Advances in quantitative Rietveld Analysis XRPD for Minerals and Mining Applications

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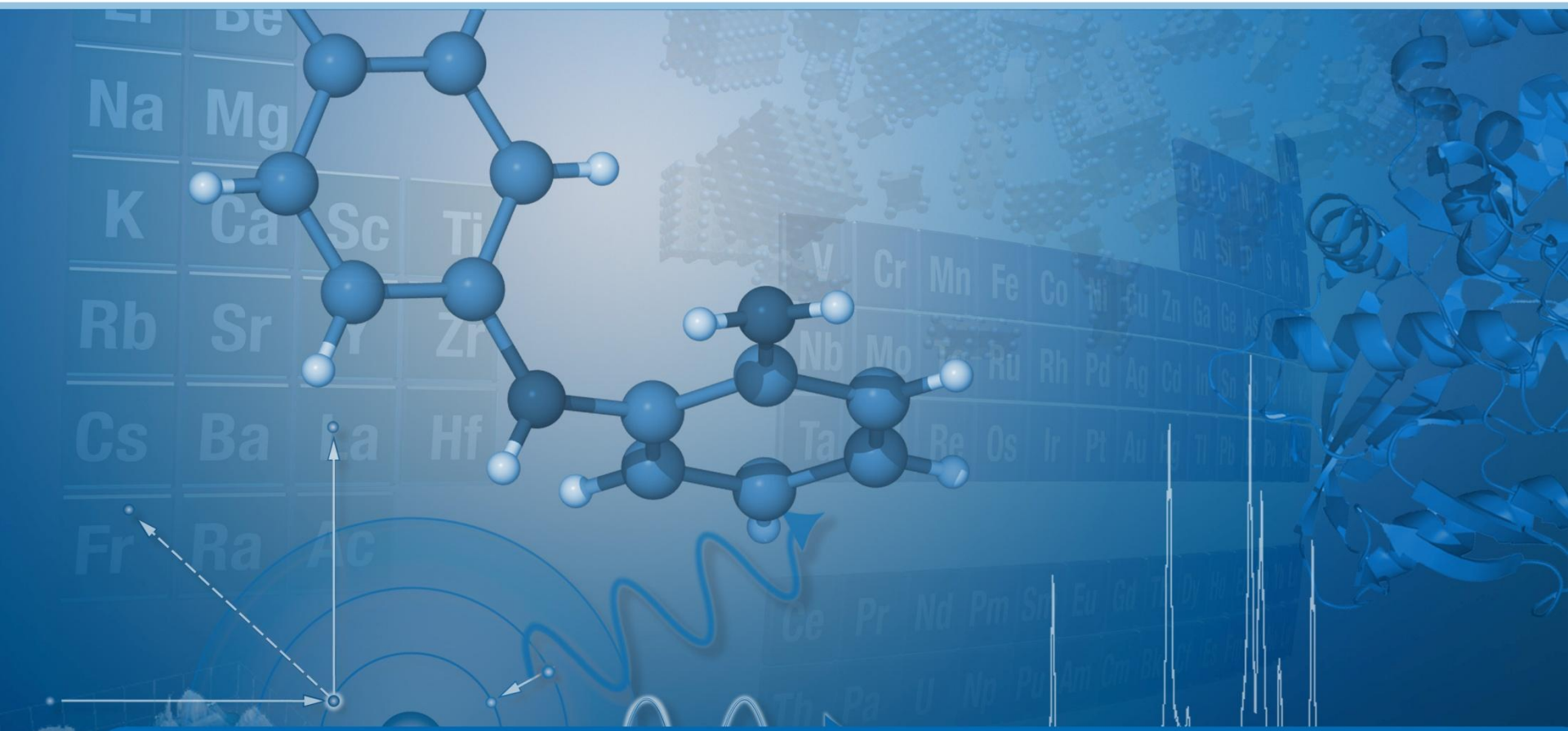


Outline

- Why X-Ray Powder Diffraction (XRPD)?
- XRPD application areas and capabilities
- Recent advances in quantitative phase analysis with XRPD
- Example applications
  - Process / production control
- Conclusions

Why X-Ray Powder Diffraction?

- X-Ray Powder Diffraction (XRPD) is an analytical tool for materials characterization, including but not limited to
  - qualitative phase analysis (phase identification),
  - quantitative phase analysis,
  - crystal structure determination and refinement
  - and much more
- XRPD is sensitive to the crystal structure of each phase present in the sample
- **The emphasis of this presentation is on quantitative phase analysis**

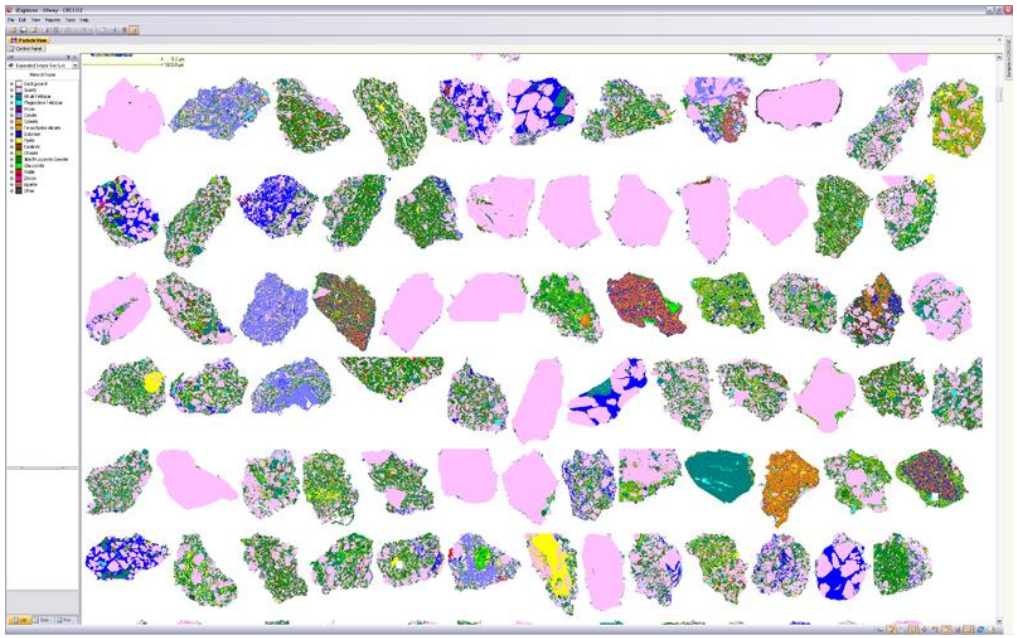
Why X-Ray Powder Diffraction?

Alternative (non XRPD) methods for quantitative phase analysis:

- Point counting
  using an optical microscope, scanning electron microscope or electron microprobe, now usually combined with digital image analysis
  - rather slow, difficult on-line automation->not usable for process
  - surface sensitive, can result in poor statistics
  - limited by fine grain size

Modern "automated" or "quantitative" mineralogy

Image processing (EDS and BSE) to obtain:



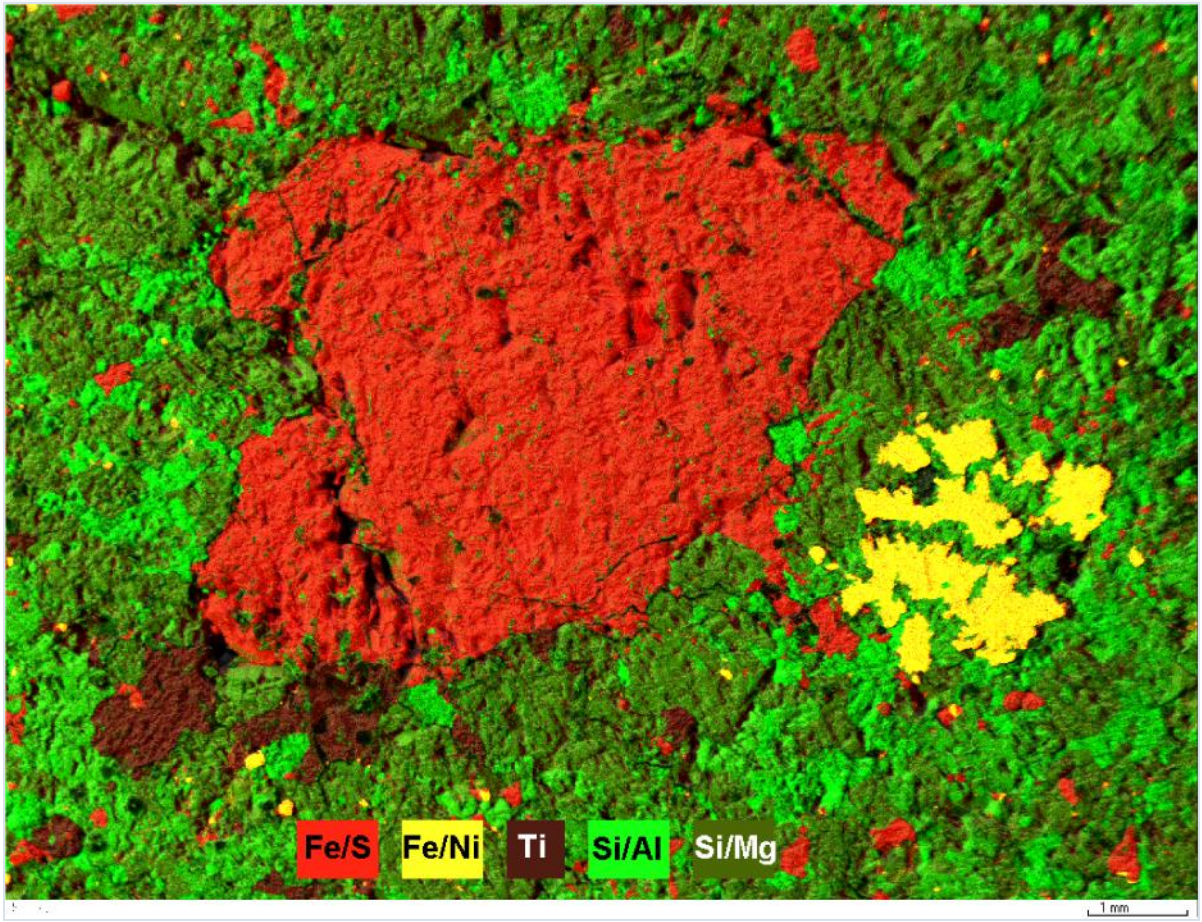
- Chemical assay(s)
- Modal mineral proportions

+

- Grain size
- Mineral associations and liberations
- Porosity

→ important information for mining and processing

Ultra fast element mapping + Mineral ID
Automated MINERALOGY (SEM/BSE)



- Mineral
- 20 kV / 10 nA
- 250 kcps
- 1024 x 768
- 15 min (1 detector)

Why X-Ray Powder Diffraction?

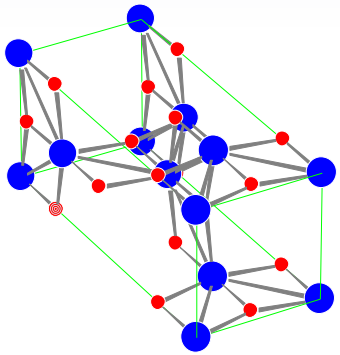
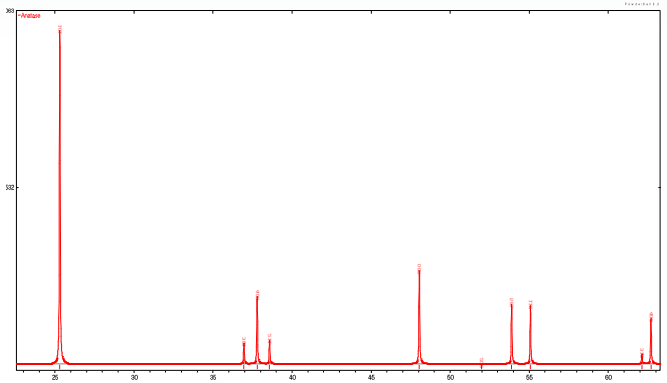
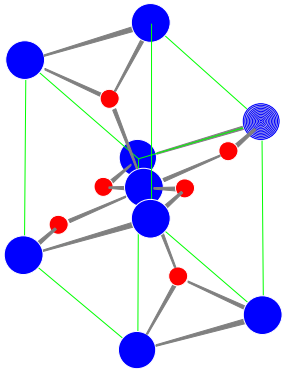
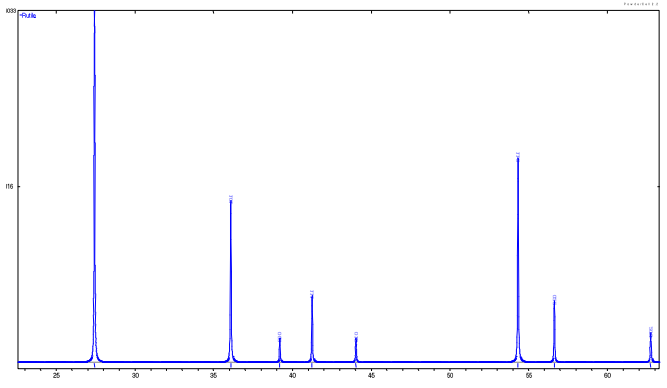
- Example: TiO_2

Anatase (with calcite)

Rutile (with hematite)

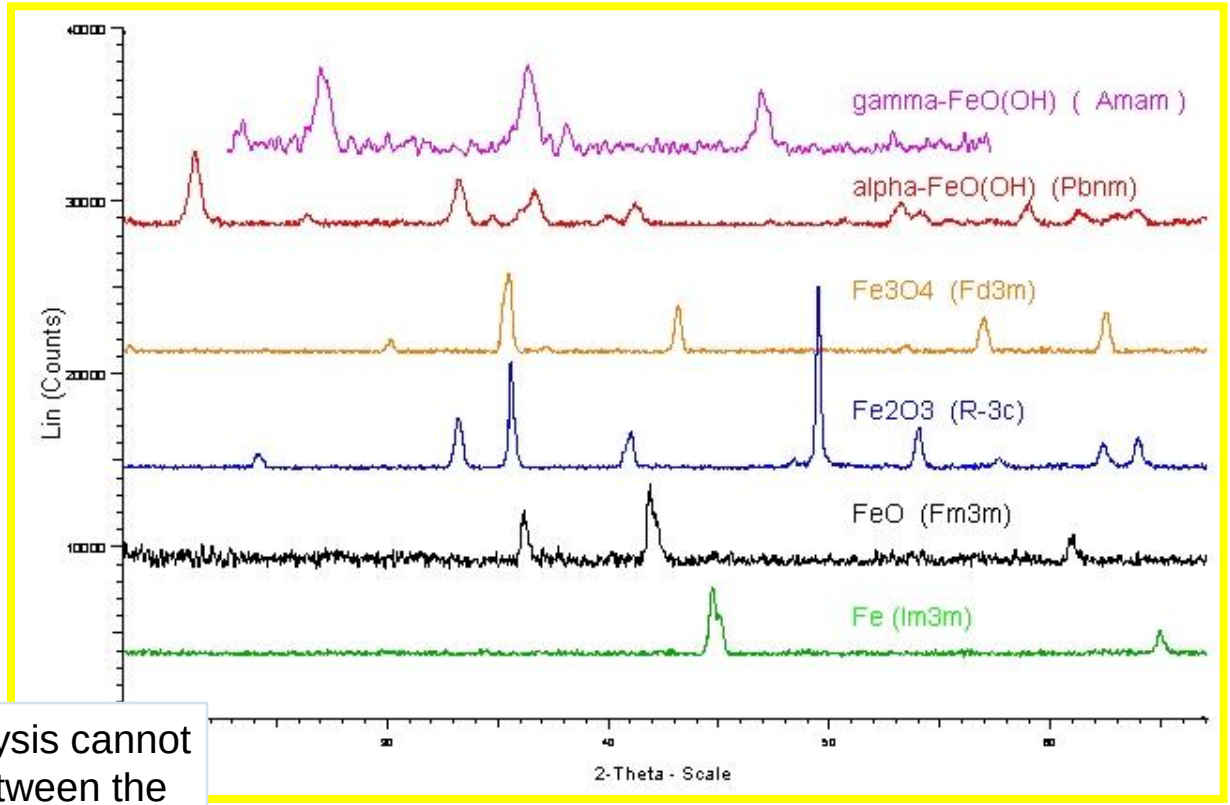
"Give rutile and anatase to chemists and they will tell you they are both 100% TiO_2"
(Ian Madsen, CSIRO)

Why X-Ray Powder Diffraction?

	Crystal structure	X-ray powder pattern
Anatase	 Tetragonal TiO_2	
Rutile	 Trigonal TiO_2	

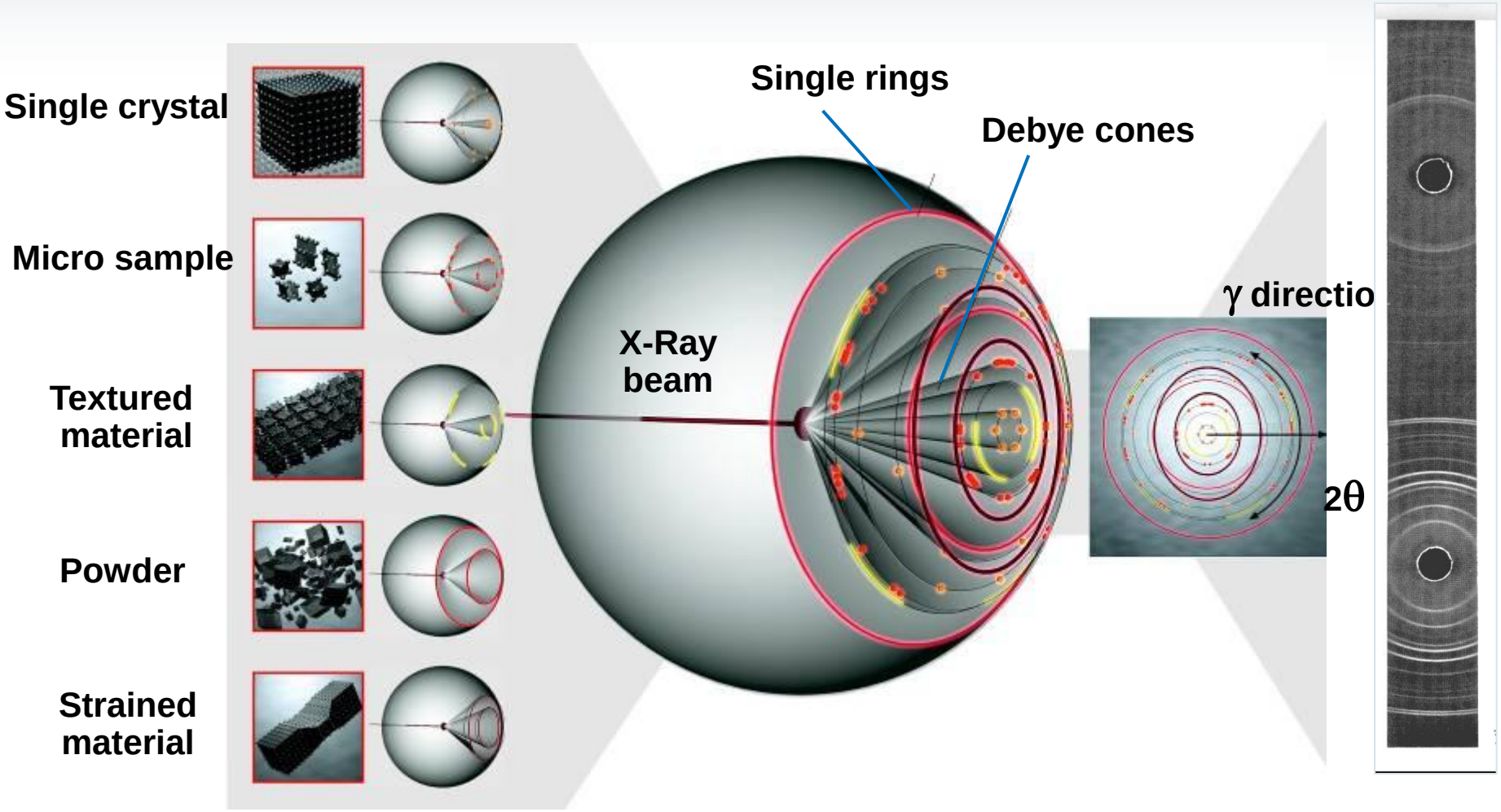
Why X-Ray Powder Diffraction?

- Example: Iron, iron oxides, iron hydroxides



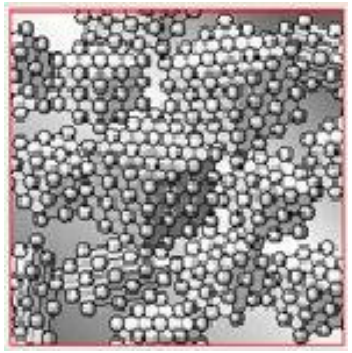
Elemental analysis cannot distinguish between the different Fe phases

X-Ray Diffraction and Scattering



Why X-Ray Powder Diffraction?

- Peak positions and intensities are functions of the crystal structure of a crystalline phase
- In mixtures, intensities are related to phase abundance
  - ⇨ Quantitative phase analysis
- An X-ray powder pattern is characteristic for a crystalline phase with its particular elemental composition and crystal structure
  - ⇨ "Fingerprint" phase identification



Why is this important?

Why X-Ray Powder Diffraction?

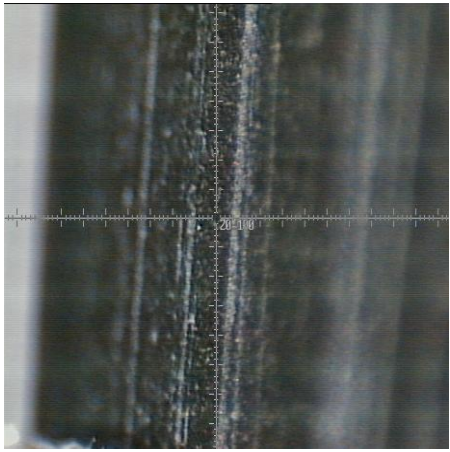
- Materials properties are not solely determined by their chemistry as e.g. determined by XRF, but by its mineralogy, i.e. the crystal structure (s) of the constituent compound (s)
- Crystal structure governs properties such as
  - Crystal habit / morphology
    - Crystal surfaces
  - Surface charge distribution
    - Hardness
    - Density
    - ...
  - Grindability
  - Flowability
  - Solubility
  - Floatation properties
    - ...
- Knowledge of these properties is a prerequisite for optimum processing

XRPD application areas and capabilities

XRPD capabilities

- Sample amounts: μ–grams (micro-diffraction) up to grams
- Ideal grain size required: <10μ
  - XRPD is sensitive to fine grain size
  - XRPD cannot provide information about particle size and shape, mineral association and liberation
- Quantitative analysis:
  - linear concentration range from 0.1-3%*) to 100%
  - typical accuracy 0.1-3%*) and reproducibility <0.1%*) absolute
  - typical detection limits: 0.1-1%*)

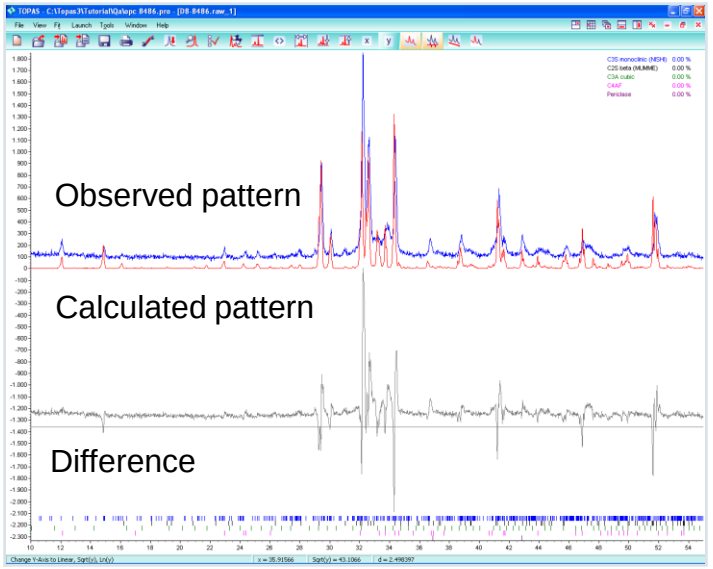
*) depends strongly on sample presentation and sample properties, such as elemental composition (scattering power), crystal structure symmetry, degree of crystallinity



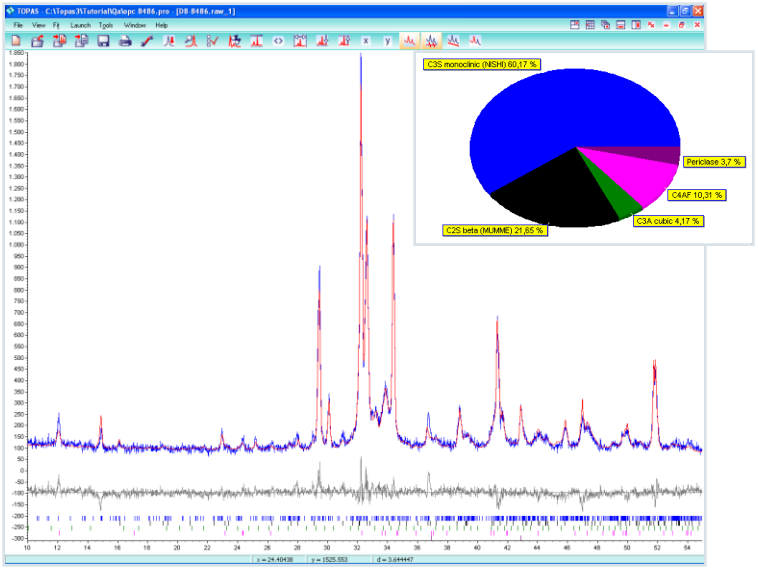
Recent advances in quantitative phase analysis with XRPD

The Rietveld method

- The Rietveld method generates a calculated diffraction pattern that is compared with the observed data
  - Qualitative phase analysis required
- The differences between observed and calculated diffraction patterns are minimized using least-squares procedures



Refinement



Quantitative X-ray Mineralogy using the Rietveld Method

- Hill & Howardt (1987)
  J. Appl. Cryst. 20, 467-74
  - all phases identified
  - all phases crystalline
  - all crystal structures known

- Benefits
  - No need for artificial calibration mixtures
  - ZMV is the calibration constant
  - ZMV known from crystal structure

$$W_\alpha = \frac{S_\alpha (ZMV)_\alpha}{\sum_{k=1}^{n} S_k (ZMV)_k}$$

W= Weight %

S = Rietveld scale factor

Z = No. of formula units in unit cell

M = Molecular mass of formula unit

V = Unit cell volume

Recent advances in quantitative phase analysis with XRPD

A new generation of Rietveld software: TOPAS (since 1997)

In addition to RECIPE based ONE button use:

- A convolution based instrument function approach for describing observed X-ray line profile shapes
  ⇨ Fundamental Parameters Approach
  - REDUCES PARAMETERS which need to be fitted DRAMATICALLY and enables REAL STABLE REPEATABLE refinements
  - No divergence approach….

Recent advances in quantitative phase analysis with XRPD

Fundamental Parameters Approach

- The observed line profile shapes in a powder pattern are calculated from the known instrument geometry
- This allows a more reliable decomposition of peak overlaps at much higher degrees of peak overlap, compared to traditional analytical profile functions (e.g. pseudo-Voigt, PearsonVII)
- The number of refineable profile parameters and therefore parameter correlation is significantly reduced
  - Analytical profile fitting : ~7 (U,V,W,X,Y,Z,Asymmetry)
  - Fundamental parameters approach : ~1-2 (size, strain)
- Complex line profile shapes as found in clays can be modeled

Quantitative X-ray Mineralogy
Amorphous material – PONKCS

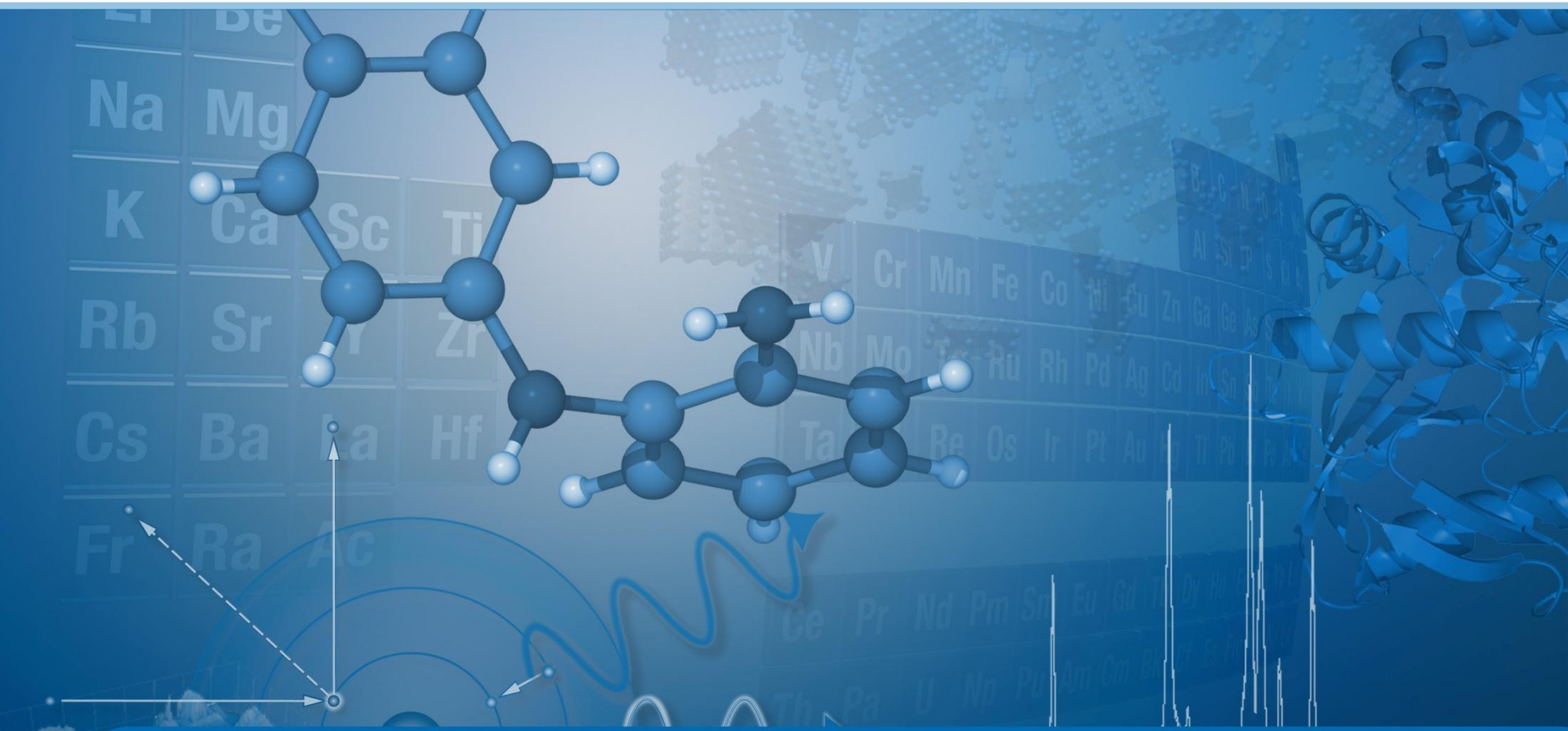
- Use if spiking not feasible
- Quantification of **P**hases **O**f **N**o **K**nown **C**rystal **S**tructure
  - amorphous
  - unknown or partly known structure
- Scarlett & Madsen (2006)Powder Diffraction 21(4), 278 – 284
- Calibration of an unknown phase α via internal standard *s* in TOPAS as
  - unindexed peaks phase
  - indexed hkl-phase

$$(ZMV)_\alpha = \frac{W_\alpha}{W_s} \cdot \frac{S_s}{S_\alpha} \cdot (ZMV)_s$$

W= Weight %
S = Rietveld scale factor
Z = No. of formula units in unit cell
M = Molecular mass of formula unit
V = Unit cell volume

ZMV known for standard,
but calibrated for unknown

Example applications: production control / industrial

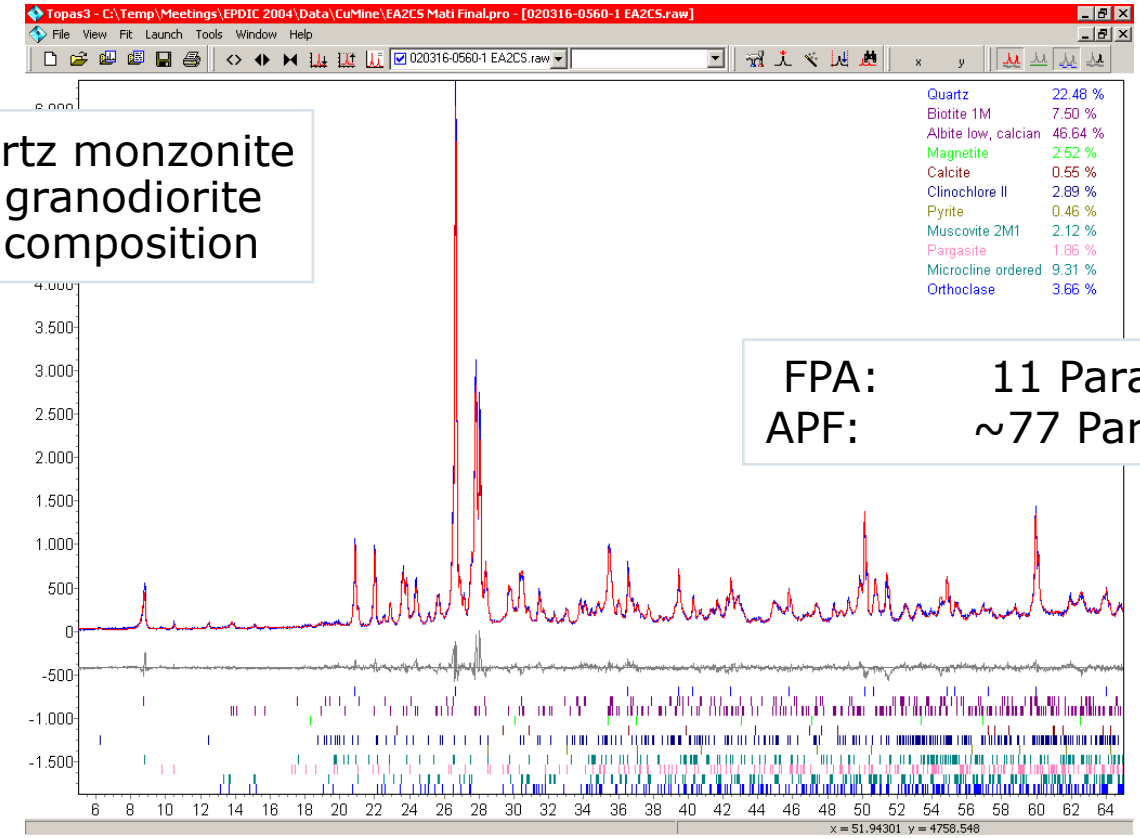


Quantitative Rietveld Analysis
Typical Recent Subjects

- Mineral processing products at mining operations
- Composition of ores
- Mine tailings and waste rocks (environmental mineralogy)
  - Acid mine and rock drainage
- Mineralogy of asbestos mine tailings (CO_2 sequestration)
- Undesirable deposits, clogs, etc. in furnaces, boilers, pipes, etc.
  - E.g. early warning of blockage
- Mineralogy of (exotic) slags
- Miscellaneous corrosion products

Quantitative Rietveld Analysis
Porphyry Copper Deposit Host Rock

- E.g. determination of the acid producing / neutralisation potential

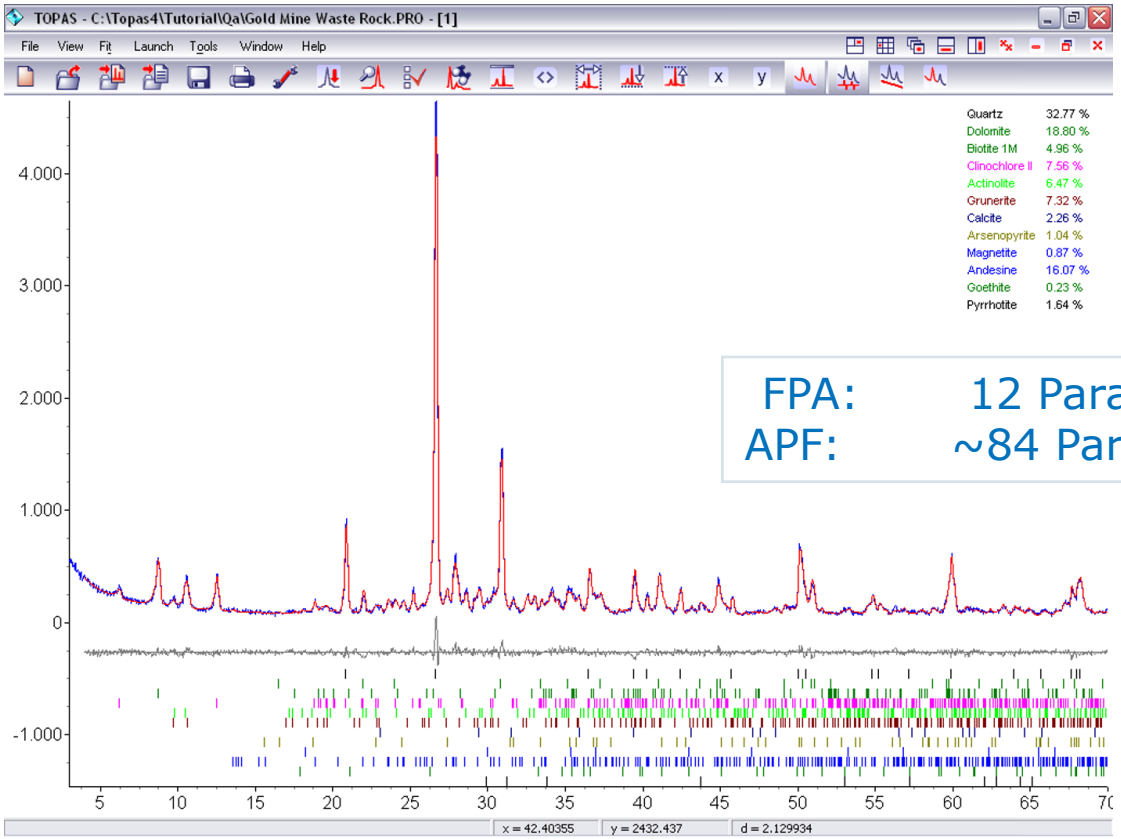


Quartz monzonite to granodiorite in composition

FPA: 11 Params
APF: ~77 Params

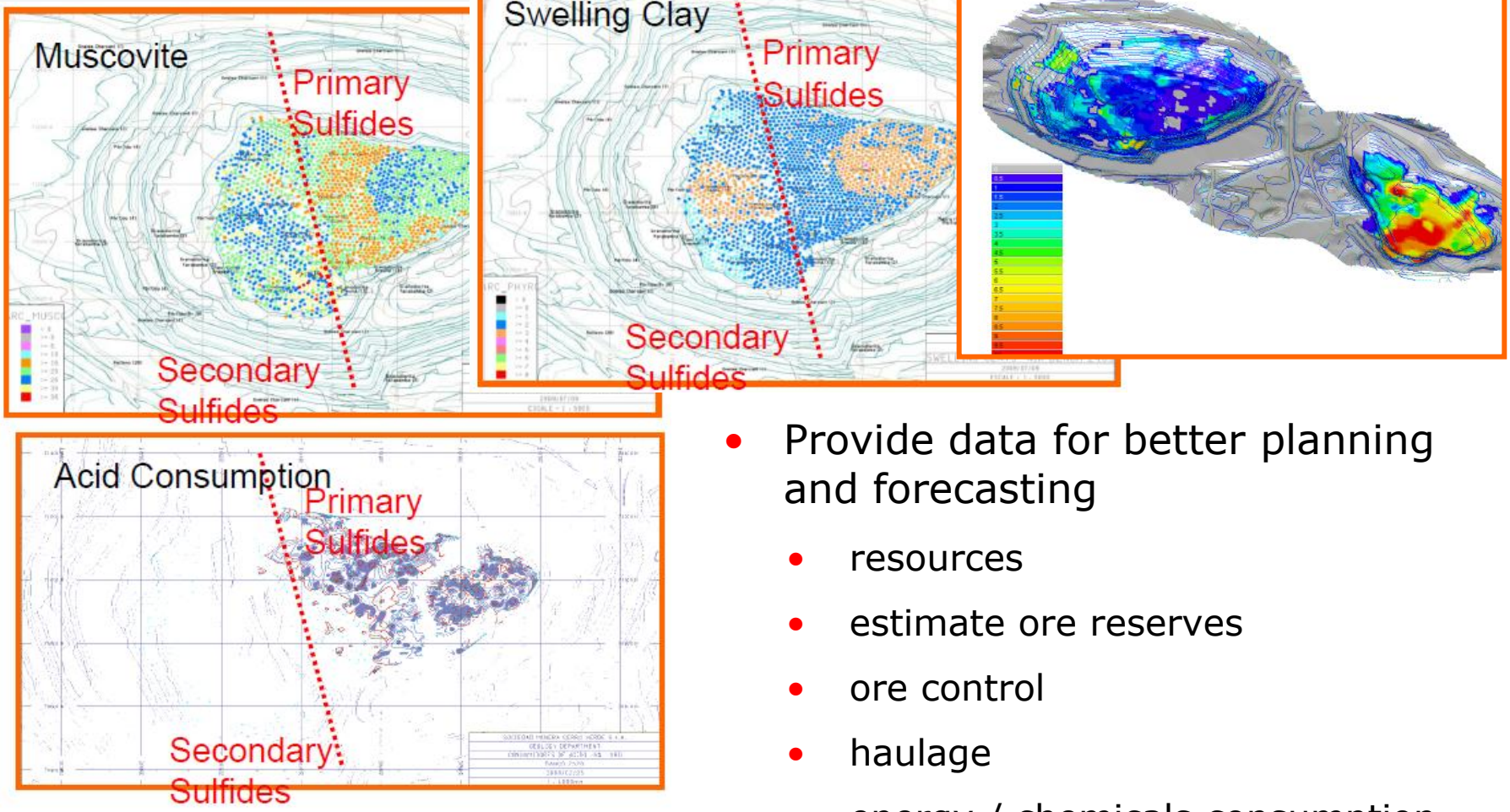
Quantitative Rietveld Analysis
Gold Mine Waste Rock

- E.g. determination of the acid producing / neutralisation potential



FPA: 12 Params
APF: ~84 Params

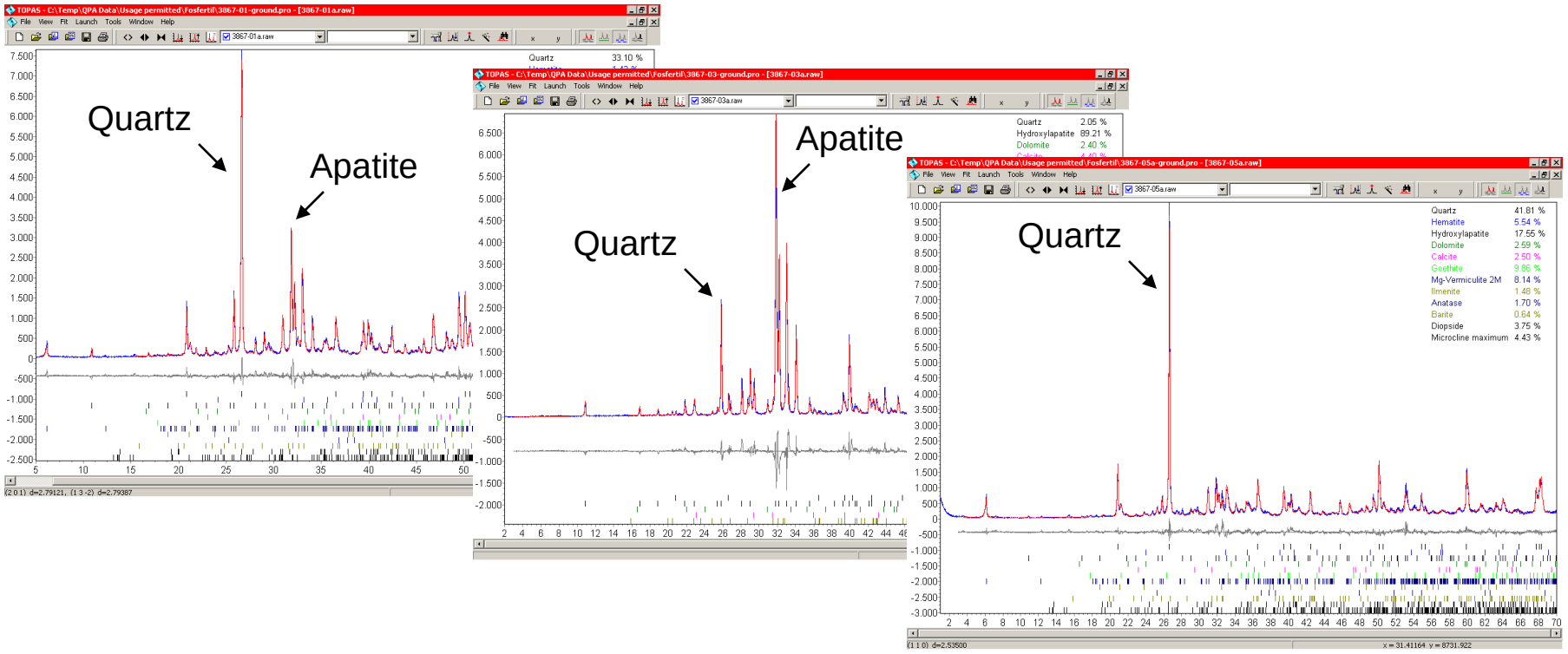
Objective: XRD to support mine operation and ore processing



- Provide data for better planning and forecasting
  - resources
  - estimate ore reserves
  - ore control
  - haulage
  - energy / chemicals consumption

Quantitative Rietveld Analysis
Phosphate Ore

As extracted **Concentrate** **Tailing**

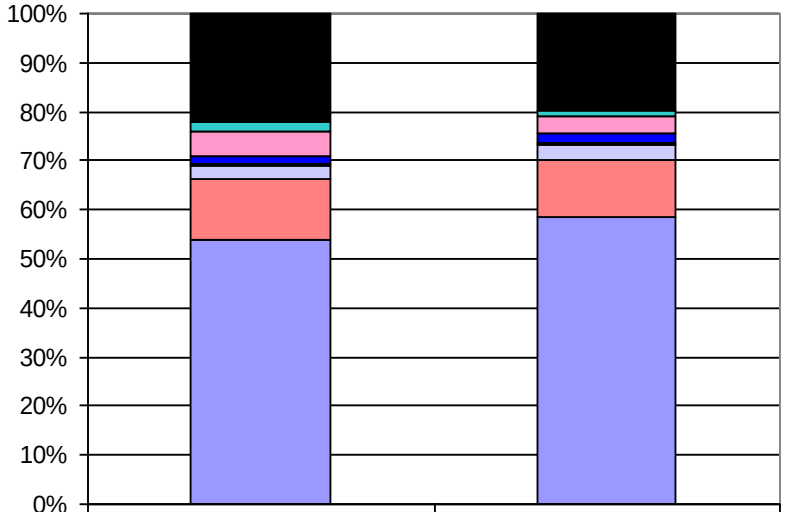


Quantitative Rietveld Analysis Phosphate Ore

Phase	As extracted	Concentrate	Tailing
• Quartz	33.10	2.05	41.81
• Hematite	1.42		5.54
• Hydroxyapatite	38.20	89.20	17.55
• Dolomite	3.33	2.40	2.59
• Calcite	2.93	4.40	2.40
• Goethite	6.23		9.86
• Vermiculite	4.83		8.14
• Ilmenite	3.49		1.48
• Anatase	1.31		1.70
• Barite	0.41	1.95	0.64
• Diopside	2.36		3.75
• Microcline	2.40		4.43

Quantitative X-ray Mineralogy
Results reconciliation

- Accuracy of the XRD method can be validated by comparing against independent methods
  - chemical analysis (XRF, ICP-MS, AA, …)
  - optical microscopy (quantitative point counting)
  - SEM-EDS



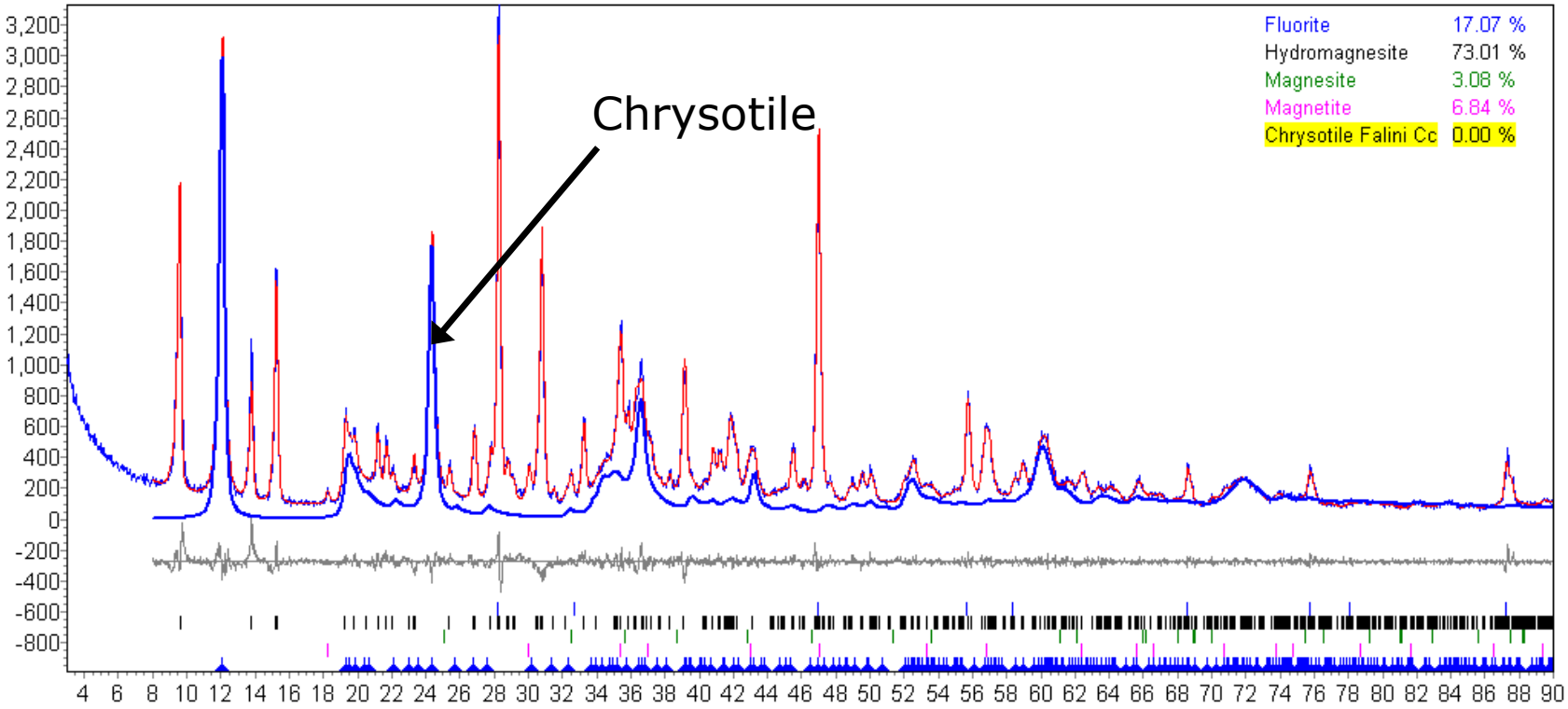
	XRD_secondary	QUEMSCAN_secondary
Total Silicate	21.95	20.03
Total Ca Sulfate	1.93	1.22
Total Carbonate	5.34	3.68
Total Fe Oxide	1.28	1.87
Total Pb-Sulfide	0.32	0.32
Total Mo Sulfide	0	0
Total Zn Sulfide	3.04	3.04
Total Fe Sulfide	12.42	11.76
Total Cu Sulfide	53.73	59.38

XRD and QUEMSCAN secondary minerals list

Quantitative Rietveld Analysis
CO_2 Sequestration

- **Wilson, S.A., Raudsepp, M. & Dipple, G.M. (2006). American Mineralogist 91, 1331-1341.**
- The sequestration of anthropogenic CO2 may be required to meet Canada's commitment to the Kyoto Protocol
- The carbonation of serpentine-group minerals in ultramafic mine tailings presents an opportunity to implement carbon sequestration in the mining industry
  - **Globally, ultramafic mines could sequester 10^8 tonnes of CO_2/year**
- The trouble with serpentine: Stacking disorder - no reliable crystal structure

Quantitative Rietveld Analysis
Structureless Fitting of Crysotile



CO_2 Sequestration
Clinton Creek Mine, BC, Canada

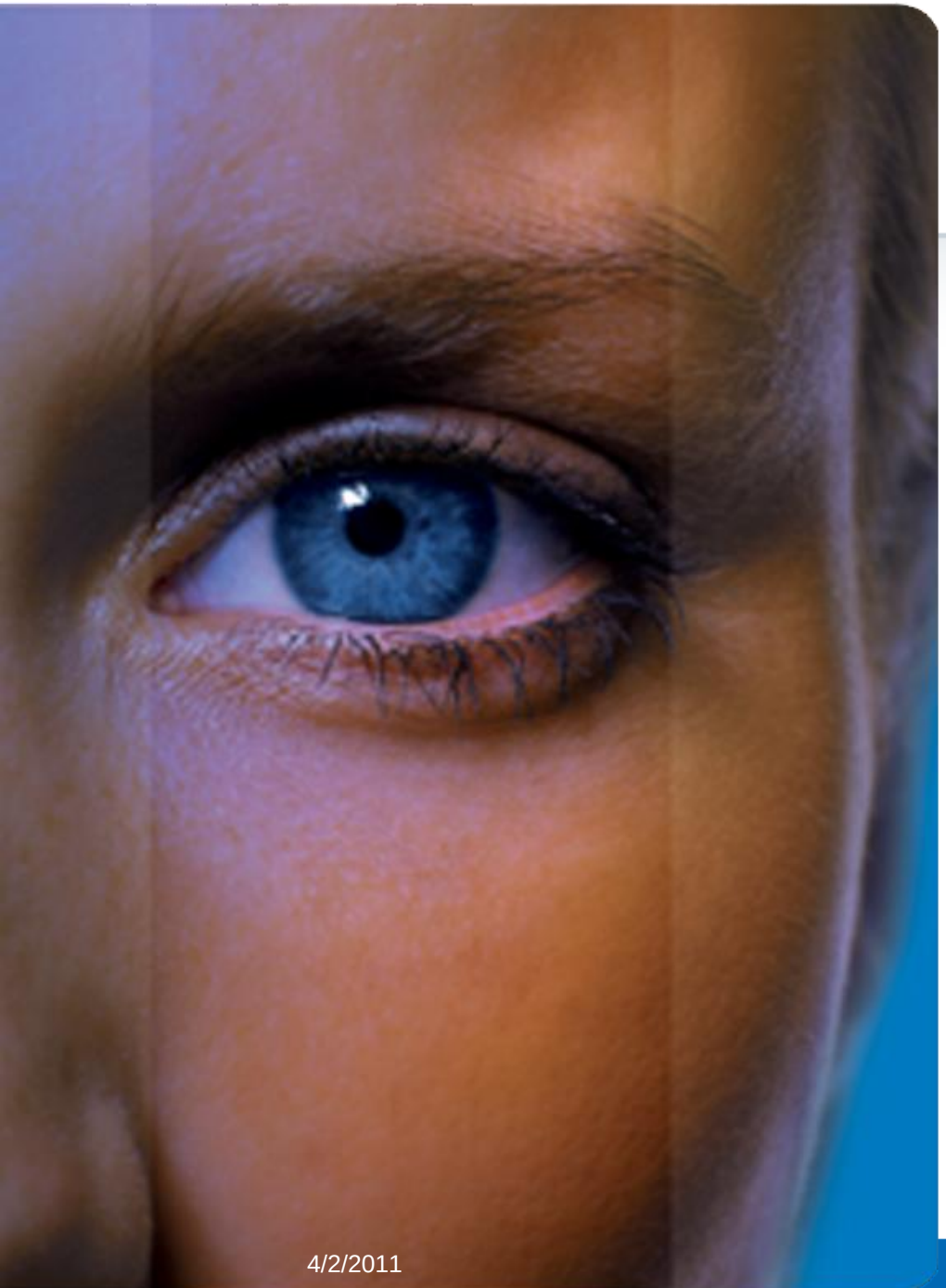
Conclusion

- XRPD is a direct and accurate analytical method for determining the presence and absolute amounts of mineral species in a sample
- STANDARDLESS QUANTIFICATION is a reality and PROCESS ready with accuracies of better than 5% relative
- Significant advances have been made in quantification of disordered materials (e.g. clays) with new functionality in TOPAS
- IN LEACHING (HEAP) XRD is used as THE CONTROL TOOL

Conclusion

- Important limitations are
  - The relatively high lower limit of detection, particularly for poorly crystalline phases
  - The requirement for appropriate sample preparation. Overgrinding may destroy soft phases, resulting in an underestimation.

Note, that microscopes/microprobes,
XRF, and XRD are highly complementary methods,
but they look at different samples!



QUESTIONS ?

References

Scarlett, N.V.Y. & Madsen, I.C. (2006)

Quantification of phases with partial or no known crystal structure

Powder Diffraction, 21(4), 278-284

Wilson, S.A., Raudsepp, M. & Dipple, G.M. (2006).
American Mineralogist 91, 1331-1341.

Webinars (recorded) or Online Classes

TOPAS WEBINAR, 2008 , please contact Karen.Roscoe@bruker-axs.com

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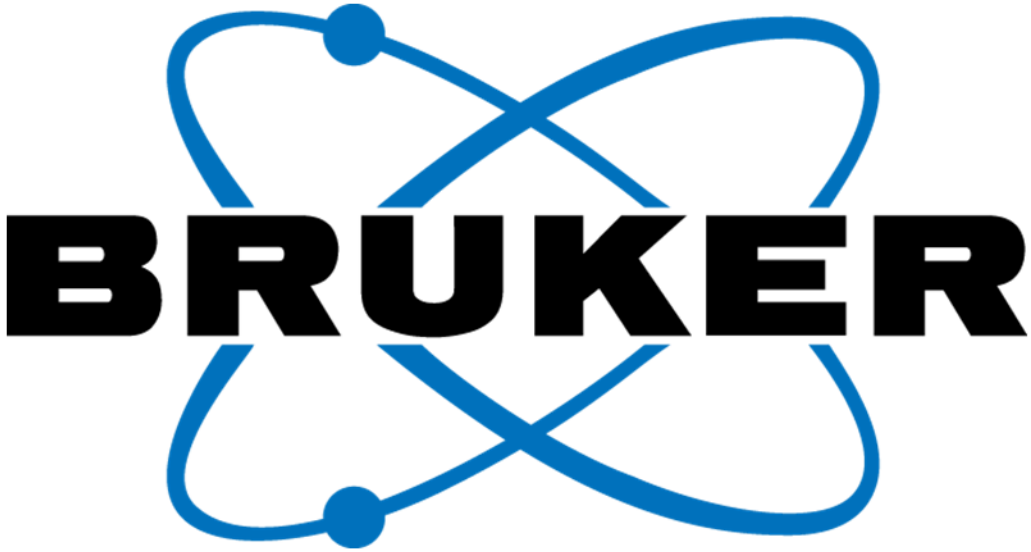

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