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State-of-the-art microspectroscopic characterisations of cementitious materials used for the engineered barrier of a deep geological repository

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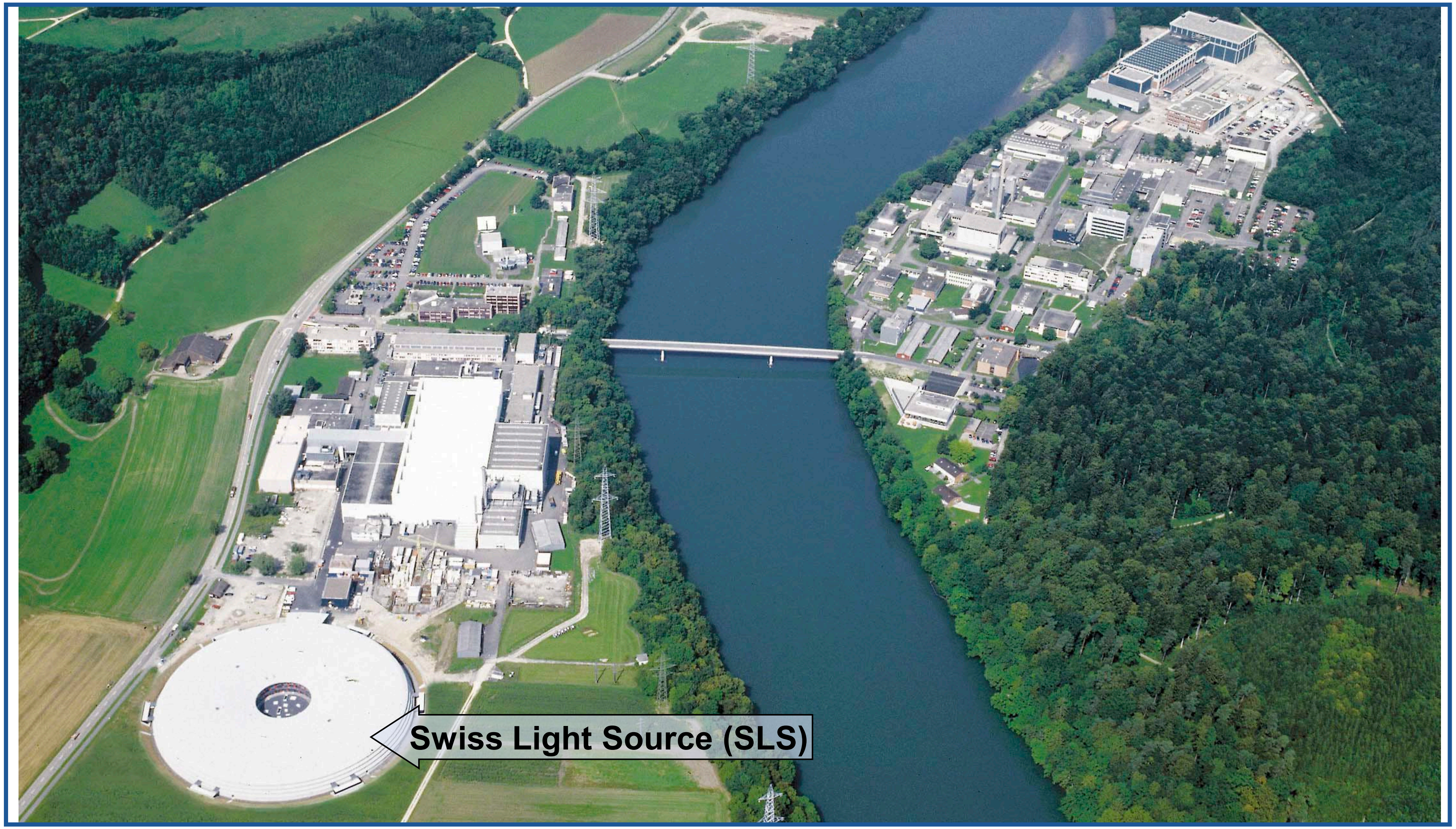
Synchrotron light sources (~50 worldwide)



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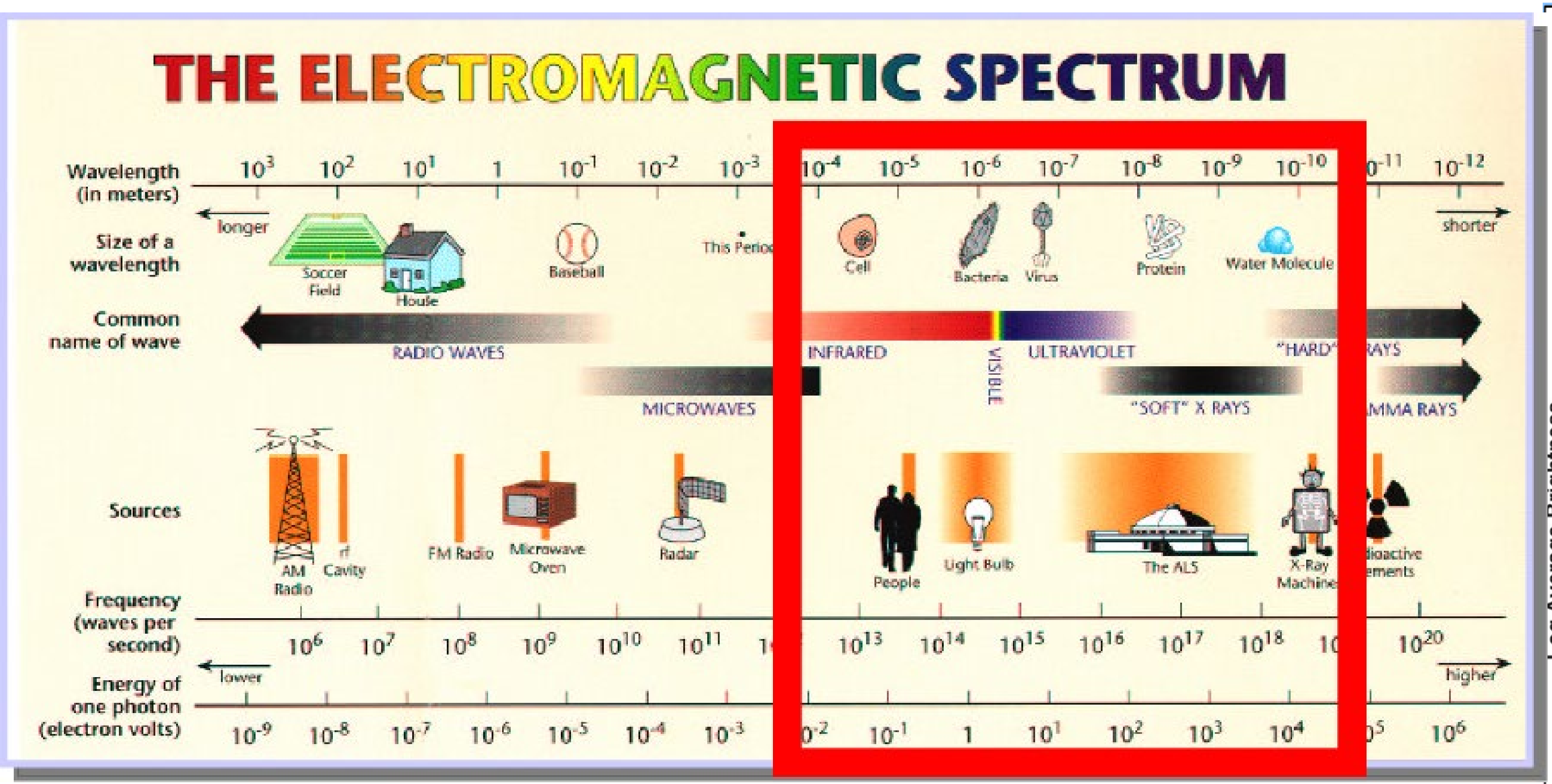
Swiss Light Source

Synchrotron radiation



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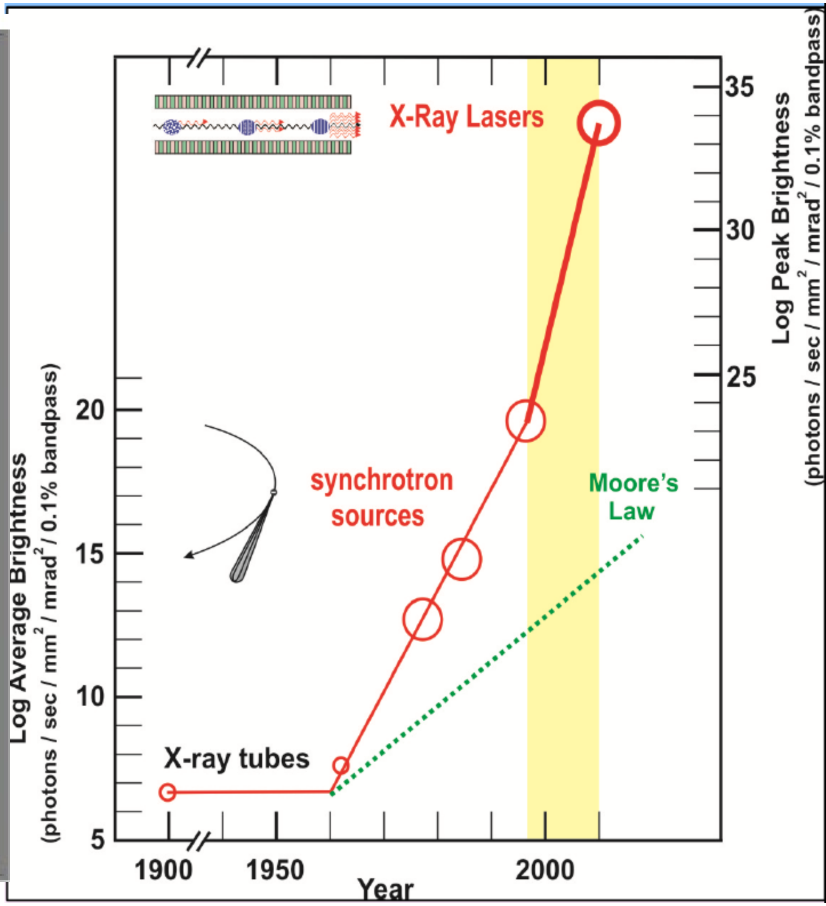


Cement hydration

Sulfate-resisting cement: CEM I 52.5 N HTS

heterogeneous material & highly alkaline (pH>12.5)

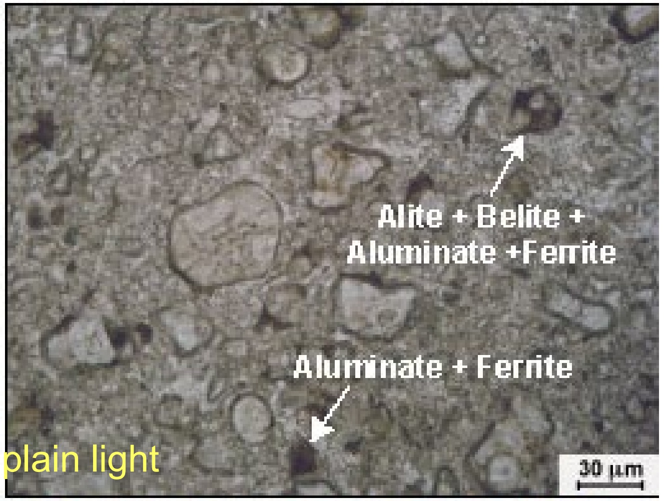
- **Clinker phases in non hydrated cement wt%:**

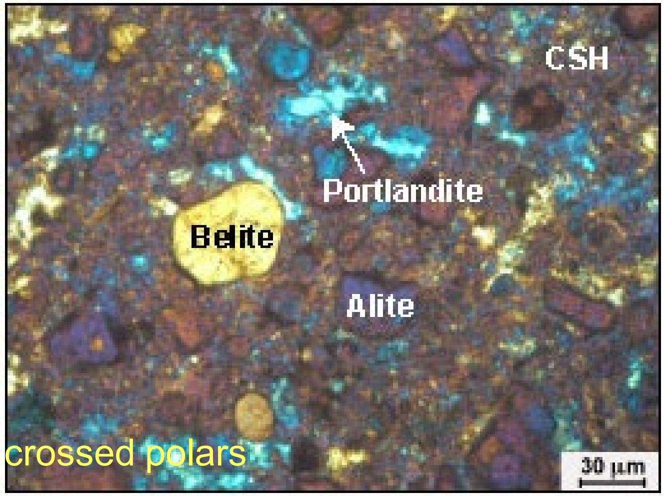
Alite	$3CaO{\cdot}SiO_2$	**~61**
Belite	$2CaO{\cdot}SiO_2$	**~19**
Aluminate	$3CaO{\cdot}Al_2O_3$	**~3.9**
Ferrite	$4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$	**~5.8**
$CaCO_3$		**~3.7**
Anhydrite	$CaSO_4$	**~3.6**
Others		**≤ 2**

$+ H_2O$

- **Hydrated cement phases in wt% (w/c 0.4):**

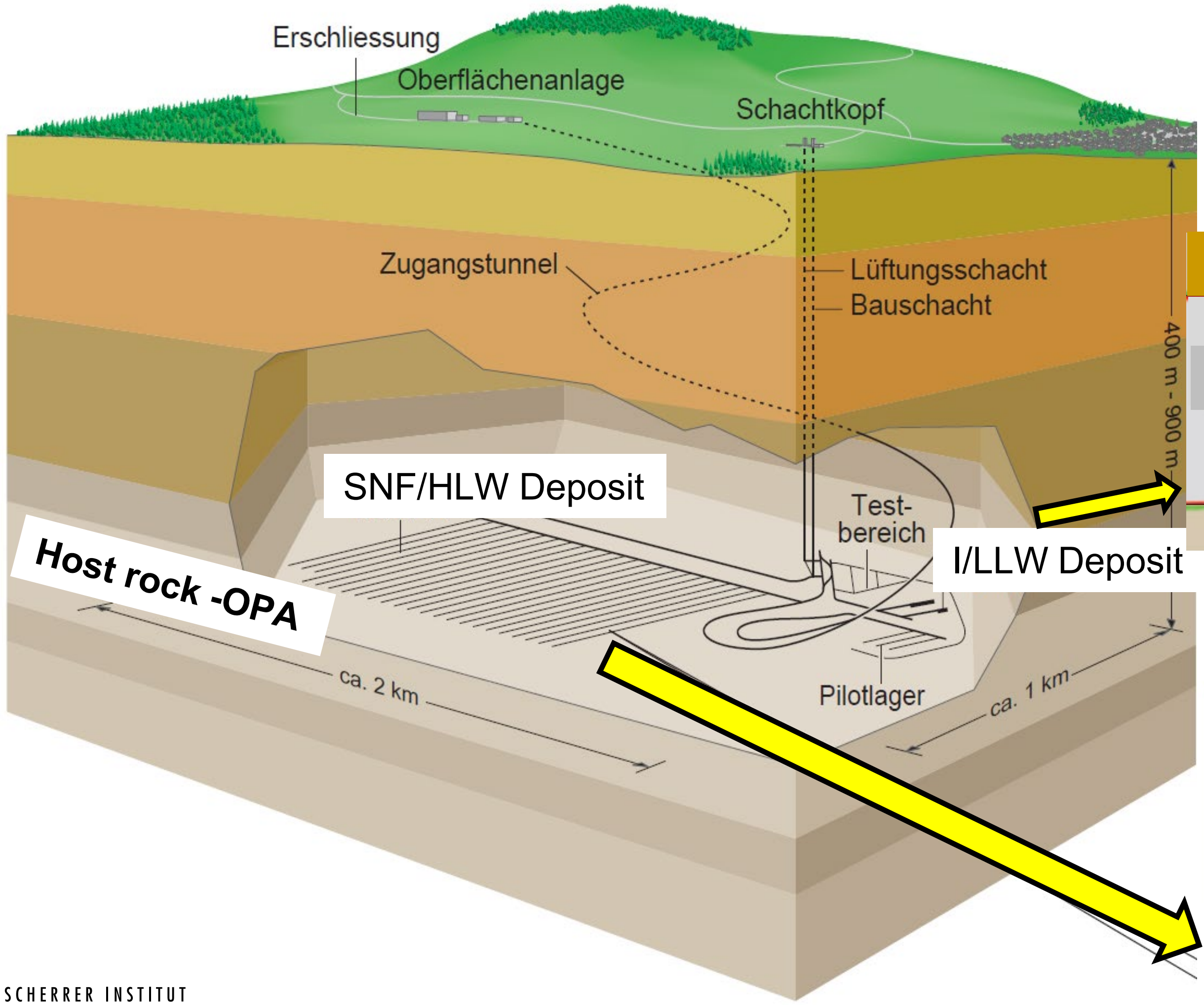
Calcium silicate hydrate	(C-S-H)	**~46**
Portlandite	$Ca(OH)_2$	**~18**
Calcium aluminates	(AFt, AFm)	**~17**
Hydrotalcite		**~1.4**
$CaCO_3$		**~1.9**
Minor phases	Fe, Mn oxides	**<<1**
Non-hydrated clinker minerals		**~15.6**

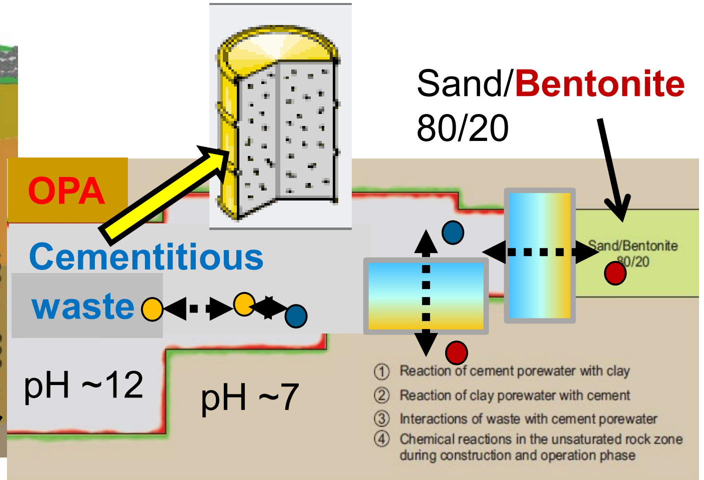


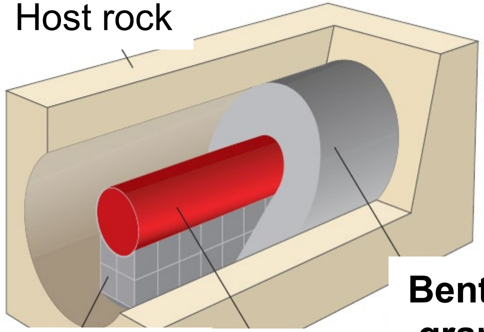


Motivation

- Cementious waste
- Cement (backfill, Liner HLW tunnel)
- Clay – Cement interaction





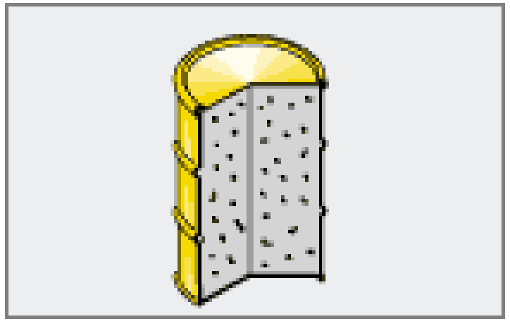


NTB 14-12 & 08-07

Case studies

- Co uptake mechanisms on hardened cement paste
  - X-ray absorption spectroscopy (XAS) at the macro/micro/nano-scale
- Investigation of Mg-containing phases
  - X-ray absorption near-edge spectroscopy (XANES)
  - Ab initio calculations
- Alkali Silica Reaction (ASR)
  - Micro-XRD

Interaction of Co with cement

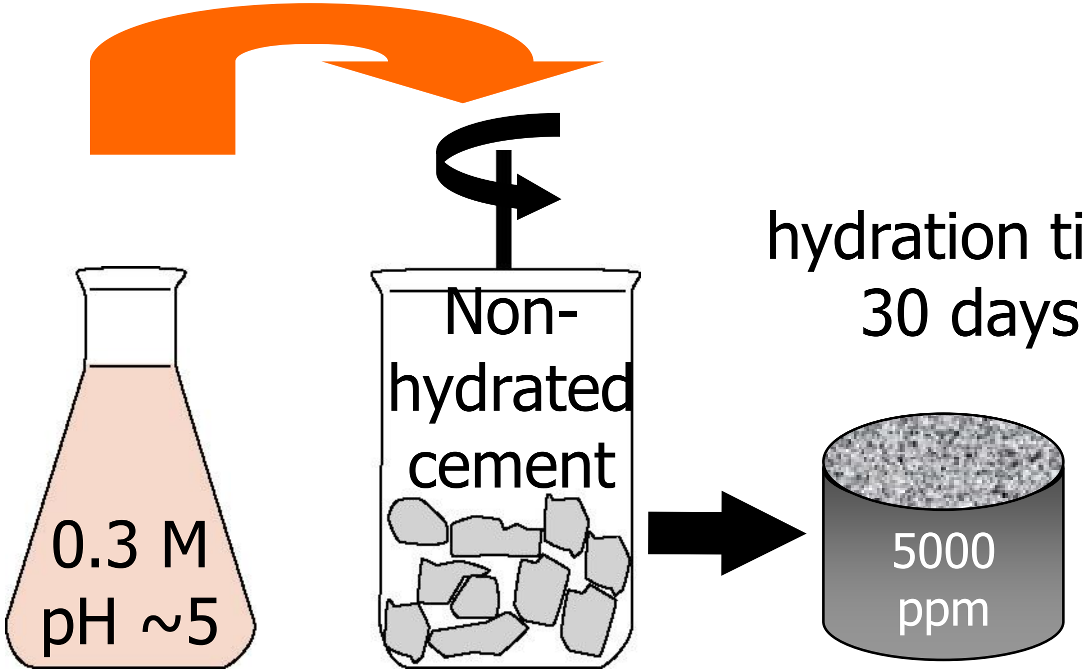


Uptake of Co during the hydration of cement

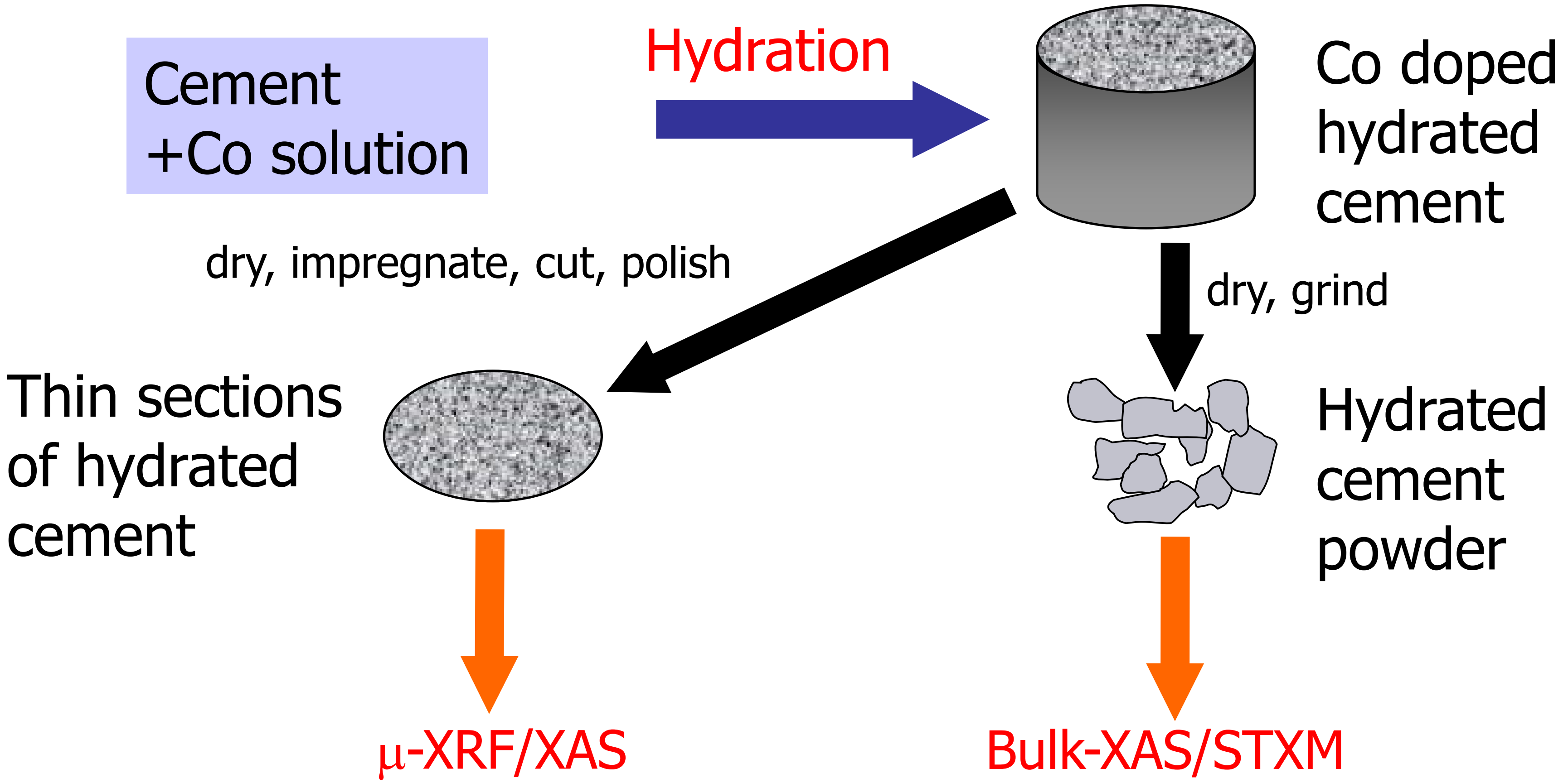
w/c = 0.4

hydration time
30 days

$Co(NO_3)_2 + H_2O$



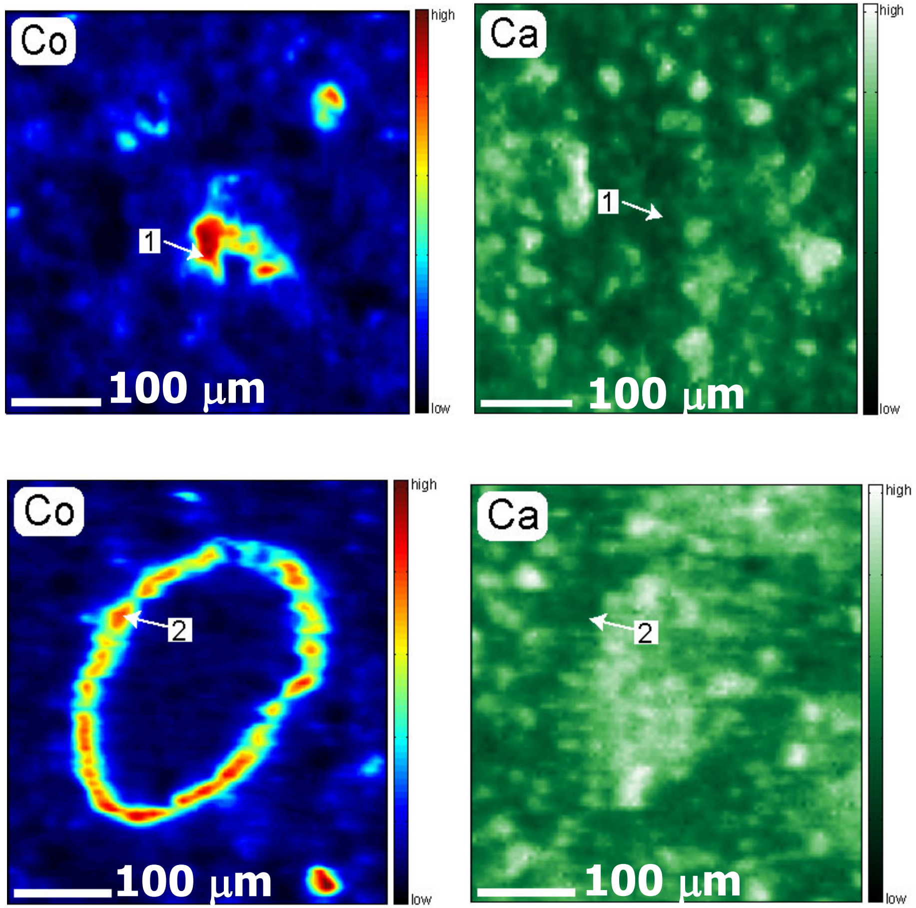
Co doped hydrated cement



Micro-XRF results

Spatial resolution 5x5 μm

- Form of immobilized Co?
- μ-XAS experiments at selected Co-rich hot spots
- μ-XRF: significant micro-scale heterogeneity
- Presence of small (≤30 μm) Co-rich hot spots (spot 1)
- Co-rich coatings (~10-50 μm thick) around some Ca-rich particles (spot 2)



Vespa et al., 2007

Micro-XAS results

Spot 1 (hot spot)

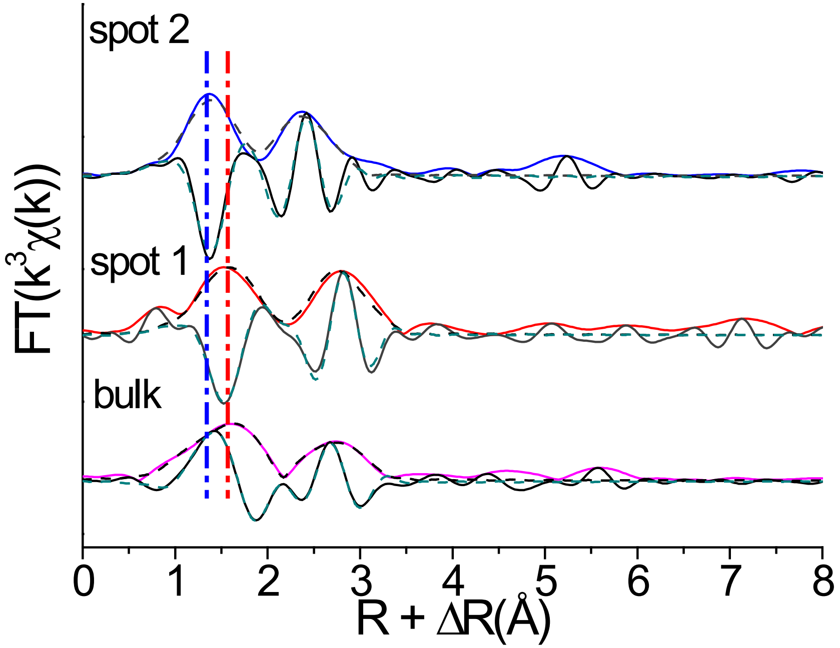
- Co-O (~2.06 Å) & Co-Co (~3.16 Å)
- Characteristic for Co(II)-phases

Spot 2 (ring-like)

- Co-O (~1.90 Å) & Co-Co (~2.80 Å)
- Characteristic for Co(III)-phases

Bulk-XAS

- Co-O (~2.06 Å & ~1.90 Å) & Co-Co (~3.13 Å)
- Mixture of Co(II) & Co(III) phases



➔ Formation of a predominant Co(II) phase in the overall matrix

➔ Different oxidation state at distinct regions

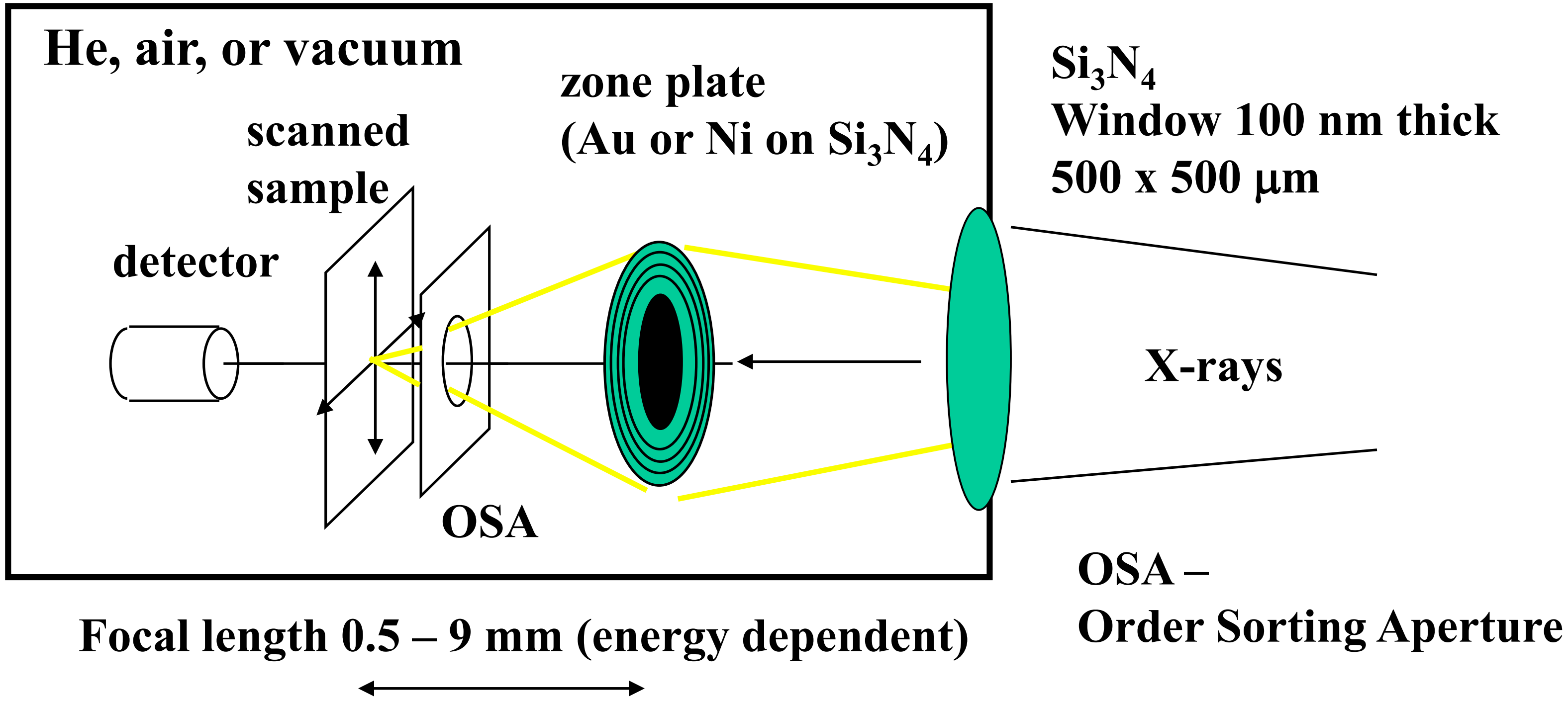
Summary of XAS results

Co(II):

- heterogeneous system with respect to:
  - Co distribution
  - oxidation state (2+/3+)
  - speciation
- what kind of Co(II) and Co(III) phases formed?
  - Co(II): $Co(OH)_2$ or Co-phyllosilicate
  - Co(III): CoOOH or Co-phyllomangate

→ Nano scale is required

Scanning transmission X-ray microscopy (STXM)



X-rays are focused on the sample by the zone plate, the sample is scanned, and the transmitted intensity is plotted as a function of sample position

STXM

2-d spectromicroscopy using soft X-ray transmission

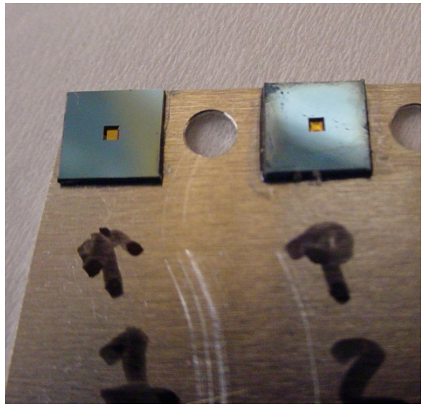
Spatial resolution: ~25 nm

Energy range: 120-2160 eV

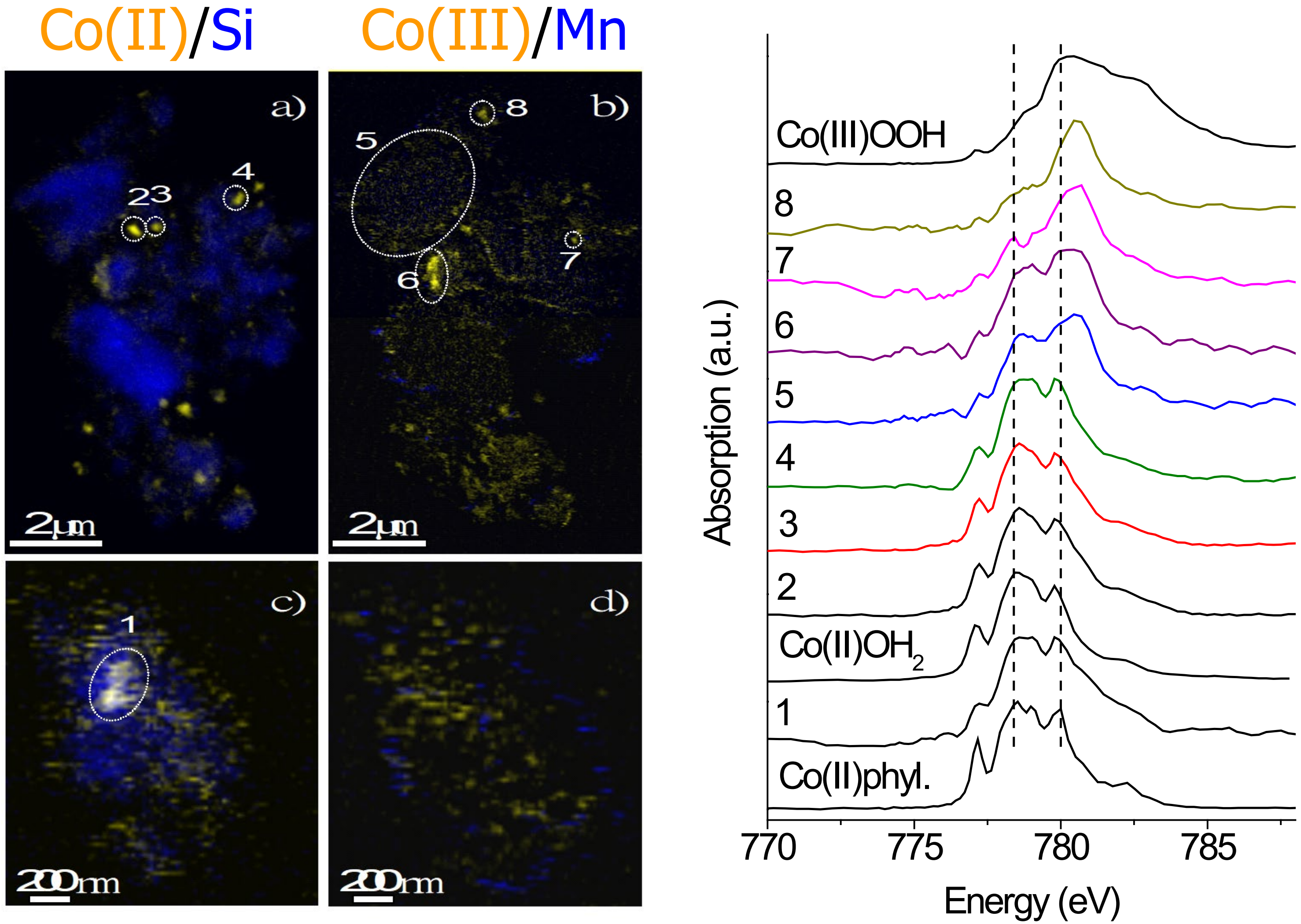
Energy resolution: $E/\Delta E=5000\text{-}7500$

Ambient atmosphere or “purged”

Si_3N_4 window “sandwich” sample packages for wet or radioactive samples



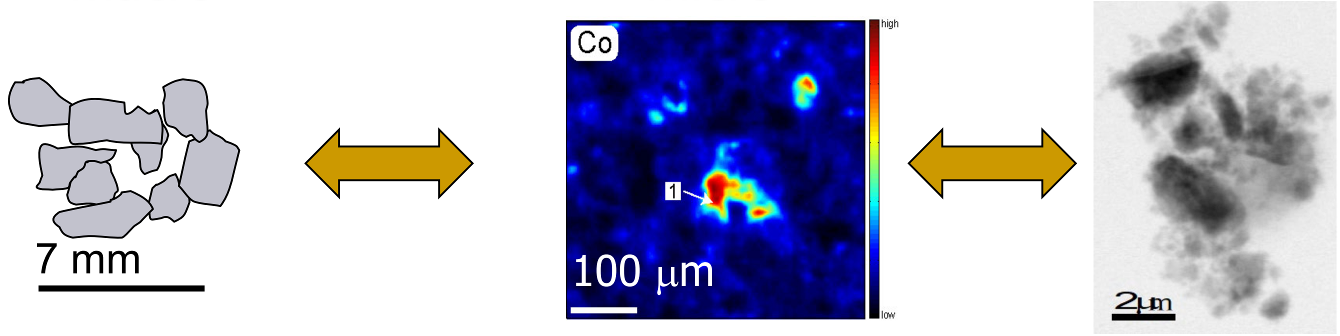
Co(II)/Co(III) speciation in Co-doped cement



Dähn et al., 2011

Summary: Co(II) uptake by cement

macro micro nano



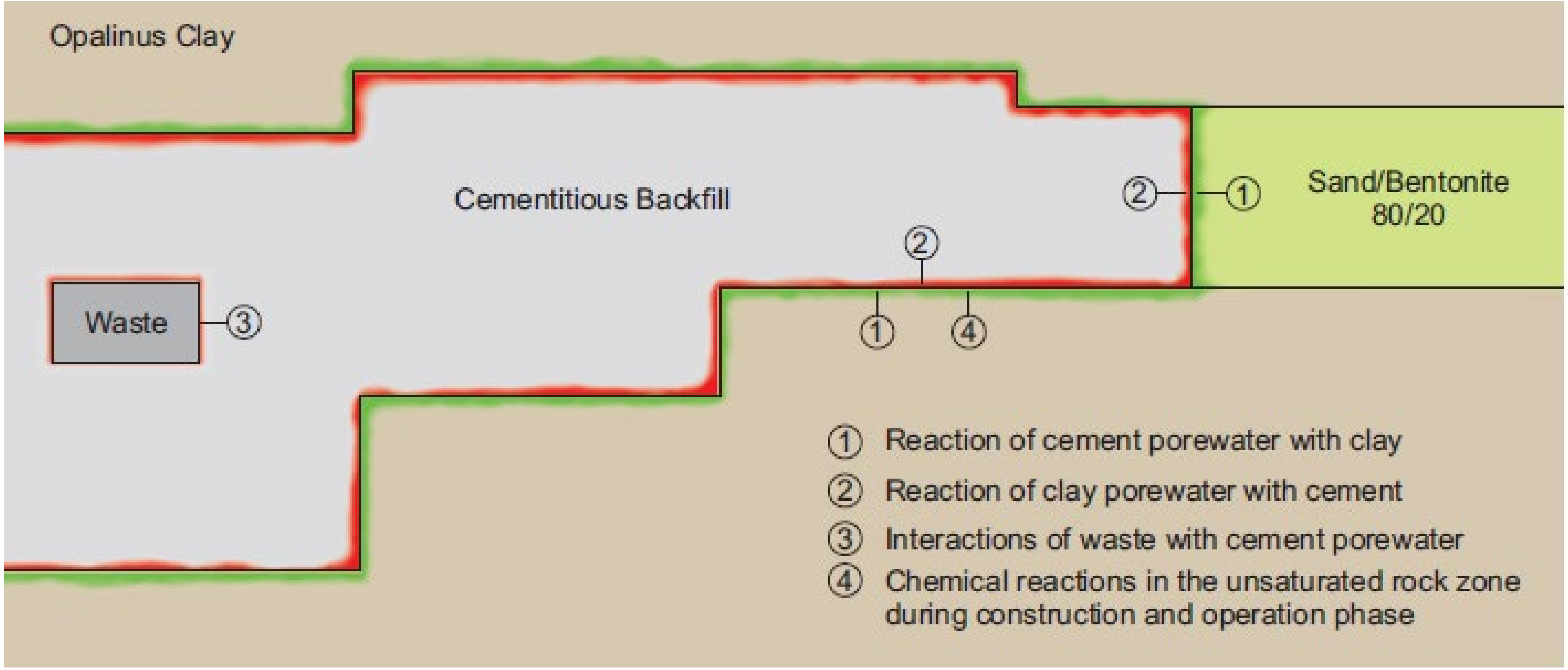
- Co(II): **$Co(OH)_2$ and Co-phyllosilicate**
- Co(III): **CoOOH**

➔ Co oxidation on a nano-level during cement hydration

➔ Decreased solubility of Co(III) vs. Co(II) phases in cement

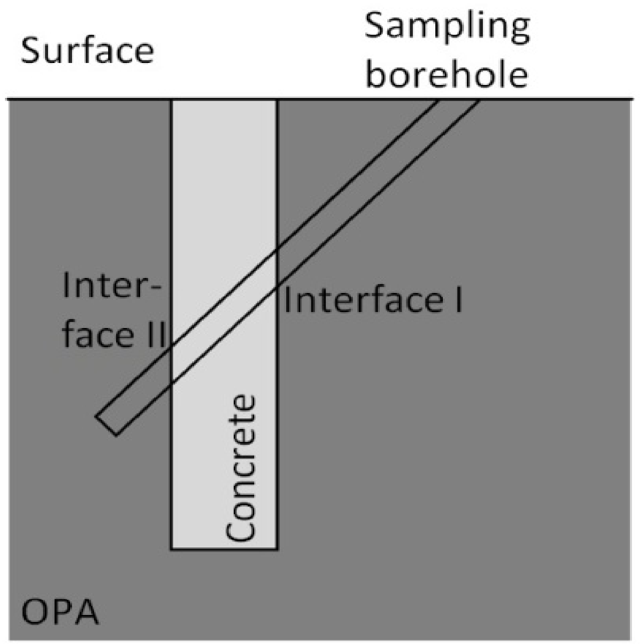
-> increased retardation of Co(III) compared with Co(II)

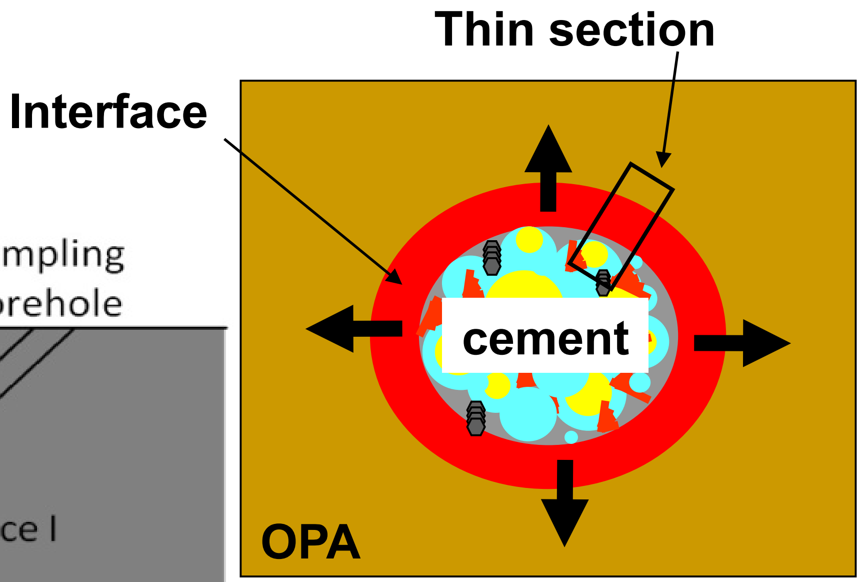
Cement-Clay (CI) interaction

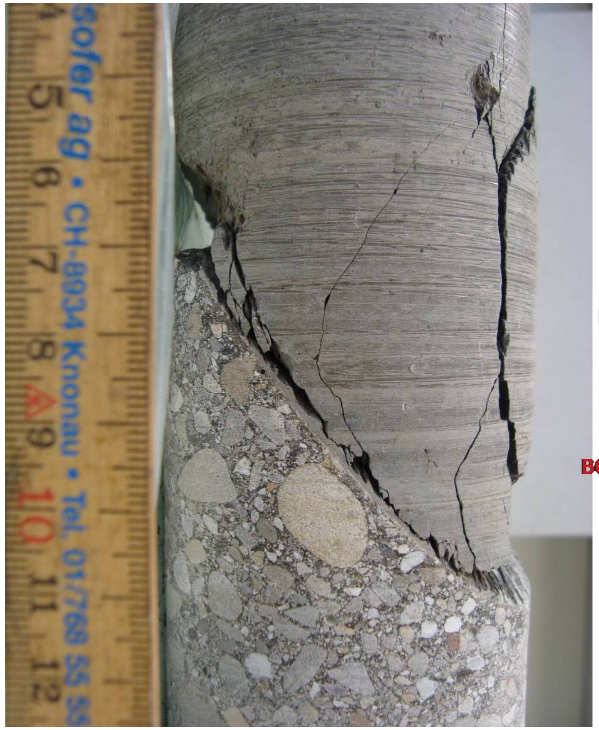


NAGRA NTB 08-07

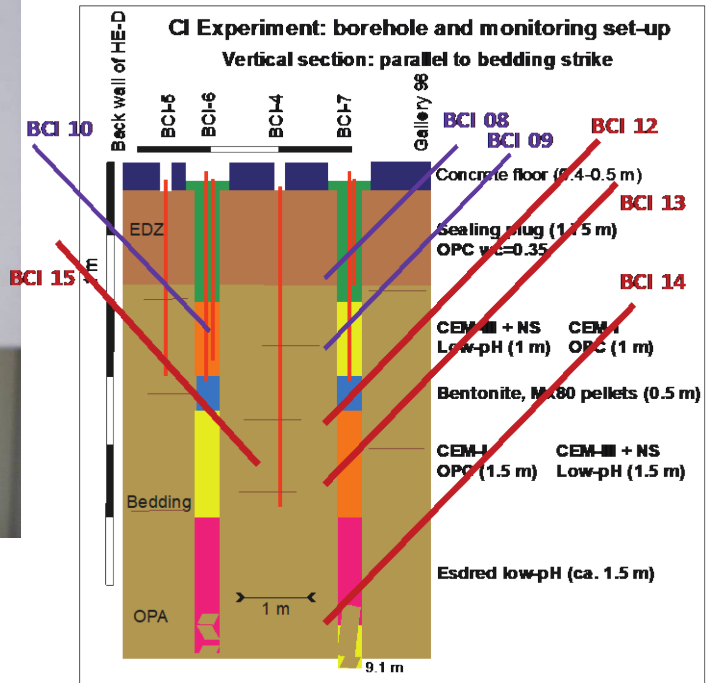
Multi-year field experiment (CI) at Mont Terri Rock Laboratory







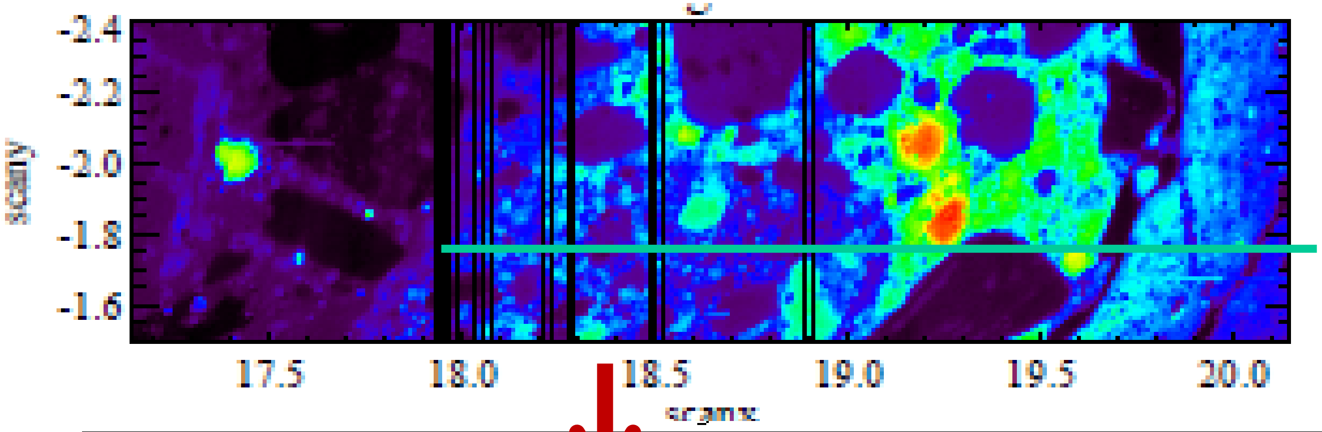
Jenni et. al., 2014

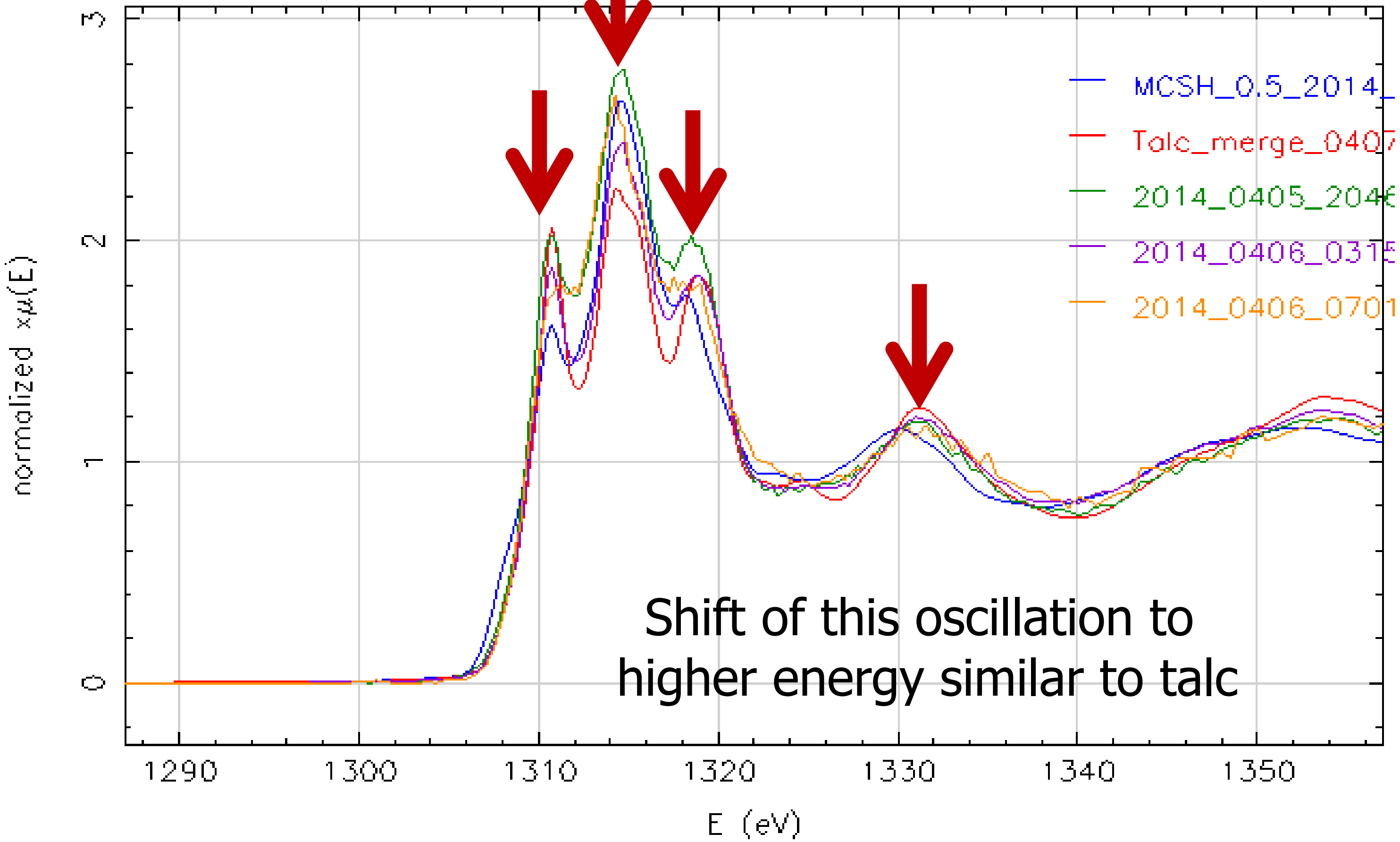


Mg containing phase

- Mg-poor region in the cement
- Mg-rich region in the interface
- Mg-poor region in clay

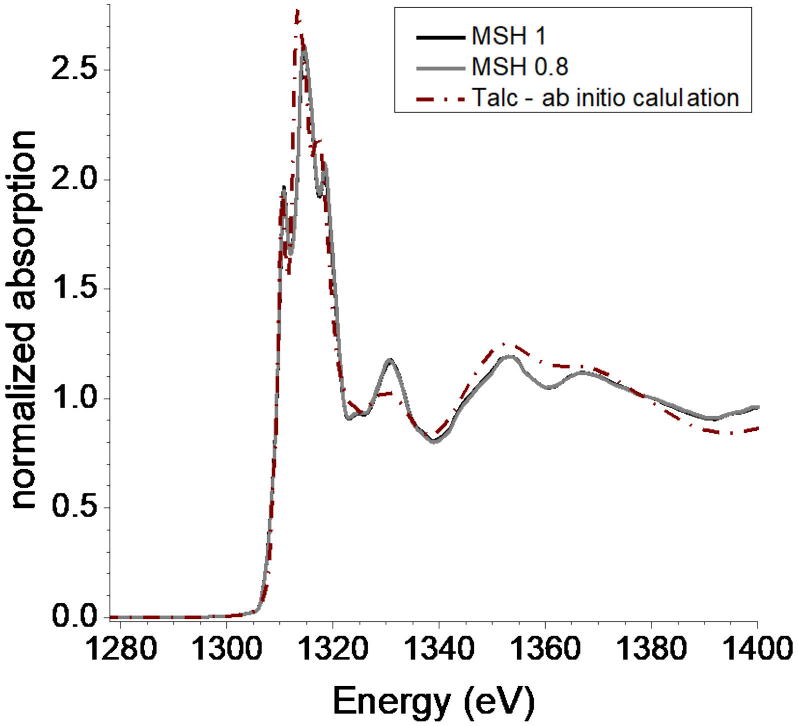
All very similar to the references





Vespa et al., 2017/2018

Ab initio calculations of XANES spectra.



- Employment of FDMNES (Joly 2001)
  - Crystal structures
  - Crystal symmetry
  - Cluster size
  - Crystallographic position

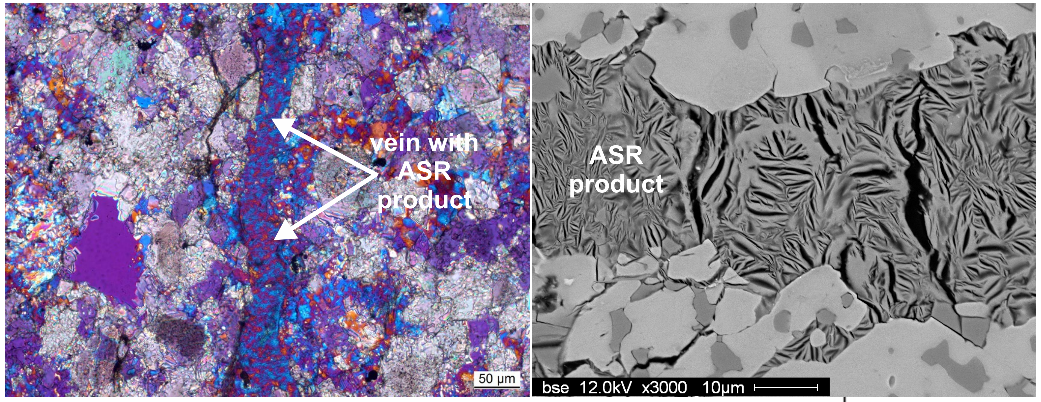
- M-S-H phases have a layered structure similar to talc
- Indication of the presence of a hydroxide layer similar to brucite

Alkali Silica Reaction (ASR)

Bridge constructed in 1969

- Dark cracks formed in bridges, dam walls and other structures made from concrete are caused by ASR (>400 structures in Switzerland (Merz et al., 2006)): Concrete cancer/disease
- Slow process which takes decades
- In the course of ASR, a material forms that takes up more space than the original concrete and thus gradually cracks the concrete from within as the decades go by
- It was believed up to now that this material is a non-crystalline gel

Optical and SEM image of the ASR material



PSI media release from 5th November 2015:
Structure of "concrete disease" solved

Not only bridges (e. g. Seabrook Nuclear Power Plant 2009-2019)

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REACTOR OPERATIONAL EXPERIENCE

- Access Authorization Programs
- Baffle-Former Bolts
- Buried Piping Activities
- **Concrete Degradation at Seabrook Nuclear Power Plant**
- Davis-Besse Reactor Vessel Head Degradation
- Fire Protection Program
- Fitness-for-Duty Programs
- Groundwater Contamination (Tritium) at Nuclear Plants
- Human Factors
- Japan Lessons Learned
- Open Phase Conditions in Electric Power Systems
- Operating Experience Smart Sample (OpESS) Program
- Operating Reactor Maintenance Effectiveness
- Point Beach 2003-2006 - Multiple/Repetitive Degraded Cornerstone Column
- Post-Fukushima Safety Enhancements

Home > Nuclear Reactors > Operating Reactors > Operational Experience > **Special NRC Oversight: Concrete Degradation**

Special NRC Oversight at Seabrook Nuclear Power Plant: Concrete Degradation

In 2009, NextEra Energy Seabrook, LLC (NextEra) realized that the intrusion of moisture into sections of walls in certain below-grade structures at the Seabrook nuclear power plant, in Seabrook, N.H., could cause the degradation of some of the concrete. The NRC and NextEra confirmed in 2010 that the degradation at Seabrook is caused by alkali silica reaction, or ASR. The result of this reaction is a gel, which can expand and cause micro-cracks in the concrete. Graphics detailing the chemical reaction and the expansive gel can be viewed on slide 9 of the May 10, 2012 presentation "Seabrook Station Safety in Light of the Alkali-Silica Reaction Occurring in Plant Structures."

Subsequently, NextEra identified that the cumulative effect of ASR-induced micro-cracking has led to larger macro-cracking (bulk expansion) and the displacement of some concrete walls.

NextEra has determined that the structures affected by ASR can continue to perform their safety functions—the regulatory term for this is that they are "operable but degraded and nonconforming." The basis for continued operability includes confirmatory engineering design reviews using computer-based finite element analysis and detailed reviews of structural design calculations that demonstrate that sufficient safety margins remain based upon field measurements and/or bounding (worst-case) ASR degradation values. Reinforced concrete structural design margins for Seabrook were established in accordance with American Concrete Institute (ACI) Code 318-1971 and ensure that the as-built (design) structural capacity exceeds

RELATED INFORMATION

Report on Aging of Nuclear Power Plant Reinforced Concrete Structures, NUREG–CR-6424

https://www.nrc.gov/reactors/operating/ops-experience/concrete-degradation.html

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Preventing ASR in nuclear reactor radiation shielding concrete

NOVEMBER 27, 2018 | LISA MCDONALD

[Image above] The Seabrook Station Nuclear Power Plant is the only commercial nuclear plant known to suffer from an alkali-silica reaction in the United States. ASR prevention is an important concern when constructing nuclear plants. Credit: Jim Richmond, CC BY-SA 2.0

Though nuclear power currently faces an uncertain future in the United States, other countries—like China and Russia—are capitalizing on the growing global nuclear power market. As countries prepare for the construction of sophisticated nuclear reactors, plant designers turn to a familiar material to safeguard against failure: concrete.

Nuclear power reactors are typically lined with concrete, which in turn are housed in a larger steel containment vessel and then surrounded by an outer concrete structure. Unlike

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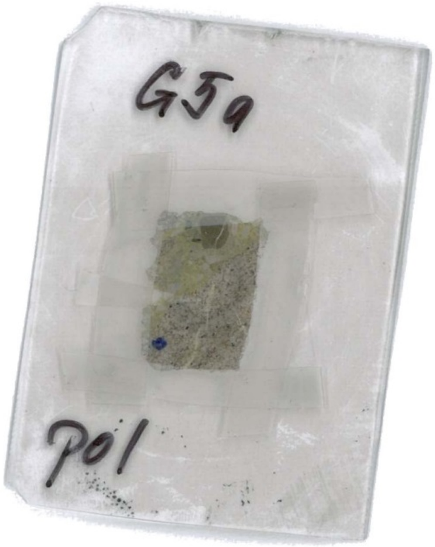
https://ceramics.org/ceramic-tech-today/construction/preventing-asr-in-nuclear-reactor-radiation-shielding-concrete

Strength of micro-XRD

micro-XRD can be used:

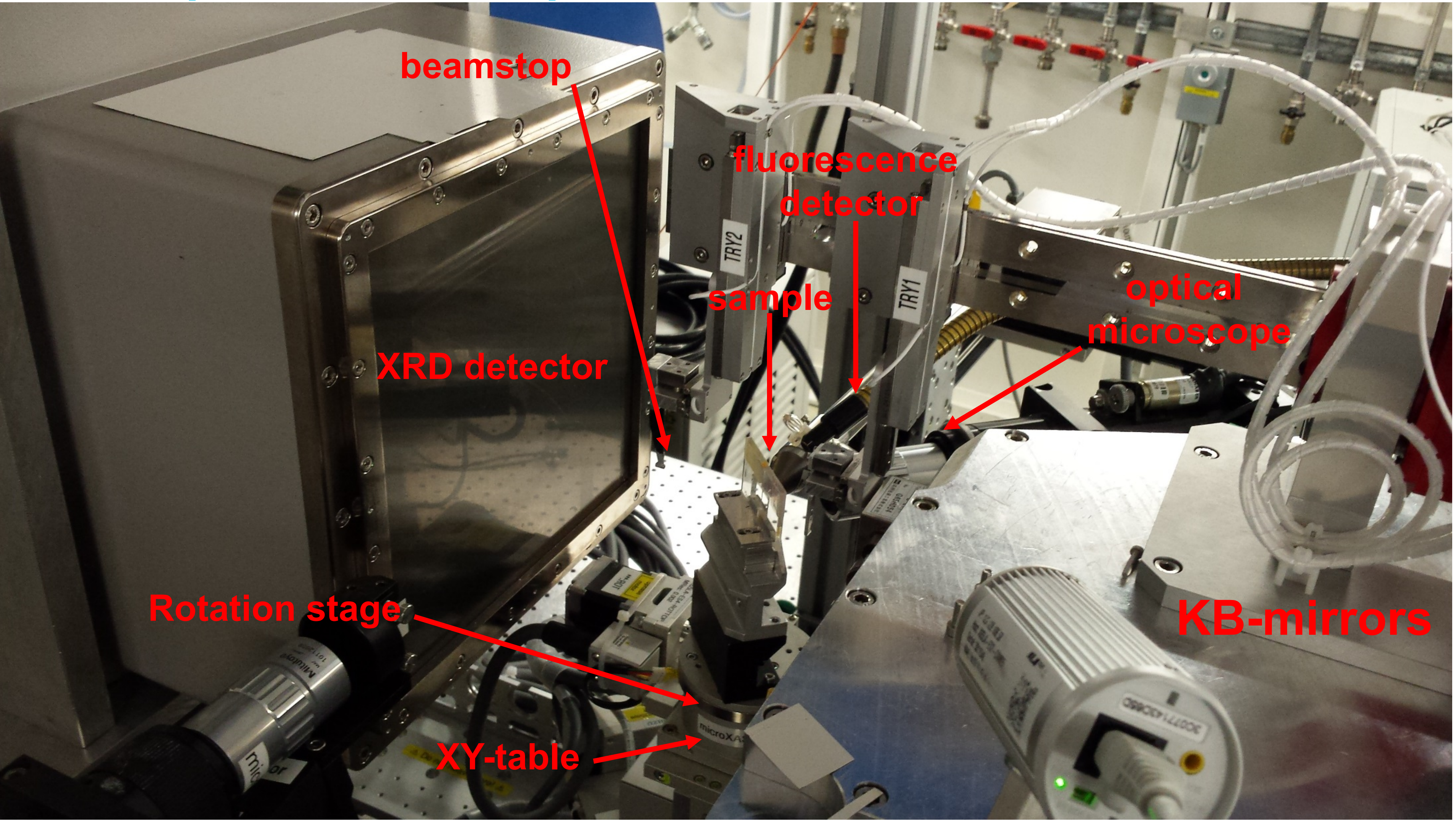
- to assess the crystallinity of phases
- to determine the reactive minerals responsible for sorption and precipitation processes
- to identify newly formed crystalline phases

Challenge: apply micro-XRD to thin sections

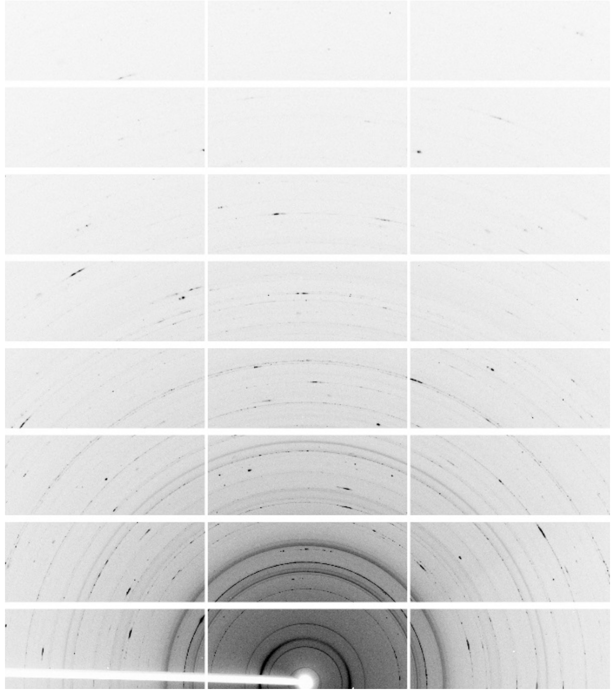


Usually on a glass support 25 x 45 mm

Experimental setup: Microxas/SLS

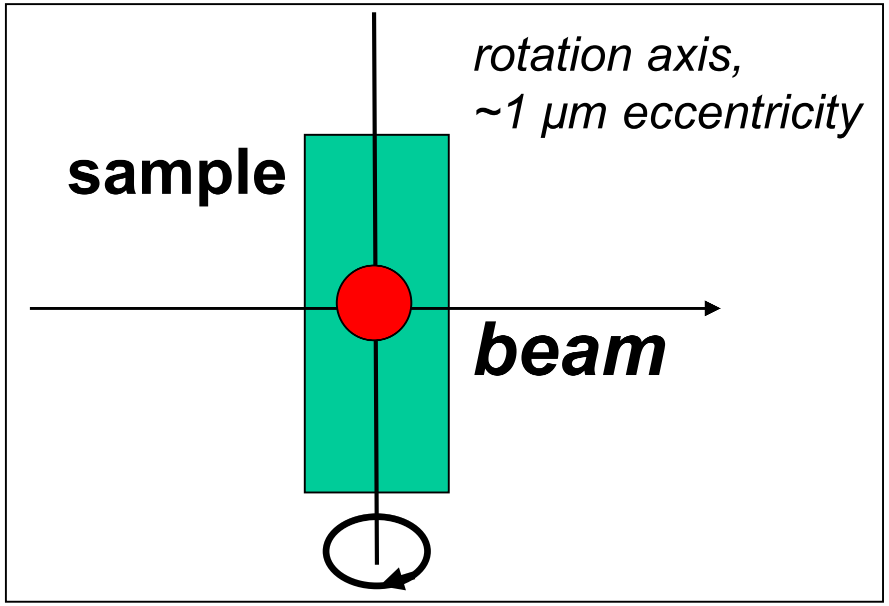


PILATUS 2M



Micro-XRD on thin sections

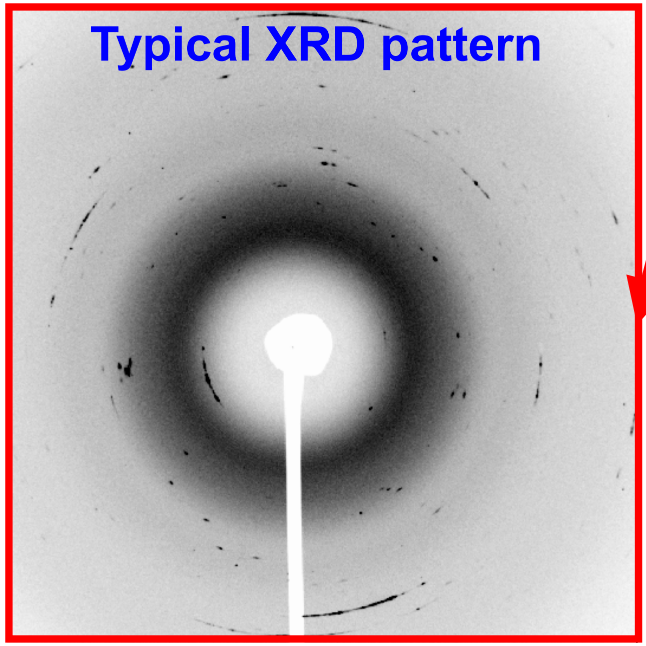
Approach: Turning the sample as in classical single crystal diffraction

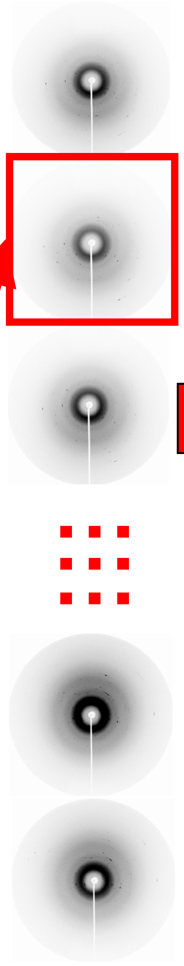


Challenge: keep the probed crystal in the center of rotation

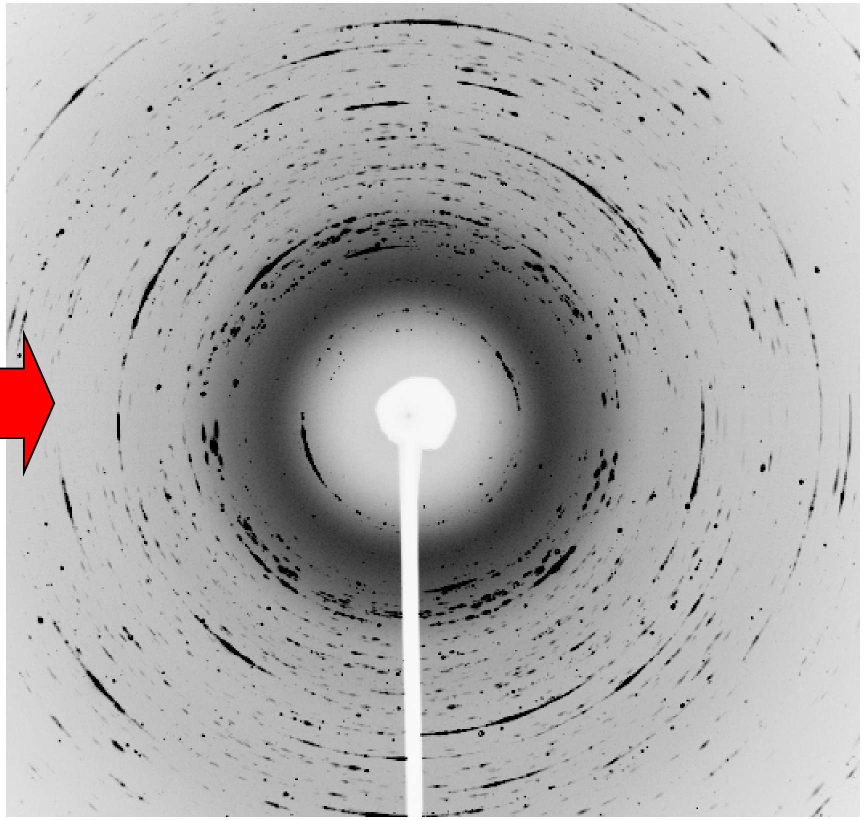
Approach

Series of 60-90 XRD pattern

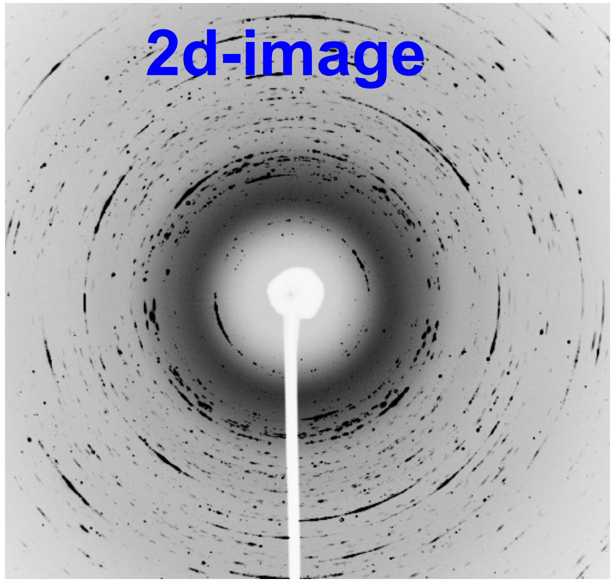


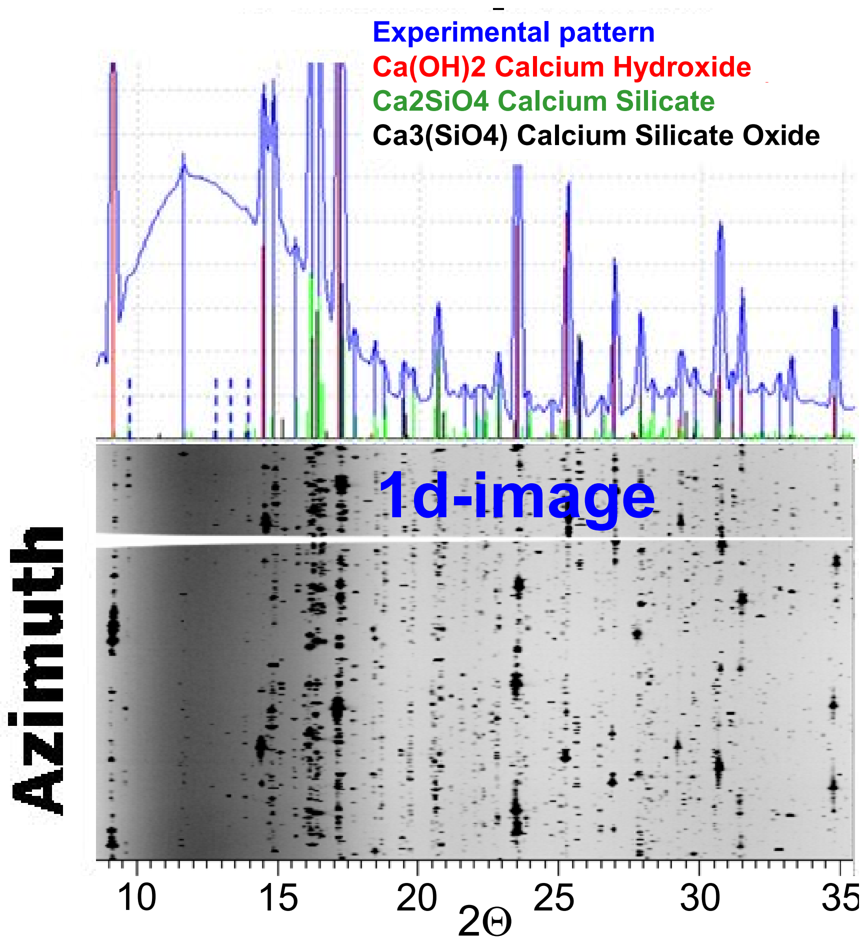


Composite image



2D-1D





- ➢ crystal structure refinement
- No a priory information needed
- Time consuming, can be applied to unknown phases

- ➢ search within cryst. database
- Elemental composition→XRF or EDS

Dähn et al., 2014

Technical challenges

- sample preparation

e.g. need to avoid diffuse scattering and absorption of x-rays in sample carrier, contrast in hardness, …

- sample handling and positioning in micro-beam; sample position has to remain stable
- huge amount of collected data

e.g. profile line scan:

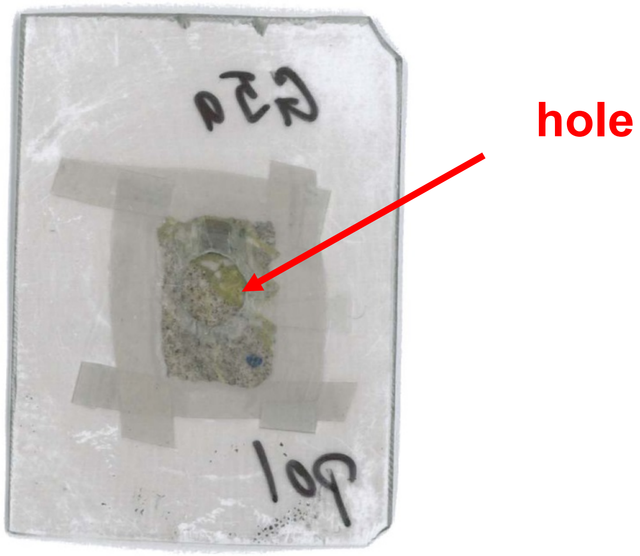
per data point: 1 rotational scan with $\Delta\varphi$= 50º, angular increment: 0.5°

→ 100 frames totally 17 rotational scans along profile line → 1700 frames

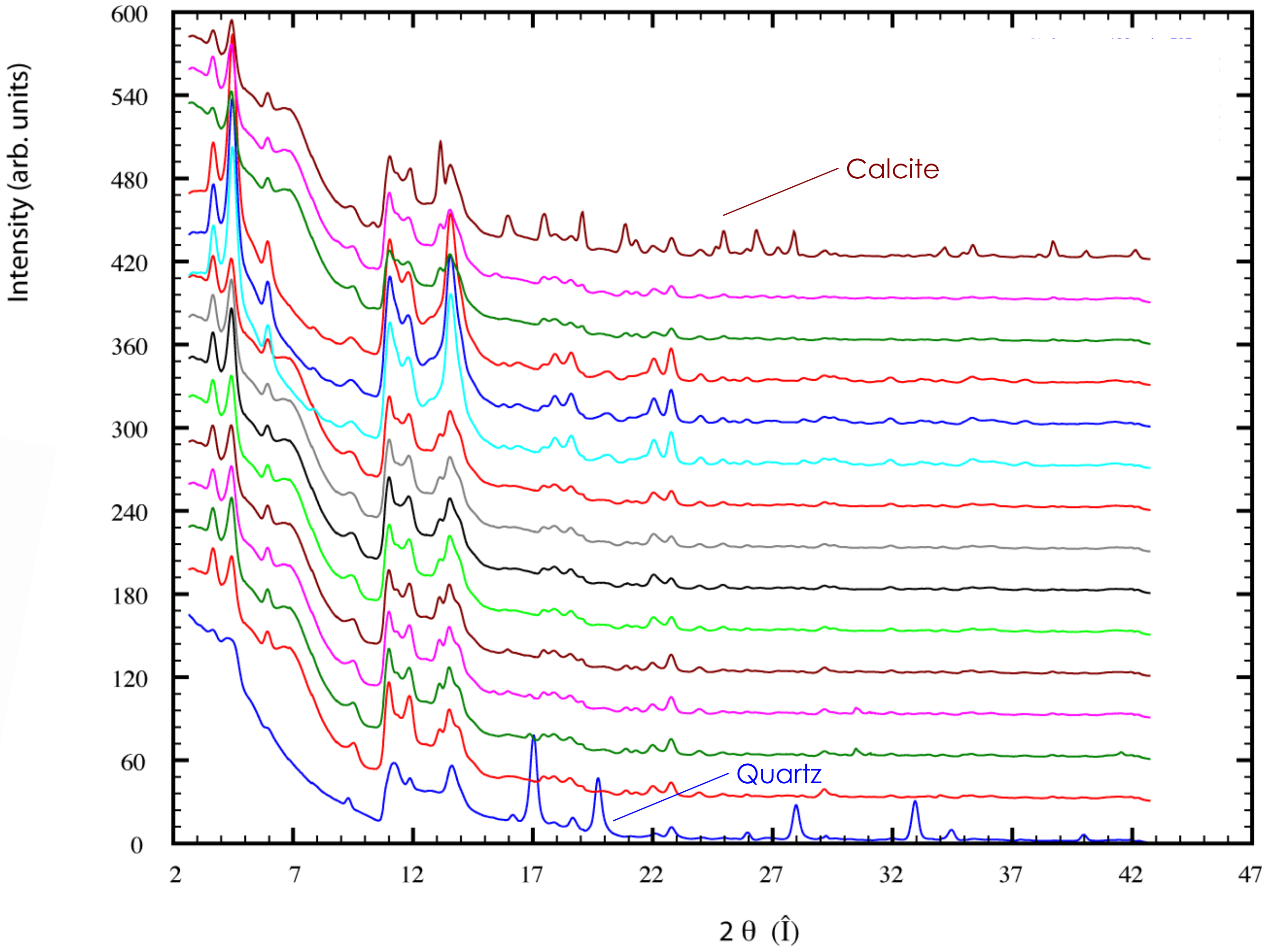
area detector PILATUS 2M: 1475 x 1679px = 2’476’525px per frame

→ totally 4.2 billion pixels recorded

→ complete dataset: 17GB



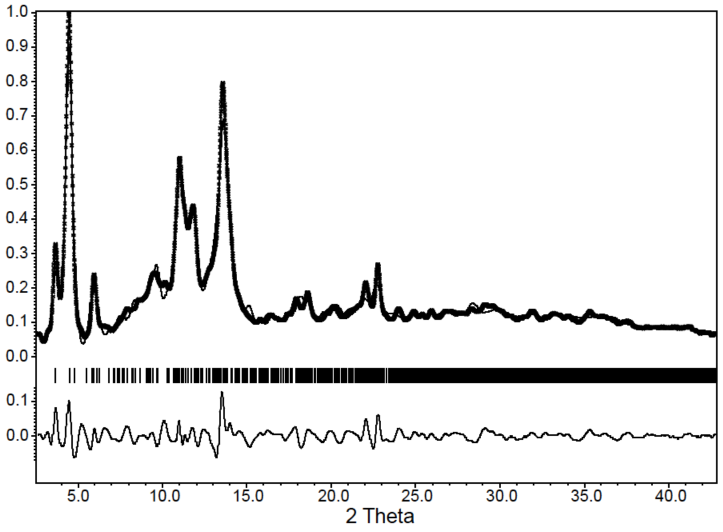
Comparison of different locations (1 x 1μm^2 beam size)

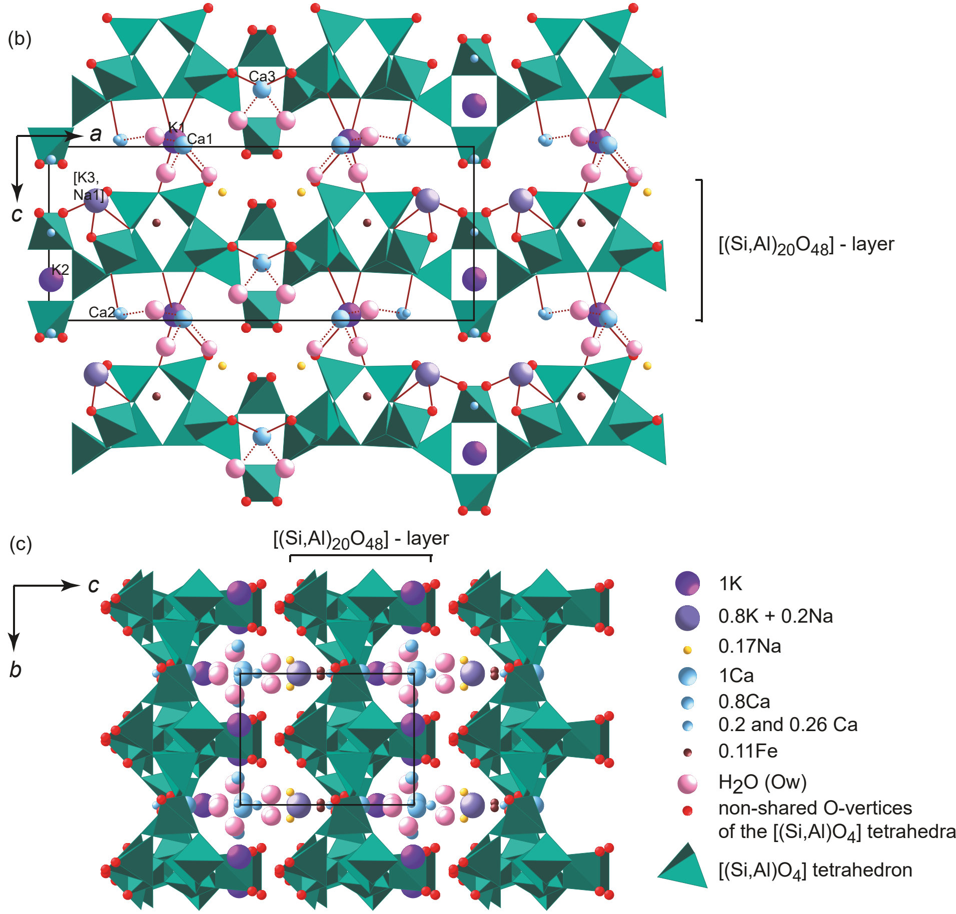


Dähn et al., 2016

Rietveld refinement

$[Ca_{5.34}K_{4.6}Na_{0.74}Fe_{0.22}\cdot 7.66H_2O]$
$[Si_{19.33}Al_{0.66}O_{48}]$
Monoclinic, *P*112
a (Å) 21.35(3)
b (Å) 6.635(9)
c (Å) 8.725(11)
γ (º) 92.31(17)





Rietveld refinement identified the so far unknown material as a layered sheet-silicate mineral similar to the mountainite family

Understanding the structure of ASR can help to improve the durability of cement based construction materials

Conclusions

- Synergy of synchrotron-based investigations from macro to nano scale & ab initio calculations are a powerful tool for material & environmental sciences to gain:
- Overall understanding of radioactive elements behaviour
- Detailed mineralogical information and characterization of:
  - newly-formed phases
  - metal complexes formed at the mineral surface
- Results can help to reduce conservatism in performance assessment
- System understanding gives strong public credibility

Acknowledgement

- Nagra and the NES/PSI division for partial financial support
- European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 701647
- SNSF-funded Sinergia project CRSII5_171018.4
- Empa
- Synchrotron light sources of:

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