UNIVERSITÀ DEL PIEMONTE ORIENTALE

Monitoring in situ experiments with RootProf

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» Introduction
» Simulated data
» The PCA approach
» Case study n. 1
» Case study n. 2
» Case study n. 3

OUTLINE

Introduction: PCA, MED, OCCR and kinetics and dynamics analysis in simulated in situ XRPD data

Sub-structure solution by PCA- and OCCR-assisted dynamic analysis of Xe into Y zeolite in situ XRPD data

Kinetics retrieval by PCA-assisted analysis

The real world: three case studies where PCA is applied to real world data

MOTIVATION

FACE the amount of incoming data storming!

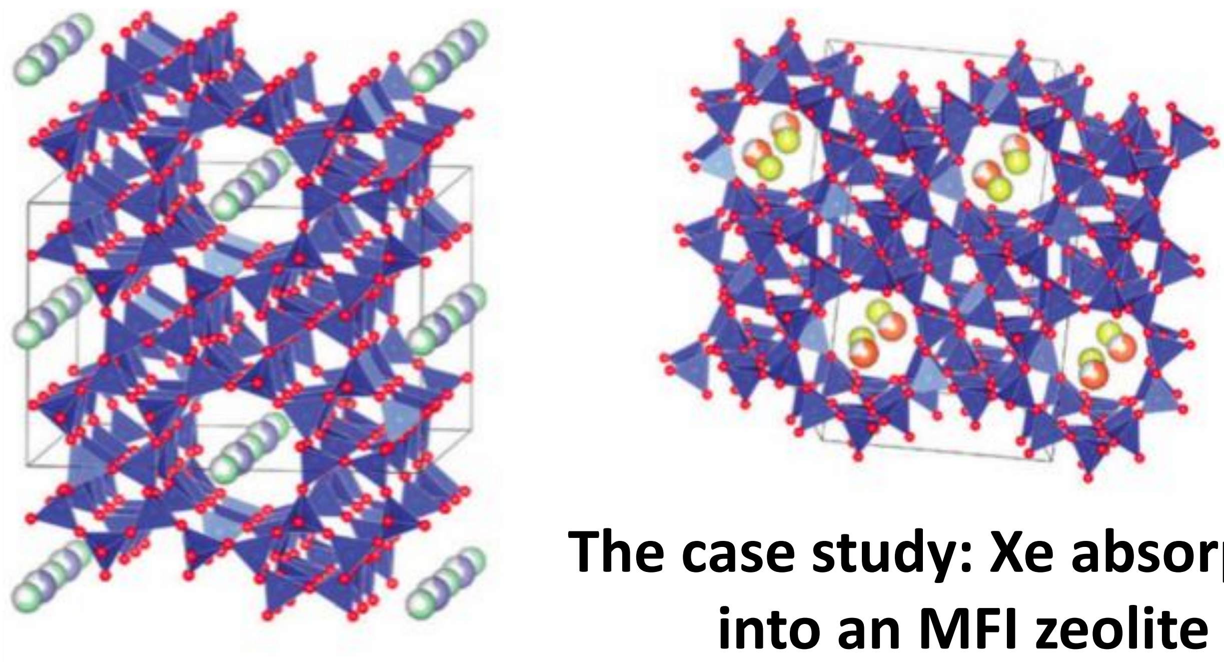
Back 1999 SNBL@ESRF
in situ experiment
20-100 XRPD patterns

Back 2009 SNBL@ESRF
in situ Raman/XRPD experiment
200-1000 Raman and 200-2000 XRPD patterns

2019 SNBL (Raman/XRPD) PSI (UV-Vis/Raman/XRPD BNL(XRPD/PDF) multiprobe experiments:
2000-10000 pattern each probe
But also lab XRPD can be used for in situ XRPD experiment with 1 min time resolution!

2029? 100000-1000000 patterns each experiment?

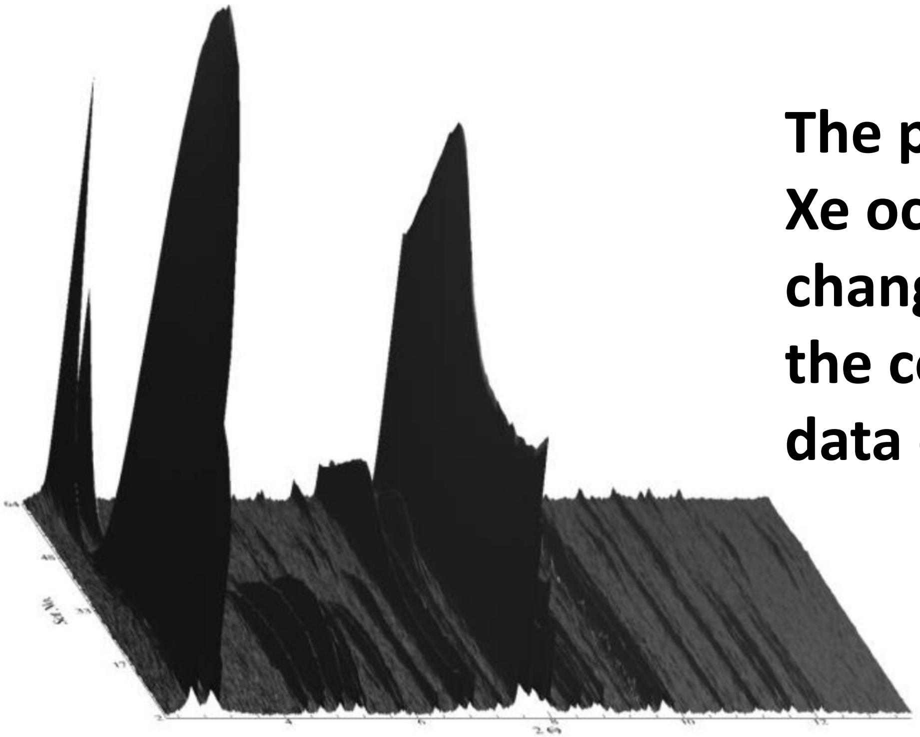
Are there alternative/complementary approaches to Rietveld refinement?



The case study: Xe absorption into an MFI zeolite

The target: speed, efficiency, selectivity, no need of crystal structure, robustness vs. Preferred Orientation, disorder, limited resolution, low data quality…

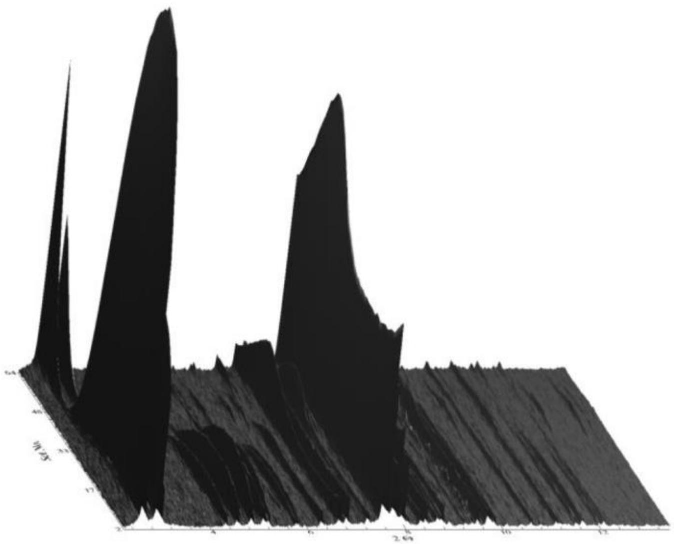
PCA, MED, OCCR and kinetics/dynamics in simulated in situ XRPD data



The playground: Xe occupancies are changed from 0 to 1 and the corresponding XRPD data calculated

The case study: Xe absorption into an MFI zeolite

Fourier analysis (PSD-MED) can retrieve both kinetics (1Ω) and substructure (2Ω)

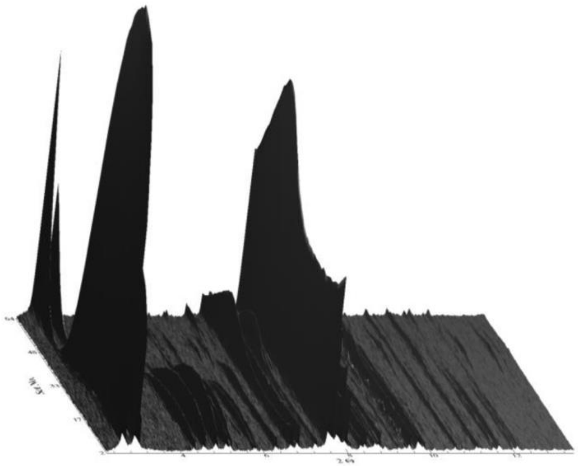


1Ω → The «direct response» to the stimulus → **Kinetic analysis**

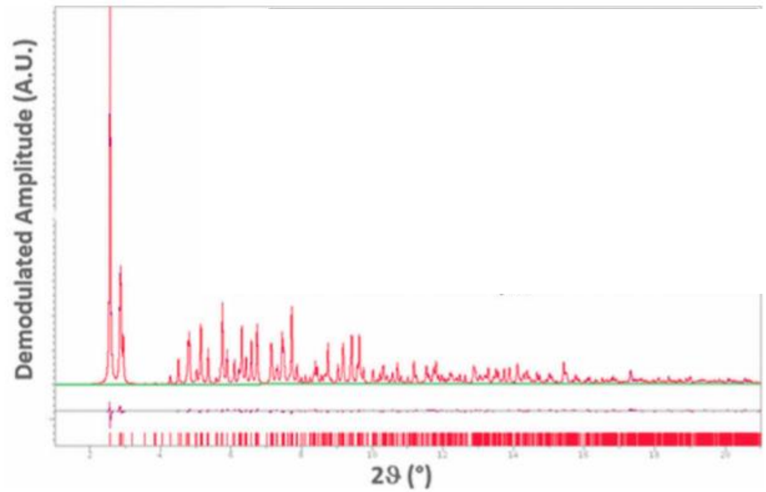
2Ω → The response of the active parte → **Structure solution of the changing part**

D. Chernyshov, et al. *Acta Cryst. Section A* A67, **2011**, 327-335;
R. Caliandro et al., **J. Appl. Cryst**., 45, 2012, *458-470.*

MED analysis of theoretical in situ XRPD data



Simulated in situ XRPD data.

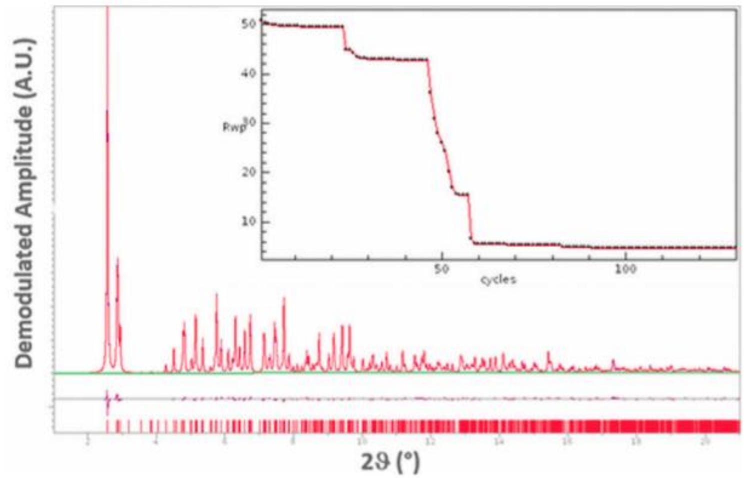


2Ω by MED

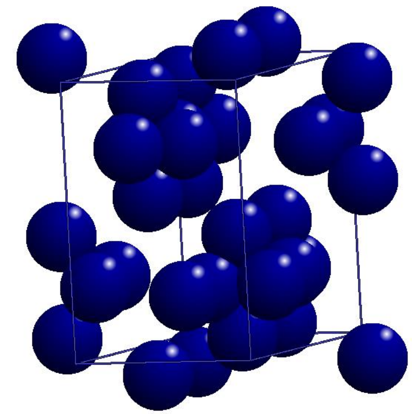
PSD-MED analysis of dynamic XRPD data gives a virtual XRPD that can be indexed by EXPO retrieving the original MFI unit cell and space group

L. Palin et al., *Phys.Chem.Chem.Phys.*, **2015**, 17, 17480.

MED analysis of theoretical in situ XRPD data



EXPO on 2Ω pattern



The model contains ONLY Xe atoms!

EXPO can solve the substructure of Xe into a MFI zeolite perfectly: <u>Chemical selectivity in X-ray diffraction!</u>

L. Palin et al., *Phys.Chem.Chem.Phys.*, **2015**, 17, 17480.

Going to real data, the good news are finished! - I

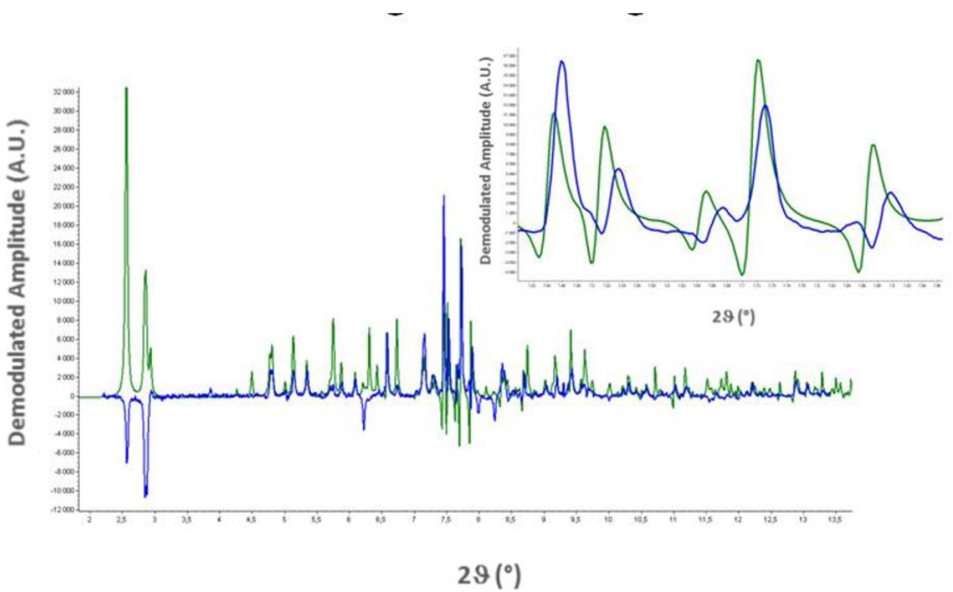


Figure SI-5: Simulated by a sinus stimulus (green) vs. experimental (blue) 2Ω demodulated pattern from the T1 experiment.

MED 2Ω (Blue) fails in real world data on Xe-MFI case study: real data 2Ω is different from simulated 2Ω.

L. Palin et al., *Phys.Chem.Chem.Phys.*, **2015**, 17, 17480.

We realized that some theoretical requirement of MED:

-) Clear distinction between active (Xe) and spectator part (MFI zeolite)

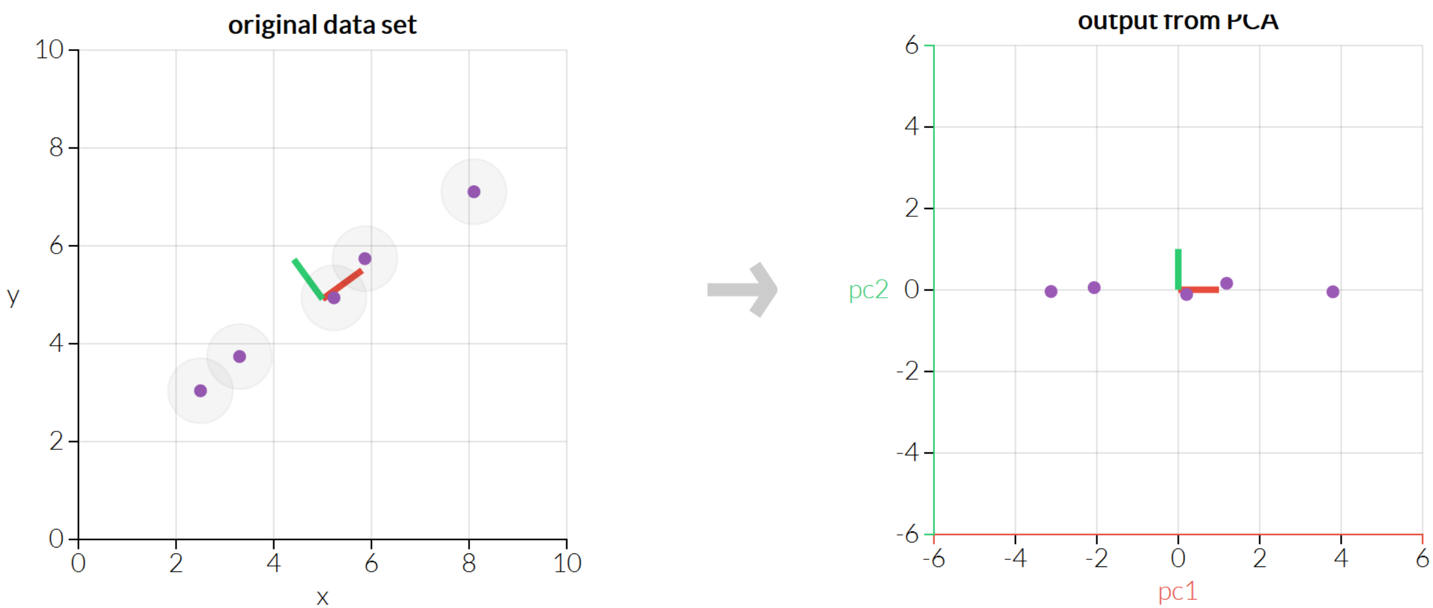
-) Linear response of the system to the stimulus

-) Absence or limited lattice variations

-) Stimulus shape should be sinusoidal

Not easy to implement in the real world on real samples. Many limitations.
Other routes than Fourier-based PSD-MED? analysis?

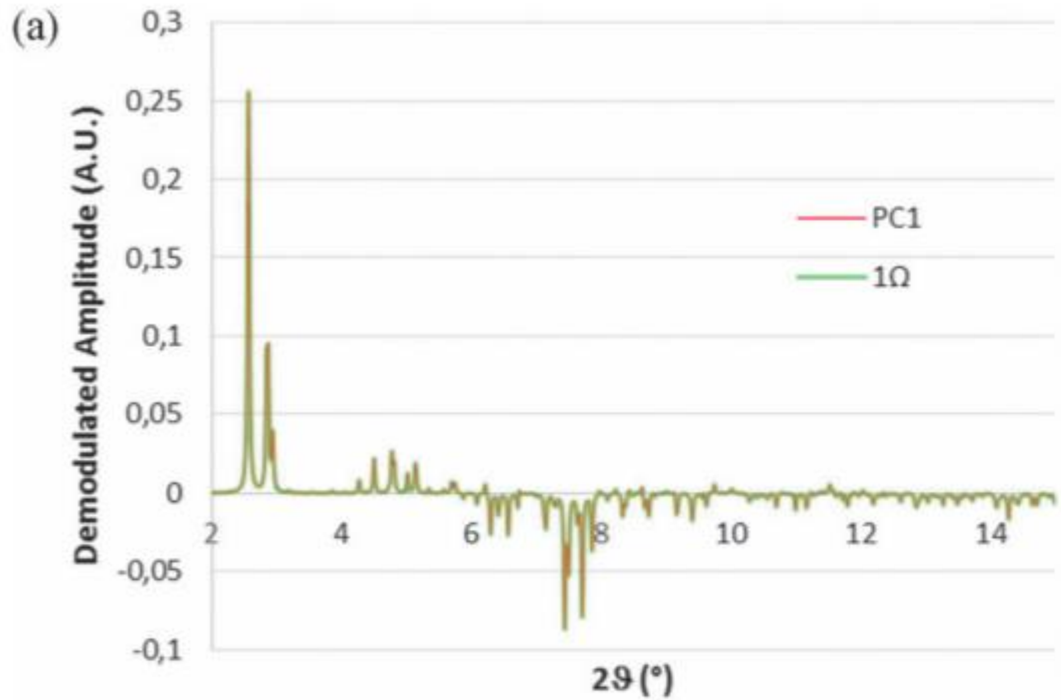
Principal Component Analysis (PCA) as alternative to PSD-MED approach



“Only” a coordinate change able to reduce dimensionality, BUT with huge power of unraveling trends in large dataset

http://setosa.io/ev/principal-component-analysis/

PCA vs. MED on in situ XRPD SIMULATED data

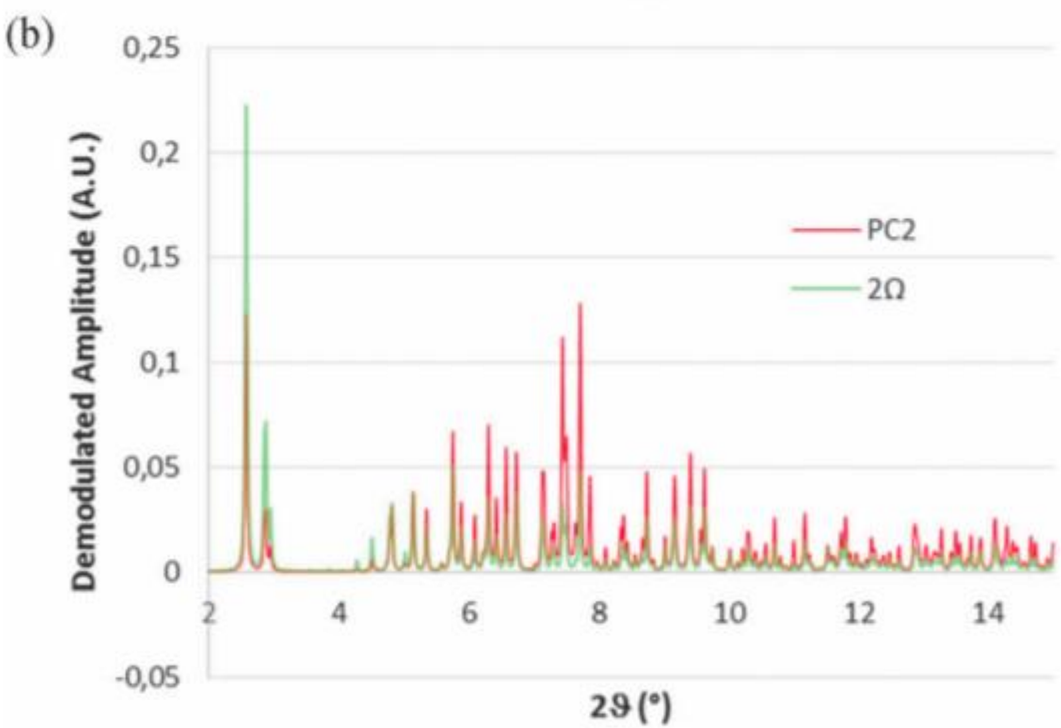


PC1 = 1Ω (PSD-MED) → PCA can be interesting for kinetic analysis

L. Palin et al., *Phys.Chem.Chem.Phys.*, **2015**, 17, 17480;

P. Guccione et al., *Phys.Chem.Chem.Phys.*, **2018**, 20, 19560 – 1957

The good news are finished! - II

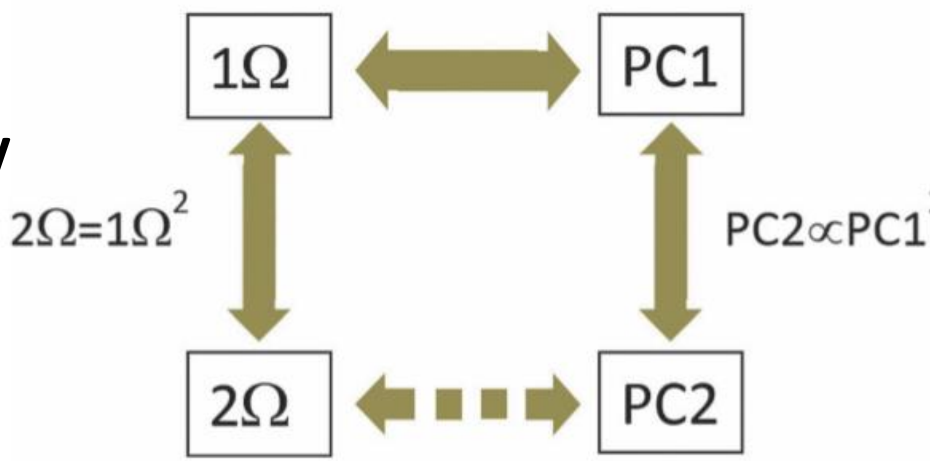


PC2 ǂ 2Ω in simulated data

L. Palin et al., *Phys.Chem.Chem.Phys.*, **2015**, 17, 17480.

Modulated Enanched Diffraction (MED) vs Principal Component Analysis (PCA) for (sub)structure solution

PSD-MED: Fourier Analysis by Phase Sensitive Detection



PCA: Variance analysis and data dimens. reduction

MED can in principle retrieve a kinetic and solve the «active» substructure in a dynamic experiment.
PCA can retrieve with a good approximation 1Ω and only rougly estimate 2Ω

L. Palin et al., *Phys.Chem.Chem.Phys.*, **2015**, 17, 17480.

Problems and solutions

Problems	Solutions
PSD-MED has limitations in real world	Adapt PSD_MED to real data Escape Lane n. 1
	Use PCA to analyze the data instead of PSD-MED, expecially for kinetics dynamics Escape Lane n. 2
PC2 ǂ 2Ω in simulated data	Use OCCR, i.e.a constrained PCA «instructed» to search for «2Ω like» information and use it for structure solution Escape Lane n. 3

Escape lane n. 1: Real world low amplitude modulation and PSD-MED

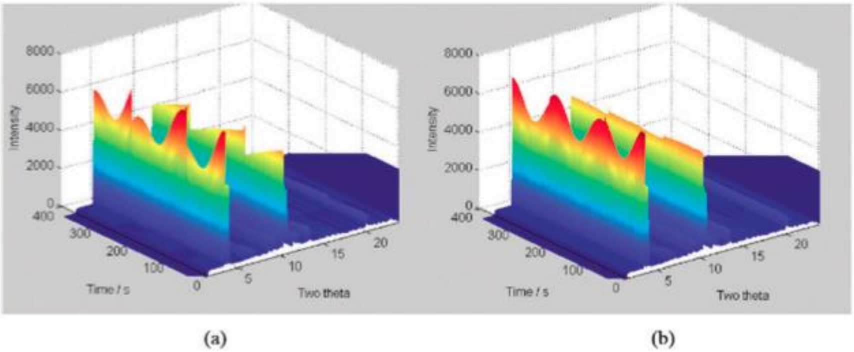
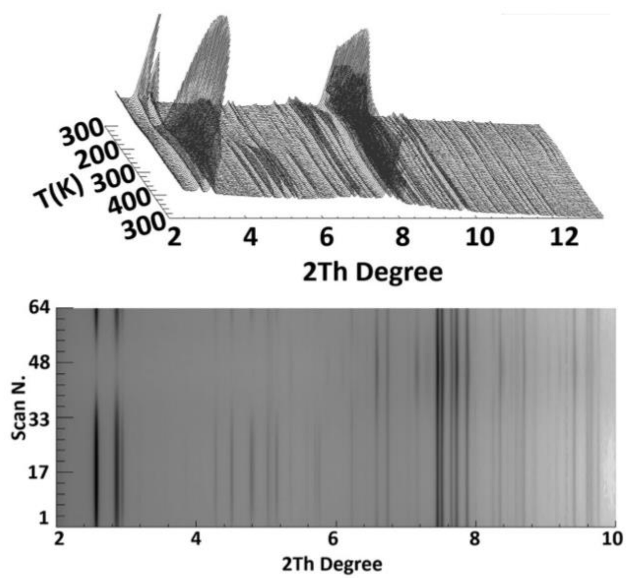


Fig. 7 Real MED data powder diffraction data on Xe occupancy variation inside a TS-1 zeolite, by a triangular small amplitude stimulus (experiment T3 in Table 1), before (a) and after (b) normalization toward beam decay.

MED 2Ω succeded in real world data on Xe-MFI case study as in simulated data BUT unique success → we moved to PCA!

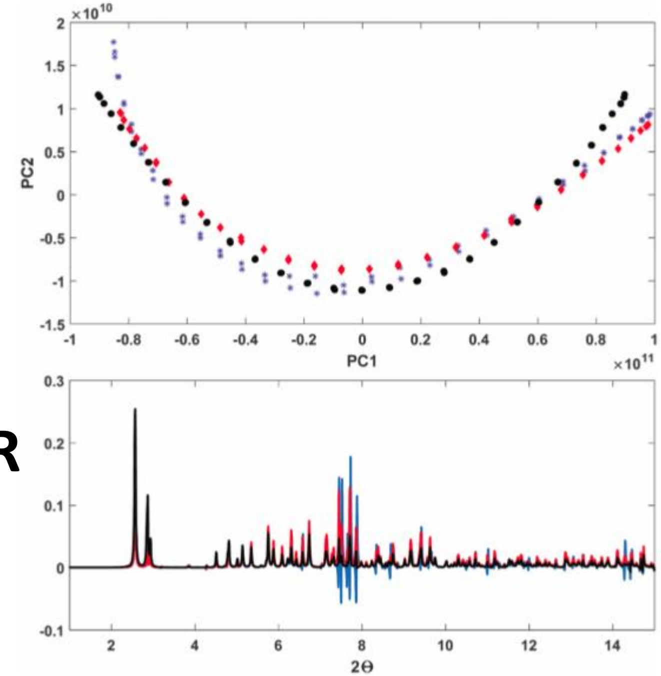
L. Palin et al., *Phys.Chem.Chem.Phys.*, **2015**, 17, 17480.

Escape lane n. 2: OCCR can reveal structural details with improved selectivity from in situ powder and single crystal



PCA

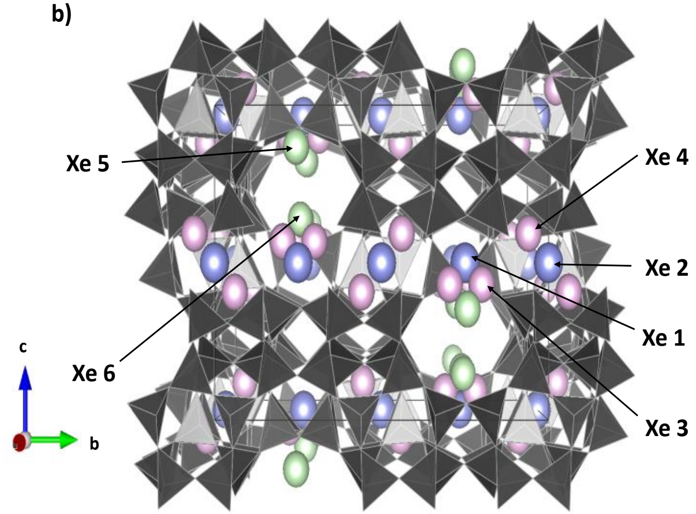
OCCR
P.A.



Scores from PCA or OCCR vs. 2Θ are a virtual XRPD pattern containing the information active atoms only

Guccione, L. et al., **PCCP**, 2018, 20**,** 2175-2187. **From themed collection [2018 PCCP HOT Articles];**

The OCCR virtual pattern was refined by Topas TA and gives experimental information on Xe only with improved chemical selectivity from in situ powder XRPD data



Two new Xe adsorption sites unraveled by PCA-OCCR assisted XRPD data analysis

POWDERS: Guccione, L. et al., **PCCP**, 2018, 20**,** 2175-2187. **From themed collection 2018 PCCP HOT Articles;**

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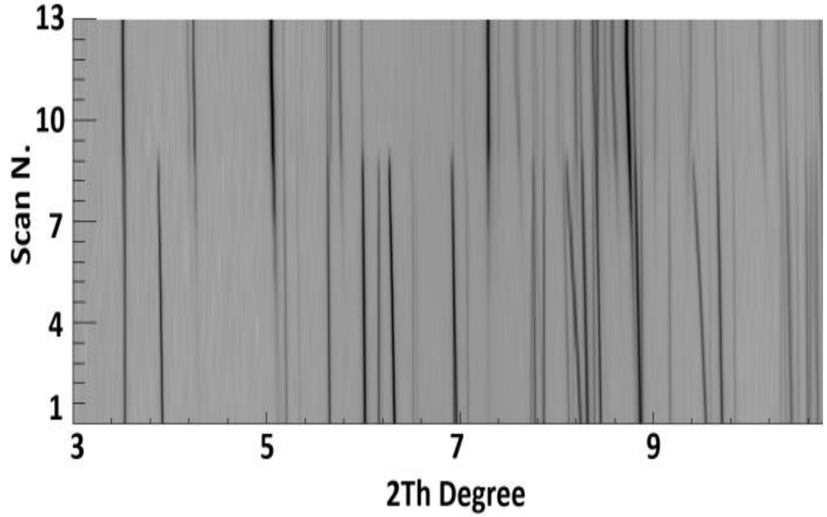
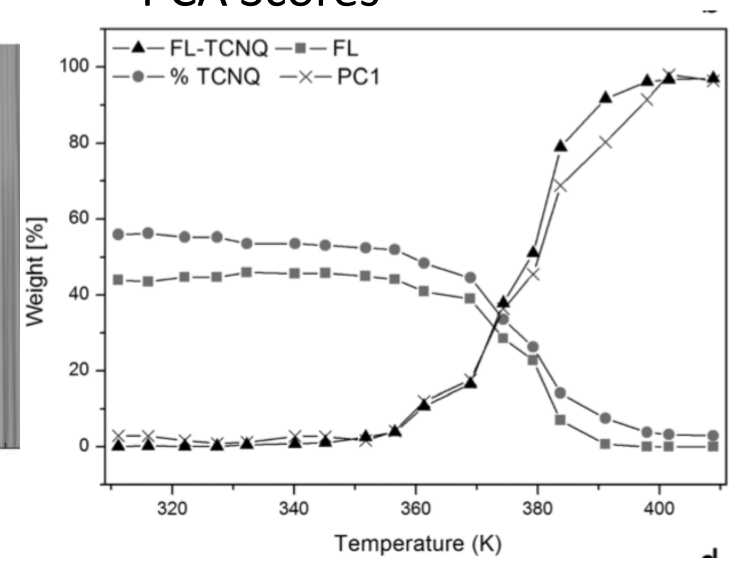
Escale lane n. 3: PCA can be used to analyse in situ XRPD data

In situ XRPD data



PCA Scores



Scores from PCA give the reaction kinetics of the solid-state reactions with good agrement with Rietveld refinement

Palin L. et al. *Cryst. Eng. Comm.*, **2016**, 18, 5930.

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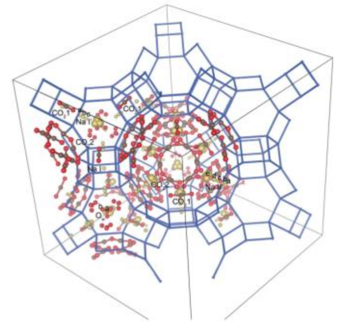
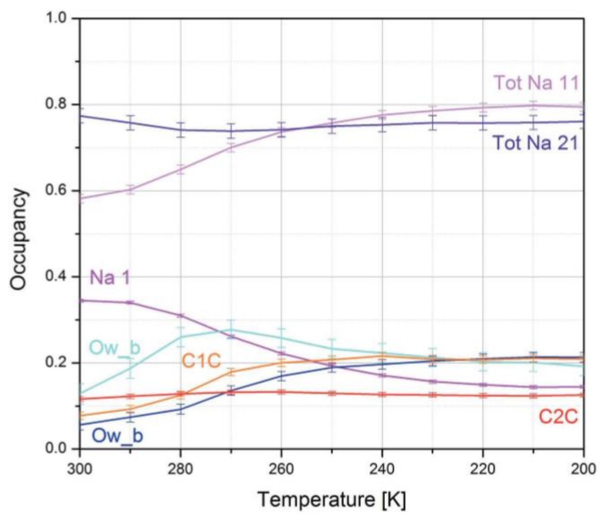
b

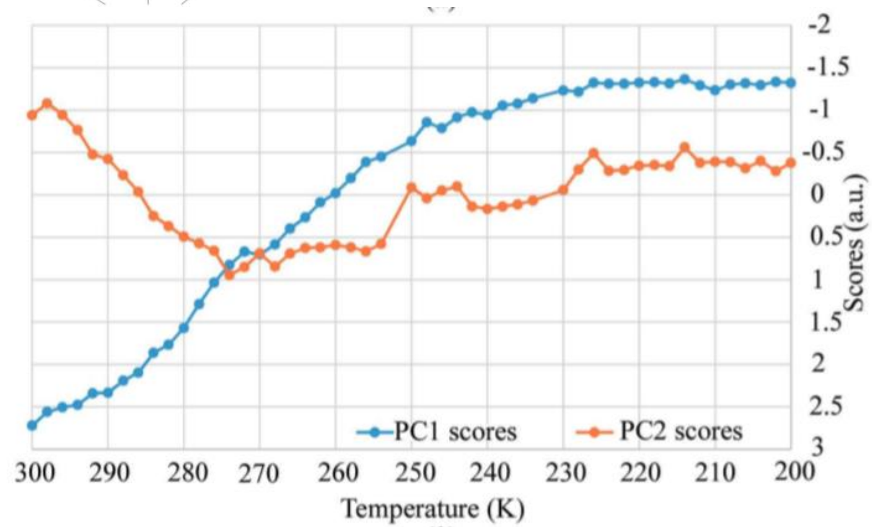
By the way, PCA can be applied also to in situ single crystal of CO_2 into a Y zeolite



Standard refinement



PCA scores



SINGLE CRYSTAL: Conterosito E. et al., **Acta Crys. Sect. A, Foundation and Advances**, 2019, 75(2), 214-222.

Three real world case studies about the PCA-assisted retrieval of the kinetics in in situ experiments

Case 1: in situ XRPD study of $BaSO_4$ sedimentation during epoxy resin curing

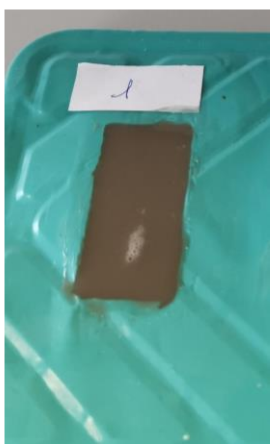
Case 2: Evolution of MOF phases whose structure is unknown

Case 3: Transformation of low ordered phases, a multitechnique approach

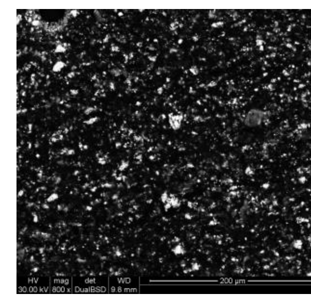
Case study n. 1: in situ XRPD study of BaSO4 sedimentation during epoxyresin curing

Radiopaque composites made of an epoxy resin additivate with $BaSO_4$

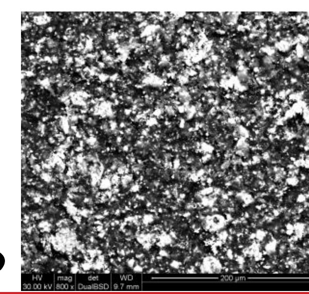
During curing (24 hours), because of gravity, $BaSO_4$ stratifies



SEM top slice



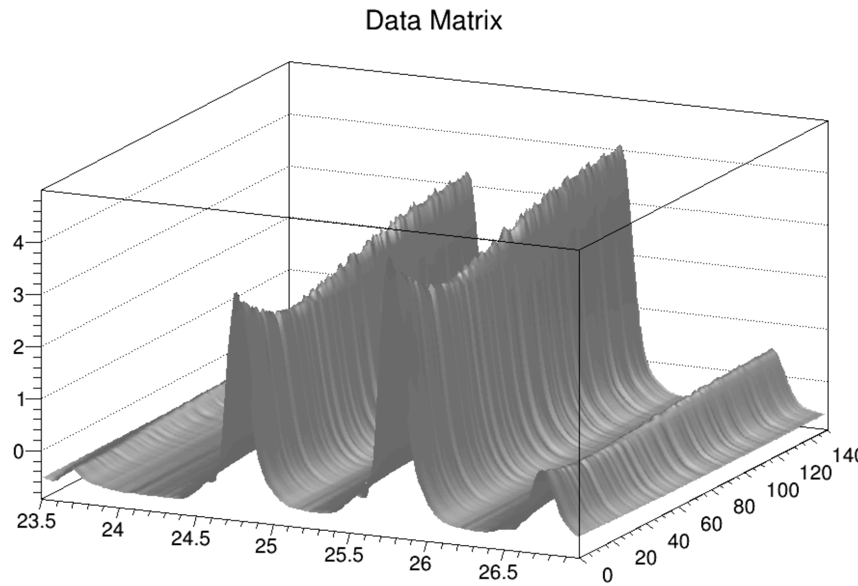
SEM bottom slice



XRPD data collection on lab diffractometer

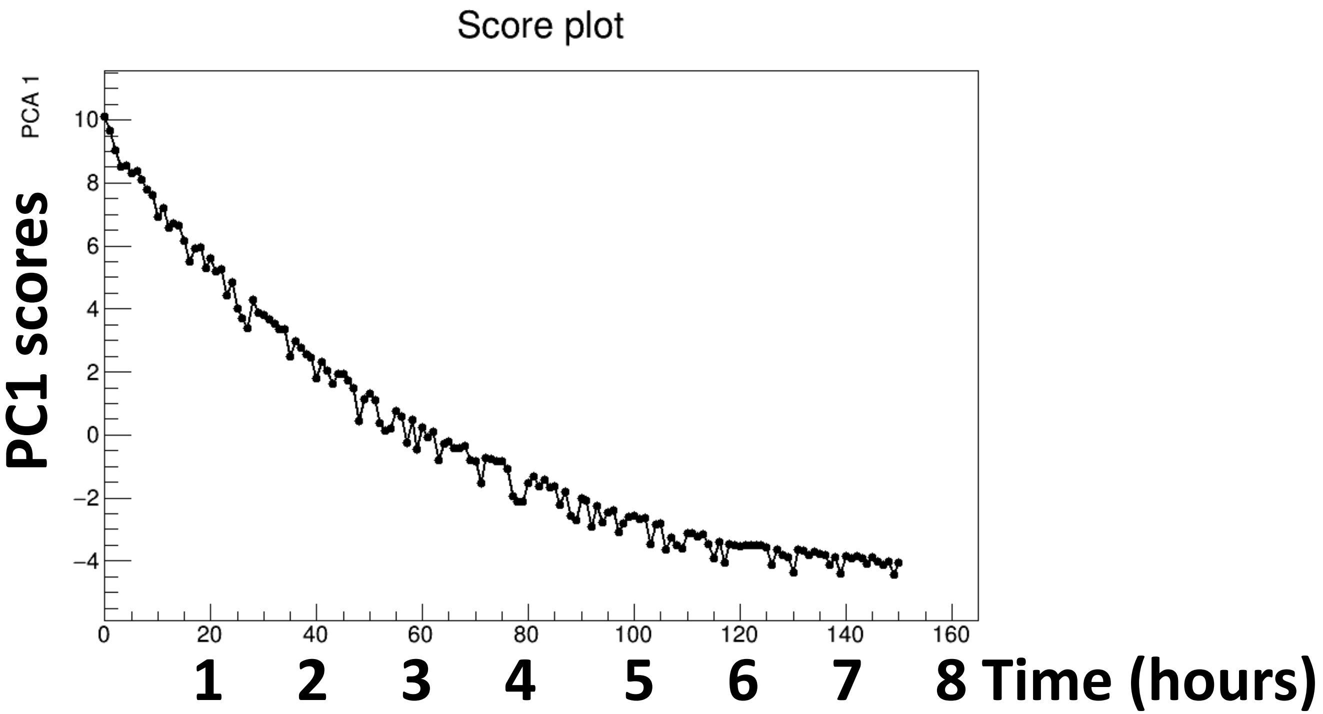
Ad hoc sample holder

(courtesy of Panero Elevatori srl)



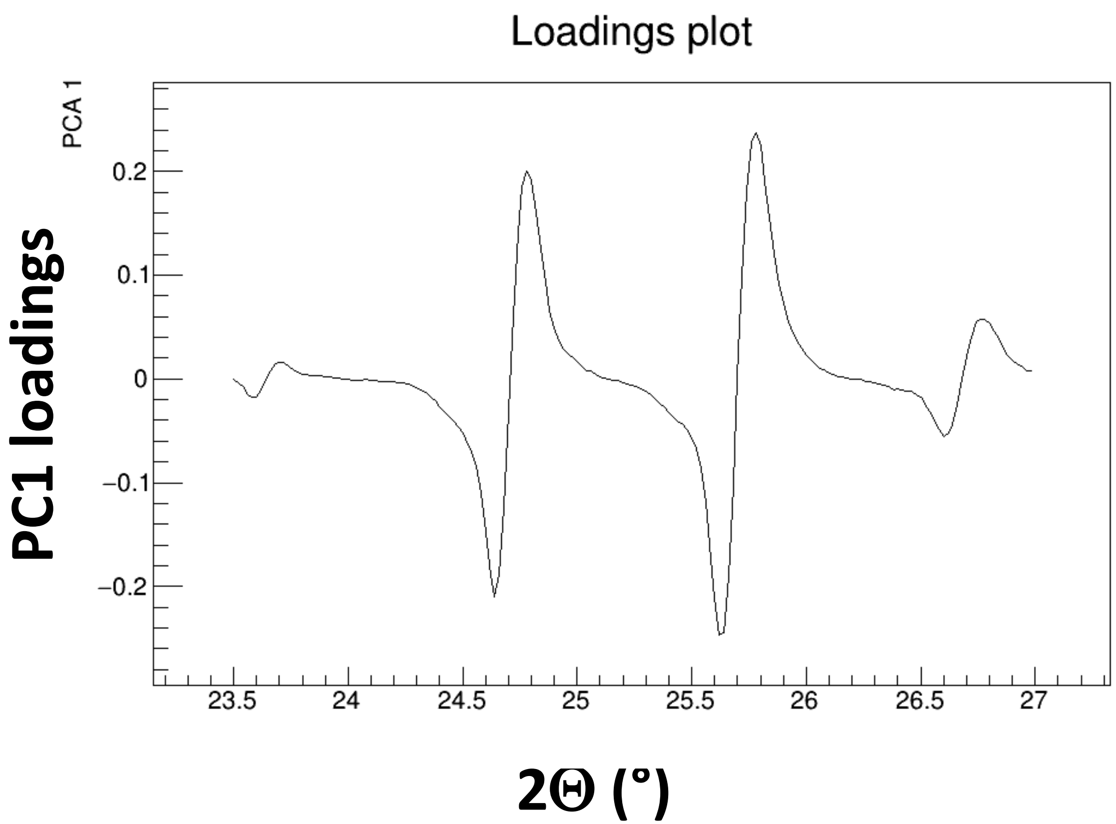
In situ XRPD lab data. Limited angular range to collect data in 3 min/pattern

PCA analysis of in situ XRPD: scores describes the dynamics of the event i.e. process advancement vs time



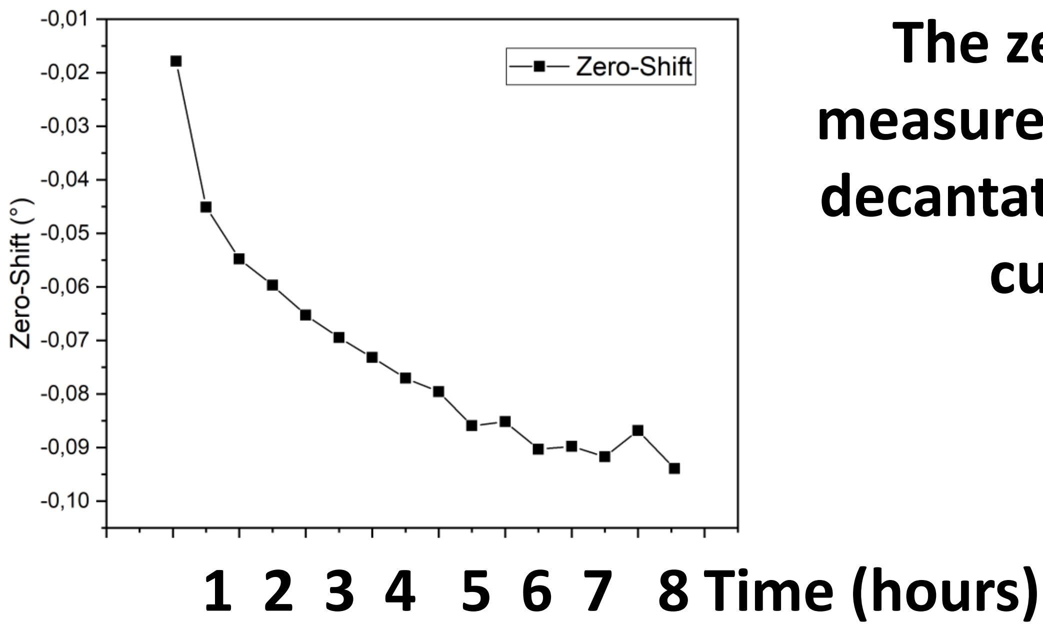
No structure needed, no problems about limited angular range, few minutes after data collection

PC loadings tell us WHAT is happening



A clear drift of the peak is observed that $BaSO_4$ is decanting down in the sample

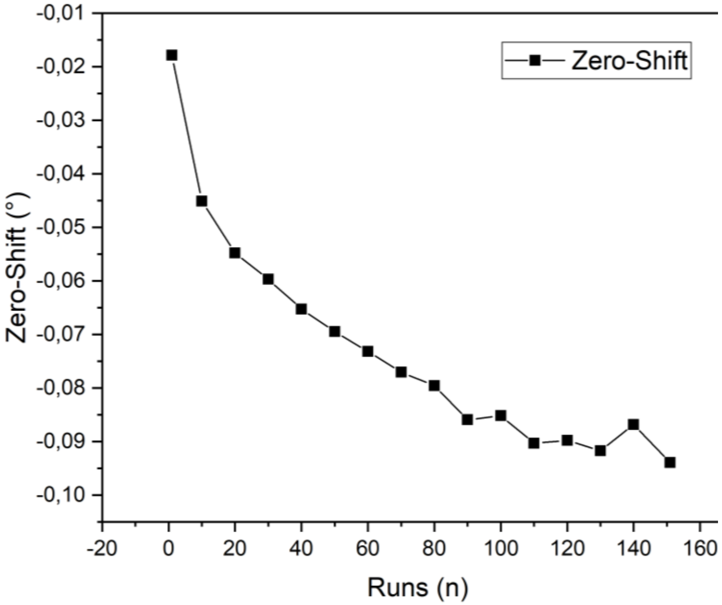
Rietveld refinement by Mattia@EXPO hands on session after knowing the result by PCA analysis

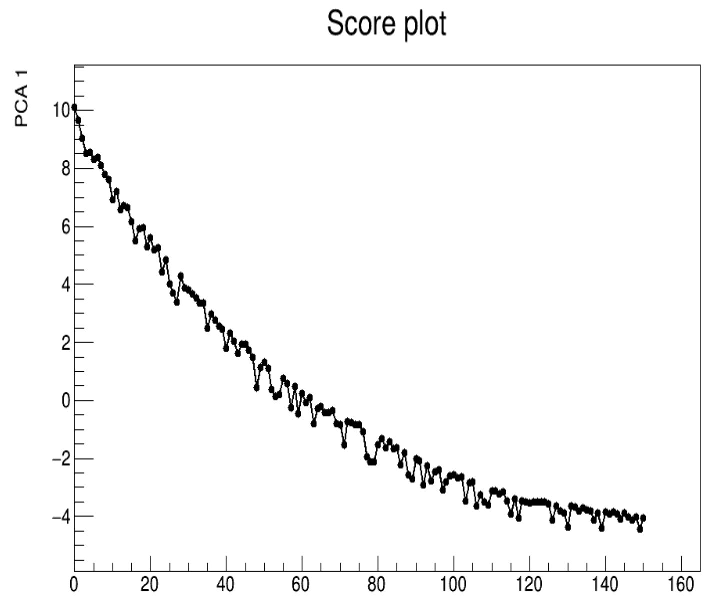


The zero shift measure the $BaSO_4$ decantation during curing

Rietveld refinement is difficult because of the limited 2Θ range and correlation between sample transparency and displacement

Rietveld refinement by Mattia@EXPO hands on session after knowing the result by PCA analysis





EXPO refinement of 16 pattern (1 out of 10) half an hour. Clear physical meaning

PCA analysis of 150 patterns: few minutes Dynamic extracted no direct physical meaning

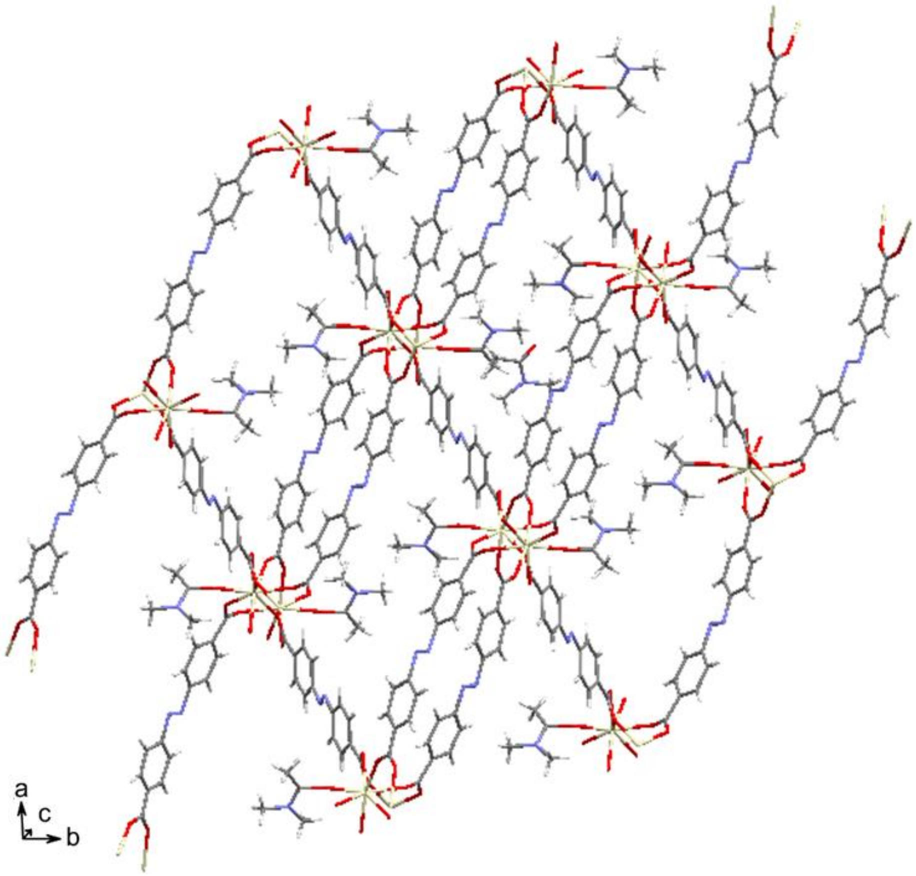
Case study n. 1 TAKE HOME message

PCA analysis is much faster and more efficient in extracting the kinetics from the whole pattern changes (peak position and intensity) BUT no physical meaning can be obtained directly, only inferred

EXPO refinement require more time but a clear physical meaning (limited to zero shift) is obtained

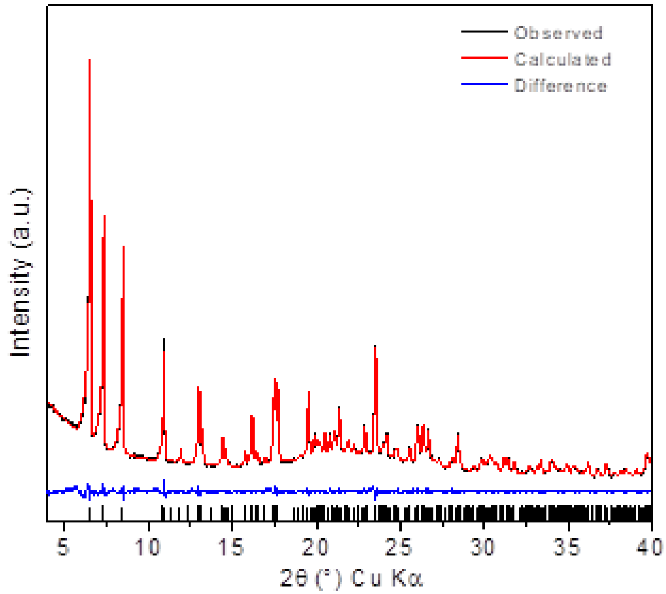
PCA is then a powerful analysis method to be used for online experiment monitoring and optimization. Besides PCA can highlight which pattern and what effect to look for in the post experiment traditional experiment

Case study n. 2: Evolution of MOF phases whose structure is unknown

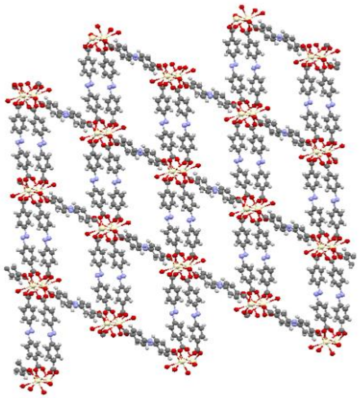


Structure and topology in the P2$_1$/*n* stable polymorph was solved

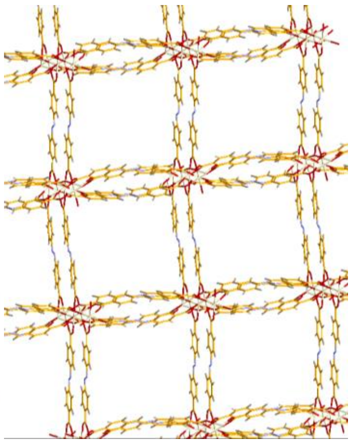
Pure $P2_1/n$ product with high area expected



XRPD refined against SC structure



P21/n structure after «graphic» DMA removal



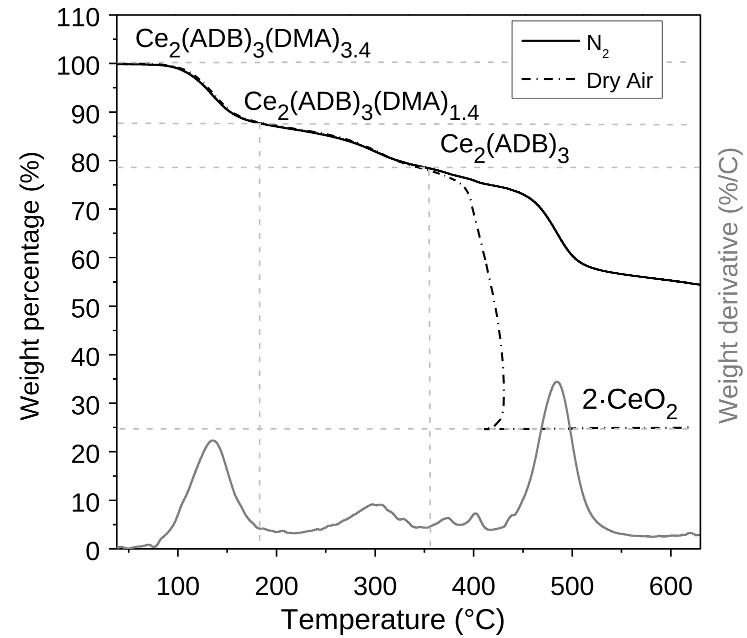
***In silico* optimized structure after DMA removal**

The bad… or good (for the crystallographer only) news

-) Thermal activation gave mixtures of phases **with small or no surface area**

-) Chemical exchange of DMA produced new phases

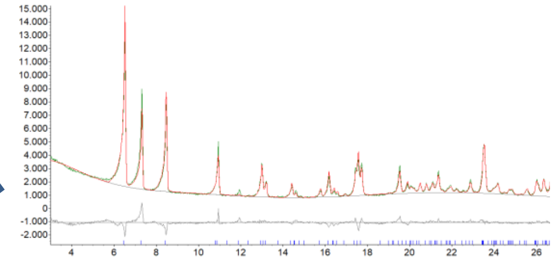
-) Exposure to air moisture or water impregnation cause new phases togheter with degradation



TGA inert atmosphere

A magic space – **the polymorph landscape** -, was studied by **oven treatments, TGA, SC- and P-XRD@Lab …….**

Monoclinic P21/n

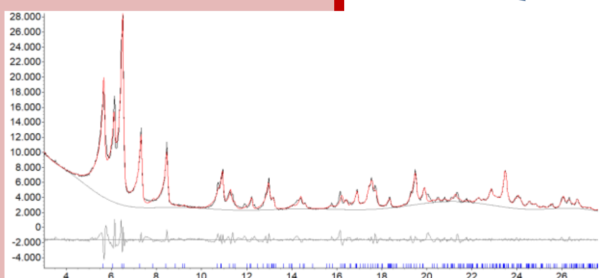


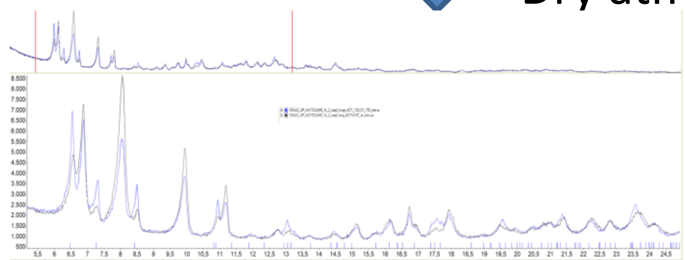
Air moisture

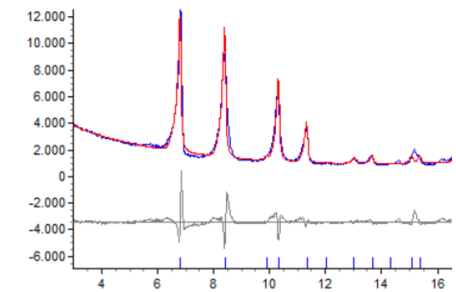
ACN washing

150-200°C

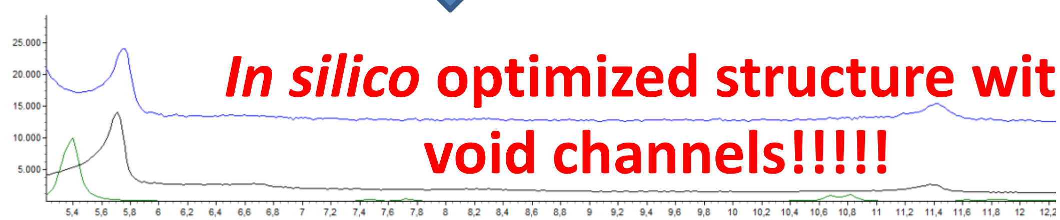
Dry atm





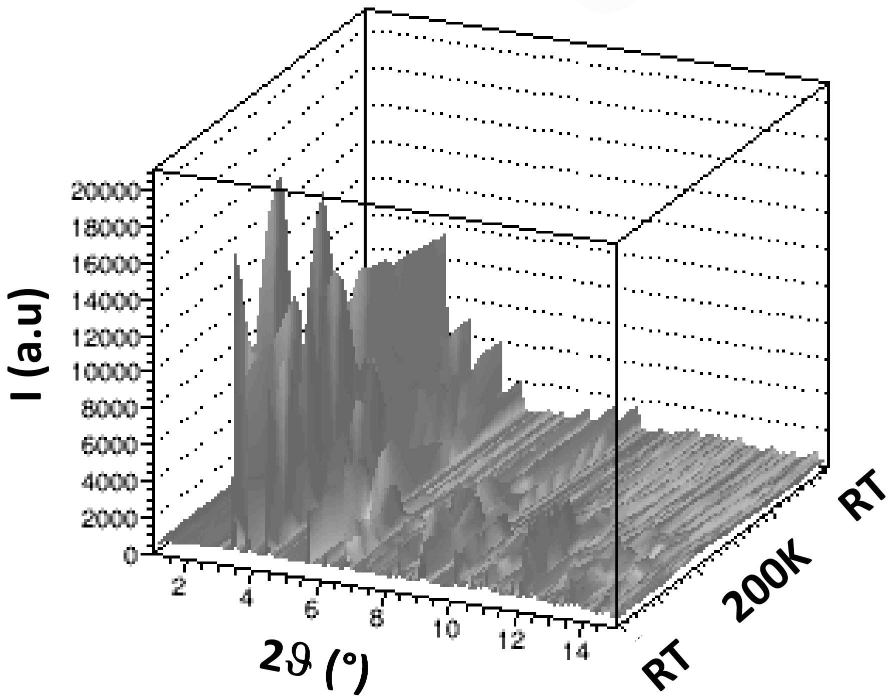


300°C dry atm or water impregnation at RT



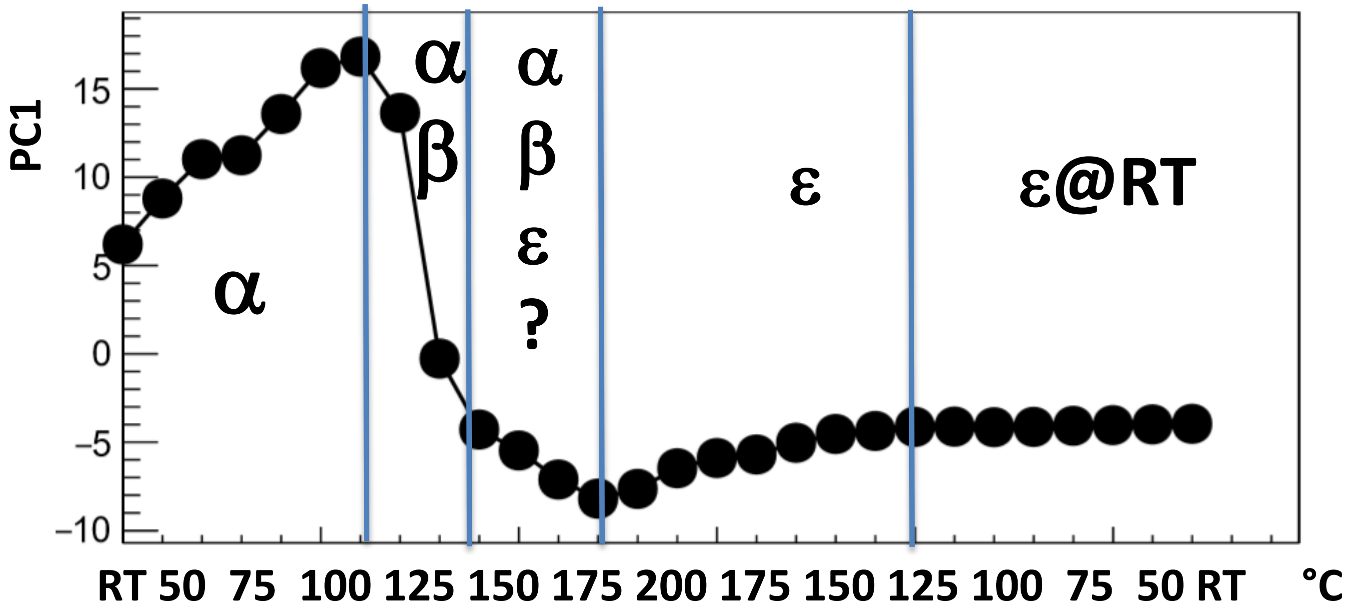
In silico **optimized structure with void channels!!!!!**

PCA-assisted in situ synchrotron XRPD to study the «intermediate» phase at 120-200 °C



PCA was used to get «online and onsite» the dynamic of the process and to optimize the experiment setup and conditions

PCA analysis of *in situ* XRPD allowed to obtain the stability range of the phases and find the ε phase



The limitation of not knowing the structures is overcome: the phase are now isolated as pure and standard structure solution can be attempted

Case study n. 2 TAKE HOME message

PCA analysis is much faster and more efficient in extracting the Dynamic without knowing the crystal structure BUT no physical meaning can be obtained directly, only inferred

Traditional strcuture solution and refinement approach is needed to characterize the unknown phases

PCA powerful on line analysis method for experiment optimization. PCA can highlight what to look for in the post experiment traditional data analysis

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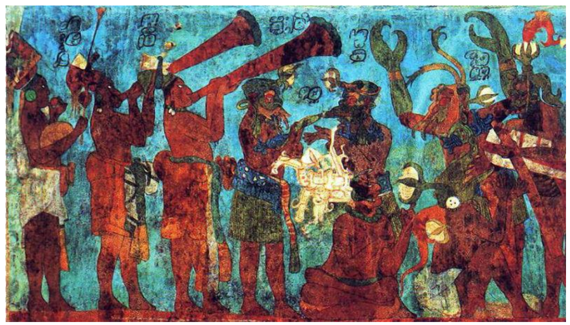
Case study n. 3: Transformation of low ordered phases, a multitechnique approach

"Musicians and dancers"



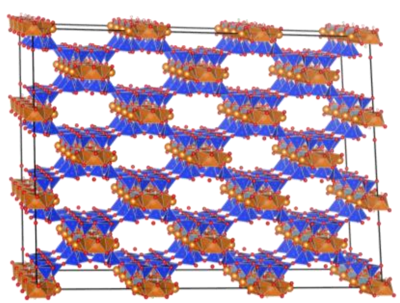
Ancient nanostructured material

The intriguing peculiarities:

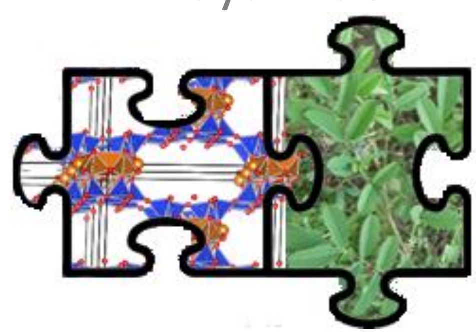
- Brightness
- hue, ranging from a bright
- turquoise to a dark greenish blue
- remarkable durability
- chemical stability

<u>The MB "technology" went lost and Maya Blue became an intriguing puzzle</u>

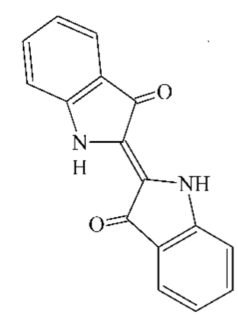
Palygorskite



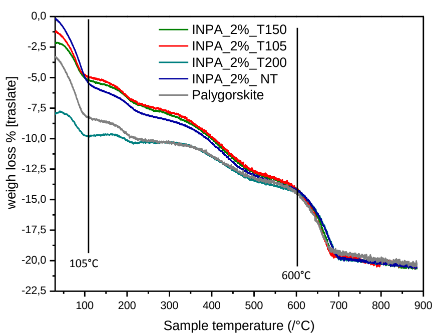
Maya Blue

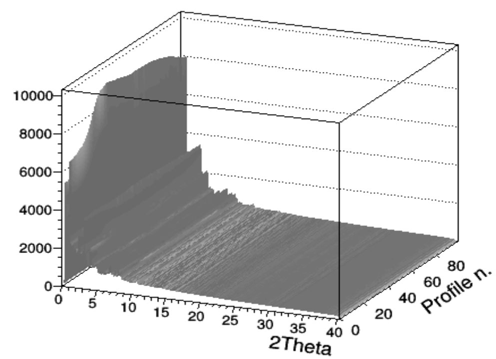


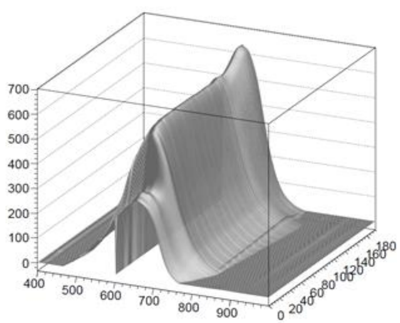
Indigo



- *Thermogravimetric analysis (TGA)*: **water adsorption/desorption**, **thermal stability**
- *In situ X-ray powder Diffraction (XRPD)*: **long range order** of water/indigo into the tunnels
- *In situ Pair Distribution Funcition (PDF)*: **short range order** into the tunnels
- *In situ Fiber Optic Reflectance Spectroscopy (FORS)*: **optical properties** of Indigo





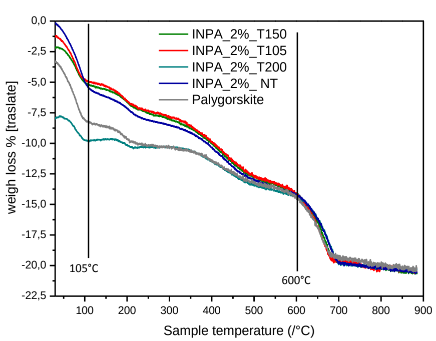


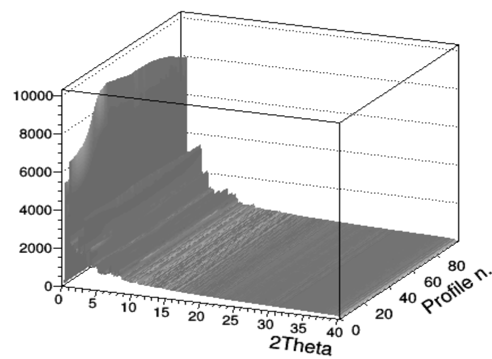
Pre-heating in the range 105-200 C of the mixtures modify tunnel content, ordering and optical features

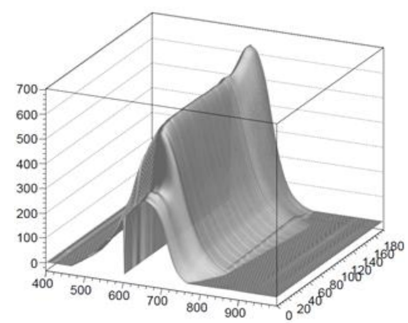
The collected data, 2 day@synchrotron, 5 day@lab

- *About 2000 XRPD pattern*
- *About 2000 PDF patterns*
- *About 1000 in situ FORS optical spectra*

HOW TO DEAL WITH?







Statistical methods to deal with complementary data

- *Principal component analysis to analyse the kinetic trends in a fast and efficient way*
- *Correlation analysis to analyze and «align» data from different probes (XRPD/PDF, XRPD/FORS …)*

The used tool: Rootprof

"*general purpose tool for processing unidimensional profiles with specific applications to diffraction and spectroscopic measurements*"

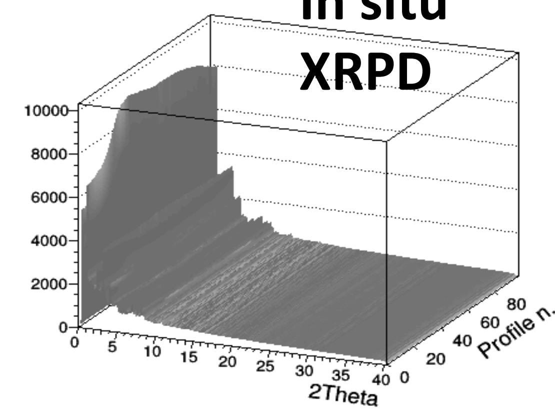
http://users.ba.cnr.it/ic/crisrc25/RootProf/RootProf_help.html

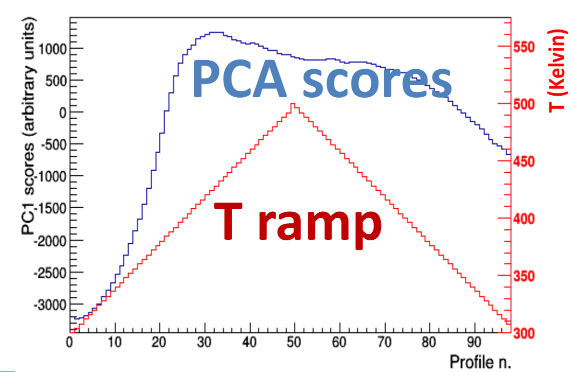
R. Caliandro et al., *J. Appl. Cryst.*, **2014**, 47 1087

Set A: Mayan materials explored by in situ XRPD to explore long range order

Mixture	sample number
Paly_indigo_2%	0
Paly_indigo_3%	1
Paly_indigo_4%	2
Paly_isatin_4%	3
Paly_isatin_6%	4
Paly_isatin_8%	5
Paly_methblue_2%	6
Paly/fuchsin 2%	7
SAP110A_indigo_4%	8
Zeo-A_indigo_4%	9
HSZ-320_NAA(Y-type)/indigo4 %	10
Halloysite/indigo 4%	11
Cloisite_indigo_4%	12
NaSap(Al)_110/indigo 4%	13

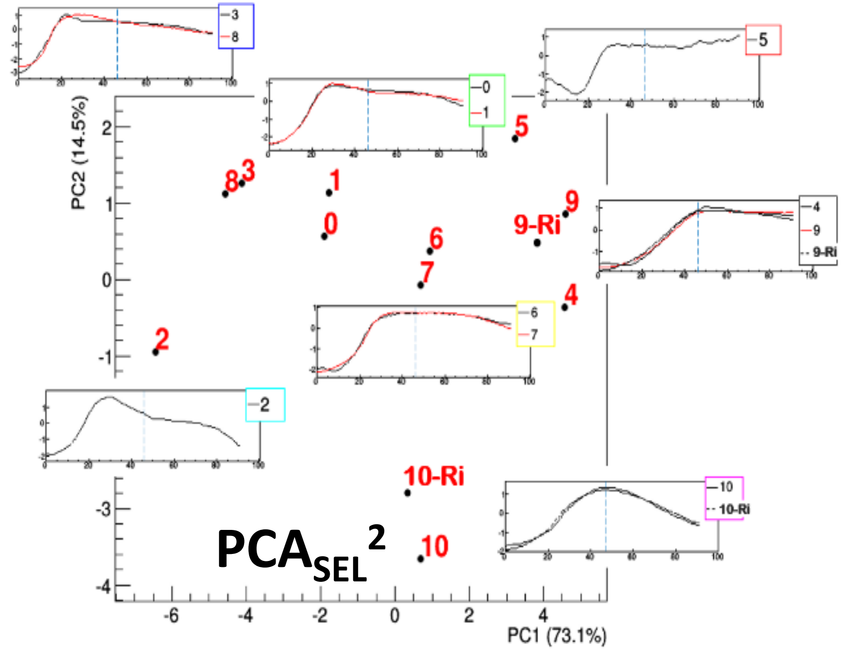
13 In situ XRPD data collected at variable temperature





After excluding the three outlayers, PCA_{SEL}^2 in situ XRPD gave info on Indigo ordering in the channels

Mixture	sample number
Paly_indigo_2%	0
Paly_indigo_3%	1
Paly_indigo_4%	2
Paly_isatin_4%	3
Paly_isatin_6%	4
Paly_isatin_8%	5
Paly_methblue_2%	6
Paly/fuchsin 2%	7
SAP110A_indigo_4%	8
Zeo-A_indigo_4%	9
HSZ-320_NAA(Y-type)/indigo4 %	10
Halloysite/indigo 4%	11
Cloisite_indigo_4%	12
NaSap(Al)_110/indigo 4%	13



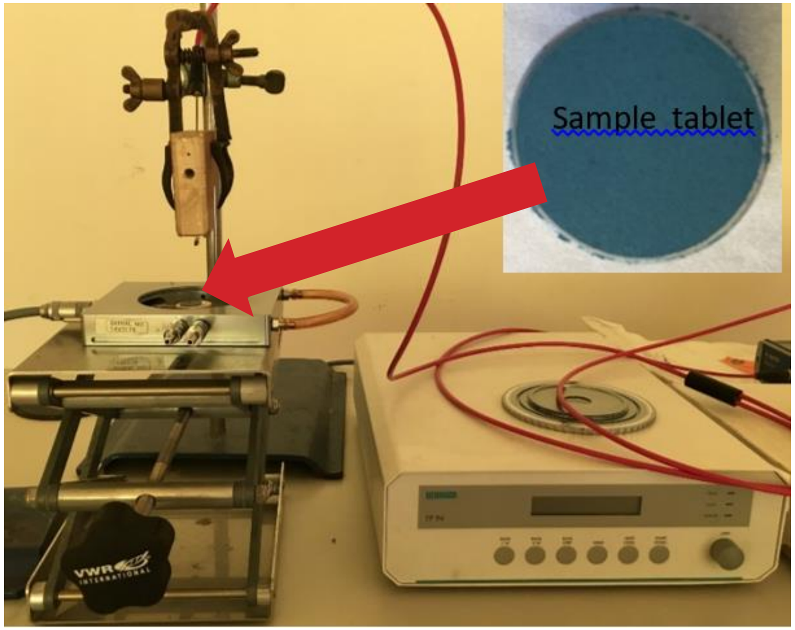
0, 1: «typical MayaBlue reaction»

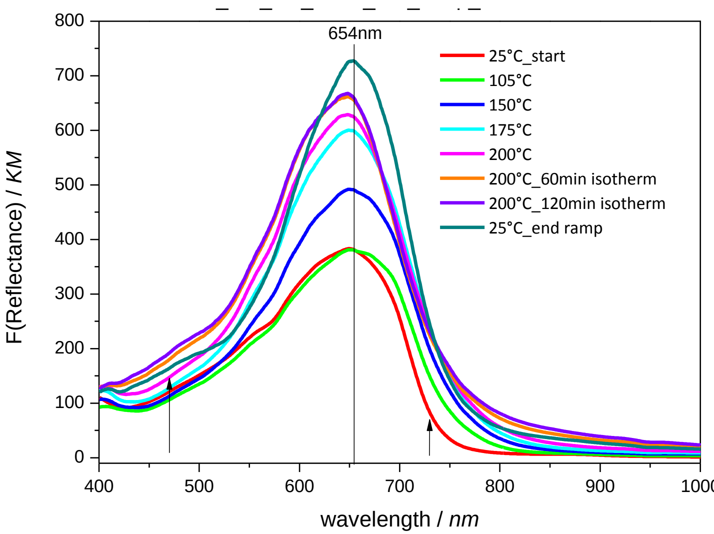
3, 6, 7, 8: similar to 0 and 1

2, 10 reversible reaction

In situ Fiber Optical Reflectance Spectroscopy (FORS) of Palygorskite indigo mixtures

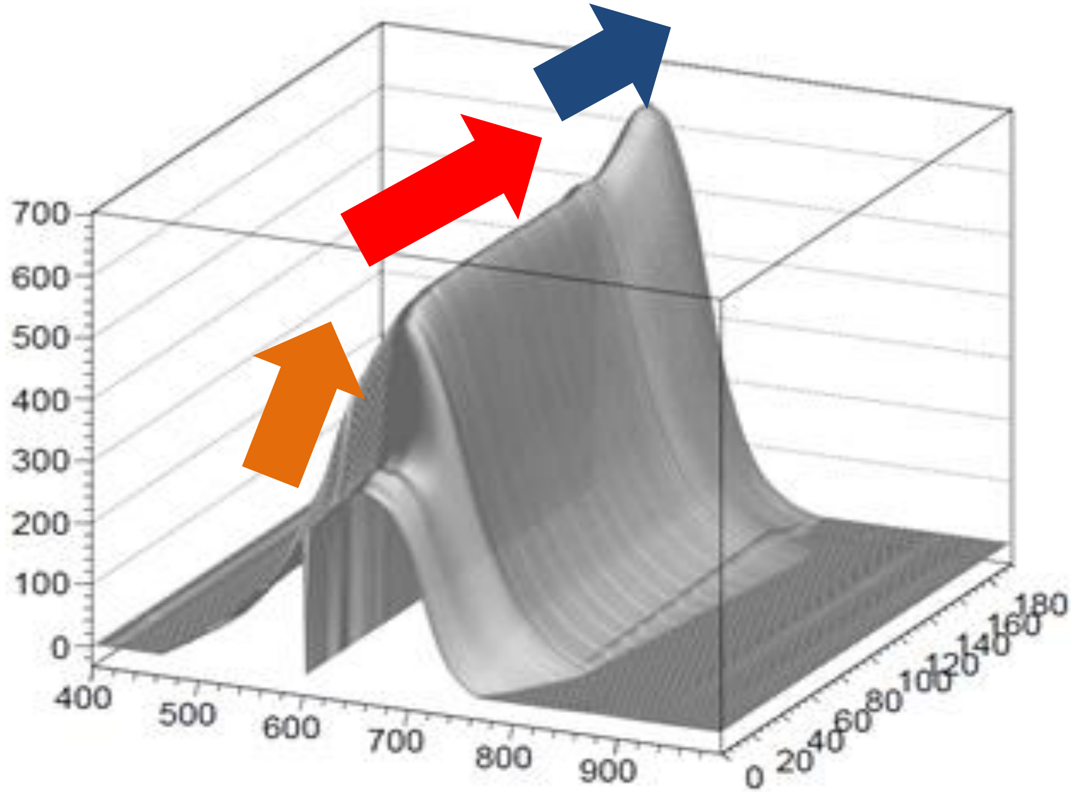
Optical spectroscopy allows evaluating the color of the Maya Blue samples and the environment of Indigo





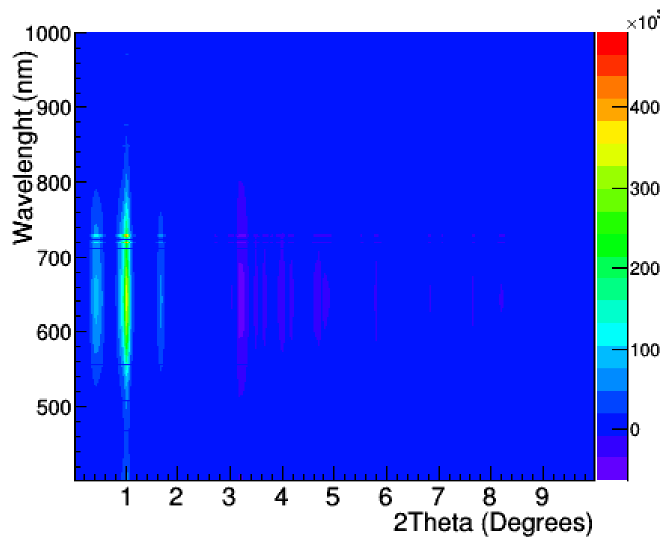
Preheating in the oven of the mixtures changes the optical features

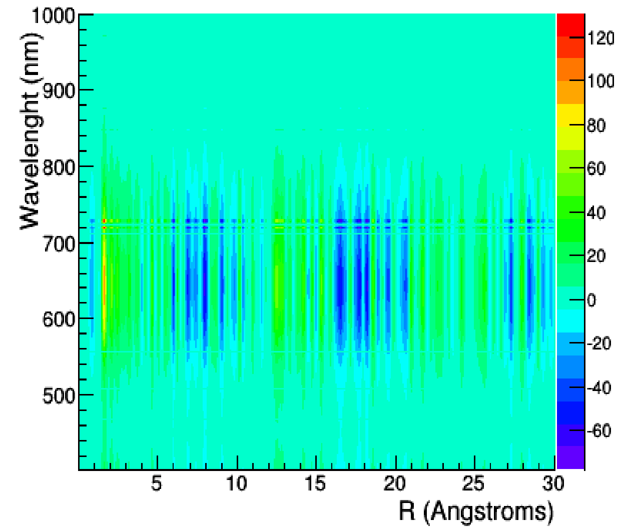
In situ FORS data



Evolution of Indigo optical reflectance during the heating dwell at 200C and cooling to RT

Are structural (in situ XRPD) and optical (in situ FORS) data correlated for the NT sample treated from RT to 200C?



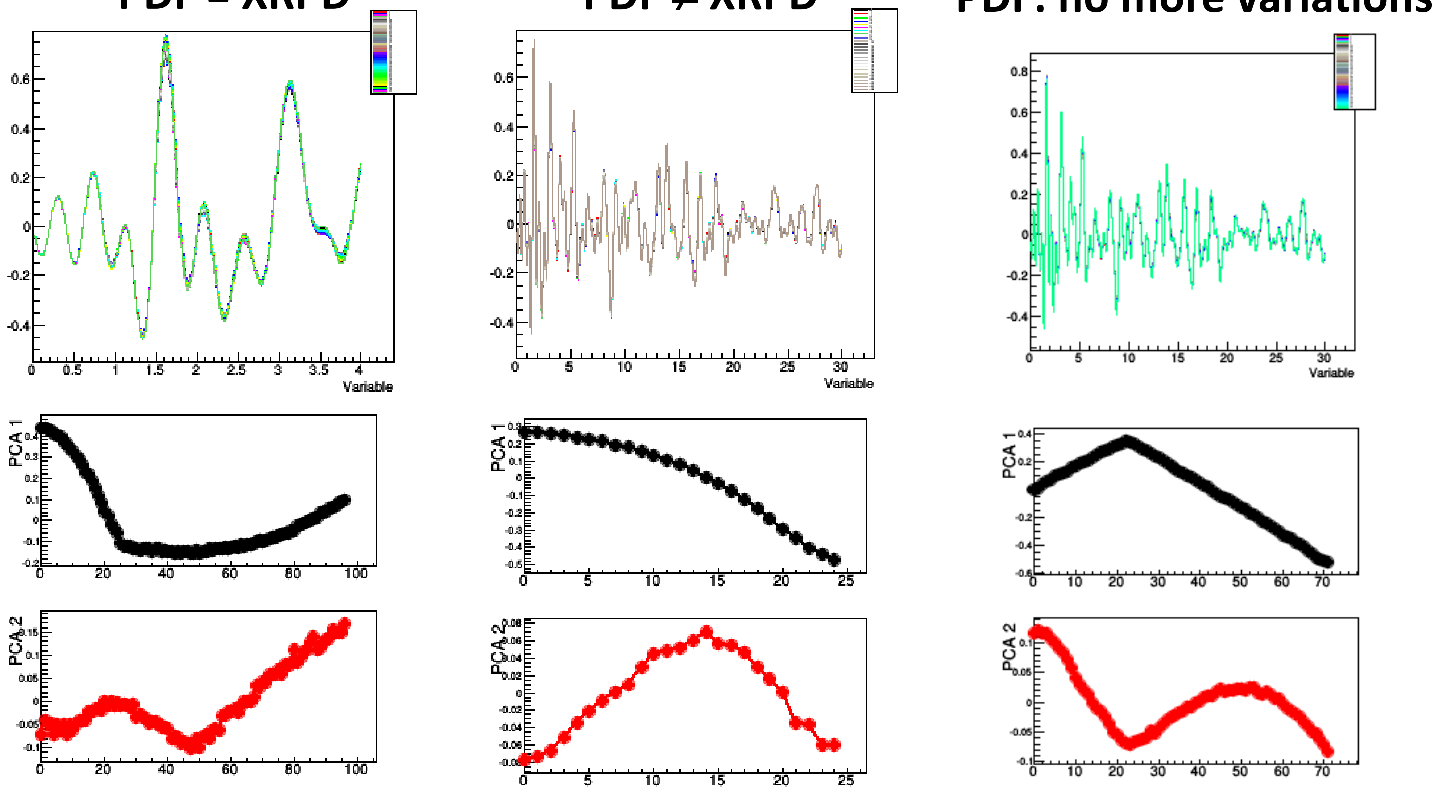


Low angles XRPD peaks correlate with FORS: water elimination is correlated with optical features

PDF correlates with FORS in region corresponding at about 10, 20, 30 Å, i.e. multiples of indigo molecule lenght

Long (XRPD) vs. short (PDF) range order by PCA

r<4 Å, all T range PDF = XRPD	T<110° PDF ≠ XRPD	T<110° PDF: no more variations



Indigo < 110C occupy channels in a disordered behaviour!

R. Caliandro et al., *New hints on Maya Blue formation process by PCA-assisted in situ XRPD and optical spectroscopy analysis, Chem Eur. J.* **2019**

Case study n. 3 TAKE HOME message

PCA and statistical analysis allowed managing succesfully 5000 experimental patterns

Correlation analysis allowed to align and correlate signals from diferent probes (FORS, XRPD, PDF)

Traditional strcuture refinement is hampered by the inability of tracking the subtle changes of the low crystallinity palygorskite sample

Moreover the traditional «manual» approach is unfeasible with 5000 patterns by different probes

Rietveld (1/2day?)

PCA (1/2 minutes)