Aplicaciones de la difracción de polvo a la identificación y caracterización de materiales

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Aplicaciones industriales del Sincrotrón ALBA en cementos, pigmentos, cerámicas y vidrios
Cerdanyola del Vallès, 6May 2016

Brief introduction to powder X-ray diffraction (XRPD)

MSPD beamline

Synchrotron XRPD benefits

Applications of XRPD to pigments, cements, ceramics or glass

- Identification of phases
- Quantification of phases
- In-situ / time-resolved experiments
- Summary and other possibilities

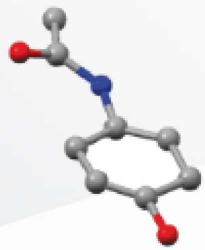
Solid state matter

Infinite and periodic 3D arrangement of scatterers = **Crystal**

lattice

\+

Atoms



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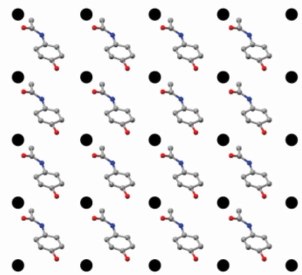


Solid state matter

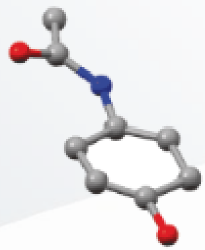
Infinite and periodic 3D arrangement of scatterers = **Crystal**

lattice

Position of the peaks

+

Atoms



Intensity of the peaks

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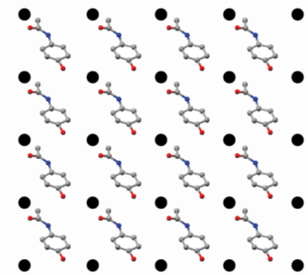
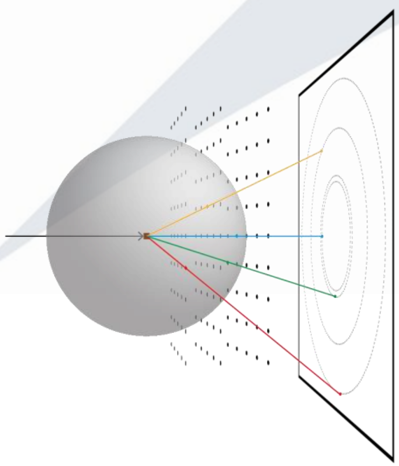
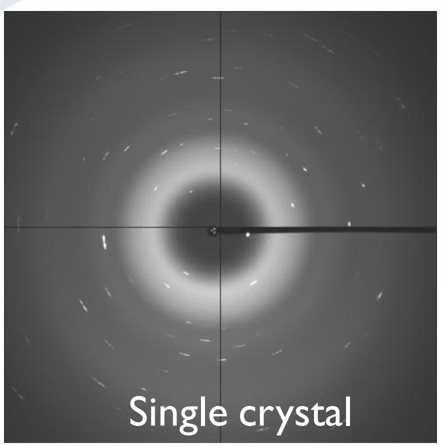






W. L. Bragg formulation of X-ray diffraction

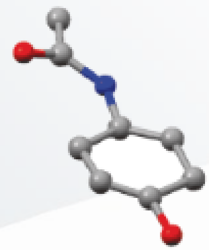
Crystalline solids produced **intense peaks** of reflected X-rays at **certain specific wavelengths and incident angles**. W. L. Bragg explained this result by modeling the crystal as a set of **discrete parallel planes** separated by a constant parameter **d**. The incident X-ray radiation would produce a Bragg peak if their reflections off the various planes interfered constructively.

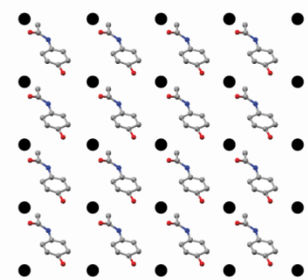
Bragg condition: $2d\sin\theta = n\lambda$

Solid state matter

Infinite and periodic 3D arrangement of scatterers = **Crystal**

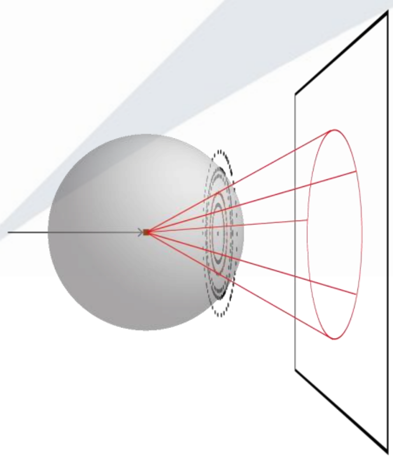
lattice + Atoms =

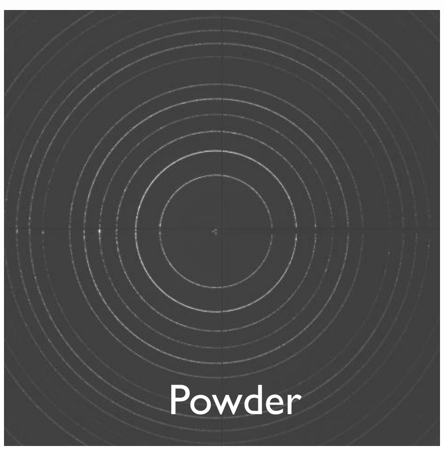


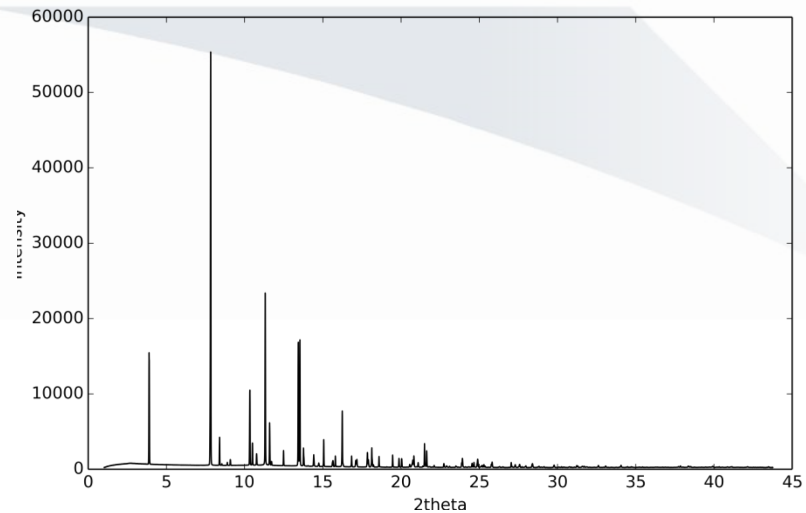


Position of the peaks

Intensity of the peaks







Outline

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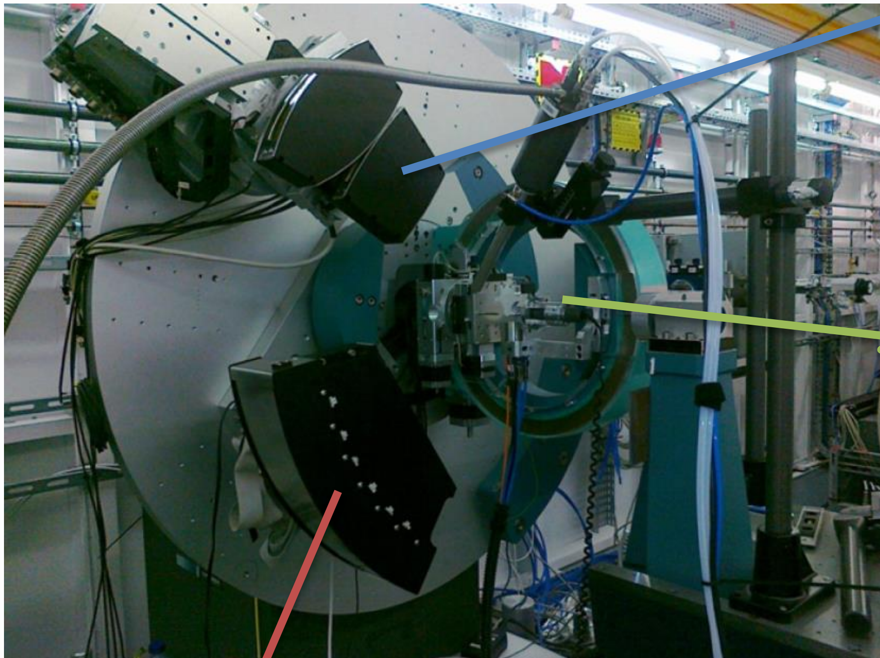
PD endstation



Multi Analyser Detector (MAD)

- 13 channels with 1.5° pitch
- Si111 or Si220 Bragg reflection
- YAP scintillator + PMT
- 10 to 50 keV

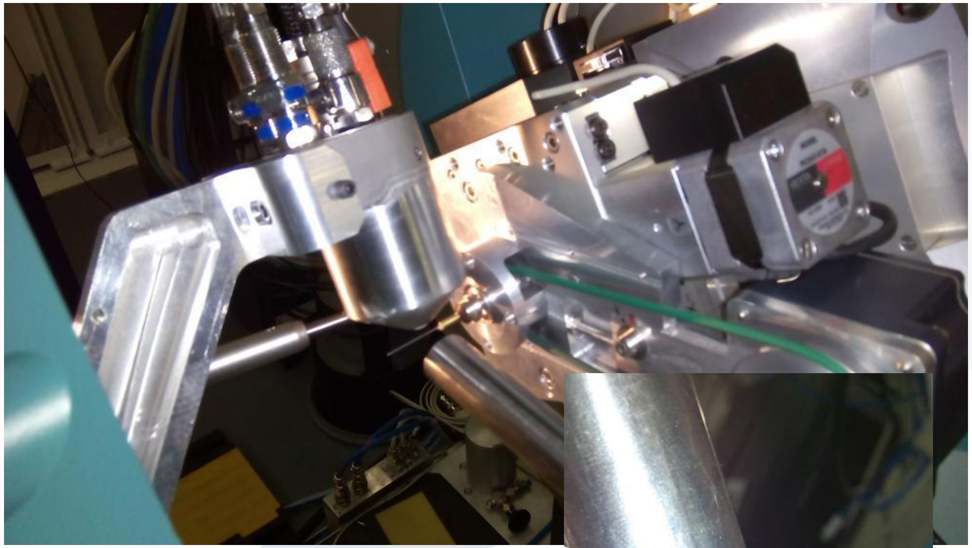
Sample environment

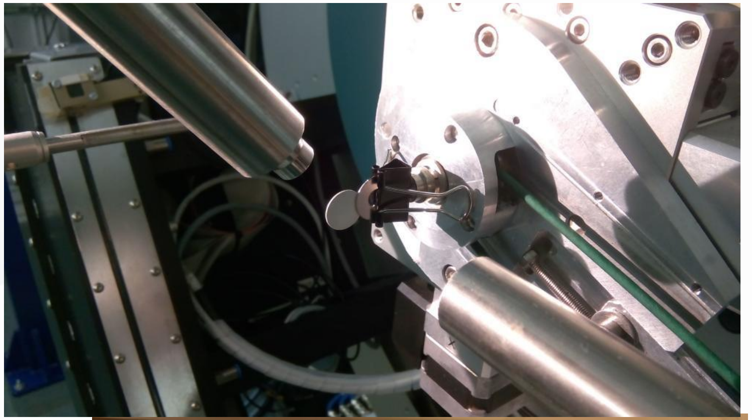
- Hot air blower (300-950°C)
- LN2 Cryostream (80-480K)
- LHe Cryostat (down to ~5K)
- Eulerian cradle
- Capillary flow cell

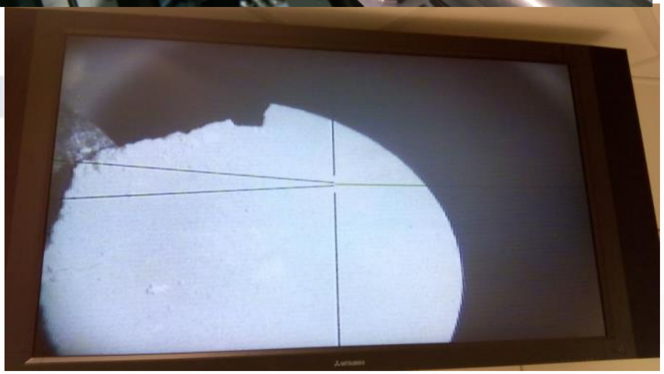
MYTHEN-II detector

- 6 modules (1280 channels, 50µm pitch)
- Sample to Det. dist. 550mm (aprox. 40° in 0.005° pitch)
- ms time resolution
- 8 to 30 keV

PD endstation







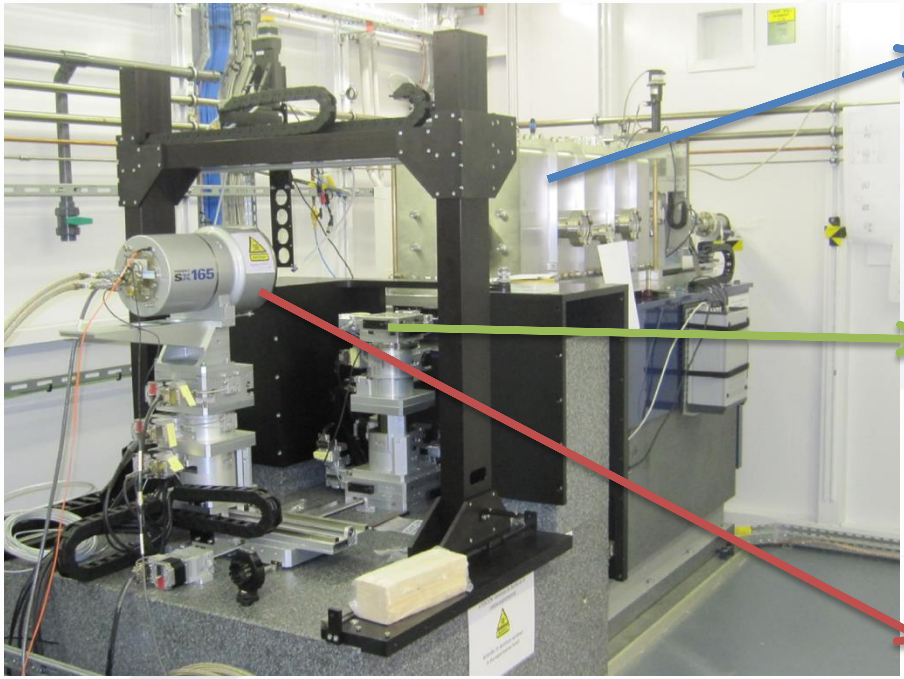
Capillaries

Standard glass 0.7mm
Quartz for HT
Other sizes

Debye-Scherrer geometry

Free standing (transmission)

High pressure / microdiffraction endstation



Kirkpatrick-Baez (KB) focusing optics

- Spot size of 15 x 15µm FWHM at sample position (20-50 keV)

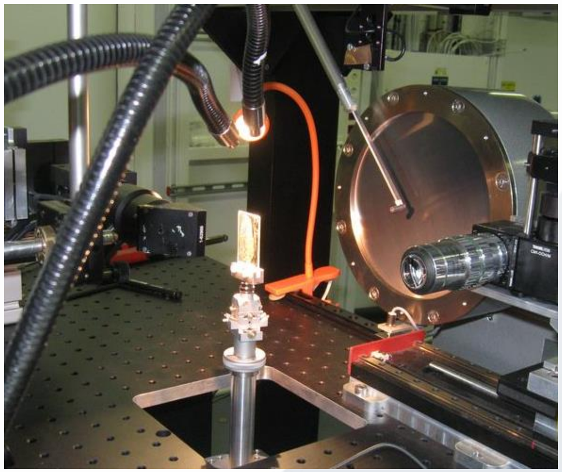
Sample mounting/environment

- XYZ stage
- Diamond anvil cells (& spectrometer)
- Online visualization system

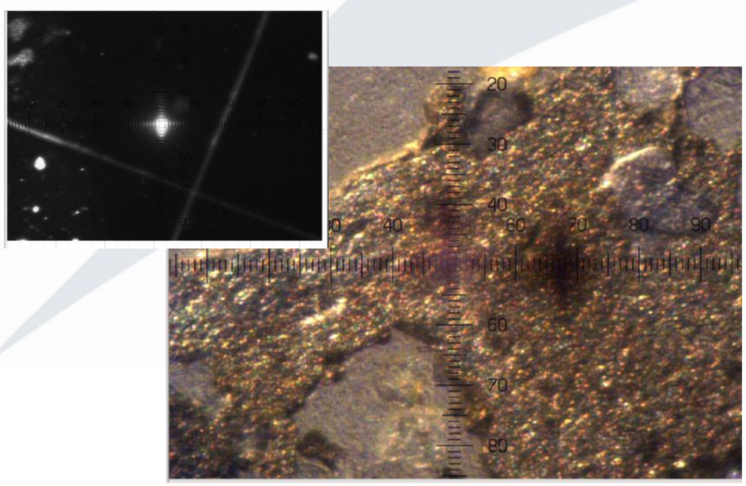
CCD camera

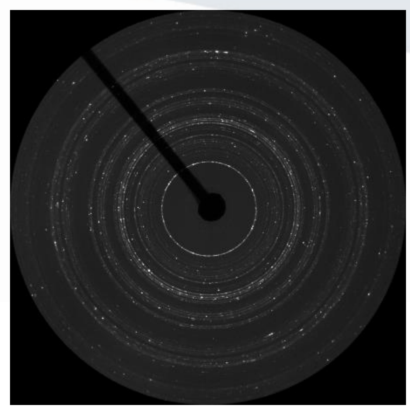
- SX165 (Rayonix)
- Round area (Ø165mm)
- 20 to 50 keV
- Dynamic range 16 bit

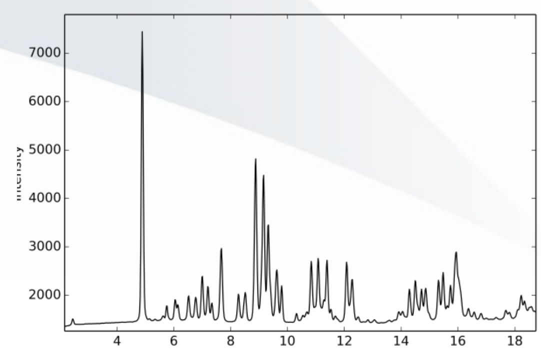
Microdiffraction



- Mounting of the sample(free standing, thin section,…)
- **Selection of the measurement points** with the online visualization system (spot ~15x15µm FWHM)
- Radial integration of the obtained image for the identification of substances







Why using Synchrotron?

Energy tunability (not limited to Cu, Mo, …)	→	Speed, control of **radiation damage**
Broad range of energies (8-50 keV at MSPD)		High statistics
High flux		Good signal to noise
Low natural beam divergence		High angular resolution
Detector systems		Penetration of absorbing materials
Small spot size		Small amount of sample required
Accommodation of sample environments		Time-resolved studies

Synchrotron X-ray powder diffraction benefits

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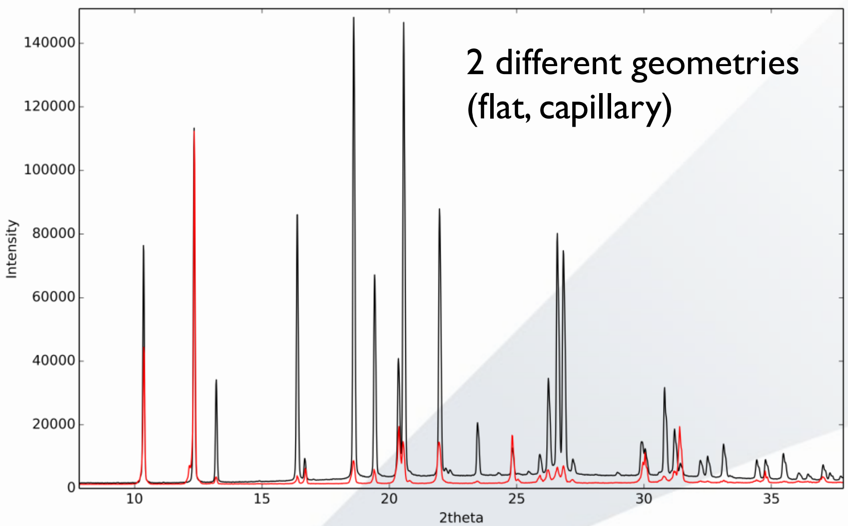
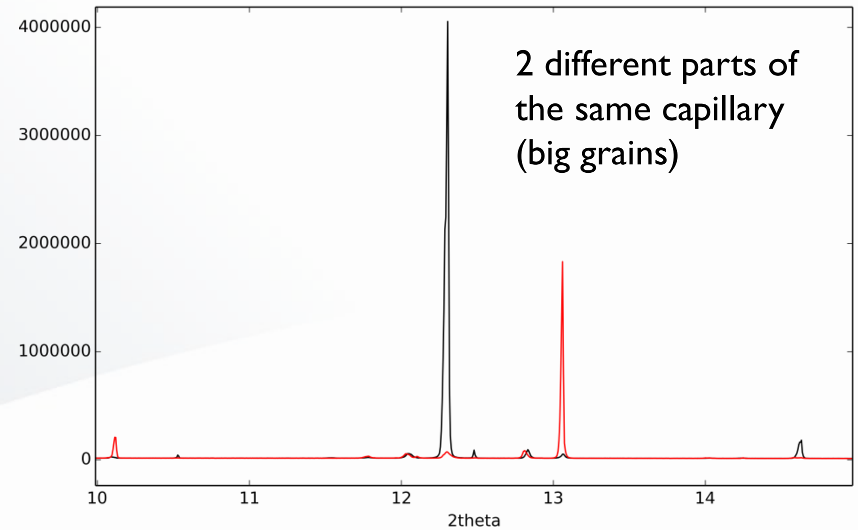
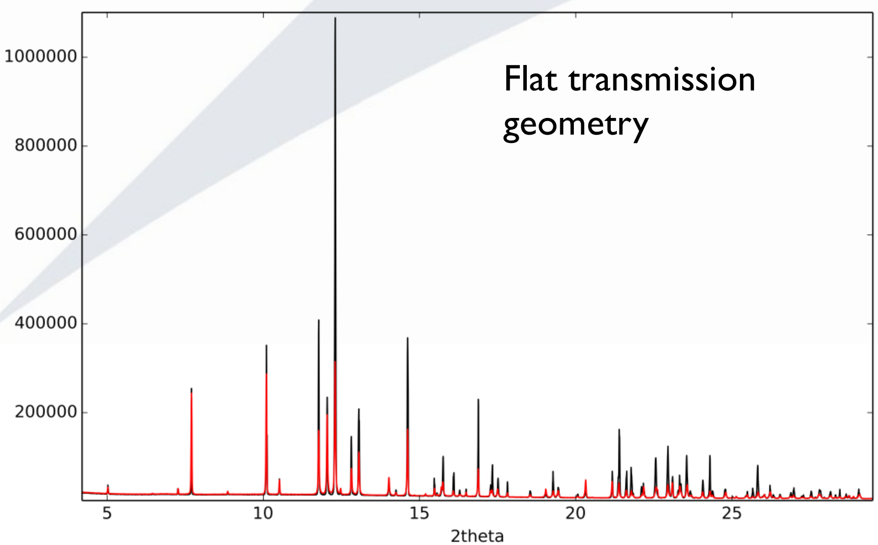
Difficulties that may be encountered (not only in synchrotron…)

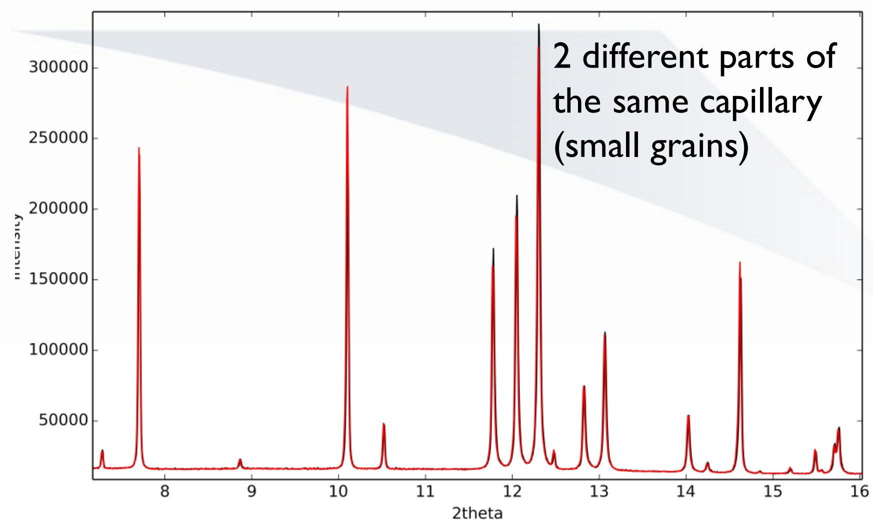
Radiation damage	→	Dose and energy control, fast measurements
Preferred orientation / grain size	➡	Debye Scherrer geometry (capillary)
Homogeneity of the sample		Averaging of different sample parts, grinding, …

Impact of preferred orientation / grain size









Brief introduction to powder X-ray diffraction (XRPD)

MSPD beamline

Synchrotron XRPD benefits

Applications of XRPD to pigments, cements, ceramics or glass

- **Identification of phases**
- **Quantification of phases**
- **In-situ / time-resolved experiments**
- **Summary and other possibilities**

Example #1: Phase identification/quantification of a pigment product

Objective:
Correlate the color properties of a pigment (obtained from different formulations or synthetic conditions) with structural parameters.

SXRPD is used to:
- Identify (and possibly quantify) the segregated phases after the pigment synthesis.
- Check for variations of the **cell parameters** (and cell volume) of the main component, related to possible small differences on the crystal structure.
- Compare between the different products.

Steps:
1) Fill capillaries with the powder samples.
2) Measurement (12 min each sample).
3) **Identification of phases**: Match the **peak positions** to **known substances** that may be expected on the final product.
4) Rietveld fit: cell parameters, quantification.

About the quantification…

Rietveld Quantitative Phase Analysis (RQPA)

Match the peak positions and **intensities**.

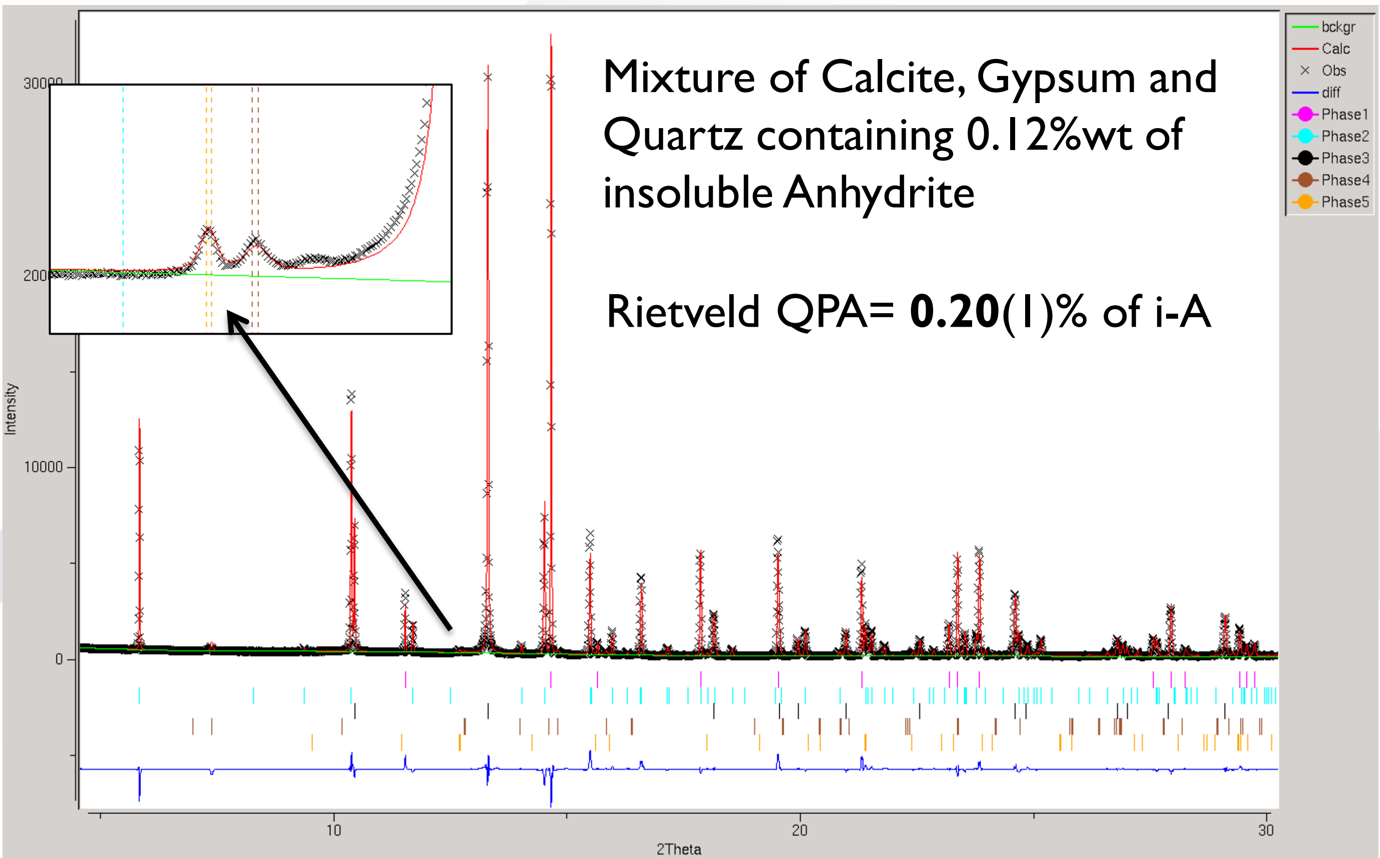
Considerations:

- Crystal structures must be known.
- Quantification of crystalline phases (relative to a total 100%)
- Low accuracy for minor components (<0.5%) which is directly related to the quality of the material, the crystal structure (model) used and the collected data.
- If a **good** RQPA can be performed, the addition of a known amount of an internal standard (well-known substance of similar composition and no amorphous content) can give the absolute wt% and thus quantify the content of amorphous/unidentified phases

L. León-Reina *et al.* (2016) J. Appl. Cryst. 49

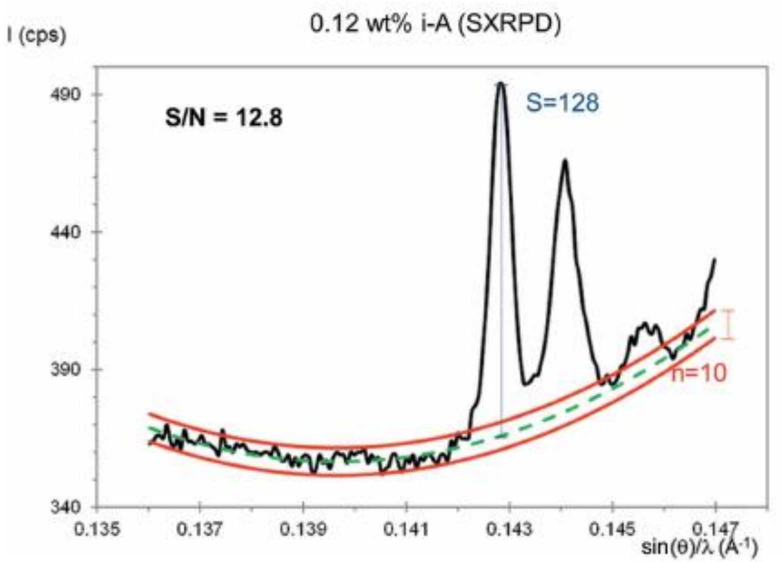
Example #2: Rietveld Quantitative Phase Analysis

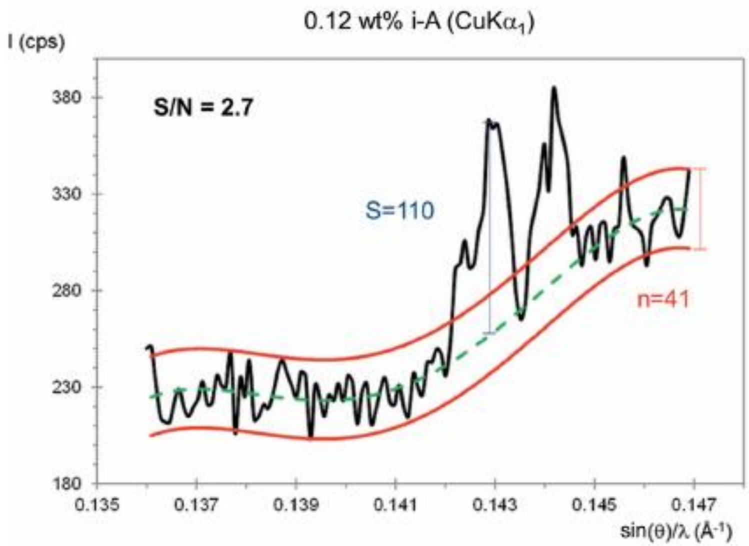
Match the peak positions and **intensities** to known substances that may be expected on the final product. Crystal structures must be known.

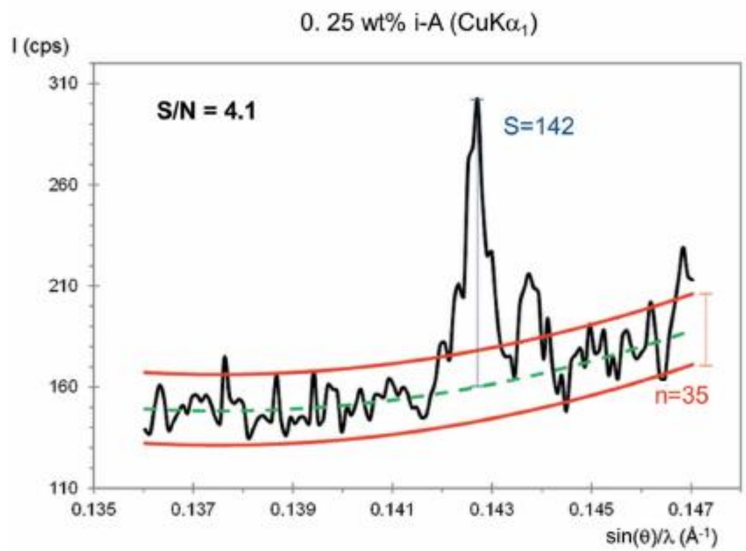


L. León-Reina *et al.* (2016) J. Appl. Cryst. 49

LoD / Quantification







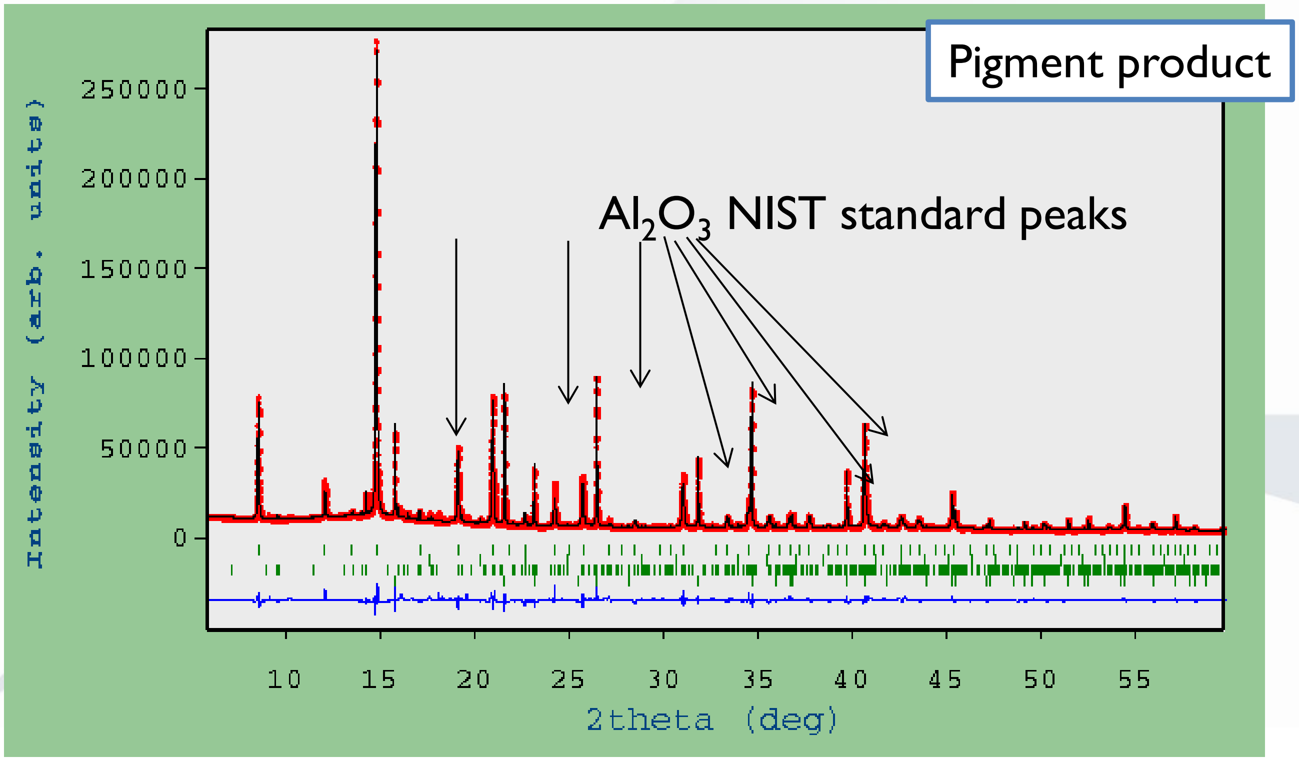
Synchrotron:

- Lower LoD
- Better accuracy on RQPA

L. León-Reina *et al.* (2016) J. Appl. Cryst. 49

Example #1 (cont.): Phase identification/quantification of a pigment product

RQPA with the addition of an internal standard.



RQPA:
Phase1=73.4%
Phase2=0.24%
Phase3=1.97%
Al_2O_3=24.4%

Real weighted Al_2O_3

16% of Amorphous/ unidentified phases

Example #3: In-situ / time-resolved study of ceramic glazes

Objective:
Study of cobalt blue glazes production process for Italian Renaissance terracotta sculptures.

SXRPD is used to:

- Follow phase transformations and evolution with temperature. Fast measurements are required to follow these transformations.
- Compare between the different starting mineral mixtures.

Steps:

1) Fill quartz capillaries with the powder samples.
2) Reproduce conditions of furnaces from XV-XVI century
3) **Identification of phases**: Match the **peak positions** to **known substances** that may be expected on the final product.

A. Zucchiatti. Proposal 2015091398

Example #3: In-situ / time-resolved study of ceramic glazes

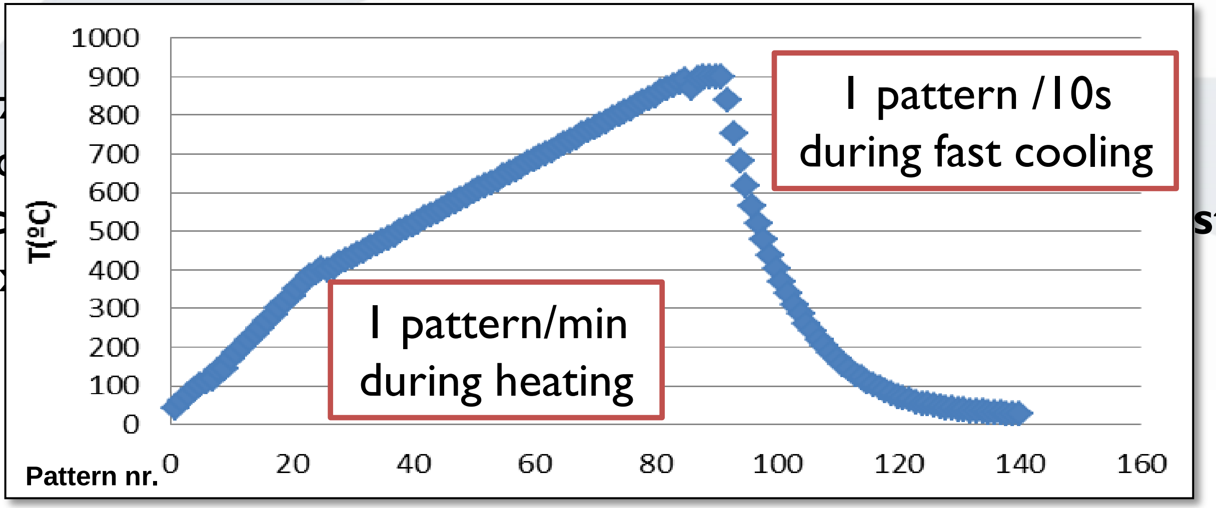
Objective:
Study of cobalt blue glazes production process for Italian Renaissance terracotta sculptures.

What SXRPD can do in this case:

- Follow phase transformations and evolution with temperature. Fast measurements are required to follow these transformations.
- Comparison between the different starting mineral mixtures.

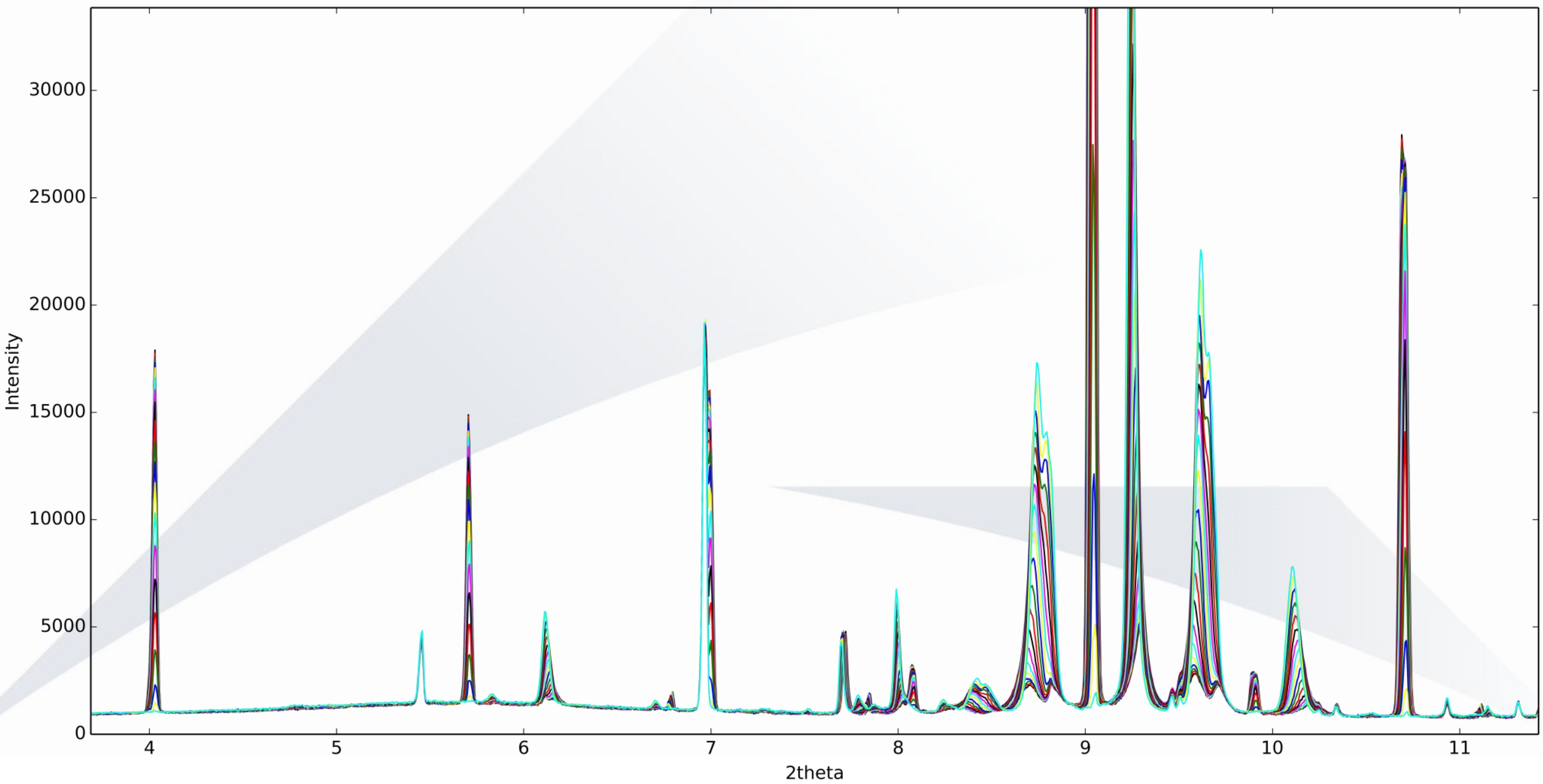
How:

1) Fill quart
2) Reproduc
3) **Identific** **stances** that may be e



A. Zucchiatti. Proposal 2015091398

In-situ study of cobalt blue glazes production process



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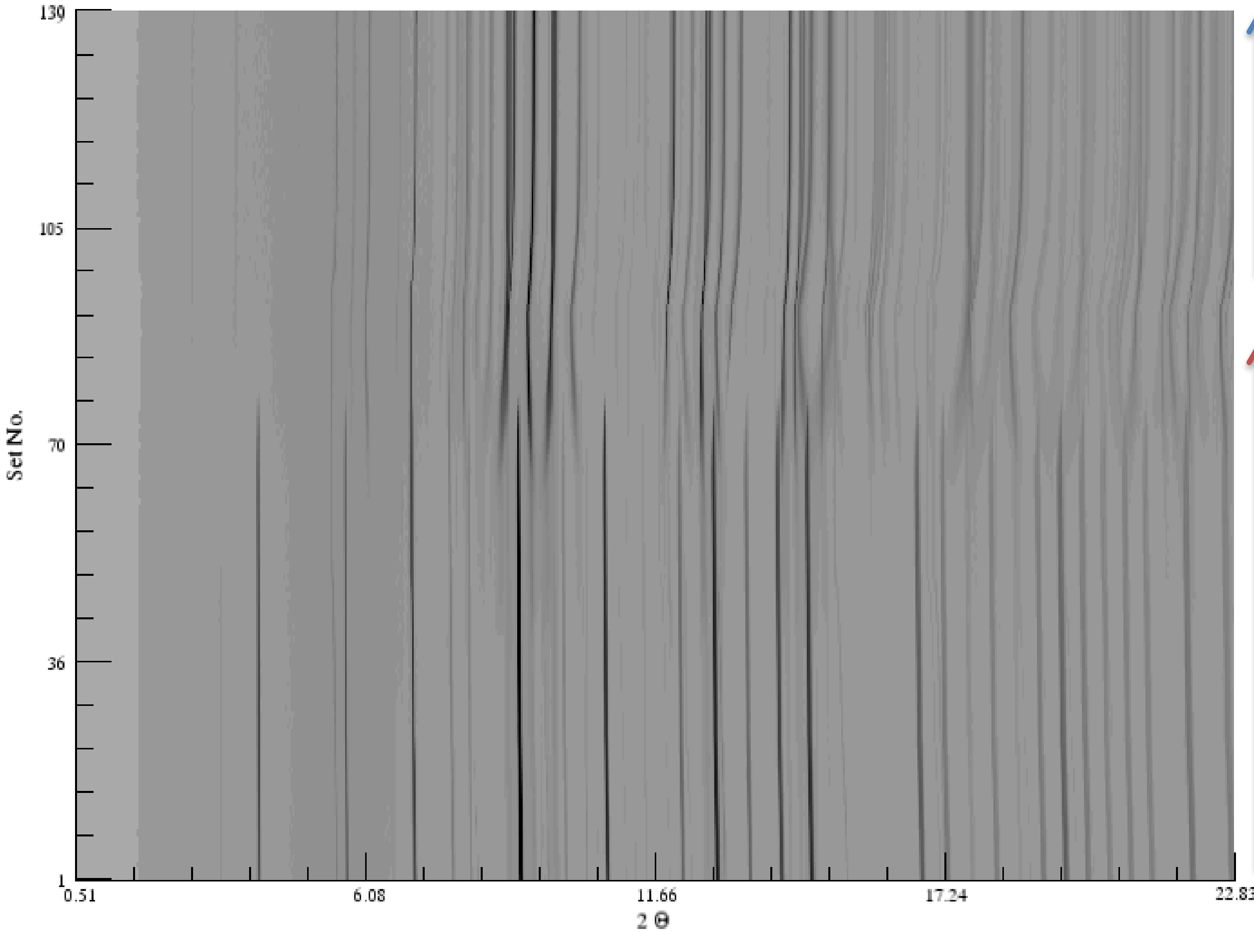
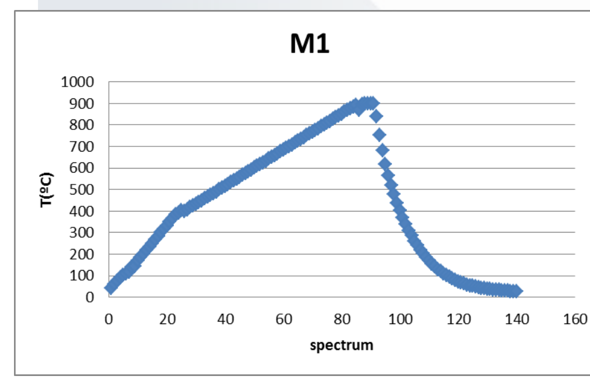


cooling

heating



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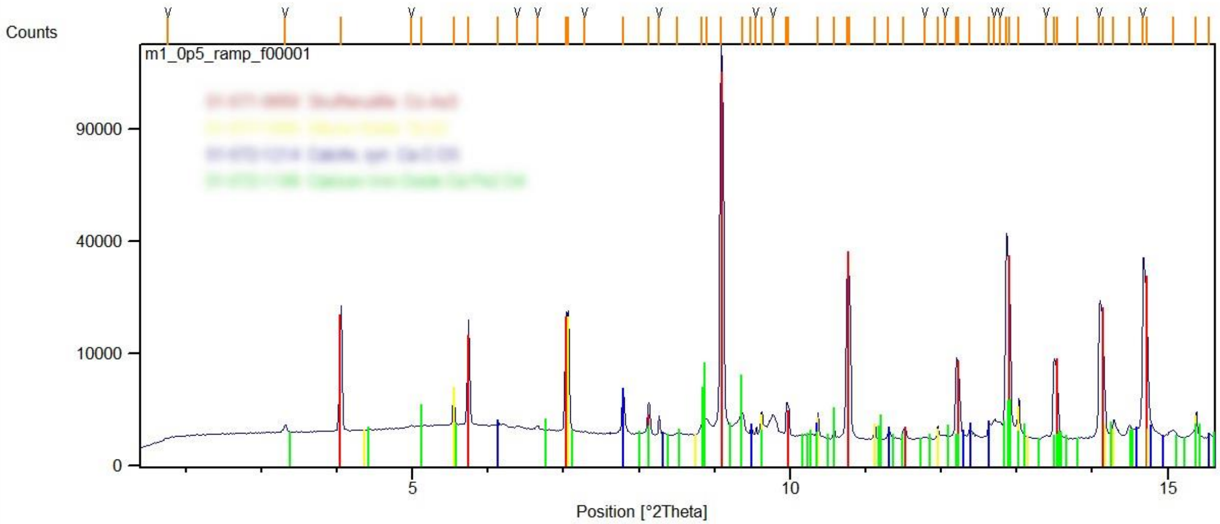
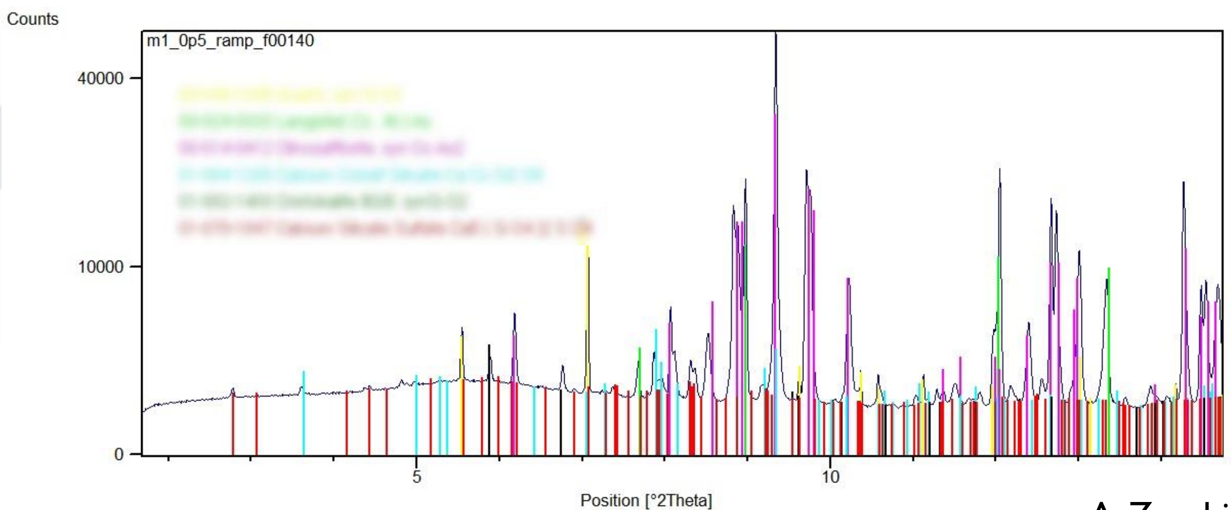


Initial pattern



Final pattern

A. Zucchiatti. Proposal 2015091398

Example #4: In-situ / time-resolved study of C_4AF phase in different environments

Objective:
Understand the hydration mechanisms of new eco-cements based on calcium sulfoaluminate which contain different polymorphs of ye'elimite with C_4AF.

SXRPD is used to:
- Follow the hydration process in time.
- Minimize microabsorption effects (useful for quantification) by using high energy SR.
- Compare between the different starting compositions.

Steps:
1) Fill capillaries with the mixtures solid-water.
2) Measurements of 15 minutes to get good s/n ratio.
3) **Identification of phases**: Match the **peak positions** to **known substances** and follow the evolution.
4) RQPA

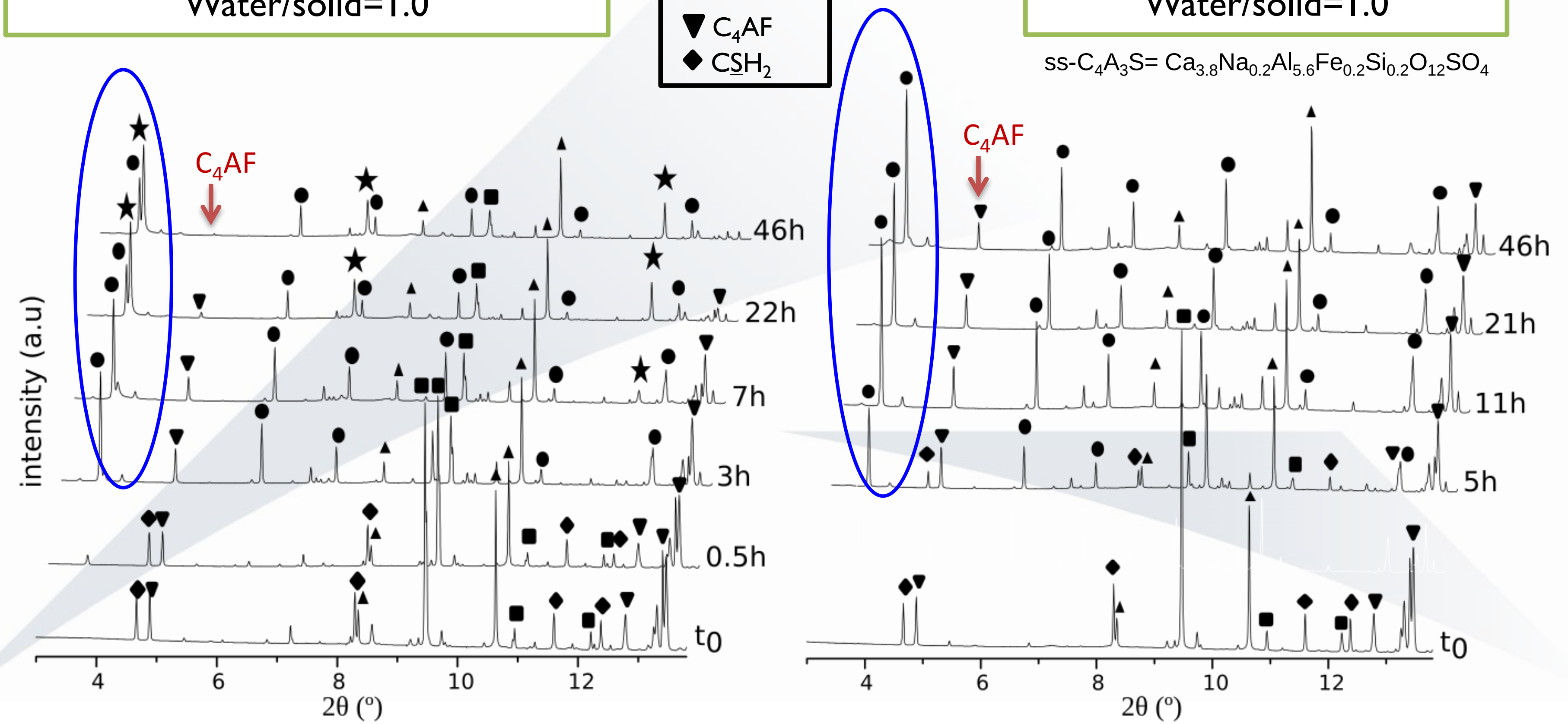
Cuesta A *et al.*(2015), Constr. Build Mater., 101, 818-827.

XRPD on cements, pigments, ceramics or glass

C_4AF
"stoichiometric" ye'elimite (st-$C_4A_3\underline{S}$)
Gypsum
Water/solid=1.0

C_4AF
"doped" ye'elimite (ss-$C_4A_3\underline{S}$)
Gypsum
Water/solid=1.0

ss-C_4A_3S= $Ca_{3.8}Na_{0.2}Al_{5.6}Fe_{0.2}Si_{0.2}O_{12}SO_4$



The dissolution of C_4AF was inhibited by the presence of the doped **ss-ye'elimite** and for this reason only small quantities of AFm were quantified

Cuesta A *et al.*(2015), Constr. Build Mater., 101, 818-827.

Example #5: Micro-XRPD to identify materials

Objective:
Study the changes in the methods of production and materials of stained glass *grisailles* from different historical periods and its relation to the conservation state of the materials.

SXRPD is used to:

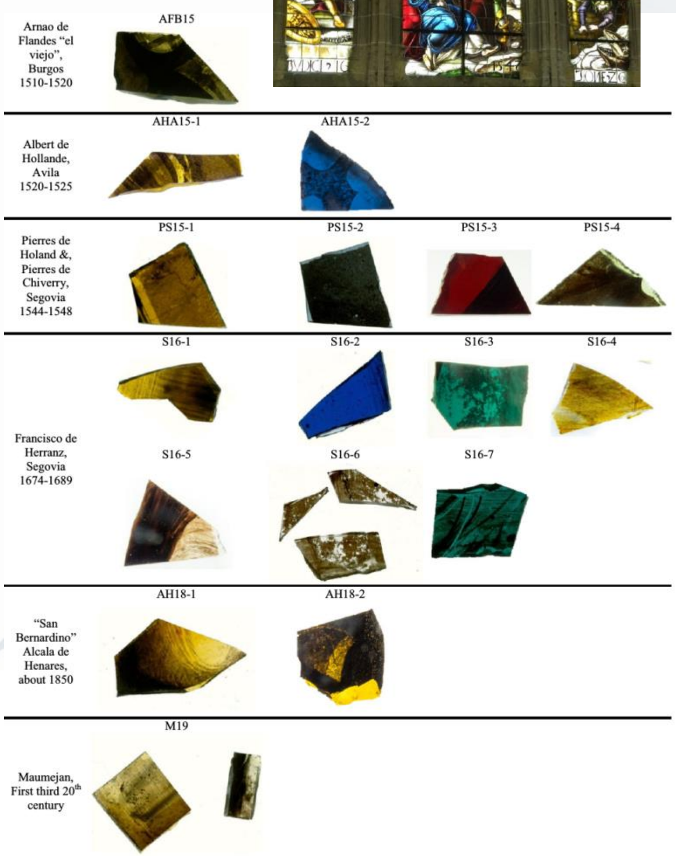
- Measure selected points of the sample with a small beam (15x15µm) to get the information of these specific regions.
- Measure samples that are highly absorbing (contain Pb)

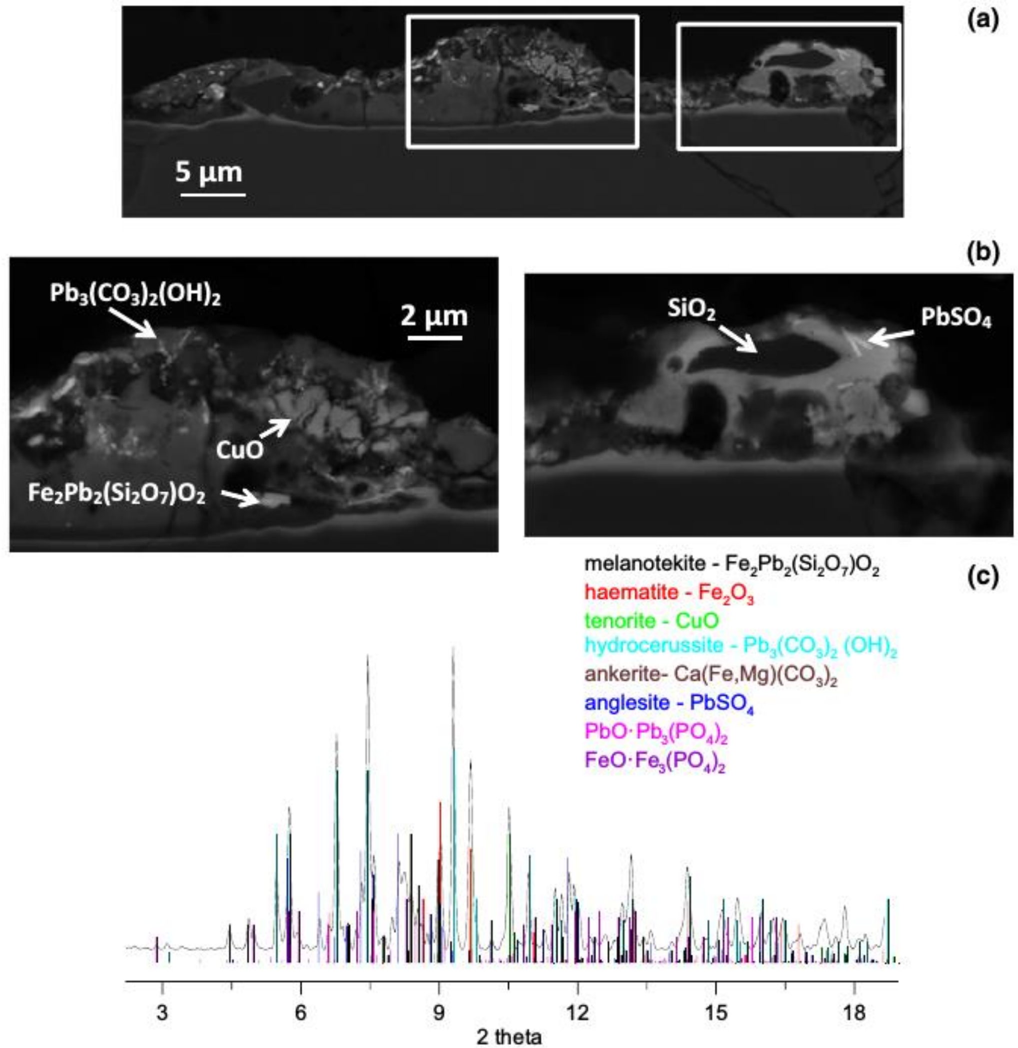
Steps:

1) Polished thin cross sections (in this case 200µm) of the stained glasses are mounted on the measurement stage.
2) **Selection of the measurement points** with the on-axis visualization system
3) Collection of the patterns with the 2D detector and radial integration of the images to obtain 1D powder patterns
4) **Phase identification**.

T. Pradell *et al.* (2016) International Journal of Applied Glass Science, 7, 41–58

Materials, techniques and conservation of historical stained glass *grisailles* (µXRPD)





T. Pradell *et al.* (2016) International Journal of Applied Glass Science, 7, 41–58

Summary of applications and possibilities of SXRPD

- Single measurement of powder samples
- Time-resolved experiments
- Point-selection/mapping of free standing samples

Phase identification

Phase quantification

Structural studies

Unit cell
Crystal structure determination

Microstructural studies

Crystallite size/strain
(not-absolute, sample comparison)

Aplicaciones de la difracción de polvo a la identificación y caracterización de materiales

Thank you!

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MSPD beamline team
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