3D Morphological Analysis of Cement over the First 24 Hours of Hydration by Holographic and Near-Field Ptychographic-Tomography

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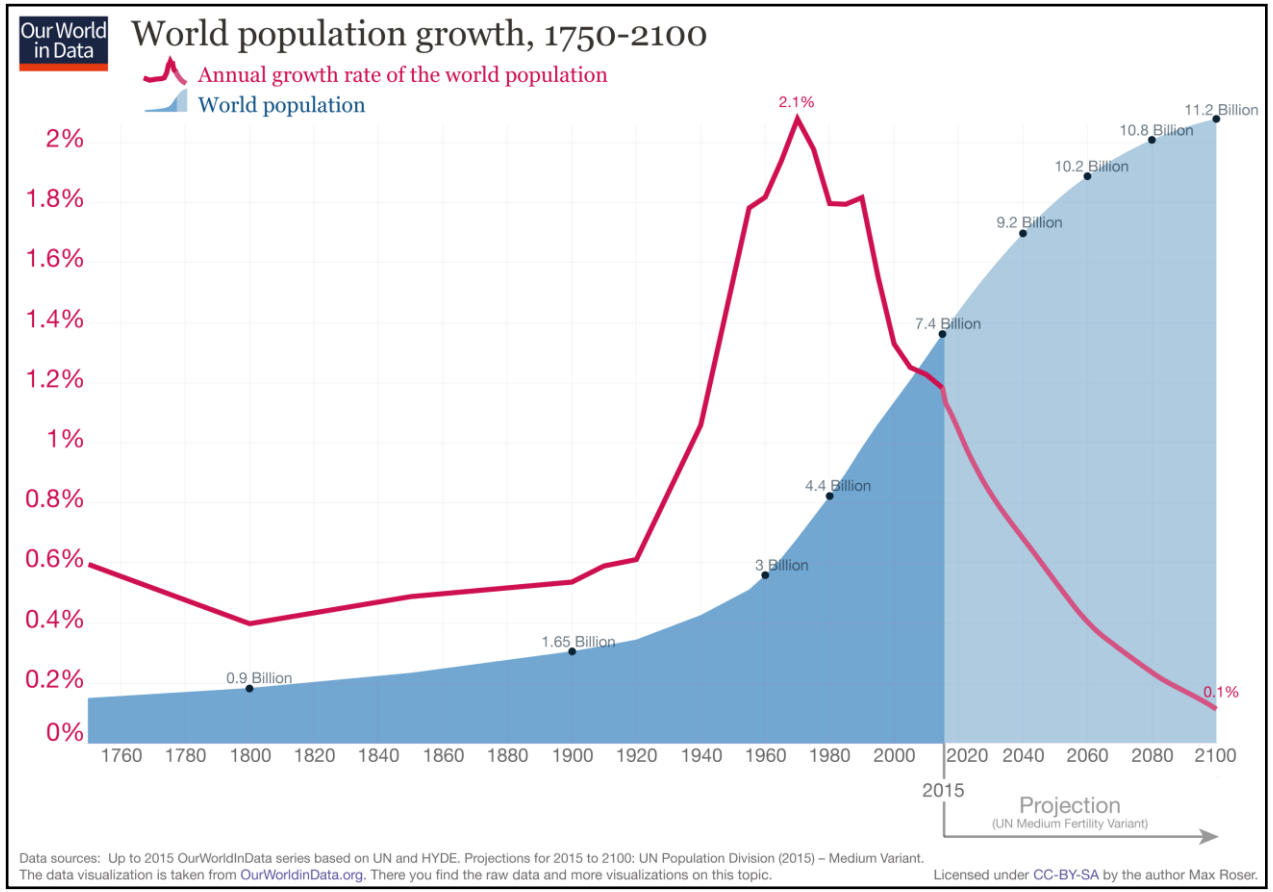
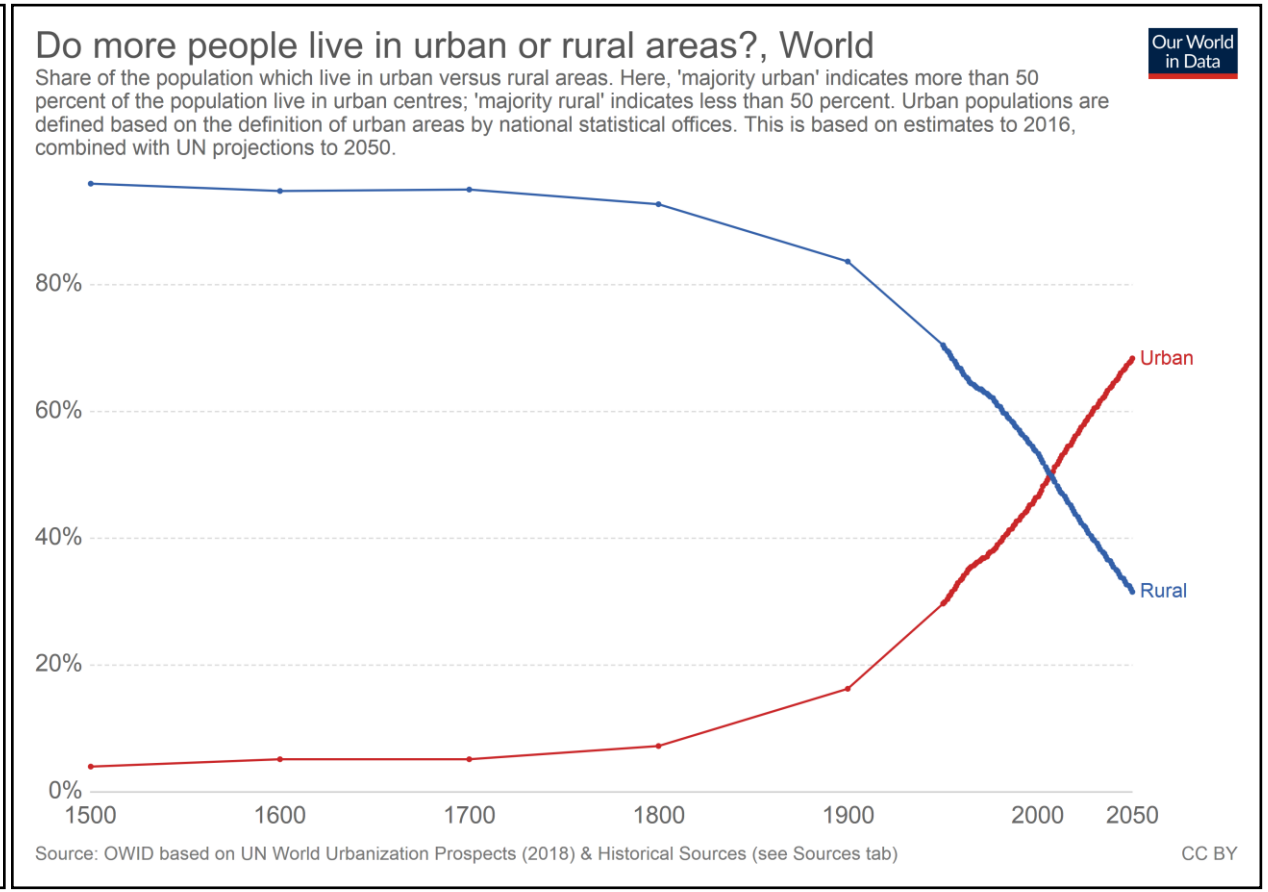
CEMENT: AN ESSENTIAL COMMODITY FOR OUR SOCIETY

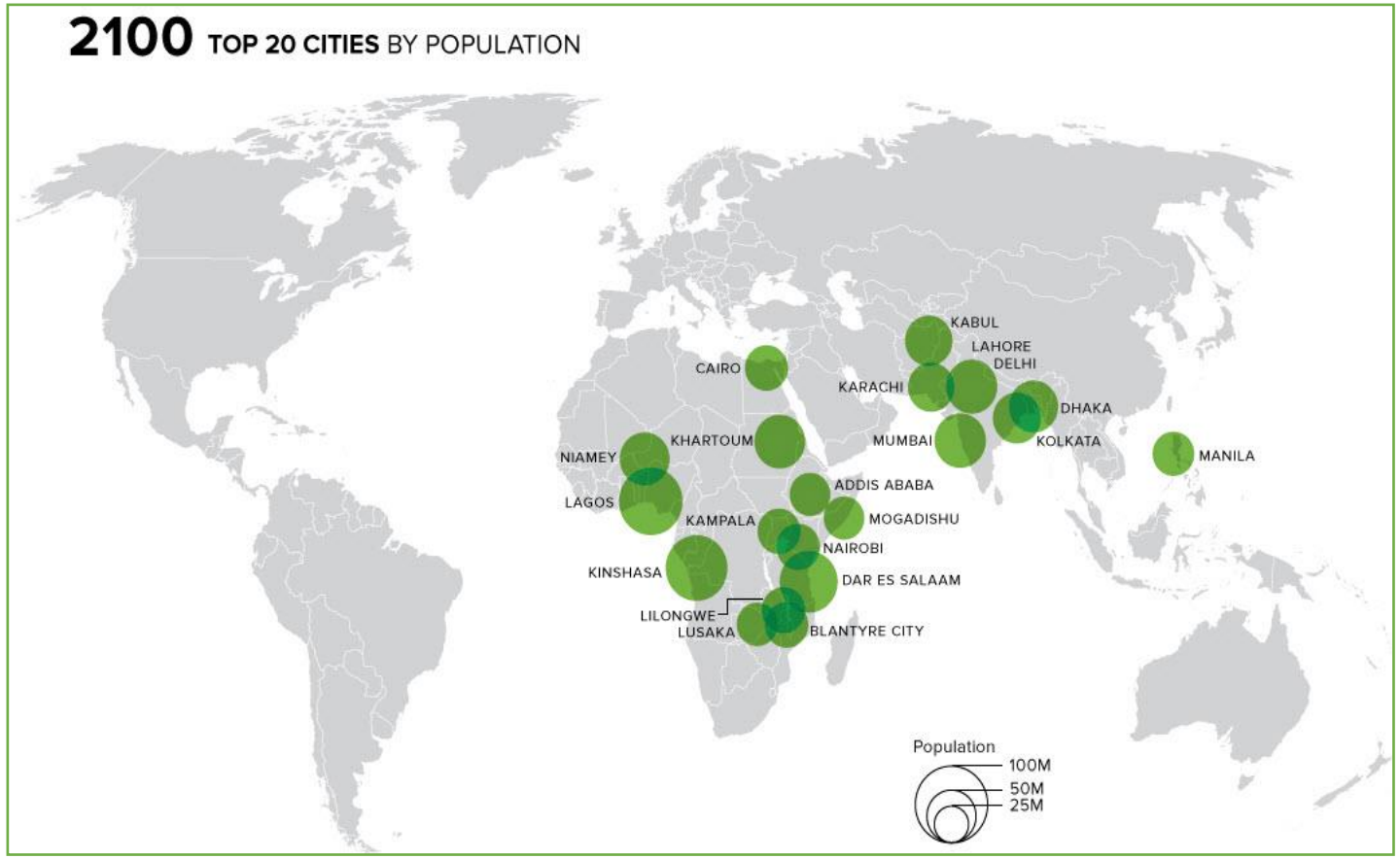
Urbanization: a global challenge



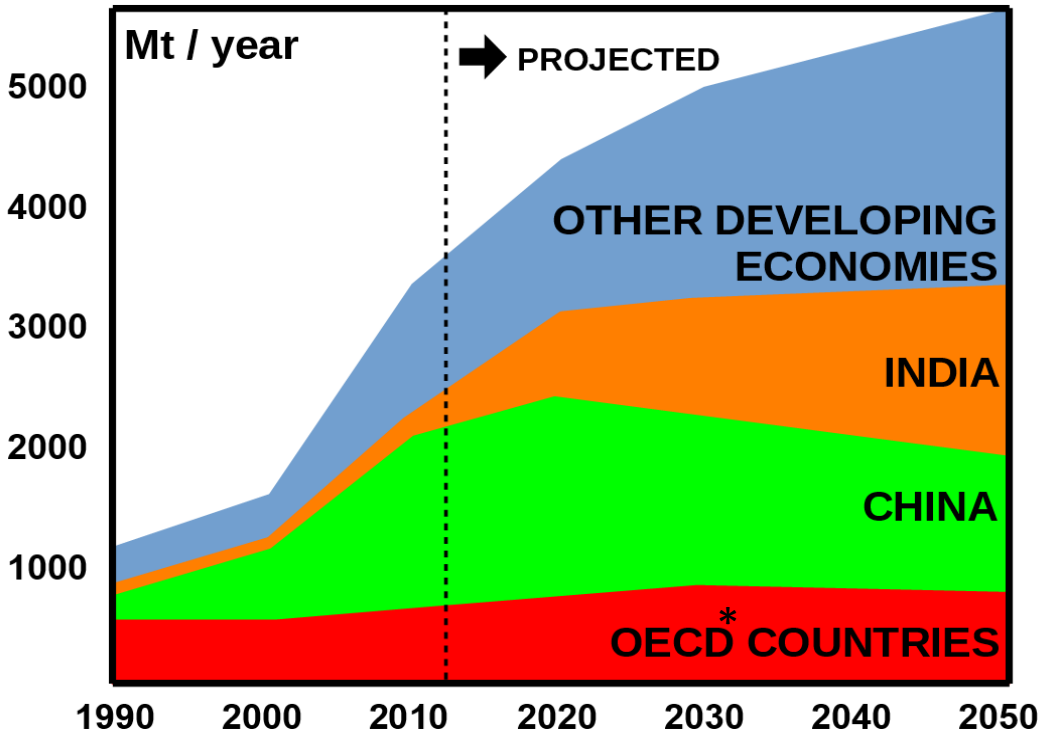


CEMENT: AN ESSENTIAL COMMODITY FOR OUR SOCIETY

WORLD URBANIZATION & MEGACITIES



WORLD CEMENT PRODUCTION



*ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT

CEMENT: A COMPLEX MATERIAL

Cement hydration and hardening occurs by a combination of basic processes (dissolution, diffusion, adsorption, precipitation) involving a series of phases characterized by different chemical composition and structure

ANHYDROUS PHASES (REACTANTS) IN CEMENT CHEMISTRY NOTATION*

C_3S	Ca_3SiO_5	**Alite**
C_2S	Ca_2SiO_4	**Belite**
C_3A	$Ca_3Al_2O_6$	**Aluminate**
C_4AF	$Ca_4Al_2Fe_2O_{10}$	**Ferrite**

MAIN HYDRATION PRODUCTS IN CEMENT CHEMISTRY NOTATION*

C-S-H	$(CaO)_{1.7}(SiO_2)(H_2O)_4$	**Calcium silicate hydrate**
CH	$Ca(OH)_2$	**Portlandite**
C_3ASH_{32}	$Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$	**Ettringite**

C_3S amounts to 70% in cement, such that simplified model cement systems consisting of C_3S only are often considered for research purposes

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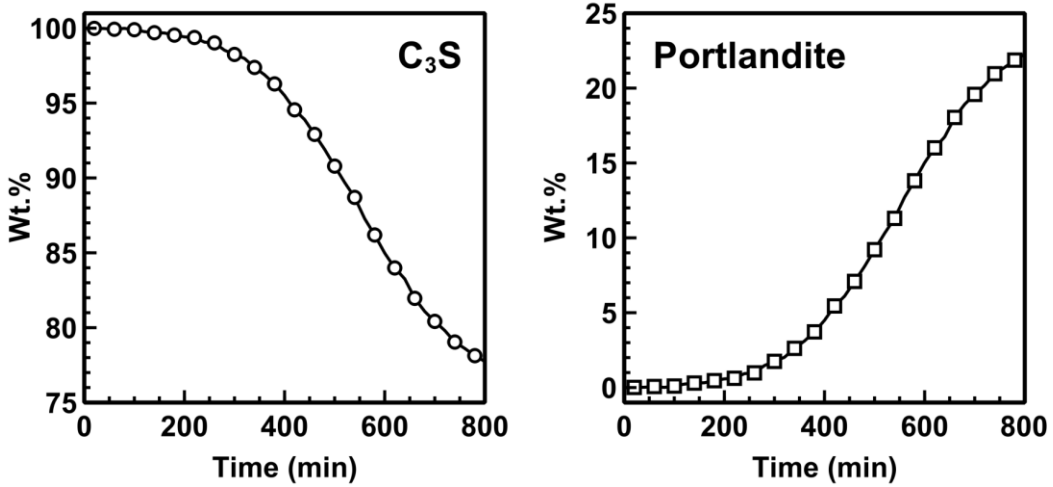
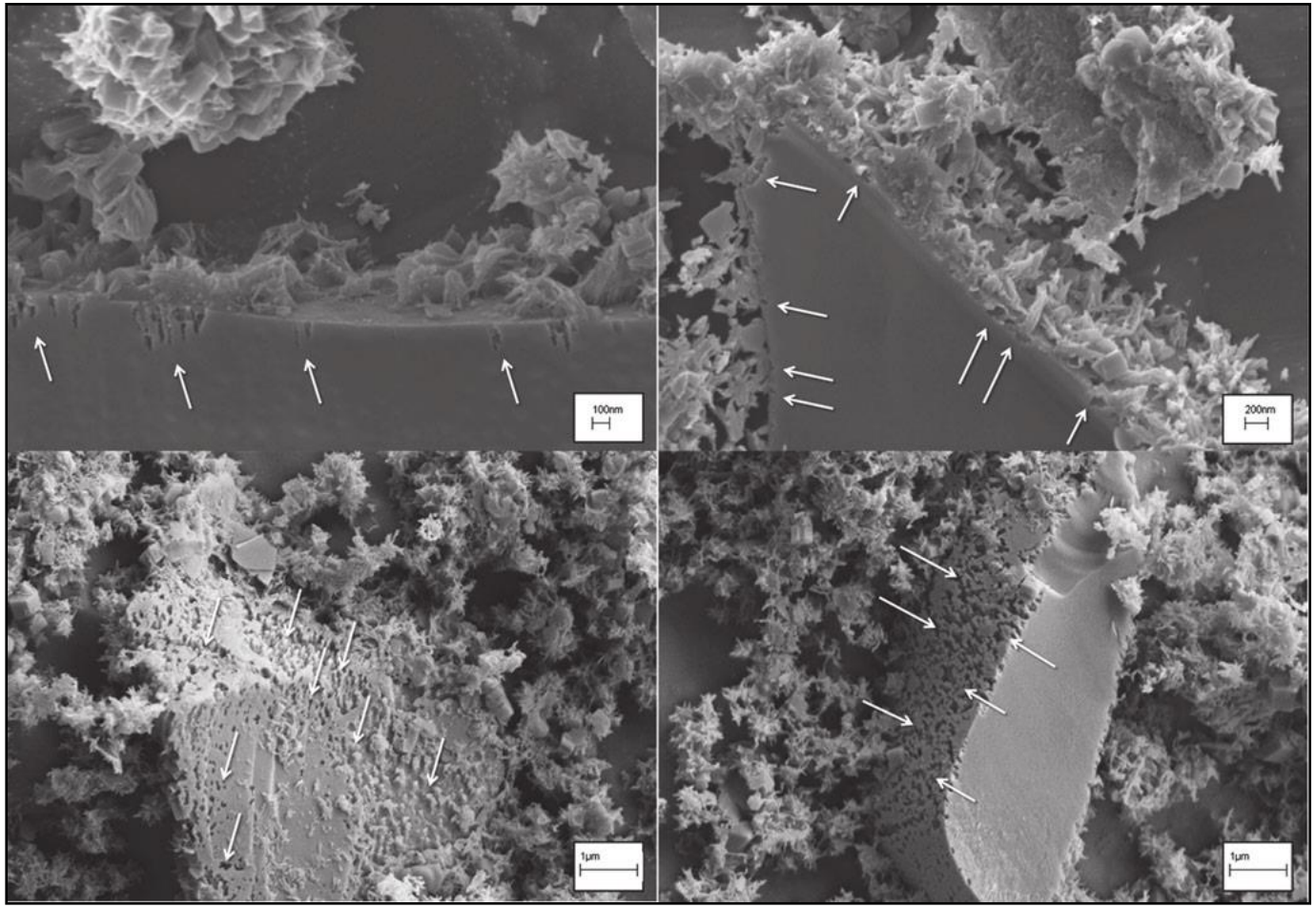
* $C = CaO$ $A = Al_2O_3$ $F = Fe_2O_3$ $S = SiO_2$ $S = SO_3$

CEMENT: A COMPLEX MATERIAL

Cement hydration and hardening occurs by a combination of basic processes (dissolution, diffusion, adsorption, precipitation) involving a series of phases characterized by different chemical composition and structure

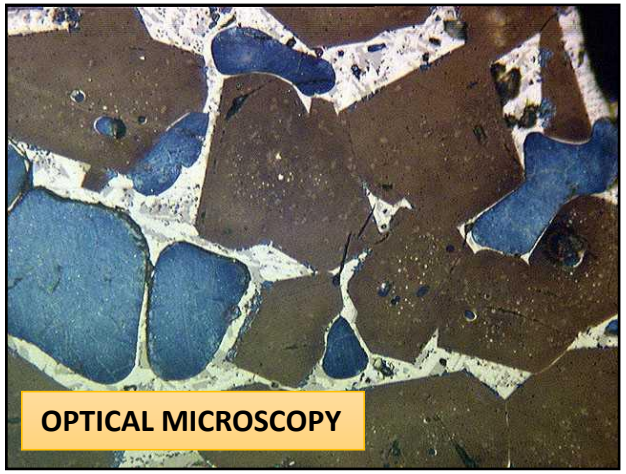


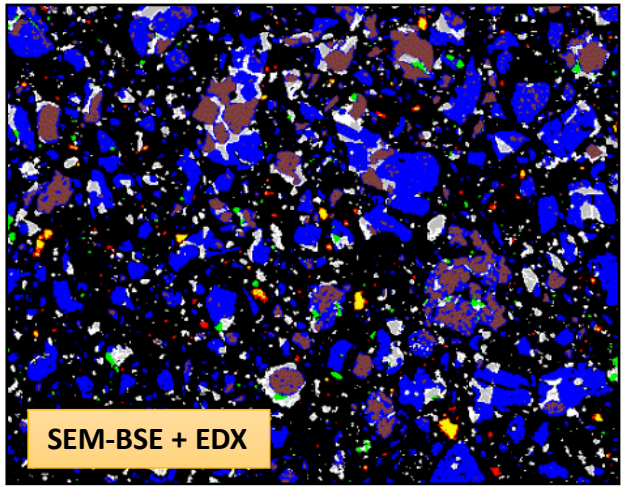


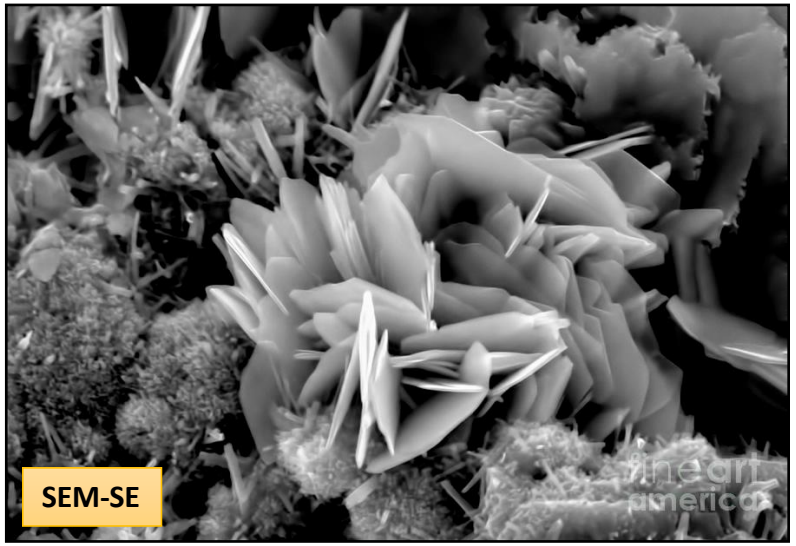
(Nicoleau and Bertolim, 2016)

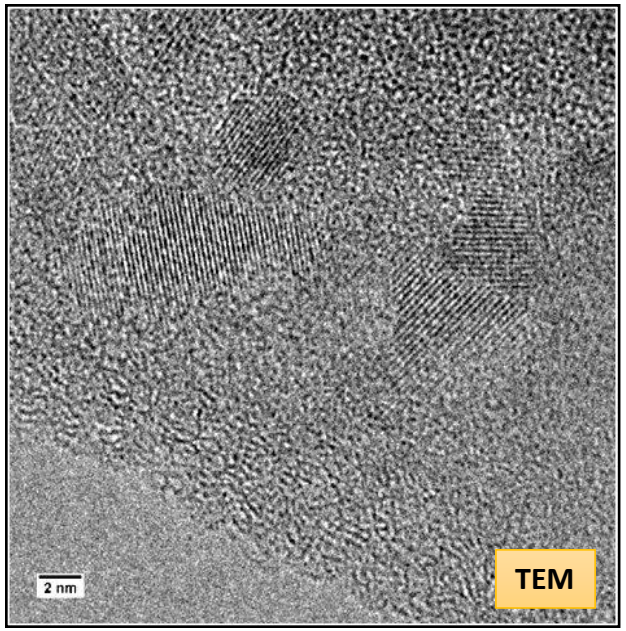
PROBING CEMENT MICROSTRUCTURE

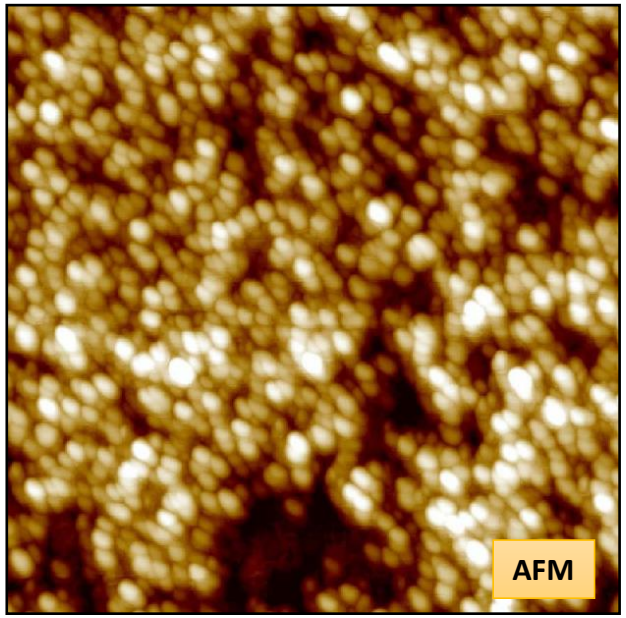
The macroscopic properties of cement are strictly related to microstructural development

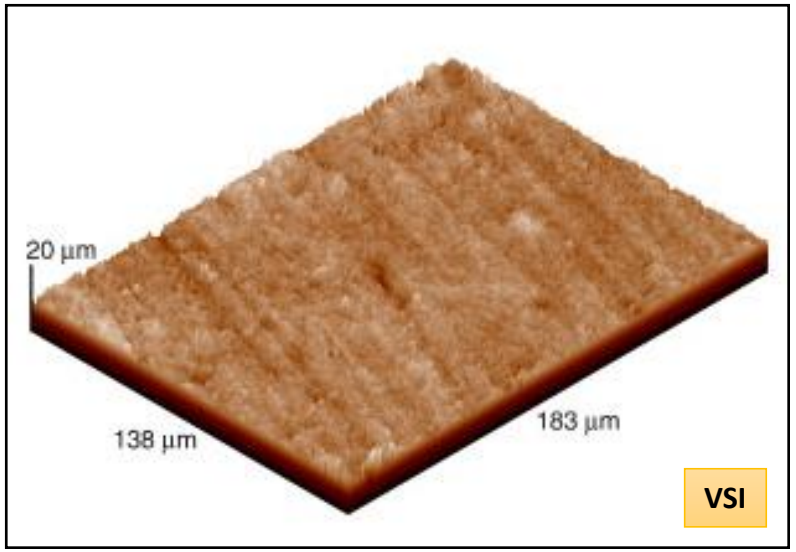








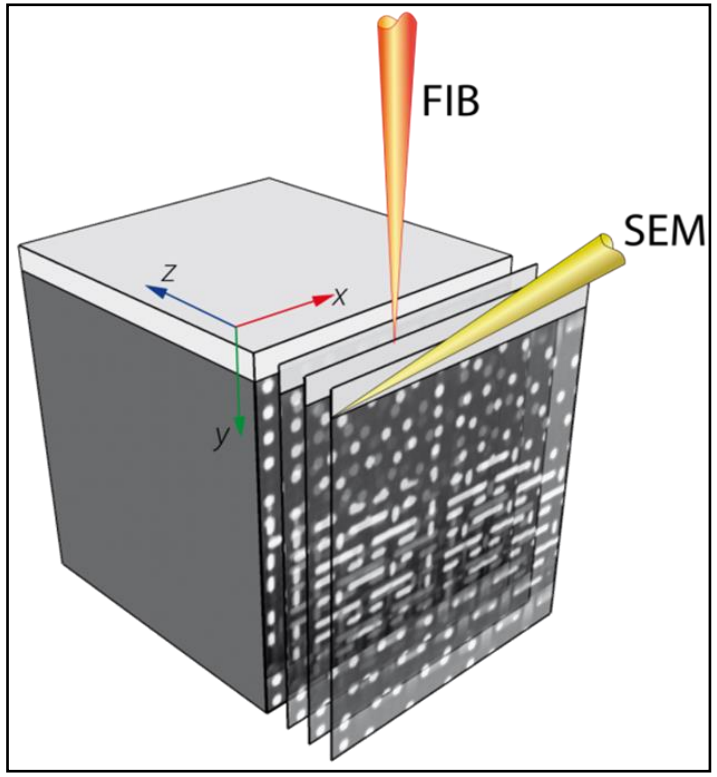


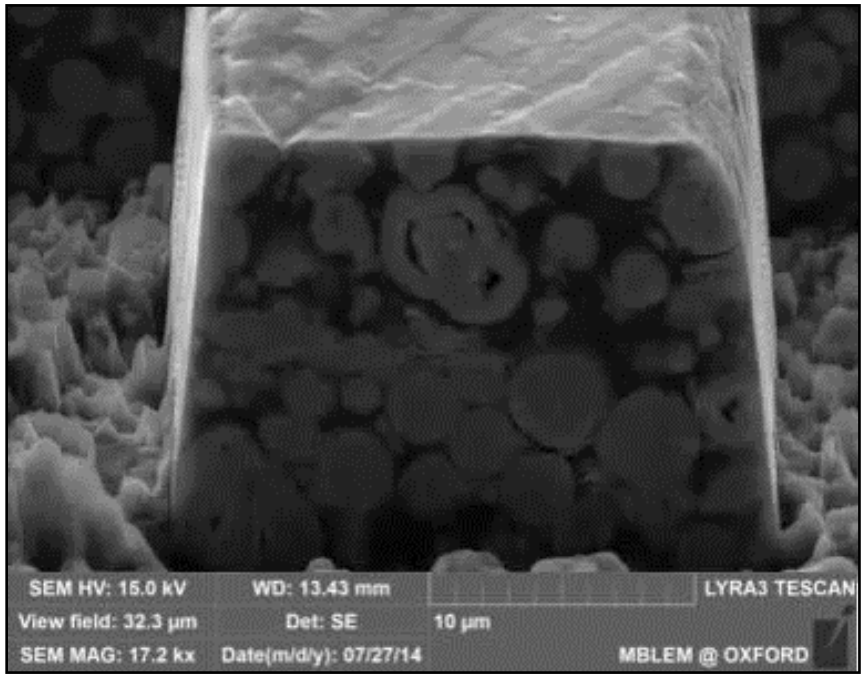


⚠ **Only 2D** **Destructive**

PROBING CEMENT MICROSTRUCTURE: ACCESSING THE 3RD DIMENSION

Serial sectioning

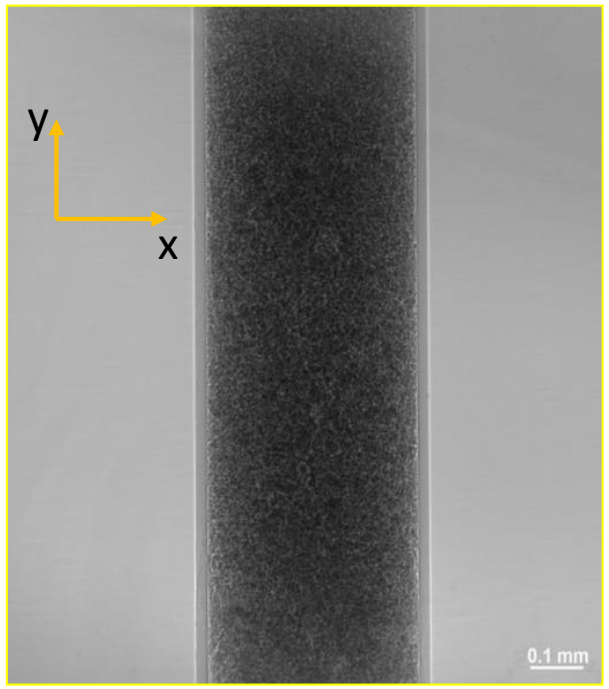


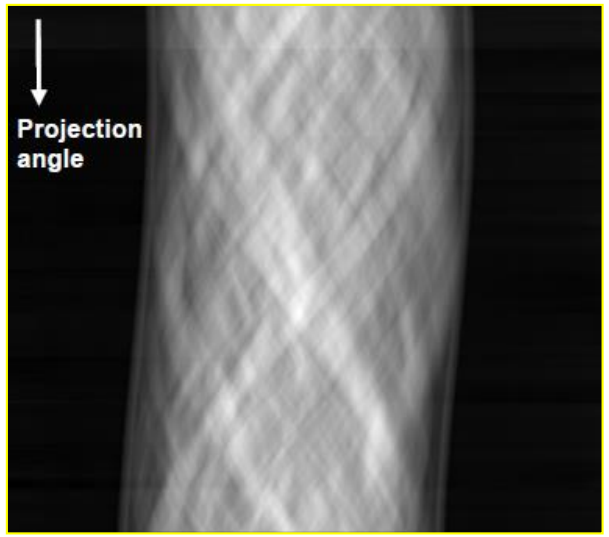


<u>FOCUSSED ION BEAM + SEM/EBSD</u>

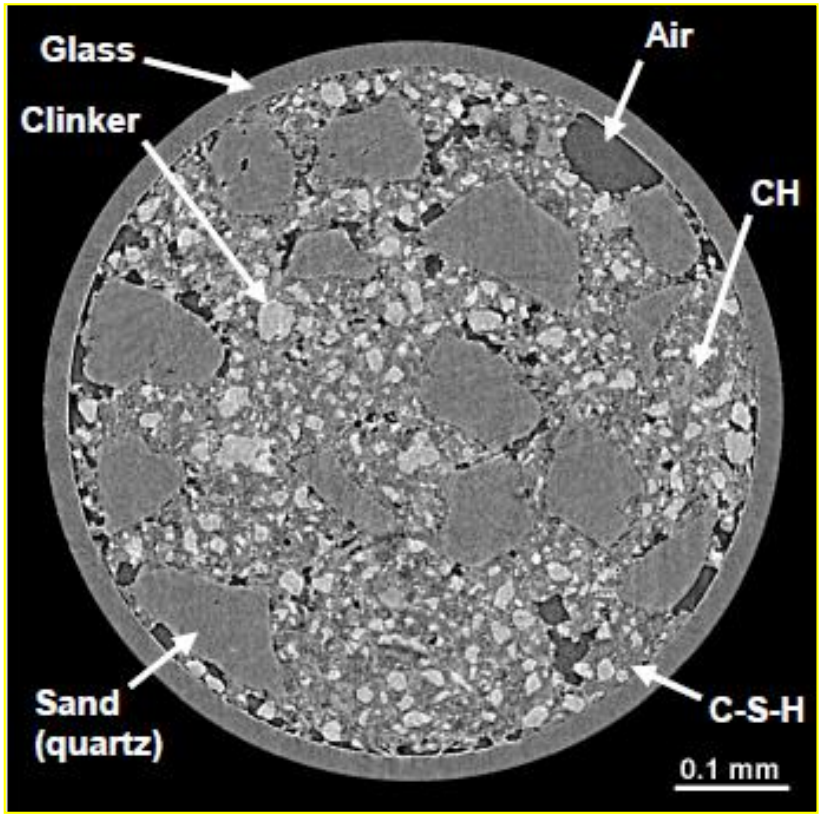
(~10 nm vertical resolution: destructive – no in-situ analysis)

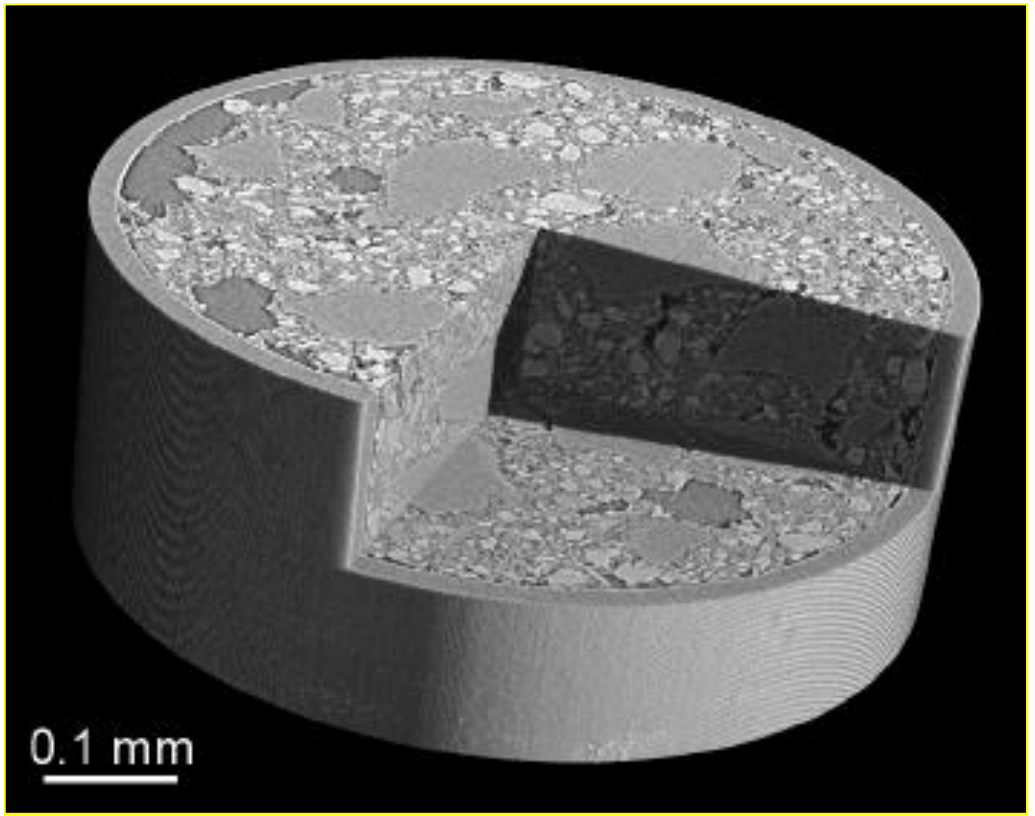
PROBING CEMENT MICROSTRUCTURE: ACCESSING THE 3RD DIMENSION





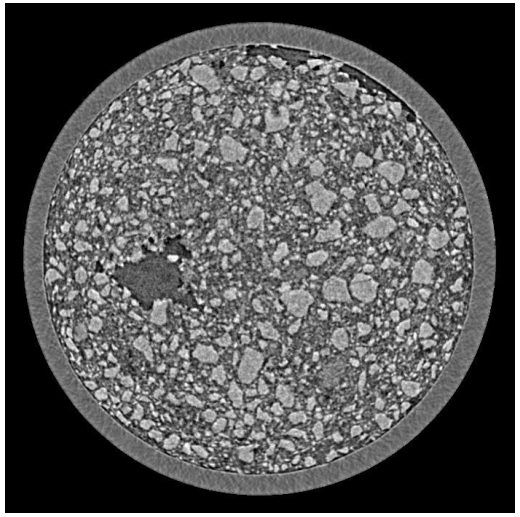
Non-destructive imaging of cement microstructure by attenuation X-ray microtomography (lab)

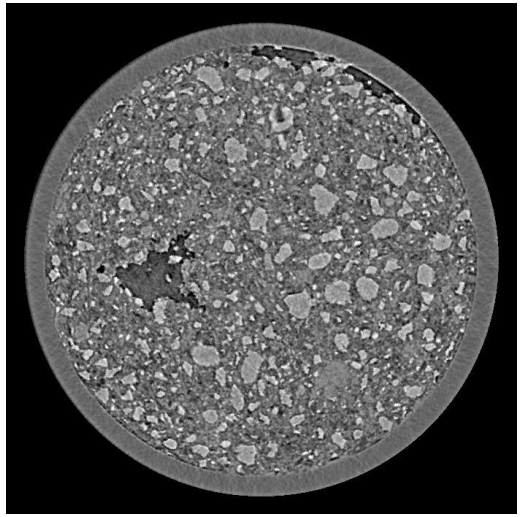


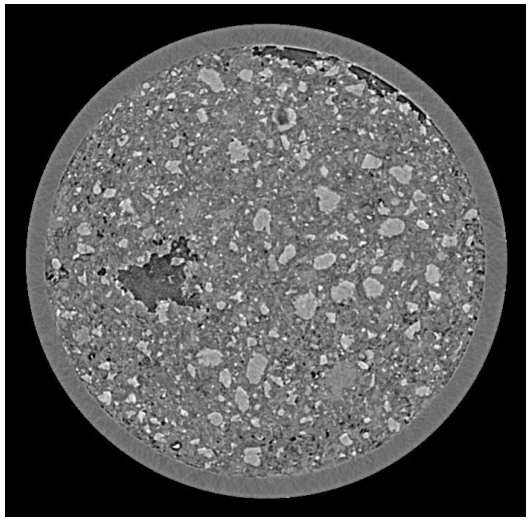


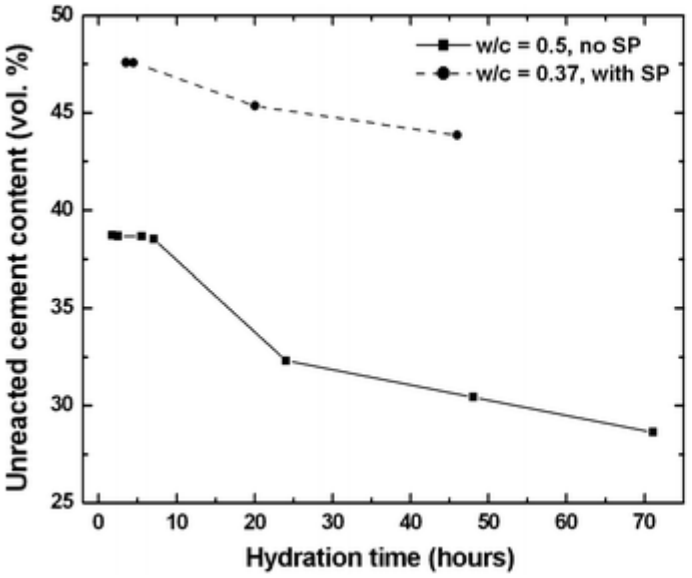
PROBING CEMENT MICROSTRUCTURE: REACTION KINETCS

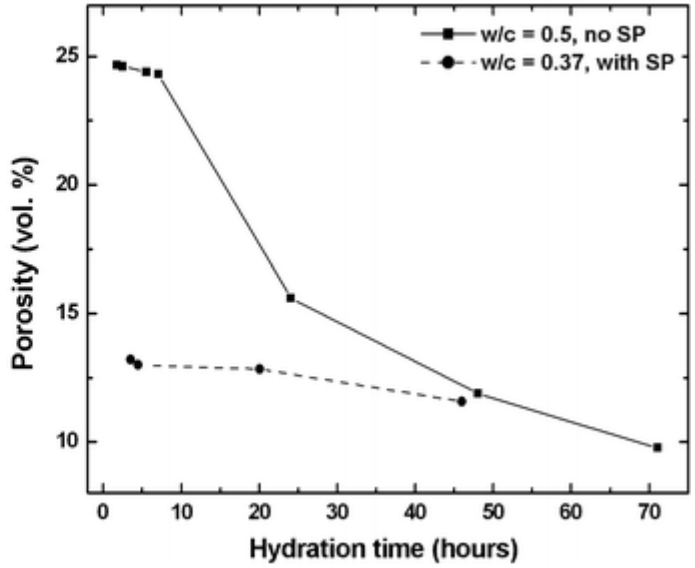
TIME











(Parisatto et al., 2015)

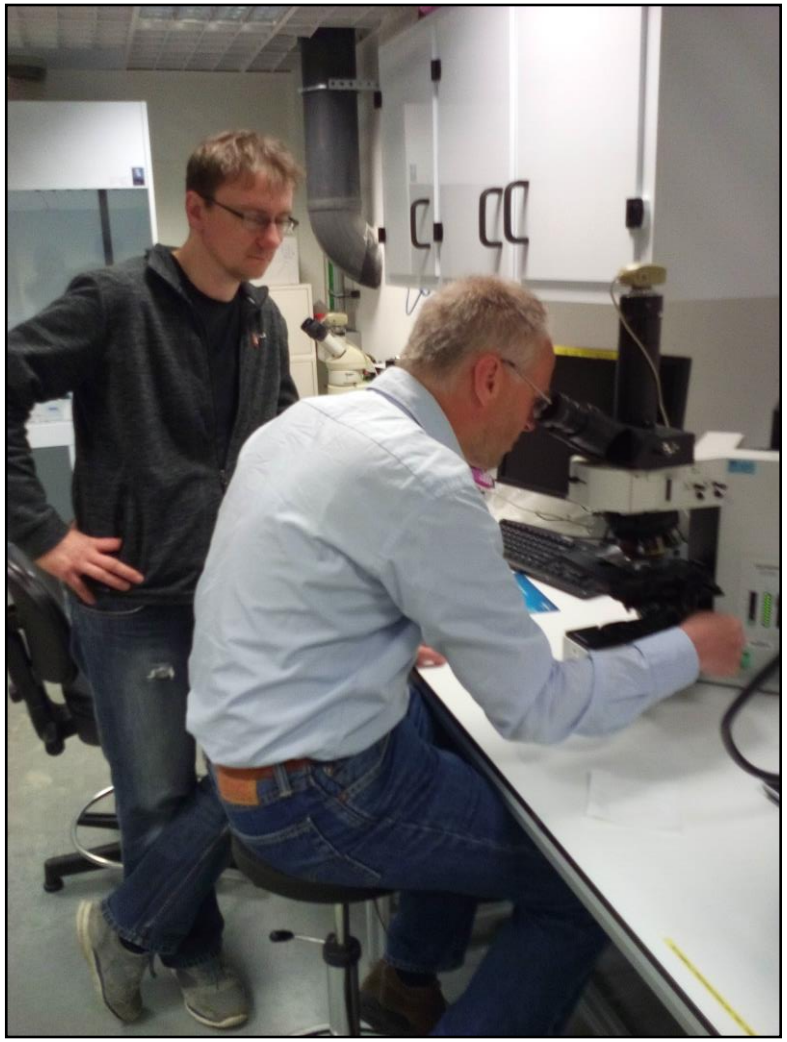
Issues: poor attenuation contrast (lack of full phase selectivity); limited time and space resolution (partial volume effects)

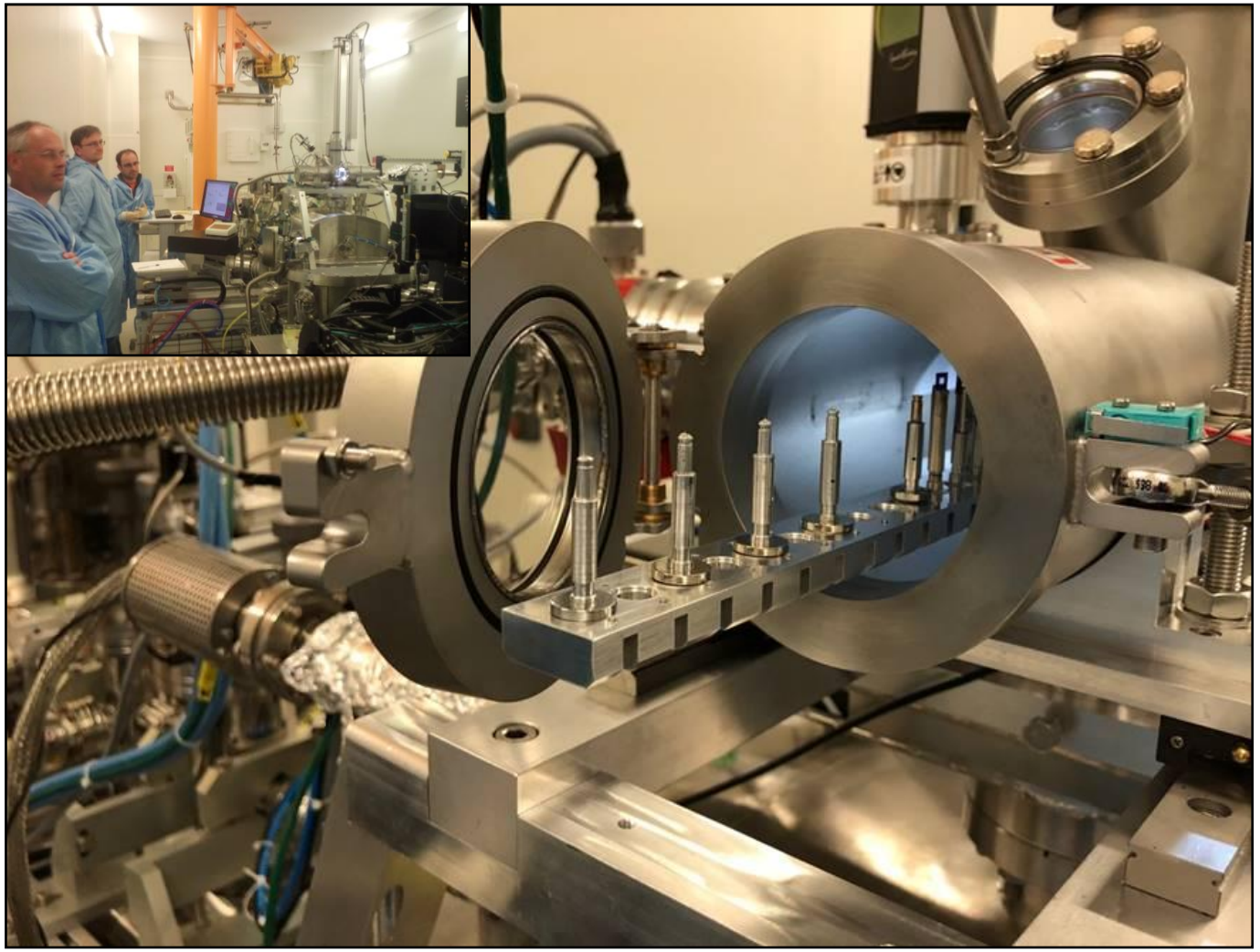
SYNCHROTRON NANO-TOMOGRAPHY @ ID16A: SAMPLE PREPARATION

1) Cement hydration stopped by solvent exchange at different times (12, 16, 20 hours)

2) Dried powders embedded in epoxy and thin filaments mounted on stage

GOAL: time-dependent PSD of dissolving C_3S to infer kinetics

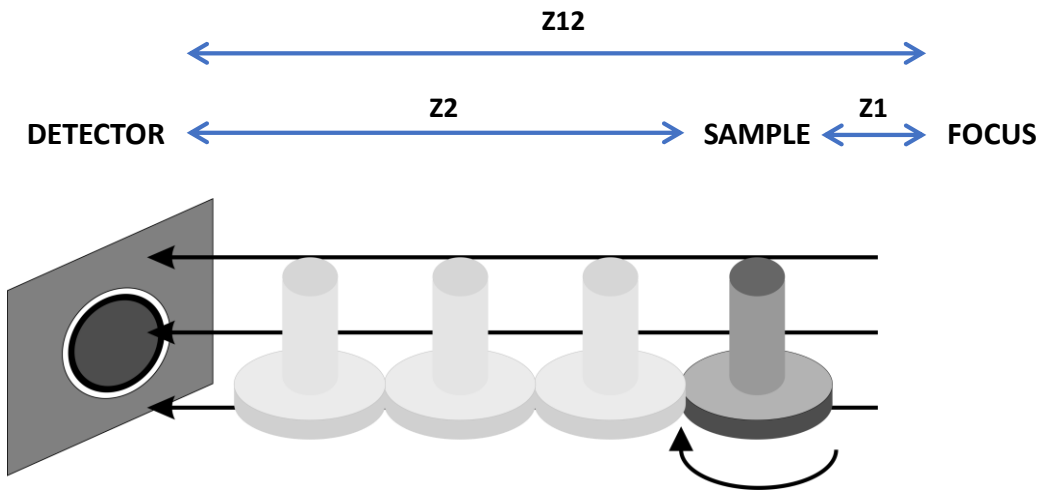




SYNCHROTRON NANO-TOMOGRAPHY @ ID16A

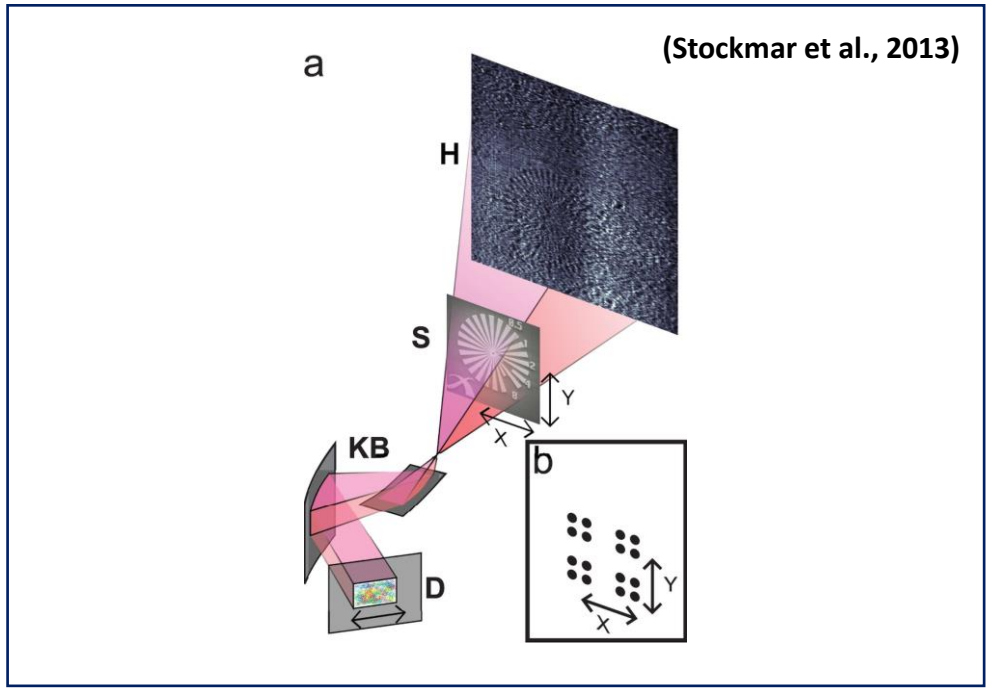
A) Holotomographic approach

- 800 projections for each z1 position (0.015 – 0.027 mm)
- 0.5 s acquisition time
- 50 nm pixel size



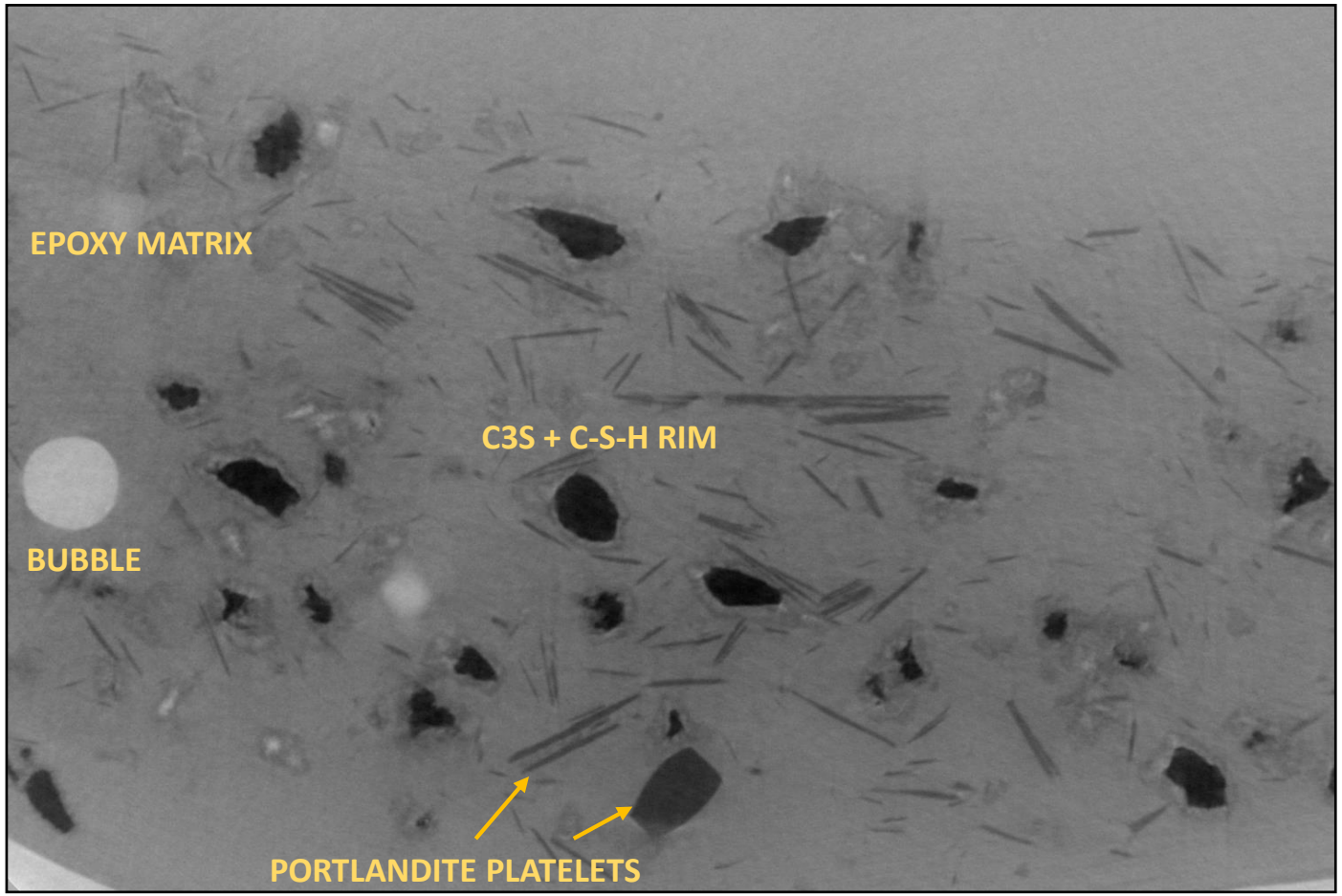
B) Near-field ptychography approach

- z12 = 1.208 m z1 = 20.13 mm
- 17 randomly distributed points at each angular position (0.3° step)
- 0.5 s acquisition time 50 nm pixel size

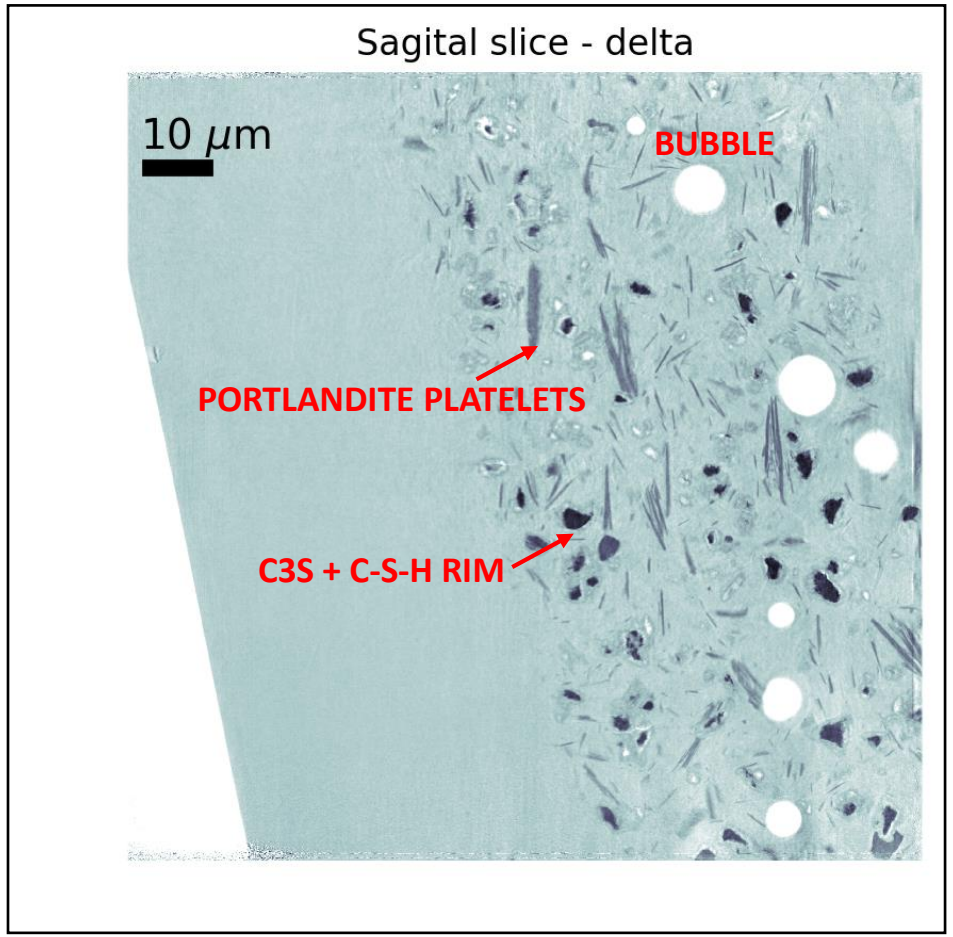


SYNCHROTRON NANO-TOMOGRAPHY @ ID16A: IMAGE RECONSTRUCTION

pre-processing + phase retrieval + tomographic reconstruction



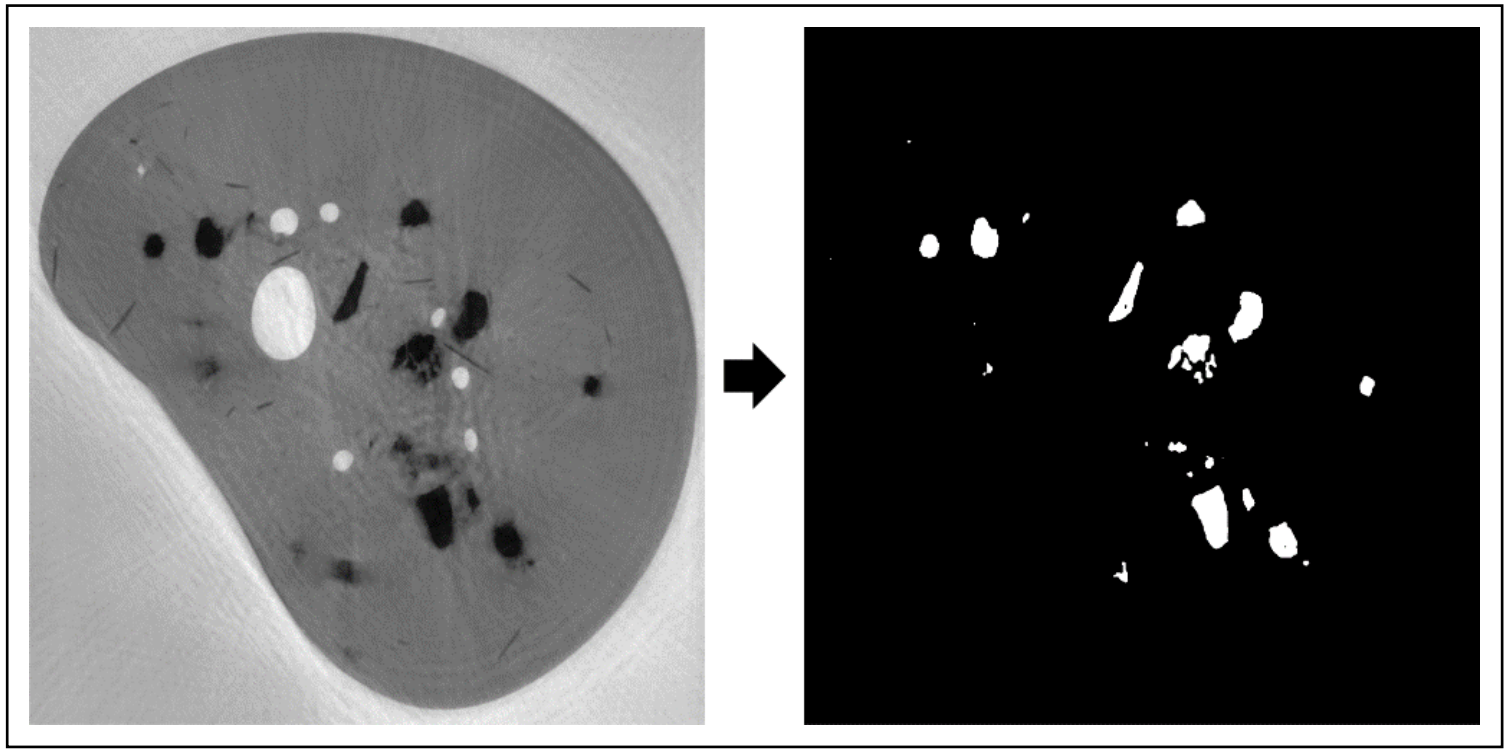
HOLOTOMOGRAPHY



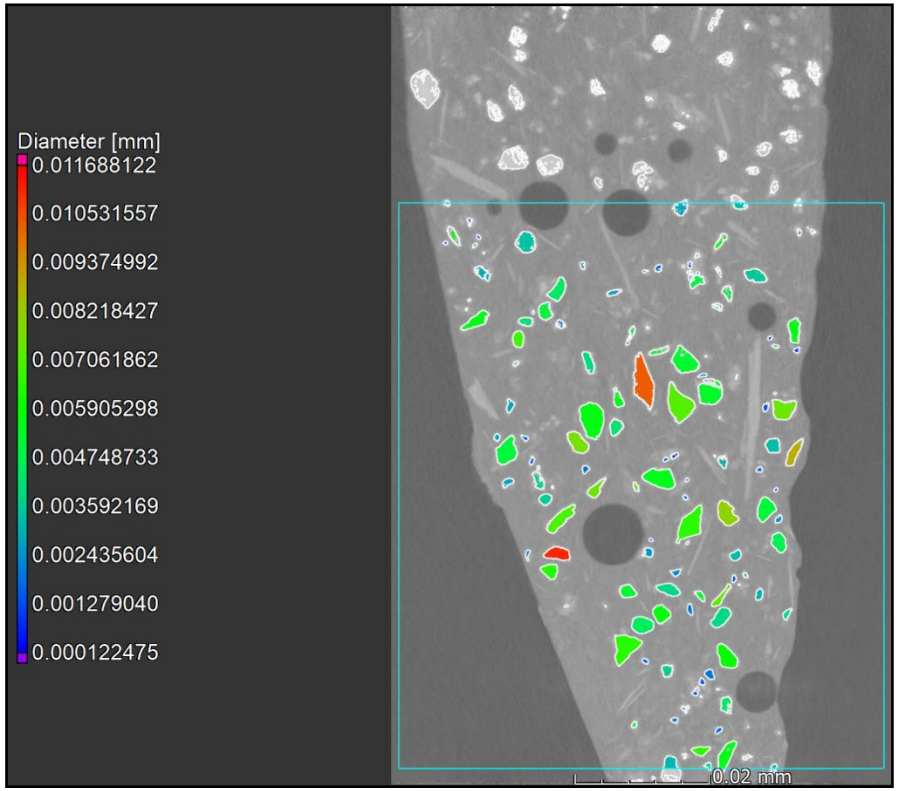
NEAR-FIELD PTYCHOGRAPHY

SYNCHROTRON NANO-TOMOGRAPHY @ ID16A: IMAGE PROCESSING

image segmentation + object measurement (PSD)



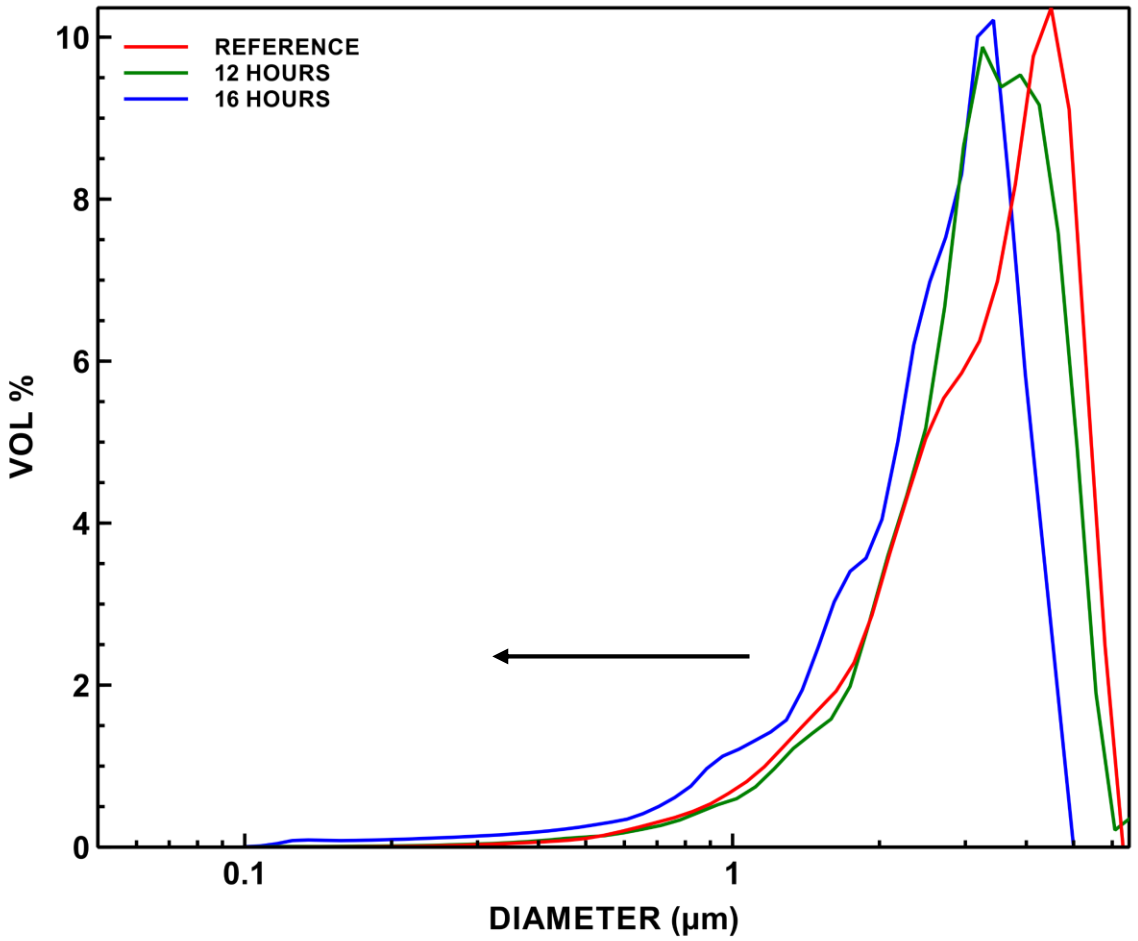
HOLOTOMOGRAPHY

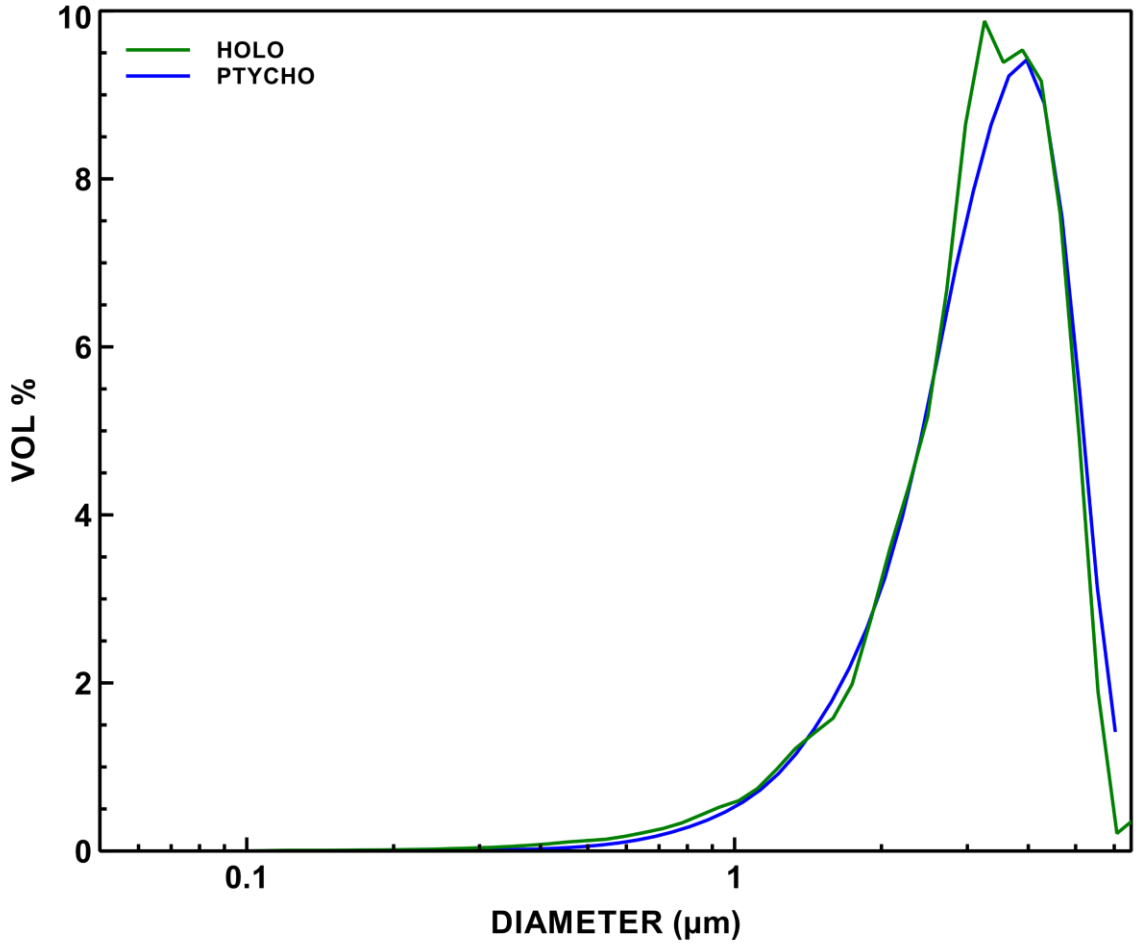


NEAR-FIELD PTYCHOGRAPHY

TIME-DEPENDENT C_3S PARTICLE SIZE DISTRIBUTION ANALYSIS

PSD obtained by commonly used methods such as laser diffraction are integrated over all cement phases (dissolving + precipitating) no data on single phase kinetics can be inferred



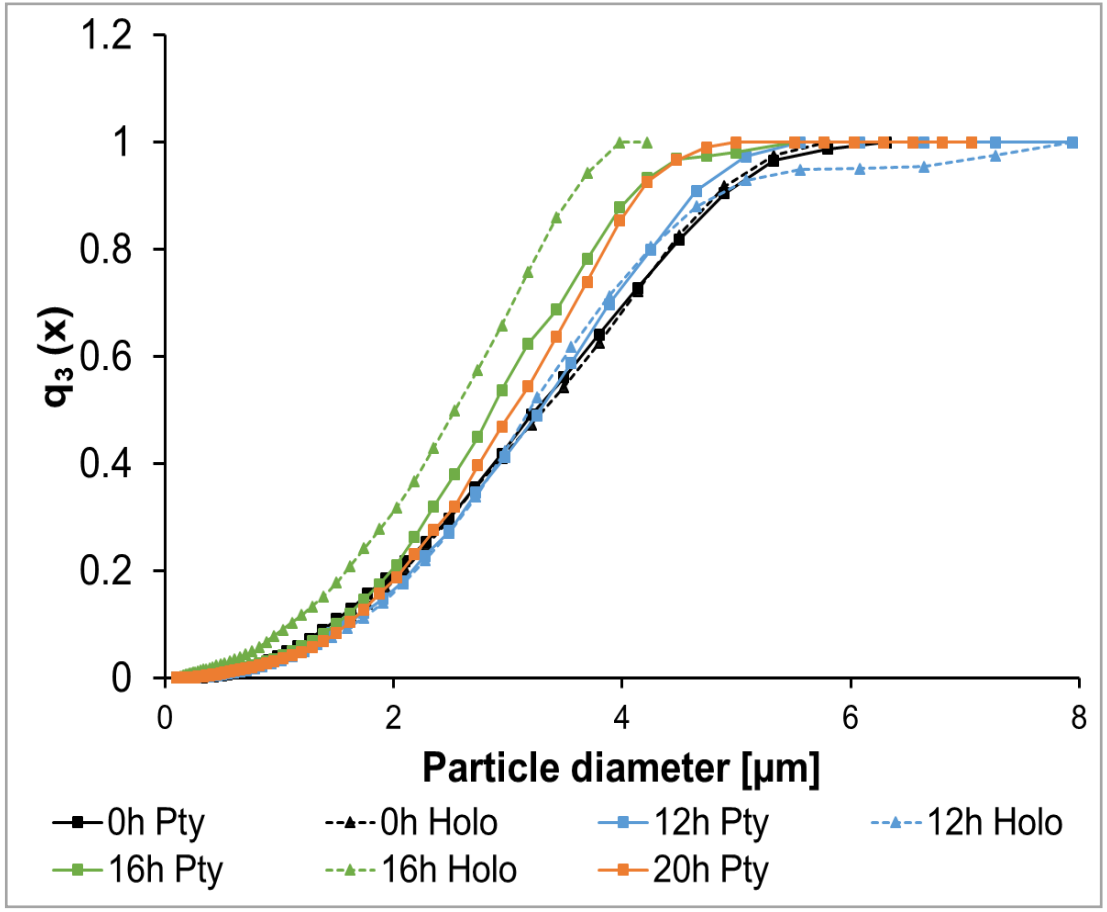


PSD shifted to the left with time due to continuous C_3S dissolution

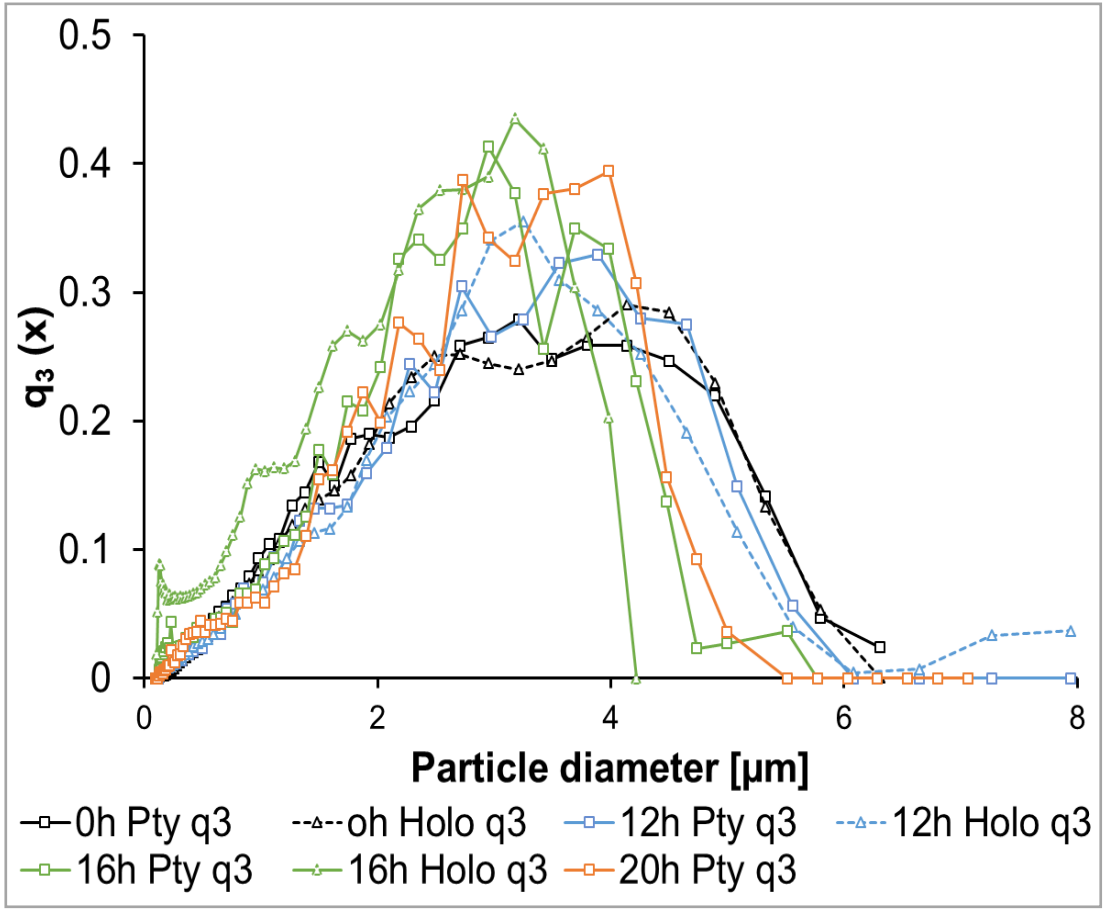
Overall good agreement between holotomography and near-field ptychography up to 12h

TIME-DEPENDENT C_3S PARTICLE SIZE DISTRIBUTION ANALYSIS

CUMULATIVE PSD (Holography and ptychography)



DIFFERENTIAL PSD (Holography and ptychography)

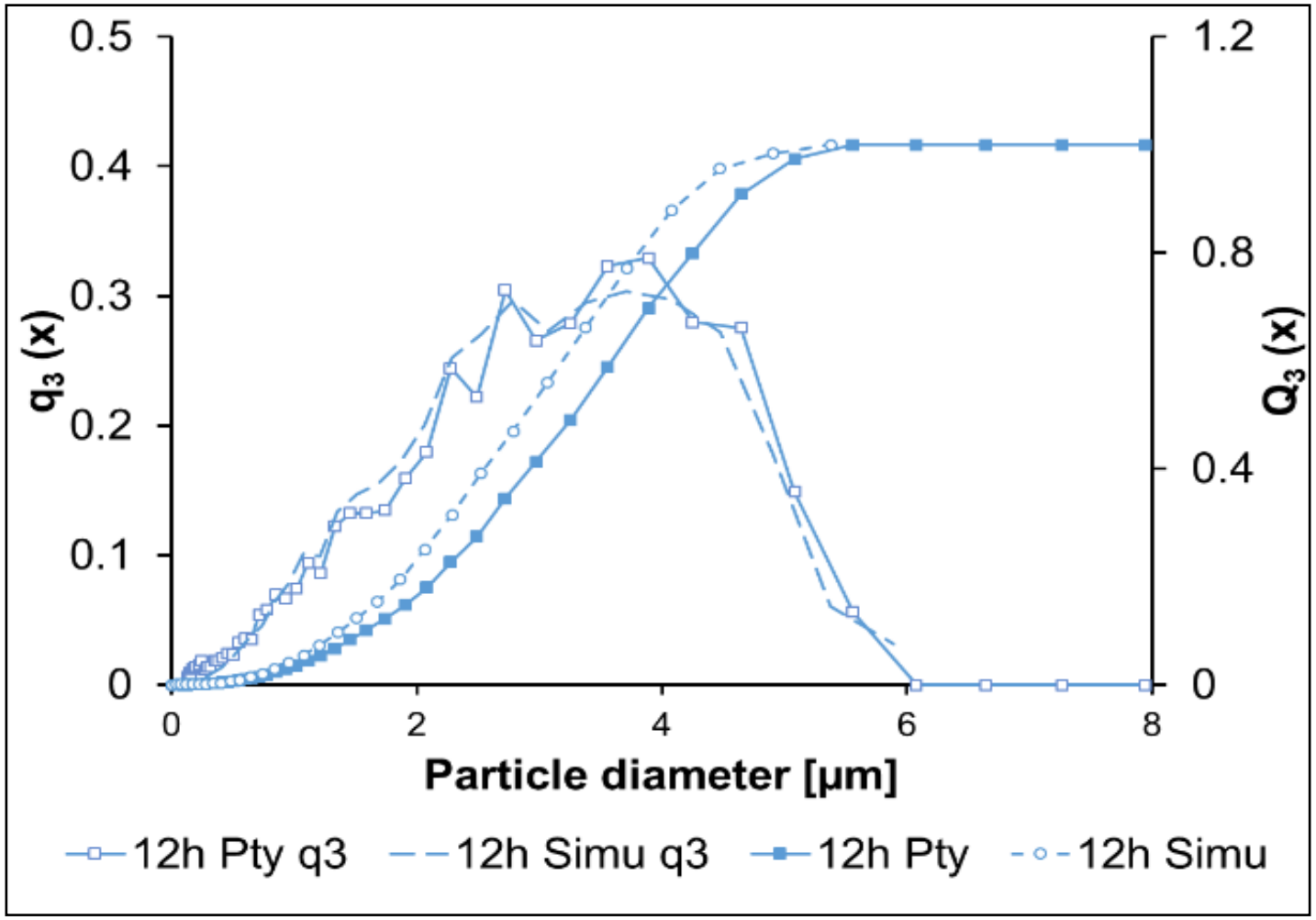


At 16h the results of holotomography give a PSD characterized by a larger amount of finer particles

TIME-DEPENDENT C_3S PARTICLE SIZE DISTRIBUTION ANALYSIS

Comparison with numerical modelling

The *reaction zone model* (Masoero et al., 2017) was used to simulate the evolution of the C_3S PSD during hydration



CONCLUSIONS

- **Synchrotron-based nanotomographic techniques can be used to probe the time evolution of cement particle sizes with excellent spatial resolution**
- **The quality of the reconstructed images allows individual mineralogical phases to be segmented**
- **The results obtained by using the holotomography and near-field ptychography approaching are in overall good agreement, although the former tend to overestimate finer particles (this point needs further insight)**
- **The obtained time-dependent PSD are in good agreement with theoretical predictions**

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