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?

Modes of permeability reduction

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

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

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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 aerogel and in their impact craters
Elemental distribution – fluorescence mapping

- Set-up ID22
Elemental distribution – fluorescence mapping

X-ray imaging techniques at the ESRF

Applications in geosciences
Elemental distribution – fluorescence mapping

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

helical = translation + rotation

high

low

Applications in geosciences
 Fluorescence tomography: helical scan

Sinograms:

Si  Ge  As  Rb

low  high
Fluorescence tomography: data processing

Volume reconstructed with a pile of 2D maps

Element found in liquid only

Element found in daughter mineral only

Element found in gas bubble only

Applications in geosciences
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.

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- 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.

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
**S⁰, S⁴⁺ and S⁶⁺ 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)

Elemental speciation

XANES mapping
Fe$^{3+}$/Fe$_{\text{total}}$ 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

Scanning the slits = energy scan

Absorption signal (a.u.)

Energy (eV)
Elemental speciation – XANES mapping

500µm

raw spectra

normalised spectra

X-ray imaging techniques at the ESRF

Applications in geosciences
Elemental speciation – XANES mapping

Muñoz et al., Geochemistry Geophysics Geosystems, 7, Q11020 (2006)
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Elemental speciation – XANES mapping

- Separation of chlorite, phengite and quartz
- Separation of chlorite (FeII) and chlorite (FeIII)

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Elemental speciation – XANES mapping

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Applications in geosciences
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

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Elemental speciation – XANES mapping

Optical image

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

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

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

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

- 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