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Rietveld Refinement

by

Filipe A. Almeida Paz

12 July 2022

Rietveld Refinement

GOAL Minimize the residual function

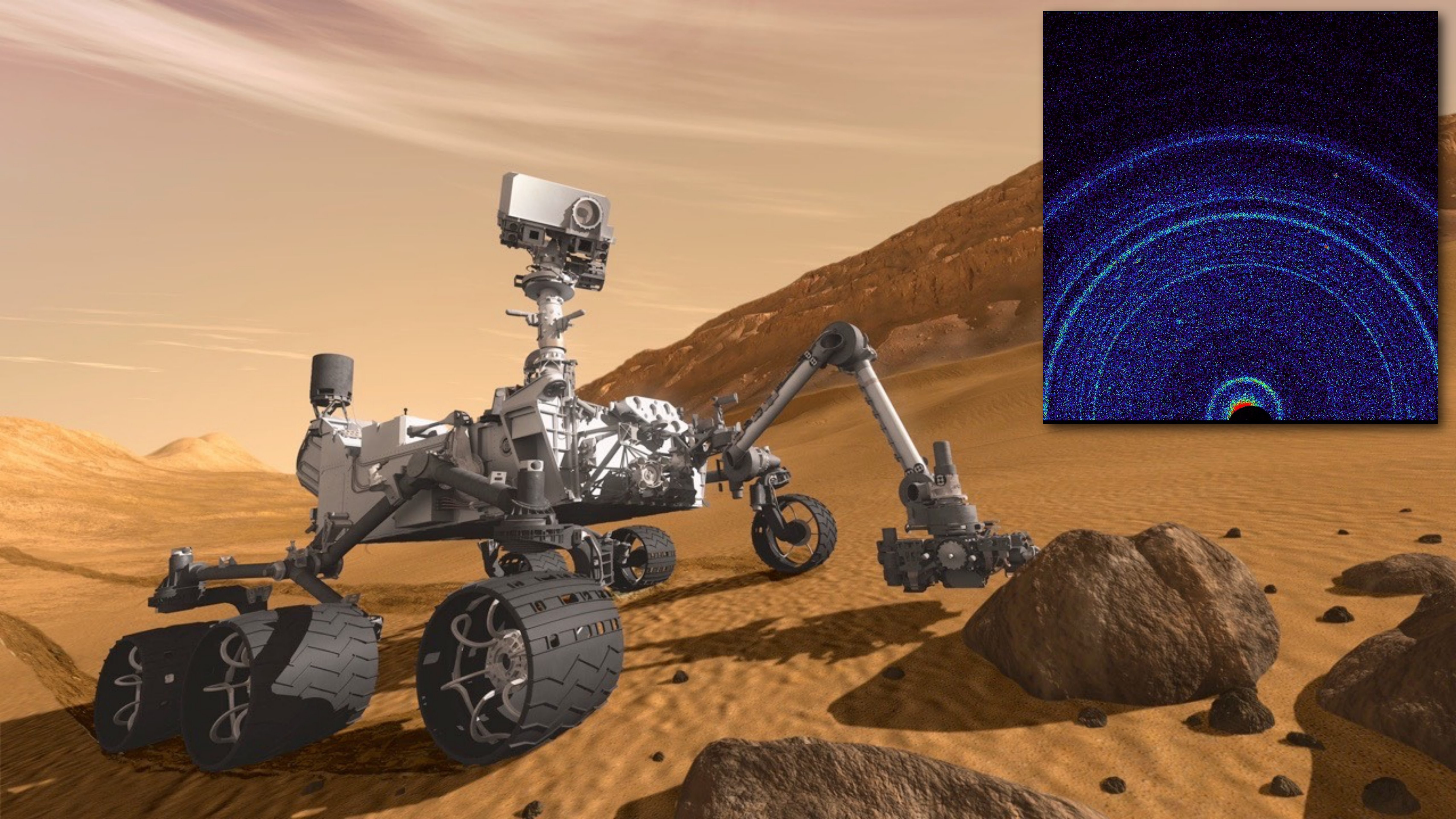
$$\sum_i w_i \left[y_i(obs) - y_i(calc) \right]^2$$

with $w_i = {}^{1}\!/\!{}_{y_i(obs)}$

$y_i(obs) =$ observed intensity at the i^{th} step

$y_i(calc) =$ calculated intensity at the i^{th} step

$$I_i^{calc} = S_F \sum_{j=1}^{N_{phases}} \frac{f_j}{V_j^2} \sum_{k=1}^{M_{peaks}} L_k \left| F_{k,j} \right|^2 S_j\left(2\theta_i - 2\theta_{k,j}\right) P_{k,j} A_j + bkg_i$$



X-ray Diffraction on Mars

Rietveld Analysis

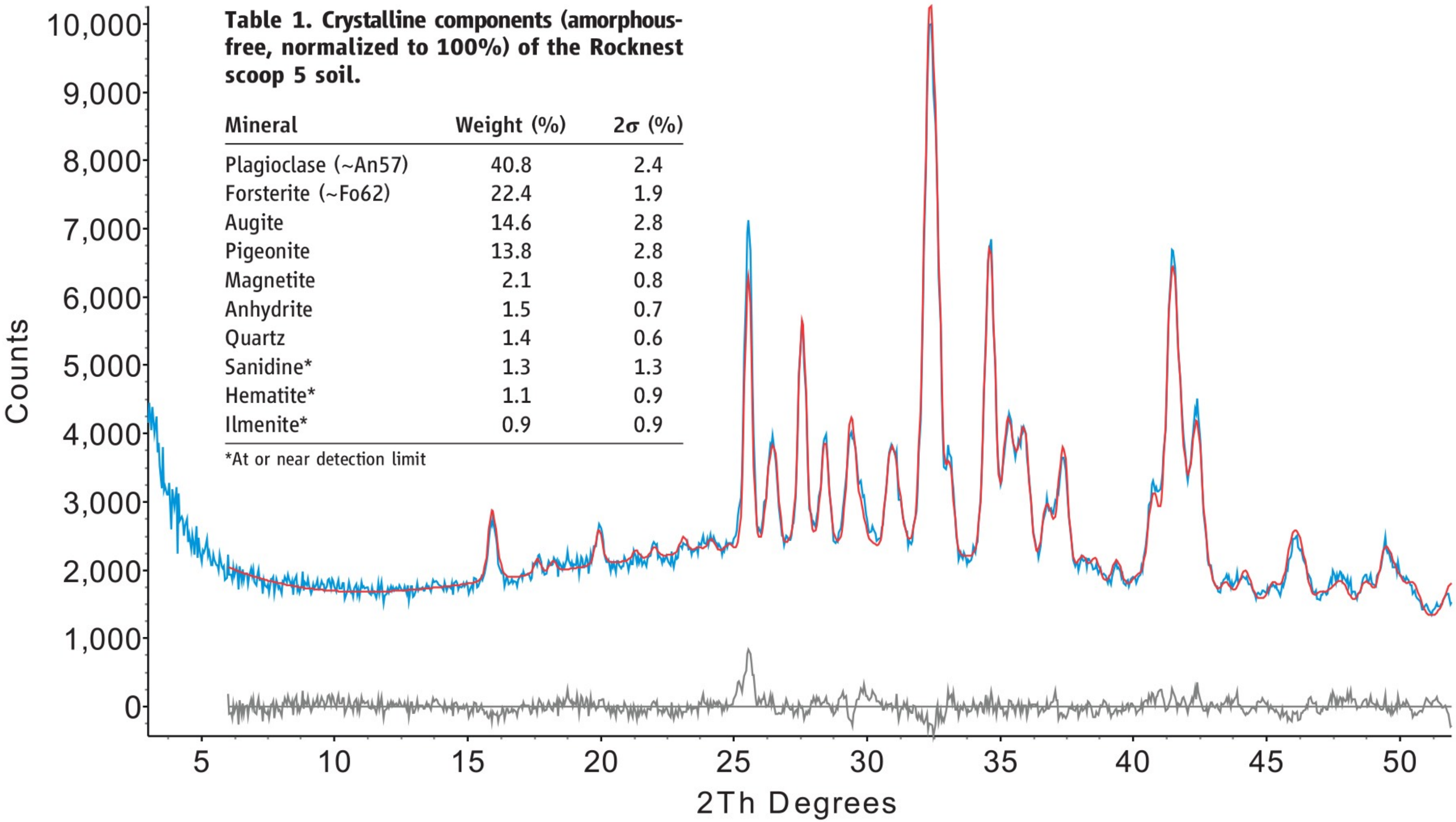
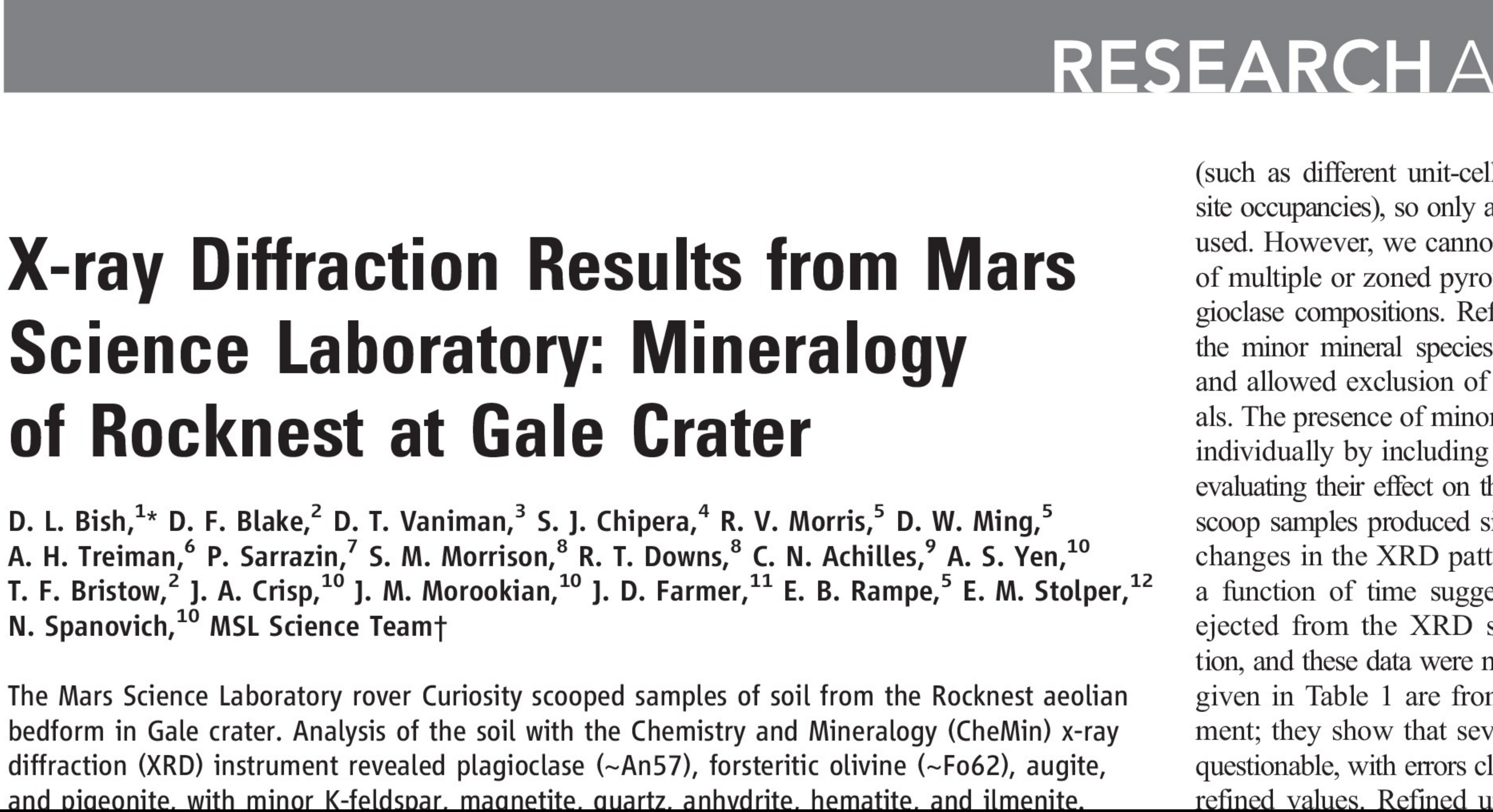


Table 1. Crystalline components (amorphous-free, normalized to 100%) of the Rocknest scoop 5 soil.

Mineral	Weight (%)	2σ (%)
Plagioclase (~An57)	40.8	2.4
Forsterite (~Fo62)	22.4	1.9
Augite	14.6	2.8
Pigeonite	13.8	2.8
Magnetite	2.1	0.8
Anhydrite	1.5	0.7
Quartz	1.4	0.6
Sanidine*	1.3	1.3
Hematite*	1.1	0.9
Ilmenite*	0.9	0.9

*At or near detection limit

Bish *et al.*, *Science* (**2013**), Vol. 341, Article Nº 1238932



RESEARCH A

X-ray Diffraction Results from Mars Science Laboratory: Mineralogy of Rocknest at Gale Crater

D. L. Bish,[1]* D. F. Blake,[2] D. T. Vaniman,[3] S. J. Chipera,[4] R. V. Morris,[5] D. W. Ming,[5] A. H. Treiman,[6] P. Sarrazin,[7] S. M. Morrison,[8] R. T. Downs,[8] C. N. Achilles,[9] A. S. Yen,[10] T. F. Bristow,[2] J. A. Crisp,[10] J. M. Morookian,[10] J. D. Farmer,[11] E. B. Rampe,[5] E. M. Stolper,[12] N. Spanovich,[10] MSL Science Team†

The Mars Science Laboratory rover Curiosity scooped samples of soil from the Rocknest aeolian bedform in Gale crater. Analysis of the soil with the Chemistry and Mineralogy (CheMin) x-ray diffraction (XRD) instrument revealed plagioclase (~An57), forsteritic olivine (~Fo62), augite, and pigeonite, with minor K-feldspar, magnetite, quartz, anhydrite, hematite, and ilmenite.

(such as different unit-cel
site occupancies), so only a
used. However, we canno
of multiple or zoned pyro
gioclase compositions. Ref
the minor mineral species
and allowed exclusion of
als. The presence of mino
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evaluating their effect on th
scoop samples produced s
changes in the XRD patt
a function of time sugge
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tion, and these data were n
given in Table 1 are fron
ment; they show that sev
questionable, with errors cl
refined values. Refined u

Bish *et al.*, *Science* (**2013**), Vol. 341, Article N° 1238932

be a contributing factor (*1*, *2*). High-quality chemical data for martian soils are available from the Pathfinder, Mars Exploration Rover (MER), and Phoenix missions (*2*–*4*), and phase information has been provided through MER thermal emission and Mössbauer spectroscopic measurements (*3*, *5*–*9*). The Chemistry and Mineralogy (CheMin) instrument onboard the Mars Science Laboratory (MSL) rover Curiosity uses x-ray diffraction (XRD), which is generally the preferred and the most definitive method for determining the nature of crystalline phases (such as minerals) in solid samples. CheMin's XRD analysis on Mars coincided with the 100th-year anniversary of the discovery of XRD by von Laue (*10*).

strument inside the body of the rover, and CheMin measured two-dimensional (2D) diffraction data (Fig. 1, scoop five) for the three samples (details are available in materials and methods). Imaging shows that the soil has a range of particle sizes, 1 to 2 mm and smaller, presumably representing contributions from global, regional, and local sources (*14*). The larger particles at the top of the bedform appear to be armoring the bedform. The term soil is used here to denote any loose, unconsolidated materials that can be distinguished from rocks, bedrock, or strongly cohesive sediments. No implication of the presence or absence of organic materials or living matter is intended, nor is the genesis of the deposit inferred.

Results

Crystalline Components

Initial analyses of the measured diffraction data from three different scoops revealed the presence of plagioclase feldspar, forsteritic olivine, augite,

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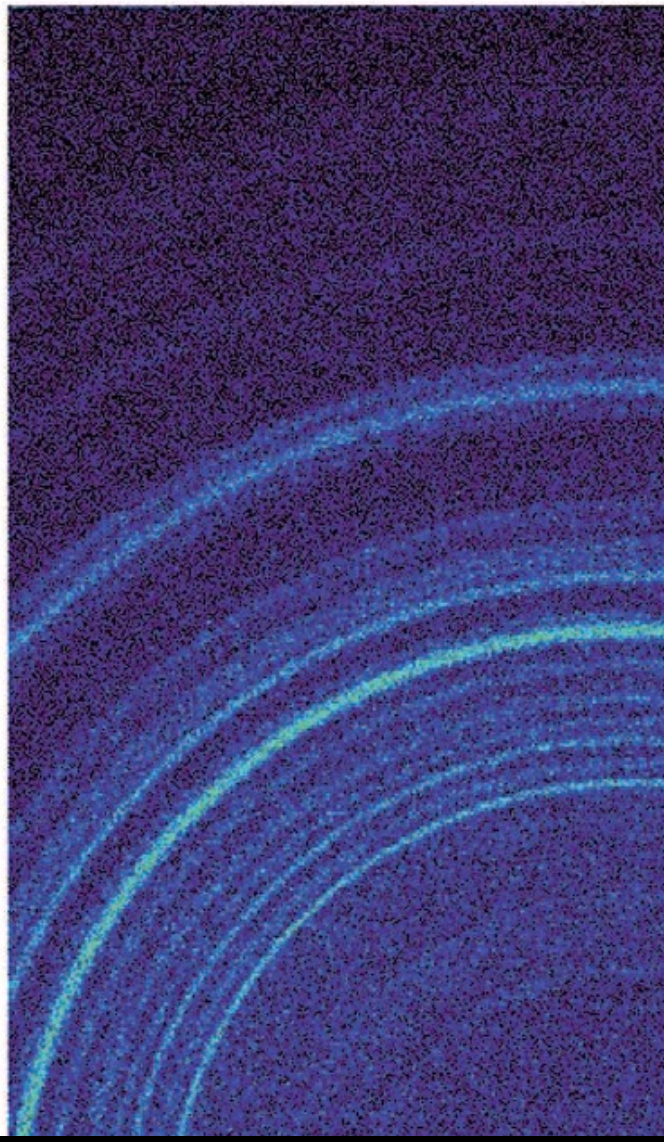

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[1]Department of Geological Sciences, Indiana University, Bloomington, IN 47405, USA. [2]NASA Ames Research Center, Moffett Field, CA 94035, USA. [3]Planetary Science Institute, Tucson, AZ 85719, USA. [4]Chesapeake Energy, Oklahoma City, OK 73154, USA. [5]NASA Johnson Space Center, Houston, TX 77058, USA. [6]Lunar and Planetary Institute, Houston, TX 77058, USA. [7]In-Xitu, Campbell, CA 95008, USA. [8]Department of Geology, University of Arizona, Tucson, AZ 85721, USA. [9]Engineering

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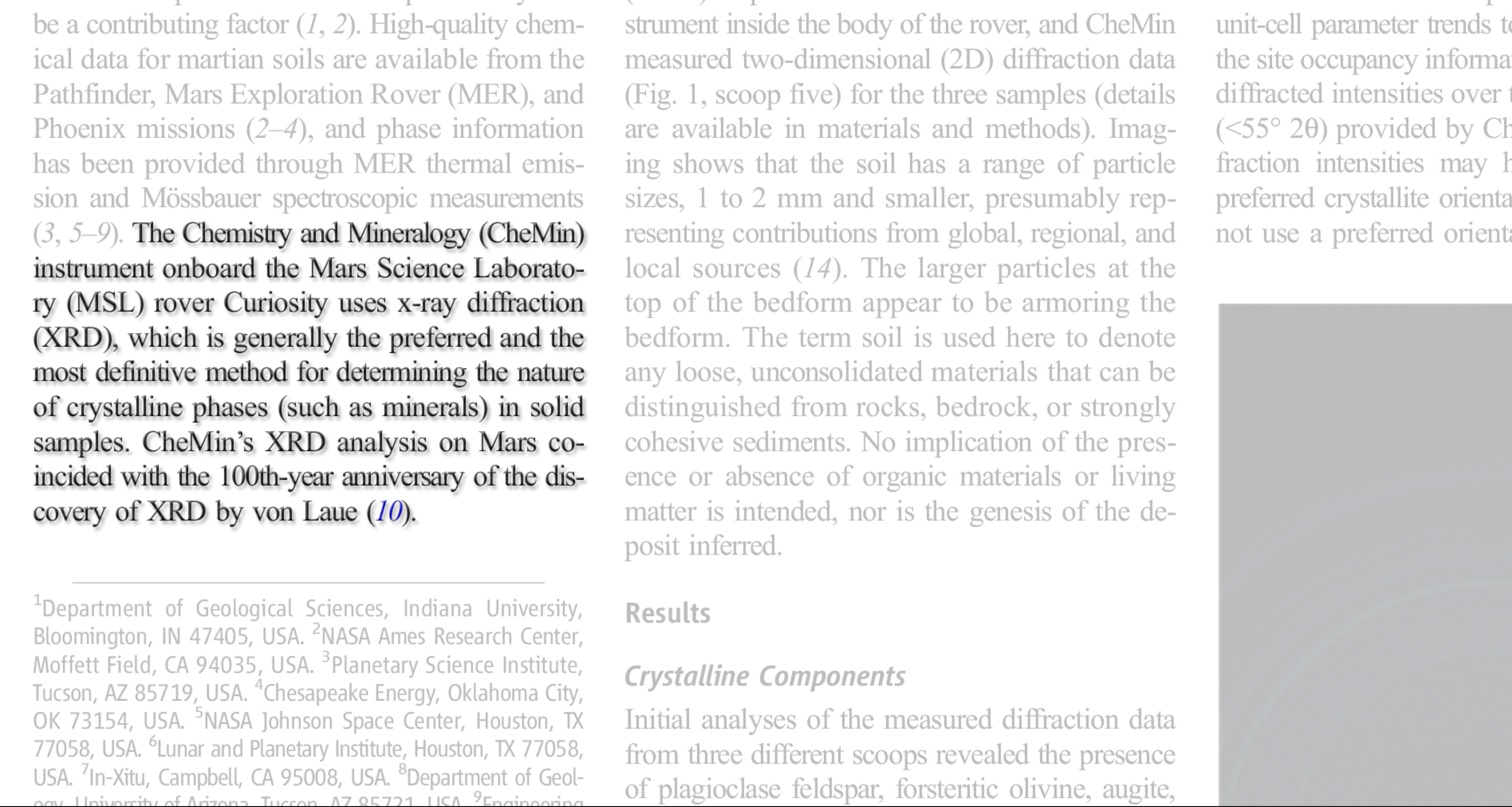

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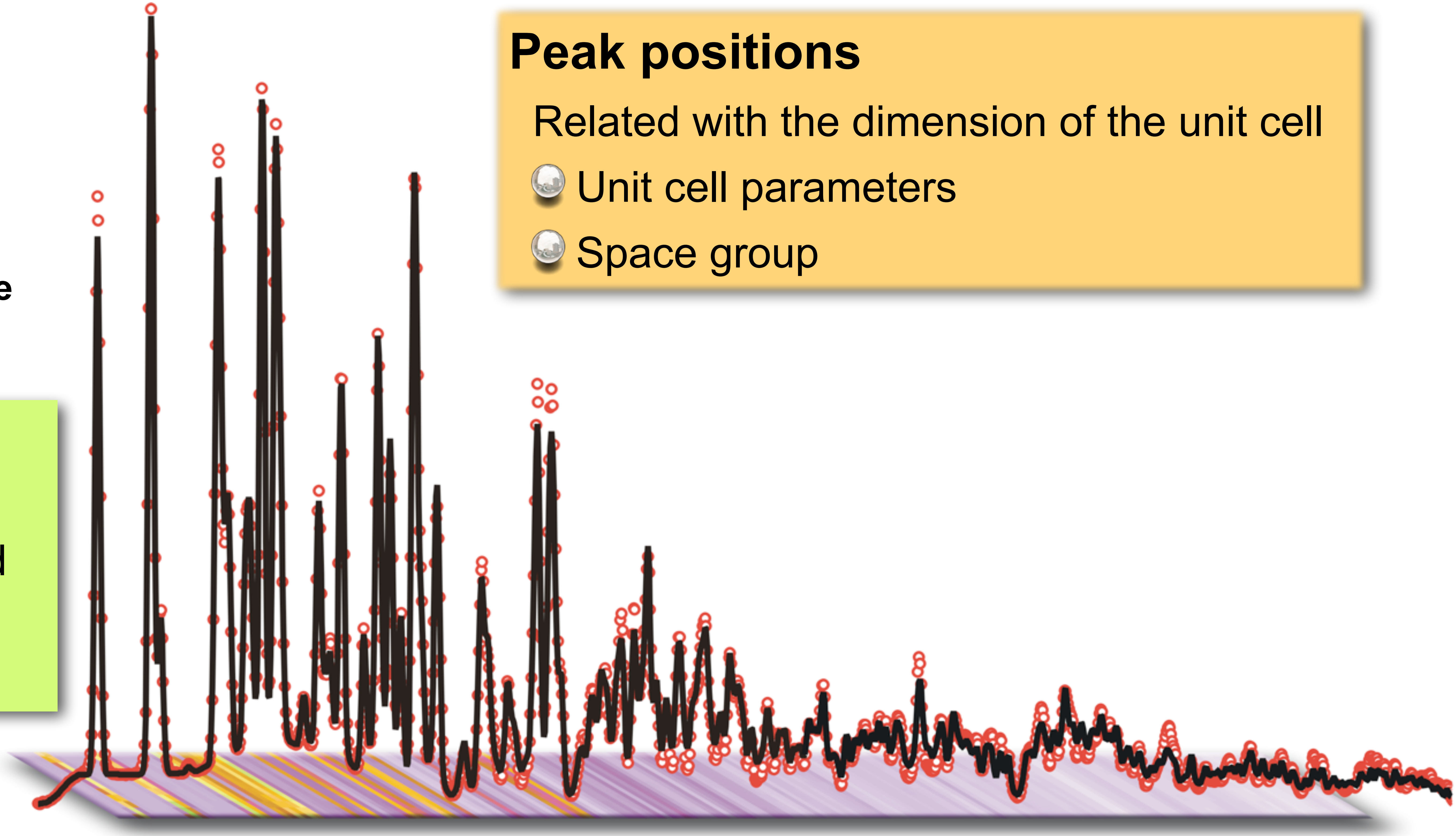
Information we take from powder X-ray diffraction pattern

Information provided by a powder X-ray diffraction pattern



What kind of information can we extract from a powder pattern?

Peak positions

Peak intensities

Profile width and shape

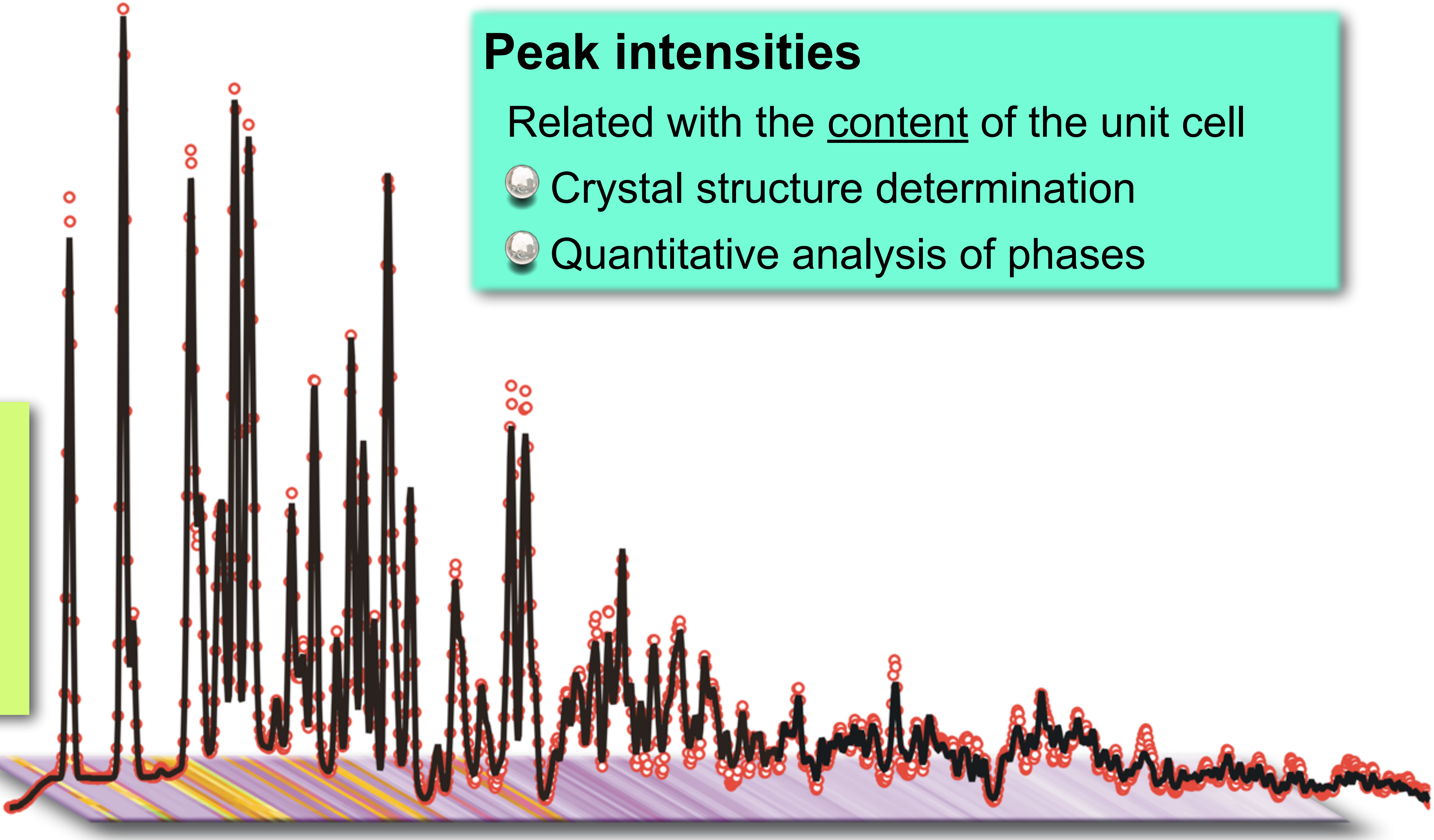
Background

Peak positions

Related with the dimension of the unit cell

- Unit cell parameters
- Space group

Information provided by a powder X-ray diffraction pattern



Peak intensities

Related with the <u>content</u> of the unit cell

- Crystal structure determination
- Quantitative analysis of phases

What kind of information can we extract from a powder pattern?

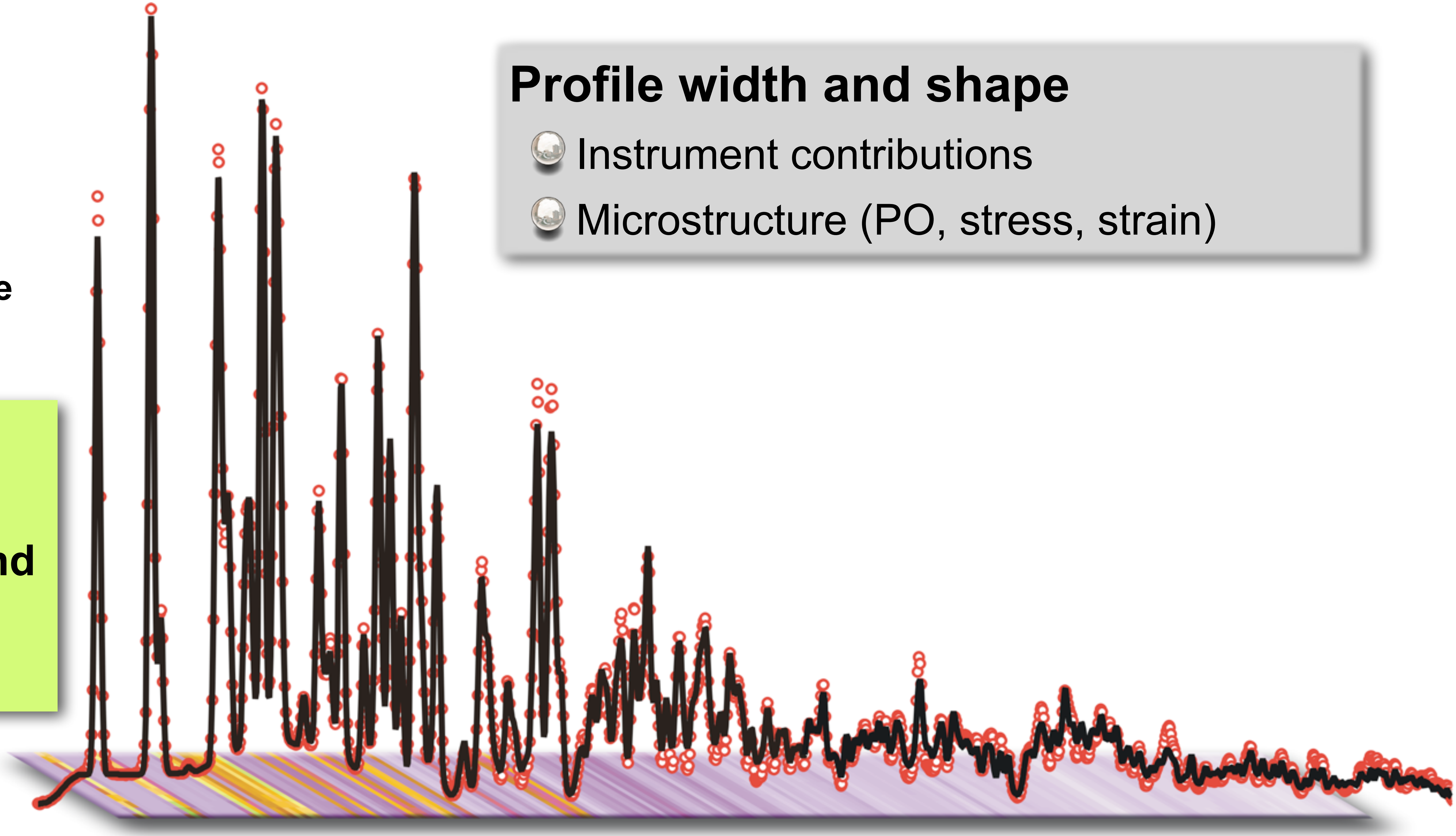
Peak positions

Peak intensities

Profile width and shape

Background

Information provided by a powder X-ray diffraction pattern



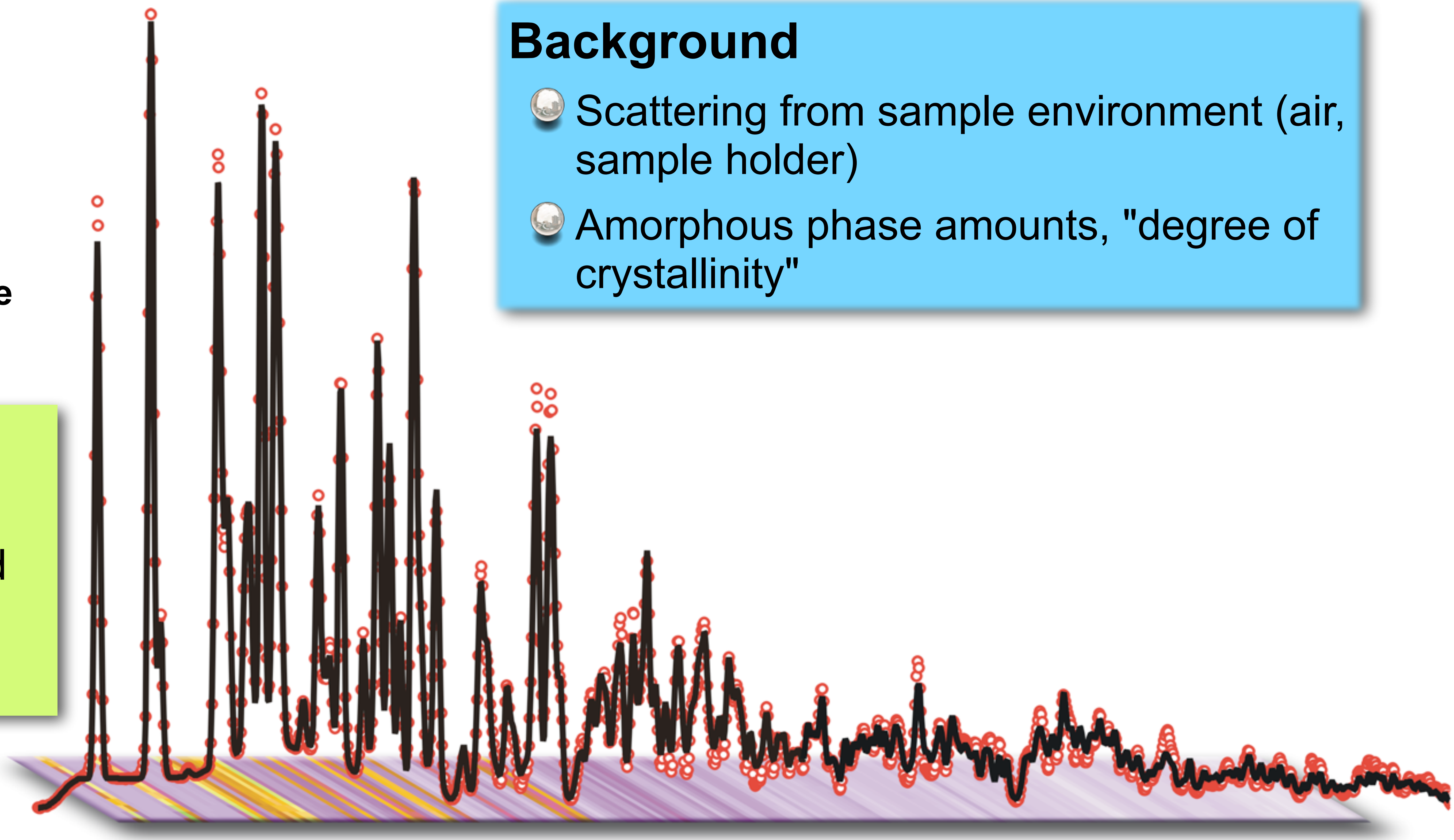
What kind of information can we extract from a powder pattern?

Peak positions
Peak intensities
Profile width and shape
Background

Profile width and shape

- Instrument contributions
- Microstructure (PO, stress, strain)

Information provided by a powder X-ray diffraction pattern



What kind of information can we extract from a powder pattern?

Peak positions

Peak intensities

Profile width and shape

Background

Background

- Scattering from sample environment (air, sample holder)
- Amorphous phase amounts, "degree of crystallinity"

Pattern Decomposition - Intensity Extraction

In the 1980's, with the advent of computer technology, two methods have been proposed to overcome this limitation in powder diffraction:

Pawley method (1980)

Diffraction profiles fitted with the following parameters:

- *I*(*hkl*) - Intensity of each reflection with indices *hkl*;
- *a, b, c, alfa, beta, gamma* - Unit-cell metric tensor parameters;
- $2\theta_{zero}$ - Instrumental zero error;
- *U,V,W* - Peak-width parameters;
- η, etc. - Other peak-shape parameters.

***Every* reflection** is assumed to have (i) a peak position and the 2θ zero error, (ii) a peak width determined by the resolution function parameters *U*, *V*, and *W*, and (ii) a peak intensity *I(hkl)*.

This requires typically a (10+N)×(10+N) square matrix, where N is the number of symmetry-independent reflections:
- for 200 reflections 170 Kb of computer memory is required;
- for 2000 reflections the memory required for the matrix alone will be 16 Mb.

Le Bail method (1988)

Diffraction profiles fitted with the following parameters:

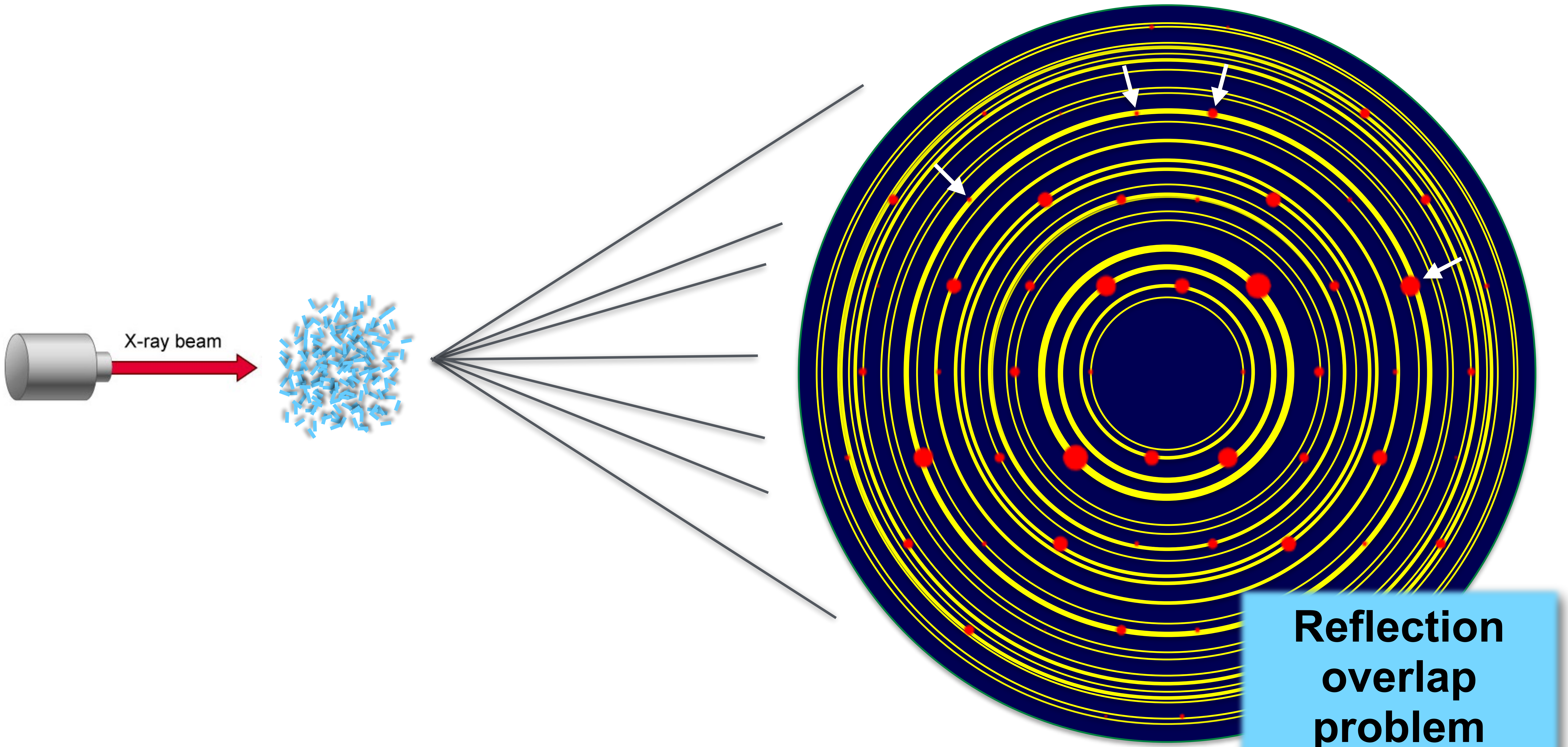
- *a, b, c, alfa, beta, gamma* - Unit-cell metric tensor parameters;
- $2\theta_{zero}$ - Instrumental zero error;
- *U,V,W* - Peak-width parameters;
- η, etc. - Other peak-shape parameters.

The intensities of the individual peaks are no longer treated as least-squares parameters and are never refined. Consequently, **each cycle of least-squares is very fast since the matrix remains small**.

The Le Bail method is faster and permits the quick probing of various possible space groups.
It lacks important information such as intensities and eds.
The method permitted a fast growth of the techniques associated with structure solution from powder data.

Both methods intrinsically have a problem with peaks that severely overlap

Single-Crystals *vs* Powder X-ray diffraction: Reflection Overlap

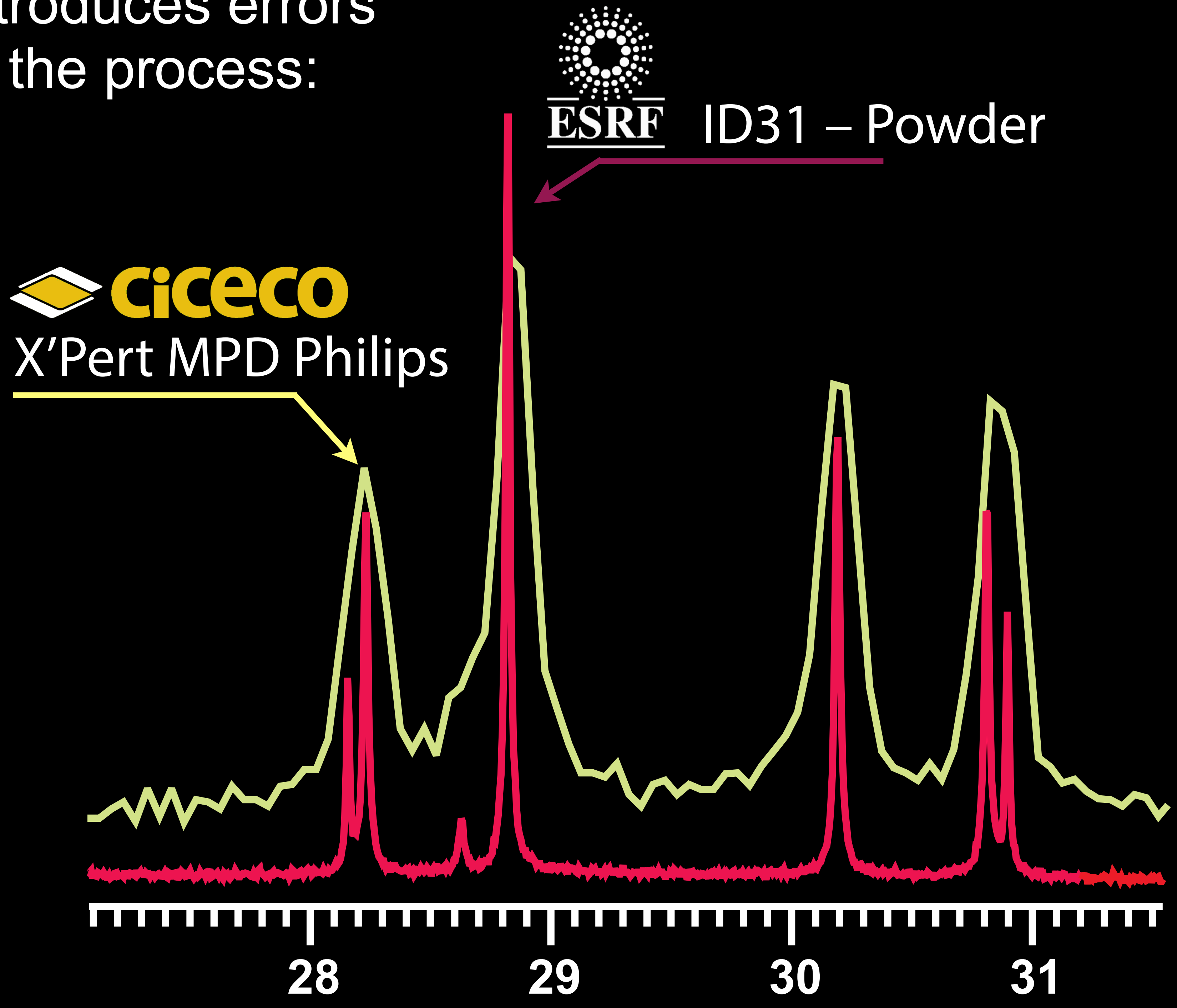


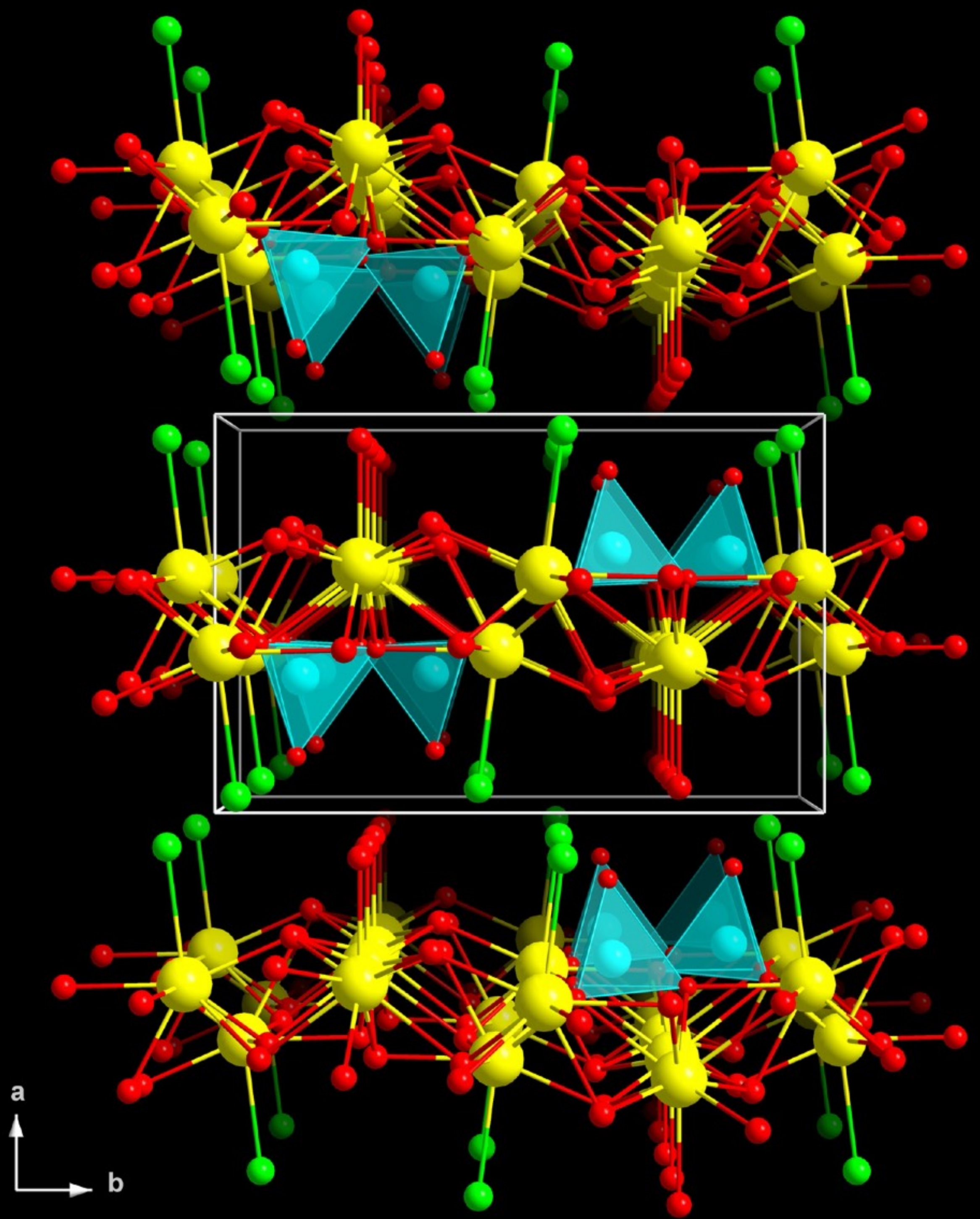
Reflection overlap problem

Adapted with permission of Professor Lynne McCusker (ETH, Zurich)

Pattern Decomposition - Peak Overlap

Solving a structure from powder data requires the extraction *hkl* and intensity values. Peak overlapping introduces errors in the process:





Ananias *et al.*, *Chemistry of Materials* (**2008**), Volume 20, Page 205-212

Crystal Structure Determination
and
Rietveld Refinement

Crystal Structure Determination and Rietveld Refinement

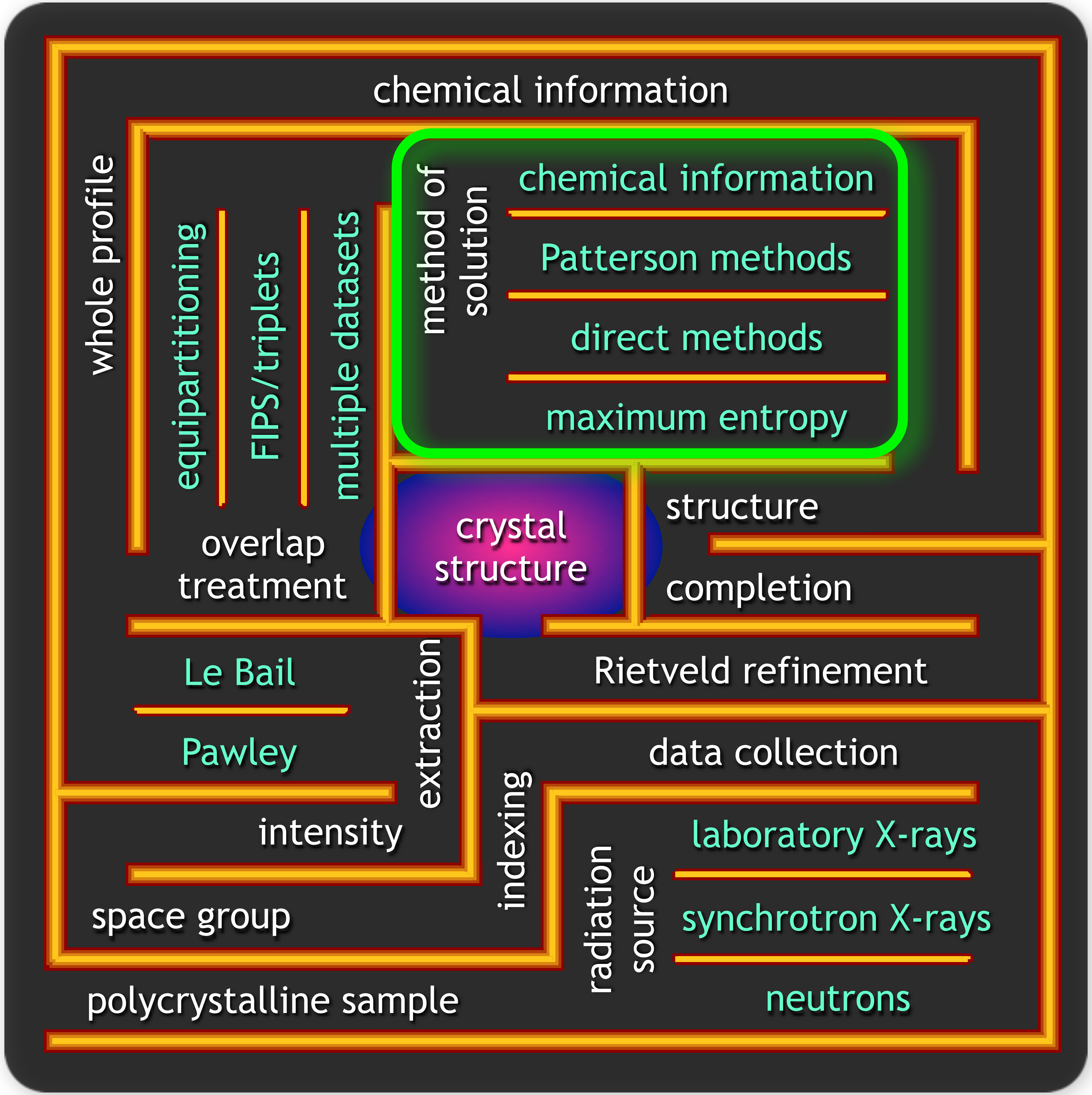
Structure Solution

Single-Crystal Methods (early 1990s)
Use of the measured reciprocal space data: $|F|^2$ values

- ***Direct Methods*** - measures the magnitude of ***F*** and not its phase. Phases have a higher "information" content than amplitudes: more than 50% of the information is lost. Direct methods attempt to determine the phases directly from the observed amplitudes.
- ***Patterson Synthesis*** - peaks correspond to the vector distances between atoms. Useful in single-crystal diffraction but limited in powder.

Direct Space Methods (late 1990s)
Concerned with the position and conformation of the molecules (or individual atoms/ions) within the unit cell

- *Simulated Annealing*
- *Monte Carlo*
- *Evolutionary methods*



chemical information

whole profile

equipartitioning

FIPS/triplets

multiple datasets

method of solution

chemical information

Patterson methods

direct methods

maximum entropy

overlap treatment

crystal structure

structure completion

Le Bail

Pawley

extraction

Rietveld refinement

intensity

indexing

data collection

space group

radiation source

laboratory X-rays

synchrotron X-rays

neutrons

polycrystalline sample

Diagram by:
Dr. Lynne McCusker
(ETH, Zurich)

Crystal Structure Determination and Rietveld Refinement

Structure Solution - Direct Space Methods

- Intuitive and strongly based of prior chemical information: atomic connectivity, chemical composition, specific bond angles and lengths, etc
- Adjustable parameters are in the real space instead of the reciprocal space

PROCEDURE

1 Trial crystal structure by randomly positioning and orienting individual atoms, molecular fragments or complete molecules taking into account (known or guessed) space group information

2 After calculating diffraction data and comparing it against the measured diffraction data, parameters of the model are adjusted in order to maximise the level of agreement between the observed and calculated data by minimising

$$\chi^2 = \sum_i w_i \left[y_i(obs) - y_i(calc) \right]^2 + w_p \sum penalties$$

Crystal Structure Determination and Rietveld Refinement

Structure Solution - Direct Space Methods

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$$\chi^2 = \sum_i w_i \left[y_i(obs) - y_i(calc) \right]^2 + \boxed{w_p \sum penalties}$$

ANTI-BUMP penalty $AB_i = \sum \left(r_{ij} - r_0 \right)^2$ for $r_{ij} < r_0$ and $i \neq j$

$r_{ij} =$ parameter for atoms i and j

$AB_i = 0$ for $r_{ij} \geq r_0$

Needs to be used with caution since may hinder the simulated annealing process

Crystal Structure Determination and Rietveld Refinement

Rietveld Refinement

The Rietveld approach refines specific parameters defined by the user in order to minimize the difference between an experimental pattern (observed data) and a crystallographic model based plus any additional instrumental parameters (calculated pattern)

It can be used for quantitative phase identification, lattice parameter and crystallite size calculations, and determine atom positions and occupancies

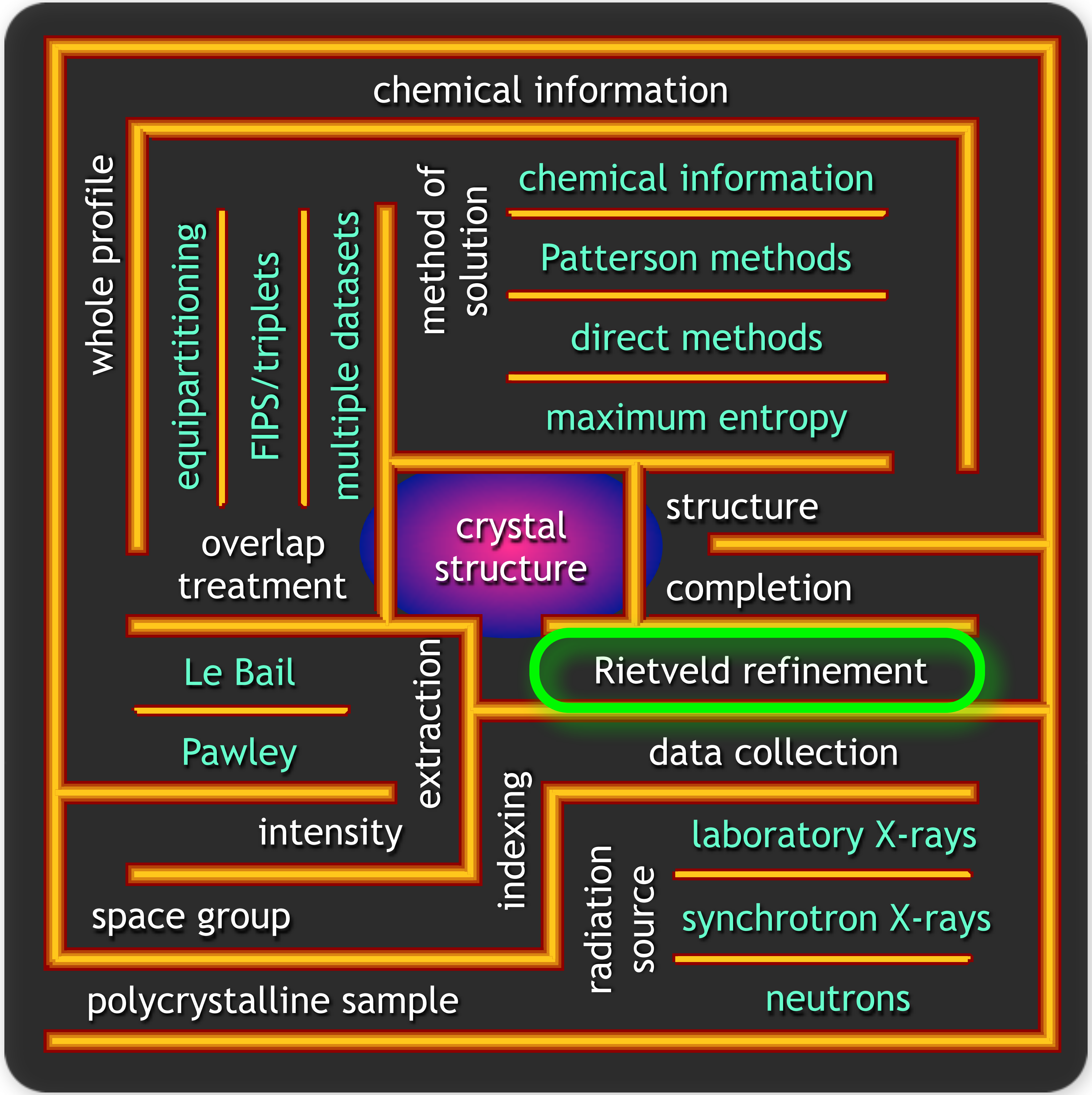


Diagram by:
Dr. Lynne McCusker
(ETH, Zurich)

Crystal Structure Determination and Rietveld Refinement

Rietveld Refinement

GOAL Minimize the residual function

$$\sum_i w_i \left[y_i(obs) - y_i(calc) \right]^2$$

with $w_i = {}^{1}\!/_{y_i(obs)}$

$y_i(obs) =$ observed intensity at the i^{th} step

$y_i(calc) =$ calculated intensity at the i^{th} step

With the value of the intensity calculated being given by:

$$I_i^{calc} = \underbrace{S_F \sum_{j=1}^{N_{phases}} \frac{f_i}{V_j^2}}_{\text{Scale Factor}} \sum_{k=1}^{M_{peaks}} \underbrace{L_k}_{\text{Lorentz Polarization Factor}} \underbrace{\left|F_{k,j}\right|^2}_{\text{Structure Factor}} S_j\left(2\theta_i - 2\theta_{k,j}\right) \underbrace{P_{k,j}}_{\text{Preferred Orientation}} \overbrace{A_j}^{\text{Volume absorption}} + bkg_i$$

Volume absorption

Scale Factor
S_F: beam intensity
f_j: volume fraction
V_j:cell volume

Structure Factor

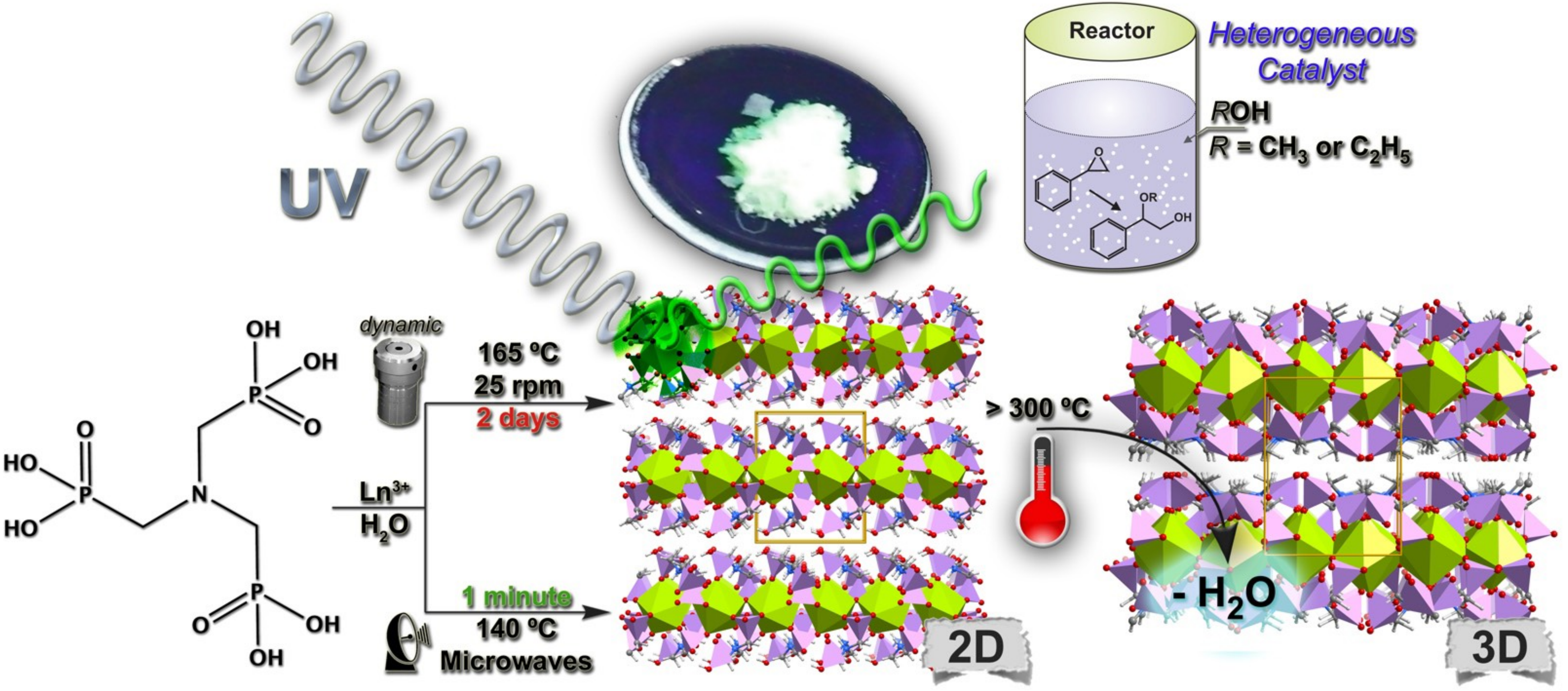
Preferred Orientation

Lorentz Polarization Factor

What can go wrong?

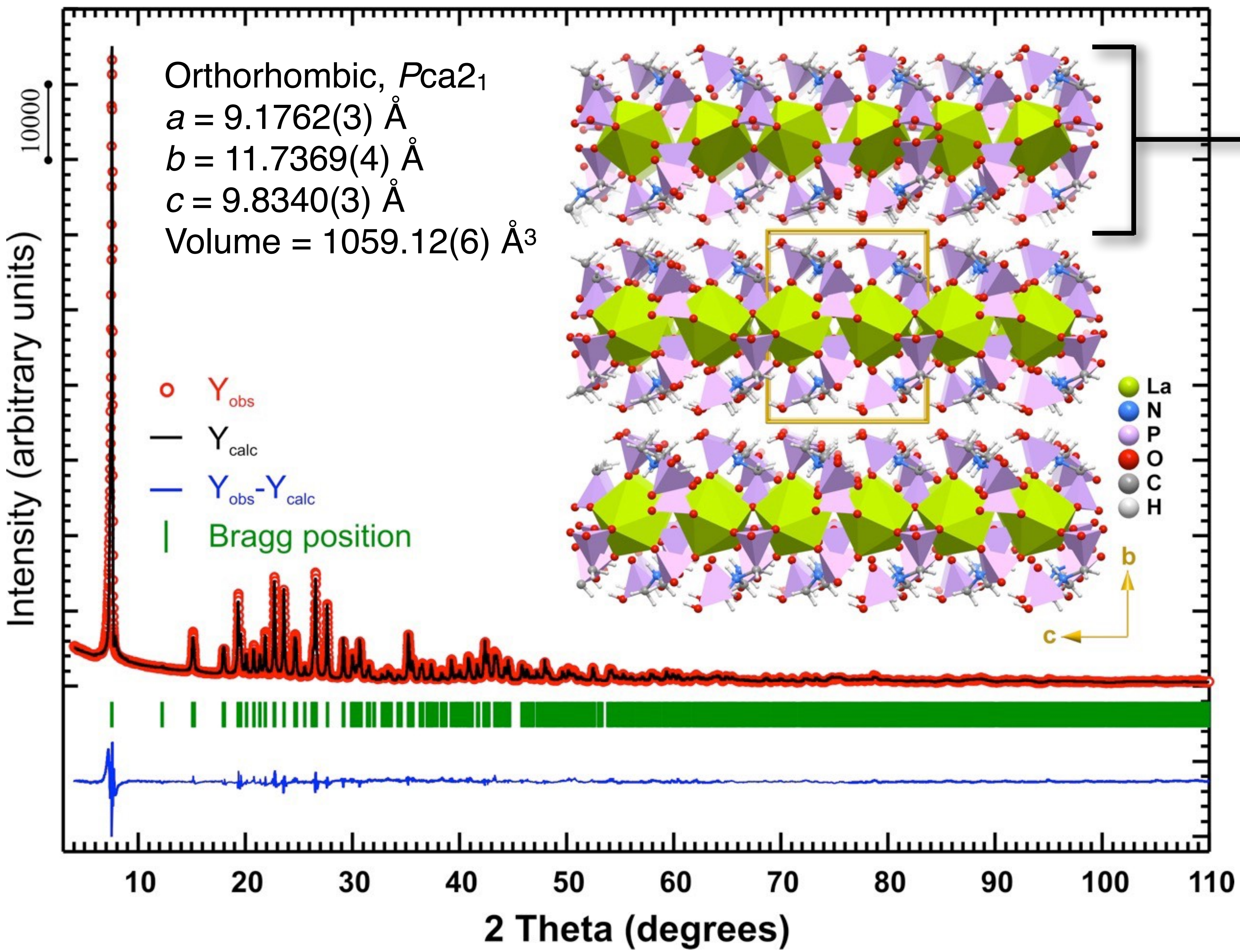
A (personal) Rietveld story…

2D → 2D by Calcination: an Infinite Phosphonate-Based Organic Linker

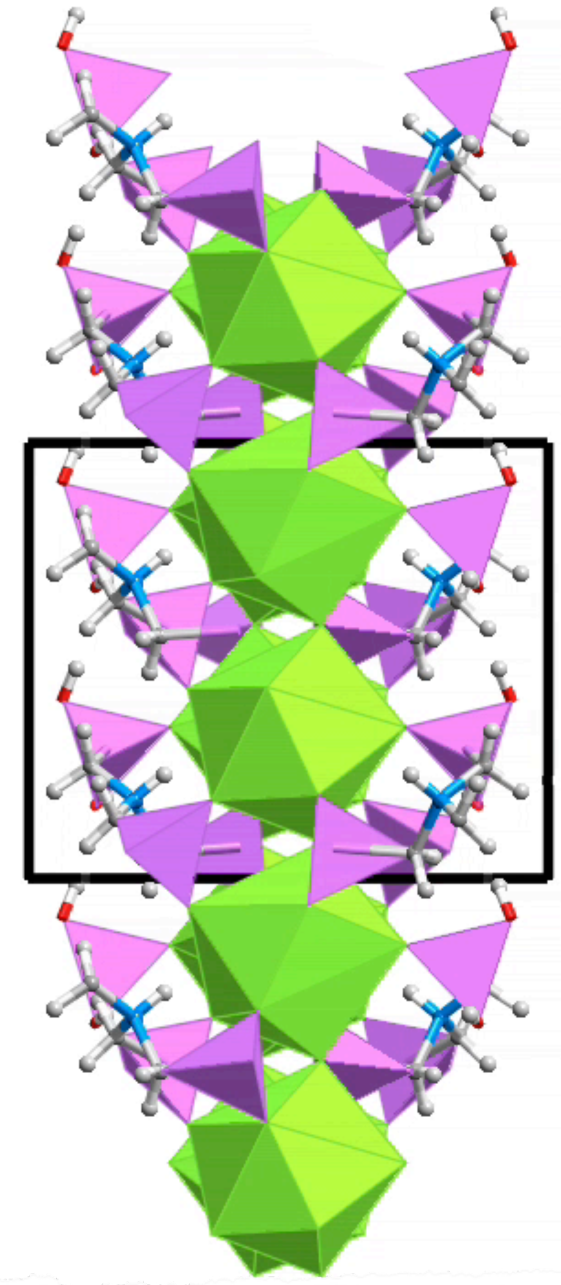


Journal of the American Chemical Society (**2011**), Volume *133*, Pages 15120-15138

2D MOF: [La(H_3nmp)]



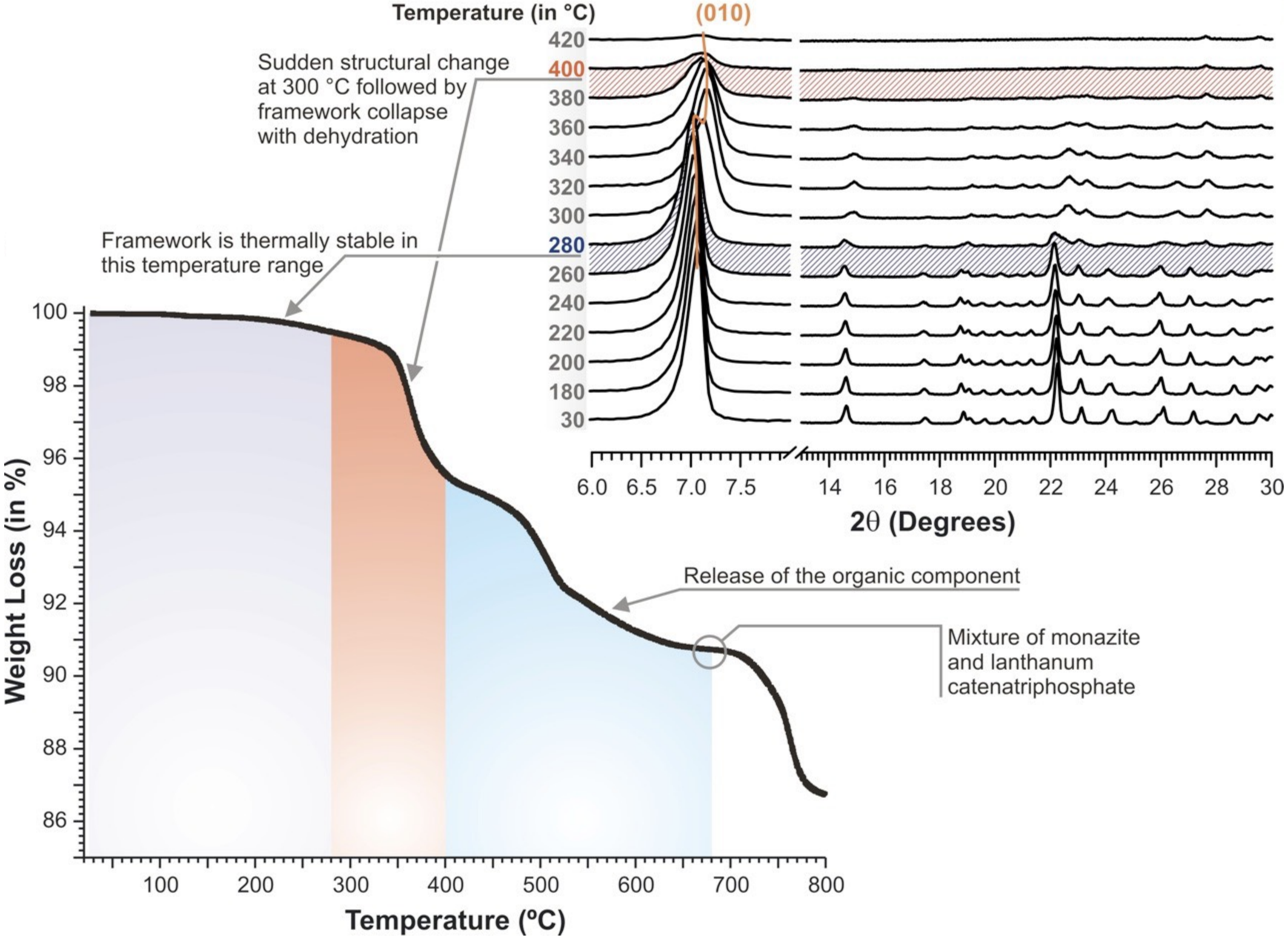
Orthorhombic, $Pca2_1$
a = 9.1762(3) Å
b = 11.7369(4) Å
c = 9.8340(3) Å
Volume = 1059.12(6) Å^3



Planar lanthanum oxide layer decorated by the H_3nmp^{3-} linkers: each {LaO_9} polyhedron is edge or corner-shared to another 4 adjacent ones

Journal of the American Chemical Society (**2011**), Volume *133*, Pages 15120-15138

Thermal Stability Studies of [La(H_3nmp)]



Sudden structural change at 300 °C followed by framework collapse with dehydration

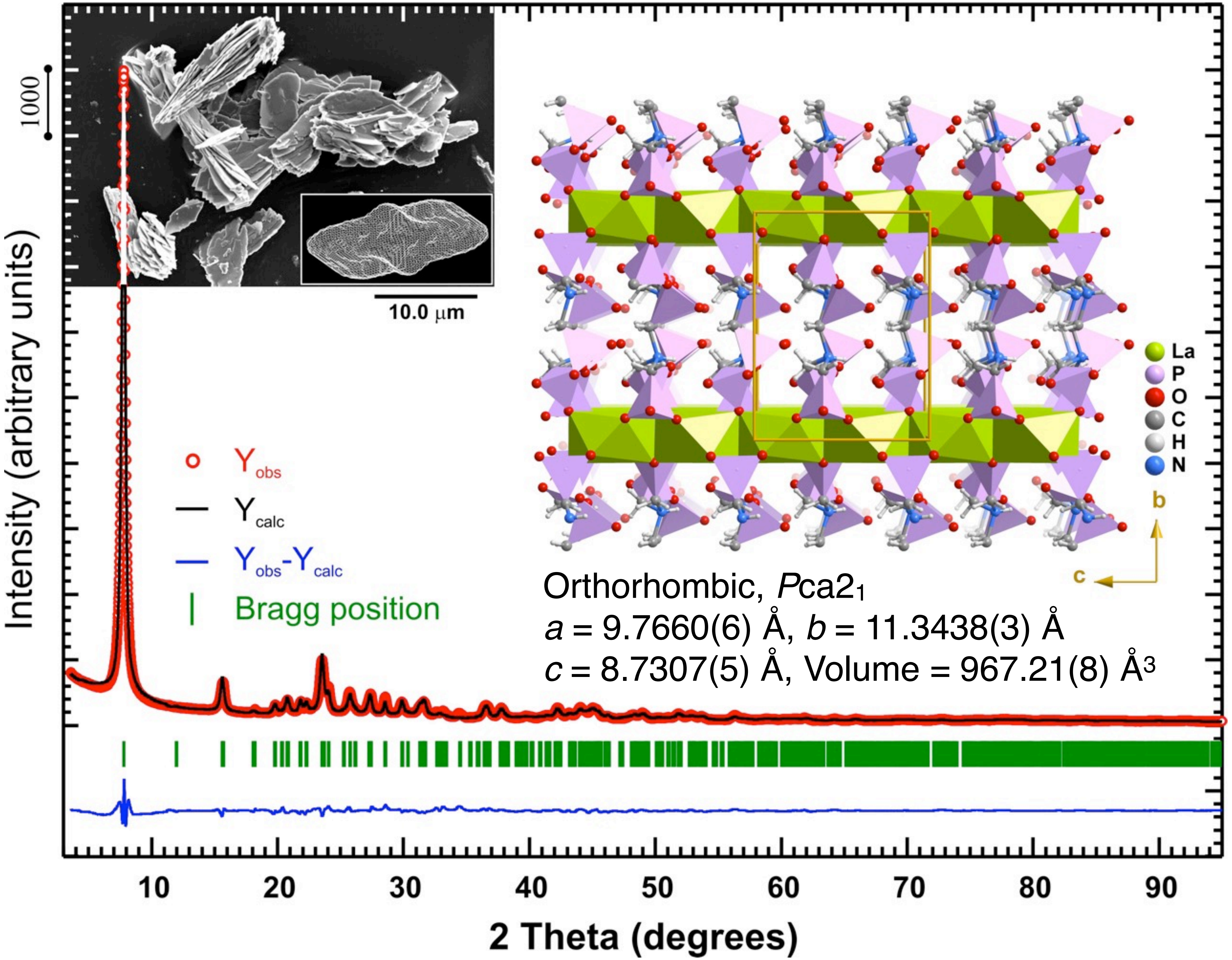
Framework is thermally stable in this temperature range

Release of the organic component

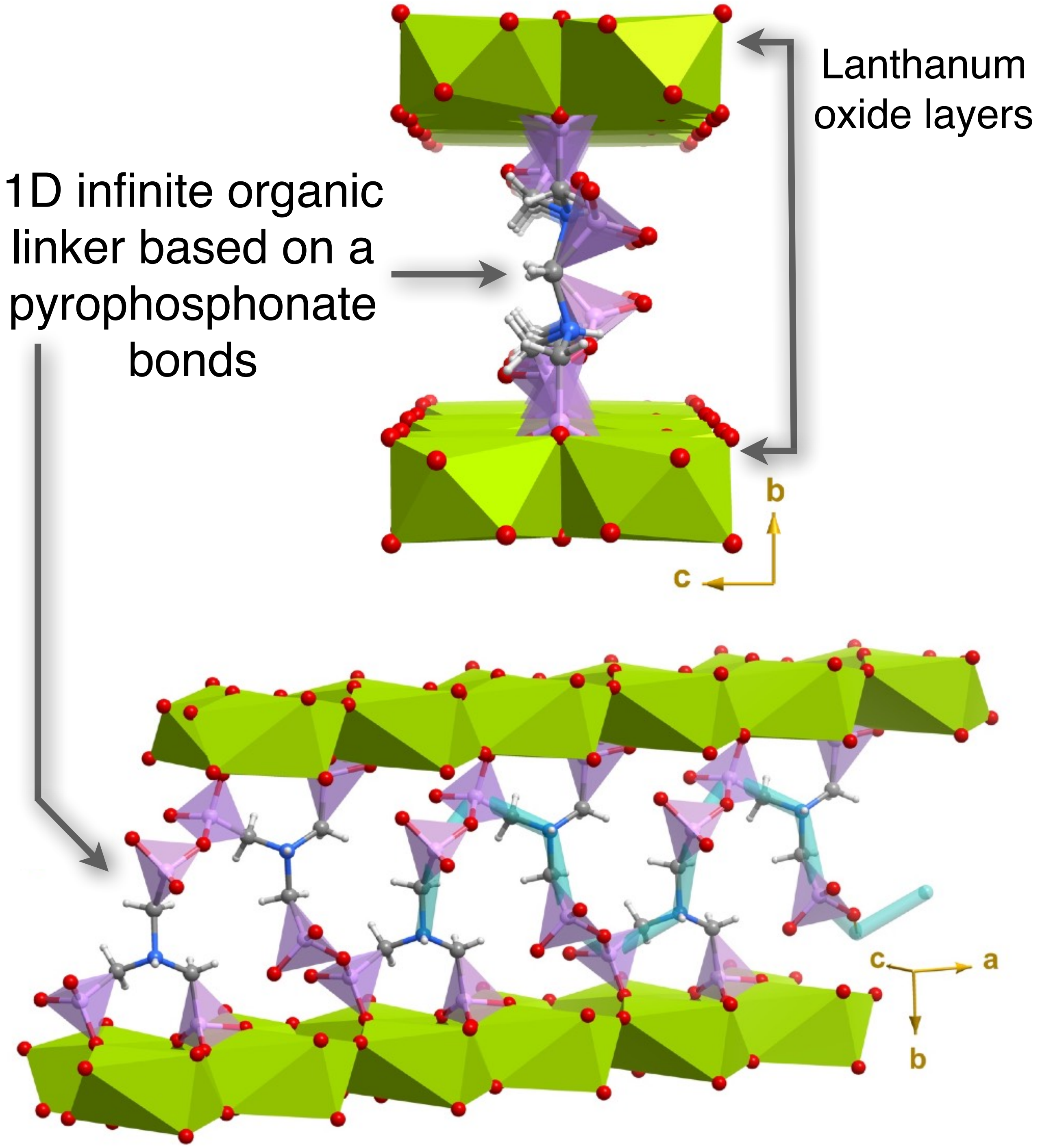
Mixture of monazite and lanthanum catenatriphosphate

Journal of the American Chemical Society (**2011**), Volume *133*, Pages 15120-15138

A possible Model for [La(*L*)]: a 3D MOF



Orthorhombic, $Pca2_1$
a = 9.7660(6) Å, b = 11.3438(3) Å
c = 8.7307(5) Å, Volume = 967.21(8) Å^3



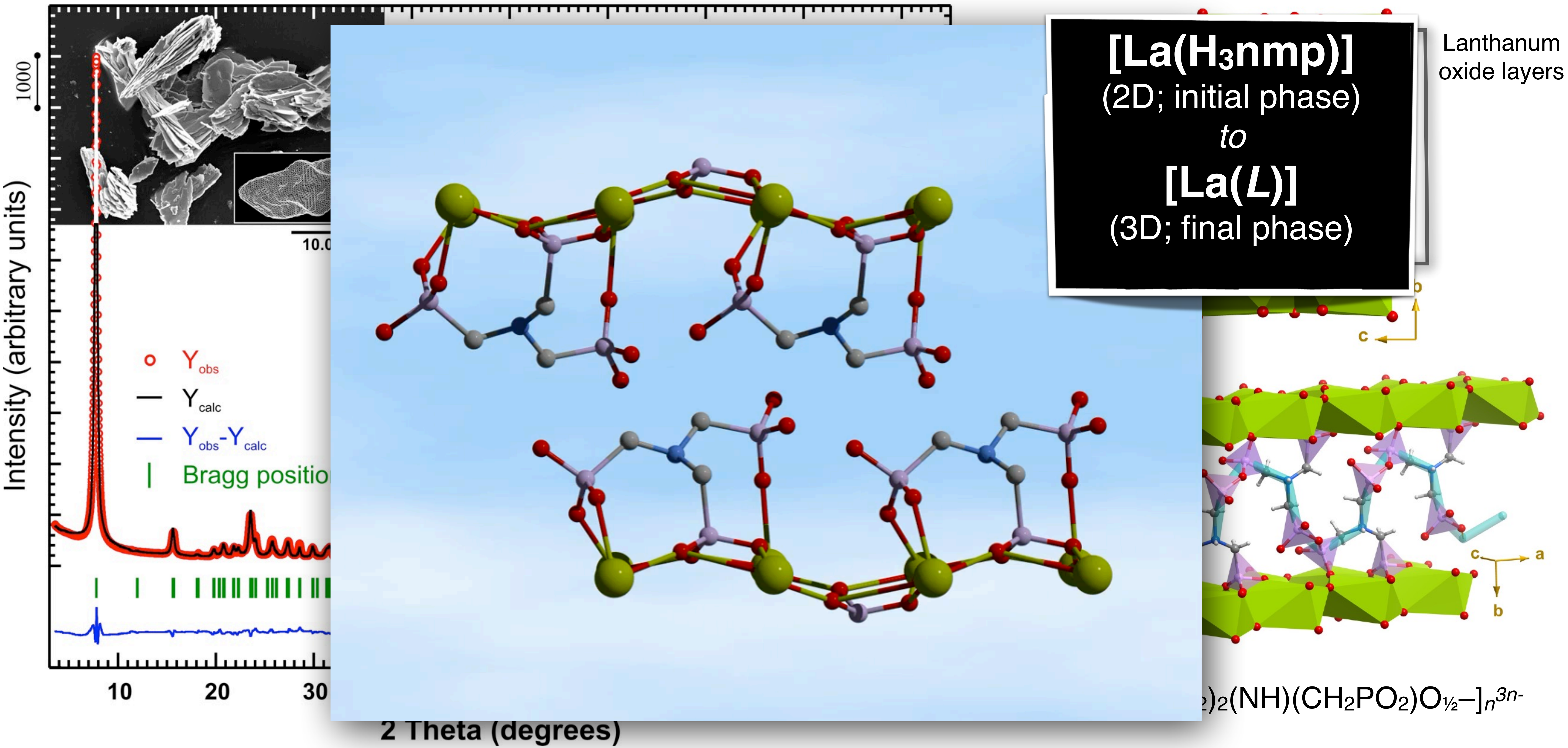
Lanthanum oxide layers

1D infinite organic linker based on a pyrophosphonate bonds

$L^{3-} = [-(PO_3CH_2)_2(NH)(CH_2PO_2)O_{½}-]_n^{3n-}$

Journal of the American Chemical Society (**2011**), Volume *133*, Pages 15120-15138

From 2D to 3D: Structural Transformation



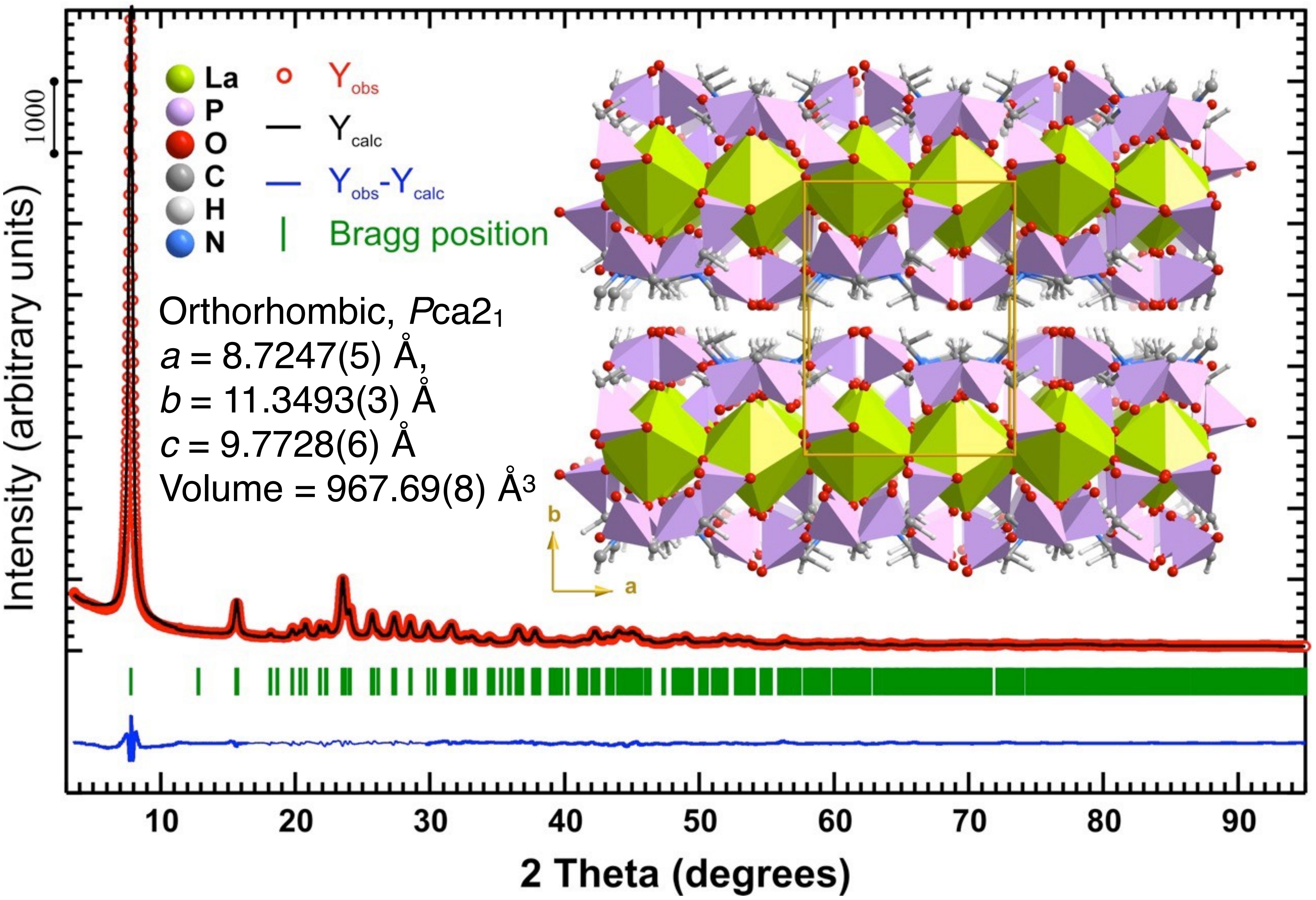
[La(H_3nmp)]
(2D; initial phase)
to
[La(*L*)]
(3D; final phase)

Lanthanum oxide layers

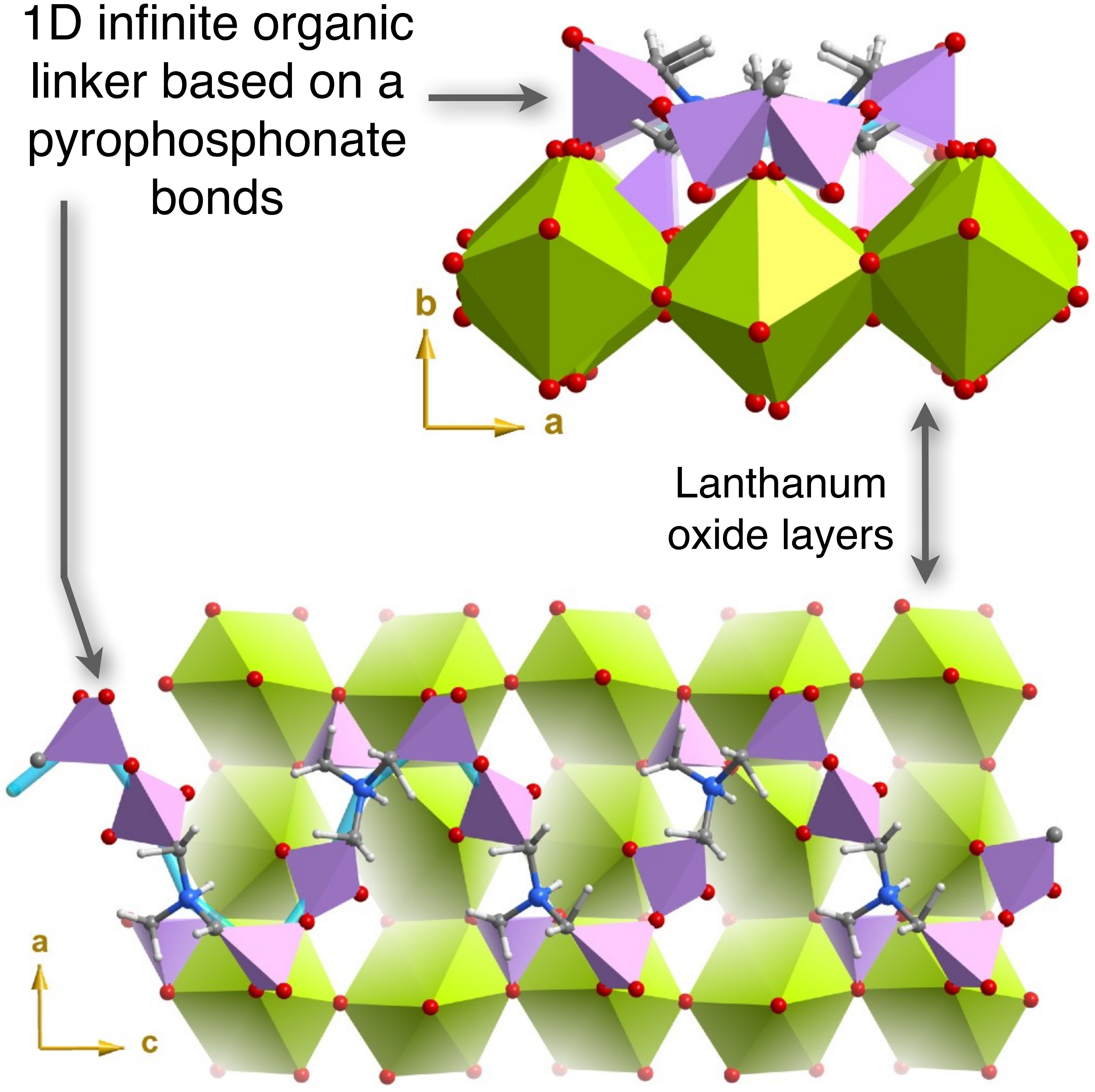
$)_2(NH)(CH_2PO_2)O_{1/2}–]_n^{3n-}$

Journal of the American Chemical Society (**2011**), Volume *133*, Pages 15120-15138

A possible Model for [La(*L*)]: a 2D MOF



Orthorhombic, $Pca2_1$
a = 8.7247(5) Å,
b = 11.3493(3) Å
c = 9.7728(6) Å
Volume = 967.69(8) Å^3



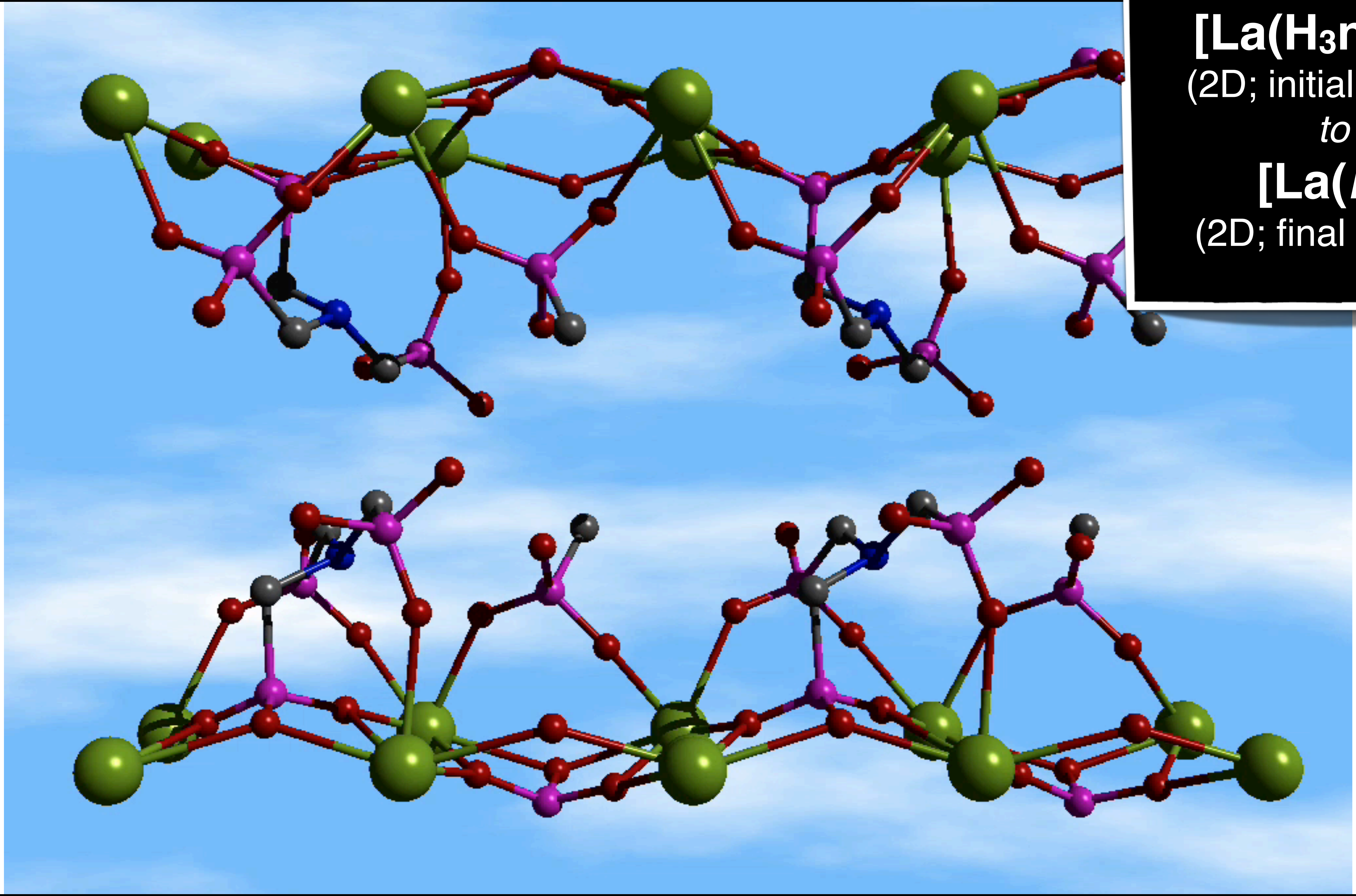
1D infinite organic linker based on a pyrophosphonate bonds

Lanthanum oxide layers

$L^{3-} = [\text{–}(PO_3CH_2)_2(NH)(CH_2PO_2)\text{–}]_n{}^{3n-}$

Journal of the American Chemical Society (**2011**), Volume *133*, Pages 15120-15138

From 2D to 2D: Structural Transformation

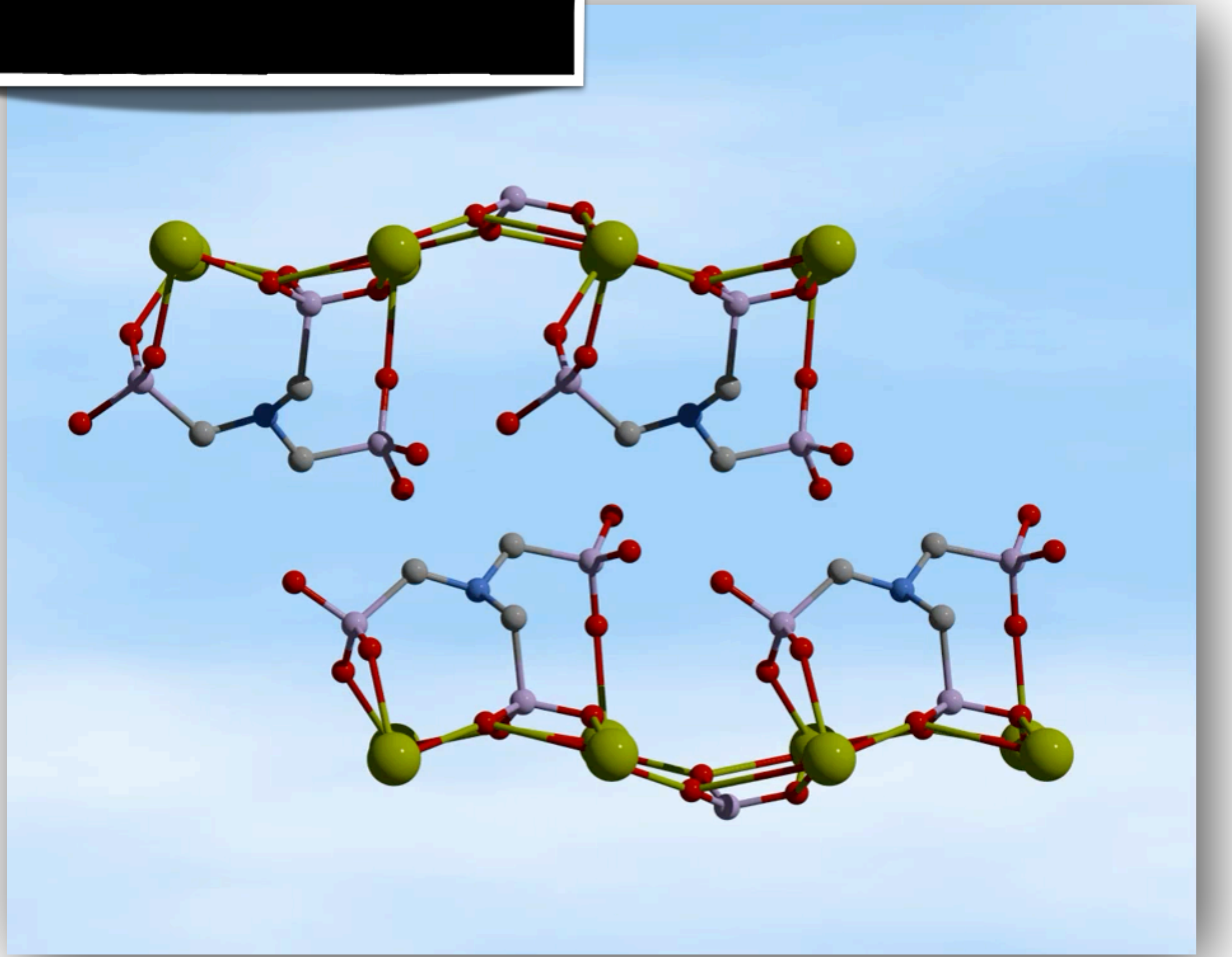


[La(H_3nmp)]
(2D; initial phase)
to
[La(*L*)]
(2D; final phase)

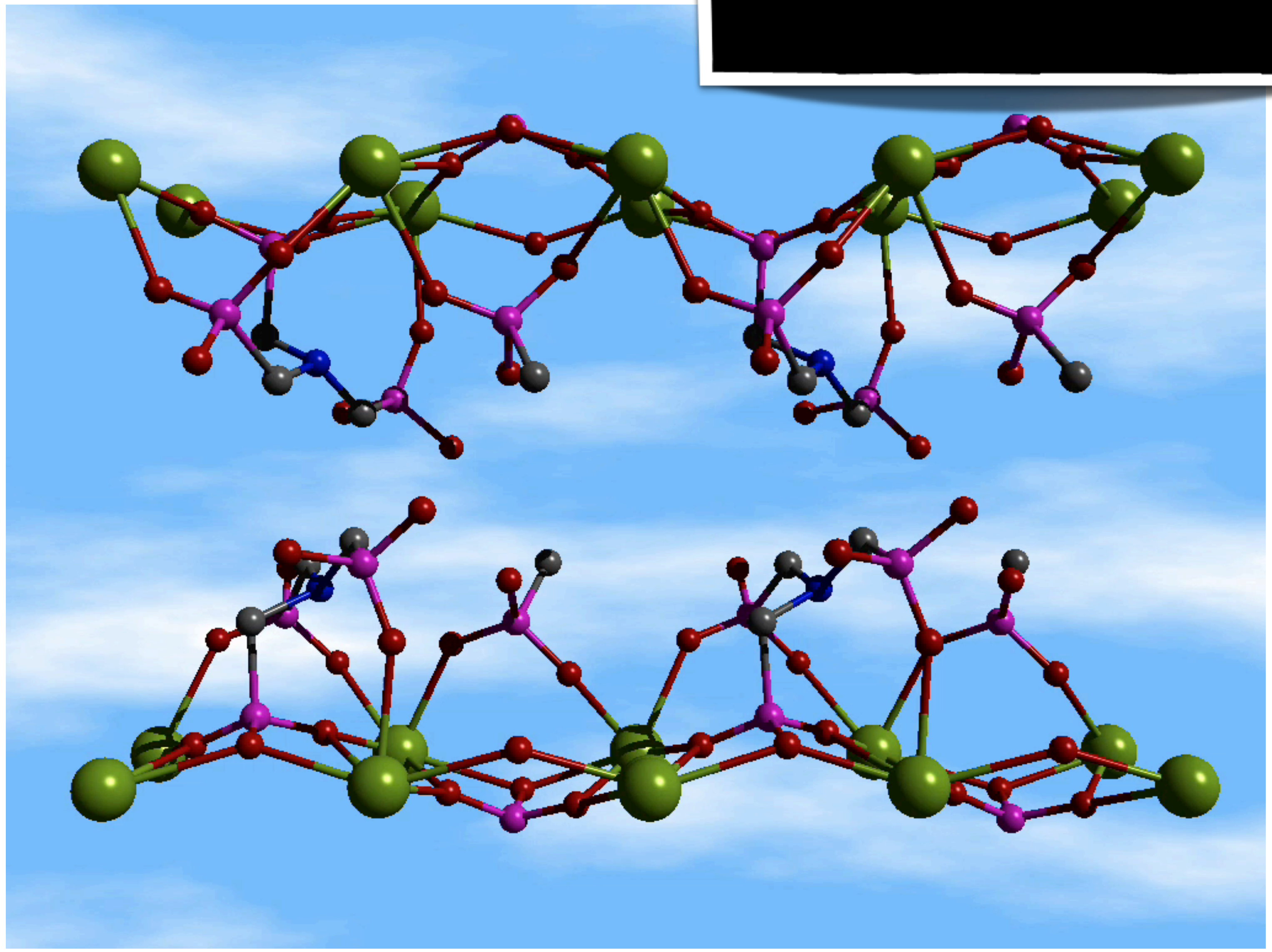
Journal of the American Chemical Society (**2011**), Volume *133*, Pages 15120-15138

Which one?

[La(H_3nmp)]
(2D; initial phase)
to
[La(*L*)]
(3D; final phase)



[La(H_3nmp)]
(2D; initial phase)
to
[La(*L*)]
(2D; final phase)



Journal of the American Chemical Society (**2011**), Volume *133*, Pages 15120-15138

Which one?

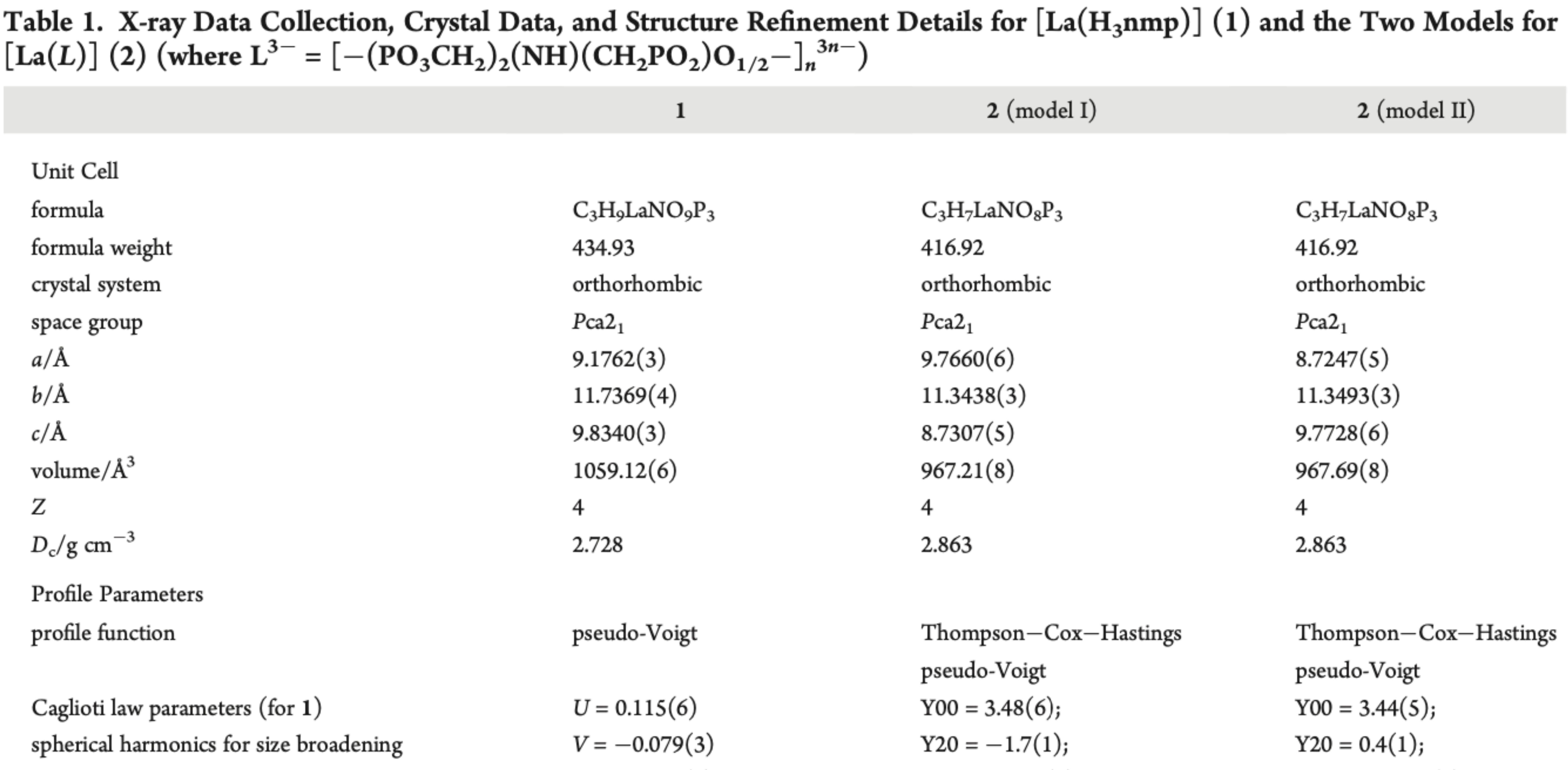


Table 1. X-ray Data Collection, Crystal Data, and Structure Refinement Details for [La(H_3nmp)] (1) and the Two Models for [La(*L*)] (2) (where $L^{3-} = [-(PO_3CH_2)_2(NH)(CH_2PO_2)O_{1/2}-]_n{}^{3n-}$)

	1	**2** (model I)	**2** (model II)
Unit Cell			
formula	$C_3H_9LaNO_9P_3$	$C_3H_7LaNO_8P_3$	$C_3H_7LaNO_8P_3$
formula weight	434.93	416.92	416.92
crystal system	orthorhombic	orthorhombic	orthorhombic
space group	$Pca2_1$	$Pca2_1$	$Pca2_1$
a/Å	9.1762(3)	9.7660(6)	8.7247(5)
b/Å	11.7369(4)	11.3438(3)	11.3493(3)
c/Å	9.8340(3)	8.7307(5)	9.7728(6)
volume/Å^3	1059.12(6)	967.21(8)	967.69(8)
Z	4	4	4
D_c/g cm^{-3}	2.728	2.863	2.863
Profile Parameters			
profile function	pseudo-Voigt	Thompson−Cox−Hastings pseudo-Voigt	Thompson−Cox−Hastings pseudo-Voigt
Caglioti law parameters (for **1**)	$U = 0.115(6)$	Y00 = 3.48(6);	Y00 = 3.44(5);
spherical harmonics for size broadening	$V = -0.079(3)$	Y20 = −1.7(1);	Y20 = 0.4(1);

Journal of the American Chemical Society (**2011**), Volume *133*, Pages 15120-15138

Which one?

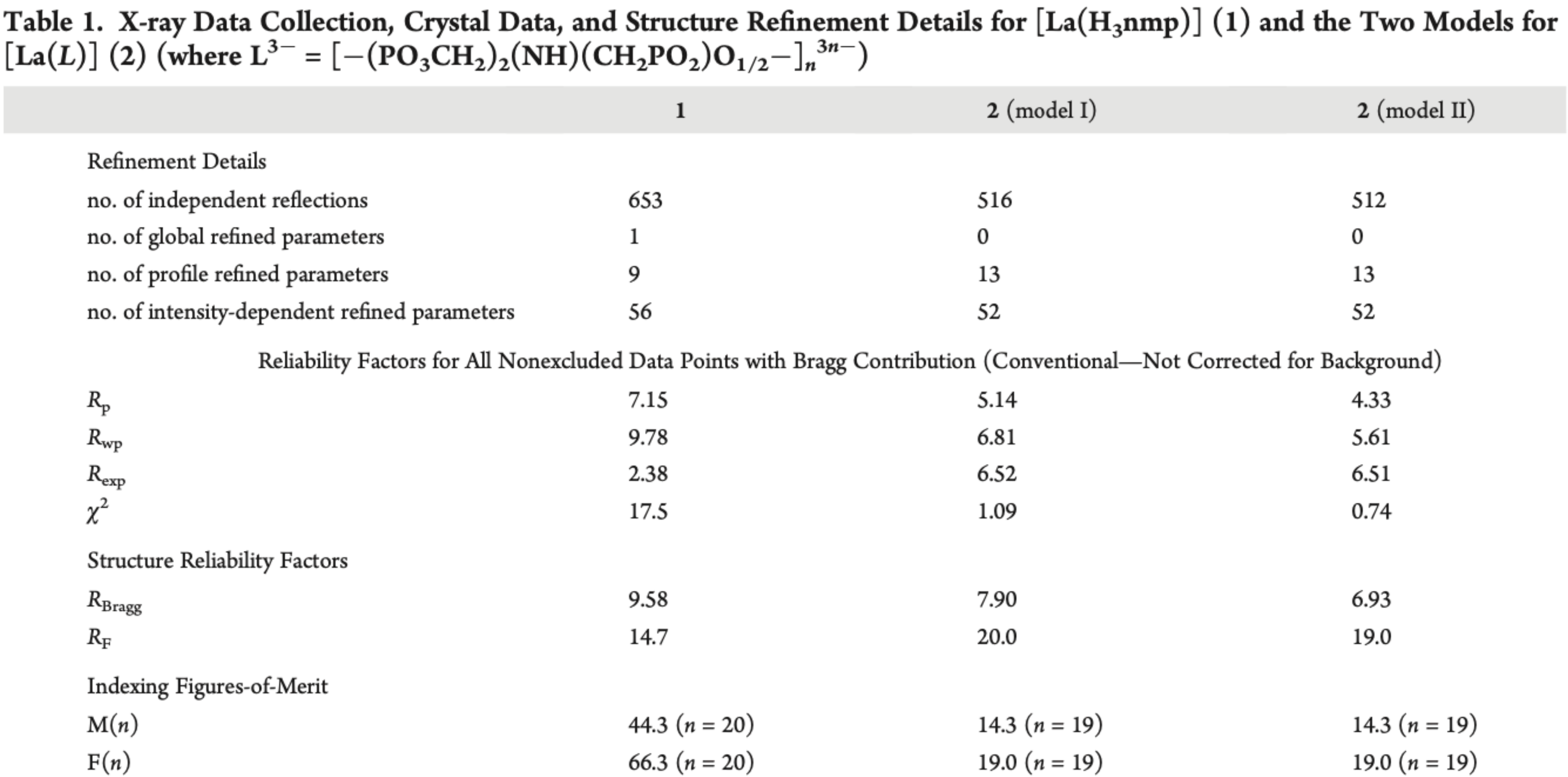
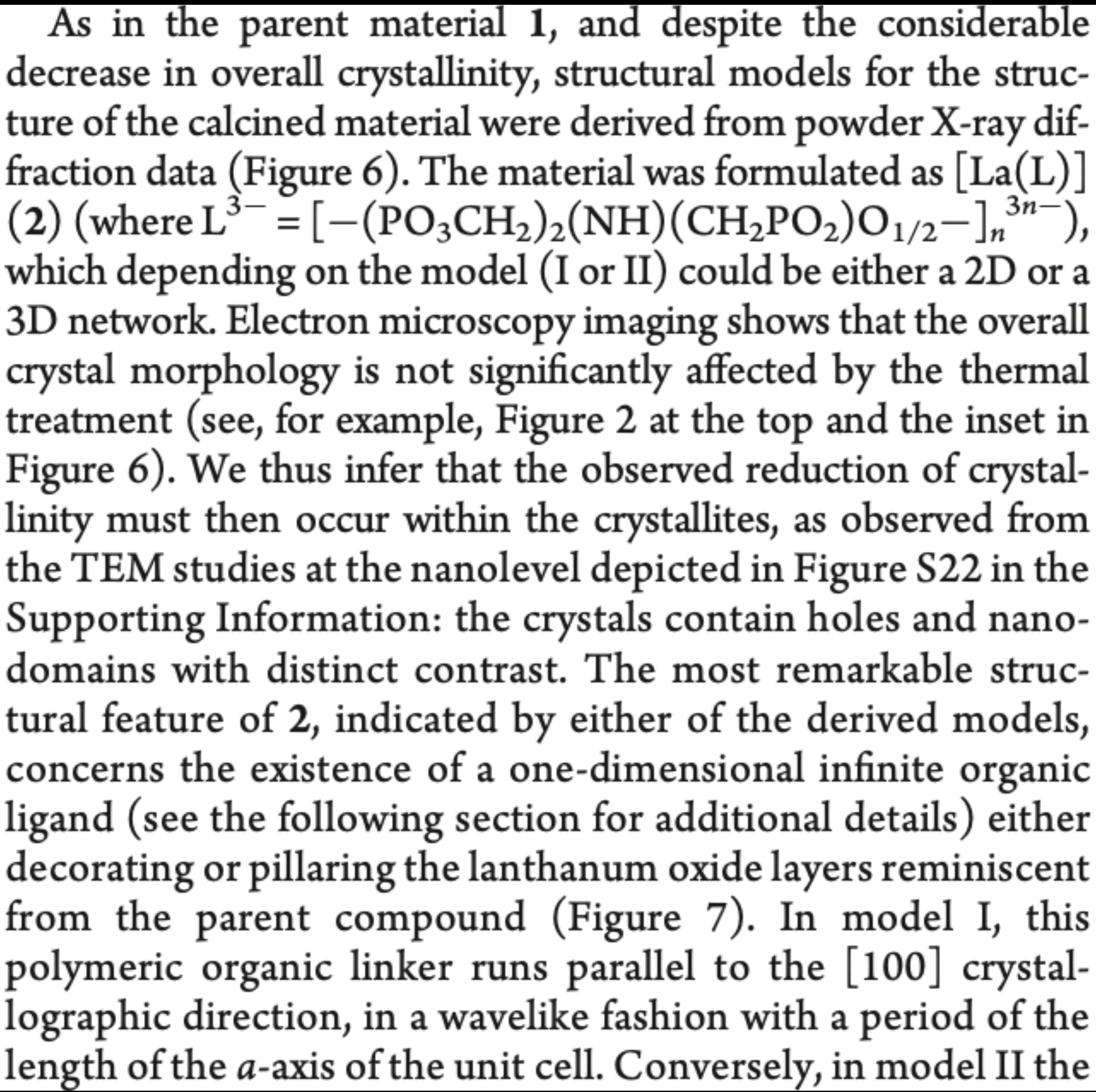


Table 1. **X-ray Data Collection, Crystal Data, and Structure Refinement Details for [La(H_3nmp)] (1) and the Two Models for [La(*L*)] (2) (where L^{3-} = $[-(PO_3CH_2)_2(NH)(CH_2PO_2)O_{1/2}-]_n{}^{3n-}$)**

	1	**2** (model I)	**2** (model II)
Refinement Details			
no. of independent reflections	653	516	512
no. of global refined parameters	1	0	0
no. of profile refined parameters	9	13	13
no. of intensity-dependent refined parameters	56	52	52
Reliability Factors for All Nonexcluded Data Points with Bragg Contribution (Conventional—Not Corrected for Background)			
R_p	7.15	5.14	4.33
R_{wp}	9.78	6.81	5.61
R_{exp}	2.38	6.52	6.51
χ^2	17.5	1.09	0.74
Structure Reliability Factors			
R_{Bragg}	9.58	7.90	6.93
R_F	14.7	20.0	19.0
Indexing Figures-of-Merit			
M(*n*)	44.3 (*n* = 20)	14.3 (*n* = 19)	14.3 (*n* = 19)
F(*n*)	66.3 (*n* = 20)	19.0 (*n* = 19)	19.0 (*n* = 19)

Journal of the American Chemical Society (**2011**), Volume *133*, Pages 15120-15138

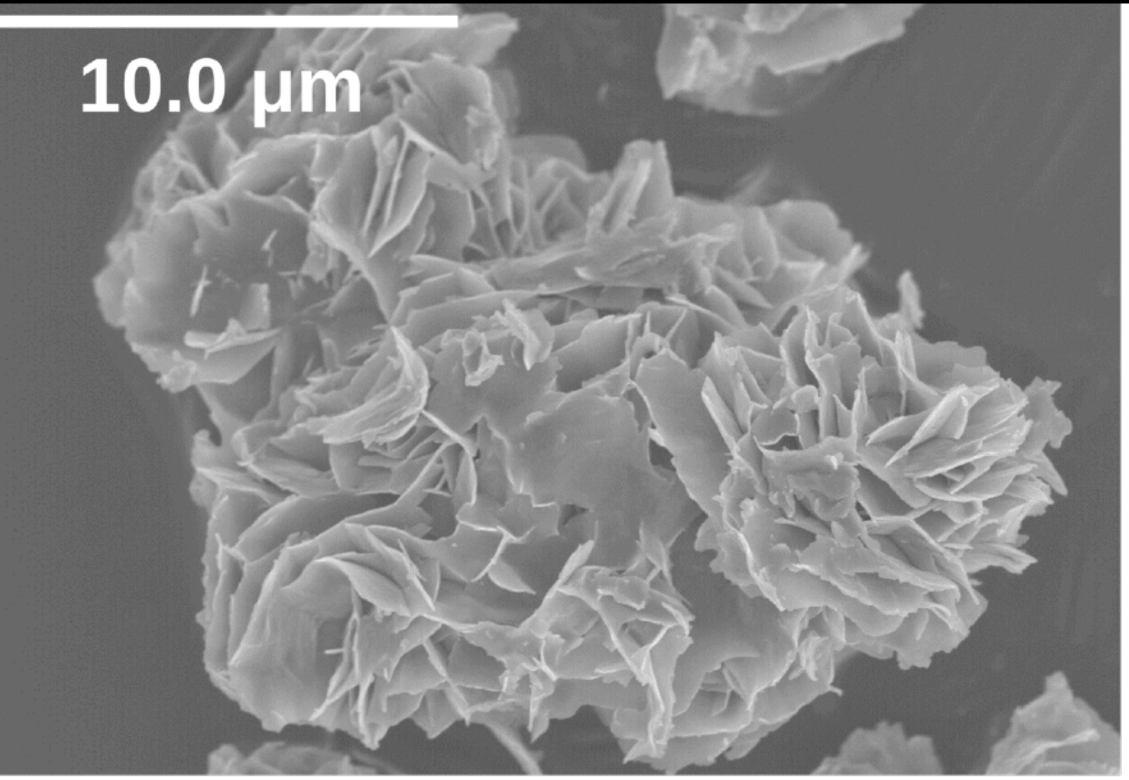
Which one?



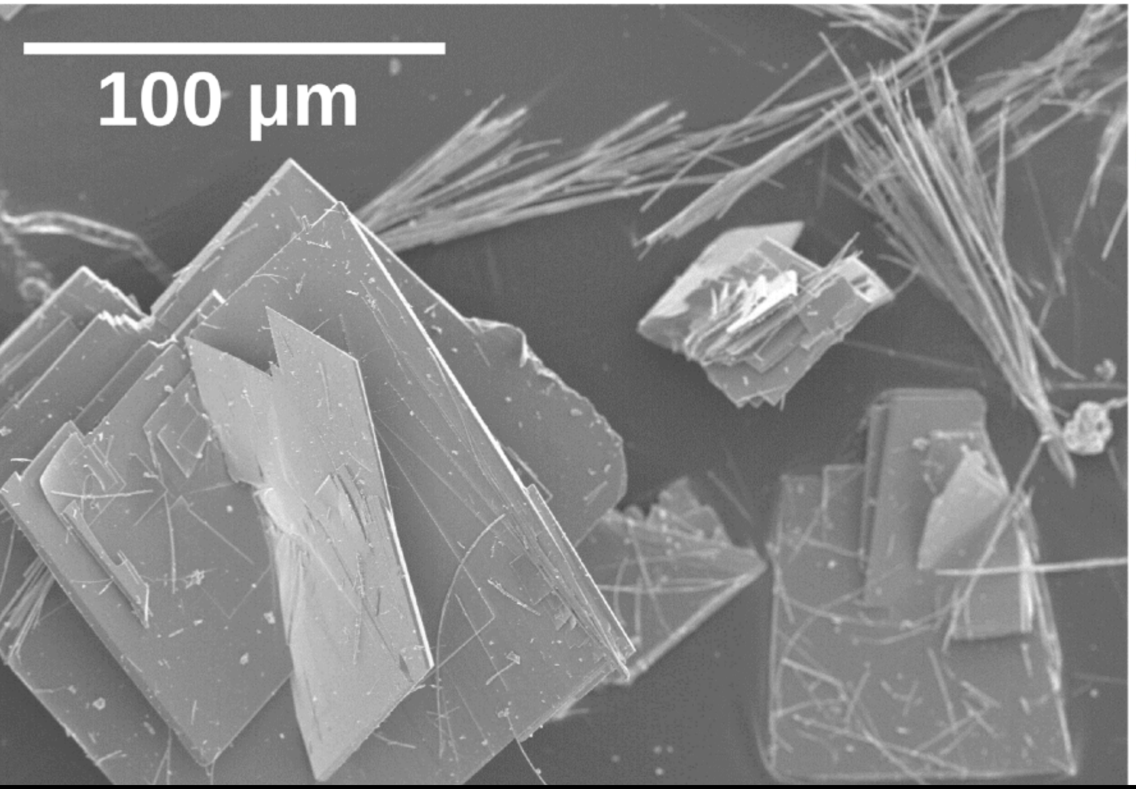
As in the parent material **1**, and despite the considerable decrease in overall crystallinity, structural models for the structure of the calcined material were derived from powder X-ray diffraction data (Figure 6). The material was formulated as [La(L)] (**2**) (where $L^{3-} = [-(PO_3CH_2)_2(NH)(CH_2PO_2)O_{1/2}-]_n^{3n-}$), which depending on the model (I or II) could be either a 2D or a 3D network. Electron microscopy imaging shows that the overall crystal morphology is not significantly affected by the thermal treatment (see, for example, Figure 2 at the top and the inset in Figure 6). We thus infer that the observed reduction of crystallinity must then occur within the crystallites, as observed from the TEM studies at the nanolevel depicted in Figure S22 in the Supporting Information: the crystals contain holes and nanodomains with distinct contrast. The most remarkable structural feature of **2**, indicated by either of the derived models, concerns the existence of a one-dimensional infinite organic ligand (see the following section for additional details) either decorating or pillaring the lanthanum oxide layers reminiscent from the parent compound (Figure 7). In model I, this polymeric organic linker runs parallel to the [100] crystallographic direction, in a wavelike fashion with a period of the length of the *a*-axis of the unit cell. Conversely, in model II the

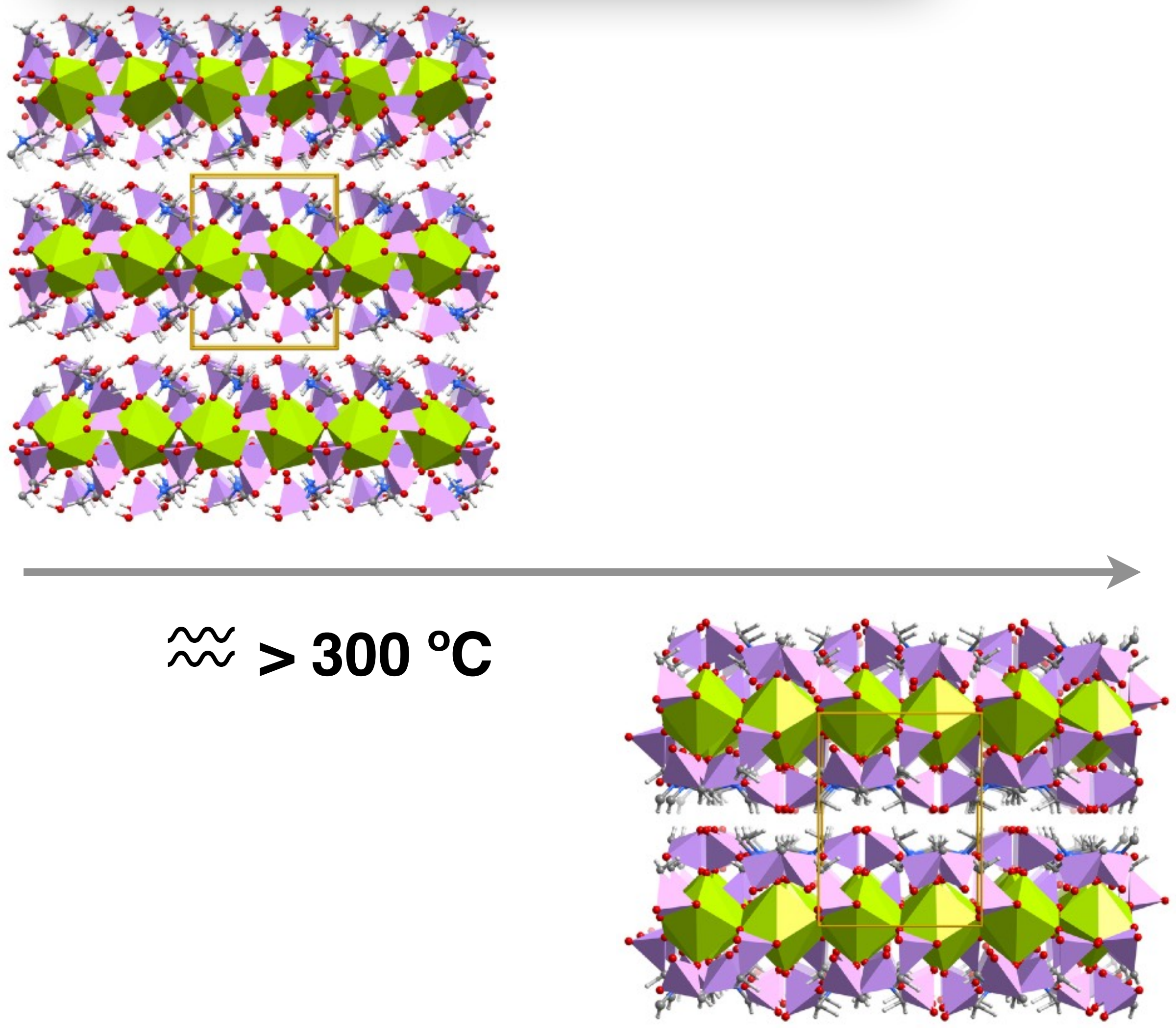
Journal of the American Chemical Society (**2011**), Volume *133*, Pages 15120-15138

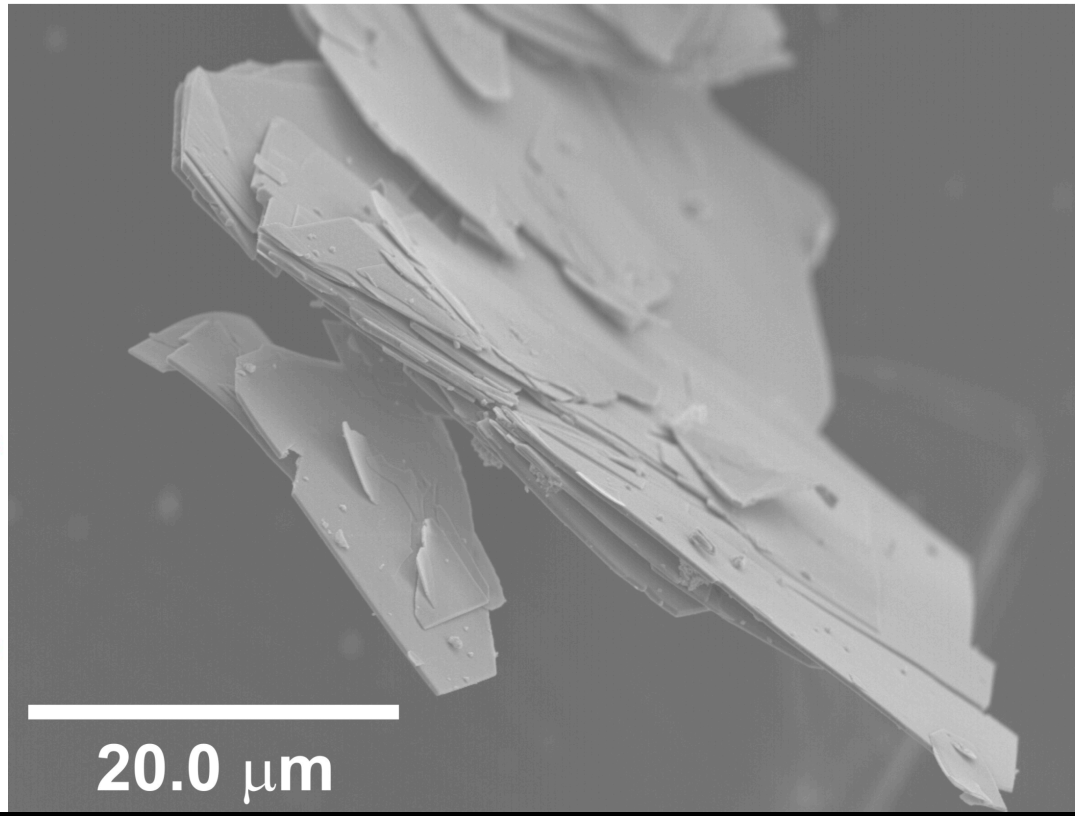
Murphy's Law



Changes in the synthesis route:
- Use of **lanthanide oxide** and the metal source
- Use of **static hydrothermal synthesis**

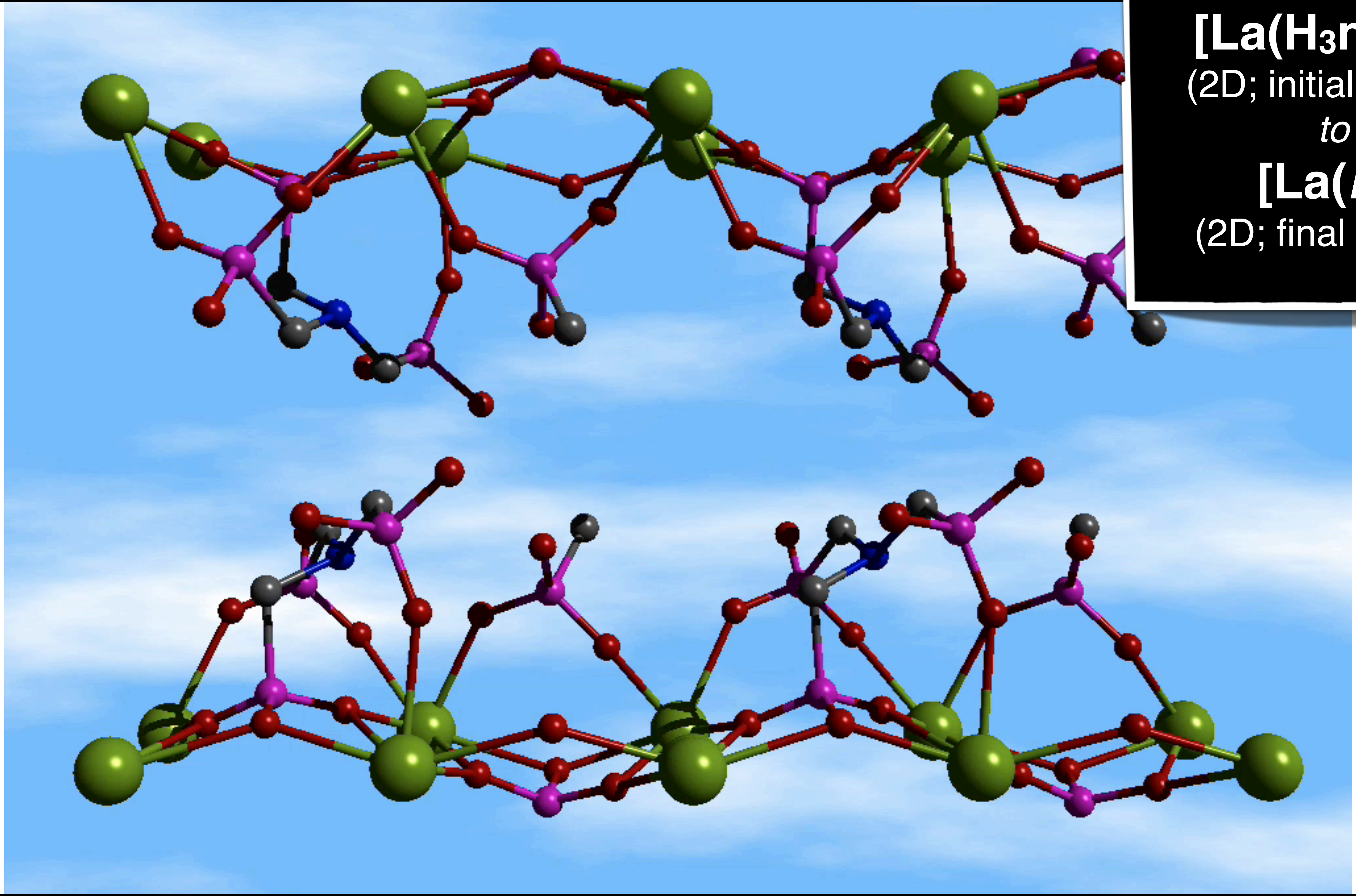






Paz *et al.*, *Acta Crystallographica - Section E* (**2012**), Volume *E68*, Pages m294-m295
Paz *et al.*, *Journal of Chemical Crystallography* (**2013**), Volume *43*, Pages 165-170

From 2D to 2D: Structural Transformation

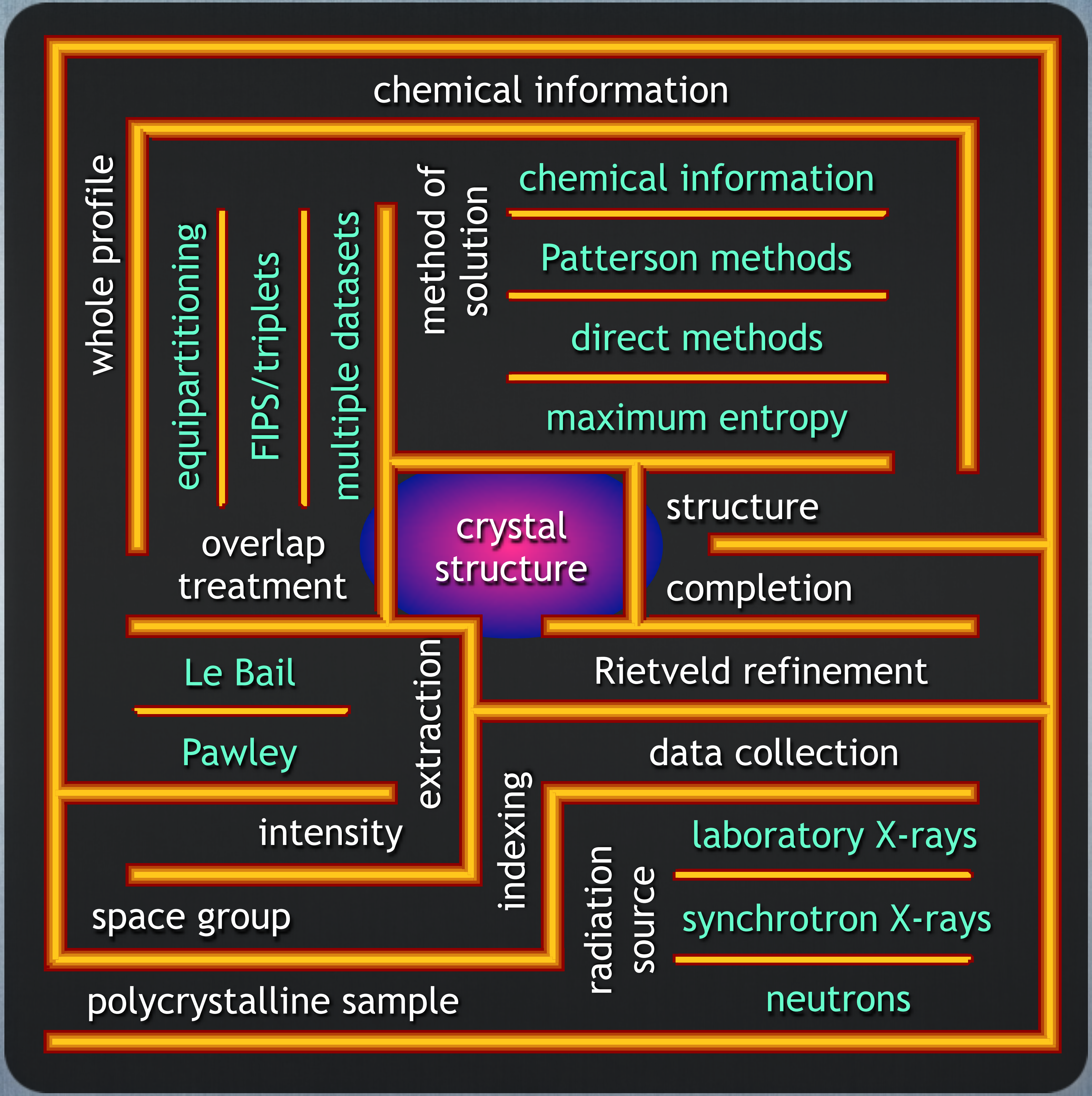


[La(H_3nmp)]
(2D; initial phase)
to
[La(*L*)]
(2D; final phase)

Journal of the American Chemical Society (**2011**), Volume *133*, Pages 15120-15138

Take home this:

You will make mistakes, even when being extremely careful…



chemical information

whole profile

equipartitioning

FIPS/triplets

multiple datasets

method of solution

chemical information

Patterson methods

direct methods

maximum entropy

overlap treatment

crystal structure

structure

completion

Le Bail

Pawley

extraction

Rietveld refinement

data collection

intensity

indexing

space group

radiation source

laboratory X-rays

synchrotron X-rays

neutrons

polycrystalline sample

The Rietveld Method

Wiki Loves Earth photo contest:
Upload photos of natural heritage sites in Portugal to help Wikipedia and win prizes!

Hugo Rietveld

From Wikipedia, the free encyclopedia

Hugo M. Rietveld (7 March 1932 – 16 July 2016[1][2]) was a Dutch crystallographer who is famous for his publication on the full profile refinement method in powder diffraction, which became later known as the Rietveld refinement method. The method is used for the characterisation of crystalline materials from X-ray powder diffraction data. The Rietveld refinement uses a least squares approach to refine a theoretical line profile (calculated from a known or postulated crystal structure) until it matches the measured profile. The introduction of this technique which used the full profile instead of individual reflections was a significant step forward in the diffraction analysis of powder samples.

Contents [hide]

Biography [edit]

Hugo M. Rietveld
(1932-2016)

The Rietveld Method

Obituary

Hugo Rietveld (1932-2016)

excerpted from *J. Appl. Cryst.* (2016). **49**, 1394-1395
doi:10.1107/S1600576716012061

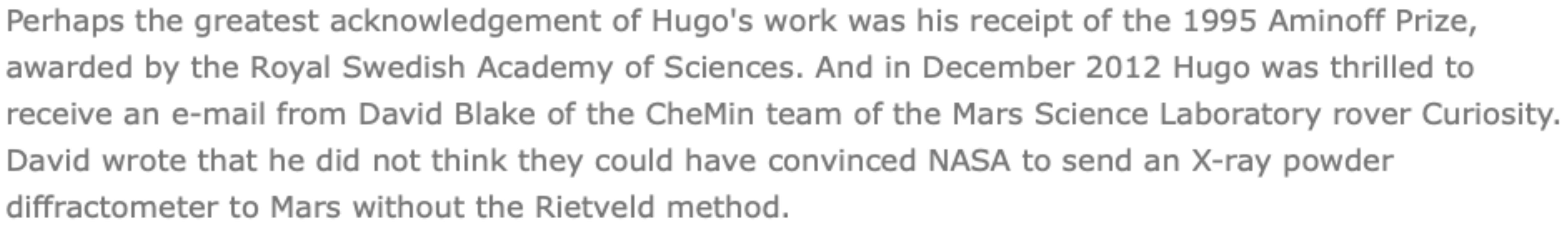
Hugo Rietveld has died at the age of 84 after a short illness. He leaves behind his wife, a son and two daughters, to whom we extend our heartfelt sympathy on behalf of the more than one thousand members of the Rietveld Mailing List.

Hugo was born on 7 March, 1932, in The Hague and migrated to Western Australia, where in 1957 he enrolled at the U. of Western Australia at the same time as Brian O'Connor and Syd Hall. He obtained his PhD under the supervision of Ted Maslen. Hugo pioneered single-crystal neutron diffraction at Lucas Heights Sydney with Terry Sabine, and their first paper was published in *Nature* in 1961.

Hugo Rietveld (left) receiving the Gregori Aminoff Prize from King Carl Gustaf of Sweden in Stockholm in 1995. (More detail given at http://home.wxs.nl/~rietv025/.)

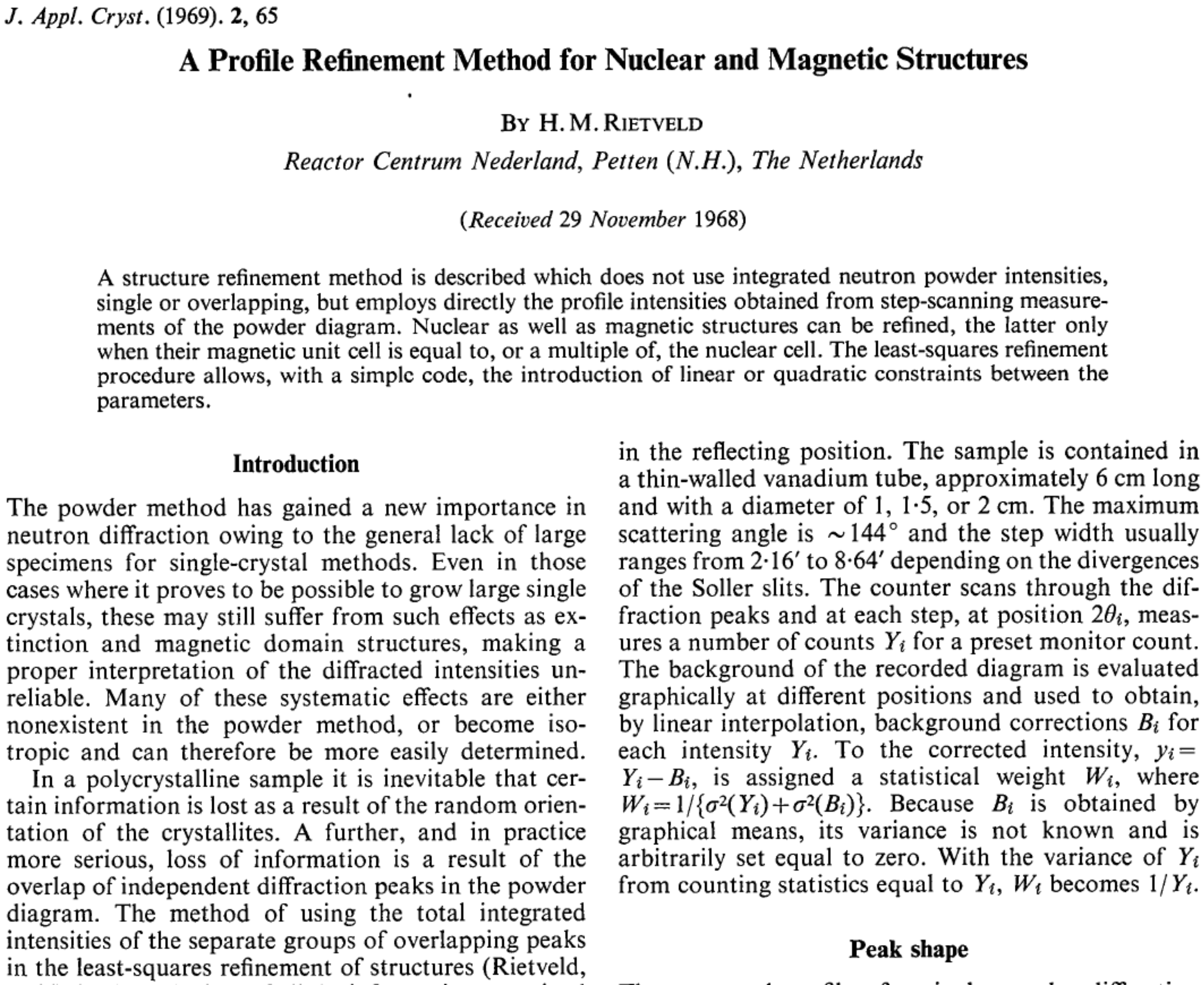
Hugo's experience with manual data collection and refinement convinced him of the need to computerize such tasks. He programmed two of the first IBM 1620 mainframes in Fortran II. After obtaining his PhD in 1964, he joined the neutron diffraction group of the Reactor Centrum Nederland in Petten and his interest turned to powder diffraction because large single crystals were not available for the inorganic materials of

The Rietveld Method



Perhaps the greatest acknowledgement of Hugo's work was his receipt of the 1995 Aminoff Prize, awarded by the Royal Swedish Academy of Sciences. And in December 2012 Hugo was thrilled to receive an e-mail from David Blake of the CheMin team of the Mars Science Laboratory rover Curiosity. David wrote that he did not think they could have convinced NASA to send an X-ray powder diffractometer to Mars without the Rietveld method.

The Rietveld Method



J. Appl. Cryst. (1969). **2**, 65

A Profile Refinement Method for Nuclear and Magnetic Structures

By H. M. Rietveld

Reactor Centrum Nederland, Petten (N.H.), The Netherlands

(*Received 29 November* 1968)

A structure refinement method is described which does not use integrated neutron powder intensities, single or overlapping, but employs directly the profile intensities obtained from step-scanning measurements of the powder diagram. Nuclear as well as magnetic structures can be refined, the latter only when their magnetic unit cell is equal to, or a multiple of, the nuclear cell. The least-squares refinement procedure allows, with a simple code, the introduction of linear or quadratic constraints between the parameters.

Introduction

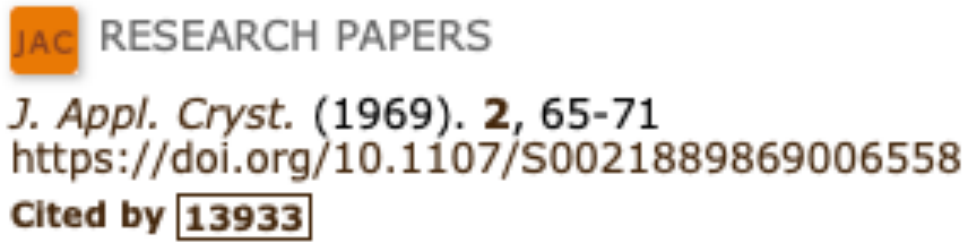
The powder method has gained a new importance in neutron diffraction owing to the general lack of large specimens for single-crystal methods. Even in those cases where it proves to be possible to grow large single crystals, these may still suffer from such effects as extinction and magnetic domain structures, making a proper interpretation of the diffracted intensities unreliable. Many of these systematic effects are either nonexistent in the powder method, or become isotropic and can therefore be more easily determined.

In a polycrystalline sample it is inevitable that certain information is lost as a result of the random orientation of the crystallites. A further, and in practice more serious, loss of information is a result of the overlap of independent diffraction peaks in the powder diagram. The method of using the total integrated intensities of the separate groups of overlapping peaks in the least-squares refinement of structures (Rietveld,

in the reflecting position. The sample is contained in a thin-walled vanadium tube, approximately 6 cm long and with a diameter of 1, 1·5, or 2 cm. The maximum scattering angle is ~144° and the step width usually ranges from 2·16′ to 8·64′ depending on the divergences of the Soller slits. The counter scans through the diffraction peaks and at each step, at position $2\theta_i$, measures a number of counts Y_i for a preset monitor count. The background of the recorded diagram is evaluated graphically at different positions and used to obtain, by linear interpolation, background corrections B_i for each intensity Y_i. To the corrected intensity, $y_i = Y_i - B_i$, is assigned a statistical weight W_i, where $W_i = 1/\{\sigma^2(Y_i) + \sigma^2(B_i)\}$. Because B_i is obtained by graphical means, its variance is not known and is arbitrarily set equal to zero. With the variance of Y_i from counting statistics equal to Y_i, W_i becomes $1/Y_i$.

Peak shape

Hugo M. Rietveld
(1932-2016)



RESEARCH PAPERS

J. Appl. Cryst. (1969). **2**, 65-71
https://doi.org/10.1107/S0021889869006558
Cited by 13933

The Rietveld Method

- First proposed for neutron diffraction in 1969 being indicated as a diffraction pattern analysis using a procedure to fit curves.
- Applied to X-ray diffraction in the 1970s and then to quantitative phase analysis in the 1980s.

Hugo M. Rietveld
(1932-2016)

The Rietveld Method - Applications

- Crystal structure refinement
- Crystal structure determination
- Phase identification and quantification
- Microstructure analysis

Hugo M. Rietveld
(1932-2016)

Cement Industry

Portland-limestone cements are the most widely used cements in Europe

Limestone is widely used in all other European common cement types as 0-5% minor additional constituents

Key properties of cement

- Strength
- Workability
- Resistance to chemical attack
- Colour (manufacture of white cement)

Properties governed by **mineral content** not composition

Influences **burnability** of raw feed and **grindability** of raw materials

On-line quality control requires measurements in real time of the quantities

- C_3S (Alite)
- C_2S (Belite)
- C_4AF (Ferrite)
- C_3A (Celite)

Anhydrous cement clinker

- $CaSO_4 \cdot 2H_2O$
- $CaSO_4 \cdot 0.5H_2O$

Added to control setting time

Dhanjal & Young & Storer, *Cement Industry Technical Conference* (**2006**), IEEE, 8978522
De la Torre & Aranda, *Journal of Applied Crystallography* (**2003**), Volume *36*, Pages 1169-1176

Cement Industry

Portland-limestone cements are the most widely used cements in Europe

Limestone is widely used in all other European common cement types as 0-5% minor additional constituents

On-line quality control requires measurements in real time

X-ray Fluorescence

Information on elemental composition which can be used to infer mineralogical composition by means of Bogue calculations

- Lack of thermodynamical equilibrium
- Does not take into account the elemental substitutions in a given phase
- Relative changes can not be monitored

Disadvantages

X-ray Diffraction

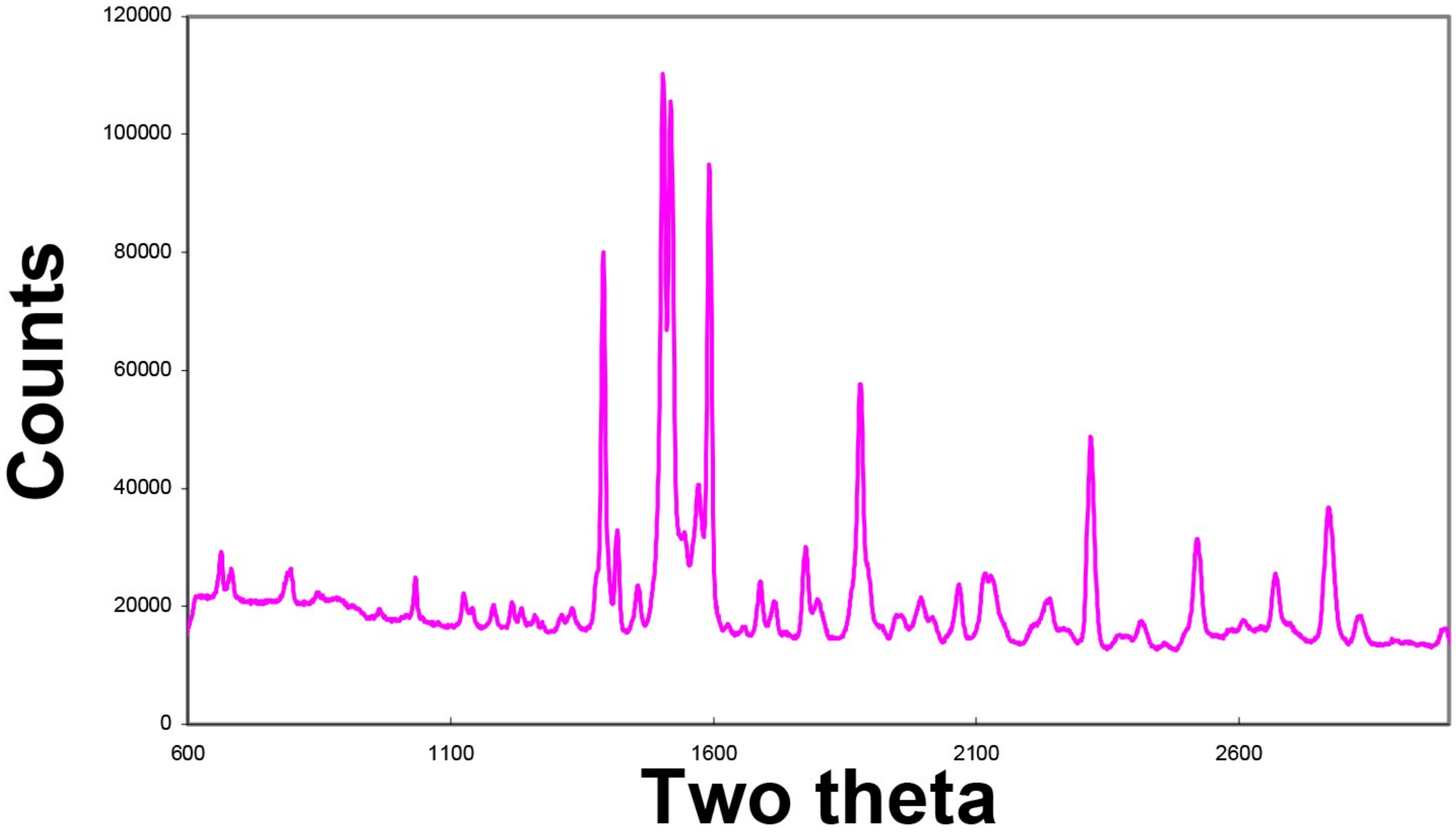
- Continuous XRD analysis provides the ability to control processes 'on-line'
- Rietveld method is the most auspicious alternative to control on-line the production process

Dhanjal & Young & Storer, *Cement Industry Technical Conference* (**2006**), IEEE, 8978522

De la Torre & Aranda, *Journal of Applied Crystallography* (**2003**), Volume *36*, Pages 1169-1176

Cement Industry

X-ray Diffraction



Powder X-ray diffraction pattern of a typical cement

Rietveld analysis based on powder X-ray diffraction allows for the complete mineralogical analysis of cement :

- C_3S (Alite)
- C_2S (Belite)
- C_4AF (Ferrite)
- C_3A (Celite)
- CaO
- $Ca(OH)_2$
- $CaCO_3$
- $CaSO_4 \cdot 2H_2O$
- $CaSO_4 \cdot 0.5H_2O$

Problems in the quantification

Dhanjal & Young & Storer, *Cement Industry Technical Conference* (**2006**), IEEE, 8978522
De la Torre & Aranda*, Journal of Applied Crystallography* (**2003**), Volume *36*, Pages 1169-1176

Cement Industry

X-ray Diffraction

Online continuous systems work for fixed and predictable mineral compositions

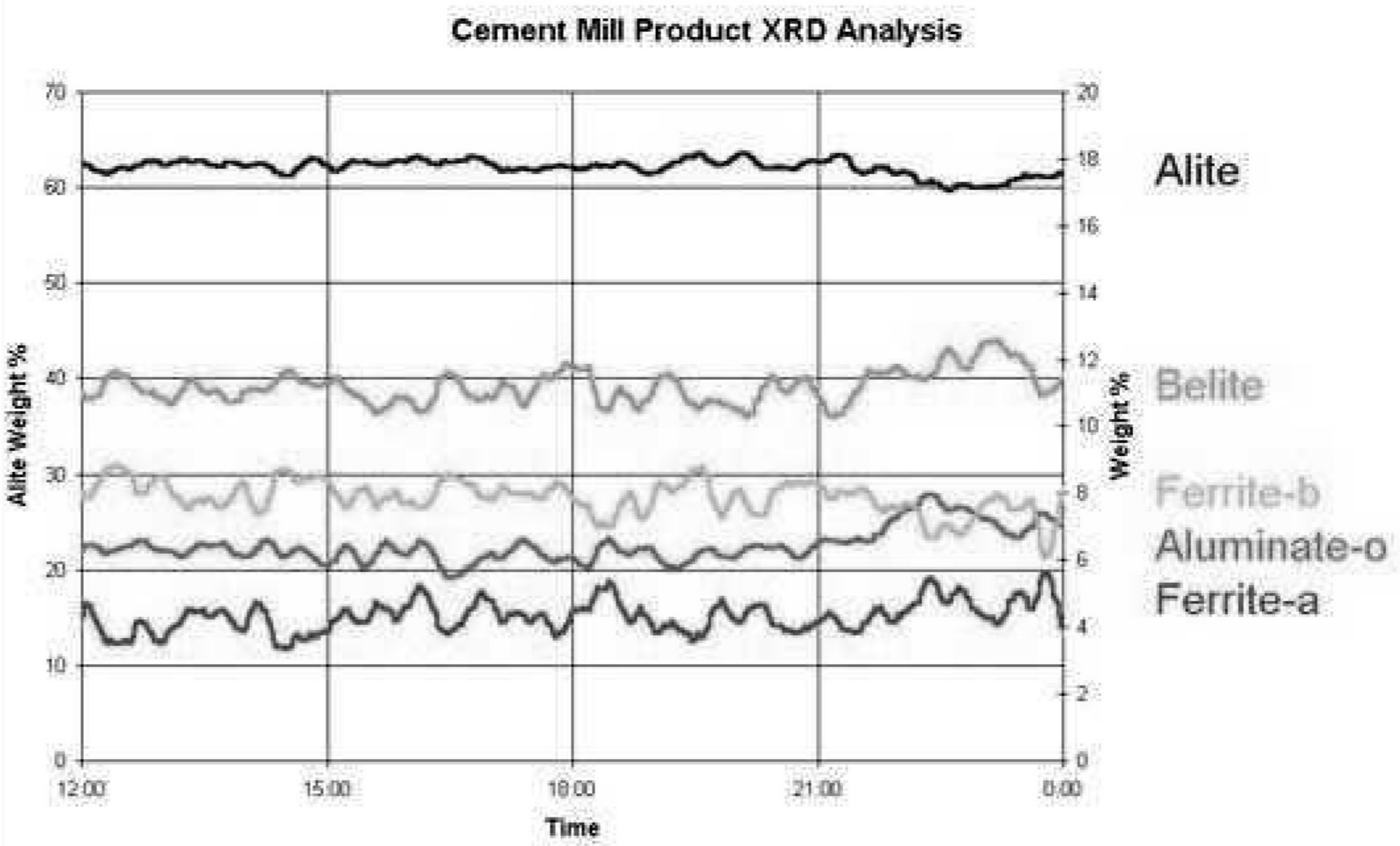
And if mineral composition varies?

↓

Phase identification

↓

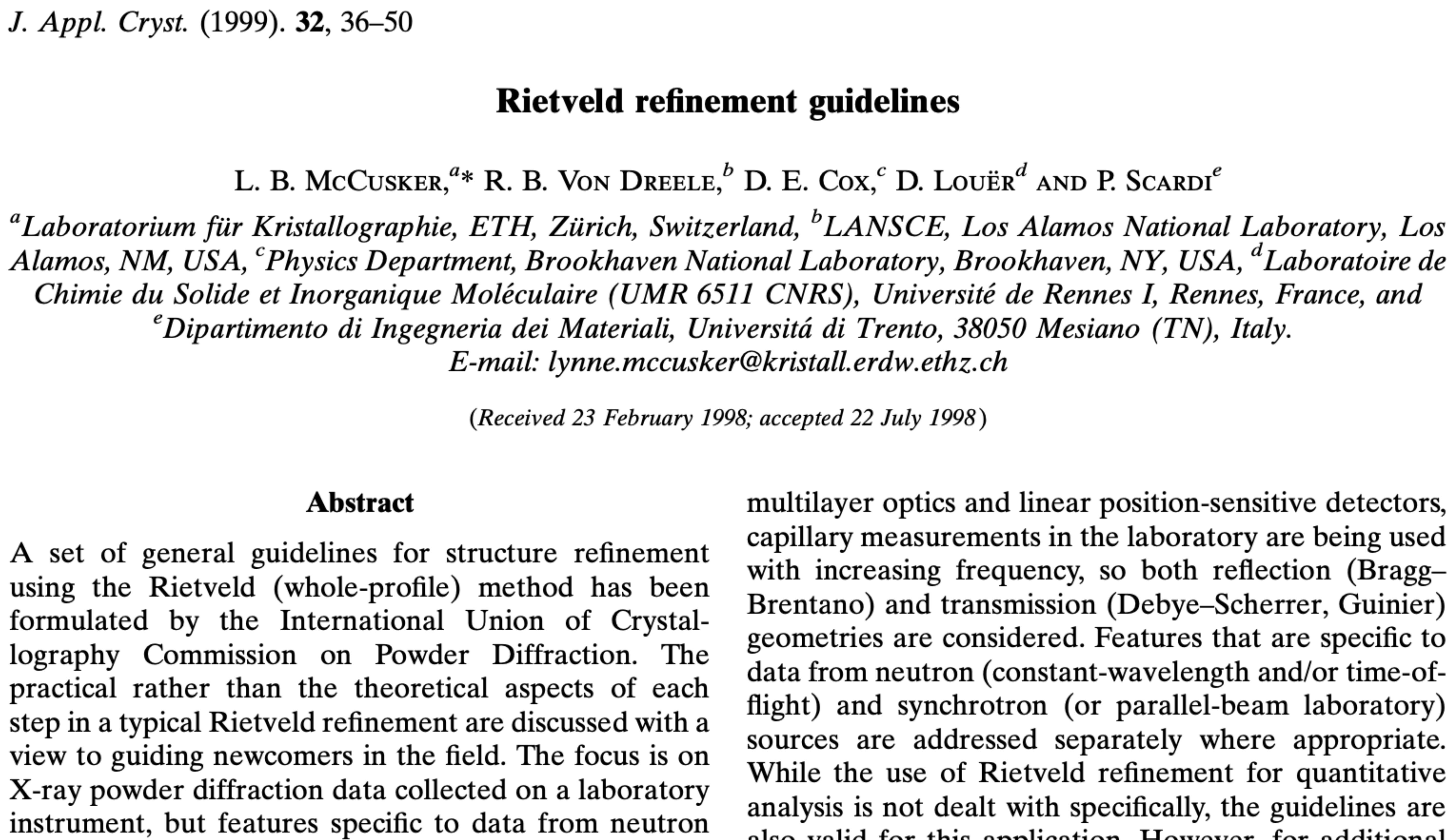
Intervention **required** of a **Rietveld expert**



Online powder X-ray diffraction patterns of a continuous cement production

Dhanjal & Young & Storer, *Cement Industry Technical Conference* (**2006**), IEEE, 8978522
De la Torre & Aranda, *Journal of Applied Crystallography* (**2003**), Volume *36*, Pages 1169-1176

Rietveld Refinement Guidelines



J. Appl. Cryst. (1999). **32**, 36–50

Rietveld refinement guidelines

L. B. McCusker,[a]* R. B. Von Dreele,[b] D. E. Cox,[c] D. Louër[d] and P. Scardi[e]

[a]Laboratorium für Kristallographie, ETH, Zürich, Switzerland, [b]LANSCE, Los Alamos National Laboratory, Los Alamos, NM, USA, [c]Physics Department, Brookhaven National Laboratory, Brookhaven, NY, USA, [d]Laboratoire de Chimie du Solide et Inorganique Moléculaire (UMR 6511 CNRS), Université de Rennes I, Rennes, France, and [e]Dipartimento di Ingegneria dei Materiali, Universitá di Trento, 38050 Mesiano (TN), Italy.
E-mail: lynne.mccusker@kristall.erdw.ethz.ch

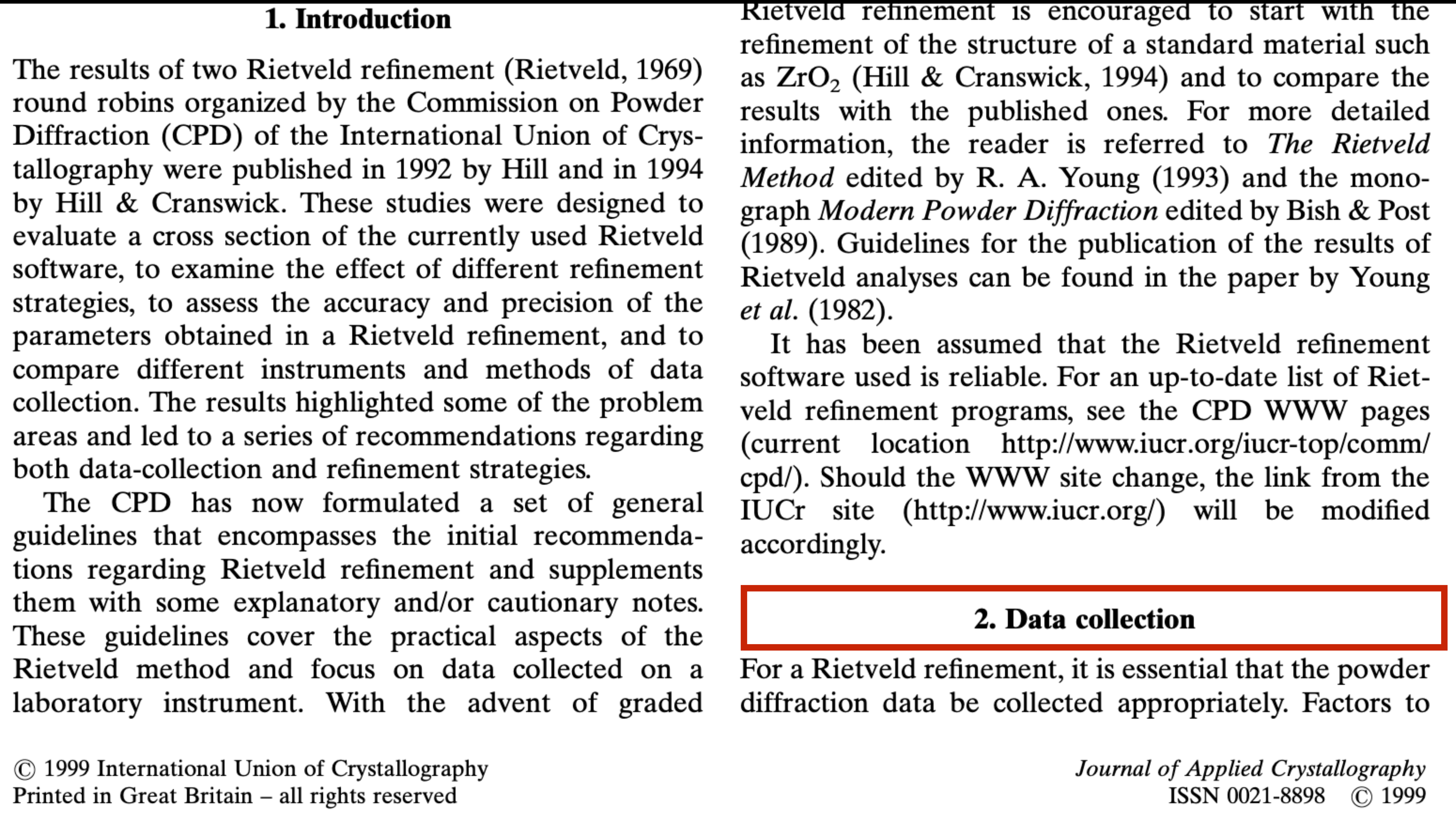
(*Received 23 February 1998; accepted 22 July 1998*)

Abstract

A set of general guidelines for structure refinement using the Rietveld (whole-profile) method has been formulated by the International Union of Crystallography Commission on Powder Diffraction. The practical rather than the theoretical aspects of each step in a typical Rietveld refinement are discussed with a view to guiding newcomers in the field. The focus is on X-ray powder diffraction data collected on a laboratory instrument, but features specific to data from neutron

multilayer optics and linear position-sensitive detectors, capillary measurements in the laboratory are being used with increasing frequency, so both reflection (Bragg–Brentano) and transmission (Debye–Scherrer, Guinier) geometries are considered. Features that are specific to data from neutron (constant-wavelength and/or time-of-flight) and synchrotron (or parallel-beam laboratory) sources are addressed separately where appropriate. While the use of Rietveld refinement for quantitative analysis is not dealt with specifically, the guidelines are also valid for this application. However, for additional

Rietveld Refinement Guidelines



1. Introduction

The results of two Rietveld refinement (Rietveld, 1969) round robins organized by the Commission on Powder Diffraction (CPD) of the International Union of Crystallography were published in 1992 by Hill and in 1994 by Hill & Cranswick. These studies were designed to evaluate a cross section of the currently used Rietveld software, to examine the effect of different refinement strategies, to assess the accuracy and precision of the parameters obtained in a Rietveld refinement, and to compare different instruments and methods of data collection. The results highlighted some of the problem areas and led to a series of recommendations regarding both data-collection and refinement strategies.

The CPD has now formulated a set of general guidelines that encompasses the initial recommendations regarding Rietveld refinement and supplements them with some explanatory and/or cautionary notes. These guidelines cover the practical aspects of the Rietveld method and focus on data collected on a laboratory instrument. With the advent of graded

Rietveld refinement is encouraged to start with the refinement of the structure of a standard material such as ZrO_2 (Hill & Cranswick, 1994) and to compare the results with the published ones. For more detailed information, the reader is referred to *The Rietveld Method* edited by R. A. Young (1993) and the monograph *Modern Powder Diffraction* edited by Bish & Post (1989). Guidelines for the publication of the results of Rietveld analyses can be found in the paper by Young *et al.* (1982).

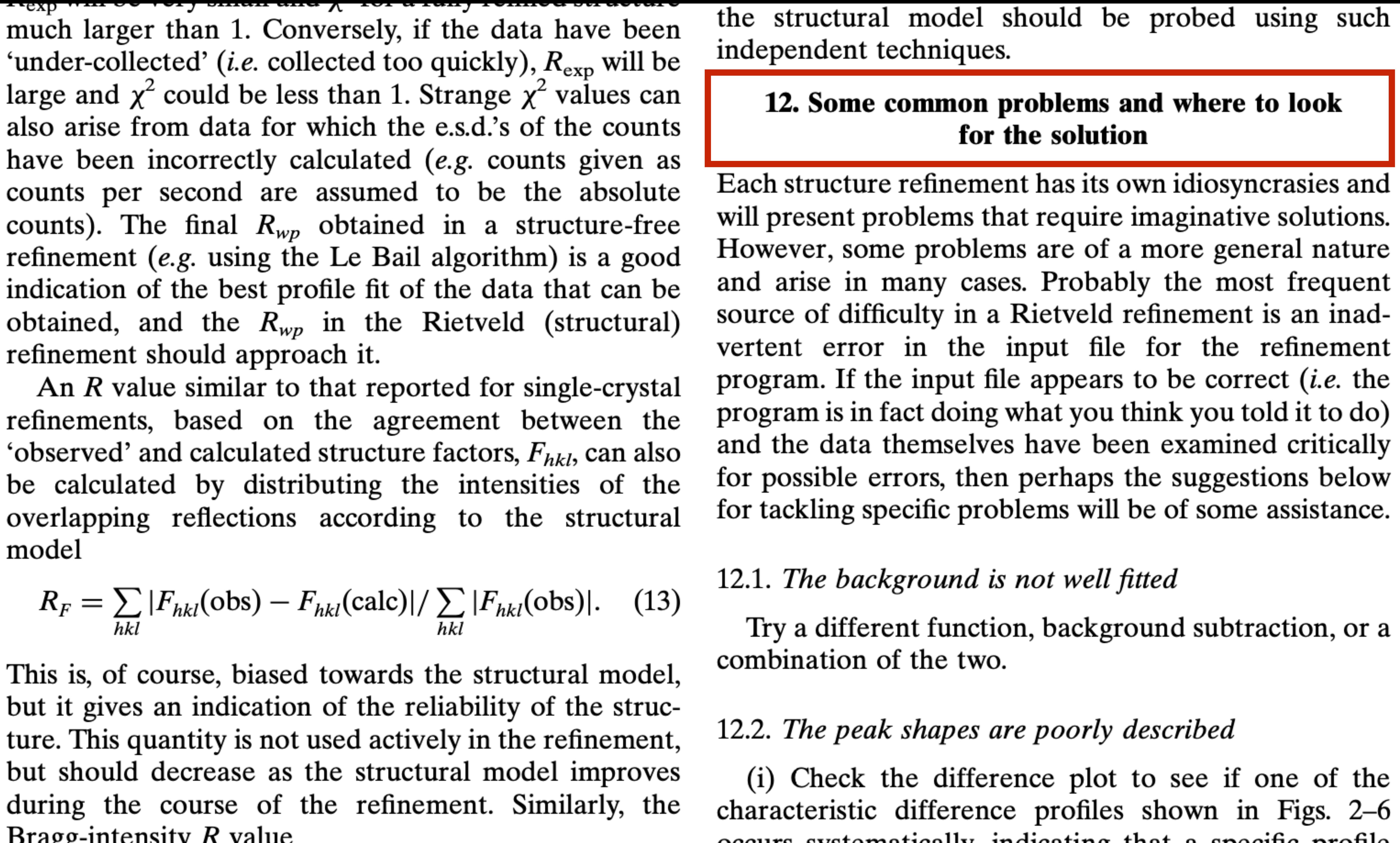
It has been assumed that the Rietveld refinement software used is reliable. For an up-to-date list of Rietveld refinement programs, see the CPD WWW pages (current location http://www.iucr.org/iucr-top/comm/cpd/). Should the WWW site change, the link from the IUCr site (http://www.iucr.org/) will be modified accordingly.

2. Data collection

For a Rietveld refinement, it is essential that the powder diffraction data be collected appropriately. Factors to

Journal of Applied Crystallography
ISSN 0021-8898 © 1999

Rietveld Refinement Guidelines



much larger than 1. Conversely, if the data have been 'under-collected' (*i.e.* collected too quickly), R_{exp} will be large and χ^2 could be less than 1. Strange χ^2 values can also arise from data for which the e.s.d.'s of the counts have been incorrectly calculated (*e.g.* counts given as counts per second are assumed to be the absolute counts). The final R_{wp} obtained in a structure-free refinement (*e.g.* using the Le Bail algorithm) is a good indication of the best profile fit of the data that can be obtained, and the R_{wp} in the Rietveld (structural) refinement should approach it.

An R value similar to that reported for single-crystal refinements, based on the agreement between the 'observed' and calculated structure factors, F_{hkl}, can also be calculated by distributing the intensities of the overlapping reflections according to the structural model

$$R_F = \sum_{hkl} |F_{hkl}(\text{obs}) - F_{hkl}(\text{calc})| / \sum_{hkl} |F_{hkl}(\text{obs})|. \quad (13)$$

This is, of course, biased towards the structural model, but it gives an indication of the reliability of the structure. This quantity is not used actively in the refinement, but should decrease as the structural model improves during the course of the refinement. Similarly, the Bragg-intensity R value

the structural model should be probed using such independent techniques.

12. Some common problems and where to look for the solution

Each structure refinement has its own idiosyncrasies and will present problems that require imaginative solutions. However, some problems are of a more general nature and arise in many cases. Probably the most frequent source of difficulty in a Rietveld refinement is an inadvertent error in the input file for the refinement program. If the input file appears to be correct (*i.e.* the program is in fact doing what you think you told it to do) and the data themselves have been examined critically for possible errors, then perhaps the suggestions below for tackling specific problems will be of some assistance.

12.1. *The background is not well fitted*

Try a different function, background subtraction, or a combination of the two.

12.2. *The peak shapes are poorly described*

(i) Check the difference plot to see if one of the characteristic difference profiles shown in Figs. 2–6

The Rietveld Method

GOAL The Rietveld method consists in refining a crystal structure model my minimising the weighted squared difference between the observed and the calculated pattern against the parameter vector β

$$\boxed{\chi^2 = \sum_{i=1}^{n} w_i \{y_i - y_{ci}(\beta)\}^2}$$

with

$$\boxed{w_i = \frac{1}{\sigma_i^2}}$$

σ_i^2 *is the variance of the observed y_i*

The optimization method is based on Least Squares

- The least squares procedure provides (when it converges) the value of the parameters constituting the local minimum closest to the starting point
- Good starting values for all parameters is strongly required: the importance of a good starting model!
- If the starting model is poor for some reason the procedure will not converge

The Rietveld Method

$$\frac{\partial \chi^2}{\partial \boldsymbol{\beta}} = 0$$ Condition for the Least Squares Algorithm

ITERATIVE PROCESS

A Taylor expansion of $y_{ci}(\beta)$ around β_0 is used
The shifts applied to the parameters at each cycle are obtained by solving a linear system of equations (normal equations)

$$\boldsymbol{\beta}_1 = \boldsymbol{\beta}_0 + \boldsymbol{\delta}_{\boldsymbol{\beta}_0}$$

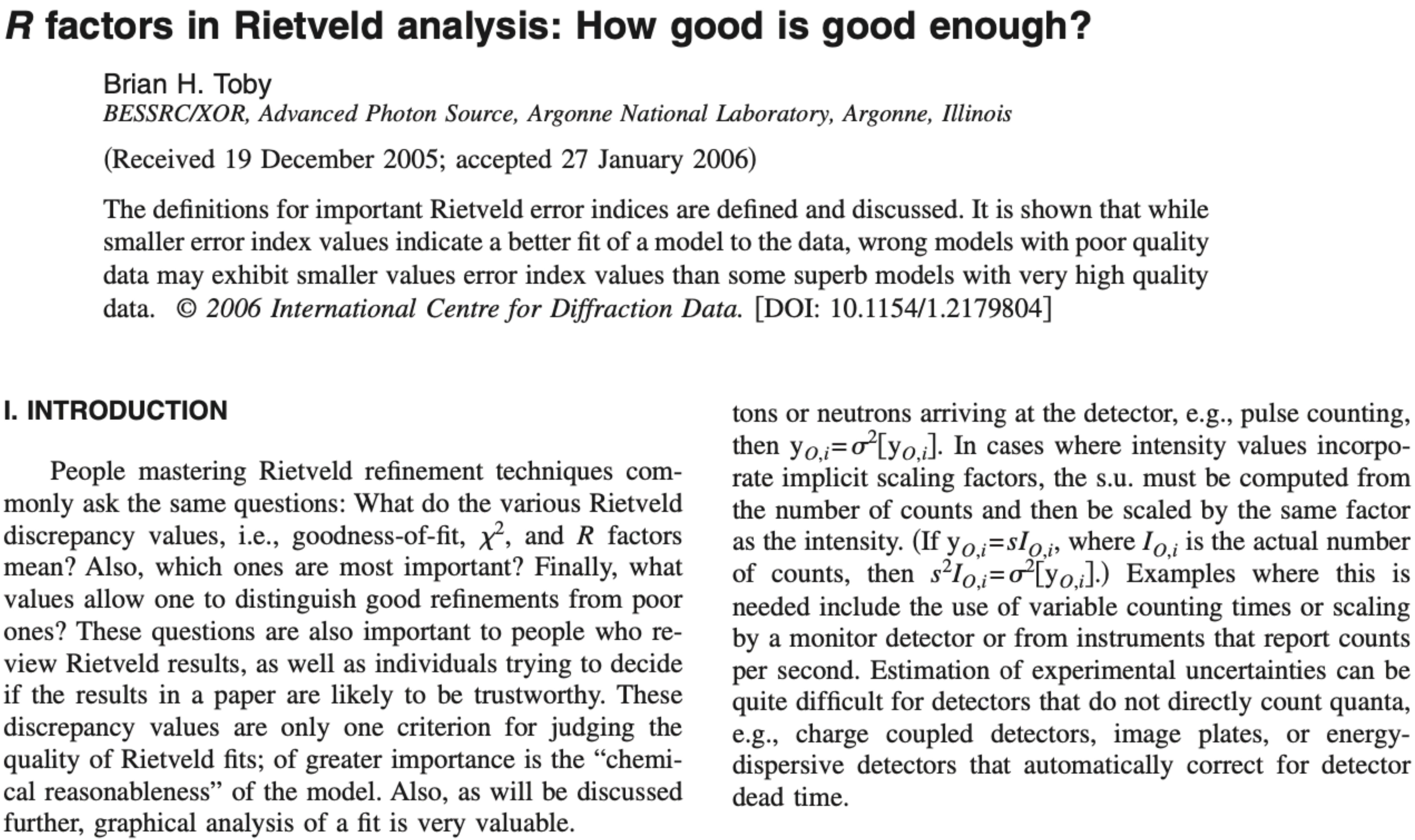
The new parameters are the starting ones in the next cycle and the process is repeated until a convergence criterion is satisfied.

The Rietveld Algorithm

Scheme by:
Juan Carvajal
(ILL, Grenoble)

```
Do for N_cycles
  Do for Patterns                         ⇐ may be done in parallel
    Do for points in Patterns
      Do for contributing reflections
        Calculate broadening w.r.t to IRF
        Calculate structure factors+derivatives
        Sum contributions (LSQ matrix + vector)
         calculate profile for current point and reflections
         contributing to it (convolution ⇒ neighbours needed)
         profile derivatives
      End do reflections
    End do points in Patterns
  End do Patterns
   Invert LSQ matrix and update the free parameters
  Tests for convergence (if convergence is reached exit!)
End do N_cycles
```

R Factors



R factors in Rietveld analysis: How good is good enough?

Brian H. Toby
BESSRC/XOR, Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois

(Received 19 December 2005; accepted 27 January 2006)

The definitions for important Rietveld error indices are defined and discussed. It is shown that while smaller error index values indicate a better fit of a model to the data, wrong models with poor quality data may exhibit smaller values error index values than some superb models with very high quality data. [DOI: 10.1154/1.2179804]

I. INTRODUCTION

People mastering Rietveld refinement techniques commonly ask the same questions: What do the various Rietveld discrepancy values, i.e., goodness-of-fit, χ^2, and *R* factors mean? Also, which ones are most important? Finally, what values allow one to distinguish good refinements from poor ones? These questions are also important to people who review Rietveld results, as well as individuals trying to decide if the results in a paper are likely to be trustworthy. These discrepancy values are only one criterion for judging the quality of Rietveld fits; of greater importance is the "chemical reasonableness" of the model. Also, as will be discussed further, graphical analysis of a fit is very valuable.

tons or neutrons arriving at the detector, e.g., pulse counting, then $y_{O,i}=\sigma^2[y_{O,i}]$. In cases where intensity values incorporate implicit scaling factors, the s.u. must be computed from the number of counts and then be scaled by the same factor as the intensity. (If $y_{O,i}=sI_{O,i}$, where $I_{O,i}$ is the actual number of counts, then $s^2I_{O,i}=\sigma^2[y_{O,i}]$.) Examples where this is needed include the use of variable counting times or scaling by a monitor detector or from instruments that report counts per second. Estimation of experimental uncertainties can be quite difficult for detectors that do not directly count quanta, e.g., charge coupled detectors, image plates, or energy-dispersive detectors that automatically correct for detector dead time.

R Factors

$$R_p = 100 \frac{\sum_i \left| y_{obs,i} - y_{calc,i} \right|}{\sum_i \left| y_{obs,i} \right|}$$

R-pattern

$$R_{wp} = 100 \left[\frac{\sum_i w_i \left| y_{obs,i} - y_{calc,i} \right|^2}{\sum_i w_i \left| y_{obs,i} \right|^2} \right]^{1/2}$$

R-weighted pattern

$$R_{exp} = 100 \left[\frac{(N - P + C)}{\sum_i w_i y_{obs,i}^2} \right]^{1/2}$$

Expected R-weighted pattern

R Factors

$$\chi_\nu^2 = \left[\frac{R_{wp}}{R_{exp}}\right]^2$$

Reduced chi-squared

$$S = \frac{R_{wp}}{R_{exp}}$$

Goodness-of-fit

- The sums over “i” may be extended to solely the regions containing Bragg reflections
- R_p and R_{wp} may contain or not the background

Strategy for Setting up a (Good) Rietveld Refinement

Use the best possible starting model for the chemical problem

This can be done by **properly selecting the background**, have a **good indexing of the powder pattern** and find the **most suitable space group**

- Collect all the information you can gather on your sample: physical and chemical
- Sets of different unit cell parameters and/or space groups need to be tested to guarantee a good level of confidence
- Have the best possible powder pattern to be studied: it is important to understand the limitations and advantages of the instrument that was used
- Do not start by refining all parameters at once! Some are more important affecting strongly the residuals while others only lead to small improvements.

Strategy for Setting up a (Good) Rietveld Refinement

Possible Sequence for Rietveld Refinement

1 - Scale factor
2 - Zero point
3 - Background parameters and lattice constants
4 - Atomic positions
5 - Peak shape and asymmetry parameters
6 - Atom occupancies if required by the atomic model
(7 - Displacement parameters)
8 - Microstructural parameters: size and strain effects

Constant Monitoring of the Refinement is required

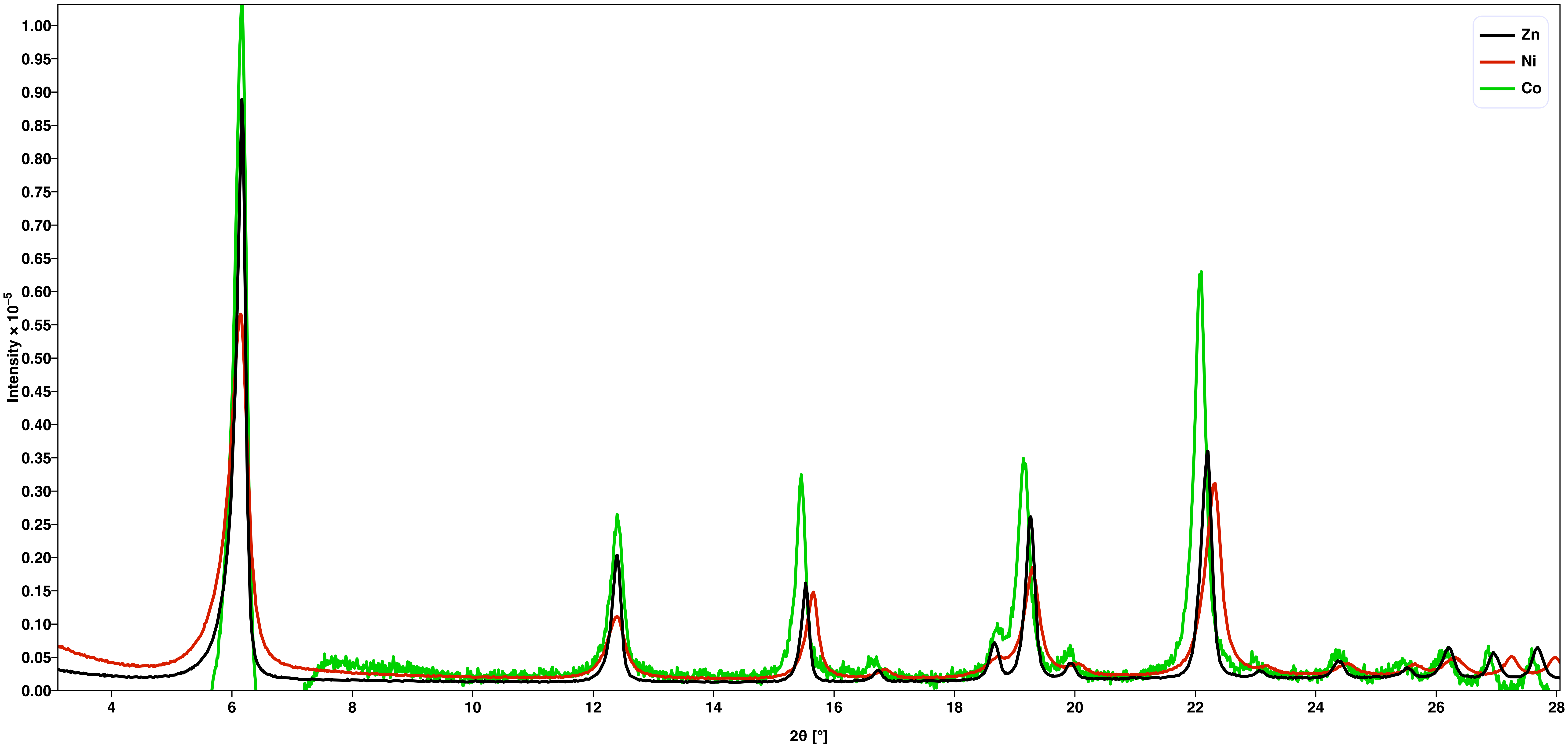
Visual examination of the difference pattern is a quick and efficient method to detect problems in the model or in the refinement process.
Its behaviour may give useful hints on the sequence to refine the whole set of model parameters for each particular case

Strategy for Setting up a (Good) Rietveld Refinement

- Refinement of complex structures typically requires very good resolution and the absence of systematic errors
- Rietveld refinement may be more difficult than solving the structure itself because of the intrinsic loss of information in powder diffraction compared to single crystals
- **Good idea:** try to employ constraints/restraints, even if the Rietveld refinement is worse
    - **Constraints:** reduce the number of free parameters (*e.g.*, rigid body refinements)
    - **Restraints:** same number of free parameters plus additional observations (allowing some interatomic distances and/or angles to vary between some min and max limits)

Another (recent) story…

Simple work: you just do a Rietveld refinement for a paper…



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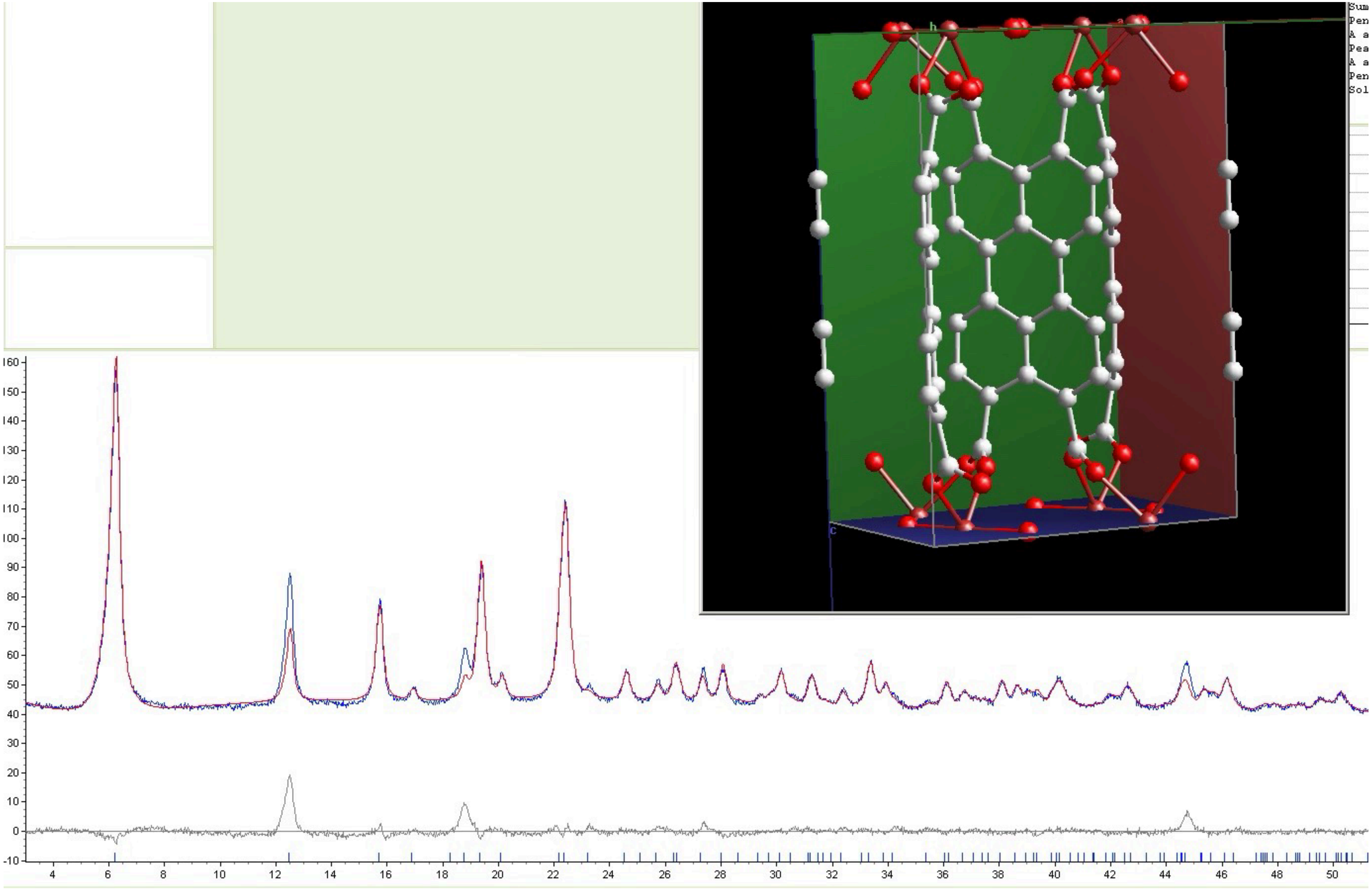

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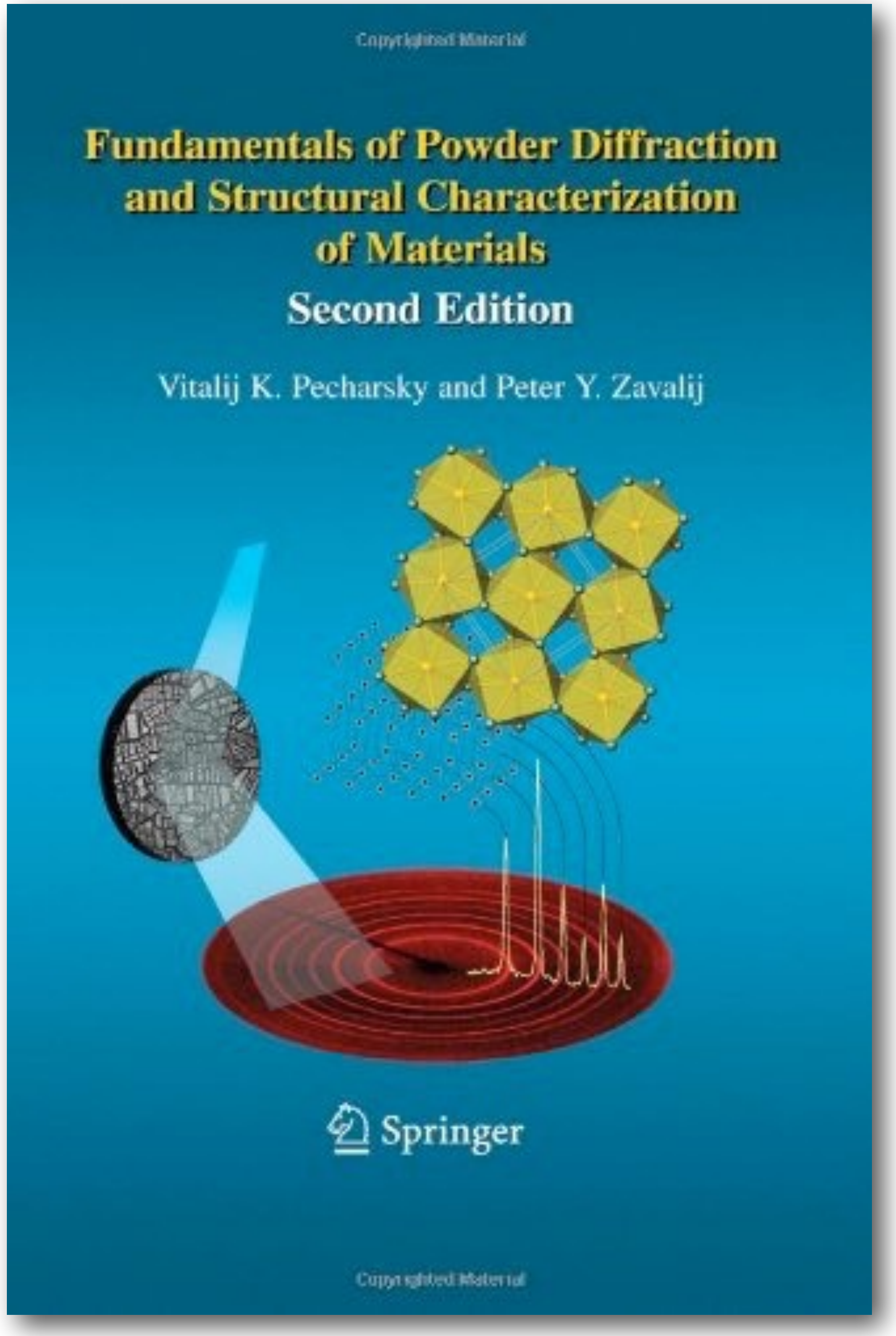
Literature



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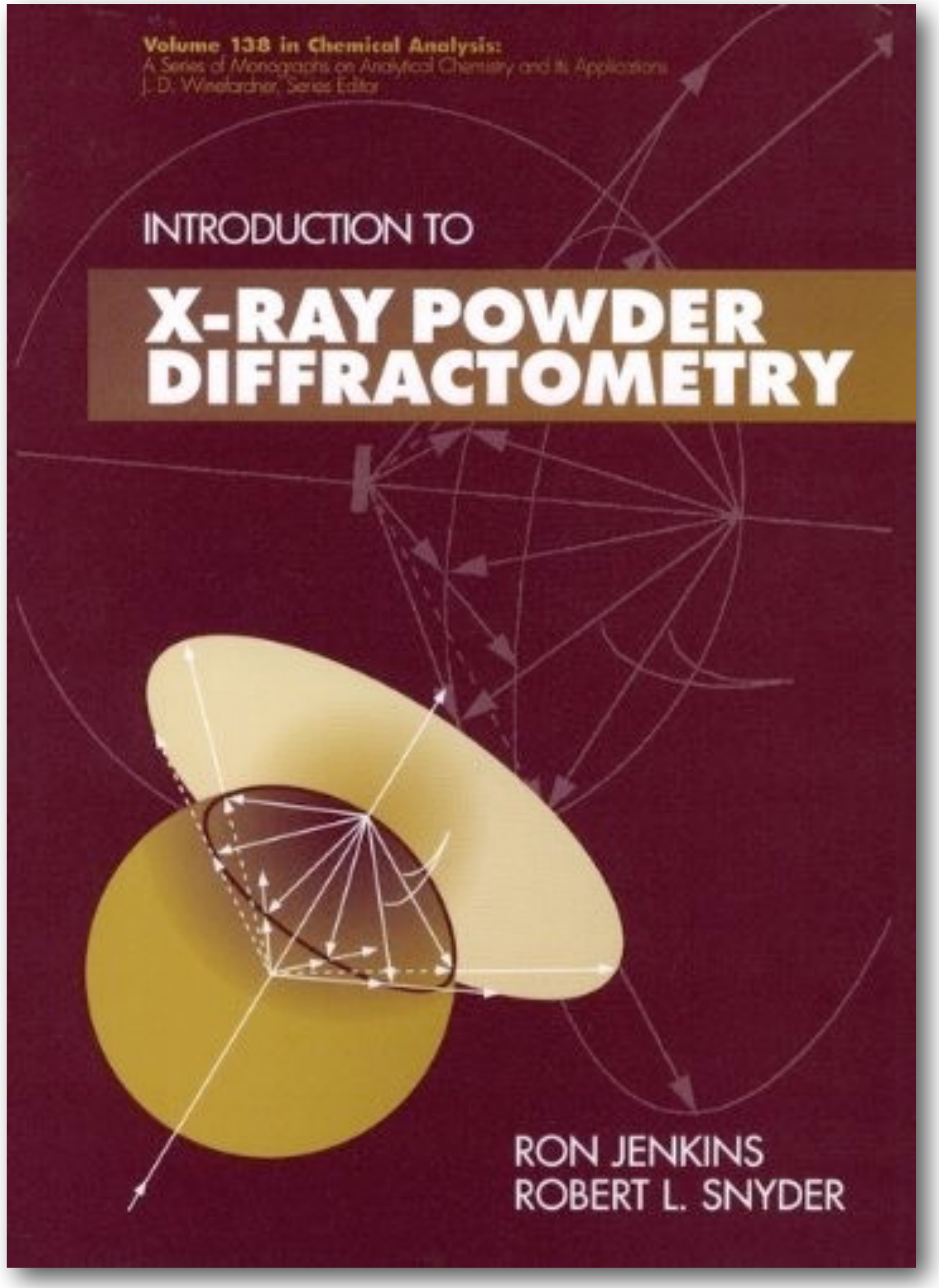

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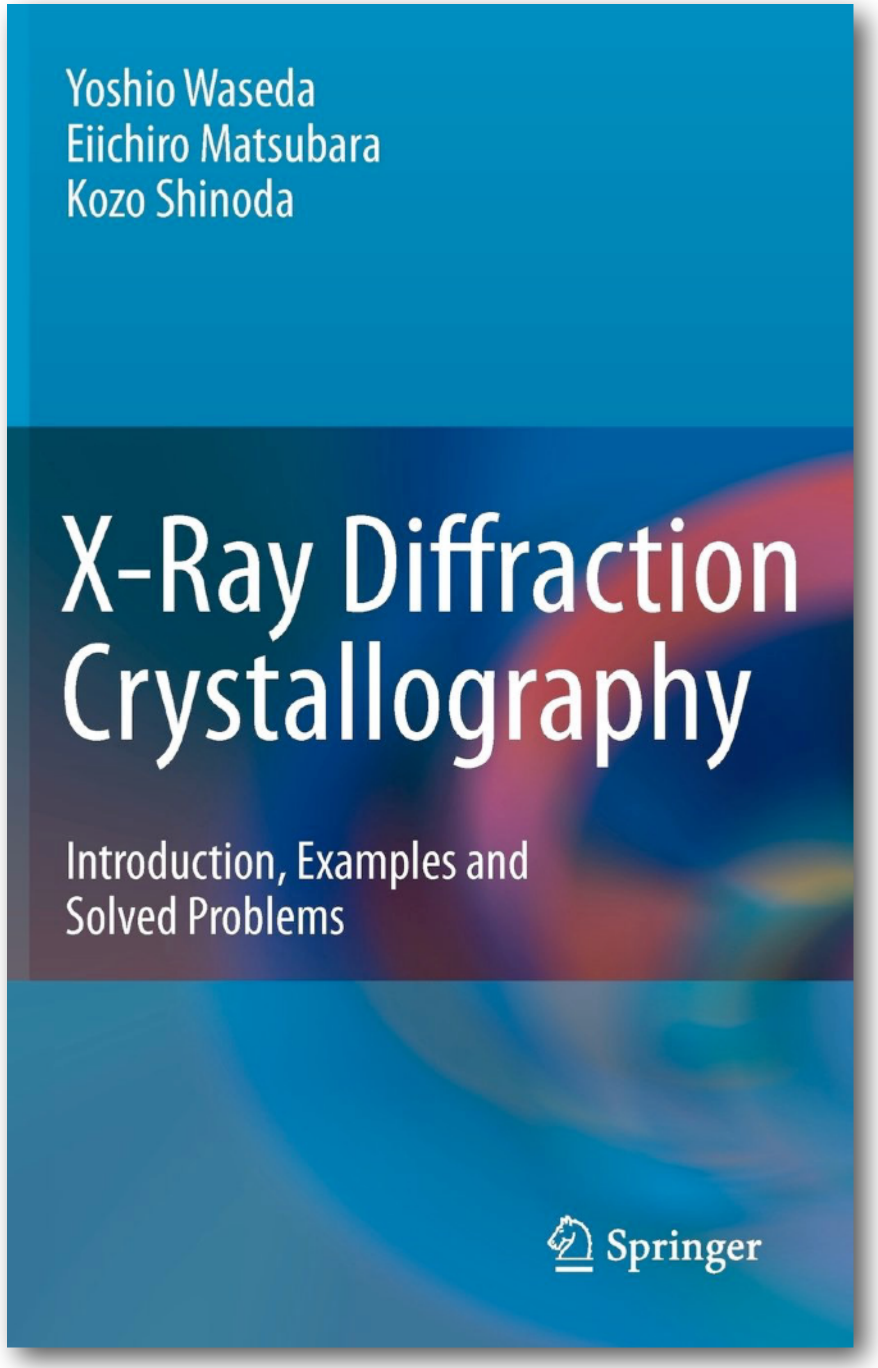

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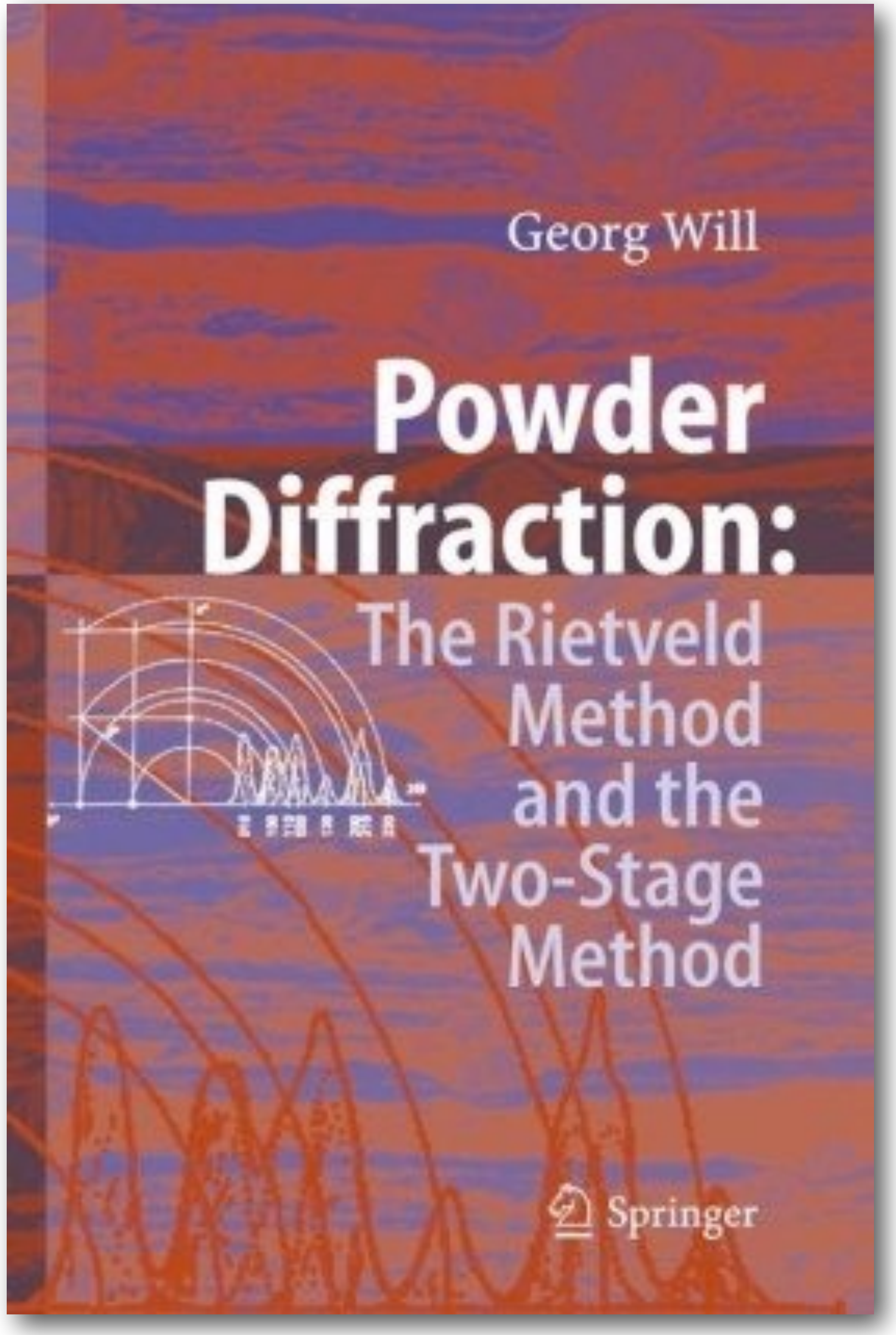

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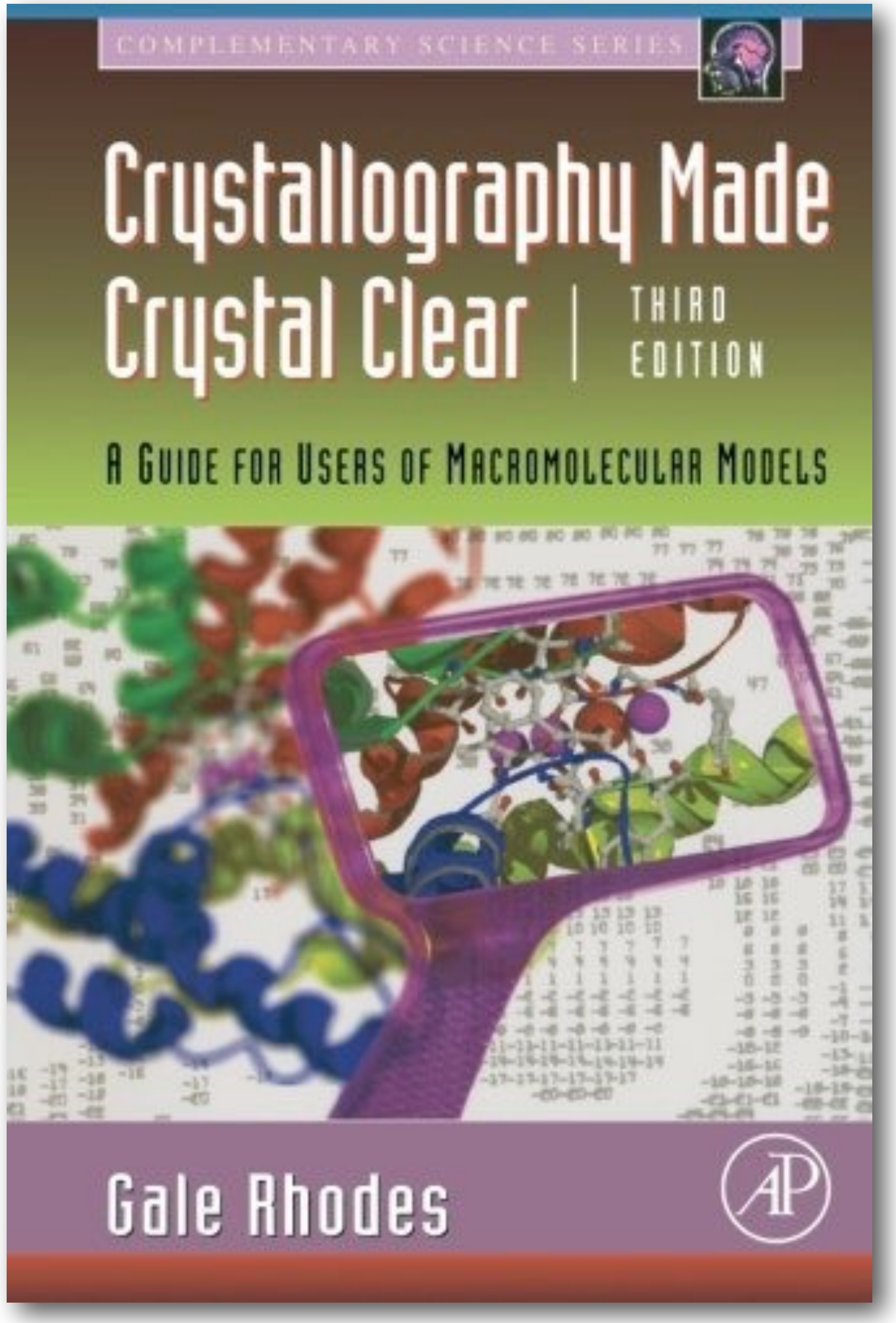

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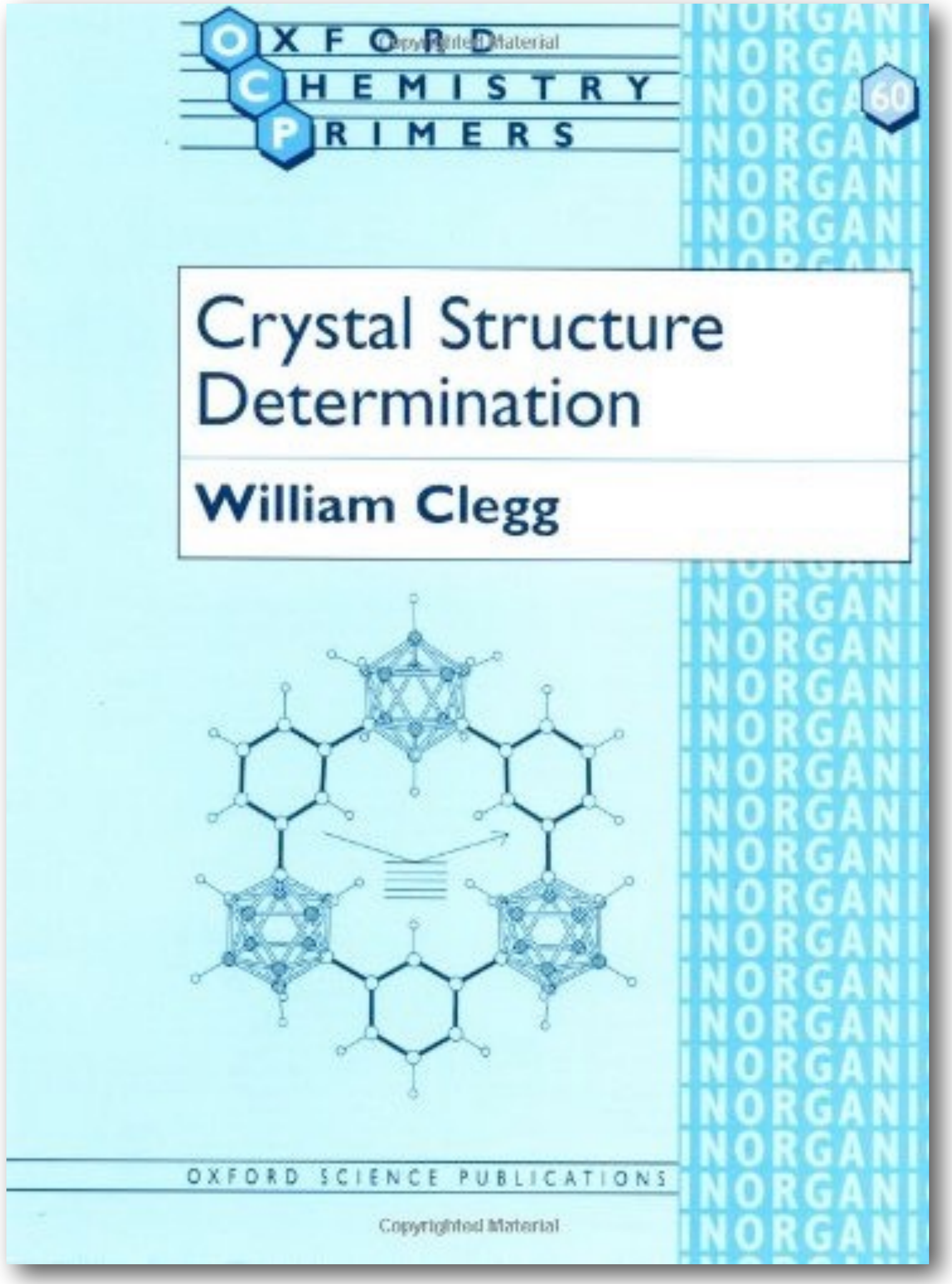

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