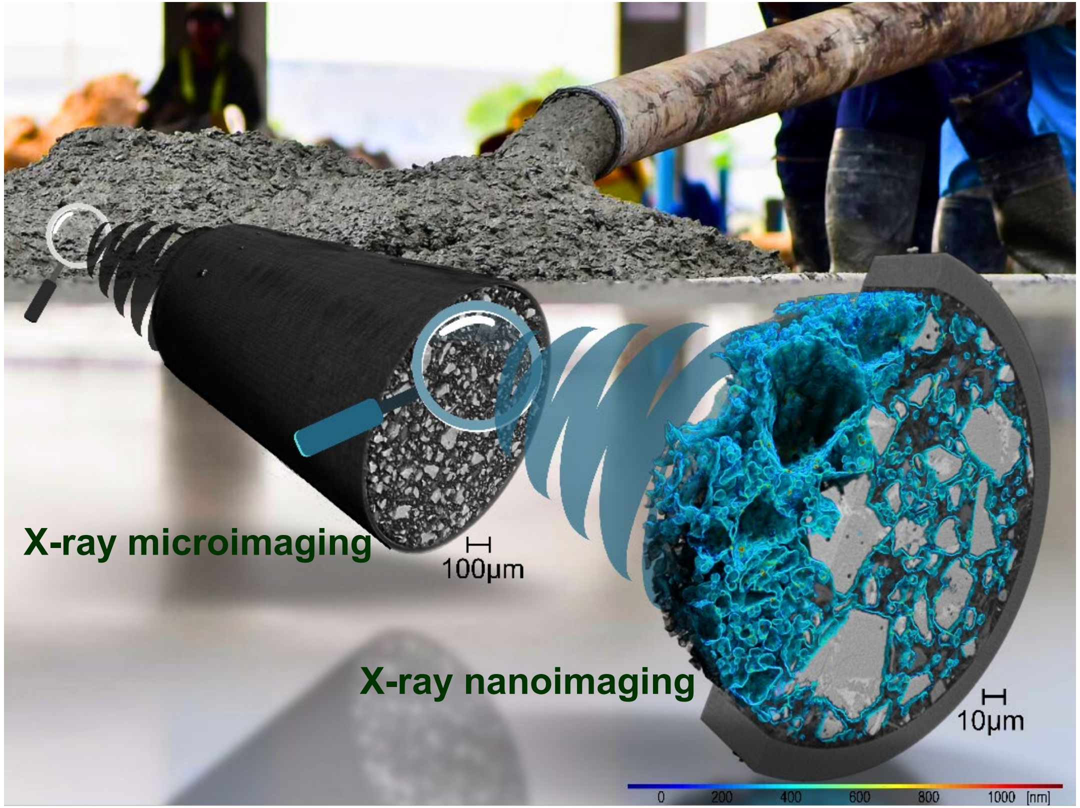
UNIVERSIDAD DE MÁLAGA

Multilength Scale Relevant Imaging of Cement Hydration

Miguel A. G. Aranda
Depart. Química Inorgánica, Universidad de Málaga, 29071-Málaga, g_aranda@uma.es



Outline

1. The relevant societal challenge #2

2. Concrete: length scales #4

3. Caveat about data analysis #1

4. **4D synchrotron nano-CT** (near-field ptychographic imaging) #12

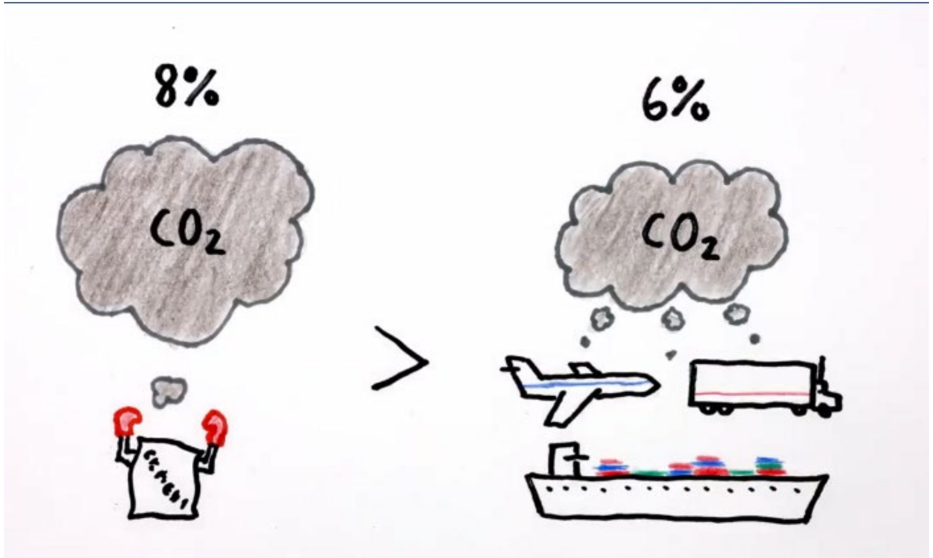
5. CoDI at ALBA-II #1

6. Summary and acknowledgement #1

UNIVERSIDAD DE MÁLAGA

1. Problem #1

To decrease CO_2 footprint / emissions (direct & indirect)



Portland cement (PC) world production is **~4 Gt/yr, 4.4 Gt in 2020**. 3441 PC integral plants in the world, 33 in Spain.
PC production is expected to range 4-8 Gt/yr by 2100, depending upon the world growth pattern(s).

On average, for every ton of type-I PC, ~0.95 CO_2 t are released, from (i) limestone decomposition, (ii) burning fuel, and (iii) electricity consumption for grinding. This translates into **~7-8% of the total anthropogenic CO_2** emissions, **3.5 Gt/yr.**

600 Millions house units are needed by 2040. 40 M/units per year. The average house unit size in Hong Kong is 33 m^2 and in the USA/Australia is 230 m^2. The average size of a slum room/unit is ~9 m^2, and there are 1.2-1.5 billion people living in slums. Finally, Africa is predicted to increase from 1.2 billions to 2 billions, in next 30 years. This means many houses (or immigration)…

1. Problem #2. To decrease Construction and Demolition Wastes (CDW)

The Empire State Building in 1932;

- Today, the concrete use is **~20-25 Gt/yr**.
- The estimated world concrete stock is **315 Gt** which results in 0.3 Gt/yr of CDW.
- The newest model predicts a skyrocket increase of CDW to **~30 Gt/yr by 2100**.

This could not be processed as aggregates, as it will be more than two times the predicted need.

→ Cements with lower CO_2 footprint and more durable/sustainable.

Todays expected service live of buildings and infrastructures: <100 years!

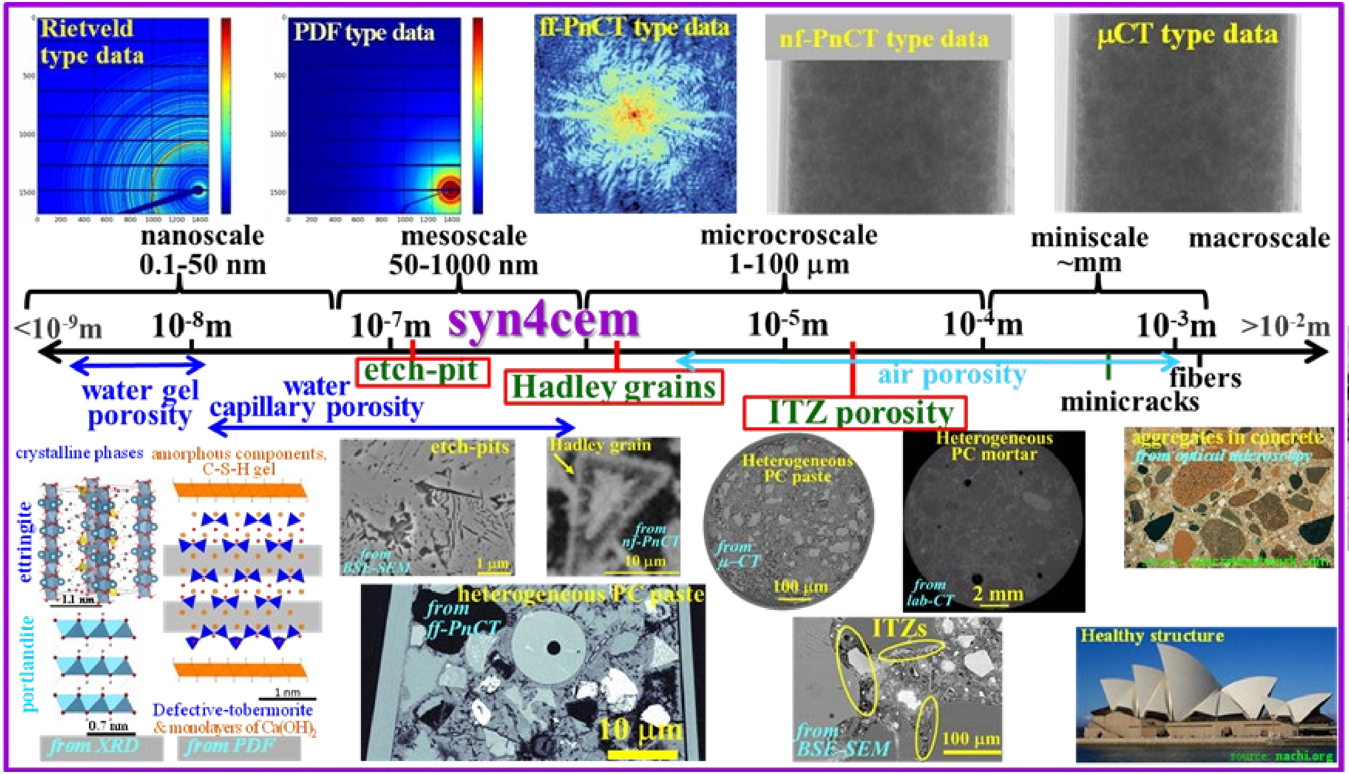
UNIVERSIDAD
DE MÁLAGA

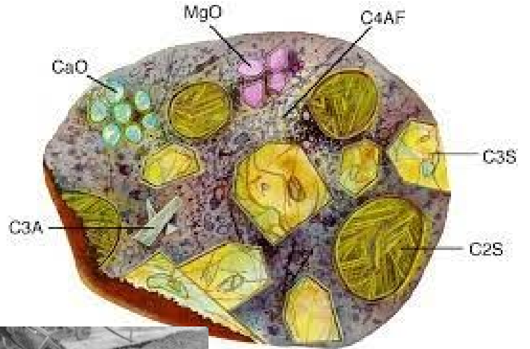
Outline

1. The relevant societal challenge #2
2. Concrete: length scales #4
3. Caveat about data analysis #1
4. **4D synchrotron nano-CT** (near-field ptychographic imaging) #12
5. CoDI at ALBA-II #1
6. Summary and acknowledgement #1

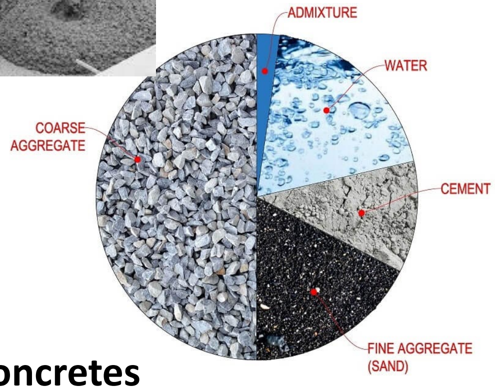
UNIVERSIDAD
DE MÁLAGA

2. Concretes/mortars/pastes: length scales – multiscale/multimodal





concrete



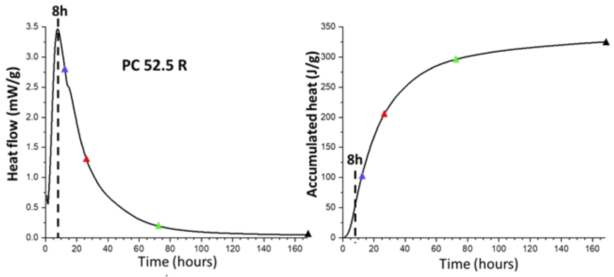
Complexity increases from **cement pastes, to mortars, to concretes, to reinforced concretes**

RESEARCH: To replace the largest fraction of Portland clinker by other materials with much lower CO_2 footprints: **FA, Slag, CC, …**

Cement hydration as seen by:

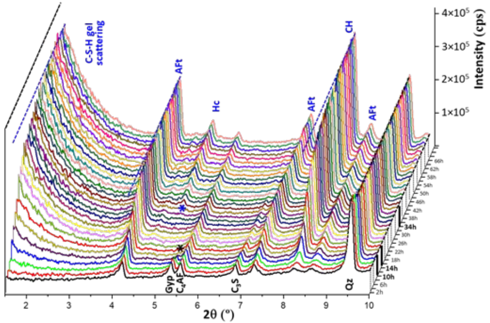
→ **Calorimetry**: isothermal

(~5 kB per dataset, #1, 1960' – continues)



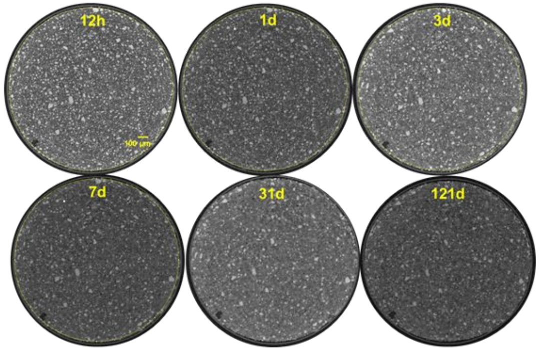
→ **Powder diffraction**: SXRPD & LXRPD

(~15 kB per dataset, #20-30, 1990' – continues)



→ **µCT**: synchrotron & lab CTs

(~5 GB per dataset, #3-10, 2010' – continues)



Advantages

Calorimetry:
- simple, robust
- continuous, fast
- widely-available
- well-established
- many data available
- provides an envelope

Powder diffraction:
- widely-available, fast
- well-established
- PC phase-dependent information
- hydrate formation information
- may give an overall amorphous content

µCT:
- fast (synchr. µCT)
- sensitive to the particle sizes
- sensitive to amorphous phases
- microstructure-related information
- porosity data

Main drawbacks

Calorimetry:
- compound function (of all reactions)
- unrelated to microstructure

Powder diffraction:
- blind to amorphous components
- the reactivity of a given phase is integrated for all particle sizes
- unrelated to microstructure

µCT:
- **limited spatial resolution**, ~1µm (for our needs)
- **very limited contrast** (between hydrated phases)

note: data processing and analysis requirements skyrocketed to the bottom (***data deluge***)

UNIVERSIDAD
DE MÁLAGA

Caveat

Difficult and challenging (but rewarding) problems require a wide set of techniques to **extract relevant information.**
But we are always adding (not replacing!) characterization techniques. **Is this sustainable?**

*BUT, there is already a **tsunami of data** at large facilities and at laboratory imaging equipments* $\rightarrow$ *ML approaches*

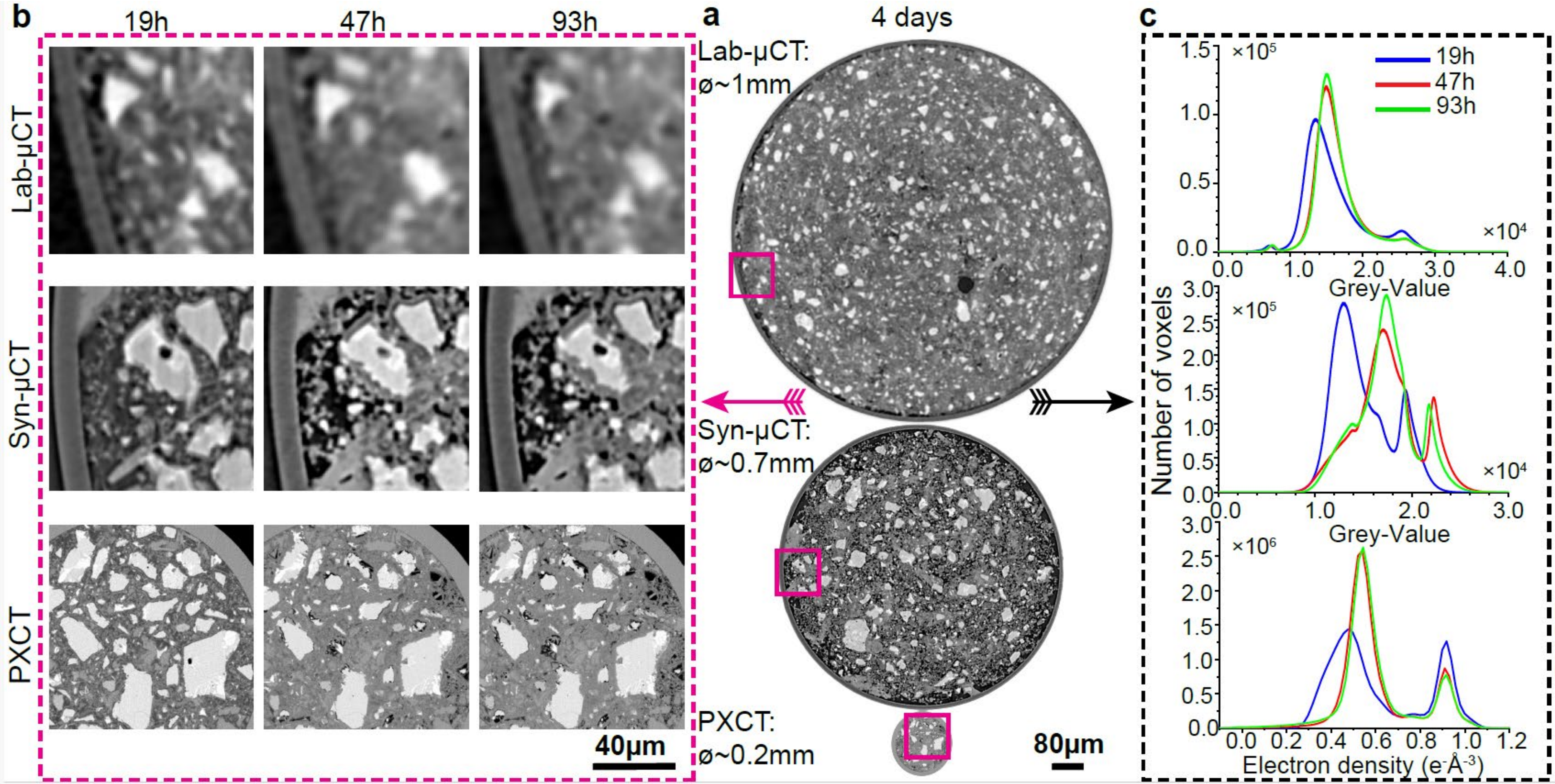
ONE EXAMPLE FOR SYNCHROTRON DATA (but lab data is not very far):

Our recent work: Shirani, et al. "Influence of curing temperature on belite cement hydration: a comparative study with Portland cement", *Cement and Concrete Research*, **2021**, 147, 106499. (About one year of data analysis).

Contained (in addition to several other characterization techniques):
34 X-ray synchrotron tomograms amounting 743.4 GB of reconstructed data &
18 Rietveld quantitative phase analyses of Laboratory Mo-Kα_1 powder diffraction data
Raw data could not be deposited at Zenodo as it only allows 100 GB per doi

UNIVERSIDAD DE MÁLAGA

Spatial resolution vs. time resolution vs. contrast in the components vs. FoV vs. relevant conditions



syn4cem sketch

CO_2 emission reduction

Technological leap

Mechanistic understanding

1d cement activation by admixtures

Outer vs. Inner C-S-H gel

Former descriptors f (admixtures)

Scientific breakthrough

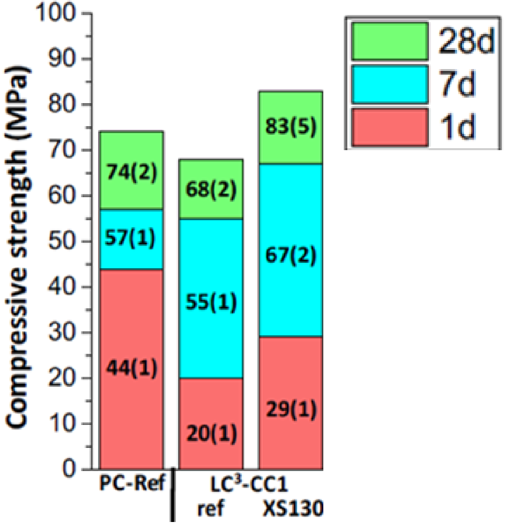
early age cement hydration

- C-S-H gel growth rate –related
- C_3S/alite dissolution rate -related

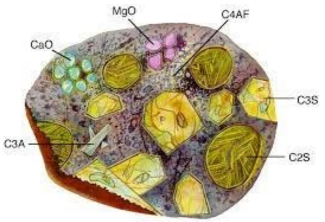
Technique development

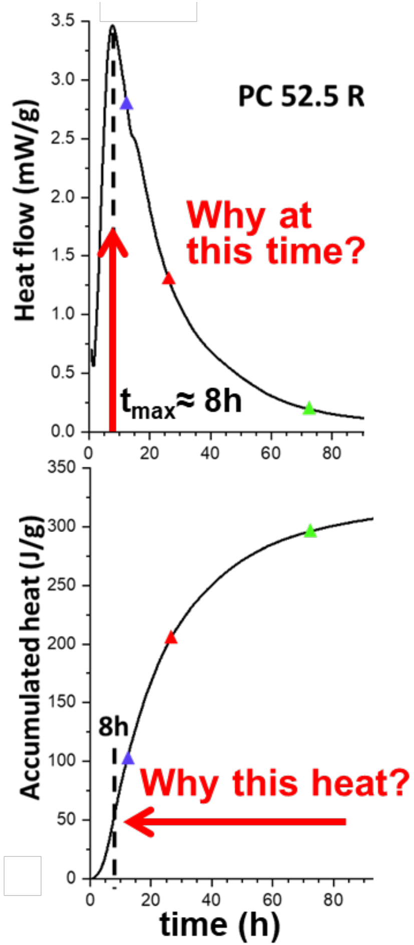
Fast HR relevant 4D nanoimaging

- 100min
- 100nm
- 200×30μm
- 30me⁻Å⁻³



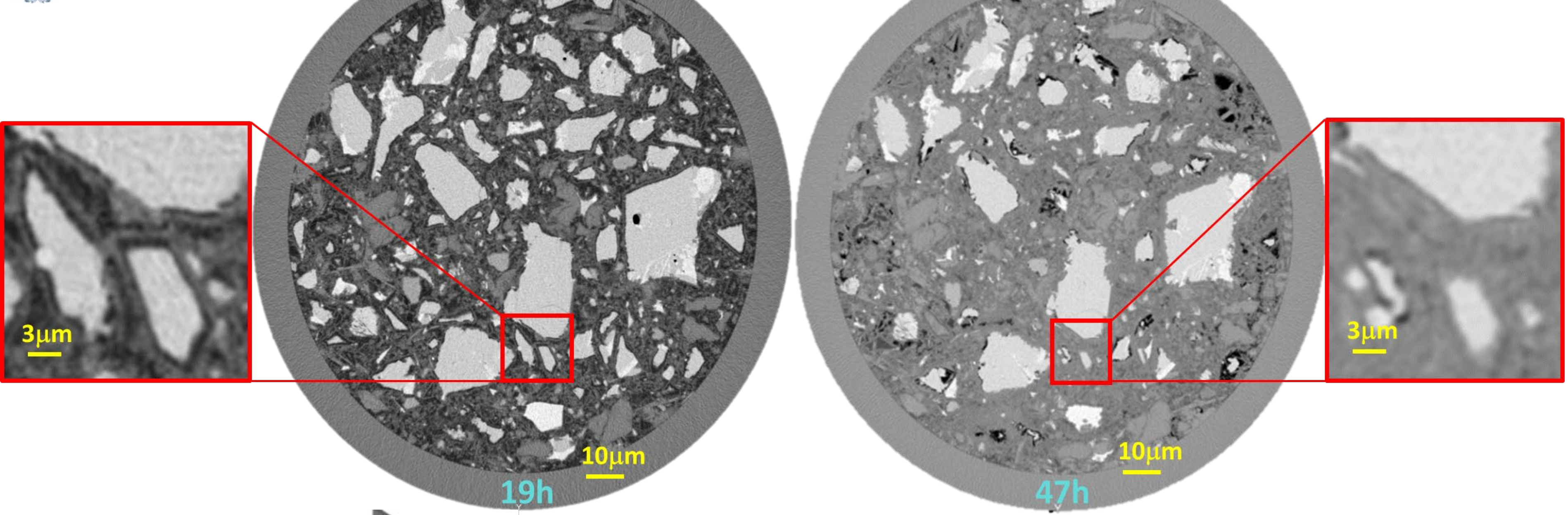
Sound development of admixtures

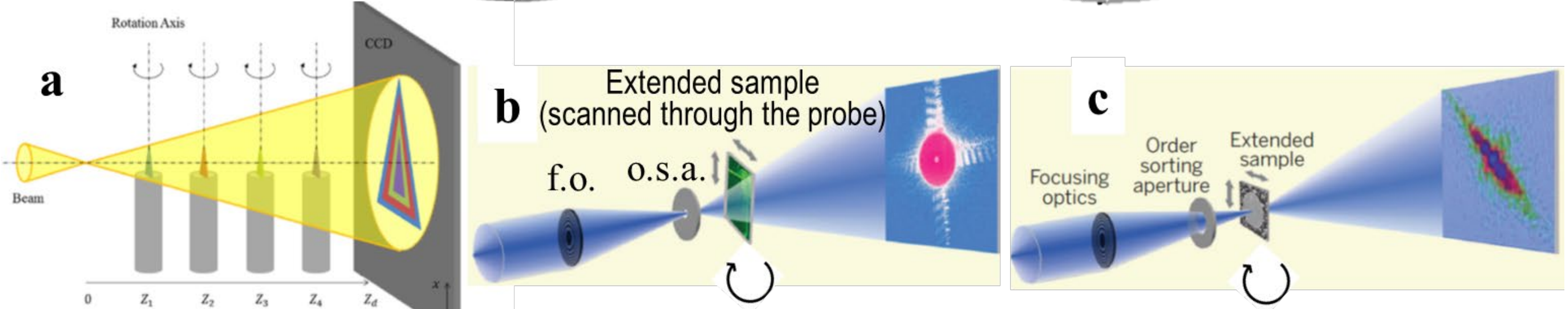




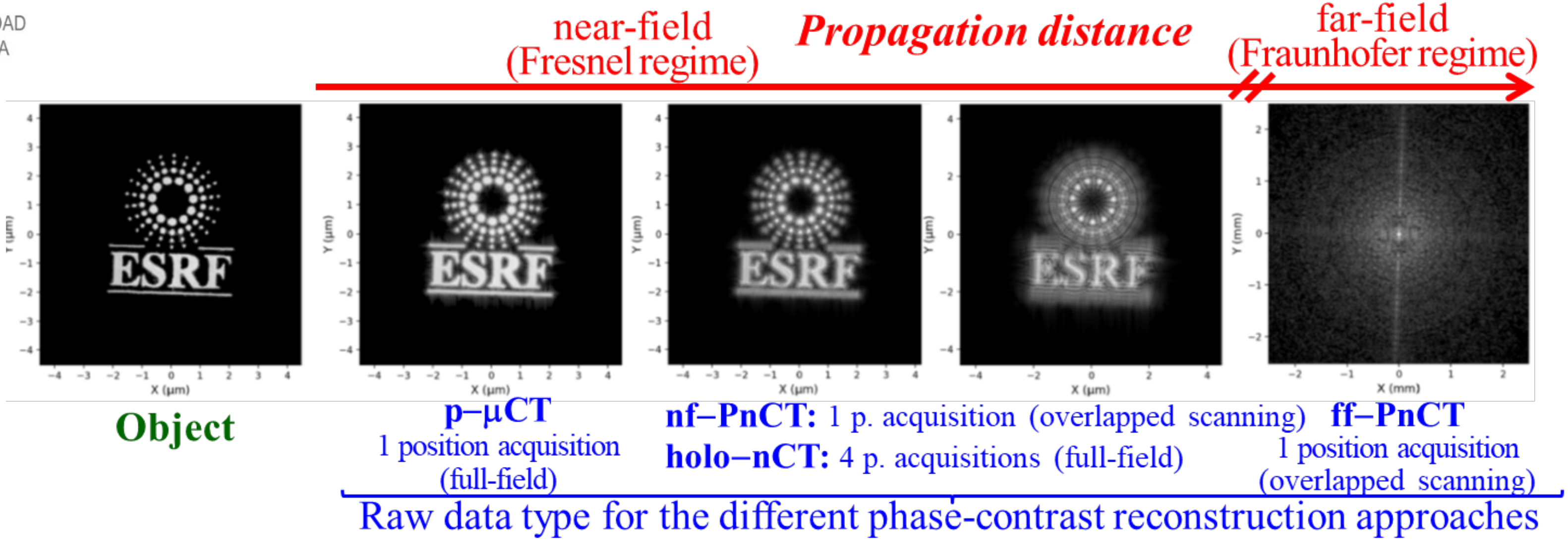
1. The relevant societal challenge #2
2. Concrete: length scales #4
3. Caveat about data analysis #1
4. **4D synchrotron nano-CT** (near-field ptychographic imaging) #12
5. CoDI at ALBA-II #1
6. Summary and acknowledgement #1

UNIVERSIDAD DE MÁLAGA





holo-nCT nf-PnCT ff-PnCT



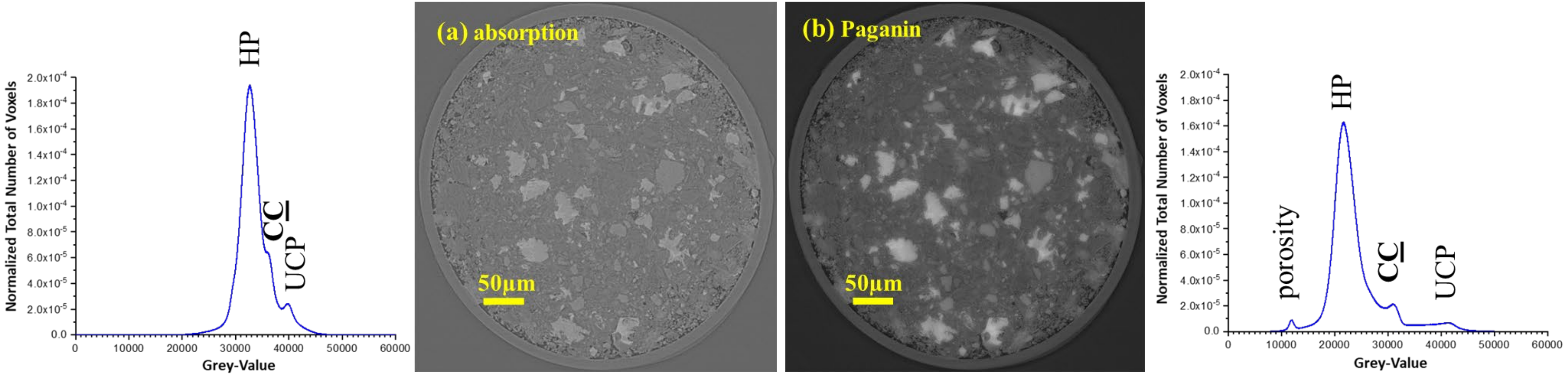
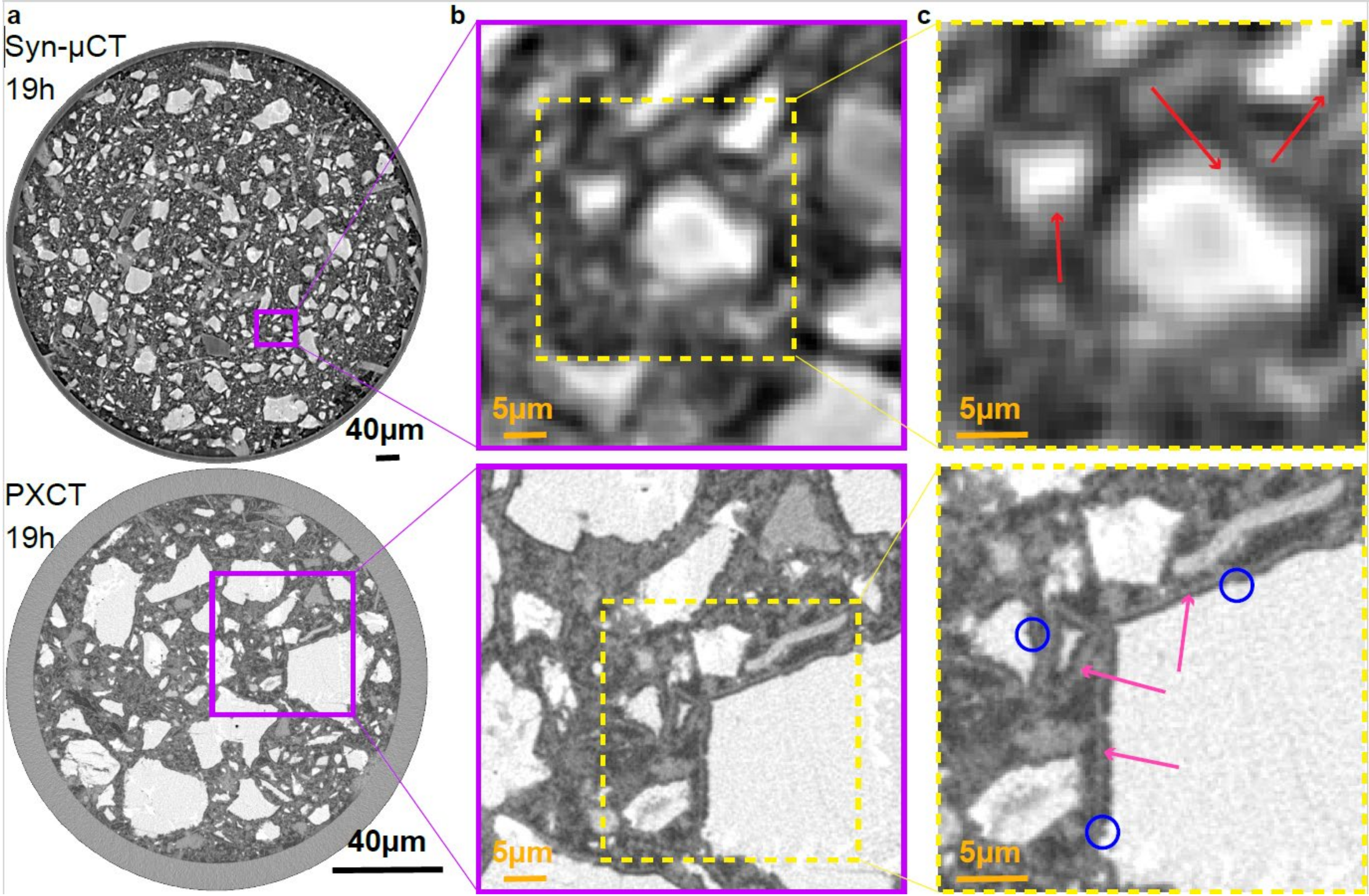
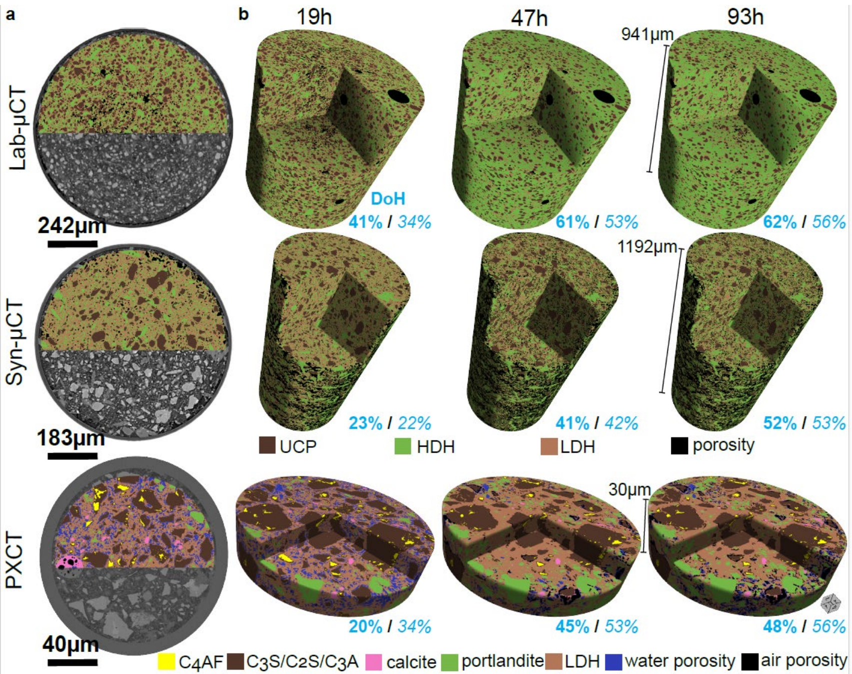
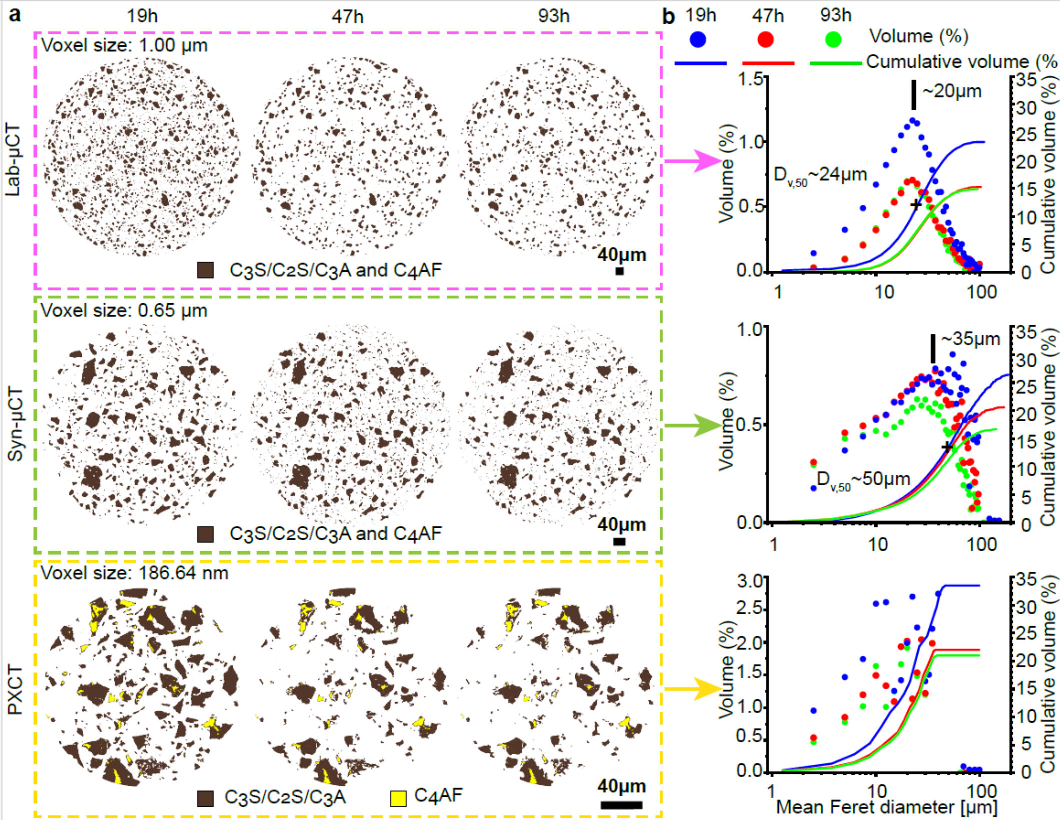


Fig. Attenuation vs. Paganin synchrotron p-µCT


a
Syn-μCT
19h
40μm
b
5μm
c
5μm
PXCT
19h
40μm
5μm
5μm

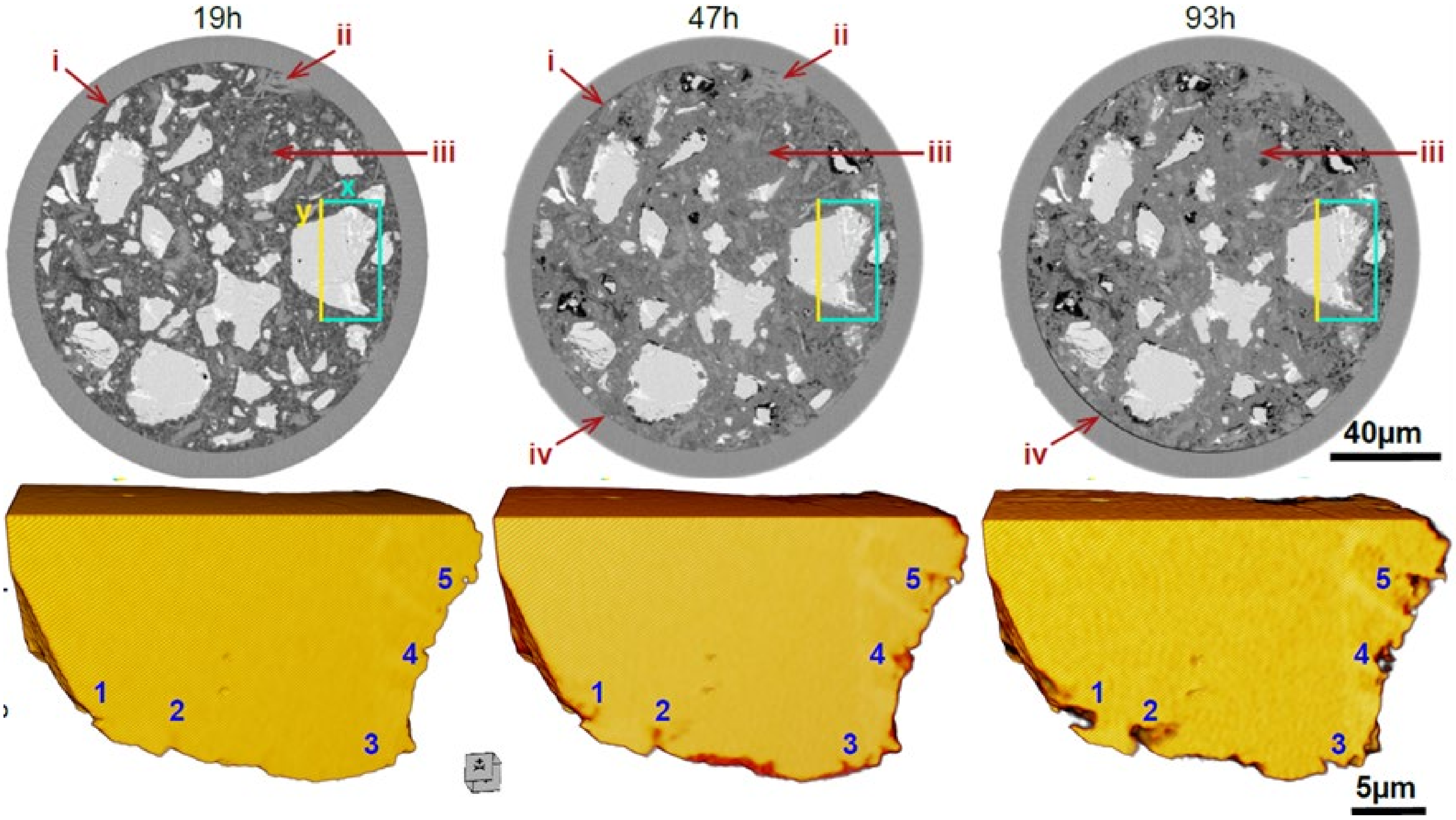


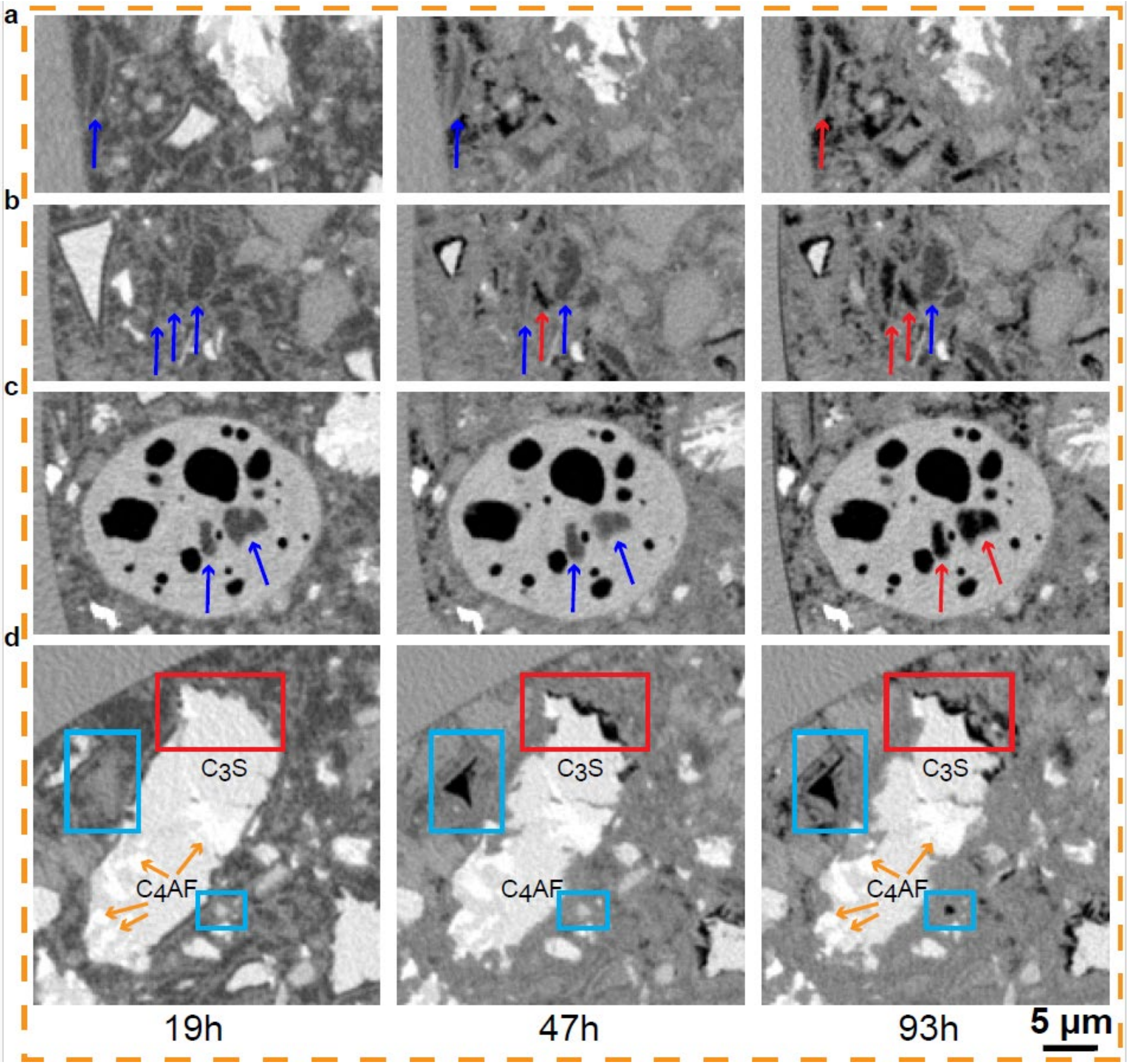


Shirani, et al. 2023. Nat. Comm. Doi: 10.1038/s41467-023-38380-1

UNIVERSIDAD DE MÁLAGA

4D nanoimaging by near-field ptychotomography. FoV=180×30 μm. Spatial resolution=3h. Time resolution=3h per tomo. Excellent component contrast. Relevant conditions: just ok.

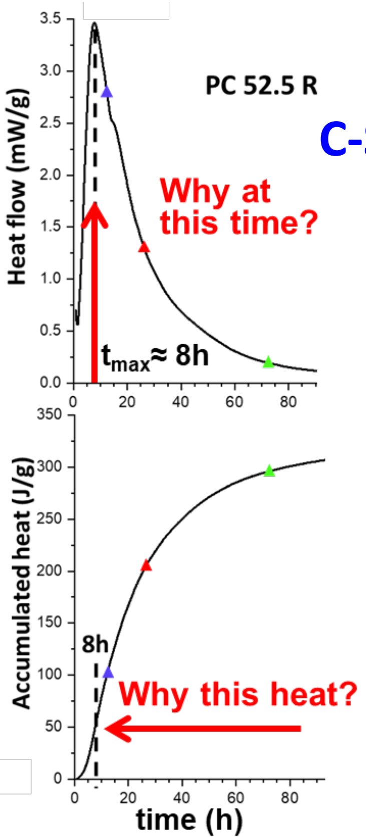


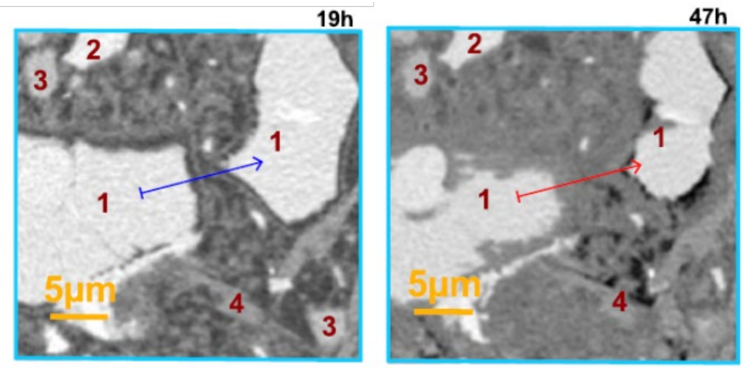

a
b
c
d
C3S
C3S
C3S
C4AF
C4AF
C4AF
19h
47h
93h
5 µm

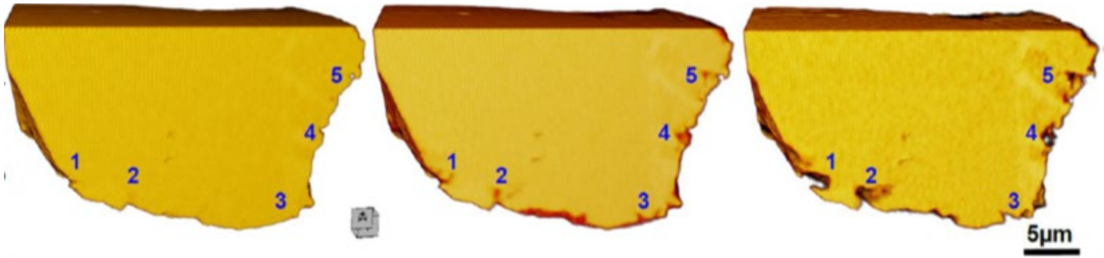
Main features to explain the acceleration-deceleration transition

C_3S
- ♦ Particle size-dependent spatial dissolution rate(s)
- ♦ Defects-enhanced spatial dissolution
- ♦ Particle size-dependent etch-pit growth rate(s)

C-S-H gel
- ♦ Decrease of diffusion because of shell growth and densification
- ♦ Gel growth rate drops because of impingement



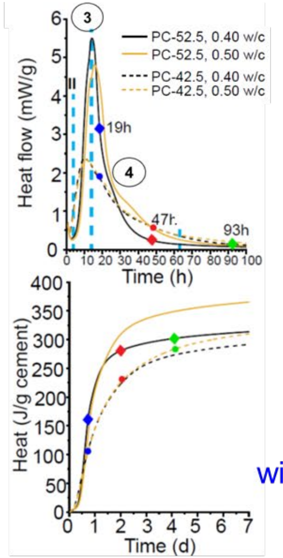


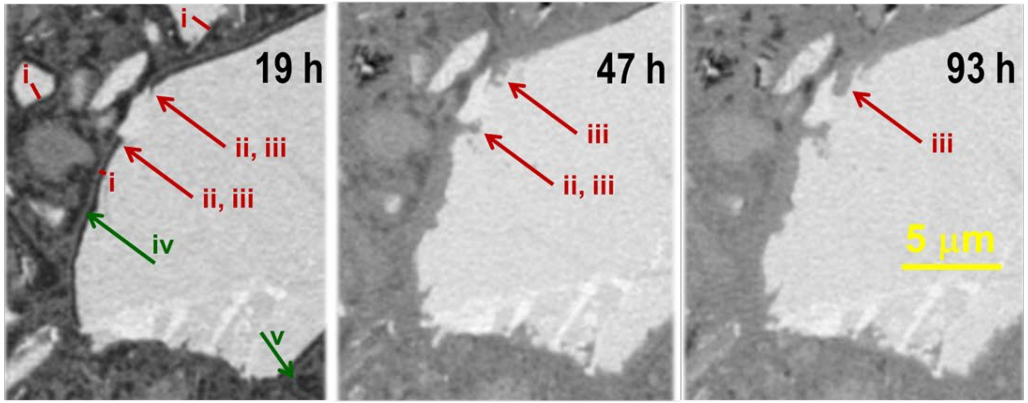


Highlights of our recently published work: *4D nanoimaging of cement hydration (2023)*

UNIVERSIDAD DE MÁLAGA

Shirani, et al. 2023. Nat. Comm. Doi: 10.1038/s41467-023-38380-1

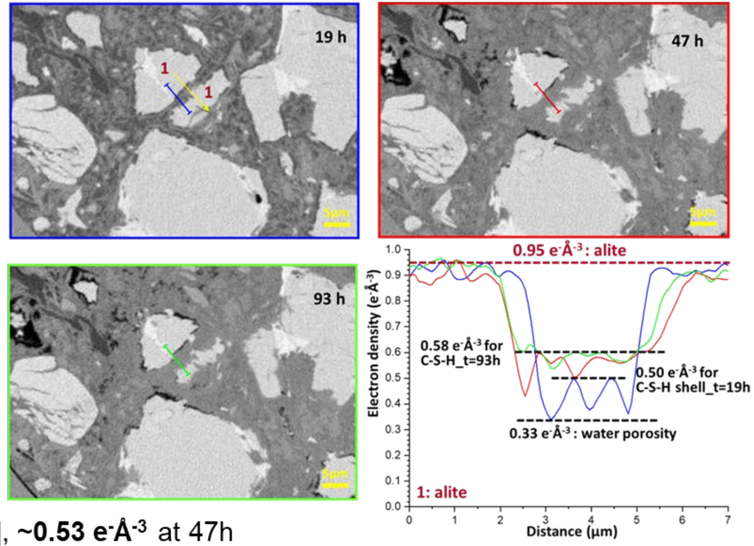




The key five numbers,

with **270 nm** of spatial-resolution

180 min of time-resolution



(i) **~100 nm/h** (indirect) spatial dissolution rate for particles smaller than 3 µm [4-19h, ③]

(ii) **~33 nm/h** (indirect) spatial dissolution rate for particles larger than ~6 µm [4-19h, ③]

(iii) **20-25 nm/h** (direct) spatial dissolution rate for particles larger than ~8 µm [19-47h, ④]

(iv) **~41 nm/h** (direct) etch-pit growth rate for particles larger than ~8 µm [19-47h, ④]

(v) **~0.47 $e^-Å^{-3}$** (direct) C-S-H gel shell electron density for particles larger than ~10 µm [at 19h, ④], **~0.53 $e^-Å^{-3}$** at 47h

Fast high-resolution relevant 4D nanoimaging

spatial resolution

~270 nm

100 nm

temporal resolution

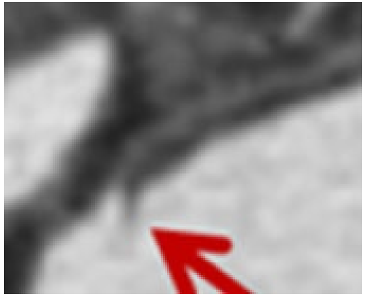
180 min

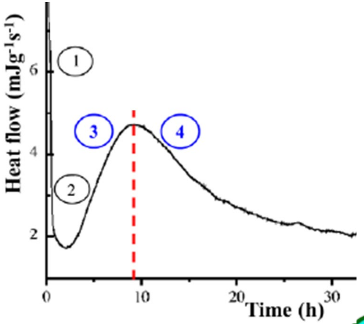
100 min

current (best) values

syn4cem target values

syn4cem relaxed values





(H×V FoV)

200×30 μm

200× 20-15 μm

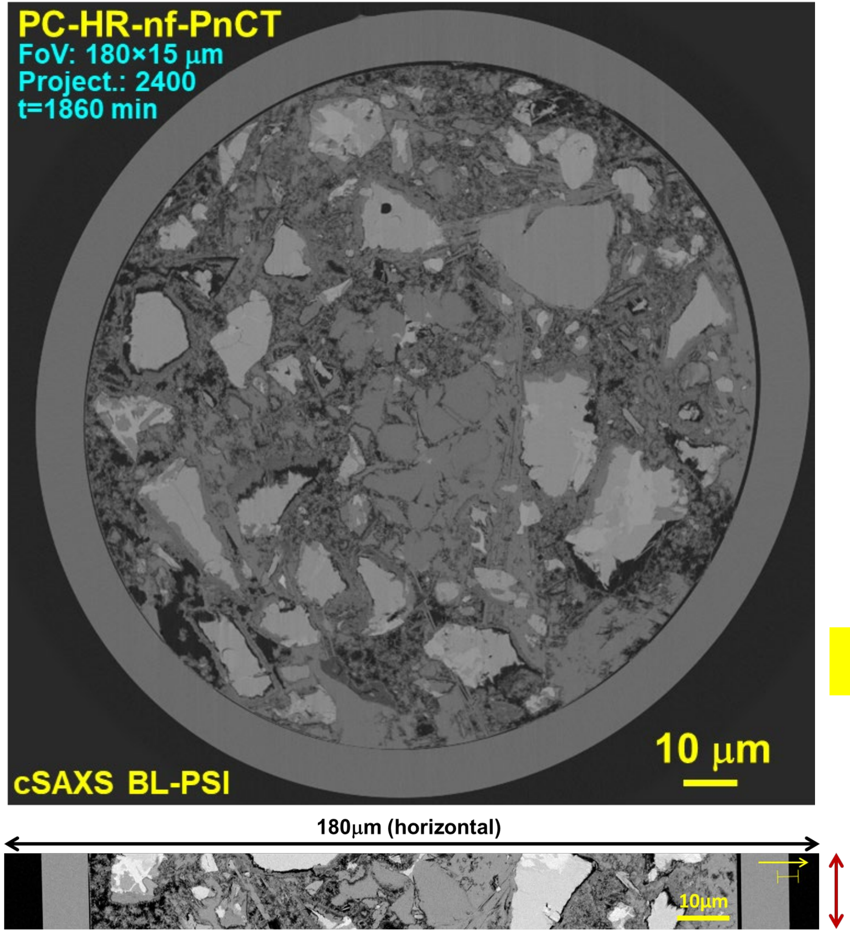
relevant conditions

30 me-Å-3, (≈CNR)

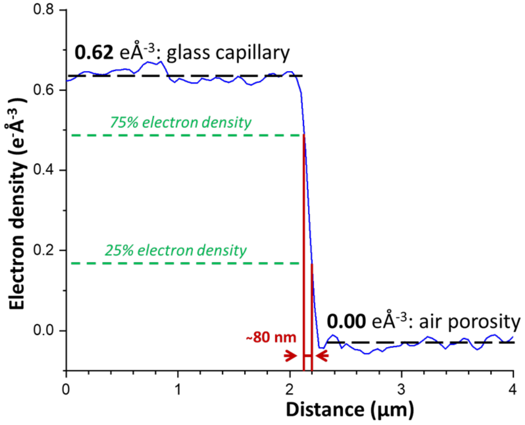
~40 me-Å-3, if needed

more than data → scientific information

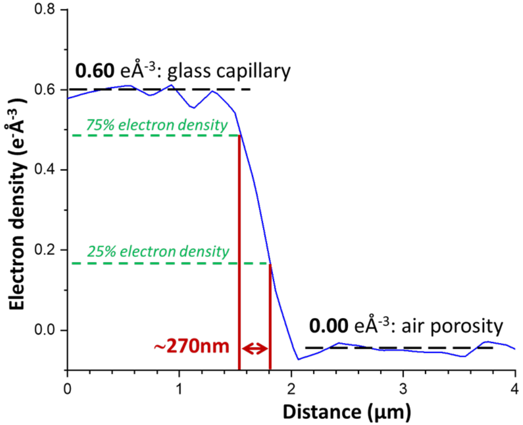
Preparatory High-Resolution nf-PnCT experiment at cSAXS in 2023



HR-nf-PnCT
voxel size: 55 nm



standard-nf-PnCT
voxel size: 186 nm



The challenge, **fast** HR-nf-PnCT: **2000 → 100** min

unpublished

UNIVERSIDAD DE MÁLAGA

High Resolution nf-PnCT (of very large samples, for nCT)

♦ *nanoCTs of voxel size: 55 nm, spatial resolution: ~90 nm*

→ FZP of highest focusing performances

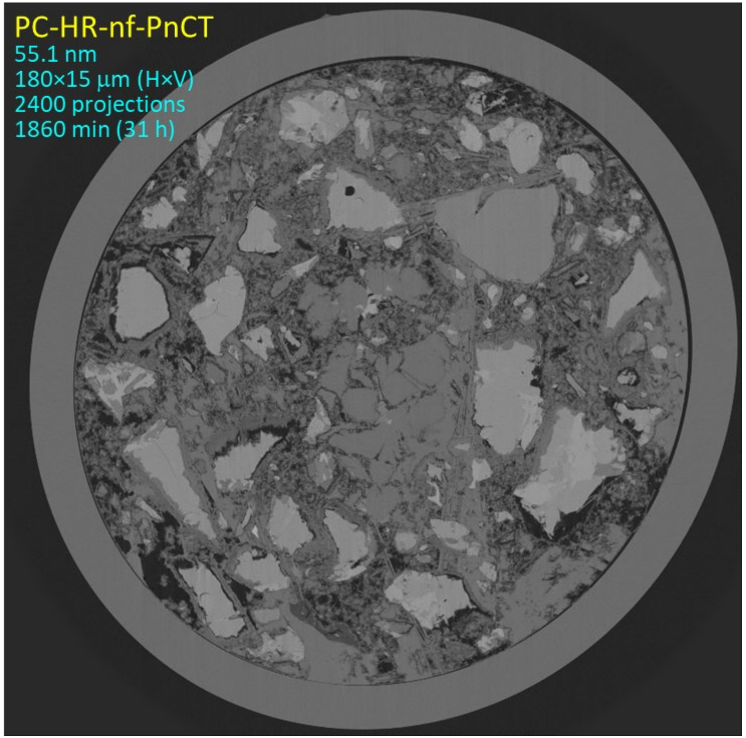
→ Maximum sample-detector distance

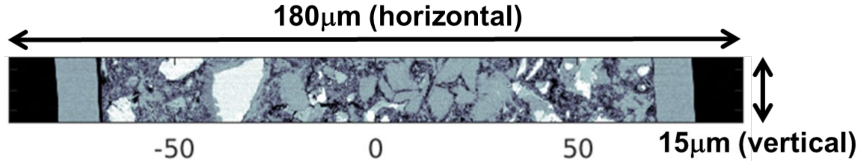
→ Shortest focus-sample distances, within near field

→ 2400 projections   Crowther limits:

5140 projections for 180μm @ 55nm. Hence, 2400 was **47%**

1520 projections for 180μm @ 186nm. Hence, 420 was **28%**





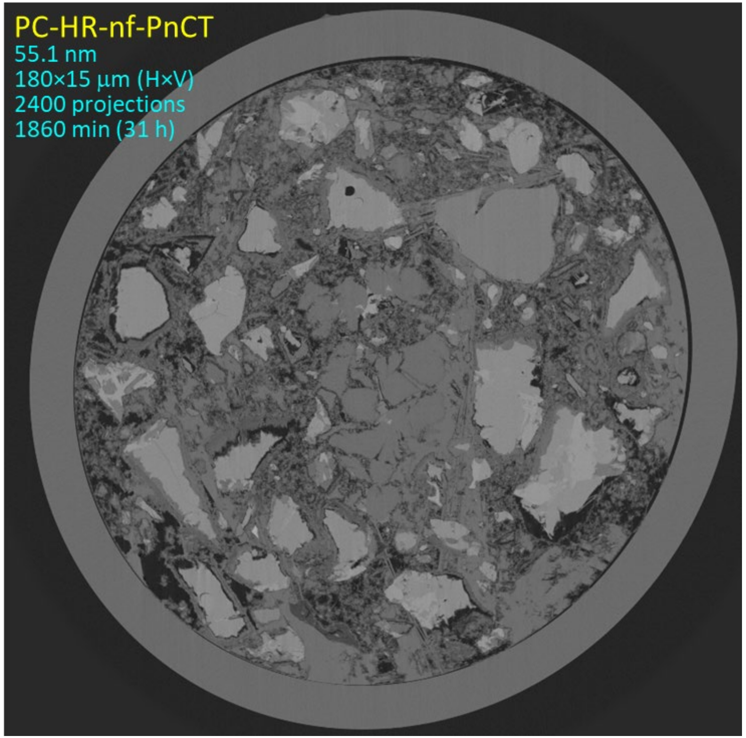
Experimental comparison details:	In situ	HR-test
Energy (keV)	8.939	8.939
Detector: Eiger 1.5M, 75 μm pixel size	– same –	
Number of projections:	420	2400
Sample-detector (mm):	5240	7210
FZP details		
outer-most zone width (nm):	60	**30**
diameter (μm):	120	250
focal distance (mm):	51.9	54.1
distance focus-sample (mm):	13.0	**5.3**
beam size @ sample (μm):	30.0	24.5
average step size (μm):	7.0	**4.0**
exposure time (s):	0.1	**0.2**

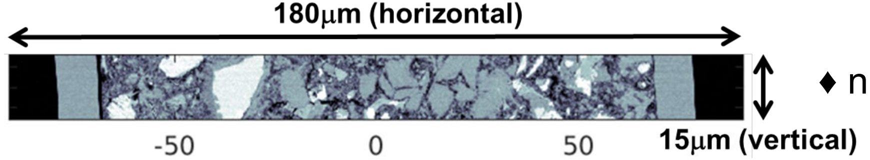
unpublished

UNIVERSIDAD DE MÁLAGA

Fast High Resolution nf-PnCT

The key challenge, **fast nanoCTs: 2000 ⟶ 100 min**





→ To profit from the increase of coherent flux at 4th generation synchrotron sources (f.i. **SLS upgrade, EBS-ESRF, MAX-IV**)

→ To decrease the detector counting time from 0.2 to ~0.01 s (Eiger 1.5M can read at 250 Hz in continuous mode, i.e. 4 ms)

→ Scan speed from 5 to 15 Hz (or higher, under BL development)

→ To collect ~1500 projections, (it may impact spatial resolution)

→ The average step size could be increased to ~6-8 μm, it will impact the spatial resolution

The resulting data (taken to the limits) will be noisier. Programs:

→ To adapt/use, when needed, **TomoGAN**
→ To adapt/use, when needed, **GANrec**
→ To adapt/use, when needed, **Noise2Inverse**

Optimization of:

♦ counting time; ♦ average ptychographic step size;
♦ number of projections; ♦ size of the vertical FoV; ♦ *scan speed*

unpublished

Backup

1. The relevant societal challenge #2
2. Concrete: length scales #4
3. Caveat about data analysis #1
4. **4D synchrotron nano-CT** (near-field ptychographic imaging) #12
5. CoDI at ALBA-II #1
6. Summary and acknowledgement #1

UNIVERSIDAD DE MÁLAGA

This document details the proposal for the **Co**herent **D**iffraction **I**maging beamline (CoDI) at ALBA II. The main scope and uniqueness of CoDI is to perform *in situ* and *operando* characterization of thick samples with nanometer resolution exploiting:

(i) the coherence of ALBA II;
(ii) the possibility of building a 250 meters long beamline;
(iii) the availability of room for a unique sample detector distance of 20 m, as a new building will be constructed.

To achieve these goals, CoDI is optimized for:

(i) A range of energies between 10-30 keV to probe thick samples in their relevant conditions,
(ii) An efficient control of the coherence and flux using a secondary source to tailor the beam features of the experiments to be carried out,
(iii) The use of a nano-focusing Kirkpatrick–Baez (KB) mirror (sub-50 nm focus) that enable a long working distance, more than 150 mm, that allows to accommodate *in situ* and *operando* sample environments,
(iv) Multilayer Laue lenses (MLLs) to produce the ultimate efficient nano-focus (sub-10 nm focus) for ultra-high resolution X-ray imaging,
(v) A long sample to detector distance that enables high-solid angle resolution with current direct-conversion detectors.

These features will make CoDI not only one of the forefront beamlines for scanning nanoimaging techniques (X-ray diffraction or X-ray fluorescence) but also for coherent imaging in the forward direction (ptychography and holography) and in diffraction conditions (Bragg-CDI, Bragg-ptychography, and tele-ptychography)

BUT, please do not forget this would be a nanoimaing BL, therefore pay attention to:

software, software, software, software, software, software, software, software, software, software, software, software, software, software, software, software,…

UNIVERSIDAD DE MÁLAGA

Take home message & acknowledgements

Multilength scale imaging is relatively easy by taking data at different beamlines.

Relevant multilength scale imaging (at least in cement hydration) is very challenging (difficult) as the conditions for sample preparation and data acquisition must be such that samples are not altered and they are kept in the *appropriate environment*.

Relevant multilength scale 4D imaging is even more challenging but it can be done and it is being improved

We thank financial support from Spanish government and Andalucía regional government.
We thank: (i) SLS/PSI for beamtime at cSAXS and TOMCAT; (ii) ESRF for beamtime at ID19.
Laboratory μ-CT data are taken at SCAI-UMA

I thank all collaborators from UMA, SLS/PSI, ESRF, ALBA, …. This is a team effort!