Anthropogenic and natural nanoparticles in the environment – dynamics and interaction

J. Thieme[1], J. Sedlmair[2], S.-C. Gleber[2], J. Rieger[3], J. Niemeyer[4], J. Coates[5]

[1]Brookhaven National Laboratory, NSLS-II,USA
[2]Institute for X-Ray Physics, University of Goettingen, Germany
[3]Harvard University, USA and BASF Ludwigshafen, Germany
[4]Department of Economic Plant Sciences, University of Goettingen, Germany
[5]University of California Berkeley, USA

U.S. DEPARTMENT OF ENERGY

BROOKHAVEN NATIONAL LABORATORY
BROOKHAVEN SCIENCE ASSOCIATES

Outline

- Nanoparticles in the environment
- Basics of X-ray spectromicroscopy
- X-ray spectromicroscopy of Nanoparticles
  - Imaging
  - Tomography
  - Elemental mapping
  - Spectromicroscopy

Studies performed at
ALS, Berkeley, USA (XM-1, Peter Fischer)
BESSY, Berlin, Germany (U41TXM, Peter Guttmann, U41STXM, self)
ELETTRA, Trieste, Italy (TwinMic, Burkhards Kaulich)
NSLS, Brookhaven, USA (X1A, Sue Wirick)

Looking into the Nanoworld using X-rays

Definition of Nanoparticles:

At least one dimension is below 100 nm in size

1D Nanofilms
2D Nanotubes
3D Nanoparticles

Most of the nanoparticles have sizes in the few nm – range.

Definition of Colloids:

At least one dimension is in the range of 1nm to 1 μm in size

Nanoparticles are a sub-class of Colloids.

Nanoparticles in the environment

Natural nanoparticles

organic: humic substances, coal, bacteria, fungi
inorganic: silicates, oxides, carbonates, metal sulfides

Anthropogenically introduced nanoparticles

organic: CNT, soot, fly ash
inorganic: TiO_2, SiO_2, ZnO

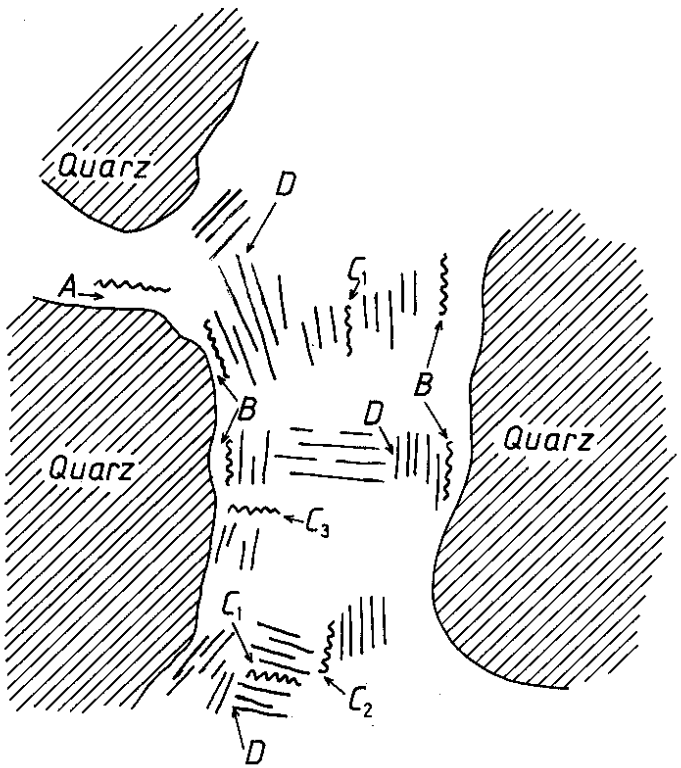
Effects:

Uptake by plants via roots
Adsorption to other particles, transport, subsequent resuspension and remobilization possible => circulation

Toxicity:

Toxic effect of nanoparticle itself (e.g. asbestos)
Interaction with toxic compounds => storage and reduction of impact as well as amplification

Soil structure



A. Quarz — org. S. — Quarz B. Quarz — org. S. — Tonmineral
C. Tonmineral — org. S. — Tonmineral
(C_1: Fläche — Fläche, C_2: Kante — Fläche, C_3: Kante — Kante
D. Tonmineral — Tonmineral (Kante — Fläche)

- Oxides (large volume, small surface)
- Clay minerals (small volume, large surface)
- Organic substances (roots, bacteria, colloids, etc.)

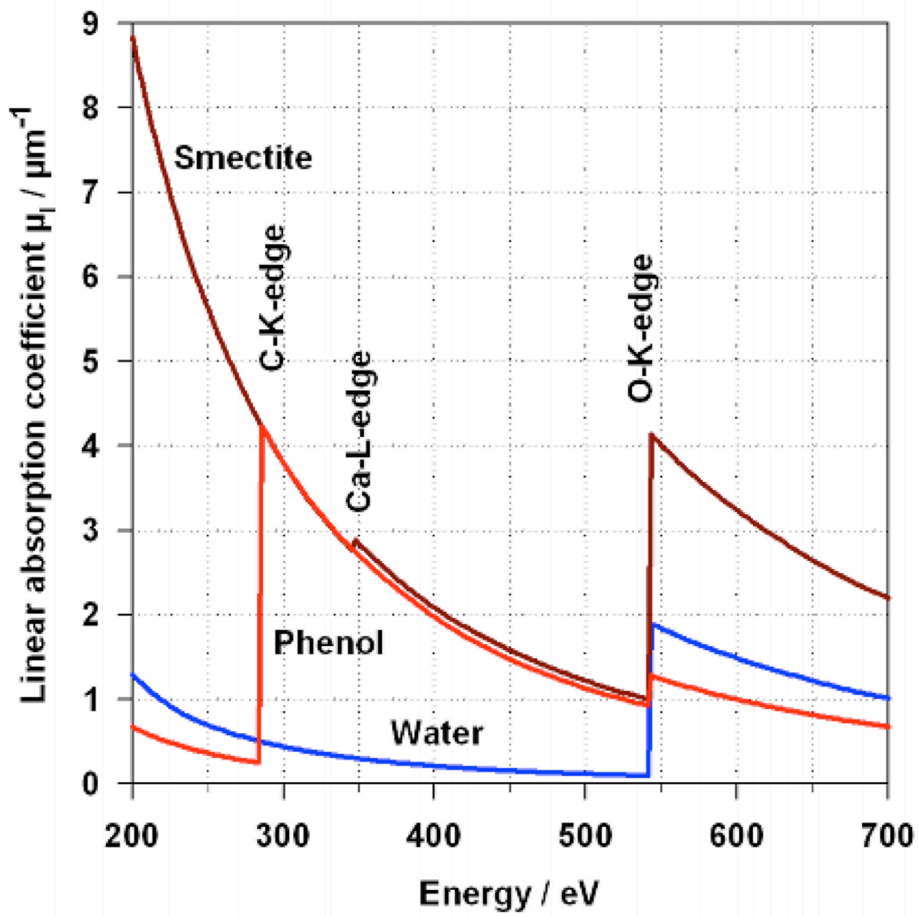
(Scheffer, Schachtschabel – Lehrbuch der Bodenkunde)

Contrast

"Water Window"
(H. Wolter: Spiegelsysteme streifenden Einfalls als abbildende Optiken für Röntgenstrahlen Ann. Phys. 6 (10), 94–114, 1952)

Between K-absorption edge
of
Oxygen @ 2.28 nm (543 eV)
and
Carbon @ 4.36 nm (284 eV)

⇒ no drying, fixation, or staining !



U.S. DEPARTMENT OF ENERGY

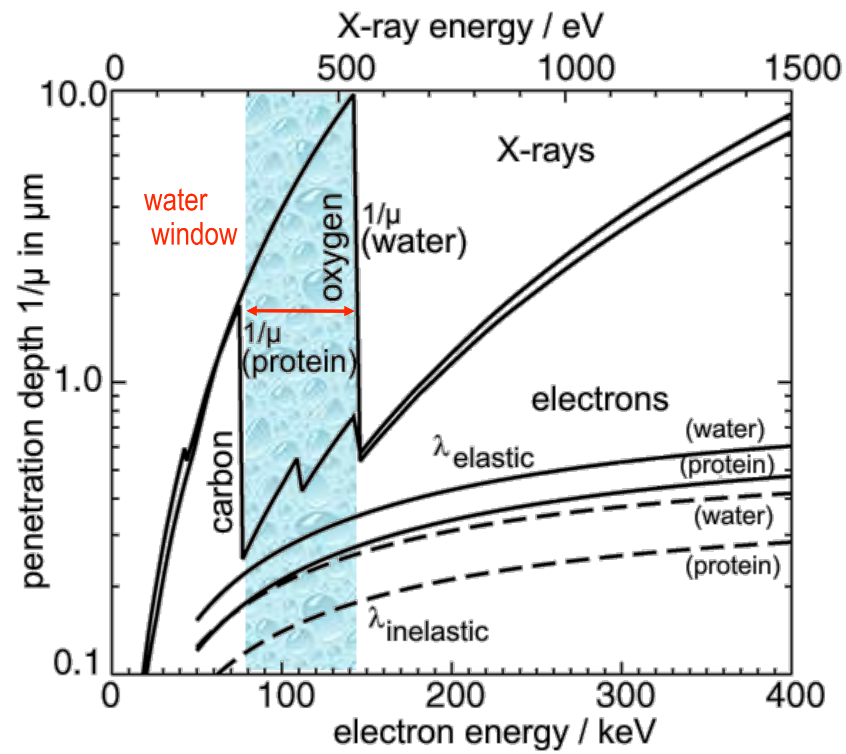
BROOKHAVEN NATIONAL LABORATORY
BROOKHAVEN SCIENCE ASSOCIATES

Some basics on X-ray microscopy

1. **Resolution**
   X-radiation: λ = 10 - 0.001 nm

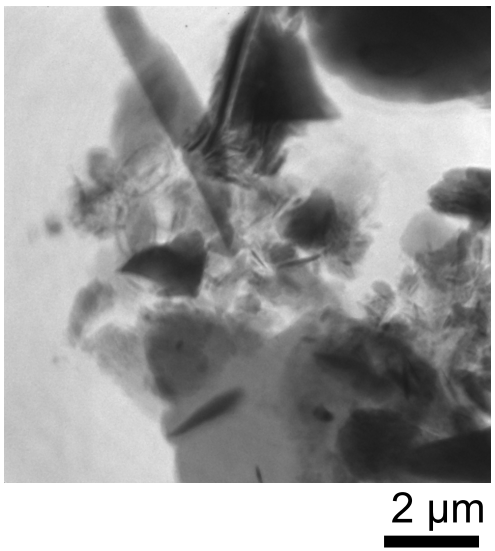
2. **Refractive index**
   $n = 1 - \delta - i\beta$ close to 1

3. **High penetration depth**
   sample thickness up to 10µm



4. **Chemical contrast + water window (284-543eV)**
   elemental mapping at absorption edges
   + additional information about binding forms via XANES
   ➔ **Spectromicroscopy**

Colloidal structures in soils and sediments



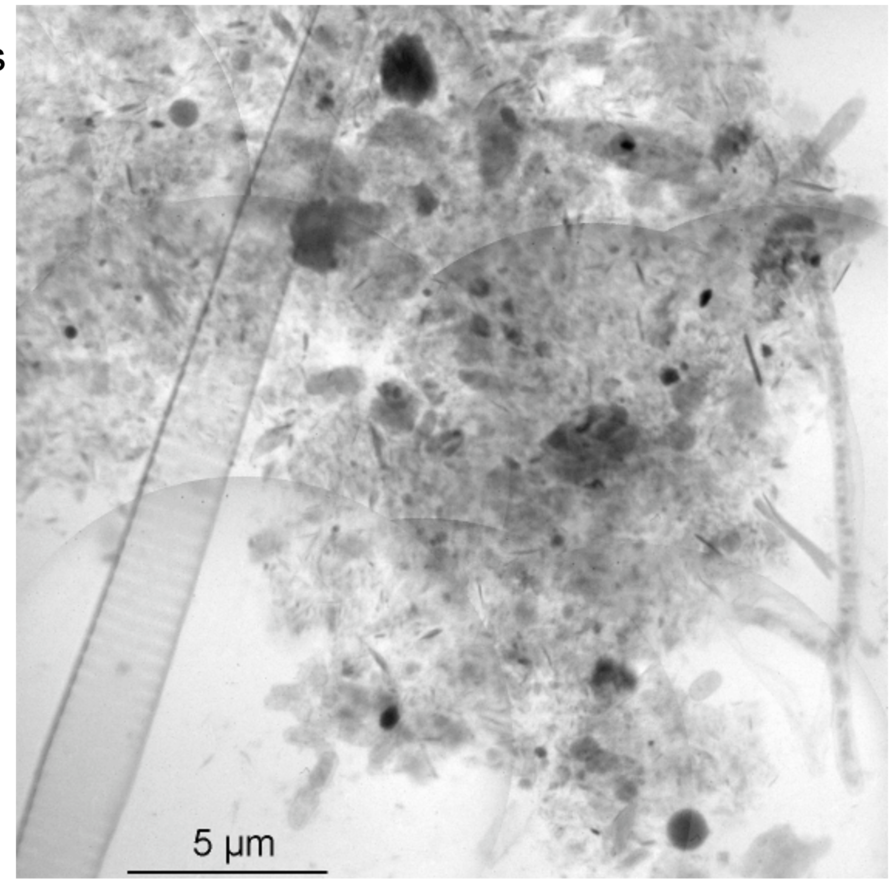
Soils and sediments in aqueous media

Images taken with **TXM @ BESSY II**

Resolution ≈ 25 nm

Soils: Luvisol
Gleysol

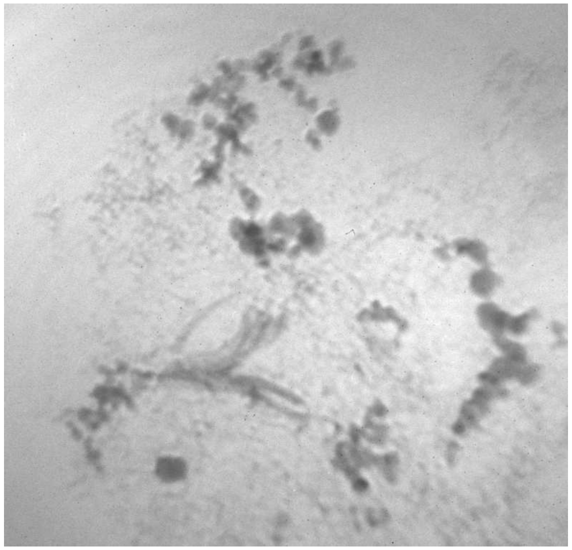
J.Thieme et al. (2007) Opt. Prec. Eng.



Harbor sediment, composed image

J.Thieme et al. (2010) J. Synchr. Rad.

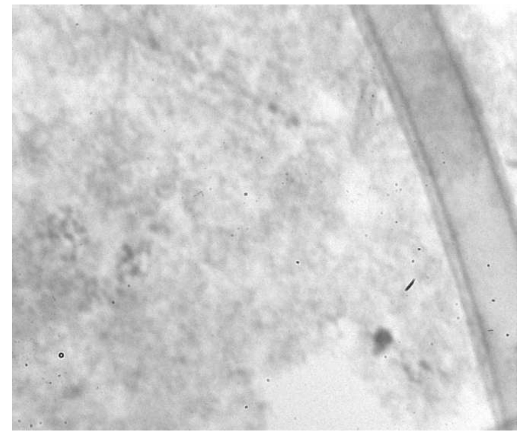
Microbial influence on recent mineralization

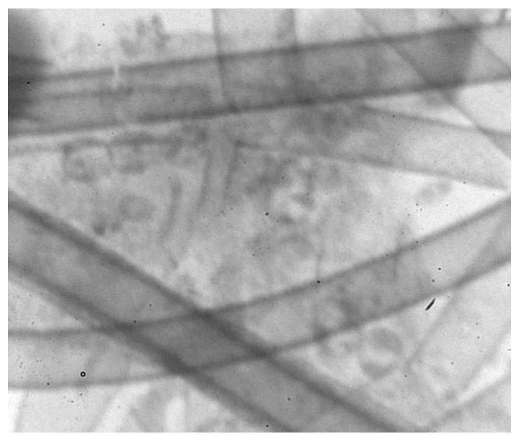


2 µm

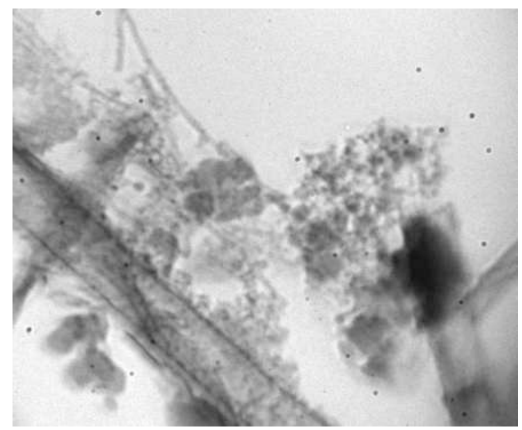
Rothschönberger Stolln

2 µm





2 µm



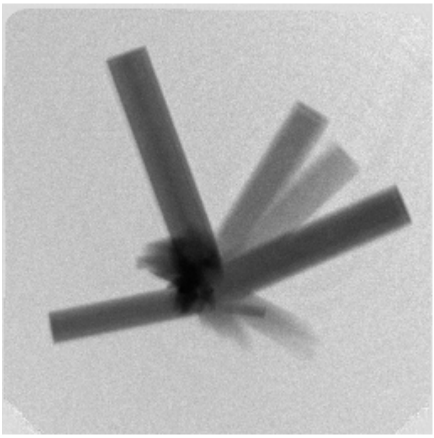
2 µm

Recent mineralization
in Ernst-August-Stollen,
Lauthental, Harz

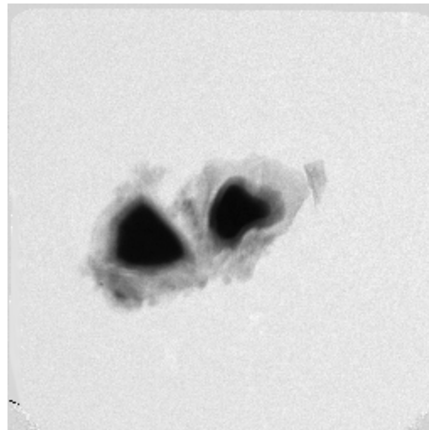
Identified Bacteria :
Gallionella ferruginea
Lepthotrix ochracea

S. Dietrich et al. (1993)
XRM IV

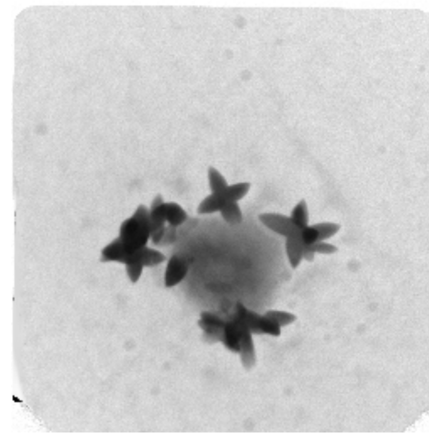
Cement phases



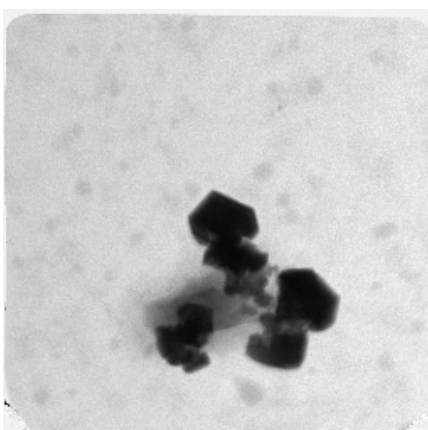
C_3A +pore solution

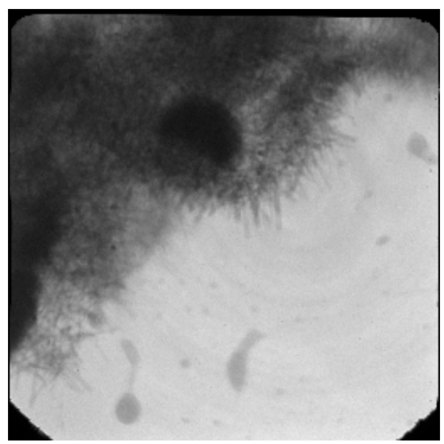


C_3S + pure H_2O



C_3S + polymer additive





All samples in aqueous media

Images taken with **TXM @ BESSY II**

Image 12 x 12 μm^2

Resolution ≈ 25 nm

U.S. DEPARTMENT OF ENERGY

C_3S +pore solution

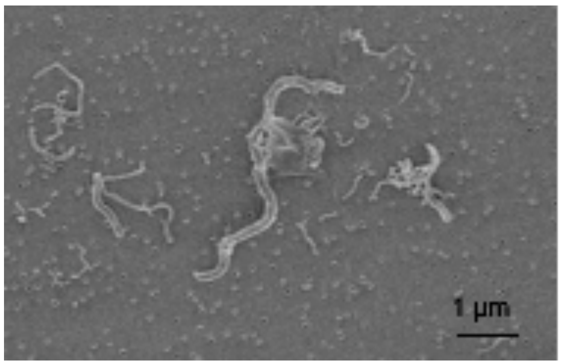
BROOKHAVEN NATIONAL LABORATORY
BROOKHAVEN SCIENCE ASSOCIATES

Carbon nanotubes (CNT)

Study structural and chemical properties of CNTs and their interaction with other molecules using x-ray spectromicroscopy

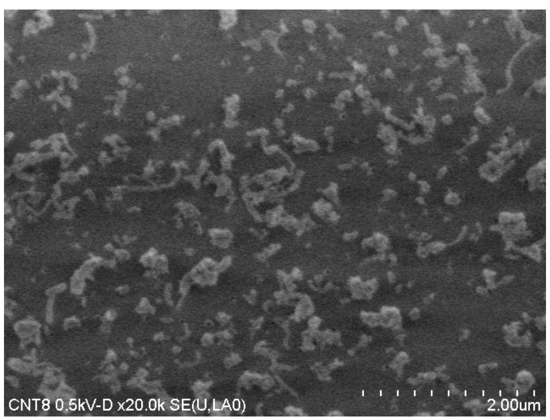
SEM

pristine CNTs



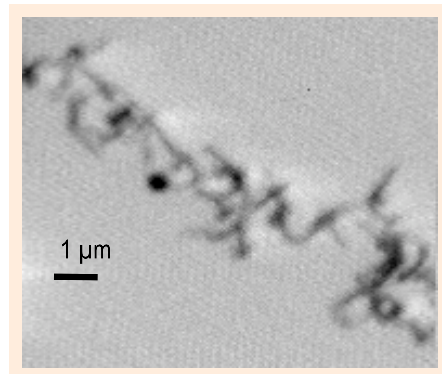
A Schierz et al., *Surf. Env. Pollut.*, 2008

CNTs + COOH -groups

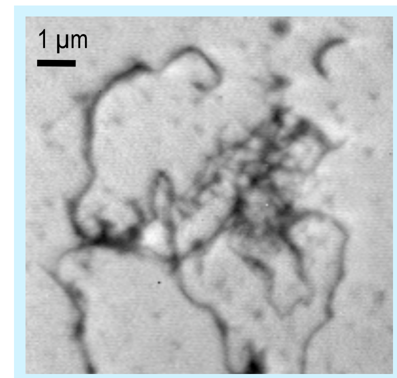


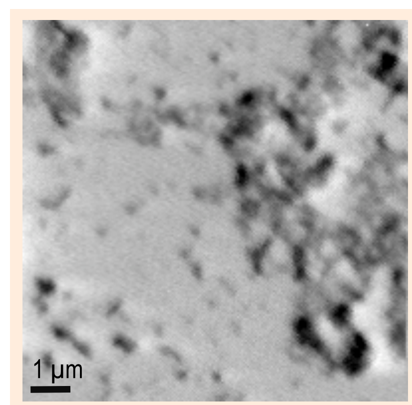
STXM

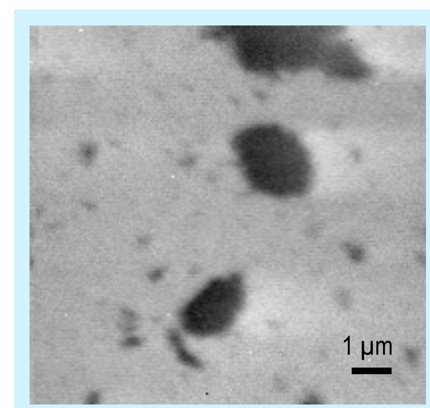
dry



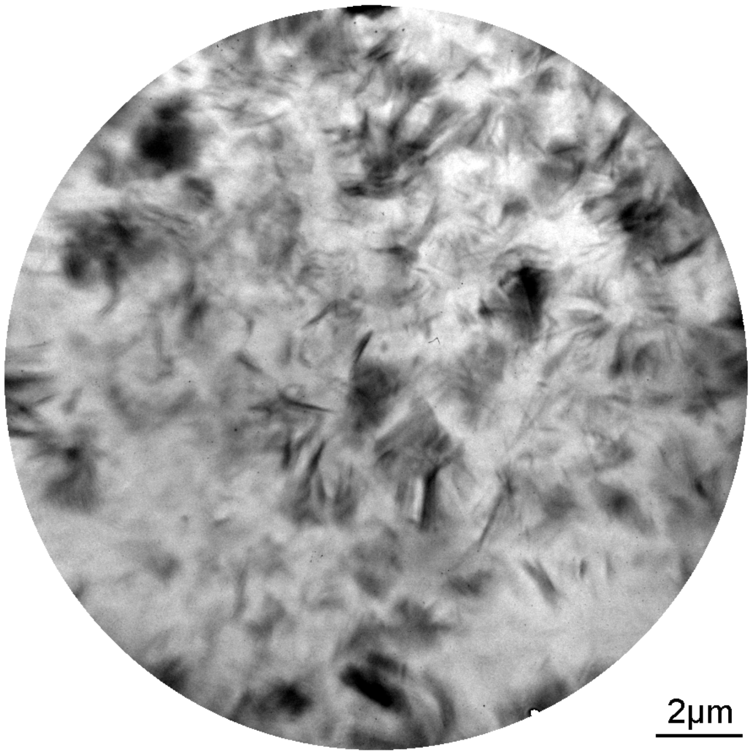
aqueous

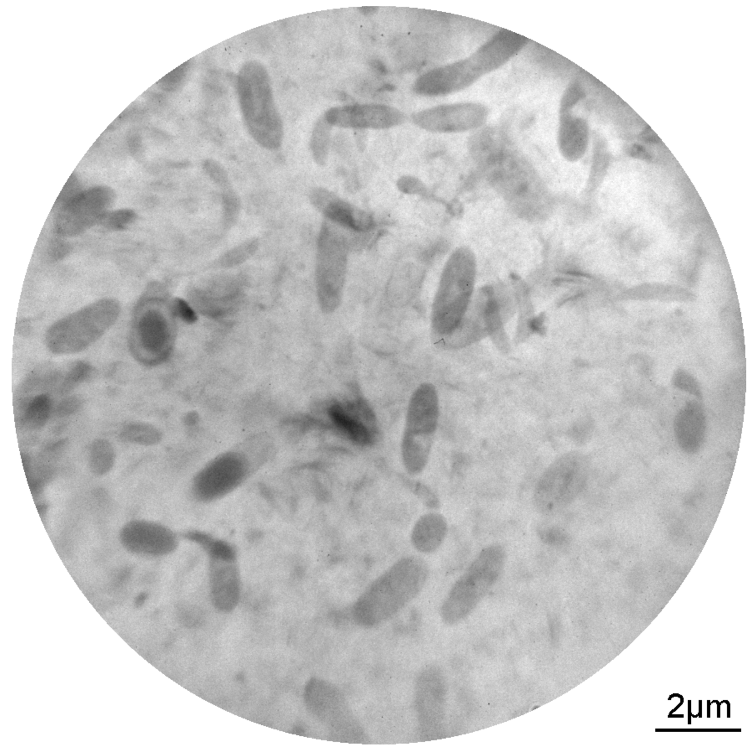






Bacteria and clay dispersion





Destruction of associations of clay particles by soil mícrobes

TXM at BESSY

G. Machulla et al. (1998)
XRM V, Springer

Interaction of soil colloids with cations

Evaluation of structure

by fractal dimension

Cations:

a) Ca^{2+}

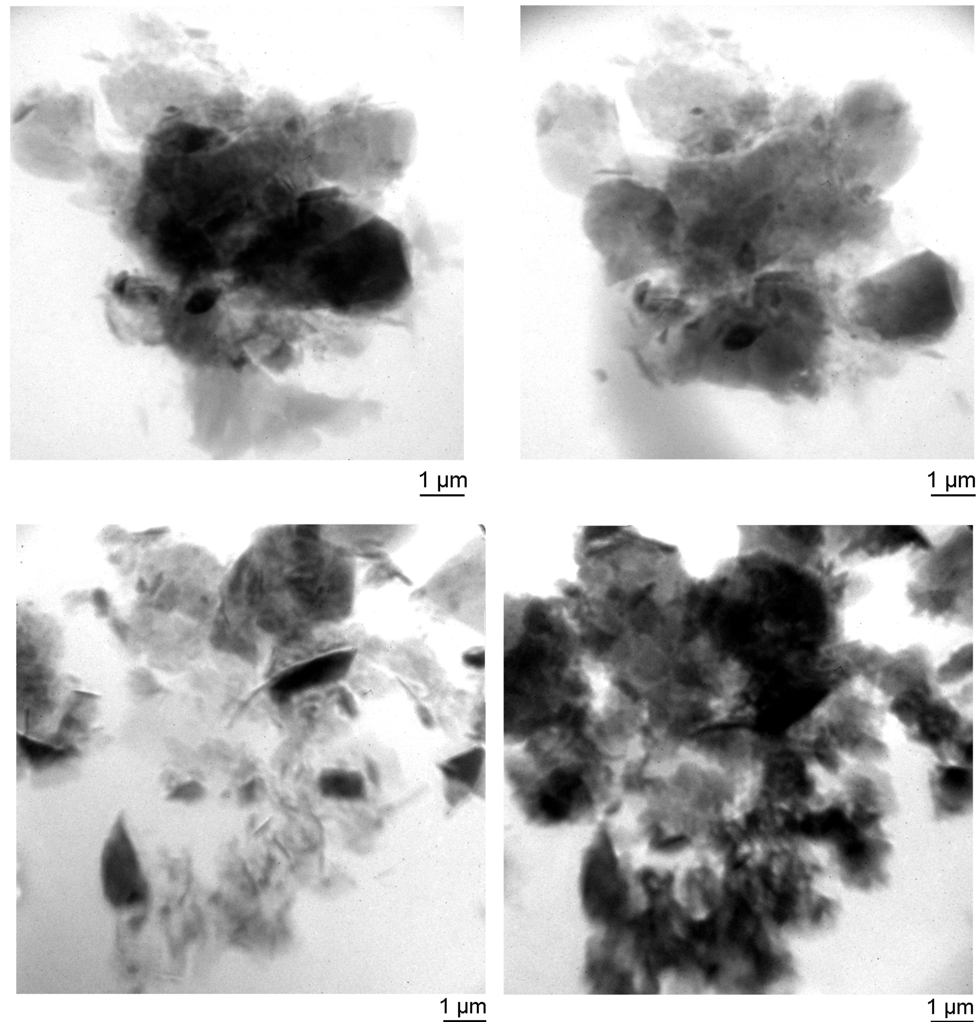
D_F : 1.73 ⇒ 1.70

b) Fe^{3+}

D_F : 1.75 ⇒ 1.81

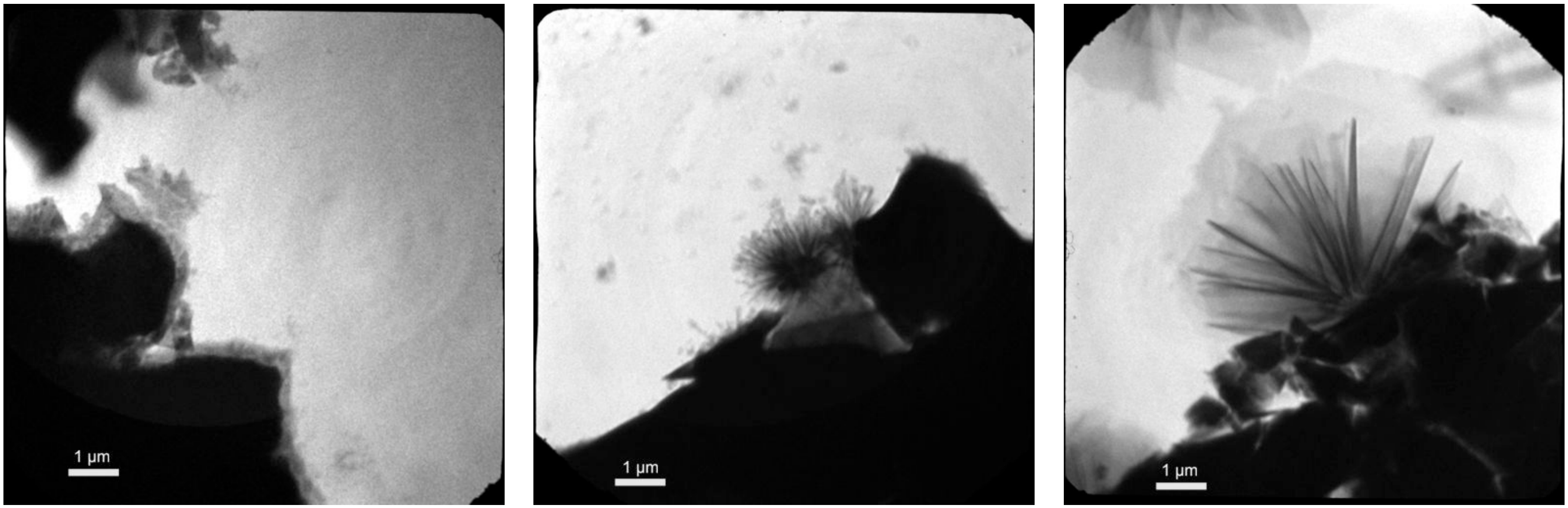
Soil: Dystric Planosol

TXM at BESSY



Growth of cement phases

Cement phases imaged with TXM @ BESSY II



Time →

Sample: Tricalciumsilicate / Tricalciumaluminate + H_2O

Start with H_2O: Gel is formed, retards further activity

After some time: C-S-H phases start to form

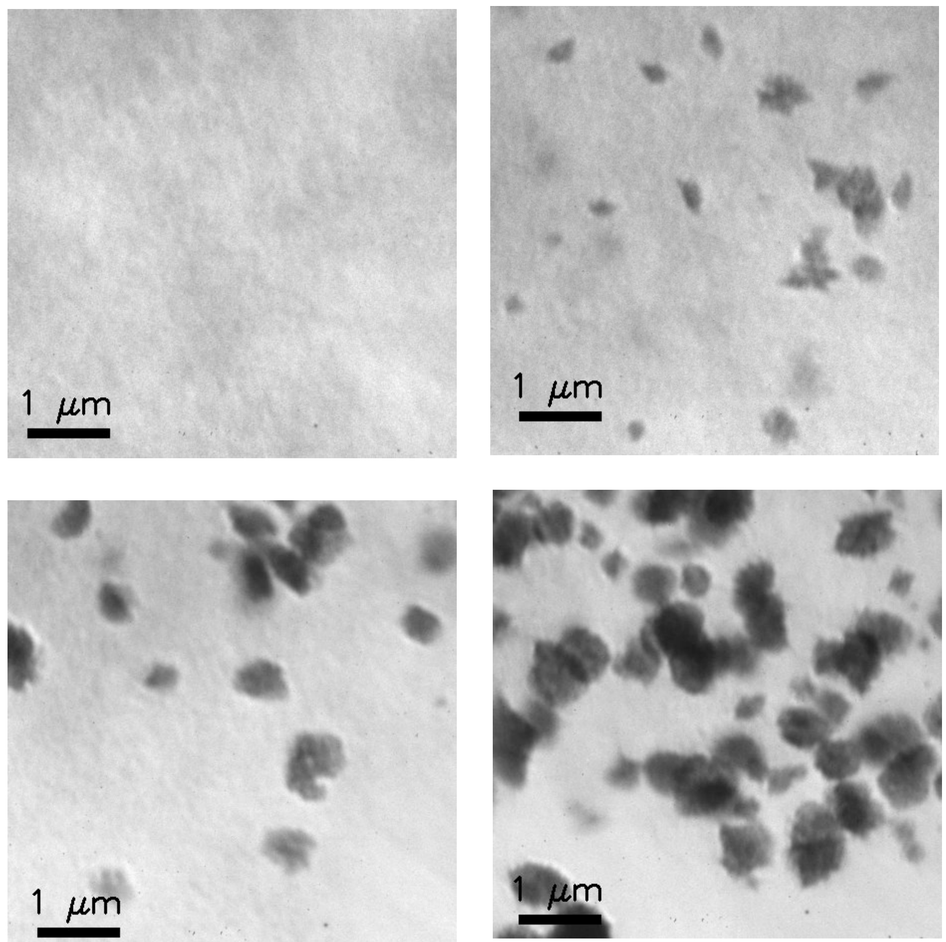
Precipitation of $Zn(OH)_2$

$Zn(OH)_2$ particles in aqueous dispersion

TXM at BESSY II
resolution approx. 25 nm
E = 520 eV

Time spans over 50 minutes after the first mixing of $ZnCl_2$ and NaOH solutions.

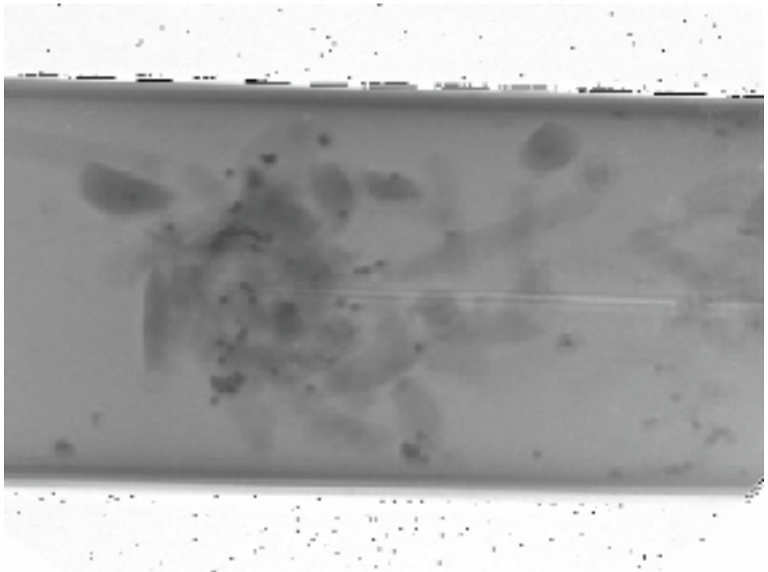
J.Thieme et al. (2009) Springer



U.S. DEPARTMENT OF ENERGY

BROOKHAVEN NATIONAL LABORATORY
BROOKHAVEN SCIENCE ASSOCIATES

3D-structure of a flock of soil colloids



Aligned X-ray images,

Capillary diameter 8 µm

sample: Chernozem soil
and microbial habitat

XM-1 at ALS

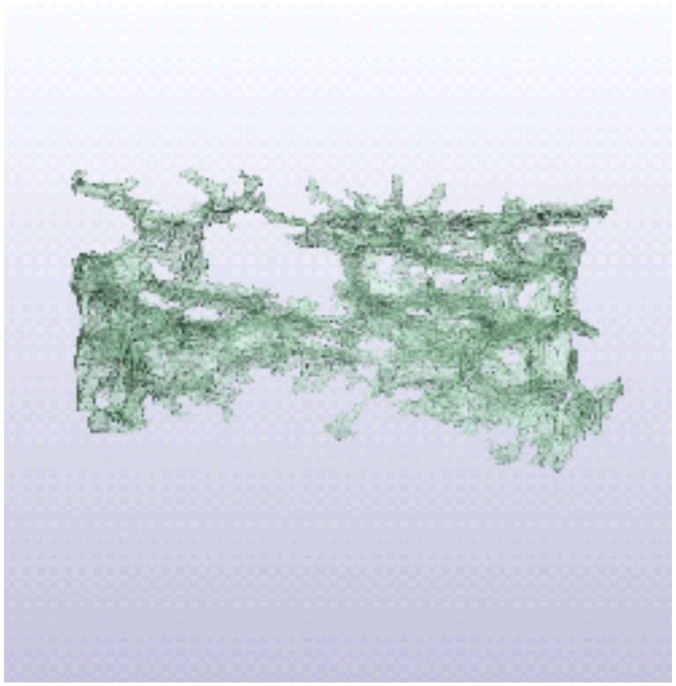
Computer generated slices,

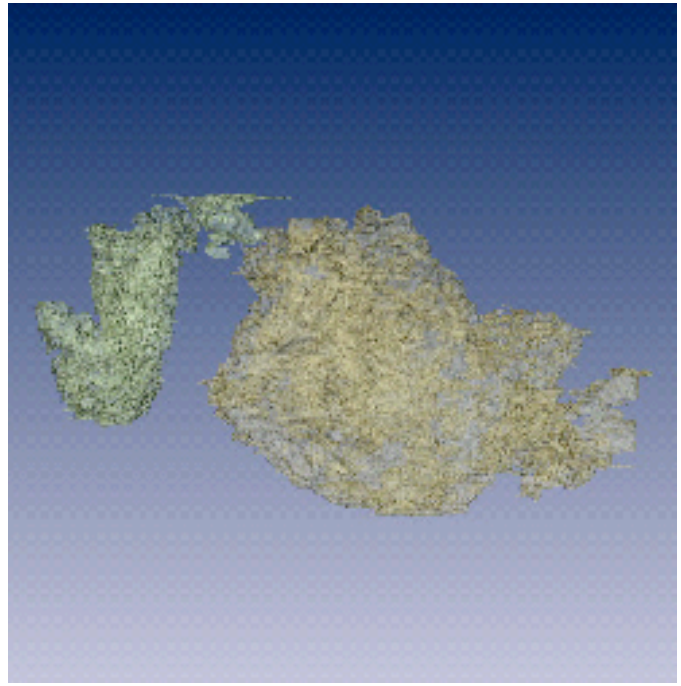
thickness 100 nm

sample: Chernozem,
soil and bacteria

Thieme et al. (2003)
Micron

Cryo tomography of humic substances





XM-1 at ALS

reduced reoxidized

Humic substances undergo a conformational change on changing their redox state

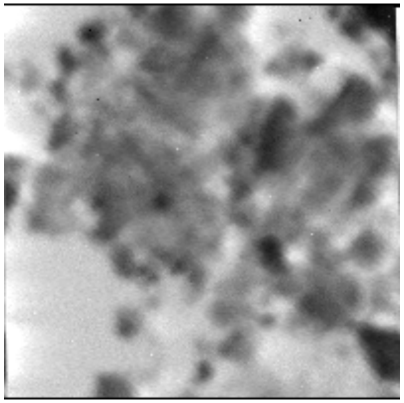
Influence on transport properties

binding capacities

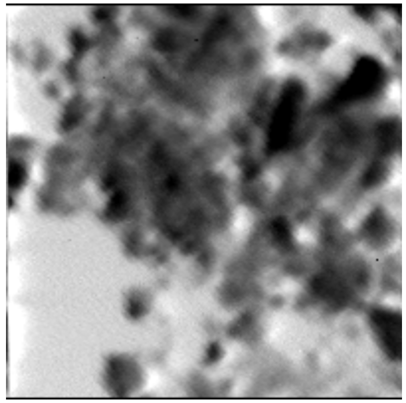
⇔ chemical studies

Thieme et al. (2007)
Env Sci Technol

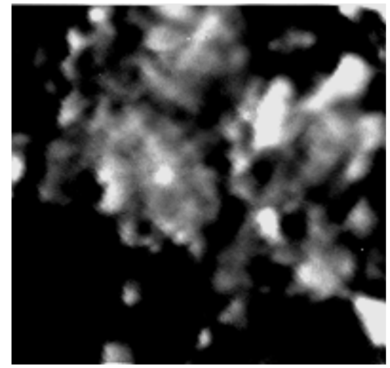
Carbon distribution by elemental mapping



E = 280 eV

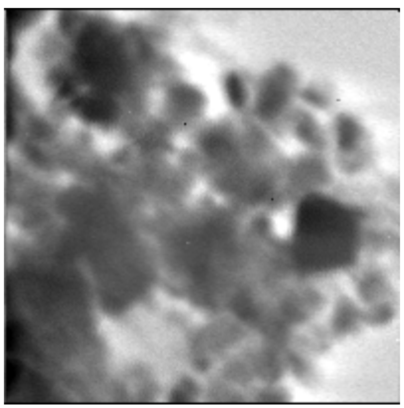


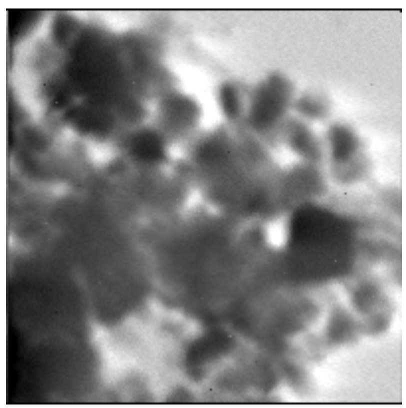
E = 310 eV

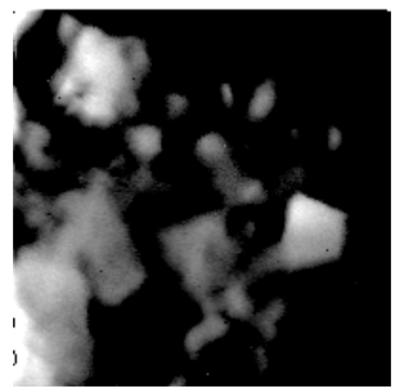


Soil colloids from Chernozem

STXM at BESSY







Colloids in seepage water from waste deposit

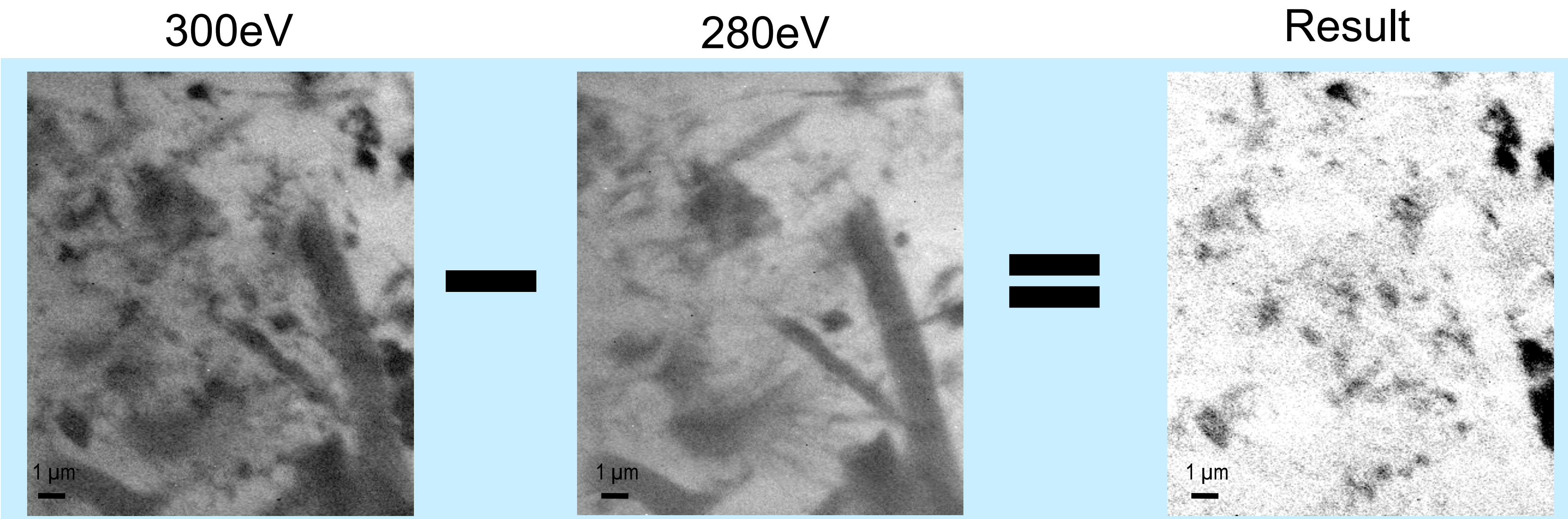
10 x 10 μm², 200 x 200 pxl, 50 nm step

G. Mitrea et al. (2008) J. Synchr. Rad.

Interaction of CNTs with clay (aqueous)

COOH-CNTs with Na-montmorillonite in water:

Elemental Mapping for identification possible, as Na-montmorillonite has no organic content.

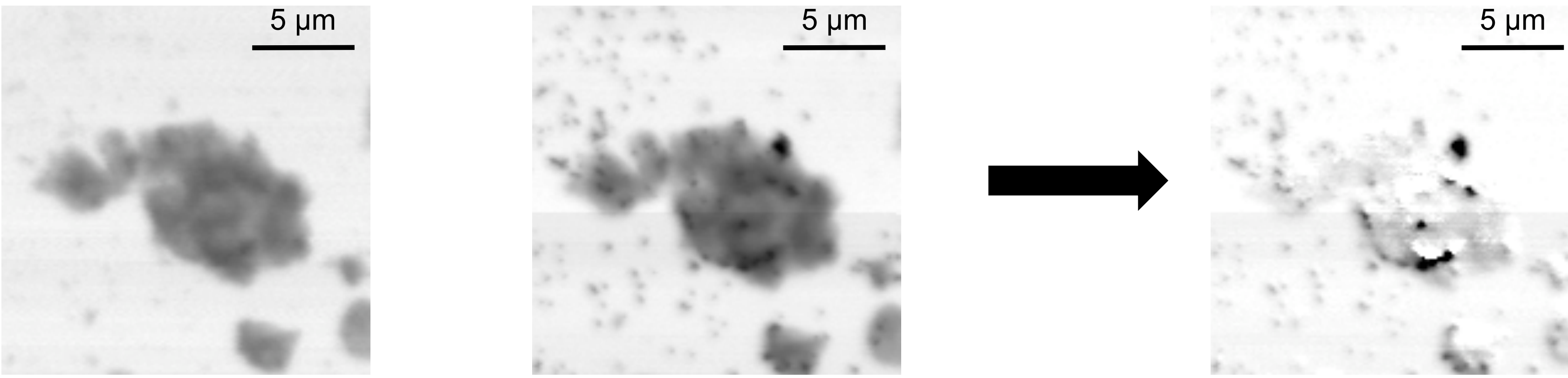


From NEXAFS-spectra it is possible to distinguish the CNTs, too.

J. Sedlmair et al.
In preparation

Hematite associates with humics

The images show a humic substances agglomeration with hematites.
scale bar: 5 µm, 0.12 µm/pxl

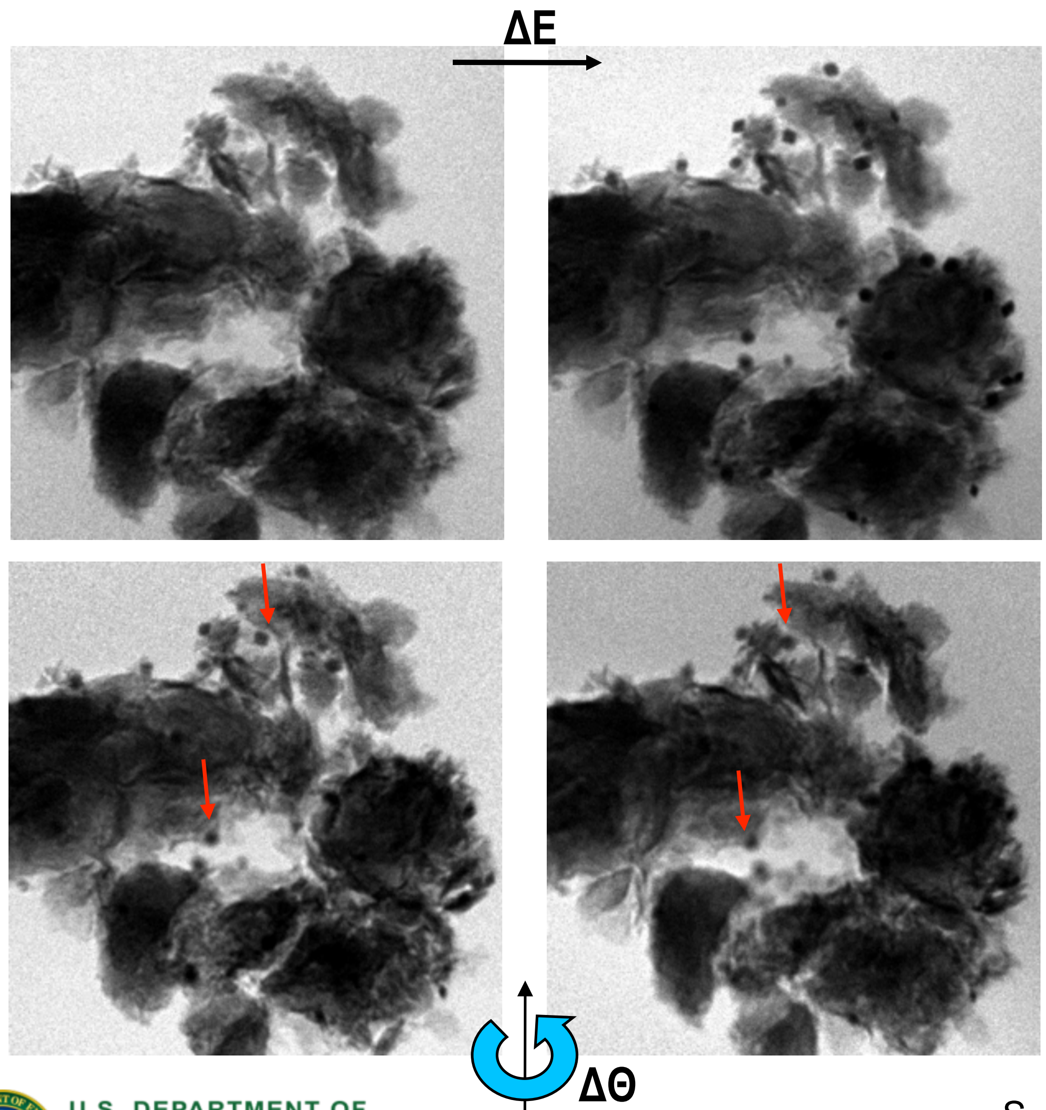


a) 700 eV b) 708 eV b / a

- bigger hematite clusters stick to the HS particle
- smaller hematites are spread out over the sample area.

  ➔ affinity Fe ⟷ C

Stereo imaging and elemental mapping



Sample: clay aqueous with hematite particles

Images taken at XM-1, ALS

Top:
left: E = 704 eV, below L-absorption edge of Fe
right: E = 711 eV, above edge, hematite particles visible

Bottom:
E = 711 eV
tilting angle = 15°
contact between clay and hematite particle visible

S Gleber et al. (2009)
J. of Microscopy

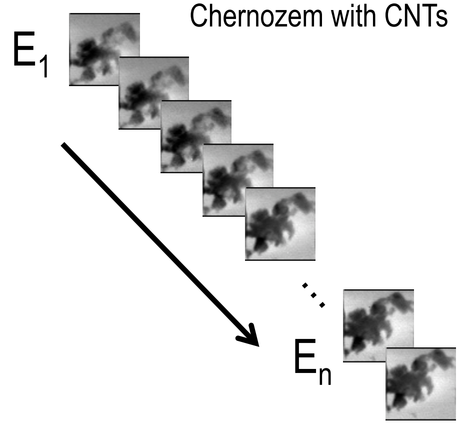
U.S. DEPARTMENT OF ENERGY

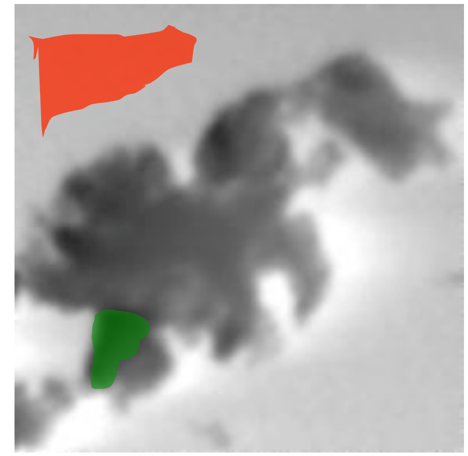
BROOKHAVEN NATIONAL LABORATORY
BROOKHAVEN SCIENCE ASSOCIATES

Chemical and spatial information combined

- image sample at different energies ascending over an absorption edge
  =: record a "**stack**"
- evaluation with Stack_Analyze
  (C. Jacobsen et al., *J Microscopy*, **197**(2), 2000):
  - alignment
  - define reference intensity $\mathbf{I_0}$
- each pixel of stack contains its own NEXAFS-spectrum with intensity **I**

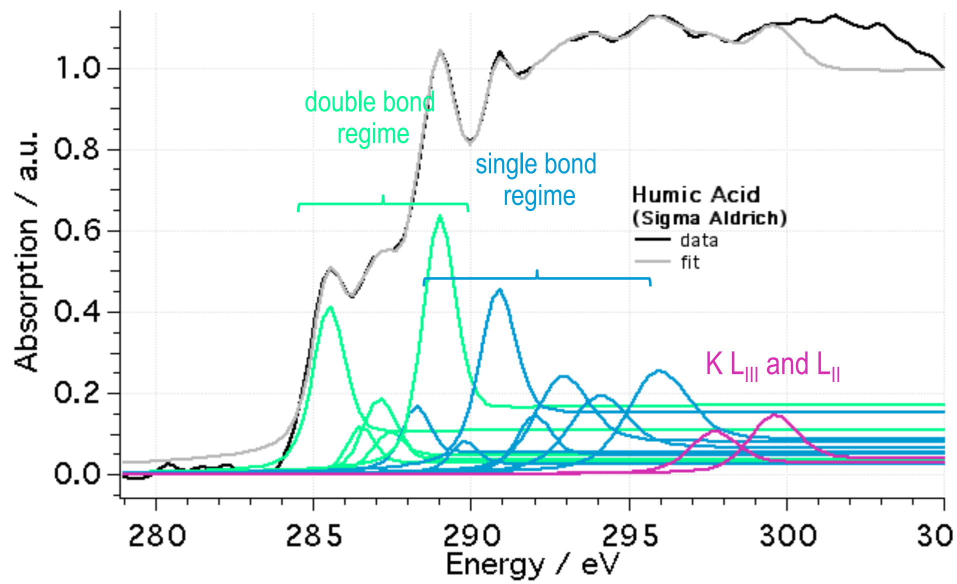
Example: STXM-image
Chernozem with CNTs





Example of a **NEXAFS** spectrum at the C 1s absorption edge (284 eV)

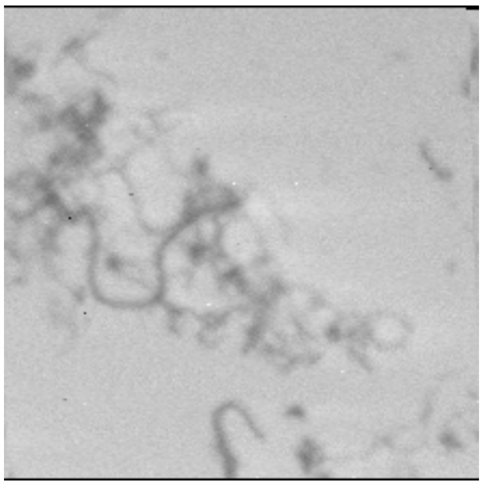
J. Sedlmair et al.
In preparation

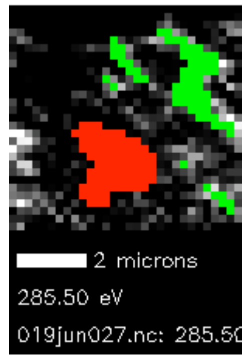


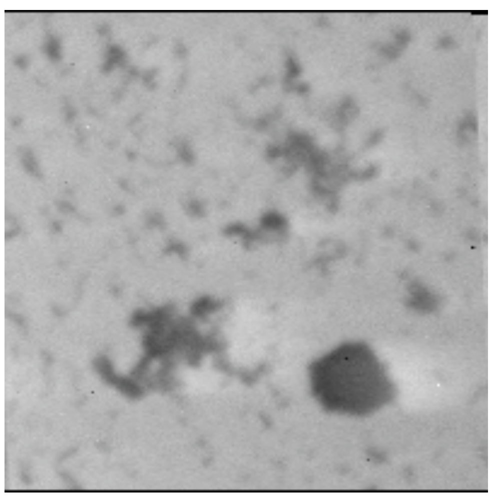
U.S. DEPARTMENT OF ENERGY

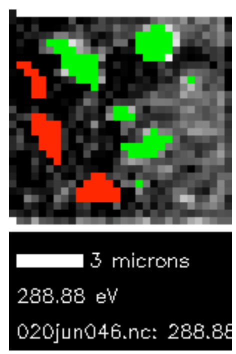
BROOKHAVEN NATIONAL LABORATORY
BROOKHAVEN SCIENCE ASSOCIATES

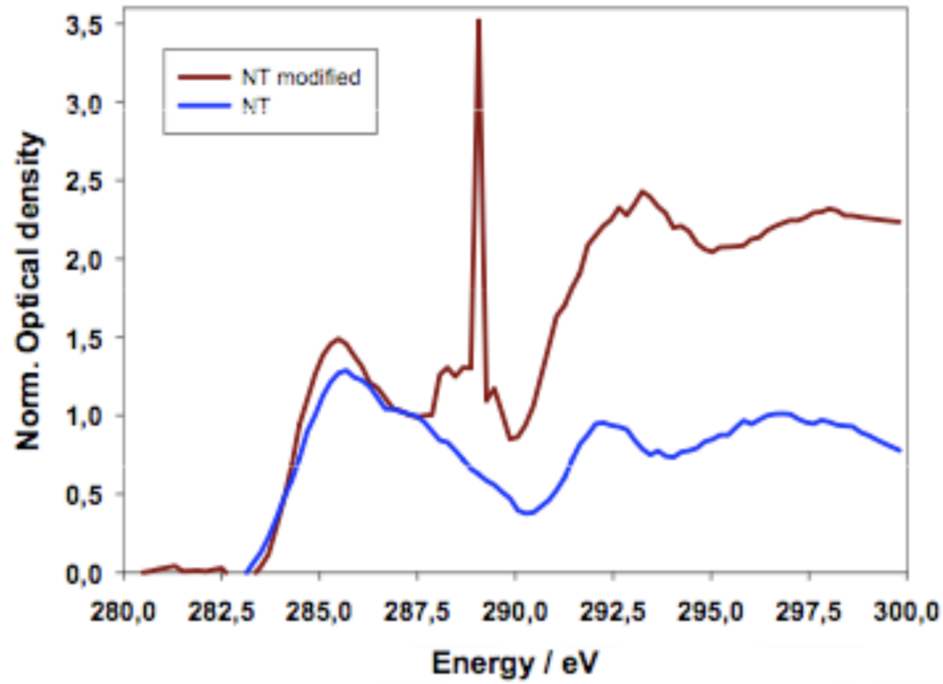
Pristine and functionalized CNT











Top image: Carbon nanotubes

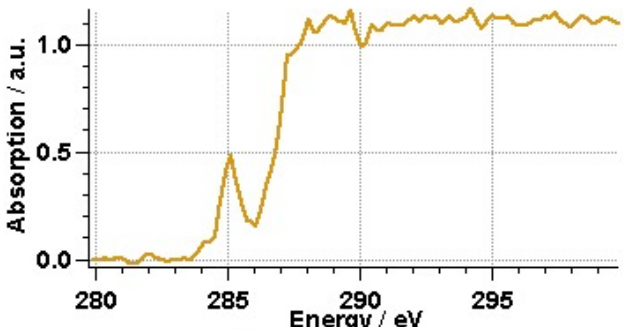
Lower image: functionalized CNT
10 µm x 10 µm, resolution 50 nm

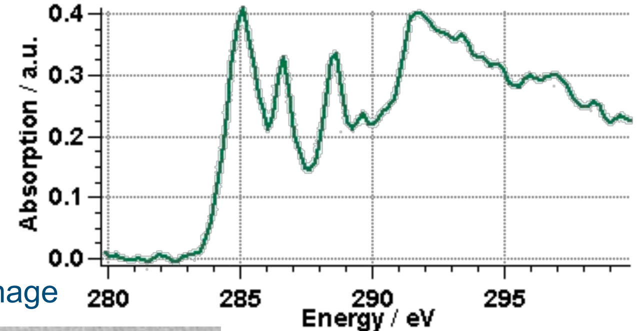
Spectrum shows C=O

J. Sedlmair et al.
In preparation

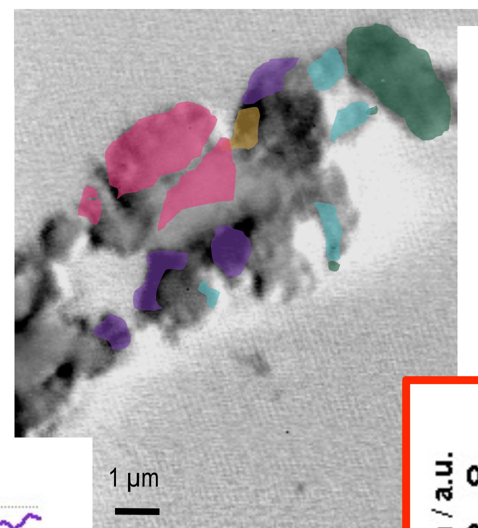
Interaction of CNTs with soil sample (dry)

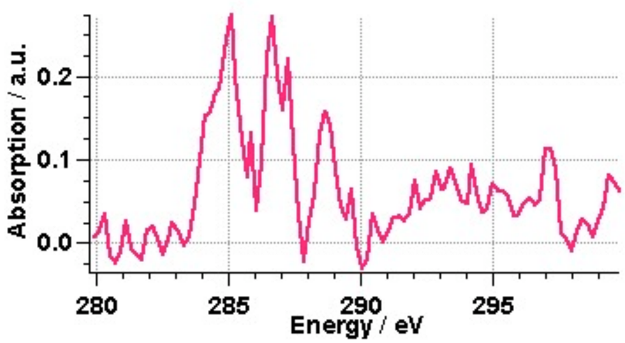
evaluation of stacks shows spectra of different components:

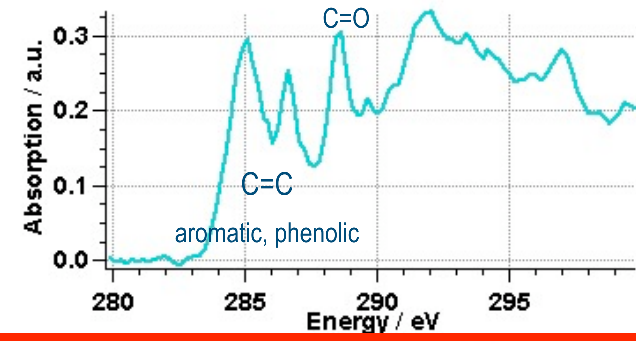


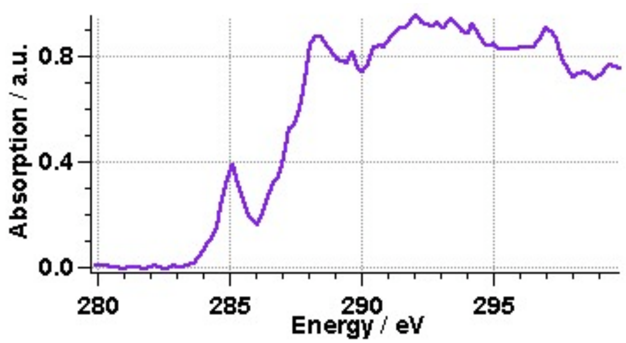


resulting image

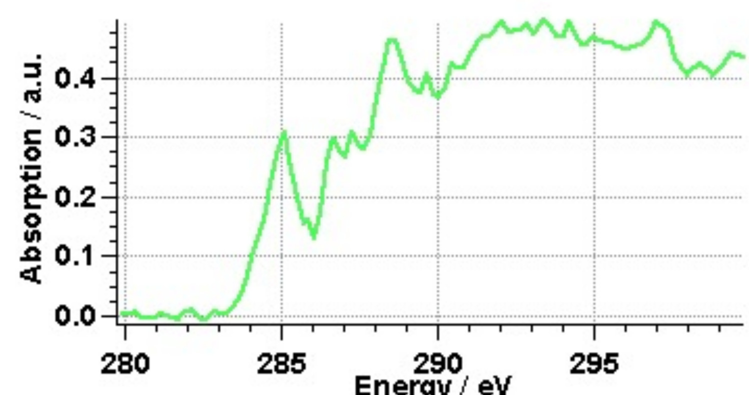








spectrum of total cluster



X-ray microscopy – a tool to study the nanoworld

Summary:

2D– / 3D– imaging		Visualization
Elemental mapping	=>	Dynamics
Spectroscopy		Interaction

Benefit of XM-3 for these studies:

Enhanced spatial resolution ⇔ nanoparticles
Tomography for 3D information ⇔ agglomerations
Cryo-capabilities for organic structures ⇔ biofilms
Spectroscopic capabilities ⇔ interactions