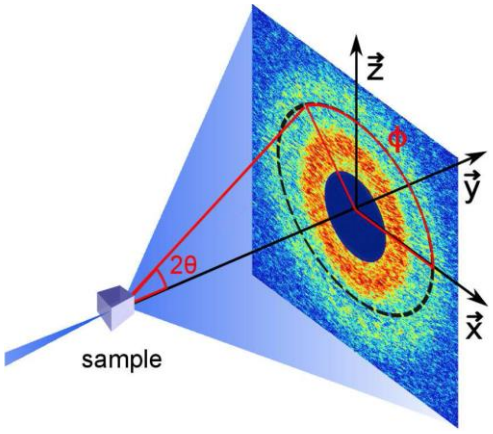
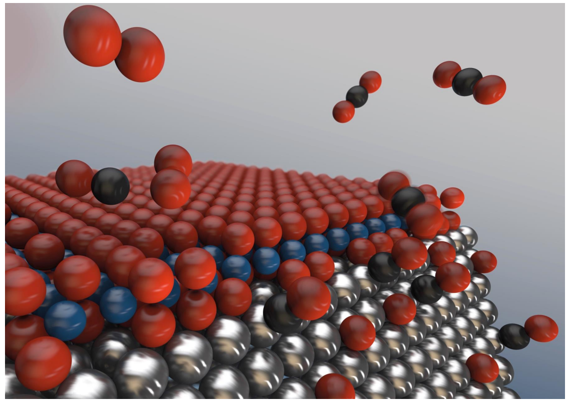
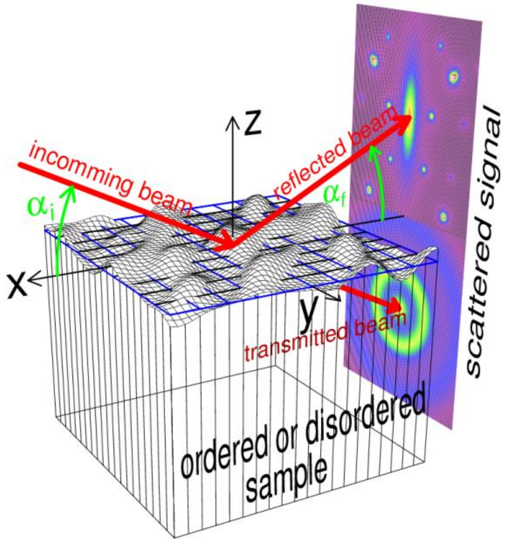
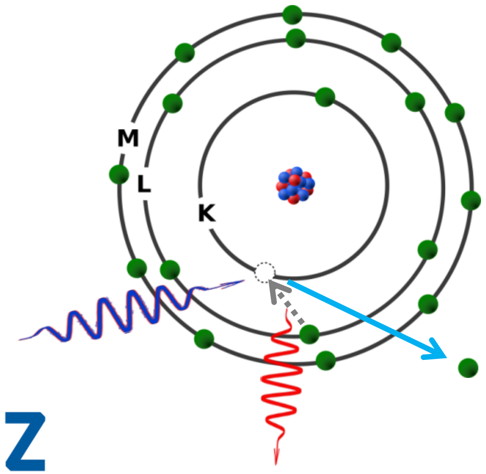
Exploring properties of the microcosm with brilliant X-rays









Wolfgang Drube

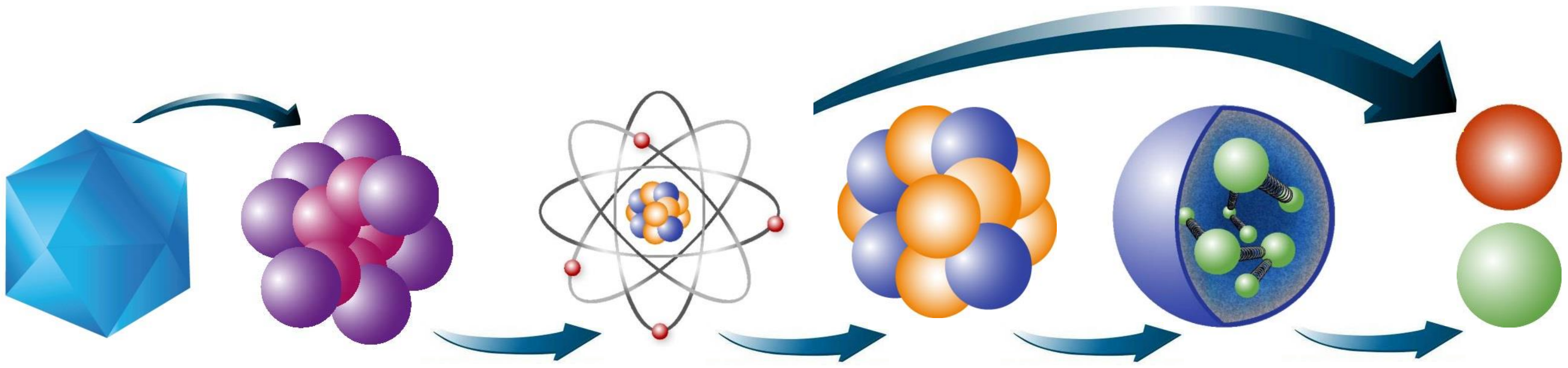
Deutsches Elektronen-Synchrotron DESY
Hamburg, Germany

HELMHOLTZ
RESEARCH FOR GRAND CHALLENGES

Scientific Evening, University of Nova Gorica, 15 Nov. 2018

DESY.

Building blocks of matter

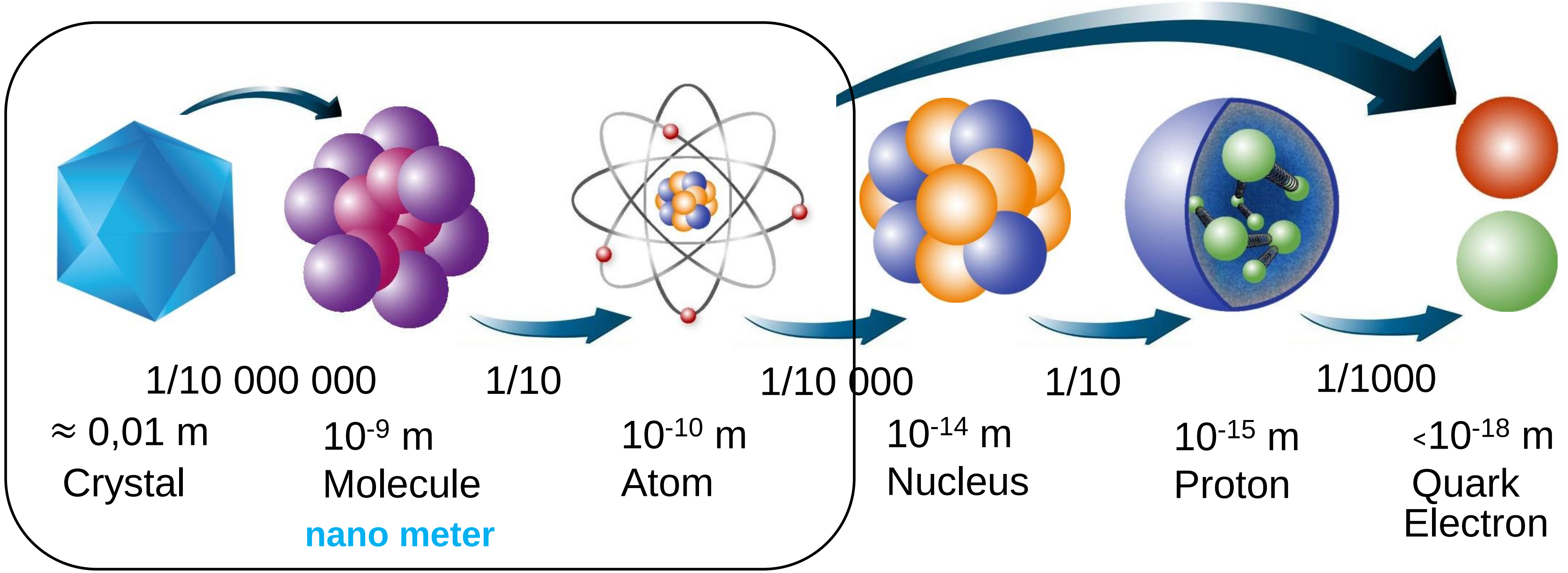


1/10 000 000	1/10	1/10 000	1/10	1/1000	
≈ 0,01 m	10^{-9} m	10^{-10} m	10^{-14} m	10^{-15} m	$<10^{-18}$ m
Crystal	Molecule	Atom	Nucleus	Proton	Quark Electron

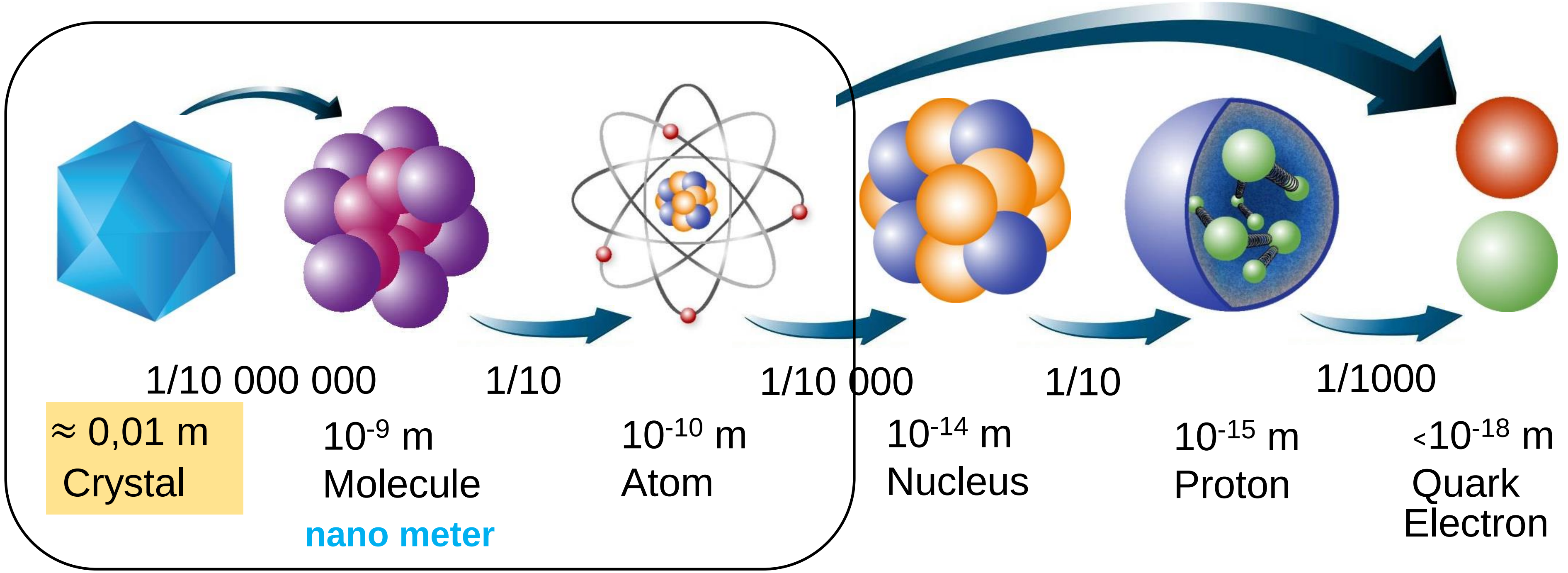
Pin head **10^{-3} m = 0,001 m**

Electron **10^{-18} m = 0,000 000 000 000 000 001 m**

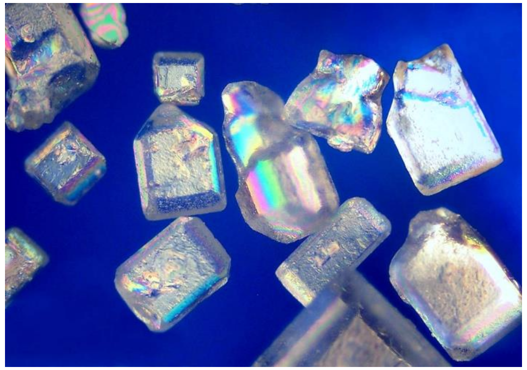
Building blocks of matter



Building blocks of matter



Salt: NaCl

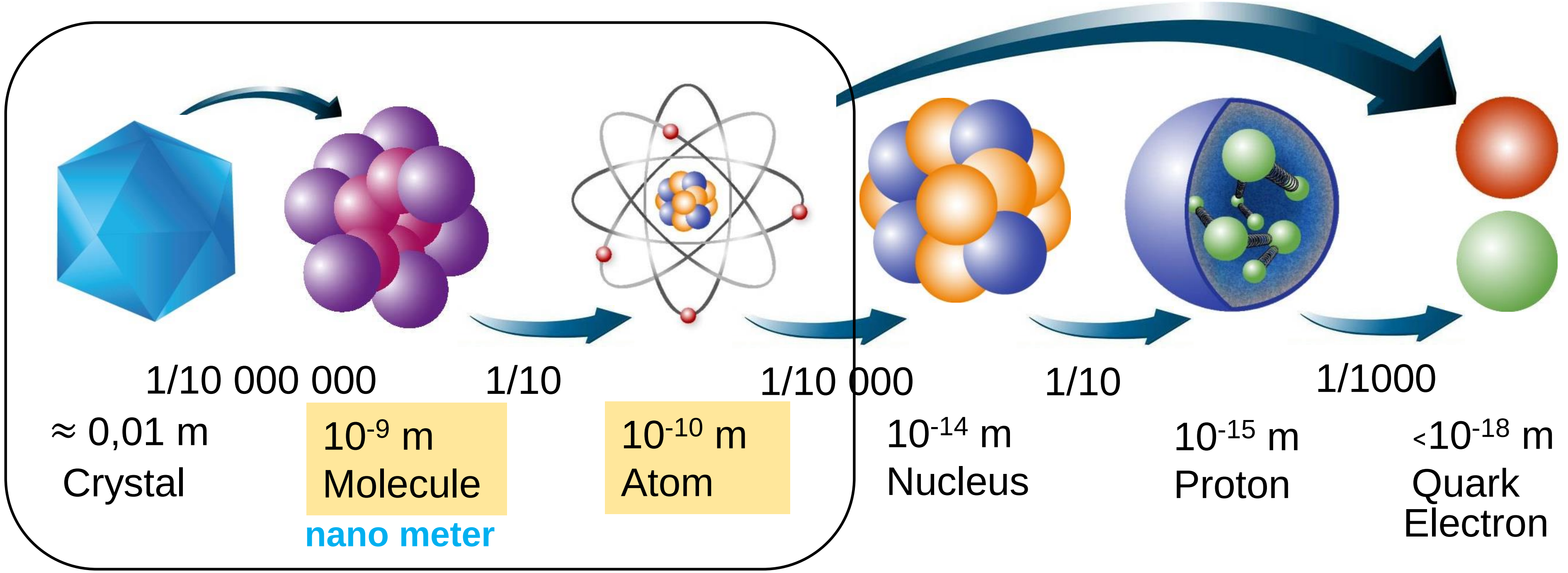


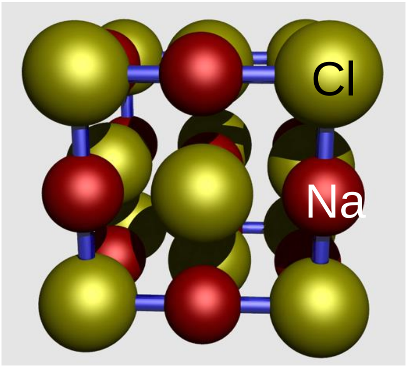
Sugar (sucrose): $C_{12}H_{22}O_{11}$

Diamond: C

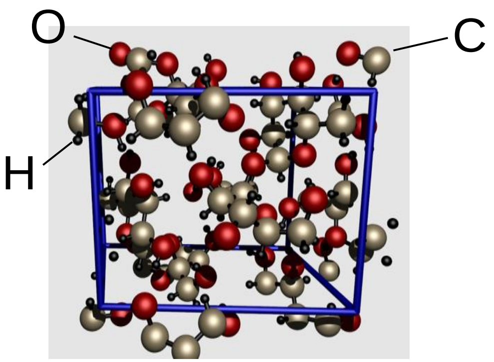
Rock crystal (quartz): SiO_2

Building blocks of matter

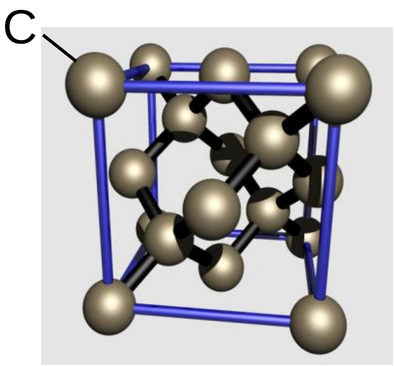




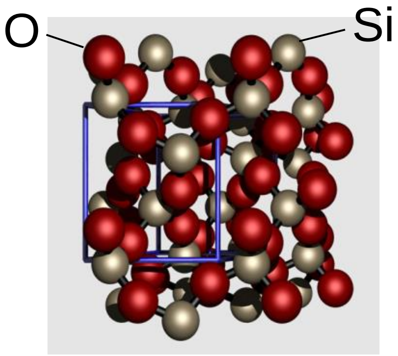
Salt: NaCl



Sugar (sucrose): $C_{12}H_{22}O_{11}$



Diamond: C

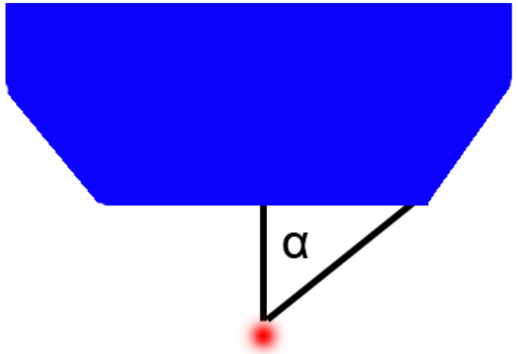


Rock crystal (quartz): SiO_2

Light as a probe: „zoom in“ with a microscope

(source: wikipedia)

Resolution of an optical microscope



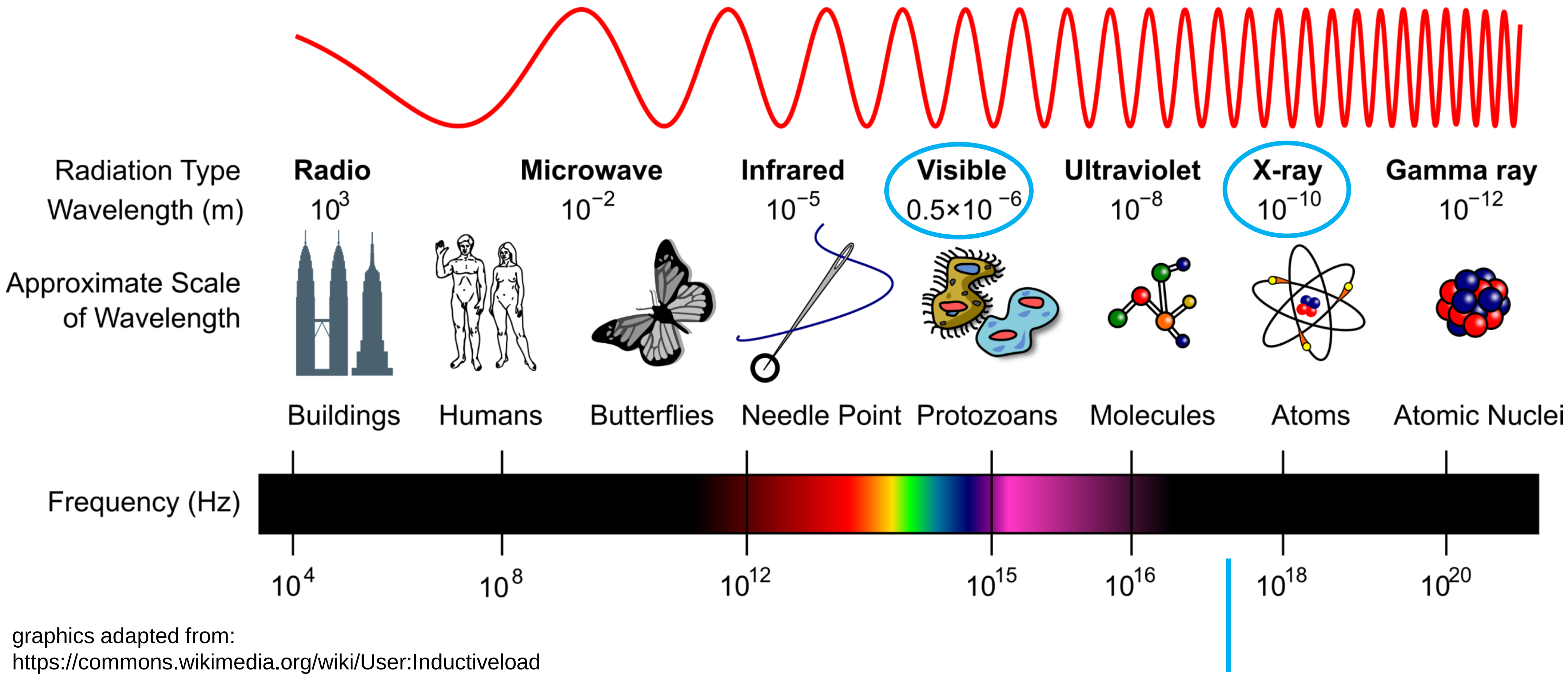
smallest separation d of two lines to be distinctly visible:

$$d = \frac{\lambda}{(2) n \sin\alpha}$$

Index of refraction: n ~ 1

Ernst Abbe
(Jena , ≈ 1870)

Electromagnetic waves



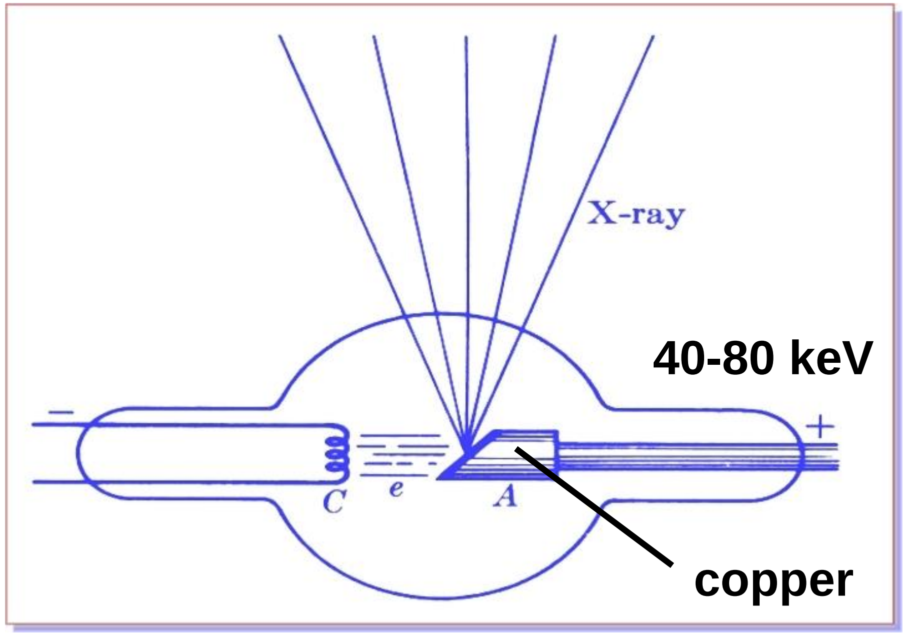
graphics adapted from:
https://commons.wikimedia.org/wiki/User:Inductiveload

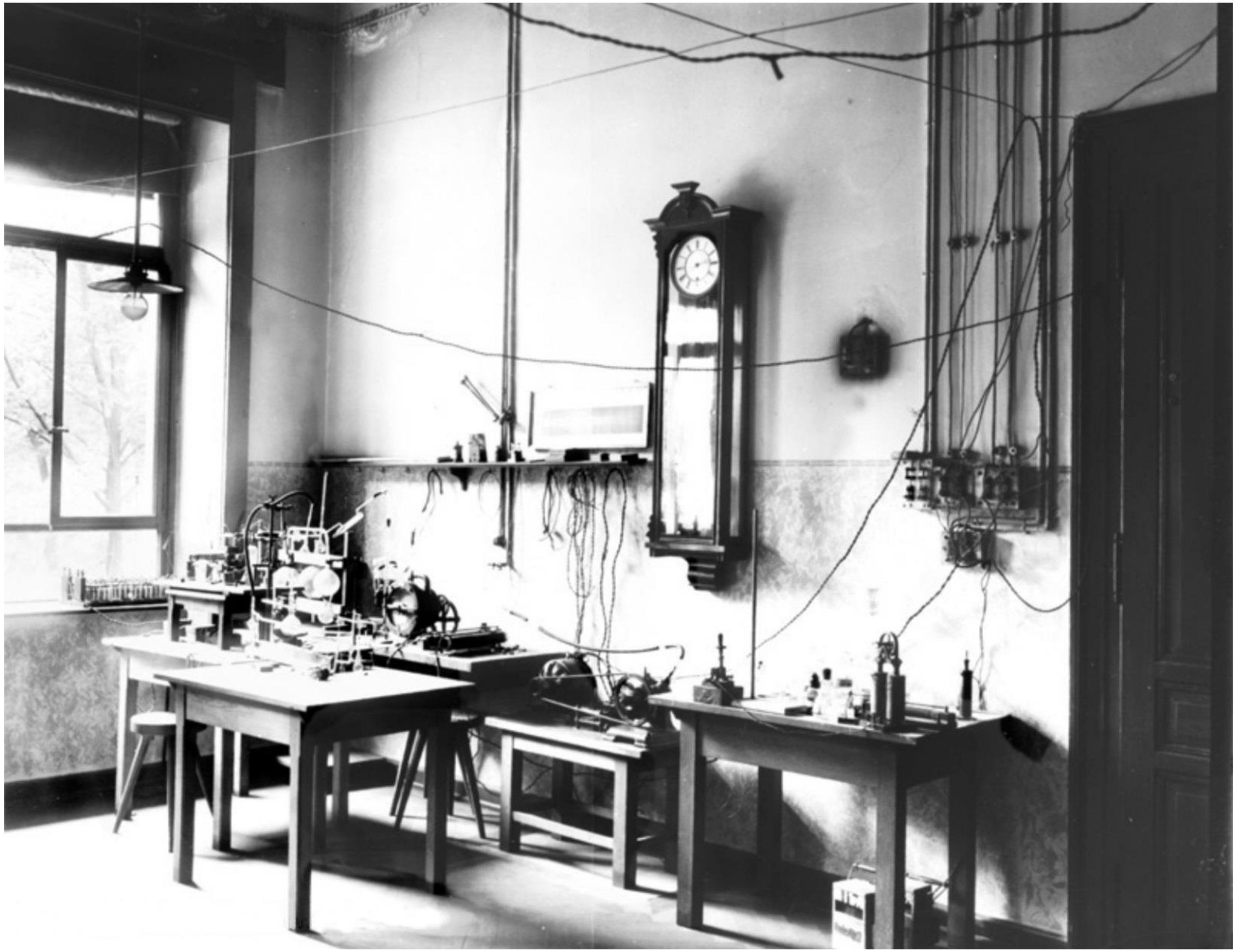
10 keV (energy)

10 000 electron volt

Discovery of X-rays

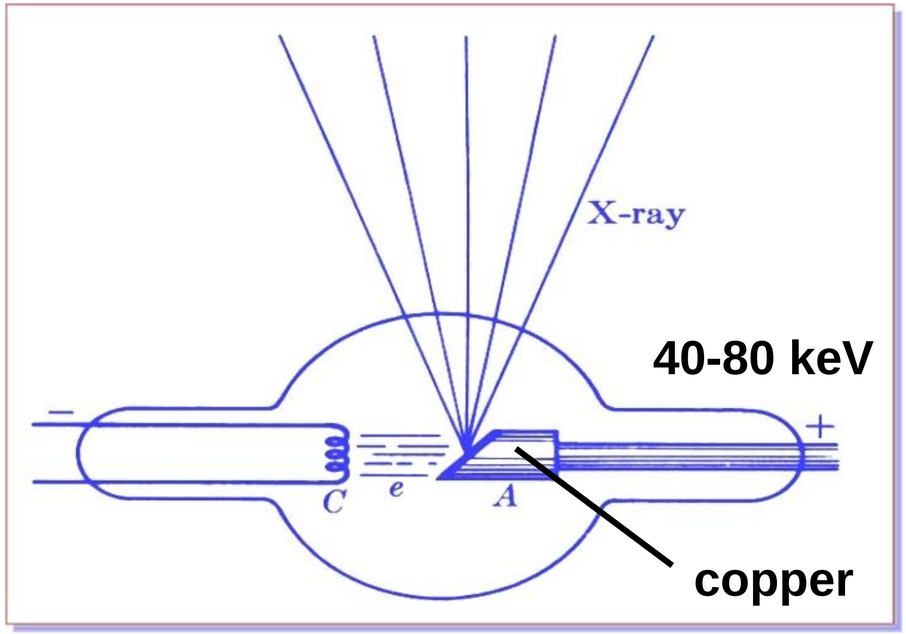
Discovered by
Wilhelm Conrad Röntgen
in Würzburg 1895
(First Nobel prize 1901)





Discovery of X-rays

Discovered by
Wilhelm Conrad Röntgen
in Würzburg 1895
(First Nobel prize 1901)



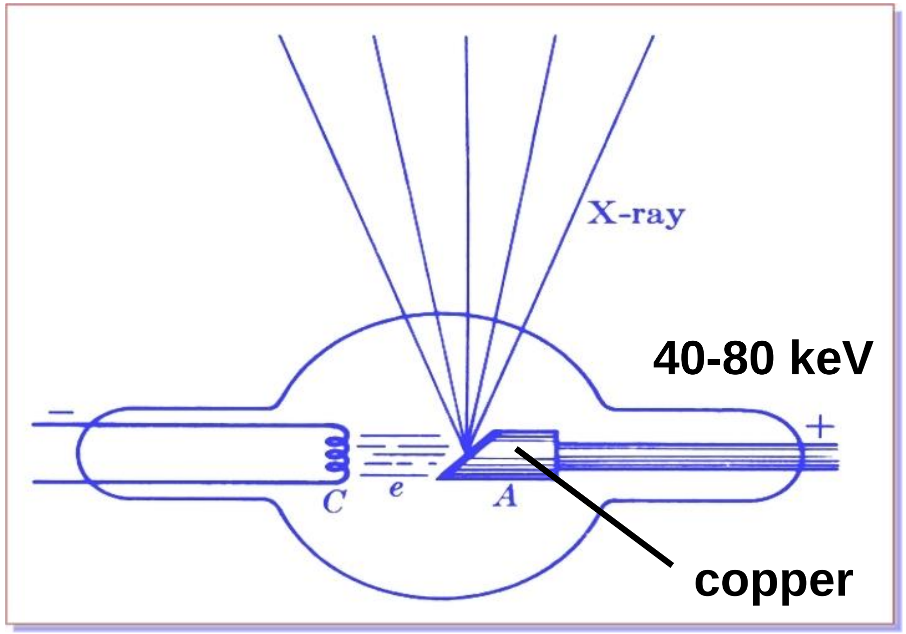
X-rays can penetrate (rather thick) material)

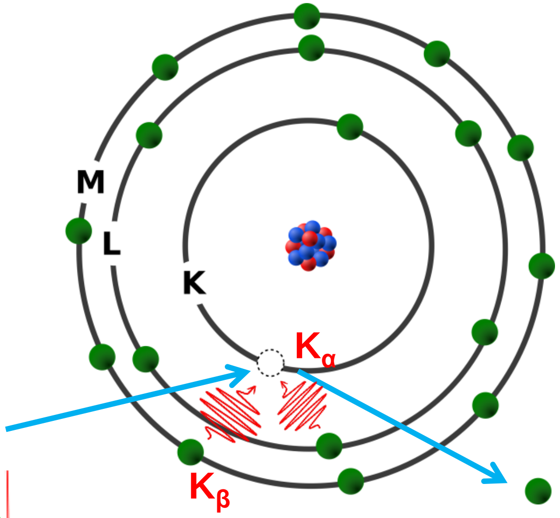
X-rayed hand of his wife
Anna Bertha Ludwig
(22. December 1895)

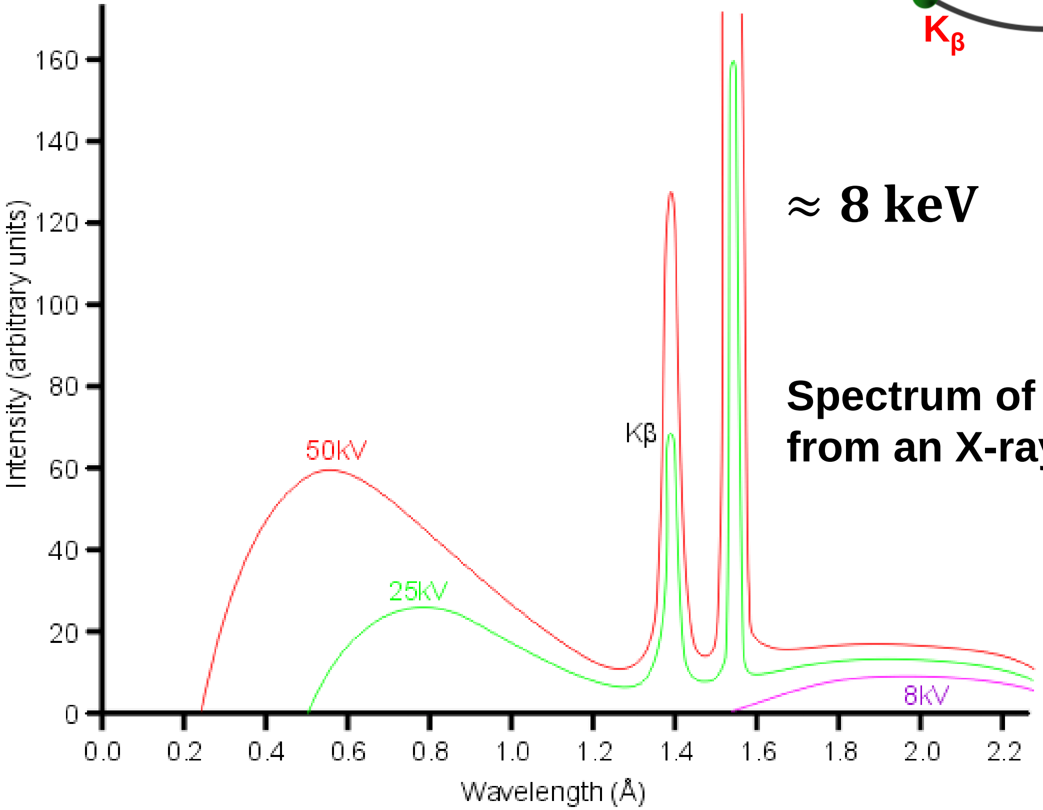
the image contrast is caused by
different X-ray absorption in
soft tissue and bones

Discovery of X-rays

Discovered by
Wilhelm Conrad Röntgen
in Würzburg 1895
(First Nobel prize 1901)



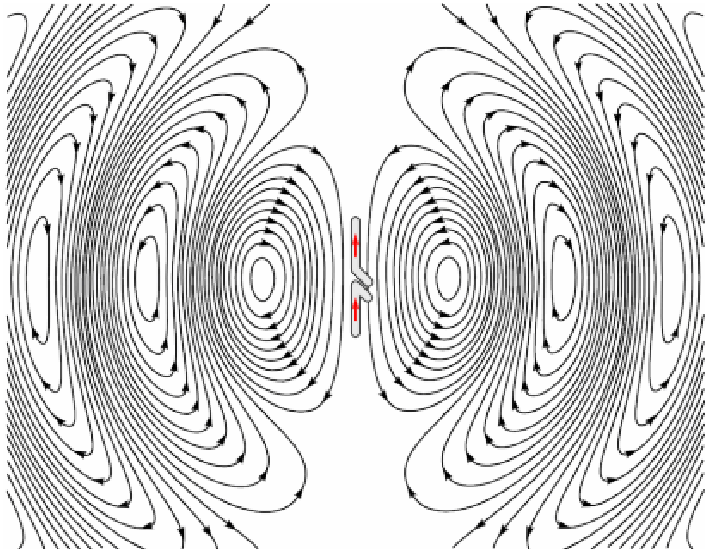




$\approx$ **8 keV**

Spectrum of X-rays emitted from an X-ray tube (Cu anode)

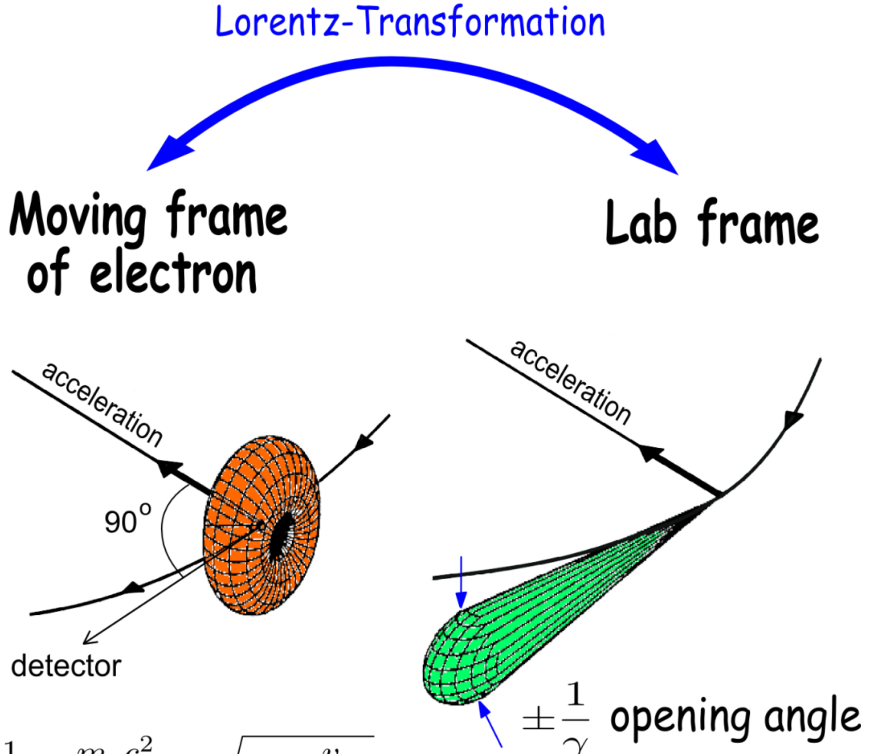
Accelerated electrons emit radiation



an accelerated charge emits electromagnetc radiation

the angular distribution: Hertz dipole

“very fast” electrons (~ speed of light)



$$\frac{1}{\gamma} = \frac{m_o c^2}{E} = \sqrt{1-(\frac{v}{c})^2}$$

highly collimated !

opening angle $1/\gamma$ = 0.5 MeV/6 GeV ≈ 0.005°

(PETRA III storage ring) 80 µrad

In pratice:

large particle accelerators:

circular motion in an electron storage ring

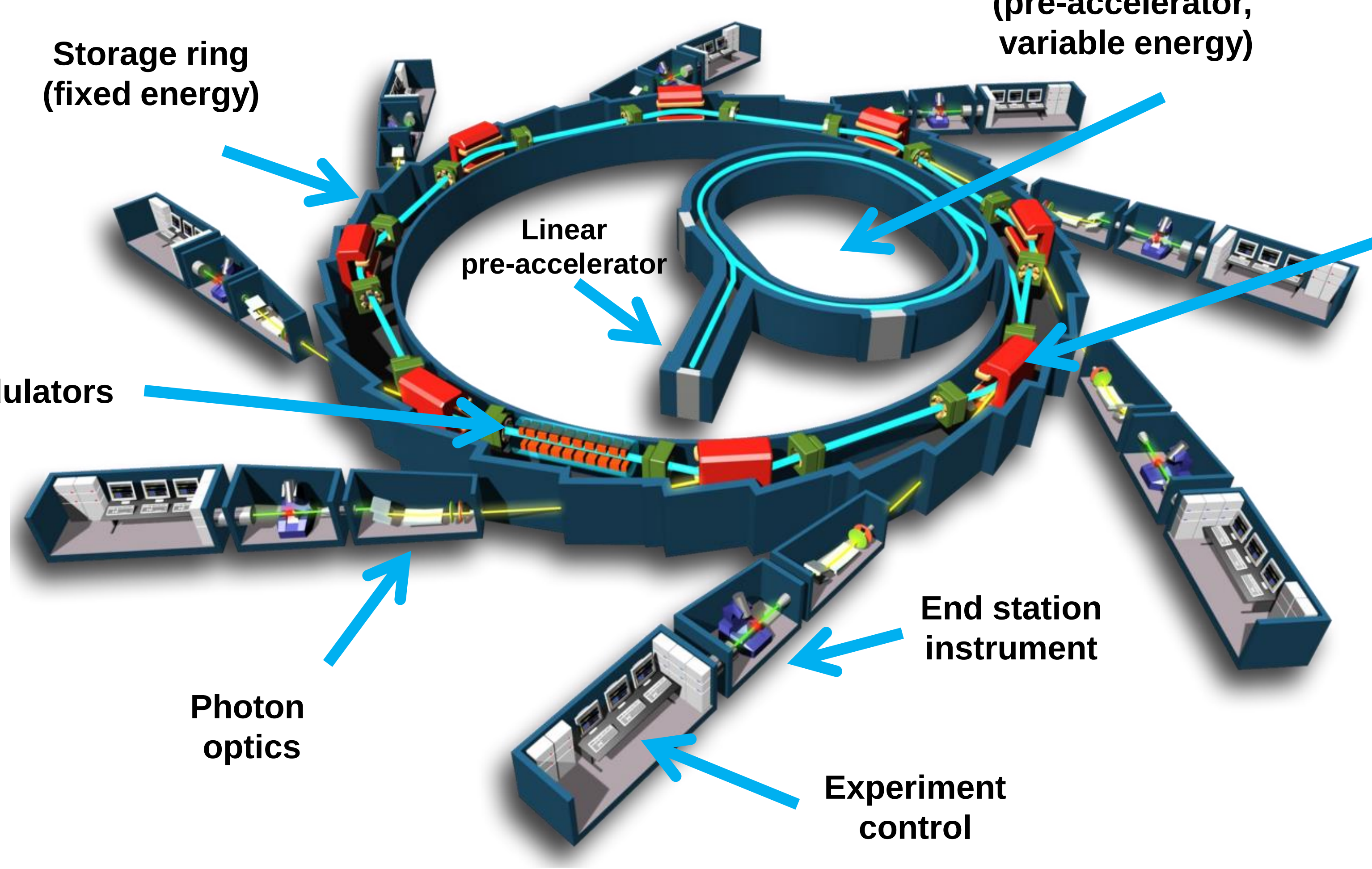
radiated power P_s (Lamor)

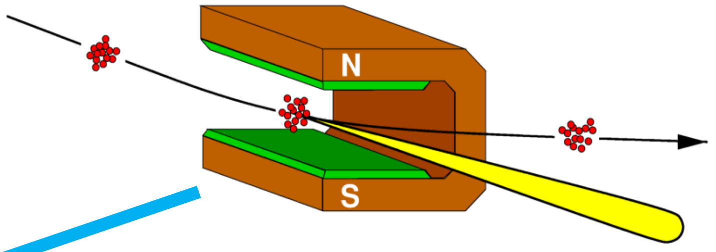
$$P_s = \frac{e^2 c}{6\pi\varepsilon_0 (m_0 c^2)^4} \frac{E^4}{R^2}$$

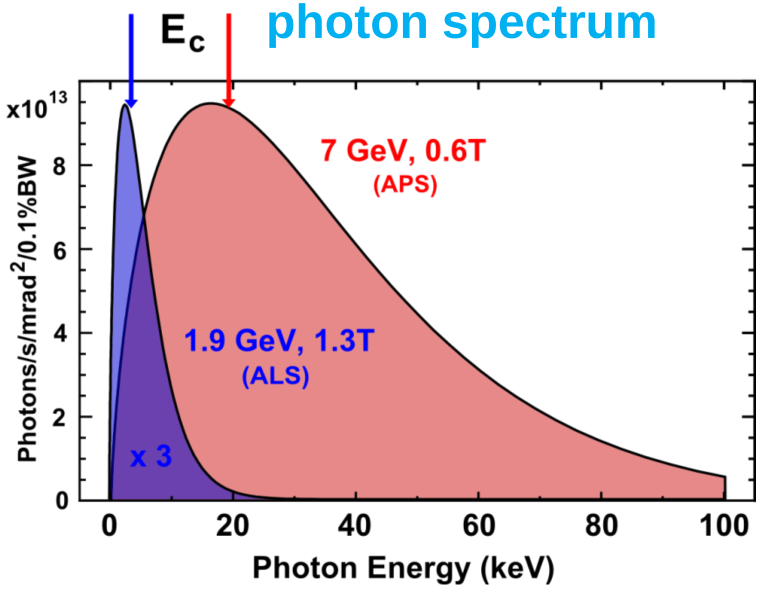
electron energy loss per turn $\Delta E \sim E^4/R$

E ~ GeV   R ~ m

Schematic Synchrotron Radiation Facility



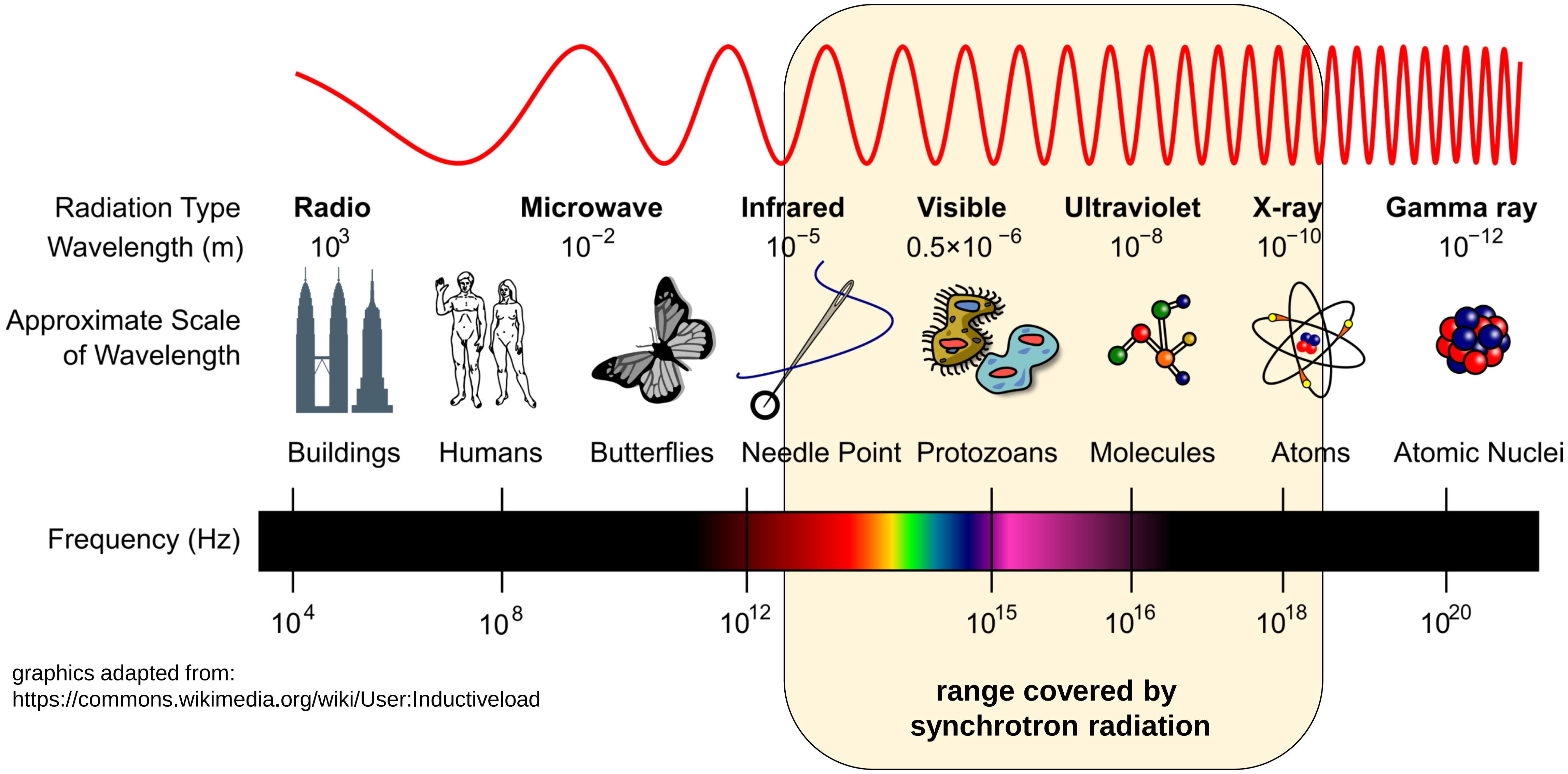




Big machines: circumference 300 – 2300 m

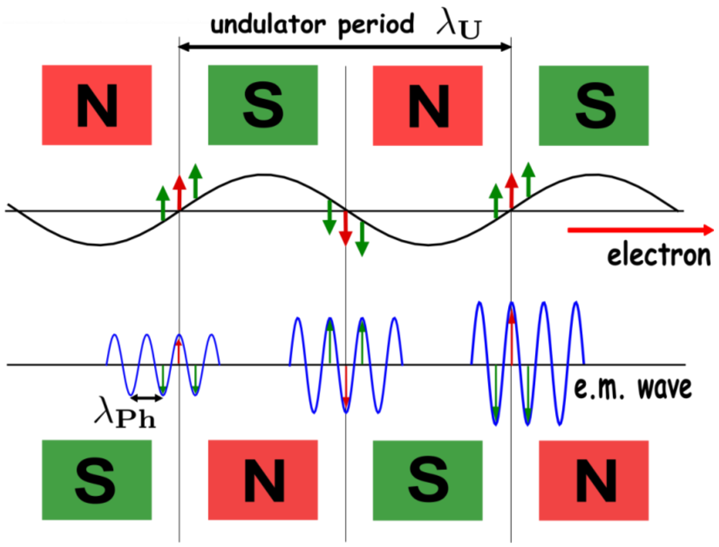
E_c (keV) = 0.665·E_e^2(GeV) · B_0(T)

Electromagnetic waves



graphics adapted from:
https://commons.wikimedia.org/wiki/User:Inductiveload

Intense X-ray beams from „undulators“



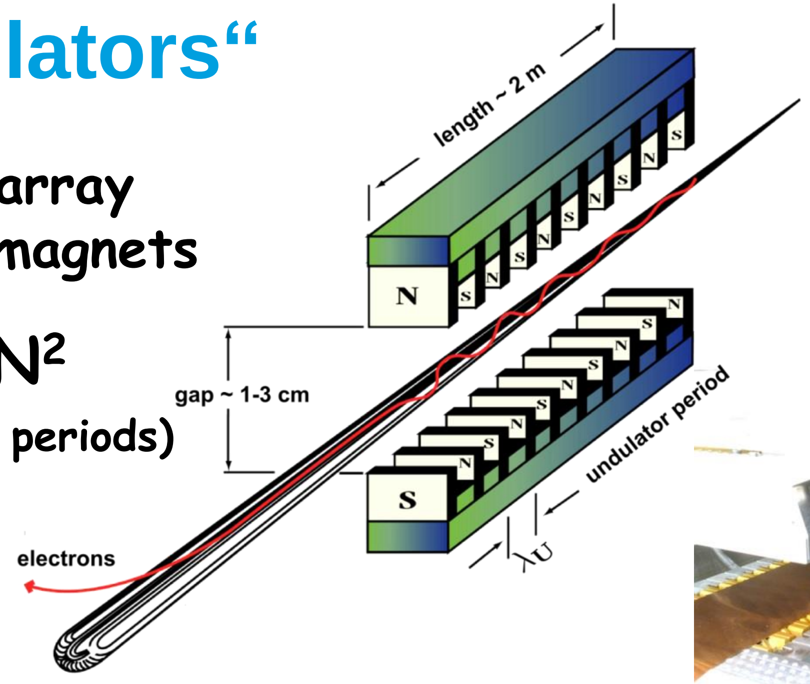
$$\lambda_{ph} = \frac{\lambda_u}{2\gamma^2}\left(1 + \frac{K^2}{2}\right)$$

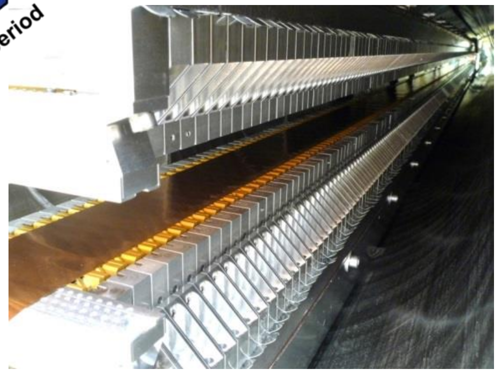
K = 0.934 λ_u [cm] B[T]

periodic array
of strong magnets

$I \sim N^2$

(N = no. of periods)

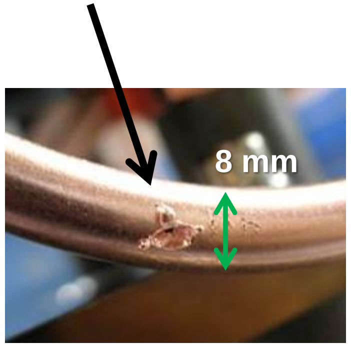


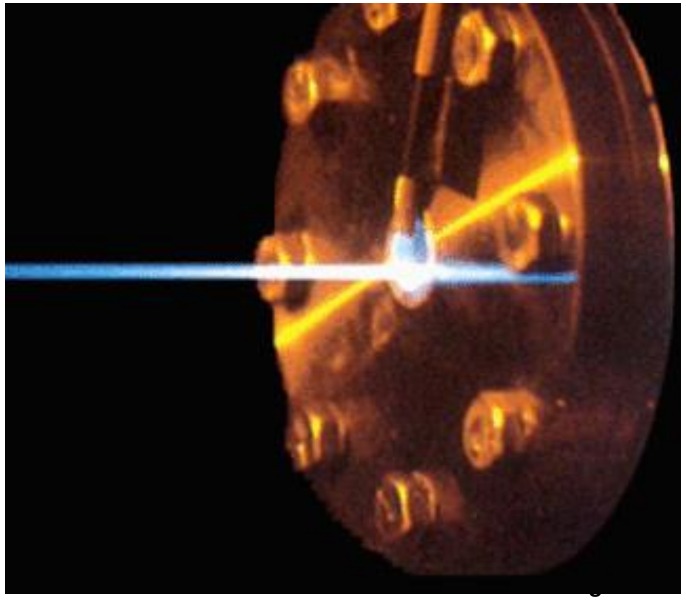


Light power:

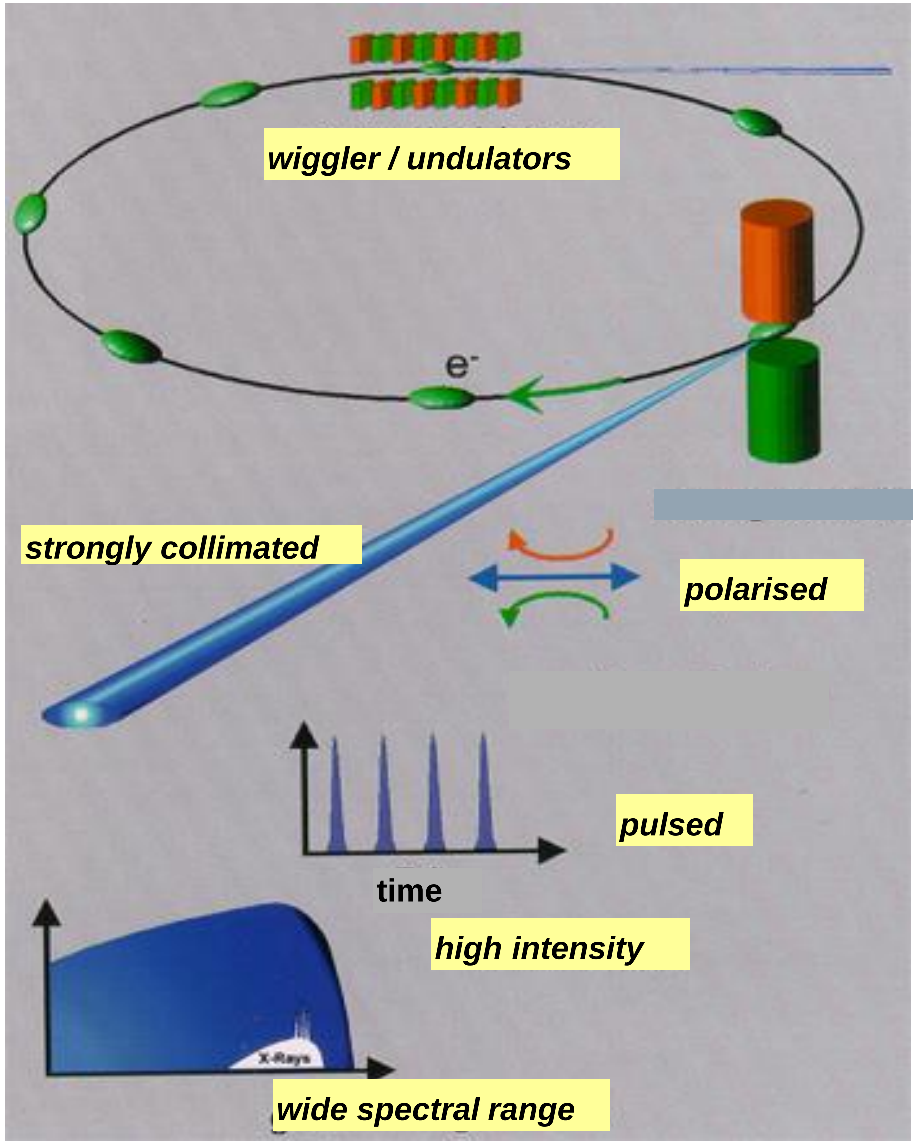
Sunlight on earth: $P_{sol} \approx 0.0013$ **W/mm²**

SR undulator: $P_{SR} \approx 8000$ **W/mm²**





Synchrotron radiation at a glance



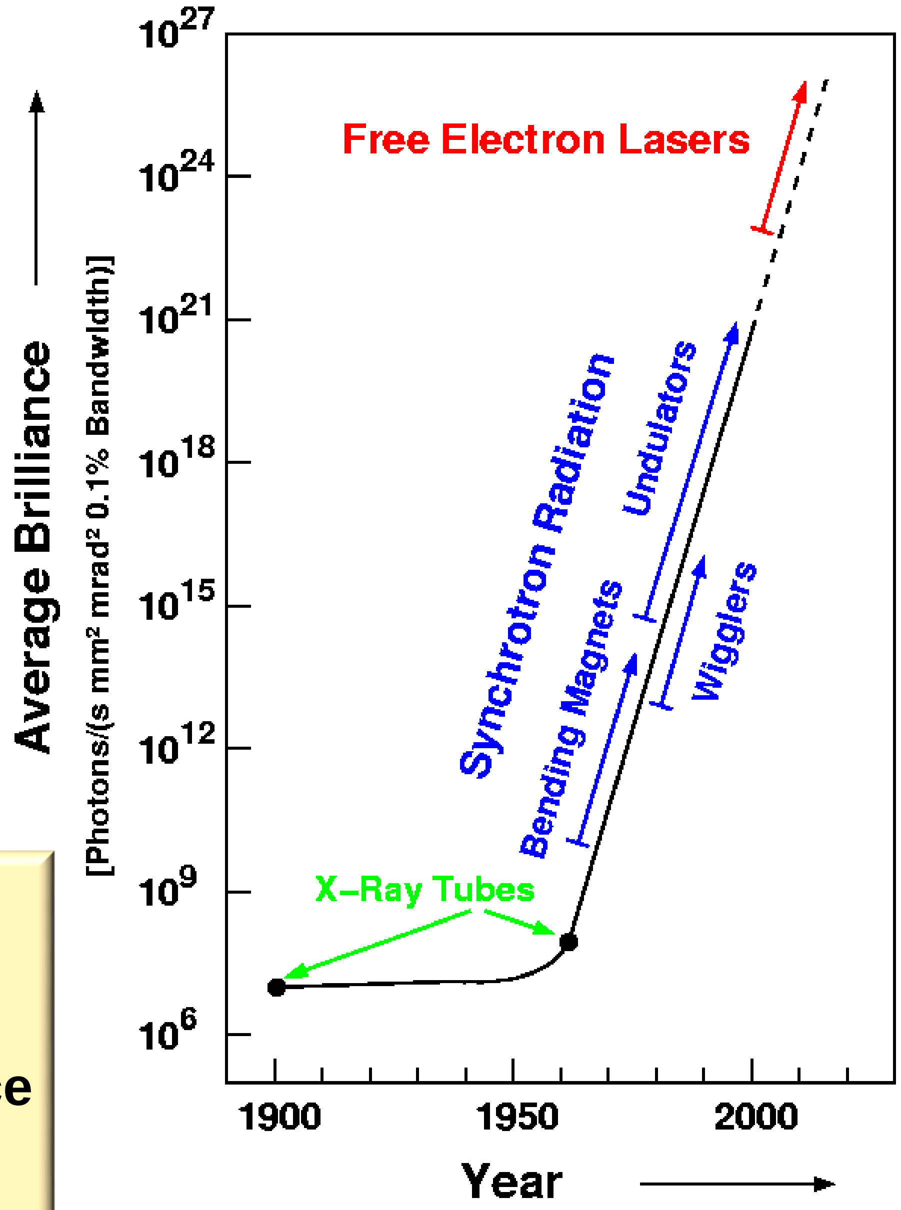
high intensity

>10 000 times
more intense
than
the most modern
X-ray lab source

strong collimation

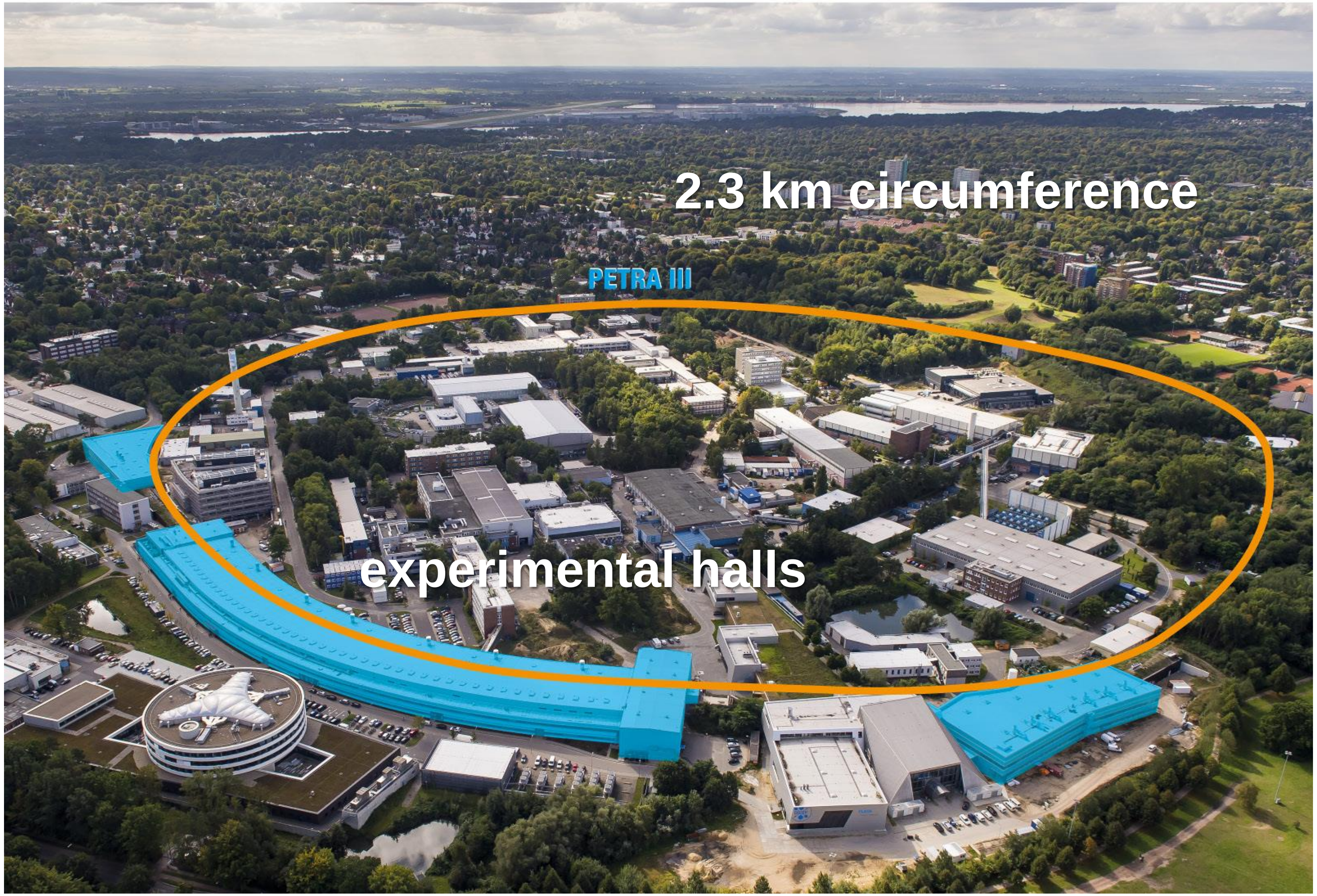
beam size (vertical)
from undulator source
~1 mm at 100 m !

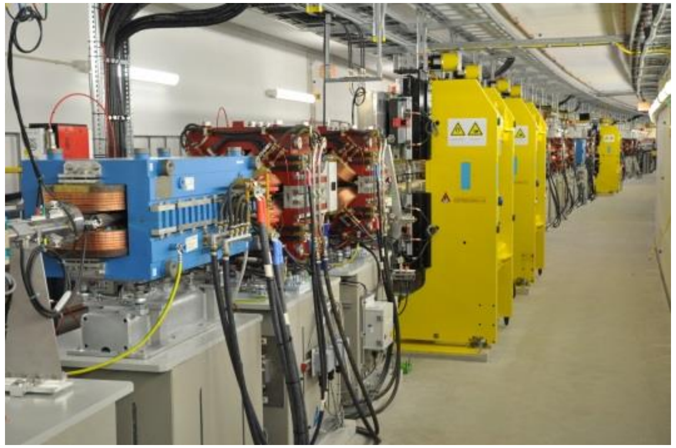
(without focusing)



10.000 x "more light"
per decade since 1965

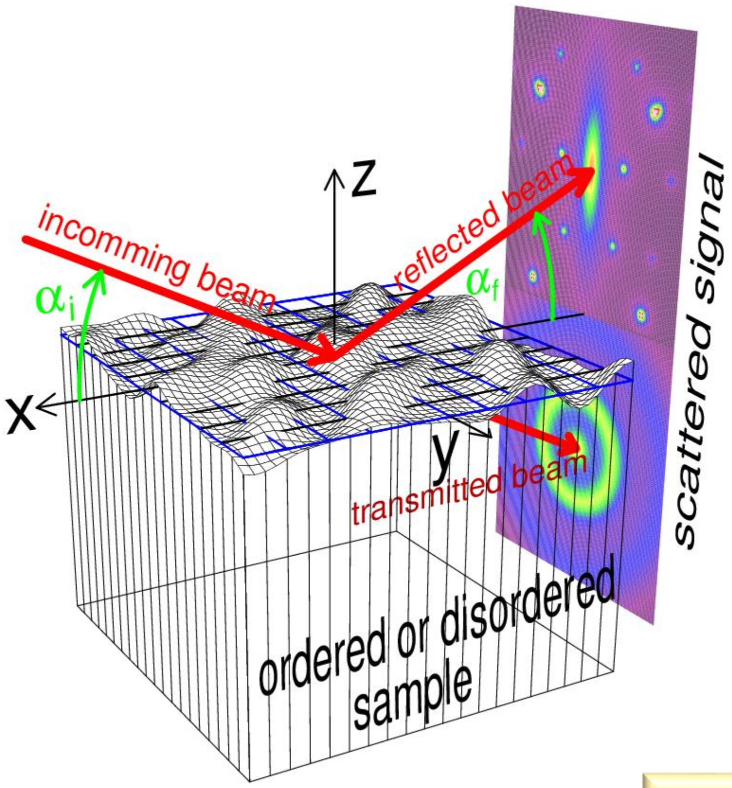
Synchrotron radiation facility (PETRA III in Hamburg)

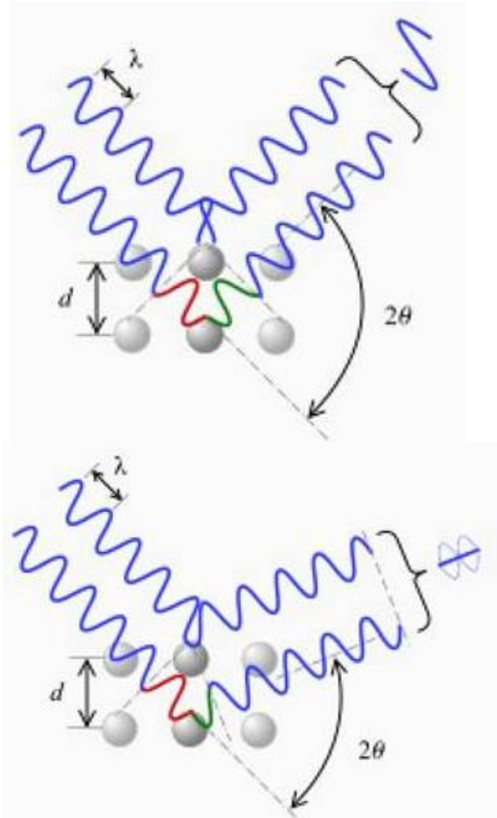




X-rays: excellent probe for the study of material properties

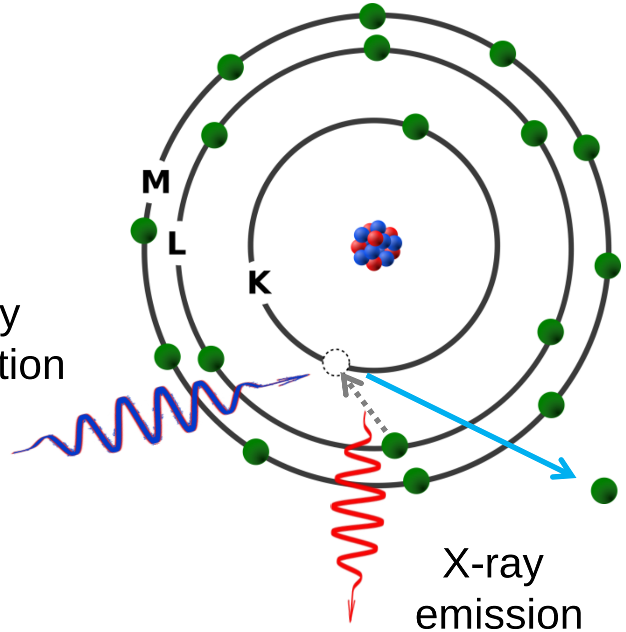
(Elastic) scattering, diffraction, imaging:
geometrical atomic structure, nano particle shapes



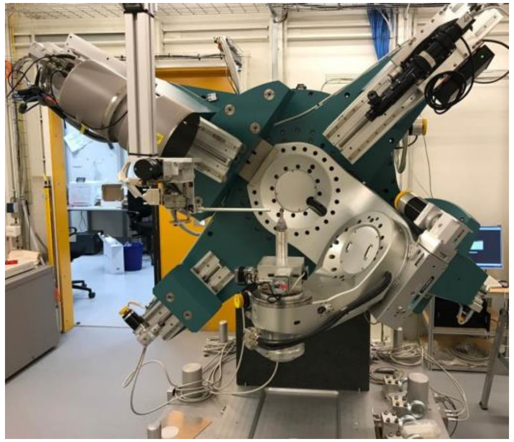


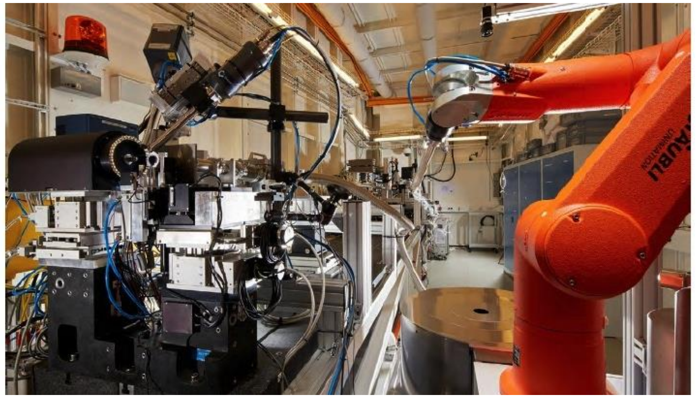
wave interference from atomic scatteres
→ structural information

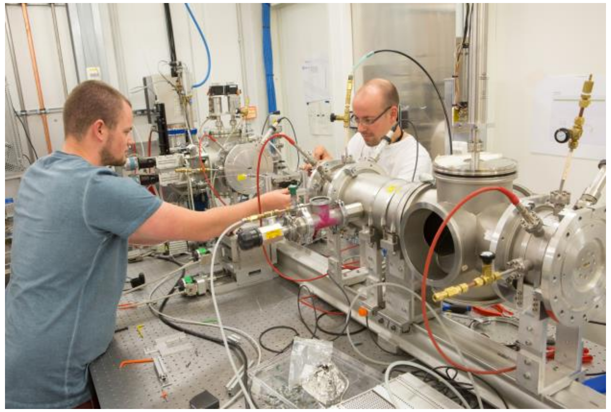
(Inelastic) atomic excitations:
elemental composition and distribution,
chemical bonding,
electronic structure (magnetism, super-conductivity, …)

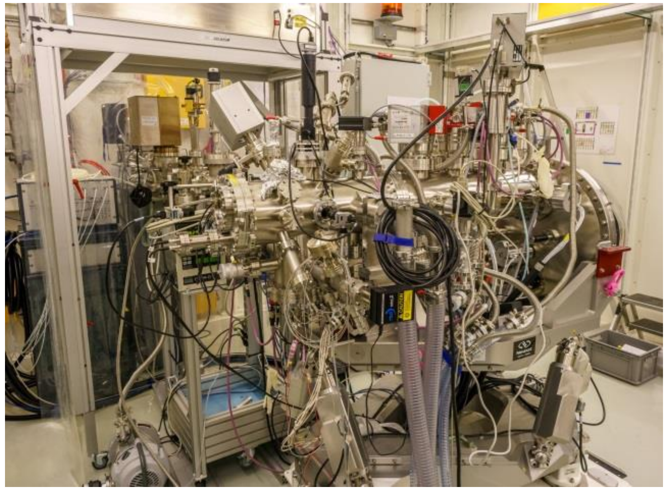


Specialized experimental stations for different applications





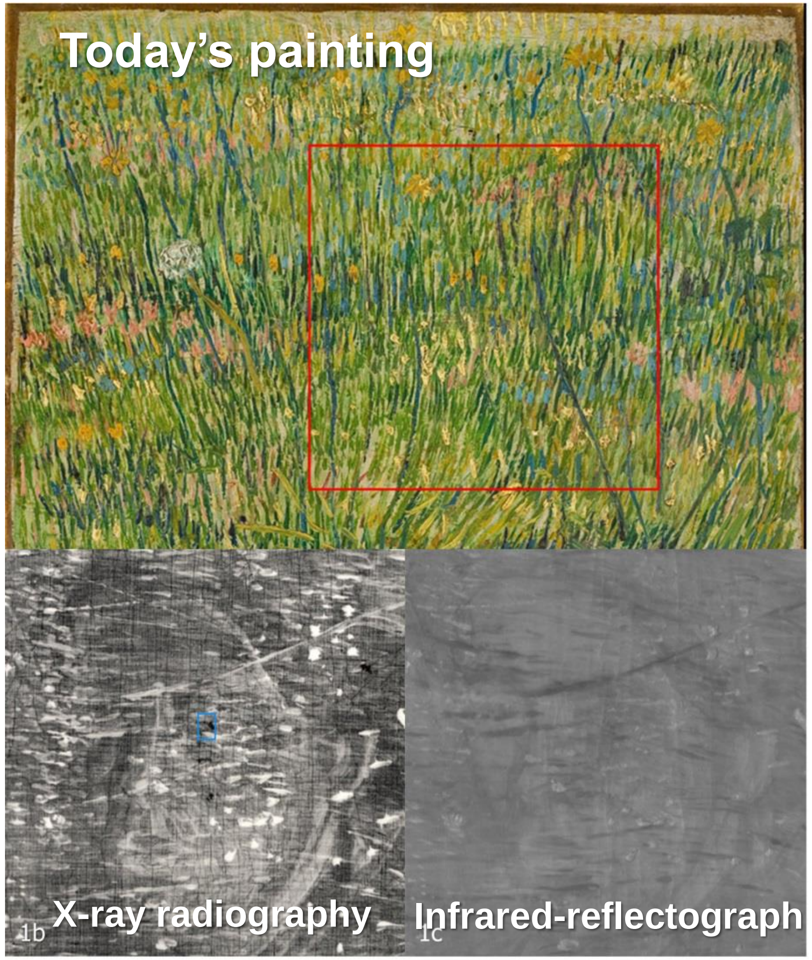




X-rays uncover hidden master pieces

Vincent van Gogh
Patch of Grass
Paris, 1886

Kroeller Mueller Museum
Otterlo, the Netherlands



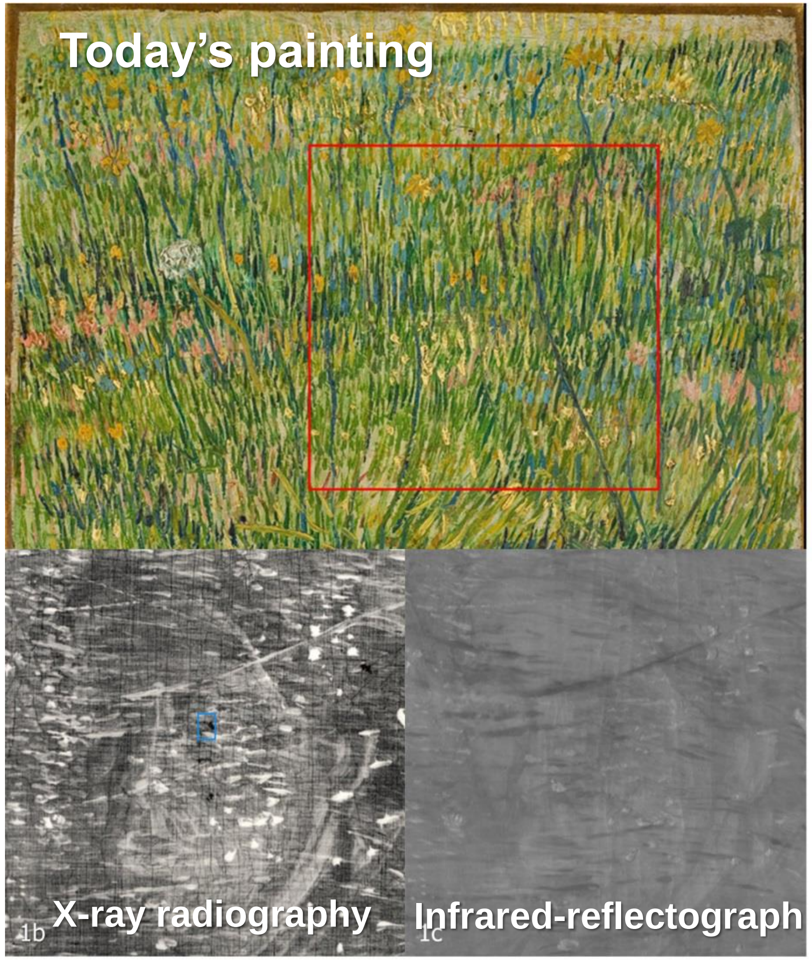
Let‘s begin with an example relating to cultural heritage

van Gogh often re-used his canvaces (by overpainting)

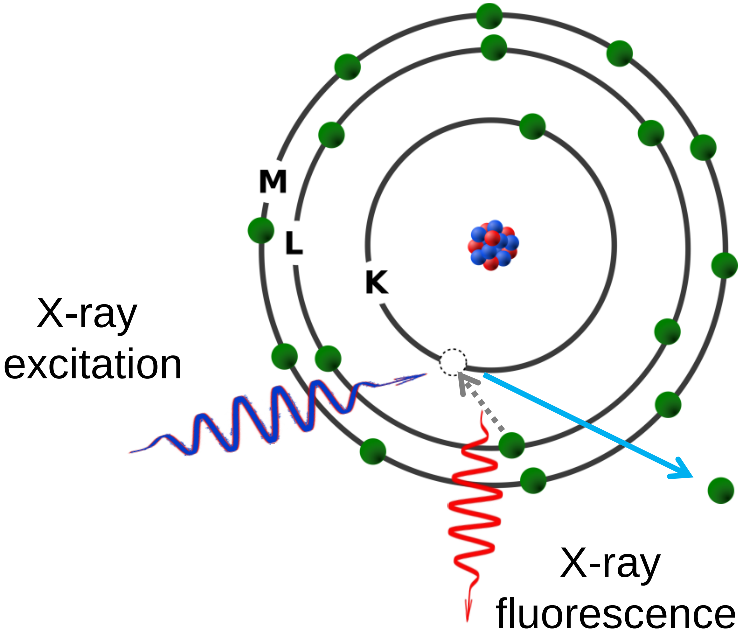
X-rays uncover hidden master pieces

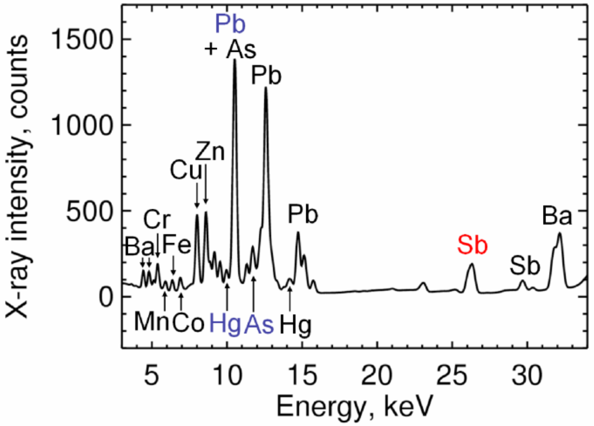
Vincent van Gogh
Patch of Grass
Paris, 1886

Kroeller Mueller Museum
Otterlo, the Netherlands



Idea:
study paint chemistry
by element selective
X-ray fluorescence

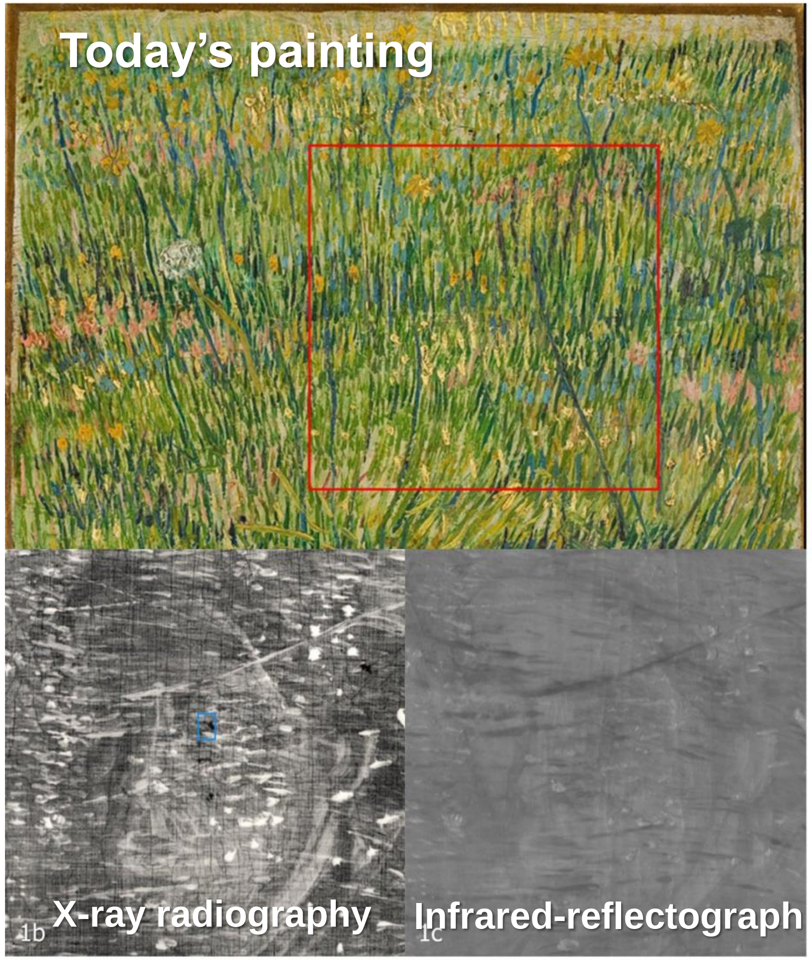




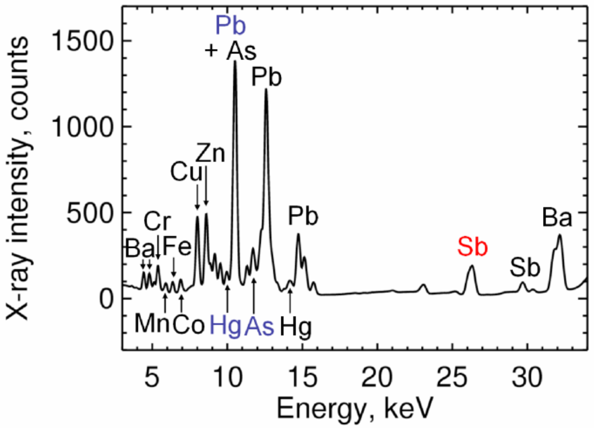
X-rays uncover hidden master pieces

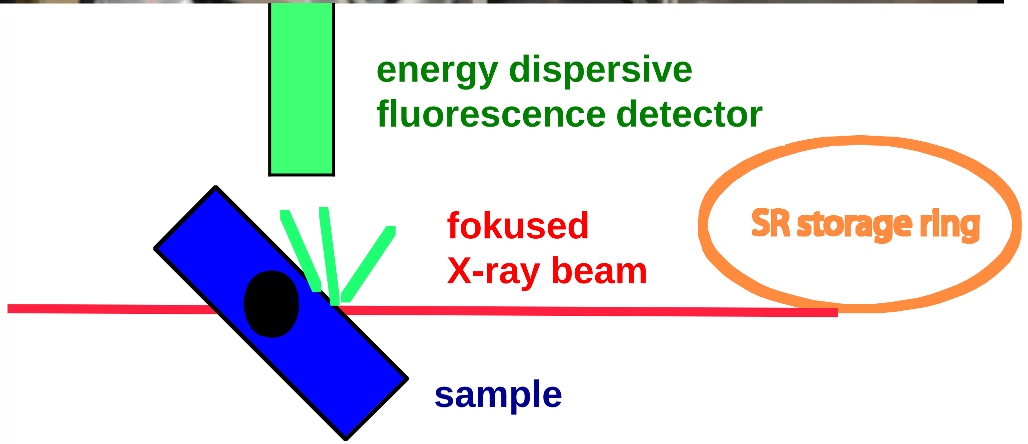
Vincent van Gogh
Patch of Grass
Paris, 1886

Kroeller Mueller Museum
Otterlo, the Netherlands



„pencil beam“
0.5x0.5mm^2

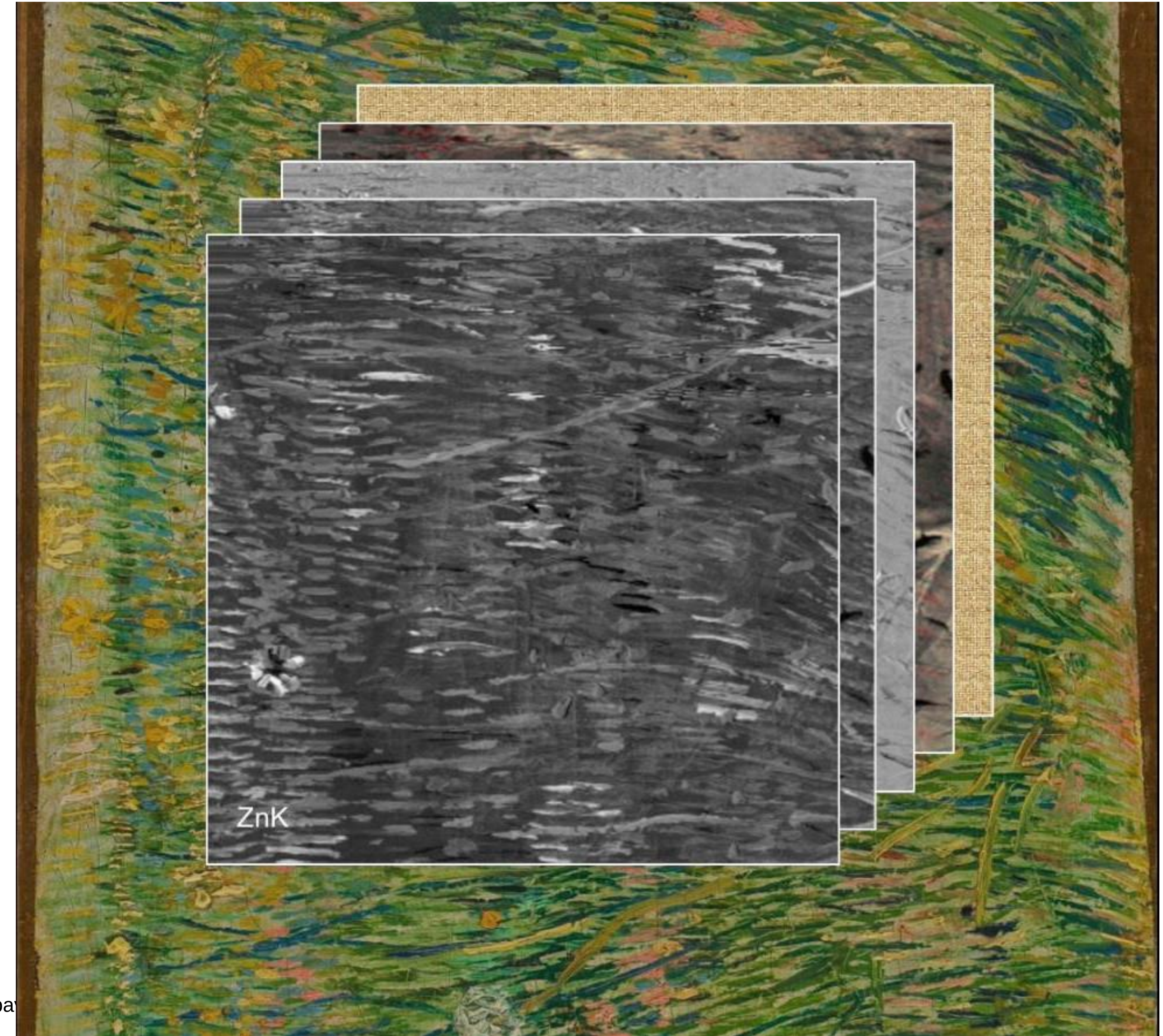




view marked area by paint elements

view marked area by paint elements

Zink



view marked area by paint elements

Barium

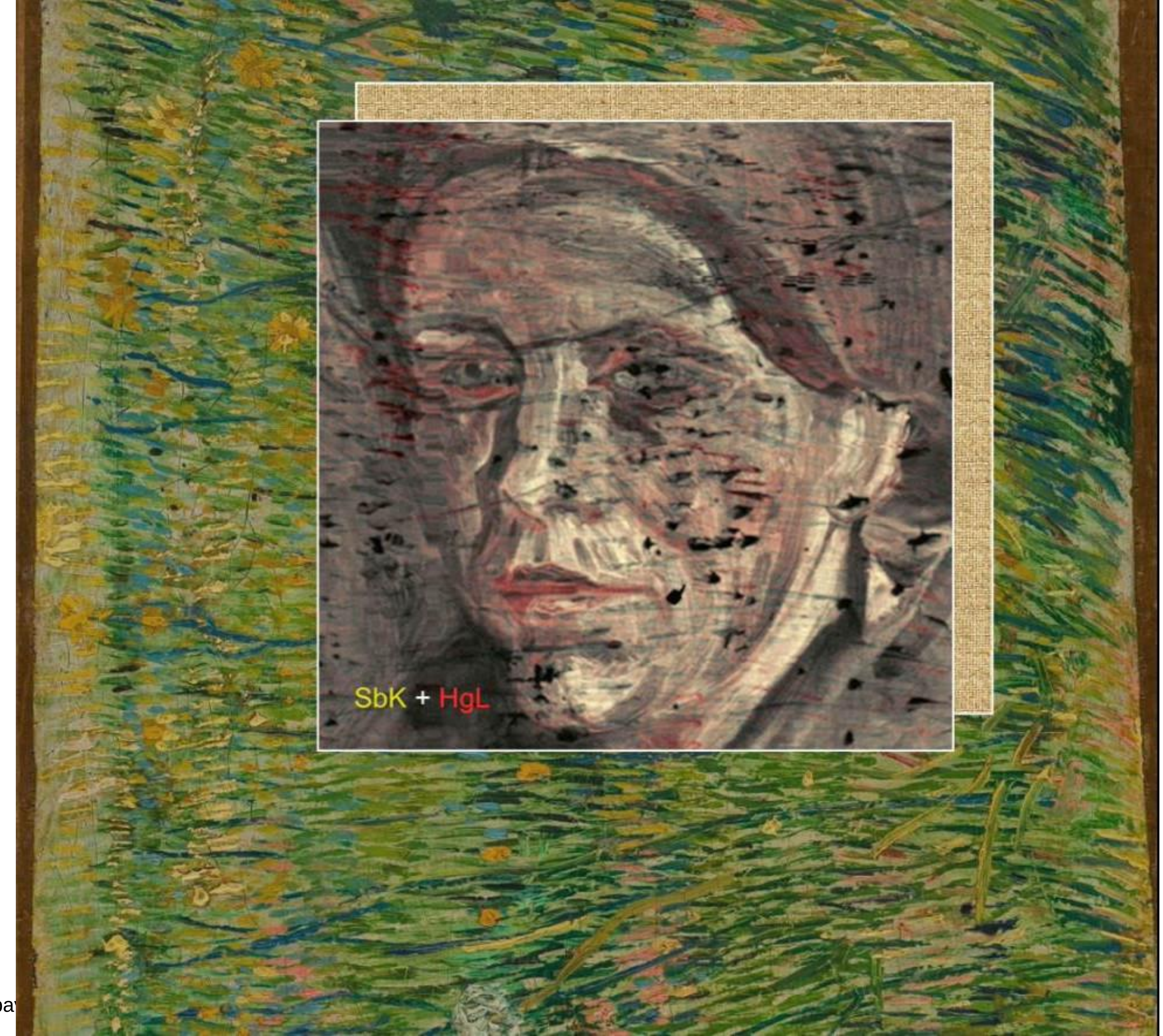
view marked area by paint elements

Lead

view marked area by paint elements

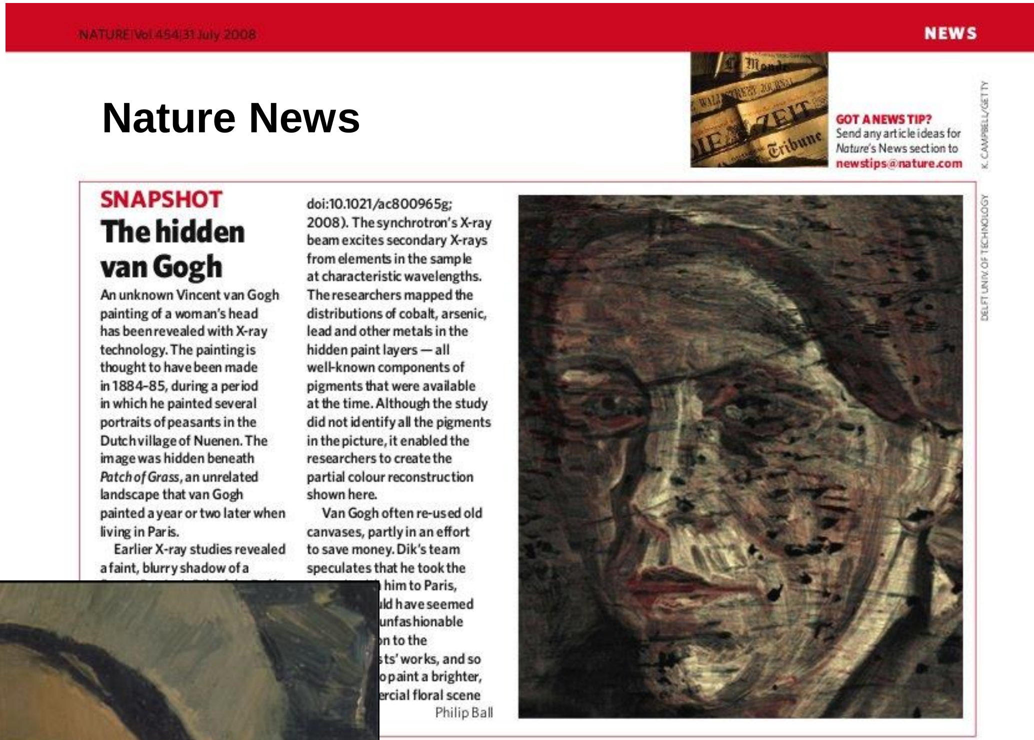
Antimony & Mercury

„Naples yellow“



X-rays uncover hidden master pieces

Nature News



NATURE|Vol 454|31 July 2008

NEWS

GOT A NEWS TIP? Send any article ideas for *Nature's* News section to newstips@nature.com

K. CAMPBELL/GETTY

SNAPSHOT

The hidden van Gogh

An unknown Vincent van Gogh painting of a woman's head has been revealed with X-ray technology. The painting is thought to have been made in 1884–85, during a period in which he painted several portraits of peasants in the Dutch village of Nuenen. The image was hidden beneath *Patch of Grass*, an unrelated landscape that van Gogh painted a year or two later when living in Paris.

Earlier X-ray studies revealed a faint, blurry shadow of a

doi:10.1021/ac800965g; 2008). The synchrotron's X-ray beam excites secondary X-rays from elements in the sample at characteristic wavelengths. The researchers mapped the distributions of cobalt, arsenic, lead and other metals in the hidden paint layers — all well-known components of pigments that were available at the time. Although the study did not identify all the pigments in the picture, it enabled the researchers to create the partial colour reconstruction shown here.

Van Gogh often re-used old canvases, partly in an effort to save money. Dik's team speculates that he took the ... him to Paris, ...ld have seemed ... unfashionable ...n to the ...sts' works, and so ...o paint a brighter, ...ercial floral scene

Philip Ball

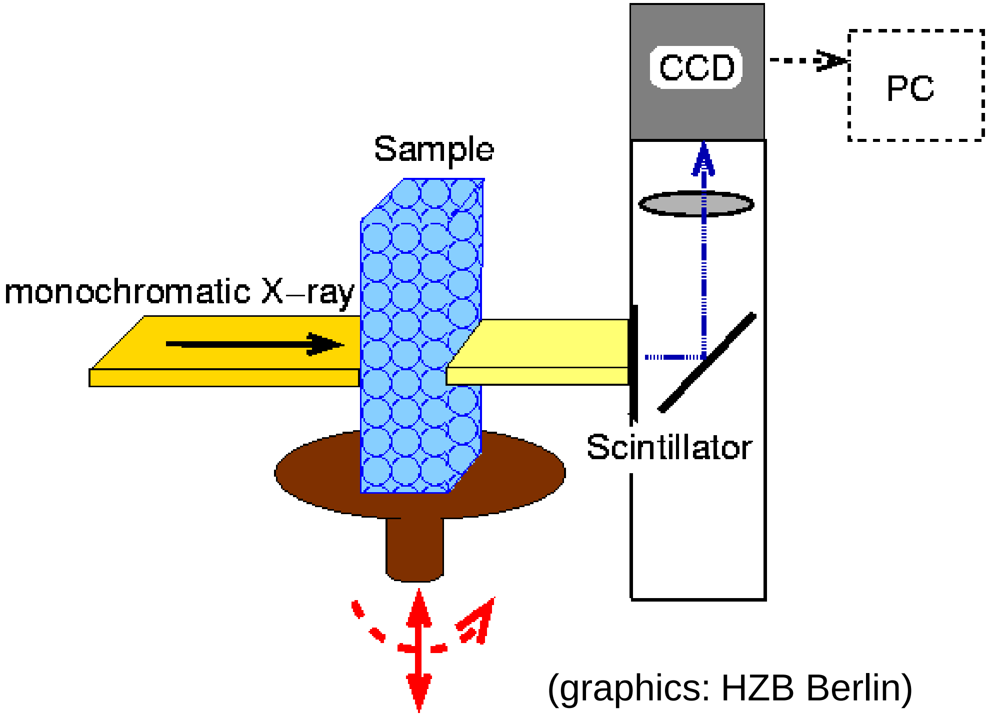
DELFT UNIV. OF TECHNOLOGY

conventional X-ray radiograph

colour reconstruction based on XRF elemental mapping

other, existing painting by Van Gogh

Computed tomography (CT)



(graphics: HZB Berlin)

micro-tomography (µCT)
with highly collimated synchrotron radiation
non-destructive!

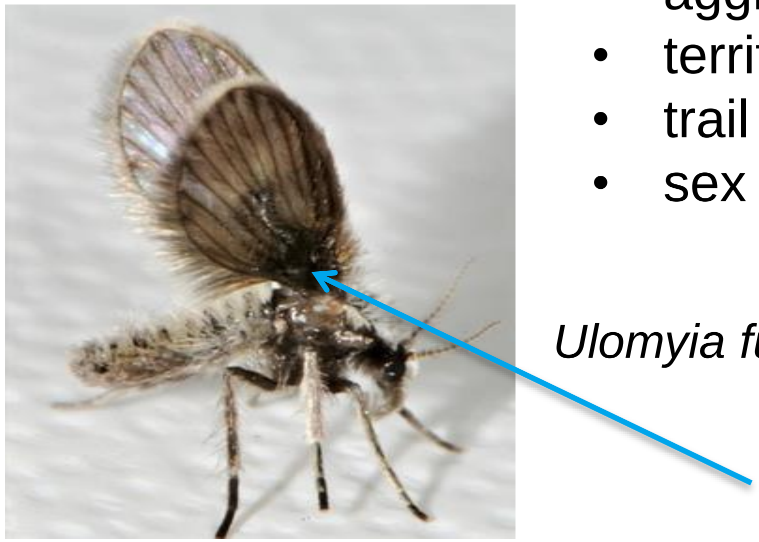
resolution from **µm down to 10 nm**
(with coherent imaging techniques)

Fossil insects preserved in amber (micro-CT)

Pheromones:
trigger certain social responses in members of the same species

They serve different purposes
- alarming
- aggregation
- territorial
- trail
- sex (mating)

Challenge:
can we get any information relating to this from fossils?

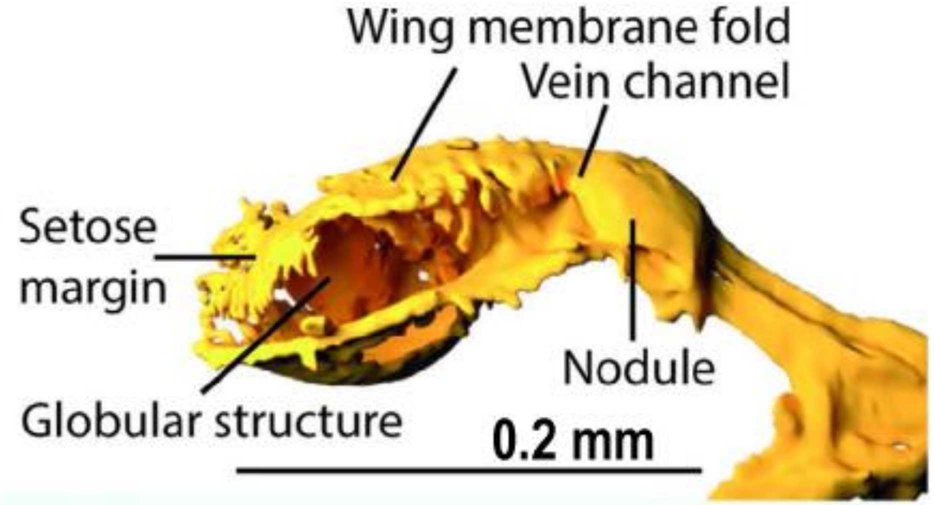


Ulomyia fuliginosa (recent)

pheromone glands
(pocket-like pouch)

Biting midge (Ceratopogonidae)
in 54 million-year-old Indian amber

Fossil insects preserved in amber (micro-CT)



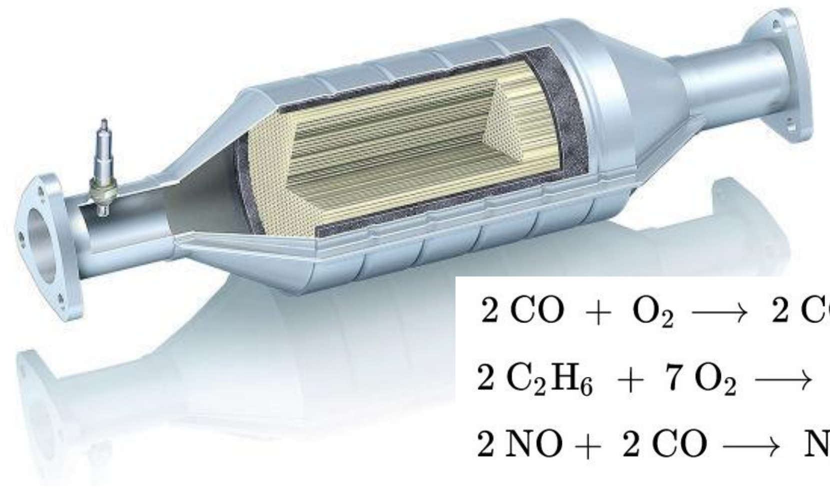
- Pheromone releasing structures on the wings have evolved independently in biting midges
- might be much more widespread in fossil as well as modern insects than known so far
- existed already > 50 Million years ago

Similar to recent *Ulomyia fuliginosa* pheromones may be created by wing veins

SR-μCT pixel size $2.4 \times 2.4\ \mu m^2$

F. Stebner et al., Sci. Rep. 6, 34352 (2016)

Aging of an exhaust gas catalyst (Pt/Al_2O_3)



Typically, the active parts of a catalyst are noble metal particles, e.g. on alumina, deposited on structured supports.

$$2\,CO + O_2 \longrightarrow 2\,CO_2$$

$$2\,C_2H_6 + 7\,O_2 \longrightarrow 4\,CO_2 + 6\,H_2O$$

$$2\,NO + 2\,CO \longrightarrow N_2 + 2\,CO_2$$

Aging of exhaust catalyst in air at 950 C: **µCT (1.27 µm voxel size)** to study deactivation mechanisms (quasi "in-situ")

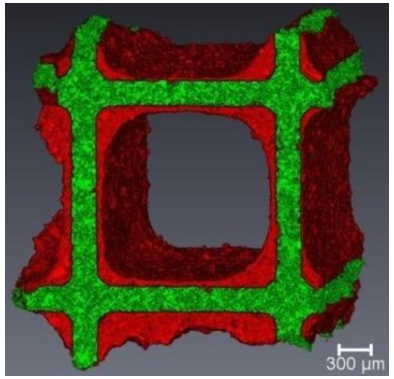
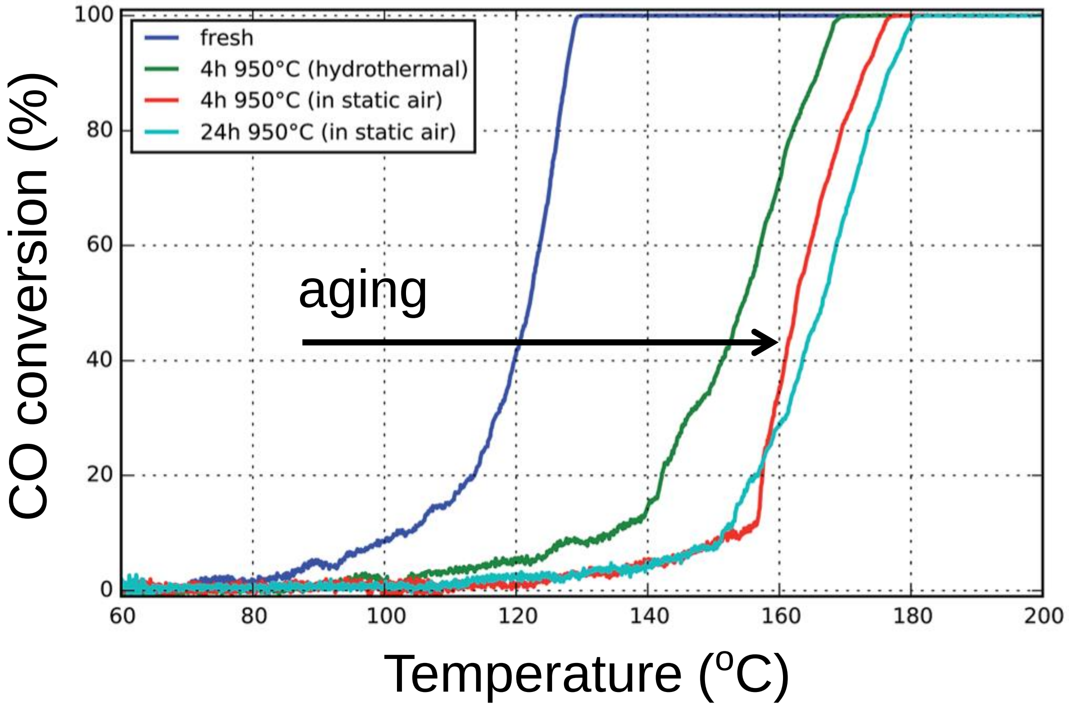
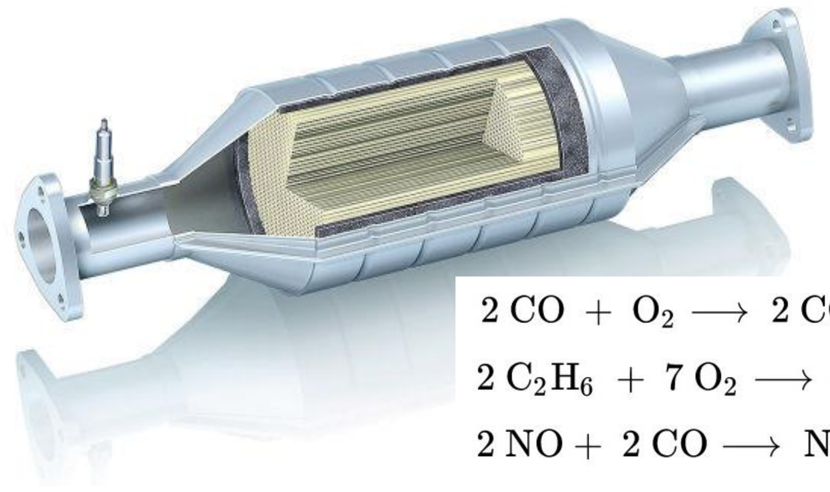


image by electron probe micro analyzer



G. Hofmann et al, *RSC Adv.* **2015**

Aging of an exhaust gas catalyst (Pt/Al_2O_3)



Typically, the active parts of a catalyst are noble metal particles, e.g. on alumina, deposited on structured supports.

$$2\,CO + O_2 \longrightarrow 2\,CO_2$$

$$2\,C_2H_6 + 7\,O_2 \longrightarrow 4\,CO_2 + 6\,H_2O$$

$$2\,NO + 2\,CO \longrightarrow N_2 + 2\,CO_2$$

Aging of exhaust catalyst in air at 950 C:
µCT (1.27 µm voxel size) to study deactivation mechanisms (quasi “in-situ”)

Initially nm-sized Pt particles grow into larger crystals and agglomerate preferentially in voids between support grains

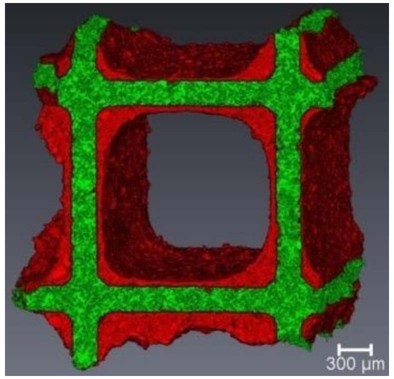
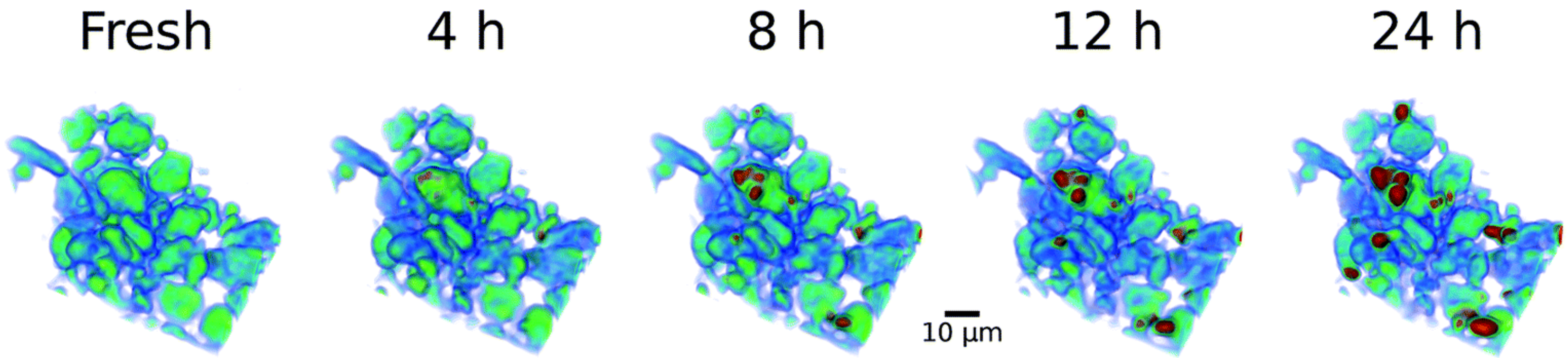


image by electron probe micro analyzer



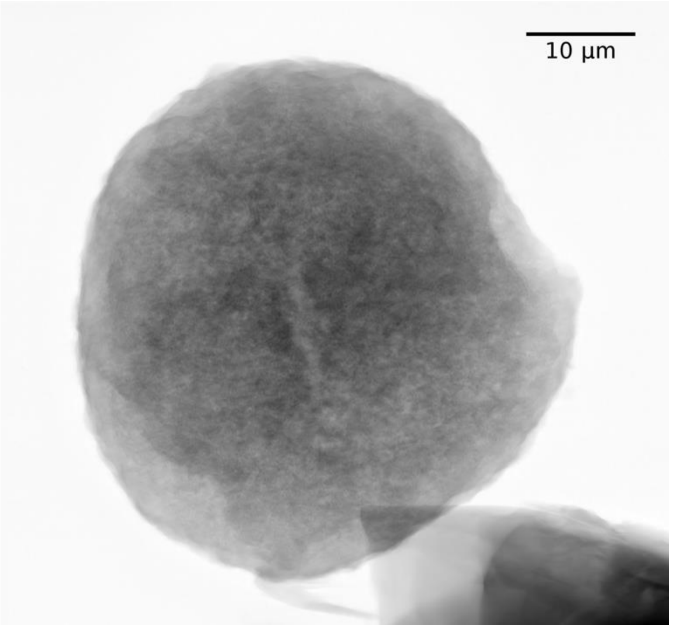
G. Hofmann et al, *RSC Adv.* **2015**

Again: catalyst aging

Fluid catalytic 'cracking'

- Conversion of the high-boiling parts of crude oil into more valuable low-boiling parts such as petrol
- Catalysts lose their effectiveness over time

Catalyst particle

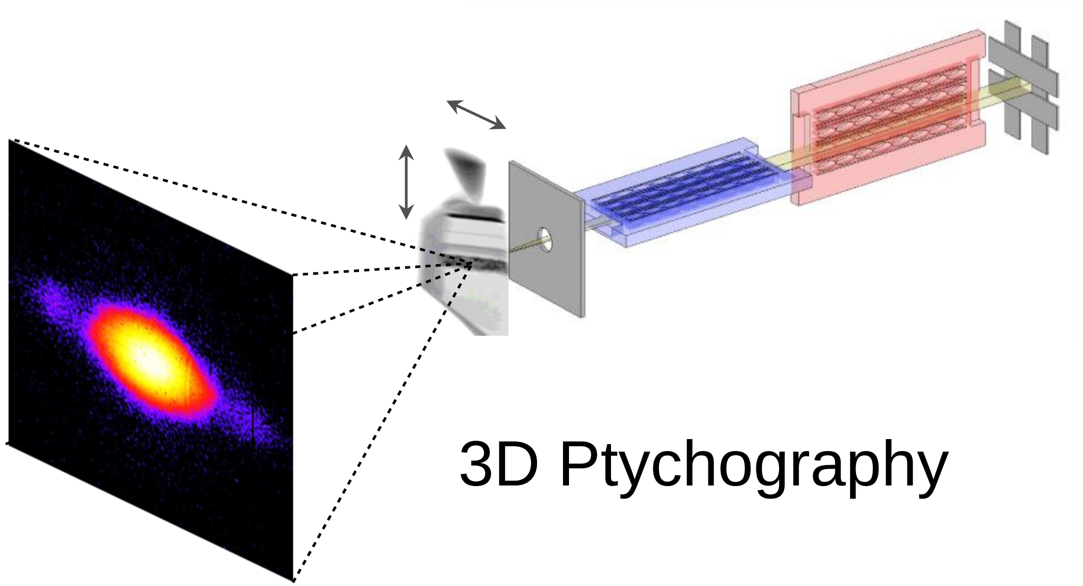


Zeolit

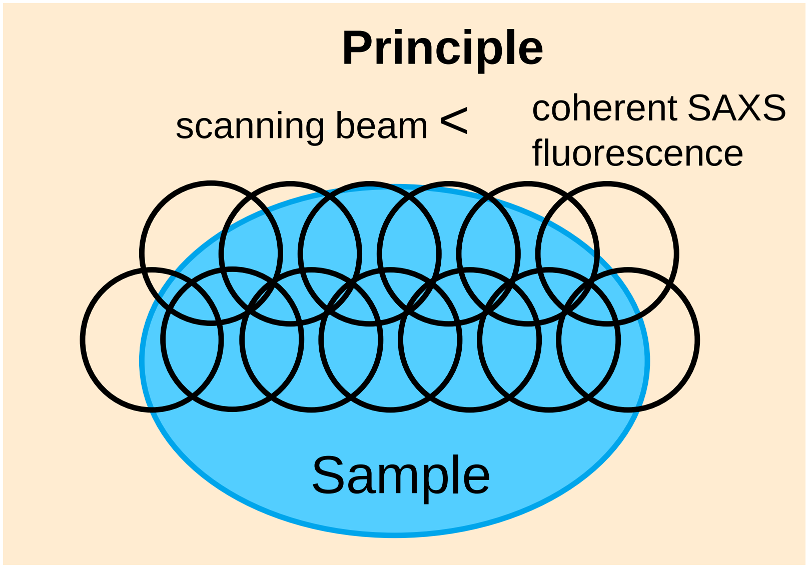
J. Garrevoet, S. Kalirai, *et al.*, unpublished

3D X-ray fluorescence tomography of (aged) catalytical particles

Combined X-ray ptychography and XRF imaging:
simultaneously structural and element specific data with **< 1µm resolution**



3D Ptychography



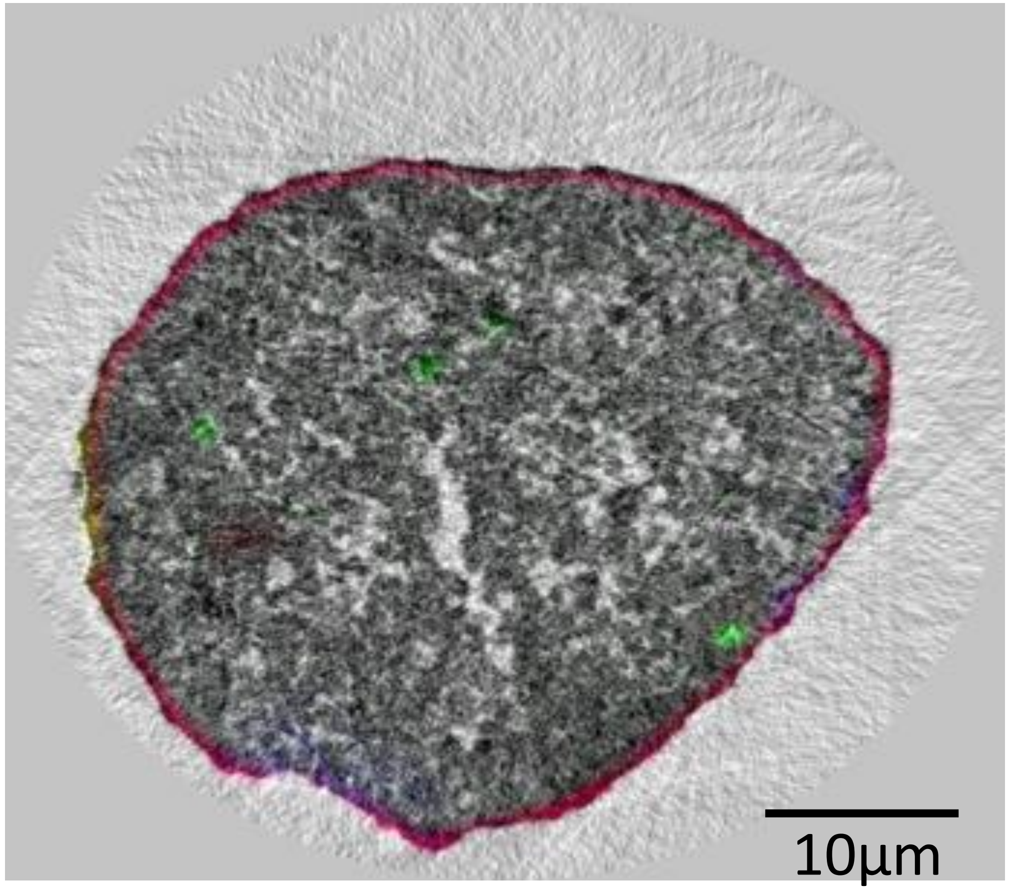
computational imaging from
set of full-field images
with coherent illumination

Data challenge: tomography dataset
Field of view 100 x 100 µm, beam size 300 x 300 nm
130,000 spectra/diffraction patterns per projection, 12 min/projection
178 projections → **3 TB/tomogram** (compress. factor >40)

3D X-ray fluorescence tomography of (aged) catalytical particles

Finding:
metal residuals poison the catalyst: transport into into the particle is clogged by built up of Fe/Ni layer

Tomographic reconstruction



Simultaneous reconstruction of element distribution:

- Fe
- Ni
- Ti
- Ga (marker)

resolution (by beam size): 300 nm

structural data (electron density): resolution (by ptychography): <100nm

J. Garrevoet, S. Kalirai et al. (2017)

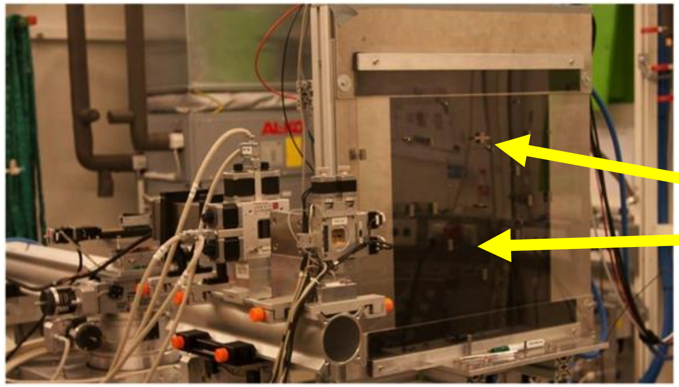
Catalyst at work on the atomic scale

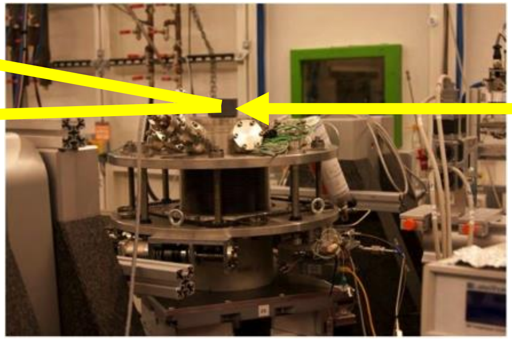
study of catalytic under realistic conditions
with structural information on the atomic scale

$$2\,CO + O_2 \longrightarrow 2\,CO_2$$

$$2\,C_2H_6 + 7\,O_2 \longrightarrow 4\,CO_2 + 6\,H_2O$$

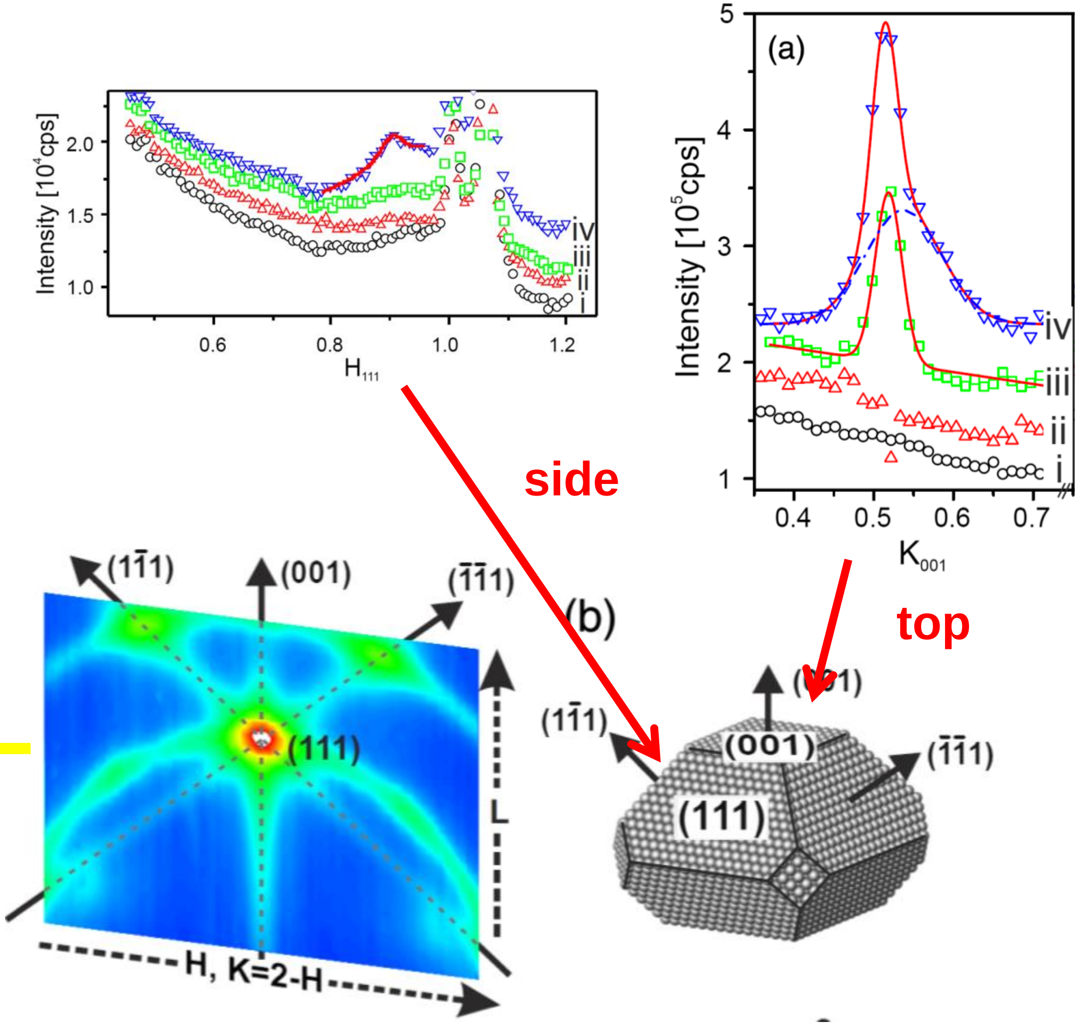
$$2\,NO + 2\,CO \longrightarrow N_2 + 2\,CO_2$$





Hejral et al., PRL (2018)

CO oxidation over PtRh nano particles
in-situ X-ray diffraction during the
catalytic process

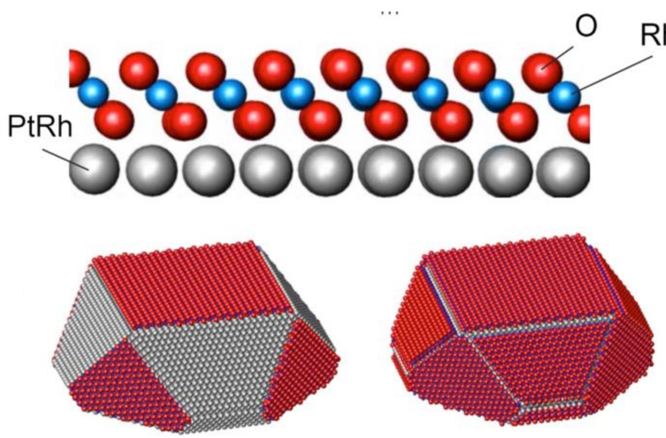


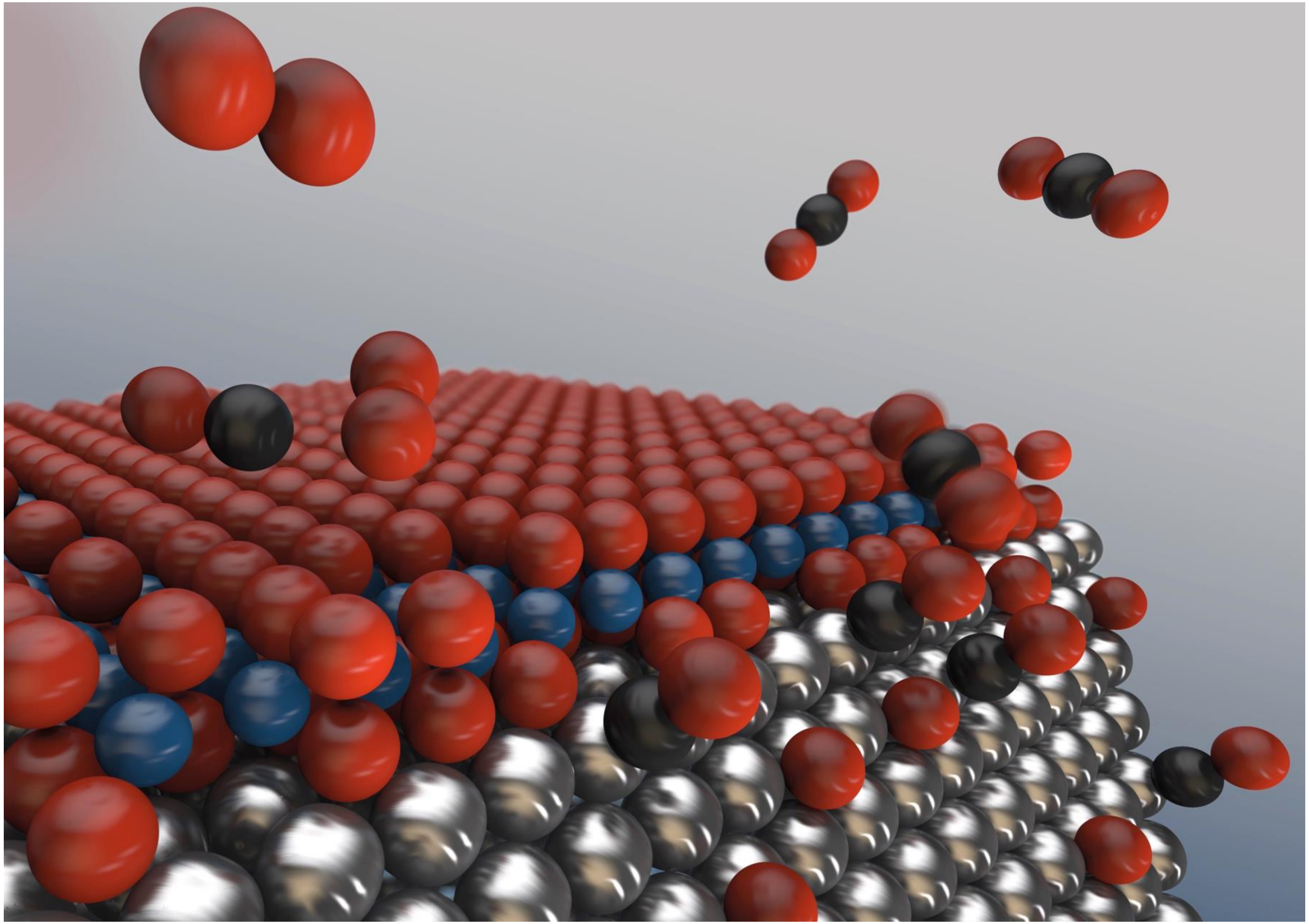
Catalyst at work on the atomic scale

Increasing O2 (red) concentration:
→ O-Rh-O sandwiches form
→ CO→CO_2 reaction inhibited

At the edges:
sandwiches brake up
→ free active sites for catalysis

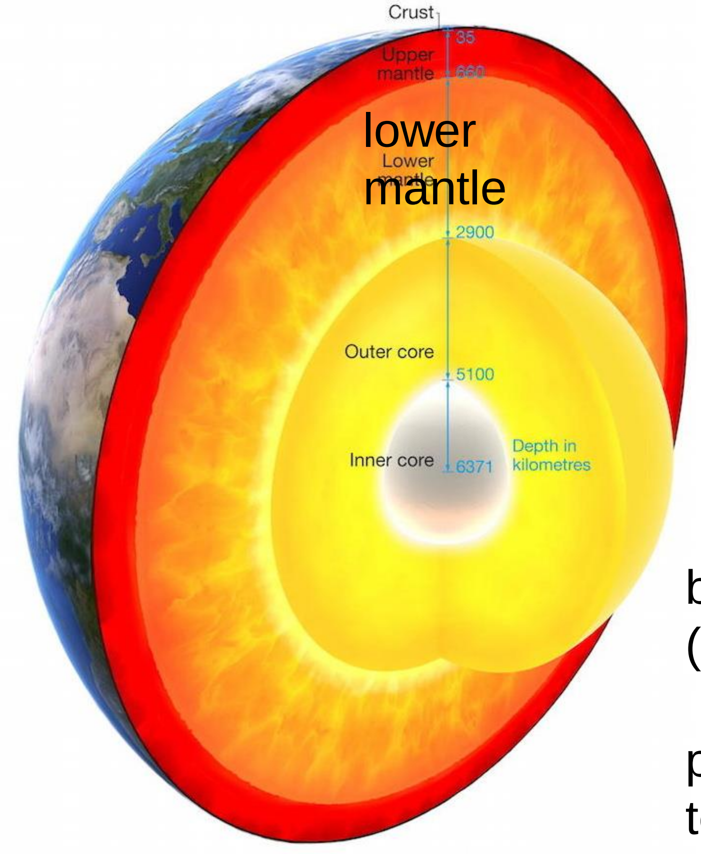
Conclusion:
more edges
→ more catalytic efficiency

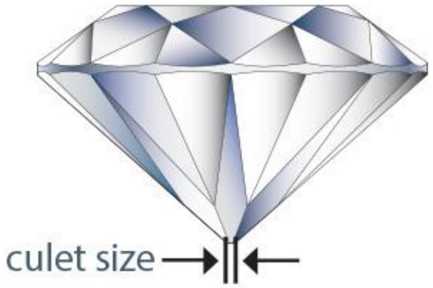




Materials under extreme conditions

- structure and dynamics of our planet ?
  physical and chemical properties of lower mantle
- try to generate similar conditions in the lab
- lower mantle: about ½ the Earth volume
  ~80% is bridgmanite [(Mg,Fe)(Si,Al)O_3]



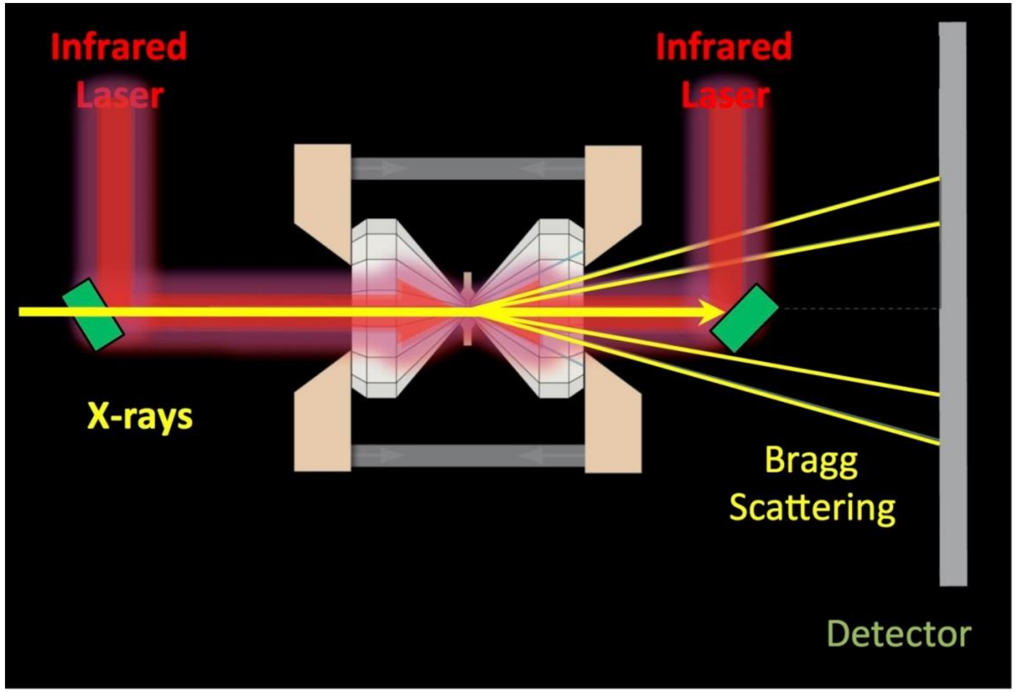


120 µm

bottom of the lower mantle (~2900km):

pressure ~136 GPa (1.4 Mbar)
temperature ~ 3000 K

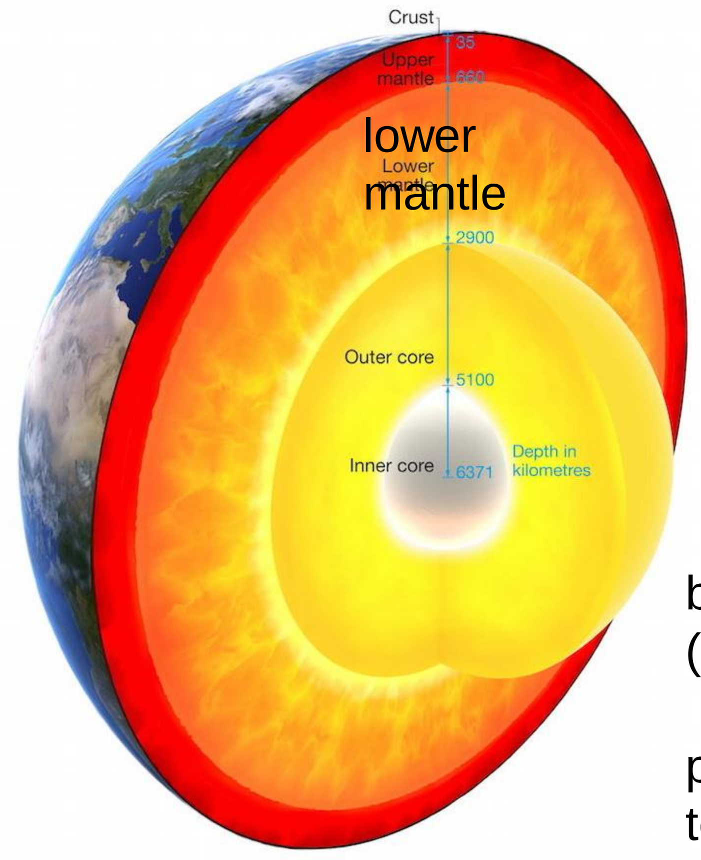
Experiment:
- **laser-heated diamond anvil cell**
- brilliant synchrotron X-rays for diffraction
- crystal size ~10x10x5 µm^3
- **X-ray beam size ~3x5 µm^3**



range: 32 to 130 GPa
2200 to 3100 K

Materials under extreme conditions

- structure and dynamics of our planet ?
  physical and chemical properties of lower mantle
- try to generate similar conditions in the lab
- lower mantle: about ½ the Earth volume
  ~80% is bridgmanite [(Mg,Fe)(Si,Al)O_3]



bottom of the lower mantle (~2900km):

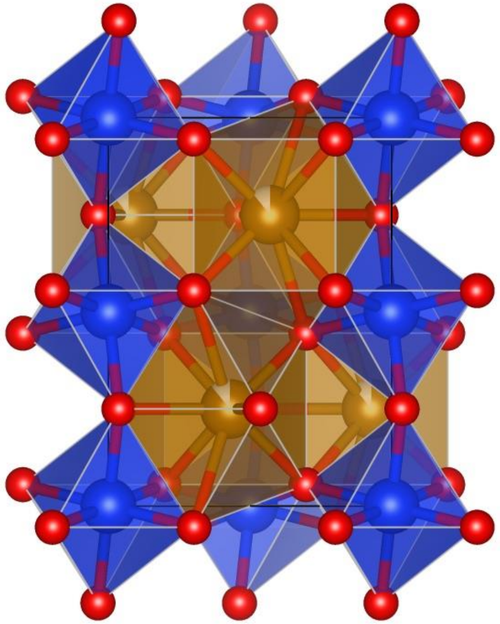
pressure ~136 GPa (1.4 Mbar)
temperature ~ 3000 K

very few data on bridgmanite structure under these conditions & inconclusive results

Result here:

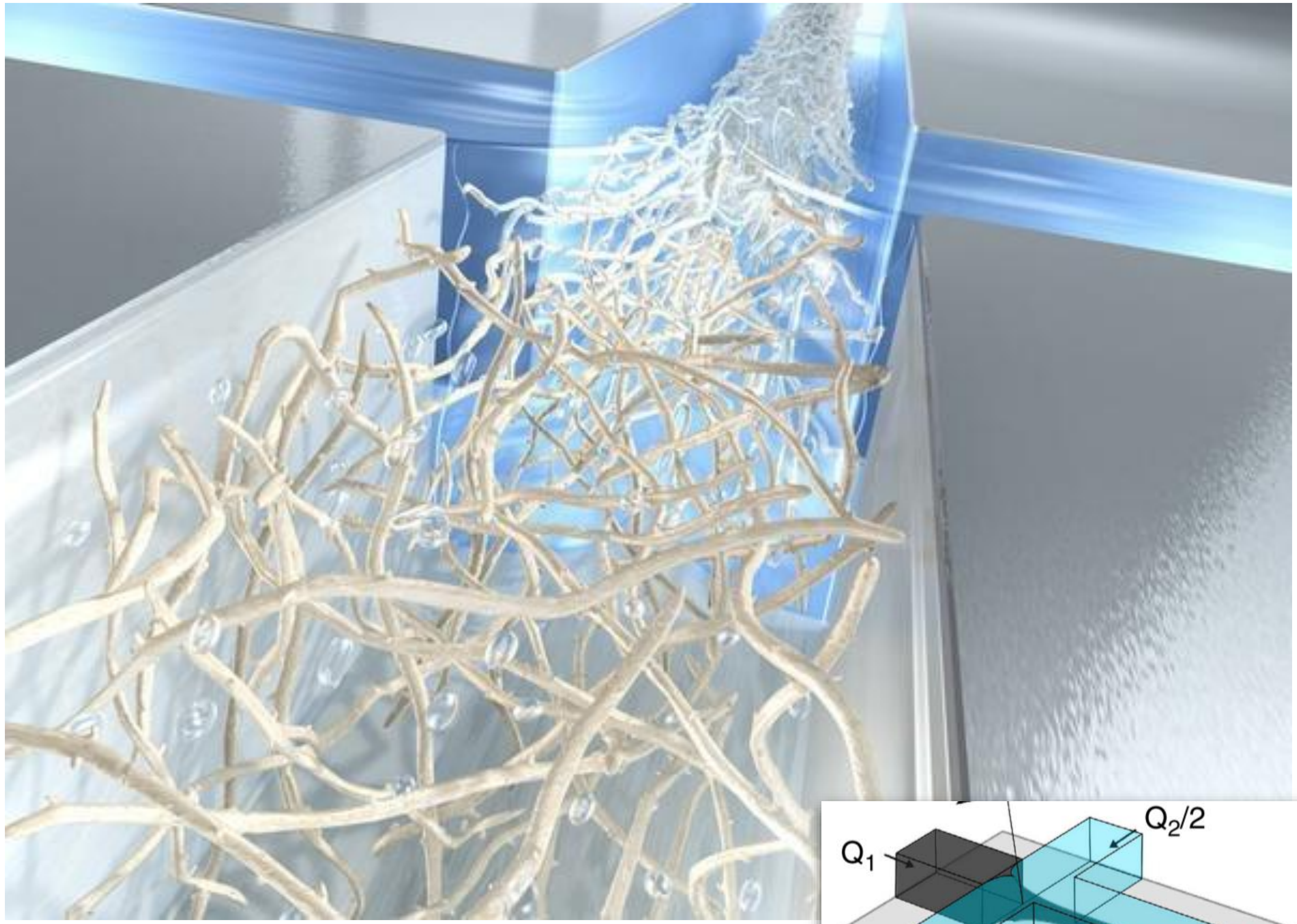
- bridgmanite forms Fe-bearing varieties (not synthesized before)
- stable up to 120 GPa and 3000 K
- compressibility is different from any known bridgmanite

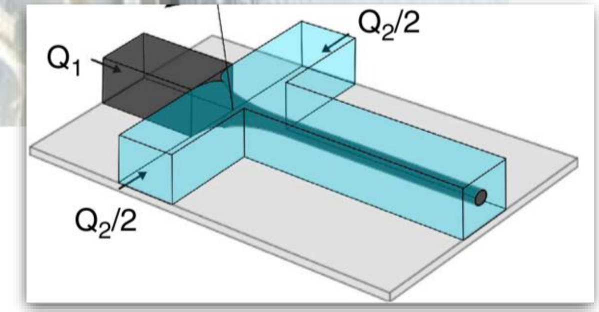
→ **direct implications for interpretation of seismic data**



Ismailova et al. Sci. Adv. (2016)

Learning from nature: biomimetic materials from cellulose





Cellulose nano fibrils:

- Building blocks for bio-based materials
- Nanostructure determines material properties (controlled fabrication needed)

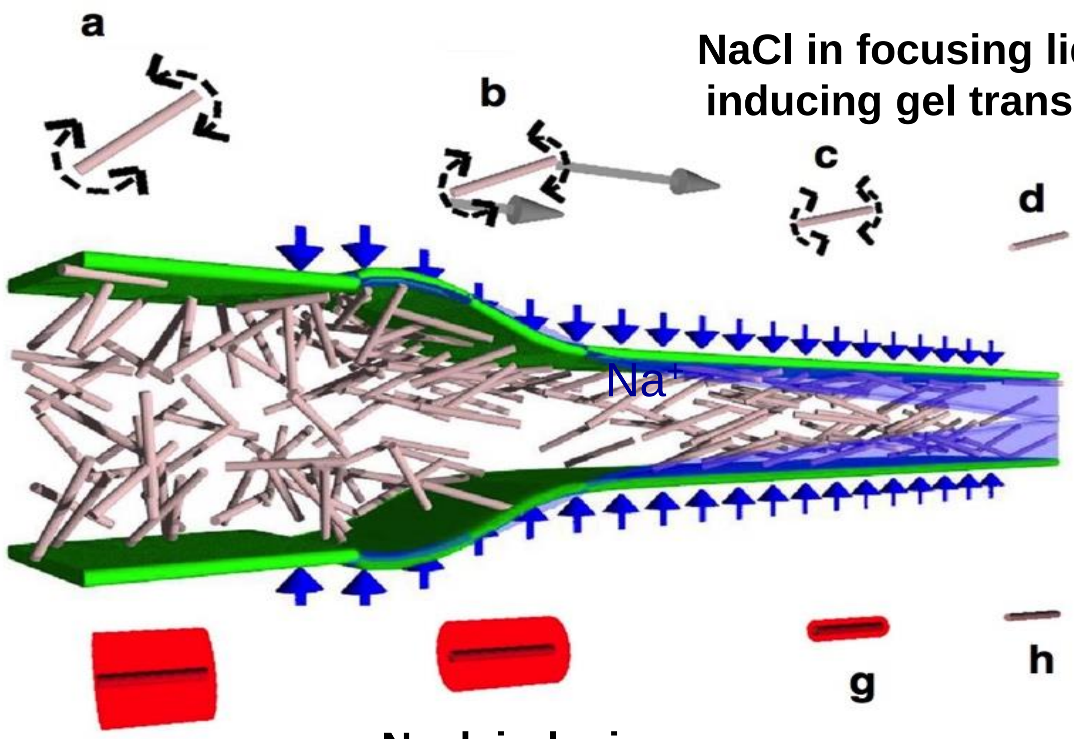
Here:

- Use hydrodynamic alignment with dispersion-gel transition
- fibril orientation controlled by process parameters

Result:

- specific ultimate strength highest among filaments made of nanofibrils (comparable to wood)

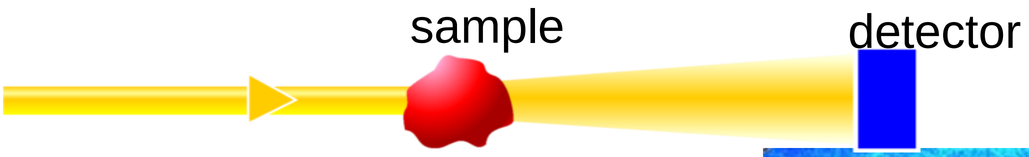
Microfluidic alignment of nano fibrils



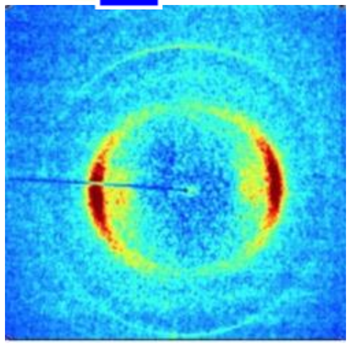
NaCl in focusing liquid inducing gel transition

Unoriented nanofibrils in dispersion

Neck inducing order of nanofibrils

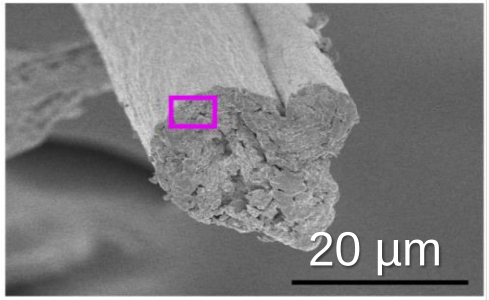


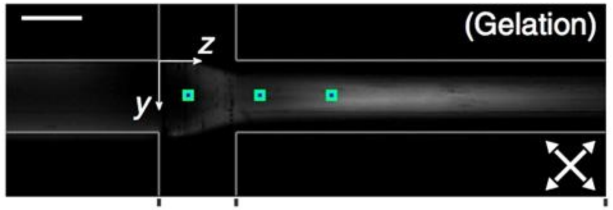
ca. 1 μm² X-ray beam

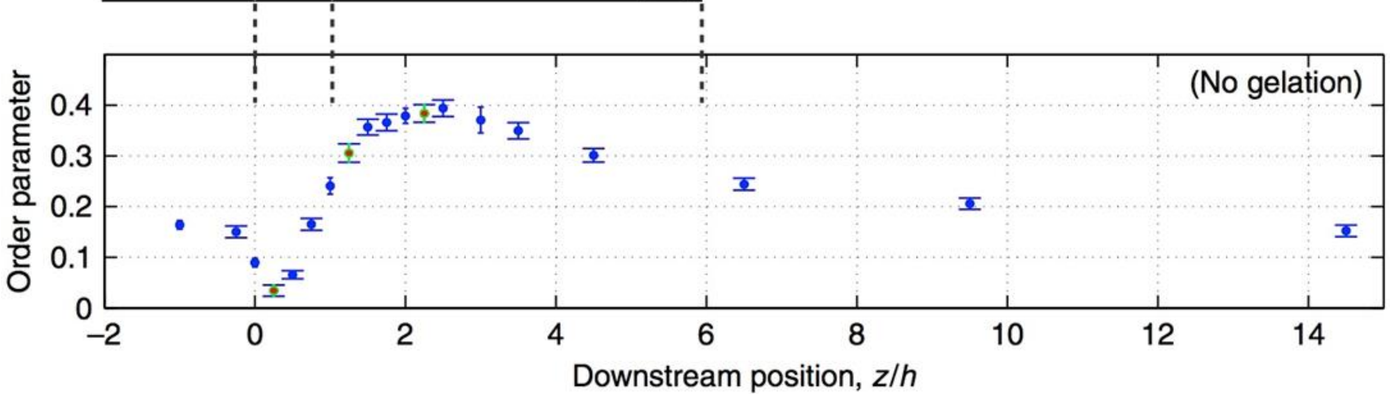


X-ray scattering reveals strong orientational order → strong fiber

Strong cellulose filament out (20 μm thick)





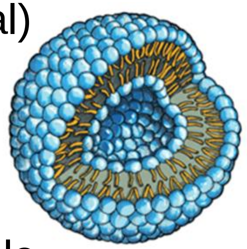


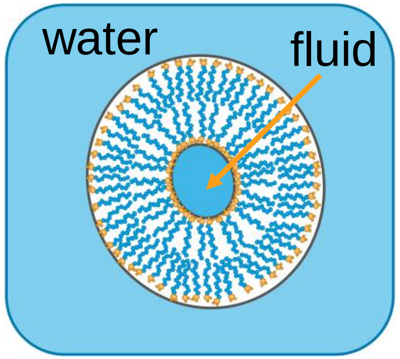
K. M. O. Håkansson, et al., Nature Commun. **5**, 4018 (2014).

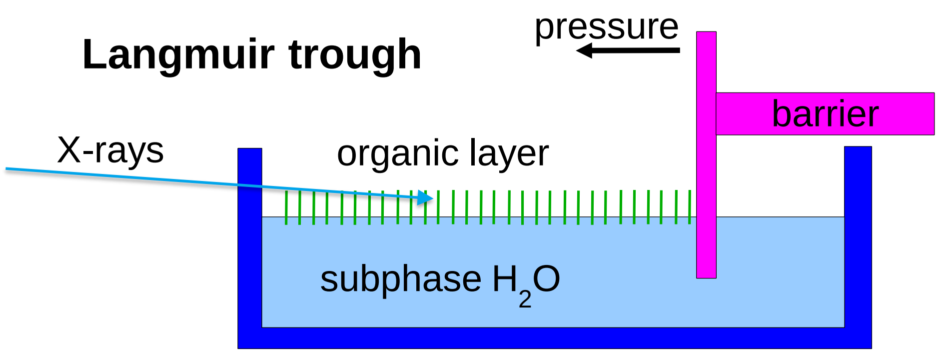
Towards controlled drug delivery inside the body

Tailored vesicles from lipid membranes

- Vesicles are natural containers (surface tension: typically spherical)
- Potential medical application in drug delivery
- Difficulty:
  ➔ spherical vesicles are very stable
  ➔ no “break on demand” for medical applications







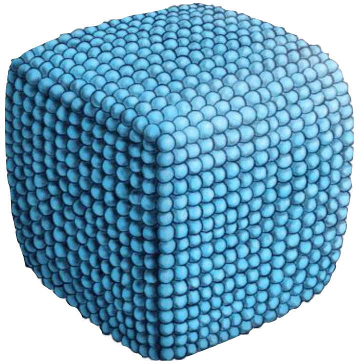
Grazing Incidence X-ray diffraction

- reveals the in-plane structure
- depending on pressure

Here: very stiff lipid (1,2-diamidophospholipid)

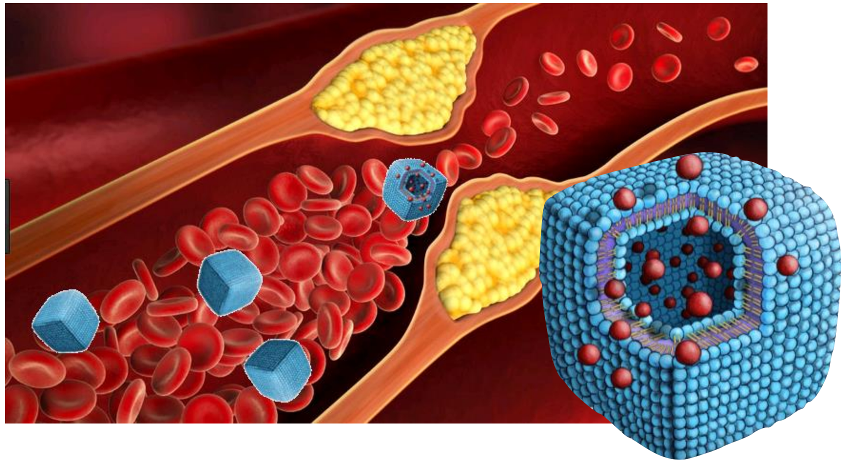
➔ opposes bending

➔ cubic vesicles



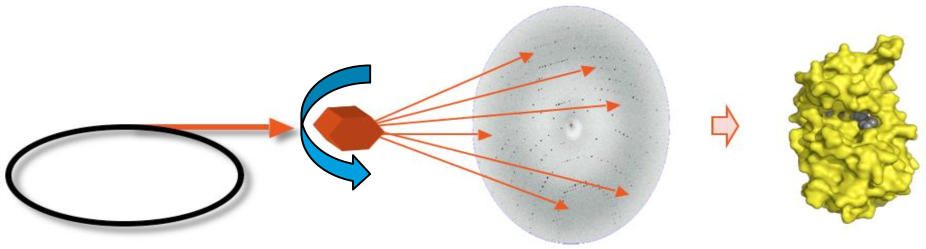
What molecular structure creates this effect?

- Already crystalline at very small pressures
- vesicle can be designed to break easily at edges
- good for drug delivery

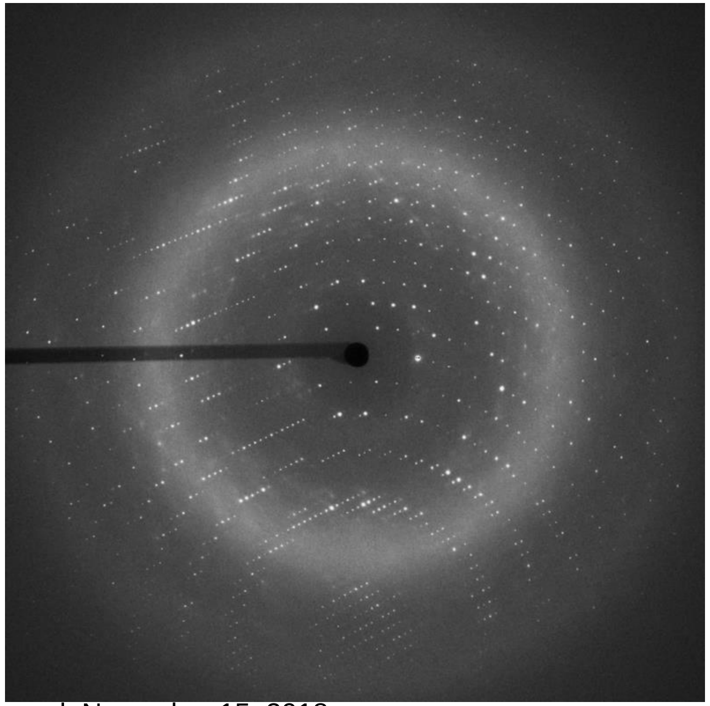


F. Neuhaus, et al. Angew. Chemie Int. Ed. **56**, 6515 (2017)

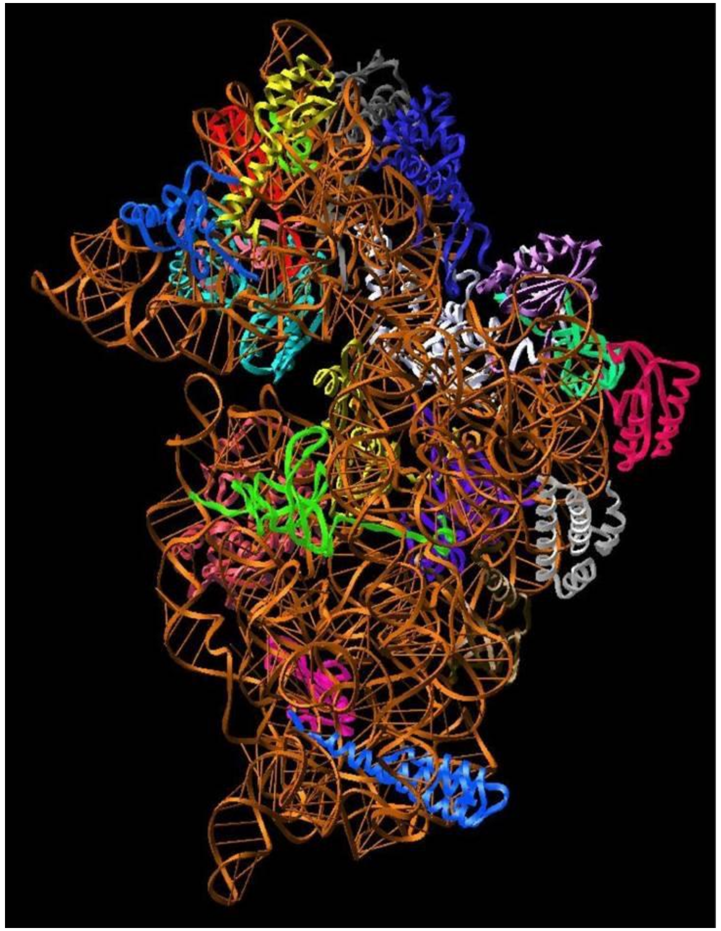
Life sciences: detailed structure of macro molecules



Diffraction of bright, well collimated X-rays ideal for structure determination of (µm-sized) crystals of bio material



Structure of the Ribosome molecule

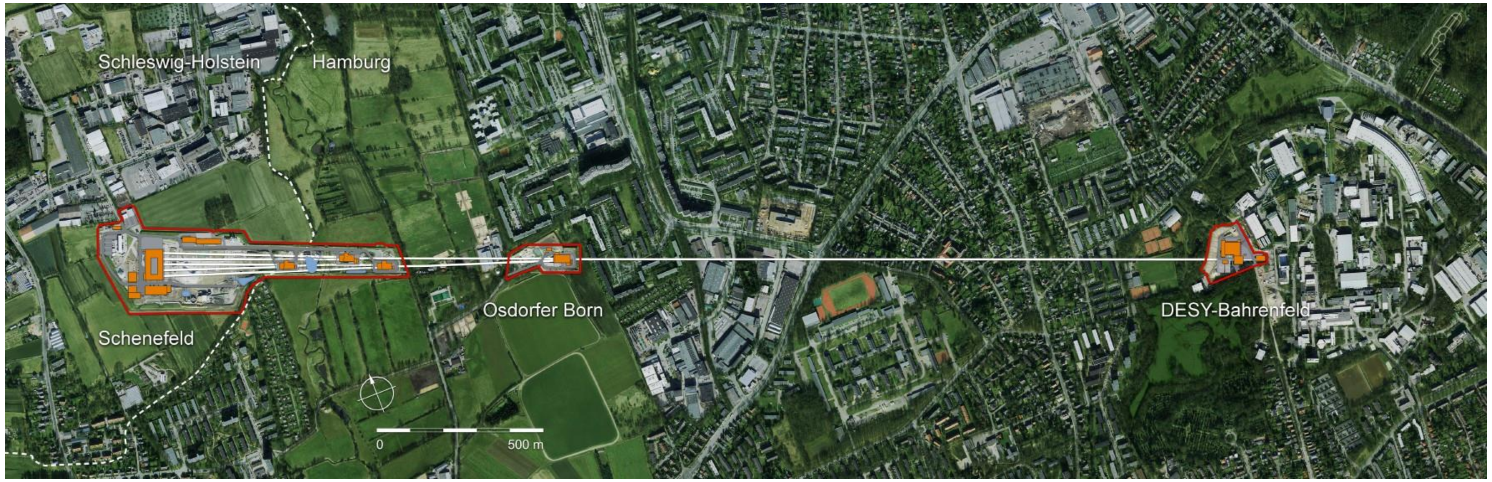


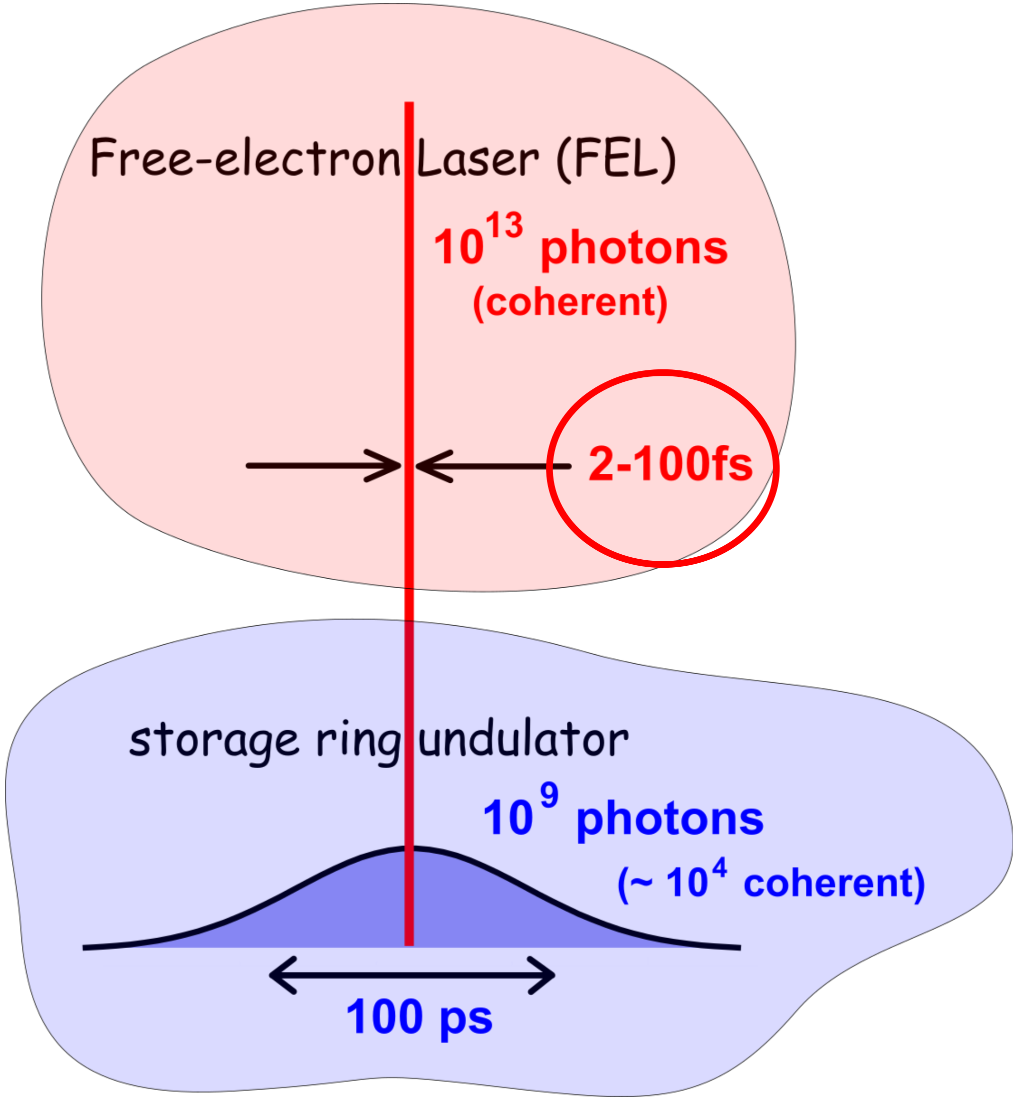
Ada Yonath
Nobel prize in chemistry (2009)

Detour: new X-ray sources: Free-Electron Lasers

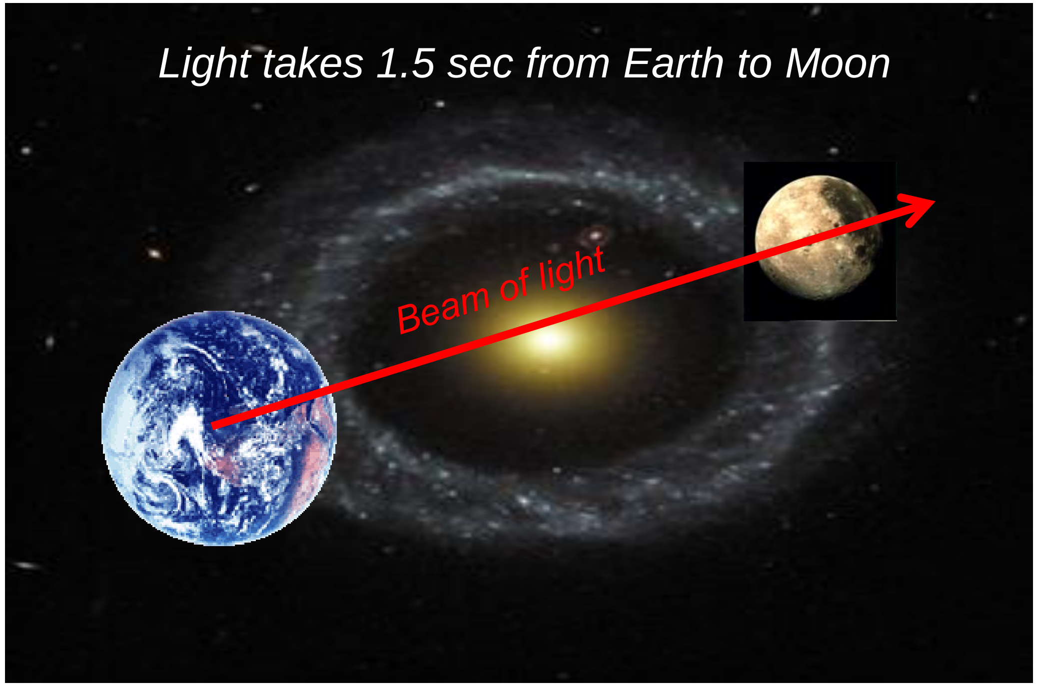
Linear electron accelerators with undulators producing **ultra-short and intense** X-ray pulses

e.g. the new European XFEL (Hamburg)

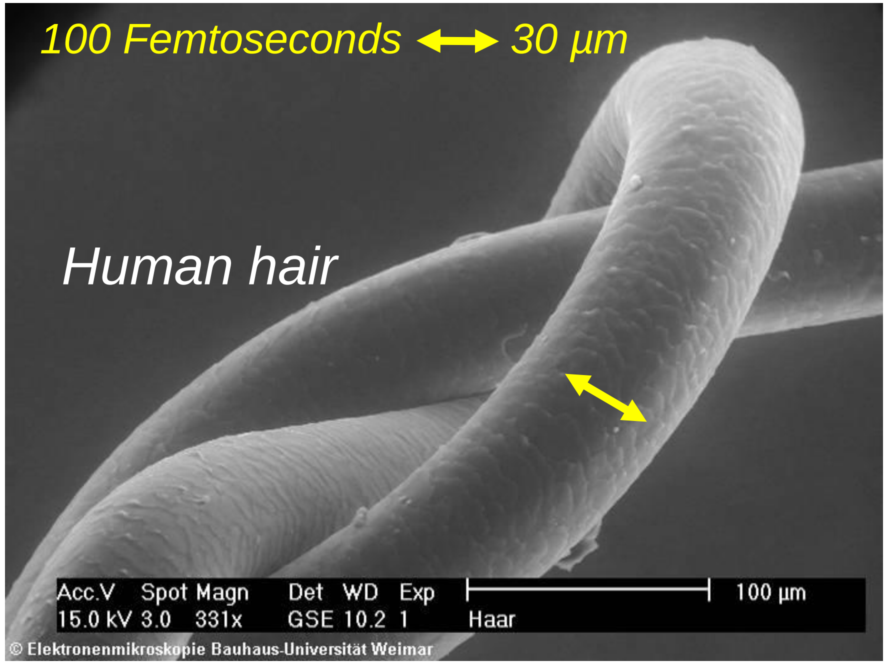




How short is short?



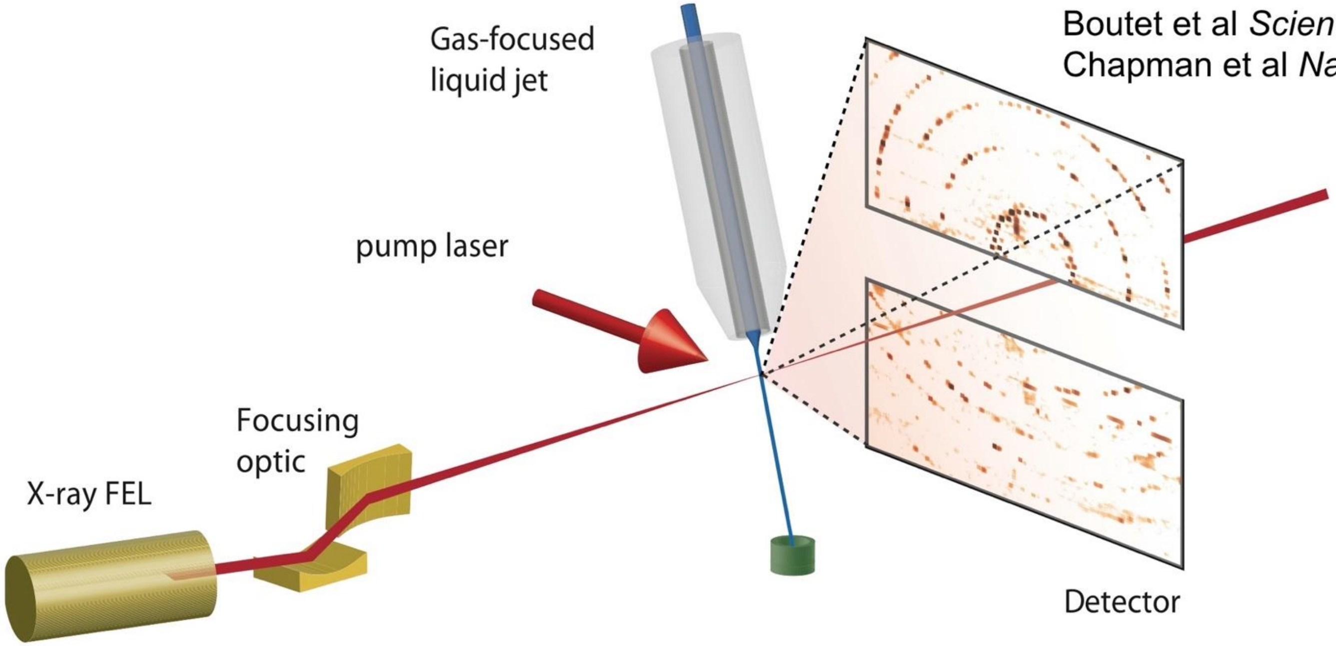
100 fs



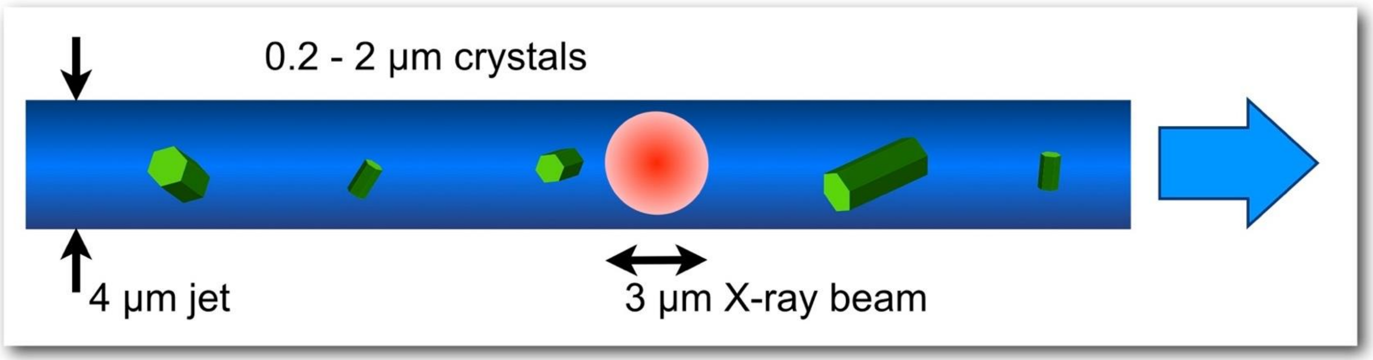
Speed of light: ~300000 km/s

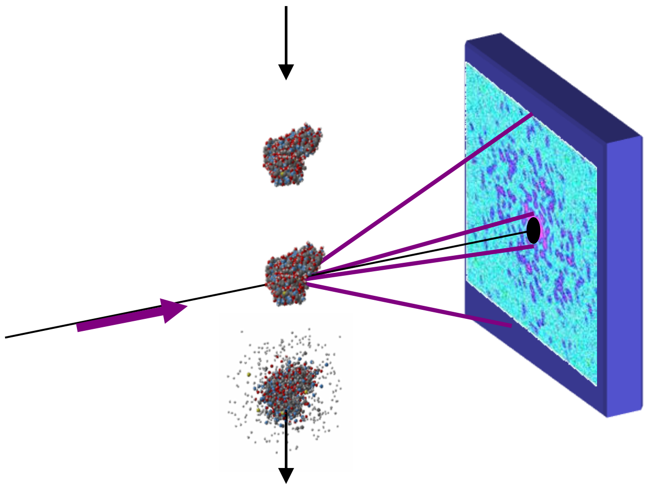
Serial femto-second crystallography

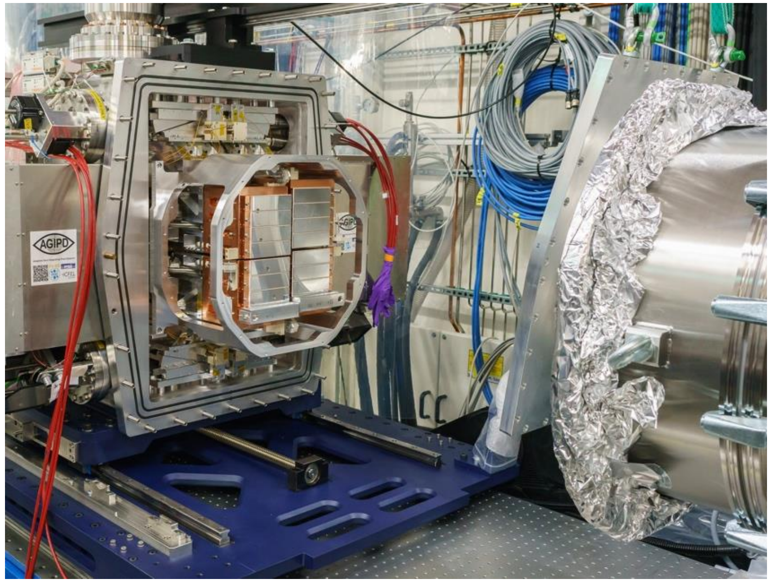
particle is destroyed by the X-ray pulse
BUT: the structural imformation is obtained,
before it „falls apart“



Boutet et al *Science* (2012)
Chapman et al *Nature* (2011)

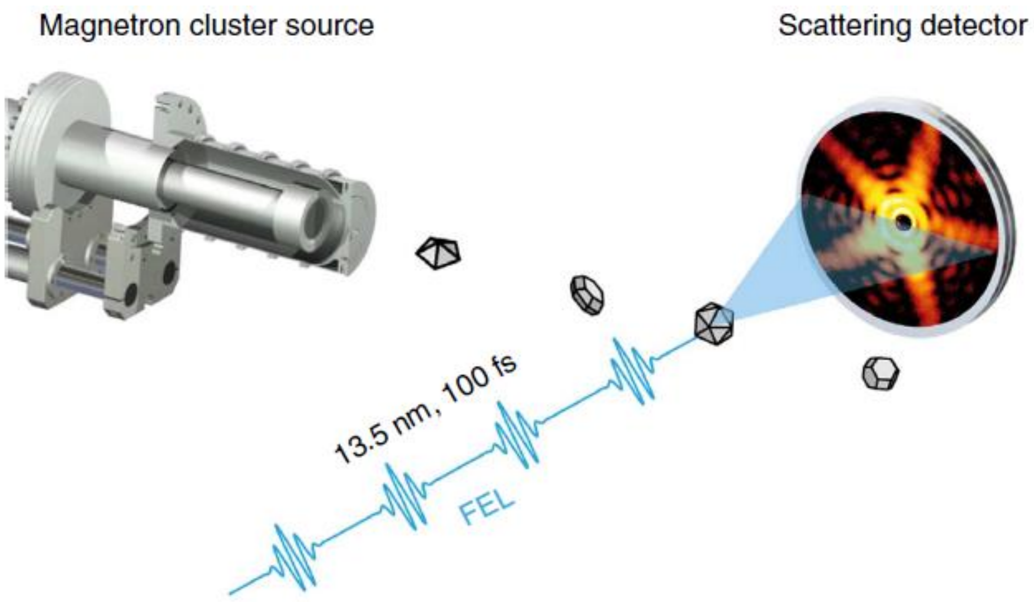




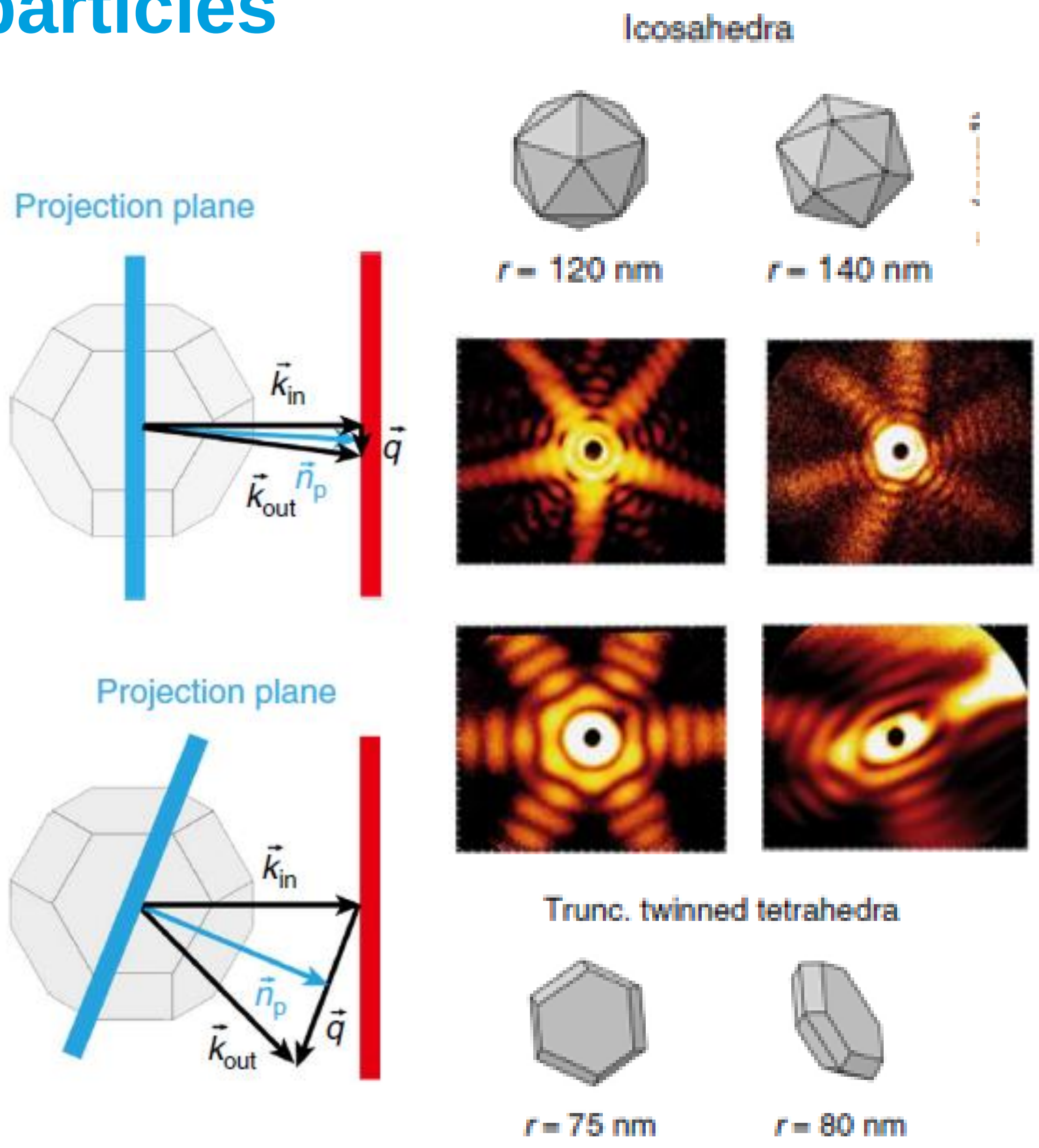


3D Imaging of Individual Ag Nanoparticles

Single „shot“ imaging of metastable states with specialized 2D detectors



Numerous highly symmetrical three dimensional shapes revealed, including several types known as Platonic and Archimedean bodies



I. Barke et al., Nature Comm. 6:6187 (2015)

At the end:
Summary of what has not been talked about

Applications of SR X-ray techniques in materials‘ science

> generation (sun, wind, water, gas, …)
> storage (batteries, hydrogen, …)
> transport (super-conducting power lines)

chemistry, catalysis
(from macroscopic to atomic length scales)

electronic, magnetic, optical properties of nanostructured functional materials

Understanding the Complexity of Matter

structure-based rational drug design
(atomic scale structure & dynamics)

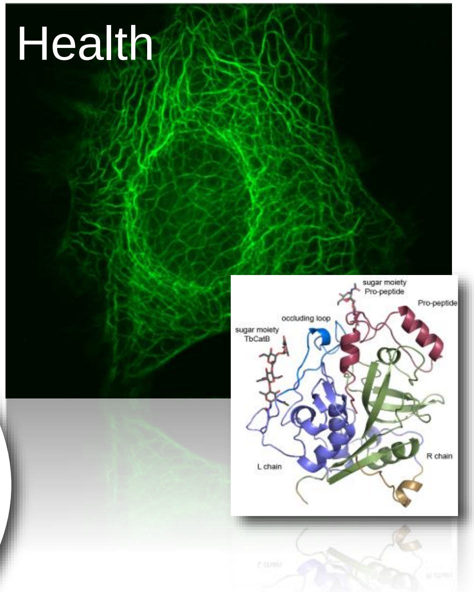
extreme states of matter
(extremely small volumes)

tailored mechanical properties, engineering
(down to nanoscale)

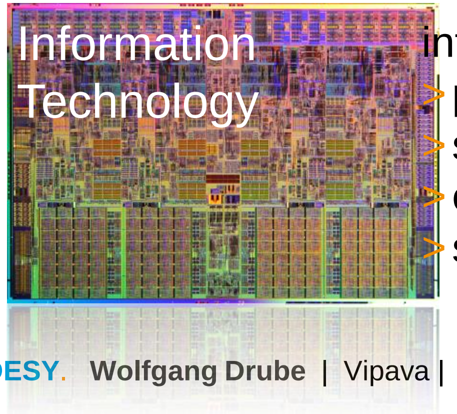
tribology

materials design

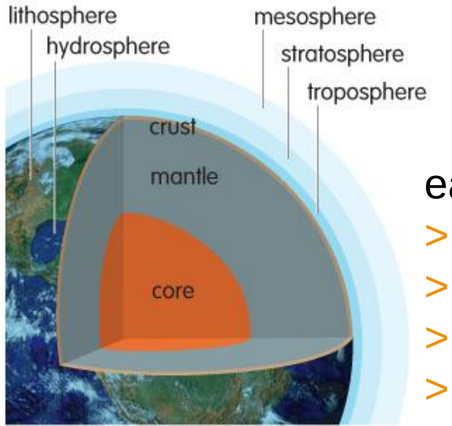
Building blocks of life
> structure
> function



> efficiency
(light-weight structures, propulsion, …)
> safety



information:
> processing
> sensors
> exchange
> storage



earth & environment:
> natural resources
> volcanos and earthquakes
> pollution
> …

Thank you for your attention