Soft X-ray Spectromicroscopy on nanoscale

Tolek Tyliszczak

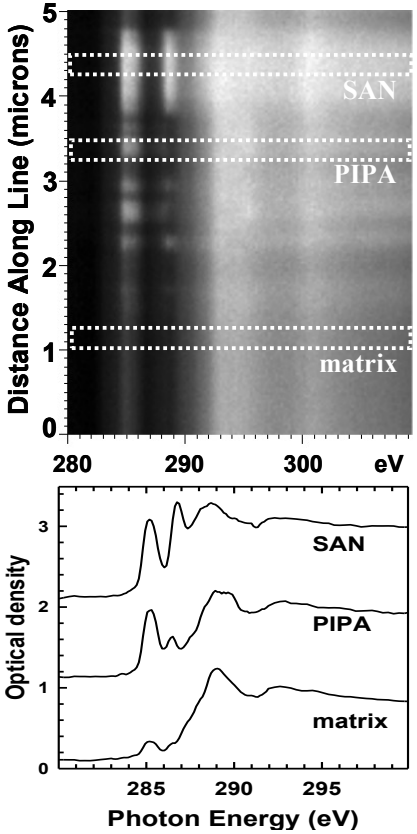
Advanced Light Source

Transmission X-ray Microscope – best tool for soft x-ray spectroscopy

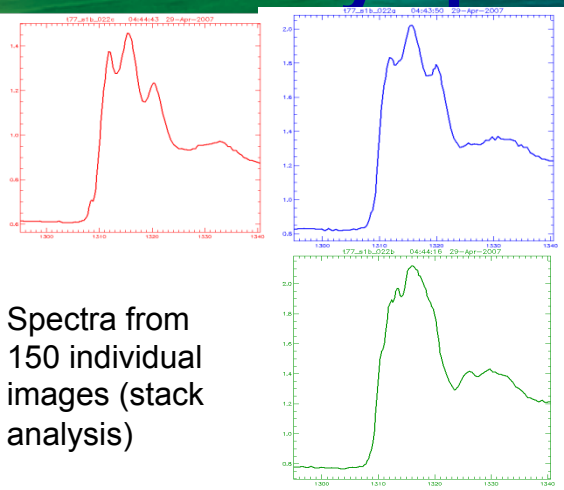
$I = I_0 e^{-\rho\mu d}$

Can be measured at the same way as the I

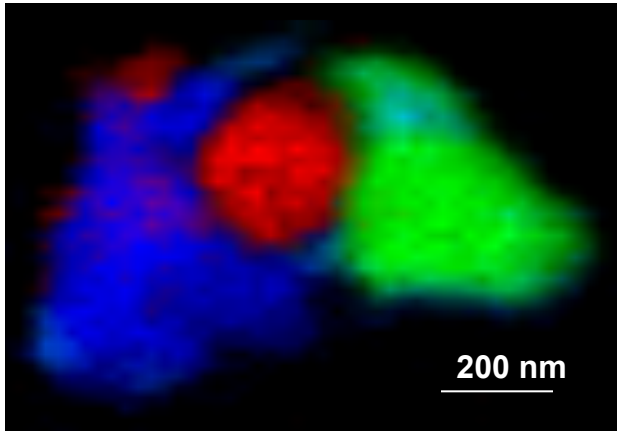
Spectra from line scan

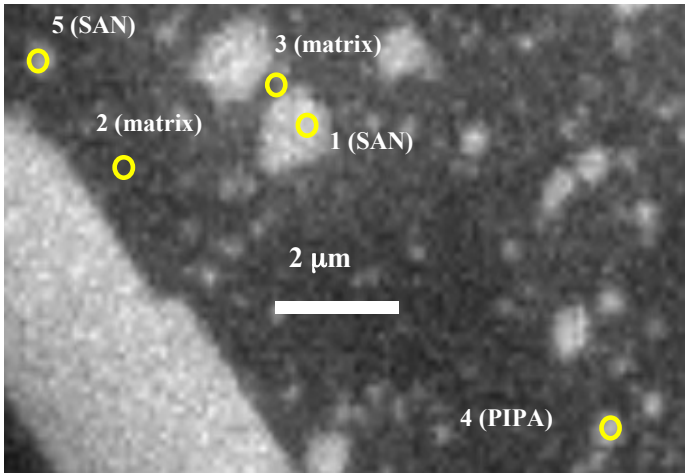


Spectra from 150 individual images (stack analysis)



MgaMgbMgc





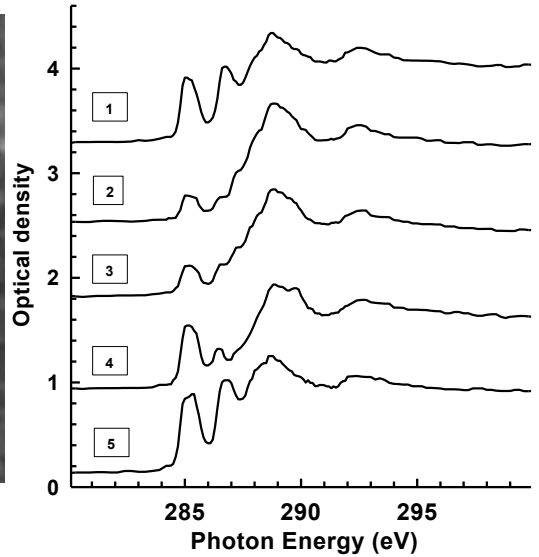
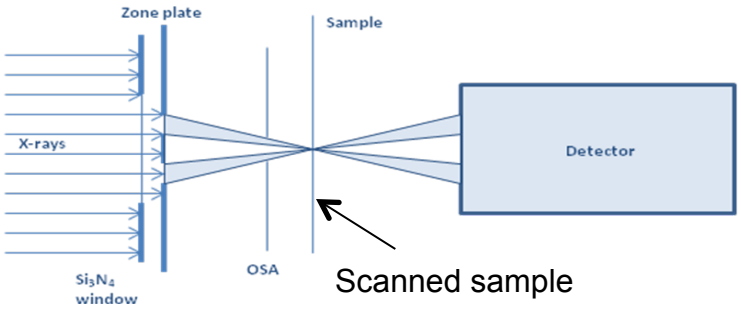
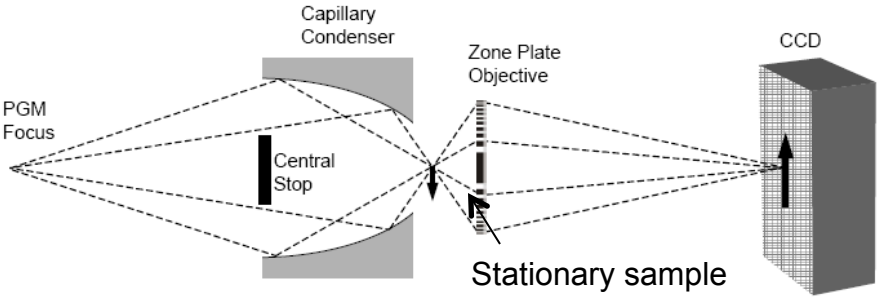


Fig. 3.6 Point spectra of multiple regions of Dow#355 sample, recorded simultaneously. (left) location of points). (right) spectra derived from point signals and hole signal (out of image range) recorded at same

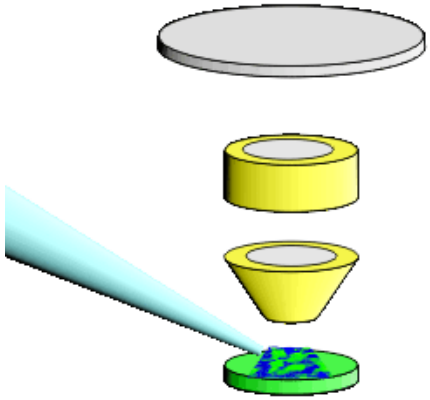
Soft X-ray Microscopy



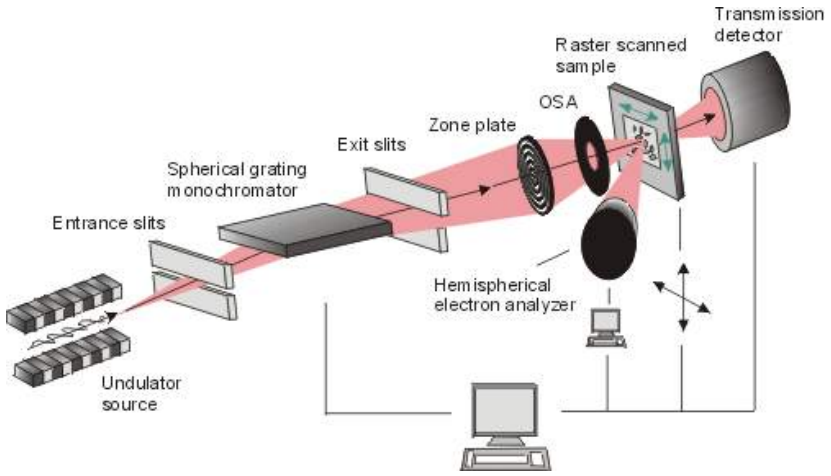
Scanning Transmission X-ray Microscope (STXM)



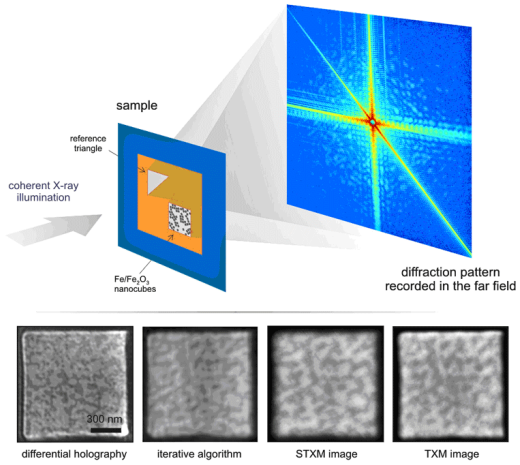
Transmission X-ray Microscope (TXM) - BESSY implementation



Photoelectron Emission Microscope (PEEM)

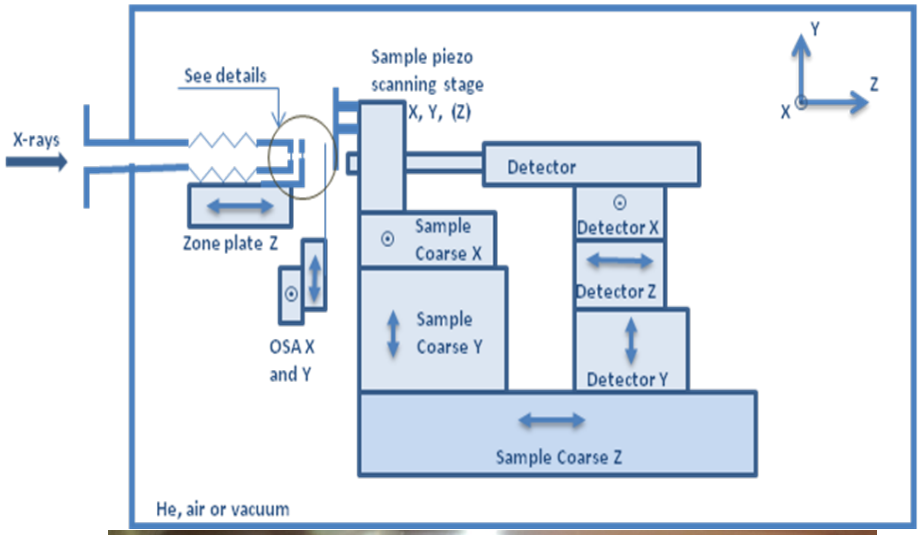


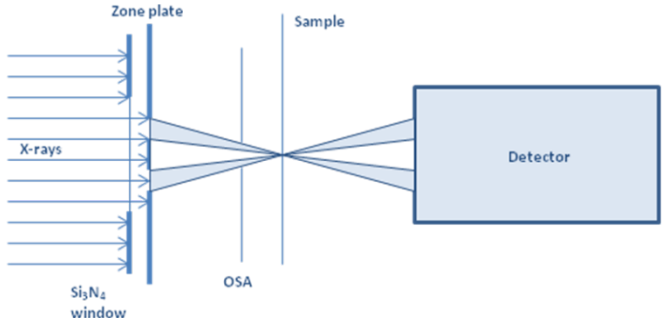
Scanning Photoemission Electron microscopy (SPEM)

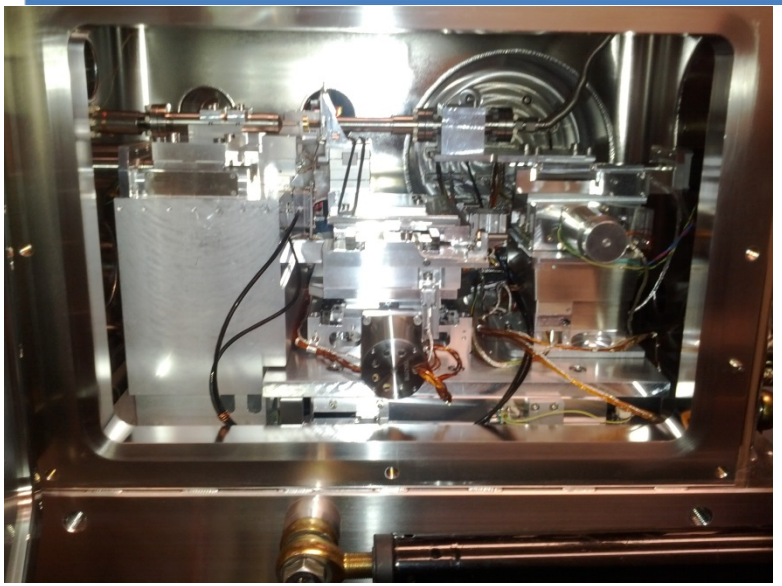


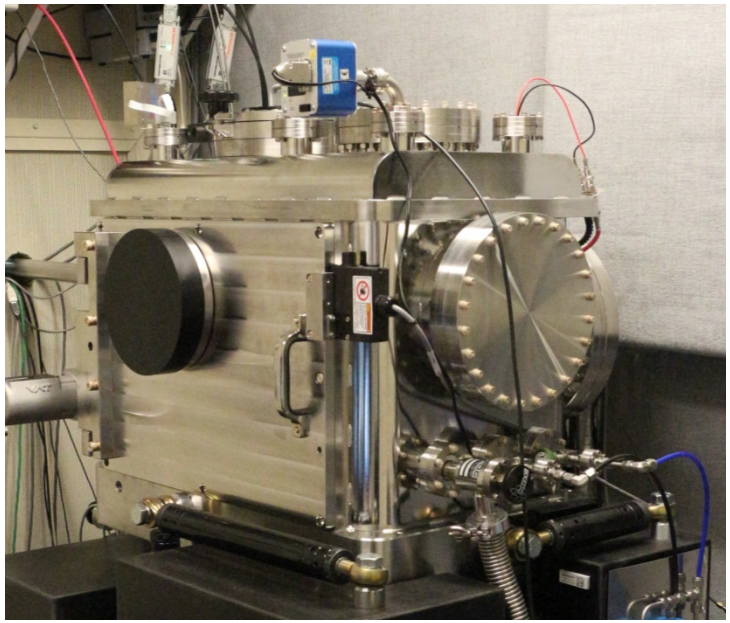
Coherent Diffraction Imaging (CDI)

STXM


See details
Sample piezo scanning stage X, Y, (Z)
Y
Z
X
X-rays
Detector
Zone plate Z
Sample Coarse X
Detector X
Detector Z
Sample Coarse Y
OSA X and Y
Detector Y
Sample Coarse Z
He, air or vacuum


Zone plate
Sample
X-rays
Detector
OSA
Si_3N_4 window





Soft X-ray Spectromicroscopy summary

Soft X-ray spectroscopy has high chemical sensitivity
Combined with a microscope provide high chemical sensitivity on nanoscale
Current x-ray microscope spatial resolution:

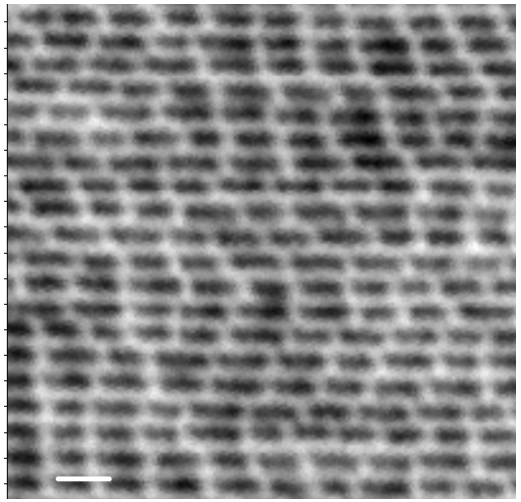
- 10 nm for imaging
- 50 nm for spectroscopy

Ways to improve resolution:

- Ptychography (combination of transmission scanning microscope with diffraction) – very promising
- Improvement of the zone plates – technical limitation
- Laue lenses - difficult to make for soft X-rays
- Combination of the scanning transmission microscope and scanning probe microscope for modification of the X-ray beam shape -
- PEEM – demonstrated 5nm at VUV, for x-rays needs better aberration correction, energy filters

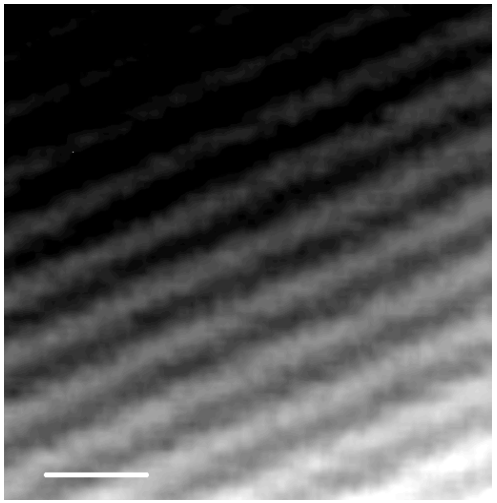
Zone plates and achieved resolution

25 nm zone plate



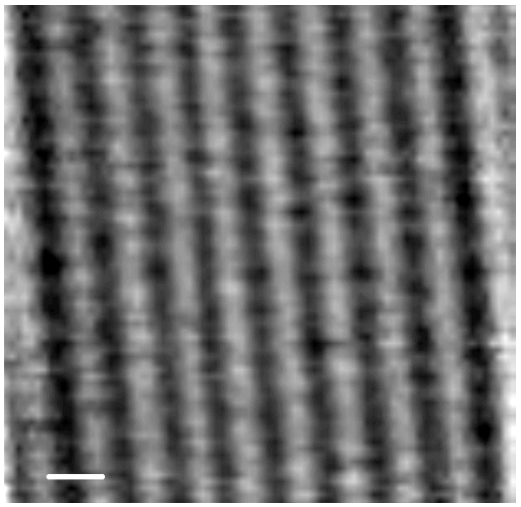
20 nm (vertical) Au lines

20 nm zone plate

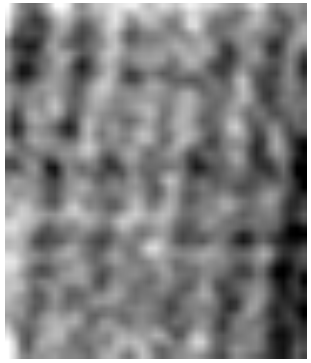


12 nm lines Si/Mo

17 nm zone plate



10 nm lines Si/Mo

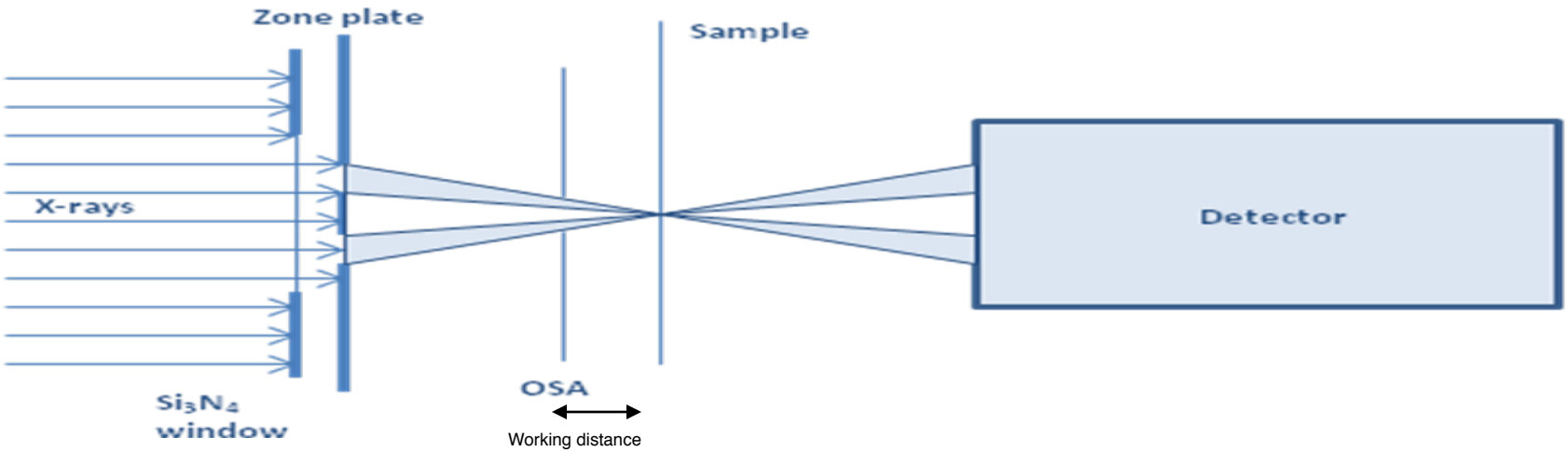


9 nm lines Si/Mo
Imaged by 17 nm zone plate

All images taken at 700 eV
Structures have equal line/space nominal dimensions
Dimensions of half periods are quoted

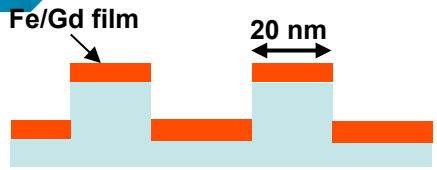
Zone plates and working distance

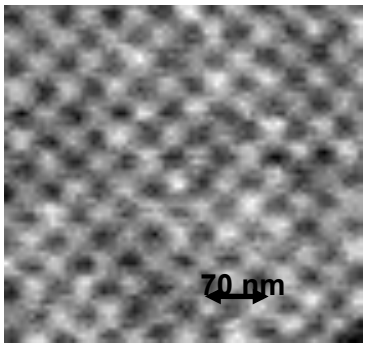
Beam size d = 1.22 * ΔR



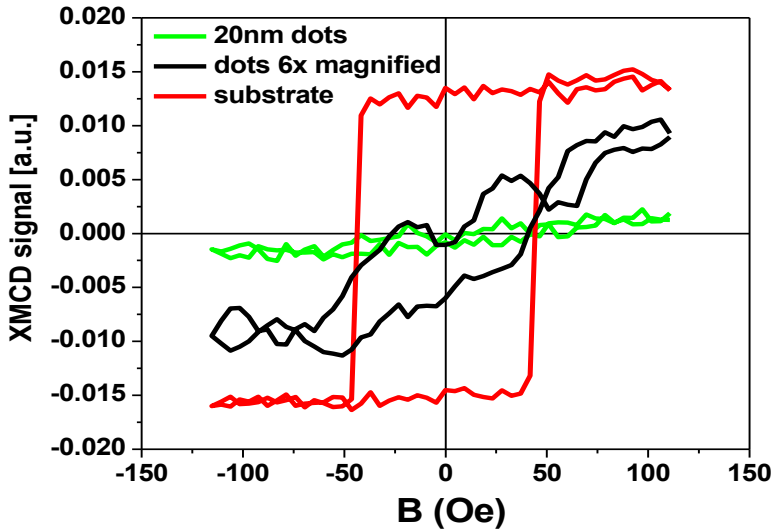
ΔR [nm]	D [μm]	Working distance	Focal length [mm]		
		at 300 eV	300 eV	700 eV	1800 eV
45	240	700	2810	6790	17460
25	240	350	1467	3423	8802

spectroscopy – XMCD - magnetism





STXM image of EUV structured Fe/ Gd dots with a diameter of 20 nm and a periodicity of 70 nm recorded at the Fe L_3 edge



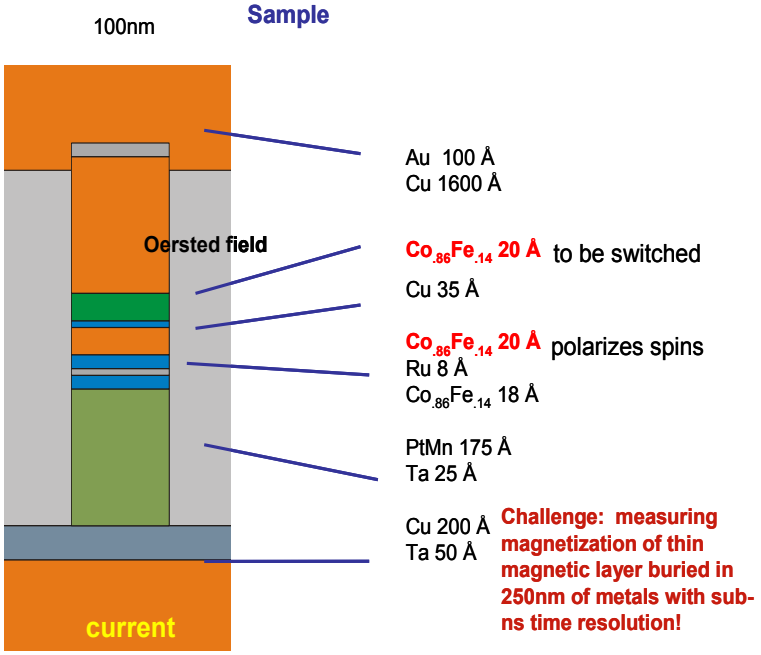
Hysteresis loop of 20 nm dots (ensemble) and of the film between the dots measured by XMCD

Nanopattern magnetic structure – investigations of magnetization of technologically important behavior in external magnetic/electric field

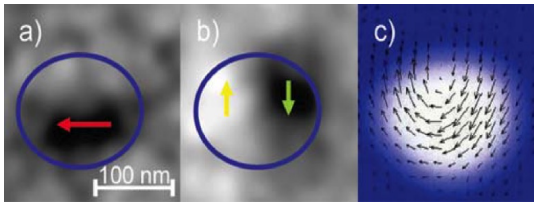
T. Eimüller, E. Amaladass, F. Luo, T. Tyliszczak,

Direct observation of magnetization reversal by spin injection – ultimate X-ray microscope challenge

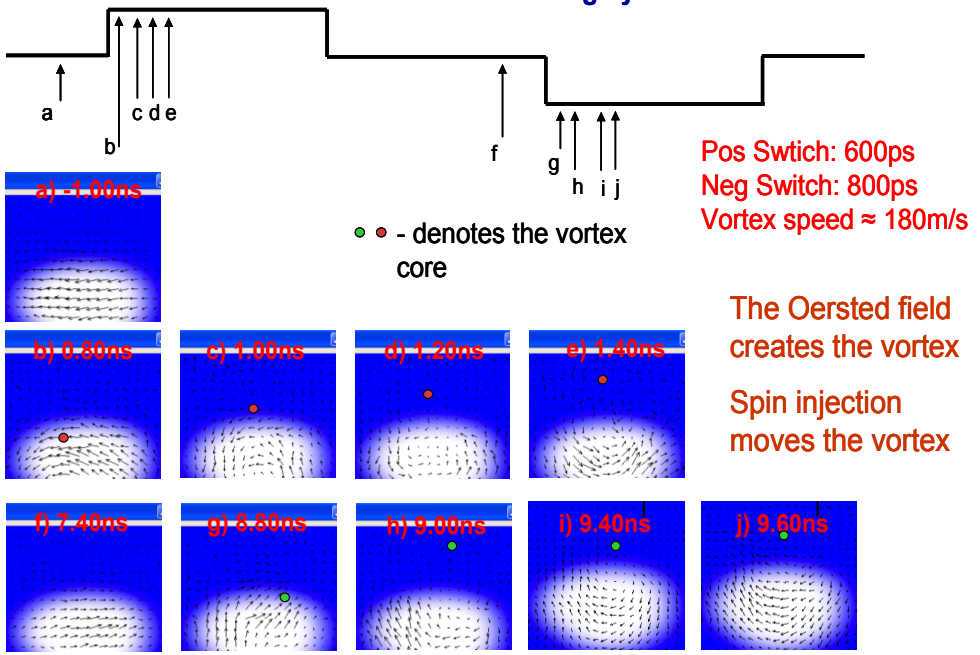
Magnetization Reversal by Spin Injection



Sample prepared by Jordan Katine, *Hitachi Global Storage*



From magnetization measured in 2 directions (Fig a and b) magnetization vectors are constructed (Fig c)



- X-rays allow us to image the switching process
- The vortex provides an alternative switching mechanism
- Smaller structures switch by a different mechanism (C-state flip-over?)

Time Resolved Imaging of Spin Transfer Switching: Beyond the Macro-Spin Concept, Y. Acremann, J. P. Strachan, V. Chembrolu, S. D. Andrews, T. Tyliszczak, J. A. Katine,M. J. Carey, B. M. Clemens, H. C. Siegmann, and J. Stohr, Phys.Rev. Lett. **96** 217202 (2006.)

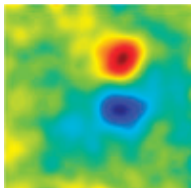
Software defined photon counting system for time resolved x-ray experiments Y. Acremann, V. Chembrolu, J. P. Strachan, T. Tyliszczak, and J. Stöhr, Rev. Sci. Instrum. **78**, 014702 (2007).

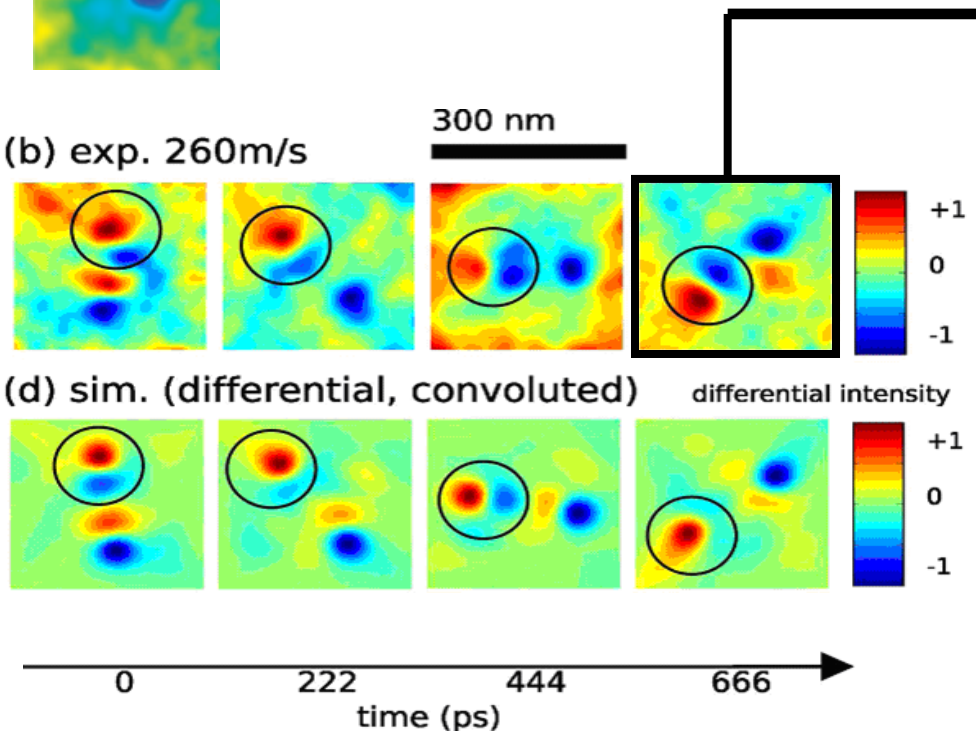
Measurements of magnetization distribution dinamics of 2 nm layer buried in 200 nm metal of 100 nm diameter pillar with 70 ps resolution

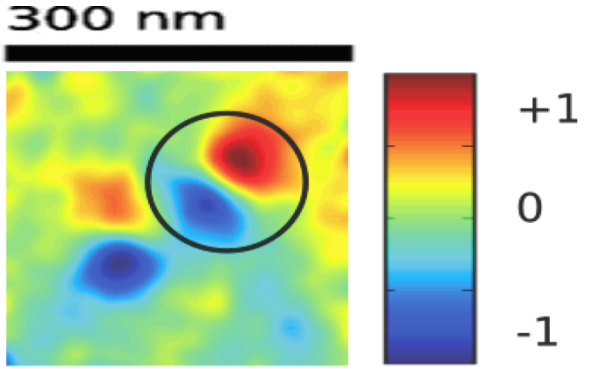
X-ray imaging of the dynamic magnetic vortex core deformation

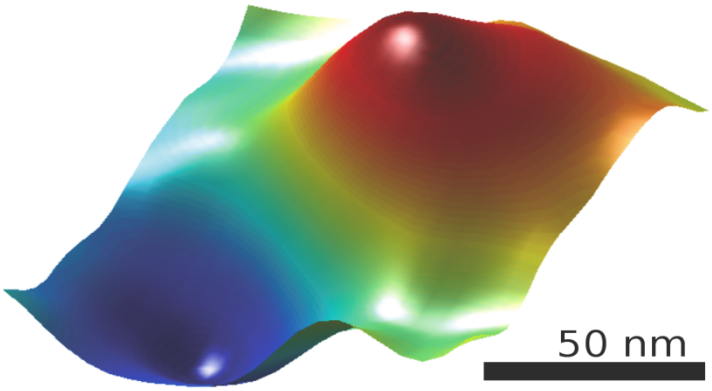
Vortex core size 10-20 nm

Exp. 160 m/s





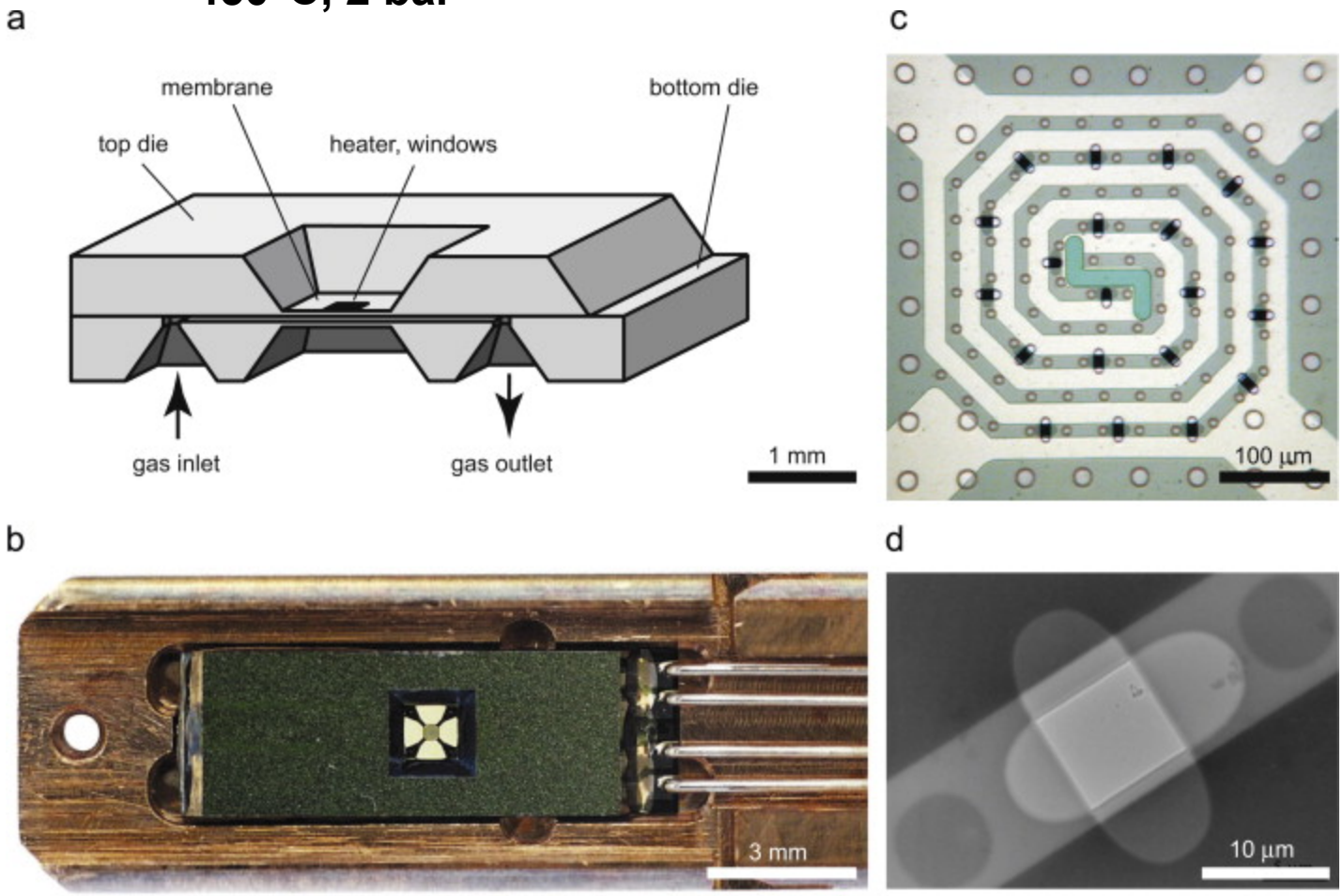




A. Vansteenkiste, K.W. Chou, M.Weigand, M. Curcic, V. Sackmann, H. Stoll, T. Tyliszczak, G.Woltersdorf, C. H. Back, G. Schütz and B. VanWaeyenberge, Nature Physics, 2009

In-Situ STXM environmental cell #2

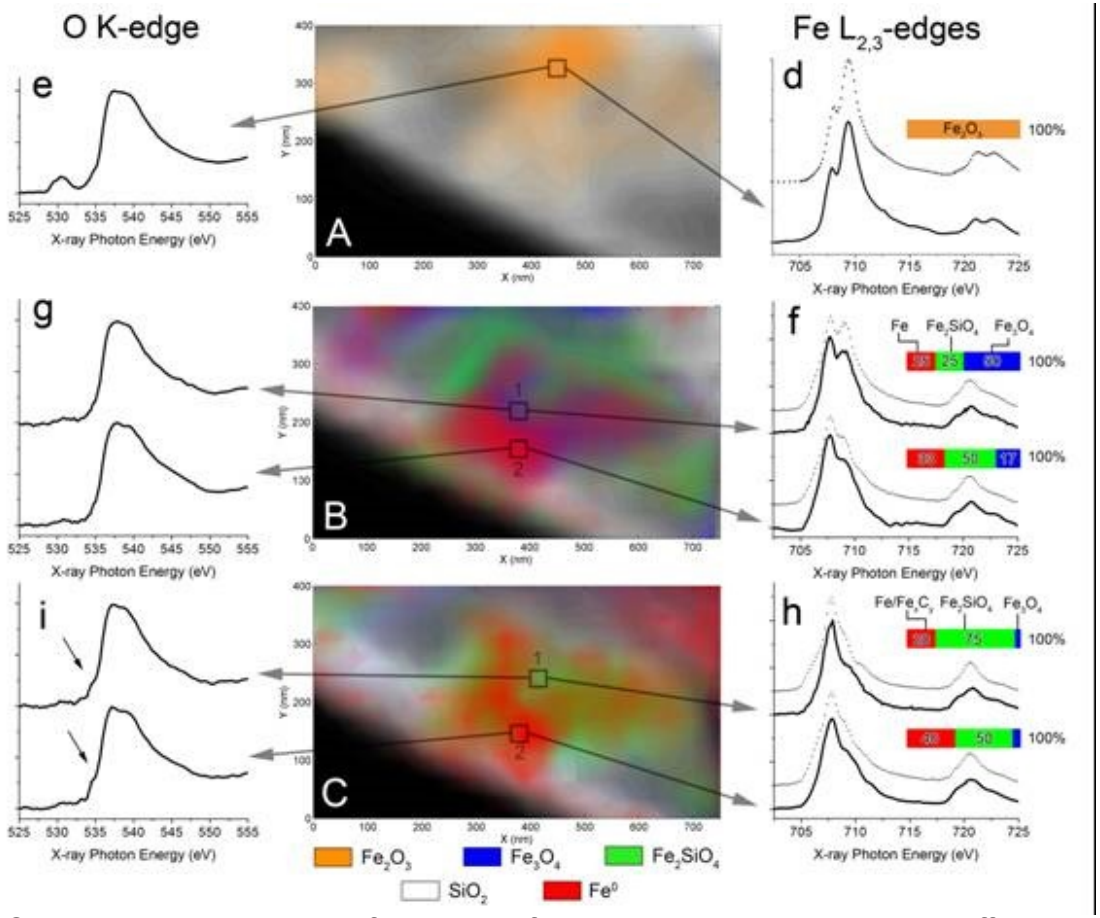
450°C, 2 bar

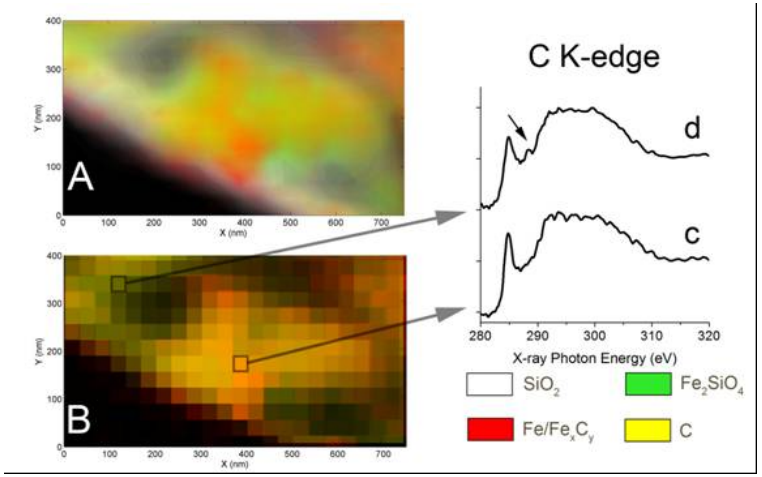


Creemer, J. F. et al., Ultramicroscopy 108, 993–998

In situ catalytic reactions

complex iron oxide based Fischer-Tropsch catalyst



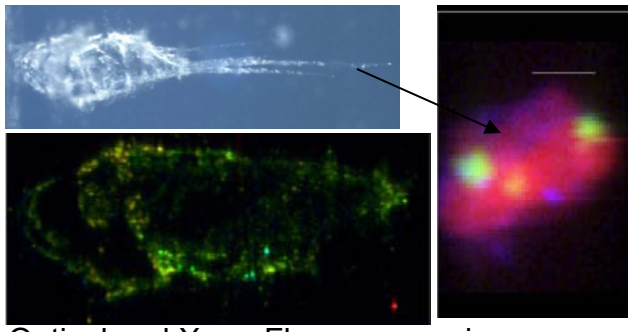


:Chemical contour maps of a region of a catalyst particle during the different stages of reaction. A: Before treatment at RT in 1 bar He. B: After 2h in H2 at 350°C. C: After 4h in CO/H2 at 250°C. The corresponding regions of the O K-edge (e, g, i) and Fe L2,3-edge spectra (d, f, h) are indicated in the figures. Dotted lines indicate the linear combination fits, with the bars representing the contribution of the different phases to the spectra.

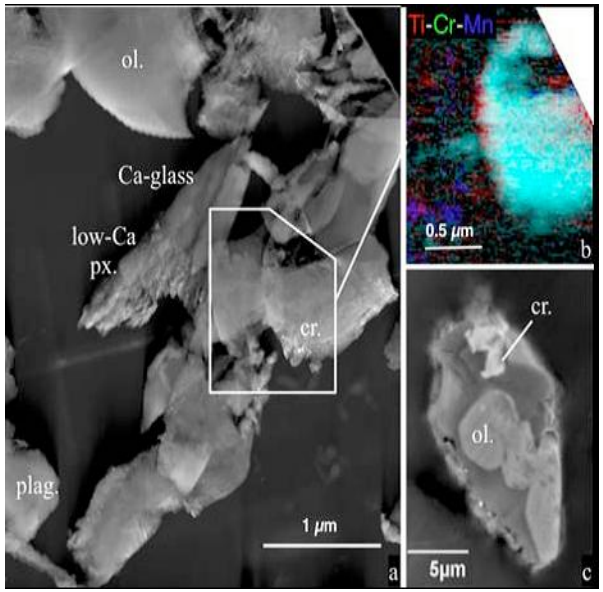
E. de Smit, I. Swart, J. Creemer, G. H. Hoveling, M. K. Gilles, T. Tyliszczak, P. J. Kooyman, H. W. Zandbergen, C. Morin, B. M. Weckhuysen and F. M. F. de Groot, Nature **456**, 222 (2008).

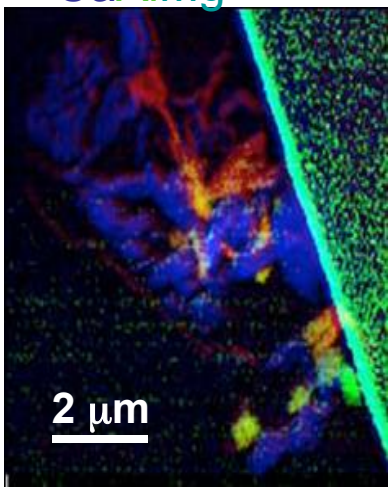
Cometary Particles

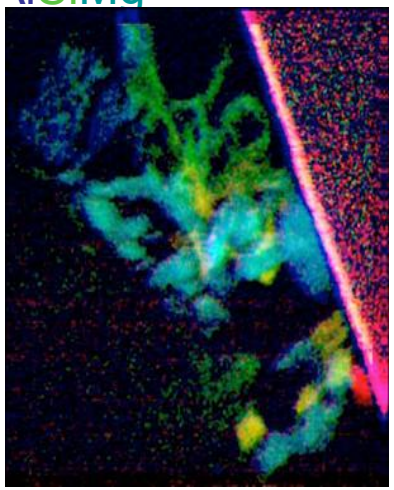
TYPE IIA CHONDRULE FRAGMENT FROM COMET 81P/WILD2 IN STARDUST TRACK C2052,2,74



Optical and X-ray Fluorescence images





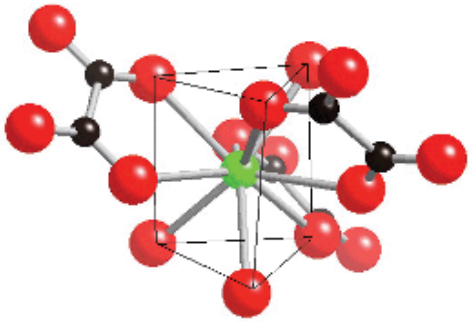


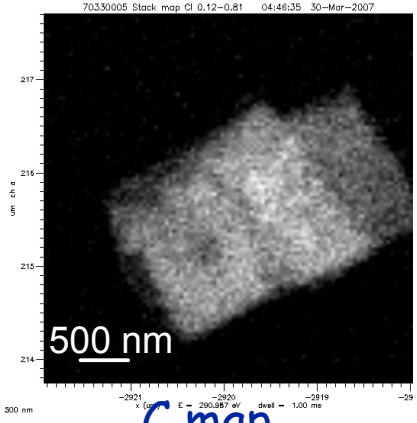
STXM element maps of Iris,9. Absorption difference maps, pixel size 100 nm. a) Ca-Al-Mg-. Yellow regions are Ca-Al rich, Purple regions are Ca-bearing Mg-Fe silicates. b) Al-Si-Mg map, the minerals are labeled as for Fig. 3.

STXM provided detail understanding of chemical composition before the TEM work to identify crystalline structure

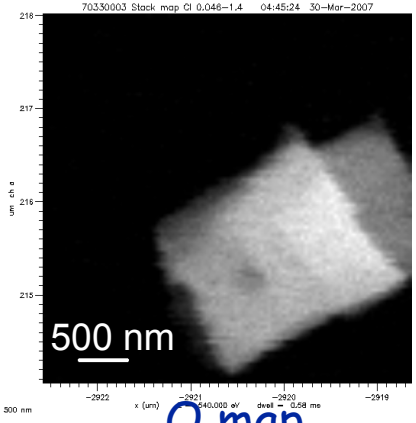
A. L. Butterworth Z. Gainsforth, A. Bauville, L. Bonal, D. E. Brownlee, S. C. Fakra, G. R. Huss, D. Joswiak, M. Kunz, M. A. Marcus, K. Nagashima, R. C. Ogliore, N. Tamura, M. Telus, T. Tyliszczak, A. J. Westphal

Pu(III) Oxalate

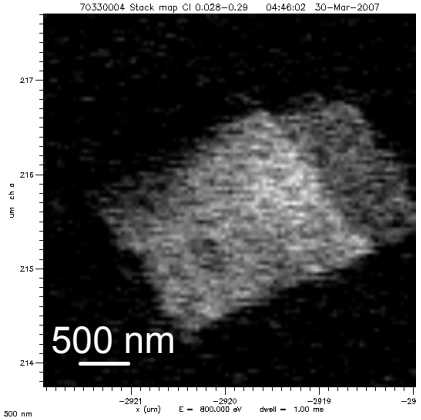




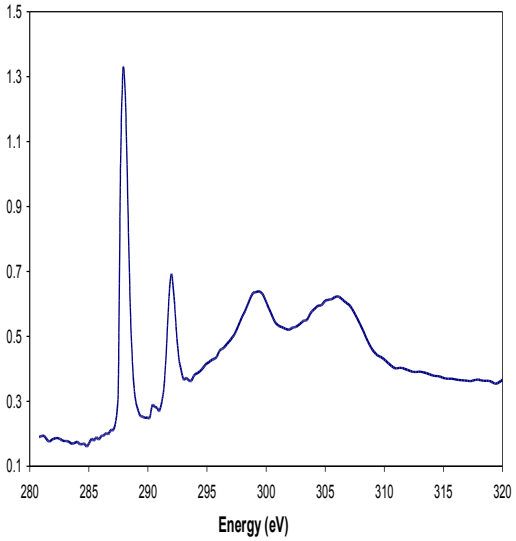
C map

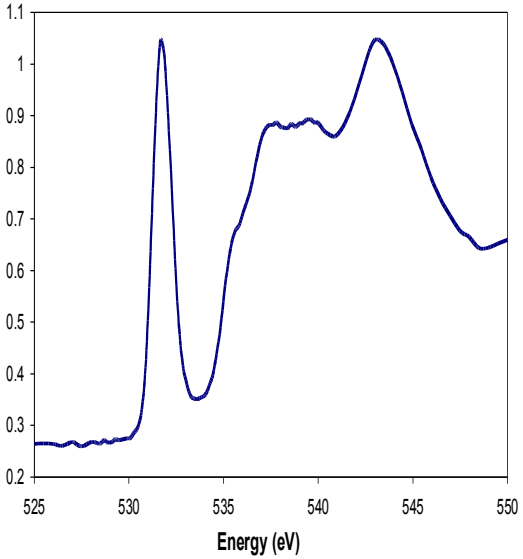


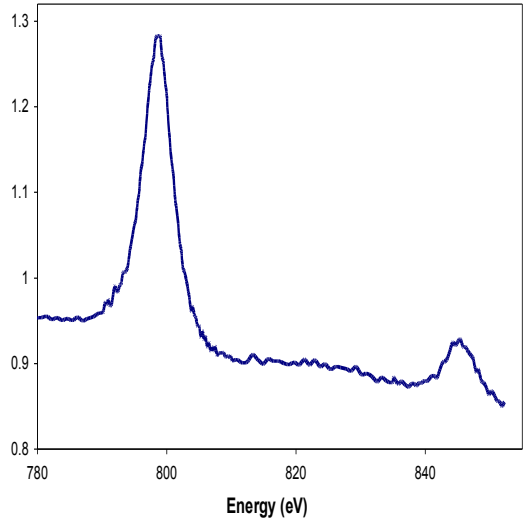
O map



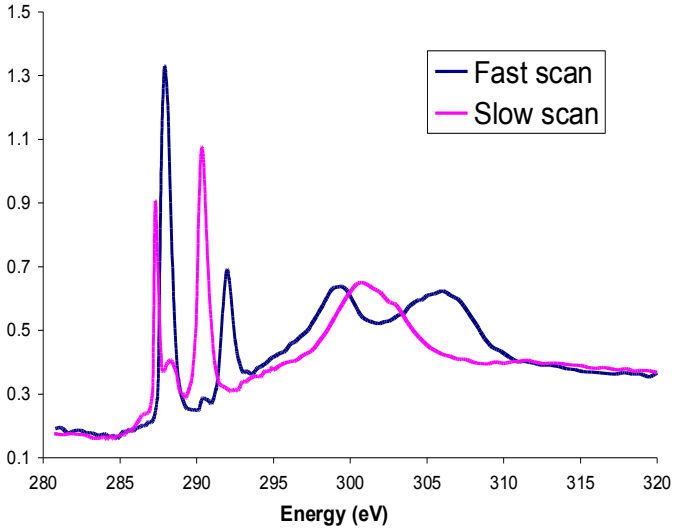
Pu map

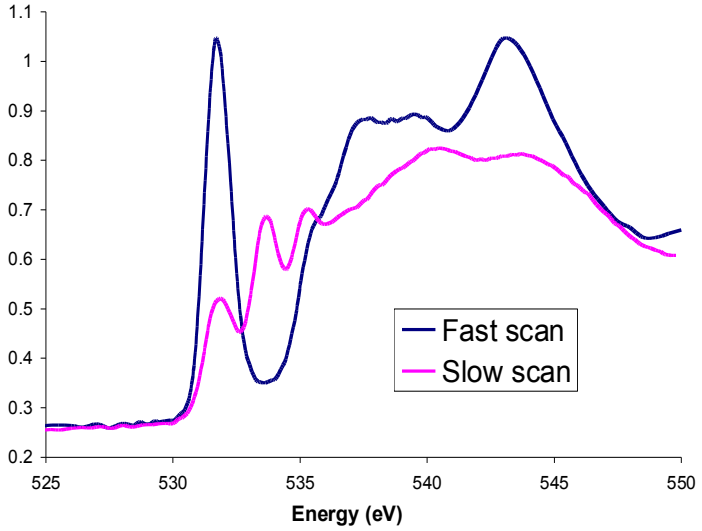


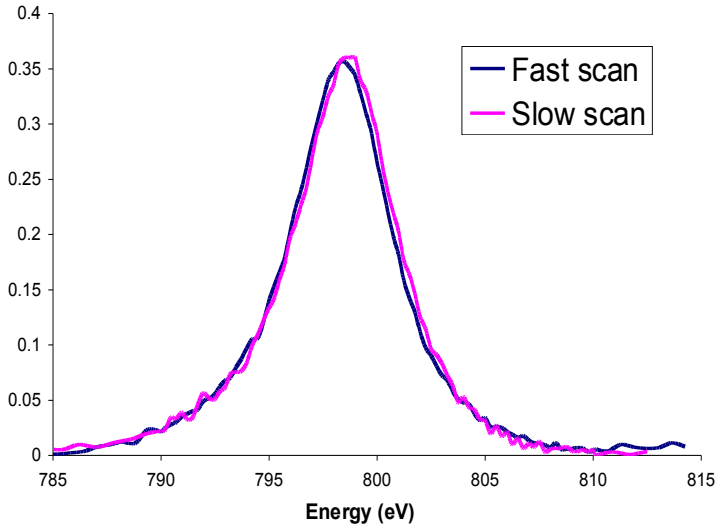




Pu(III) Oxalate Radiation Damage



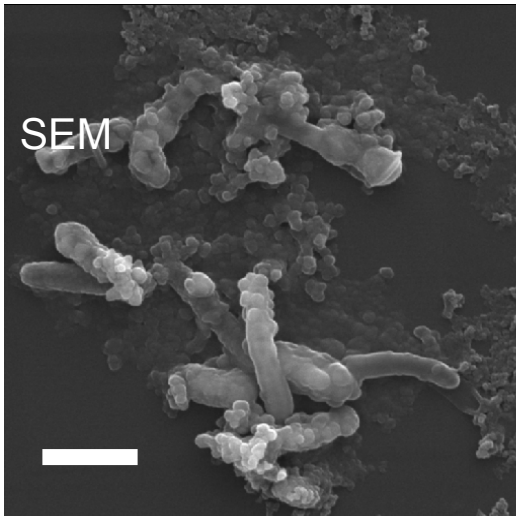




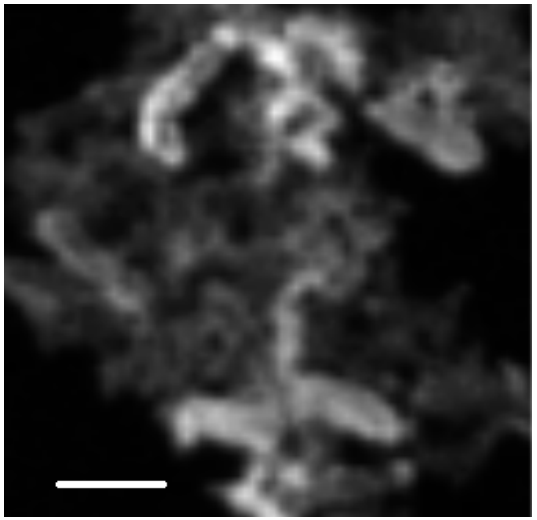
Fast scan – 100 μs/pixel + reduced flux + fewer points
Slow scan - 1 ms/pixel

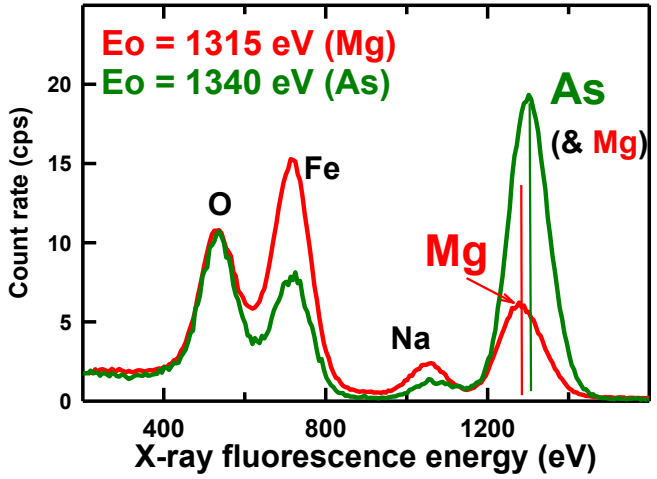
X-ray fluorescence in STXM

Adam Hitchcock (McMaster), *Martin Obst (Tuebingen), Tolek Tyliszczak (ALS)*

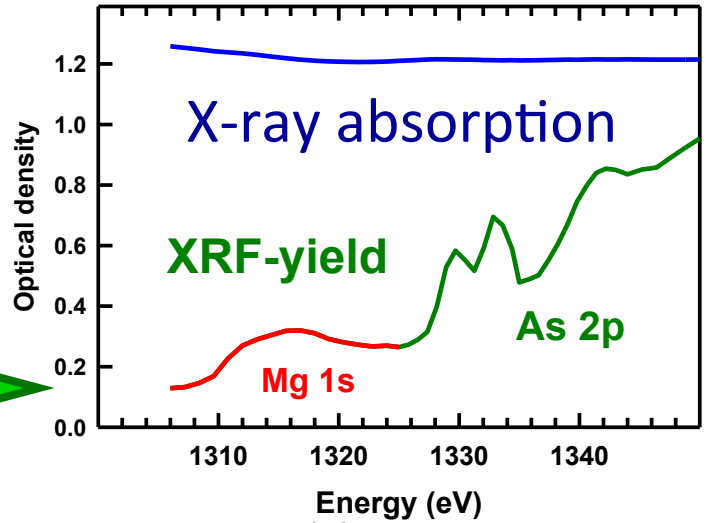


As map





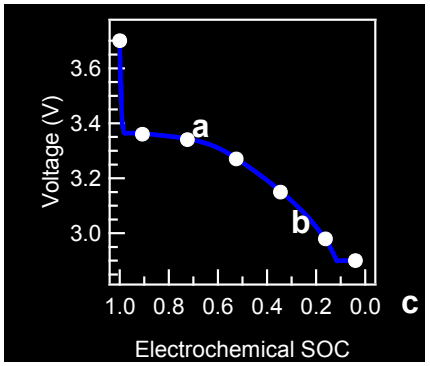
X-ray fluorescence yield X-ray absorption provides a reliable **As map and spectra** in a case where the conventional **transmission signal** does not detect it.

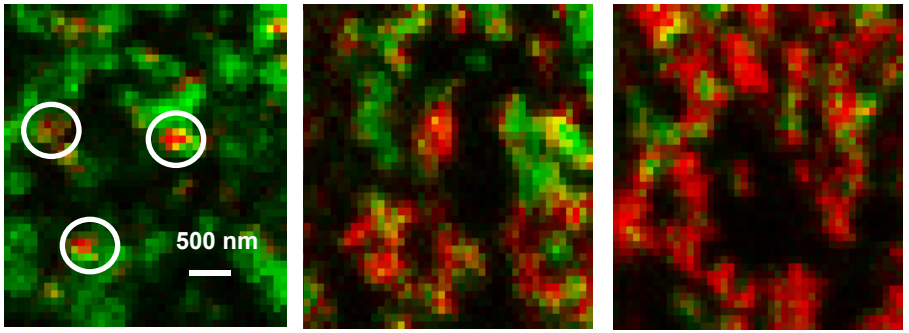


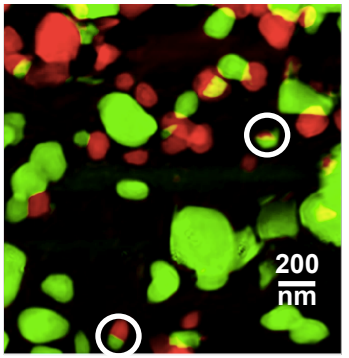
Lake Constance Acidovoris biofilm (BoFeN) cultured on 10 mM **Fe**(II). & 1 mM **As**

RELEVANCE: species is very tolerant to high As levels - WHY ?

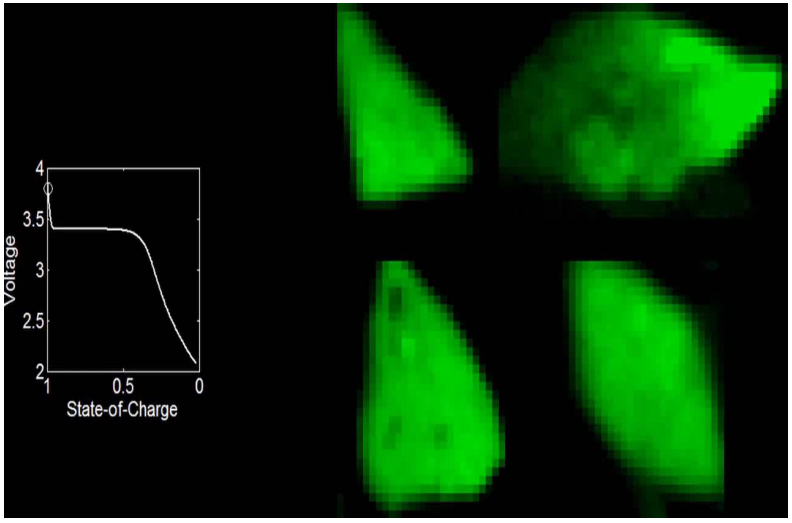
Tracking Lithiation in Real Time in Liquid

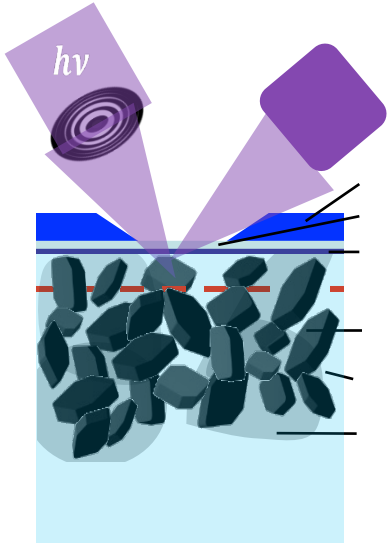


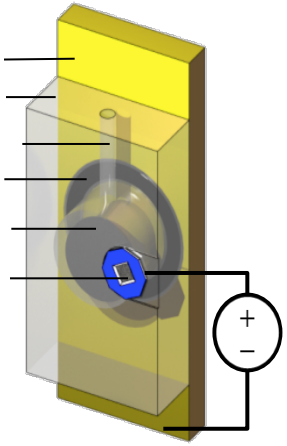




Particle-by-particle intercalation pathway







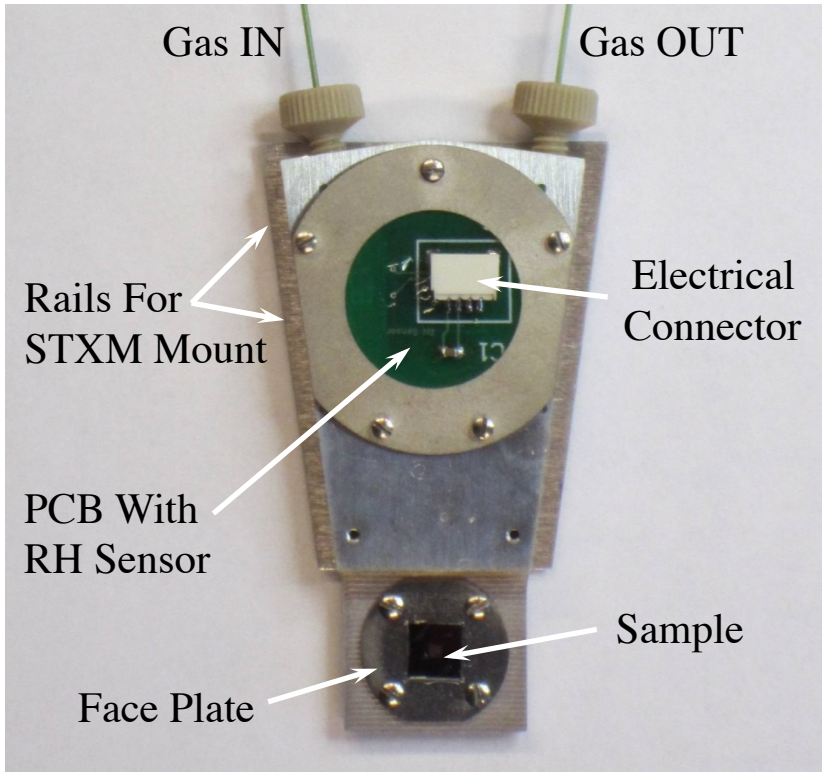
SOC

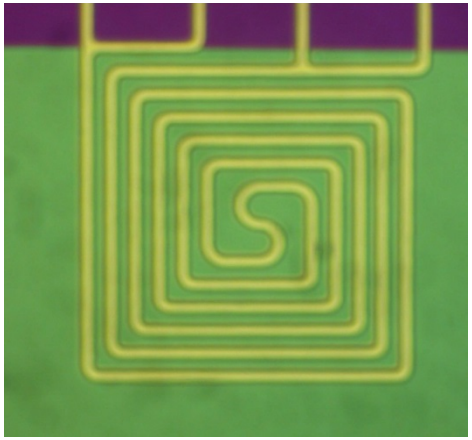
0% 100%

Y. Li, T. Tyliszczak, W. Chueh *et al. Adv. Funct. Mater.*

Gas flow nonoreactor

- Measurements under realistic conditions
  - CO_2, H_20, etc.
- *In situ* observation of chemical changes
- Mounts to existing STXM sample holder
- Real-time on-board measurement of relative humidity

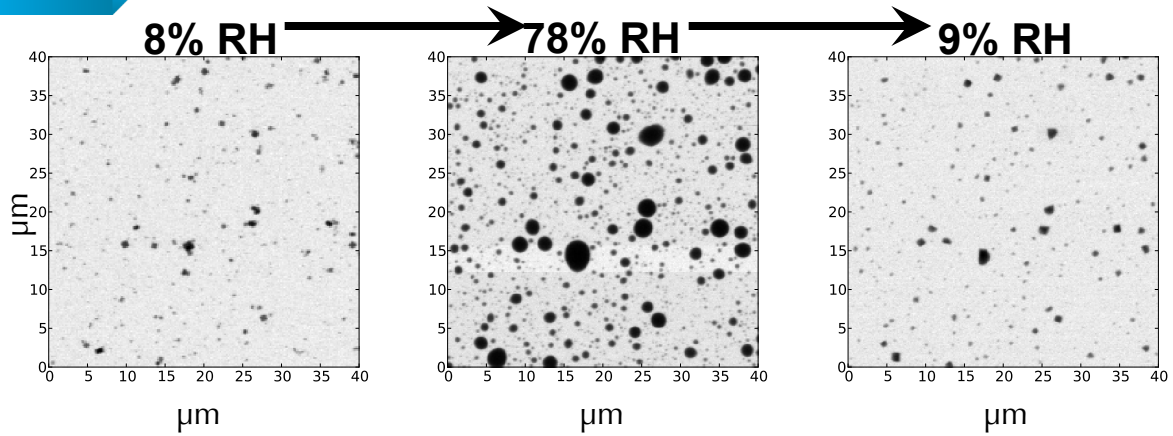


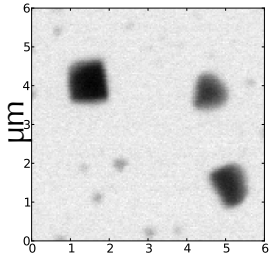


- Gold and platinum coils
- Four contacts:
  - 2 x Voltage (measure)
  - 2 x Current (supply)
- Resistively heats Si_3N_4 sample area
- Coil resistance gives *average* temperature measurement

Stephen T. Kelly, Gregory T. Carroll, Tobias Roedel, Pascal Nigge, Shruti Prakash, Alexander Laskin and **Mary K. Gilles**

Relative Humidity test

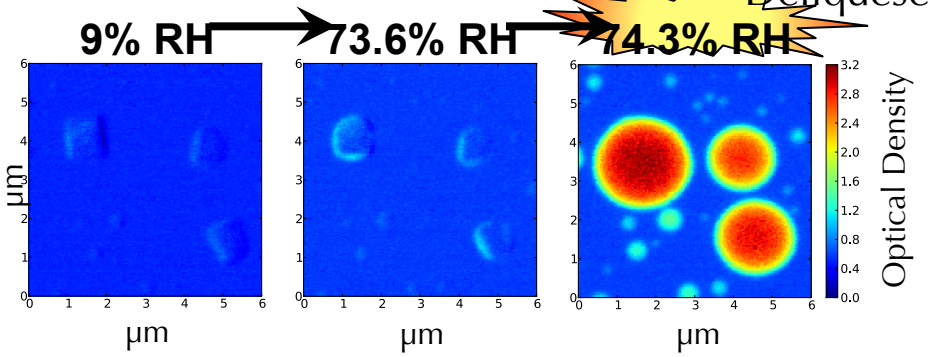




540 eV Image

NaCl Deliquecence Relative Humidity – 75%

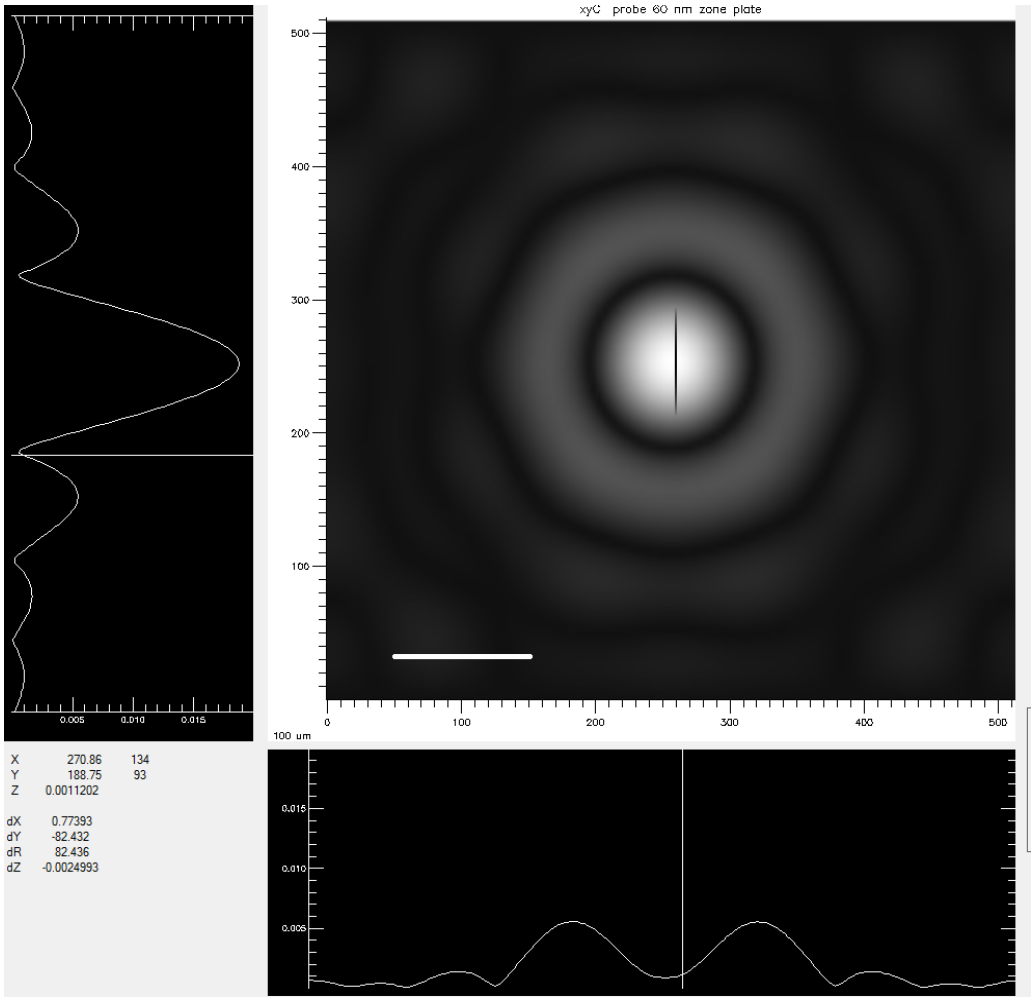
Deliquescence!



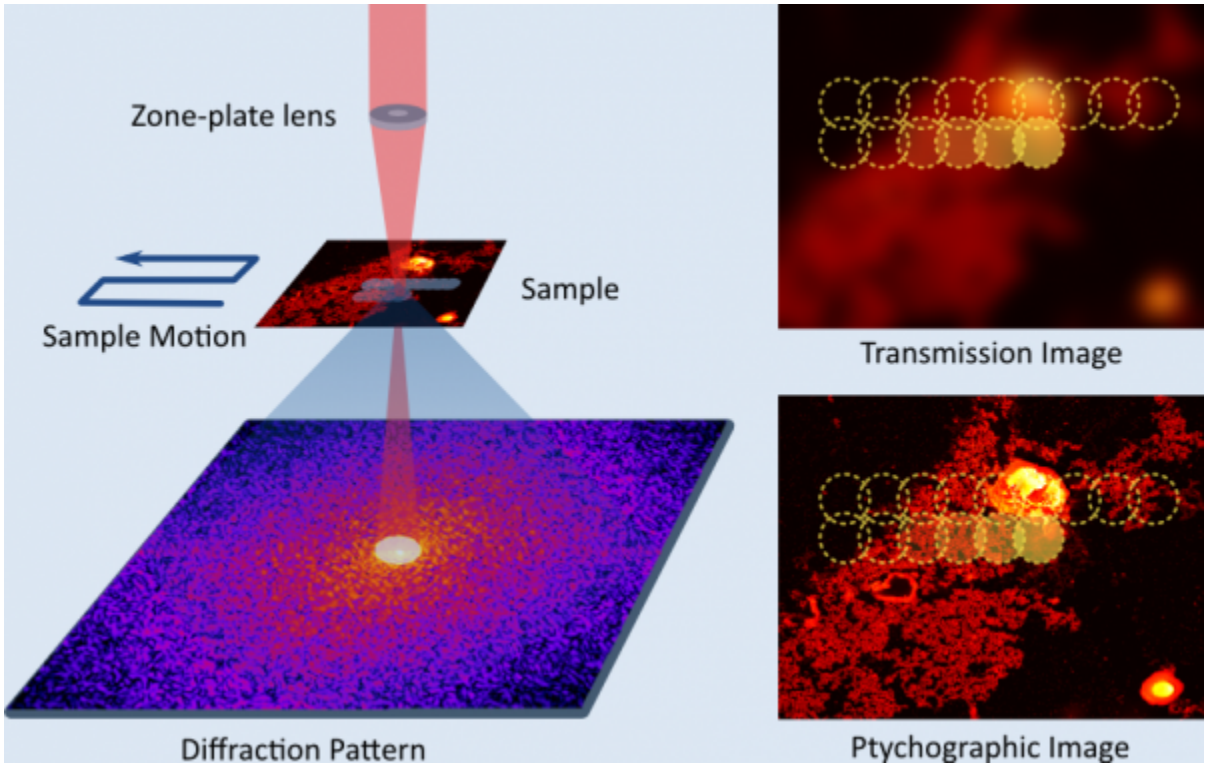
Oxygen Maps

Mary Gilles group has also liquid flow cell

Beam profile and its consequences

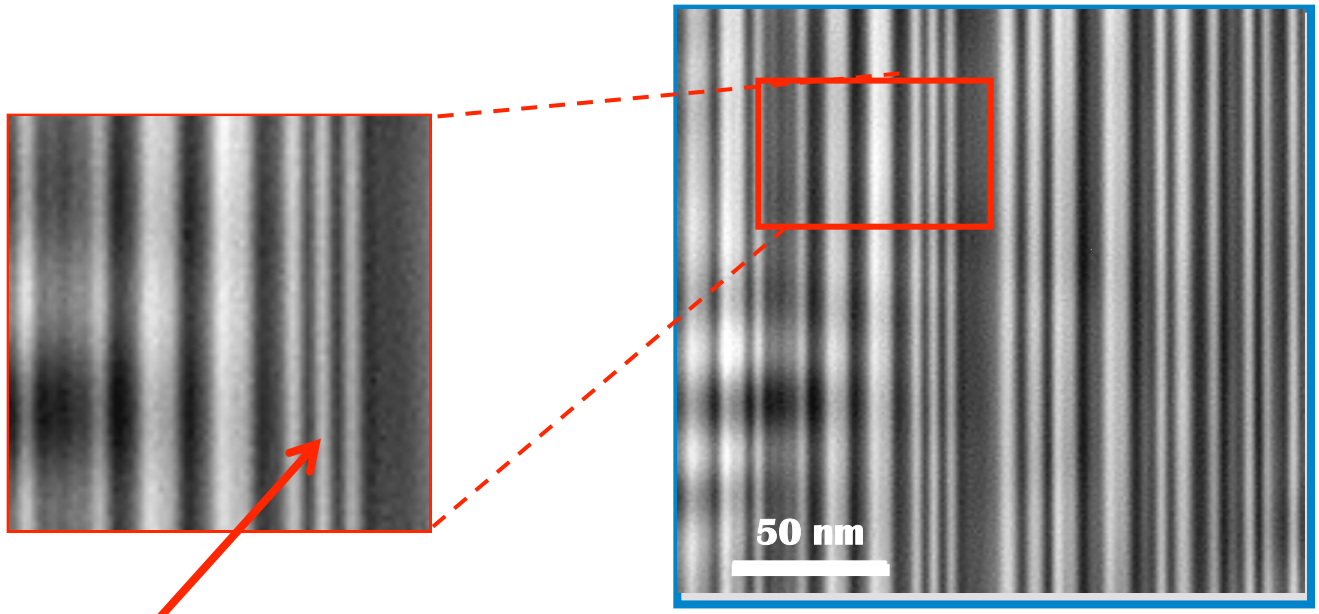


Ptychography



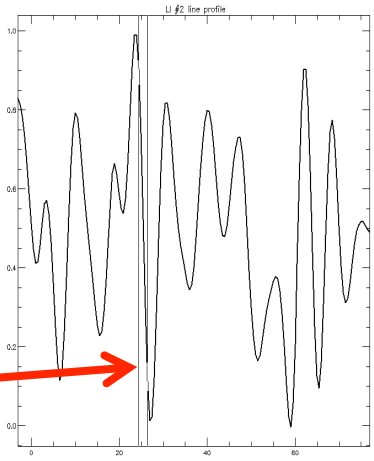
Sample is scanned in the plane of focused, coherent X-ray beam with steps smaller than the beam size. At each step, a diffraction pattern is recorded. Amplitude and phase shift images of the sample are reconstructed with much higher resolution than the beam size.

The Best Spatial Resolution of Soft X-ray Microscopy
< 2 nm resolution



2.8 nm line

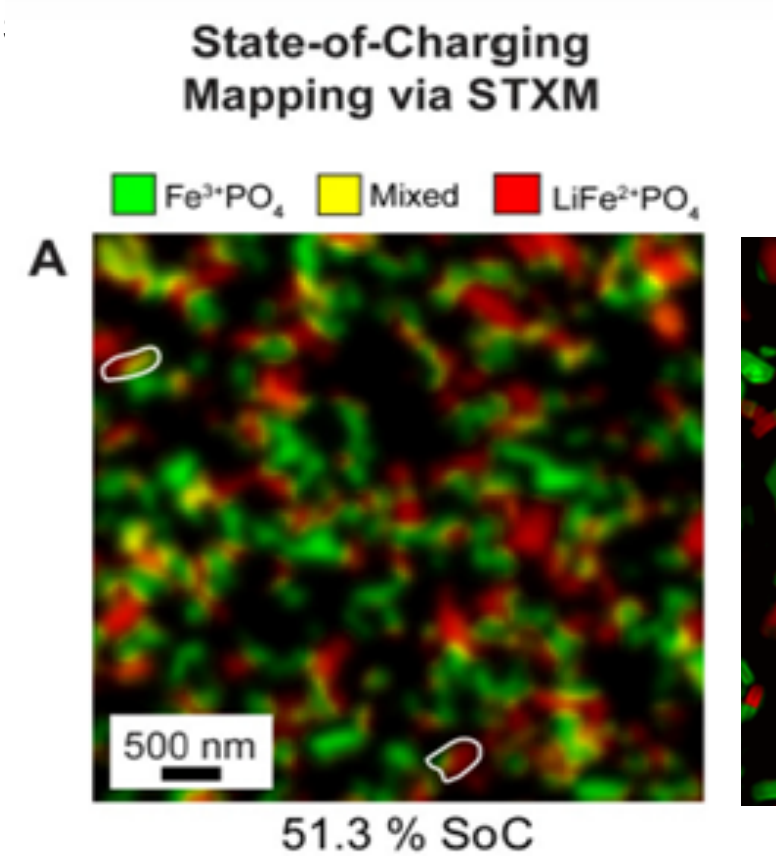
Line profiles
2 nm edge



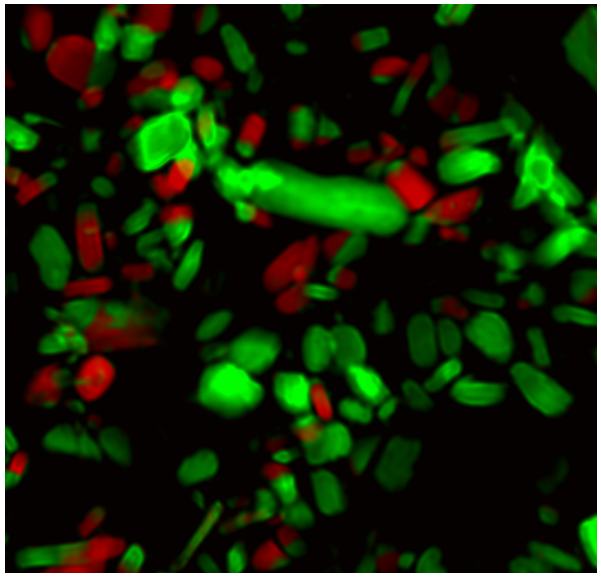
Ptychography at 11.0.2

Ptychography

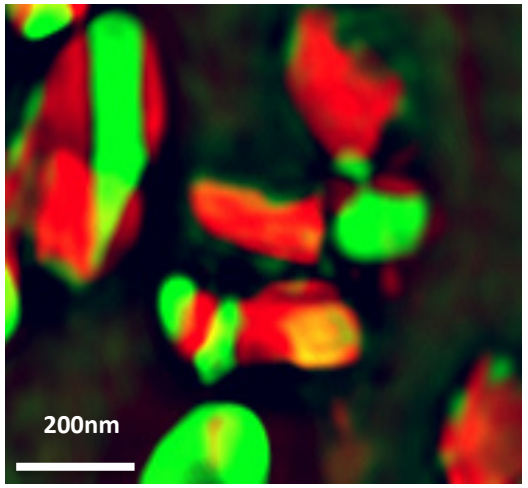
Ptychography – 6 nm resolution for chemical mapping

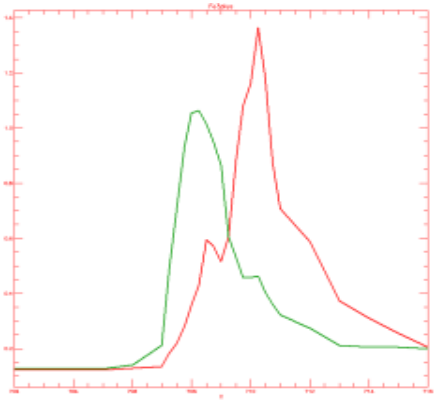


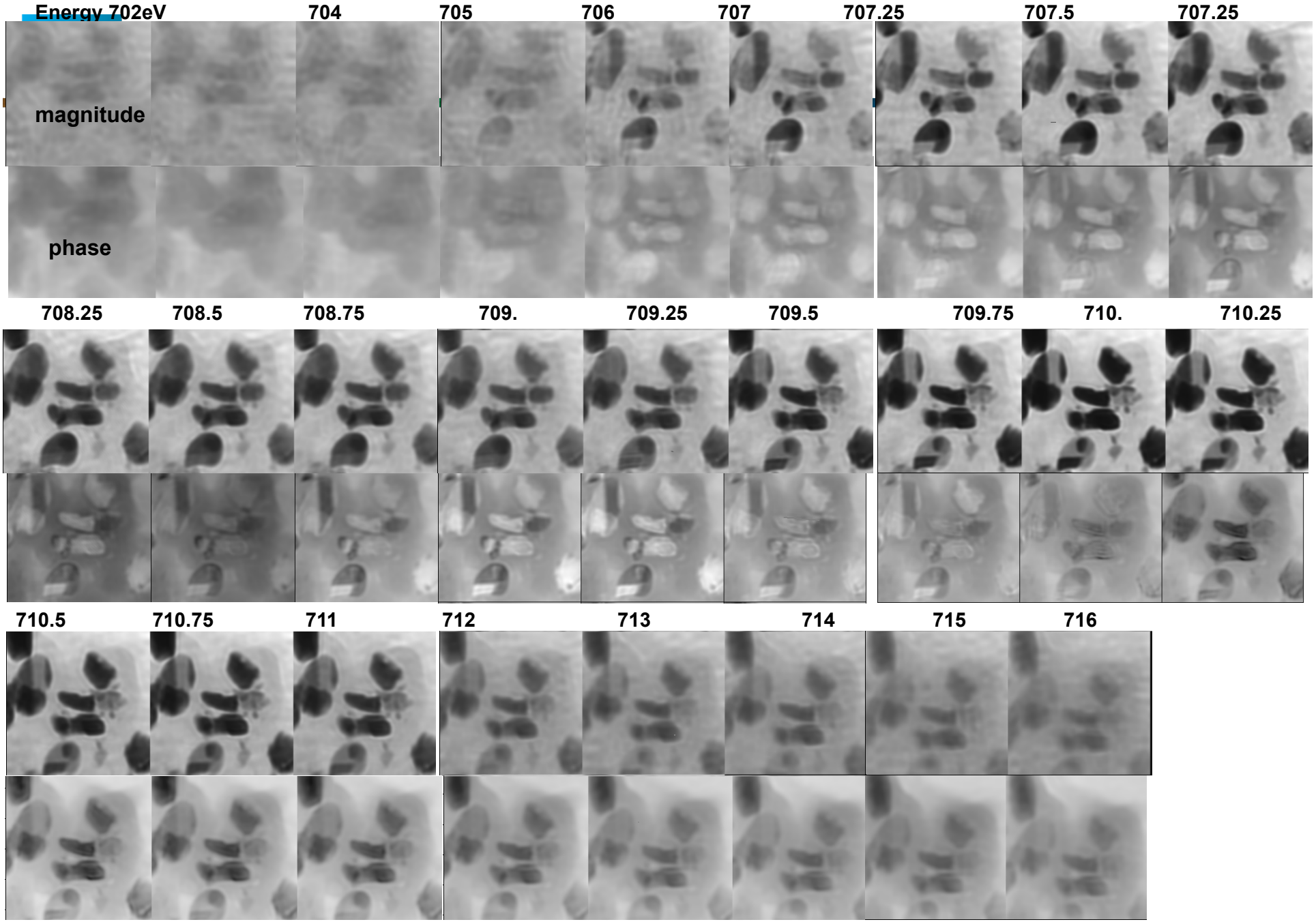
Chemical mapping from 3 energy



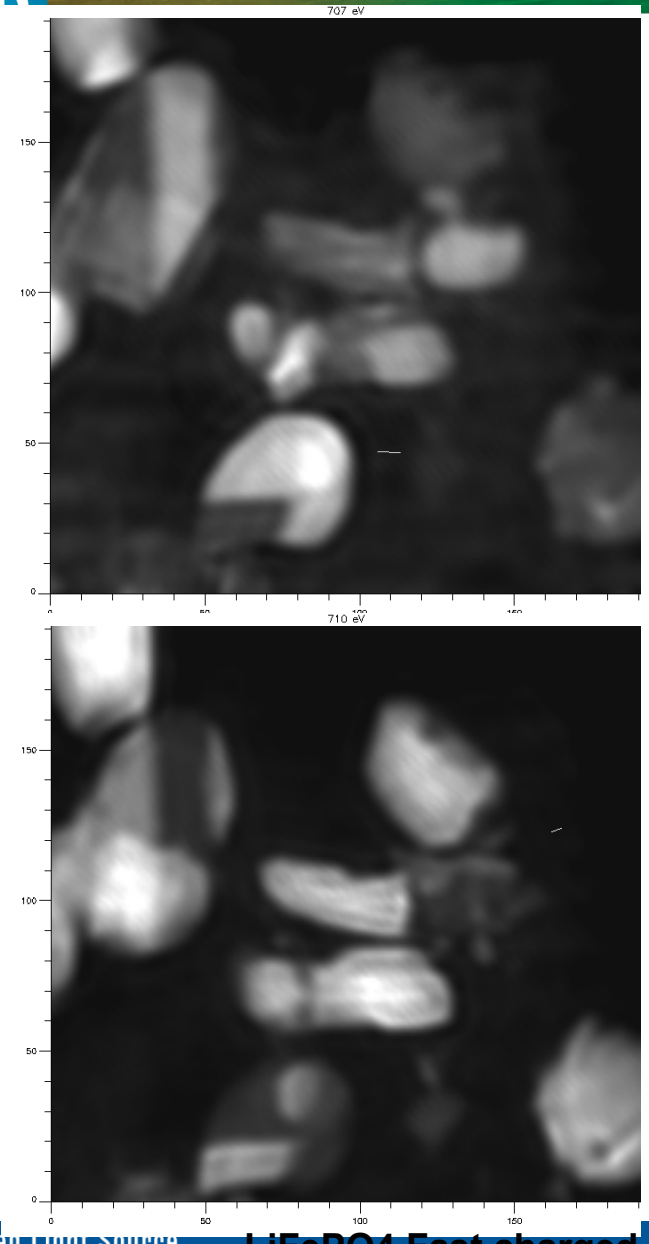
Chemical mapping from a stack

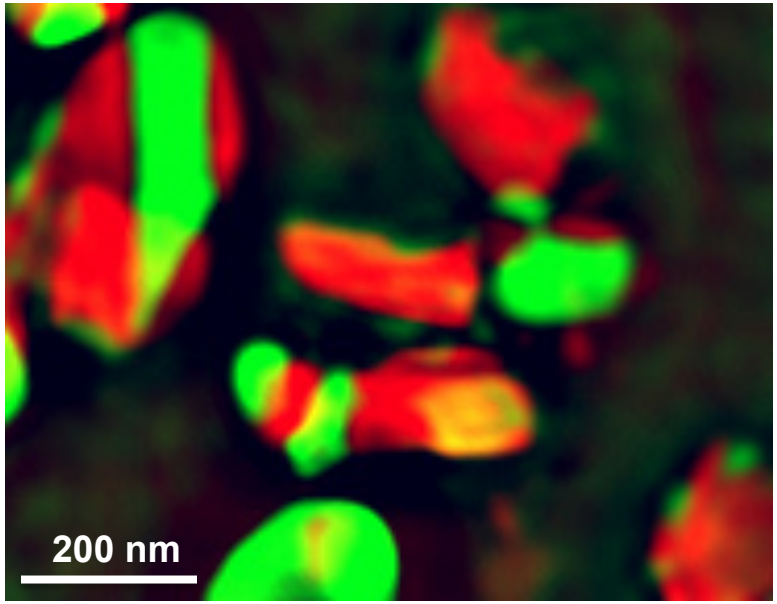


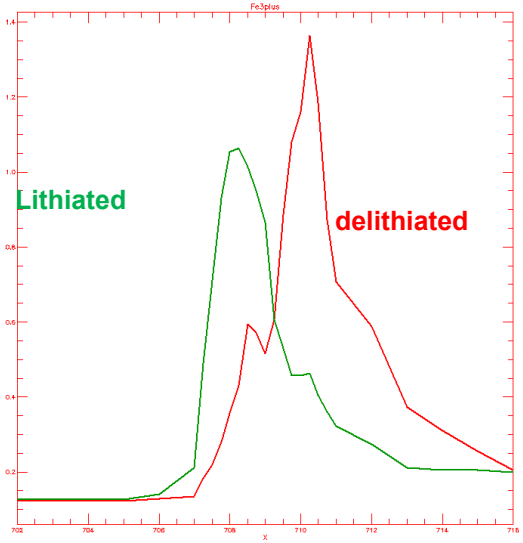



Energy 702eV
704
705
706
707
707.25
707.5
707.25
magnitude
phase
708.25
708.5
708.75
709.
709.25
709.5
709.75
710.
710.25
710.5
710.75
711
712
713
714
715
716

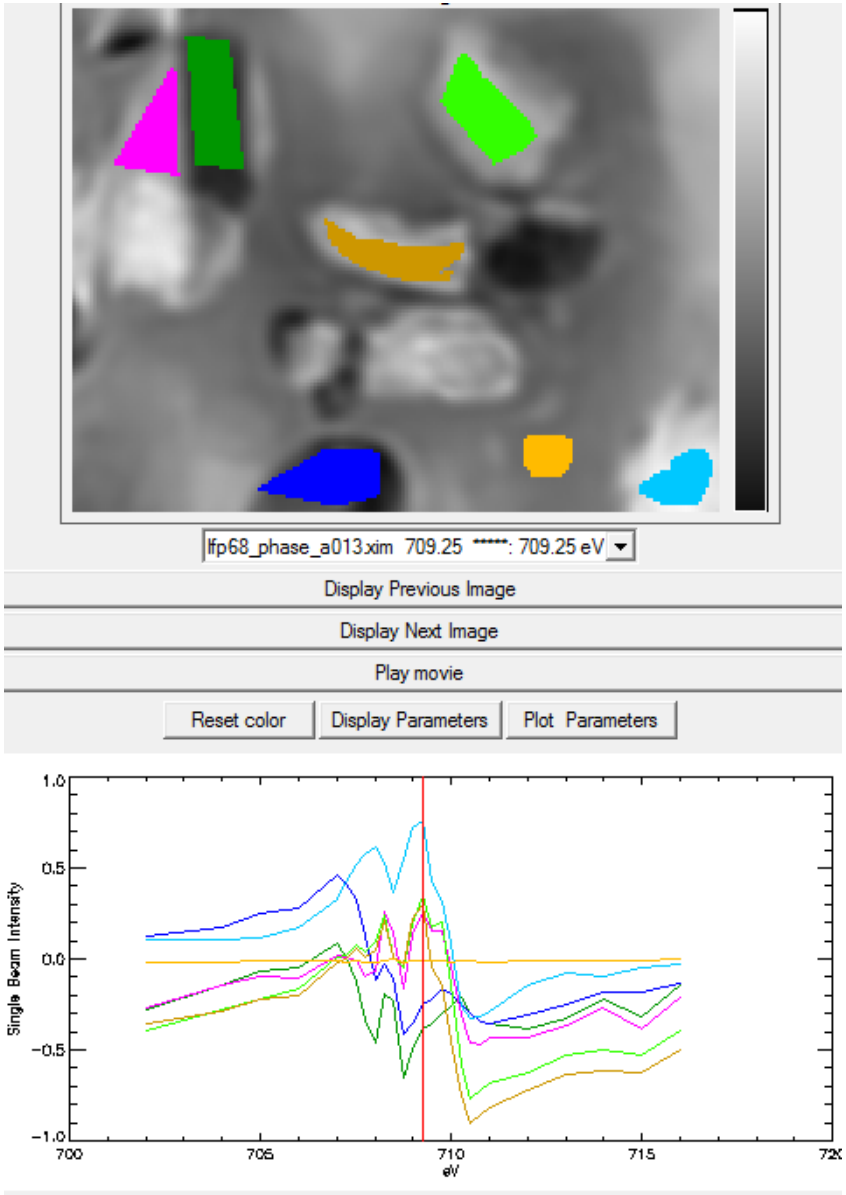
Ptychography spectromicroscopy





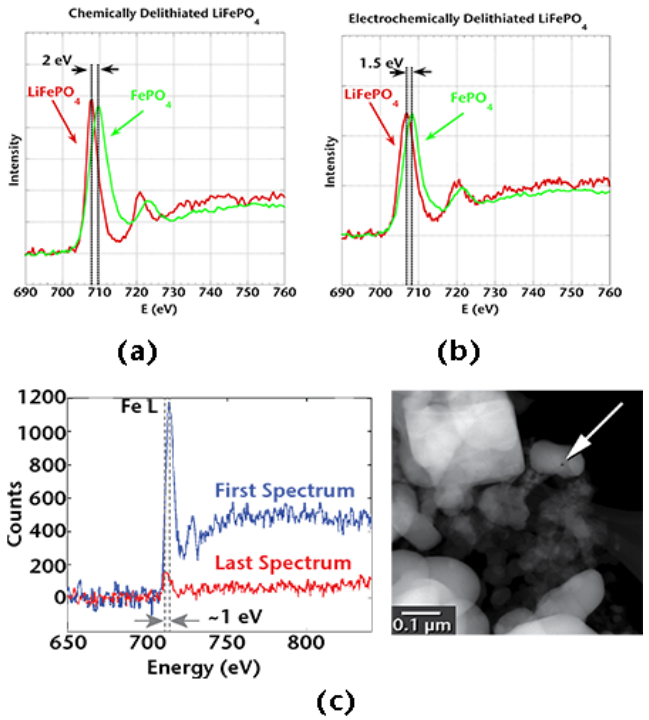


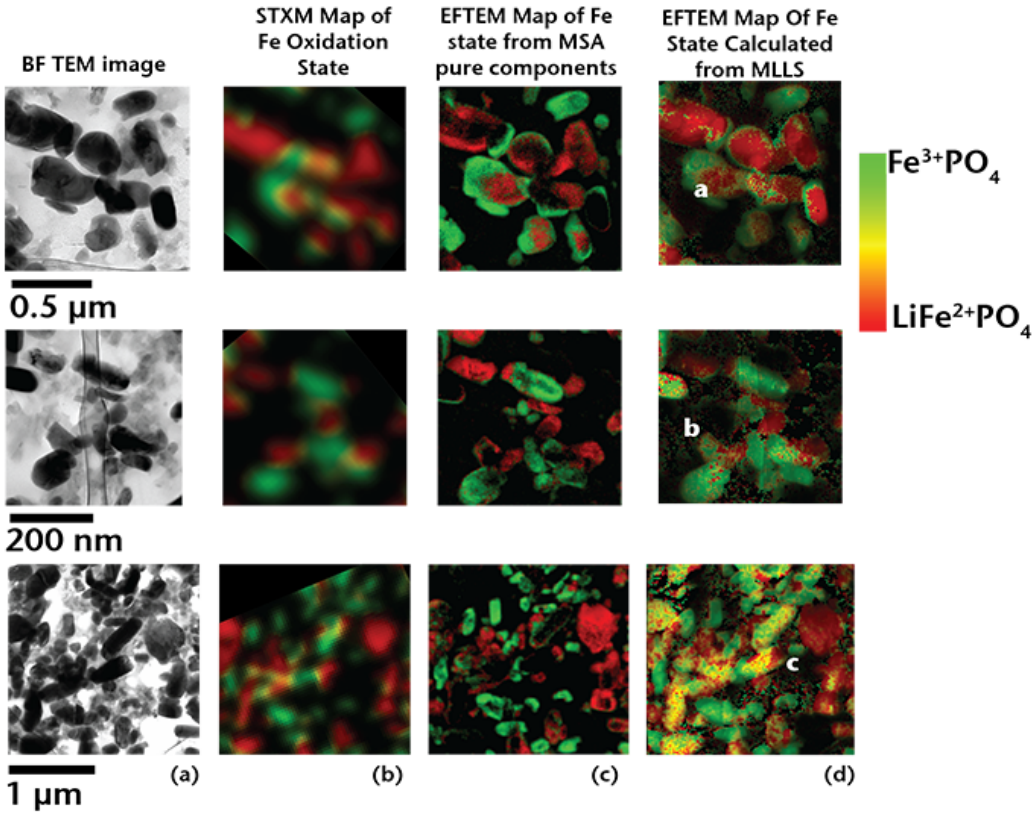
LiFePO4 Fast charged measured at bl 11.0.2 in ptychography mode

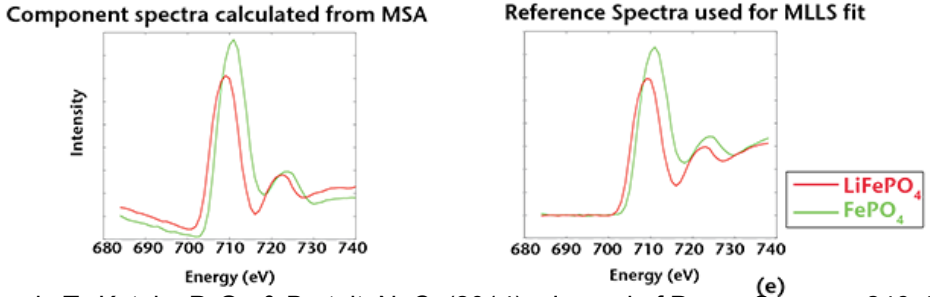


Phase analysis
Normalized to orange area

EELS studies

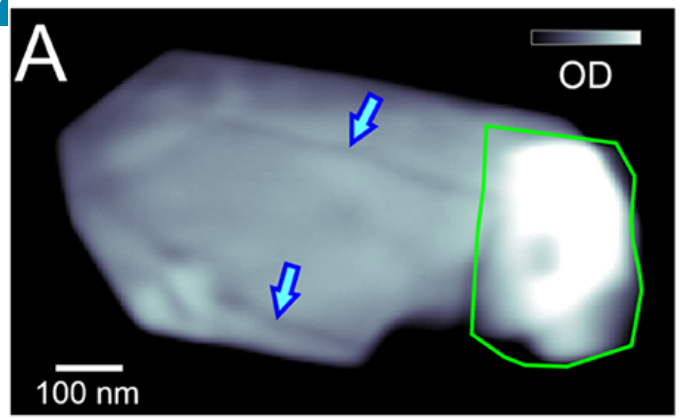


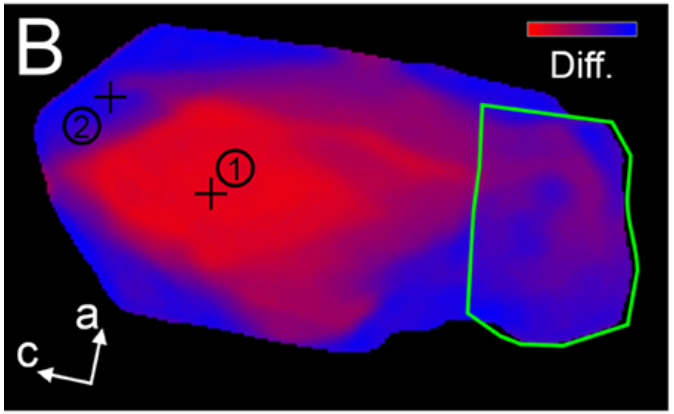


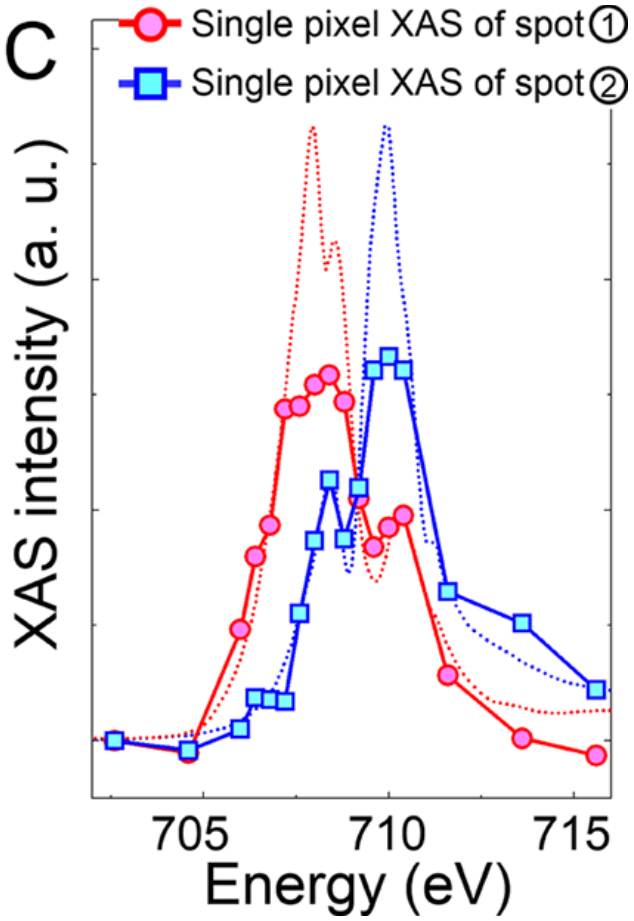


Sugar, J. D., El Gabaly, F., Chueh, W. C., Fenton, K. R., Tyliszczak, T., Kotula, P. G., & Bartelt, N. C. (2014).. Journal of Power Sources, 246, 512-521.

$LiFePO_4$ chemically partly delithated

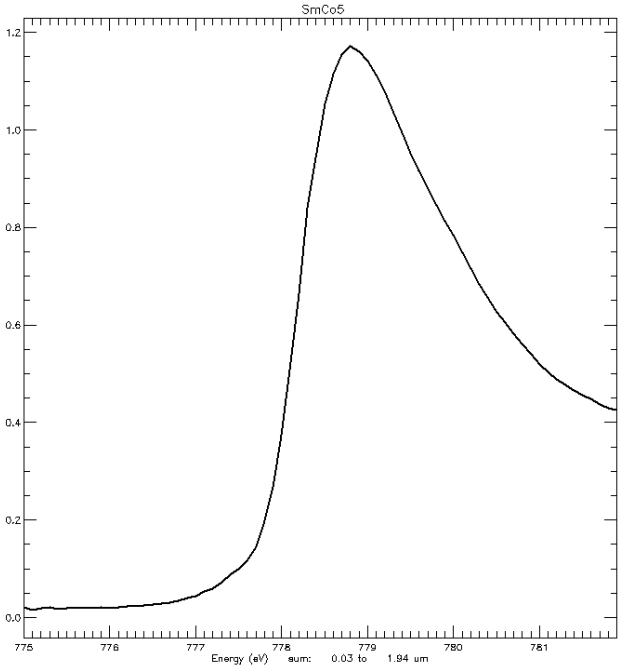


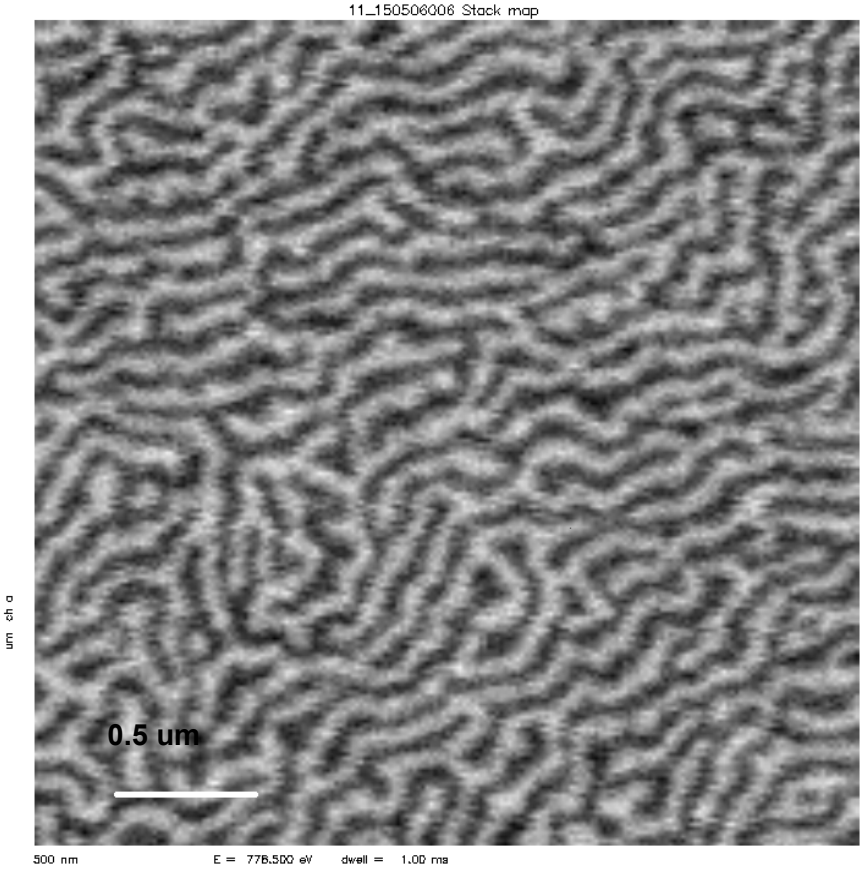




Yu, Young-Sang, et al. "Dependence on crystal size of the nanoscale chemical phase distribution and fracture in LixFePO4." Nano letters (2015).

$SmCo_5$ sample – STXM XMCD

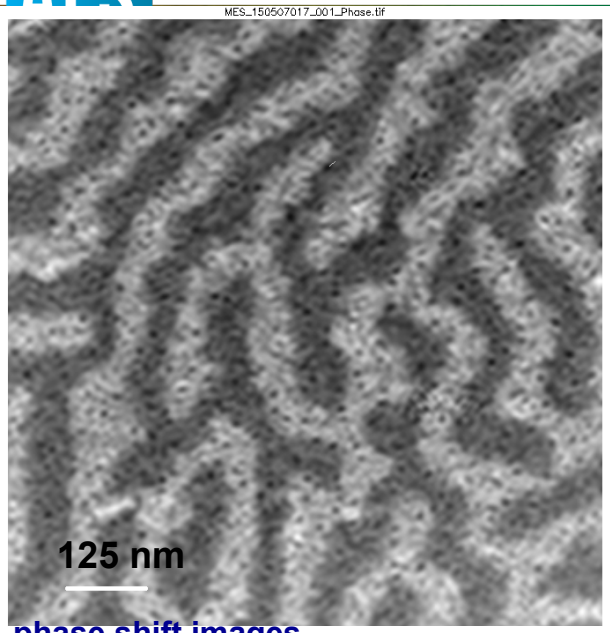


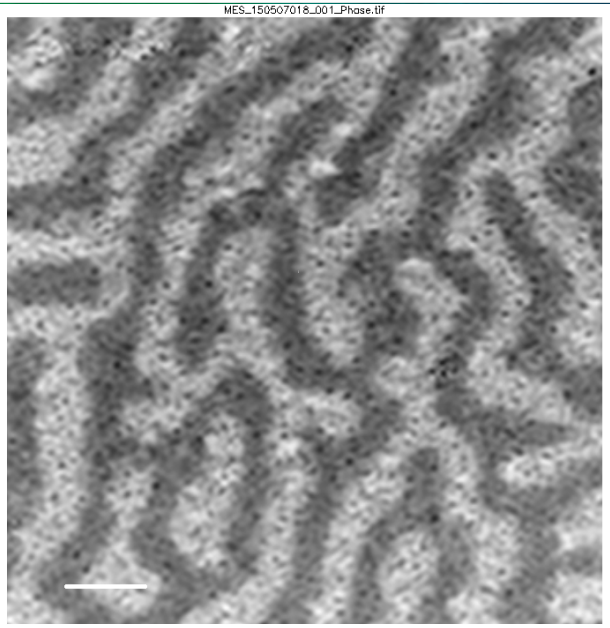


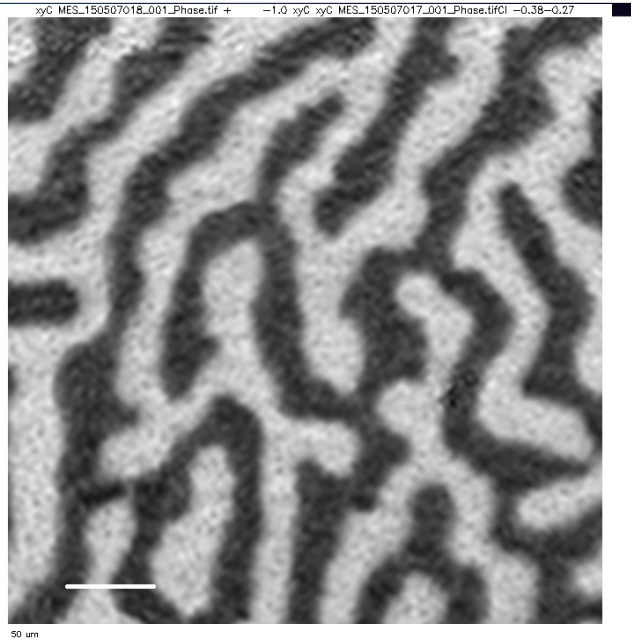
Work in progress

Xiaowen Shi, Hung Wei Shiu, Sujoy Roy, Peter Fisher, David Shapiro, Stephen Kevan, Youn-Sang Yu, Maryam Farmand

$SmCo_5$ at 778 eV – ptychography reconstruction





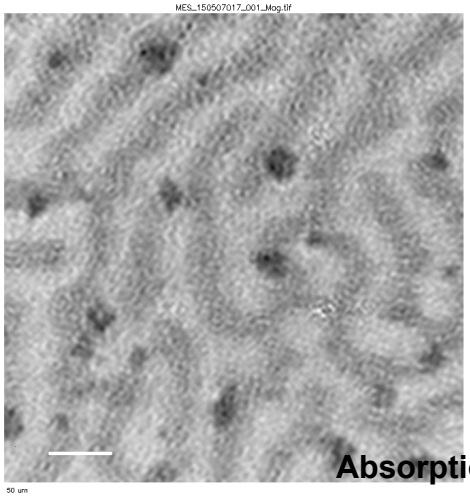


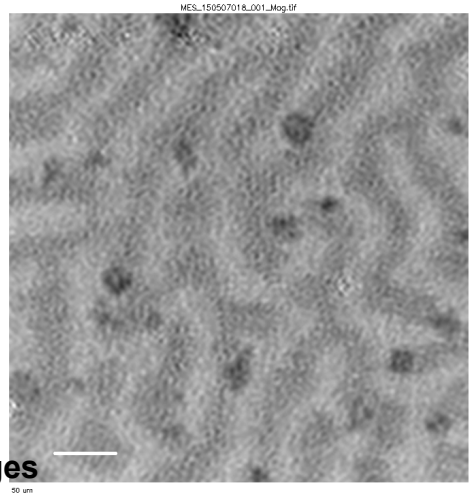
phase shift images

Polarization elliptical left

Polarization elliptical right

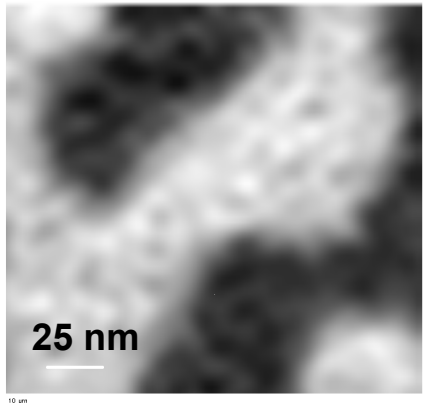
XMCD



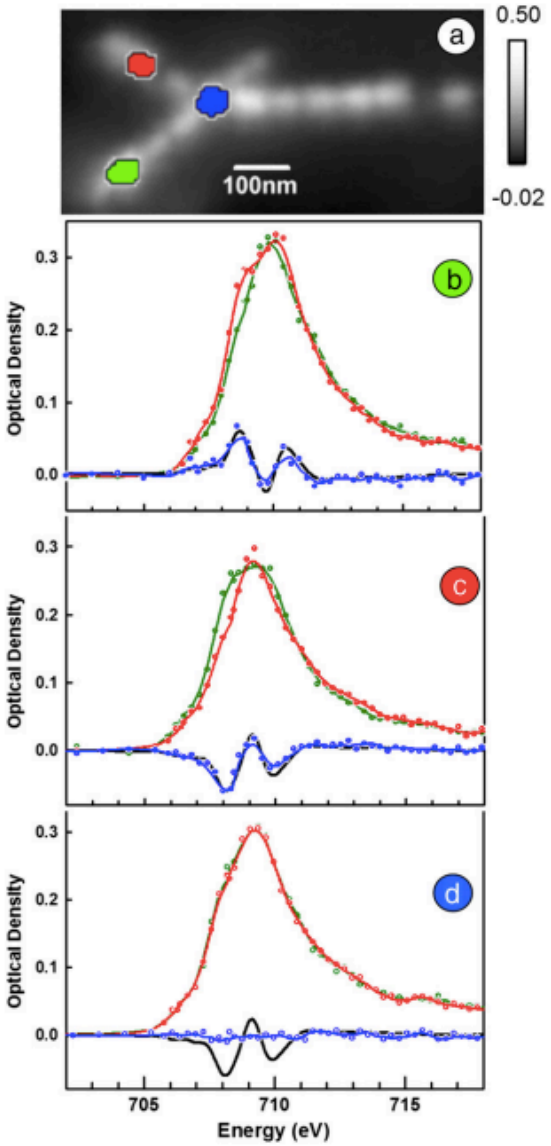


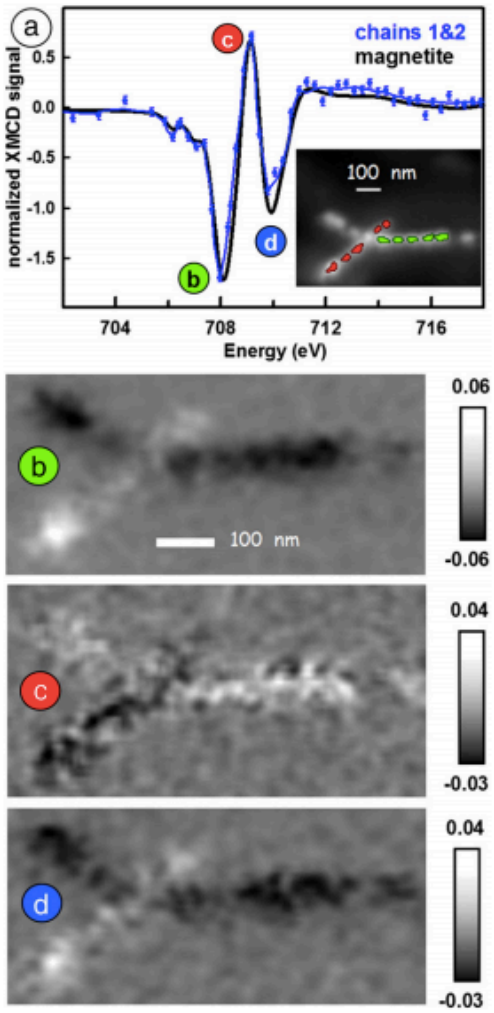
Absorption images

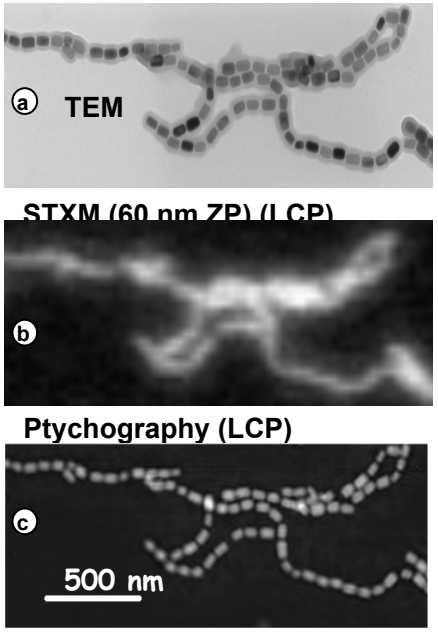
zoom



magnetism of magnetotactic bacterium Candidatus Magnetovibrio blakemorei strain MV-1







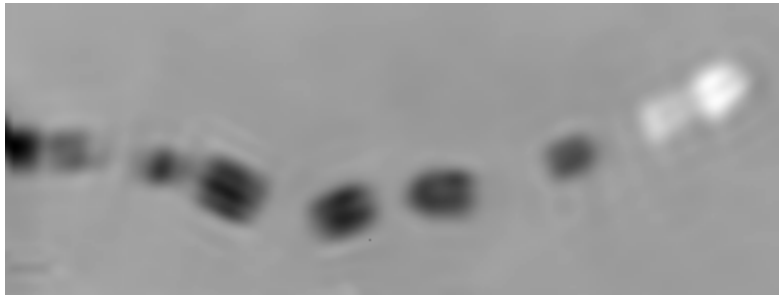
S.S. Kalirai et al. / Chemical Geology 300-301 (2012) 14–23

Intact MV-1 Cells

STXM Image of the Cell (708eV)

Left EP X-ray beam

XMCD (LCP-RCP)



Right EP X-ray beam

Ptychography - Work in progress

Xiaohui Zhu, T. Tyliszczak, H.-W. Shiu, D. Shapiro, D.A. Bazylinski, U. Lins[5] and A.P. Hitchcock[1]

Memristors – HP Lab

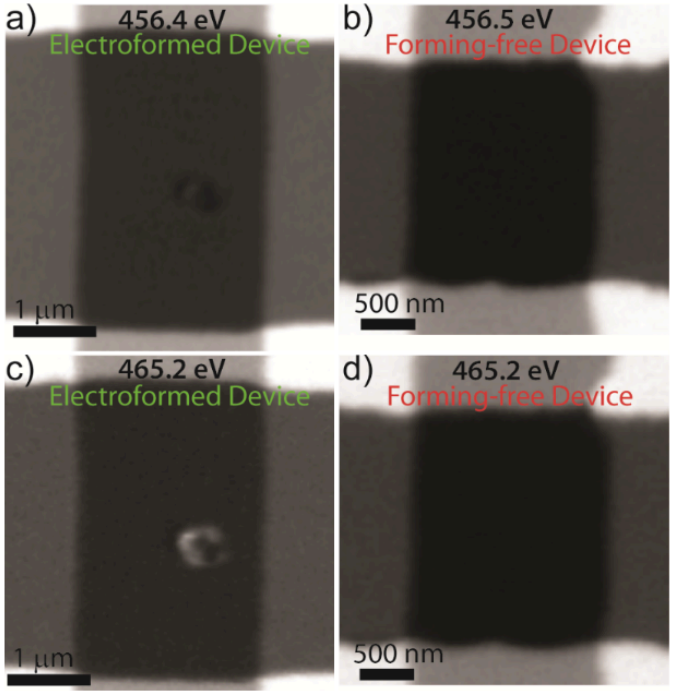


Figure 2: Comparison of scanning transmission X-ray micrographs for electroformed and forming-free devices. Contrast was derived from spatially-resolved X-ray absorption using incident monochromatic X-rays at the indicated energy which is before (456.4/456.5 eV) and within (465.2 eV) the main Ti L_3 edge. For the electroformed device, (a) and (c), a strong contrast was observed within the junction which reversed at the different X-ray energies, and

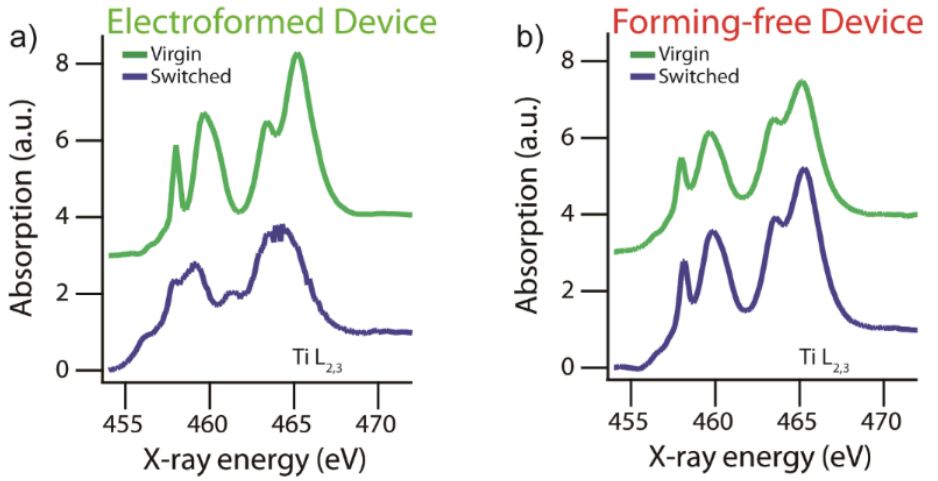
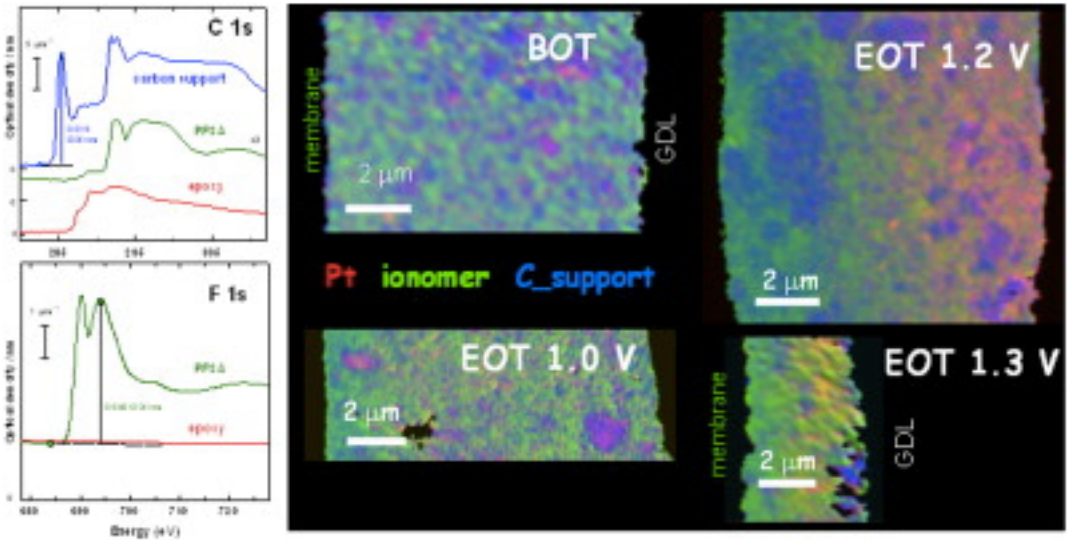


Figure 3: X-ray absorption spectroscopy within the junction region of an electroformed and forming-free device. The Ti L_3 absorption edge is shown, which is sensitive to chemical composition and structure state. (a) The "Virgin" NEXAFS spectrum (green curve) was derived from a neighboring, simultaneously grown device which was not electrically biased, while the "switched" spectrum (blue curve) came from within the materially altered nanoscale region in the electroformed device of Figure 2 with a size of roughly 200 nm × 200 nm. (b) Both "Virgin" and "switched" spectra (green and blue curves, respectively) were derived from the junction region in the forming-free device of Figure 2, before and after the application of electrical bias, respectively.

Strachan, J. P., Yang, J. J., Montoro, L. A., Ospina, C. A., Ramirez, A. J., Kilcoyne, A. L. D., ... & Williams, R. S. (2013). Characterization of electroforming-free titanium dioxide memristors. Beilstein journal of nanotechnology, 4(1), 467-473, 2013

Fuel cell membrane

Combination of open and proprietary research
Ballard Power Systems Inc, 9000 Glenlyon Parkway, Burnaby, BC V5J 5J9, Canada
Adam P. Hitchcock group, McMaster University, Hamilton, Canada



A.P. Hitchcock – AFCC (Automotive Fuel Cell Corporation)

Spectro-ptychography of a PEM-FC cathode

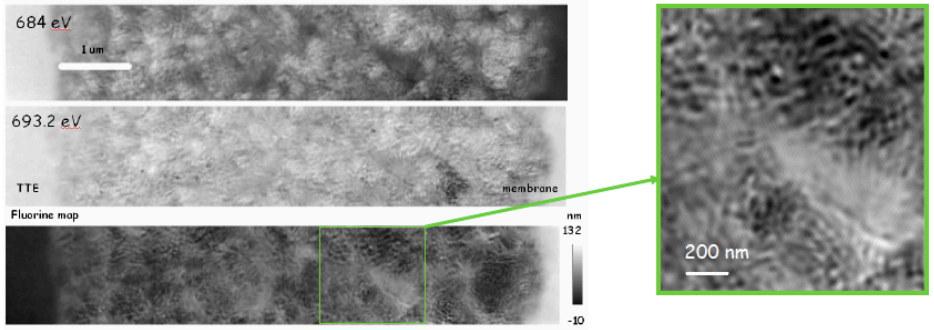
ALS STXM1102
17 Apr 2015

Xiaohui Zhu, Juan Wu, Adam Hitchcock (McMaster), *H.-W. Shiu, David Shapiro,, Tolek Tyliszczak* (ALS); *Viatcheslav Berejnov, Darija Susac, Juergen Stumper* (AFCC)

GOALS: (1) explore spatial resolution improvements using ptychography
(2) determine if F 1s signal in cathode (ionomer) can be measured using ptychography

EXPERIMENTAL: AFCC sample A (from fall 2010) used. Microtomed sections were made in Aug 2011. These are embedded in TTE and mounted on formvar coated grid. Plate M150413-2.
Start 6:30 – did stxm stack for F 1s energy; beam lost 7:30 – 13:00 (!!); 13:00 – 15:00 ptycho set-up
15:00 – 17:00 – Ptycho Fluorine 1s stack map (693.2/684) over 8.5 um x 1.5 um (width of cathode) – 2.6 Gb

RESULTS:



CONCLUSION: F-mapping CAN be done with ptychography with not much more damage than regular STXM

BASF – catalyst group

Collaboration with Bert Weckhuysen – Utrecht University

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Conclusions

- Strong side of using soft X-rays – chemical information – spectroscopy on < 100 nm scale, especially good for C, N, O
- Relatively low radiation damage
- In-situ measurements
  - Many different environmental cells are used
  - In STXM – temperature 450 ^{o}C and 2 bar pressure
  - Working electrochemical cell
  - Working batteries (using fluorescence yield)
- Magnetization dynamics
- Ptychography – a new method allowing to use zone plates with much larger working distances. Much better spatial resolution (demonstrated 2 nm – potentially diffraction limited, C 4 nm, Mg 1 nm).