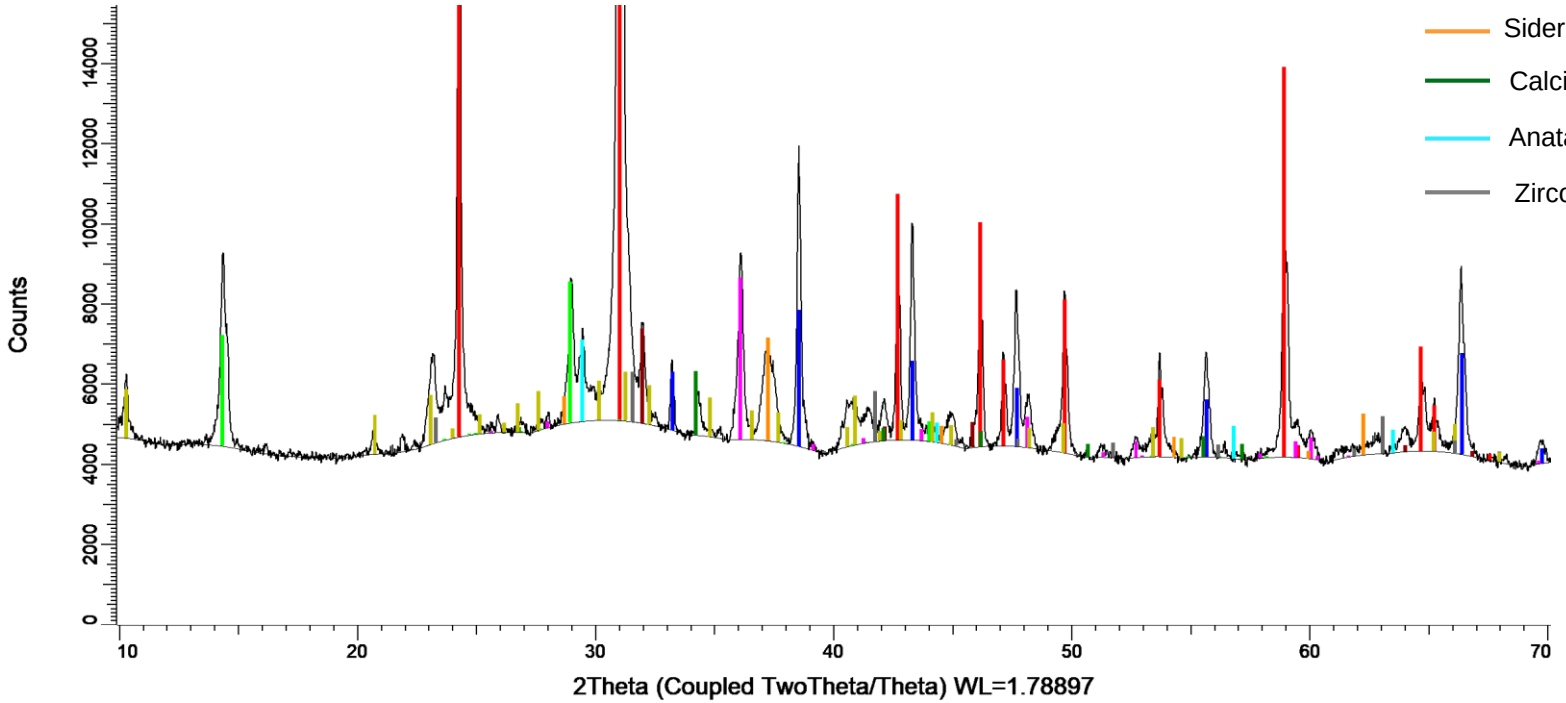
Clay Minerals

- Sample preparation techniques for clay minerals
- Identification of clay minerals and associated minerals
- Identification of mixed-layered clay minerals
- Quantitative analysis
- Disorder in smectite, illite/smectite, and illite

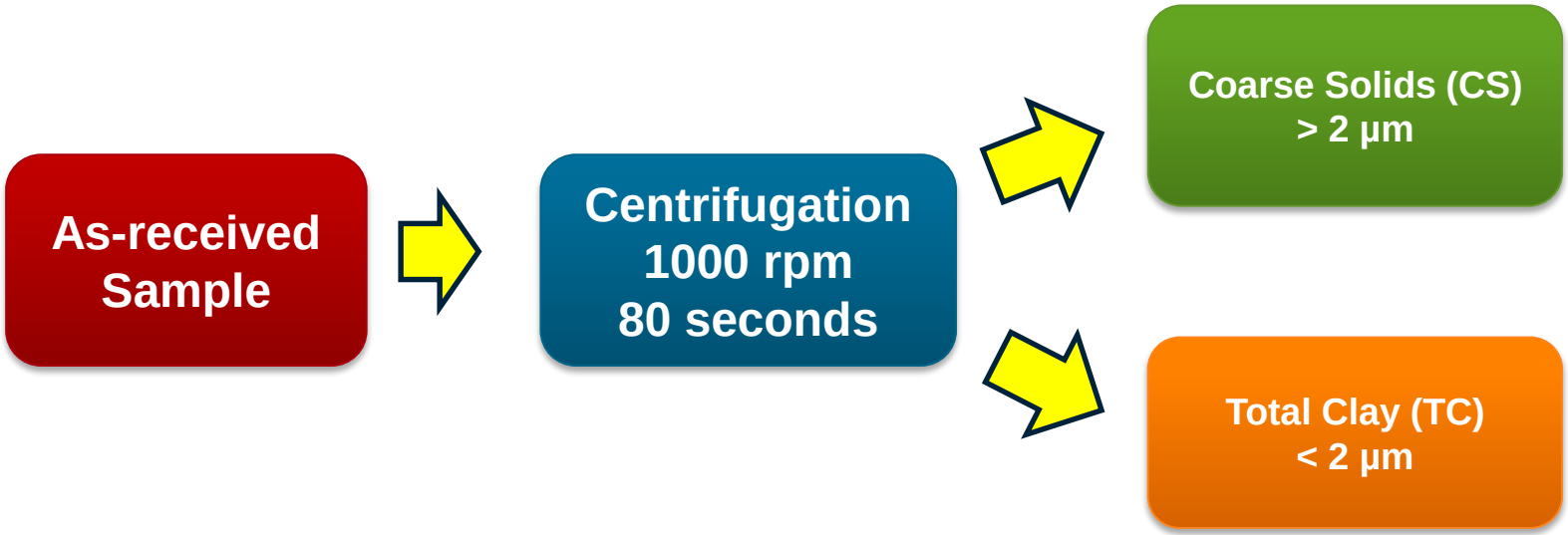


Clay Minerals

Identification of smectite or interstratified clay minerals in <2um clay solids

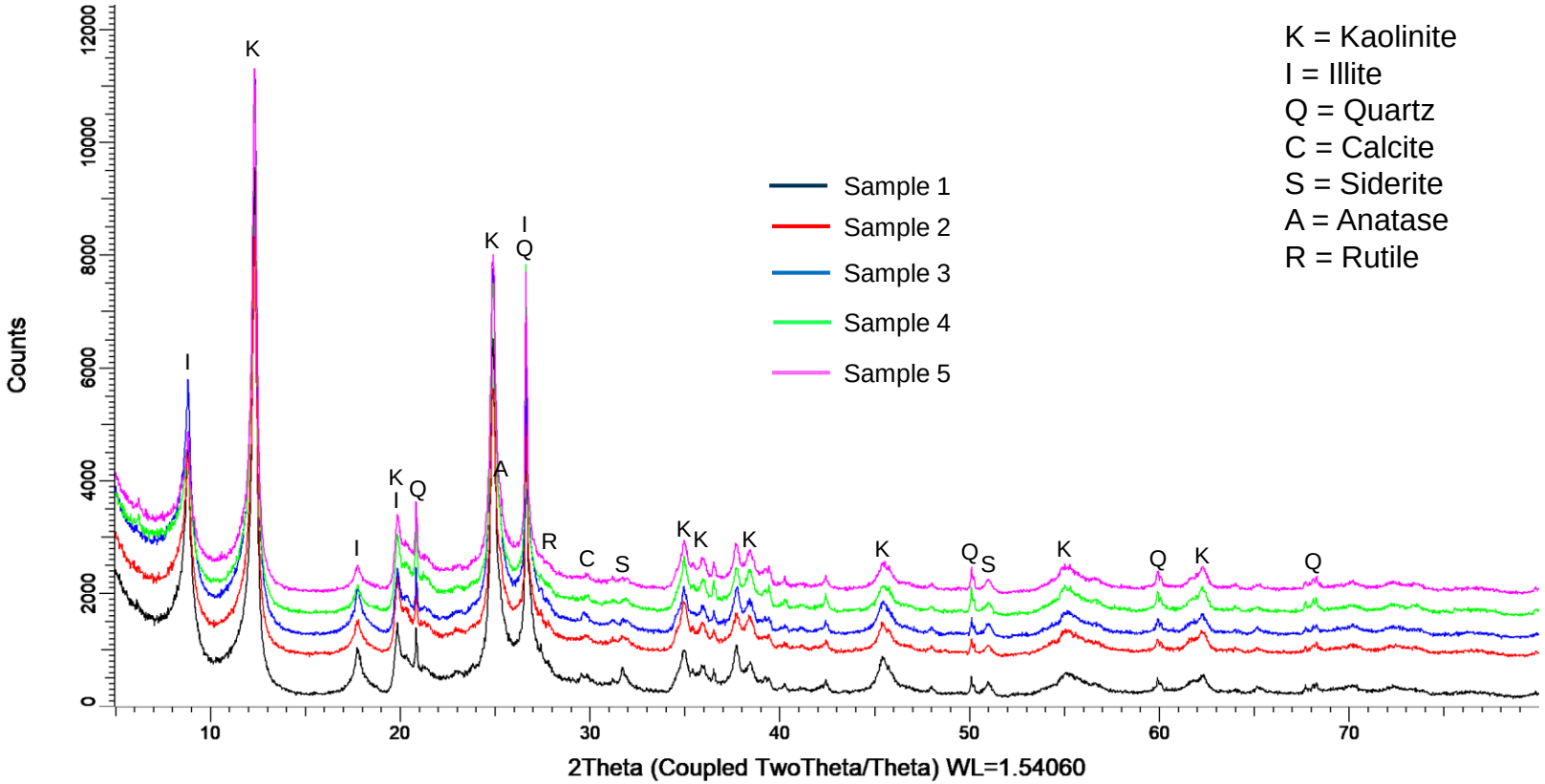


Clay Minerals



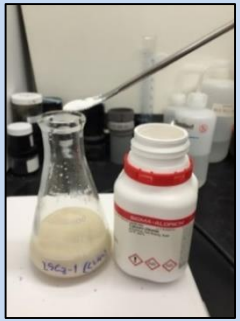
Mercier et al. (2019) Fuel 237: 961-976

Clay Minerals



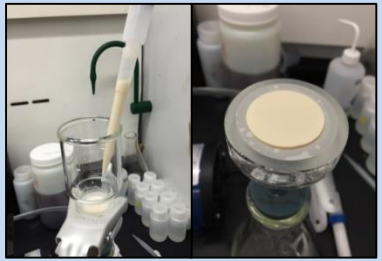
Clay Minerals

Ca Saturated suspension



Add $CaCl_2$ into 50mL clay suspension and stir to allow the salt to dissolve

Remove excess chlorides



Filter the Ca-saturated clay suspension and wash away any excess chlorides

Oriented clay slides

Place the wet filter cake up side down on a glass slide. Peel off the filter paper

"XRD analysis of illite-smectite interstratification in clays from oil sands ores"
Patarachao, B. et al. Advances in X-ray analysis. 2019, 62: 22-31

Clay Minerals

Air dry (AD)
at 54% Relative Humidity for 24hrs

XRD measurement

Ethylene Glycol Solvation (EG)
at 65ºC for 24hrs

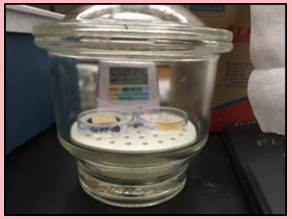
XRD measurement

Heat treatment at 375°C for 2hrs (HT375)

XRD measurement

Heat treatment at 550°C for 2hrs (HT550)

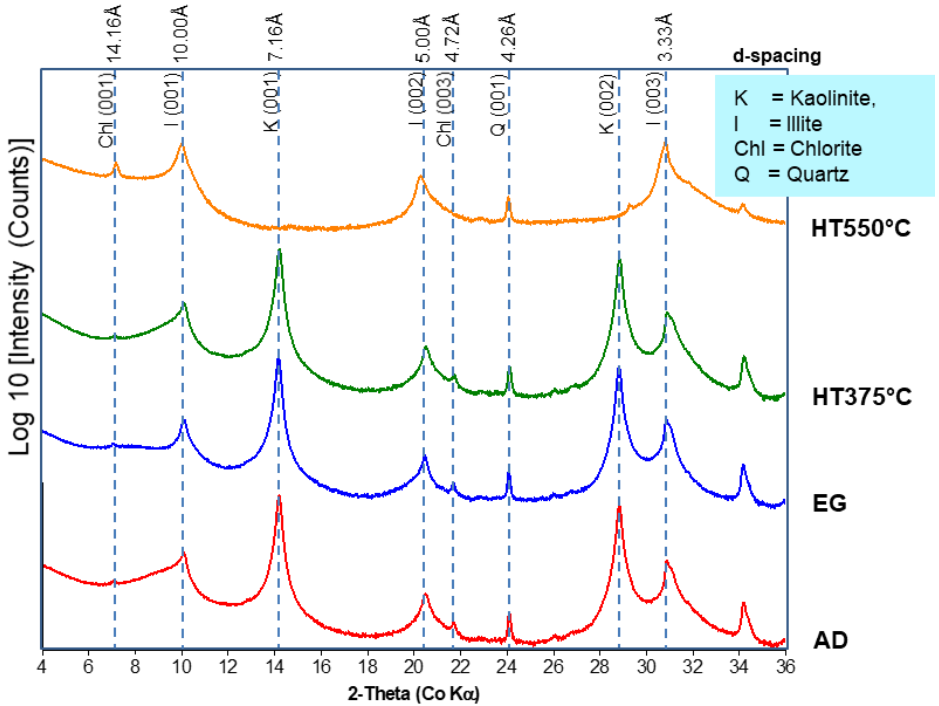
XRD measurement



super saturated solution of $MgNO_3$

Patarachao, B. et al. Advances in X-ray analysis. 2019, 62: 22-31

Clay Minerals



- Illite and Kaolinite are the main non-swelling clay minerals
- No distinct Smectite in detectable quantities – *no peak above 15Å in AD preparation*
- Evident of interstratified illite-smectite – *changing of illite 001 diffraction peak shape after ethylene glycol solvation*
- Detectable chlorite – *a peak observed at 14.16Å after decomposition of kaolinite at 550°C*

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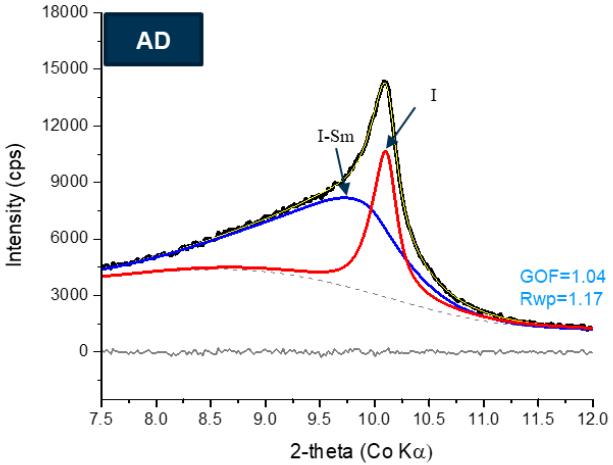
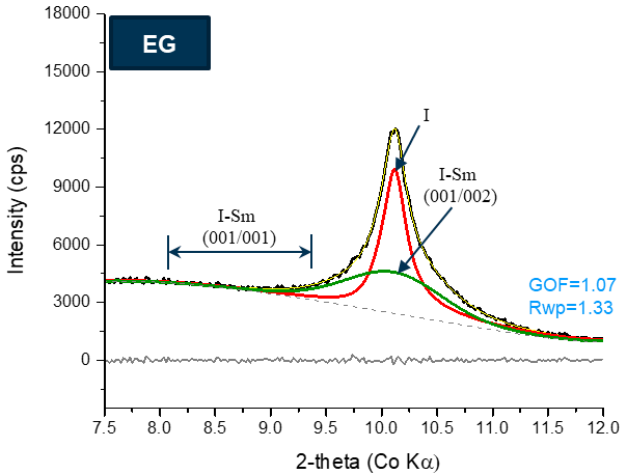
Clay Minerals

Degree of interstratification can be determined using peak fitting by Rietveld analysis





- Interstratified illite-Smectite phase (I-Sm) appears at low-angle side of Illite 001 diffraction peak

- I-Sm 001/002 reflection appears at high-angle side
- I-Sm 001/001 reflection is hidden in the background at low-angle side

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Clay Minerals

Reynolds Cup Competition

- Open to anyone interested in quantitative mineral analysis, with particular emphasis on clay mineralogy
- Each set comprises three samples of ~3–4 g with mineral mixtures commonly found in clay-bearing rocks.
- The top three contestants with the most accurate results will be announced

The Clay Minerals Society

https://www.clays.org/reynolds/

Nano Materials

"Tutorial on Powder X-ray Diffraction for Characterizing Nanoscale Materials."
ACS Nano 2019, 13, 7359−7365

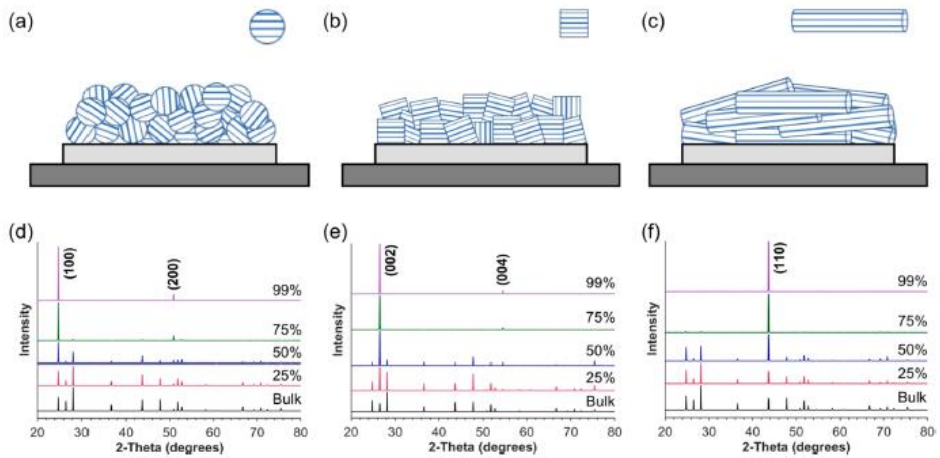


Figure 3. Graphical representation of preferred orientation for nanoparticles having different shapes: (a) spheres, (b) cubes, and (c) rods. Simulated X-ray diffraction patterns for varying degrees of alignment (*i.e.*, preferred orientation) of wurtzite CdS particles along specific crystallographic directions: (d) [100], (e) [001], and (f) [110].

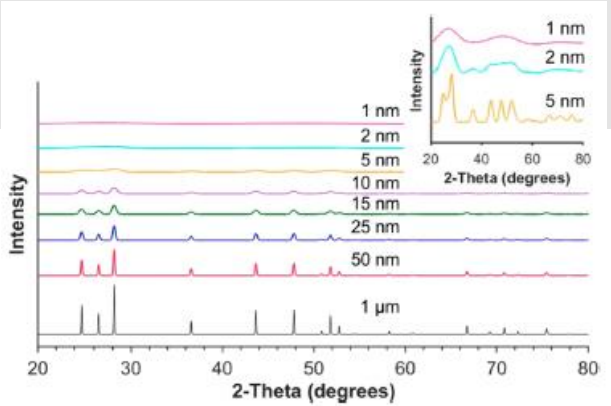


Figure 2. Simulated powder X-ray diffraction patterns for wurtzite CdS spherical particles of different sizes that range from 1 μm to 1 nm. The inset shows the 1, 2, and 5 nm XRD patterns on an expanded *y*-axis scale for clarity.

It is important to recognize the capabilities and limitations of powder XRD for nanoscale materials when collecting and analyzing data as well as to ensure that claims based on XRD data are accurate, appropriate, and not overreaching.

Cellulose

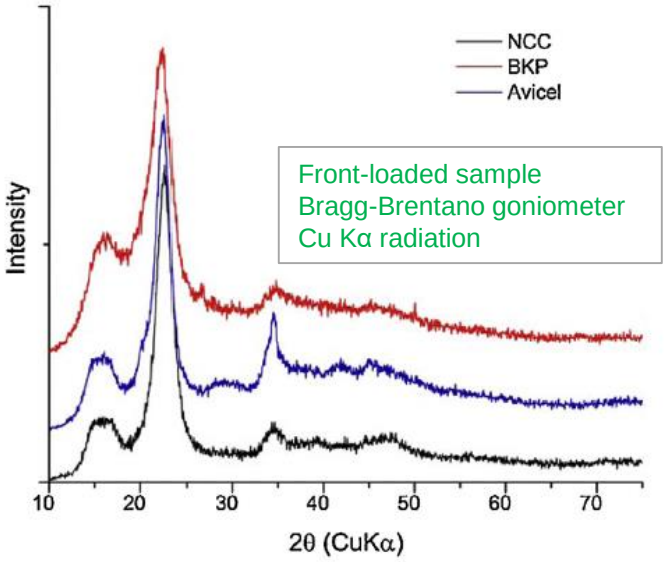


Fig. 5. Measured XRD patterns of the cellulose samples, scaled to the same maximum intensity and offset for clarity.

- Determination of cellulose crystallinity index
- Nanocrystalline cellulose (NCC)
- Rietveld refinement
- Preferred orientation

"An improved X-ray diffraction method for cellulose crystallinity measurement"

Ju, X. et al. Carbohydrate Polymers. 2015, 123: 476-481

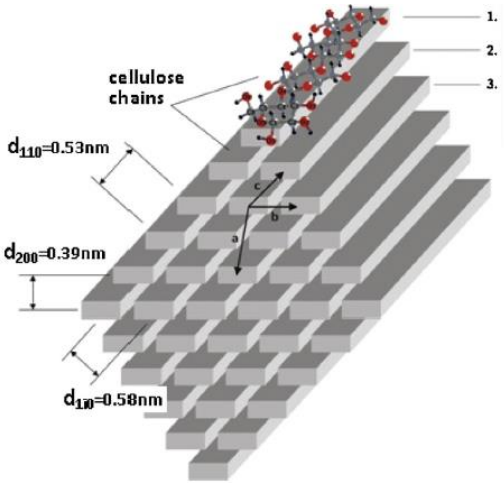


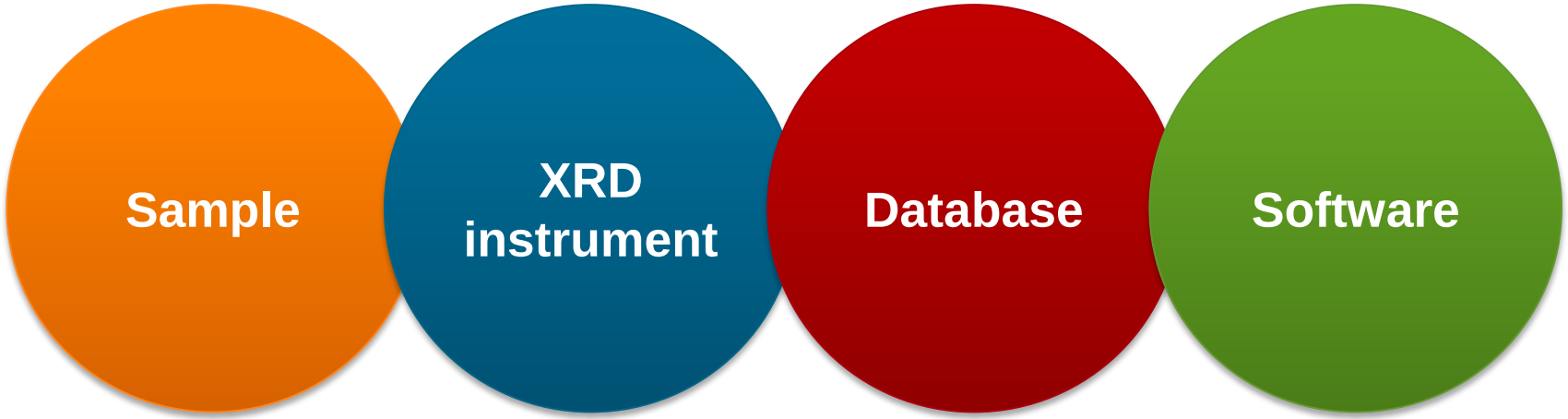
Fig. 6. Proposed crystallite structure of nanocrystalline cellulose.

Other type of samples

- Cement and concrete
- Metals and steels
- Polymers
- Catalysts
- Battery materials
- Pharmaceuticals
- etc.

Summary

Better understanding of……..



……..Better chance of successful phase identification

THANK YOU

Bussaraporn Patarachao

Research Council Officer
Bussaraporn.Patarachao@nrc-cnrc.gc.ca