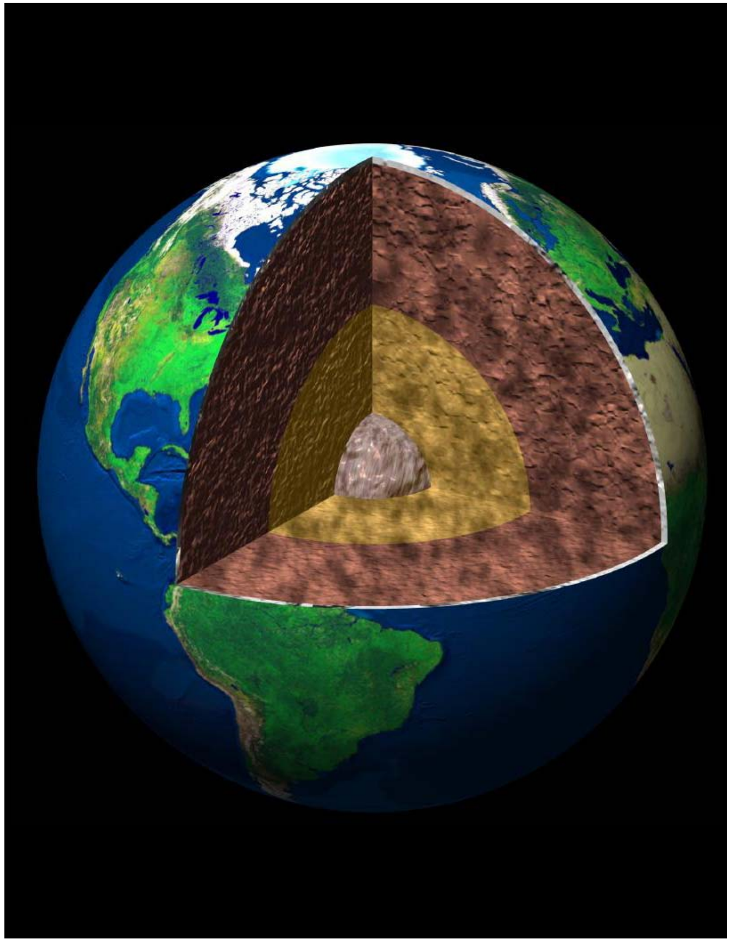
X-ray Imaging Techniques at the ESRF:

Applications in geosciences

One missing data – one available technique

- Internal structure: tomography
  - Rock permeability
- Elemental distribution: fluorescence
  - 2D – Solar nebula composition
  - 3D – fly-ash particles
- Elemental speciation: energy-dependent signal
  - S redox in microfossils
  - Fe^{3+}/Fe_{total} ratio
- Gathering complementary data: Combined studies
  - Fluid-fluid immiscibilities



3D internal structure

Tomography

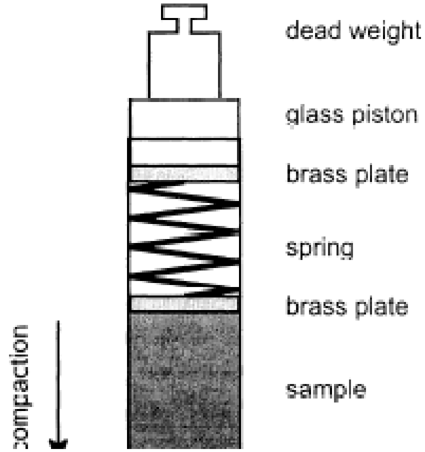
Permeability and pressure solution creep

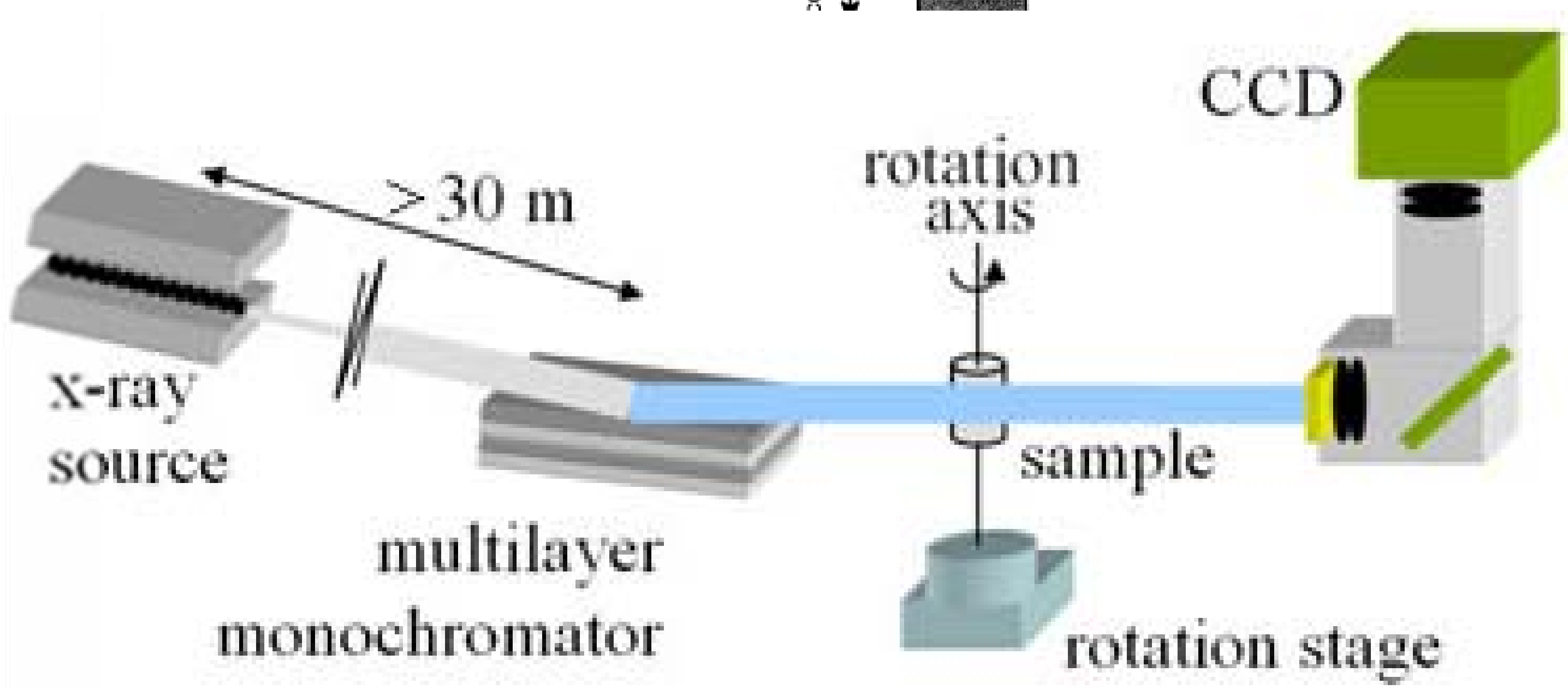
- Aim:
  - evaluate the influence of pressure solution (Dissolution – transport – precipitation) in permeability (connected porosity) changes upon compaction in geological settings
- Scientific background:
  - Pressure solution is an important ductile deformation mode in sedimentary rocks during diagenesis and in compaction of fault sealing in between earthquakes
- Method:
  - Evolution of the internal geometry in samples of aggregated grains
  - Observation of grain boundaries at selected steps during compaction
- System:
  - NaCl + saturated solution in monoaxial pressure cylinders

Tomography

Talk "Absorption imaging 2D + 3D" given by Pierre Bleuet

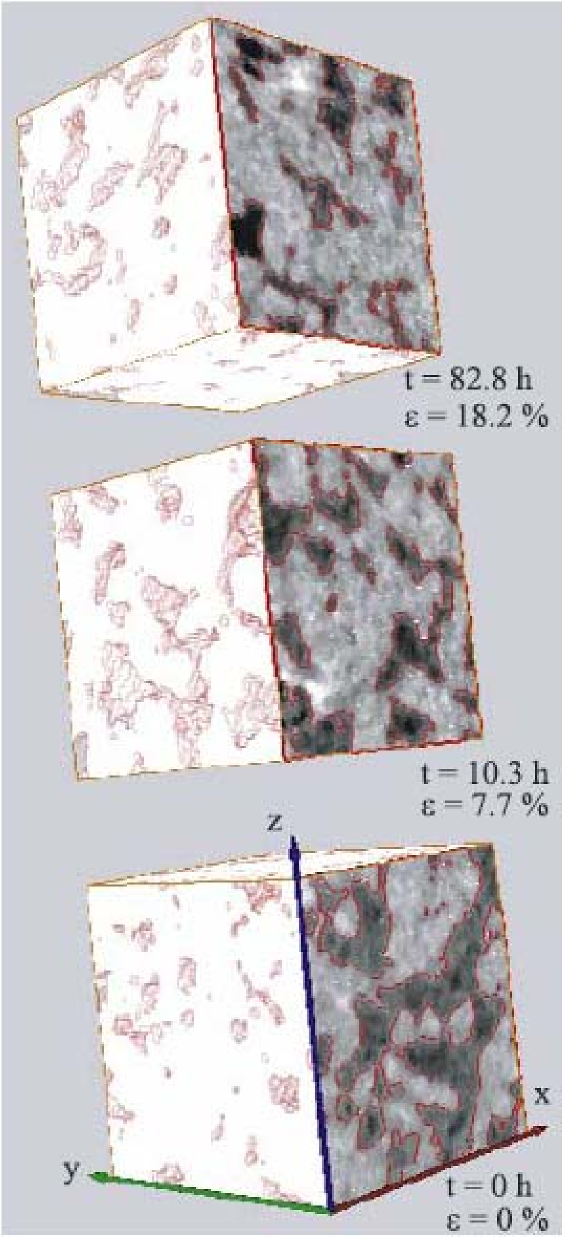
- Set-up ID19





Permeability reduction

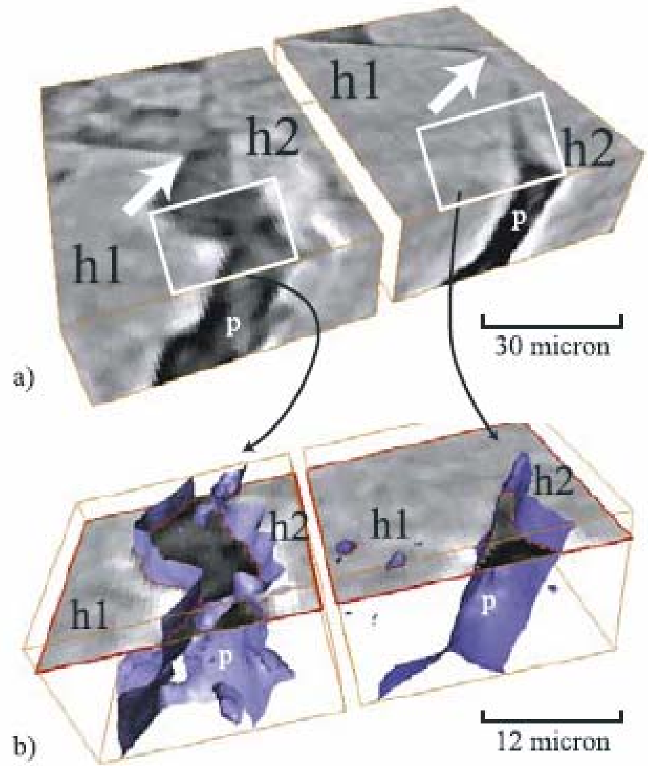
- Compaction (ε) corresponds to a decrease of the volume of halite+solution.
- It decreases by 18.2% (compaction = ε) in 82.8h
- Porosity (grey parts) decreases with compaction (ε)
- What about permeability?



Renard *et al*., Geophysical Research Letters, 31, L07607 (2004)

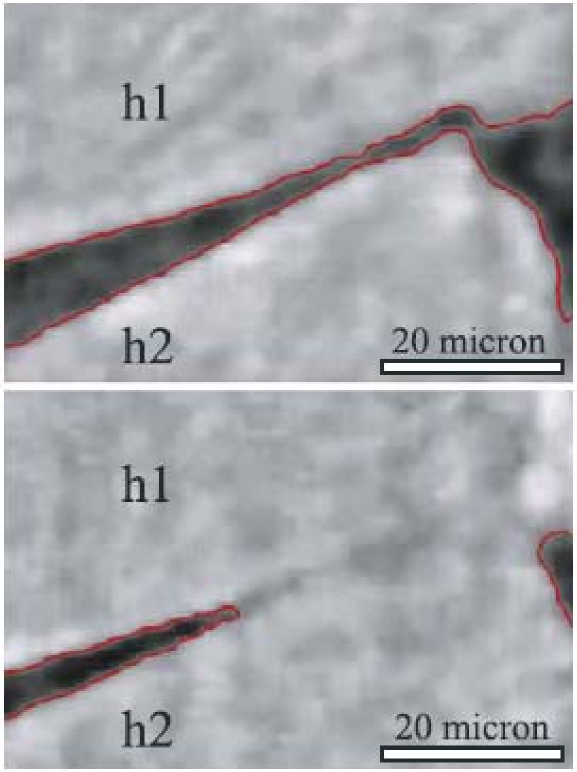
Modes of permeability reduction

- Grain indentation
  - grains are displaced
  - Strengthening of the halite skeleton

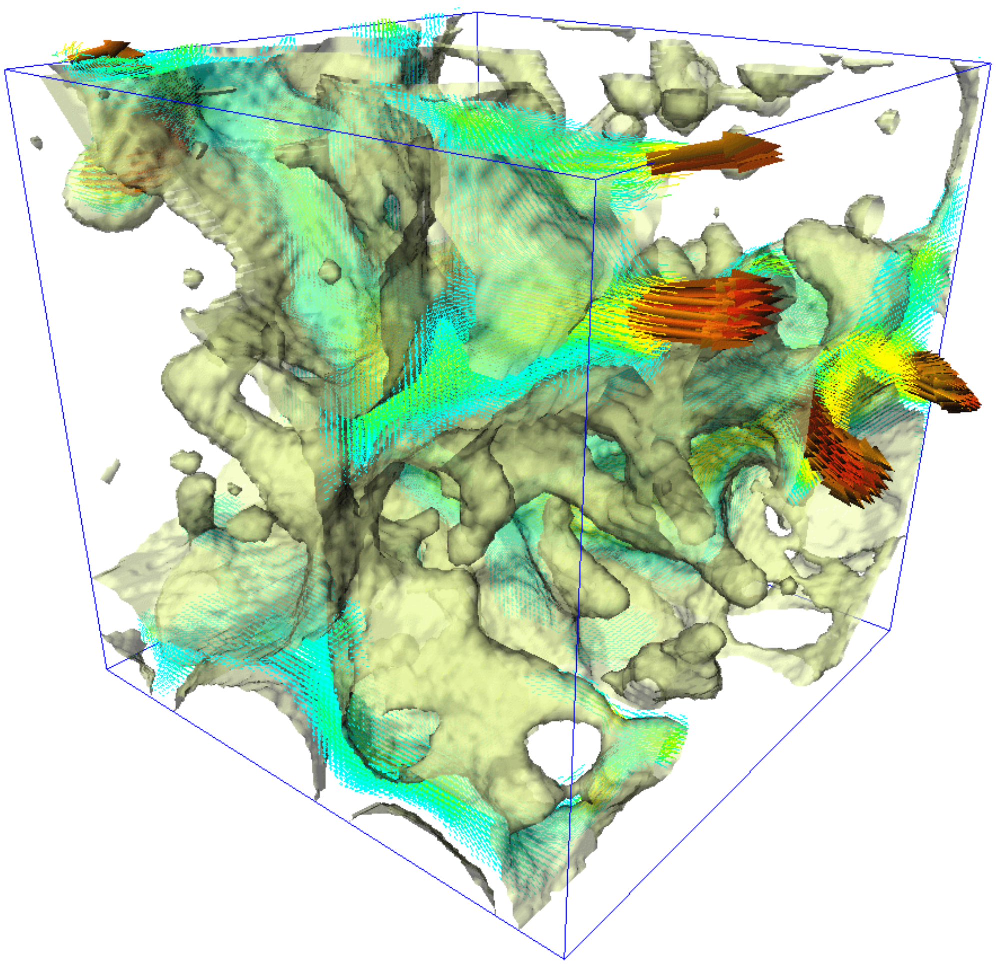


Renard *et al*., Geophysical Research Letters, 31, L07607 (2004)

- Pore throat closure
  - grains do not move
  - Disconnection of porosity



Permeability and pressure solution creep



- 3D data enables calculating the permeability tensor

Elemental distribution 2D

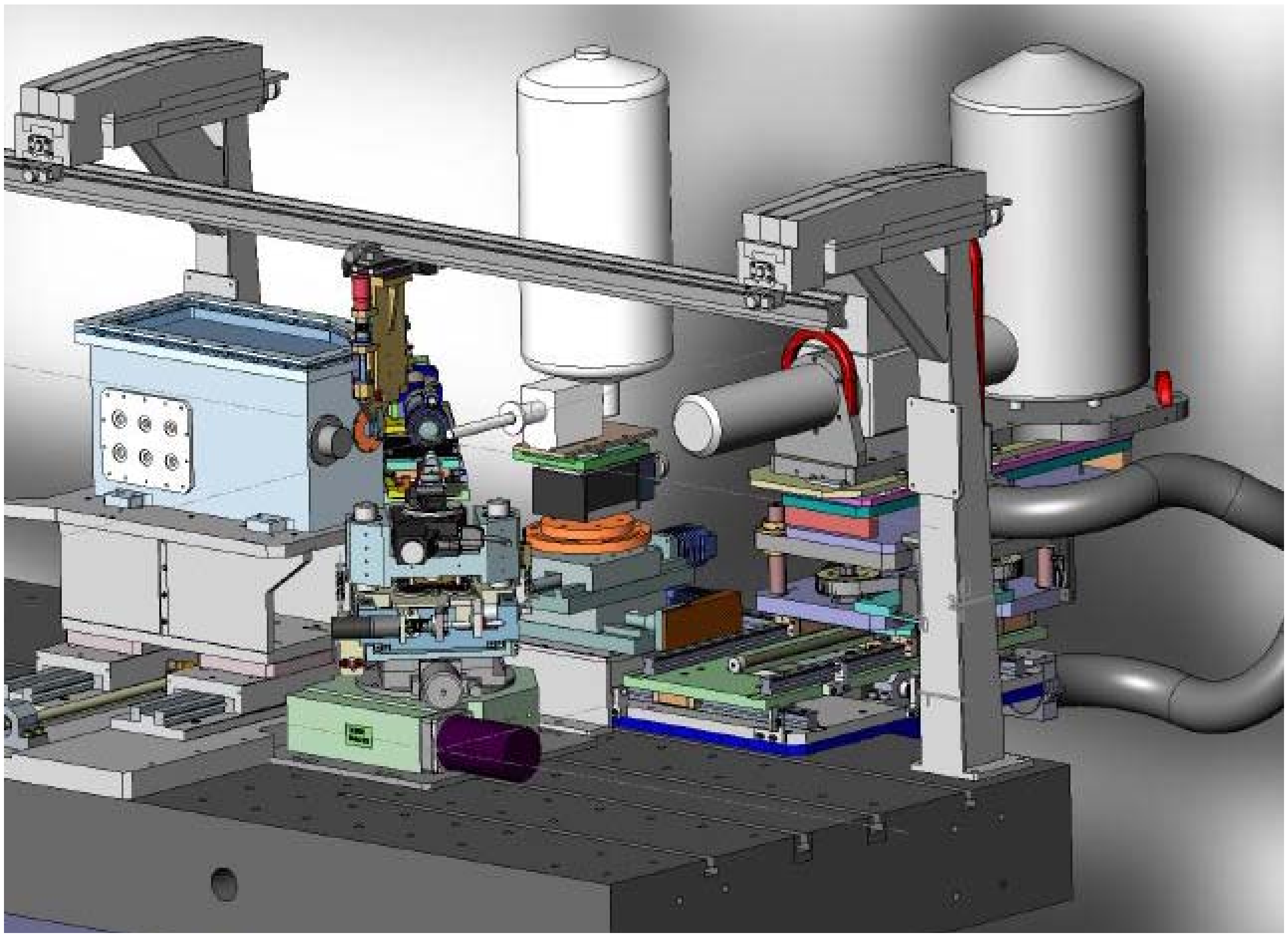
fluorescence mapping

Composition of preserved solar dust

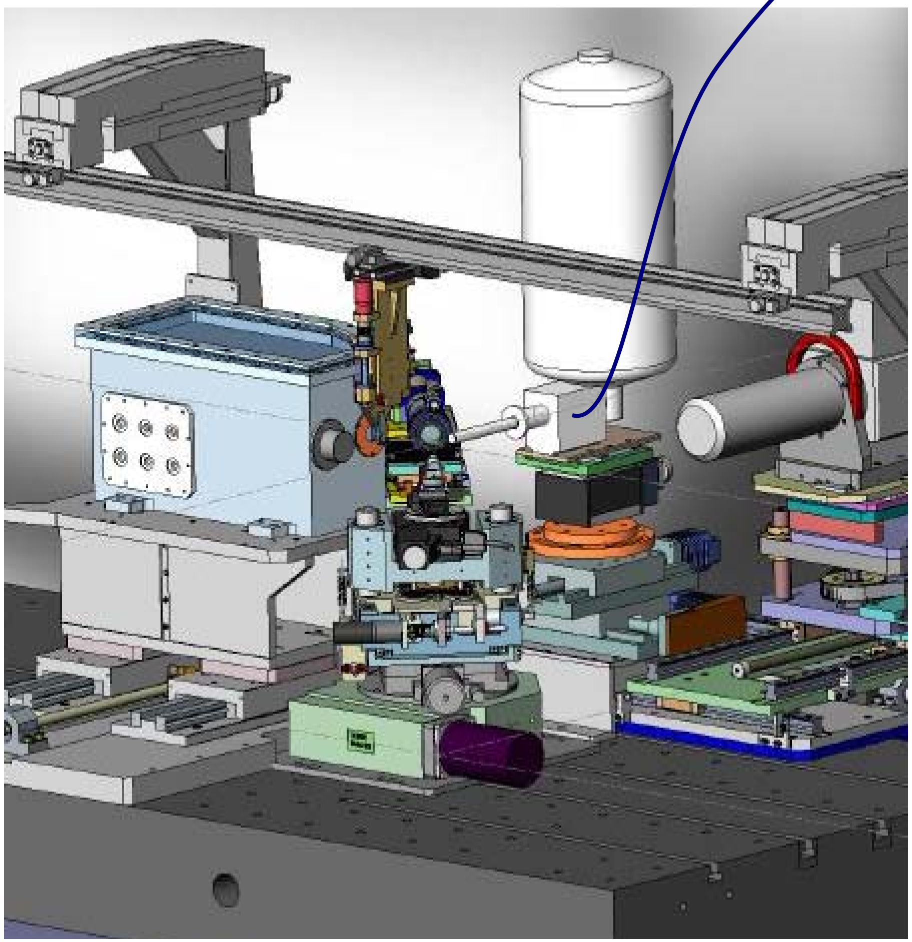
- Aim:
  - Calculate concentrations in dust grains sampled from comet 81P/Wild2
- Scientific background:
  - Comets are representative of the solar nebula composition
  - Stardust brought back more matter from comets than did any previous mission
  - It gives the opportunity to better constrain the solar nebula composition by direct measurements
  - The amount of collected matter is however still small and trapped by aerogel in which dust particles break while being stopped
- Method:
  - Fluorescence mapping of grains trapped in aeorogel and in their impact craters

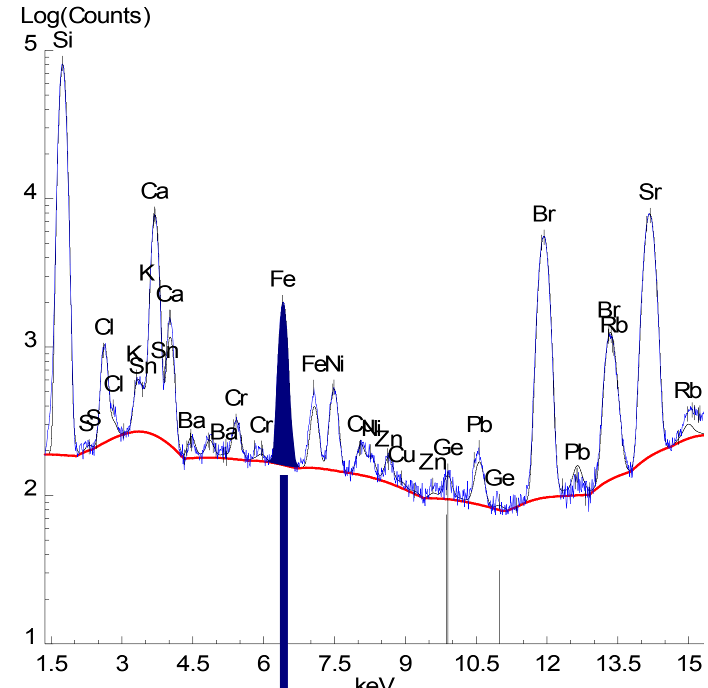
Elemental distribution – fluorescence mapping

- Set-up ID22



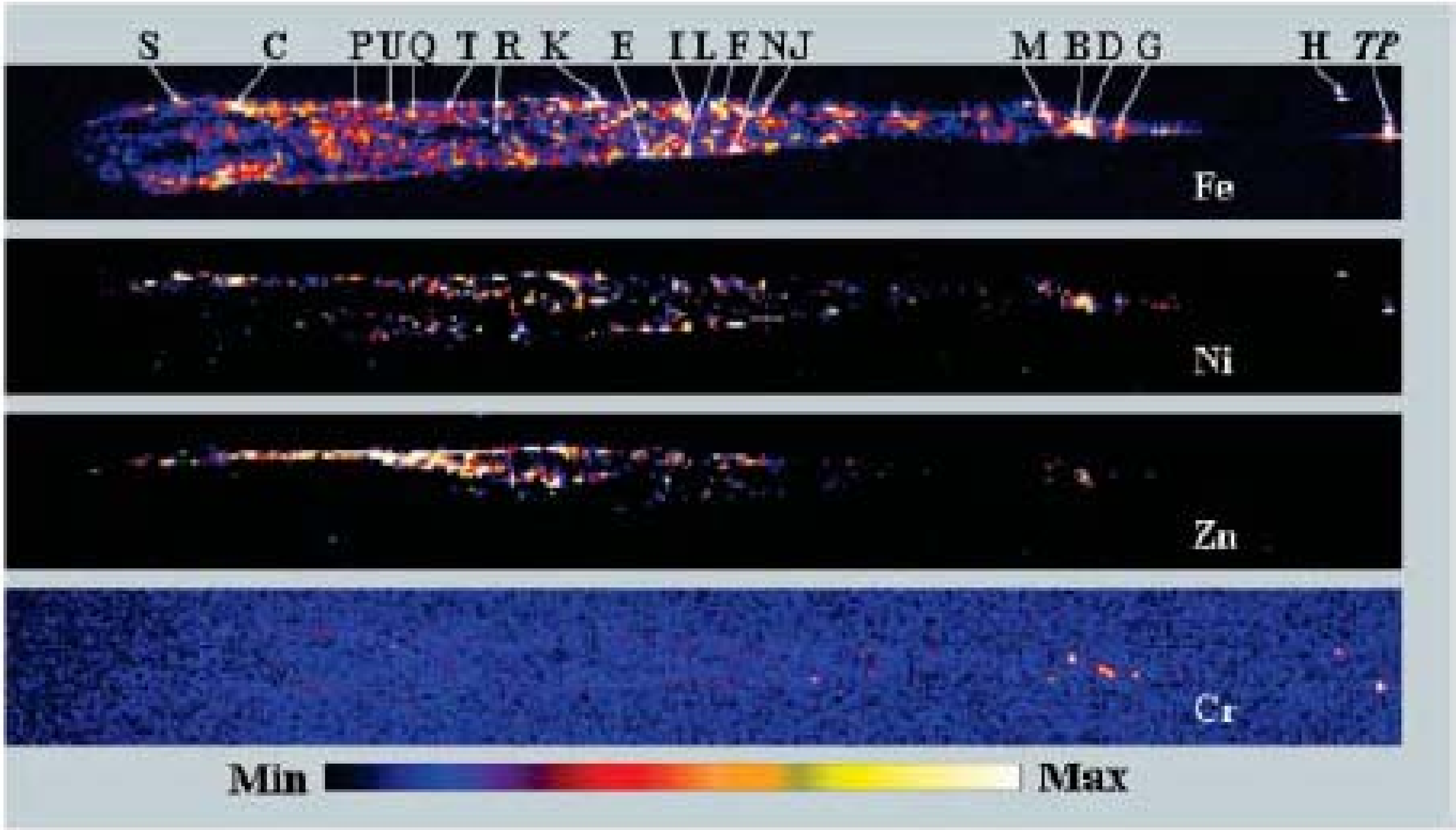
Elemental distribution – fluorescence mapping





N_{Fe}

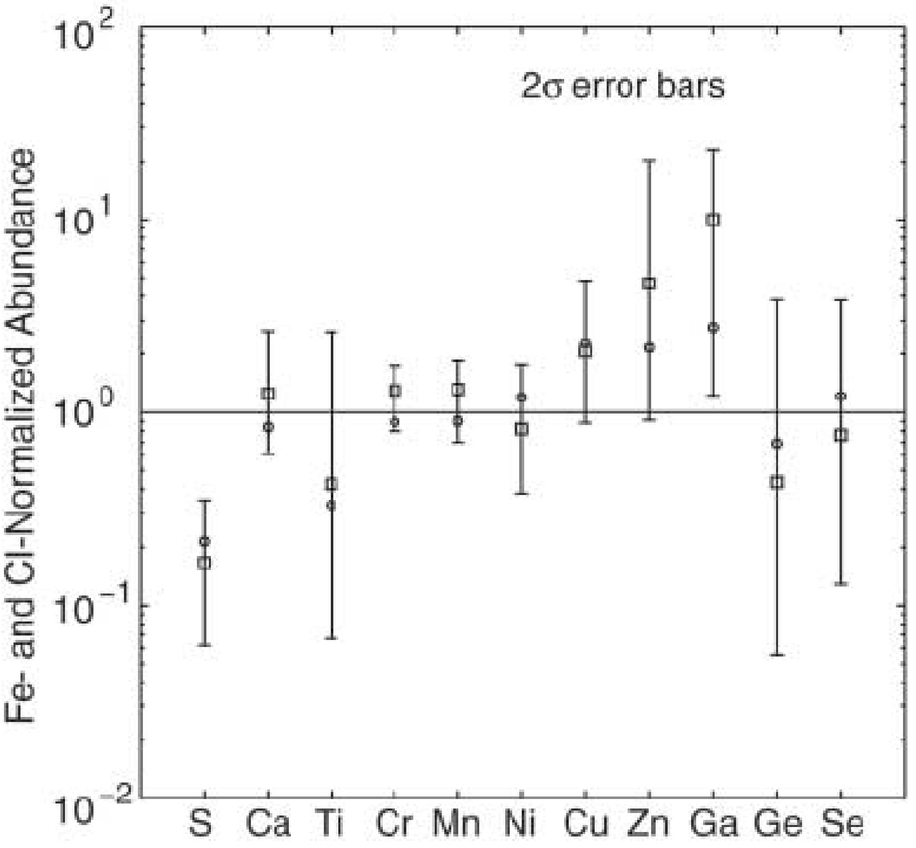
Elemental distribution – fluorescence mapping



Flynn *et al*., Science, 314, 1731 (2006)

Composition of preserved solar dust

- Results:
  - Composition are consistent with previously estimated values
  - Composition of the initial solar nebula may be more enriched in moderately volatile minor elements such as Cu, Zn and Ga



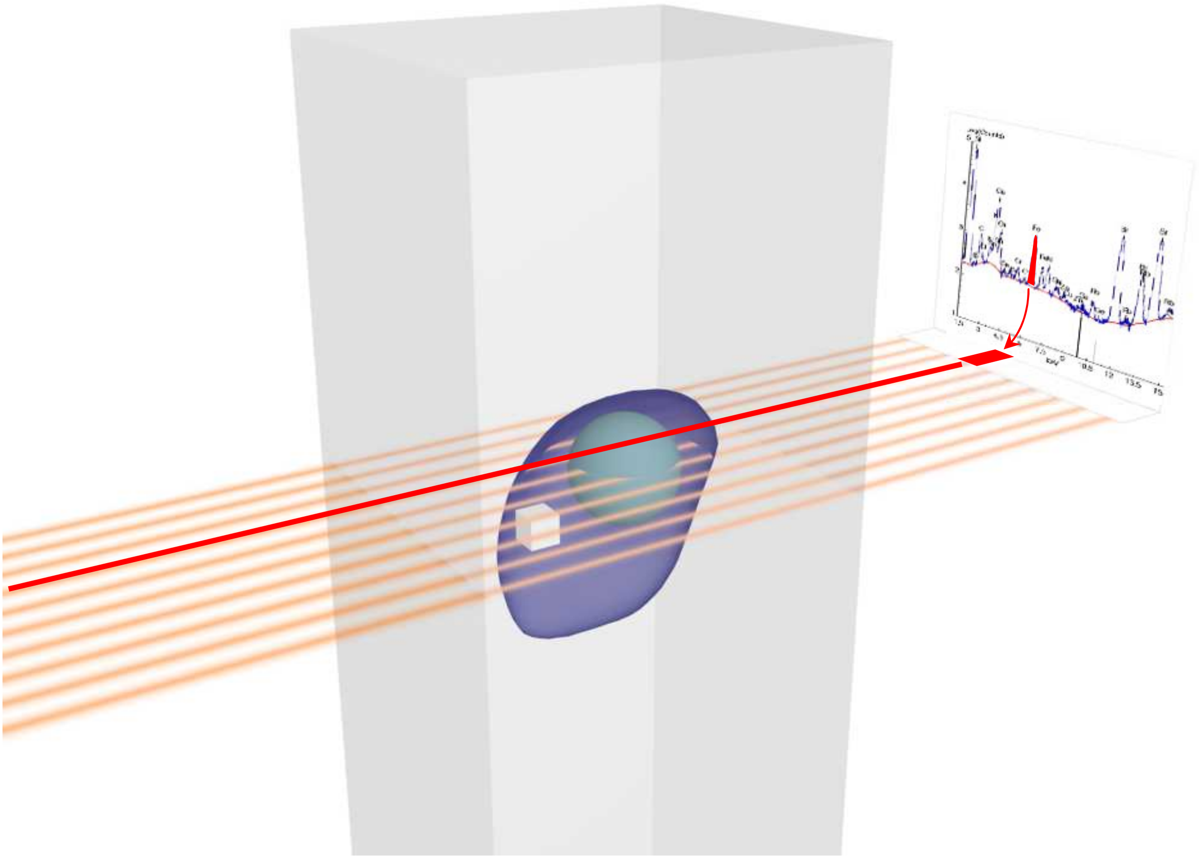
Elemental distribution 3D

fluorescence tomography

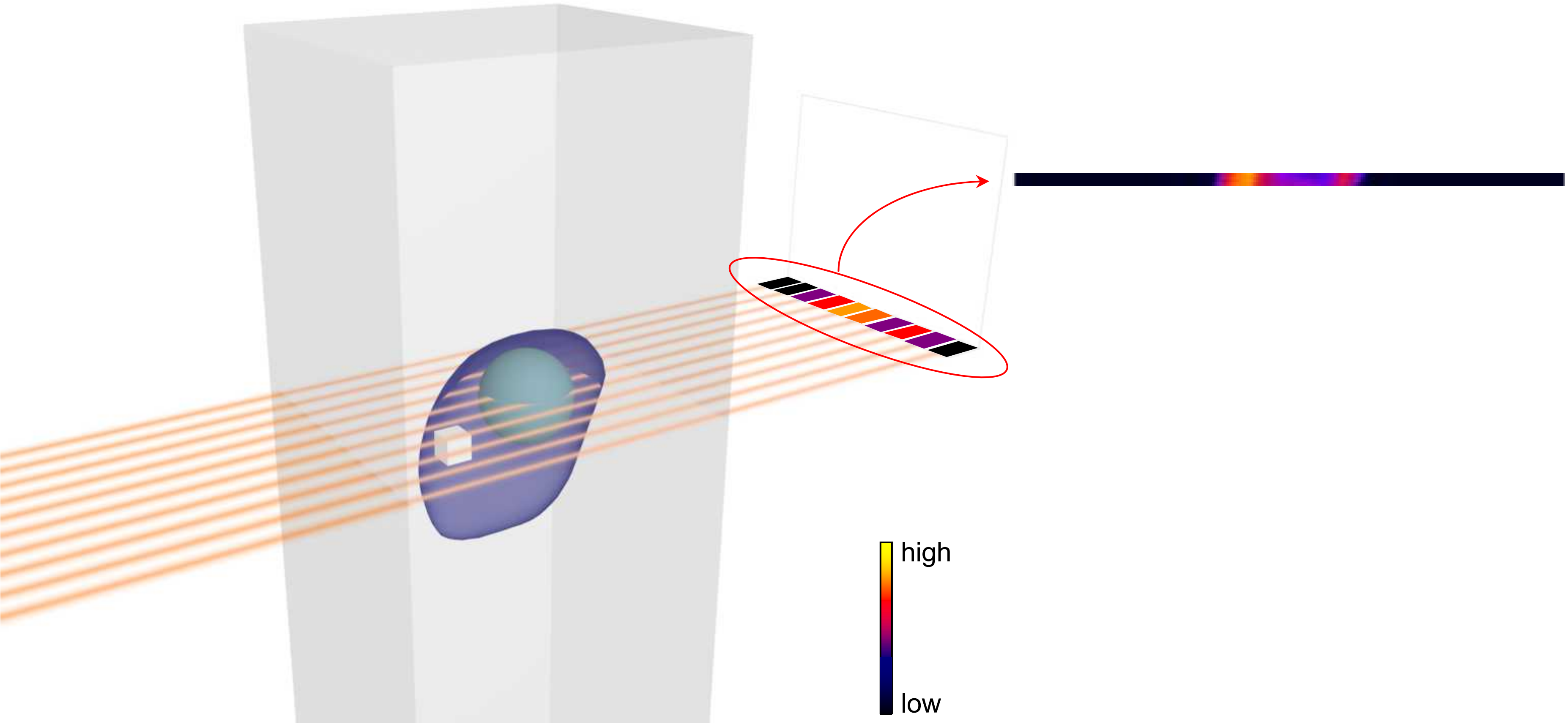
Environmental science: fly-ash particles

- Aim:
  - Investigate 3D imaging with a combination of absorption, Compton and fluorescence tomographies in fly ash particles
- Scientific background:
  - Fly ash produced by burning of biofuels or municipal waste has to be disposed.
  - Concentrations and distributions of potentially toxic elements have to be known before disposal to evaluate possible threat to the environment
- Sample:
  - Single fly-ash particle glued on the top of a quartz capillary
- Method:
  - Imaging the sample with helical scan and simultaneous recording of absorption, Compton and fluorescence signals

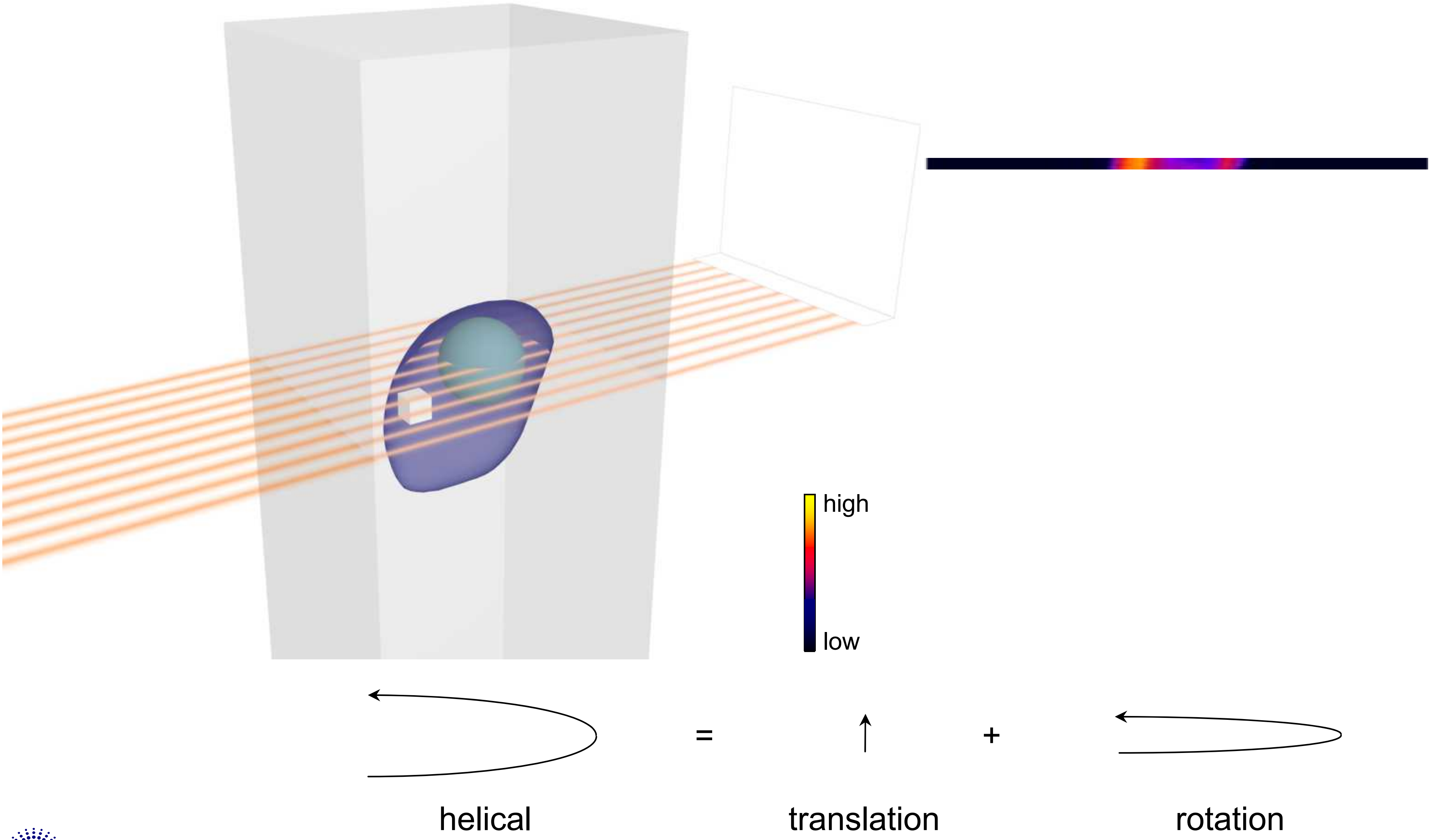
Fluorescence tomography : helical scan



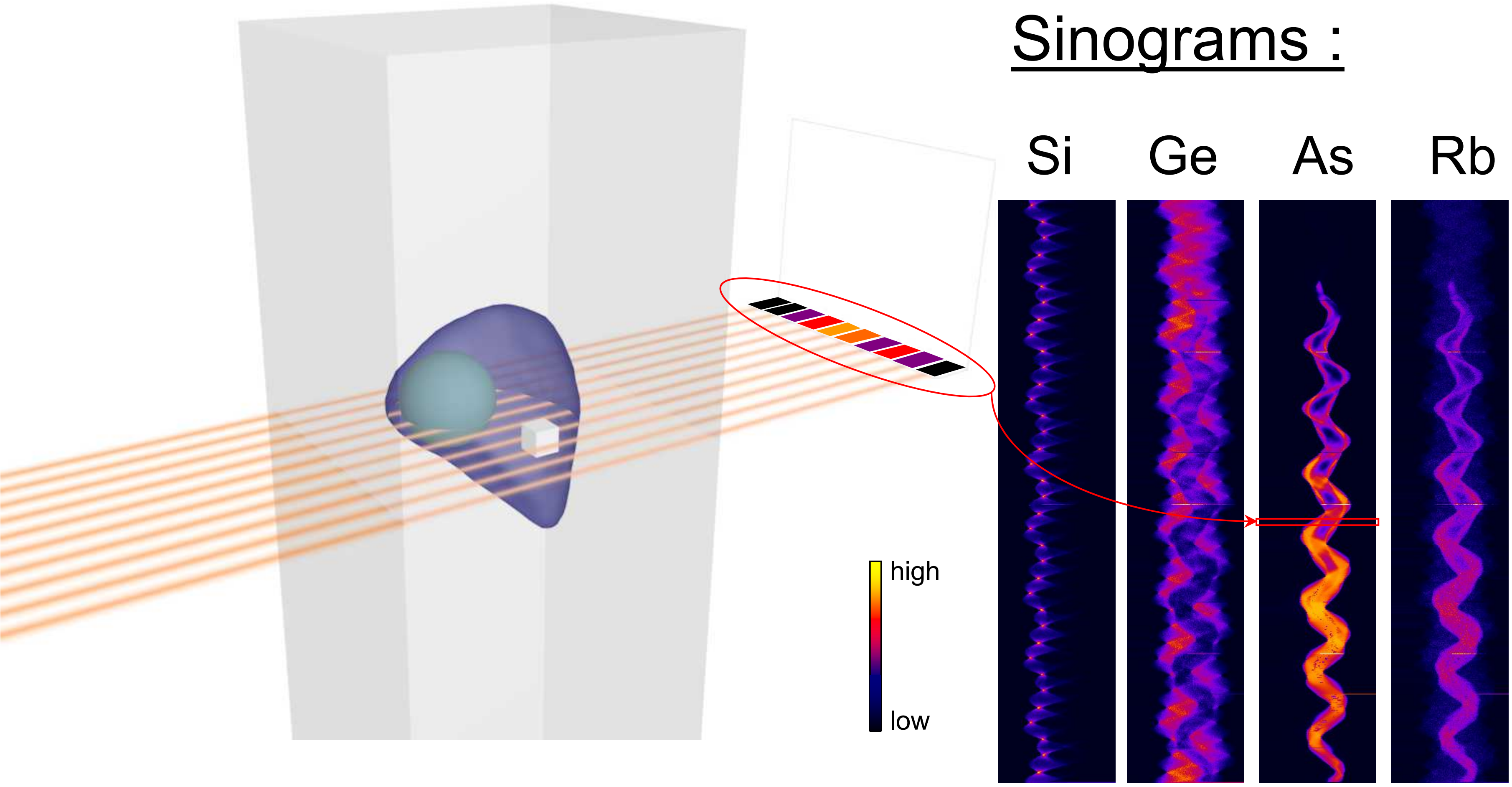
Fluorescence tomography : helical scan



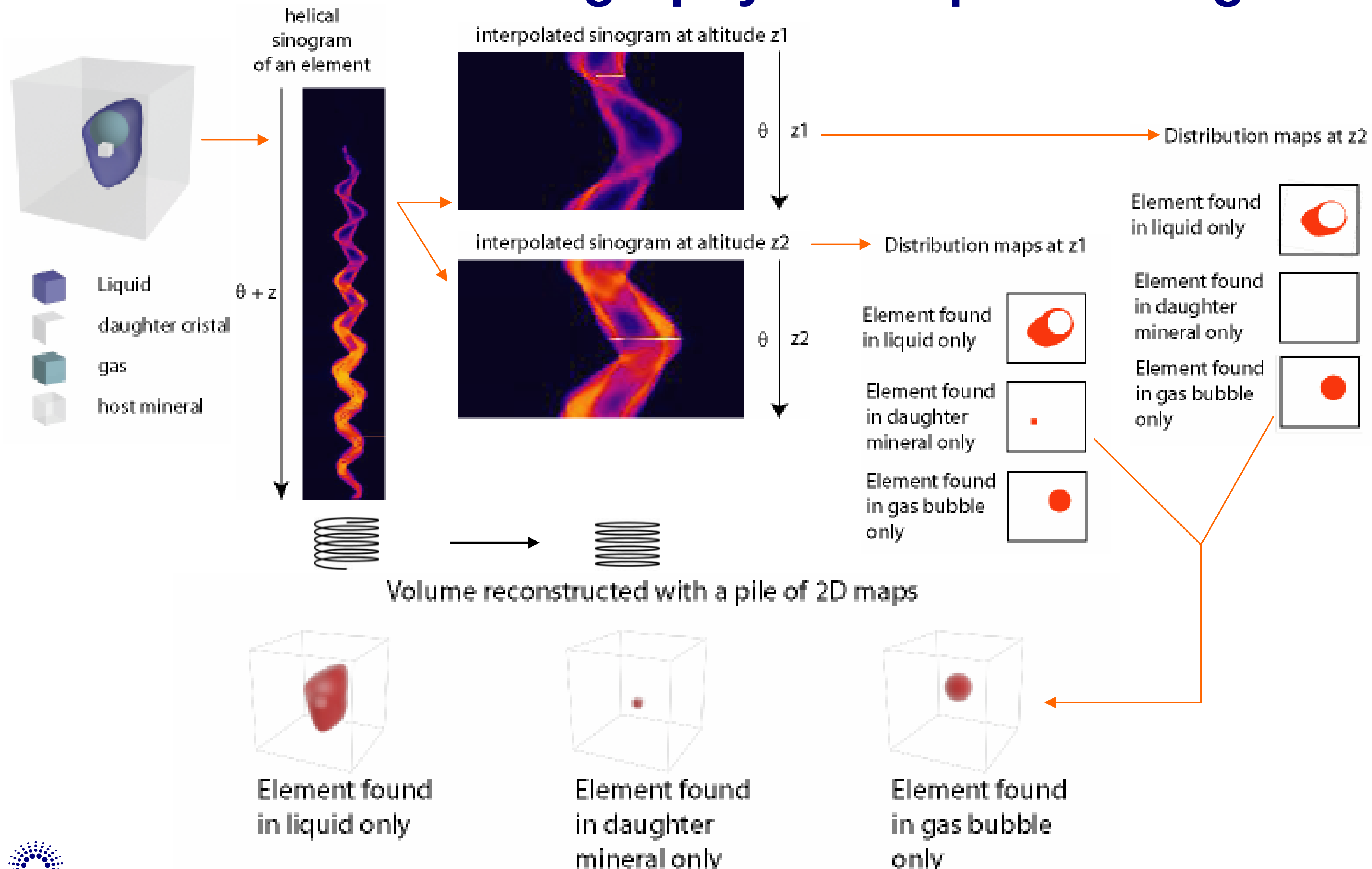
Fluorescence tomography : helical scan



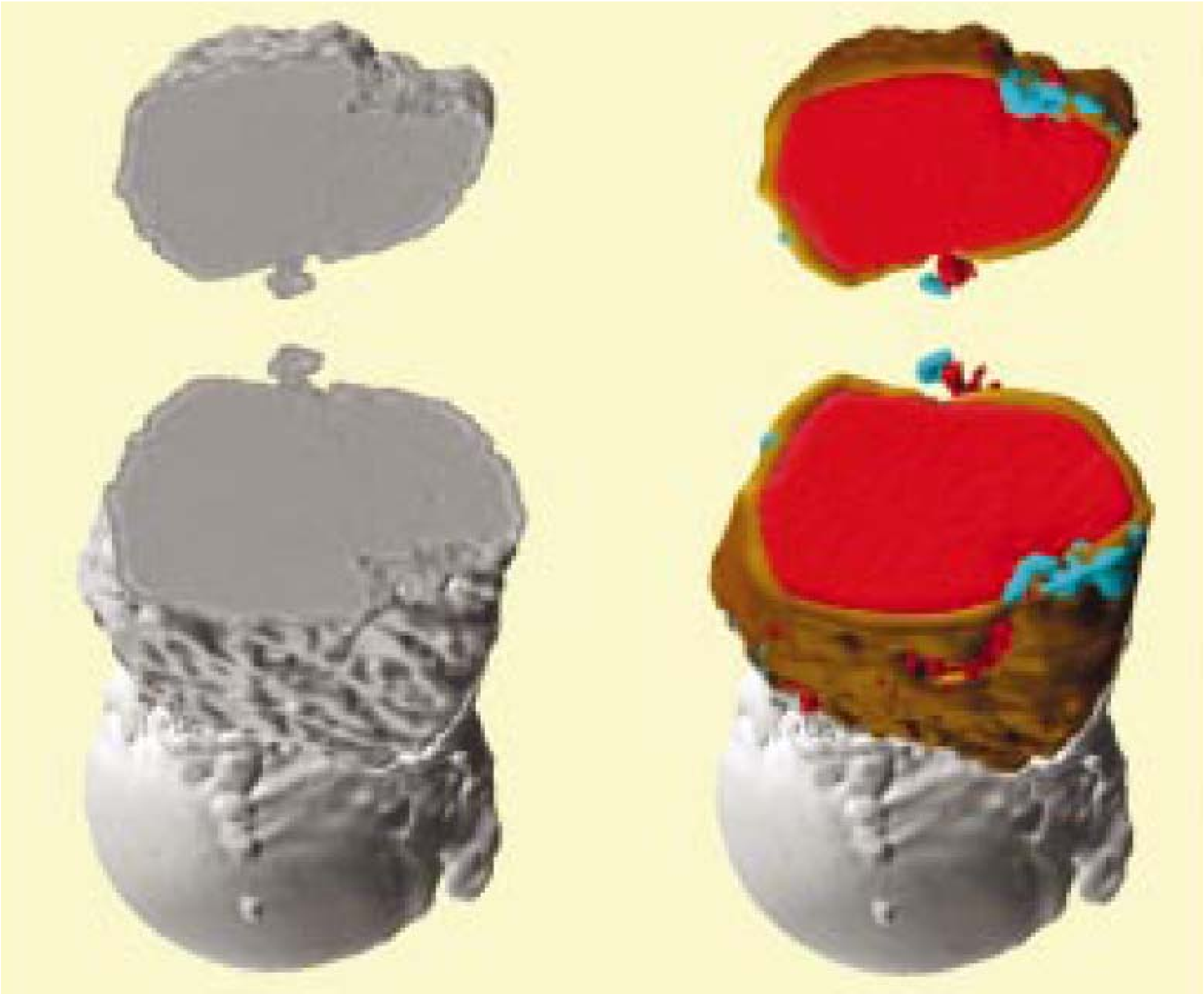
Fluorescence tomography : helical scan



Fluorescence tomography : data processing

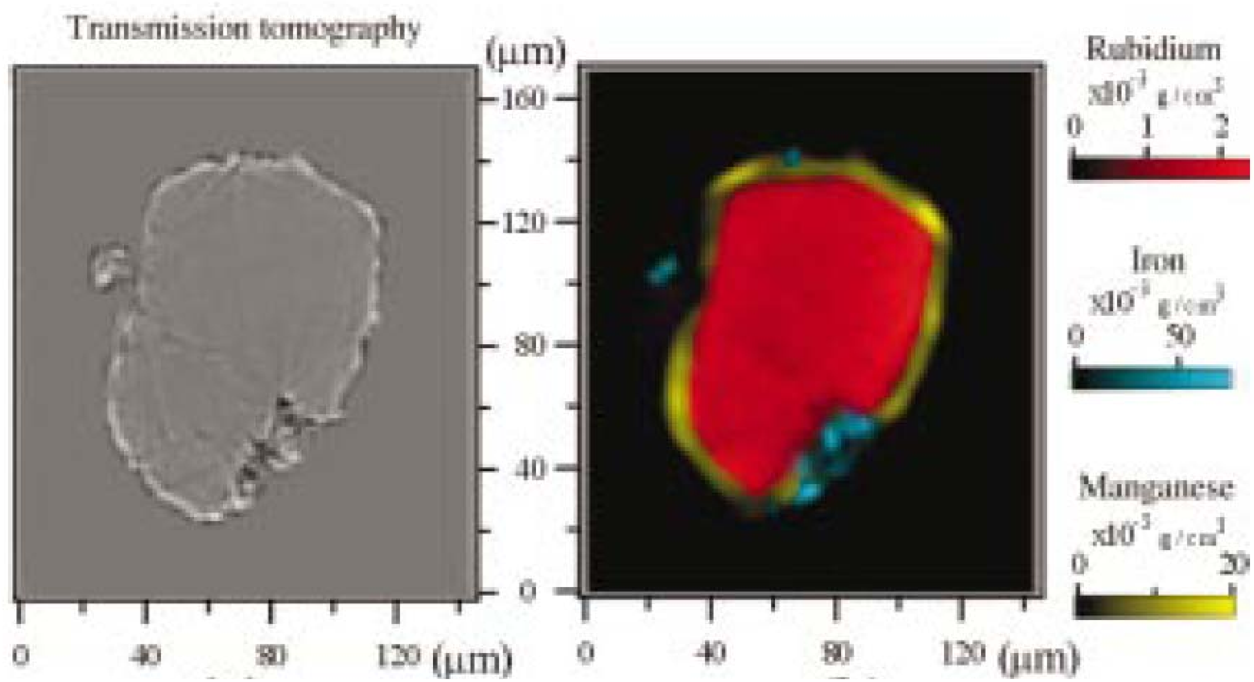


- Results:
  - Elements are not homogeneously distributed.
  - Elements (Rb, red) protected by the Mn shield (brown) are less easily leached or made available to the environment



Golosio *et al*., Applied Physics Letters, 84, 2199-2201 (2004)

- Results:
  - Elements are not homogeneously distributed.
  - Elements (Rb, red) protected by the Mn shield (brown) are less easily leached or made available to the environment
  - Images are quantitative



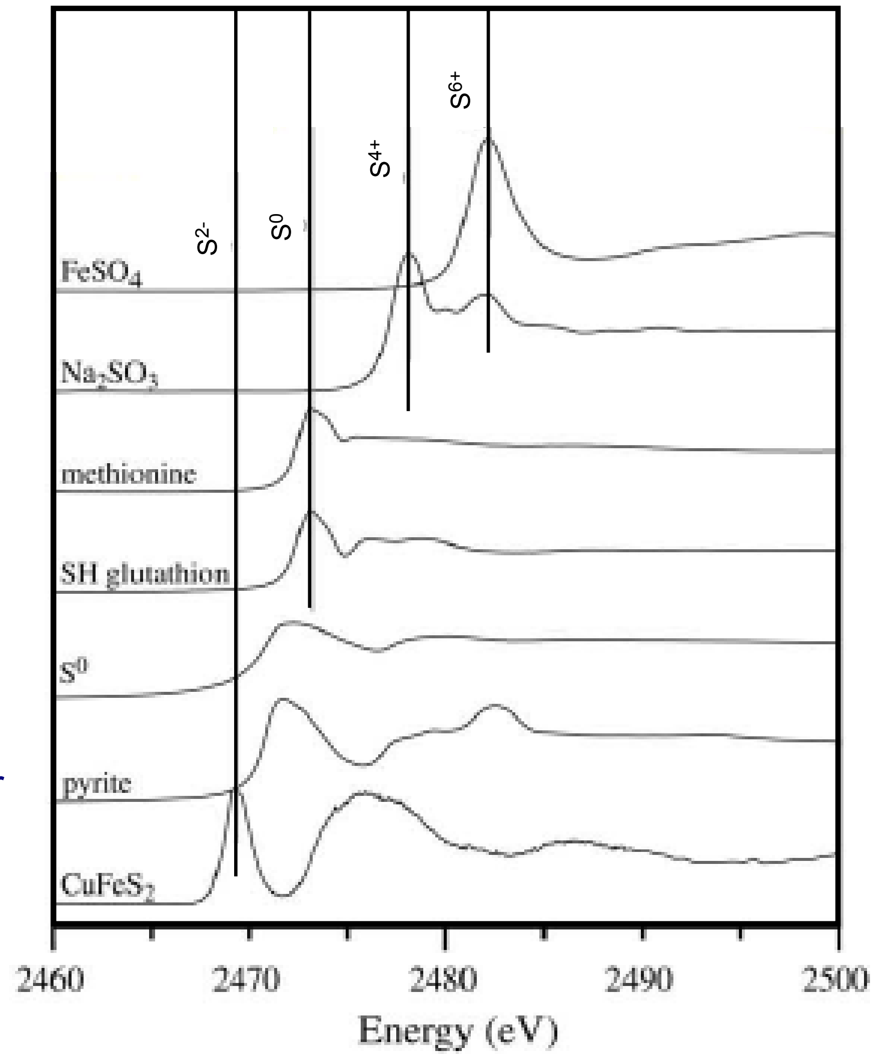
Golosio *et al*., Applied Physics Letters, 84, 2199-2201 (2004)

Elemental oxidation state

fluorescence mapping at selected energies

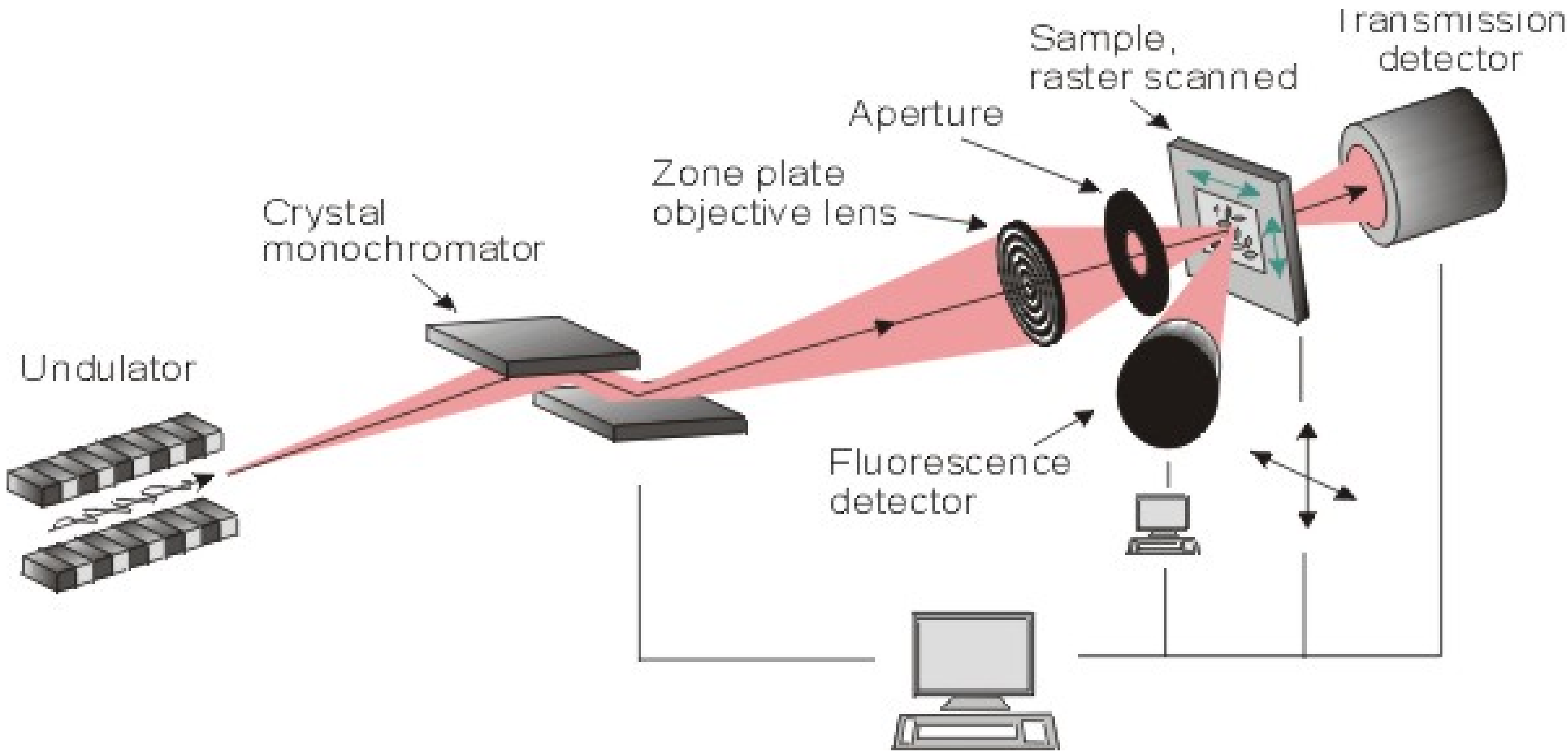
Early life – which traces?

- Aim:
  - Map S oxidation state in microfossils and living bacteria
- Scientific background:
  - No specific morphology enable discriminating biogenic from abiotic processes
  - Look for a specific biogeochemical signature
  - Is S oxidation state preserved in fossils?
  - Ultimate goal: define chemical signatures valid up to the early life (>3.5 Gyr)
- Sample:
  - living bacteria
  - analogues encapsulated in an Silica-rich matrix sampled on a deep ocean smoker
- Method
  - Fluorescence mapping of S at selected incident energies



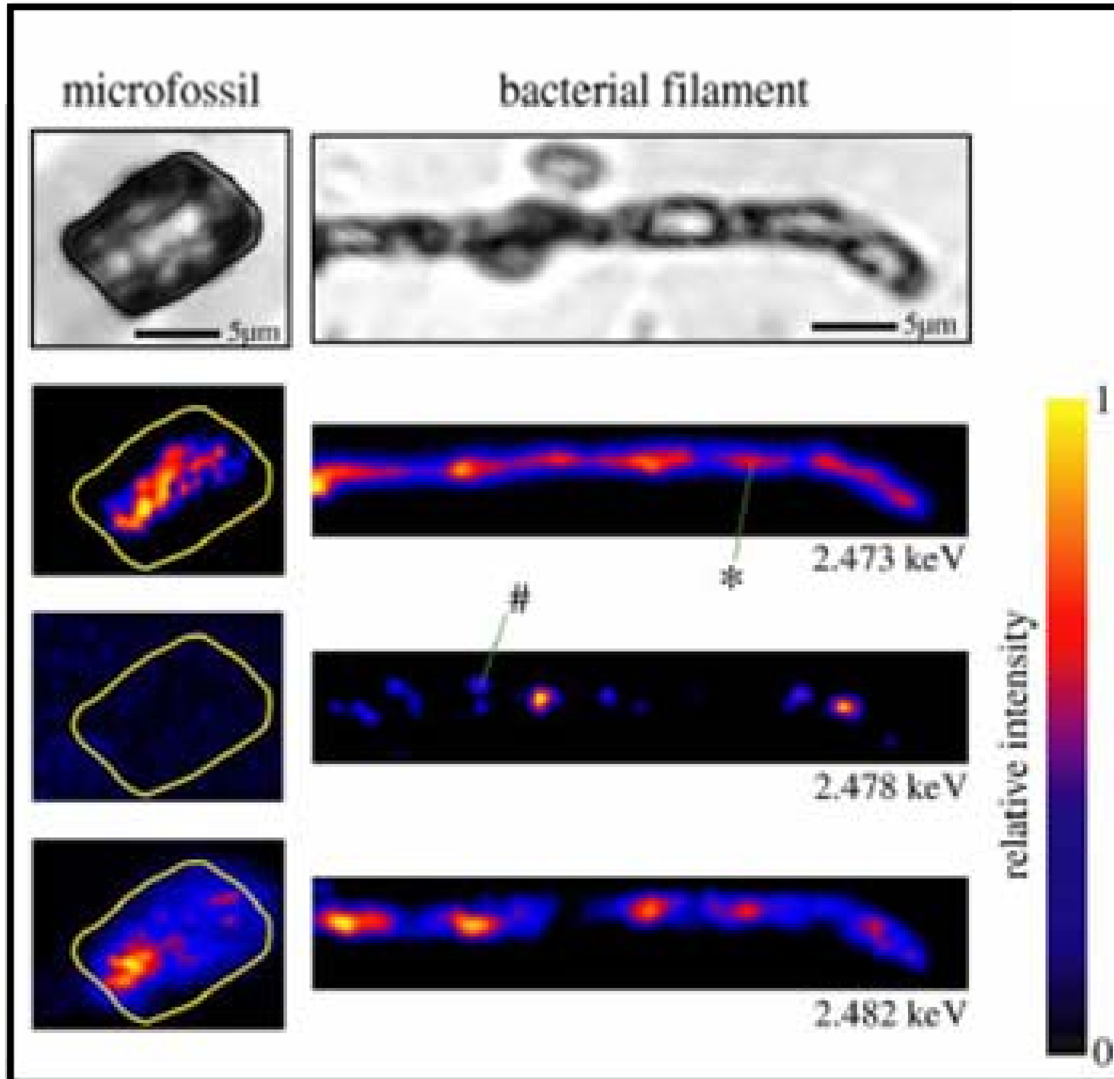
Elemental oxidation state – fluorescence mapping at selected energies

- Set-up ID21



S^0, S^{4+} and S^{6+} distributions

- Results:
  - S is spatial distributions are comparable in both samples → X-ray fluorescence mapping can help discriminating true fossils
  - S oxidation state is comparable in both samples → S could be an indicator of early biogenic activity
  - Is S oxidation state preserved in older fossils (>3.5 Gyr)



Foriel *et al*., Geochimica et Cosmochimica Acta, 68, 1561-1569 (2004)

Elemental speciation

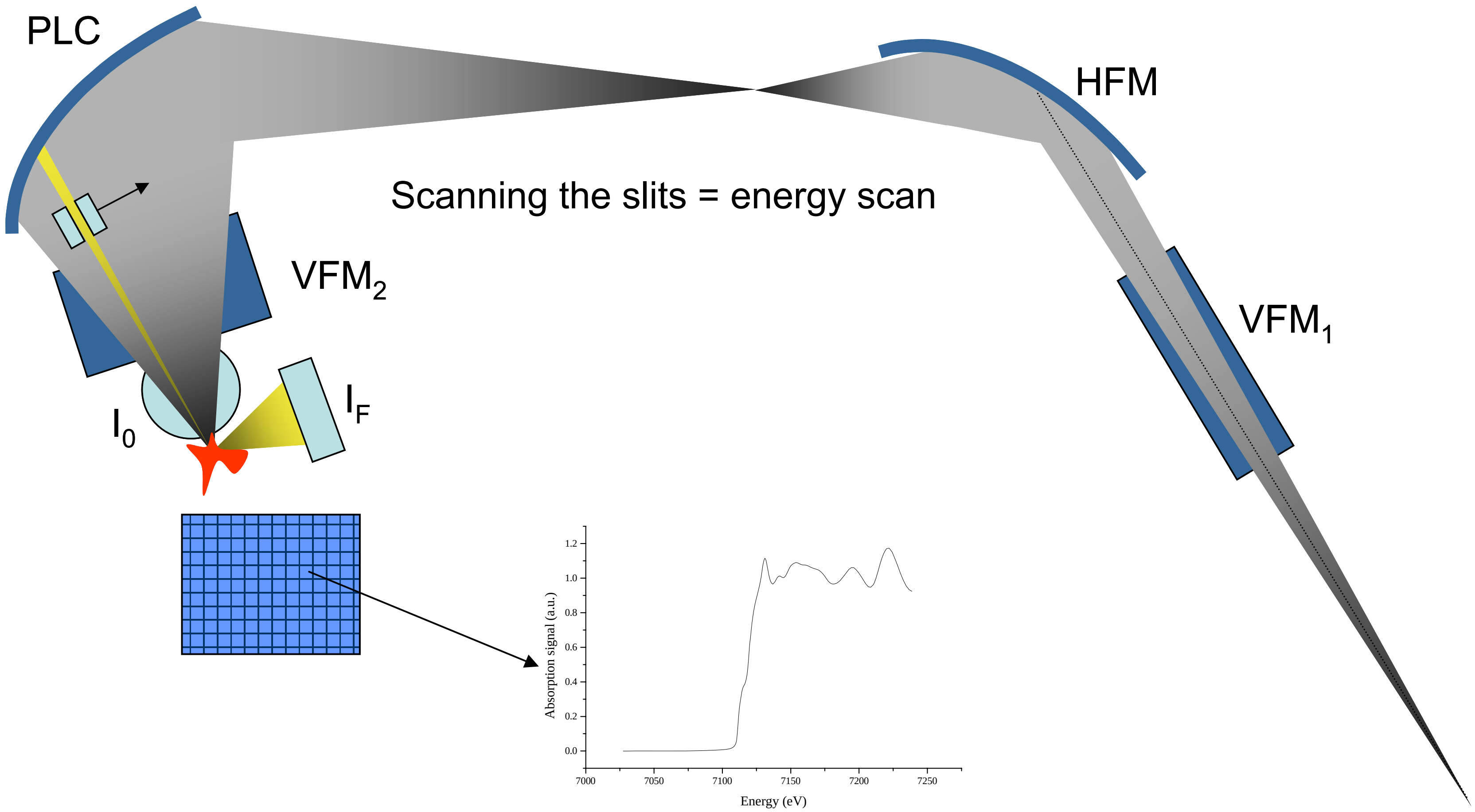
XANES mapping

Fe^{3+}/Fe_{total} in pressure shadow fillings

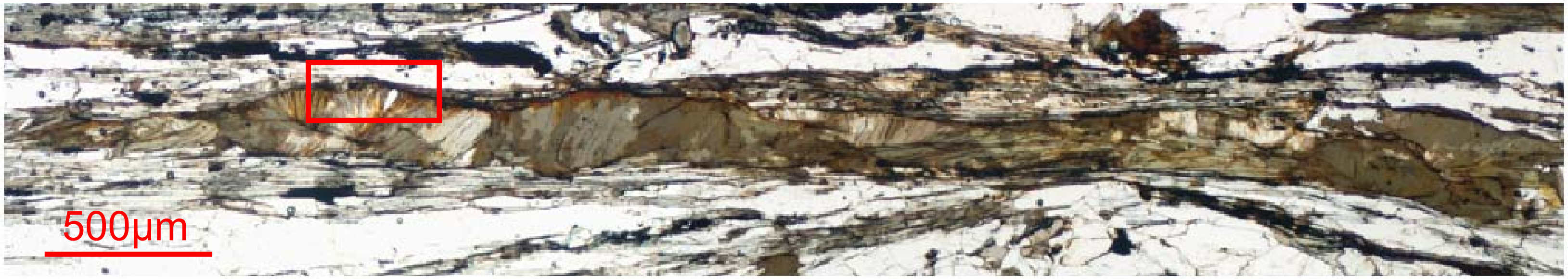
- Aim:
  - Test a thermodynamic procedure to evaluate oxidation state of some elements in mineralogical assemblages
- Scientific background:
  - There is a need of evaluating temperature and pressure at which minerals formed
  - Thermodynamics can provide those information in a mineralogical assemblage provided phases are exactly known
  - Electron microprobe provides elemental concentrations but do not give any information about chemical structure
  - A method based on multiequilibrium thermodynamic calculations have been established to fill this gap but need to be tested by comparing its **prediction** with the comparable **measured** information
- Samples:
  - Chlorite, phengite and quartz assemblage from a metamorphic rock from Sambagawa (southwestern Japan)
- Method
  - XANES mapping at the Fe K edge

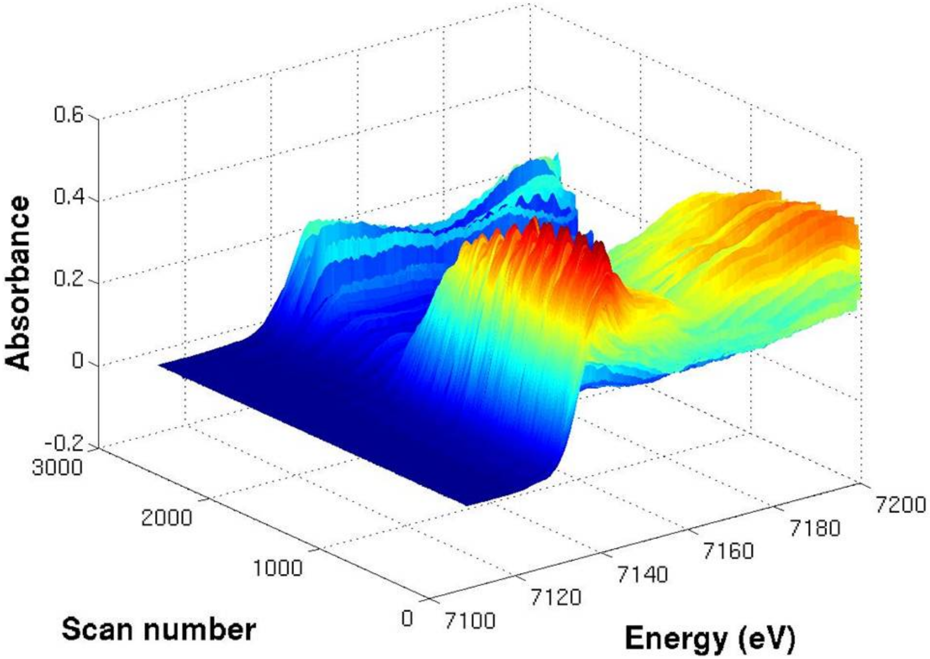
Elemental speciation – fluorescence mapping at selected energies

- Set-up ID24

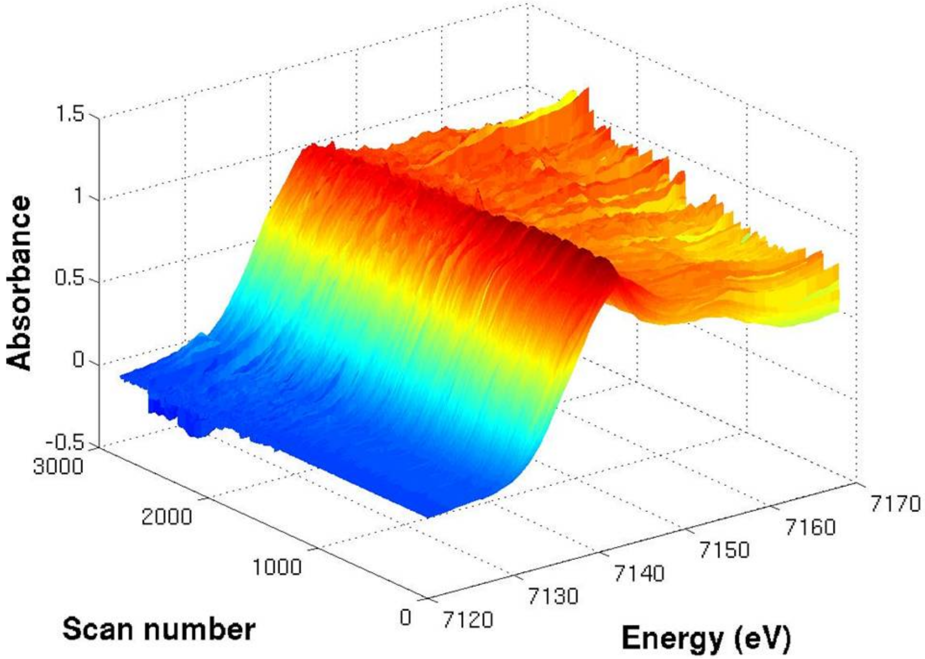


Elemental speciation – XANES mapping



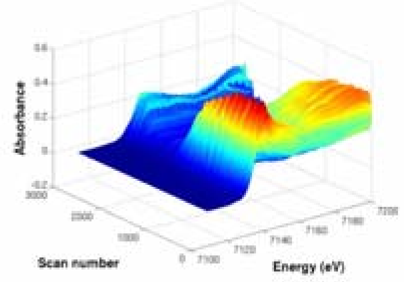


raw spectra

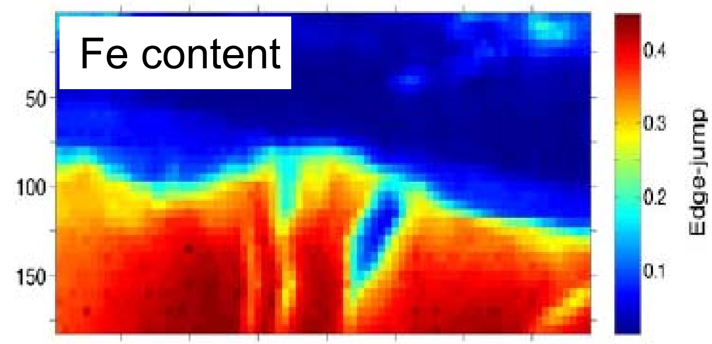


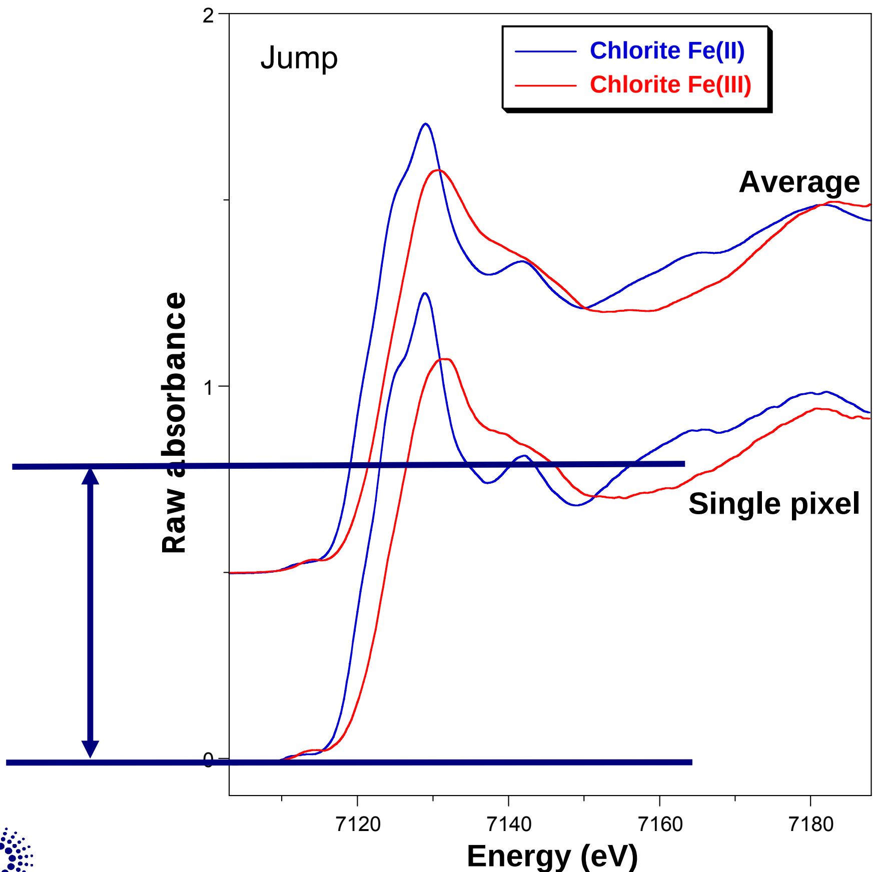
normalised spectra

Elemental speciation – XANES mapping

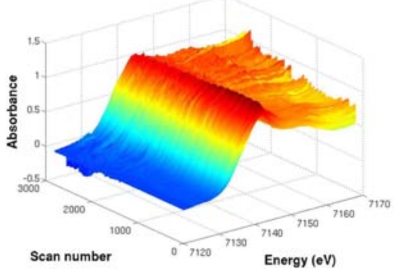


Muñoz *et al*., Geochemistry Geophysics Geosystems, 7, Q11020 (2006)

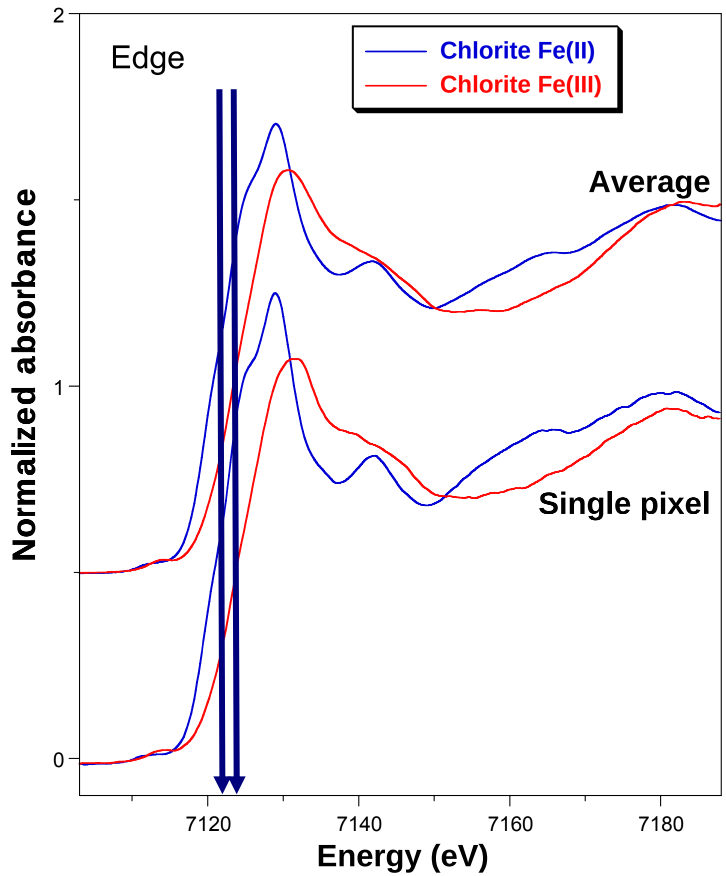


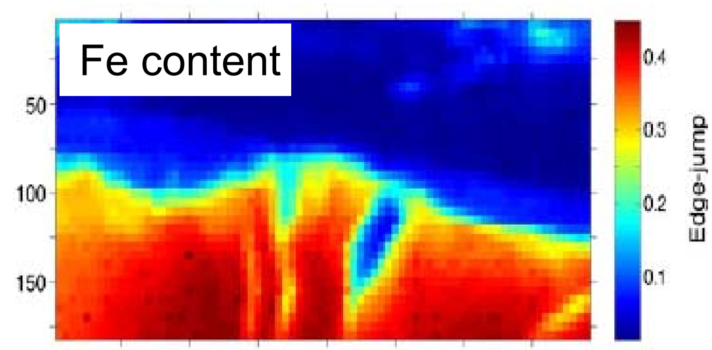


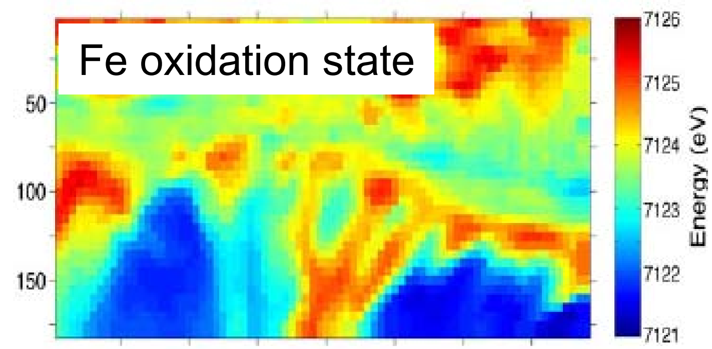
Elemental speciation – XANES mapping



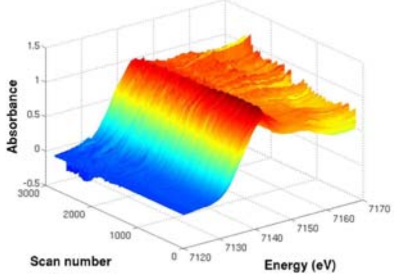
Muñoz *et al*., Geochemistry Geophysics Geosystems, 7, Q11020 (2006)



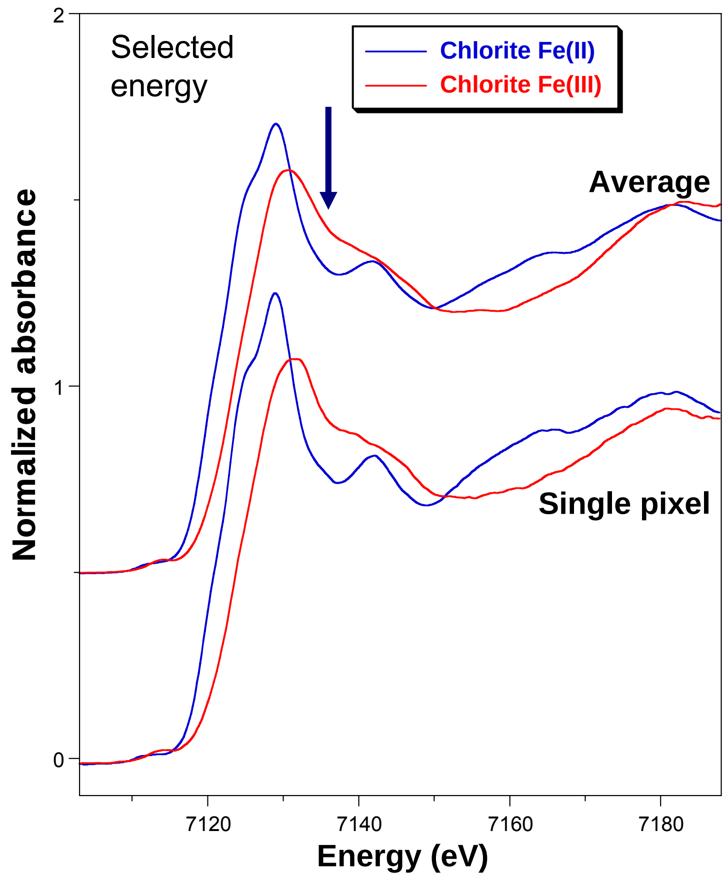


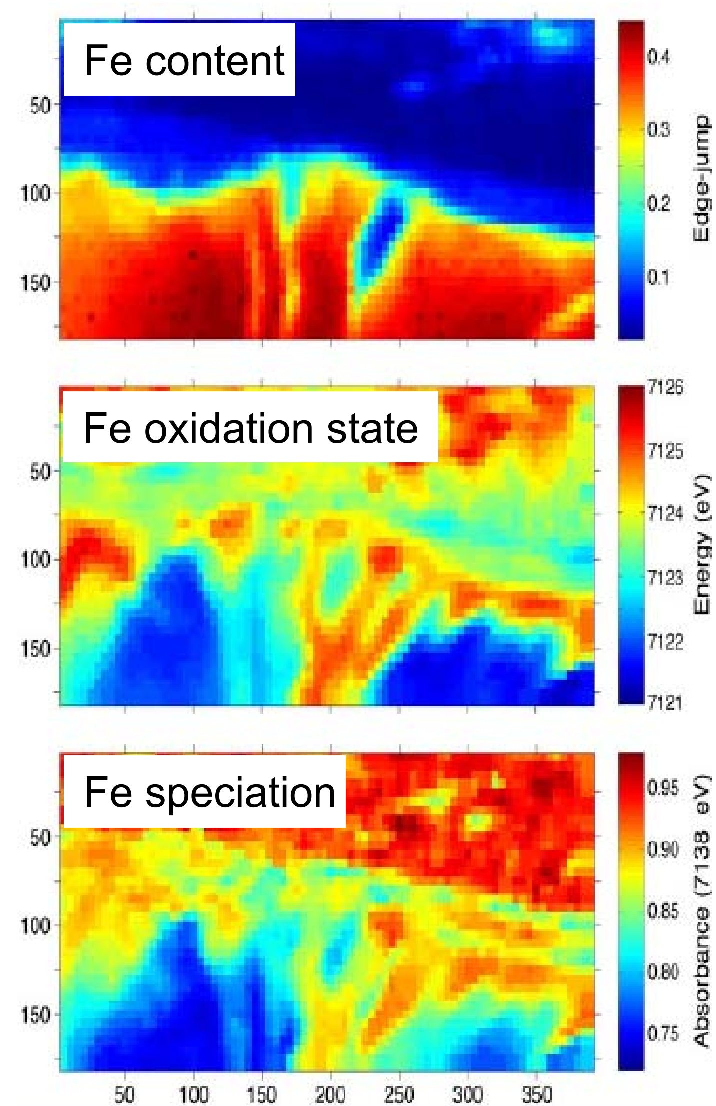


Elemental speciation – XANES mapping



Muñoz *et al.*, Geochemistry Geophysics Geosystems, 7, Q11020 (2006)



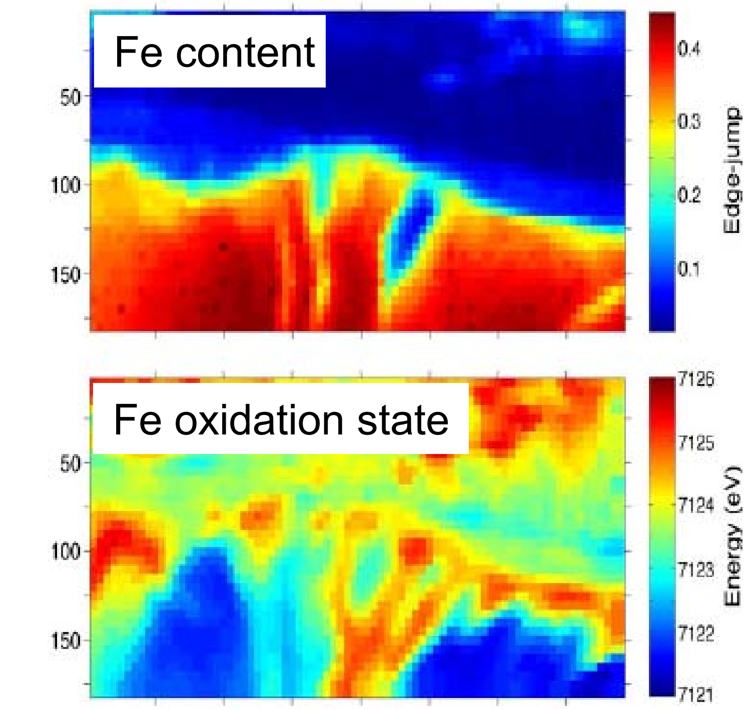


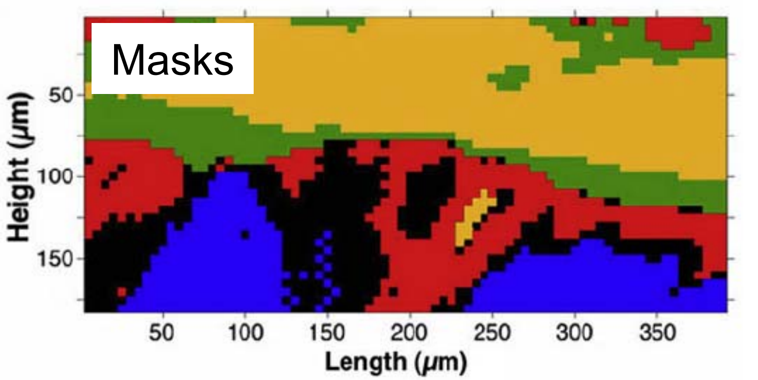
Elemental speciation – XANES mapping

Muñoz *et al*., Geochemistry Geophysics Geosystems, 7, Q11020 (2006)

Separation of chlorite, phengite and quartz

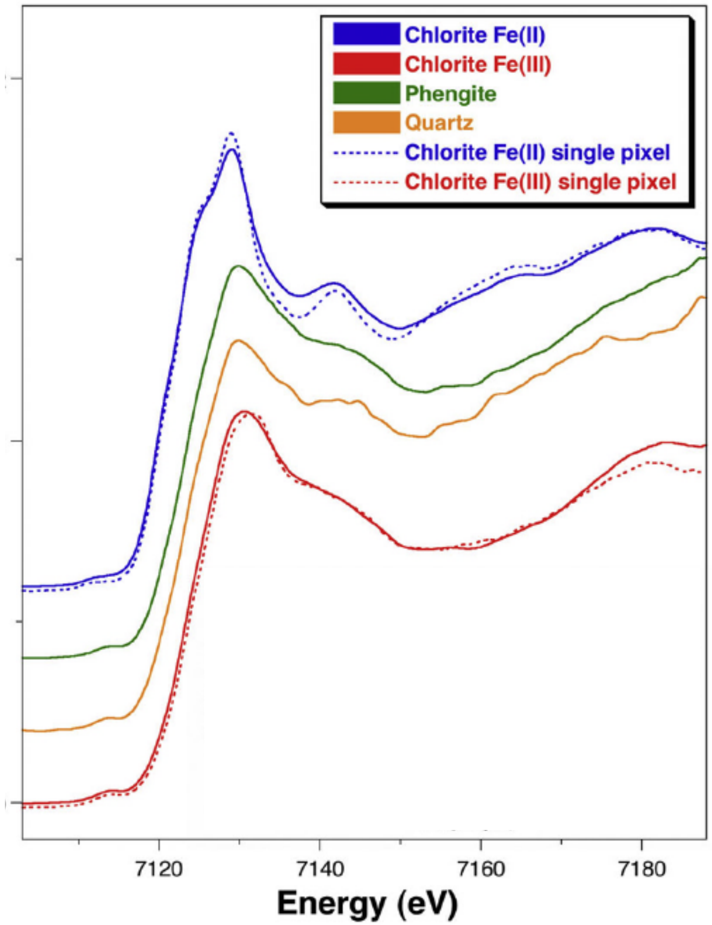
Separation of chlorite (FeII) and chlorite (FeIII)

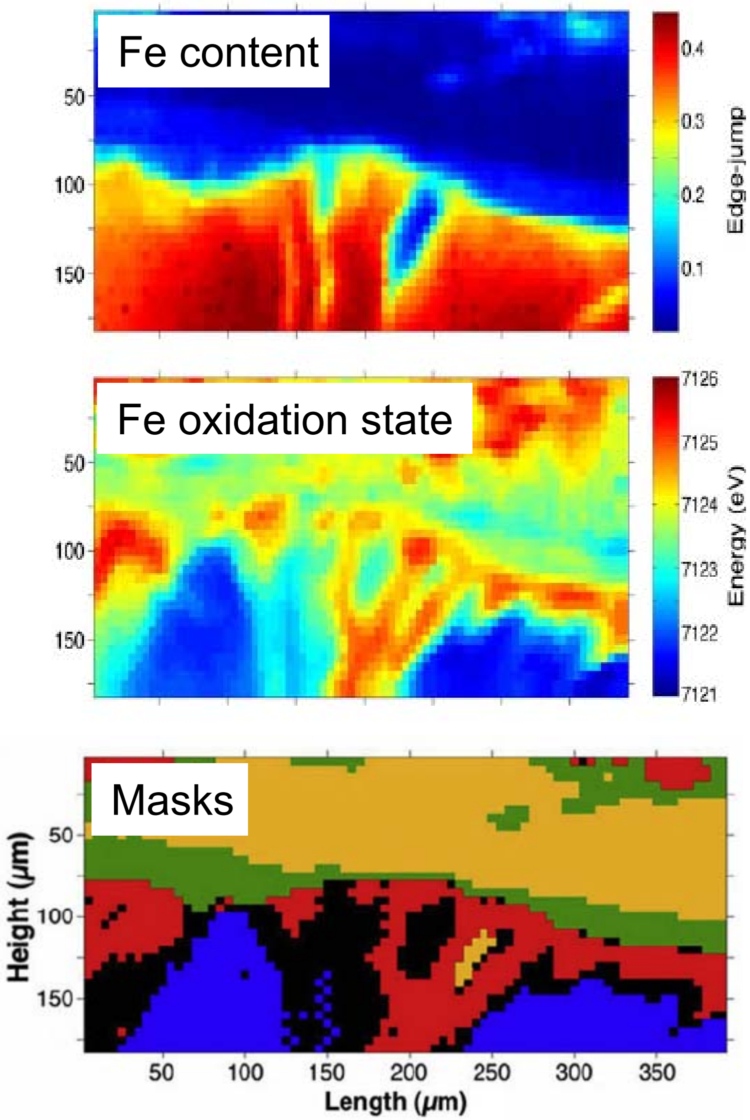




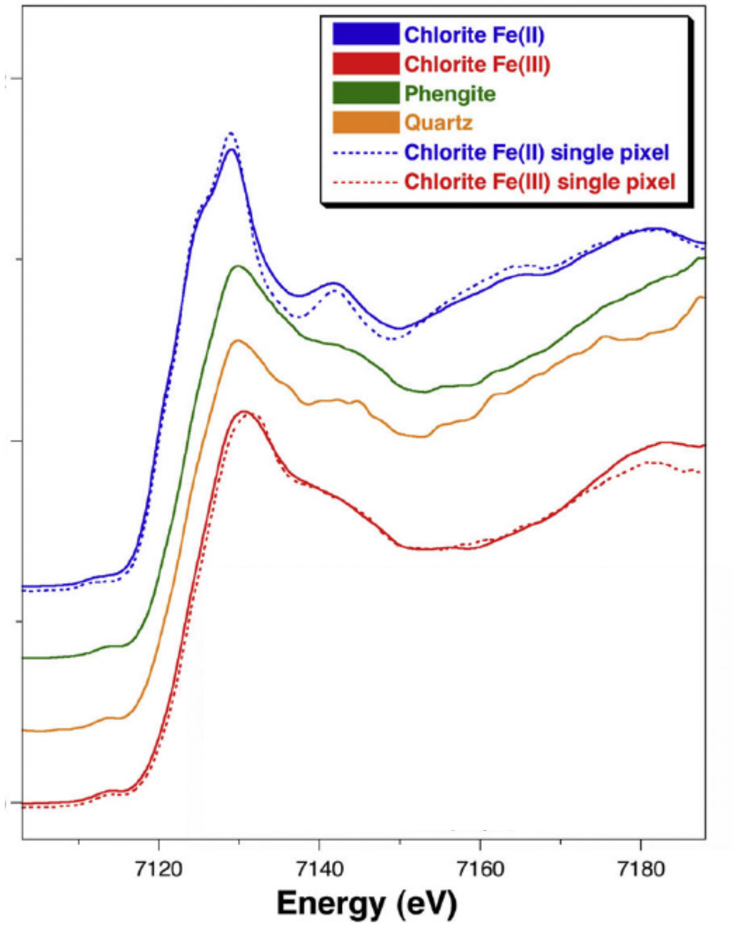
Elemental speciation – XANES mapping

Muñoz *et al*., Geochemistry Geophysics Geosystems, 7, Q11020 (2006)





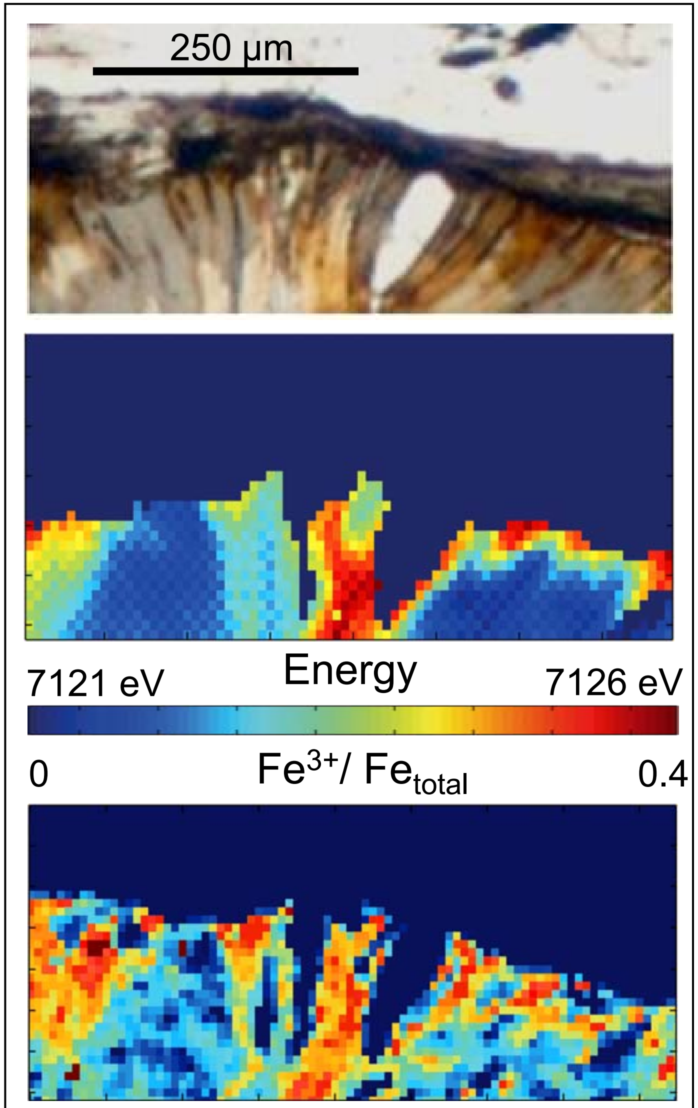
Elemental speciation – XANES mapping



- Results:
  - Ab initio calculations on averaged spectra suggest that Fe(II) is in octahedral sites whereas Fe(III) is preferentially located in octahedral interfoliar layers

Muñoz *et al*., Geochemistry Geophysics Geosystems, 7, Q11020 (2006)

Elemental speciation – XANES mapping



Optical image

Measured map of Fe^{3+}/Fe_{total} (XANES)

Calculated map of Fe^{3+}/Fe_{total} (thermodynamics)

- Results:
  - Ab initio calculations on averaged spectra suggest that Fe(II) is in octahedral sites whereas Fe(III) is preferentially located in octahedral interfoliar layers
  - Measured data corresponds to prediction using the multiequilibrium calculations

Muñoz *et al*., Geochemistry Geophysics Geosystems, 7, Q11020 (2006)

Gathering several information

Combining techniques

Conclusions

- Choose the technique depending on:
  - Type of data:
    - Morphology: 2D or 3D absorption imaging and/or enhanced by phase contrast,…
    - Elemental distribution: fluorescence
    - Elemental speciation: fluorescence mapping at selected energy, XANES mapping
  - Beamtime available:
    - Absorption imaging: fast
    - 2D fluorescence or XANES mapping: slower
    - 3D fluorescence imaging: slowest
  - Spatial resolution:
    - Fluorescence mapping and absorption imaging: 1 µm and below
    - XANES mapping: 5 µm
  - number of samples required for representativity

- Benefit from complementary techniques (absorption, fluorescence, spectroscopy, diffraction) :
  - 2D pencil beam imaging allows simultaneous analysis with various methods.
  - 2D imaging is appropriate to choose representative or interesting locations for complementary analysis

- Demand in-situ capabilities
  - Reproducing HT-HP conditions
  - Work under pressure (uniaxial, isotropic)
  - Accessing new elements with He/vacuum chambers

References

- Renard F. et al. Synchrotron 3D microtomography of halite agregates during experimental pressure solution creep and evolution of the permeability. Geophysical Research Letters, 31, L07607 (2004)
- Flynn et al., Elemental Compositions of Comet 81P/Wild 2 Samples Collected by Stardust. Science 314, 1731 (2006) DOI: 10.1126/science.1136141
- Golosio B. et al. Non-destructive three-dimensional elemental microanalysis by combined helical x-ray microtomographies. Applied Physics Letters 84, 2199-2202 (2004)
- Foriel J. et al. High-resolution imaging of sulfur oxidation states, trace elements, and organic molecules distribution in individual microfossils and contemporary microbial filaments. Geochimica et Cosmochimica Acta, 68, 1561–1569 (2004)
- Muñoz M. et al. Redox and speciation micromapping using dispersive X-ray absorption spectroscopy: Application to iron in chlorite mineral of a metamorphic rock thin section. Geochemistry Geophysics Geosystems, 7, Q11020 (2006)
- Cauzid et al. Quantification of Single Fluid Inclusions by Combining Synchrotron Radiation-Induced µ-X-ray Fluorescence and Transmission. Analytical Chemistry, 76, 3988-3994 (2004)
- Cauzid et al. Contrasting Cu-complexing behaviour in vapour and liquid fluid inclusions from the Yankee Lode tin deposit, Mole Granite, Australia. Chemical Geology, in revision
- Cauzid et al. 3D imaging of vapour and liquid inclusions from the Mole Granite, Australia, using helical fluorescence tomography. Spectrochimica Acta Part B, in revision