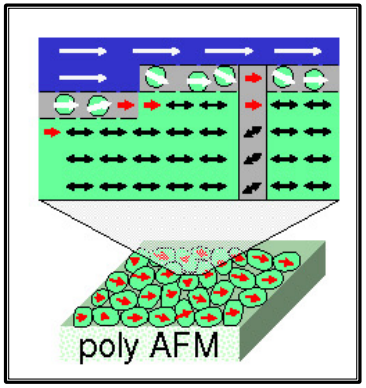
Microscopie X au Synchrotron pour l'étude de matériaux complexes et expériences operando

HERMES Beamline - SOLEIL

R. BELKHOU

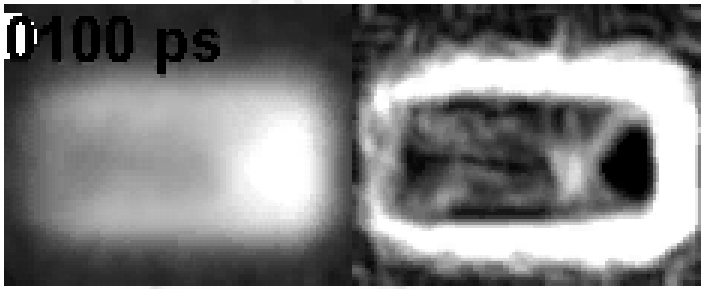
Challenges for X-ray Microscopy

Spatial Resolution + Chemistry, Electronic..



Complex Materials, Nanostructures, In-Operando…

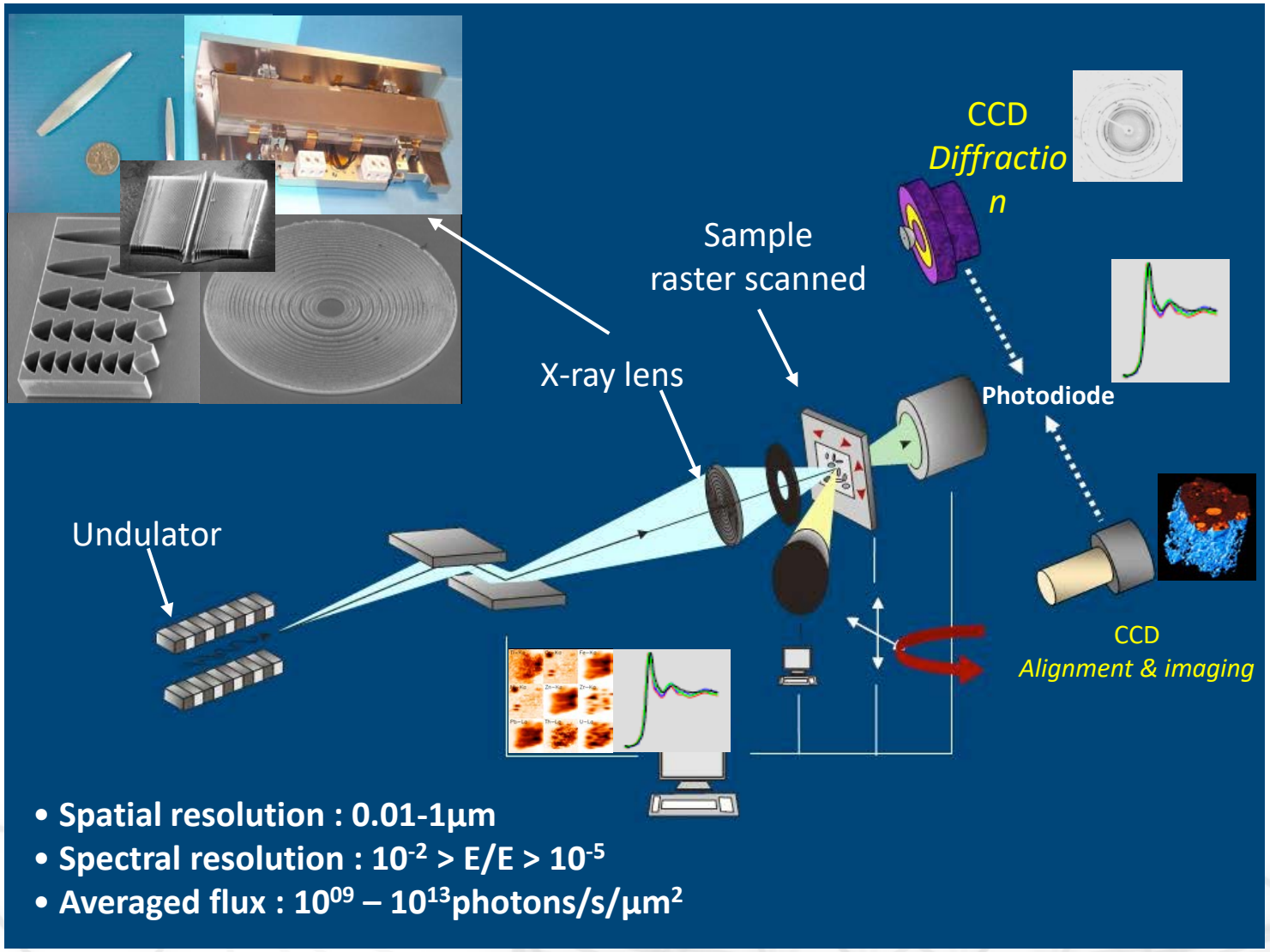
Time Resolution



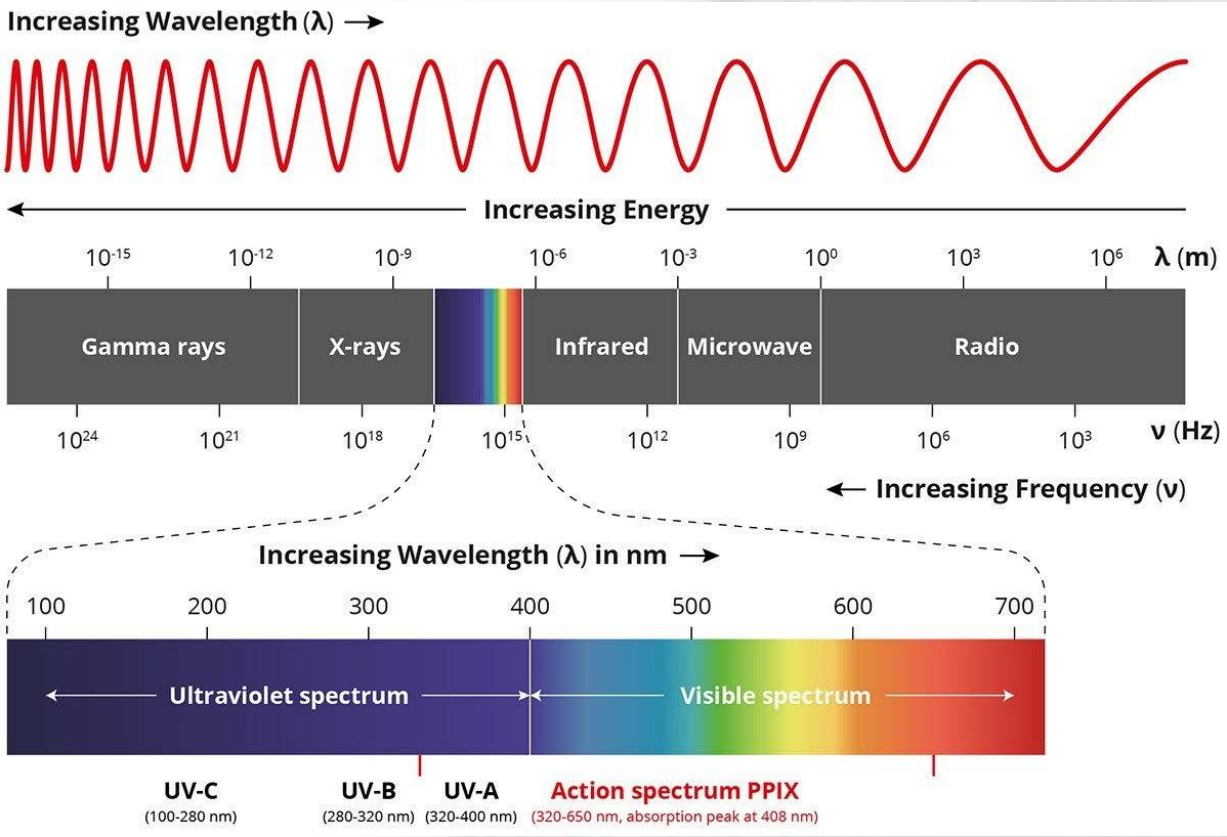
Dynamical Processes

New and Advanced microscopies

X-ray Microscopy : HOW?



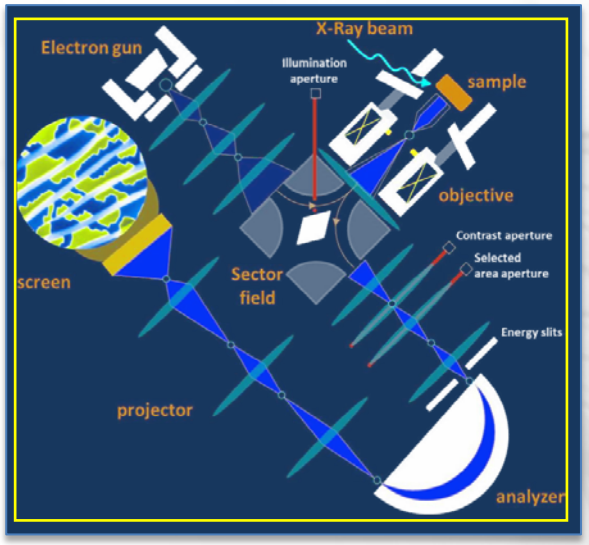
Why Soft X-rays ?



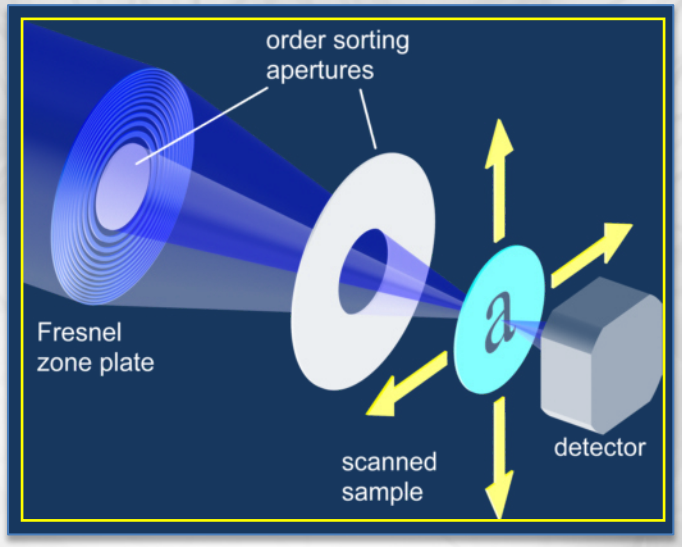
- Broad energy range to detect all the elements
- High spatial resolution
- « Water window » to study liquid adn in-vivo samples
- Combination of Spectroscopy + Microscopy

Photon-electron and Photon-Photon µcroscopy

XPEEM



STXM



Combining two microcopies:
Photon-Electron and Photon-Photon

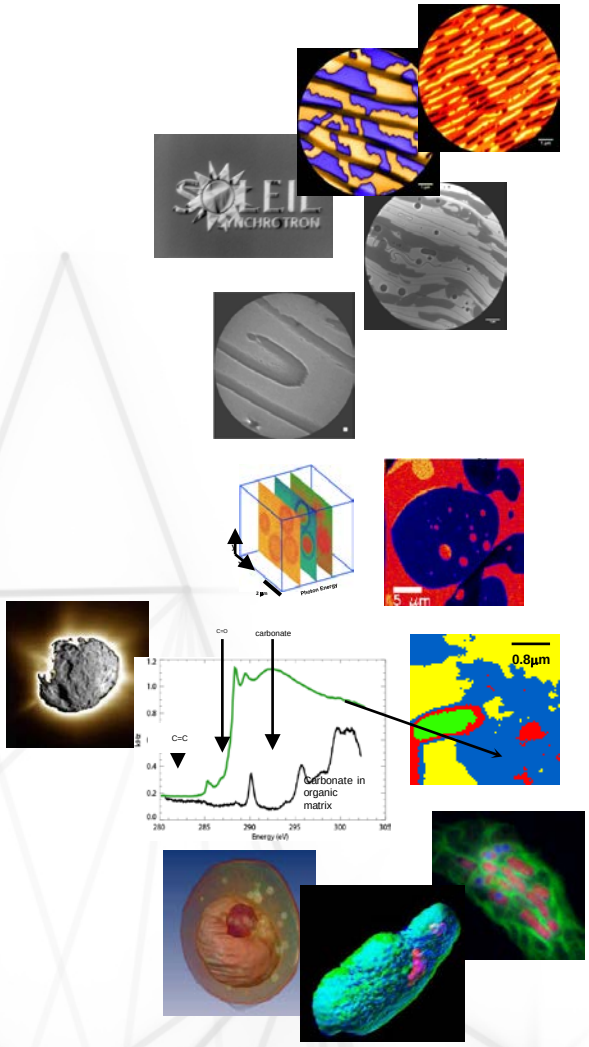
- ✓ *Surface/Interface Science*
- ✓ *Depth Analysis < 10nm*
- ✓ *Spectroscopic capabilities*
- ✓ *Fast acquisition time: Parallel mode*
- ✓ *UHV and controlled gas phase environment*
- ✓ *In and Ex-situ sample preparation.*
- ✓ *Time resolved measurements*

- ✓ *"Bulk" hard and soft matter science*
- ✓ *Depth Analysis < 500nm*
- ✓ *No UHV requirement*
- ✓ *Raster scanning mode*
- ✓ *Easy sample environment control:*
  High magnetic field, Cryogenic stage, wet cell, living cells …..

R. Belkhou & al., J. Synchrotron Rad. 22 (968) 2015

Broad Scientific programm

- ***Nanomagnetism and magnetic domain imaging***
  - *Ferro/Ferro, Ferro/Antiferro magnetic coupling*
  - *Current-induced magnetization switching, Magnetization dynamics,…*
  - *Nanostructures, Nanoparticles, Buried interfaces,…*
  - *Biogenic and geological magnetic minerals (Magnetite, Ferrites,..)*
- ***Surface and Interface Sciences:***
  - *Thin film growth mode*
  - *Elemental, topological and morphological inhomogeneities.*
  - *Diffusion, segregation, phase transition*
  - *Charge transfer, band gap mapping, electronic structure, Photoelectron diffraction….*
- ***Catalysis and surface chemistry:***
  - *Chemical reaction mechanism*
  - *Catalytic reaction, adsorbate diffusion, chemical waves….*
- ***Soft condensed matter:***
  - *Polymers wetting, de-wetting, Bonding, Matrix interaction, aggregation…*
  - *Biomineralisation, Nanoparticles, …*
  - *Component quantization, Polymer blends,…*
  - *Self assembled surfactant*
- ***Earth and environmental science:***
  - *Trace element analysis*
  - *Bacteria and microbes biomineralization*
  - *Extraterrestrial and spatial dust and meteorites chemical analysis*
  - *Bimolecular characterization and speciation maps in soils, rivers… Toxic and polluted soils*
  - *Archeology, Paleoclimatology,..*
- ***Biology, pharmacology and medicine science:***
  - *Nuclear architecture characterization.*
  - *Chromosomal translocation mechanisms*
  - *Intracellular drug probing, toxicity,*
  - *Biopolymer, biominerals and biomaterials*
  - *Cell and tissue recognition in cancer research*
  - *Metals in cells: toxicity and physiological functions*



Spectromicroscopy: Spectroscopy at nm Scale

Goal:

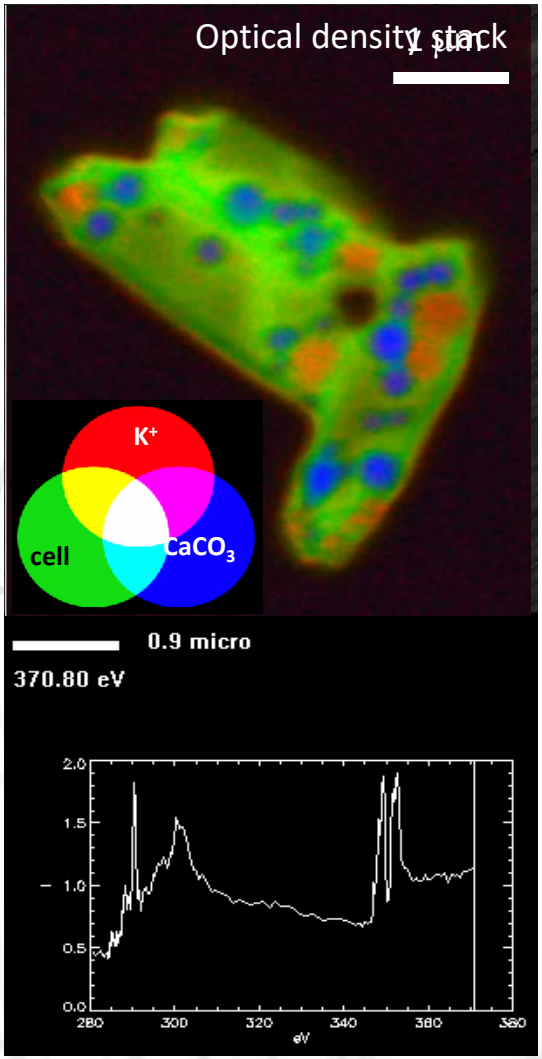
- *Measure chemistry of internal particles in C7-350* ***cyanobacteria*** *cultured in controlled levels of* Ca^{2+} *and* CO_3^{2-}

Experimental:

- Planktonic cells dispersed on hydrophilic silicon nitride window. Measured dry.

Results:

- ✓ Spherical $CaCO_3$ particles are well defined
- ✓ $CaPO_4$ deposited more uniformly in cells
- ✓ Significant amounts of localized K^+

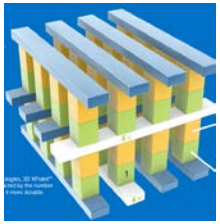


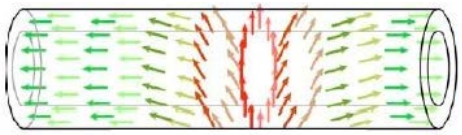
Collab. K. Benzerara (UPMC, FR))

C.L. Monteil, ISME Journal., 15 (1) 2021

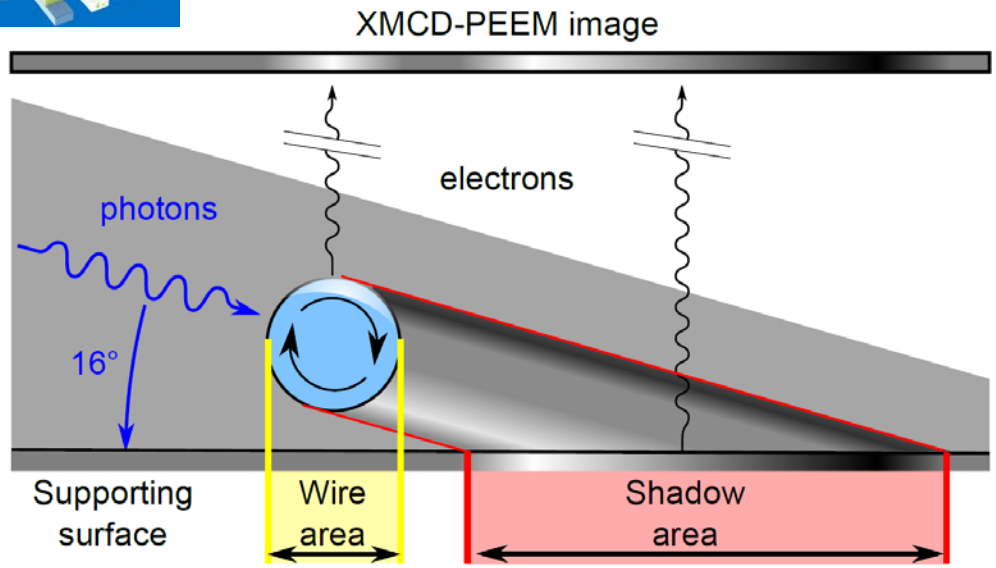
Magnetic Imaging

❖ ***Internal magnetic domains structure of CoNi nanotubes in the framework of 3D magnetic memories***



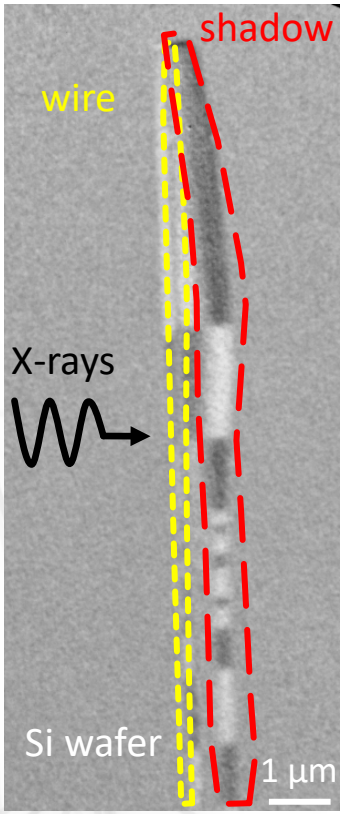


Shadowing effect



● **XAS**

● **XMCD Image**

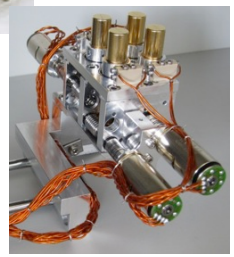


S. Da Col et al. , PRB 89, 180405(R) (2014)
S. Michal et al. Sub. Nano Letters (2018)

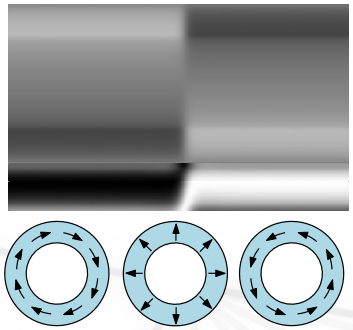
Imaging of surface vs. bulk magnetic domains onset of nanotube

In-Operando Magnetic Imaging

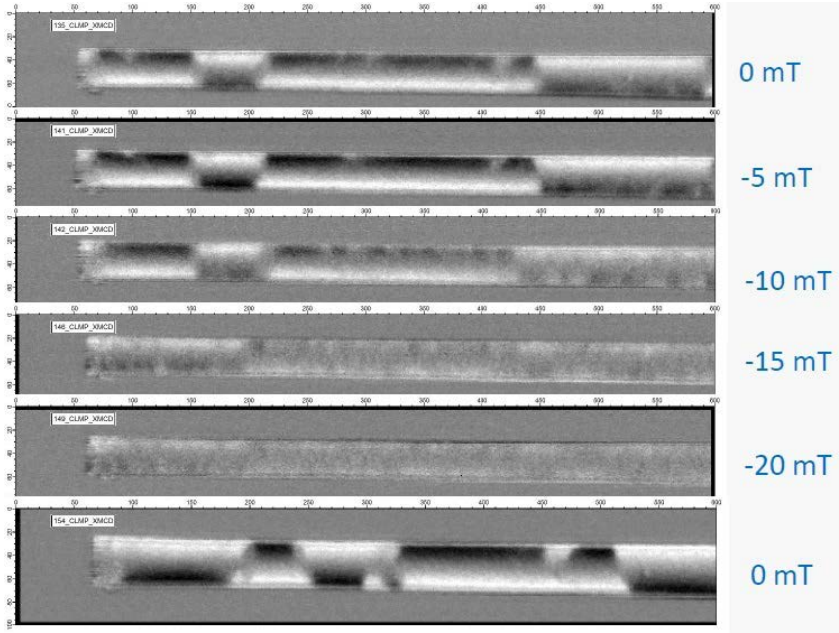
Rotary stage for Magnetic Tomography



Magnetic quadripole for vectorial magnetisation Current injection…



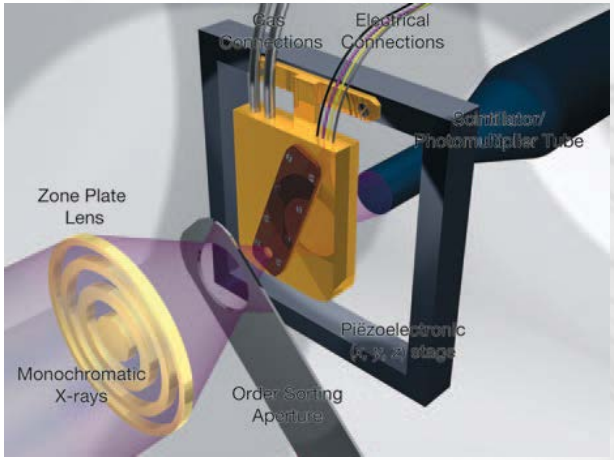
Magnetic anisotropy evaluation: CoNi nanotubes

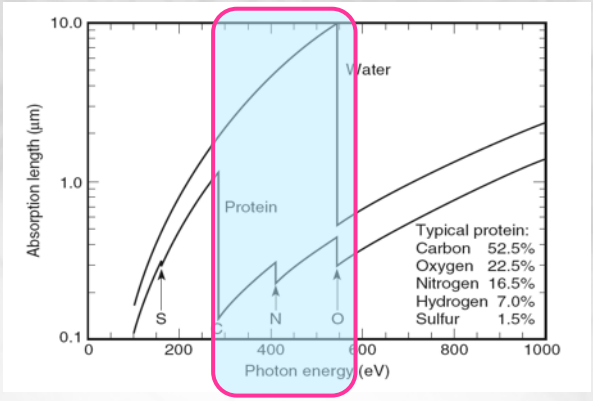


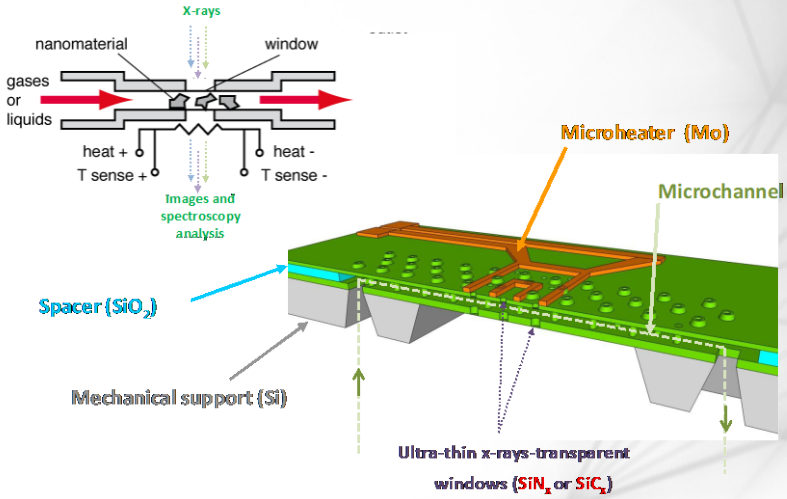
Collab. O. Fruchart (I. Nèel - Spintec, Grenoble)

Bloch DW's separating azimuthal magnetic domains

In-Operando X-ray Microscopy



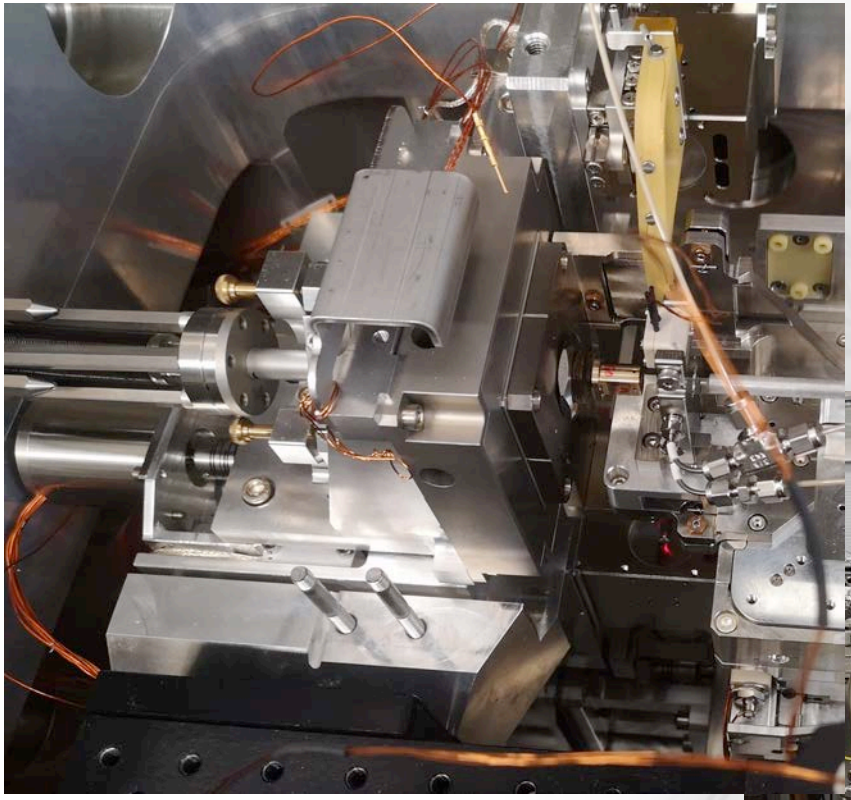


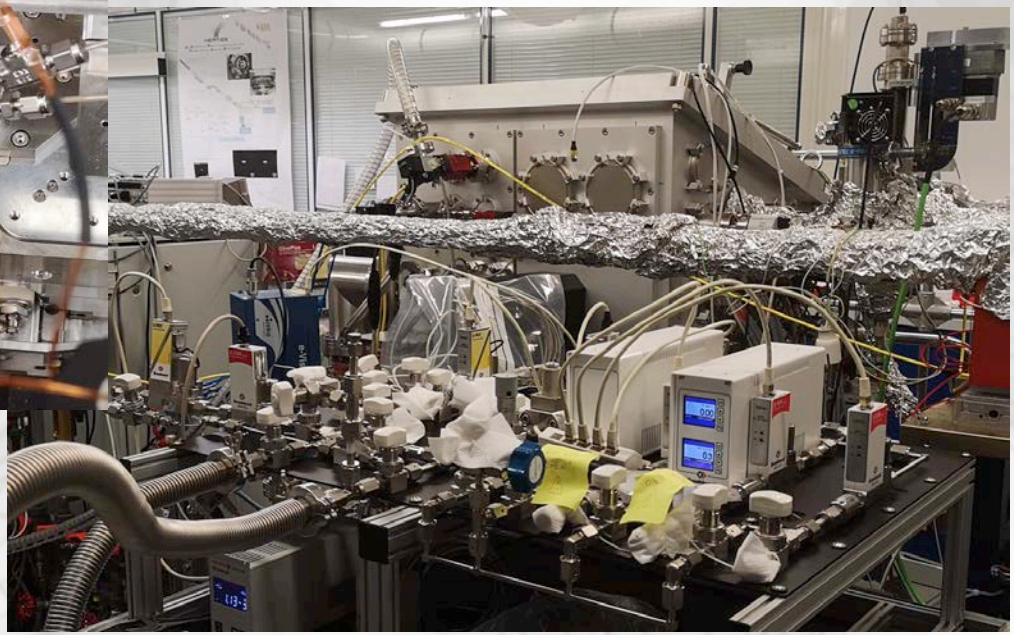


Sample environment has to be 'tailored' for various specific applications:

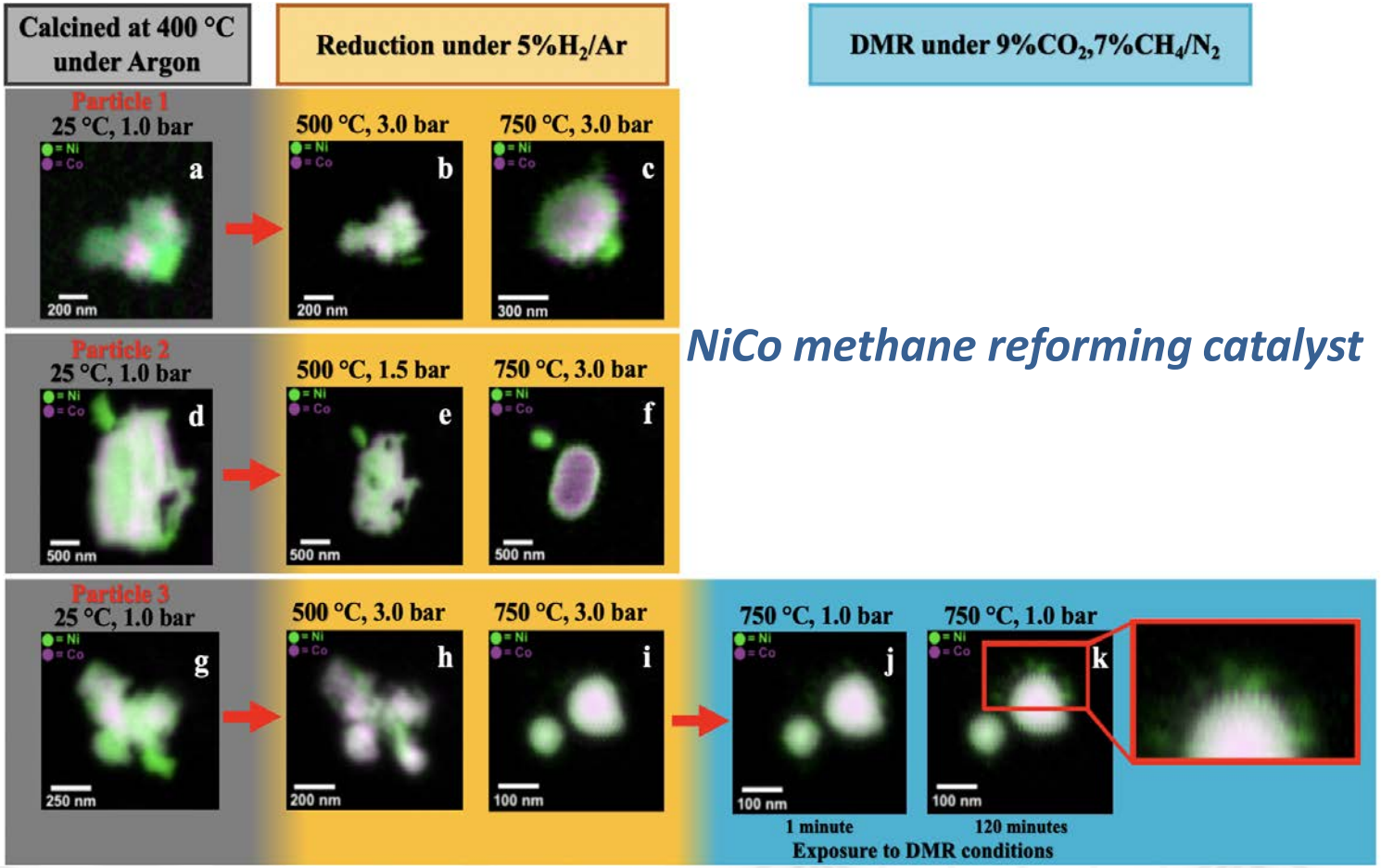
- *Fuel, MicroFluidic, Catalytic, Wet Cells ….*
- *Solid or liquid electrolytes, batteries….*
- *Organic or Inorganic solar cell*
- *In-Operando Nanoprobe*

In-Operando X-ray Microscopy





NiCo methane reforming catalyst

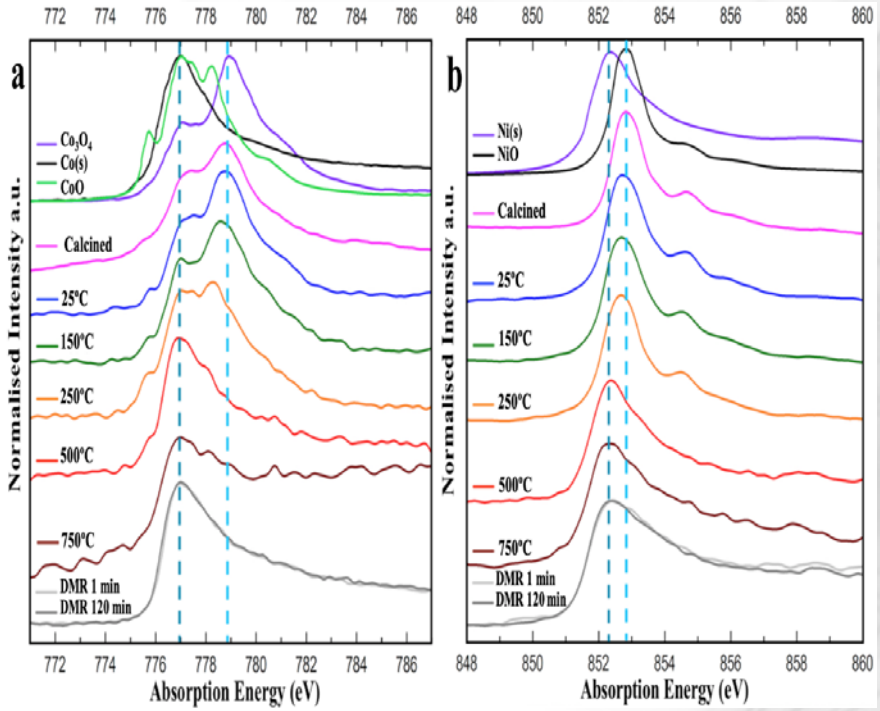


NiCo methane reforming catalyst

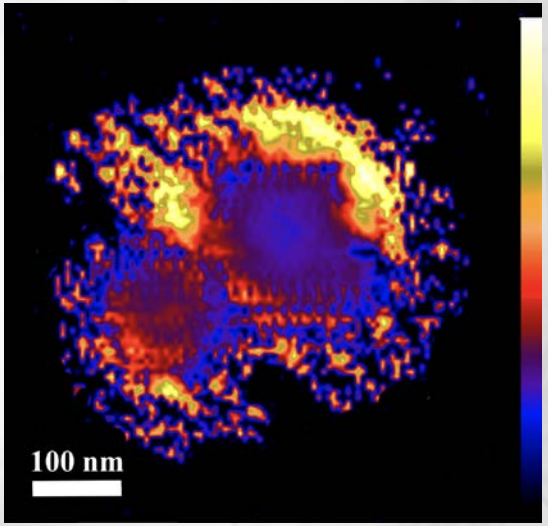
A. Askari et al., ASC Catalysis. 10 (6223) 2020 (2019)

Coll. Max Planck Gesellschaft

NiCo methane reforming catalyst



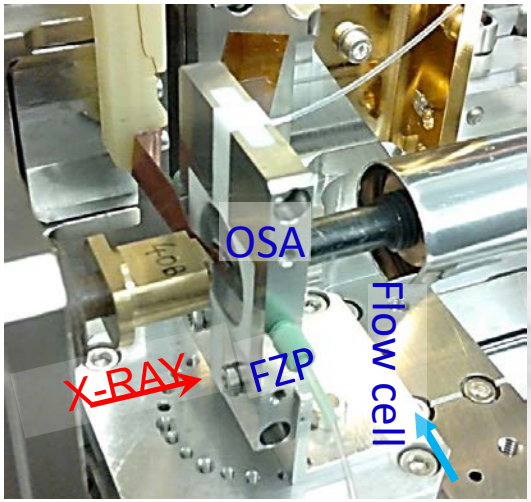
During DMR Ni migrates from the shell to the branches
9 bar – 1000°C

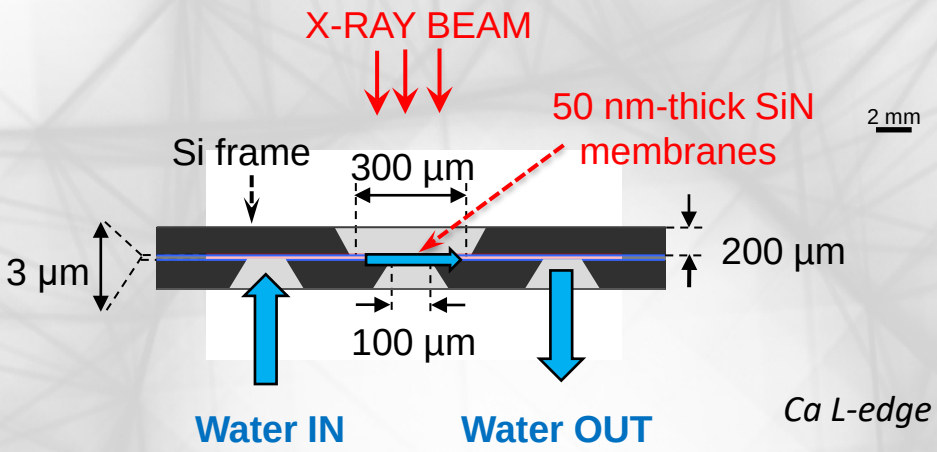


Ni is likely the primary active site, while the more readily oxidized Co may serve as an electron donor to Ni during catalysis.

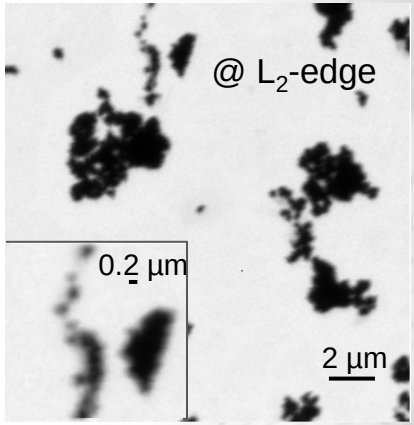
A. Askari et al., ASC Catalysis. 10 (6223) 2020 (2019)
Coll. Max Planck Gesellschaft

Liquid Flow Cell

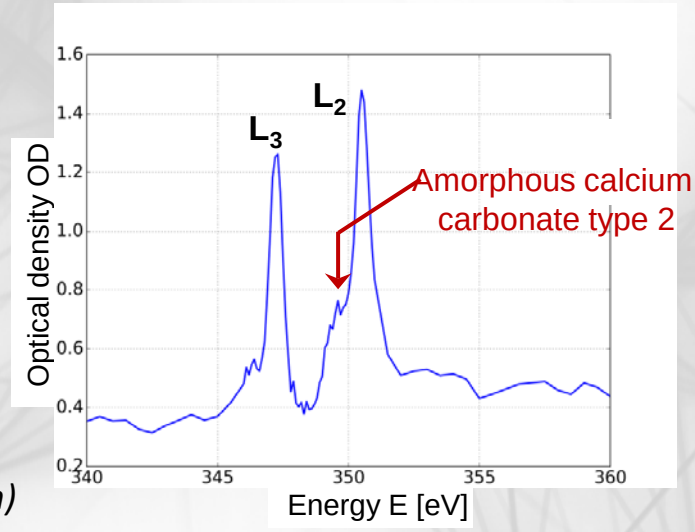




Ca L-edge



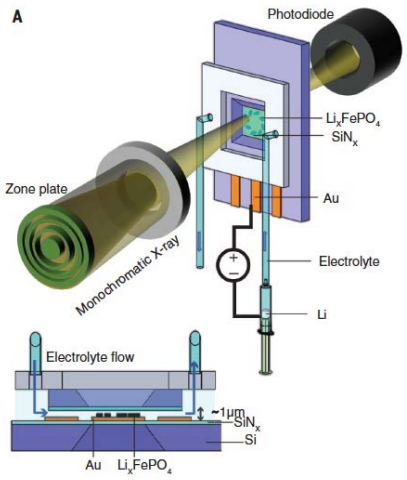
Calcite nanoparticles (90 nm)



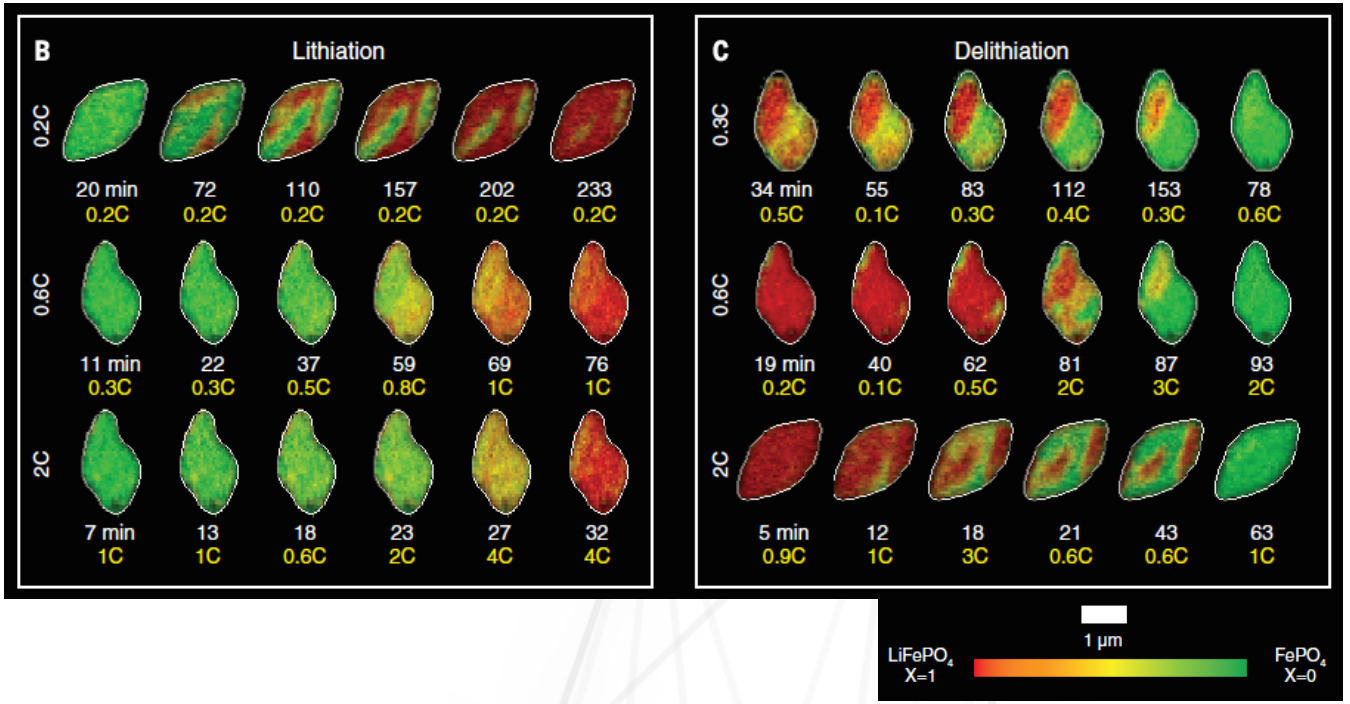
Collab. C. Chevallard & al.

C. Gosse et al., Lab Chip, 2020, 20, 3213–3229

Lithium compositional spatiodynamics



Battery primary particles



Lithiation suppress compositional nonuniformities

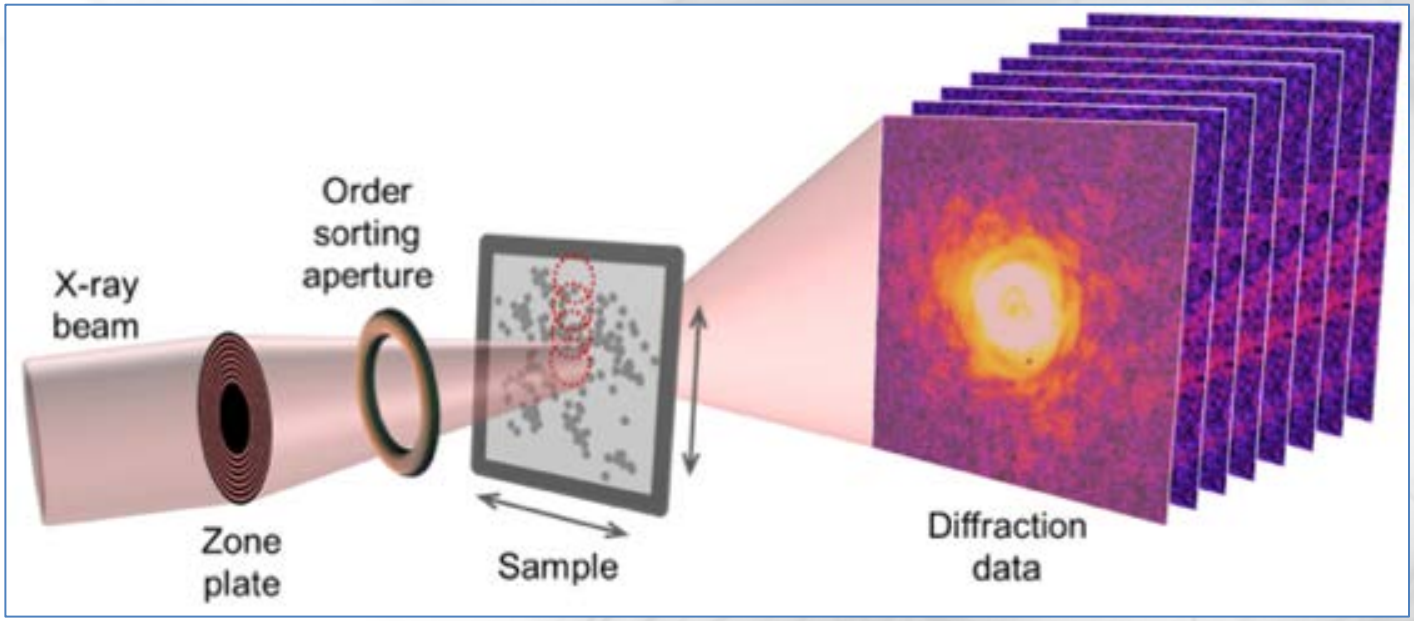
Not true for delithiation

ALS Synchrotron - Berkley

J. Lim et al., Science 353 (2016) 6299

PTYCHOGRAPHY – Sub 10nm resolution

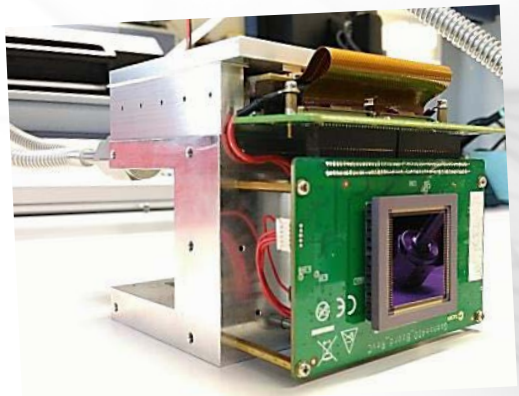
Combining Microscopy and Coherent Diffraction



- ***High X-rays Coherence --> Better scattering signal***
- ***Do not depends on the focusing optics***
- ***Gives access to the Phase and the Amplitude of the scattered beam***
- ***Possible to achieve ultimate spatial resolution (Diffraction limit 1nm)***

New back-side illuminated CMOS Camera

❖ ***New CMOS back-illuminated camera***



DhyanaX (sCMOS GSENSE400BSI)

❖ ***Main advantage with respect to CCD:***

- ✓ ***High frame rate (48fps)***
- ✓ ***High charge capacity***
- ✓ ***Low read-out noise***
- ✓ ***Low dark current***
- ✓ ***Less expensive***

Specifications GSENSE400BSI

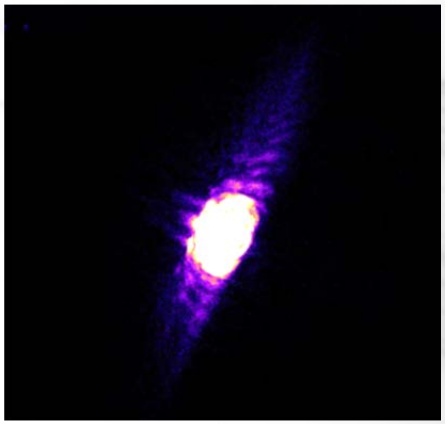
	Value	References
Gain	Low gain, High gain or HDR mode	GPIXEL® datasheet (www.gpixel.com) TUCSEN® Dhyana95 datasheet (www.tucsens.com)
Frame Rate	24 Hz Full frame (HDR) 48 Hz Full frame (LG or HG)	
Pixel Size	11 x 11 µm²	
Sensor size	4M — 2048 × 2048 pixels 22.5 mm × 22.5 mm)	
Readout noise	< 2 e- rms (HDR & HG) & < 45 e- rms (LG)	Desjardins et al, 2019 Wang et al., 2017
Dark current	~ 3 e-/s/pix (-20°C)	
FWC	30 ke- (HDR), 1700 e- (HG) & > 80 ke- (LG)	

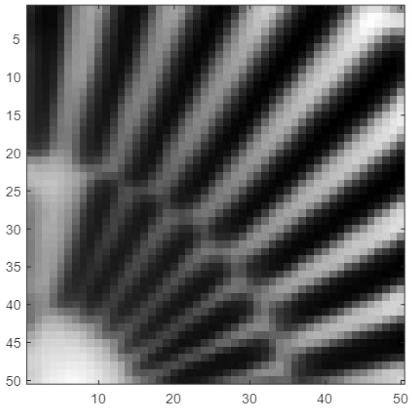
Collab. Detector Group - SOLEIL
K. Desjardin & al., J. Synchrotron Rad. 27 (2020) 1577

First PTYCHO @ HERMES

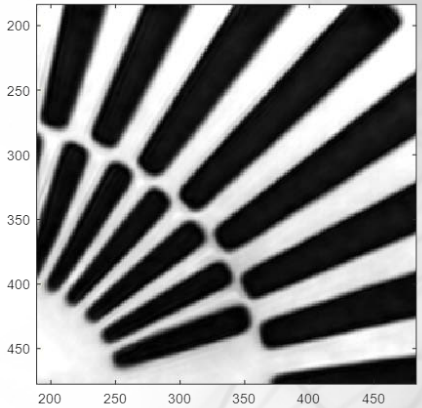
❖ *SIEMENS Star patterned sample*

Diffraction image





STXM



PTYCHO

❖ *Magnetotactic Bacteria: Magnetosoms*

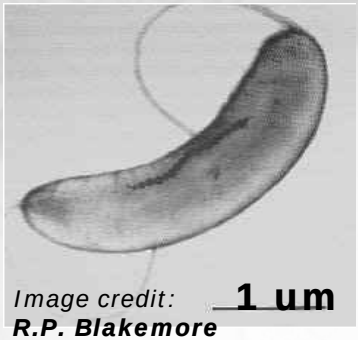
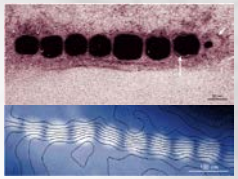
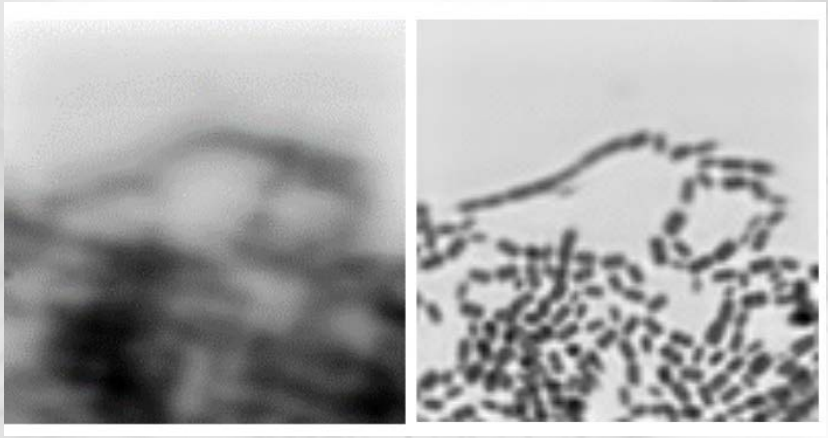


Image credit: ***R.P. Blakemore***

HR TEM



Nat. Rev. Microbiol **2004,** 2, 217.



STXM *PTYCHO*

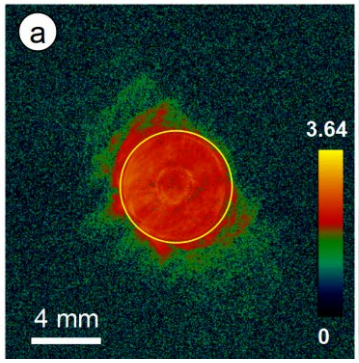
6.2nm FRC resolution

K. Desjardin & al., J. Synchrotron Rad. 27 (2020) 1577

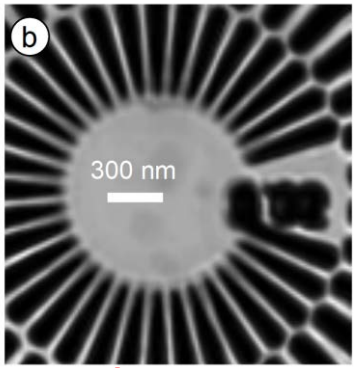
Ptychography at the Carbon edge

❖ *SIEMENS Star patterned sample @ 285eV*

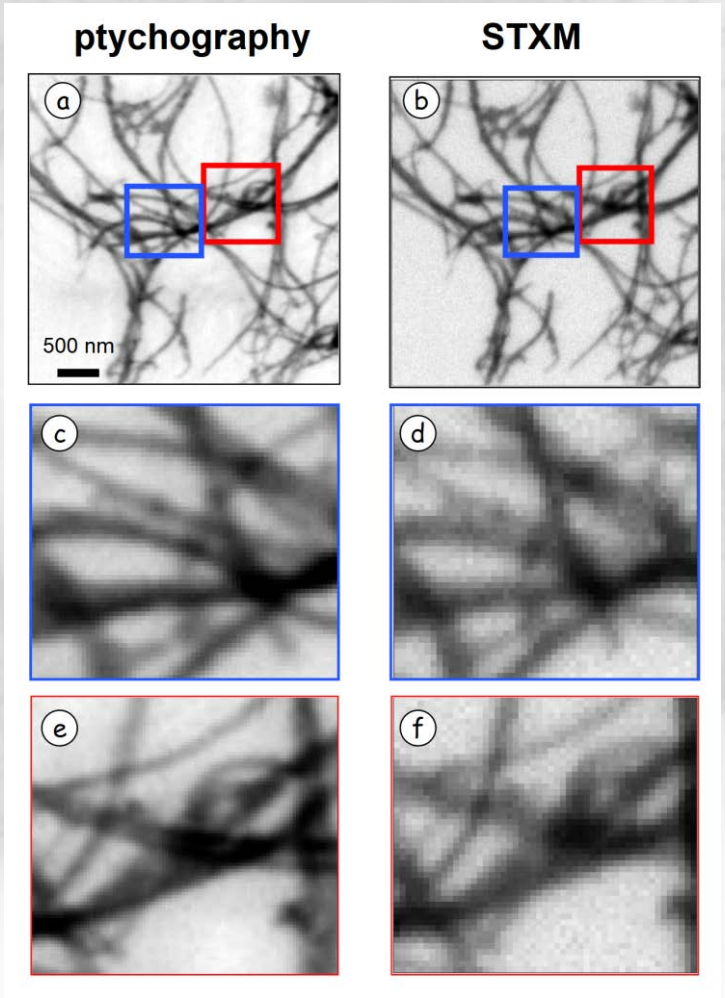
Diffraction Pattern



PTYCHO



❖ *Carbon Nanotubes*



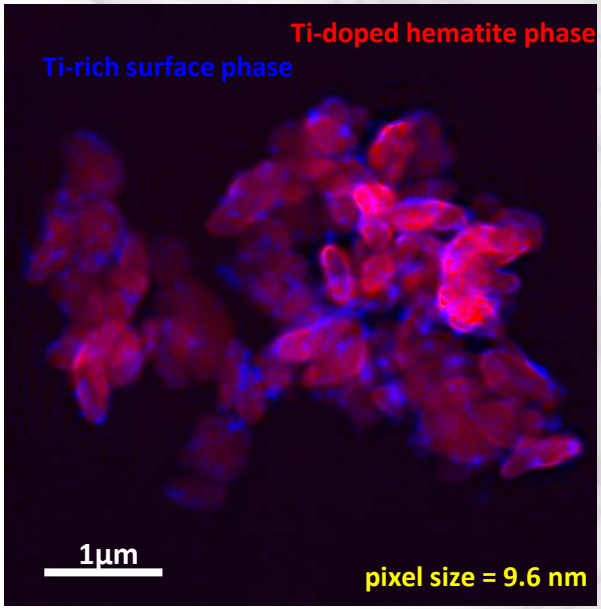
First Ptychography measurements at the Carbon edge:

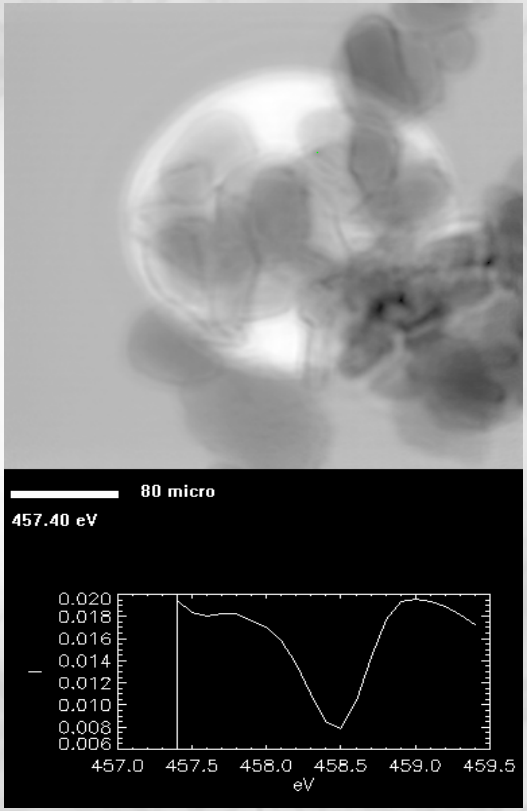
New opportunity for biology, soft matter, environmental science…

N. Mille & al., Nature Com. 3 (8) 2022.

Spectro - Ptychography

Hematite-based photoelectrochemical activity enhancement upon annealing in oxygen deficient atmosphere



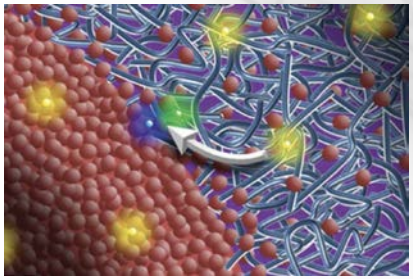


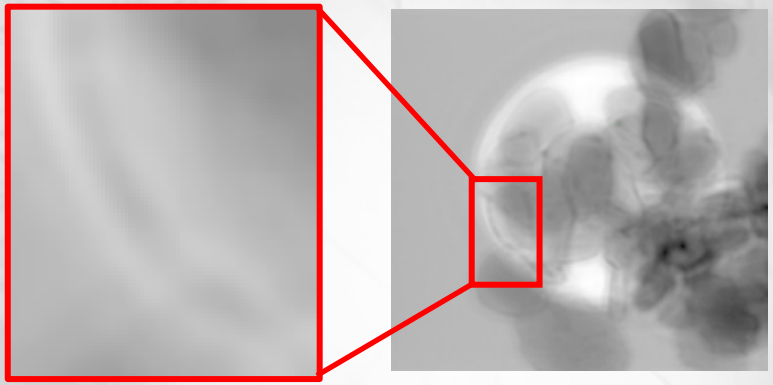
Spectro-ptychography reveals Ti L_3 t_{2g} shift of 0.11 eV in surface compared to bulk, most probably related to formation of surface $TiFeO_x$ (ilmenite-like) phase.

Conclusions & Outlooks

- ✓ Chemical, Electronic & Magnetic mapping at spatial resolution (<10nm) on a regular basis [= better Science] *(High Flux and Coherence)*

Surface, Bulk + INTERFACES





- ✓ Higher thoroughput--->Automation/high thoroughput experiments might interest industries

- ✓ Bring X-ray microscopy to an unprecedent level:

Faster, Smaller and more Efficient

- ✓ Other microscopy beamlines at SOLEIL: ANATOMIX (Tomo), ANTARES (Nano ARPES), NANOSCOPIUM (Hard X-ray microscopy), LUCIA (Tender X-ray microscopy)…..

The HERMES TEAM