



X-ray micro-spectroscopy, tomography, and operando conditions

Chemical imaging using XAS

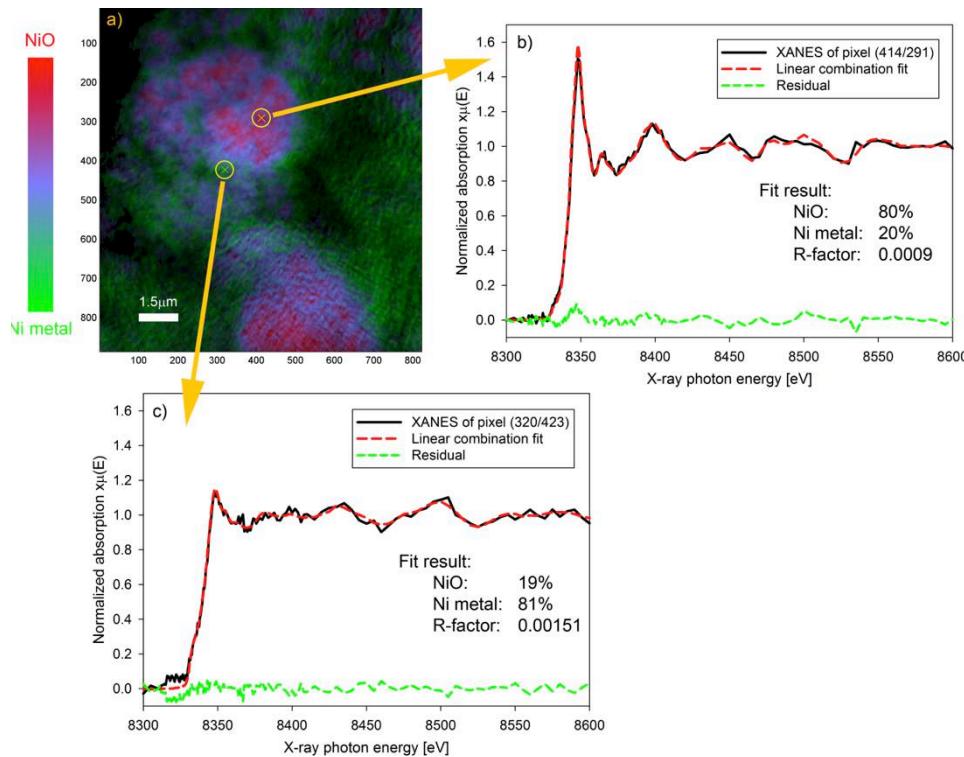
Florian Meirer
Utrecht University



Chemical Imaging

Chemical imaging is the analytical capability

-) to create a **visual image** of the distribution of the
-) **components** of a sample by
-) simultaneously collecting **spectral and spatial (or time)** information



Chemical imaging and the fundamental questions in science:

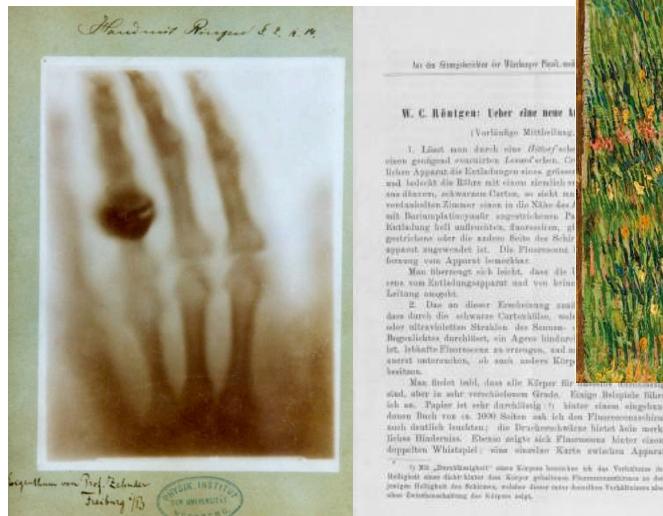
1. **What is there and where is it?**
2. How does it work?
3. How did it come to be this way?



Why X-rays?

1. What is there and where is it?

- ⇒ Create a visual image different from what you see using visible light...
- ⇒ X-rays can provide a different view of things:



Top left: Röntgen's first X-ray, of his wife's hand, taken on Dec 22th, 1895.

Top right: Röntgen's first report "Über eine neue Art von Strahlen. Vorläufige Mitteilung.", 1895



Left top: Vincent van Gogh, *Patch of Grass*, Paris, April-June 1887, oil on canvas, 30 cm × 40 cm, Kröller-Müller Museum, Otterlo, The Netherlands

Left: Tritonal color reconstruction of Sb (yellowish white) and Hg (red) representing the flesh color of the hidden face.

Reference:

J. Dik et al., *Anal. Chem.* 2008, 80, 6436–6442

Below: Kidney blood vessels. Angiography (blood vessel X-ray) footage showing a radio-opaque contrast medium (dark) being injected by a catheter (right) into a 35-year-old patient's right renal artery.

Source:

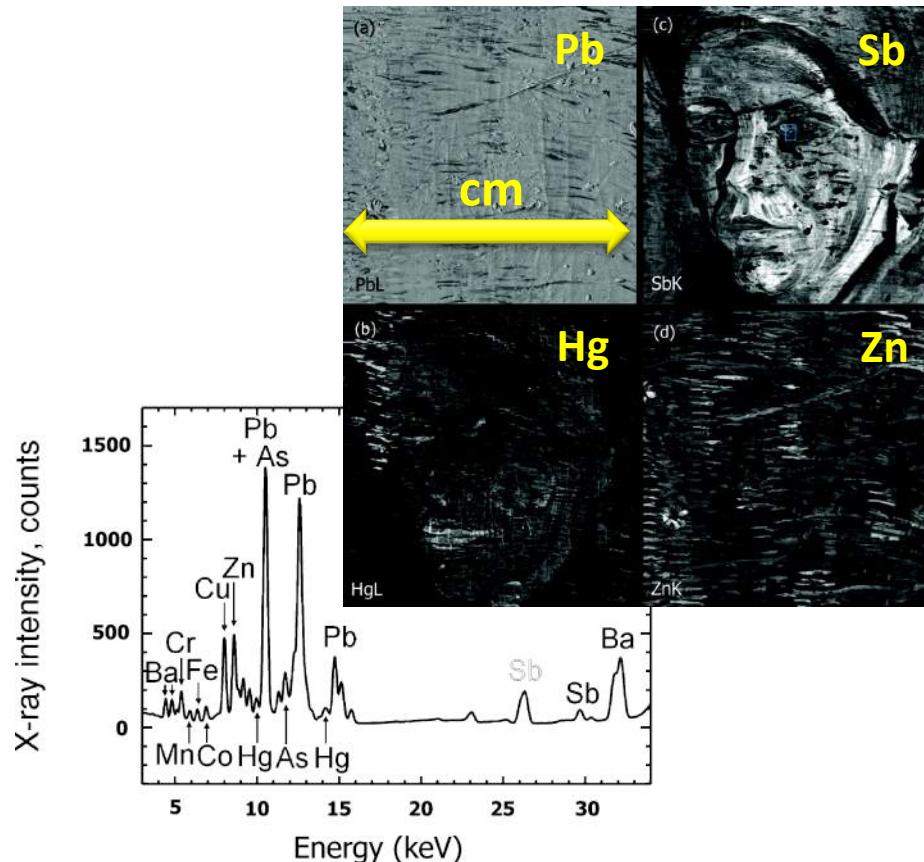
www.sciencephoto.com



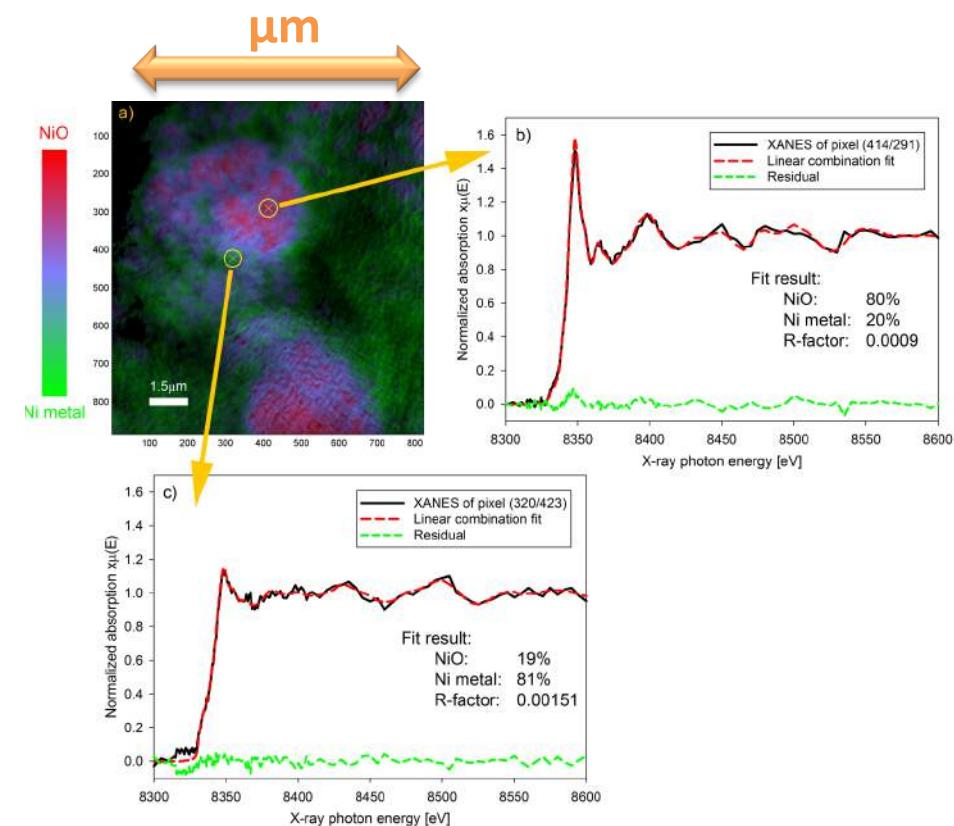
X-ray Spectroscopy

Chemical imaging is the analytical capability

-) to create a **visual image** of the distribution of the
-) **components** of a sample by
-) simultaneously collecting **spectral and spatial (or time)** information



J. Dik et al., *Anal. Chem.* (2008), 80, 6436–6442



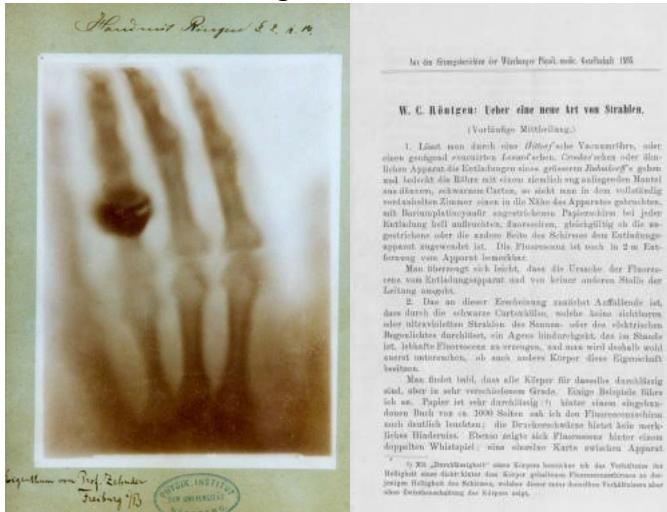
F. Meirer et al., *J. Synchrotron Rad.* (2011). 18



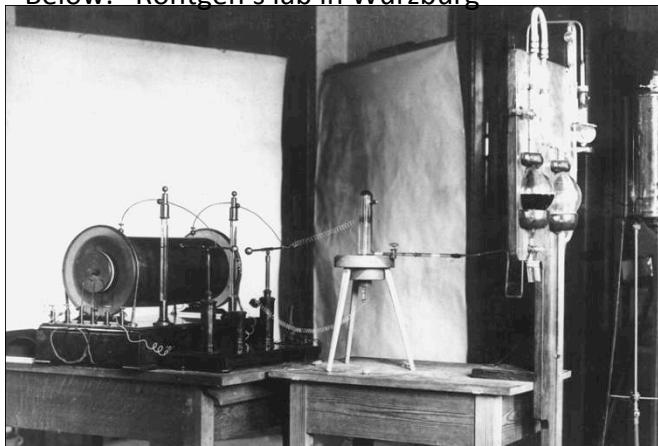
X-ray Imaging: 1895 and Today

Left: Röntgen's first x-ray, of his wife's hand, taken on Dec 22th, 1895.

Right: Röntgen's first report "Über eine neue Art von Strahlen. Vorläufige Mitteilung.", in: Aus den Sitzungsberichten der Würzburger Phys.-med. Ges. Würzburg. S 137–147, 1895;



Below: Röntgen's lab in Würzburg



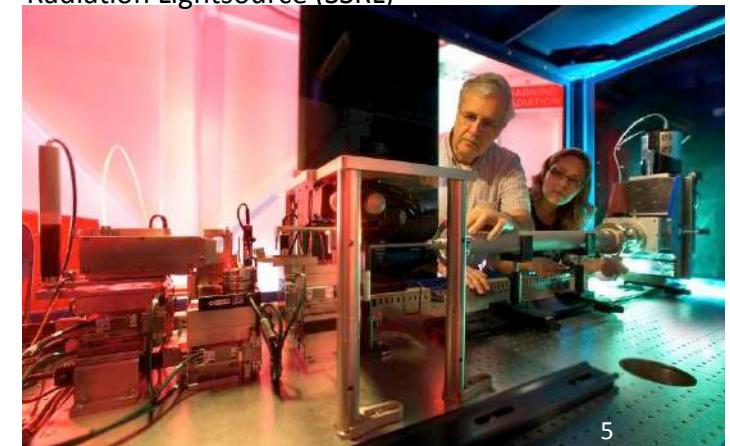
... but the tools have somewhat improved after more than 100 years of technological development

Reconstructed tomography dataset of lacuna from mouse bone (*tibia*) imaged in absorption contrast with 40nm 2D-resolution.



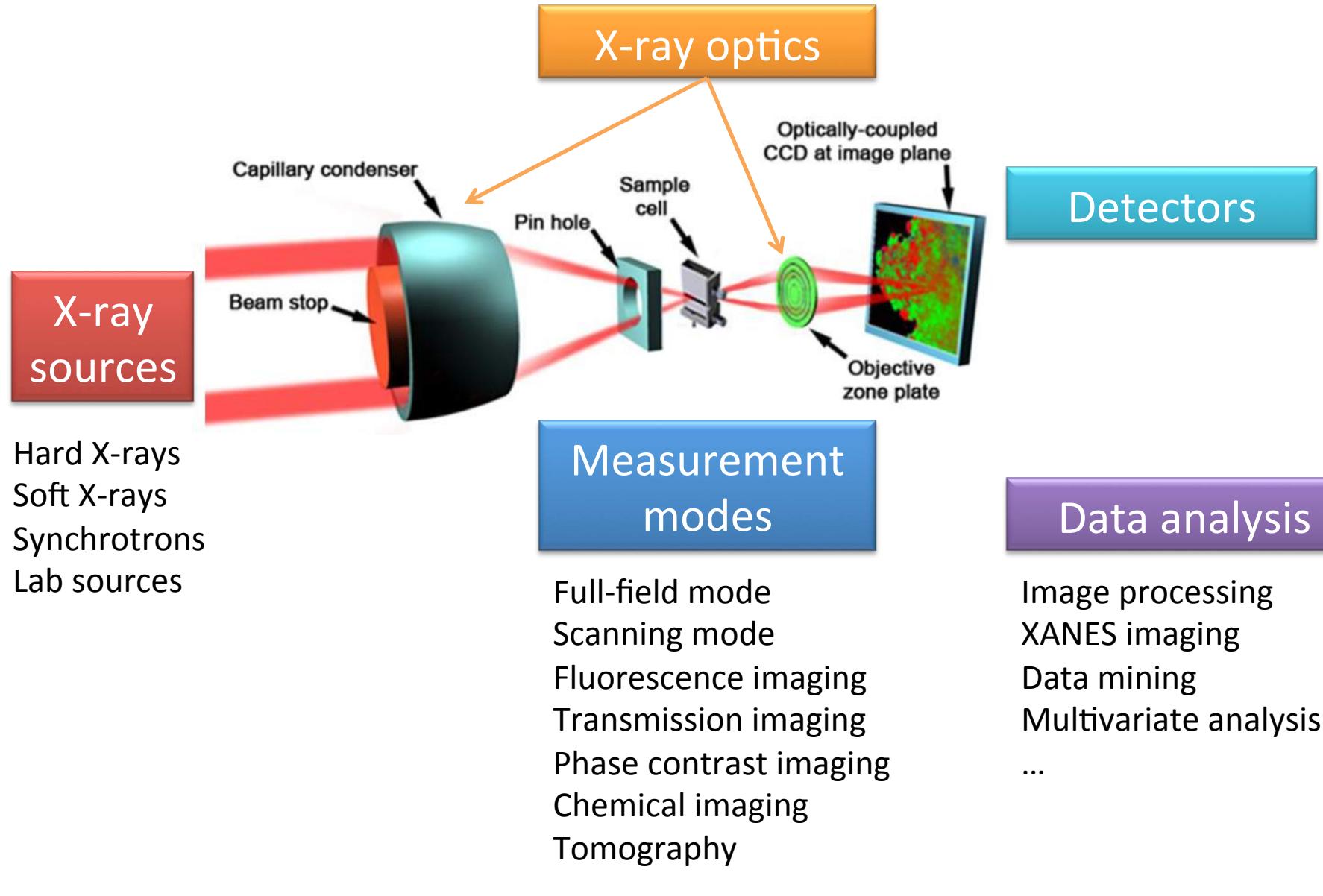
The concept is old and materials are still the same...

TXM at beamline 6-2 at the Stanford Synchrotron Radiation Lightsource (SSRL)





X-ray Microscopy



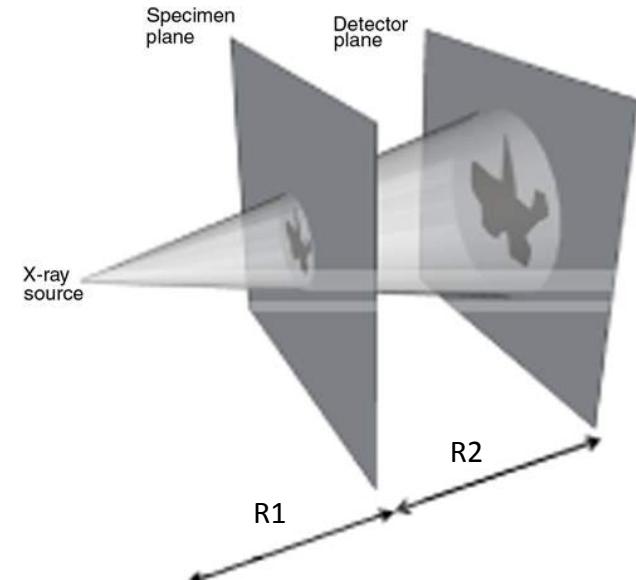


X-ray Microscopy

Types of (real-space⁽¹⁾) x-ray microscopes / imaging techniques:

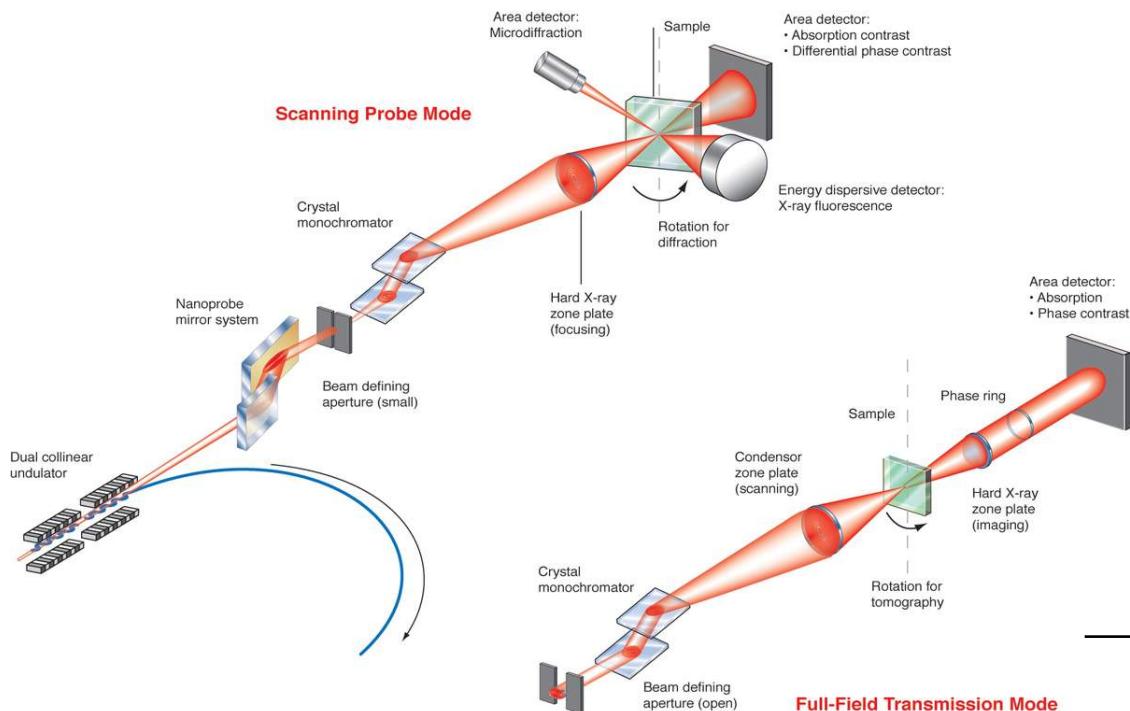
a) Projection imaging:

Lensless imaging; a small diameter X-ray source **projects the specimen onto a pixel-array detector**



b) Scanning probe X-ray Microscopy:

an X-ray micro/nano probe is formed and the specimen is **raster-scanned to build up the image**



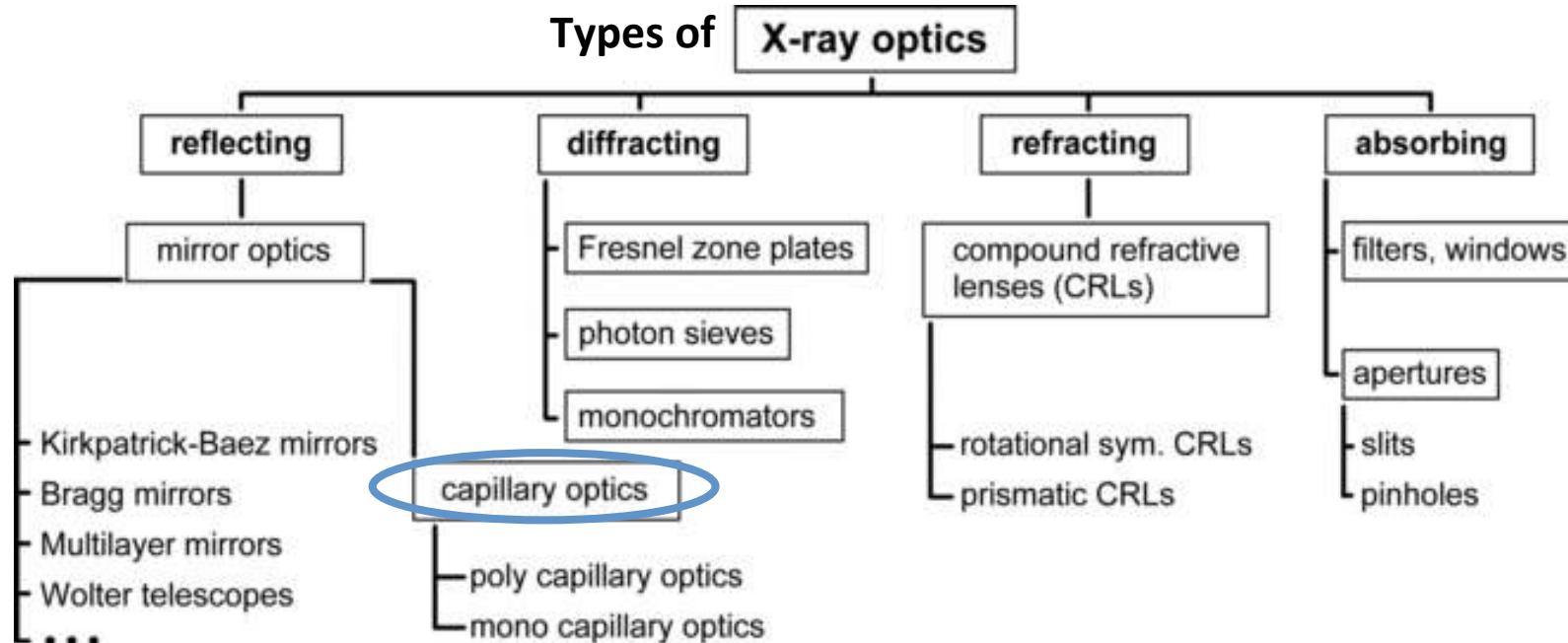
c) Full-field Transmission X-ray Microscopy (TXM):

sample is illuminated by a modestly focused x-ray source and an **objective lens magnifies the image of the sample onto a pixel-array detector**

(1): In contrast to reciprocal space techniques, i.e. diffraction imaging

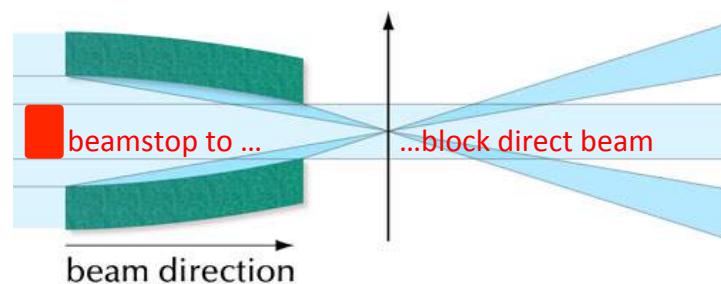


X-ray Microscopy

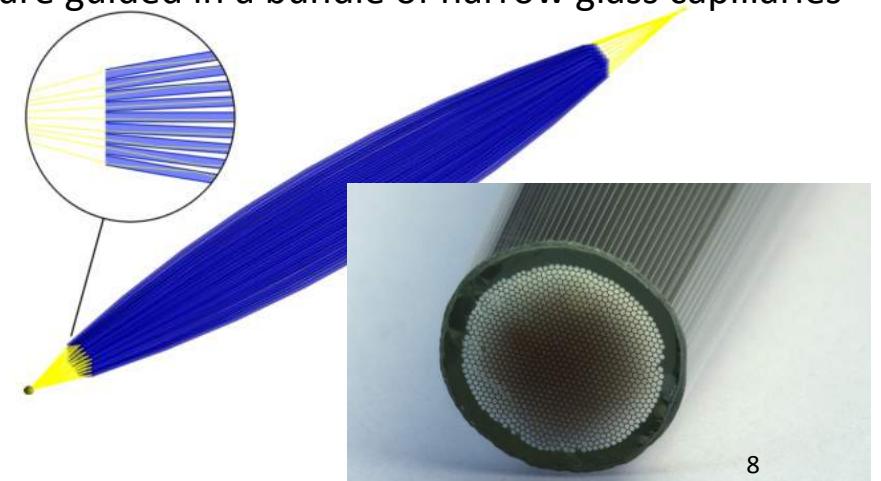


capillary optics

poly capillary optics
mono capillary optics



Polycapillary optics:
x-rays are guided in a bundle of narrow glass capillaries

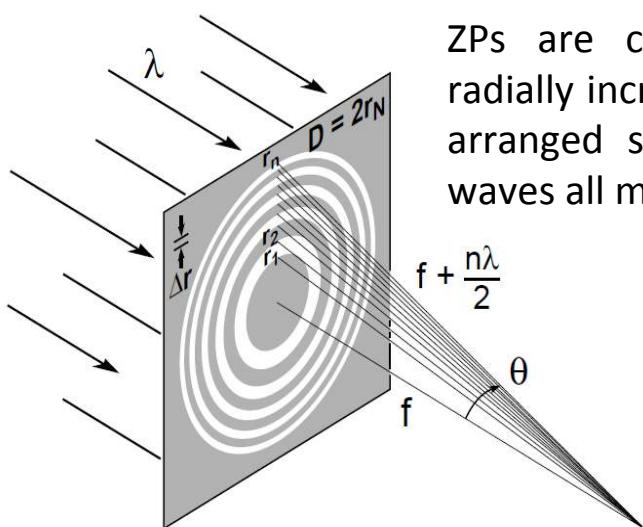
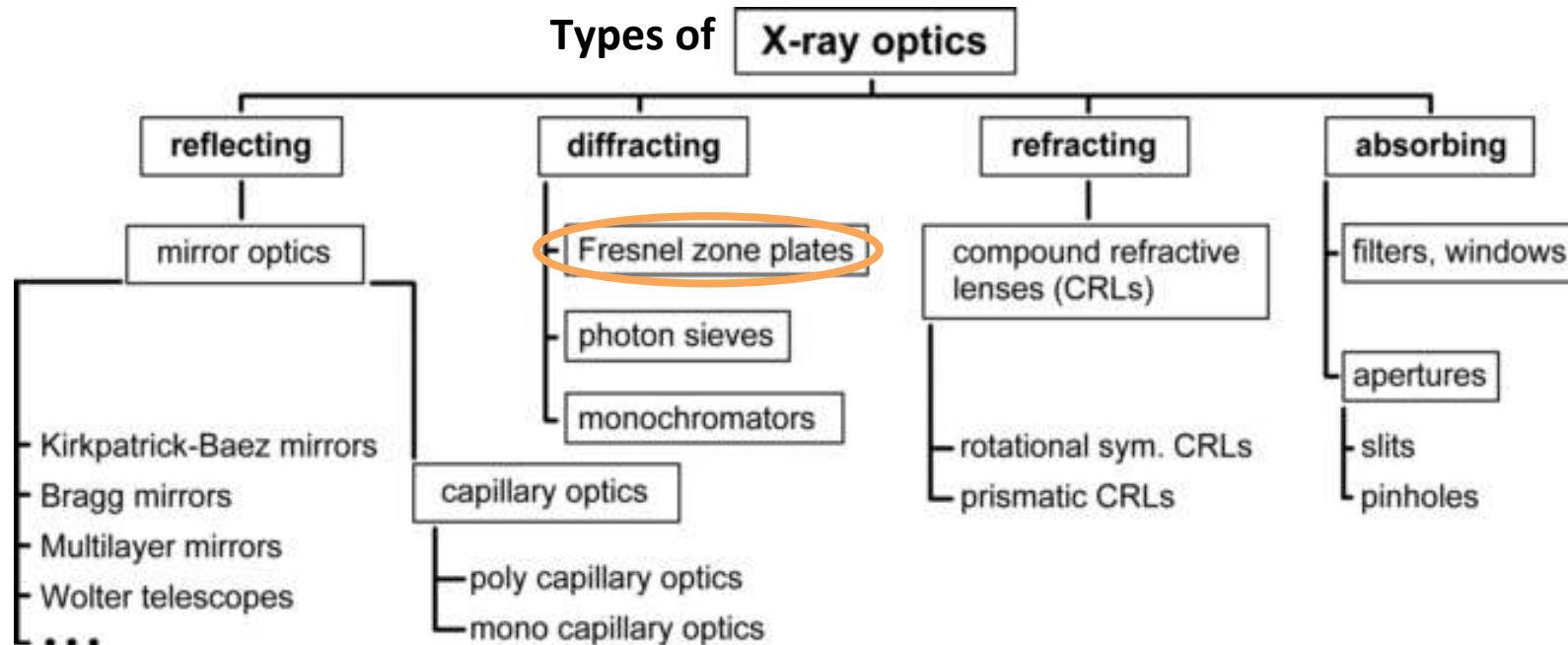


Monocapillary optics:

X-rays reflect only once inside an imaging capillary;
all rays are focused to one point.

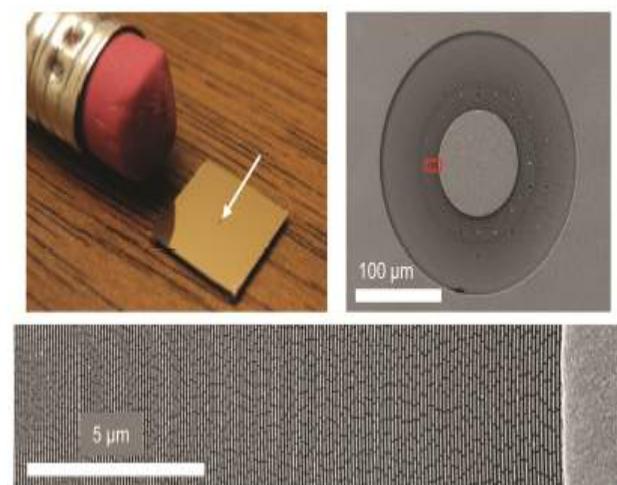


X-ray Microscopy



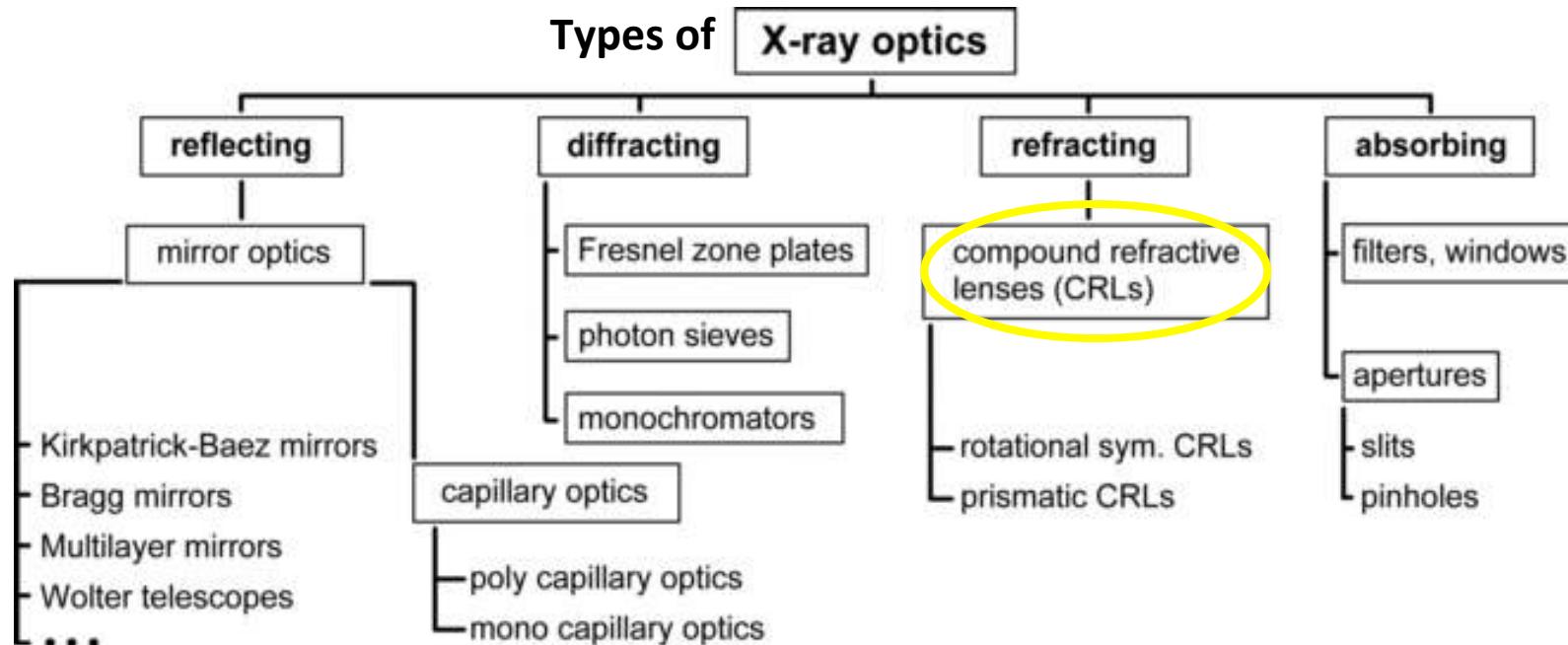
ZPs are circular diffraction gratings with radially increasing line density. The spacing is arranged so that the first order diffracted waves all meet at the primary focus.

A zone plate lens is fully specified by three parameters: wavelength λ , outer zone width Δr , and number of Zones N .

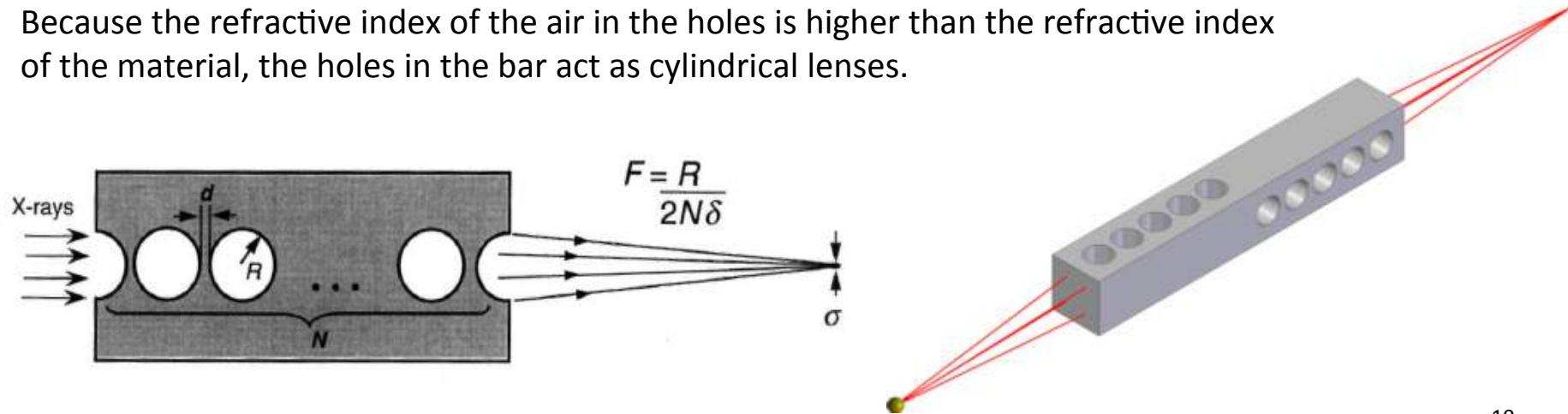




X-ray Microscopy



Because the refractive index of the air in the holes is higher than the refractive index of the material, the holes in the bar act as cylindrical lenses.





Is it all about resolution?

Microscopy today – what do we have?

Microscope Type	Detect	Resolution	Contrast
visible light	transmitted light	500 nm	bright field
		500 nm	phase contrast
	scattered light	500 nm	dark field
	fluorescence	50 – 500 nm	label
electron microscope (TEM)	scattered electrons	0.1 – 1 nm	heavy metal stain
scanning electron micr. (SEM)	secondary electrons	3 – 10 nm	surface relief
scanning tunneling micr. (STM)	tunneling current	0.1 nm	surface atoms
scanning force micr. (AFM)	force on probe tip	0.5 nm	surface relief
X-ray projection microscope	transmitted x-rays	>1000 nm	absorption
X-ray microscope (TXM)	transmitted x-rays	15-30 nm ^{(1), (2)}	absorption, XANES ⁽²⁾
		25 nm	phase contrast
scanning x-ray microscope (STXM)	transmitted x-rays	25 nm	absorption
			XANES (chemical)
X-ray nanoprobe / micro-probe	fluorescence	<30 nm up to mm	Elements, XAS
	diffraction	<30 nm	strain

Source:
www.xradia.com

Examples:

Soft X-rays: down to 15nm:
⁽¹⁾ LBNL, beamline 6.1.2

Hard X-rays: <30nm:
⁽²⁾ SSRL, beamline 6-2

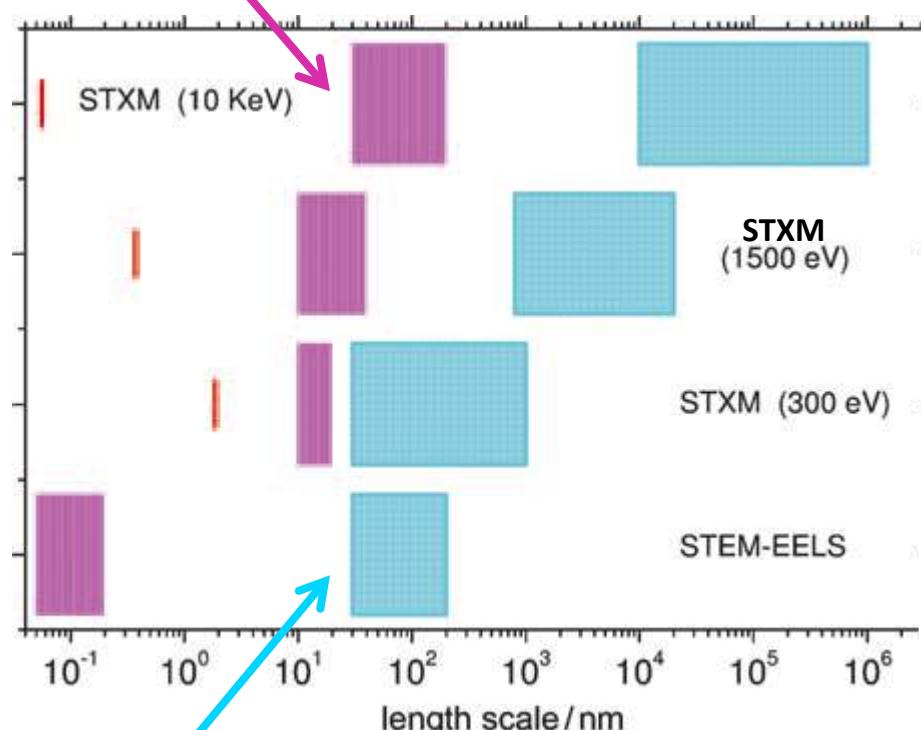
X-ray microscopes are particularly powerful where:

- a resolution better than delivered by visible light microscopes is required
- samples are opaque to visible light
- easy sample preparation is desired
- samples are too thick for transmission electron microscopy
- bulk information is required (i.e. information on the **3D structure of samples**)



X-ray Microscopy

Range of experimental spatial resolutions (pink)



Range of maximal sample thickness (blue)

The range of sample thicknesses is limited as a consequence of the **X-ray attenuation** but also by spectral deformations due to **saturation effects**. The red vertical lines indicate the diffraction limited resolution R of the X-rays, given as $R \text{ (nm)} * E \text{ (eV)} \approx 620$

	STEM EELS	Soft x-ray TXM	Hard X-ray TXM
Resolution	0.1 nm	10 nm	20 nm
Conditions	1 mbar / 300 C	1 bar / 500 C	30 bar / 1000 C
Beam damage	severe damage	damage	less damage
Sample thickness	< 300 nm	< 1 μm	< 100 μm
In-situ setup	nanoreactor	nanoreactor	capillary reactor plug flow
Detectable elements	all elements	Z > 5 (C)	Z > 21 (Ti)

From: F.M.F. deGroot et al., *ChemPhysChem* 2010, 11, 951 – 962



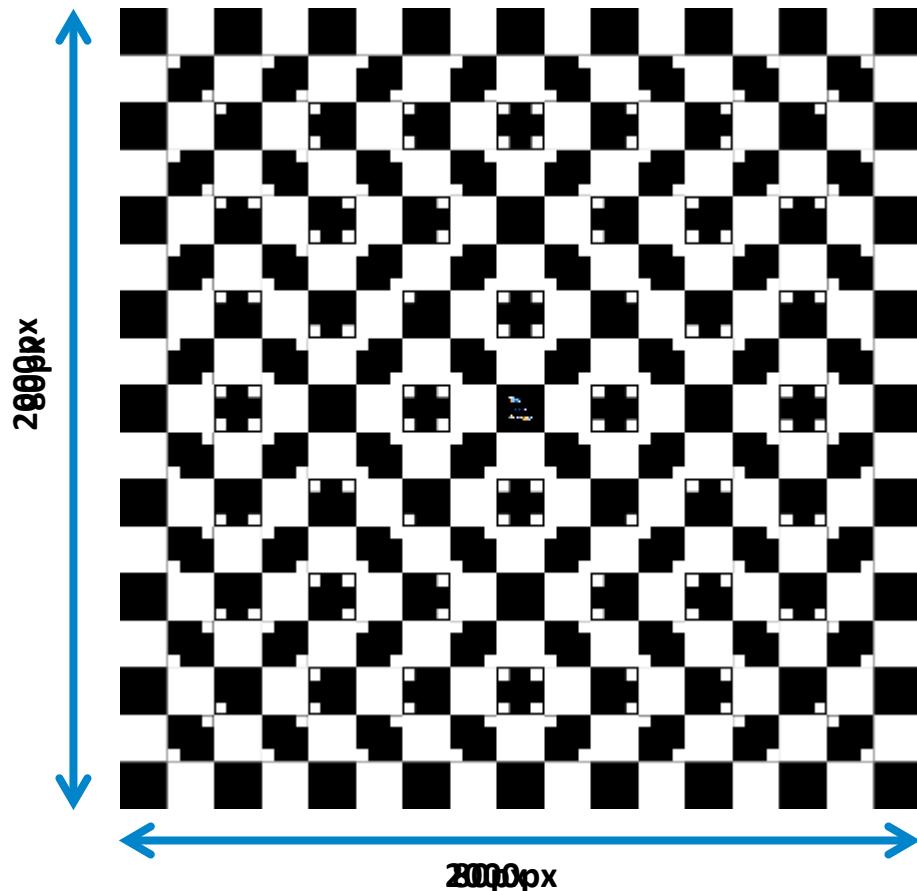
A large FOV - full field mode

1.) Example: FOV: 80×80 pixels

⇒ raster scan with 1 sec. exposure time: ~ 1.8 h

⇒ need for extremely short exposure times, e.g. 1 msec.: 6.4s for one FOV

2.) increasing the resolution with a **constant Field Of View (FOV)**



In order to study **hierarchically structured complex systems** at multiple length scales we need both:

high resolution AND a large FOV

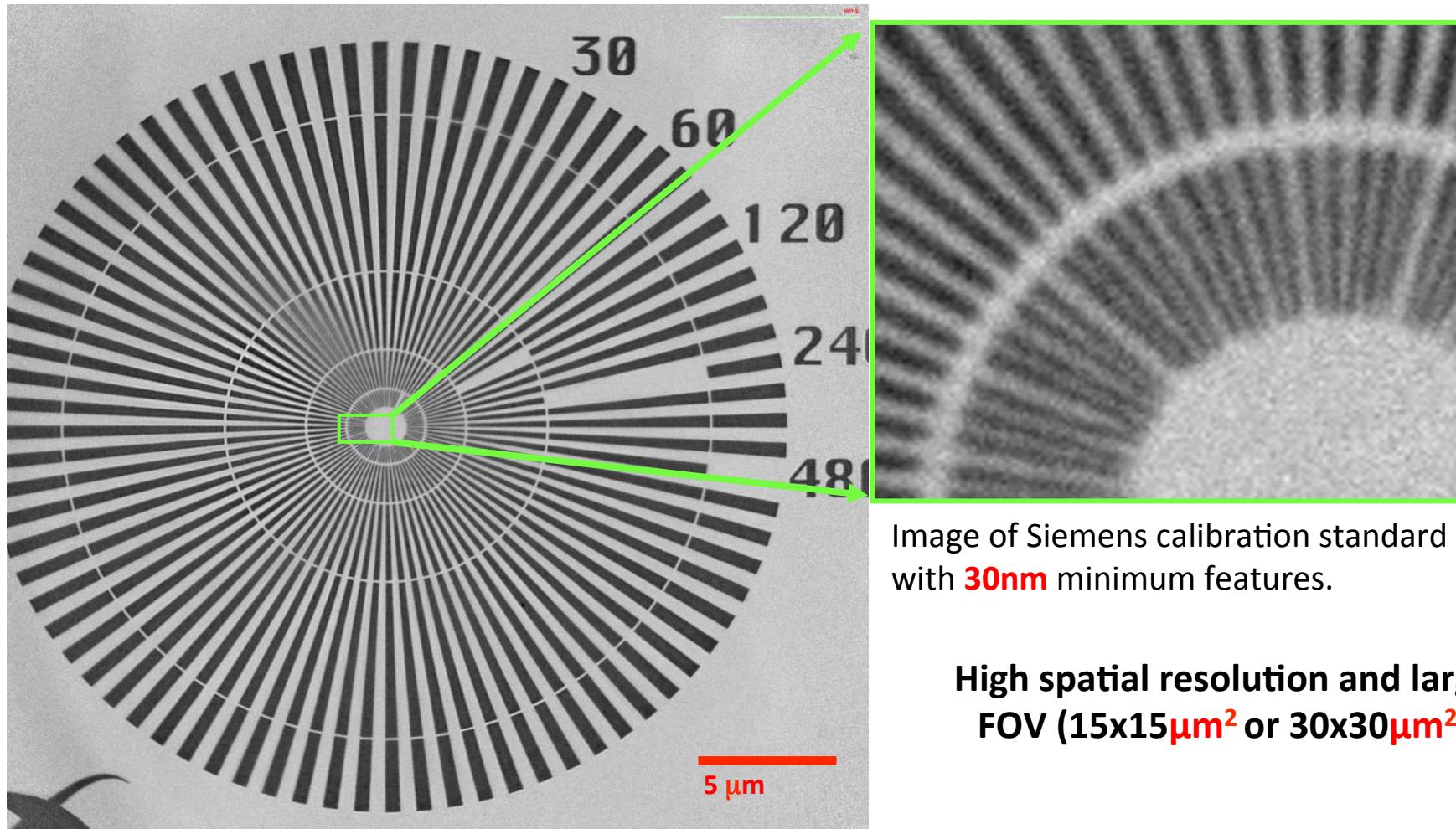
3.) increasing the FOV while **keeping high resolution**

Full field techniques do not raster scan the FOV but use a CCD sensor, typically collecting images of $2k \times 2k$ pixels.



Example: the Full Field Transmission X-ray Microscope (FF-TXM) – High resolution AND large FOV

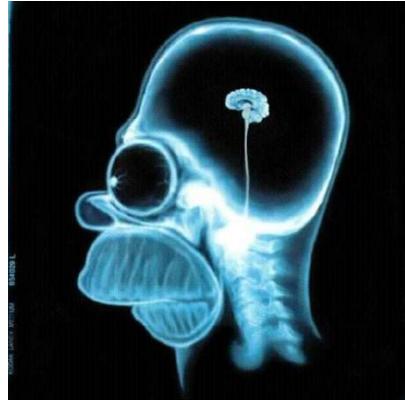
TXM image of Siemens star test pattern recorded at 5.4 keV (30-200 zone plate) at BL 6-2 of the Stanford Synchrotron Radiation Lightsource (SSRL)



**High spatial resolution and large
FOV ($15 \times 15 \mu\text{m}^2$ or $30 \times 30 \mu\text{m}^2$)**



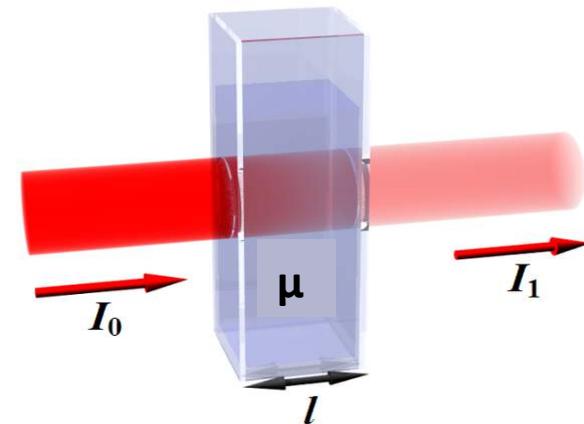
X-ray absorption and imaging



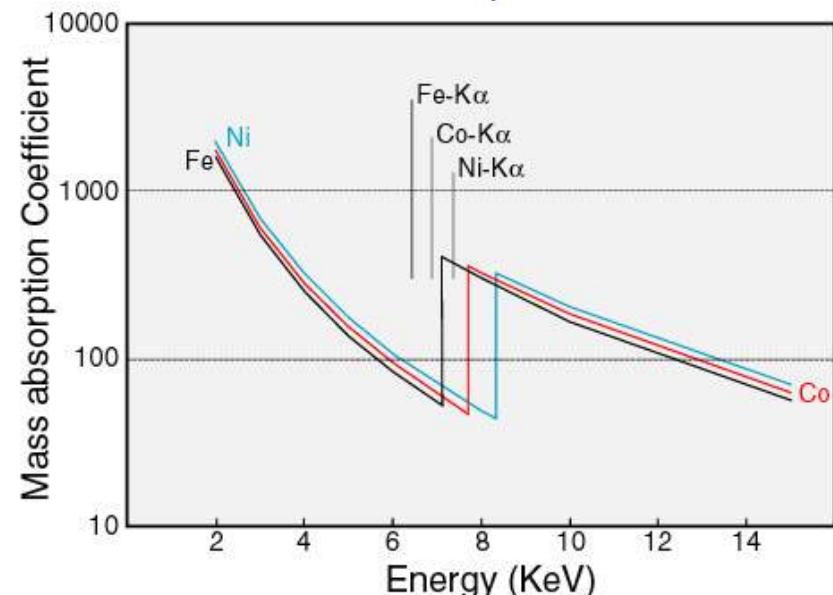
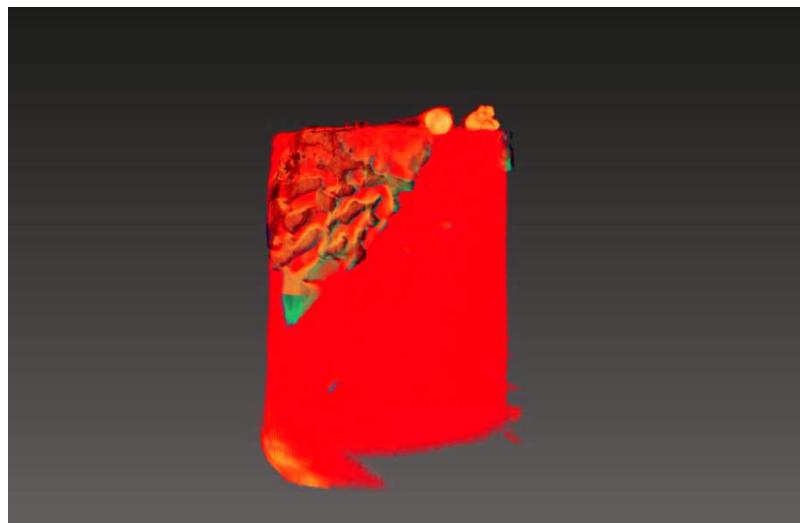
The image of the sample represents the local sample transmission of X-rays

⇒ Allows quantitative analysis following Beer-Lambert's law.

$$\text{Beer-Lambert's Law: } I_1 = I_0 e^{-\mu \cdot l}$$



Absorption contrast takes advantage of the **unique absorption of each chemical element** at a given X-ray energy => **elemental imaging**



Left: Reconstructed tomography dataset of a Ni-Cu aluminide in an AlSi10Cu5Ni2 piston alloy showing the elemental distribution of Ni and Cu.
(Voxel size: 24 nm³, Sample diameter: 20 microns)

Reference: Y. Liu, et al., Anal Bioanal Chem (2012) 404:1297–1301.

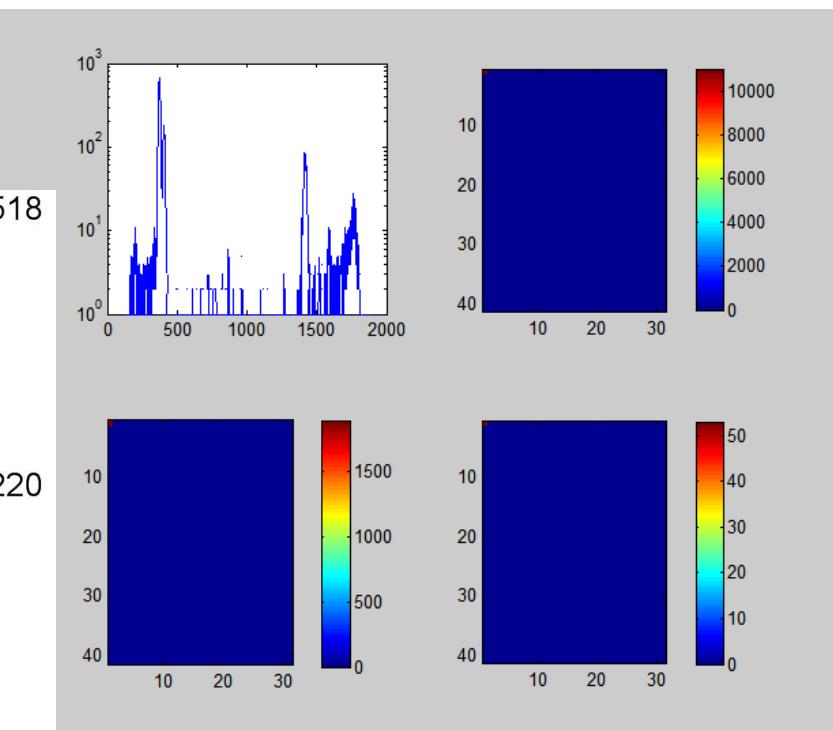
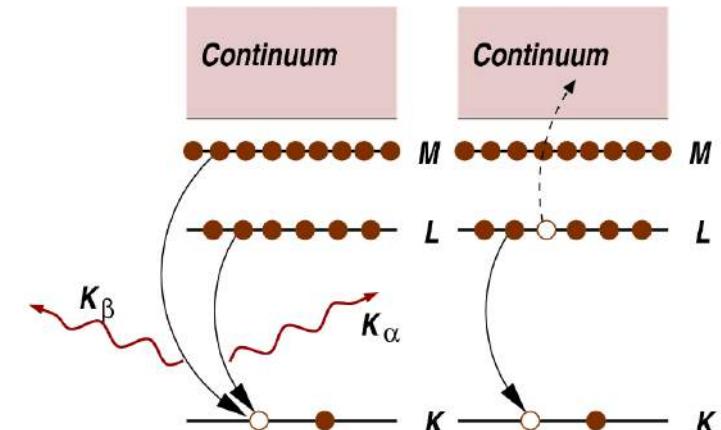
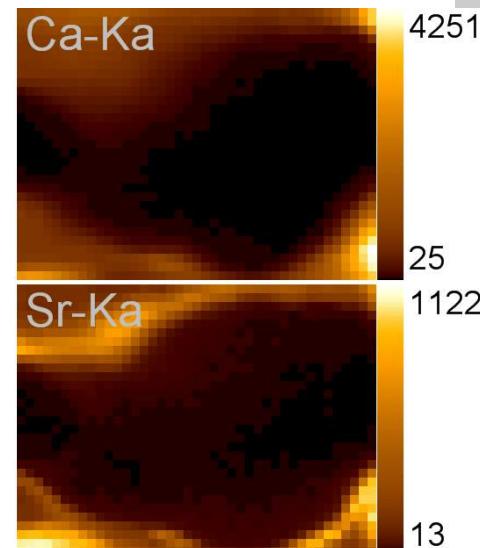
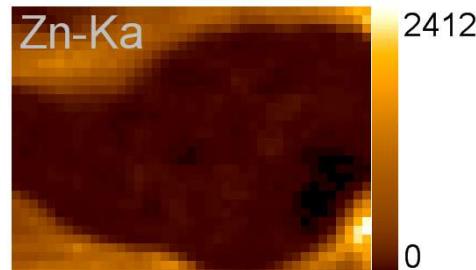


X-ray fluorescence and imaging

For elemental imaging for example we can also use the **x-ray fluorescence spectrum**

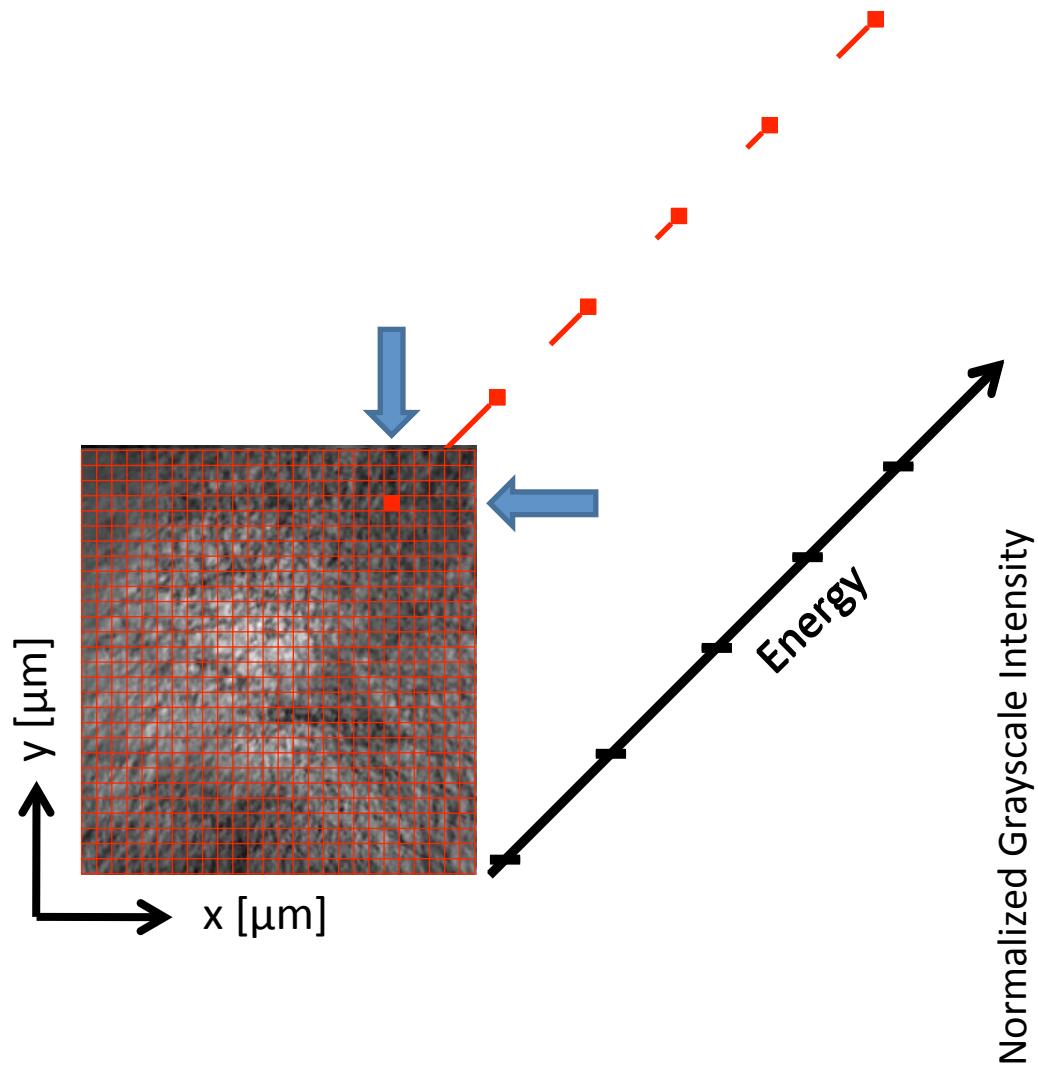
- + simultaneous information about many elements with a single measurement (e.g. tomography)
- + higher sensitivity than transmission mode
(=> better detection limits)

Name: p01_71_
Scan size: 41x31 pixel
Resolution: 10 μ m per pixel.
Normalized to cps and 100mA ringcurrent.
Counting time: 1sec. per pixel





XANES imaging



- 1) Collect one high resolution fluorescence or absorption image at each energy
- 2) Align images & correct changes in magnification
- 3) Trace the absorption value for each pixel to get single pixel XANES
- 4) The XANES provides information about the chemical state of the element of interest



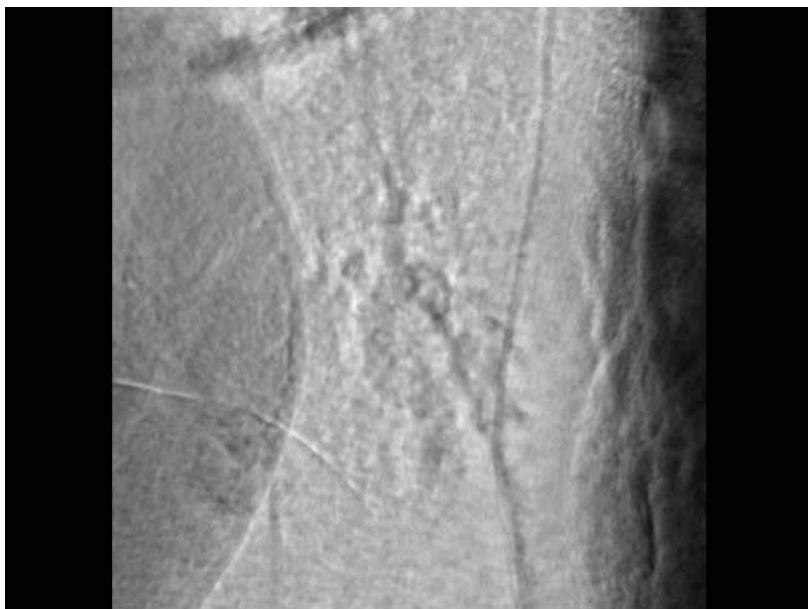
Full field XANES data evaluation - some numbers

146 images (905x927 pixels) recorded during scan across Fe K-edge:

⇒ 146 x 838,935 pixels (15nm pixel size; resolution 30nm)

⇒ **838,935 XANES**

⇒ single scan: **20 minutes – 1 hour**



Comparison to x-ray scanning techniques:

Record 838,935 XANES spectra using 1 millisecond exposure time per energy point (e.g. 146) ~ **34 hours**

Perform standard XANES data evaluation, i.e. a spectroscopist is manually processing the XANES?

Spend **10 seconds per XANES** spectrum => work for more than **97 days**

⇒ a **fast, efficient** and **reliable** way to process the data was needed



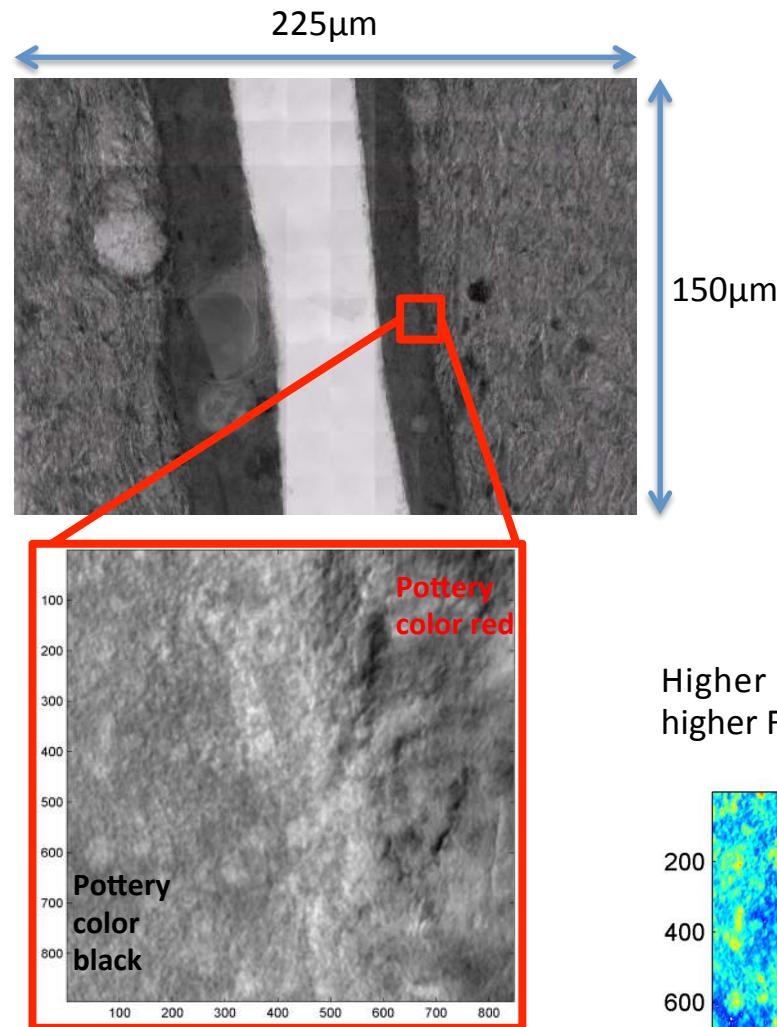
Development of software package to run TXM-XANES measurements and process datasets:

'TXM-Wizard' [1] freely available for download at sourceforge.

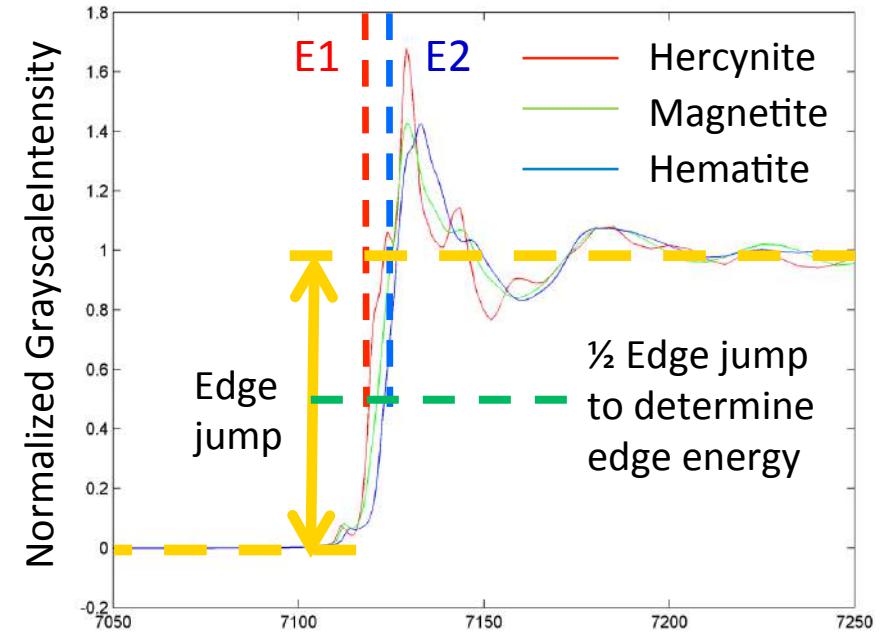
[1] Liu et al., J. Synchrotron Rad. (2012), 19, 281–287



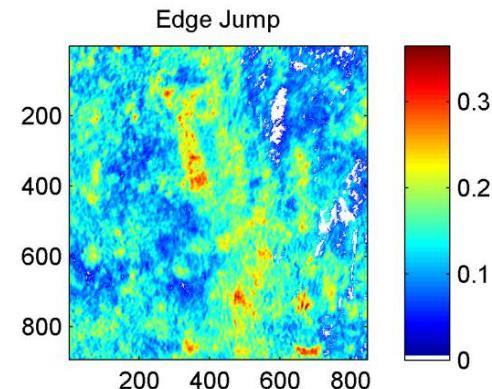
FF XANES data evaluation – analyzing millions of XANES



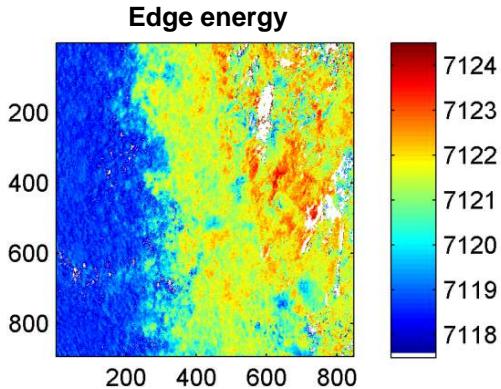
one field of view = 15x15 micron²;
pixel size 15nm; resolution 30nm



Higher edge jump means higher Fe concentrations:



Energy position of edge indicates Fe valence state:





FF XANES data evaluation – analyzing millions of XANES

Beyond the valence map:

Performing detailed speciation for each pixel
=> creating the '**Phase-Map**'

Using *a priori* knowledge of present species inside the sample:

=> least squares (LS) linear combination (LC) fitting **of known standards** to each pixel

=> ratio of the Fe compounds present in each pixel

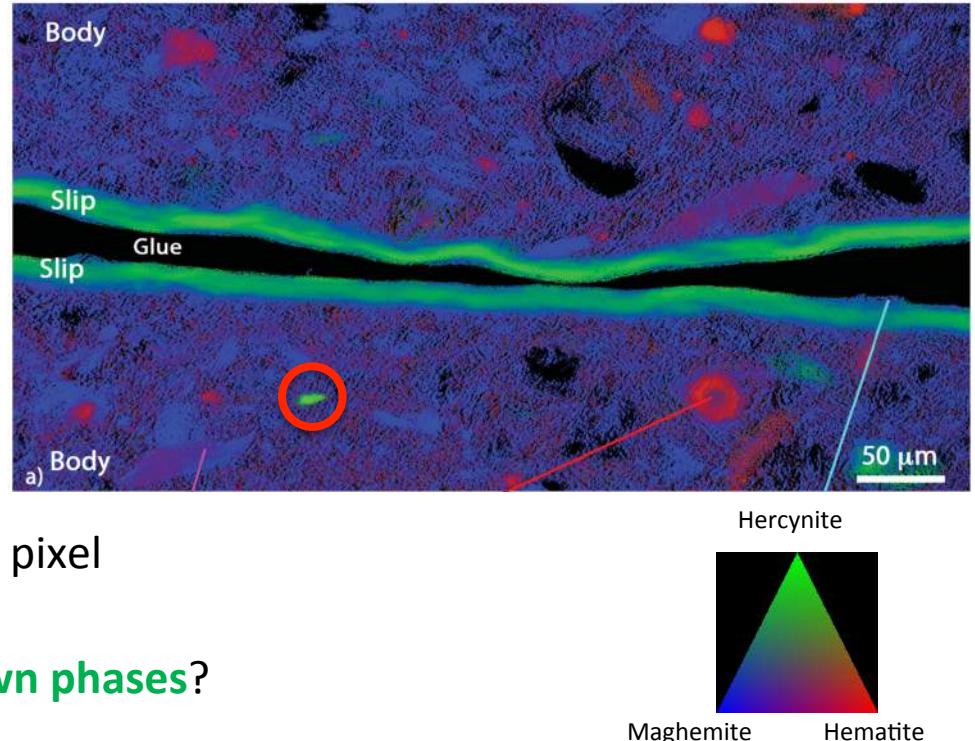
But can we find **unknown phases?**

Yes, we can...

1) 'Brute-force' approach:

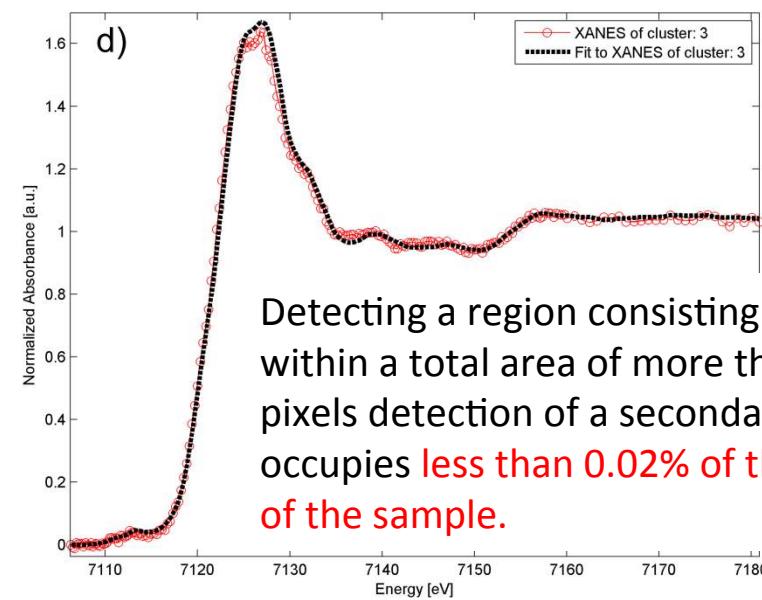
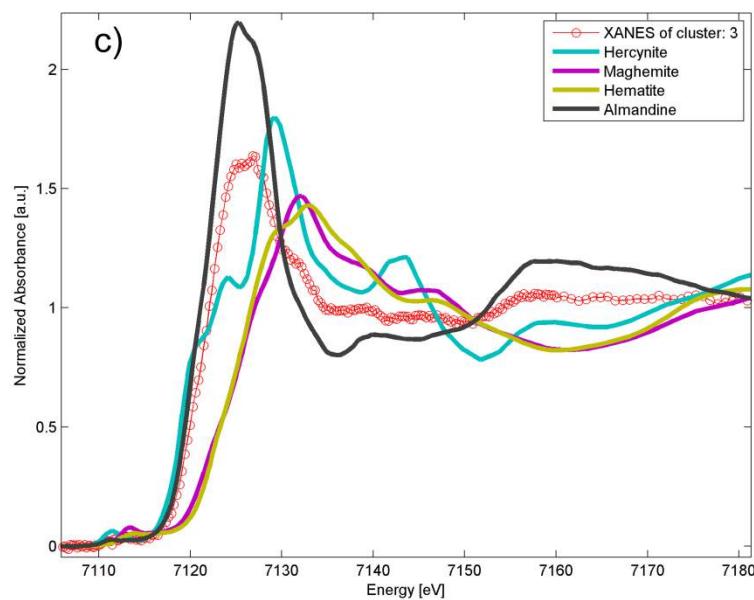
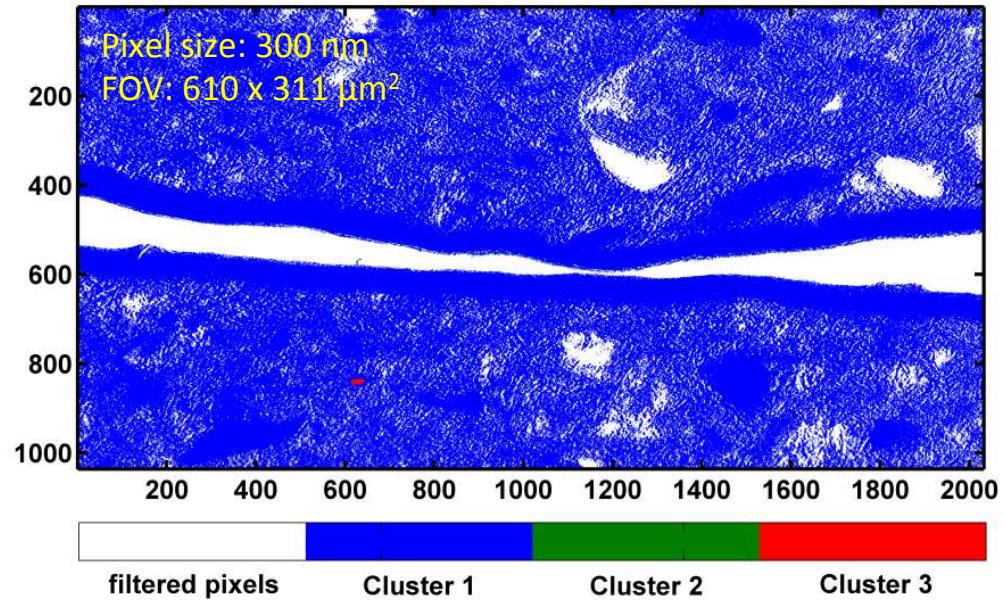
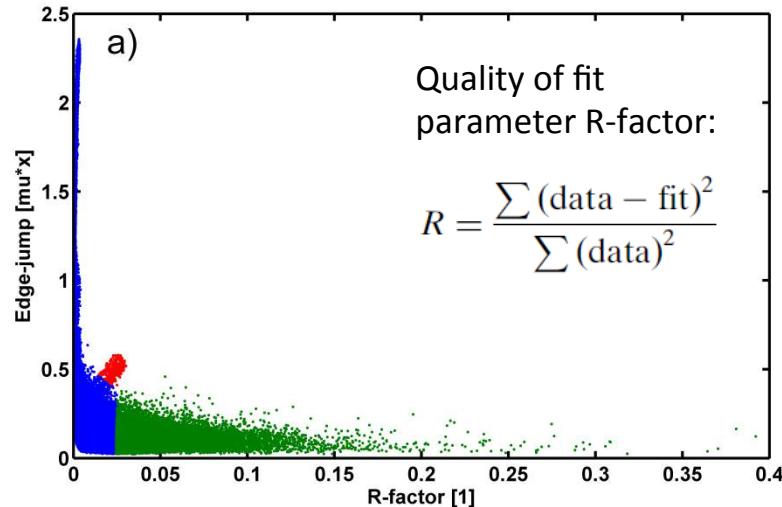
LC fit using known phases and inspection of the correlation plot of edge-jump versus the quality of fit parameter R-factor.

2) Multivariate analysis of the whole data set (PCA & K-means clustering)



FF XANES data evaluation – analyzing millions of XANES

Finding an unknown phase



Detecting a region consisting of **~400 pixels** within a total area of more than **2.1 million** pixels detection of a secondary phase that occupies **less than 0.02% of the total volume of the sample.**



FF XANES data evaluation – analyzing millions of XANES

Finding an unknown phase

Principal component analysis (PCA) & clustering

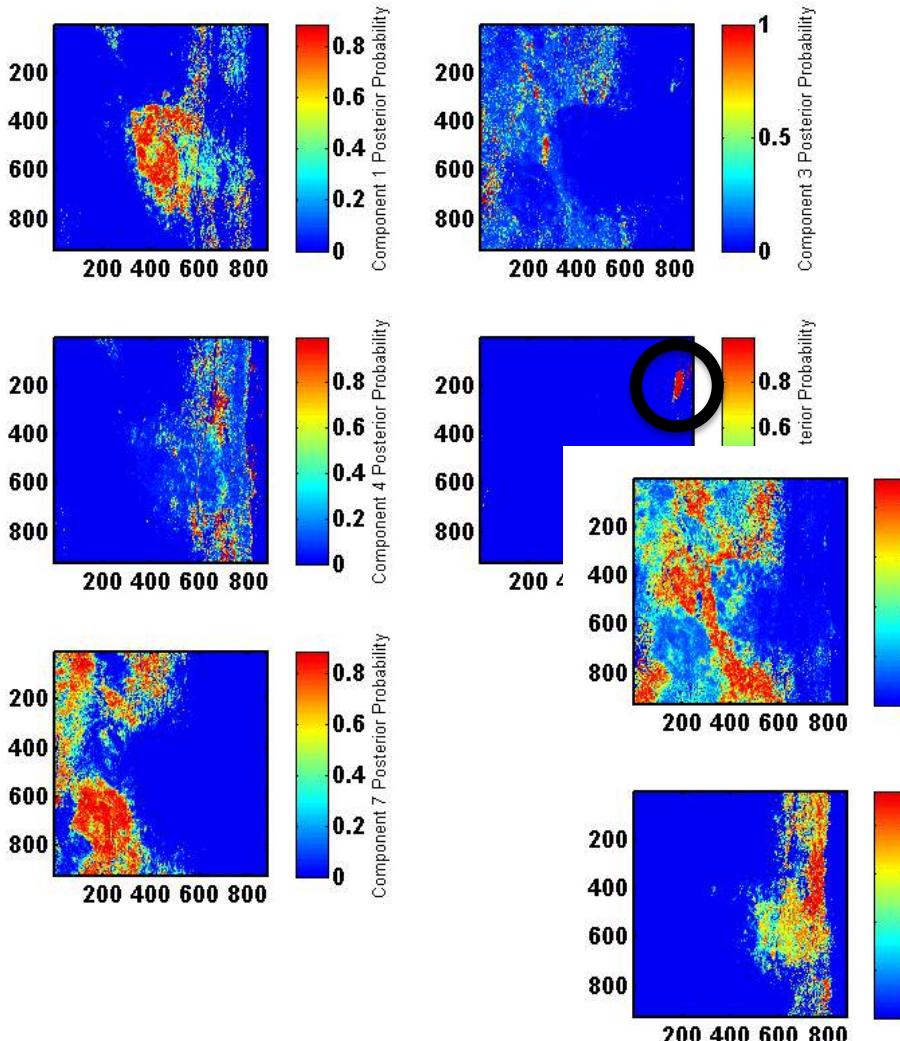
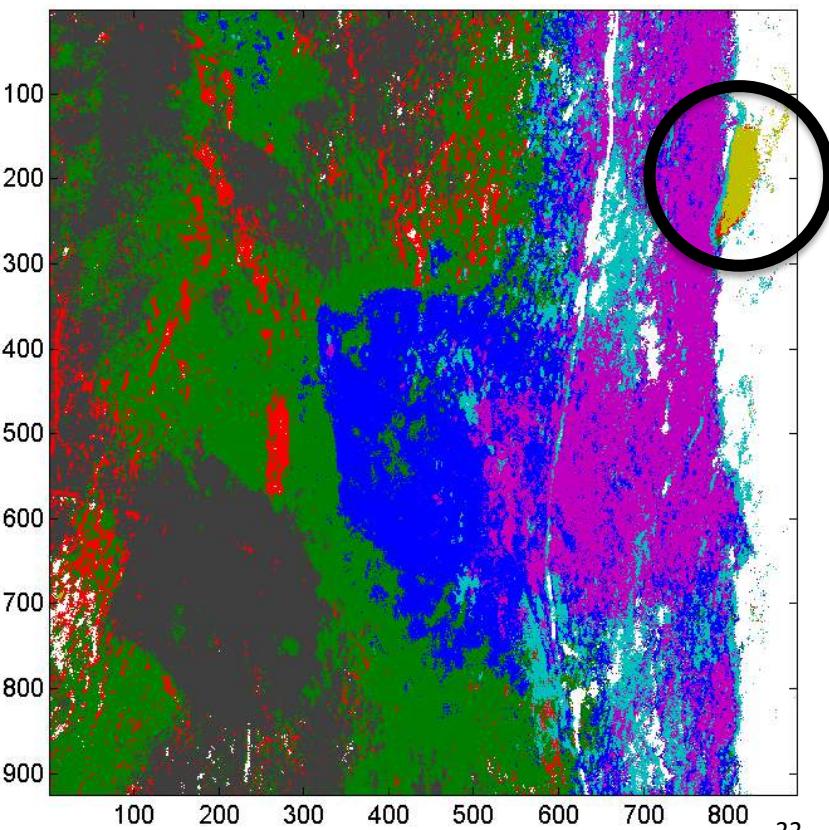


Image segmentation based on XANES similarity
without using any a priori knowledge





FF XANES data evaluation – analyzing millions of XANES

Finding an unknown phase

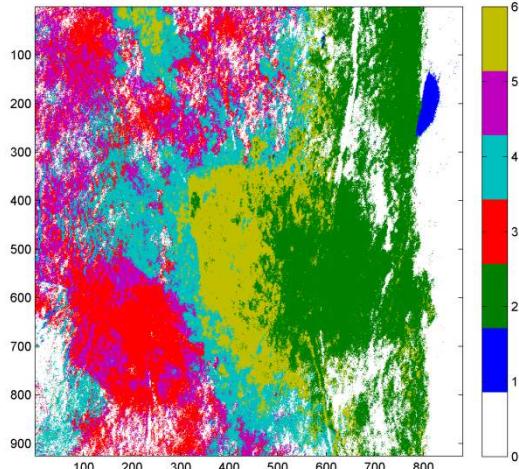
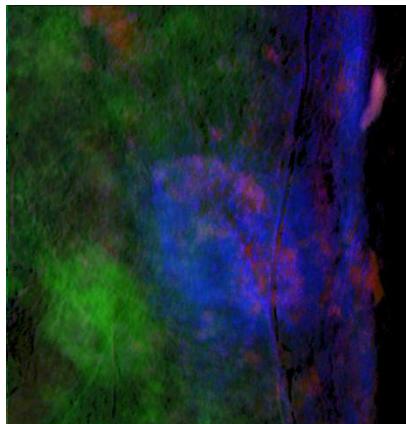
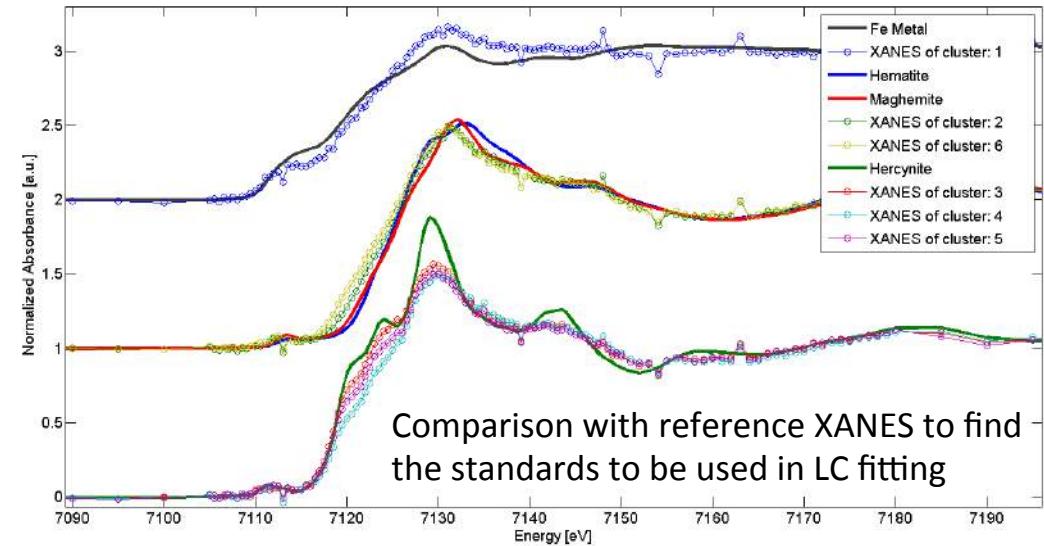


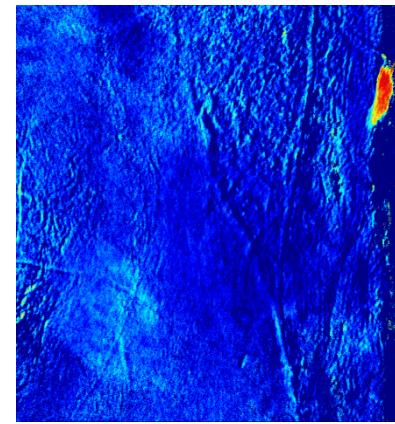
Image
segmentation
↔
based on
XANES
similarity



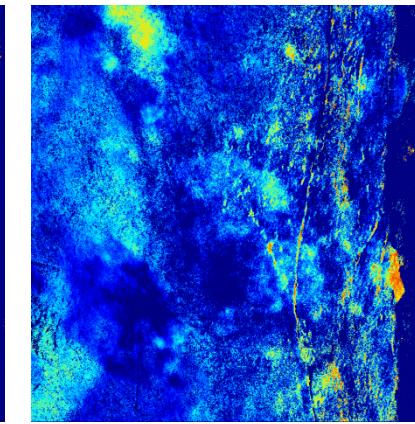
Hercynite

Maghemite Hematite & Fe Metal

10 μm



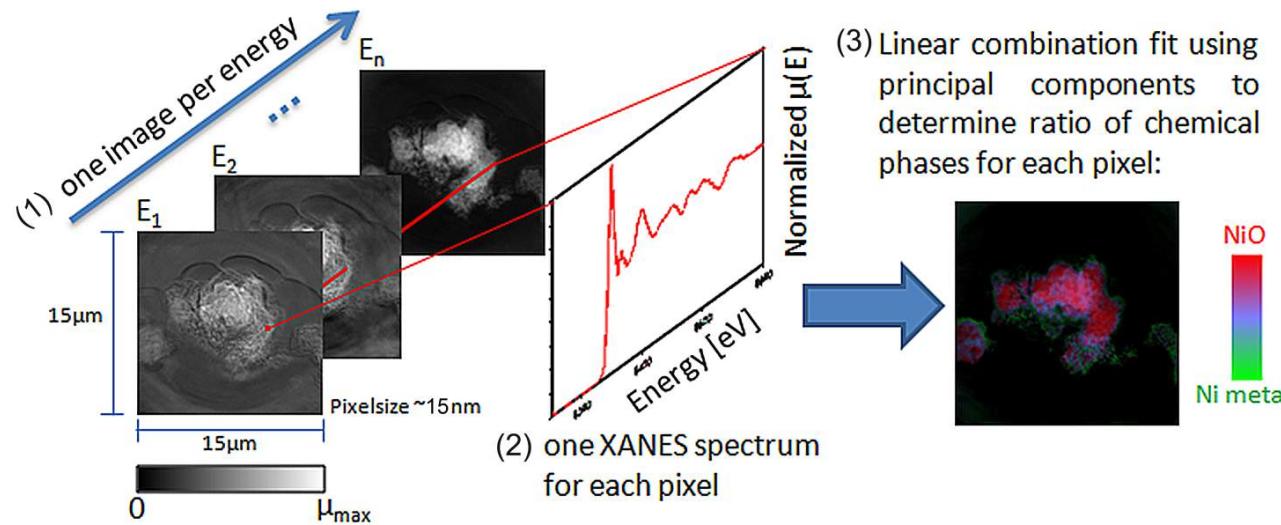
Fe metal



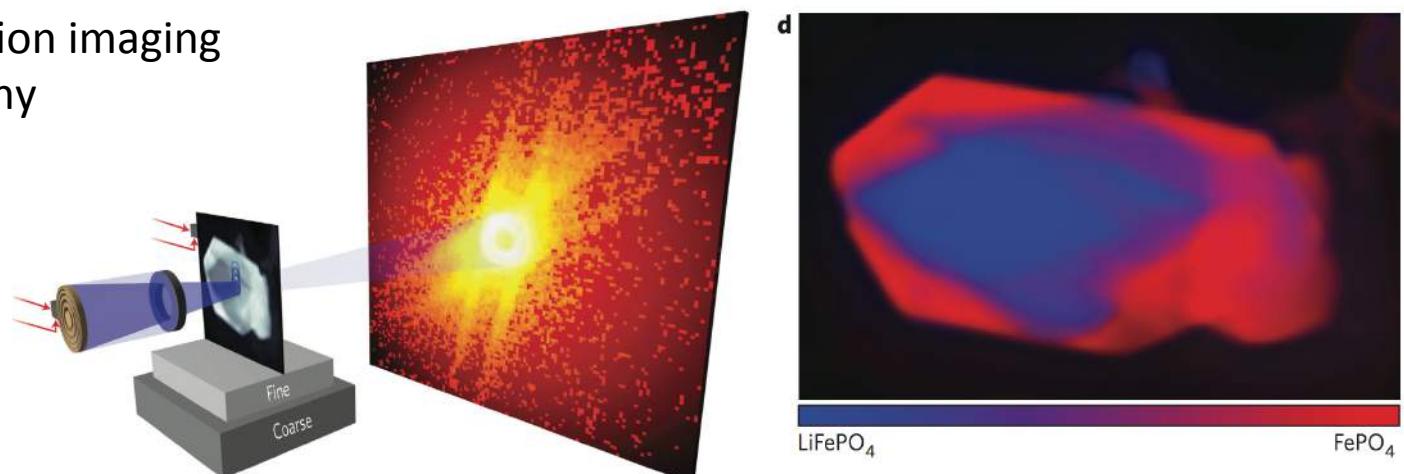
Hematite



2D XANES imaging - Summary

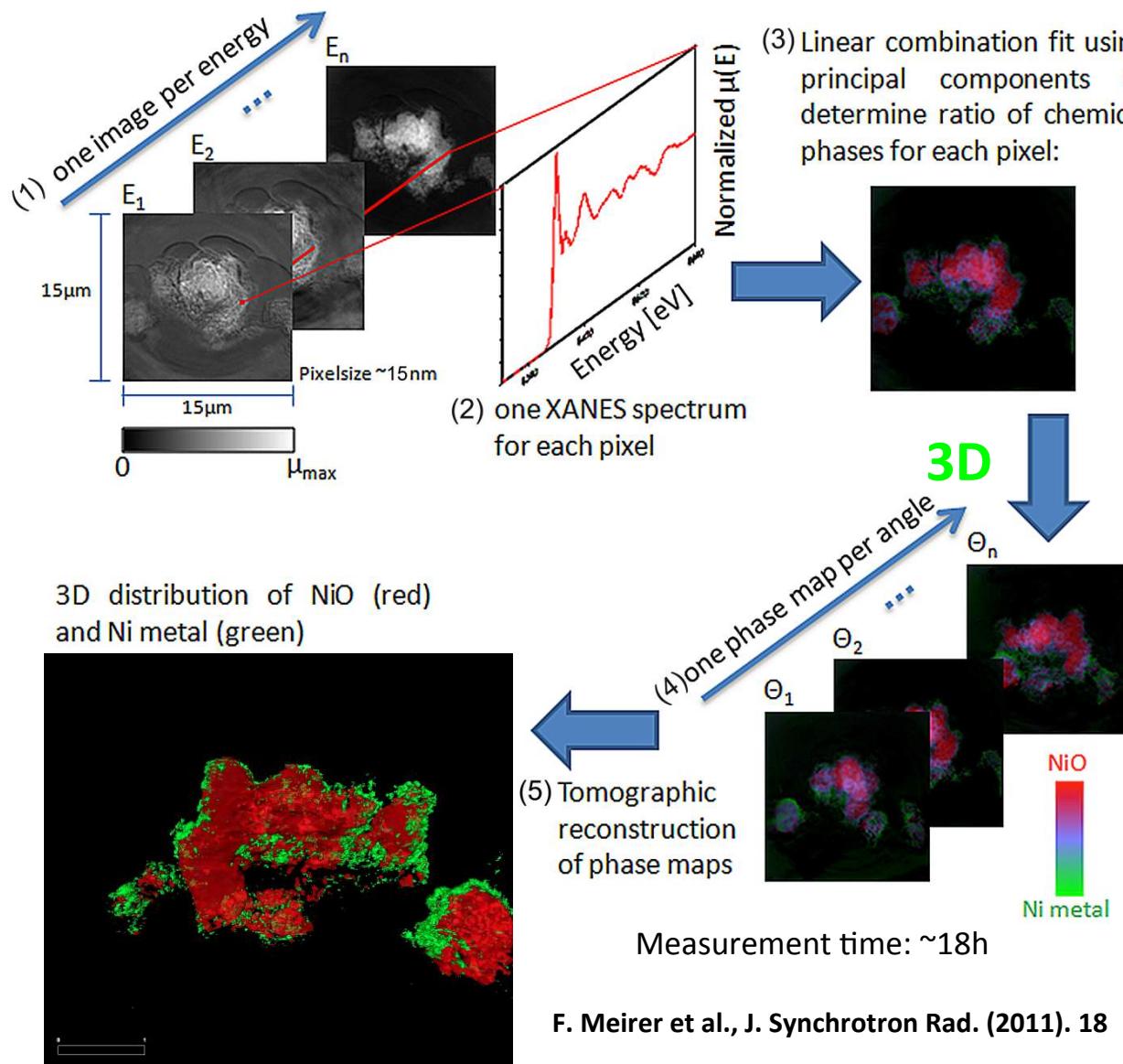


Current 'world record in spatial resolution' for chemical imaging with XAS: **5 nm**
using coherent diffraction imaging
also called ptychography



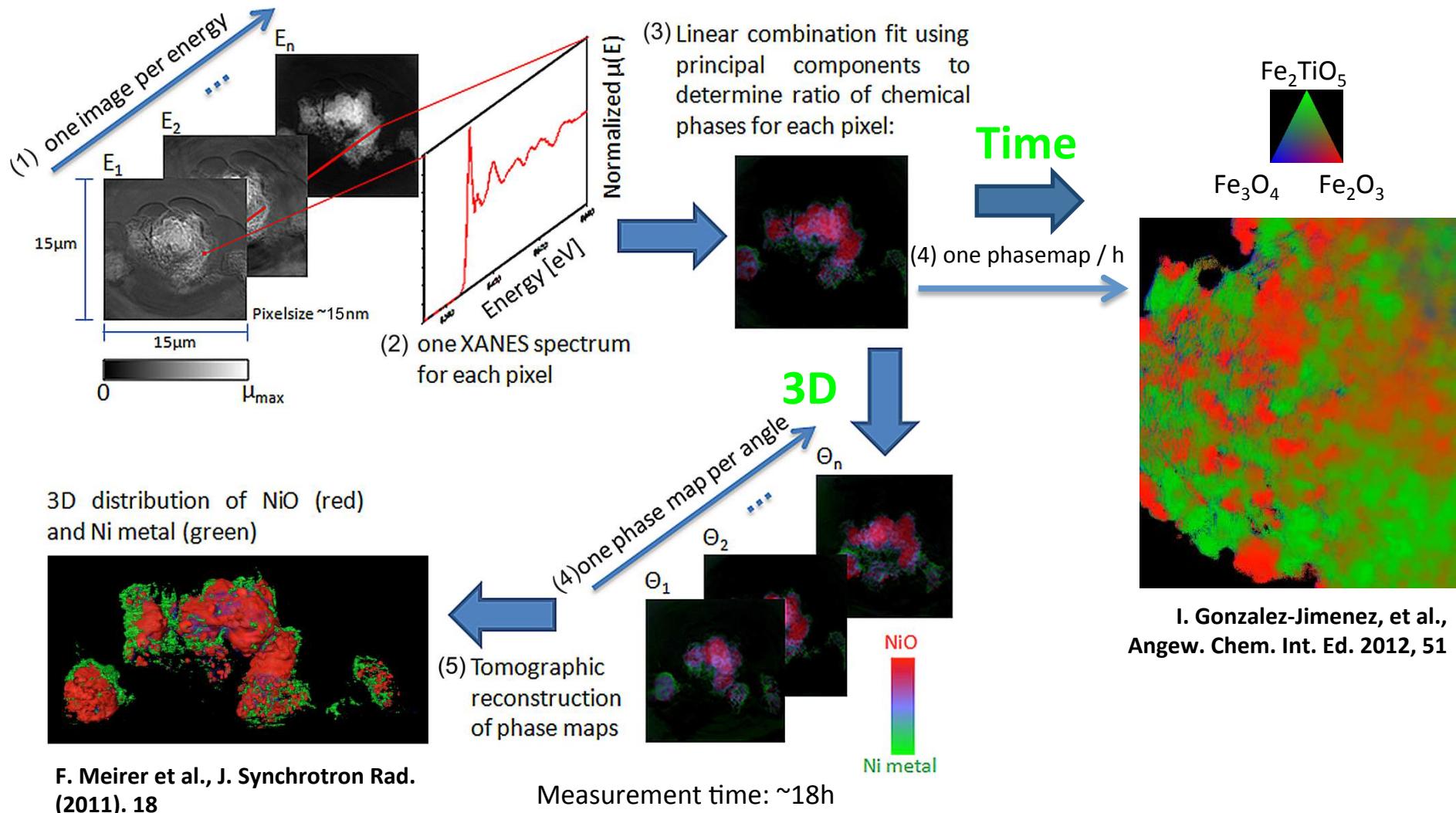


3D XANES imaging - Expansion in Space



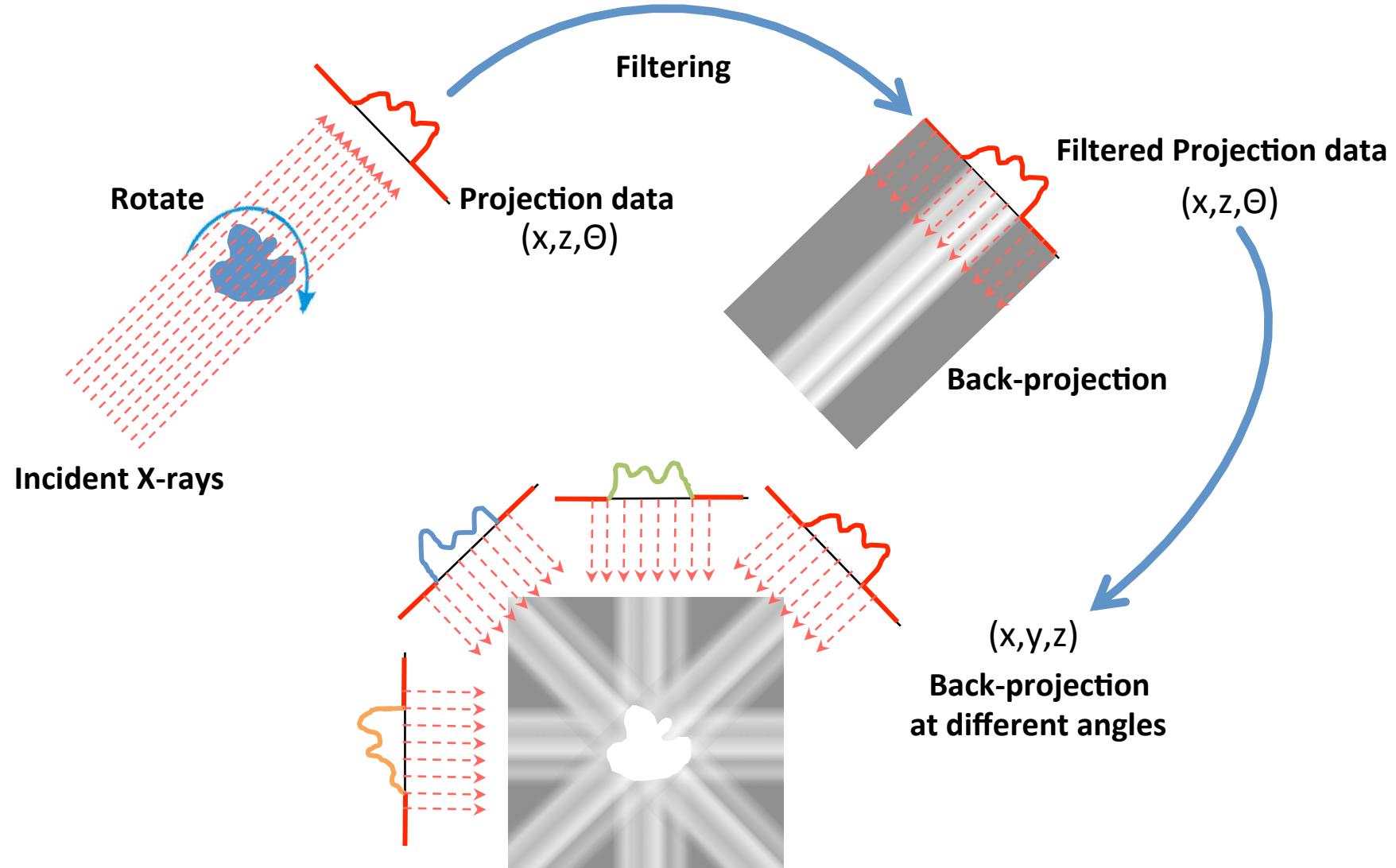


XANES imaging - Expansion in Space and Time



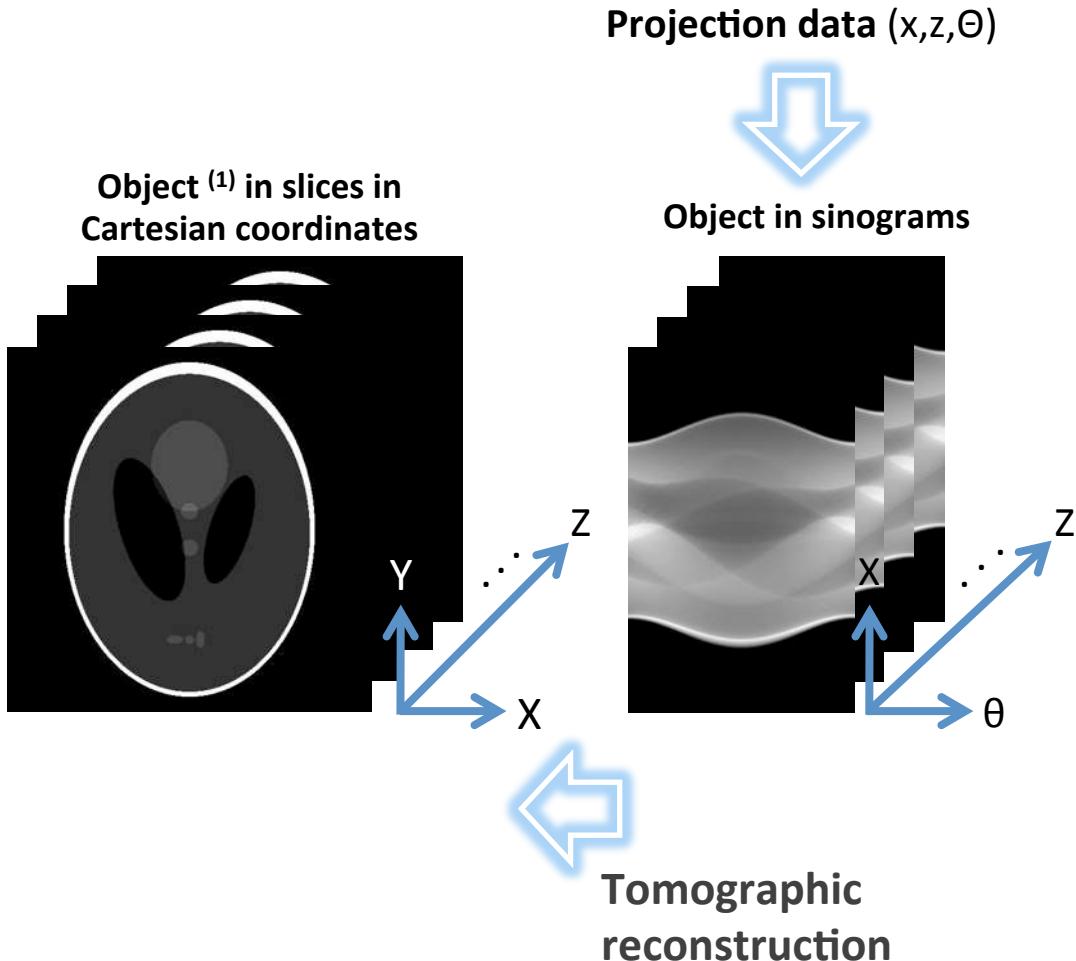


X-ray Tomography





X-ray Tomography



- **Analytical algorithms**
 - **Filtered Back Projection** (inverse Radon transform)
 - Fourier slice theorem based inverse Radon transform (in frequency domain)
- **Iterative algorithms**
 - Algebraic reconstruction technique (ART)
 - Simultaneous iterative reconstruction technique (SIRT)
 - Simultaneous algebraic reconstruction technique (SART)
 - Maximum likelihood with expectation maximization (MLEM)
 - Expectation maximization (EM)
 -

(1) Depicted is the so called 'Shepp–Logan phantom', a standard test image created by Larry Shepp and Benjamin F. Logan (*The Fourier reconstruction of a head section*, IEEE Transactions on Nuclear Science, (1974), Vol 21, 3, pp 21-43). It serves as the model of a human head in the development and testing of image reconstruction algorithms.



X-ray Tomography

Why tomography?



- **Tomographic reconstruction** converts the projection data collected at multiple viewing angles into a **3D density distribution** in Cartesian coordinates.
- This provides **full structural information** of a certain object in a 3D coordinate system.
- A simple 2D projection image can be misleading in many cases.

The word **tomography** means "*a picture of a plane*".
(i.e. the plane in focus in the projection image)

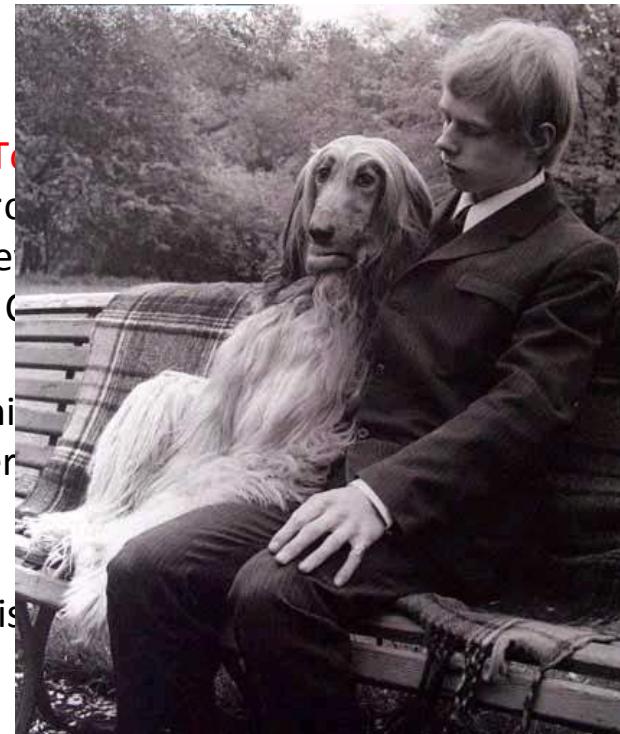


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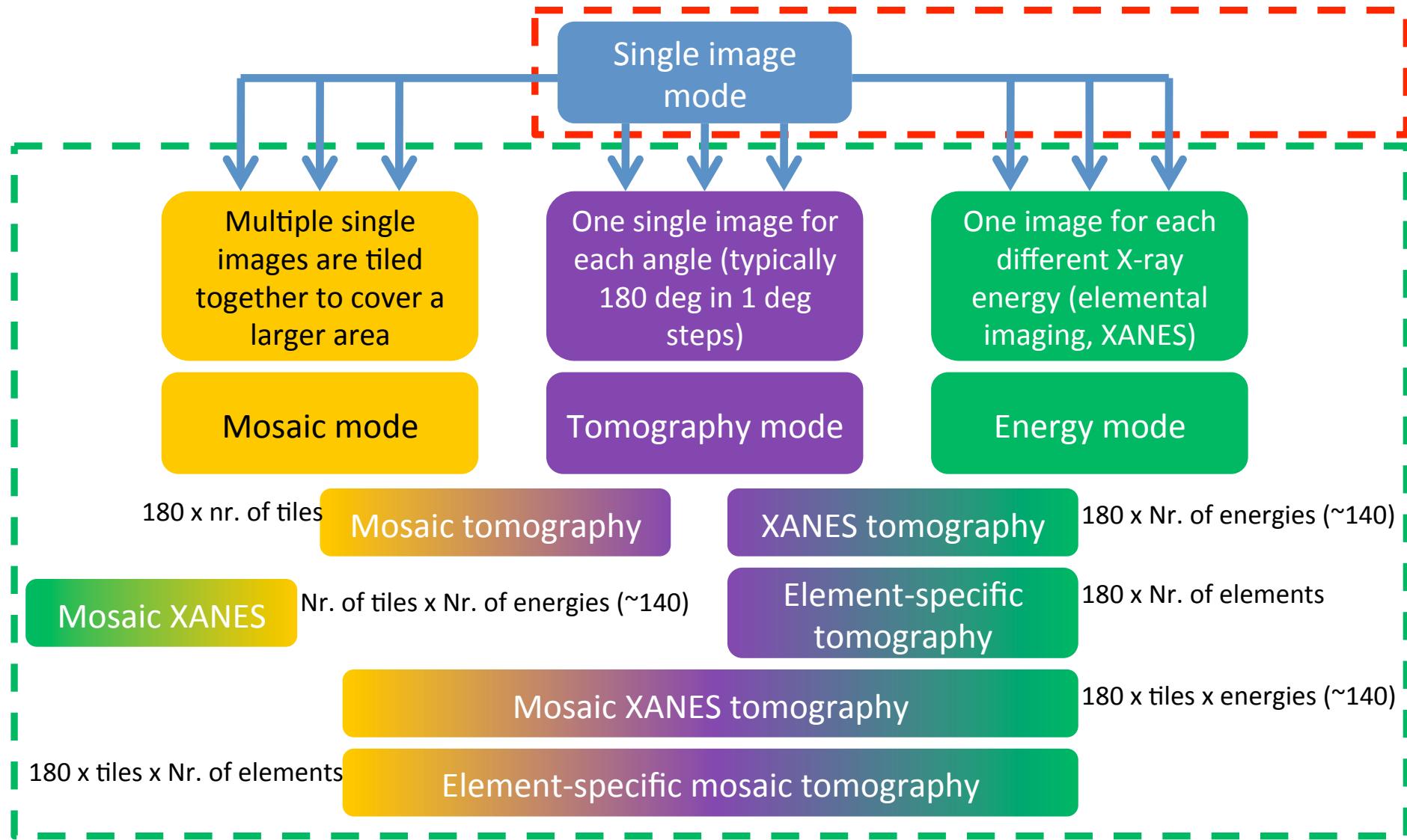
- Tomography is the process of viewing an object in cross-section.
- This can be done in a certain direction.
- A single plane can be imaged.



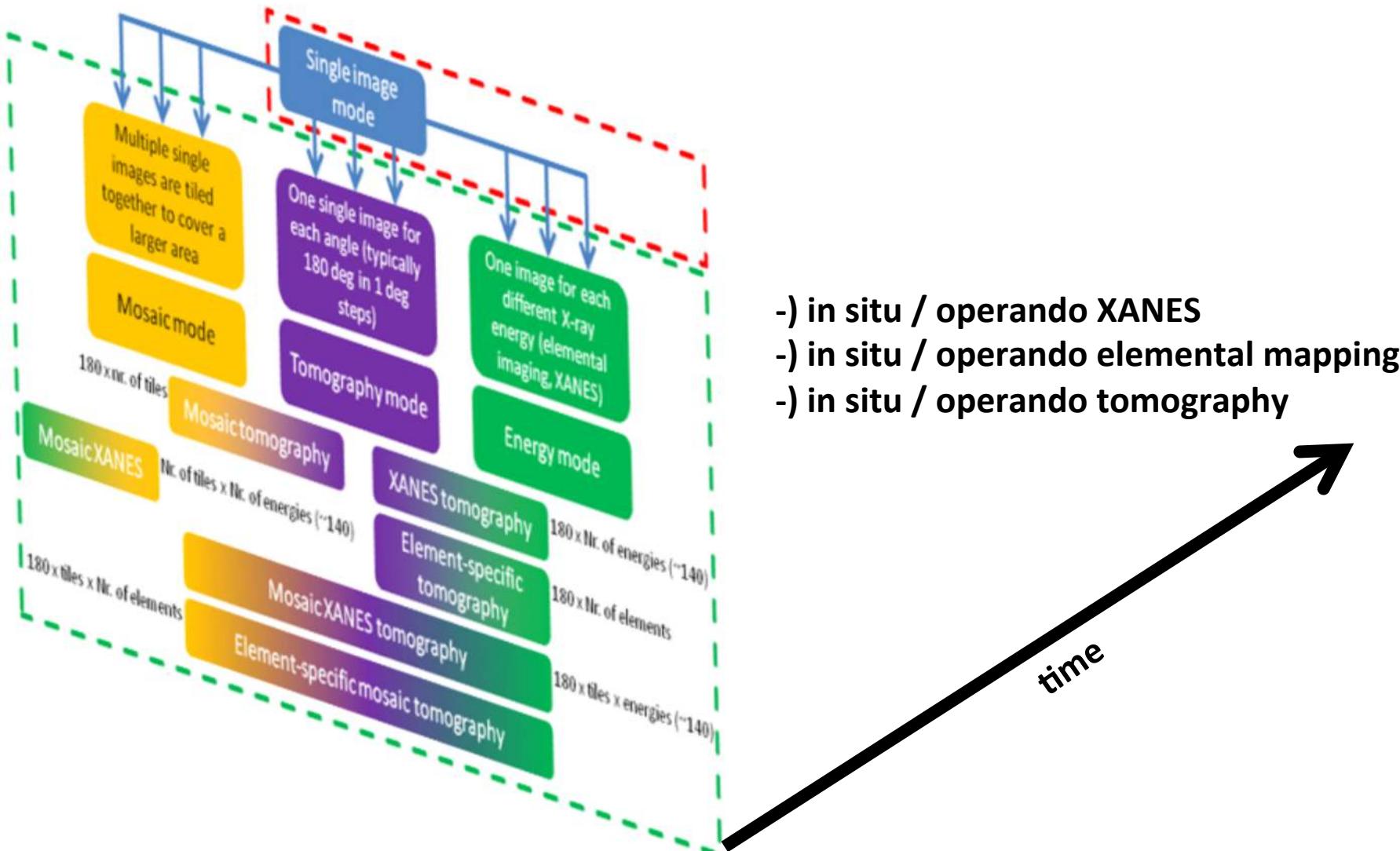
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Summary - 2D and 3D imaging



Adding another dimension – in situ and operando imaging





Expansion in time – in-situ and operando imaging

in situ

(latin for *on site*)

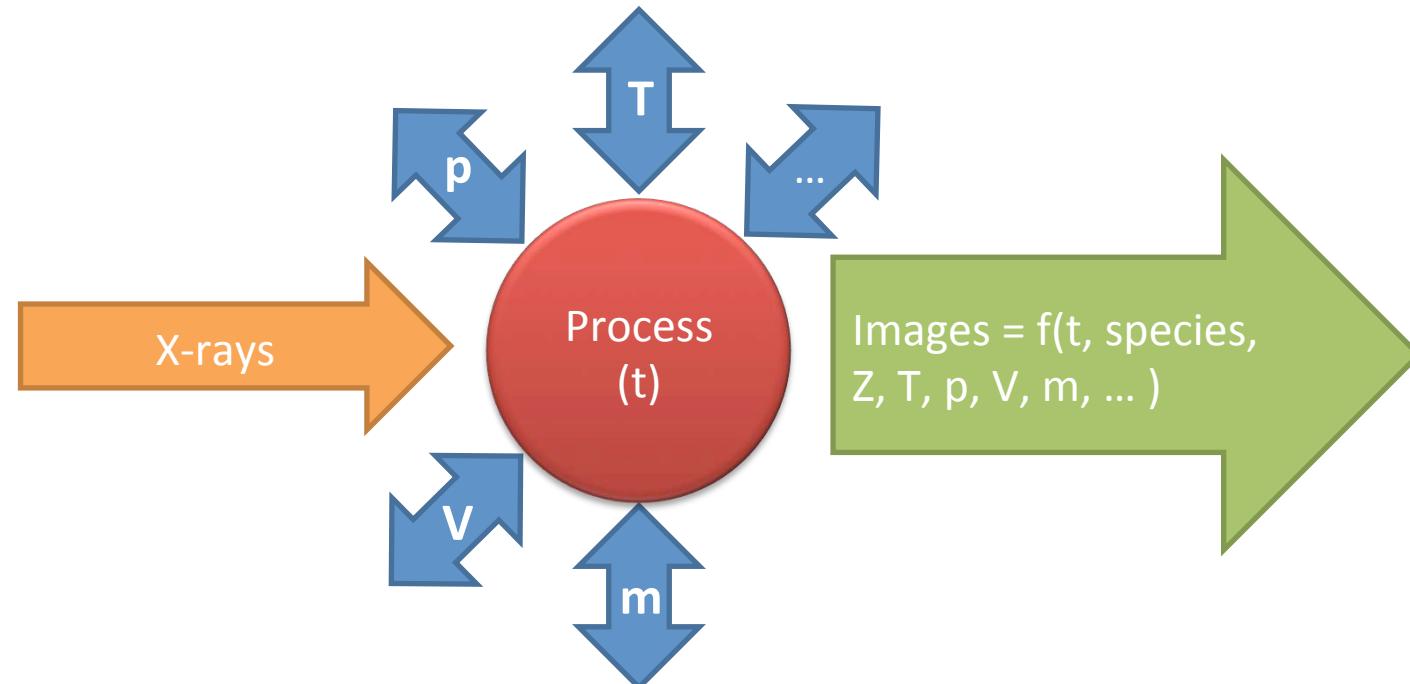
describe an event where it takes place
in chemistry: *in the reaction mixture*

in spectroscopy: measuring under operating conditions (operando?)

operando

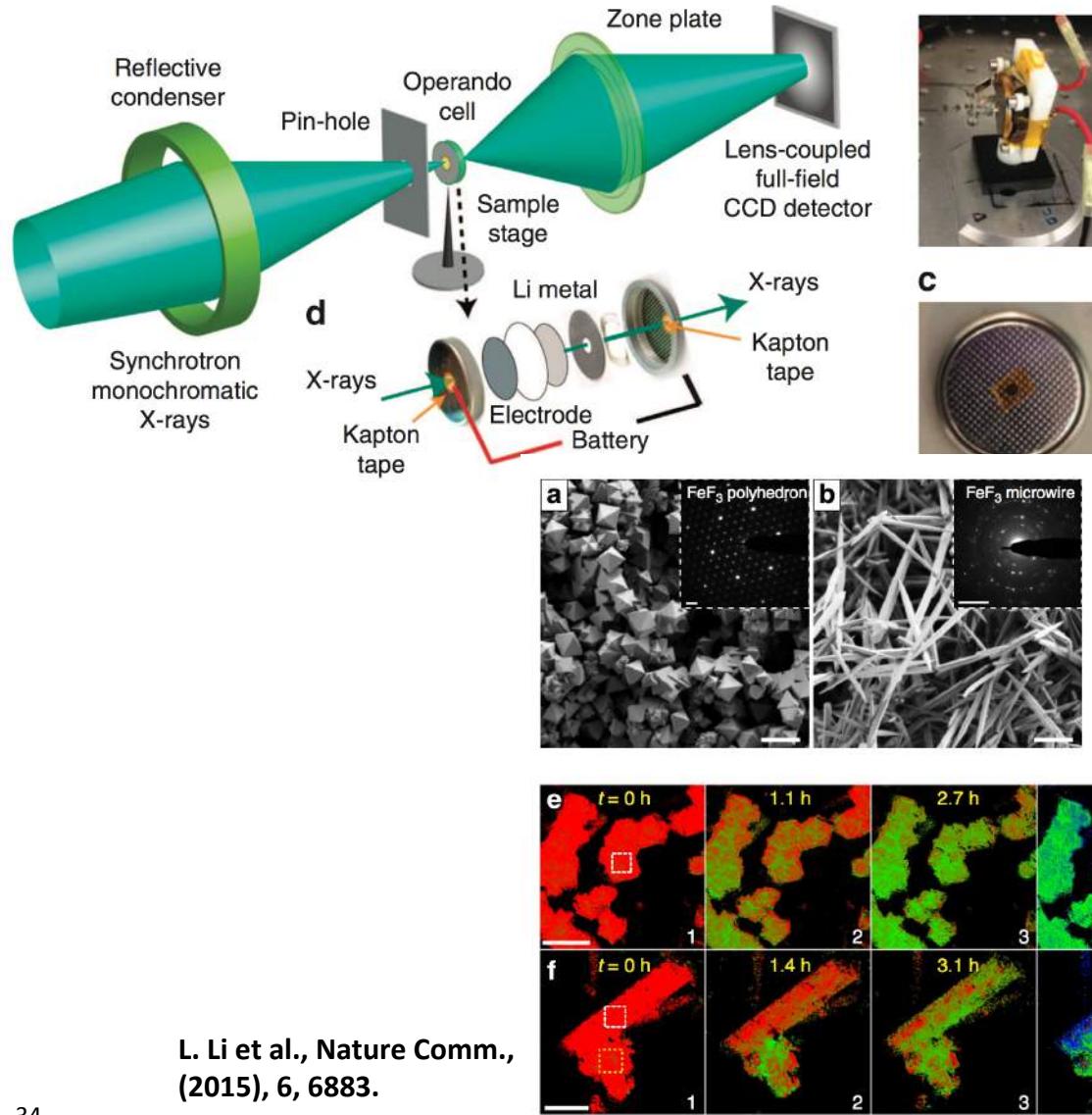
(latin for *working/operating*)

real-time measurement of a catalytic
process



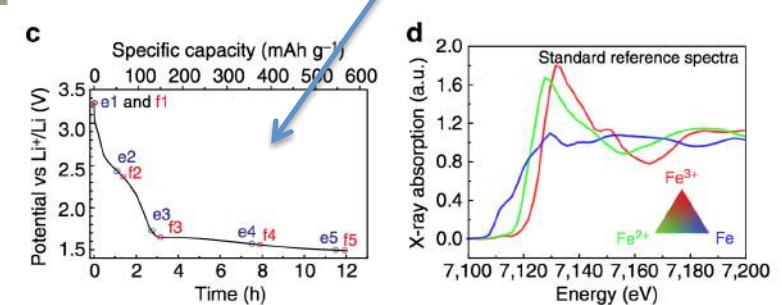
Expansion in time – in-situ and operando imaging

Operando visualization of Iron(III) fluoride electrochemical reaction

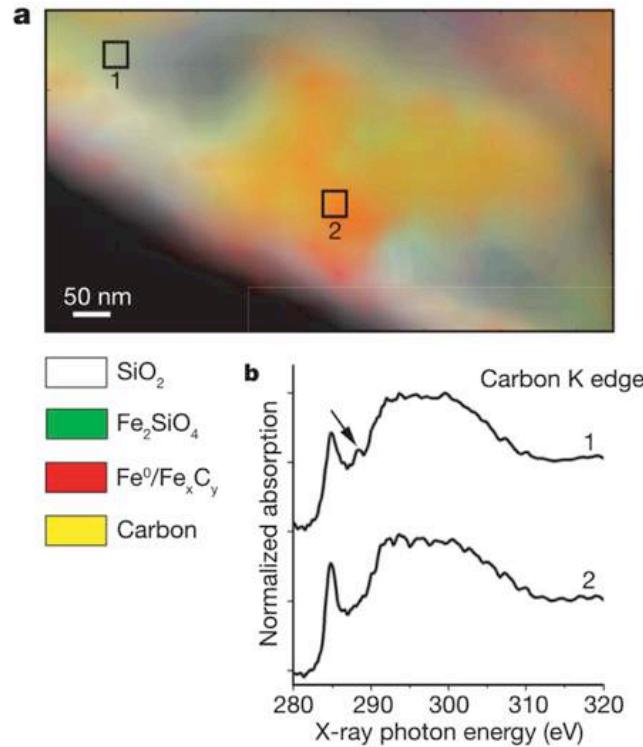


X-rays transmit through a perforated 2032-type coin-cell containing the FeF_3 cathode and all the other key components of a realistic battery, such as carbon black, polymeric binder and a liquid electrolyte.

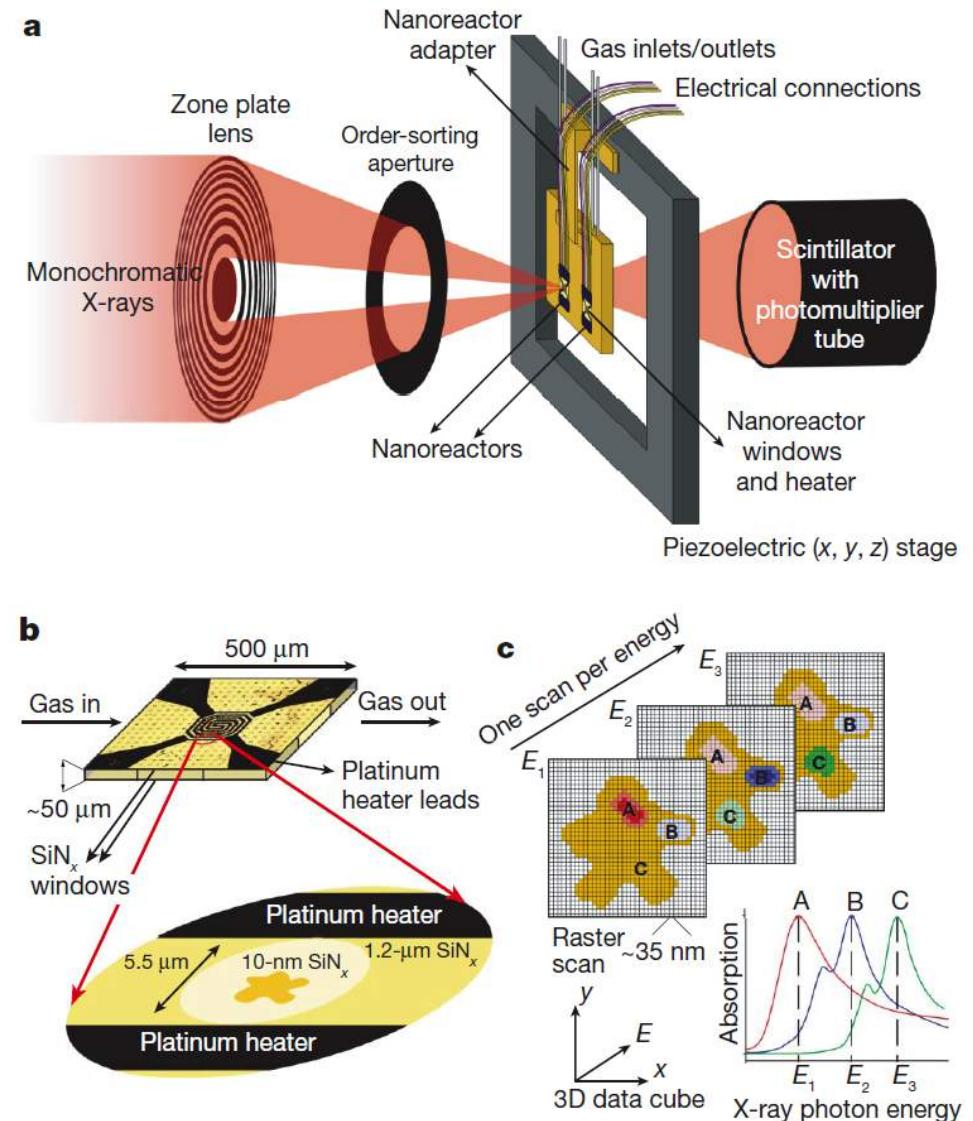
Discharge voltage profile



Expansion in time – in-situ and operando imaging



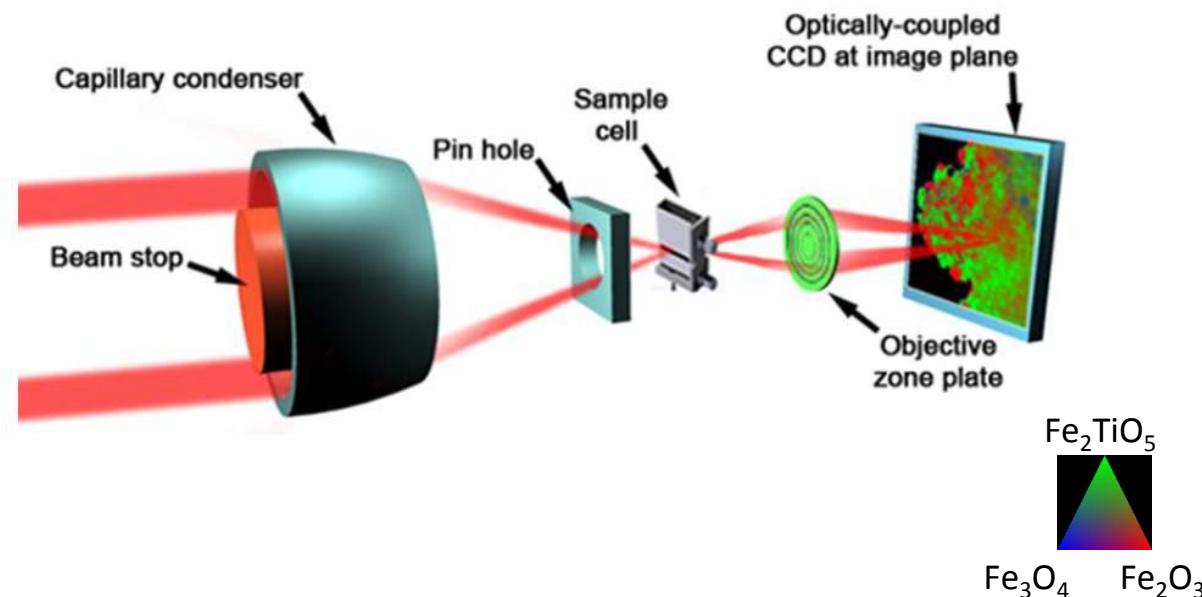
Adapting a nanoreactor (designed for high-resolution electron microscopy) for scanning transmission X-ray microscopy.
It can be used at **atmospheric pressure and up to 350°C** to monitor in situ phase changes in a complex iron-based Fisher-Tropsch catalyst and the nature and location of carbon species produced.



E. de Smit, et al., Nature, (2008), 456.

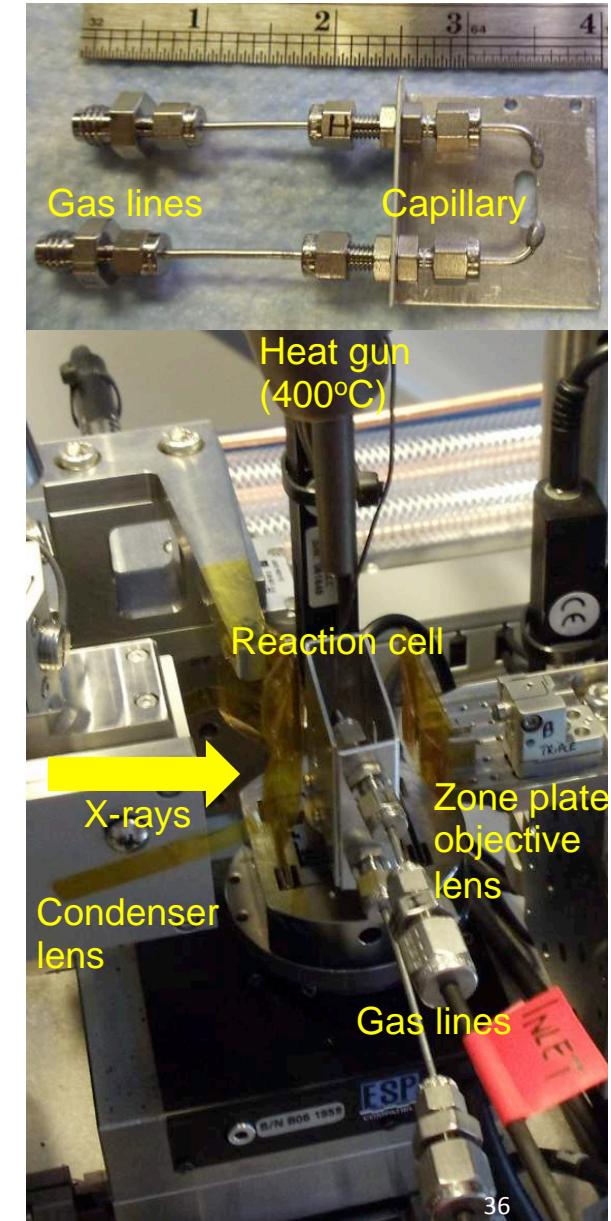


Expansion in time – in-situ and operando imaging



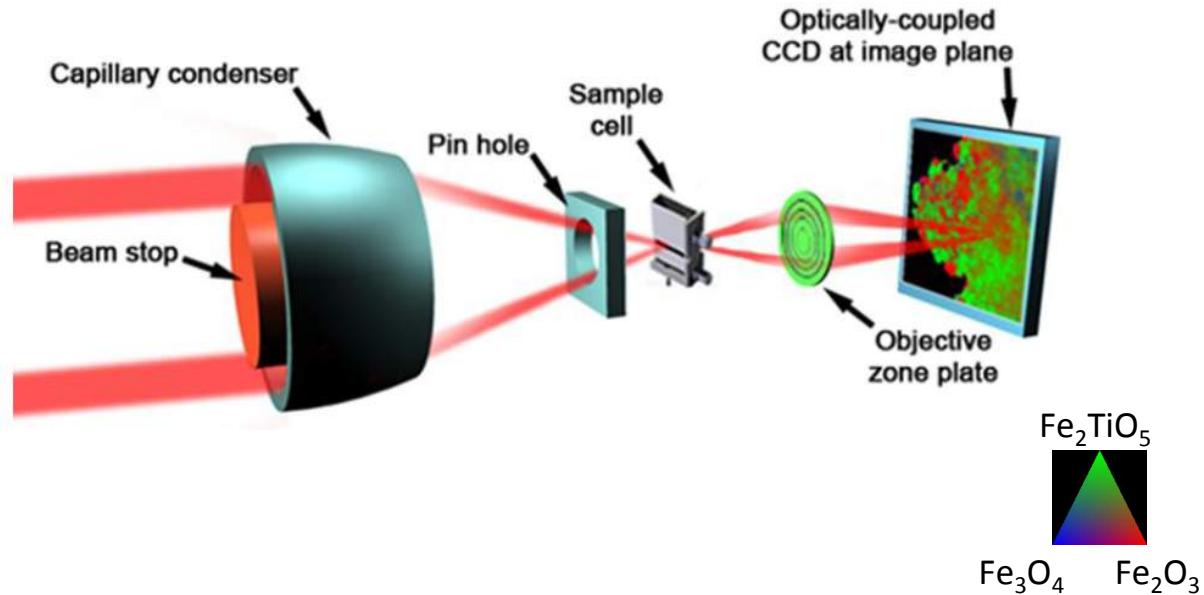
Fischer-Tropsch-to-Olefins (FTO) synthesis:

Studying the dynamic character in the catalytically active phases under **realistic reaction conditions**, i.e. high temperatures (350°C) and pressures (10bar).



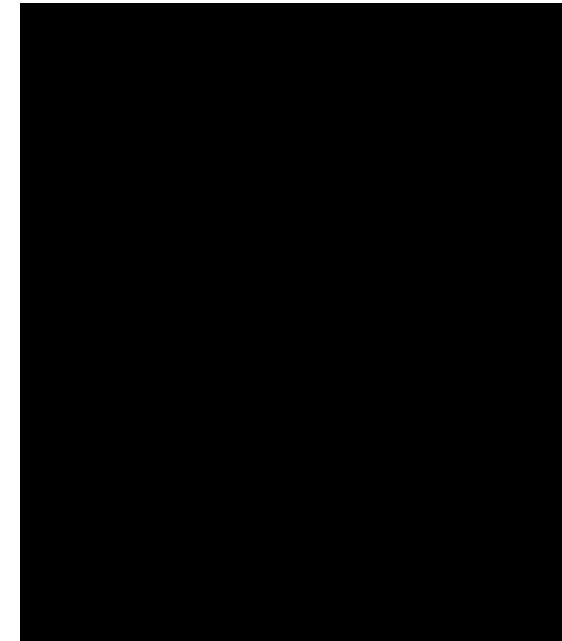


Expansion in time – in-situ and operando imaging



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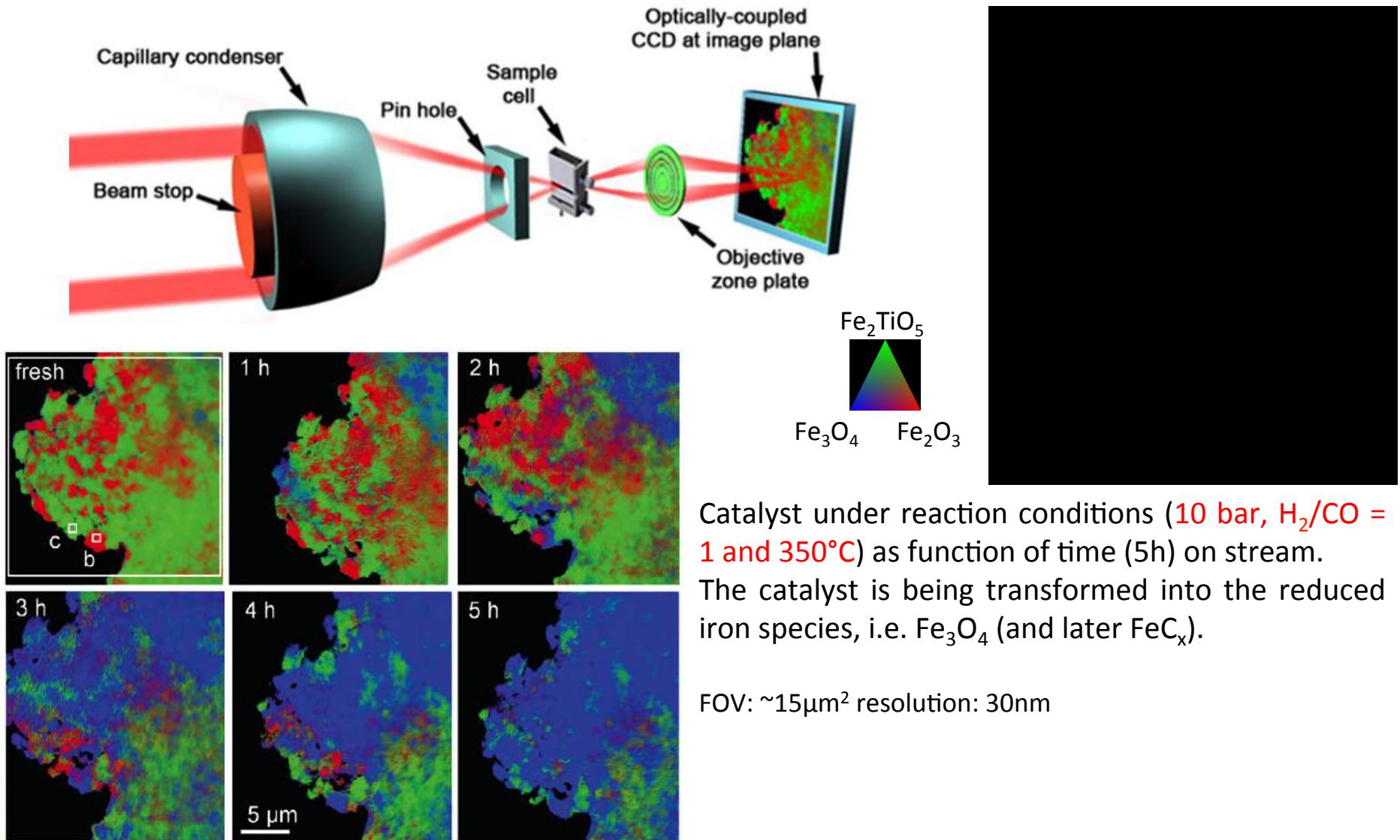


Catalyst under reaction conditions (**10 bar, H₂/CO = 1 and 350°C**) as function of time (5h) on stream. The catalyst is being transformed into the reduced iron species, i.e. Fe₃O₄ (and later FeC_x).

FOV: ~15μm² resolution: 30nm



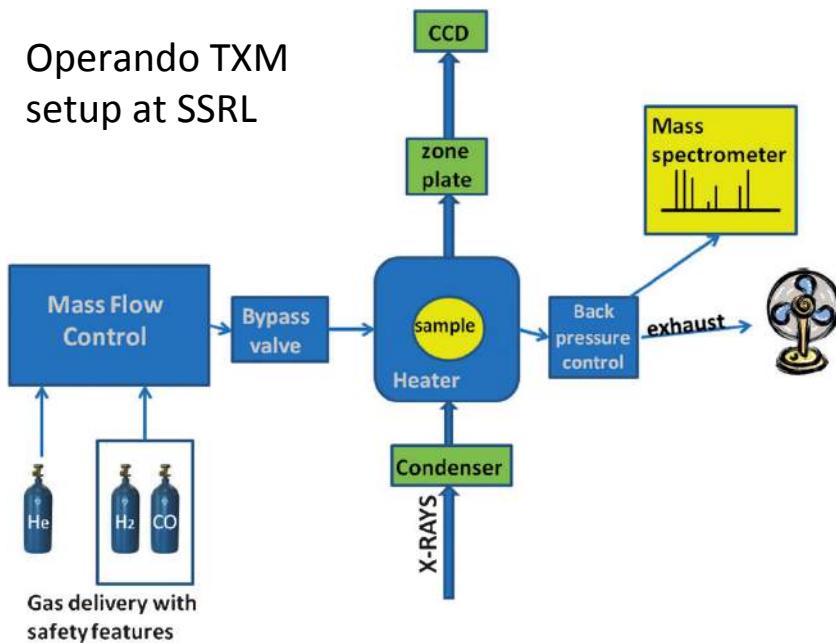
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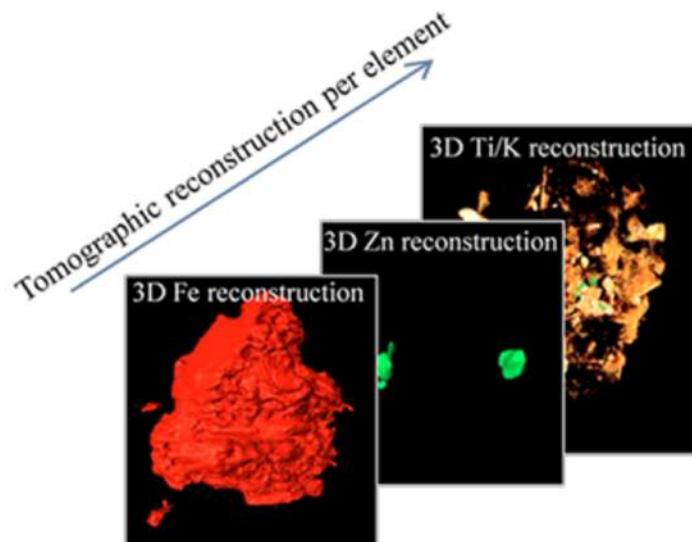
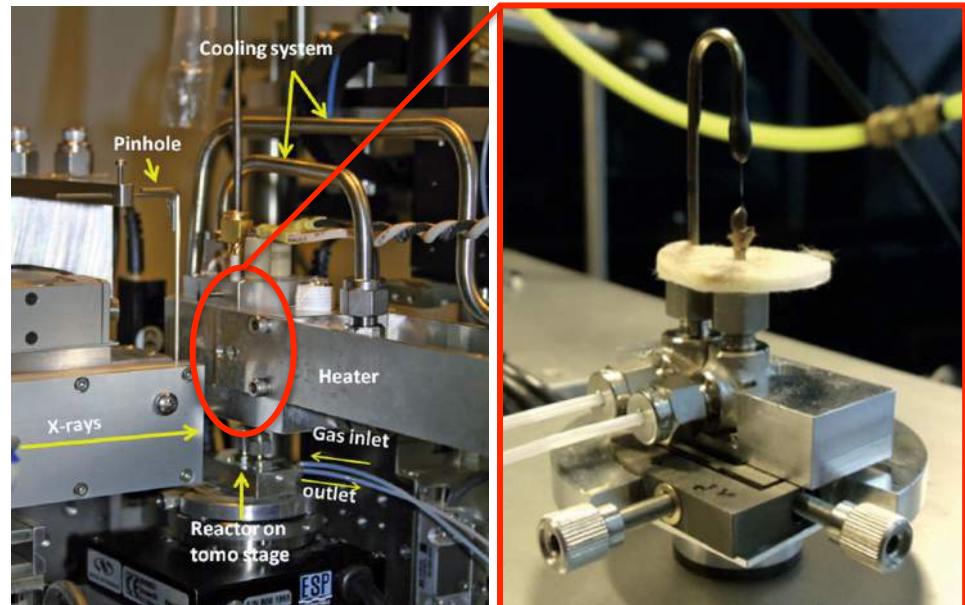


Expansion in time – in-situ and operando imaging

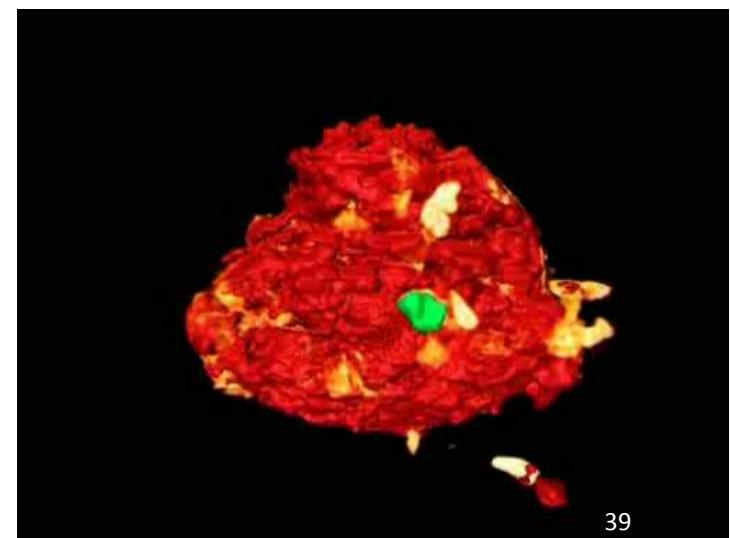
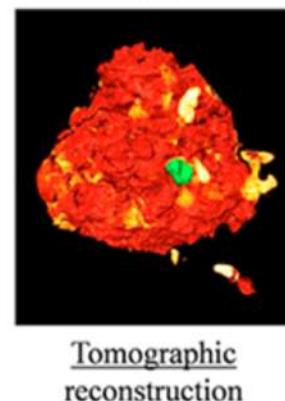
Operando TXM
setup at SSRL

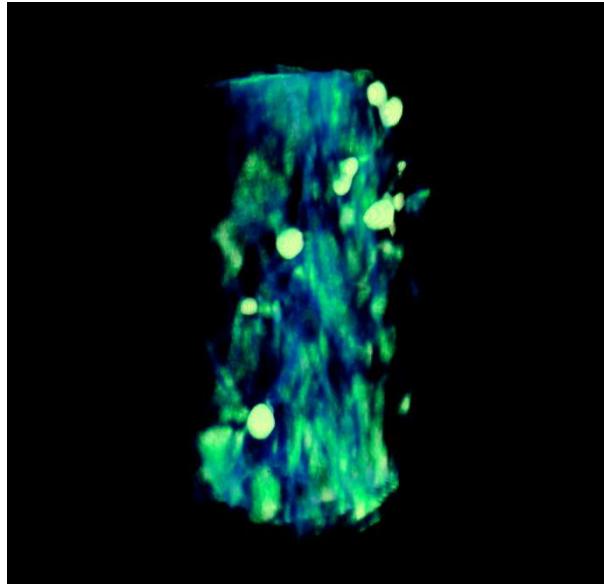


J.C. Andrews, B.M. Weckhuysen, ChemPhysChem, (2013), 14, 3655-3666

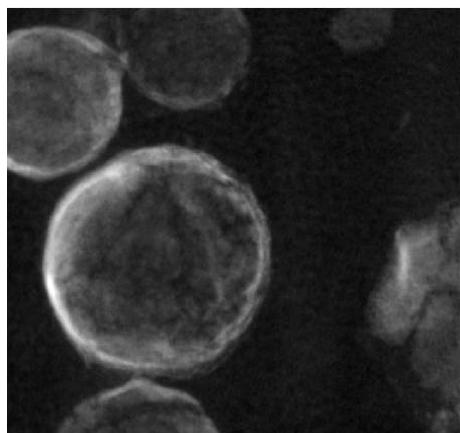


I. Gonzalez-Jimenez, et al.,
Angew. Chem. Int. Ed. (2012), 51.

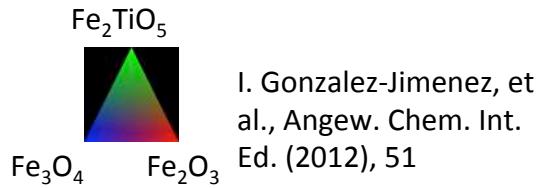




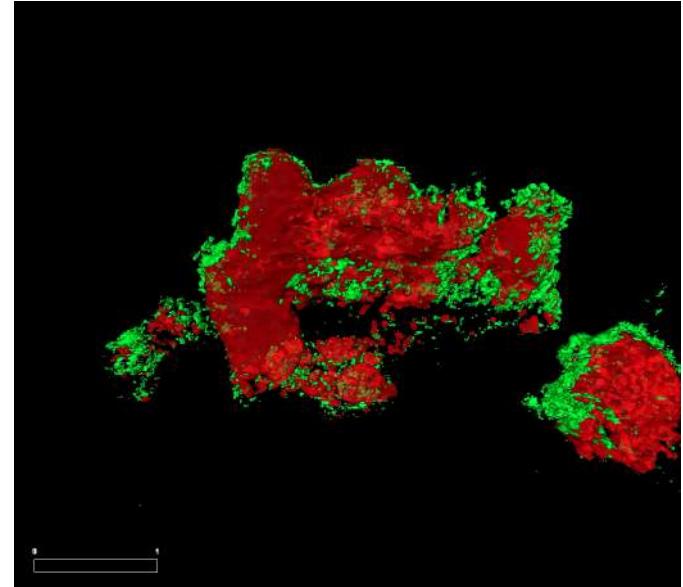
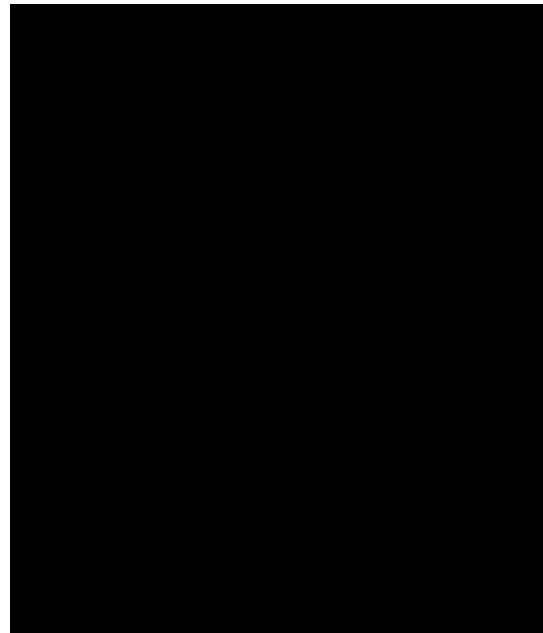
TXM tomography (SSRL beamline 6-2c);
"Snapshot" of Hg methylation in the
rhizosphere of *S. foliosa*? FOV: $30\mu\text{m}^2$,
 30nm^2 2D resolution
C. Patty, et al., Environ Sci Technol. (2009);
43(19): 7397–7402.



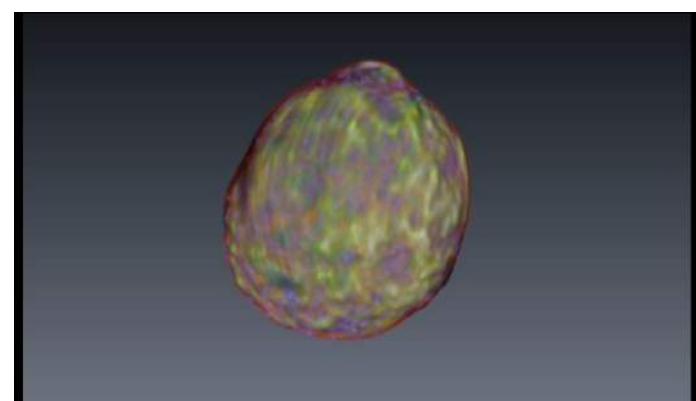
Left: exploding NiO particles
in operated Li-ion battery
electrode. FOV: $\sim 15\mu\text{m}^2$, 2D
resolution: 30nm^2



I. Gonzalez-Jimenez, et
al., Angew. Chem. Int.
Ed. (2012), 51



XANES tomography of Li-ion battery electrode
material (SSRL, TXM at BL6-2c)
F. Meirer et al., J. Synchrotron Rad. (2011), 18.



μXRF tomography (P06, PETRA III, Hamburg
Germany) of a single catalyst particle (FCC)