Search-Match & FPSM

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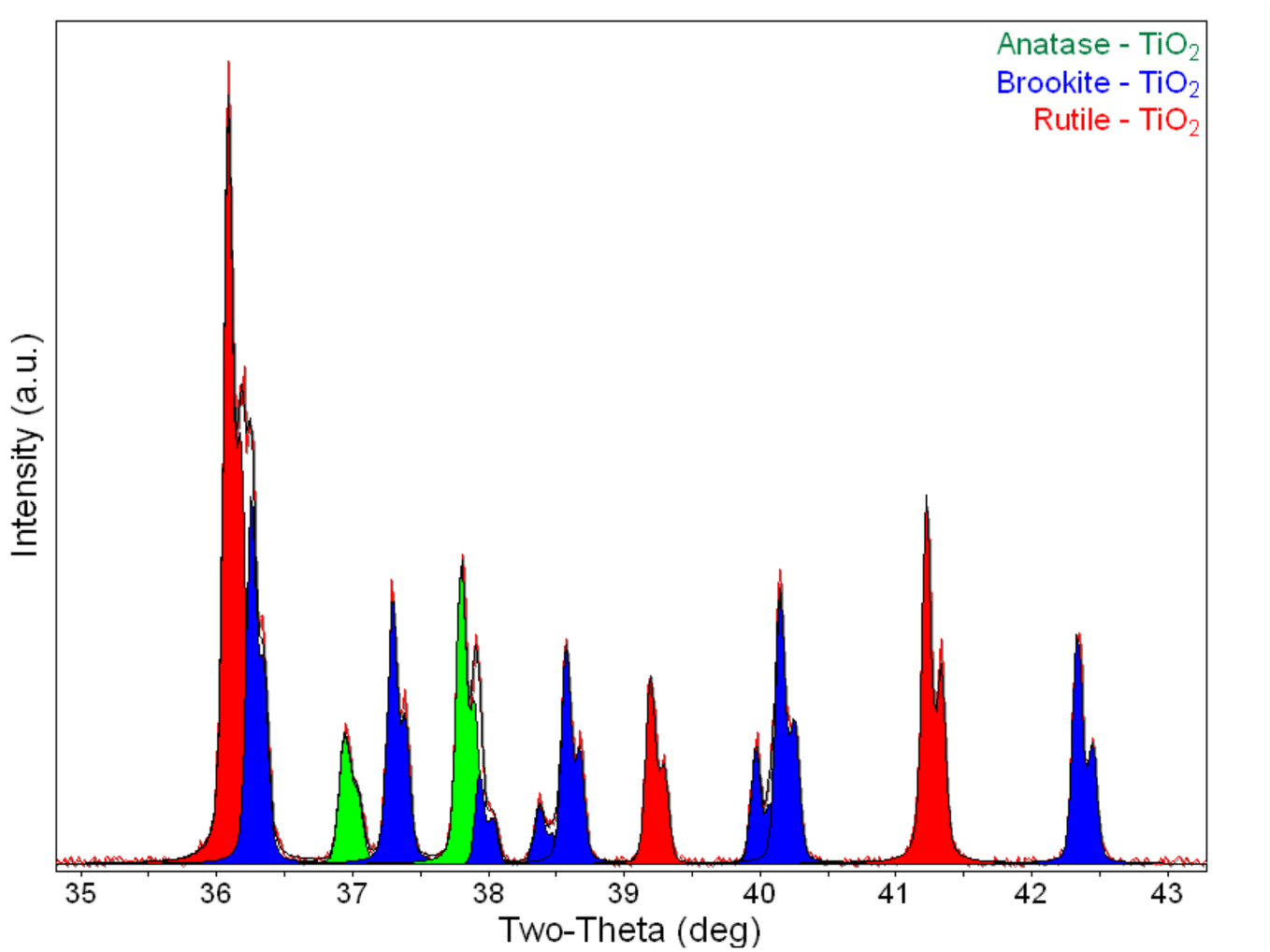
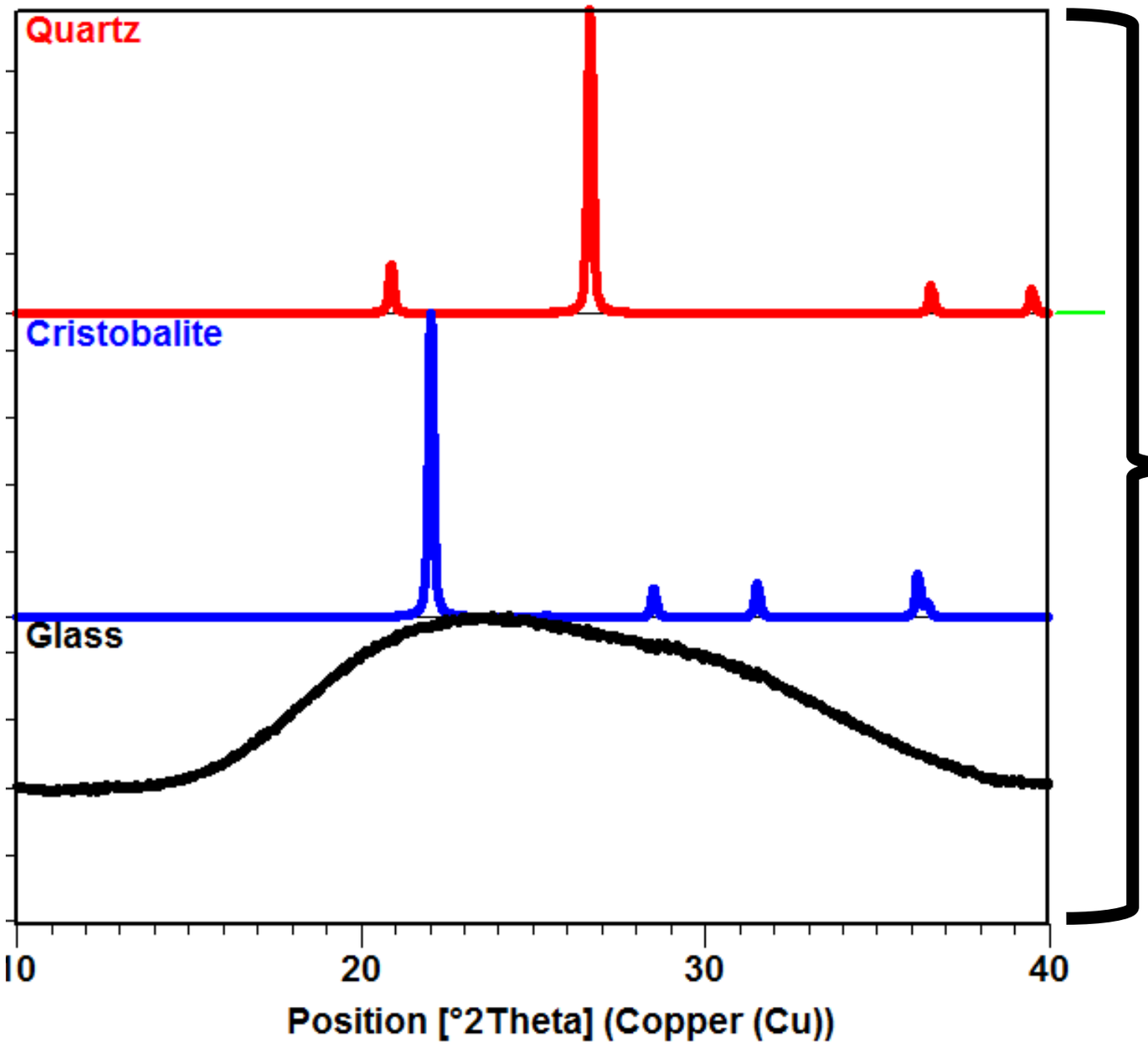
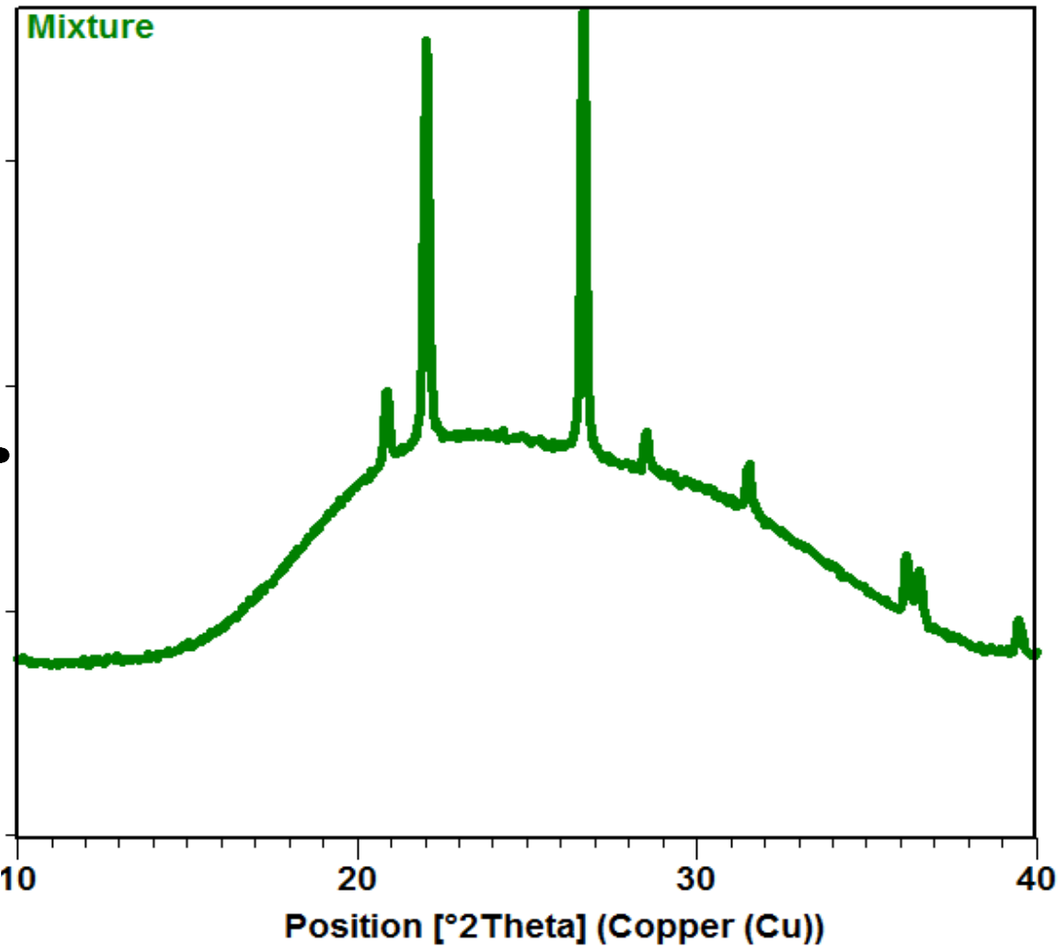
Phase Identification

- The diffraction pattern for every phase is as unique as your fingerprint
  - Phases with the same chemical composition can have drastically different diffraction patterns.
  - Use the position and relative intensity of a series of peaks to match experimental data to the reference patterns in the database



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





Databases such as the Powder Diffraction File (PDF) contain d-I lists for thousands of crystalline phases.

- The PDF contains over 300,000 diffraction patterns.
- Modern computer programs can help you determine what phases are present in your sample by quickly comparing your diffraction data to all of the patterns in the database.
- The PDF card for an entry contains a lot of useful information, including literature references.

PDF#00-021-1276(RDB): QM=Star(S); d=(Unknown); I=...

Reference | Lines(38) | Cu | 8

Rutile, syn
TiO_2 (White)

Radiation=CuKα1 Lambda=1.54056 Filter=
Calibration=Internal(W) 2T=27.447-155.866 I/Ic(RIR)=3.40
Ref:
Natl. Bur. Stand. (U.S.) Monogr. 25, v7 p83 (1969)

Tetragonal - Powder Diffraction, $P4_2/mnm$ (136) Z=2 mp=
CELL: 4.5933 x 4.5933 x 2.9592 <90.0 x 90.0 x 90.0> P.S=tP6.00
Density(c)=4.25 Density(m)=4.23 Mwt=79.9 Vol=62.43
Ref:

F(30)=107.8(0.008,32/0)

Strong Lines: 3.25/X 1.69/6 2.49/5 2.19/3 1.62/2 1.36/2 0.82/1 1.35/1 (I%-Typ

General Comments: Pattern reviewed by Syvinski, W., McCarthy, G., North Dakota State Univ, Fargo, North Dakota, USA, ICDD Grant-in-Aid (1990). Agrees well with experimental and calculated patterns. Additional weak reflections (indicated by brackets) were observed. Naturally

PDF#00-021-1276(RDB): QM=Star(S); d=(Unknown); I=...

Reference | Lines(38) | Cu | 8

#	2-Theta	d(Å)	I(f)	(h k l)	Theta	1/(2d)	2pi/d	n^2
1	27.447	3.2470	100.0	(1 1 0)	13.723	0.1540	1.9351	
2	36.086	2.4870	50.0	(1 0 1)	18.043	0.2010	2.5264	
3	39.187	2.2970	8.0	(2 0 0)	19.594	0.2177	2.7354	
4	41.226	2.1880	25.0	(1 1 1)	20.613	0.2285	2.8717	
5	44.051	2.0540	10.0	(2 1 0)	22.026	0.2434	3.0590	
6	54.323	1.6874	60.0	(2 1 1)	27.161	0.2963	3.7236	
7	56.642	1.6237	20.0	(2 2 0)	28.321	0.3079	3.8697	
8	62.742	1.4797	10.0	(0 0 2)	31.371	0.3379	4.2463	
9	64.040	1.4528	10.0	(3 1 0)	32.020	0.3442	4.3249	
10	65.479	1.4243	2.0	(2 2 1)	32.740	0.3510	4.4114	
11	69.010	1.3598	20.0	(3 0 1)	34.505	0.3677	4.6207	
12	69.790	1.3465	12.0	(1 1 2)	34.895	0.3713	4.6663	
13	72.409	1.3041	2.0	(3 1 1)	36.205	0.3834	4.8180	
14	74.411	1.2739	1.0	(3 2 0)	37.205	0.3925	4.9322	
15	76.509	1.2441	4.0	(2 0 2)	38.255	0.4019	5.0504	
16	79.821	1.2006	2.0	(2 1 2)	39.911	0.4165	5.2334	
17	82.334	1.1702	6.0	(3 2 1)	41.167	0.4273	5.3693	
18	84.260	1.1483	4.0	(4 0 0)	42.130	0.4354	5.4717	
19	87.463	1.1143	2.0	(4 1 0)	43.732	0.4487	5.6387	

Automatic analyses: FPSM

- First step (XRD only):
    - Phase identification -> Search-Match
    - Phase quantification -> Rietveld
- Second step (XRD + XRF)
- Third step (+ Raman)

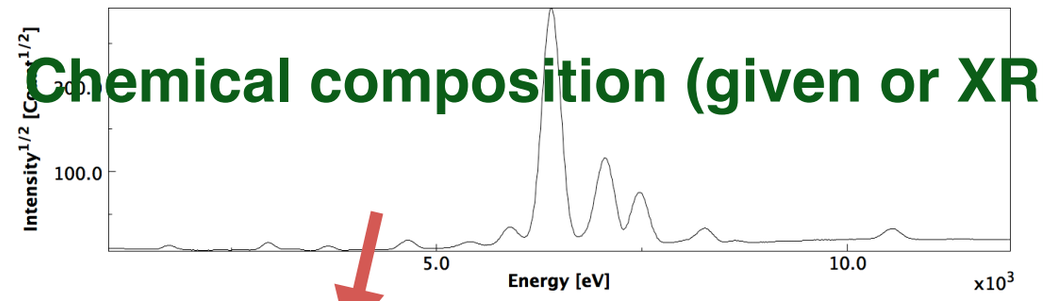
Automatic analyses: FPSM

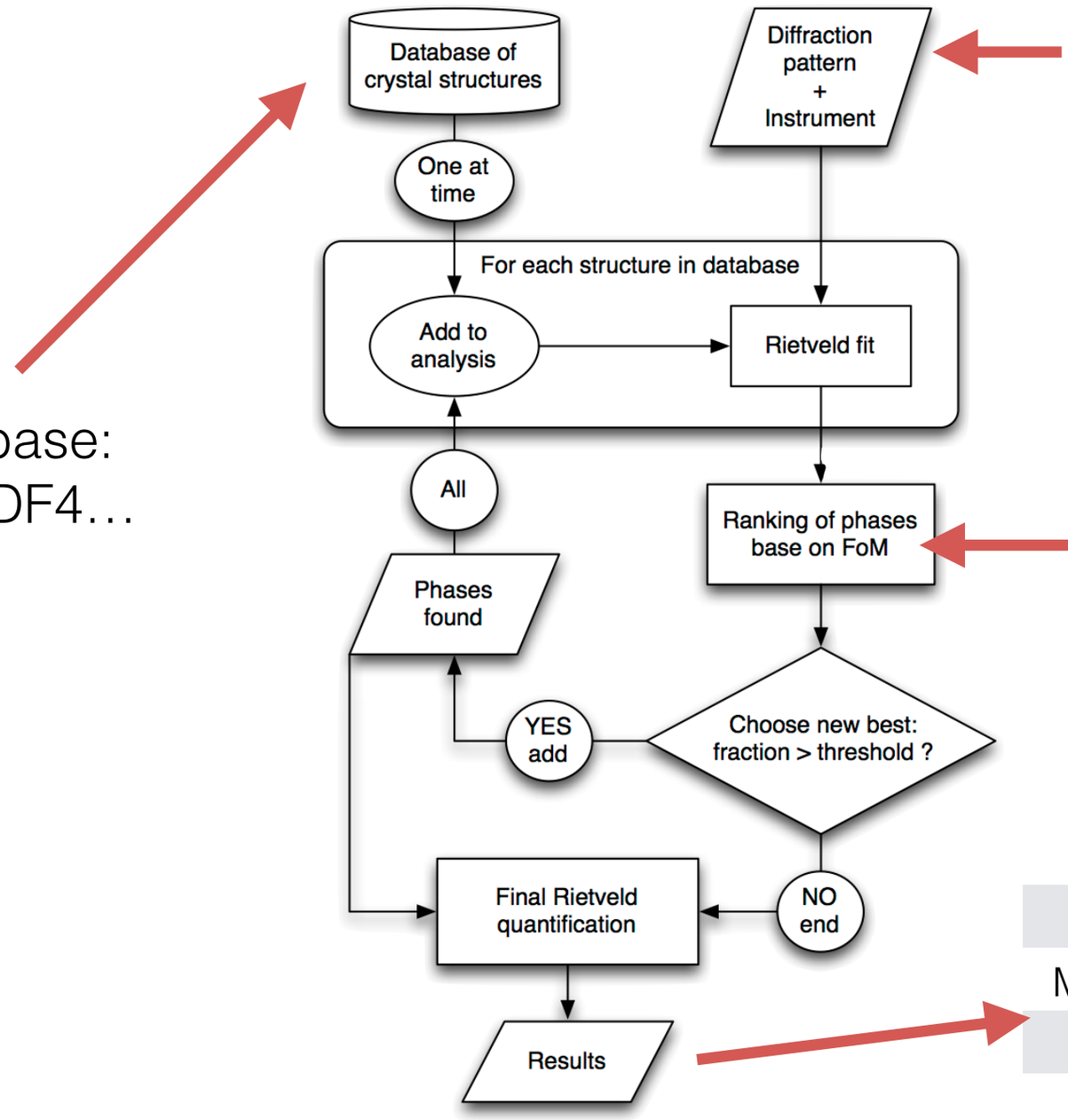
- First step (optional): XRF chemical identification (qualitative XRF analysis)
- Second step (XRD only):
    - Phase identification and quantification ->

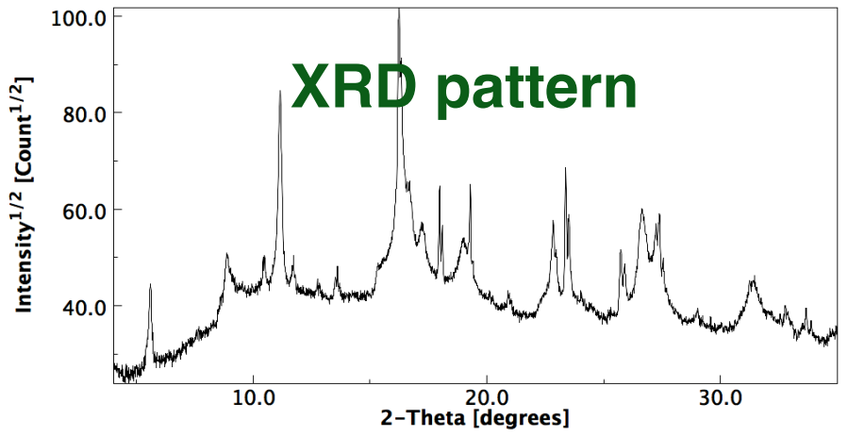
      Rietveld Search-Match ?
- Final step (XRD + XRF)

Full Pattern Search Match (FPSM)

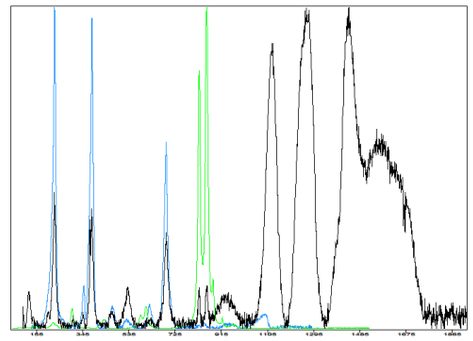
Starting database:
COD, ICSD, PDF4…







Raman



Phases identification

Early phase quantification

Microstructural characterization

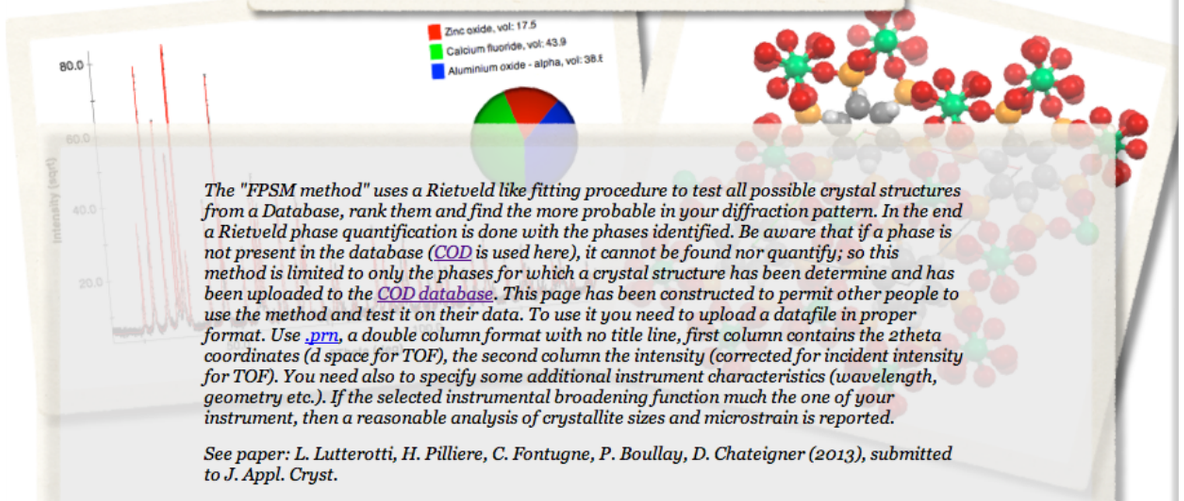
Better phase quantification

Chemical quantification

Full Pattern Search Match (Rietveld Search Match)

Full Profile Search Match

by L. Lutterotti using COD



The "FPSM method" uses a Rietveld like fitting procedure to test all possible crystal structures from a Database, rank them and find the more probable in your diffraction pattern. In the end a Rietveld phase quantification is done with the phases identified. Be aware that if a phase is not present in the database (COD is used here), it cannot be found nor quantify; so this method is limited to only the phases for which a crystal structure has been determine and has been uploaded to the COD database. This page has been constructed to permit other people to use the method and test it on their data. To use it you need to upload a datafile in proper format. Use .prn, a double column format with no title line, first column contains the 2theta coordinates (d space for TOF), the second column the intensity (corrected for incident intensity for TOF). You need also to specify some additional instrument characteristics (wavelength, geometry etc.). If the selected instrumental broadening function much the one of your instrument, then a reasonable analysis of crystallite sizes and microstrain is reported.

See paper: L. Lutterotti, H. Pilliere, C. Fontugne, P. Boullay, D. Chateigner (2013), submitted to J. Appl. Cryst.

Diffraction pattern and sample composition

Upload diffraction pattern: Choose File no file selected

Atomic elements in the sample: O Al Ca F Zn

☐ Sample nanocrystalline

Experiment details

Radiation:
◉ X-ray tube: Cu
○ Other : x-ray Wavelength (Å): 1.540598

Instrument geometry:
◉ Bragg-Brentano (theta-2theta)
○ Bragg-Brentano (2theta only), omega: 10
○ Debye-Scherrer
○ Transmission

Instrument broadening function: Medium

Structures database: CODstructures.sqlite

Search and quantify

DISCLAIMER

Your uploaded file will not be stored locally in our server and is only kept in memory during the computation. We have nor space, nor interest on keeping your experimental data or results!
The FPSM method will not be able to find a phase if it is not present in the database. At the moment the database is constructed using all phases in the COD. So it is extremely important to contribute and donate/upload crystal structures to the COD to make it more complete.
If you are willing to give us some feedback on the analysis or results, or want to contribute to ameliorate the service, send an email to: luca_lutterotti at ing_unitn_it (substitute _ with the dot).

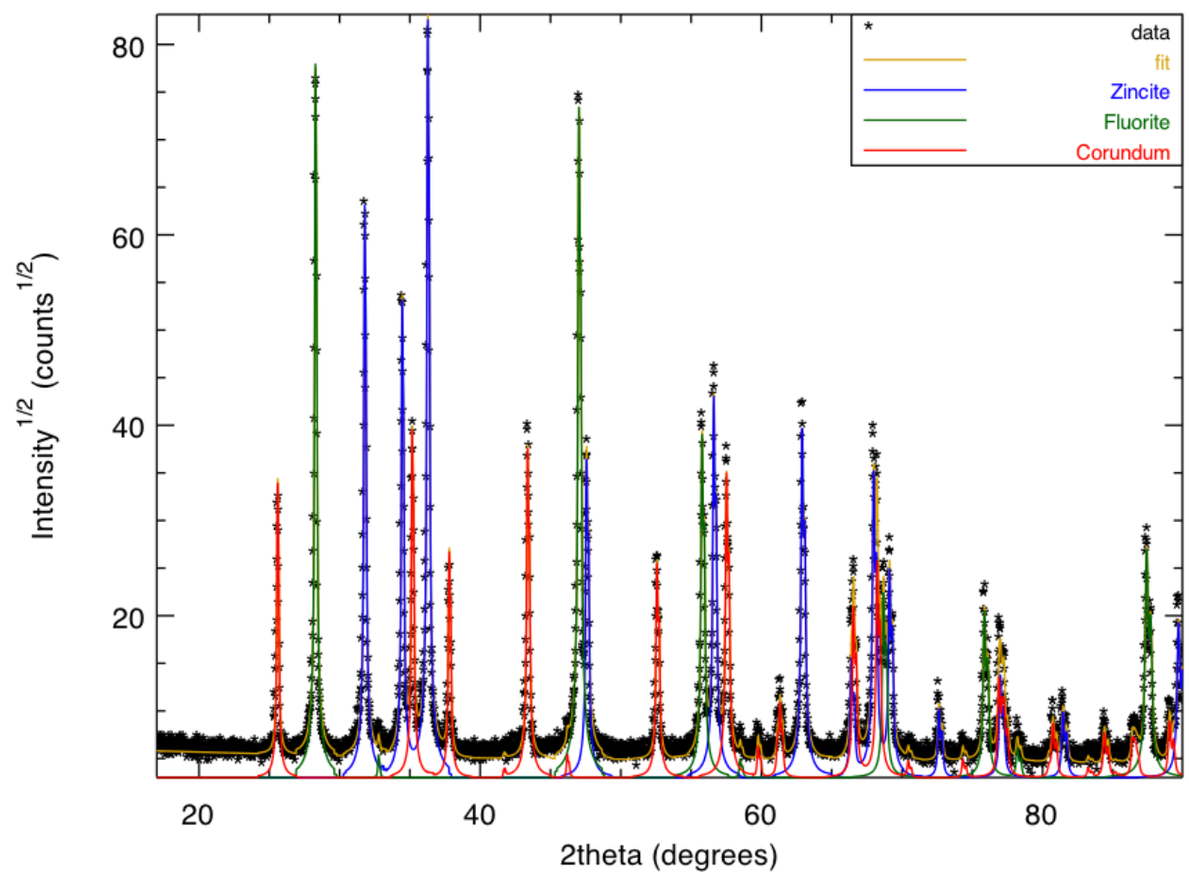
Full Pattern Search Match
Tube radiation: Cu
Using database: CODstructures.sqlite
Elements to include: O Al Ca F Zn
Number of structures to test: 271

Found phases and quantification:

Phase ID	name	vol. (%)	wt. (%)	crystallites (Å)	microstrain
9004180	Zincite	20.2448	28.8293	2067.89	0.000321462
1000043	Fluorite	42.5474	33.9434	2163.67	0.00037629
9007498	Corundum	37.2078	37.2273	1981.98	0.000294557

Final Rietveld analysis, Rw: 0.153089, GofF: 1.95965

Final Rietveld fit



FPSM computation finished!

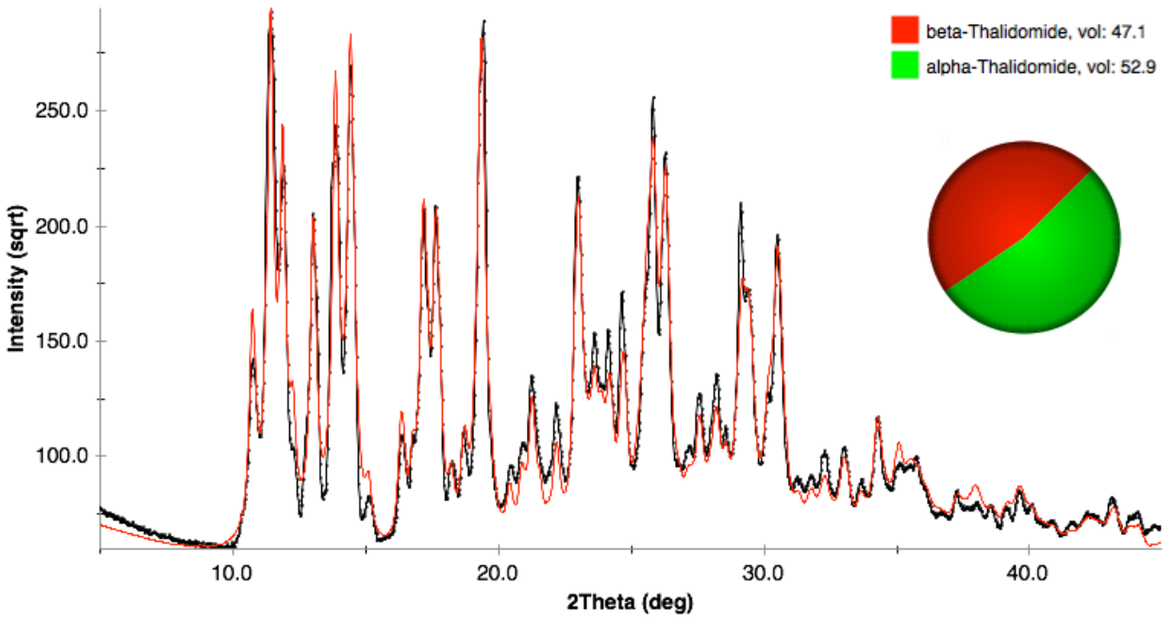
FPSM testing

http://nanoair.dii.unitn.it:8080/sfpm

Found phases and quantification:

Phase ID	name	vol. (%)	wt. (%)	crystallites (Å)	microstrain
9000098	Siderite	39.5067	45.9923	770.485	0.000874197
9002213	Hydroxylapatite	34.9531	32.5953	1000	0.0004
9010145	Quartz	1.97382	1.53981	1000	0.0004
9005624	Souzalite	12.452	11.1812	1000	0.0004
1011172	Quartz low	11.1144	8.69139	1000	0.0004

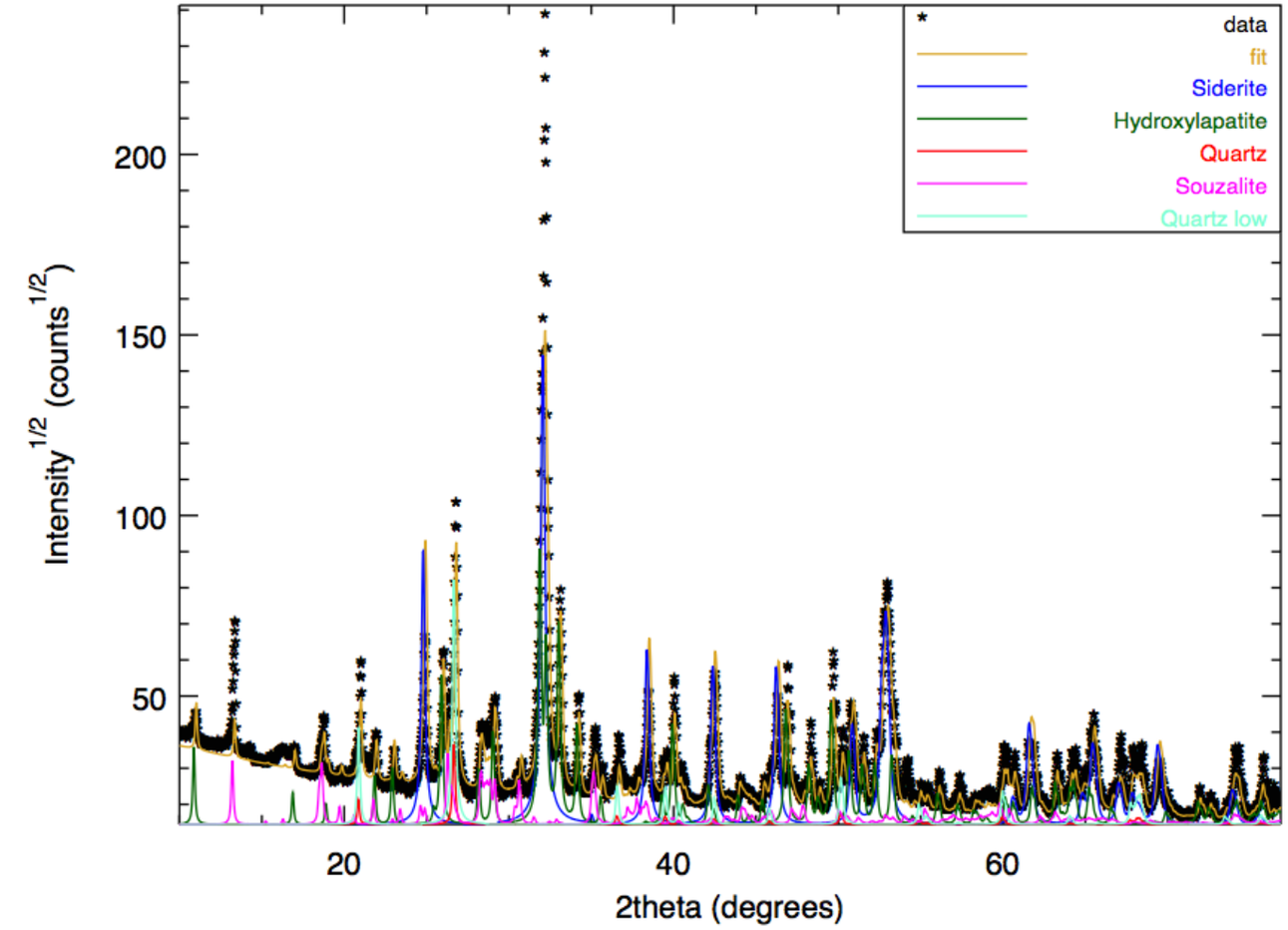
Final Rietveld analysis, Rw: 0.317671, GofF: 10.5251

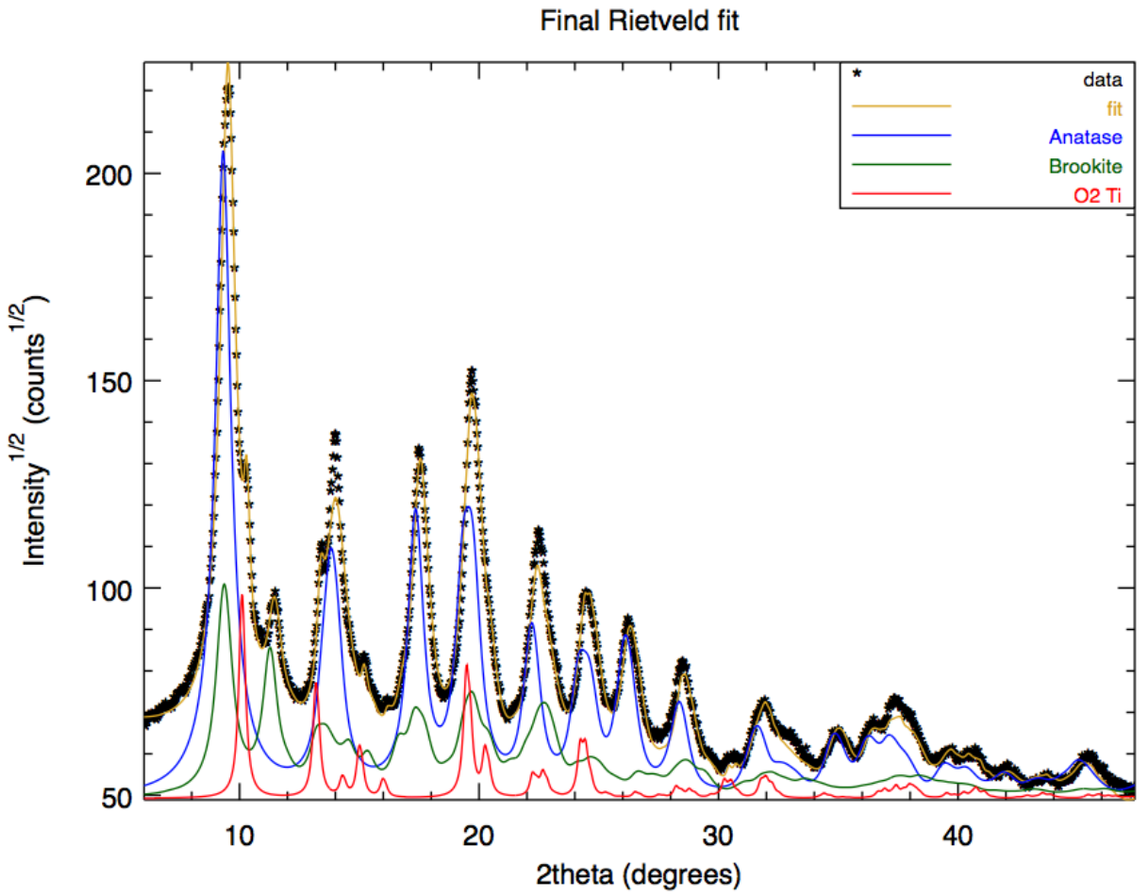


Found phases and quantification:

Phase ID	name	vol. (%)	wt. (%)	crystallites (Å)	microstrain
1010942	Anatase	65.6941	64.3453	64.7864	0.00356267
9004137	Brookite	26.4308	27.5815	57.9515	0.00122701
4102355	O2 Ti	7.87511	8.07321	152.681	0.000179707

Final Rietveld analysis, Rw: 0.0540809, GofF: 4.37766





QPA-Quantitative Phase Analysis

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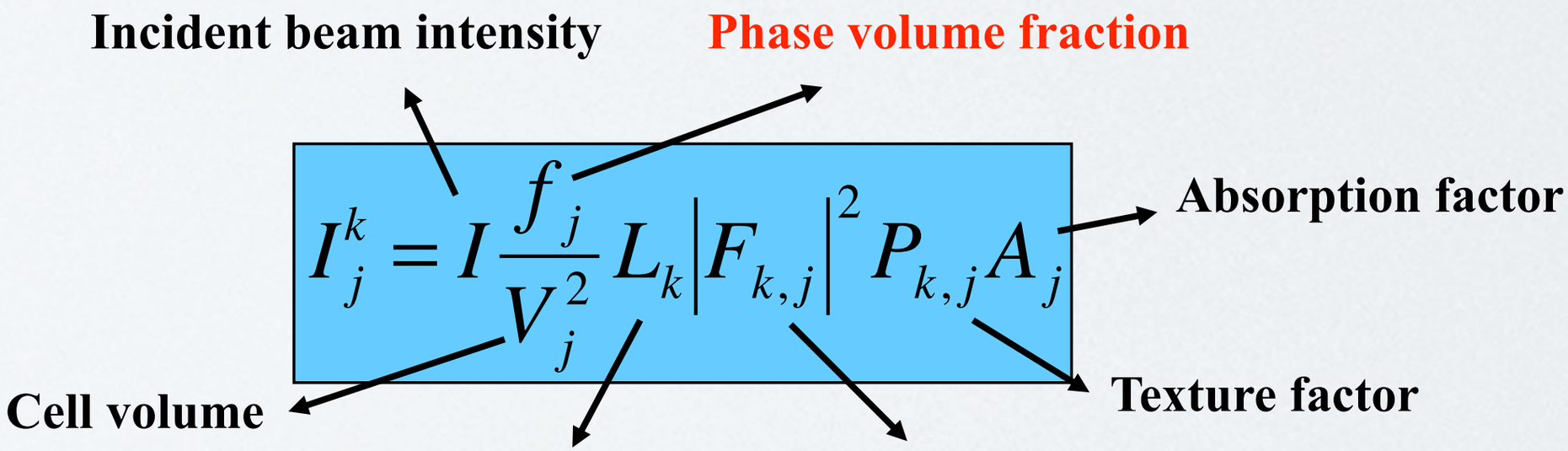
QPA methods

- Reflection intensity (reflection k of phase j):



- The intensity of a diffraction peak is directly proportional to the volume fraction
- QPA methods:
- Traditional (polymorph, internal standard, RIR….)
- Rietveld

Quantitative phase analysis

- Reflection intensity:

$$I_j^k = I \frac{f_j}{V_j^2} L_k \left| F_{k,j} \right|^2 P_{k,j} A_j$$

- In the case of random texture: $P_{k,j}=1$

- For reflection geometry and flat sample: $A_j = 1/2\mu^*$, μ^*=linear absorption coefficient of the mixture

- First problem: μ^* is unknown, but considering two phases (1 and 2) and measuring a peak k for phase 1 and peak s for phase 2:

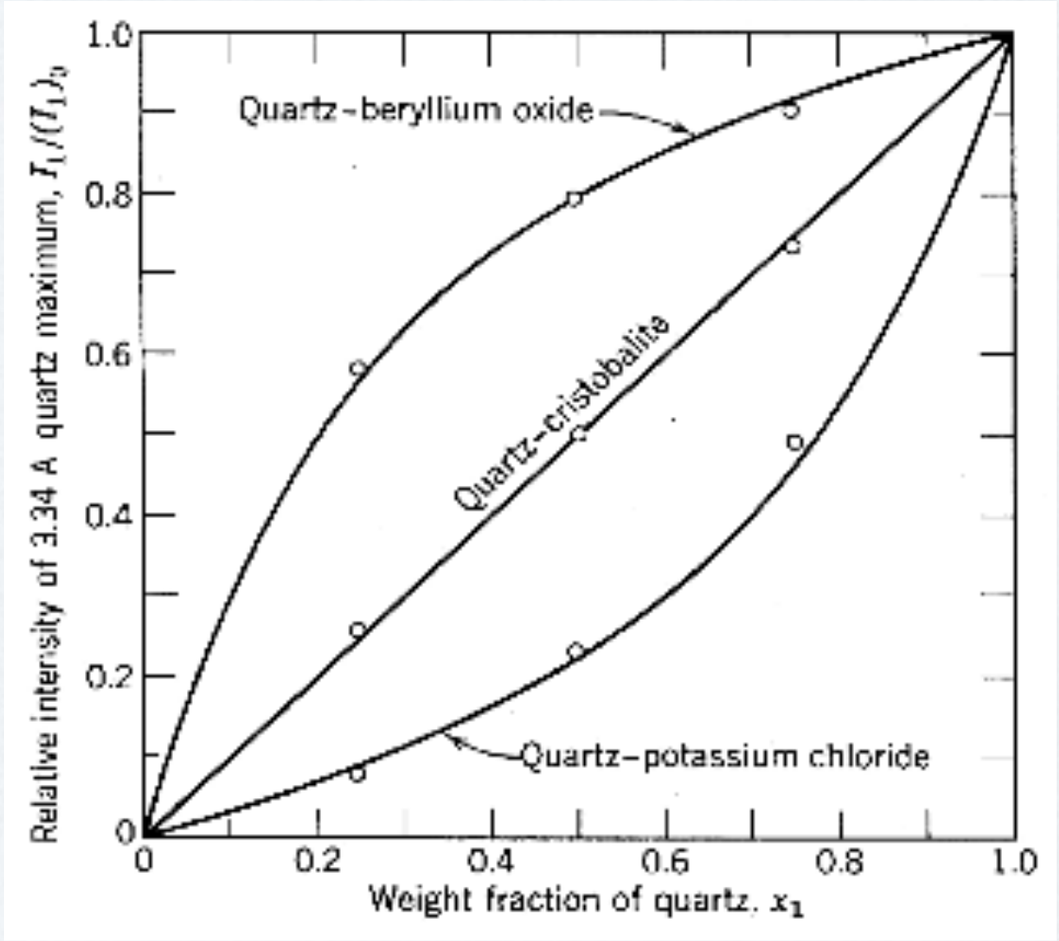
$$\frac{f_1}{f_2} = \frac{I_1^k}{I_2^s} \frac{V_1^2 L_s \left| F_{s,2} \right|^2}{V_2^2 L_k \left| F_{k,1} \right|^2}$$

Traditional methods (external standard)

- Require the measurement of a pure sample of one of the two phases at the same conditions (beam intensity, time and packing of the sample) as the mixture. Indicating with ext the peak intensity measured for the external standard or pure phase:

$$\frac{\mathrm{I}_1^{\mathrm{k}}}{\mathrm{I}_{1,\mathrm{ext}}^{\mathrm{k}}} = \frac{w_1 \mu_1^*}{w_1(\mu_1^* - \mu_2^*) + \mu_2^*}$$

- By graphical representation:
- The graph can be measured also (calibration curve)



Traditional methods (others)

- Internal standard: mixing phases 1 and 2 in know proportion we can measure K. When we add a know amount of phase 2 (the internal standard) to a sample containing phase 1, using K we determine the amount of phase 1.

- Polymorph method: developed for polymorph mixtures. The same formula is used and K is measured or computed theoretically. But no internal standard is needed. For polymorphs the absorption is the same so no matrix effects are present.

$$\frac{I_1^k}{I_2^s} = K\frac{w_1}{w_2}$$

- RIR or Reference Intensity Ratio: same principle as the internal standard that is always the corundum. Values of the RIR or intensity ratio of the more intense peak of each phase respect to the (113) peak of corundum are reported in the PDF of ICDD.

$$w_1 = \frac{I_1^k}{I_{\text{corundum}}^{113}}\frac{w_{corundum}}{RIR_{1,corundum}}$$

Limits of traditional methods and QPA

- Principal errors of traditional methods derive from:
  - Methodology to determine the peak intensity (often the height instead of the peak integral is used)
  - Use of only one peak (or few), so the results are affected more by preferred orientation etc.
  - Peak overlapping that make difficult to extract the intensity of a peak
  - In the RIR, the use of tabulated values that may not be representative of the real phase in the sample to be analysed. The multi-reflection RIR, where intensity is determine over all peaks in a certain range, has been introduced to mitigate some of these problems.

QPA by Rietveld method

- Recalling the usual intensity formula for Rietveld:

$$I_i^{calc}(\chi,\phi) = \sum_{n=1}^{Nphases} \frac{S_n}{V_n^2} \sum_k L_k \left|F_{k;n}\right|^2 S\left(2\theta_i - 2\theta_{k;n}\right) P_{k;n}(\chi,\phi) A + bkg_i$$

- Where Sn are the scale factors for the phases and remembering the intensity formula for peaks:

$$I_j^k = I \frac{f_j}{V_j^2} L_k \left|F_{k,j}\right|^2 P_{k,j} A_j$$

- It is easy to see that the scale factors incorporate the terms: incident beam intensity (equal for all phases) and the phase fraction, so we can write:

$$f_j = \frac{S_j}{\sum_{i=1}^{Nphases} S_i} \quad \text{or} \quad w_j = \frac{S_j \rho_j}{\sum_{i=1}^{Nphases} S_i \rho_i}$$

Volume fractions

Weight fractions

Phase density

Internal standard and Rietveld

- For amorphous quantitative analysis
- A know amount of crystalline phase, the standard, is added to the powder sample ($W_{std,noto}$)
- Data collection
- Rietveld analysis on all the crystalline phases
- If $W_{std,raff}$ is the weight fraction of the standard as determined by the Rietveld analysis, the unknown amorphous weight fraction is:

$$w_{am} = 1/(1 - w_{std,noto}) \cdot [1 - (w_{std,noto} / w_{std,raff})]$$

Unknown crystalline phase (the PONKS method)

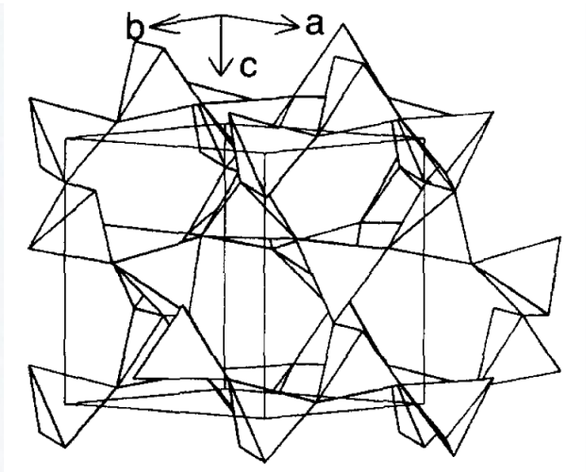
- Similar concept to RIR but for Rietveld
- We need an indexing (cell parameters) for the unknown phase
- We need a calibration: mix the unknown phase with a know amount of a well known phase (for which we have the crystal structure) and measure it
- Can be used for amorphous also
- Let's see how to do it with Maud

Pseudo-amorphous approximation

Journal of Non-Crystalline Solids 183 (1995) 39–42

Modelling the silica glass structure by the Rietveld method

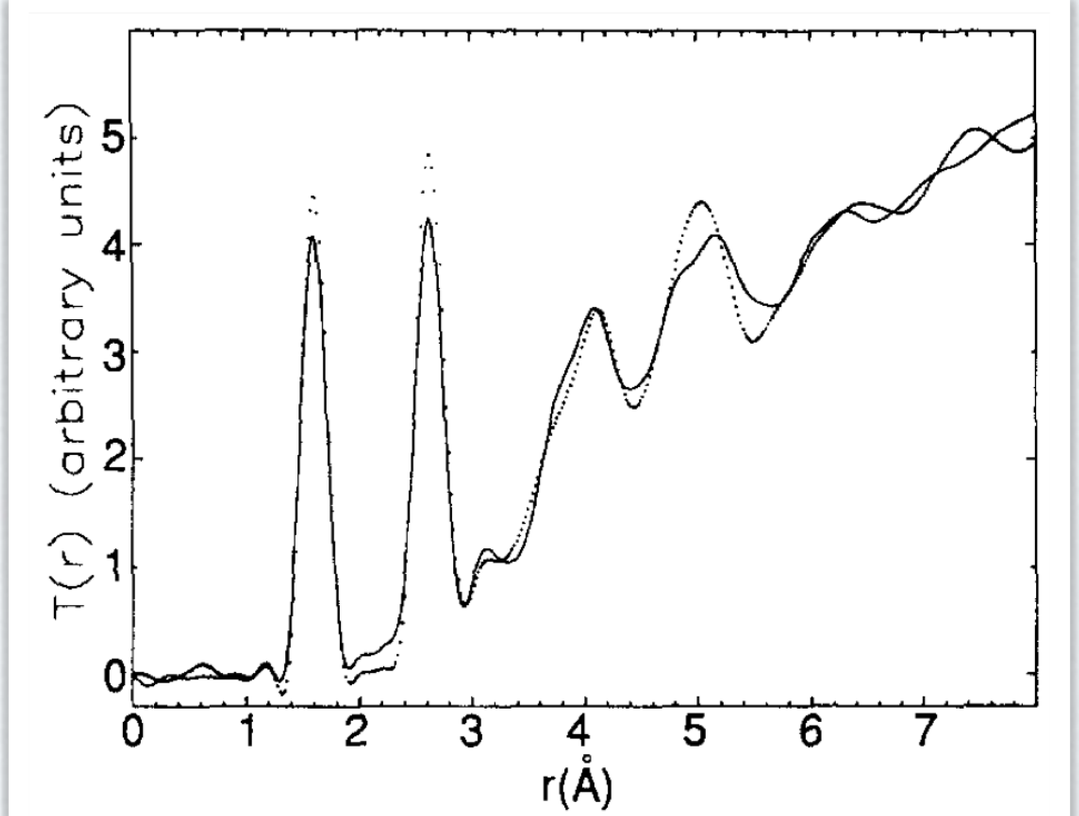
A. Le Bail *

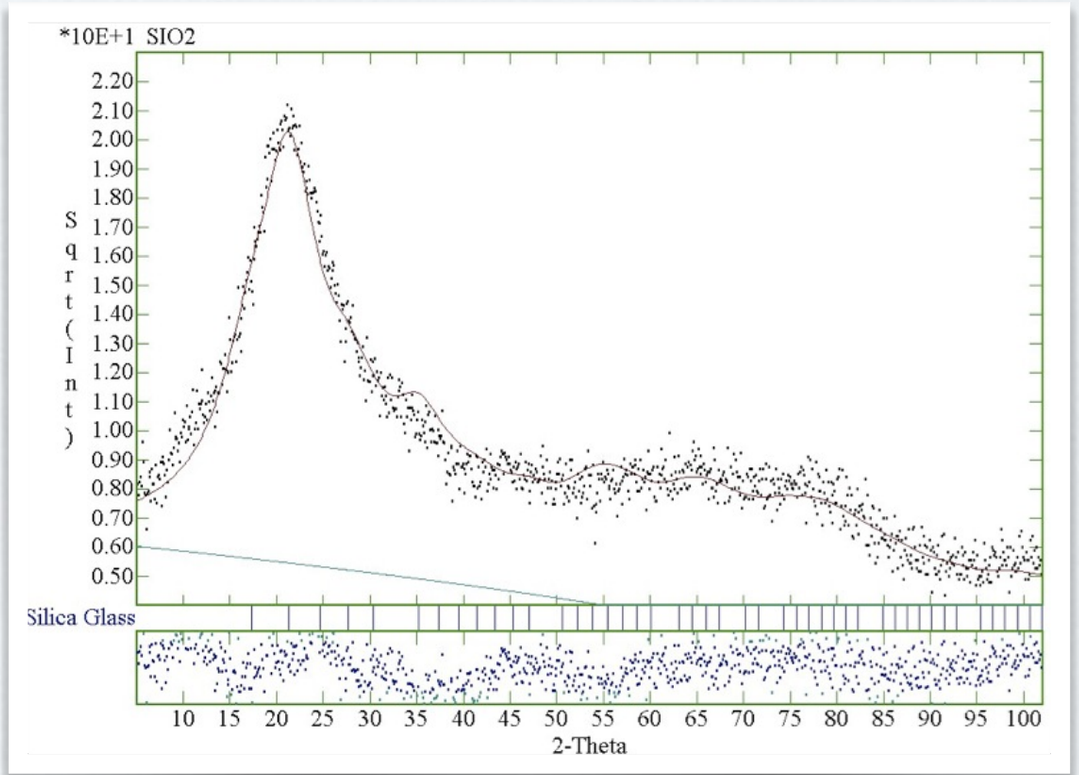


Refined parameters of the amorphous SiO_2 model in spacegroup $P2_12_12_1$

Atom	x	y	z
Si(1)	0.277(2)	0.275(2)	0.282(1)
Si(2)	0.009(1)	0.022(3)	0.016(3)
O(1)	0.125(3)	0.149(4)	0.152(3)
O(2)	0.635(4)	0.657(4)	0.061(5)
O(3)	0.065(4)	0.646(6)	0.654(7)
O(4)	0.670(3)	0.060(4)	0.621(4)

Lattice parameters: $a = 7.22(7)$ Å, $b = 7.09(6)$ Å and $c = 7.30(6)$ Å. V/molecule $= 46.7(2)$ Å^3 with $Z = 4$. Halfwidth parameters for the simultaneous fit of diffraction data rebuilt at a fictitious 2θ scale: $U = 22(6)$, $V = 0.5$, $W = 5.2(1)$ (neutron, $\lambda = 0.35$ Å) and $U = 42(11)$, $V = 1.0$, $W = 15(1)$ (X-ray, $\lambda = 0.5$ Å). The number in parentheses denotes the estimated standard deviation in the last digit.





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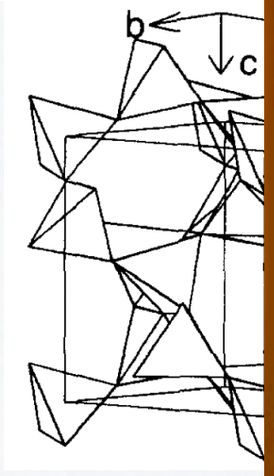
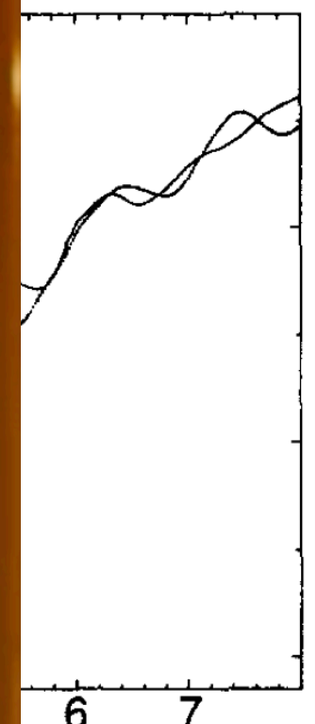
Modelling th

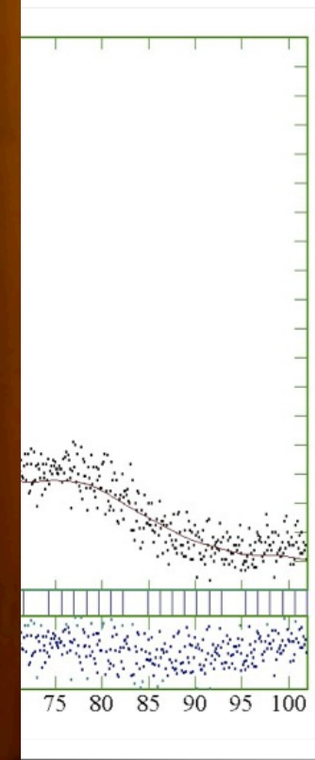


Refined parame
$P2_12_12_1$

Atom	x
Si(1)	0
Si(2)	0
O(1)	0
O(2)	0
O(3)	0
O(4)	0

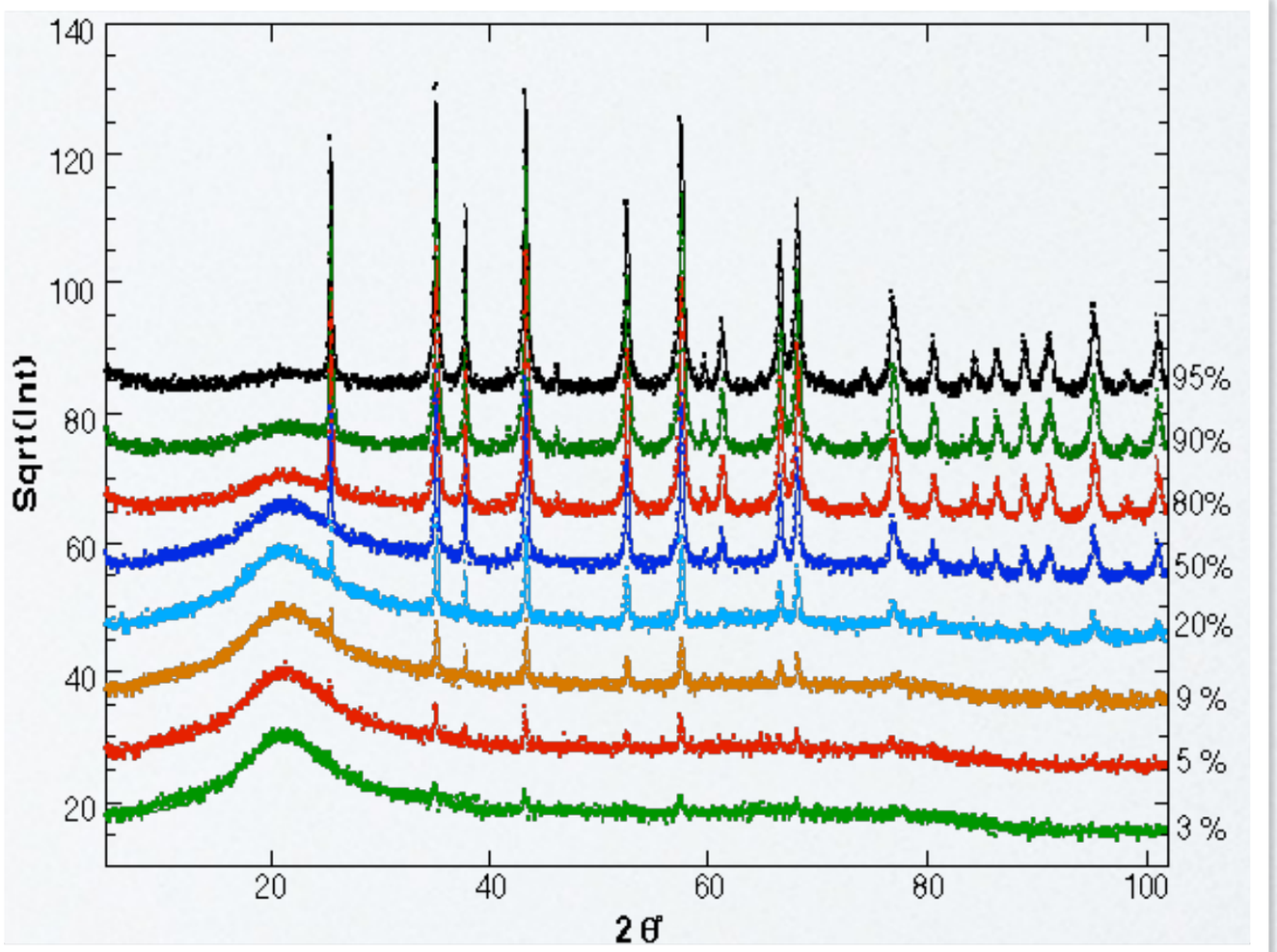
Lattice paramet
Å. V/molecul
for the simultan
scale: $U = 22(6$
$U = 42(11)$, V
in parentheses
digit.

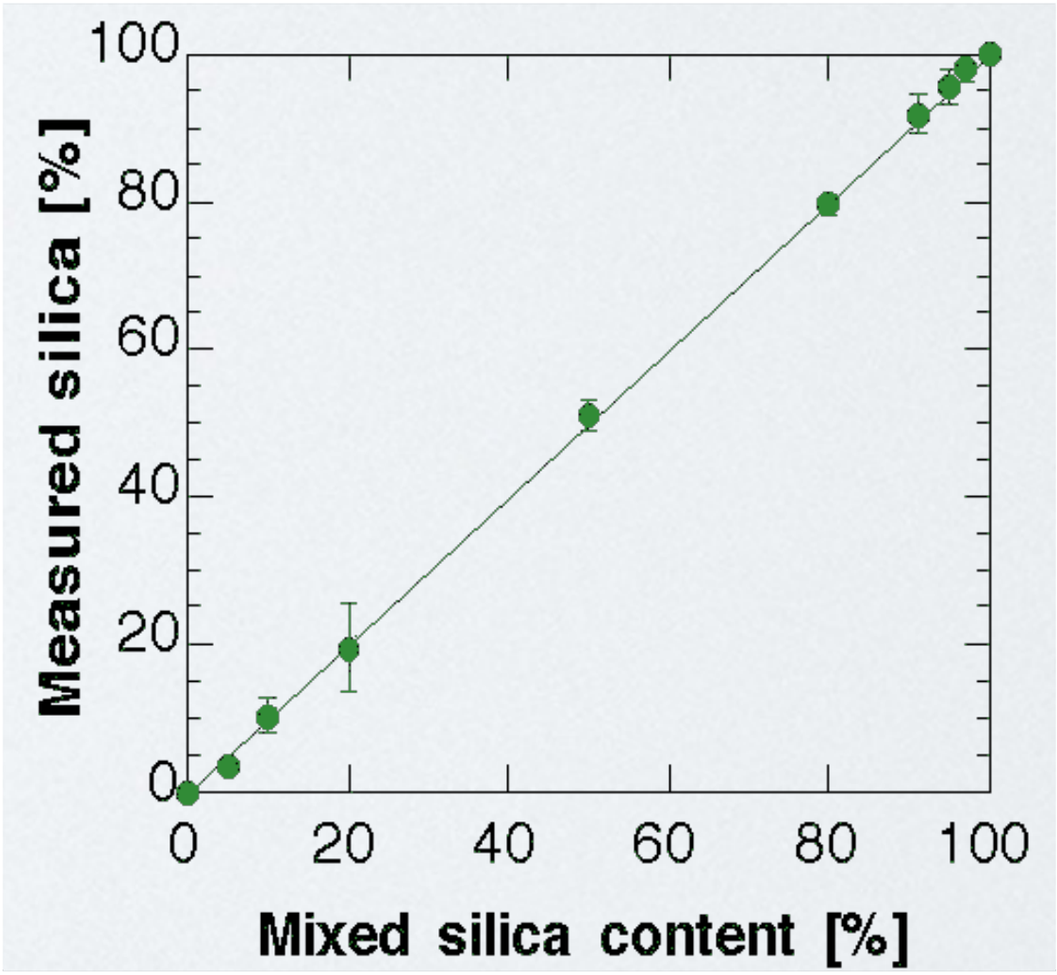




Corundum+amorphous silica mixed

Validation of the method testing with know amount of silica-alumina

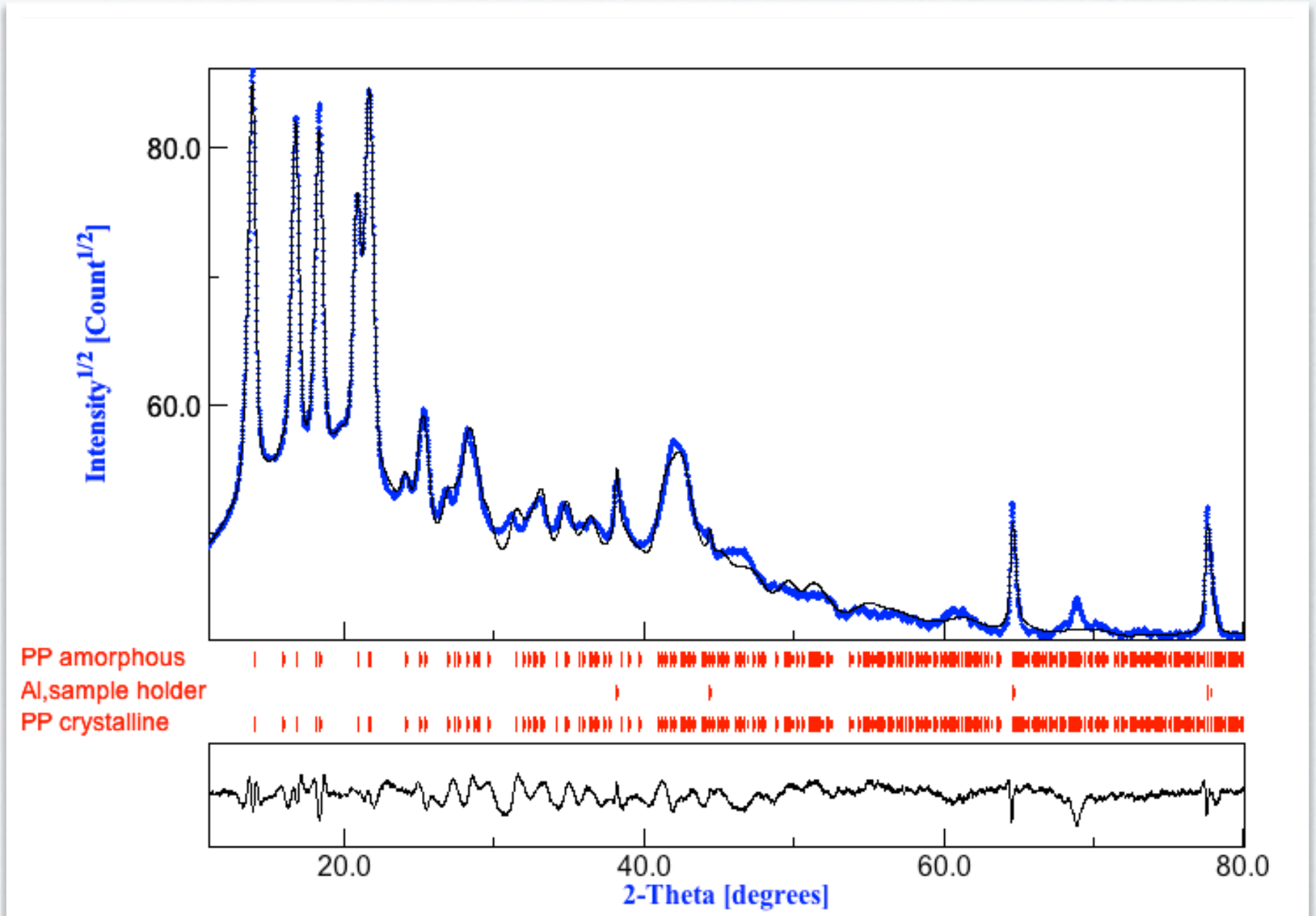




Lutterotti L., Ceccato R., Dal Maschio R., Pagani E.: Quantitative analysis of silicate glass in ceramic materials by the Rietveld method. Mater. Sci. Forum, 278-281, 87-92 (1998)

Crystalline fraction for polypropylene

- Same crystal structure for amorphous and crystalline
- Results: 43(1) % crystalline - 57(1) % amorphous



Errors in QPA

- Preferred orientation (texture): this is one of the main causes for errors in QPA, for powder samples, a correct sample preparation is fundamental

- Graininess: too few large grains contributing to the scattering; the intensity is not representative and the only solution is to improve the number of scattering grains (either by milling the sample, or spinning or enlarge the beam size)

- Microabsorption: large absorbing particles scatter more than light absorbing small grains inducing an erroneous quantitative phase analysis

Problems:

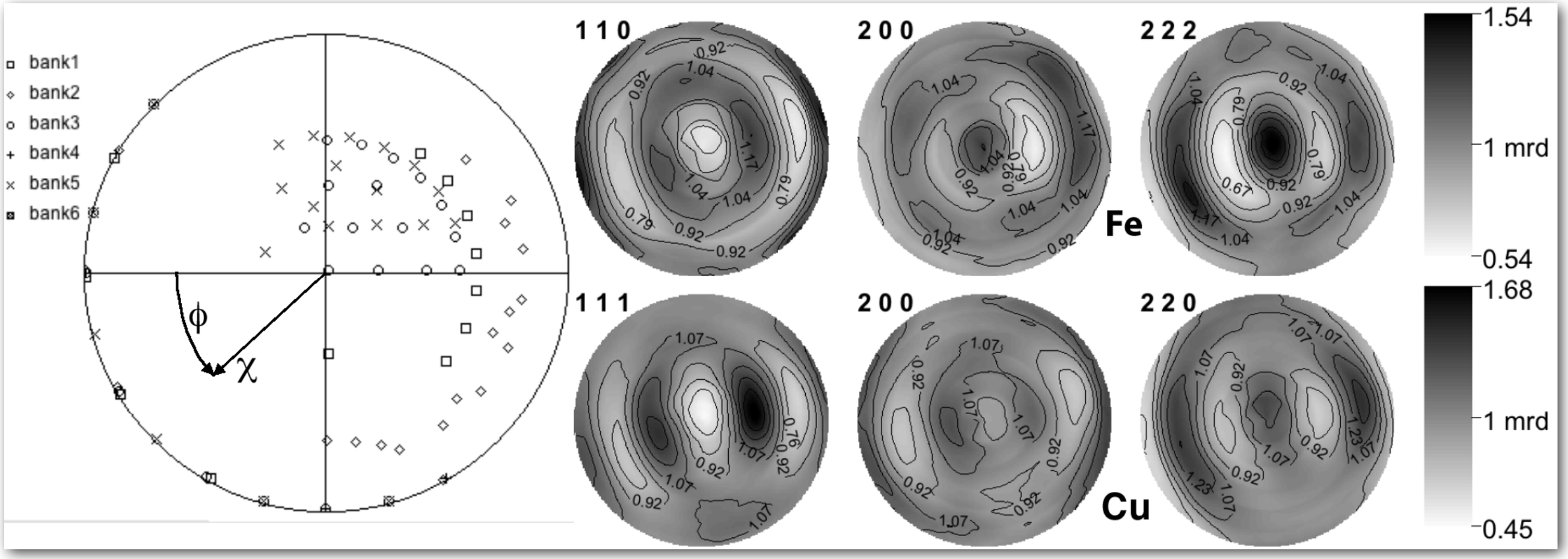
1) Texture (Preferred Orientations)

Analysis of rolled Cu67-Fe33 samples

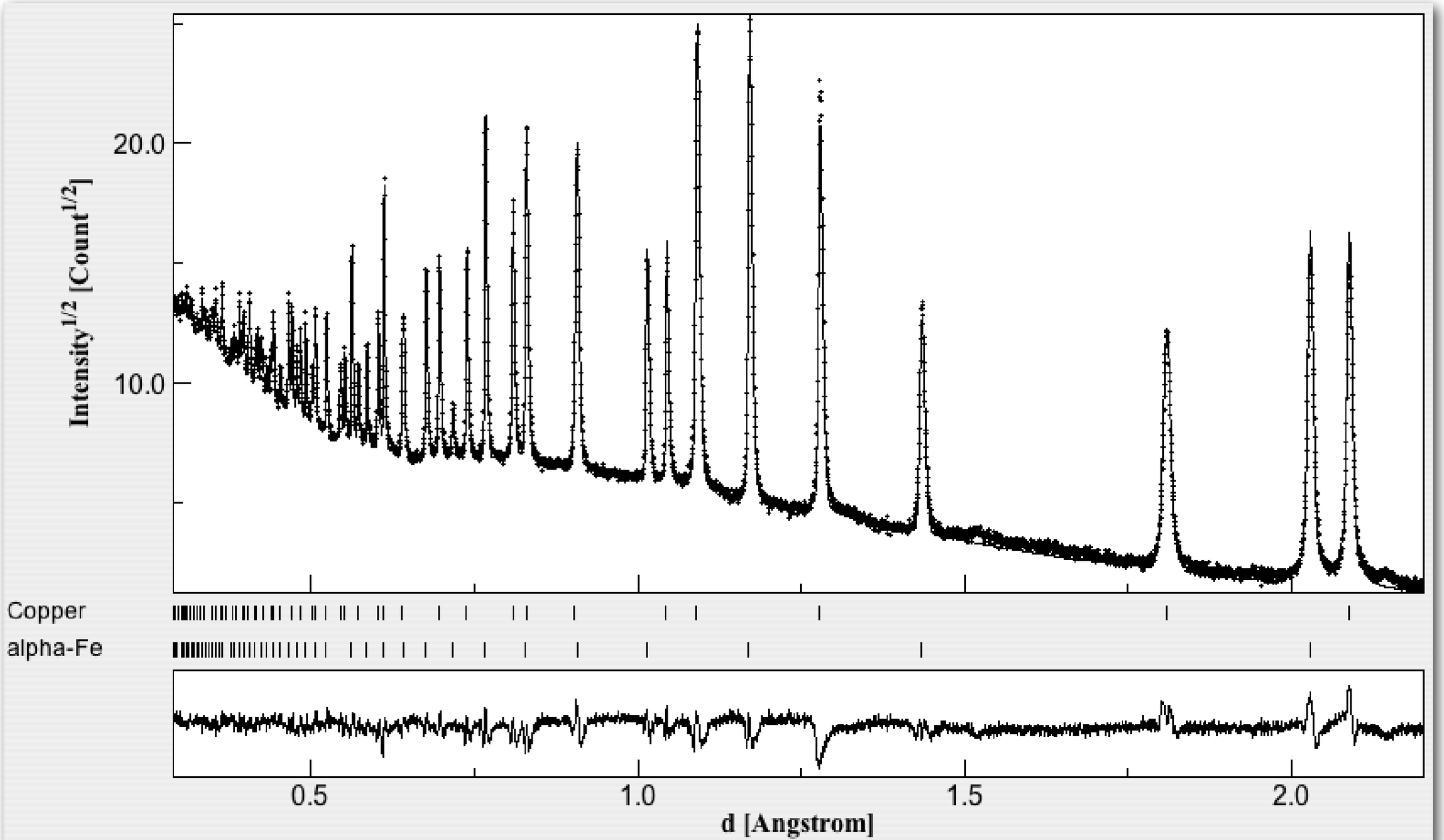
- **Production: Powder metallurgy (Technical University of Hamburg-Harburg, B. Commentz)**
- **67% of Cu - 33% of Fe**
- **Cold Isostatic Pressing (115 Mpa)**
- **Hot Pressing (750°C, 50 Mpa, 30 min)**
- **Resulting compacts: 1% porosity**
- **Rolling at 5 m/min**
  - **I: not deformed**
  - **II: 6 pass for -0.1/pass, plastic deformation: -0.607**
  - **III: 6 pass for -0.2/pass, plastic deformation: -1.142**
- **Measurements by Neutron TOF at IPNS**

Measurement and texture

- **Pole figure coverage showing the measuring points for the different banks**
- **Texture is only moderate**



Spectra sum for bank 2 with fitting by RTA



QPA analysis on one pattern

- **Only the spectrum at the center of pole figure was used**
- **For the ODF given by EWIMV we assumed the ODF was measured externally and used only to correct the spectrum**
- **We tested different texture corrections to see the effect on the QPA results**
- **The harmonic and March-Dollase corrections give erroneous quantities**
- **If the ODF is unknown, better to assume random ODF for QPA analysis**

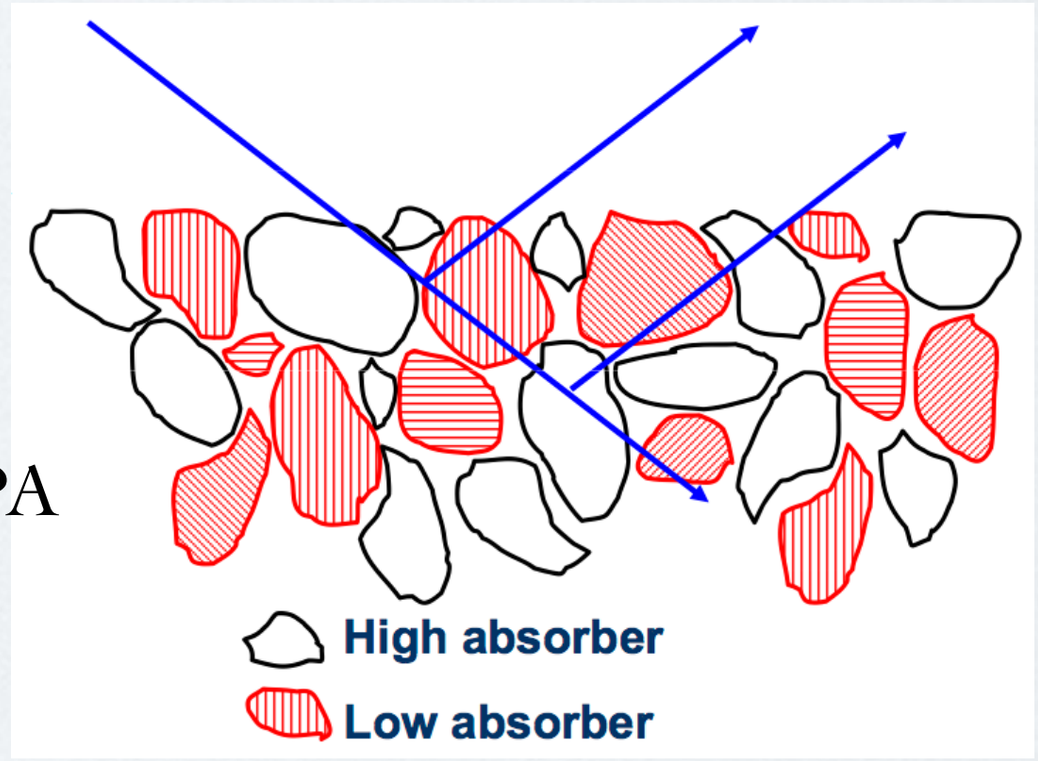
	Full range		Range 0.79-2.2 Å	
Methods	% Cu	R_w (%)	% Cu	R_w (%)
ODF given (EWIMV)	68.8(14)	14.5	66.5(19)	15.6
Random ODF	65.5(25)	31.5	63.3(37)	35
March-Dollase Fe(100) Cu(110)	58.3(20)	25	57.3(38)	29
Harmonic (fiber), L_{max} = 4	67.4(23)	27.5	62.7(41)	30.5
Harmonic (fiber), L_{max} = 6	70.0(13)	13	66.0(25)	14.5
Harmonic (fiber), L_{max} = 8	71.4(14)	12.7	70.2(40)	14.4

Problems:

2) Microabsorption (absorption contrast)

Absorption contrast

- The largest source of residual error in QPA by XRD is due to microabsorption
- Occurs when sample contains a mix of low & highly absorbing phases and grains in one of the phases are bigger than a critical value (~1 micron)
- High absorbers:
  - Beam absorbed in surface of grain
  - Only a fraction of the grain diffracting
  - Intensity under-overestimated – low QPA
- Low absorbers:
  - Beam penetrates further into grain
  - Greater likelihood of 'volume diffraction' occurring
  - Intensity over-estimated – high QPA



The Brindley correction

The correction equation:

$$w_i = \frac{I_i \rho_i}{\tau_i \sum_{j=1}^{N} \frac{I_j \rho_j}{\tau_j}}$$

where τ_i is given by Brindley in a table and the following formula is fitting it well (spherical particles):

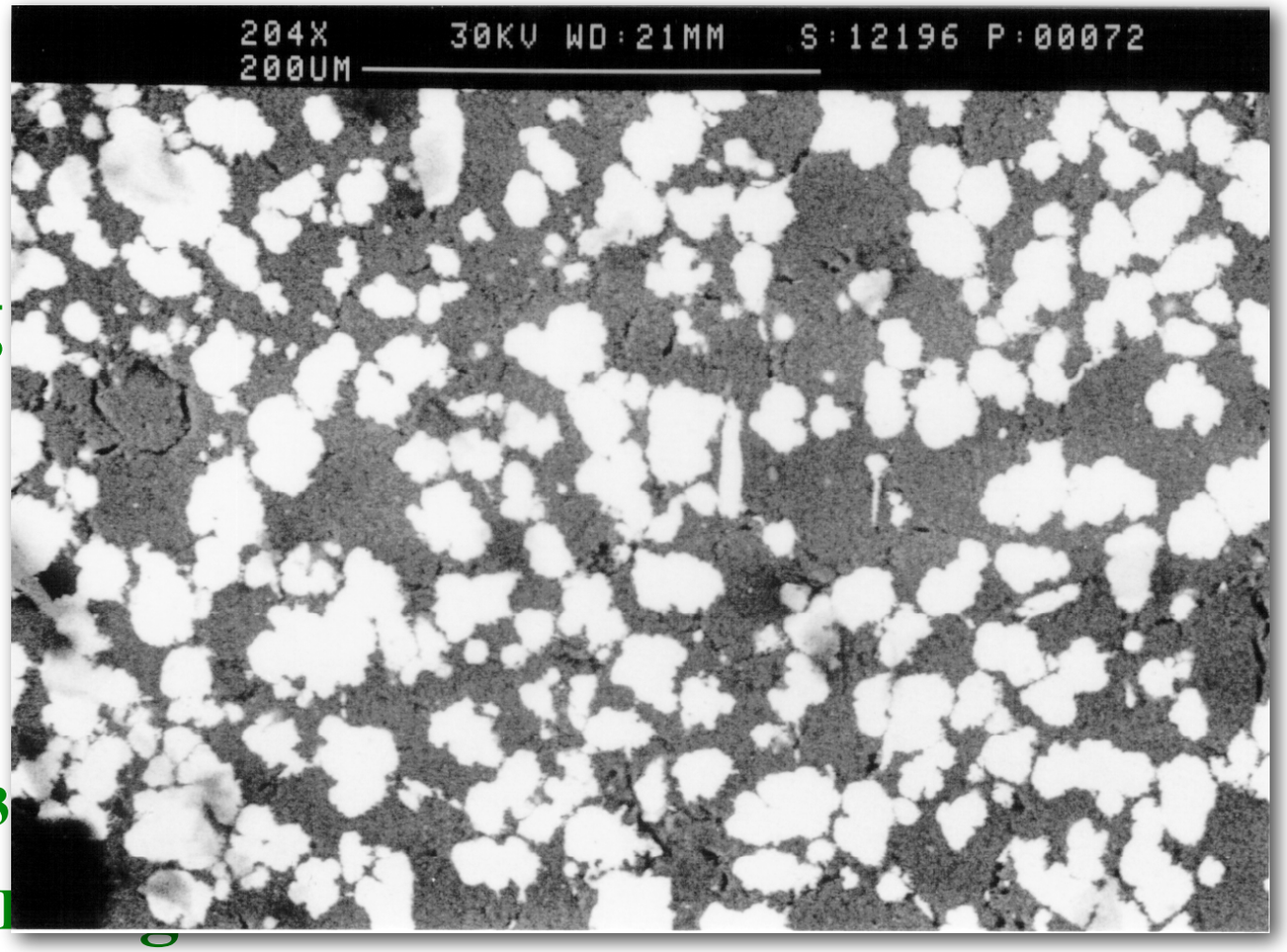
$$\tau_i = -0.00229 + 2.054e^{-\frac{(\mu_i - \bar{\mu})R_i + 0.50356}{0.69525}}$$

Brindley G. W.: A theory of X-ray absorption in mixed powders. Philos. Mag. **36**, 347-369 (1945)

Cermet production ($Ni-Al_2O_3$)

★Powder metallurgy

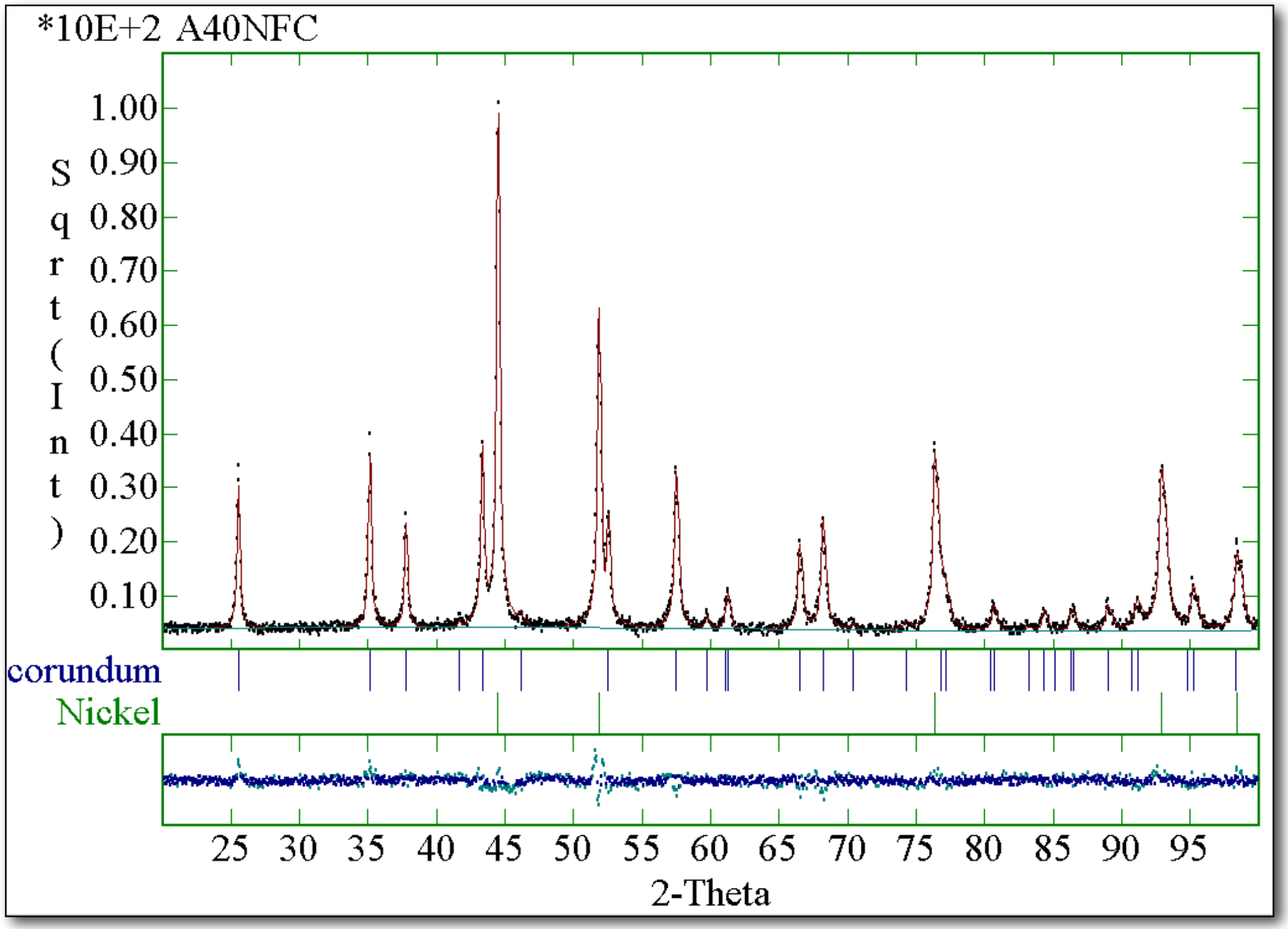
- Forming and sintering
- Cold Isostatic Pressing
- Hot Pressing



★Active binder

- Binder + powder Al_2O_3
- Polimerization and for
- Thermal treatment (decomposition) + sintering

Quantitative phase analysis (Rietquan)



Quantitative phase analysis: problems

✓ **High contrast in absorption between Ni and alumina**

	No Correction		Brindley Cubic Corr.		Brindley Spheric Corr.	
	$\%Al_2O_3$ VOL	%Ni VOL	$\%Al_2O_3$ VOL	%Ni VOL	$\%Al_2O_3$ VOL	%Ni VOL
Al_2O_3 + 40%VOL Ni Powders	72.1 (2)	27.9 (2)	61.3 (2)	38.7 (2)	63.8 (2)	36.2 (2)
Pure Al_2O_3 F1	100 (0)	0 (0)	100 (0)	0 (0)	100 (0)	0 (0)
Al_2O_3 + 10%VOL Ni F1	94.7 (1)	5.34 (1)	89.9 (1)	10.1 (1)	91.2 (1)	8.8 (1)
Al_2O_3 + 20%VOL Ni F1	88.1 (1)	11.9 (1)	79.9 (1)	20.1 (1)	82.0 (1)	18.0 (1)
Al_2O_3 + 30%VOL Ni F1	80.7 (2)	19.3 (2)	70.4 (2)	29.6 (2)	72.9 (2)	27.1 (2)
Al_2O_3 + 40%VOL Ni F1	70.1 (3)	29.9 (2)	59.2 (3)	40.8 (2)	61.7 (3)	58.1 (2)
Pure Al_2O_3 F1C23	100 (0)	0 (0)	100 (0)	0 (0)	100 (0)	0 (0)
Al_2O_3 + 10%VOL Ni F1C23	91.4 (1)	8.6 (1)	84.6 (1)	15.4 (1)	86.4 (1)	13.6 (1)
Al_2O_3 + 20%VOL Ni F1C23	88.2 (1)	11.8 (1)	79.8 (1)	20.2 (1)	82.0 (1)	18.0 (1)
Al_2O_3 + 30%VOL Ni F1C23	79.8 (2)	20.2 (2)	69.4 (2)	30.6 (2)	71.9 (2)	28.1 (2)
Al_2O_3 + 40%VOL Ni F1C23	70.6 (3)	29.4 (3)	60.4 (3)	39.6 (3)	62.9 (3)	37.1 (3)
Al_2O_3 + 20%VOL Ni HP (b)	88.4 (1)	11.6 (1)	80.4 (1)	19.6 (1)	82.4 (1)	17.6 (1)
Al_2O_3 + 20%VOL Ni HP (w)	88.4 (1)	11.6 (1)	80.3 (1)	19.7 (1)	82.4 (1)	17.6 (1)
Al_2O_3 + 20%VOL Ni HP (Mo)	89.7 (1)	10.3 (1)	78.8 (1)	21.2 (1)	81.4 (1)	18.6 (1)
Al_2O_3 + 40%VOL Ni HP (b)	73.8 (2)	26.2 (2)	63.1 (2)	36.9 (2)	65.6 (2)	34.4 (2)
Al_2O_3 + 40%VOL Ni HP (w)	70.2 (2)	29.8 (2)	59.2 (2)	40.6 (2)	61.9 (2)	38.1 (2)
Al_2O_3 + 40%VOL Ni HP (Mo)	76.1 (3)	23.9 (2)	61.5 (3)	38.5 (2)	64.7 (3)	35.3 (2)

Use neutron