

How to Analyze Minerals

Fundamentals



Acknowledgement

This tutorial was made possible by the many contributions of ICDD members working in the fields of mineralogy and geology.

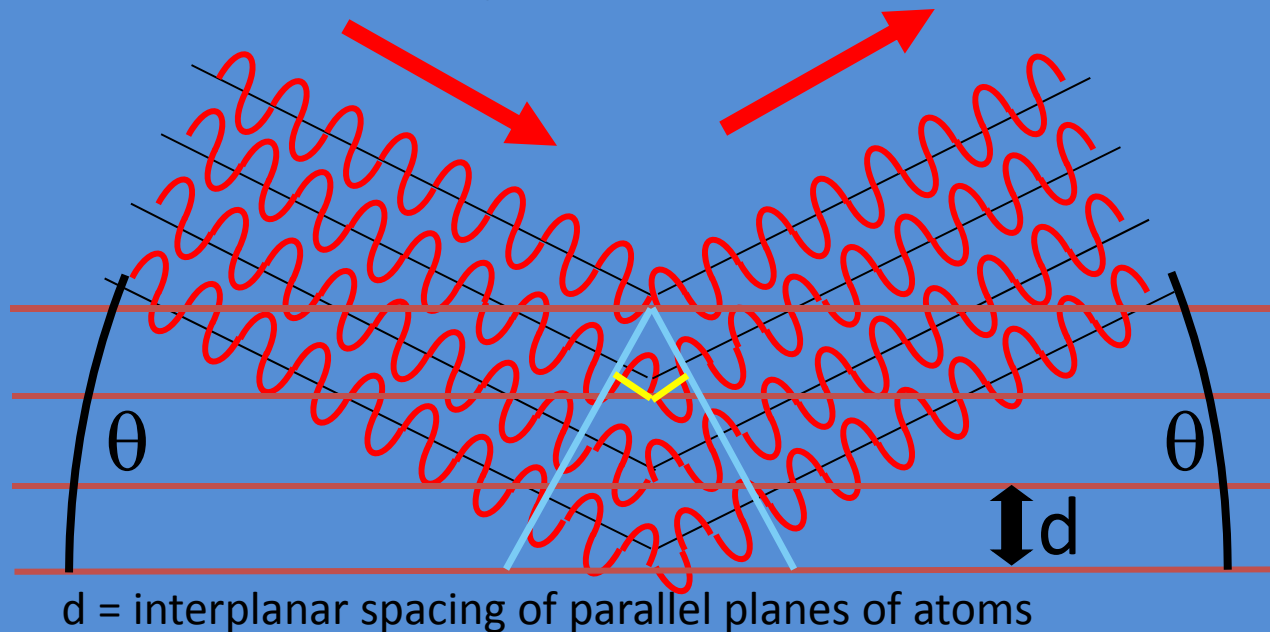
The data shown in this presentation were contributed by ICDD members and/or clinic instructors

Overview

- The vast majority of minerals are crystalline solids made of periodic arrays of atoms
- Crystalline solids, when exposed to monochromatic X-rays will diffract according to the principles of Bragg's law. This is the principle behind single crystal crystallographic analysis and powder diffraction analysis
- In powder diffraction analyses a randomly oriented, finely ground powder is required for multi-phase identification and quantitation.

Diffraction - Bragg's Law

Incident coherent X-ray beam



X-rays scattered from the second plane travel the extra distance depicted by the yellow lines. Simple geometry shows this distance = $2d \cdot \sin\theta$

When this extra distance is equal to one wavelength, the x-rays scattered from the 2nd plane are in phase with x-rays scattered from the 1st plane (as are those from any successive plane). This “constructive interference” produces a diffraction peak maximum at this angle. This is the basis of Bragg's Law:

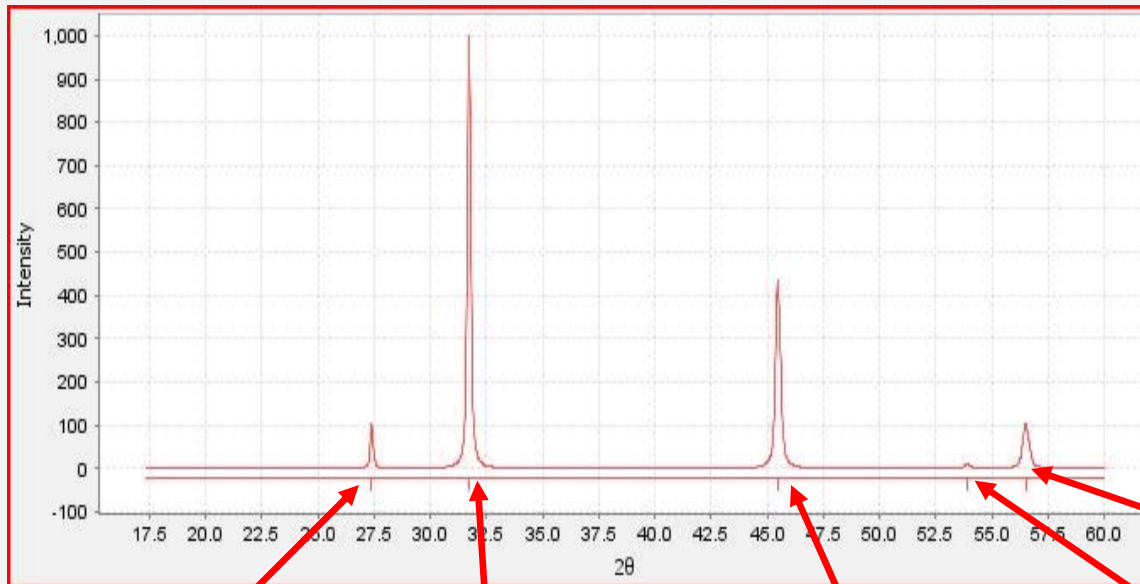
$$\lambda = 2d \cdot \sin\theta$$

XRPD Pattern for NaCl

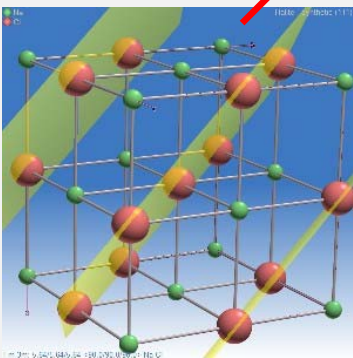
$$\lambda = 1.5406 \text{ \AA} \text{ (Cu } K\alpha_1)$$

$$a = 5.6404 \text{ \AA}$$

Bragg's law prescribes the 2θ angular position for each peak based on the interplanar distance for the planes from which it arises.



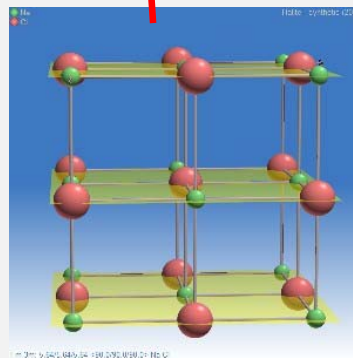
$$2\theta = 2 \text{ asin}(\lambda/2d)$$



(1 1 1)

$$d = 3.256 \text{ \AA}$$

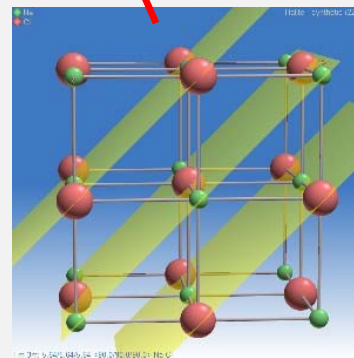
$$2\theta = 27.37^\circ$$



(2 0 0)

$$d = 2.820 \text{ \AA}$$

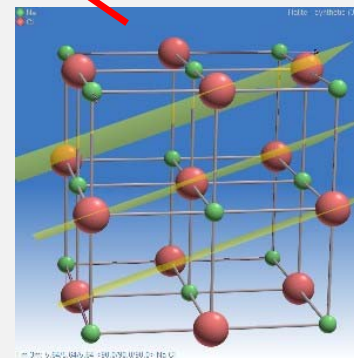
$$2\theta = 31.70^\circ$$



(2 2 0)

$$d = 1.994 \text{ \AA}$$

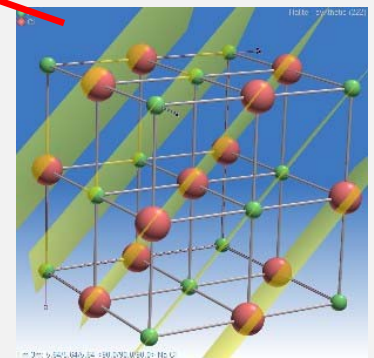
$$2\theta = 45.45^\circ$$



(3 1 1)

$$d = 1.701 \text{ \AA}$$

$$2\theta = 53.87^\circ$$



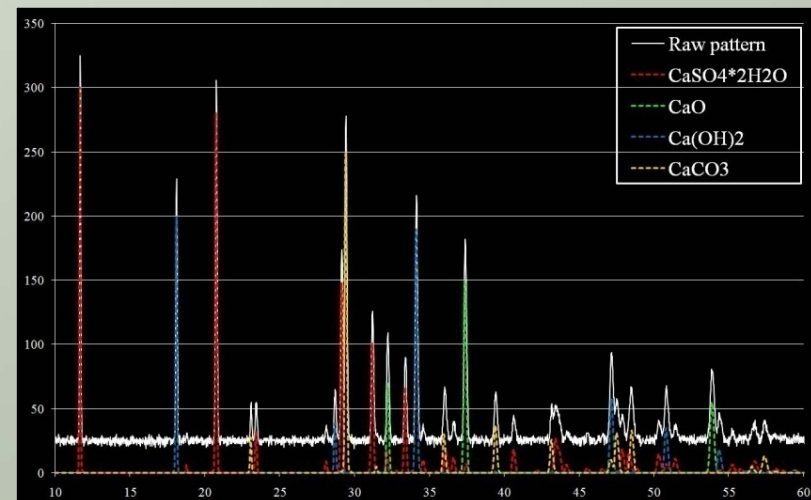
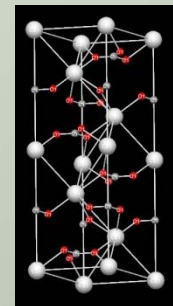
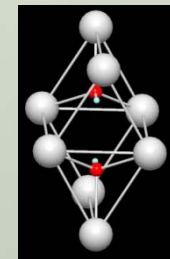
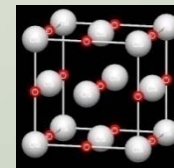
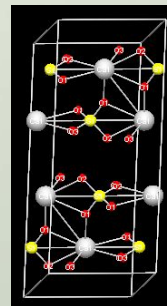
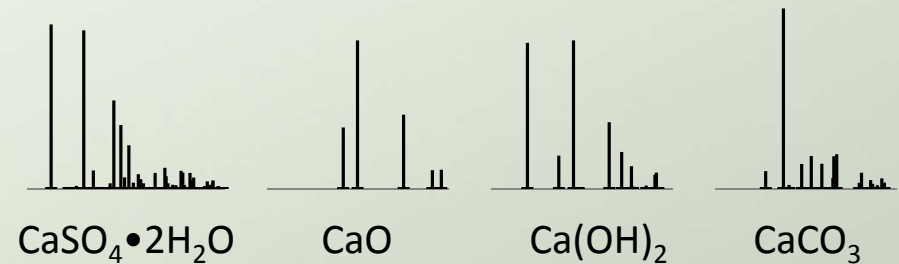
(2 2 2)

$$d = 1.628 \text{ \AA}$$

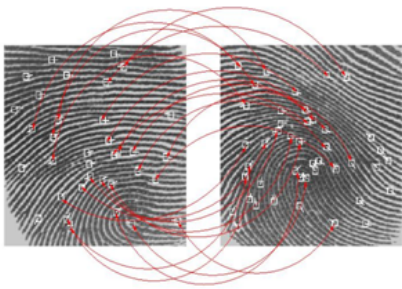
$$2\theta = 56.47^\circ$$

Why It Works

- Each crystalline component phase of an unknown specimen produces its own powder diffraction pattern.
- These patterns arise from the crystal structures of the component phases
- The pattern for a multi-component mixture consists of the weighted sum of the individual patterns for each component in the mixture.



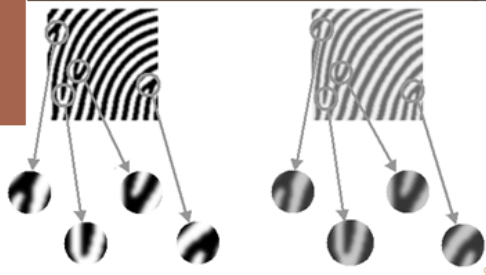
Material Identification



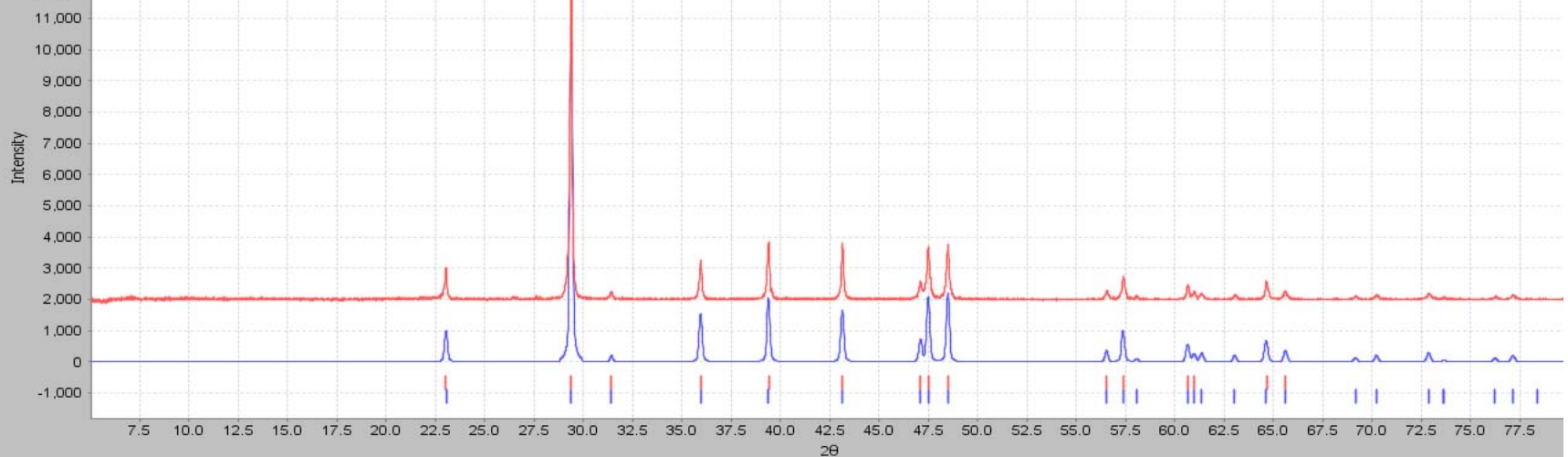
Phase Identification is called a fingerprint technique

Match the experiment with a reference

Unknown specimen Compared to a reference



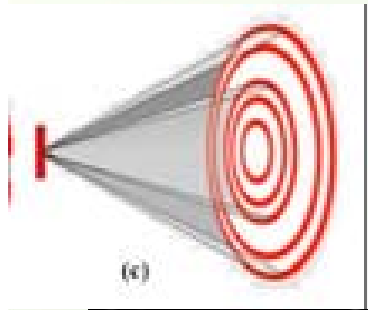
Powder XRD is called a fingerprint technique since every unknown needs to be compared to a reference. In the diffraction pattern below a specimen of oyster shell (top red) is compared to the reference diffraction pattern of calcium carbonate (bottom blue) from the Powder Diffraction File. The matching of all major peaks identifies the oyster shell as being composed of calcium carbonate.



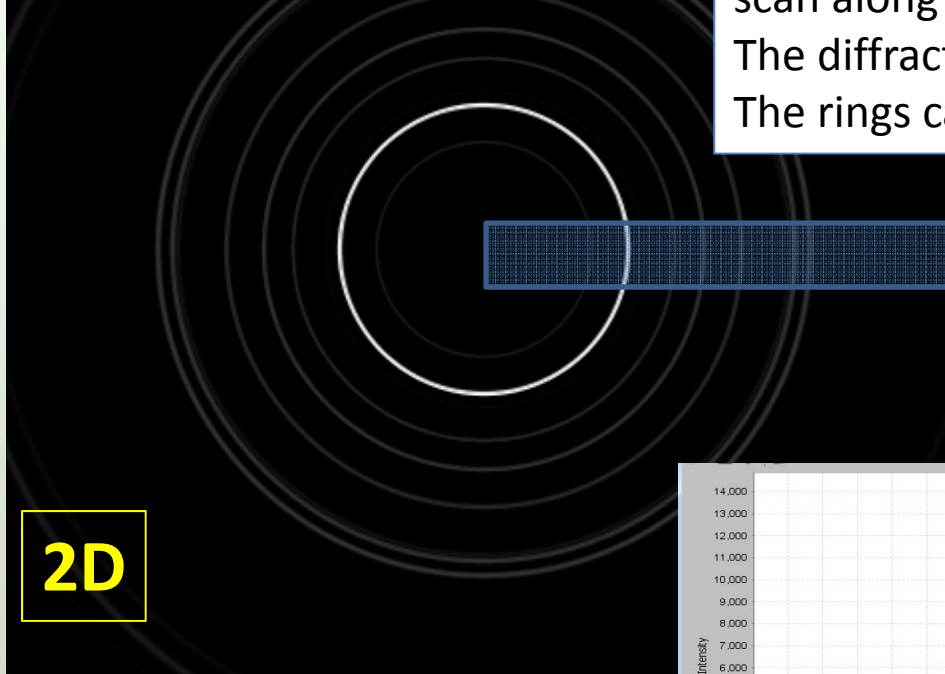
— Oyster_Ca.udf — Ca (C O3) - 01-071-3699 (Calculated, Intensity: 85.1%)



1D vs 2D detectors

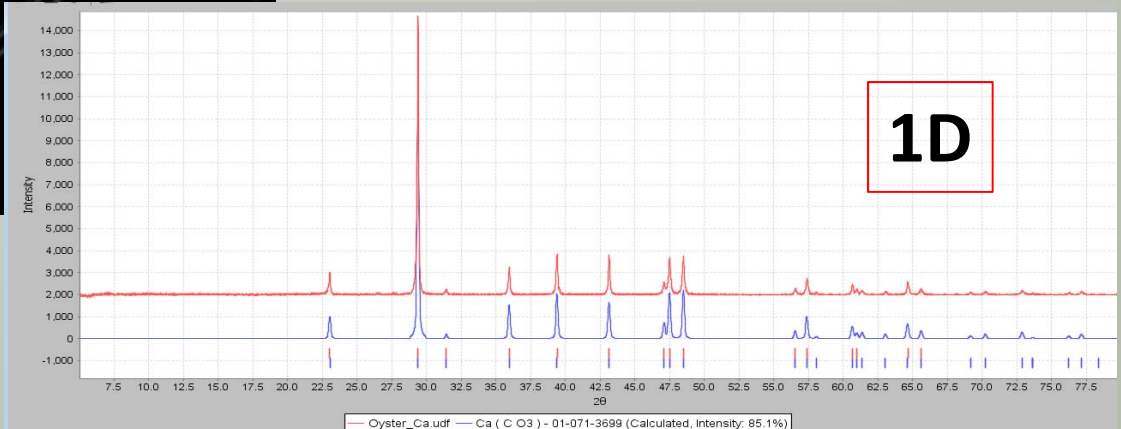


Diffraction from a polycrystalline powder will produce a series of rings (Debye rings) that satisfy Bragg's equation. If a 2D detector is used then the full ring is captured. A one dimensional detector will scan along the theta axis (blue box) and produce the diffraction pattern shown on the bottom right. The rings can also be integrated to produce 1D patterns



2D

In this presentation we show data from both 1D and 2D detectors



1D

Powder Diffraction Basics

To analyze minerals by powder diffraction you will need to have a well ground specimen where the particles are randomly oriented in order to produce a uniform intensity. For reproducible intensities diffraction physics and particle statistics of the diffraction process* require that the particles should be below 10 μm in size and preferably 1 μm in size.

Improper specimen preparation is the single largest source of error in the quantitative analysis of minerals by powder diffraction

Minimizing the particle size also diminishes the surface roughness and often helps packing of the particles into the specimen holder. Proper particle size reduction eliminates or reduces many of the common errors associated with mineral identification and analysis such as orientation, specimen transparency granularity and microabsorption. A general rule of thumb is to regrind and analyze the data again if you have a great deal of difficulty with the initial analysis.

*References with particle statistics analyses

“Introduction to X-Ray Powder Diffractometry”, Ron Jenkins, Robert L. Snyder”, Wiley-Interscience Publisher, 1996

“X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials”, Harold P. Klug and L. R. Alexander, Wiley-Interscience, 1974



The Challenge is how to get a representative sample that will produce a representative specimen for your diffractometer



The rock/mineral sample will need to be crushed into small pieces and then ultimately ground into a fine powder.



If the mineral is soft an agate mortar and pestle can be used to produce a fine powder. If the mineral is hard mechanical grinding may be required.

*Courtesy of
PANalytical*

Macro to Micro

- Mountains to molehills

- **Macro**
 - Riffle Splitters
 - Jaw Crushers
 - Sample Thieves
 - Pulverizer
 - Mills (large)
 - Slicers & Dicers
 - Diamond saws
 - Core borings
 - Tungsten Carbide drills
- **Micro**
 - Mortar & Pestle
 - Ball mill (small)
 - Particle Sieve
 - Cryogrinder
 - Attrition mill
 - Micronizing mill

These mechanical devices are used to sample minerals. Oftentimes many of these devices will be used in succession to go from tons of solid rock to a finely powdered specimen.

Particle size reduction

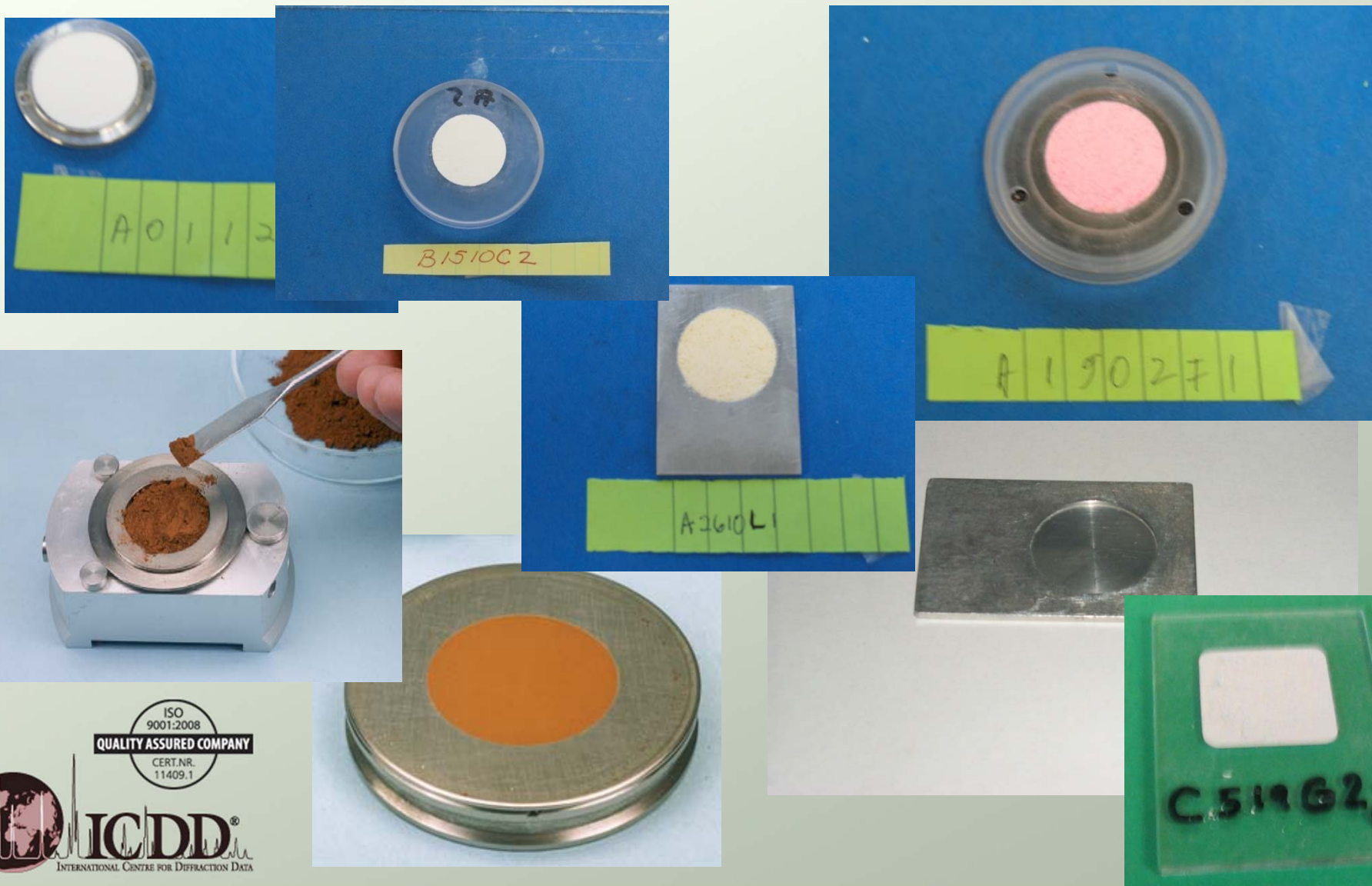
An attrition or micronizing mill is becoming a common tool used in many laboratories for particle reduction. These types of mills have been shown to be able to reduce the particle size of many hard minerals without significantly diminishing the crystallinity or contaminating the specimen with milling media. The media used in the milling process can vary from polyethylene to alumina, agate or tungsten. In general, matching the media hardness with the specimen hardness is useful if one wants to avoid significant damage to the specimen during the particle reduction process.



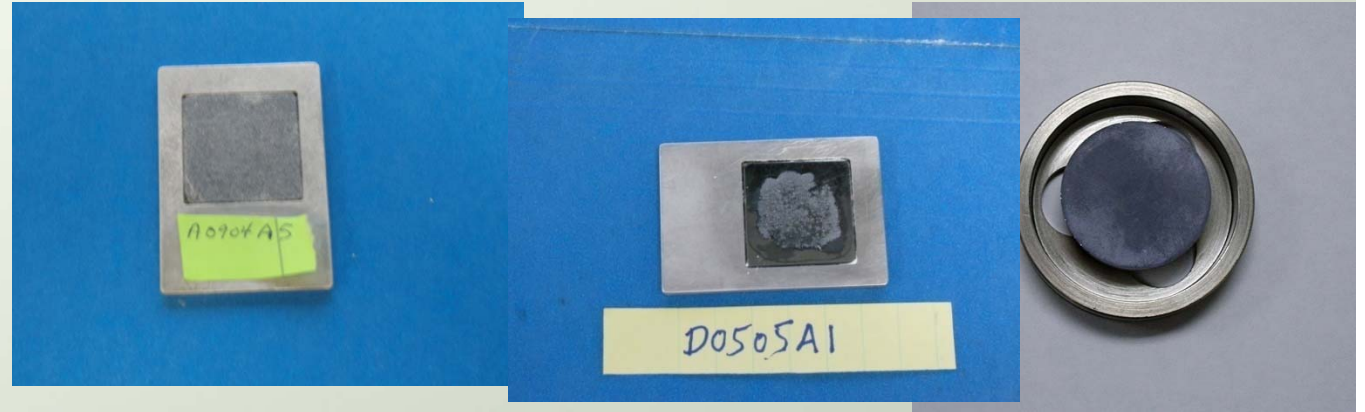
On left: Particle sieves of 100, 200 and 600 mesh

On right: Micronizing chambers from a McCrone micronizing mill using either agate media or alumina media (light pink)

Cavity Mount from ICDD clinics,
mounts by PANalytical, Rigaku, Bruker-AXS
Examples of finely ground powders ready for analysis



Zero Background Holders - off cut silicon crystal, off-cut quartz also used



An essential tool for most mineralogists is the use of a zero background holder. This is typically an off-cut single piece of quartz or silicon that will not produce any background in the pattern. This is very useful for small specimens that can be centered in the holder. This is critical if one is analyzing clays or amorphous materials that are weakly scattering. Standard glass and plastic holders contribute amorphous scatter that can interfere with the determination of clay or amorphous phases.

Effects of a Smooth Surface

Specimen Preparation Methods

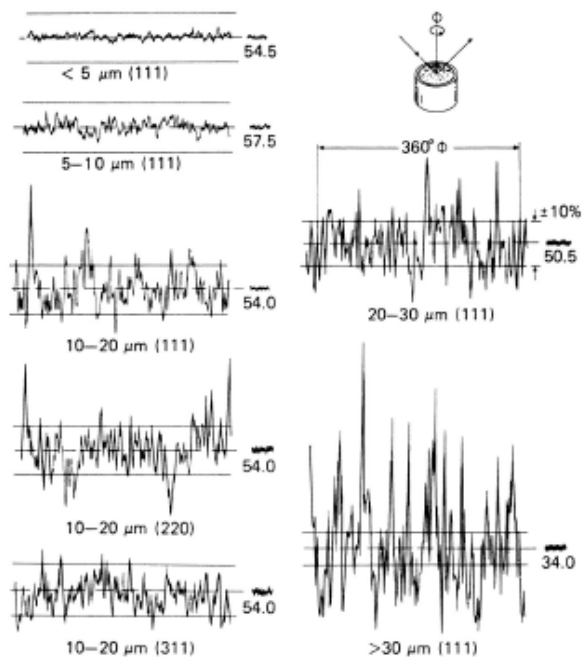
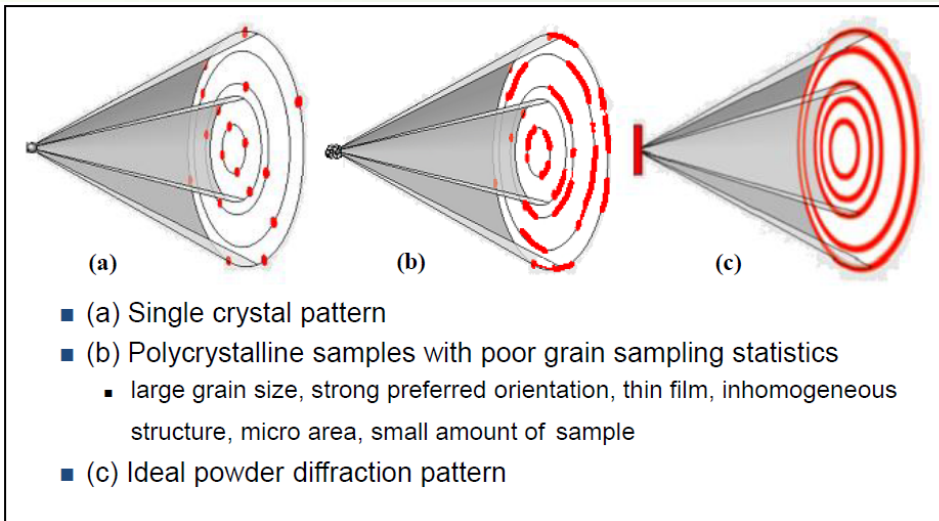


Figure 1. Recordings of intensity variations of rotating silicon powder samples of various particle sizes.

Having a small particle size and a smooth surface can also reduce noise levels as demonstrated in a systematic study by Klug and Alexander.

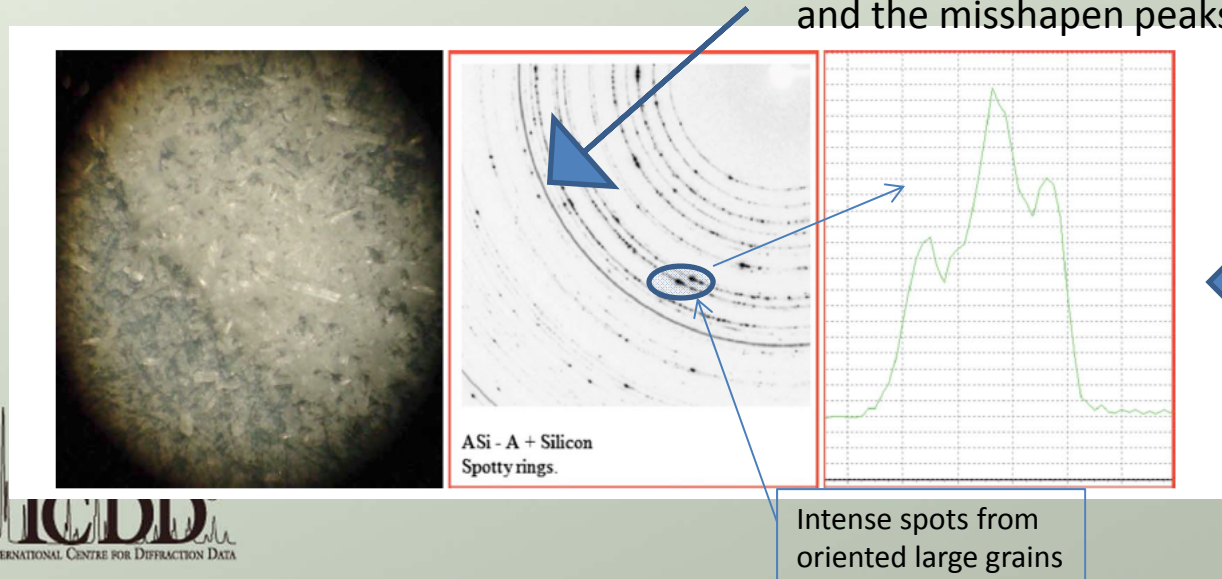
More recently some scientists are using this variation, with a gamma scan technique and two dimensional detectors, to provide estimations of particle sizes.

Diffraction patterns in 3D space



On the left are three idealized patterns from a single crystal, large grains and an ideal random powder

The middle figure below is from a two dimensional detector of a specimen of silicon and mannitol. The silicon was finely ground powder that produced a perfect Debye diffraction ring, the mannitol was asymmetric large platelets (left photo) that produced the spotted rings in the middle pattern and the misshapen peaks in the far right pattern.



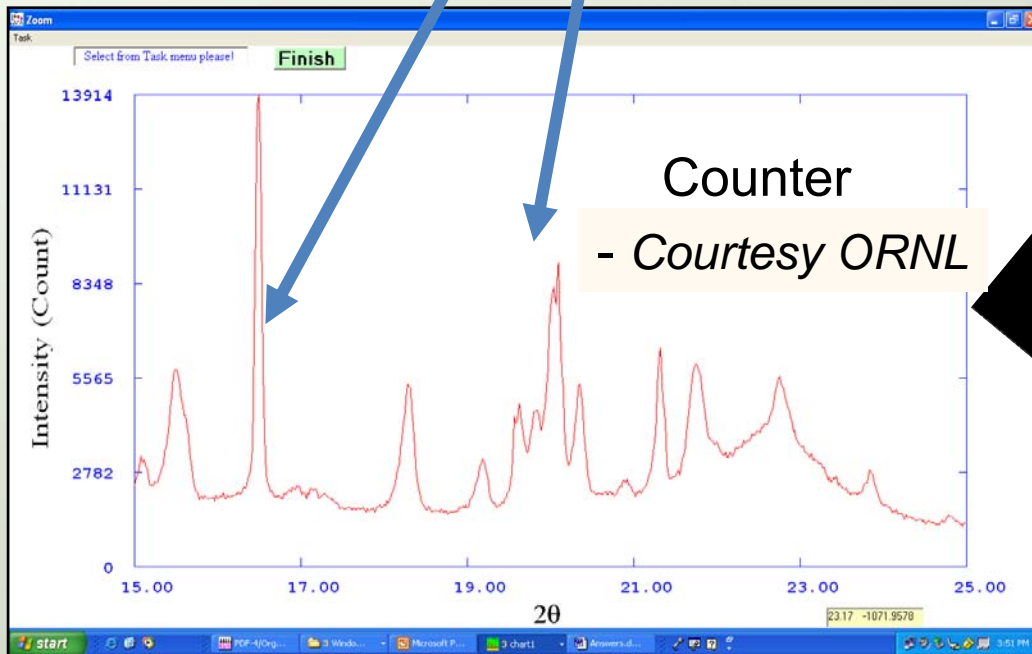
If your peaks look like this – regrind the sample. If the shape is due to large grains Then the peak will look normal on regrinding. If the peaks are due to multiple phases it will not change with regrinding

Tip: Narrow or spotty peaks may be a sign of orientation, granularity and/or poor sampling statistics (small samples)

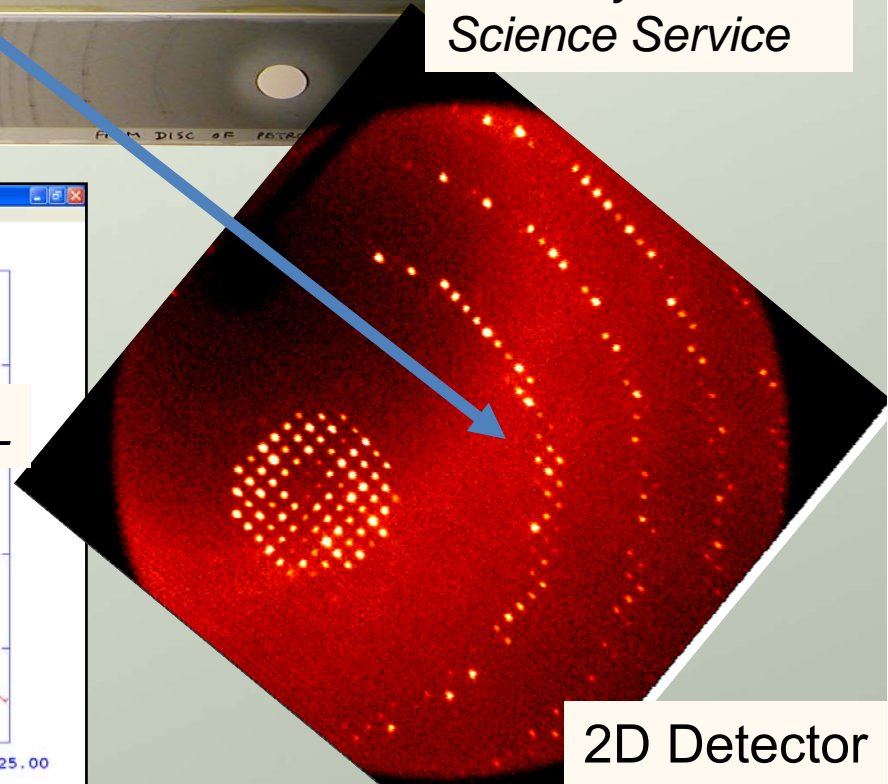


Film

Courtesy Forensic Science Service



Counter
- Courtesy ORNL



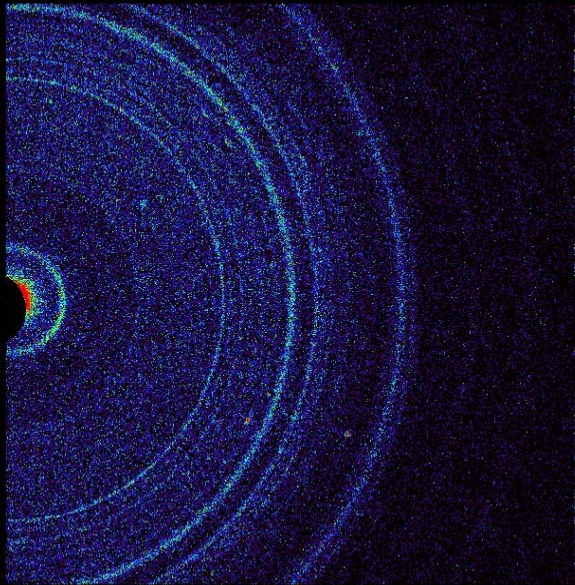
2D Detector
- Courtesy Bruker-AXS

First data from Mars

The first powder diffraction data directly from Martian soil (link below).

Notice the nice uniform Debye rings with only a small amount of granularity

This was achieved on the Mars rover by using a grinding mill and then placing the sample in a novel piezoelectric specimen holder which vibrates the soil, randomizing the particles. The holder and particle vibration from a laboratory demonstration are shown in the linked movie.



[Vibrating particles](#)

<http://www.icdd.com/resources/tutorials/files/xrd-vibrating-holder.mov>

[Martian soil](#)

http://www.nasa.gov/mission_pages/msl/multimedia/pia16217.html

Every time you prepare a sample you change it !

Make sure the sample prep technique
is not destroying, altering or masking the original
problem (*tip - analyze before and after preparation steps*)

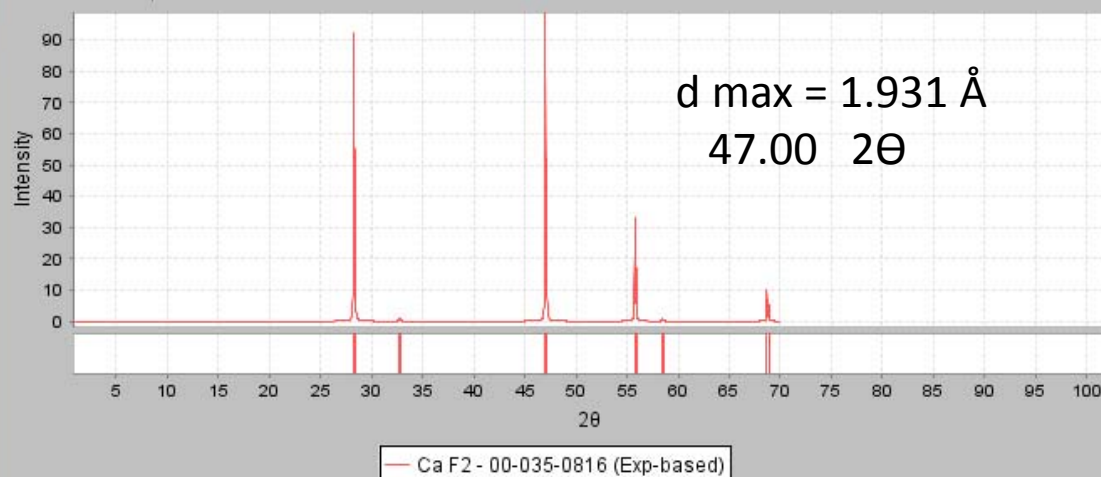
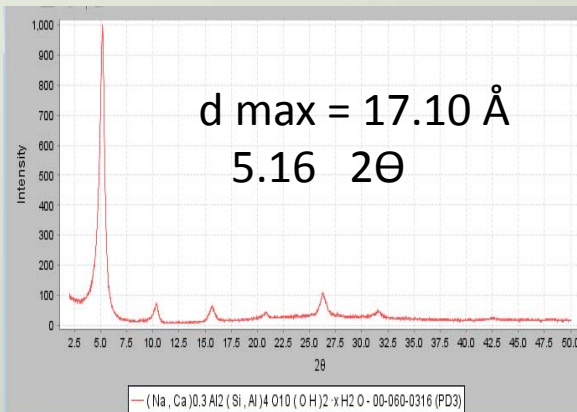
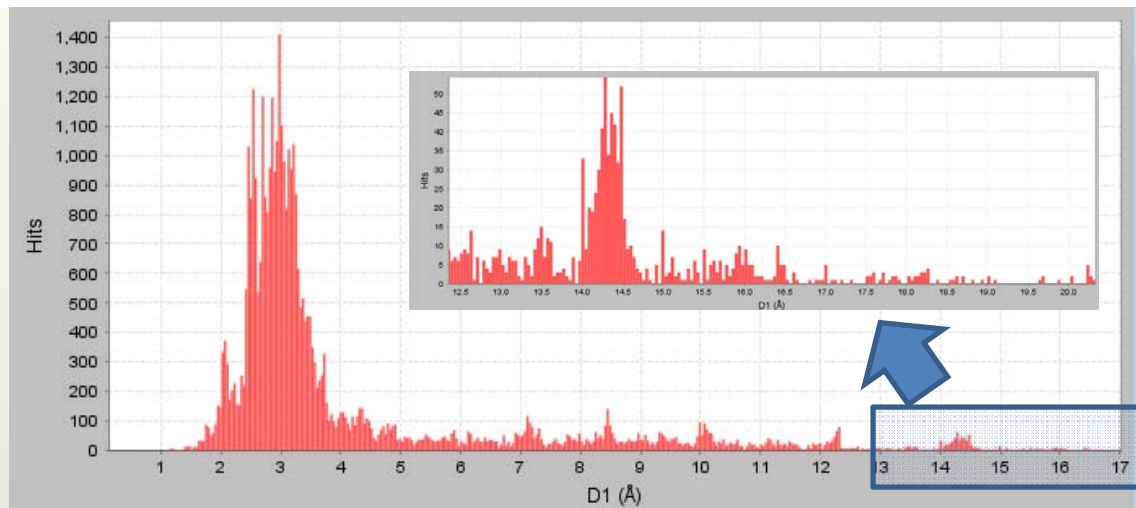
- Grinding can destroy soft materials
- Binders can mask or dilute phases
- Temperature and humidity can change phase chemistry
- Sieving may separate phases as well as separating
particle size

Material can be over ground destroying crystallinity.
Hard materials like quartz will often self grind softer materials.

Data collection

Data should be collected from 2 to 70 degrees for phase identification and 2 to 100 degrees for quantitative analysis with a step size of 0.02 degrees. (Cu radiation)

Minerals show a wide diversity in diffraction patterns which are a result of their diversity in crystal and molecular structure. The plot at the top shows the maximum d-spacing for 39,406 minerals and mineral related materials (i.e. synthetics, gems)..Many minerals have characteristic peaks at very high d-spacings (low angles) as shown by the insert of the top graph and by the reference data for montmorillonite shown in the middle graph. Alternatively fluorite has a d-max at a very low d-spacing (high angle) as shown in the bottom graph. This variety dictates a wide analysis range when analyzing mineral unknowns.



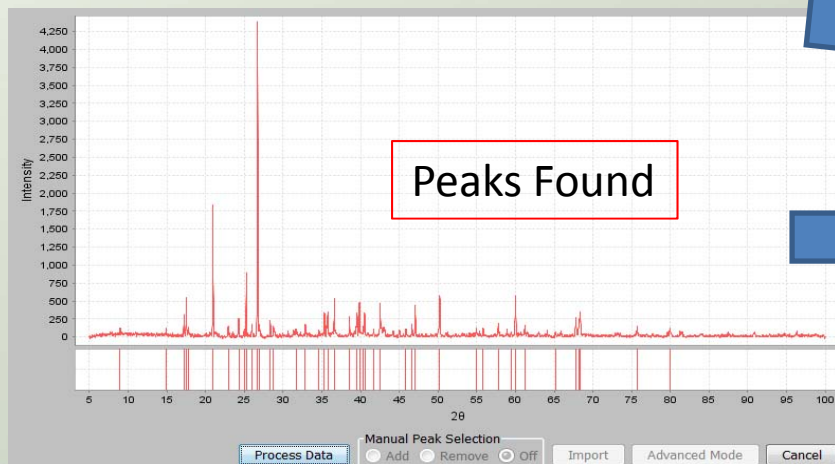
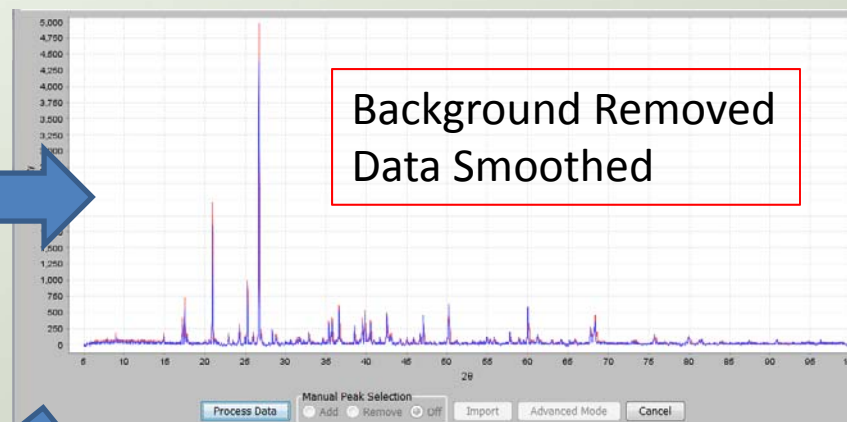
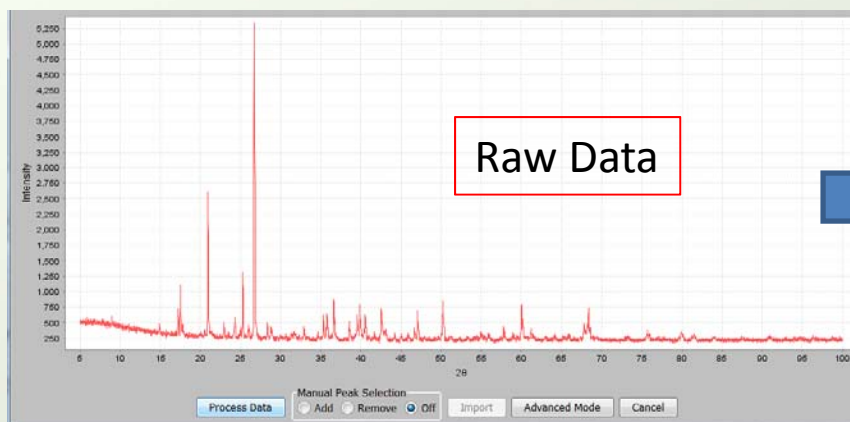
Material Identification Process

- Prepare the specimen (well ground small particle size powder)
- Collect the data
- Treat the data
 - remove background
 - smooth data if needed
 - find peaks
 - identify peak heights and areas
 - normalize all intensities
- Compare mineral data to reference data-

In many search/match programs these steps are batched processed so a single user operation does all the data treatment

Data Treatment

(graphics interface with ICDD's Sieve+ program)



Ex d	Ex I	1.97740	2
5.06211	13	1.94557	4
4.97734	2	1.92957	10
4.23765	41	1.81560	13
3.87766	4	1.66996	3
3.66128	6	1.64539	3
3.56283	2	1.59421	4
3.52169	20	1.55355	2
3.42673	4	1.54042	13
3.33498	100	1.51320	3
3.30406	4	1.43006	1
3.14450	5	1.38105	6
3.10251	3	1.37409	6
2.82385	3	1.37097	8
2.72205	4	1.25520	4
2.58760	2		
2.53798	8		
2.50765	8		

Normalized d-spacings and intensities

Search the PDF-4+ database

Or

Common Filters

Primary Patterns Mineral Related Pharmaceuticals and Excipients Common Phases

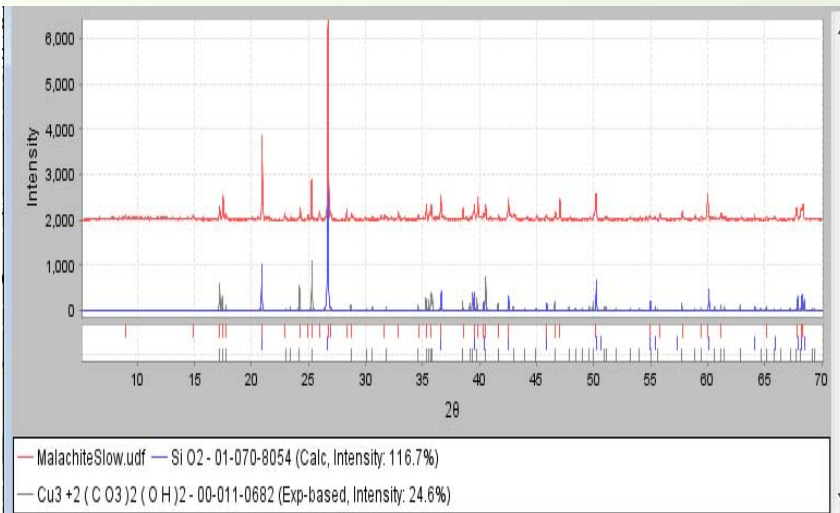
Search Match efficiency is greatly improved by using a minerals and related material subfile. This reduces the search to 39,406 entries in Release 2012. This is the largest mineral entry collection in the world for diffraction data.

GOM	PDF #	QM	Status	Coords	Compound Name	Chemical Formula	D1	D2	D3	D4	D5	D6	D7	D8	I/Ic	Rot. #
5097	01-070-8054	S	A	✓	Silicon Oxide	Si O2	3.337080	4.245170	1.814580	1.538030	2.277880	2.450950	1.372650	2.122590	3.1	1
5047	01-086-1629	S	A	✓	Silicon Oxide	Si O2	3.337800	4.246120	1.814970	1.538380	2.278360	2.451500	1.372940	2.123060	3.1	1
5045	04-006-1757	P	A	✓	Silicon Oxide	Si O2	3.337820	4.246120	1.814980	1.538380	2.278390	2.451500	1.372960	2.123060	3.03	1
5017	01-085-0865	I	A	✓	Silicon Oxide	Si O2	3.336560	4.243520	1.814370	1.537510	2.450000	2.277990	1.372610	1.378950	3.11	1
4866	01-086-1628	S	A	✓	Silicon Oxide	Si O2	3.337370	4.245340	1.814750	1.538110	2.278180	2.451050	1.372810	1.379360	3.09	1
4859	01-077-5327	B	A	✓	Copper Carbonate Hydroxide	Cu3 (C O3)2 (O H)2	3.525810	5.162210	3.662450	2.511180	5.077540	2.223220	2.281130	2.257920	1.92	3
4724	00-011-0136	B	D		Copper Hydroxide Carbonate	Cu3 (O H)2 (C O3)2	3.527000	5.150000	2.516000	3.663000	2.336000	2.287000	2.260000	2.225000		3
4631	00-011-0682	S	P	✓	Copper Carbonate Hydroxide	Cu3 +2 (C O3)2 (O H)2	3.516000	2.224000	5.150000	3.674000	2.510000	2.287000	5.080000	2.503000		3



The search matches d-spacings and immediately found quartz and azurite in this specimen.

Match



Ex d	Ex I	P1 d	P1 I	P2 d	P2 I	P3 d	P3 I
9.85630	3						
5.94230	3						
5.14925	7			5.150000	55		
5.06211	13			5.080000	30		
4.97734	2			4.990000	11		
4.23765	41	4.245170	20				
3.87766	4			3.860000	3	3.883380	20
3.66128	6			3.674000	50		
3.56283	2					3.560330	50
3.52169	20			3.516000	100		
3.42673	4					3.424380	100
3.33498	100	3.337080	100				
3.30406	4					3.301070	41
3.14450	5						
3.10251	3			3.107000	11		
2.82385	3			2.811000	7	2.823440	19
2.72205	4					2.723920	21
2.58760	2			2.590000	11		
2.53798	8			2.540000	25		
2.50765	8			2.510000	35		
2.45236	11	2.450950	8				
2.33253	6			2.336000	17		
2.27687	8	2.277880	8				
2.25995	11			2.265000	25		
2.23347	3	2.231740	4				
2.22300	7			2.224000	70		
2.16488	2			2.168000	15		
2.12405	11	2.122590	6				
1.97740	2	1.975400	3				
1.94557	4			1.948000	20		
1.92957	10						
1.81560	13	1.814580	12				
1.81560	13	1.814580	12				
1.66996	3	1.668540	4	1.667800	1		
1.64539	3						
1.59421	4			1.595300	15		
1.55355	2			1.554600	3		
1.54042	13	1.538030	9				
1.51320	3			1.514000	11		
1.43006	1			1.430600	9		
1.38105	6	1.379260	6	1.381700	3		
1.37409	6	1.372650	6	1.374600	5		
1.37097	8						
1.25520	4	1.253290	3				
1.19898	3	1.197620	3				



Third phase
Ba (Pb)SO4

The match of the complete patterns can be compared graphically, above, or by a line by line d-spacing comparison on the right. All d-spacings in blue indicate a match and the d-spacing in black are not identified. The first column is the d-spacings of the unknown and the other columns are the d's and I's of reference materials.

Quartz

Azurite



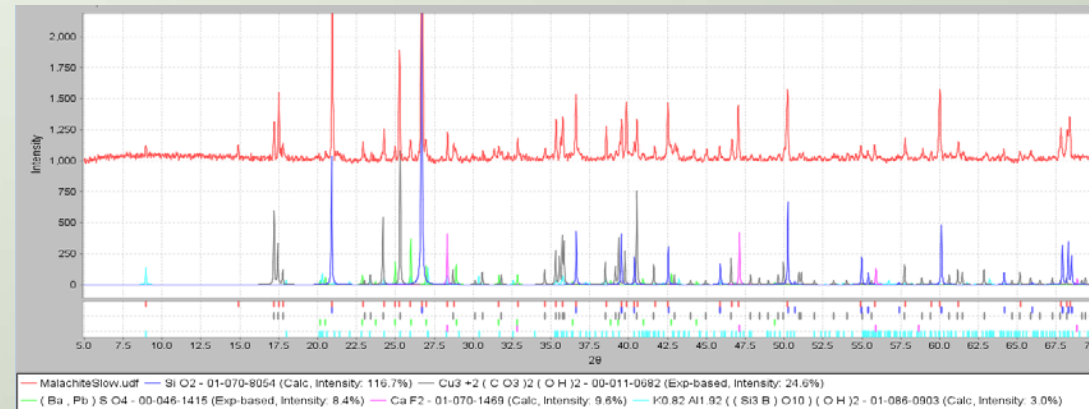
More Matches by analyzing the remaining unidentified peaks

Remaining residual d-spacings



- 9.856 d-max of Muscovite
- 5.942 Malachite
- 3.145 CaF2
- 1.929 d-max of CaF2
- 1.645 CaF2

By examining the residual d-spacings and searching minerals in the database, additional minerals can be found.



Using additional information such as microscopic examination and elemental analyses another two phases can be identified – tenorite and copper. The major peaks of these phases are in areas of heavy peak overlap which makes identification of these two phases difficult without the supplemental data. This particular specimen was also analyzed by X-ray Fluorescence which confirmed the phases identified, including the lead in the Pb doped Barite.



Can we do a quantitative analysis ?

- For the Reference Intensity Ratio method one needs an I/I_c value for each mineral

In PDF-4+ Release 2012 and PDF-4/Minerals 28,542 out of 39,406 entries (72.4%) have an I/I_c

- For the Rietveld method one needs atomic coordinates for each mineral structure

In PDF-4+ Release 2012 and PDF-4/Minerals 27,649 out of 39,406 entries (70.1%) have atomic coordinates or are cross referenced to atomic coordinates

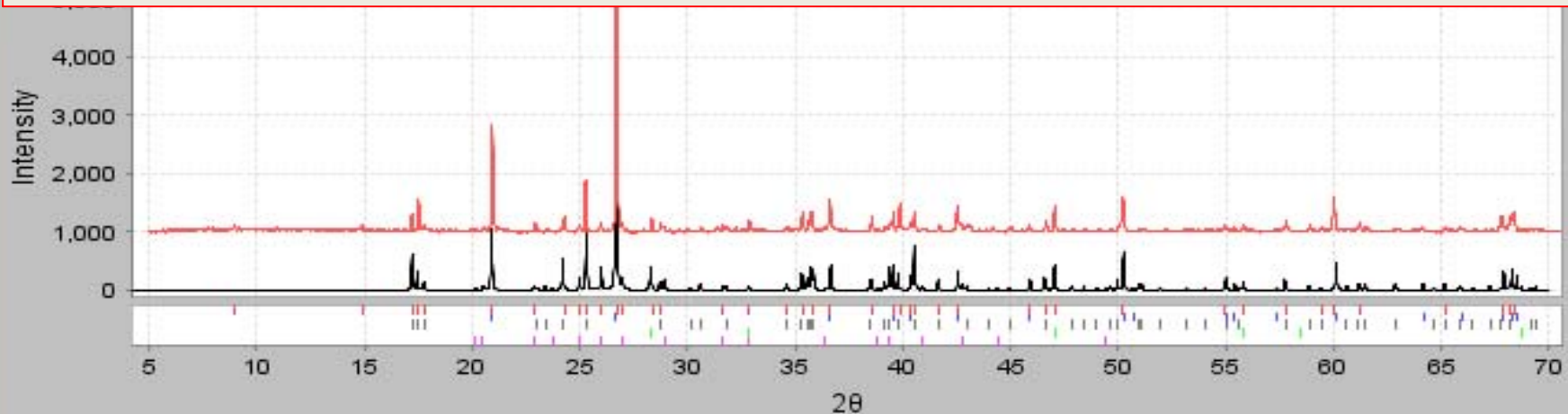
- For pattern fitting methods digital patterns would be required for all phases

In PDF-4+ Release 2012 and PDF-4/Minerals all 39,406 mineral and related mineral entries can be expressed as either an experimental or calculated digital pattern (100 %). Pattern fitting methods may be the preferred method of analysis if one is dealing with non crystalline components.

RIR Method

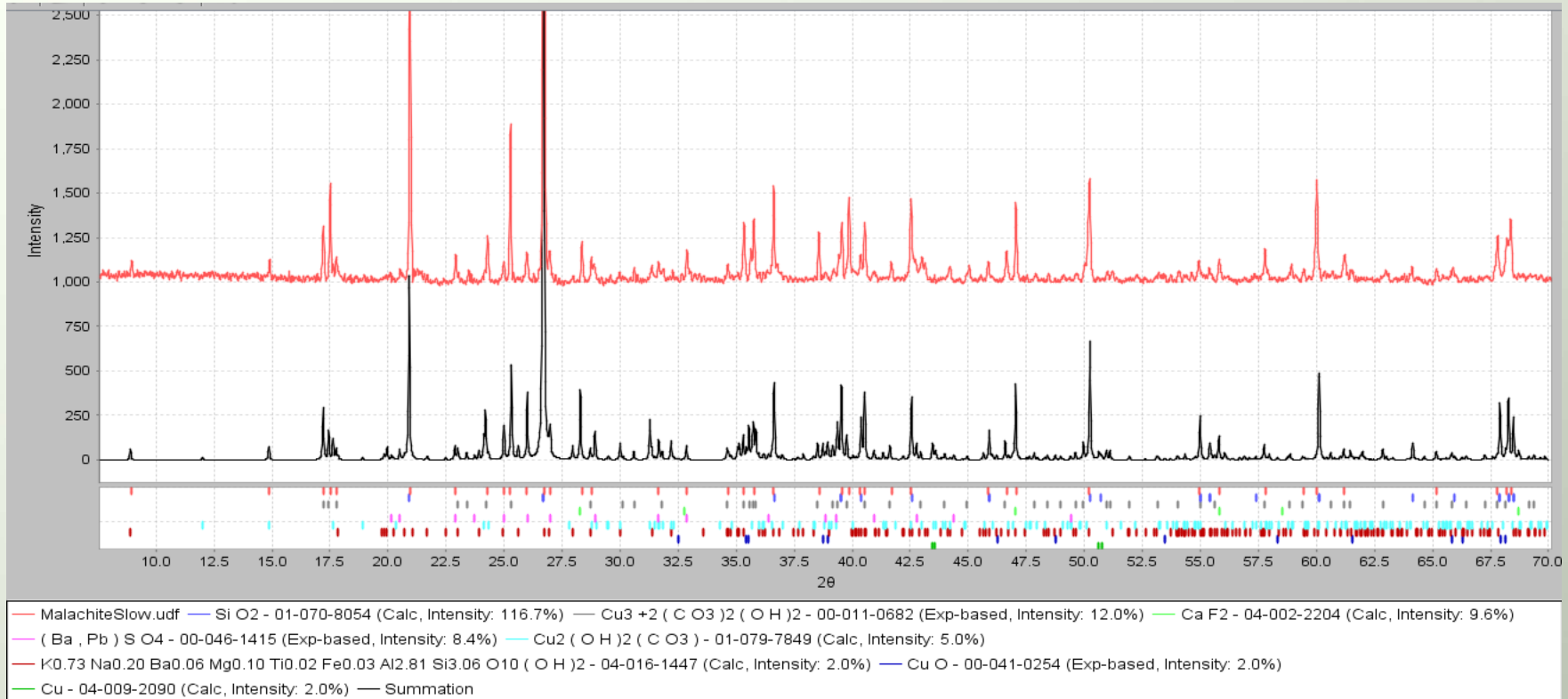
#		PDF #	Compound Name	I Ratio	I %	I/Ic	Est Wt %
1	✓	01-070-8054	Silicon Oxide	1.167	73	3.1	68
2	✓	00-011-0682	Copper Carbonate Hydroxide	0.246	15	1.9*	23
3	✓	04-002-2204	Calcium Fluoride	0.096	6	3.84	4
4	✓	00-046-1415	Barium Lead Sulfate	0.084	5	2.85*	5

The RIR method calculates an estimated concentration based on scaling all data to the intensity of corundum (I/Ic). With ICDD's software this worked well for the major phases shown here, but had trouble with autoscaling the minor phases due to the peak overlap issues. The simulation (black) shown below was based on the automatic RIR scaling



— MalachiteSlow.udf — Si O2 - 01-070-8054 (Calc, Intensity: 116.7%)
 — Cu3 + 2 (C O3)2 (O H)2 - 00-011-0682 (Exp-based, Intensity: 24.6%) — Ca F2 - 04-002-2204 (Calc, Intensity: 9.6%)
 — (Ba , Pb) S O4 - 00-046-1415 (Exp-based, Intensity: 8.4%) — Summation

Pattern Fitting



Pattern fitting was somewhat more successful since scaling can be manually adjusted and minor phases included. In ICDD software the patterns can be summed (black) and compared to the experimental data (red).

Other vendor software such as FULLPAT can shift and adjust patterns to a residual

Quantitation by Pattern Fitting

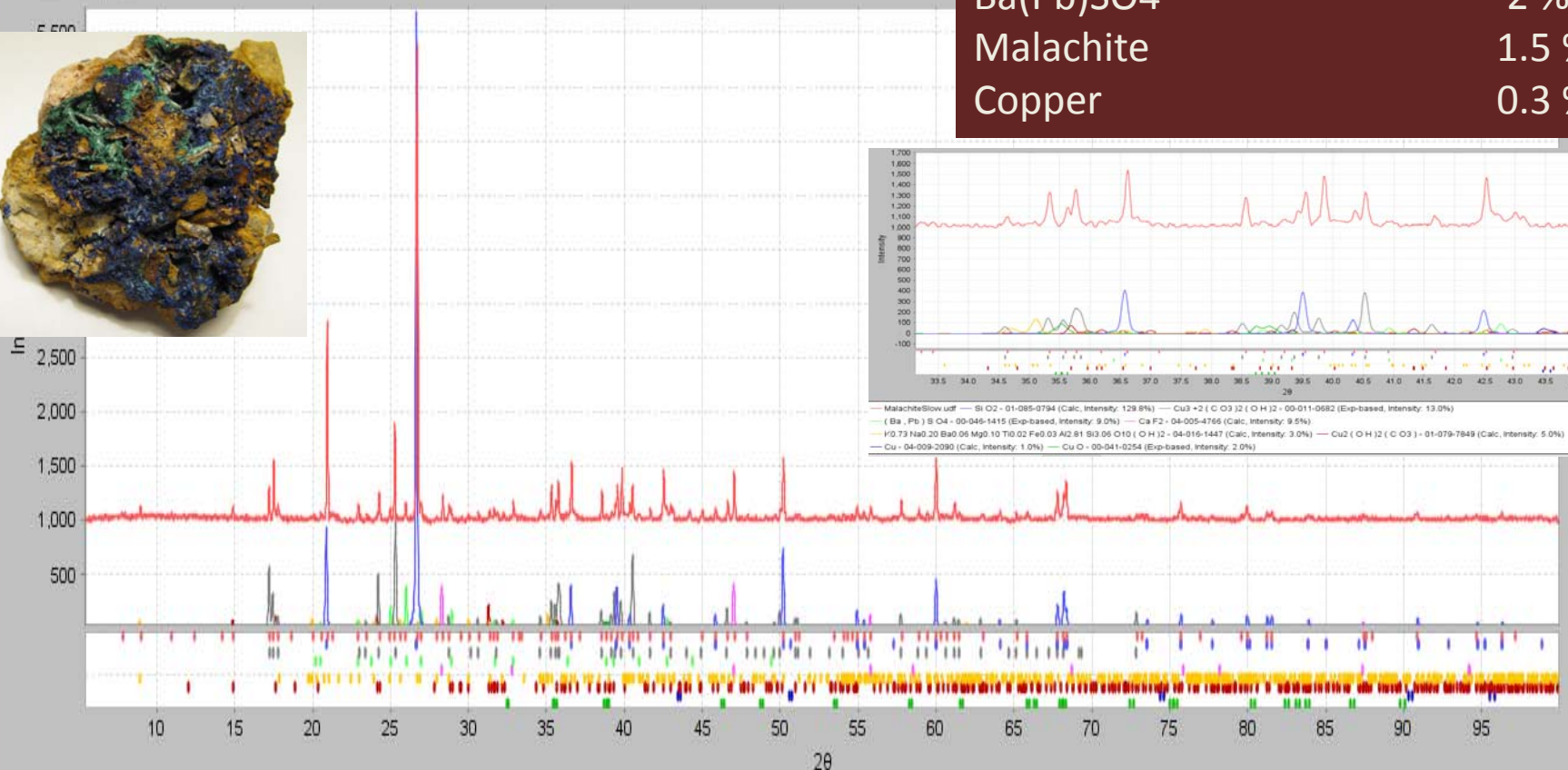
<u>Phase</u>	<u>Pattern Integrated Area</u>	<u>I/Ic</u>	<u>N</u>	<u>wt %</u>	<u>RIR</u>	<u>Rietveld</u>
Quartz	116.7	3.1	37.64	64 %	68 %	71%
Azurite	12.9	1.9	6.78	11.5	23 %	14 %
Muscovite	2.0	0.4	5.00	8.5	4 %	5 %
Copper Oxide	2.0	2.8	0.71	1.2		3.7 %
Flourite	9.6	3.84	2.50	4.2		2.5 %
Ba(Pb)SO ₄	9.4	2.85	3.29	5.6	5 %	2 %
Malachite	5.0	1.74	2.87	4.9		1.5 %
Copper	2.0	8.86	0.22	0.4		0.3 %
			59.01			

I/Ic's for each phase were obtained from the PDF database and used to scale the fitted patterns and normalize the data.

Rietveld Analysis -

Rietveld Analysis was performed by the program HighScore Plus using atomic coordinates from the PDF-4+ database. Rietveld offers the advantage of refining each phase and peak shape

Azurite	14 %
Quartz	71%
Muscovite	5 %
Copper Oxide	3.7 %
Flourite	2.5 %
Ba(Pb)SO ₄	2 %
Malachite	1.5 %
Copper	0.3 %



— MalachiteSlow.udf — Si O₂ - 01-085-0794 (Calc, Intensity: 129.8%) — Cu₃+2 (C O₃)₂ (O H)₂ - 00-011-0682 (Exp-based, Intensity: 23.0%)
 — (Ba , Pb) S O₄ - 00-046-1415 (Exp-based, Intensity: 9.0%) — Ca F₂ - 04-005-4766 (Calc, Intensity: 9.5%)
 — K_{0.73} Na_{0.20} Ba_{0.06} Mg_{0.10} Ti_{0.02} Fe_{0.03} Al_{2.81} Si_{3.06} O₁₀ (O H)₂ - 04-016-1447 (Calc, Intensity: 3.0%) — Cu₂ (O H)₂ (C O₃) - 01-079-7849 (Calc, Intensity: 5.0%)
 — Cu - 04-009-2090 (Calc, Intensity: 1.0%) — Cu O - 00-041-0254 (Exp-based, Intensity: 2.0%)

Quantitative results

In the previous 4 slides three different methods were used for quantitative results but they were not equivalent methods. All three methods identified the major phases. The automated RIR method had some difficulty with minor phases because of peak overlap whereas the other two methods were somewhat more robust since they both used full pattern data. The Rietveld technique was more rigorous than pattern fitting since the data were fit *and refined*.

The intent was to demonstrate that the reference databases can support various quantitative methods of analysis.

Reference on quantitative methods:

Madsen, I. C., Scarlett, N.V.Y., and Kern, A. (2011), "Description and survey of methodologies for the determination of amorphous content via X-ray powder diffraction", Z. Krist., 226, pp. 944-955.

Summary

- Because of the difficulties in obtaining and preparing samples mineral analyses can often be difficult
- Specimen preparation is key to obtaining good results
- There is an array of database and pattern fitting software tools that can help analyze complex multiphase mineral specimens both qualitatively and quantitatively.