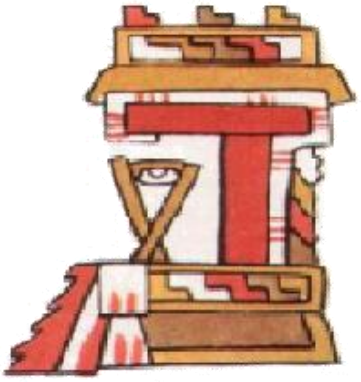

A Novel Method to Determine Amorphous Phase Concentrations Using the Rietveld Refinement Technique

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LAREC (**L**aboratorio **R**efinamiento **E**structuras **C**ristalinas)

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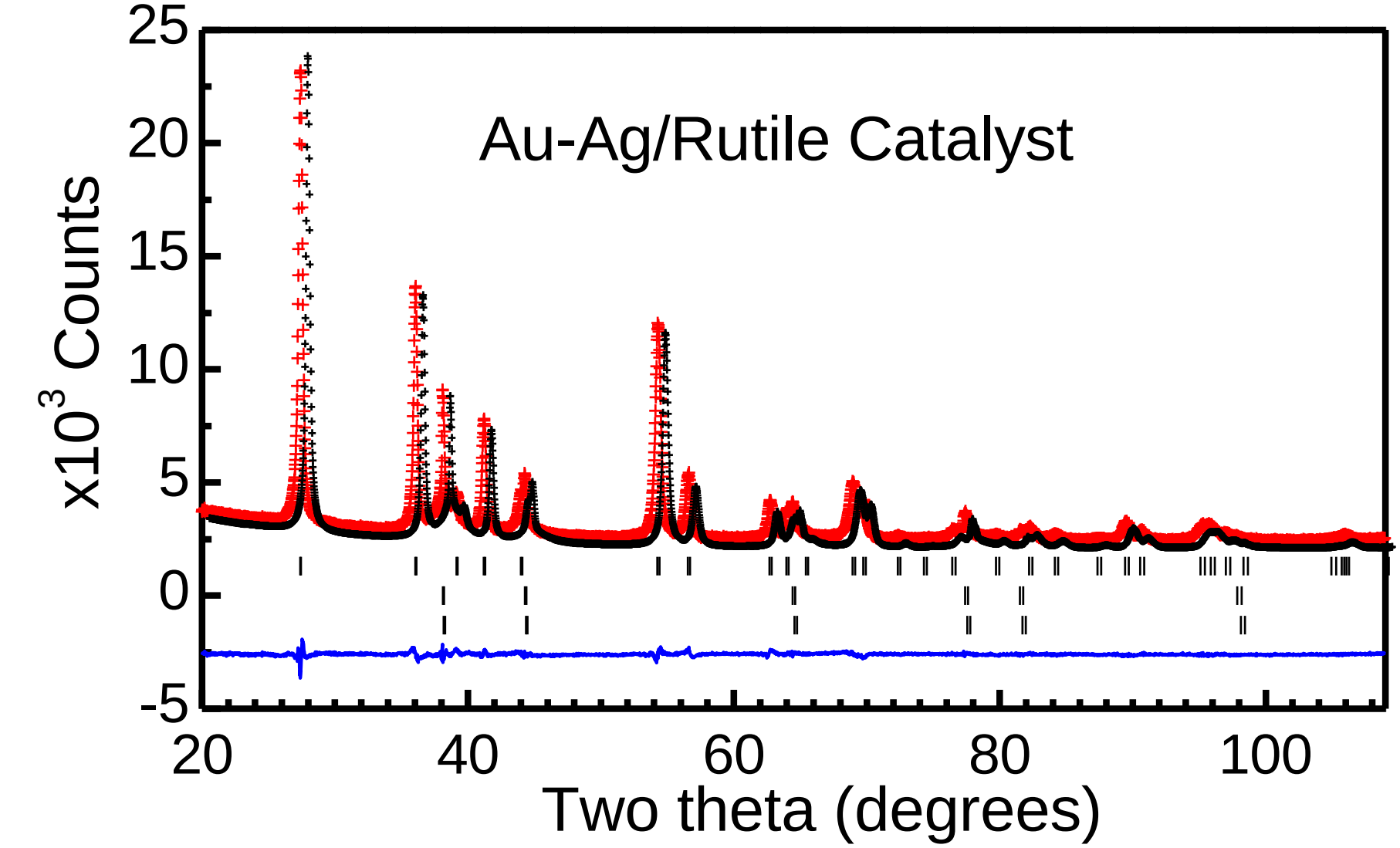
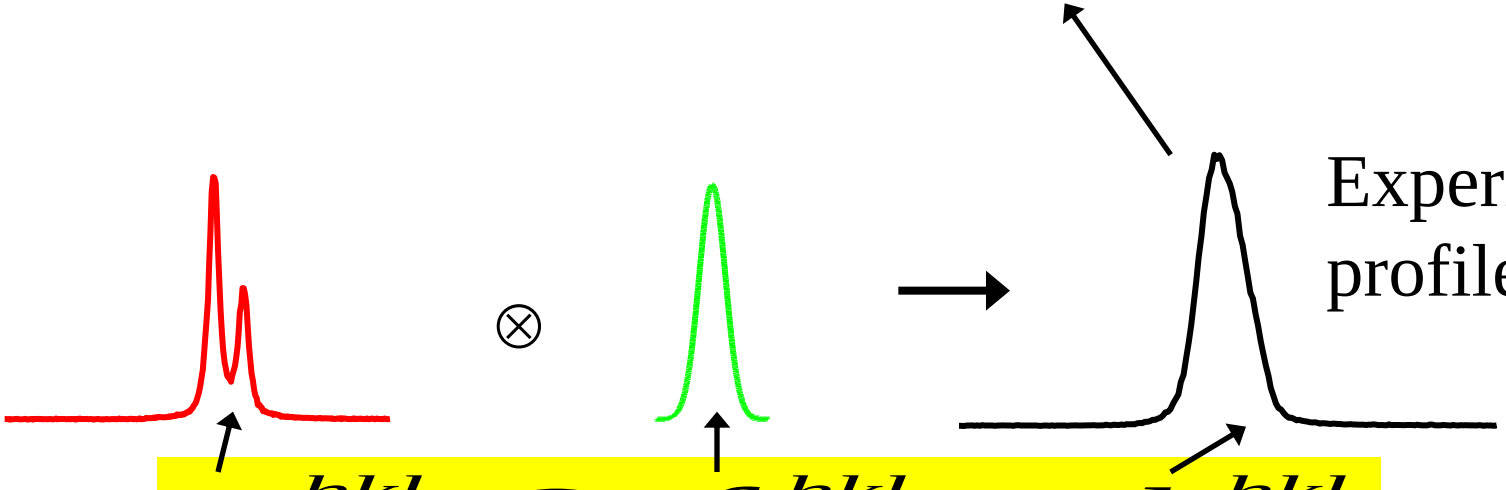
$$y_{ci}(2\theta_i) = S \sum |F_K|^2 \phi(2\theta_i - 2\theta_K) L_K P_K A + y_{bi}$$

1. Structure factor, F_K: Crystallography
2. Phase Scale, S: Phase concentration
3. ϕ Sample Microstructure
   and instrument: optics, L, A
4. Background, y_b:

$$Sy = \Sigma\, w_i\,(y_i - y_{ci})^2;\;\; w_i = 1/y_i$$



$$y_{ci}(2\theta_i) = S \sum |F_K|^2 \phi(2\theta_i - 2\theta_K) L_K P_K A + y_{bi}$$



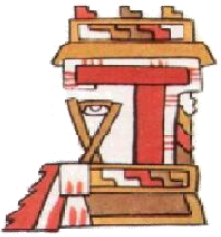
Instrumental resolution

Physical broadening

Microstructure

Atom vibration

Line Broadening



Peak diffraction profile $\phi(2\theta_K)$

Convolution of

Instrumental Function ($F_{instrument}$)

and Sample Function (F_{sample})

$$\phi(2\theta_K) = F_{instrument} \otimes F_{sample}$$

Instrumental function

$F_{instrument}$

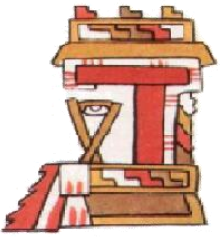
$2\theta = 83°$

-0.4°

+0.4°

$2\theta = 14°$

$2\theta = 4°$



Sample function: F_{sample}

$$F_{sample} = F_{crystallite\ size} \otimes F_{microstrain} \otimes F_{size\_distribution}$$

Crystallite size (Domain coherence)
Debye-Scherrer $\Rightarrow$ **fwhm α 1/Cos θ**

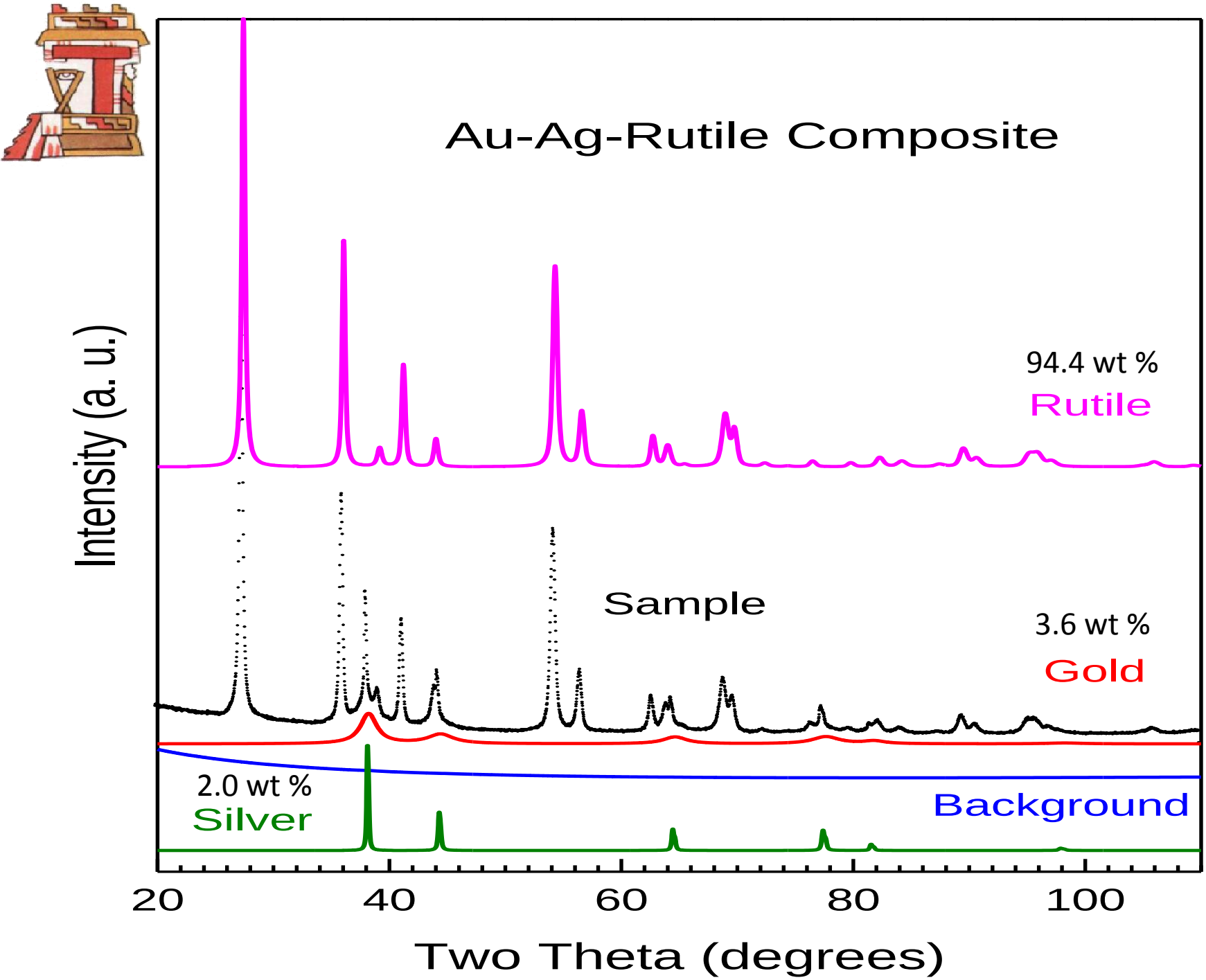
Microstrain $\Rightarrow$ **fwhm α Tan θ**

Crystallite size distribution
Log-normal distribution: the logarithm of the crystallite size distribution follow a Gaussian distribution $\Rightarrow$ **fwhm α σ ; (independent of θ)**

Scale factor -> Phase concentration

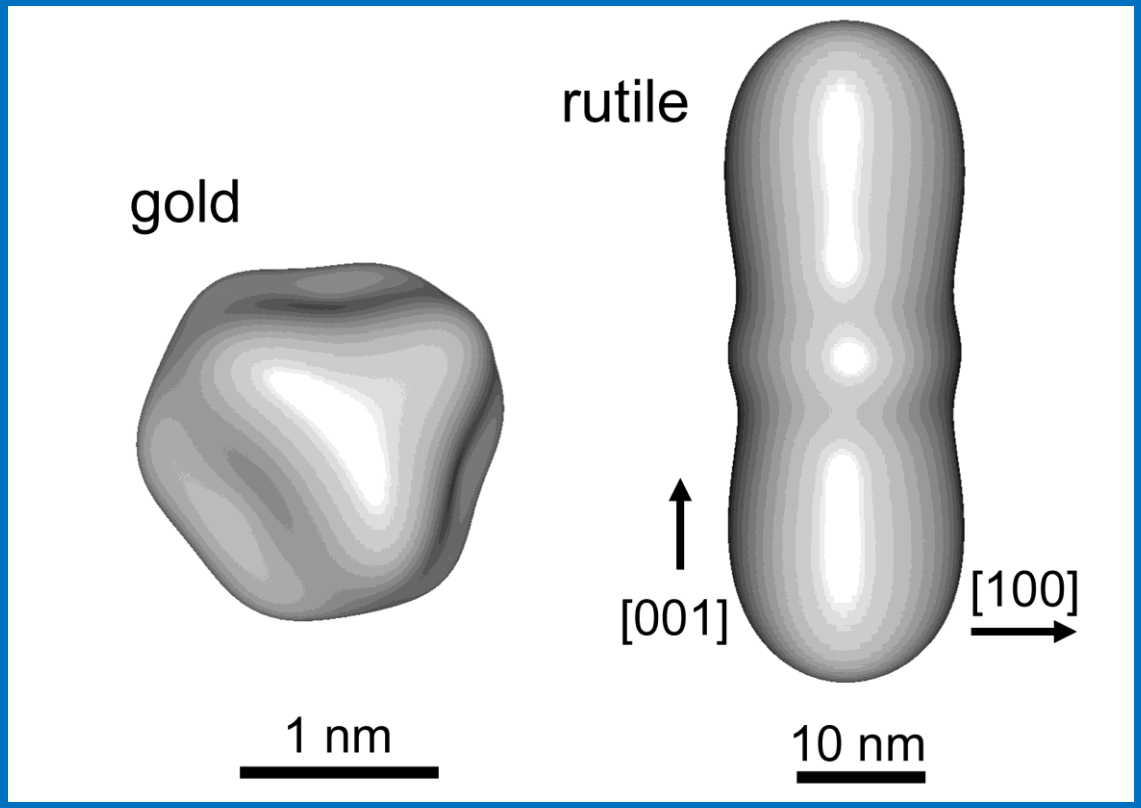
$$W_i\ (\%) = S_i\ (ZMV)_i\ /\ \Sigma_p\ S_p\ (ZMV)_p$$

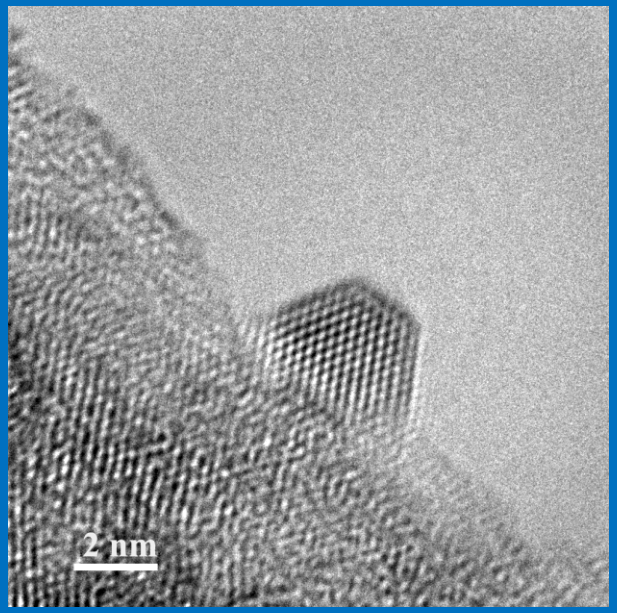
W_i	weight percent of phase i
S_i	Phase scale factor
ZM	Unit cell mass
V	Unit cell volume

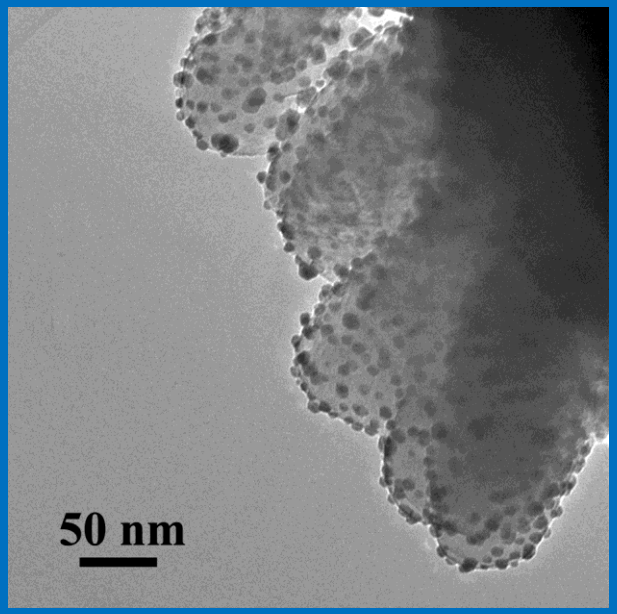

Au-Ag-Rutile Composite
Intensity (a. u.)
94.4 wt %
Rutile
Sample
3.6 wt %
Gold
2.0 wt %
Silver
Background
20
40
60
80
100
Two Theta (degrees)

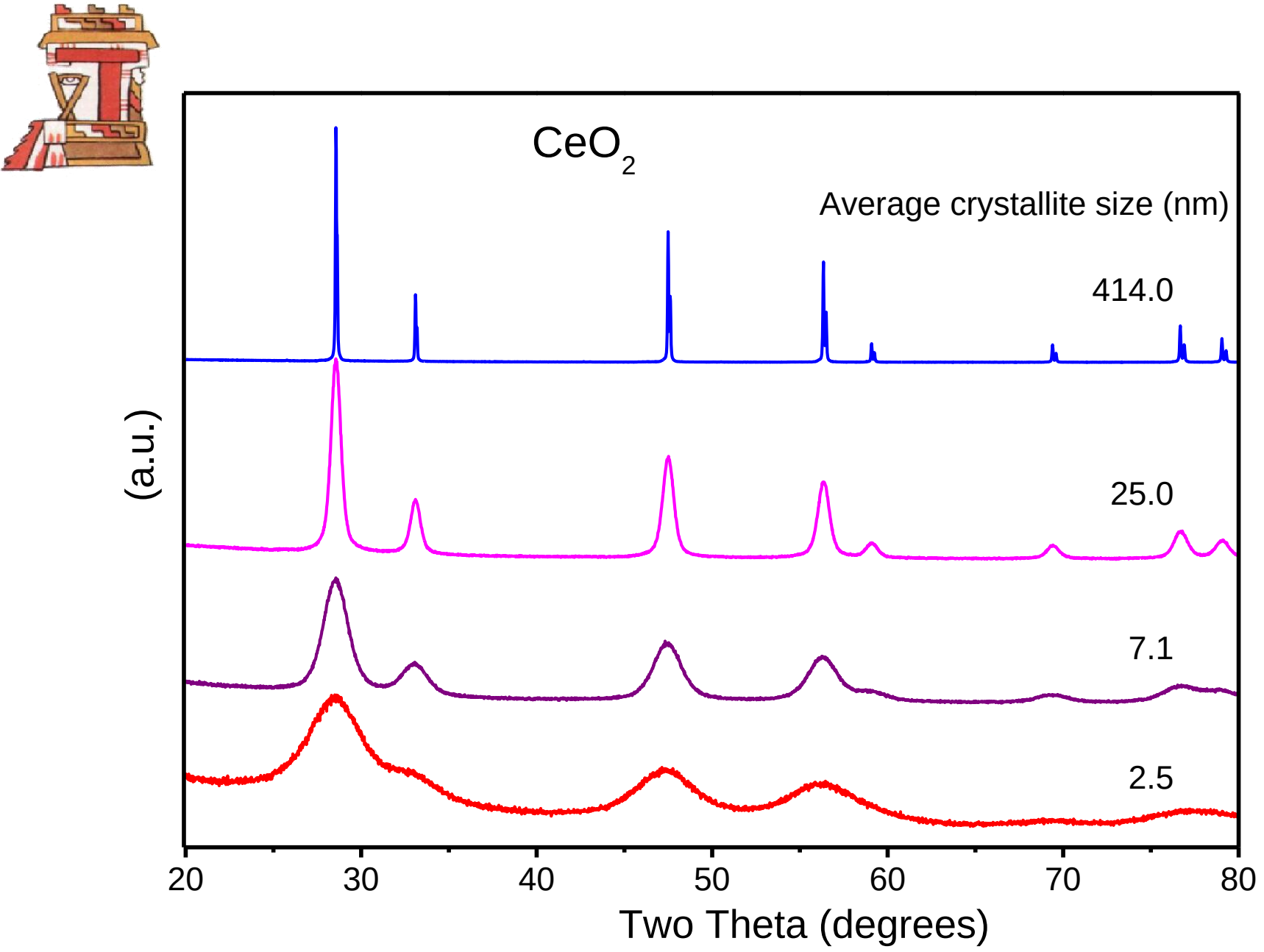
$$H_L = F_h(\alpha_z)/\cos\theta$$

$$F_h(\alpha_z) = \lambda \sum a_{lmp} Y_{lmp}(\theta, \Phi)$$

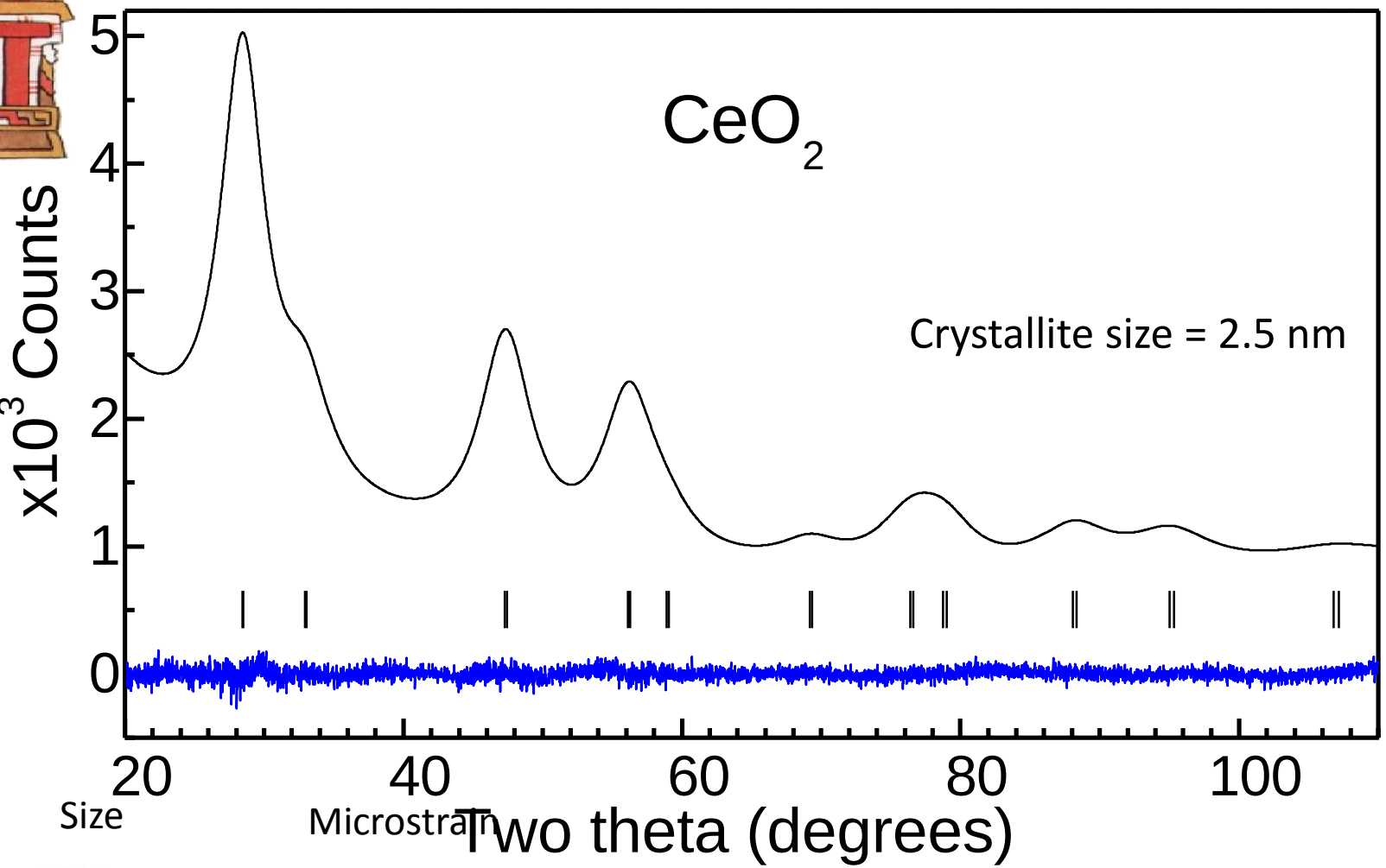


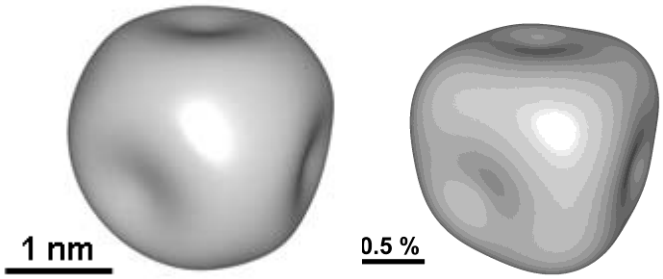





CeO2
Average crystallite size (nm)
414.0
25.0
7.1
2.5
(a.u.)
20
30
40
50
60
70
80
Two Theta (degrees)

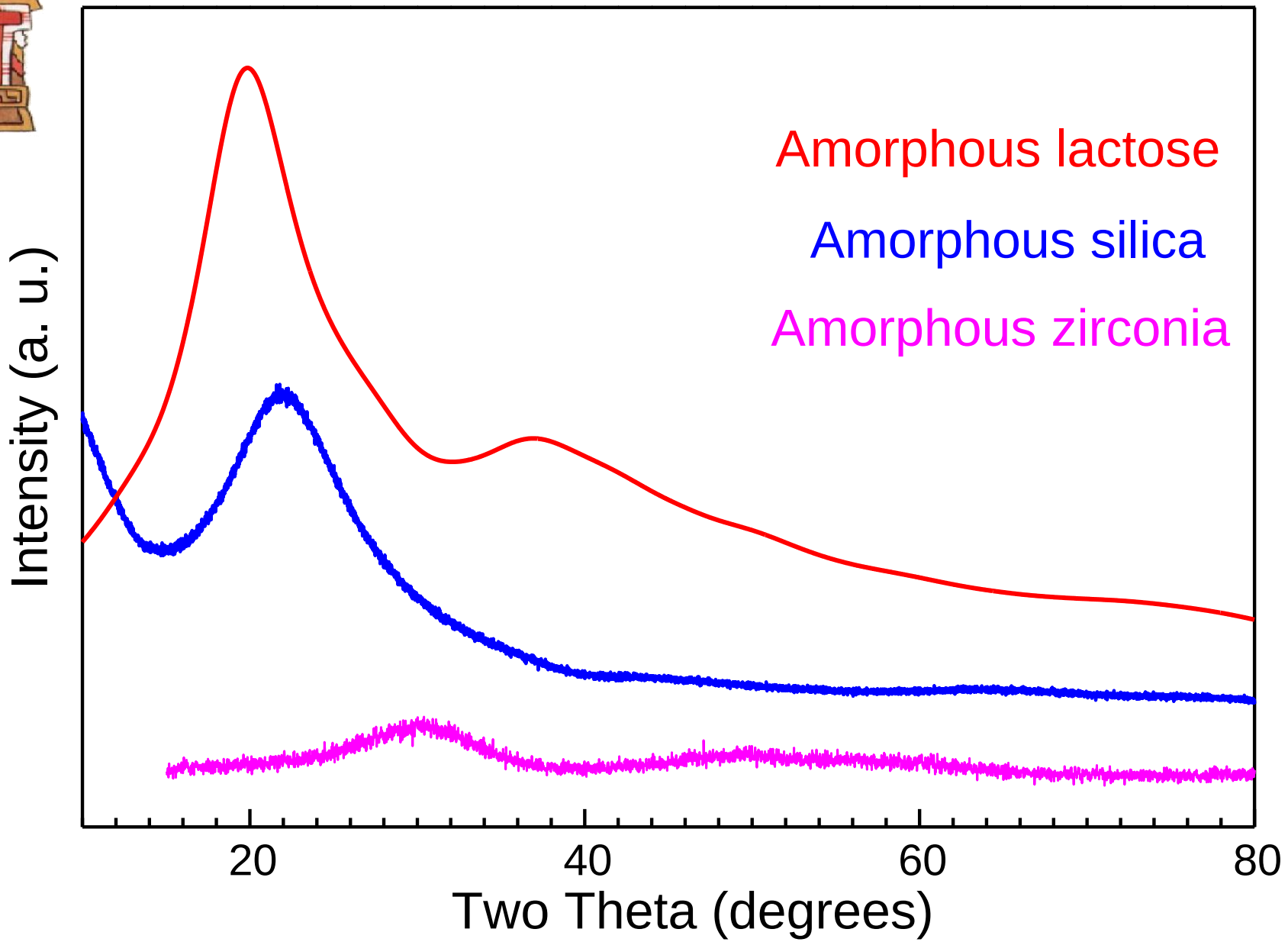
The Rietveld technique can be used to study nanocrystalline materials

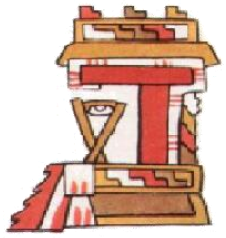




Area nm^2	Volume nm^3	Specific Area m^2g^{-1}	Number of atoms	Crystallites per gram
20.9	8.64	339	651	1.62×10^{19}

Can the Rietveld technique be used to analyze amorphous materials?



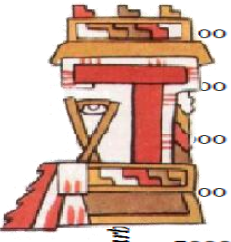


Silicon oxide has several low temperature polymorphs:

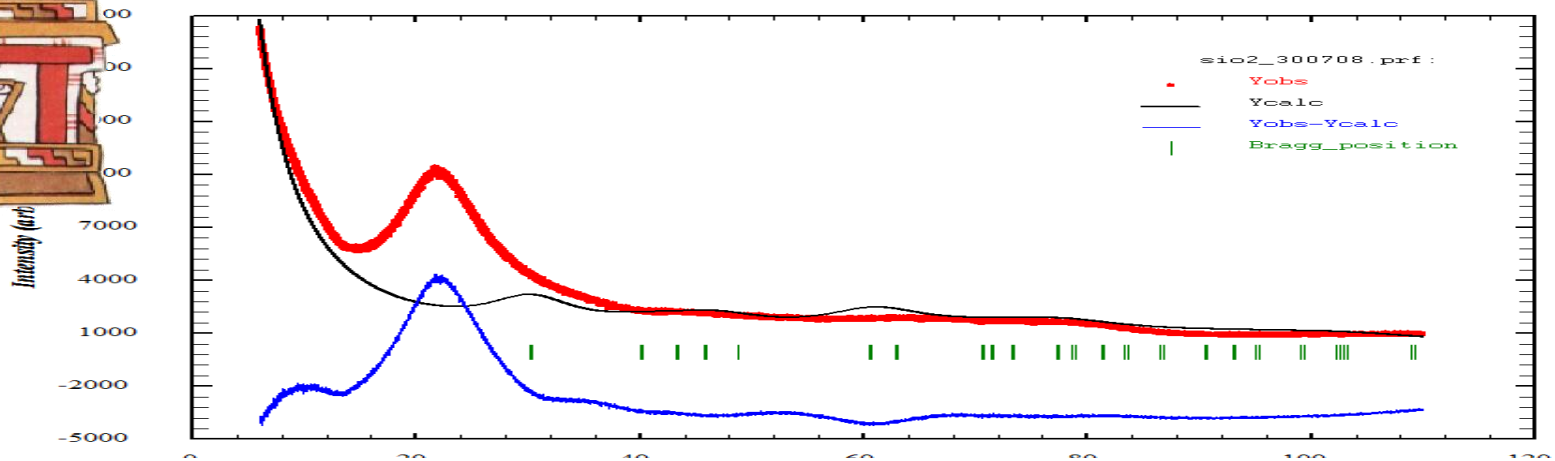
Stishovite, Tetragonal

Beta-Cristobalite, Cubic

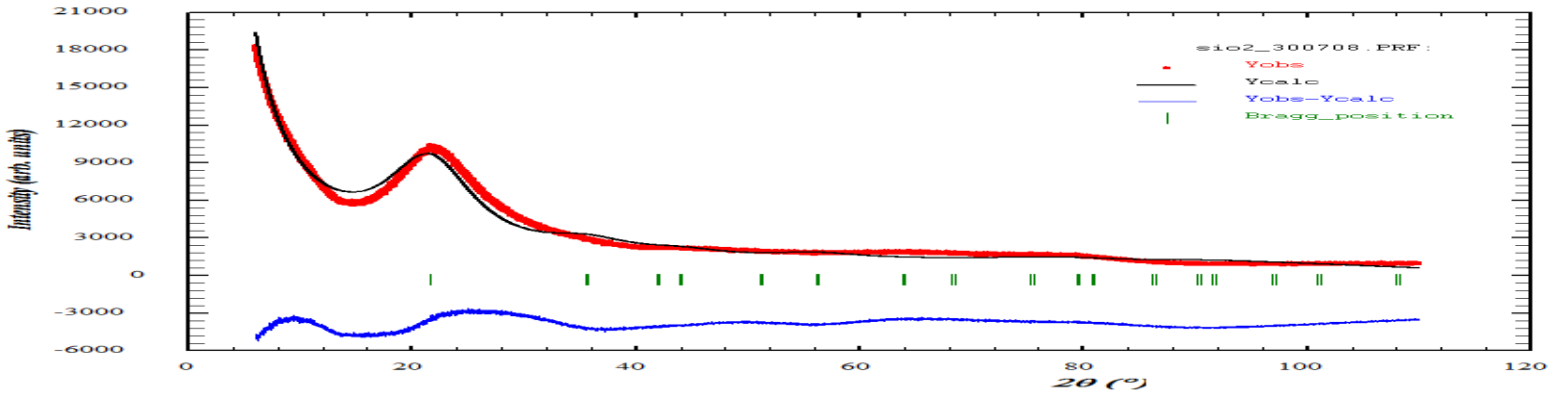
Alpha-Cristobalite, Tetragonal



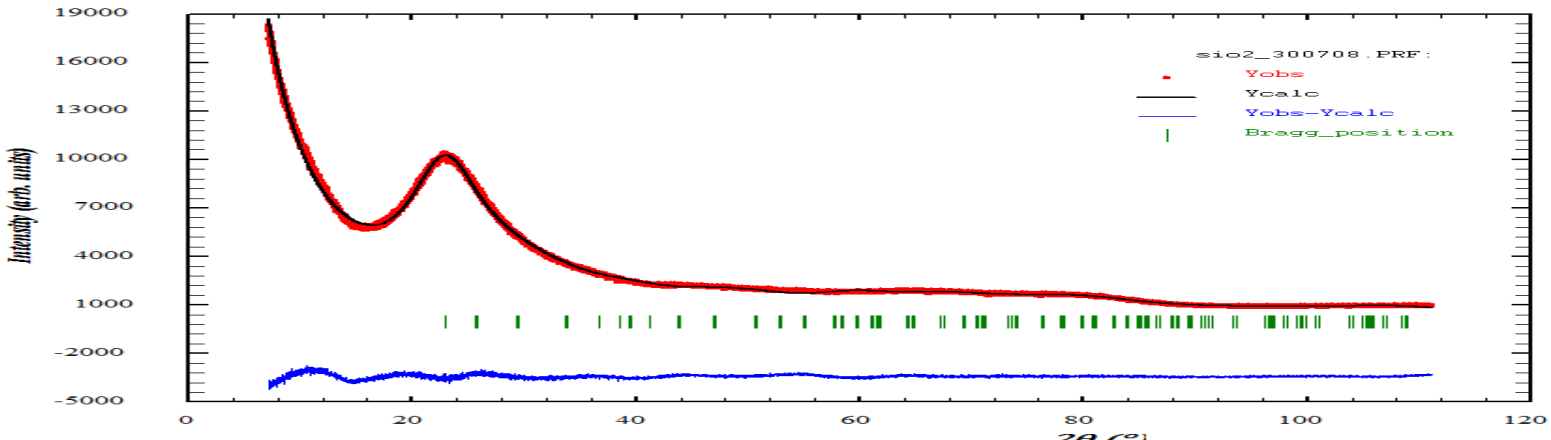
Modeled with Stishovite

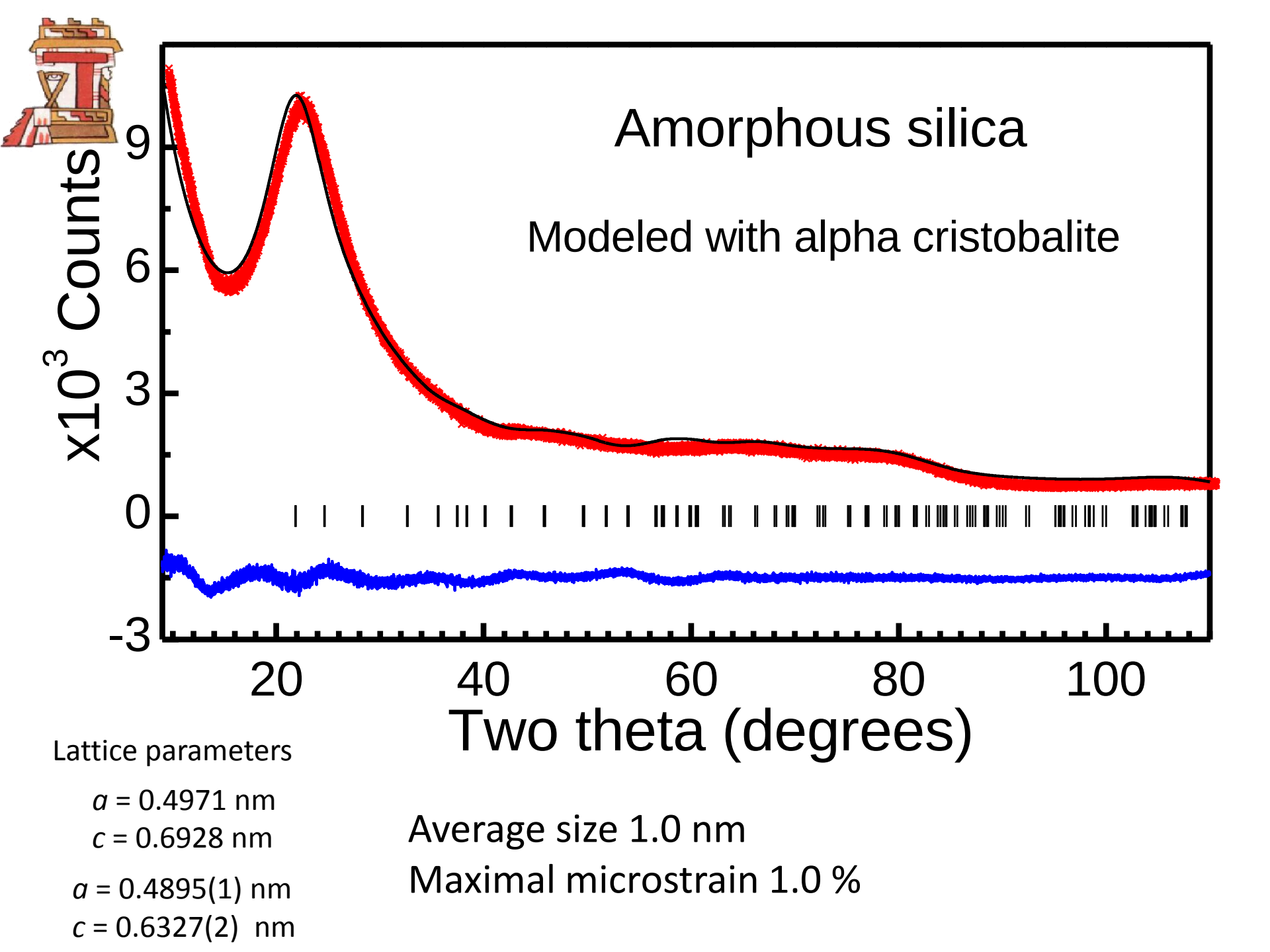


Modeled with Beta Cristobalite



Modeled with alpha cristobalite





Lattice parameters

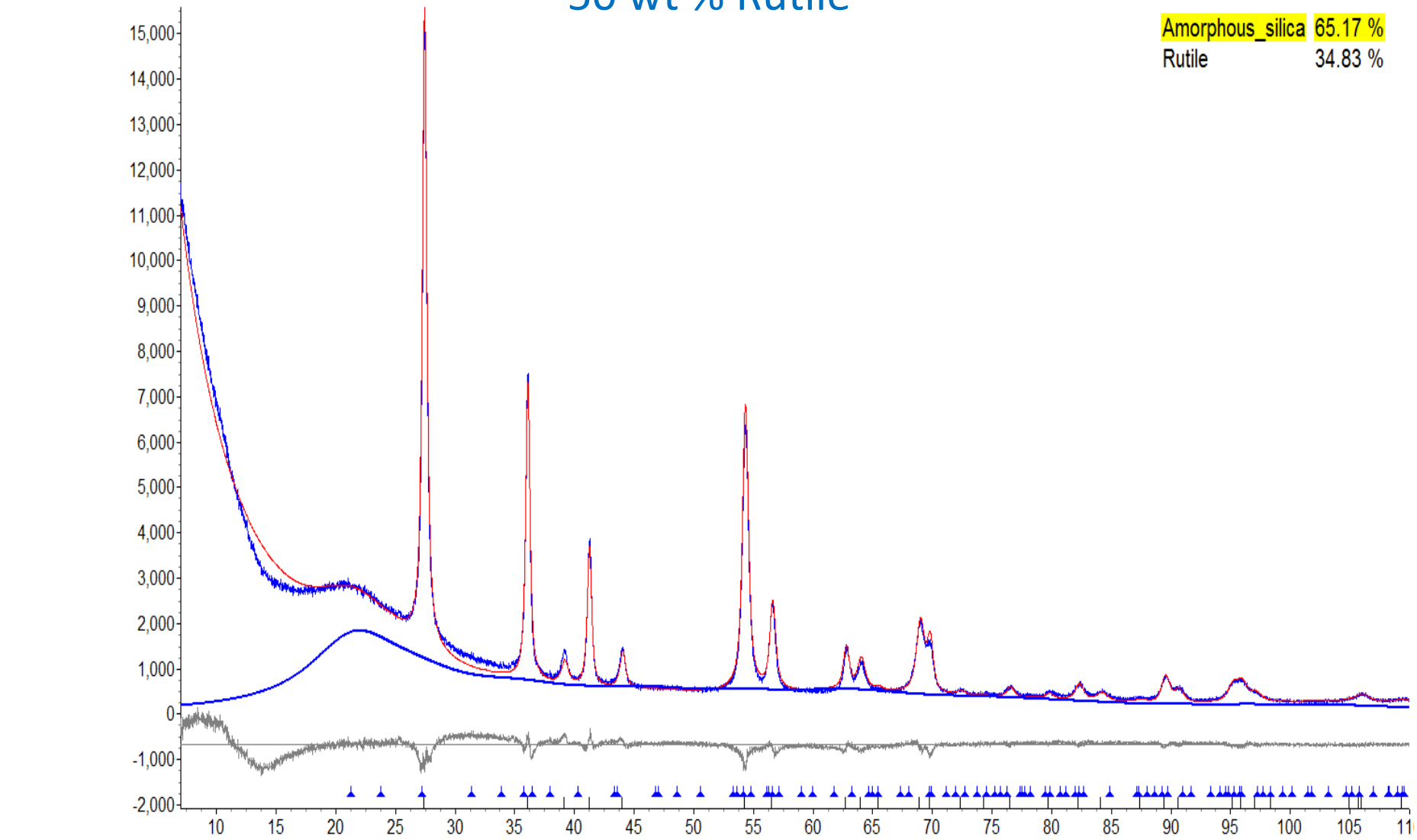
a = 0.4971 nm
c = 0.6928 nm

a = 0.4895(1) nm
c = 0.6327(2) nm

Average size 1.0 nm

Maximal microstrain 1.0 %

Nominal concentrations:
50 wt % Amorphous silica
50 wt % Rutile

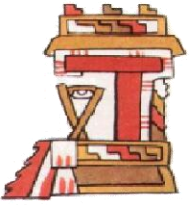


$$y_{ci}(2\theta_i) = S \sum |F_K|^2 \phi(2\theta_i - 2\theta_K) L_K P_K A + y_{bi}$$

Improving Instrument modeling
or instrument optic

Background:
Simple model Chevychev Polynomial

It is necessary to take into account the
Inelastic Compton scattering



Crystallization of amorphous lactose

Lactose crystallizes in three polymorphs:

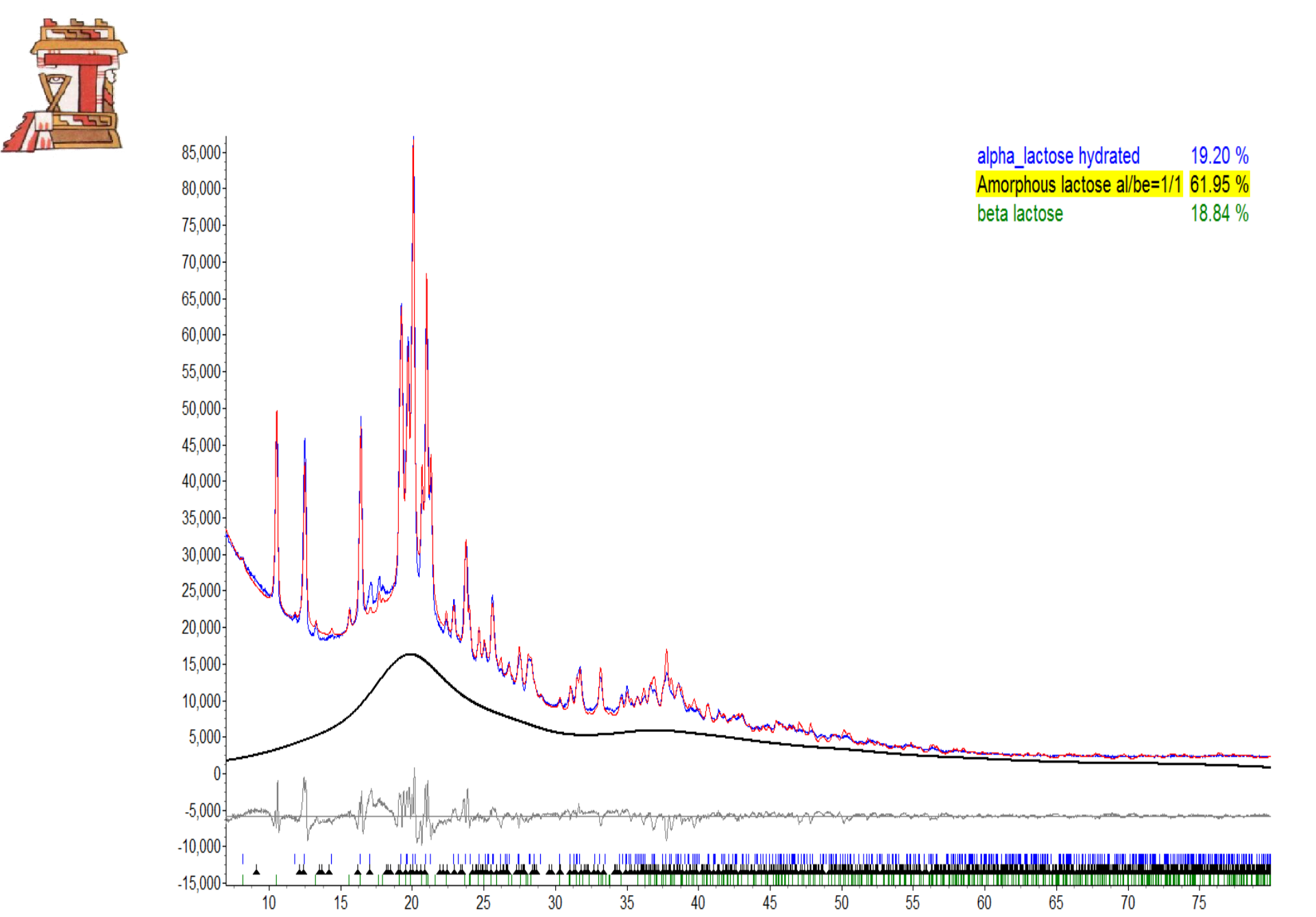
Alpha Lactose hydrated, Monoclinic

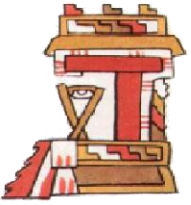
Beta Lactose, Monoclinic

1/1 Alpha/Beta phase, Triclinic

The Amorphous phase was modeled with the

Crystallography of the Triclinic phase


alpha_lactose hydrated 19.20 %
Amorphous lactose al/be=1/1 61.95 %
beta lactose 18.84 %
85,000
80,000
75,000
70,000
65,000
60,000
55,000
50,000
45,000
40,000
35,000
30,000
25,000
20,000
15,000
10,000
5,000
0
-5,000
-10,000
-15,000
10
15
20
25
30
35
40
45
50
55
60
65
70
75

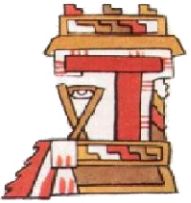


Amorphous Indomethacin:

Crystalline Alpha-Form

Crystalline Gamma-Form

From the NMR experiments:
The local atomic order of the amorphous
Phase is similar to that in the Alpha-form



Conclusions

The Rietveld refinement technique can be used to obtain Information about the concentrations of the phases in a sample inclusive when one of them is amorphous.

The amorphous phase should be modeled with the crystalline structure of the phase that crystallizes first.

The analysis requires to improve the model for the background and the optic of the diffractometer.

Some codes to refine crystalline structures

DBWS	R.A. Young
FullProf	Juán Rodriguez Carbajal
GSAS	Robert B. von Dreele
RIETAN	F. Izumi
TOPAS	Allan Coelho
BGMN	George Bergmann