Diffraction computed tomography for materials chemistry

The pioneers…

Andrew Beale

Simon Jacques, Bob Cernik

Marco Di Michiel, Gavin Vaughan, Michelle Alvarez
Pierre Bleuet, Jean Susini, Ulf Kleuker, Pekka Suortti, Per Spanne…

Jean-Louis Hodeau

Simon Billinge

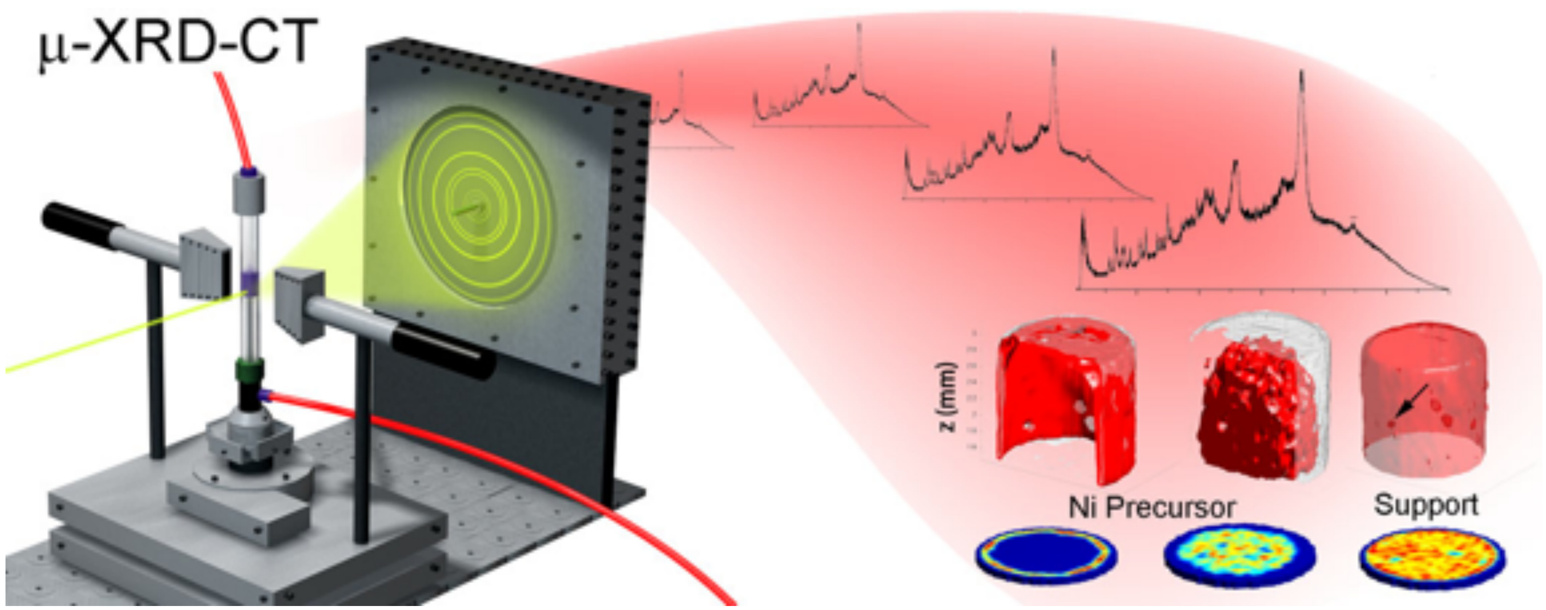
Overview– diffraction computed tomography

What is it?

How do we do it?

Applications to materials chemistry

The future…



Computed tomography

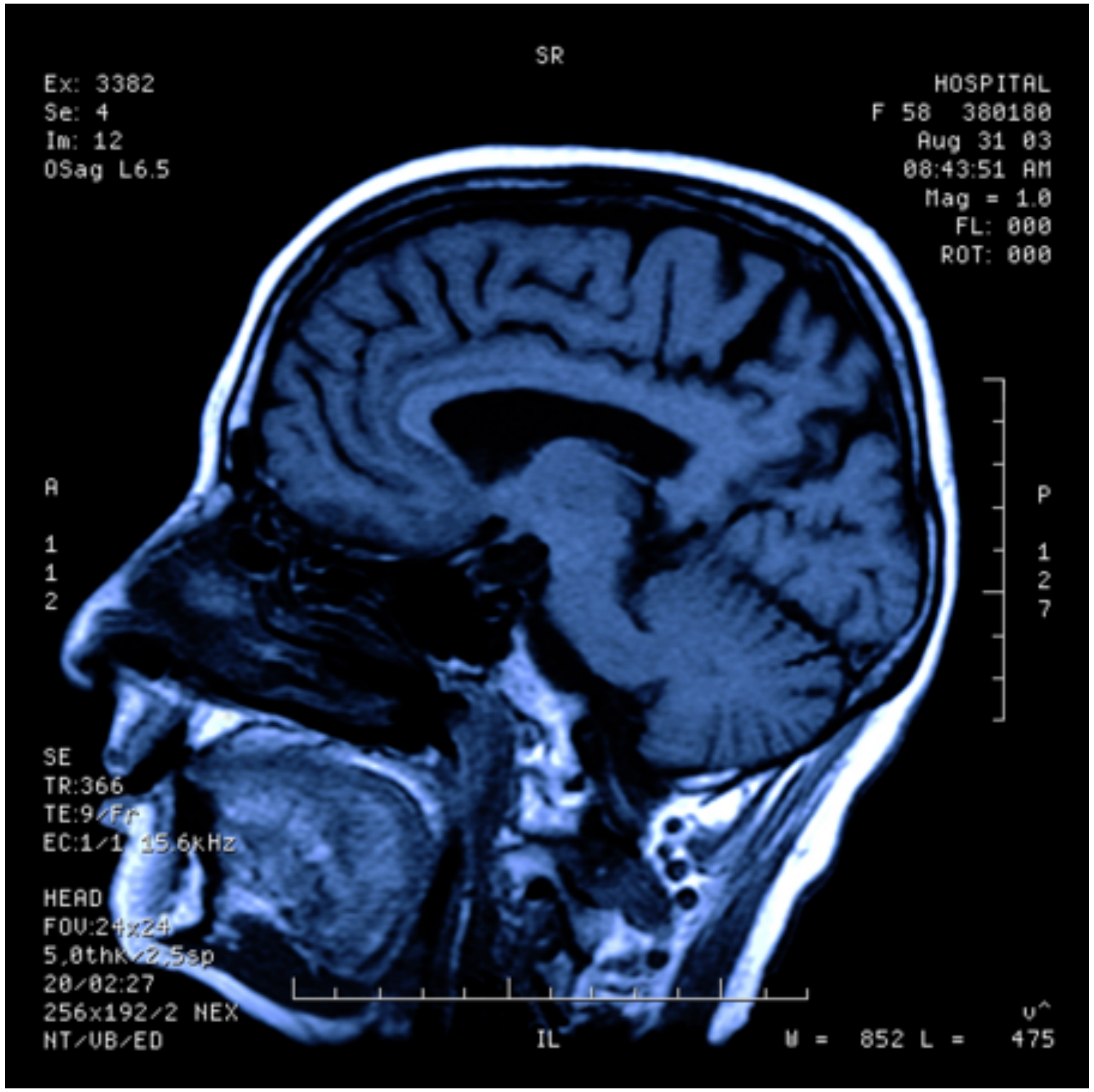
Many interesting samples which we do not wish to destructively analyze!

Relies upon taking many radiographs and performing reconstruction through back projection

Classically gives access to the absorption coefficient

What about materials with no Z contrast?

Chemical contrast?

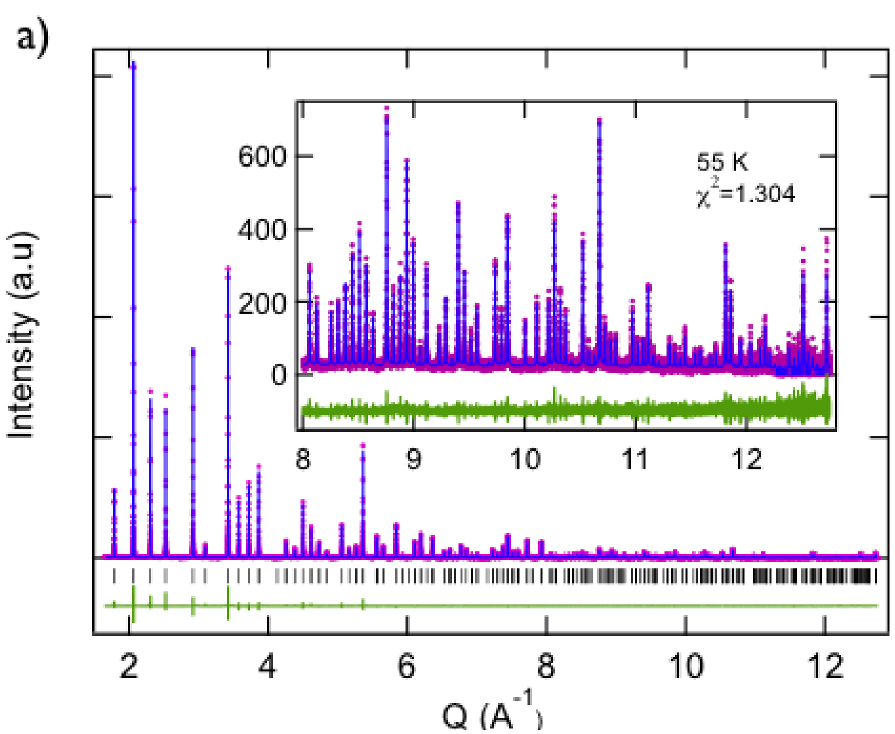


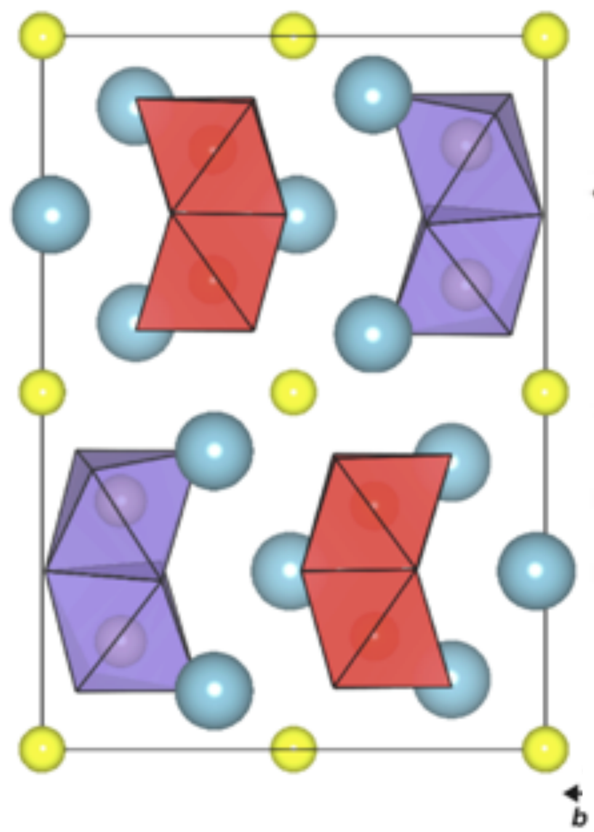
The power of powder diffraction….

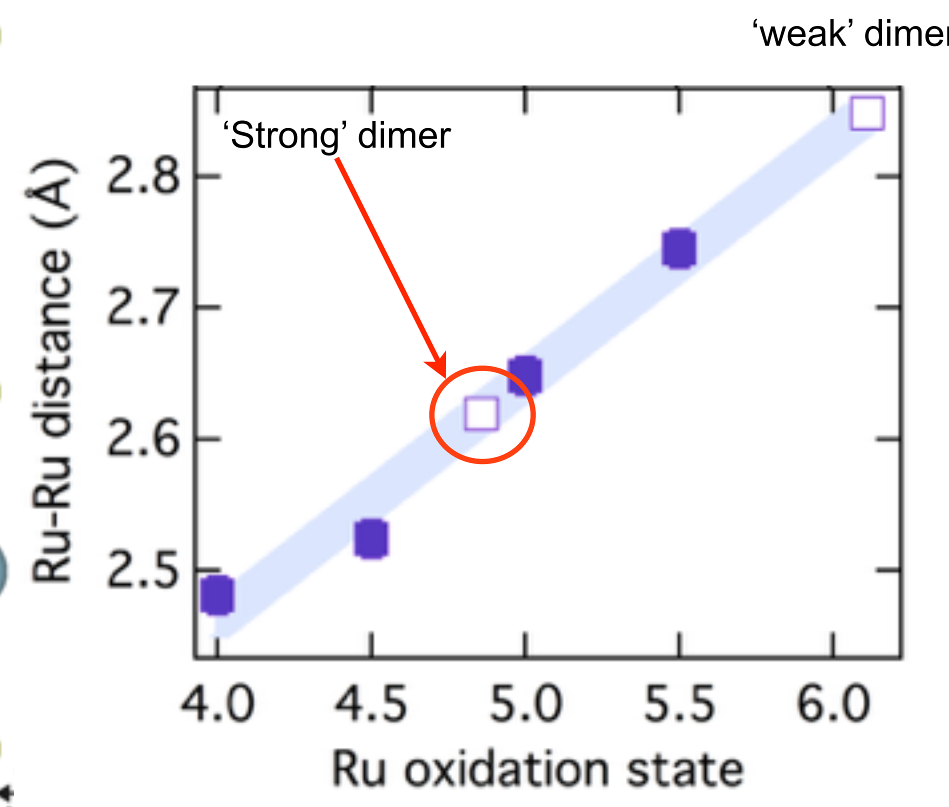
Powder diffraction easily distinguishes materials of similar density

Can extract Angstrom-level detail from each voxel

- -bond lengths and angles
- -coordination numbers
- -oxidation states

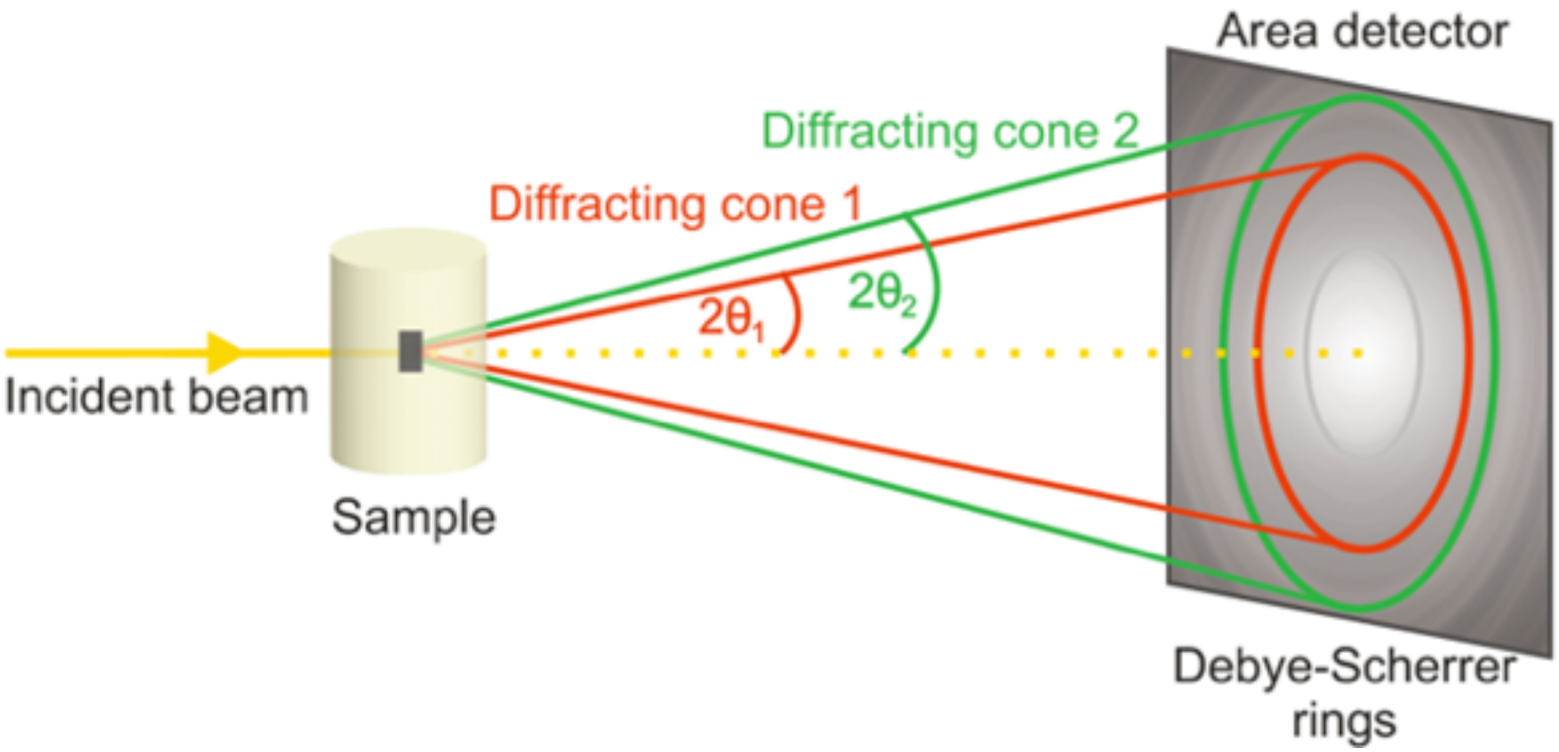


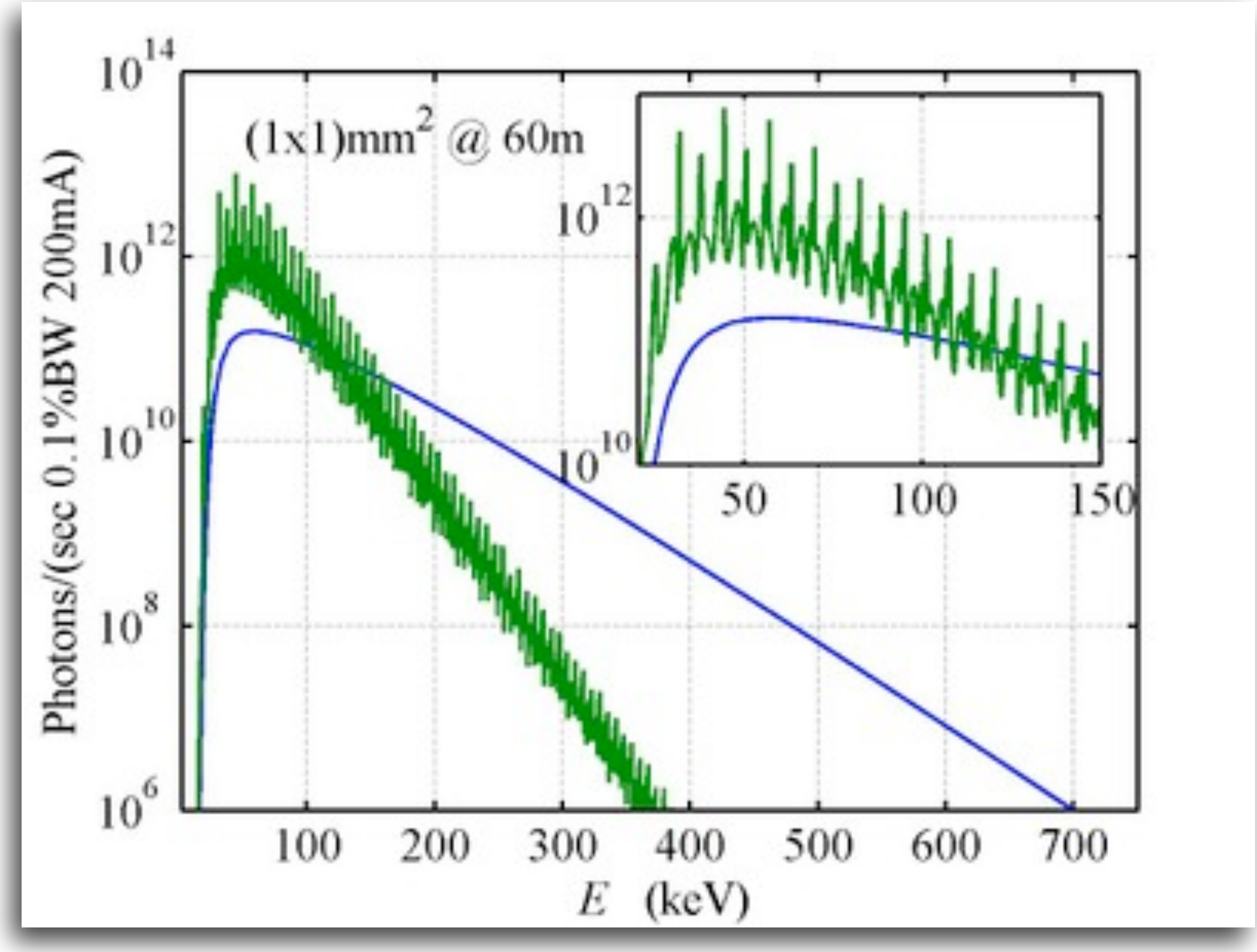




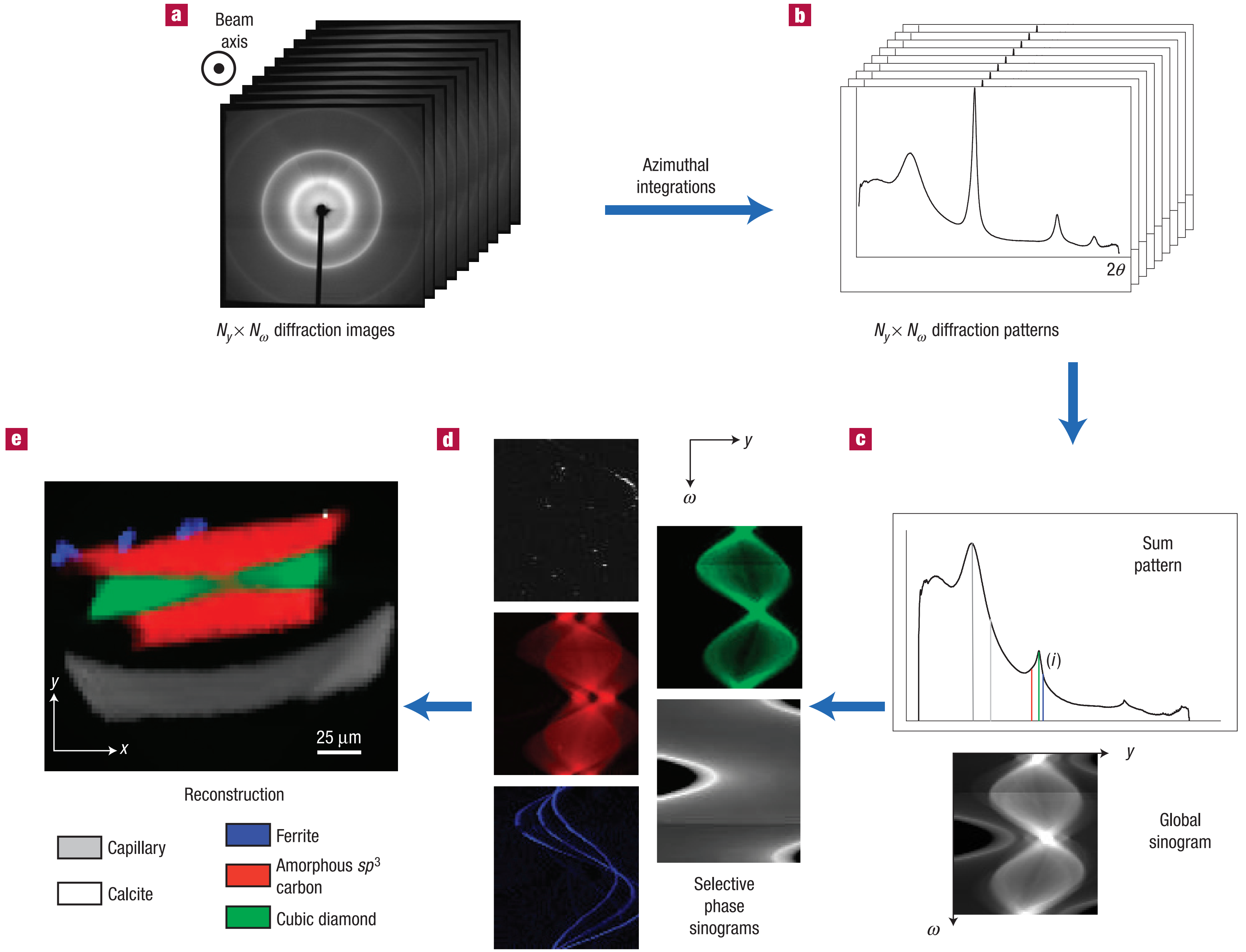
Kimber *et al* PRL (2013)

Diffraction computed tomography



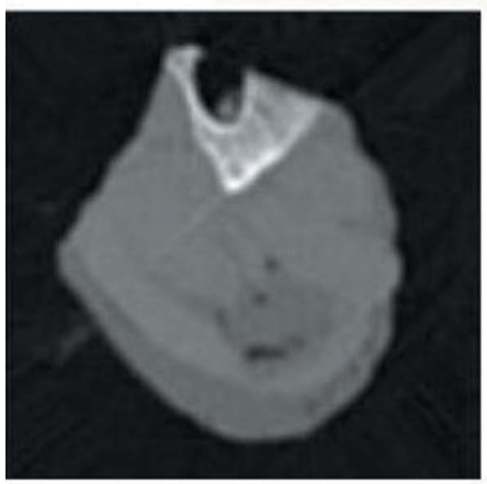


Diffraction computed tomography

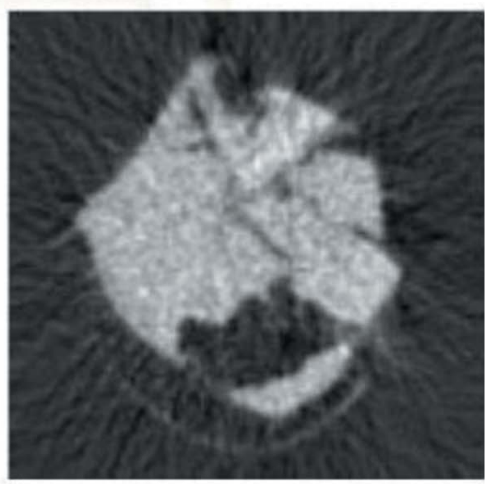


Bleuet, P., Welcomme, E., Dooryhee, E., Susini, J., Hodeau, J.-L. & Walter, P. (2008). Nat. Mater. 7, 468–472.

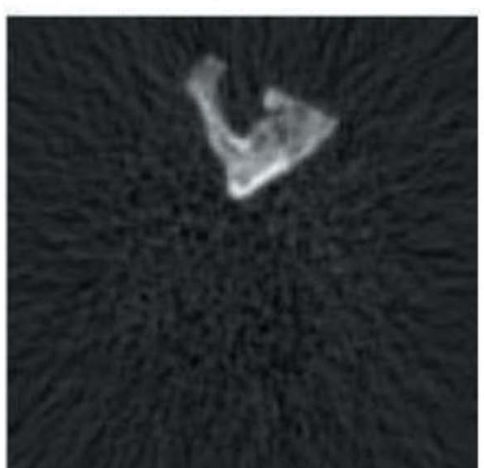
Diffraction computed tomography



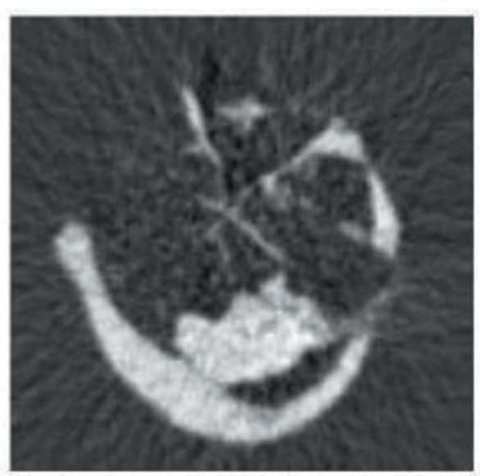
Absorption slice



Diffraction slice (muscle)



Diffraction slice (bone)



Diffraction slice (fat)

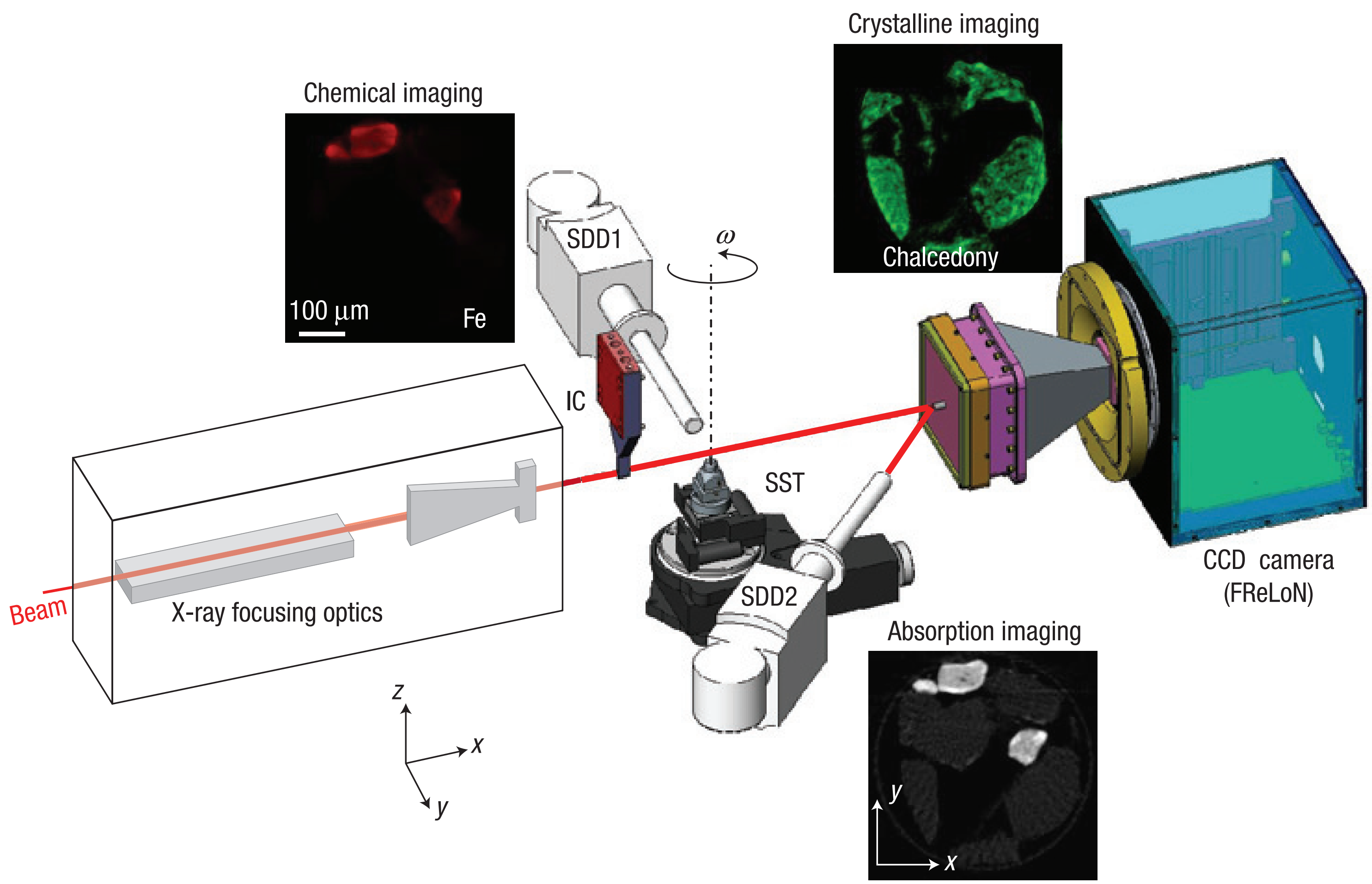
Pioneered at ESRF in 1998 by Ulf Kleuker et al

Experiments performed using ID17 and a lamb chop!

Excellent contrast using scattered signal

Kleuker, U., Suortti, P., Weyrich, W. & Spanne, P. (1998). Phys. Med. Biol. 43, 2911–2923.

Diffraction computed tomography

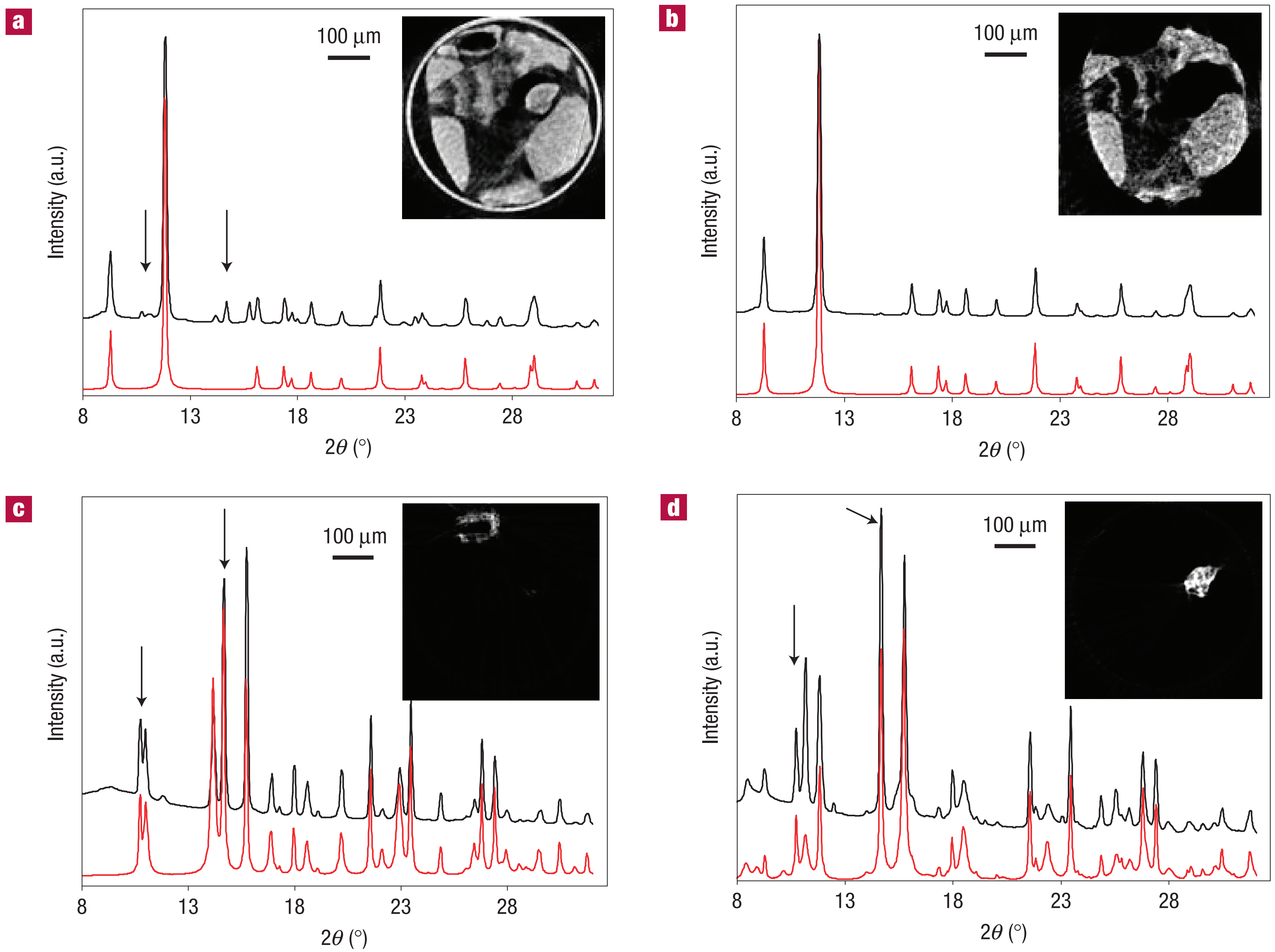


Next major advance was made at ID22 at the ESRF

18 KeV photons focused to sub-micron beam sizes

P. Bleuet *et alBleuet, P., Welcomme, E., Dooryhee, E., Susini, J., Hodeau, J.-L. & Walter, P. (2008). Nat. Mater. 7, 468–472.*

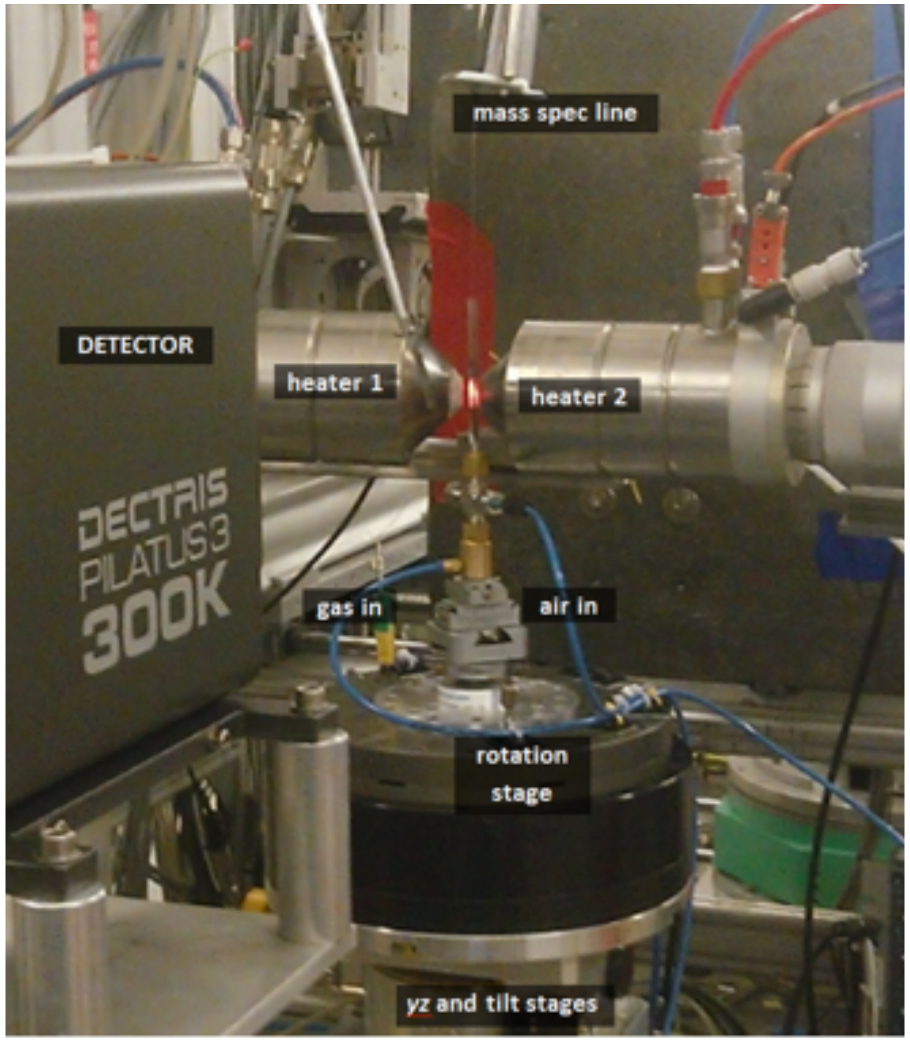
Diffraction computed tomography

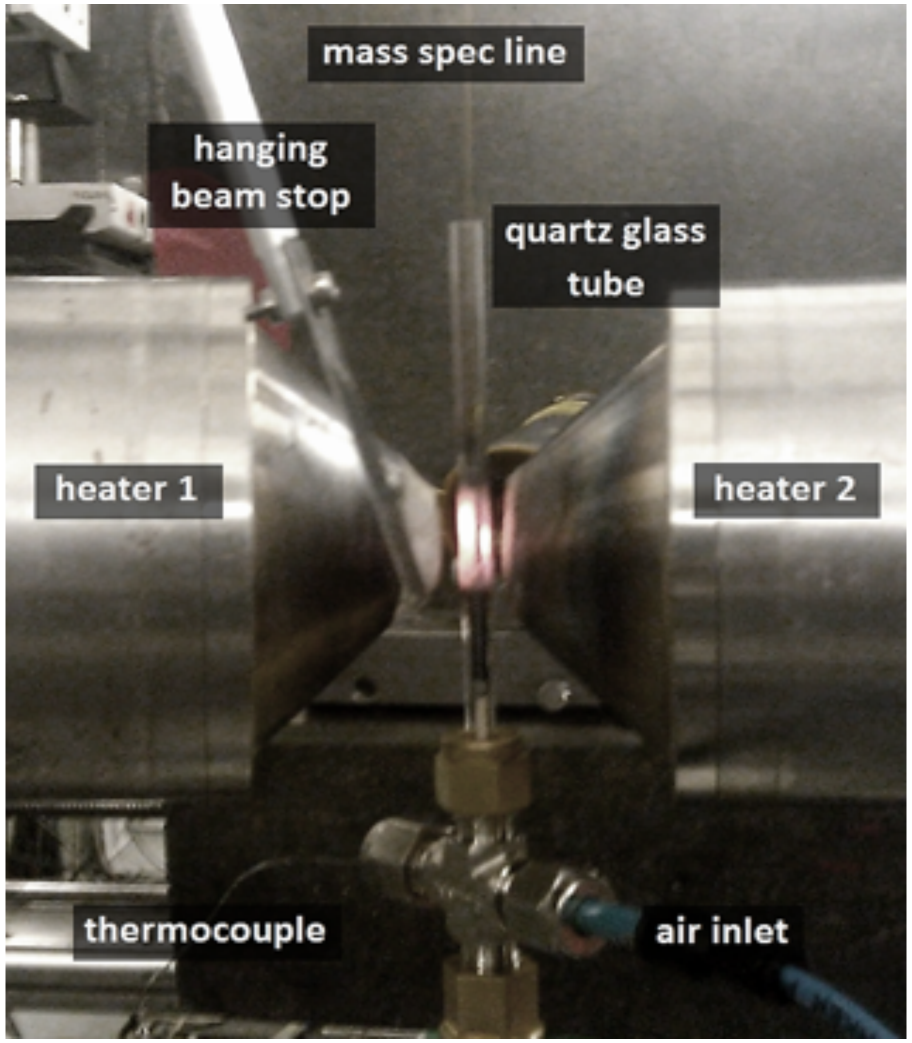


Demonstrated ability to reconstruct Rietveld quality powder patterns (Fe pigment powder)

P. Bleuet *et alBleuet, P., Welcomme, E., Dooryhee, E., Susini, J., Hodeau, J.-L. & Walter, P. (2008). Nat. Mater. 7, 468–472.*

Diffraction computed tomography

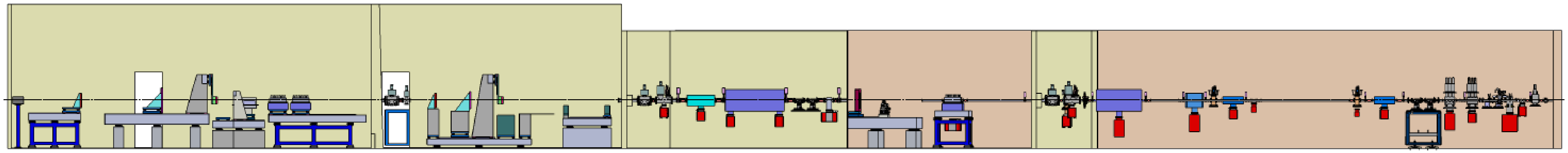


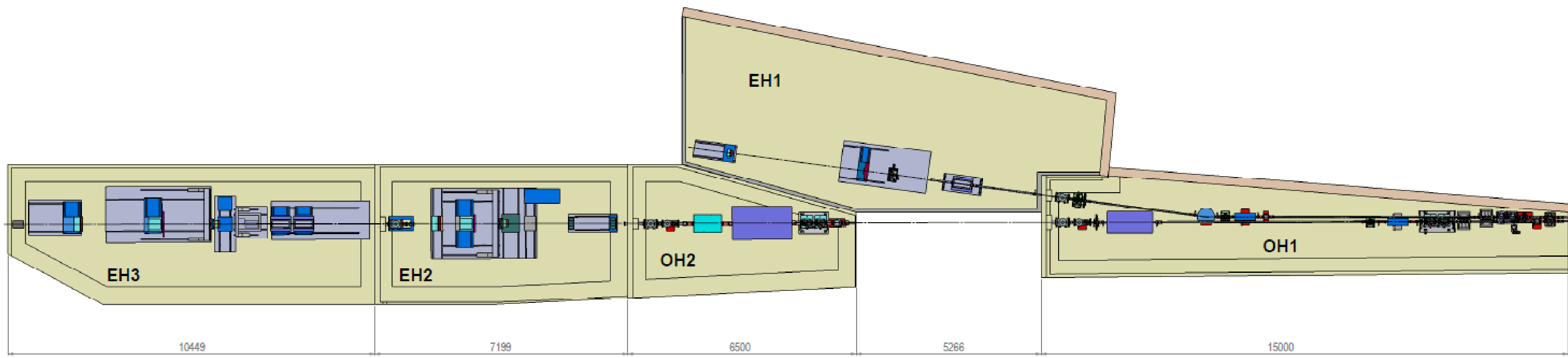


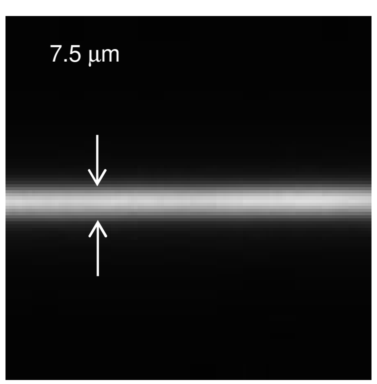
Diffraction computed tomography made *fast* and user friendly by Marco Di Michiel and collaborators on ID15A

Now ca. 10 min for 100 x 100 grid of data. Optimised for beam sizes of 1-30 µm

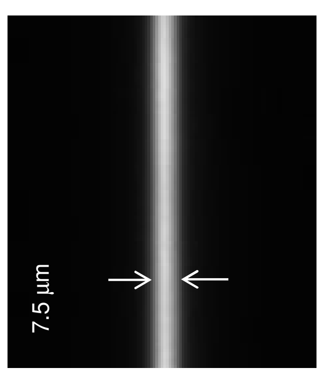
Diffraction computed tomography



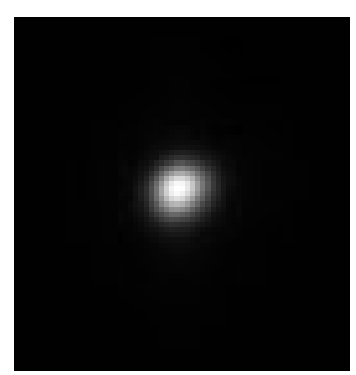




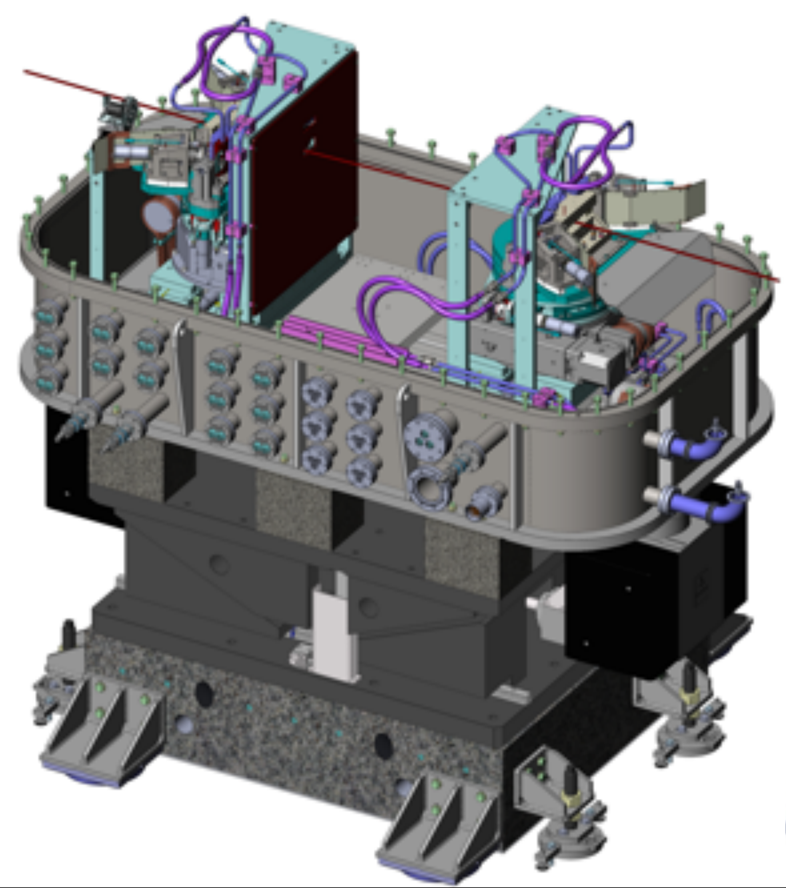
Vertical
N=17 R=300µm
L2 ~ 4m



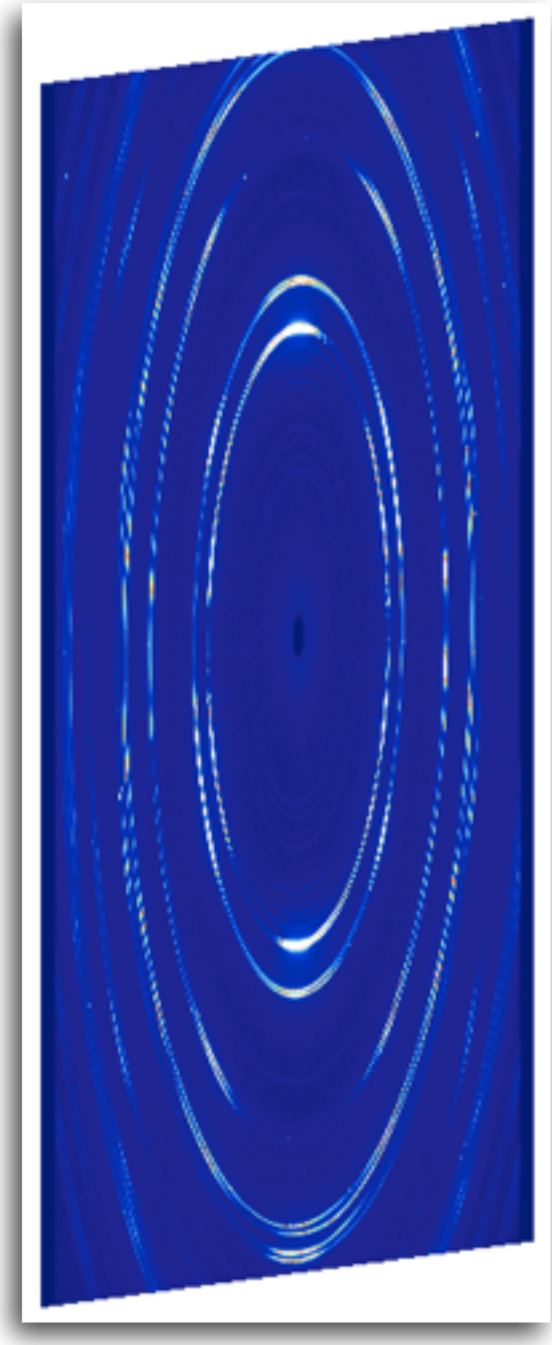
Horizontal
N=17 R=200µm
N=15 R=300µm
L2 ~ 1.4m



Crossed
gain: 1200



Diffraction computed tomography



$$n.\lambda = 2.d.sin\theta$$

Heterogeneous catalysis

Tool exceptionally well matched to problems in heterogeneous catalysis

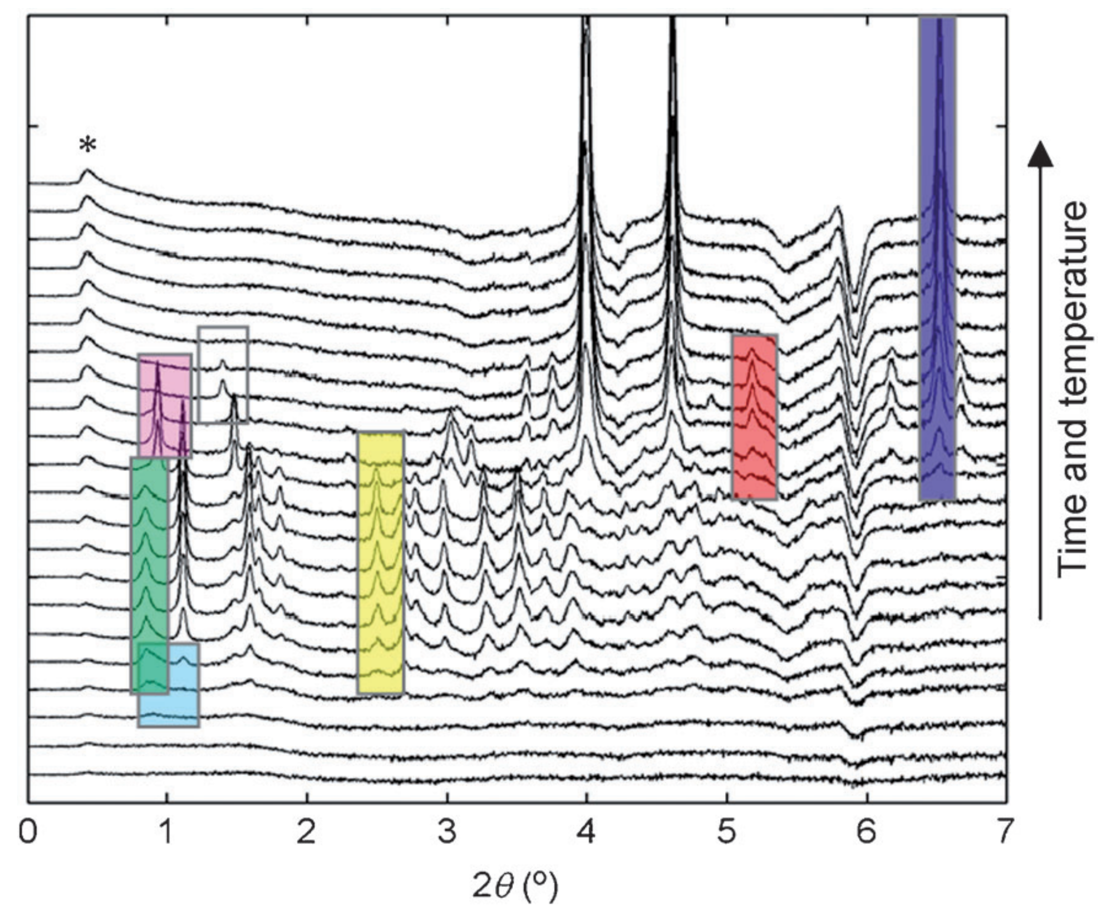
Multiple billion Euro global industry

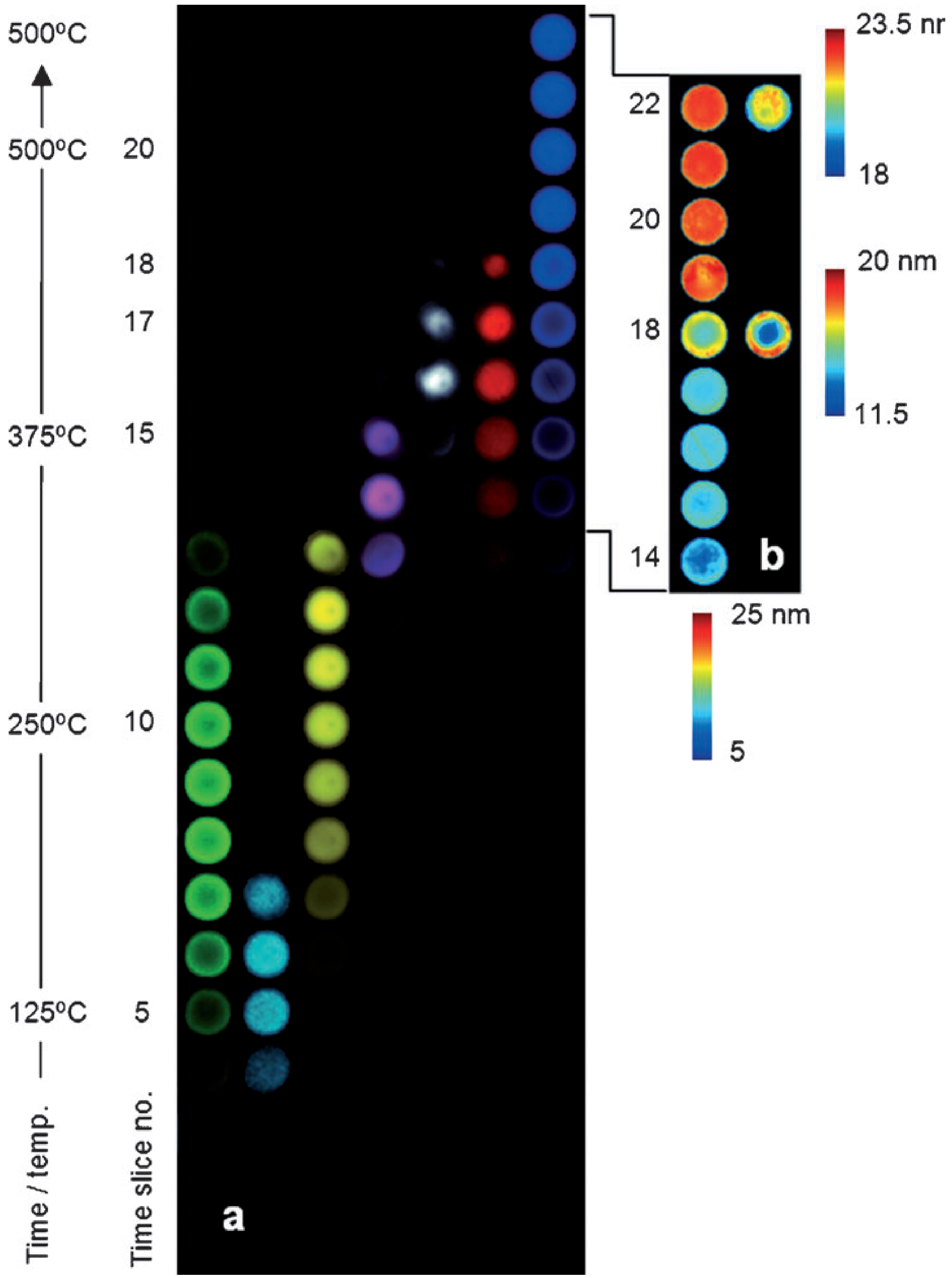
How to best optimise distribution and form of active catalyst? Begins with solution phase!

UCL

MANCHESTER 1824
The University of Manchester

Heterogeneous catalysis



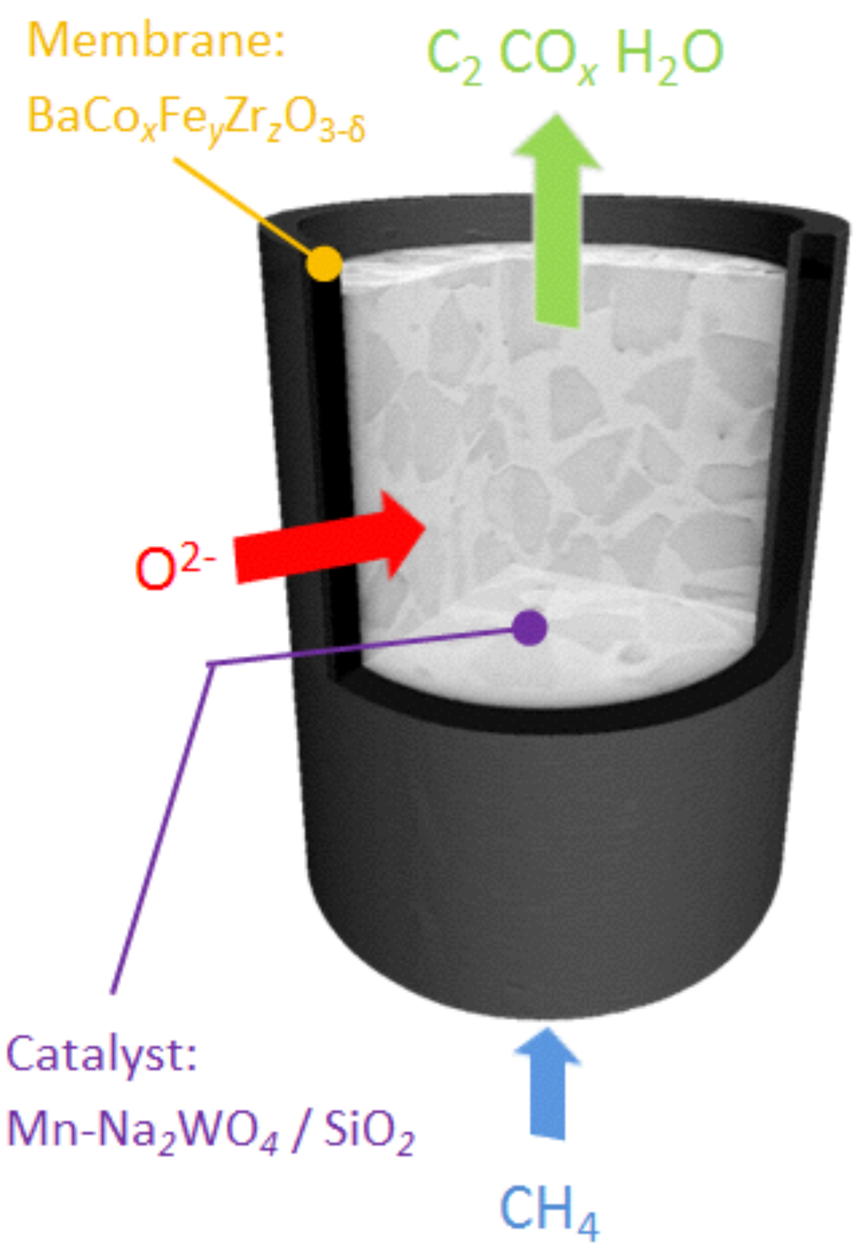


The color maps indicate the following distribution of solid-state phases accordingly : $Ni(en)_xCO_3$ (green), $Ni(en)(CO_3)_xCl_{2(1-x)}\cdot x$ H_2O (cyan), Ni(en)- $(CO_3)_xCl_{2(1-x)}$ (yellow), $Ni(en)_{0.5}(O)_xCl_{2(1-x)}$ (magneta), $Ni(en)Cl_2$ (white), hcp Ni (red), and fcc Ni (blue)

Very complex temporal and spatial development

Jacques, S. D. M., Di Michiel, M., Beale, A. M., Sochi, T., O'Brien, M. G., Espinosa-Alonso, L., Weckhuysen, B. M. & Barnes, P. (2011). Angew. Chem. Int. Ed. 50, 10148–10152.

Heterogeneous catalysis



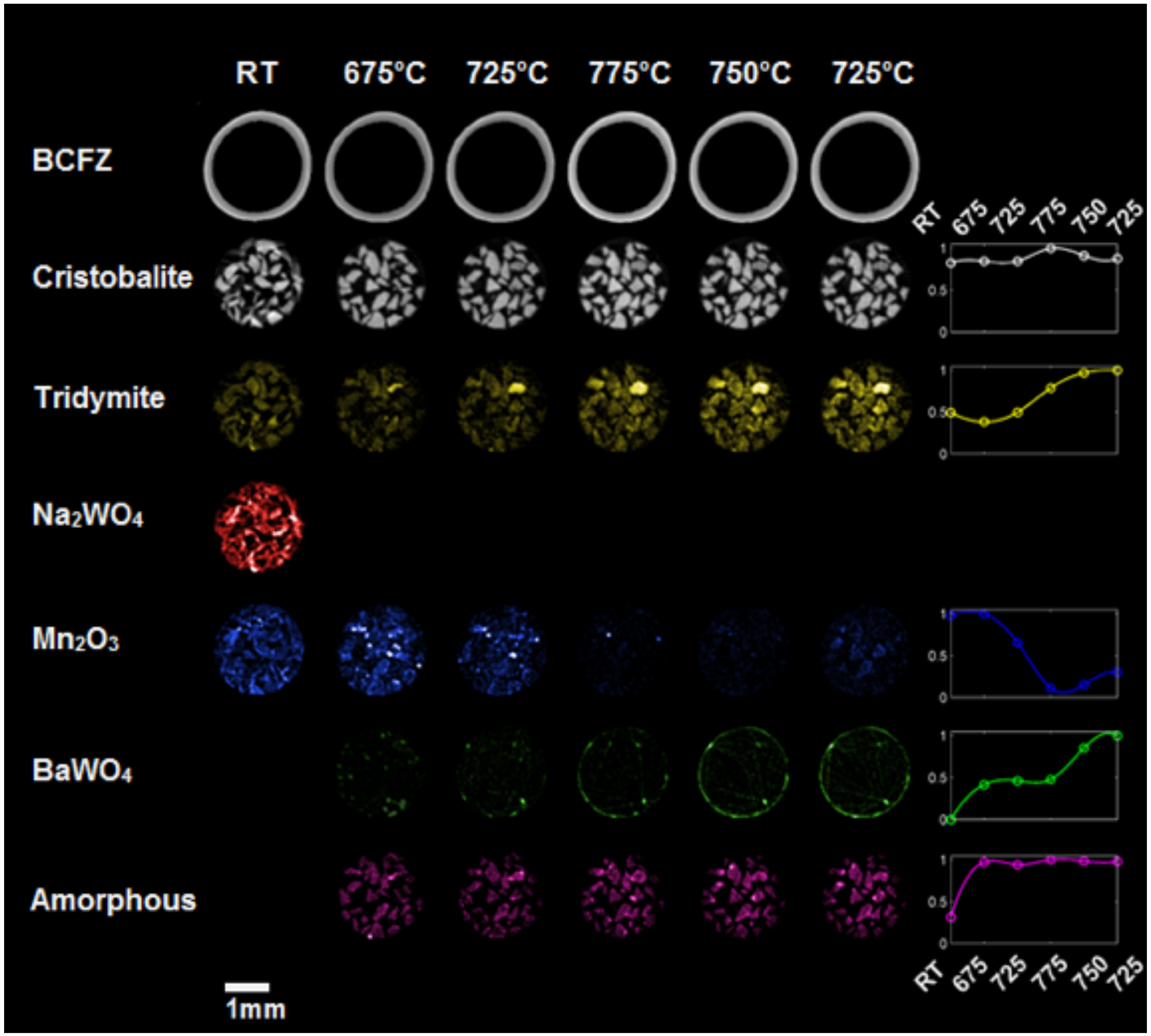
Catalytic membrane reactors developed for CH_4 to C_2 conversion

- Advantages:
  - Increased C_2 selectivity
  - Process Intensification
  - Disadvantages:
  - Long-term stability
  - Sealing at high temperatures

- Membrane ($BaCo_xFe_yZr_zO_{3-\delta}$):
  - High oxygen permeation flux
  - Chemical stability
  - $Mn\text{-}Na_2WO_4/SiO_2$ Catalyst
  - High C_2 yield
  - High stability under high temperatures

Vamvakeros *et al*, Chem. Commun., 2015,51, 12752-1275

Heterogeneous catalysis



Extremely complex system

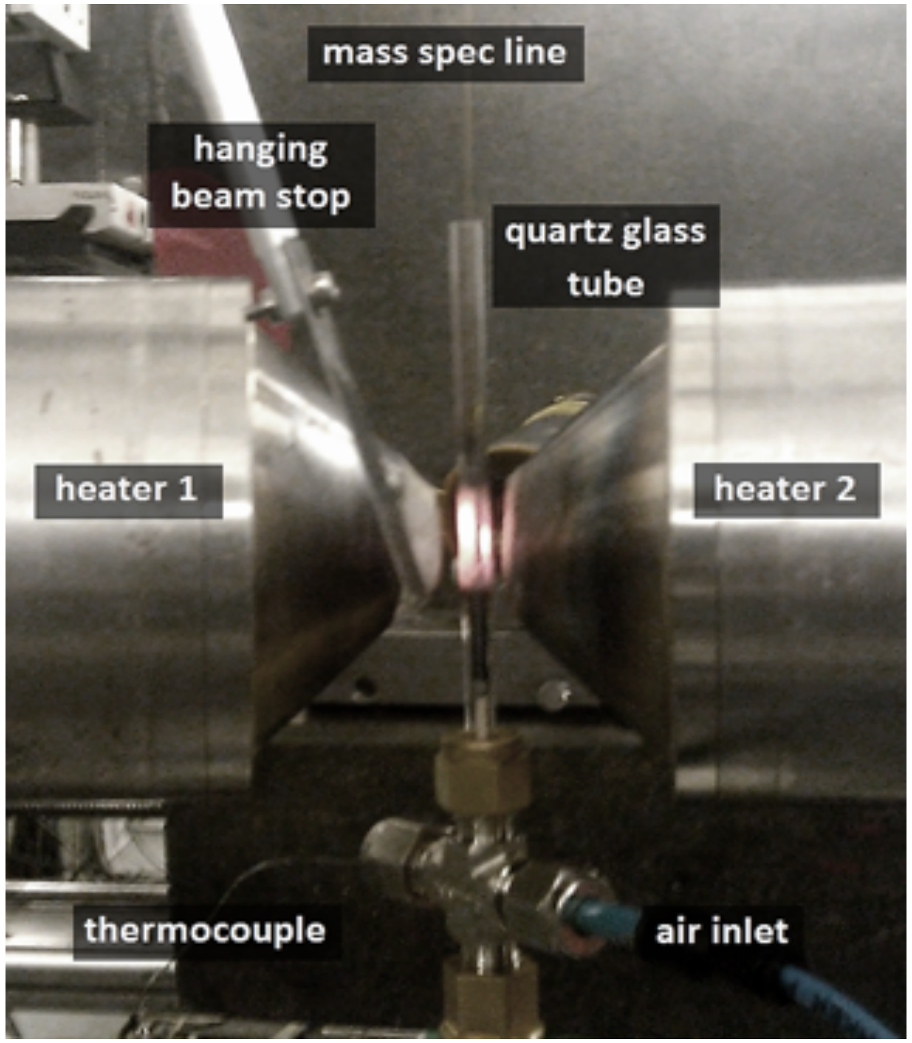
diffraction computed tomography can resolve the multiple phases present

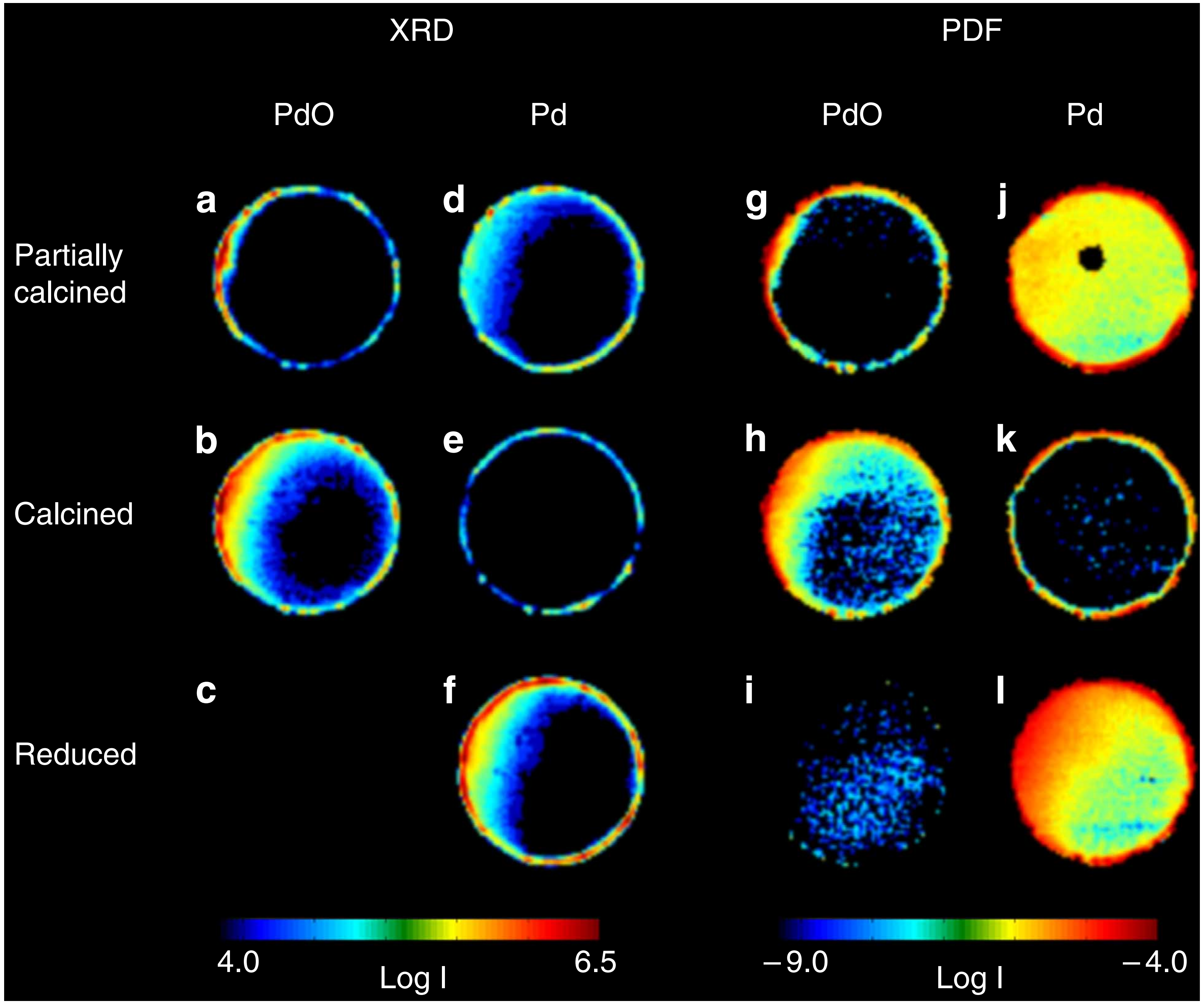
Reaction between catalyst and oxygen membrane shown to be key

Tour de force of in-situ measurement, with online reaction, mass spectrometry etc

Vamvakeros *et al*, Chem. Commun., 2015,51, 12752-1275

Heterogeneous catalysis



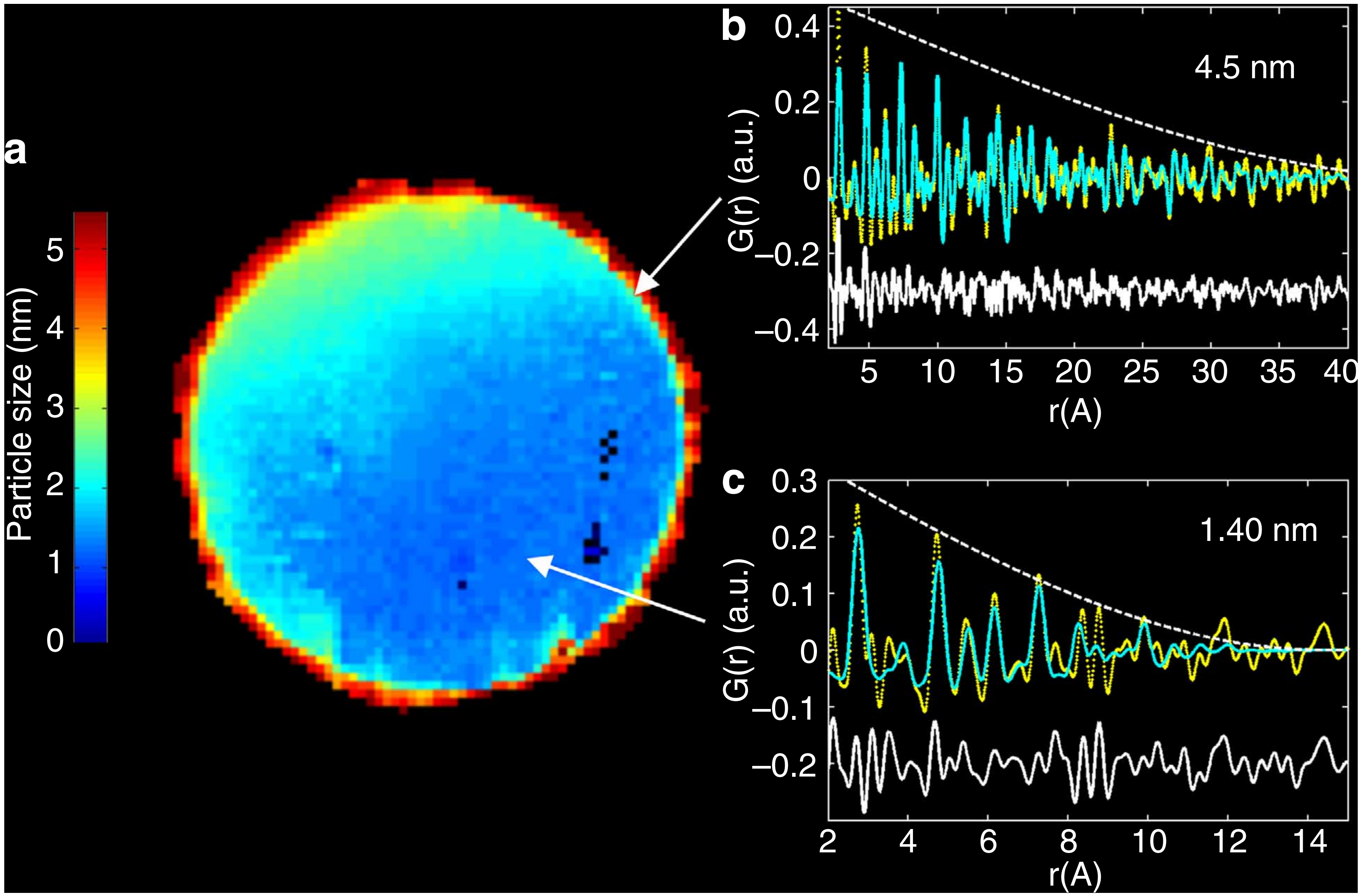


Experiments now routinely performed under reducing/oxidising conditions e.g. preparation of Pd loaded catalysts

Experiment can be easily modified to use pair distribution function contrast

Jacques *et al*, Nat. Com., 2013 ,4, 2536

Heterogeneous catalysis



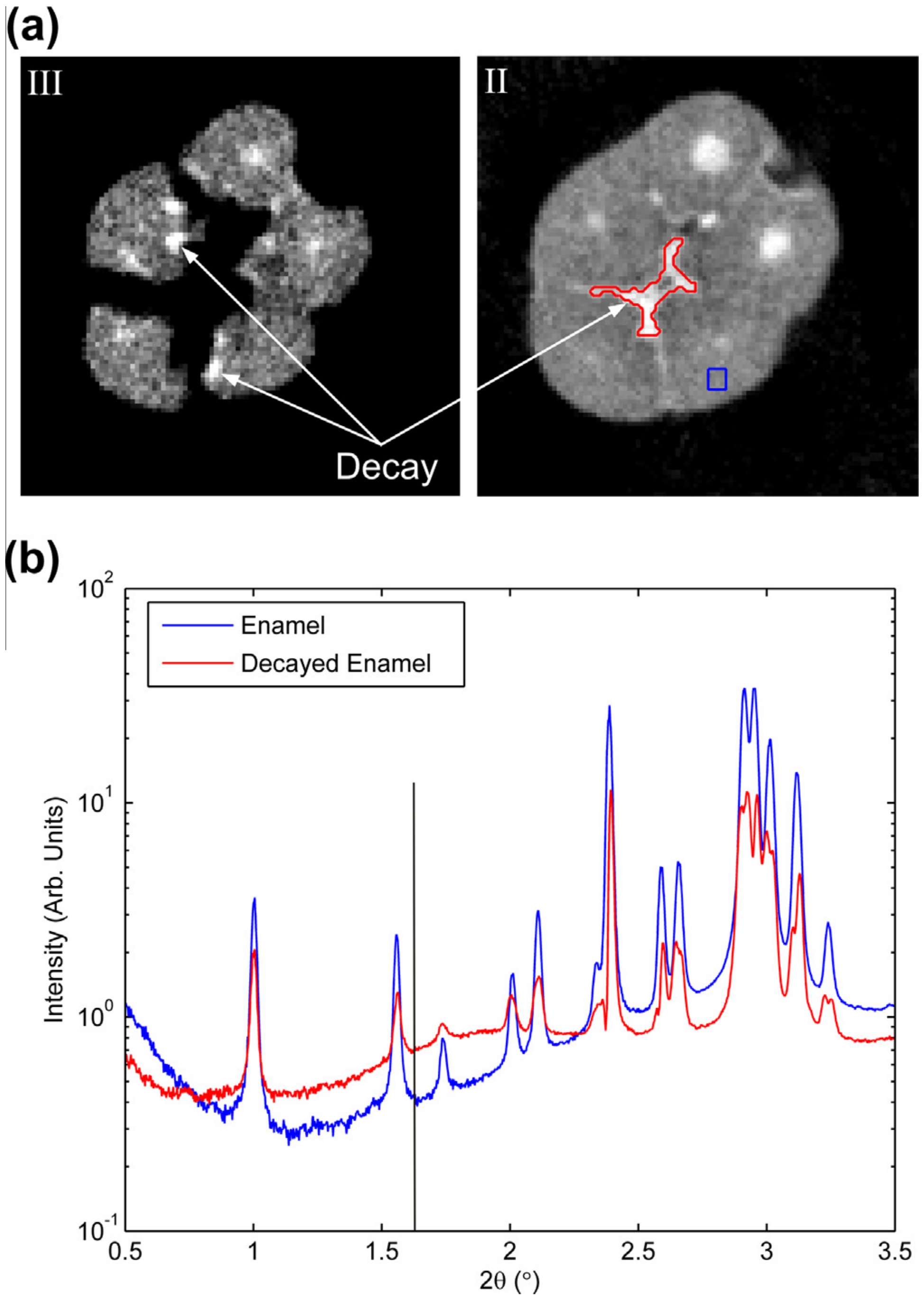
COLUMBIA UNIVERSITY

PDF method provides unique access to nanostructure, coherent domain size etc

- see talk of Simon Billinge this afternoon

Jacques *et al*, Nat. Com., 2013 ,4, 2536

Beyond phase identification…



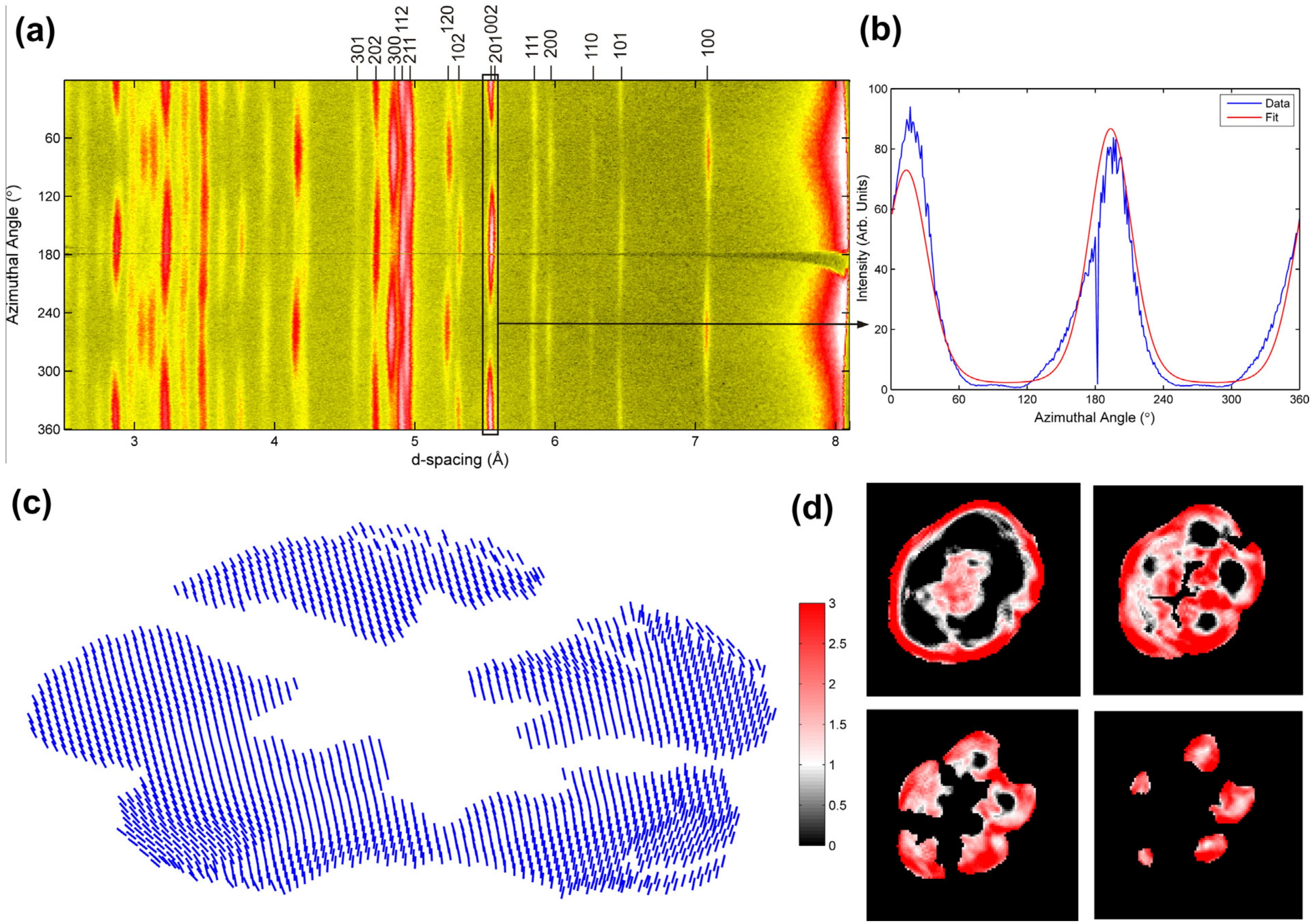
Full power of diffraction computed tomography applied to human teeth

Many questions about decay, strength of enamel (mineralised calcium hydroxy apatite)

Egan *et al*, Acta Biomaterialia 9 (2013) 8337–8345

The University of Manchester

Beyond phase identification…

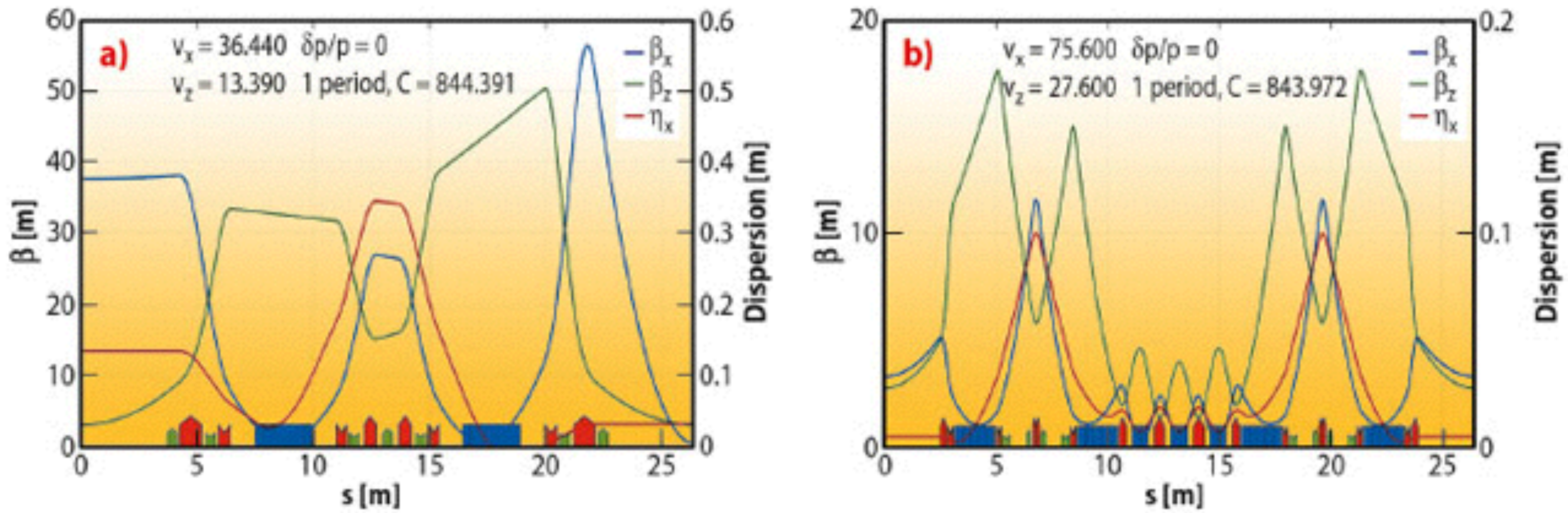


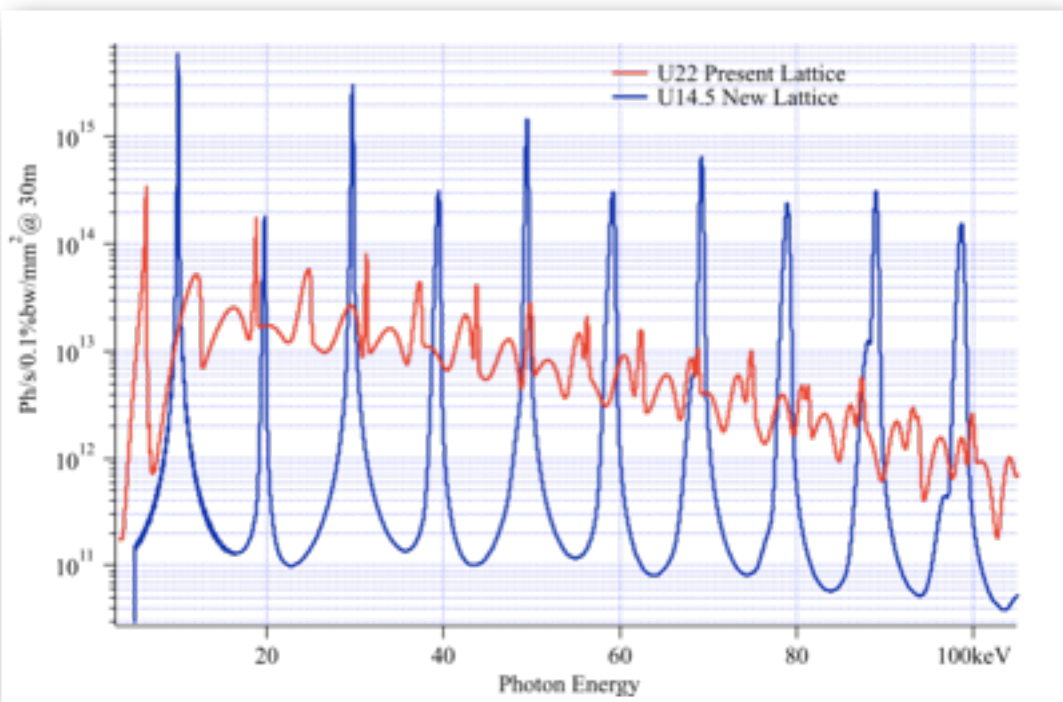
Very detailed analysis allowed extraction of preferred orientation (along load direction)

Variations in lattice parameters reflect compositional changes

Egan *et al*, Acta Biomaterialia 9 (2013) 8337–8345

What about the future?





The second phase of the Upgrade Programme, launched in 2015, is remarkably different … It includes the delivery of the first of a new kind of storage ring based synchrotron source with a normalised horizontal emittance of at least a factor 10 better than any existing or currently planned projects, and at least a factor 100 more brilliant than the ESRF source today. …ESRF Management has decided to highlight this second phase of the ESRF upgrade by choosing a name to emphasize the new project's main deliverable - a new source - and its principal attribute with respect to what is presently available or planned worldwide **- Extremely Brilliant.**

What about the future?

Next generation of light sources will be bright enough for ‘chemically resolved x-ray vision’ in 3D

WIll become a standard technique for all areas of science (chemistry, materials, cultural heritage etc), much like computed absorption tomography

ESRF upgrade will be ~20 years since technique first used on ID17

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