ADVANCED MINERAL ANALYSES BY X-RAY POWDER DIFFRACTION

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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

Whats new in X-ray diffraction

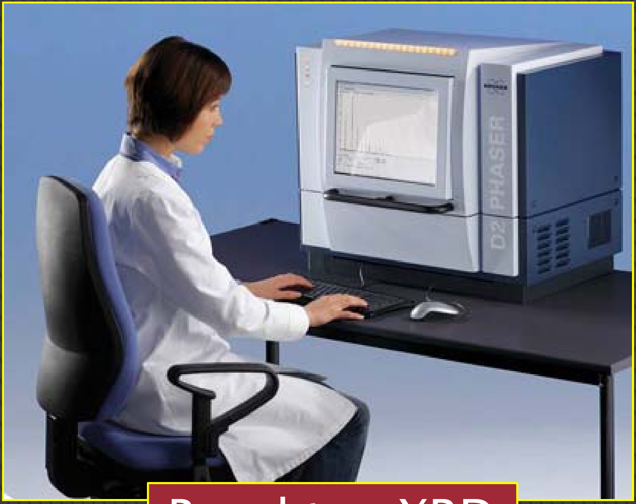
- Miniaturized sources
- Energy selective detectors
- Low noise, high dynamic range detectors
- Sophisticated self-aligning optics
- More 2D detectors (texture, particle distributions)
- Improved efficiency multilayer optics
- Growth of worldwide synchrotron facilities and their user communities

Enabling New Instruments for exploration and analysis

Handheld XRF

XRD and XRF on Mars

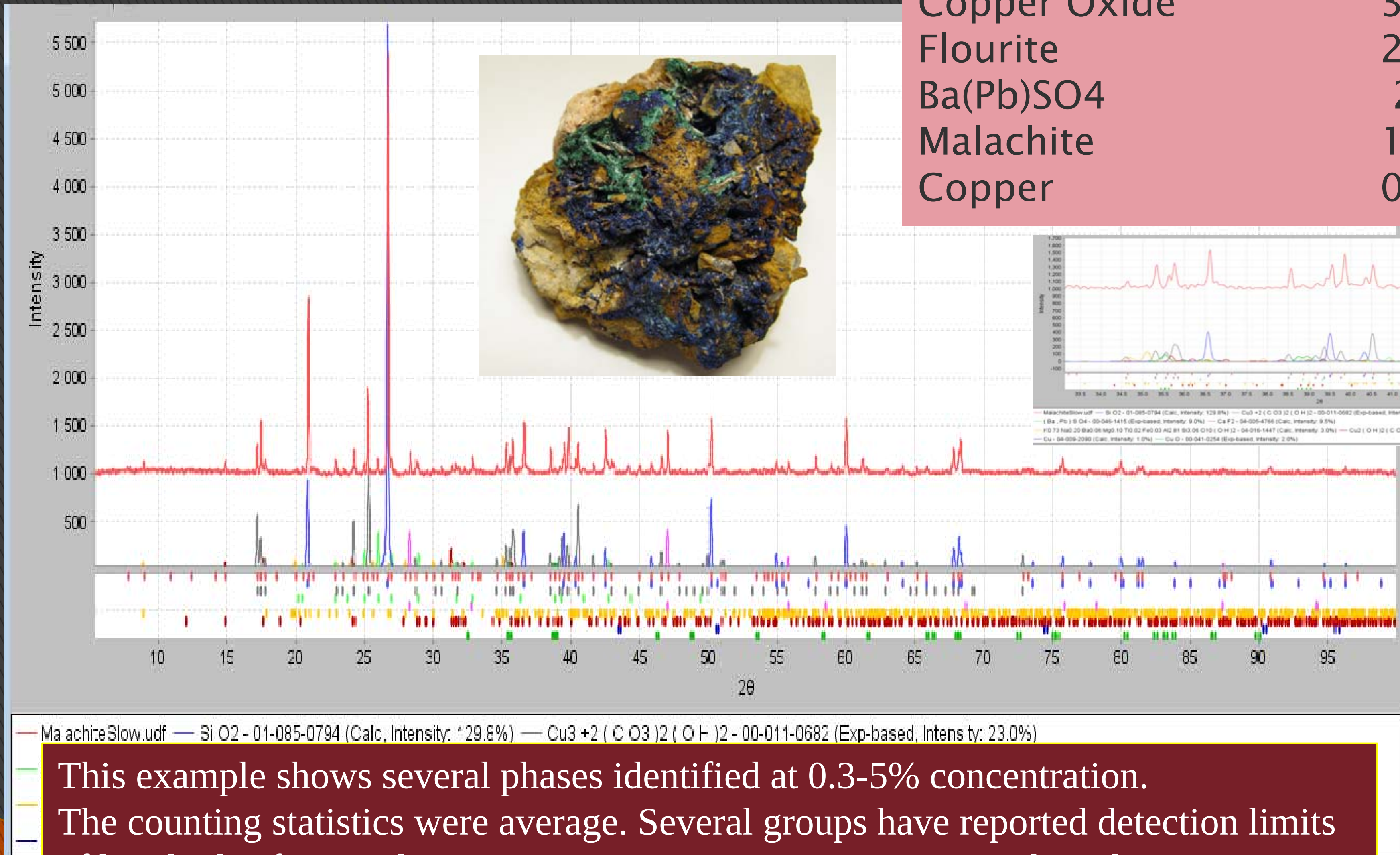
Portable XRD



Benchtop XRD

Enabling new limits of detection and analysis

Azurite	14%
Quartz	71%
Muscovite	5 %
Copper Oxide	3.7%
Flourite	2.5%
Ba(Pb)SO4	2 %
Malachite	1.5 %
Copper	0.3 %

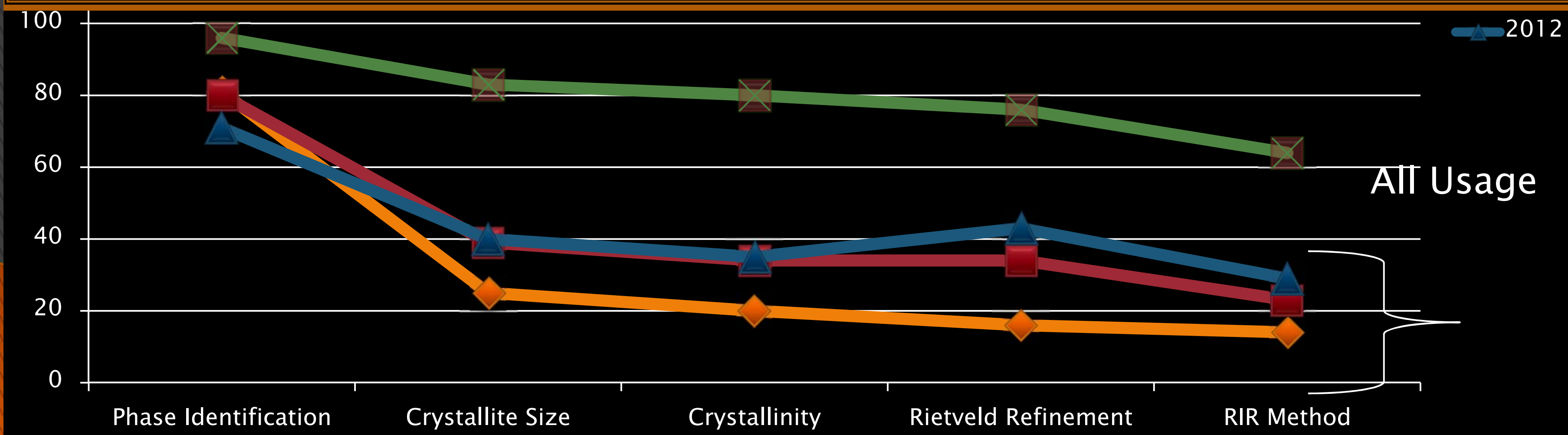


This example shows several phases identified at 0.3-5% concentration. The counting statistics were average. Several groups have reported detection limits of hundreds of ppm when using superior counting statistics such as those provided by modern position sensitive detectors and/or the use of high flux X-ray sources (rotating anodes, synchrotrons).

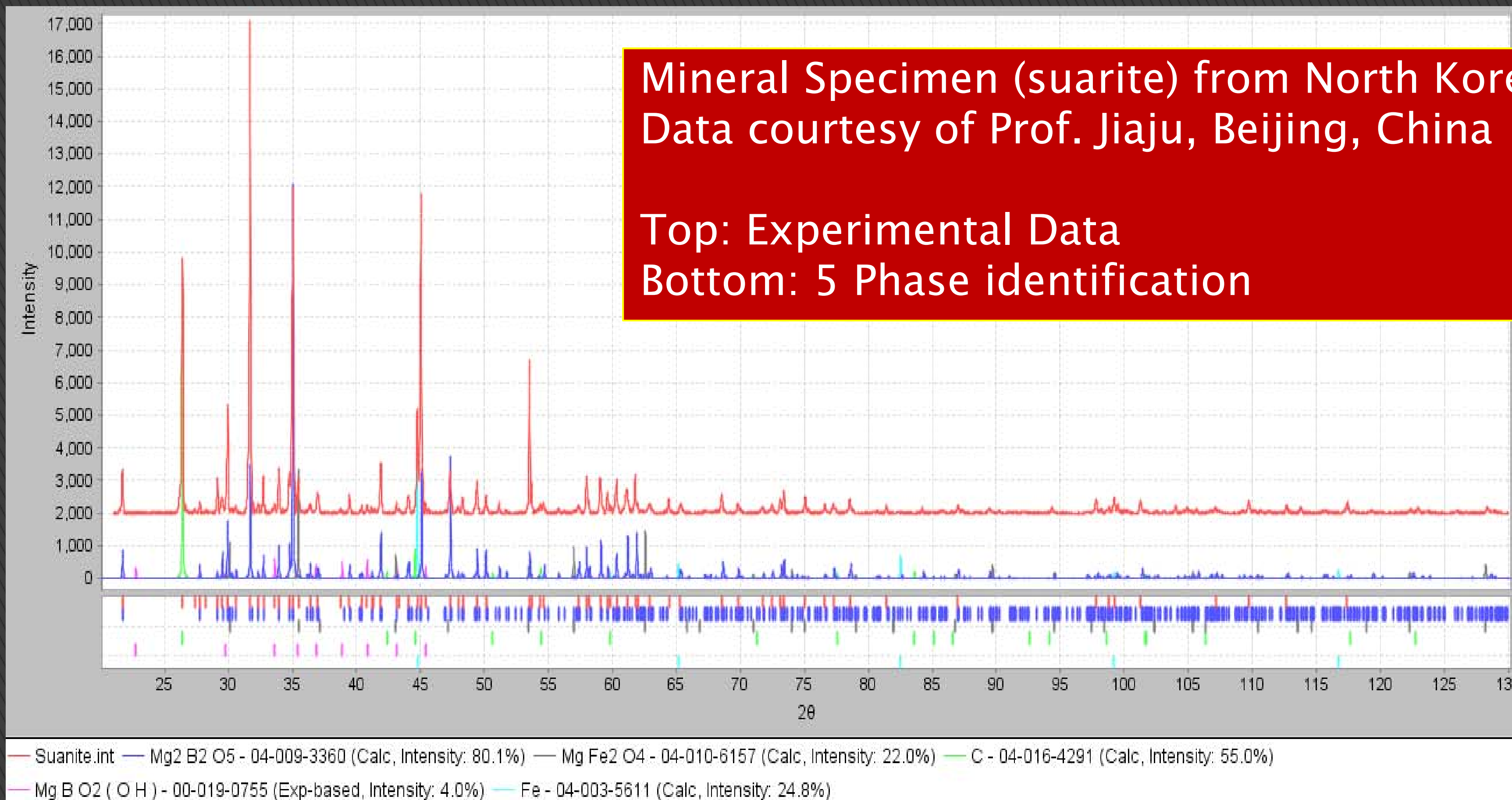
Powerful Personal Computers – *Better Analysis Programs*

- Rietveld Refinement is commonplace
- Whole pattern fitting methods (LeBail, FullPAT, FULLPROF, GSAS, PONCKS)
- Pair Distribution Function Analyses
- Modulated structure analyses
- Complex multivariant analyses

ICDD Global Users Survey – 2006, 2009 and 2012



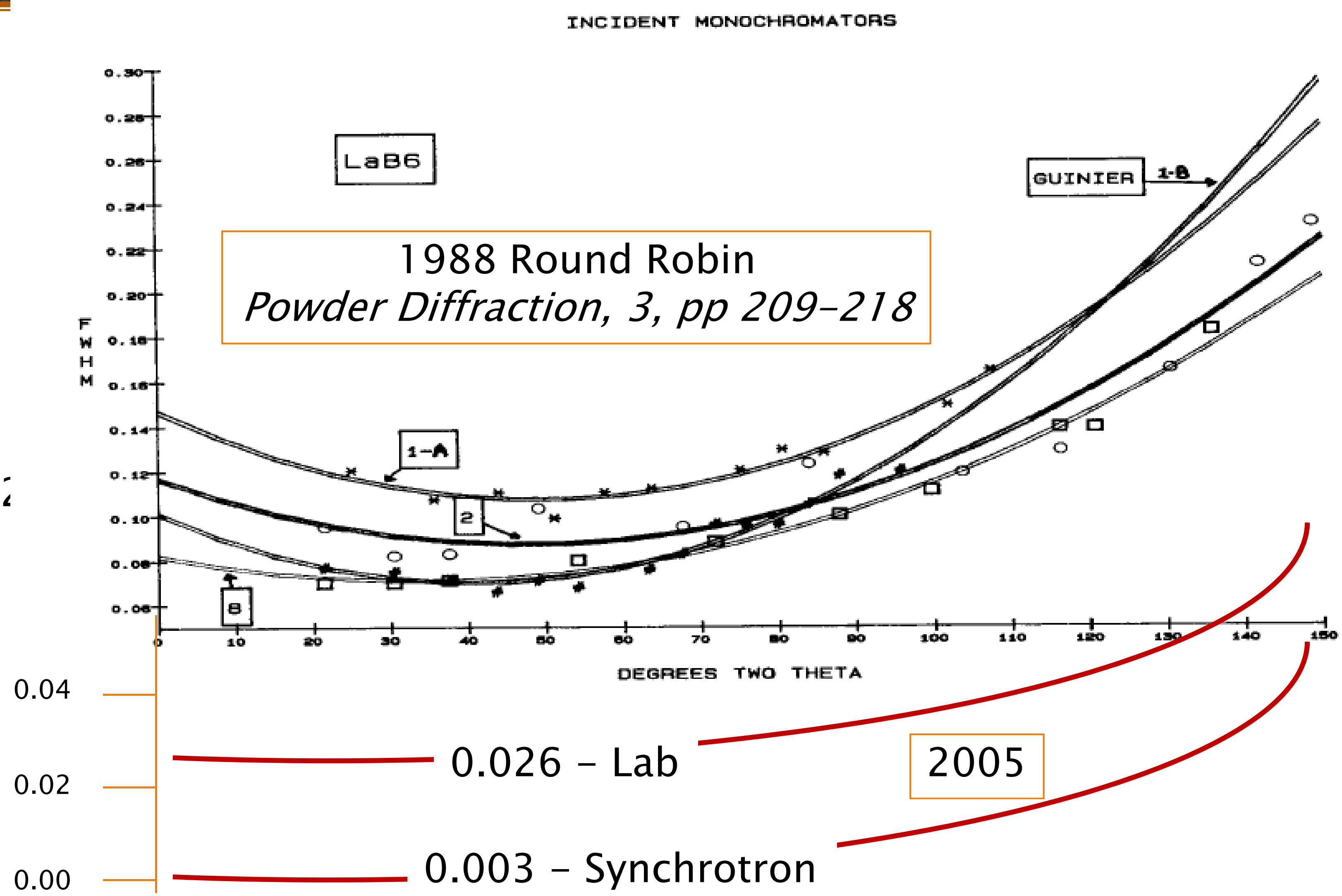
Better Data and analysis tools



Mineral Specimen (suarite) from North Korea
Data courtesy of Prof. Jiaju, Beijing, China

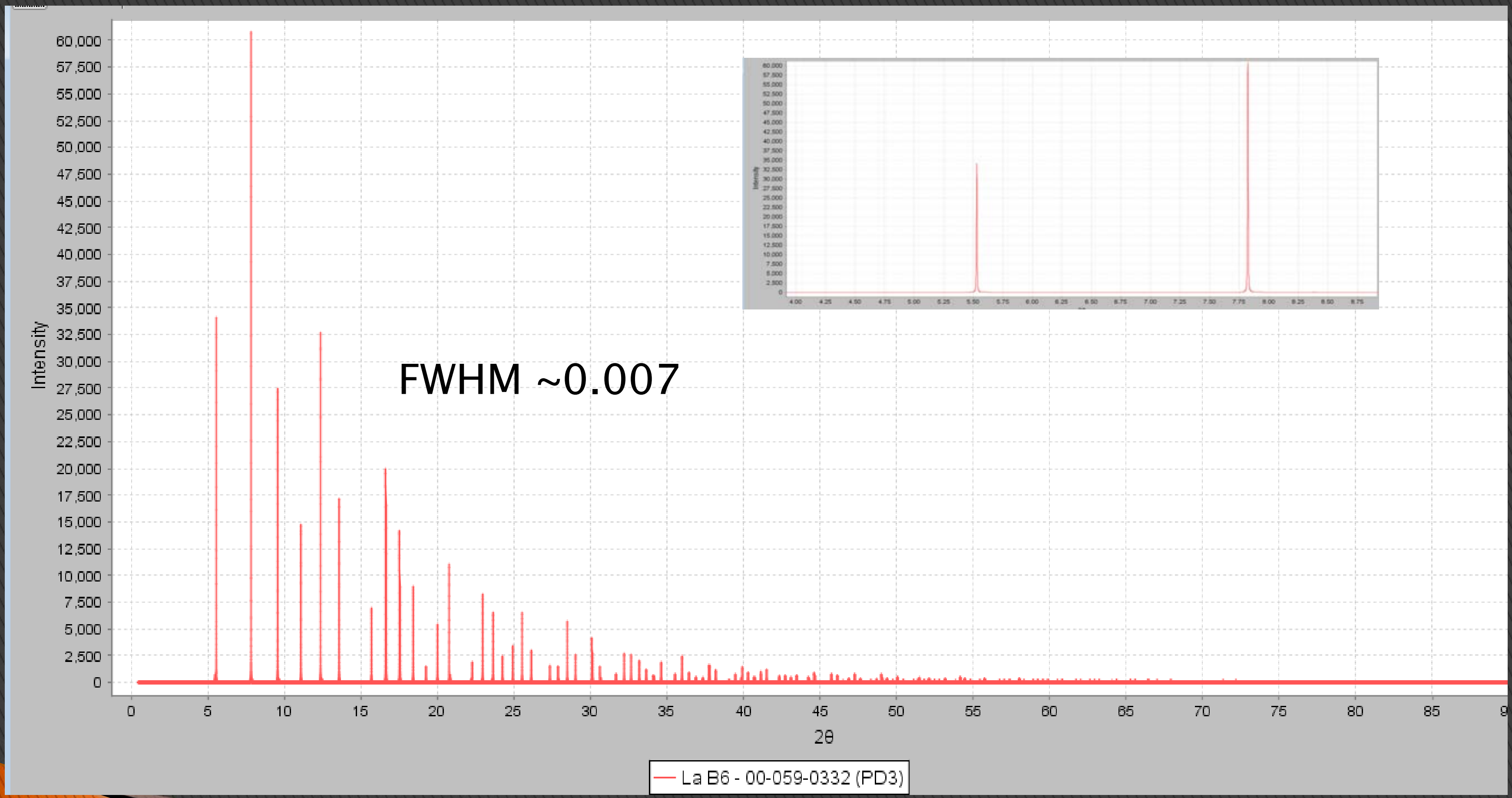
Top: Experimental Data
Bottom: 5 Phase identification

Instrumental Peak Resolution LaB6 – Better optics and detectors

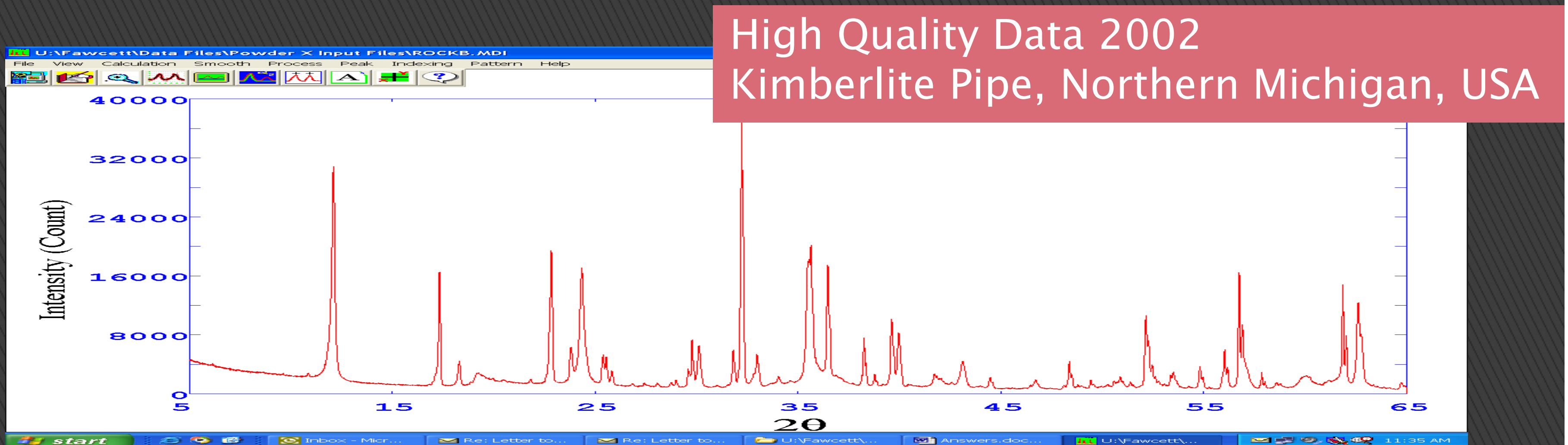


Experimental Data – LaB6, 2009

Brian Toby, Argonne National Light Source

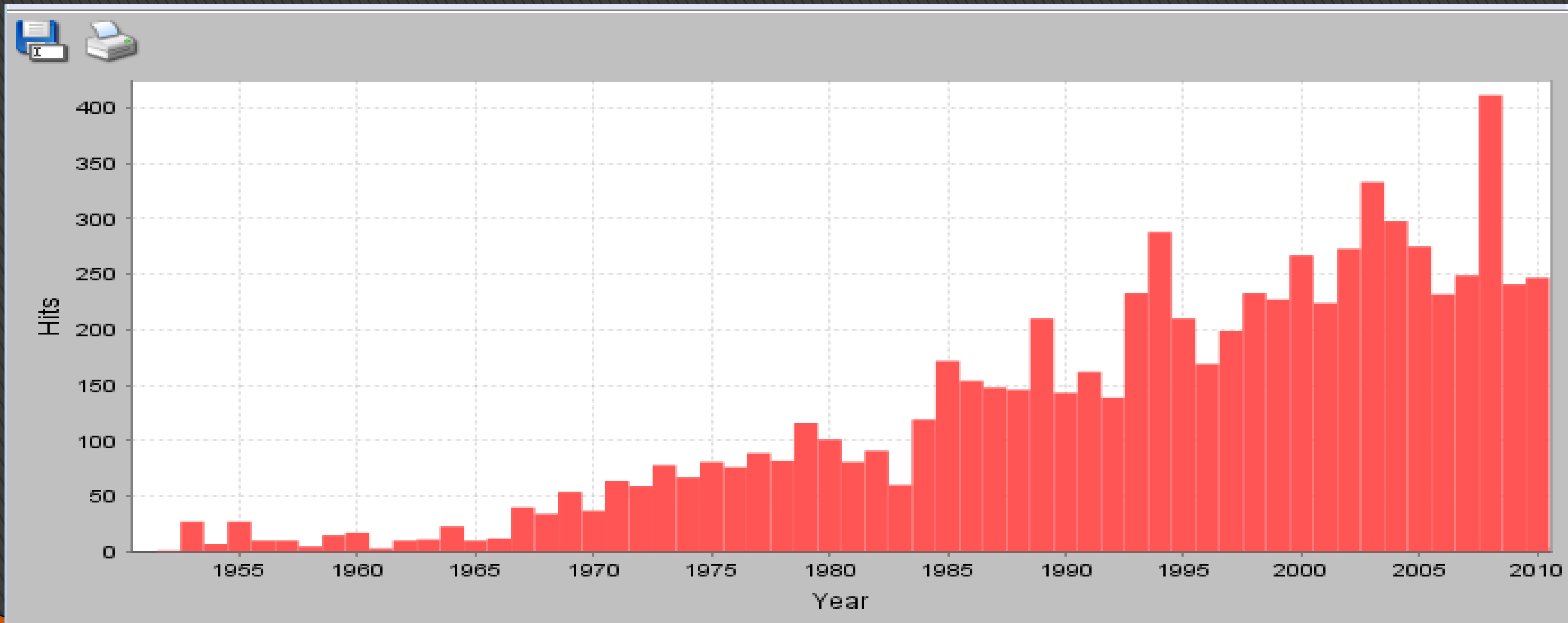


Laboratory Data



Star Quality (Highest quality) Mineral Data in the PDF by year

XRD is a “fingerprint” technique the specimen is always compared to a reference. The highest quality reference data have been produced with modern methods and instrumentation.



41 % of the highest quality data are new since the year 2000

Whats new in XRD analyses of minerals

- Higher quality reference data
- More data
- Better experimental data (optics,sources)
- High efficiency, energy selective, position sensitive detectors
- Improved methods of analysis

Database – Growth with growth in technology

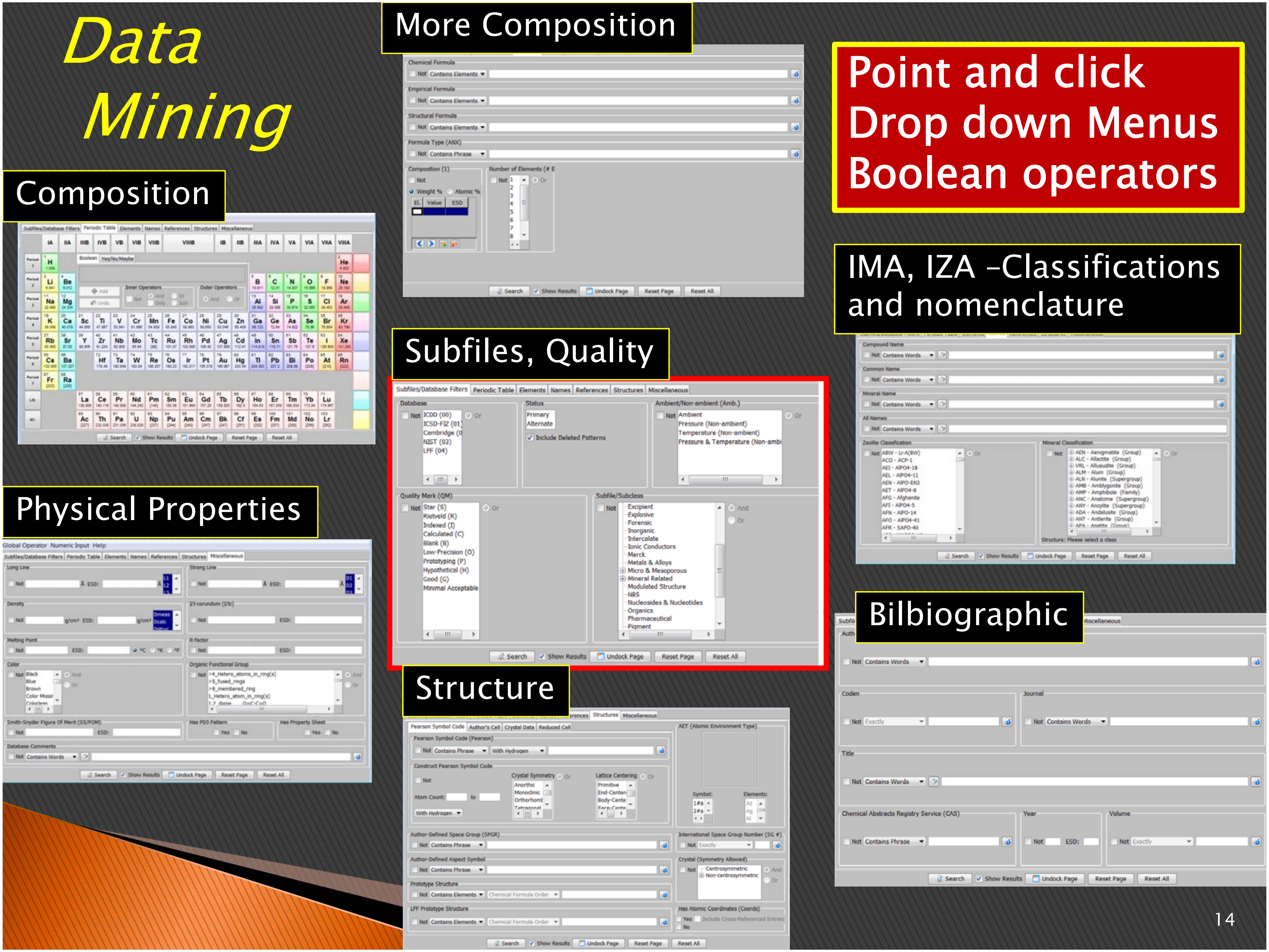
Growth of quality data references based on better experimental data

All entries expressed as digital patterns to enable whole pattern fitting methods

All calculated digital patterns can be adjusted for instrument function and crystallite size including X-ray, neutron, electron and synchrotron diffraction – This enables the study of nanomaterials.

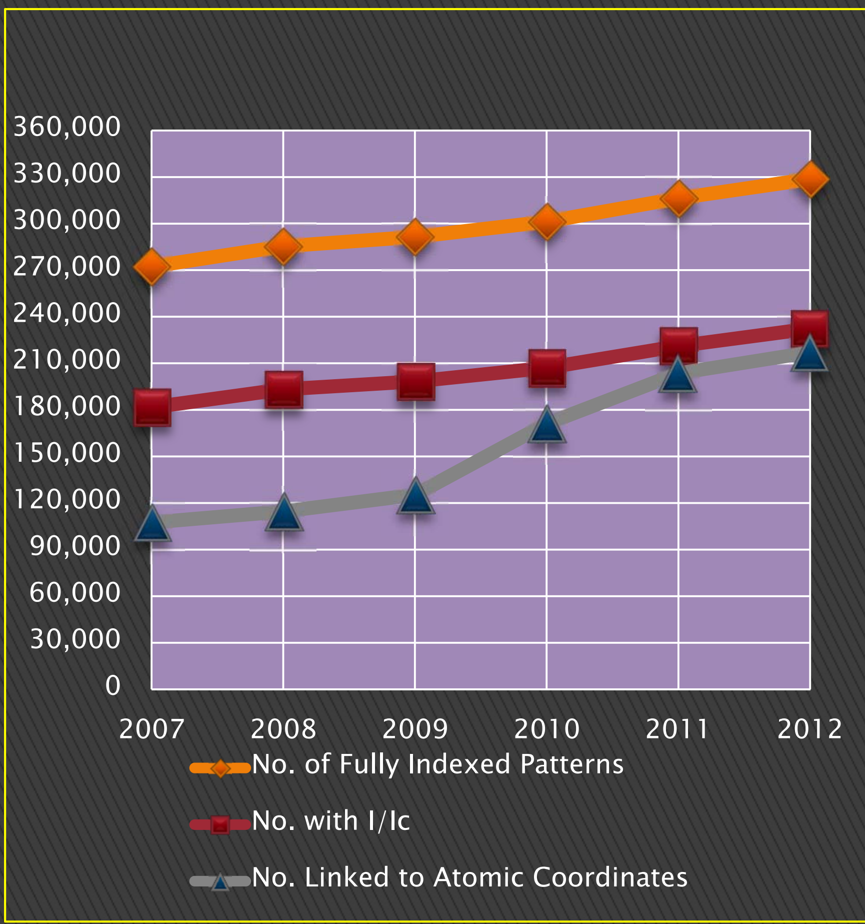
Addition of non-crystalline reference materials experimental patterns
 – clays

Addition of data mining capability and software for improved phase identification and quantitative analysis by multivariate analysis

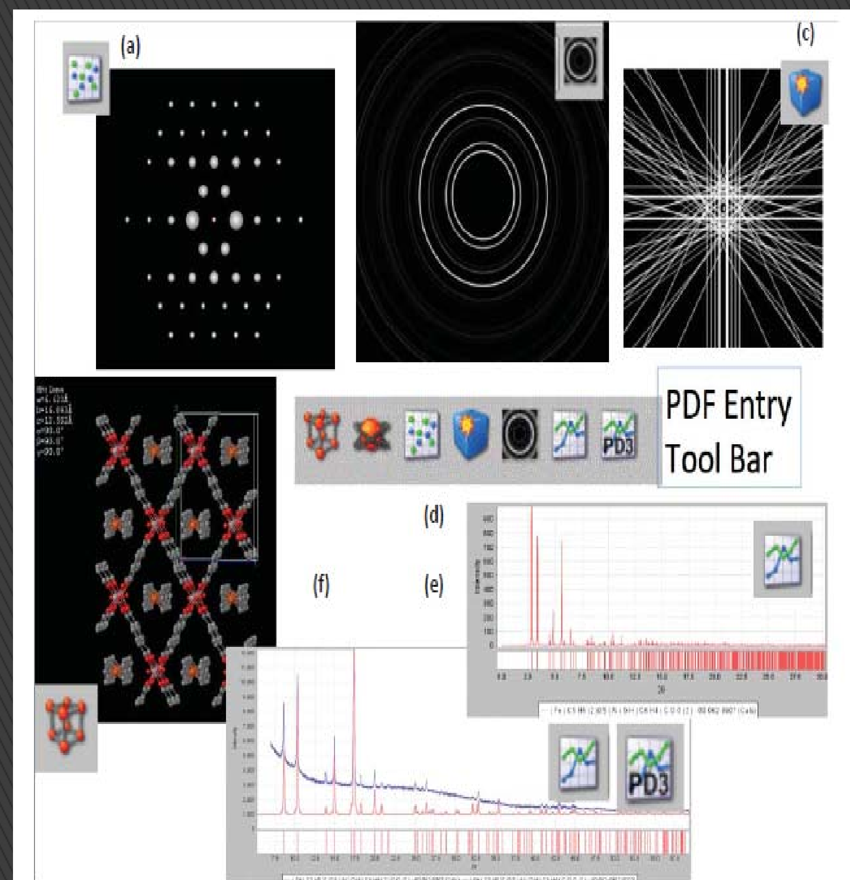

Data
Mining
Composition
More Composition
Point and click
Drop down Menus
Boolean operators
IMA, IZA –Classifications
and nomenclature
Subfiles, Quality
Physical Properties
Structure
Bilbiographic

Structural Information in PDF-4+

Quantitative Analysis



Simulations

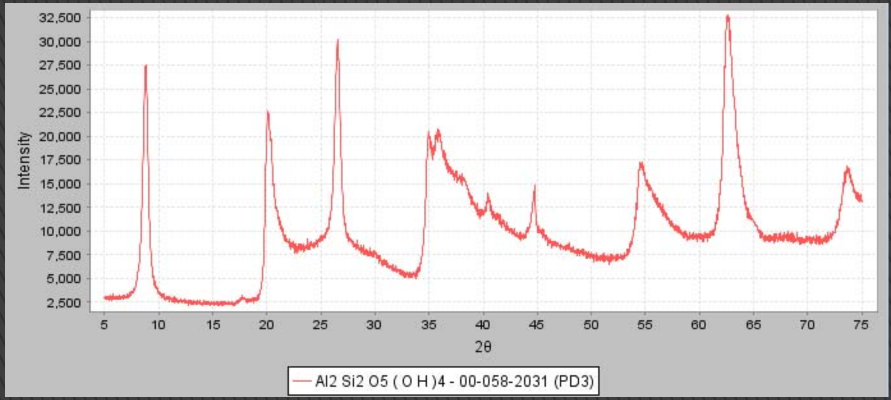


Basic Mineral Content in the PDF

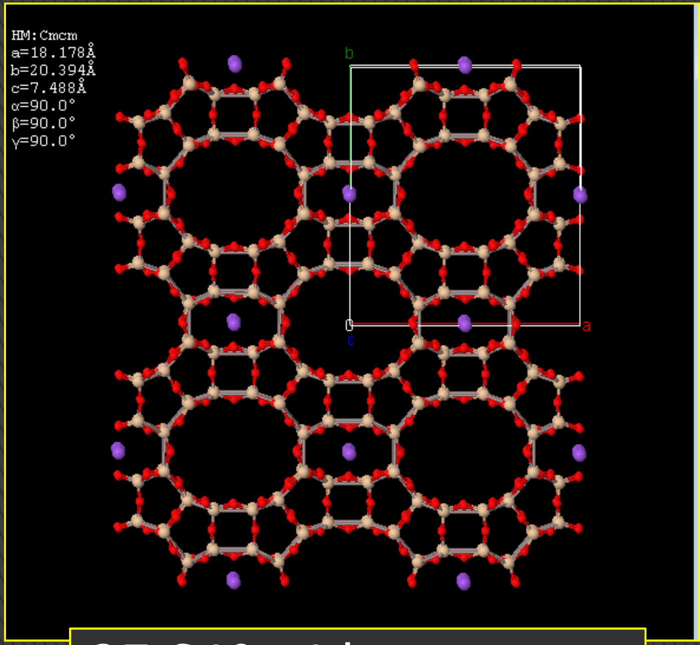
Minerals and Related Materials – 39,410 Entries
all entries have digital patterns

Bibliographic Data

No. of References	48,279
No. of Journals	1,137
No. of Authors	20,686
No. of Titles	28,474



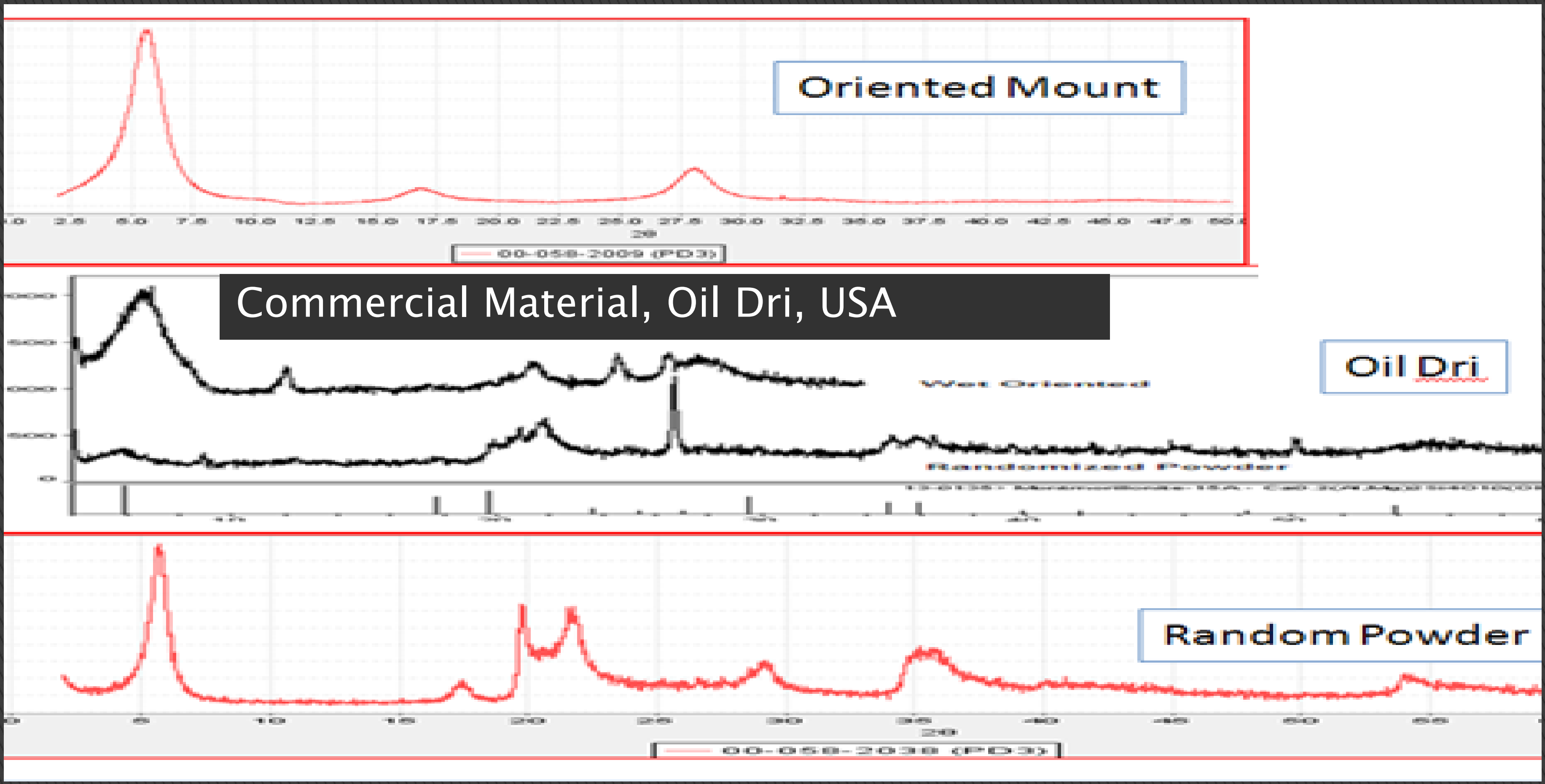
92 experimental PD3 patterns – mostly clays



27,649 with structures

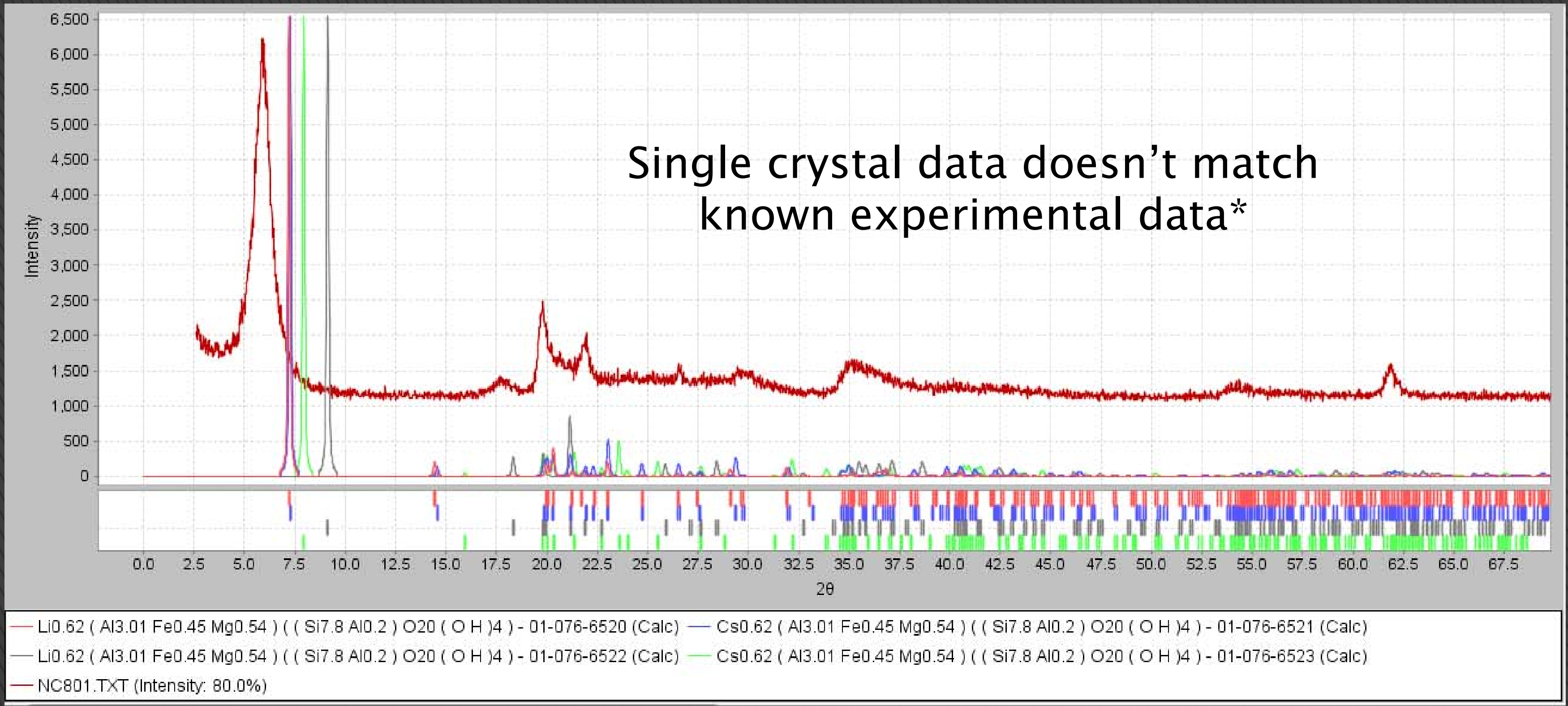
Case Studies

Identification of commercial absorbents montmorillonite and quartz



Clays from the Penn State Univ collection

Comparison of experimental data to 4 calculated data sets from four published structures of montmorillonite

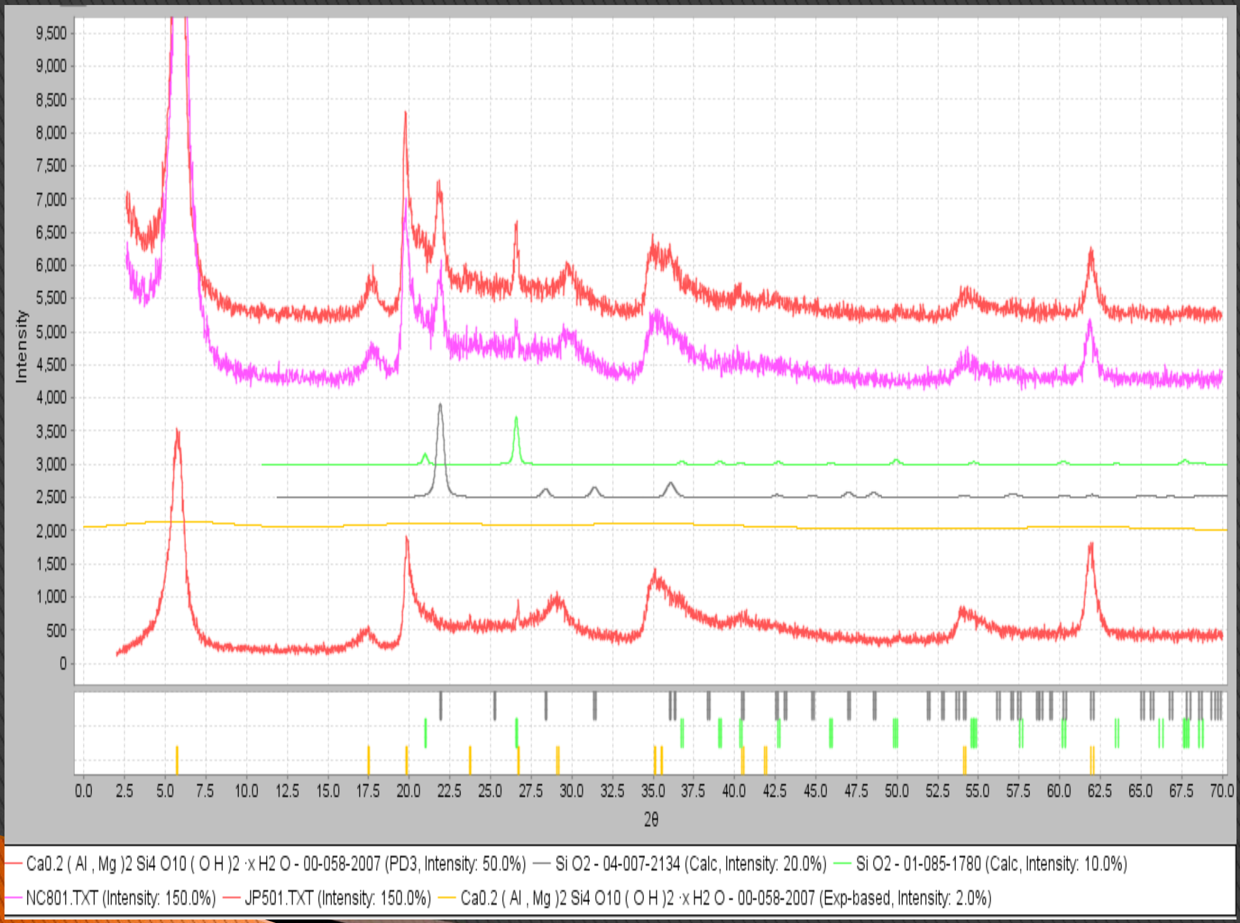


* The reference publications for the structures of montmorillonite detail extensive treatments used to induce crystallinity and refine the structure. It is the opinion of many experts that these results are not accurate representations of the mineral.

Method – Analysis of a 3 phase sample of montmorillonite, from Northern China

- Match the montmorillonite
  Use the best experimental digital pattern for montmorillonite – 19 choices
- Use calculated patterns, adjusted for crystallite size, for quartz and cristobalite

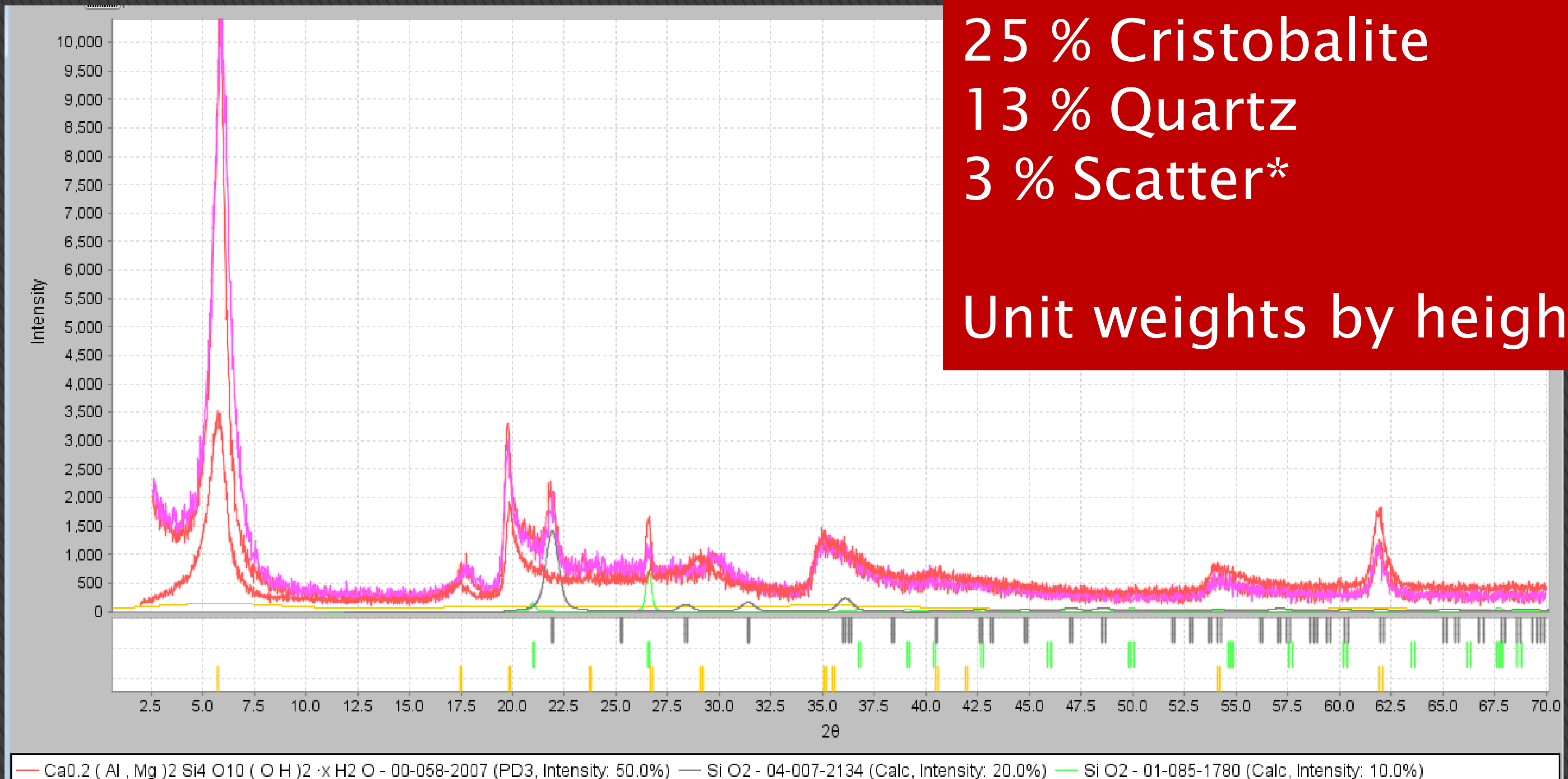
Scaled components – separated



Experimental Data

Components of the model simulation

Components

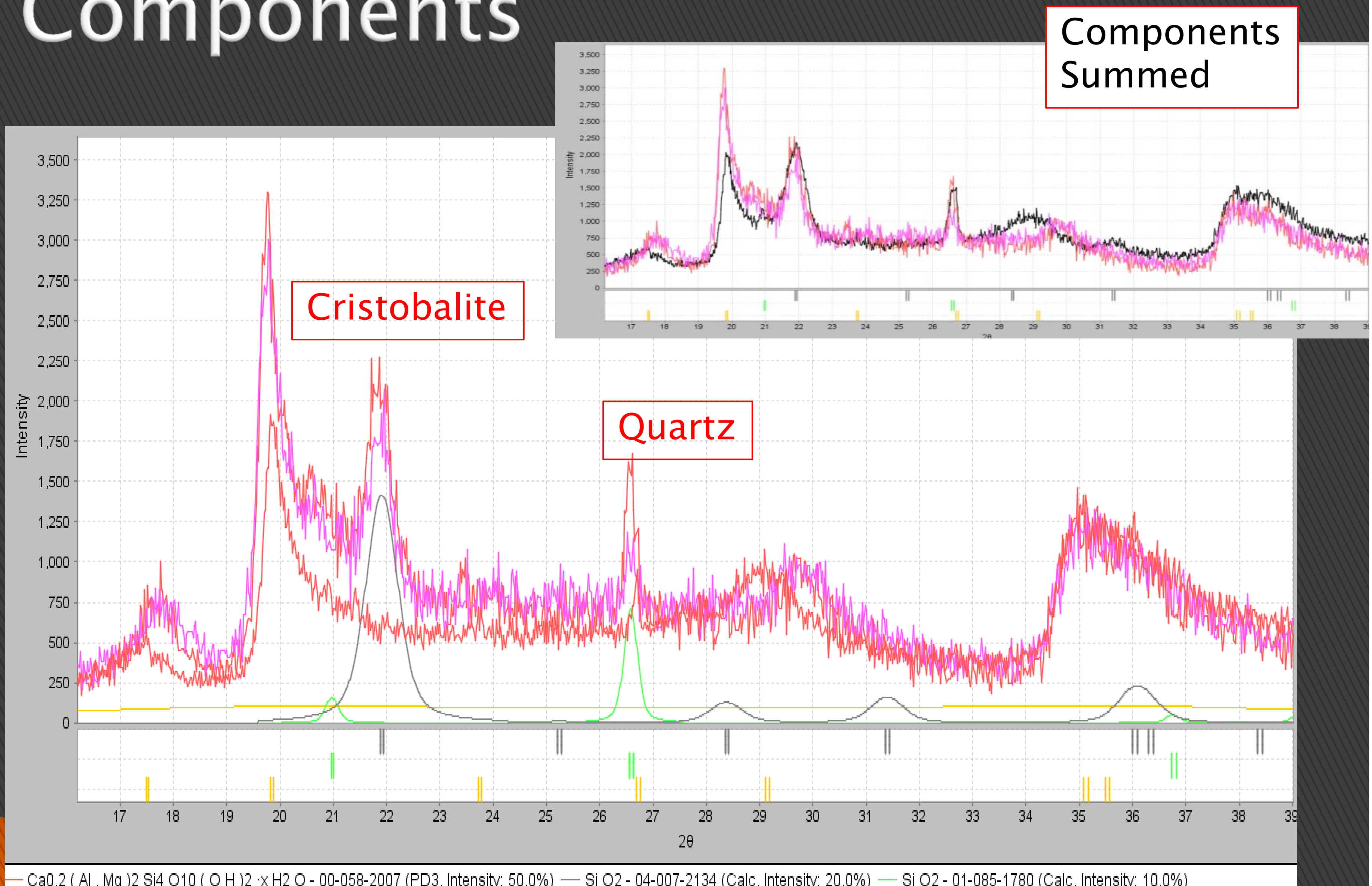


64 % Montmorillonite
25 % Cristobalite
13 % Quartz
3 % Scatter*

Unit weights by height

* A scatter function was used to adjust background levels. A more accurate representation could be made using a 2D scatter simulation for montmorillonite. X-ray diffraction from two dimensional crystals, such as montmorillonite and other minerals in the smectite group, is described by Brindley and Brown, (1980) "*Crystal Structures of Clay Minerals and their X-ray Identification*", published by The Mineralogical Society, London, UK. The program DIFFax can simulate layer stacking.
http://www.public.asu.edu/~mtreacy/DIFFaX.html

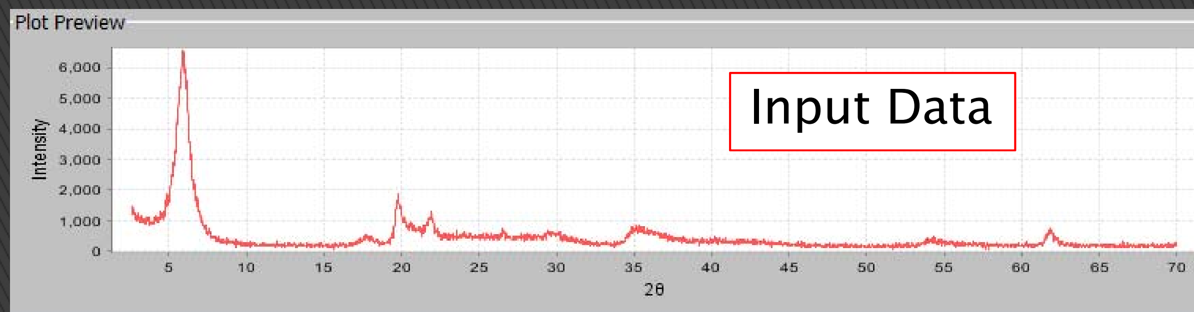
Components



Components Summed
Cristobalite
Quartz
Intensity
2θ
Ca0.2 (Al , Mg)2 Si4 O10 (O H)2 ·x H2 O - 00-058-2007 (PD3, Intensity: 50.0%)
Si O2 - 04-007-2134 (Calc, Intensity: 20.0%)
Si O2 - 01-085-1780 (Calc, Intensity: 10.0%)

Method Details

Match the best montmorillonite – use a similarity index to compare experimental data to all references



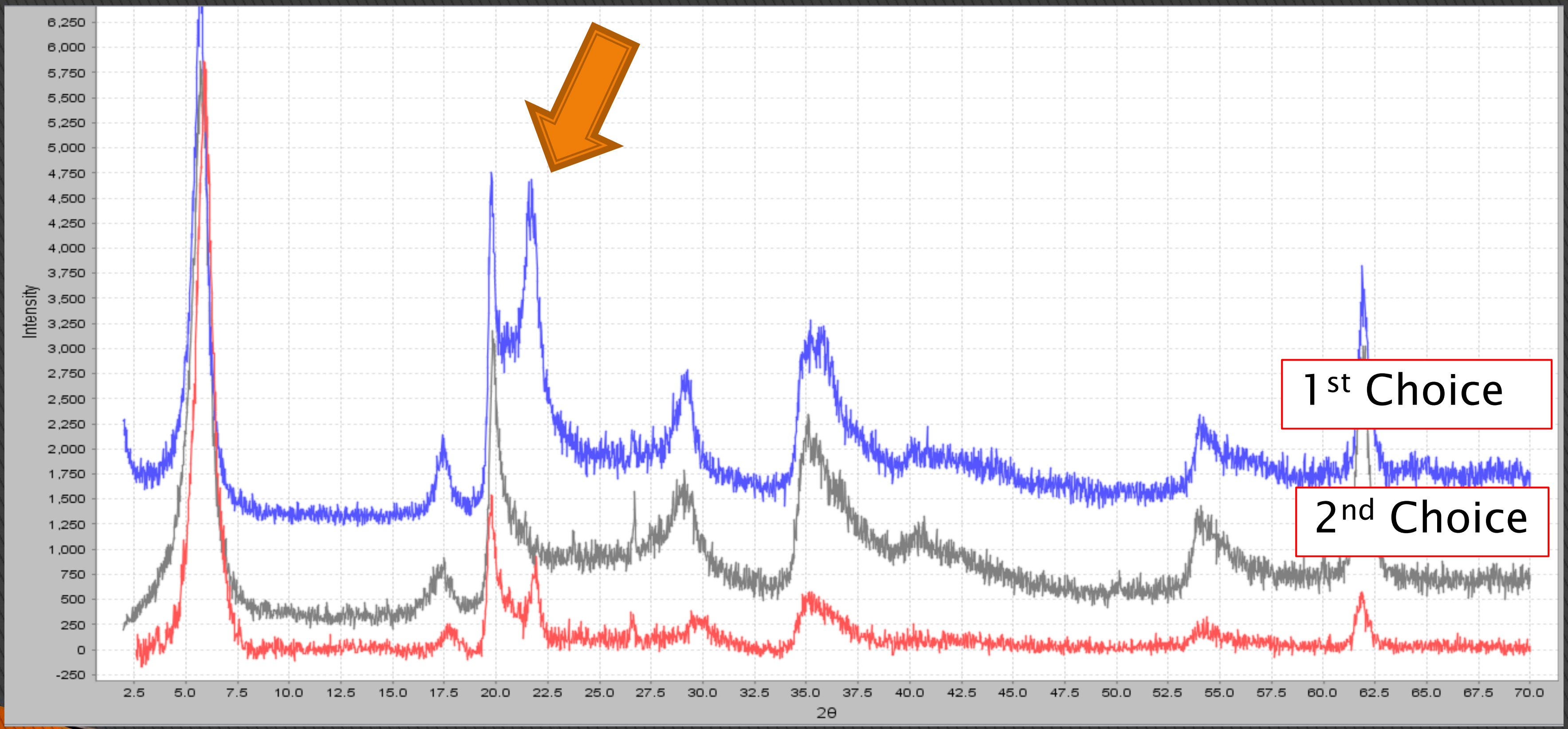
Match quality

Normalized R-index	PDF #	QM	Mineral Name	Chemical Formula	Compound Name	Coords	D1	D2	D3	SYS	Year
1.12 *(2.60° - 70.00°)*	00-058-2038	B	Montmorillonite, calcian	(Ca , Na)0.3 Al2 (Si , Al)4 O10 (...	Calcium Sodium Aluminum Silicate H...		15.445900	4.483360	4.115850	M	1983
1.16 *(2.60° - 70.00°)*	00-058-2007	B	Montmorillonite-calcian	Ca0.2 (Al , Mg)2 Si4 O10 (O H)2 ·...	Calcium Magnesium Aluminum Silicat...		15.432400	4.475070	1.496970	H	1983
1.22 *(2.60° - 70.00°)*	00-060-0318	B	Montmorillonite	(Ca , Na)0.3 Al2 (Si , Al)4 O10 (...	Sodium Calcium Aluminum Silicate H...		14.024500	4.475970	2.491340	M	1983
1.31 *(2.60° - 56.88°)*	00-060-0319	B	Montmorillonite, oriented	(Ca , Na)0.3 Al2 (Si , Al)4 O10 (...	Sodium Calcium Aluminum Silicate H...		15.628900	3.103580	5.140480	M	1983
1.37 *(2.60° - 55.64°)*	00-058-2009	B	Montmorillonite-calcian	Ca0.2 (Al , Mg)2 Si4 O10 (O H)2 ·...	Calcium Magnesium Aluminum Silicat...		15.673300	3.173450	5.258910	H	1983
1.38 *(2.60° - 57.96°)*	00-058-2008	B	Montmorillonite-calcian	Ca0.2 (Al , Mg)2 Si4 O10 (O H)2 ·...	Calcium Magnesium Aluminum Silicat...		15.853200	3.068780	5.149970	H	1983
1.44 *(2.60° - 70.00°)*	00-058-2010	B	Montmorillonite	Na0.3 (Al , Mg)2 Si4 O10 (O H)2 ·...	Sodium Aluminum Magnesium Silicat...		12.522800	3.118450	4.452390	O	1983
1.55 *(2.60° - 70.00°)*	00-060-0315	B	Montmorillonite-Na	(Na , Ca)0.3 Al2 (Si , Al)4 O10 (...	Sodium Calcium Aluminum Silicate H...		3.148310	12.478600	4.465480	M	1983
1.62 *(2.60° - 58.14°)*	00-060-0316	B	Montmorillonite, glycolated	(Na , Ca)0.3 Al2 (Si , Al)4 O10 (...	Sodium Calcium Aluminum Silicate H...		17.108600	3.385200	8.545640	M	1983
1.62 *(2.60° - 58.20°)*	00-060-0320	I	Montmorillonite, glycolated, oriented	(Ca , Na)0.3 Al2 (Si , Al)4 O10 (...	Sodium Calcium Aluminum Silicate H...		17.003200	3.399160	8.560500	M	1983
1.65 *(2.60° - 41.92°)*	00-058-2041	B	Montmorillonite, calcian, heated	(Ca , Na)0.3 Al2 (Si , Al)4 O10 (...	Calcium Sodium Aluminum Silicate H...		18.521700	4.476190	7.301200	H	1983
1.74 *(2.60° - 53.12°)*	00-058-2011	B	Montmorillonite	Na0.3 (Al , Mg)2 Si4 O10 (O H)2 ·...	Sodium Aluminum Magnesium Silicat...		12.803800	3.164290	6.232400	O	1983
1.75 *(2.60° - 53.34°)*	00-058-2039	B	Montmorillonite, calcian	(Ca , Na)0.3 Al2 (Si , Al)4 O10 (...	Calcium Sodium Aluminum Silicate H...		12.722800	3.120050	6.246850	M	1983
1.83 *(2.60° - 42.82°)*	00-058-2012	B	Montmorillonite, glycolated	Na0.3 (Al , Mg)2 Si4 O10 (O H)2 ·...	Sodium Aluminum Magnesium Silicat...		21.928900	4.854450	7.952340	O	1983
1.82 *(2.60° - 42.74°)*	00-058-2040	B	Montmorillonite, calcian, glycolated	(Ca , Na)0.3 Al2 (Si , Al)4 O10 (...	Calcium Sodium Aluminum Silicate H...		21.633500	4.874830	7.940240	M	1983
1.83 *(2.60° - 42.72°)*	00-058-2029	B	Montmorillonite, calcian, glycolated	Ca0.2 (Al , Mg)2 Si4 O10 (O H)2 ·...	Calcium Magnesium Aluminum Silicat...		21.517500	4.888960	7.932430	X	1983
1.94 *(2.60° - 57.32°)*	00-060-0321	B	Montmorillonite, heated, oriented	(Ca , Na)0.3 Al2 (Si , Al)4 O10 (...	Sodium Calcium Aluminum Silicate H...		9.737700	3.192940	4.808500	M	1983
1.95 *(2.60° - 57.30°)*	00-058-2013	B	Montmorillonite, heated	Na0.3 (Al , Mg)2 Si4 O10 (O H)2 ·...	Sodium Aluminum Magnesium Silicat...		9.803470	3.188360	4.843400	O	1983
1.96 *(2.60° - 57.36°)*	00-060-0317	I	Montmorillonite, heated, oriented	(Na , Ca)0.3 Al2 (Si , Al)4 O10 (...	Sodium Calcium Aluminum Silicate H...		3.193730	9.624450	4.790210	M	1983

Library of References

Similarity Index Matches

Note: 1st choice also matched cristobalite impurity so we used the second choice without the impurity

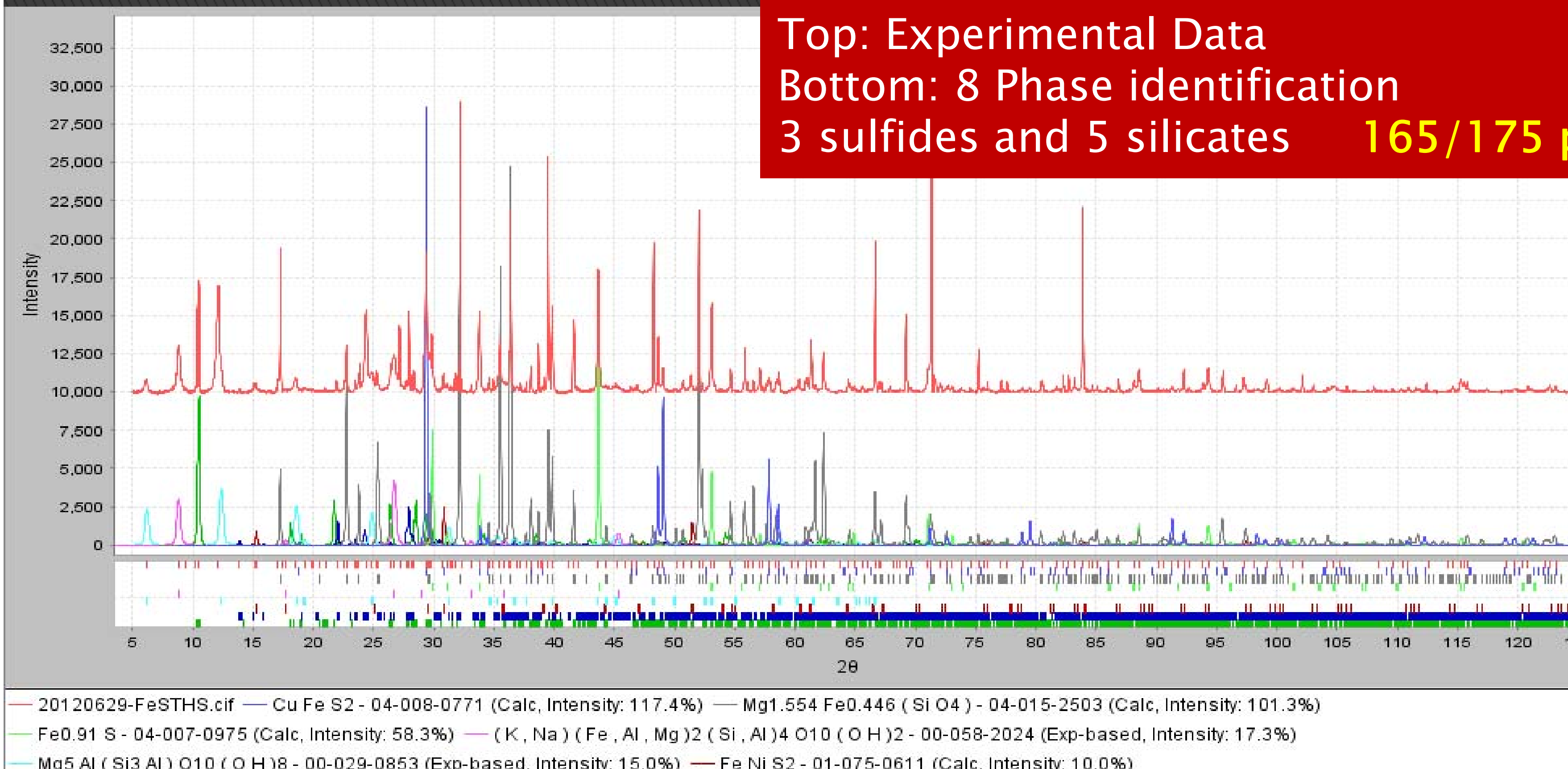


Mine Specimens

Phase identification

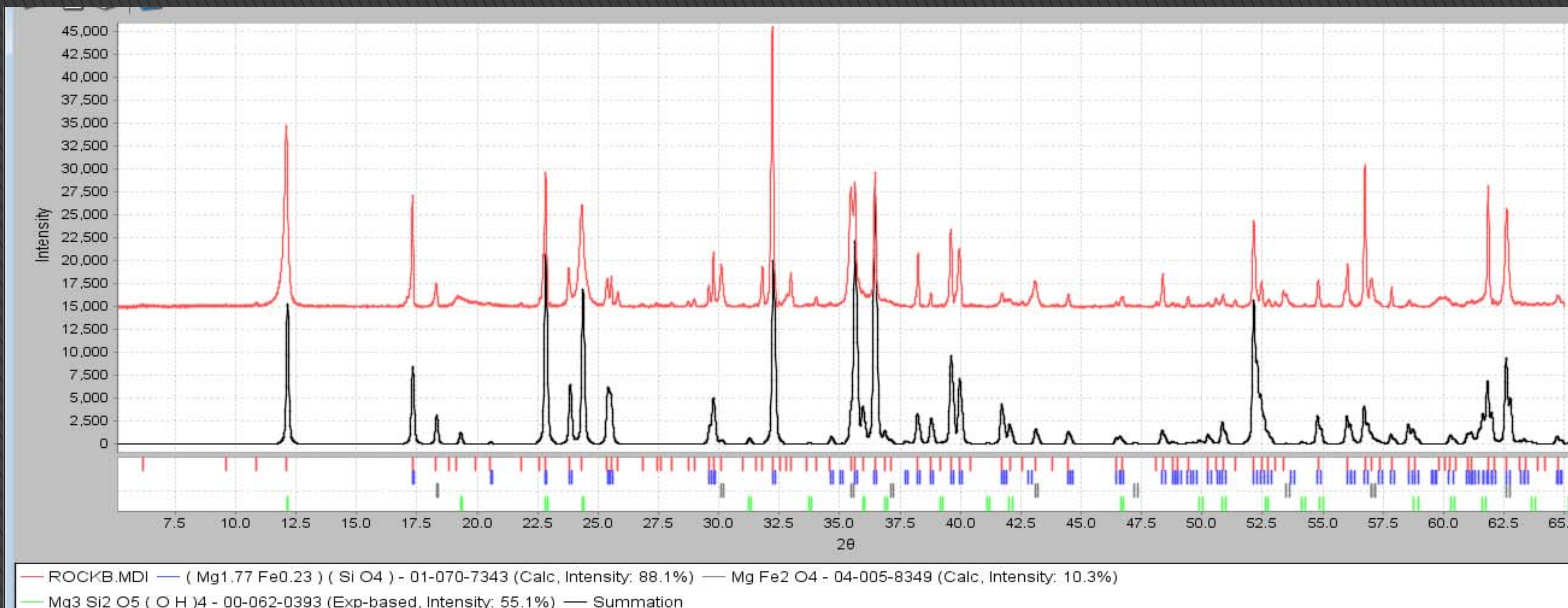
Mineral Specimen from Xinjiang Gold Mine
Data courtesy of Prof. Jiaju, Beijing, China

Top: Experimental Data
Bottom: 8 Phase identification
3 sulfides and 5 silicates 165/175 peaks

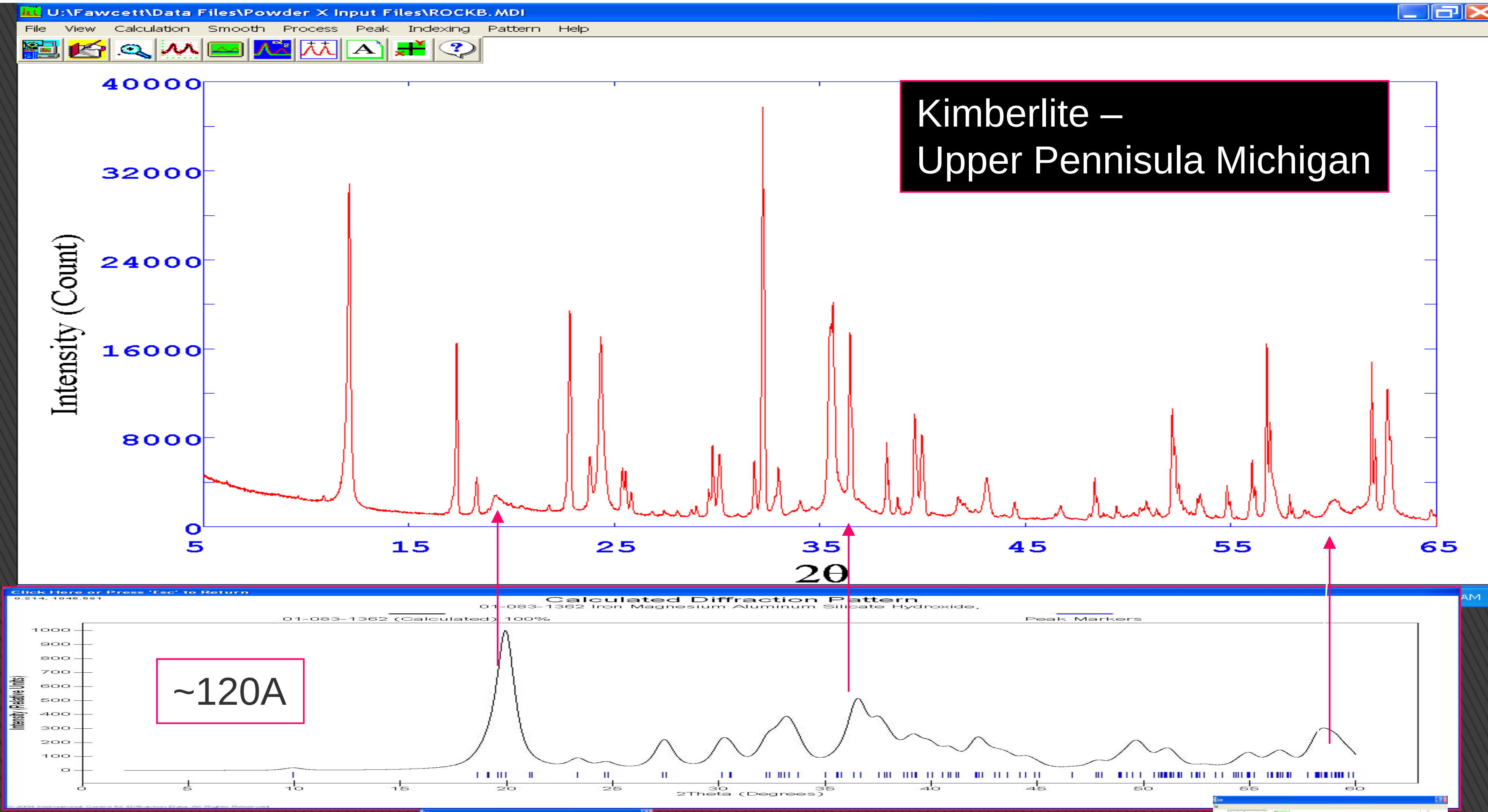


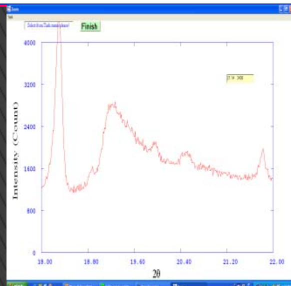
Plus cordierite and albite

Kimberlite Rock – Diamond bearing mineral

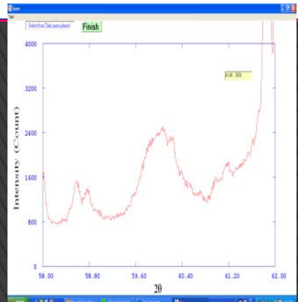


Fosterite
Magnetite (Mg)
Lizardite



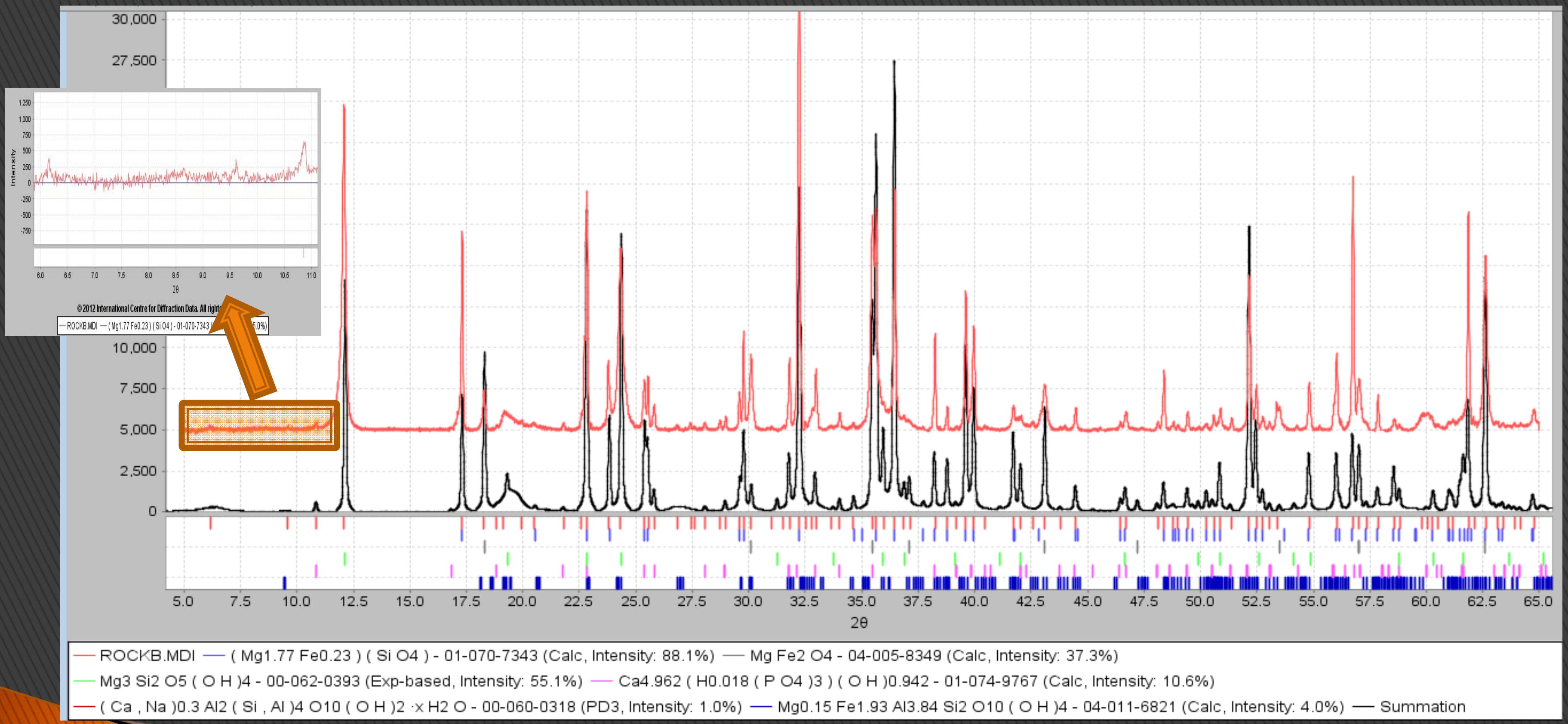


Iron Magnesium Aluminum
Silicate Hydroxide
-Quebec
Chloritoid Series

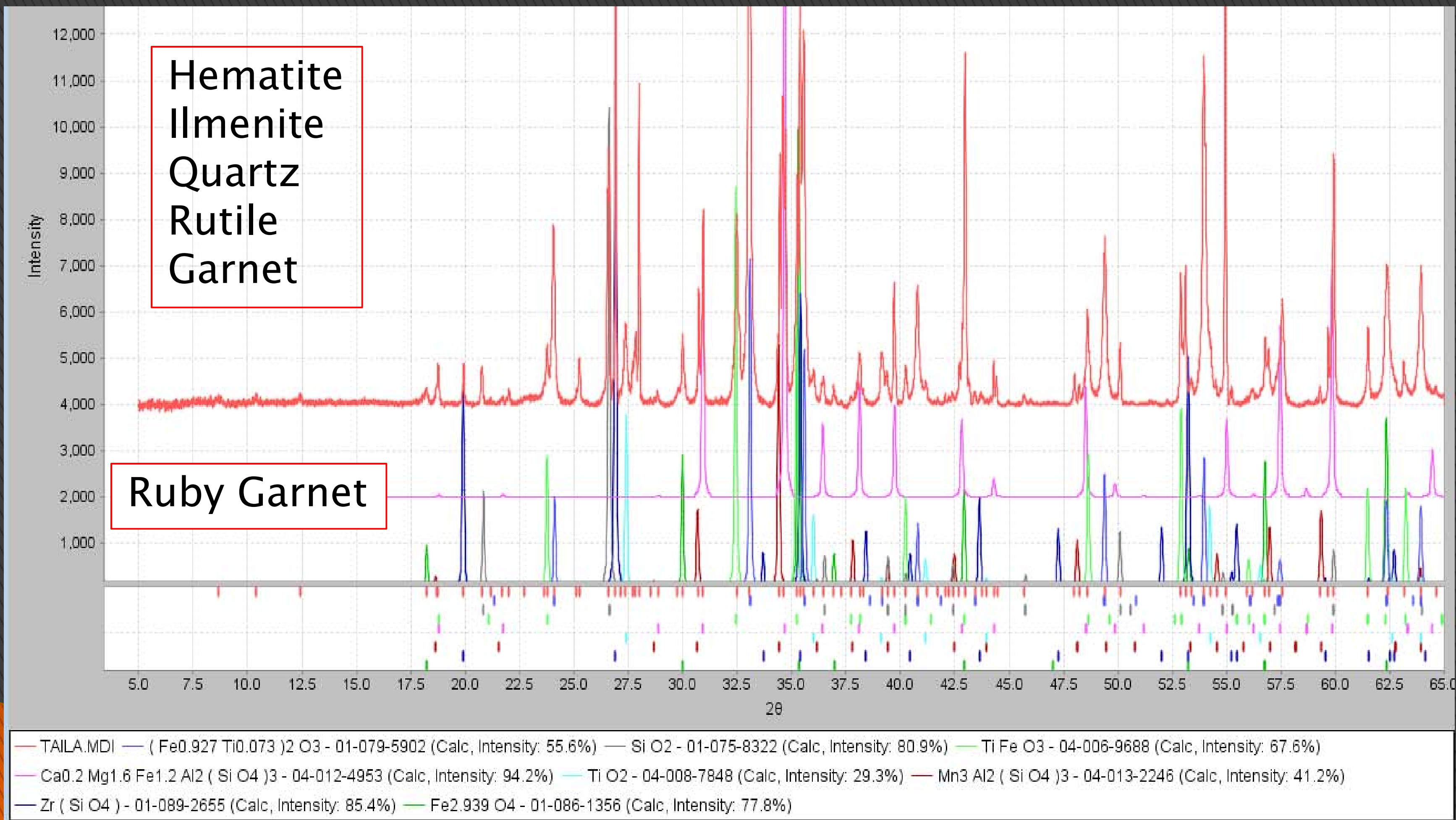


Specimen from Chibougamau – Quebec, Canada

Kimberlite rock – 6 phases
with apatite and montmorillonite

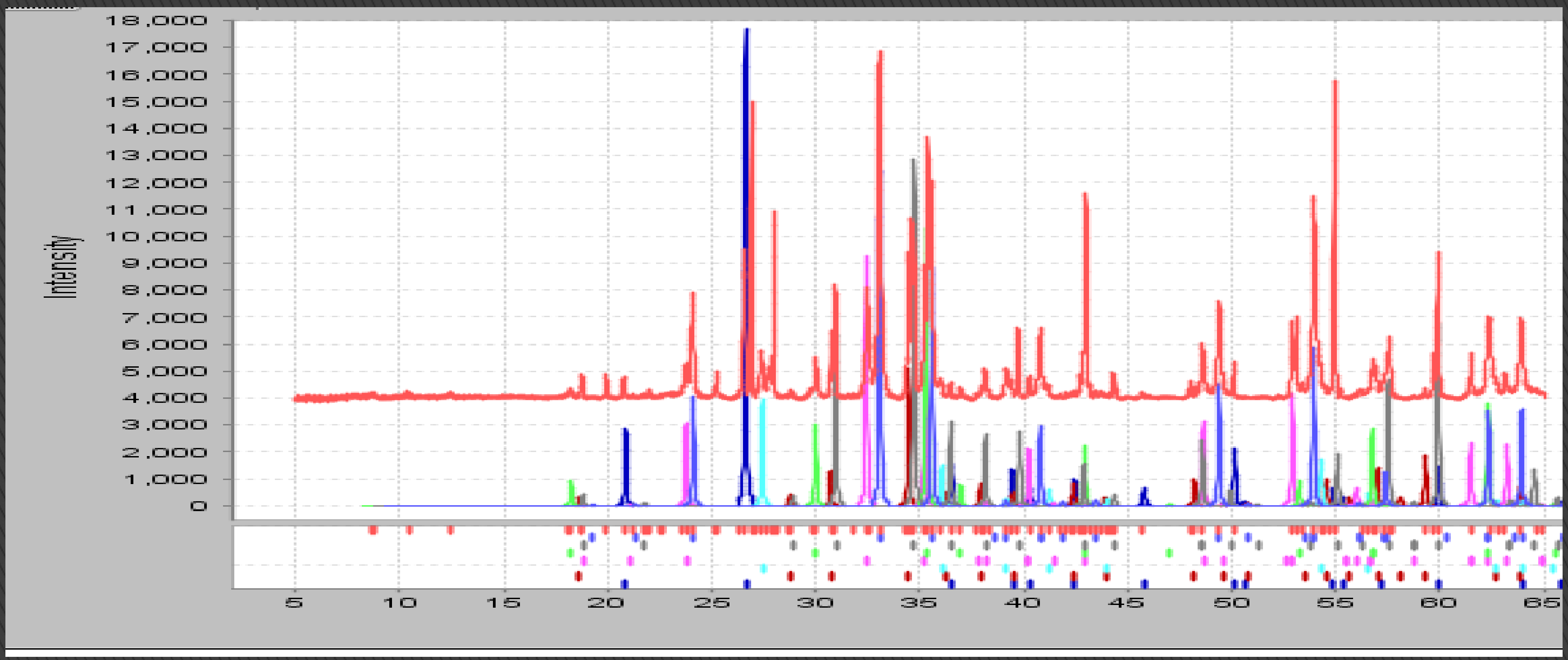


Isolated/Separated Mineral Fraction from a Kimberlite pipe core sample (clays and light density minerals removed by chemical and physical separation)



Group I Kimberlite

Hematite
Quartz
Pyrope
Rutile
Ilmenite
Garnet



Kimberlite

- Indicator minerals were initially used to identify pipe locations
- Indicator minerals isolated from ore body using physical and chemical separation
- Cr analyzed in the pyrope ruby garnet
- Diamonds identified in the pipe test cores

- 20 Kimberlite pipes eventually found in the area
- None have been commercially mined

Hunt for diamonds

At present, 15 companies have diamond exploration leases for 130,000 acres of state-owned land in a 5,000-square-mile area of Iron, Dickinson and Gogebic Counties in the western section of the Upper Peninsula. An estimated 1 million acres of privately owned land also are under lease.

Chicago Tribune, June 30th 1985

TORONTO (ResourceInvestor.com) -- The latest results from Dianor Resources [TSX-V:DOR] continue to point to the company's Leadbetter property near Wawa, Ontario, Canada hosting a significantly large body of diamondiferous rock.

The company optioned an 80% stake in the road-accessible Leadbetter property in December 2004 for close to $4 million in cash and shares over a four-year period. In excess of 330 diamonds, ranging up to 0.11 carats in size, had been collected from bedrock by prospector Joe Leadbetter in 2004. In addition, three macro diamonds were recovered from adjacent creek gravels, including a gem quality 1.39-carat stone valued at US$3,000. A pink 0.11-carat diamond is the largest stone recovered as of April 2005 from the bedrock.

Dianor started collecting and processing samples in January of this year. Initial results caused the shares to shoot up to $0.70 and were promising enough for the company to acquire a 70% interest in 49 claims located to the east and south of the original property, forming a contiguous land holding of approximately 16 square kilometres.

Resource Investor, May 30th, 2005

Dianor got $30 MM in investment funding in 2010

Role of XRD in diamond exploration and discovery

- Search for indicator minerals
- Confirmation of ruby garnets – pyrope
- Confirmation of diamonds

ADVANCED MINERAL ANALYSES BY X-RAY POWDER DIFFRACTION

- Ability to identify both crystalline and non-crystalline minerals
- Routinely identify and quantify complex multi-phase specimens (2 8-phase, 2 6-phase, a 5 and a 4 phase solution in this study)
- Detection depends on resolution and counting statistics – there are both improved optics and detectors in recent years significantly lowering detection limits
- New software tools (similarity indices, whole pattern methods, multivariant analyses) greatly facilitate search, identification and quantification.