Micro-spectroscopic investigations of the Al and S speciation in hardened cement paste

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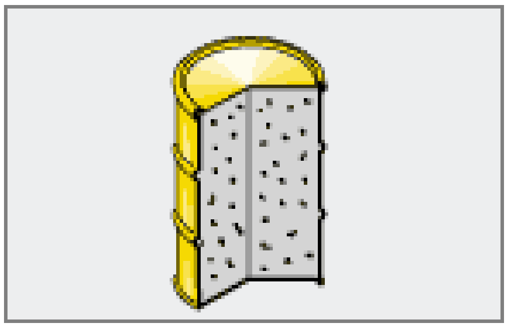
Layout

- Introduction
- Materials and methods
- Al and S speciation in cementitious materials
  - Al speciation
    - References
    - Micro-spectroscopic studies
  - S speciation
    - References
    - Micro-spectroscopic studies
- Conclusions

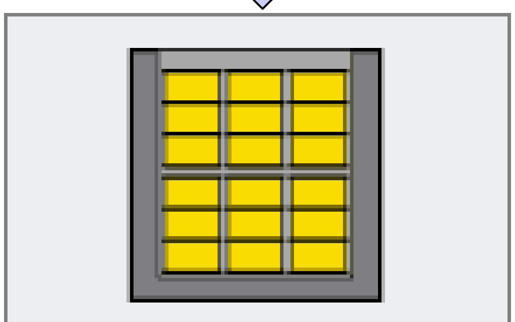
Background

Waste package (cement & steel)

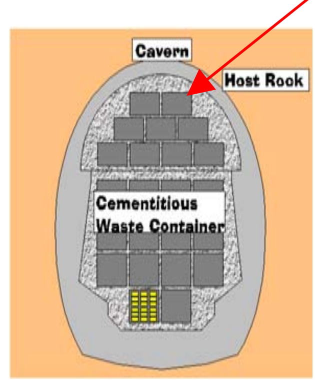


Cement – important component of the engineered barrier system of the repositories for low- (L/ILW) and intermediate-level wastes (ILW)

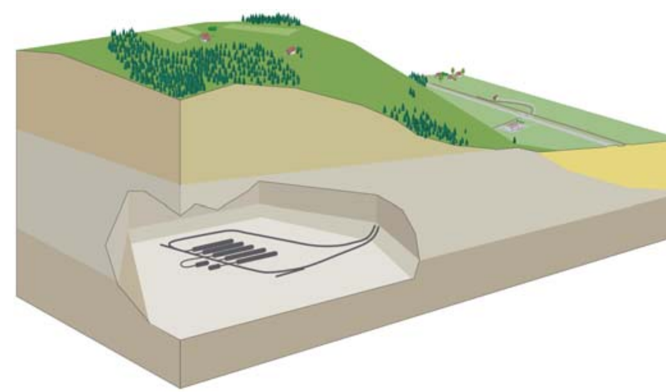
Hardened cement paste: ~ 20 wt%



Container (concrete, mortar, steel)



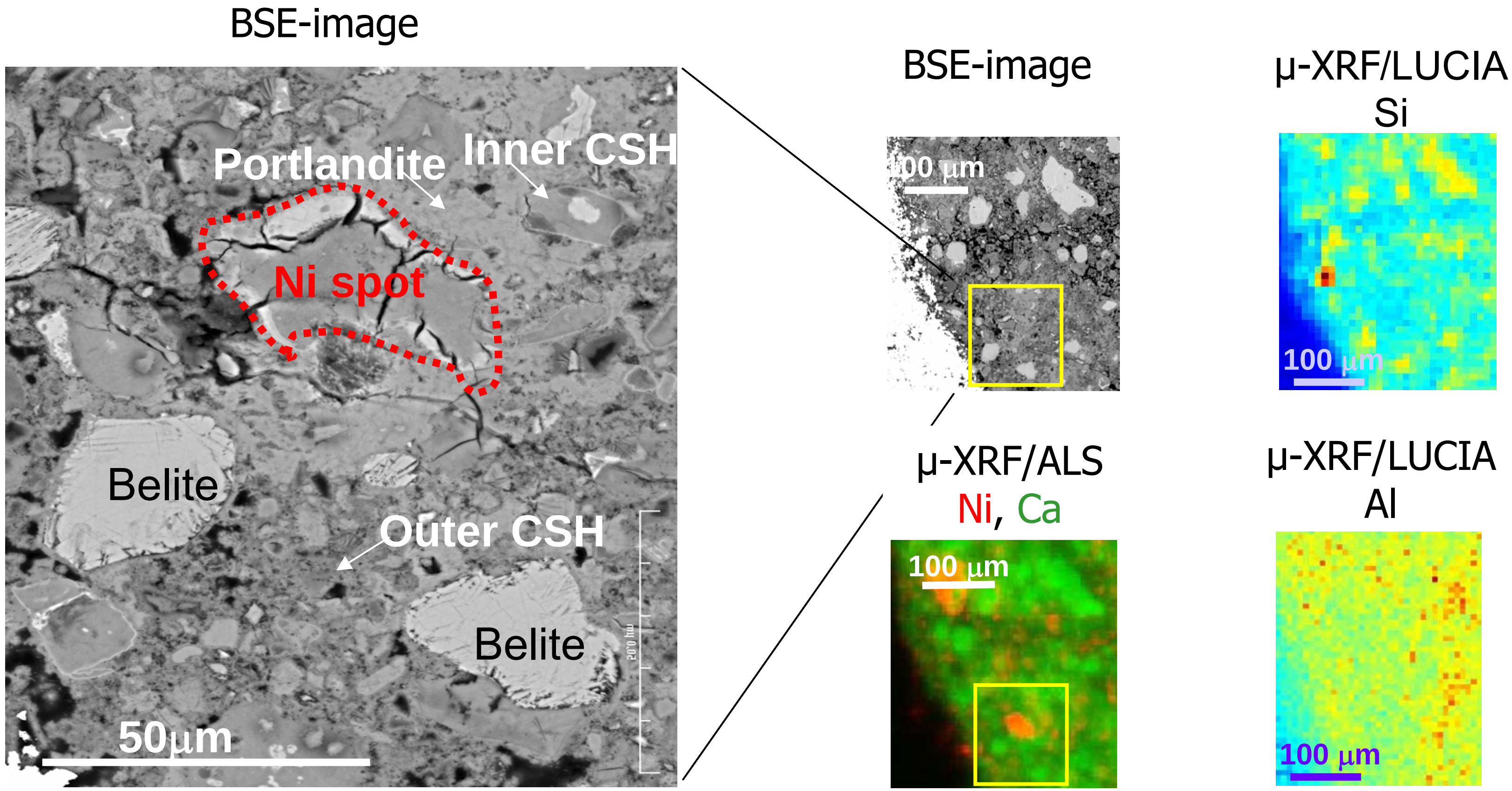
Cavern backfill (porous mortar)



Deep geological repository

Example: Ni uptake by cement

- **Combination of BSE (SEM) with μ-XRF/XAS**
- **Information on the morphology and the chemical composition of phases on the same spot**



Motivation

- X-ray absorption fine structure (XAFS) spectroscopy as complementary tool to XRD for cement phase characterization?

- In situ identification of single cement phases with micro-scale resolution in hardened cement paste?

- Identification of uptake-controlling cement phase in connection with metal cation and anion binding in hardened cement paste?

Hardened Cement Paste (HCP)

Sulphate-resisting cement: CEM I 52.5 N HTS

Clinker phases in non hydrated cement wt%:

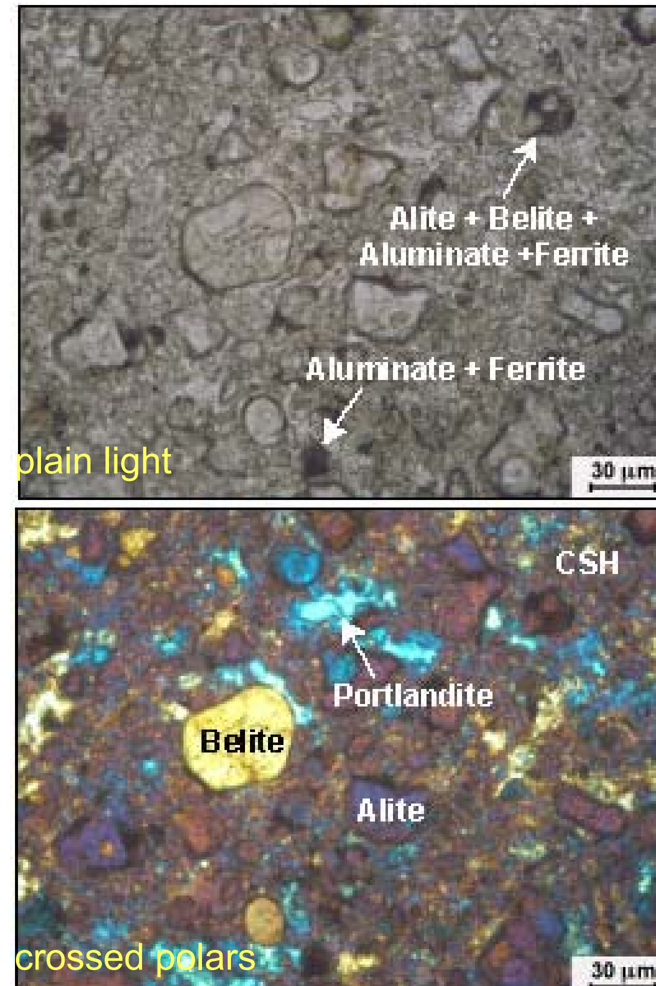
Alite	$3CaO{\cdot}SiO_2$	**61**
Belite	$2CaO{\cdot}SiO_2$	**18**
Aluminate	$3CaO{\cdot}Al_2O_3$	**3.9**
Ferrite	$4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$	**5.8**
Calcite	$CaCO_3$	**3.7**
Gypsum, Anhydrite	$CaSO_4$	**3.6**
Others		**≤ 4**

+ H_2O

Hydration products in wt% (w/c = 0.4; 1 y hydration):

Calcium silicate hydrate (C-S-H)	**~49**
Portlandite	**~20**
Calcium aluminates (AFt, AFm)	**~19**
Hydrotalcite	**~2**
$CaCO_3$	**~2**
Minor phases (Fe, Mn oxides)	**<1**
Non-hydrated clinker minerals	**~8**

Lothenbach & Wieland 2006



Materials

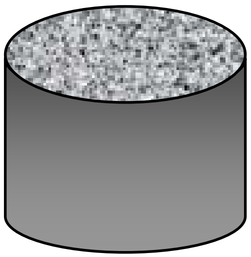
- **References**
  - S: Gypsum $CaSO_4$
  - Al: Aluminate C_3A
  - Al: Ferrite C_4AF
  - Al/S: Ettringite, Fe-Ettringite
  - Al/S: AFm (C_4AH_{13}), Monosulfate, Monocarbonate
  - Al: Hydrogarnet, Si-Hydrogarnet
  - Al: Hydrotalcite
- **Cement**
  - CEM I 52.5 N **HTS** (Lafarge, France)
- **Hardened cement pastes (HCP)**
  - HTS cement hydrated at 5°, 20°, and 50° for 28 days

Sample Preparation for Micro and Bulk XAS Studies

Cement

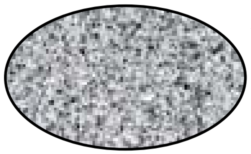
Hydration

5°/20°/50°

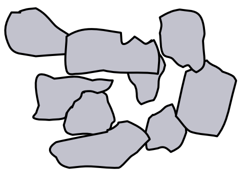


dry, impregnate, cut, polish

Thin sections of HCP



μ-XRF/XAS
@ Lucia/SLS
Beamsize: ~5 x 5 μm²

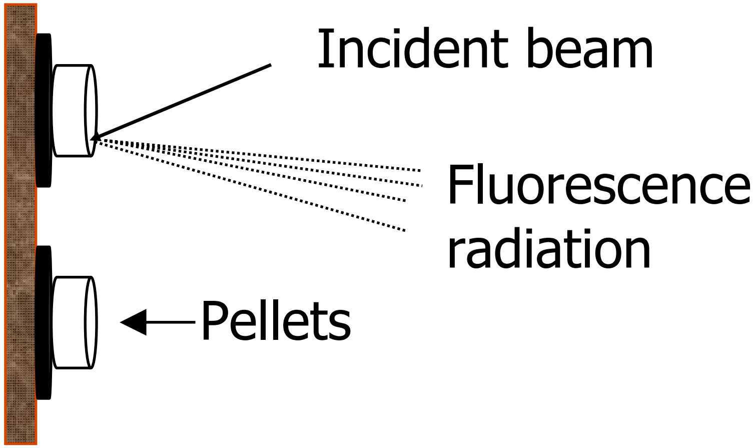


References
Clinkers
(<63μm)

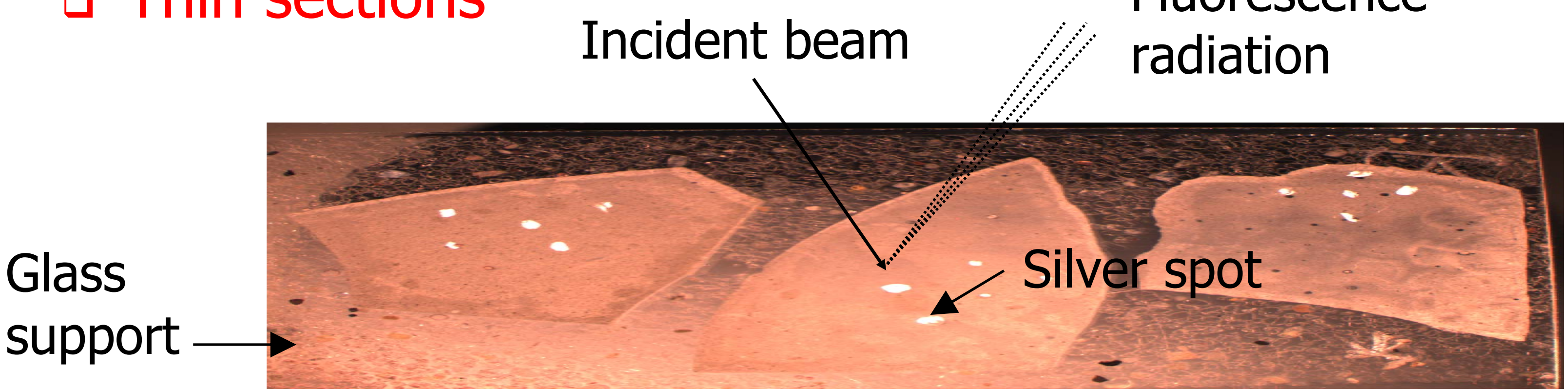
„Bulk"-XAS
@ Lucia/SLS

Sample Preparation

- Powder materials



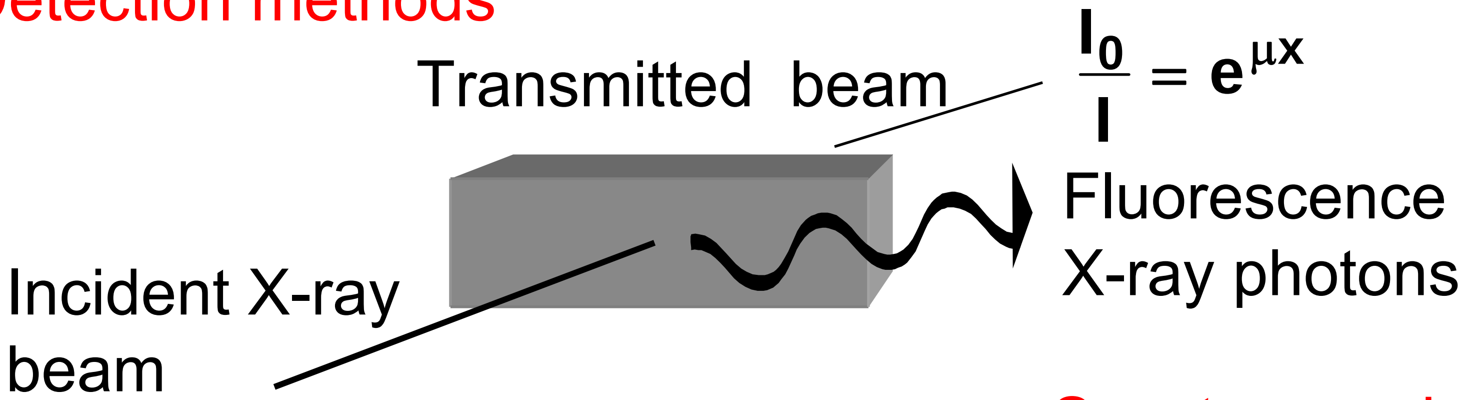
- Thin sections



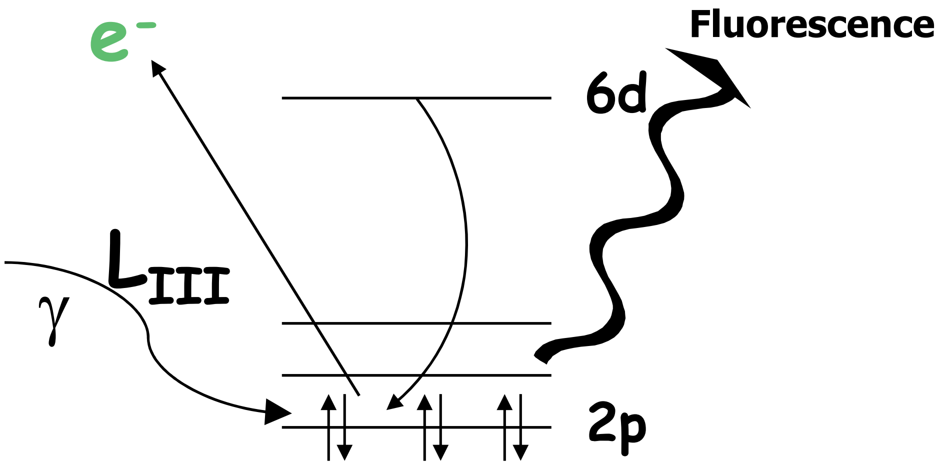
Note: Probed volume at the given energy: ~5×5×1 μm^3

X-ray Absorption Fine Structure (XAFS) Spectroscopy

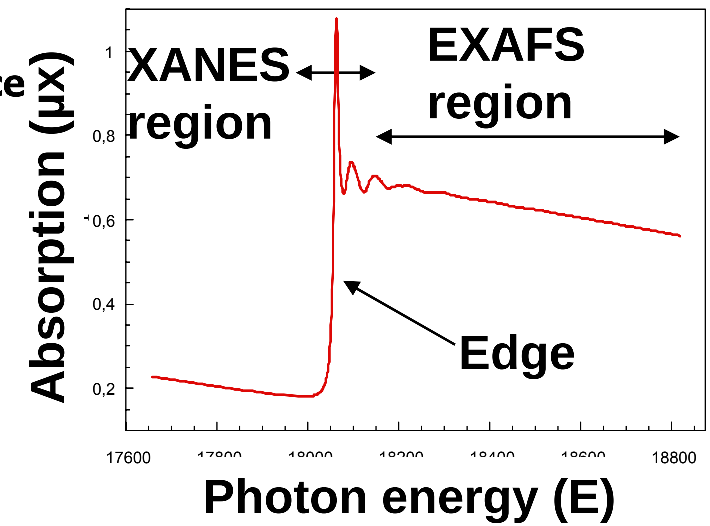
Detection methods



Photon - Matter interaction

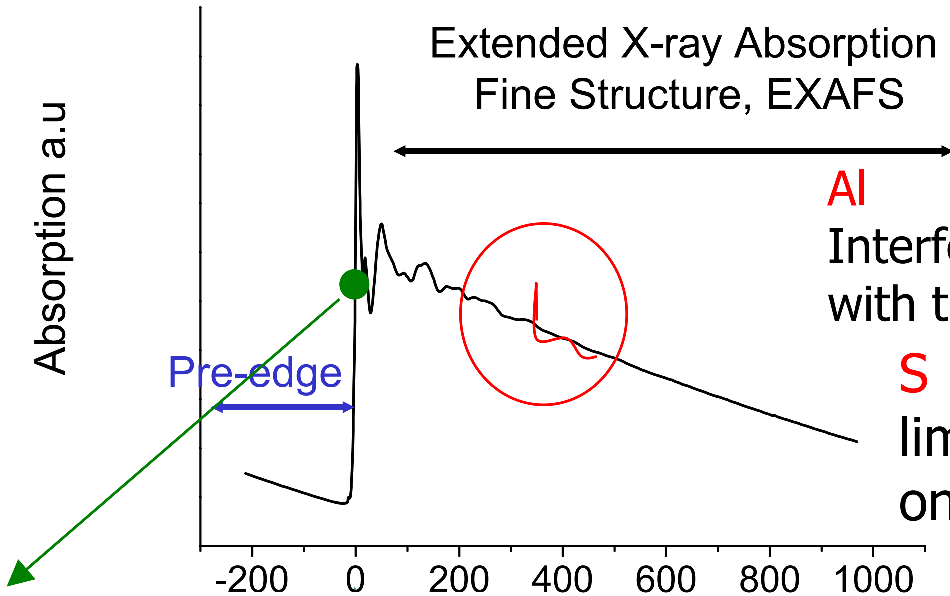


Spectra - regions



X-ray Absorption Fine Structure (XAFS) Spectroscopy

X-ray Absorption Near Edge Structure; XANES



Relative Energy [eV]

Al
Interference of Si edge@1839 eV with the Al EXAFS

S
limited structural information on the chemical environment

E_0: photoelectron threshold energy

Al K: E_0 = 1559.6 eV

S K: E_0 = 2472 eV

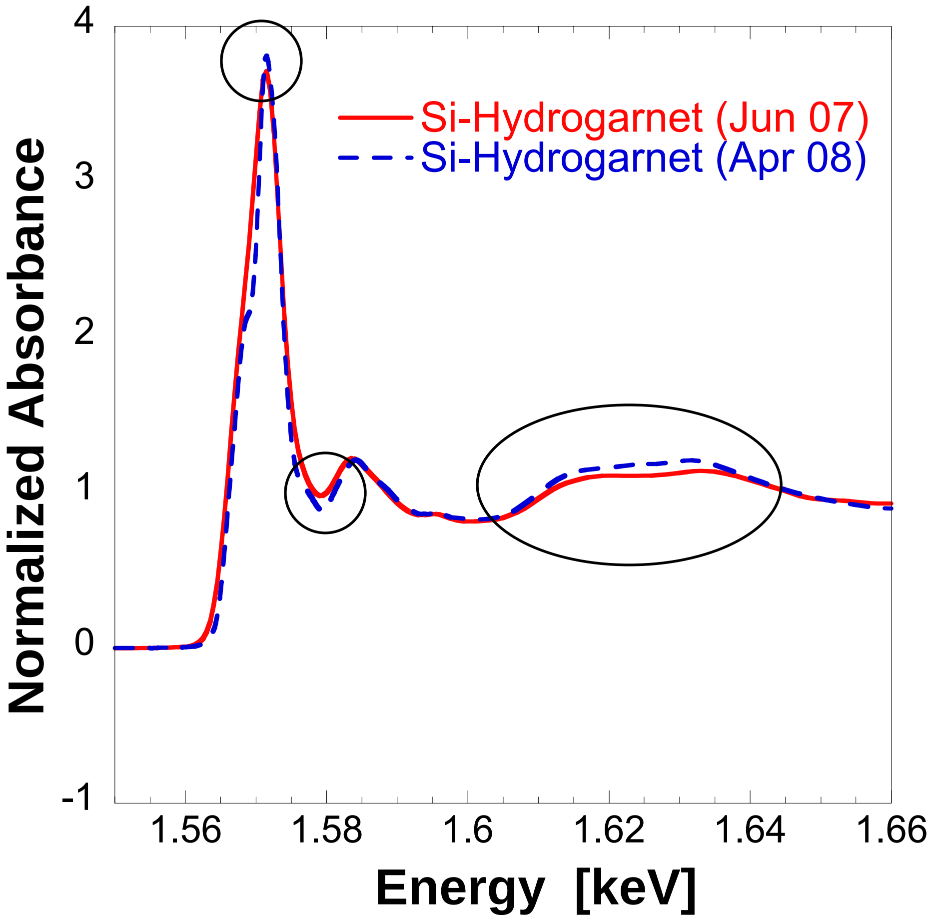
XANES Data Analysis

- **Features**
  - XANES range: to an energy of about 50 eV above the edge
  - XANES states: Excited electron populate higher unoccupied states *(unoccupied bound states and low-lying continuum states in complex ions etc.)*
  - XANES regime:
    - electronic and geometric structure
    - multiple-scattering events
    - average valence of absorber atom

- **Experimental consistency checks**
  - Same reference measured on different campaigns
  - Same compounds prepared by different groups
  - Spectra of similar compounds

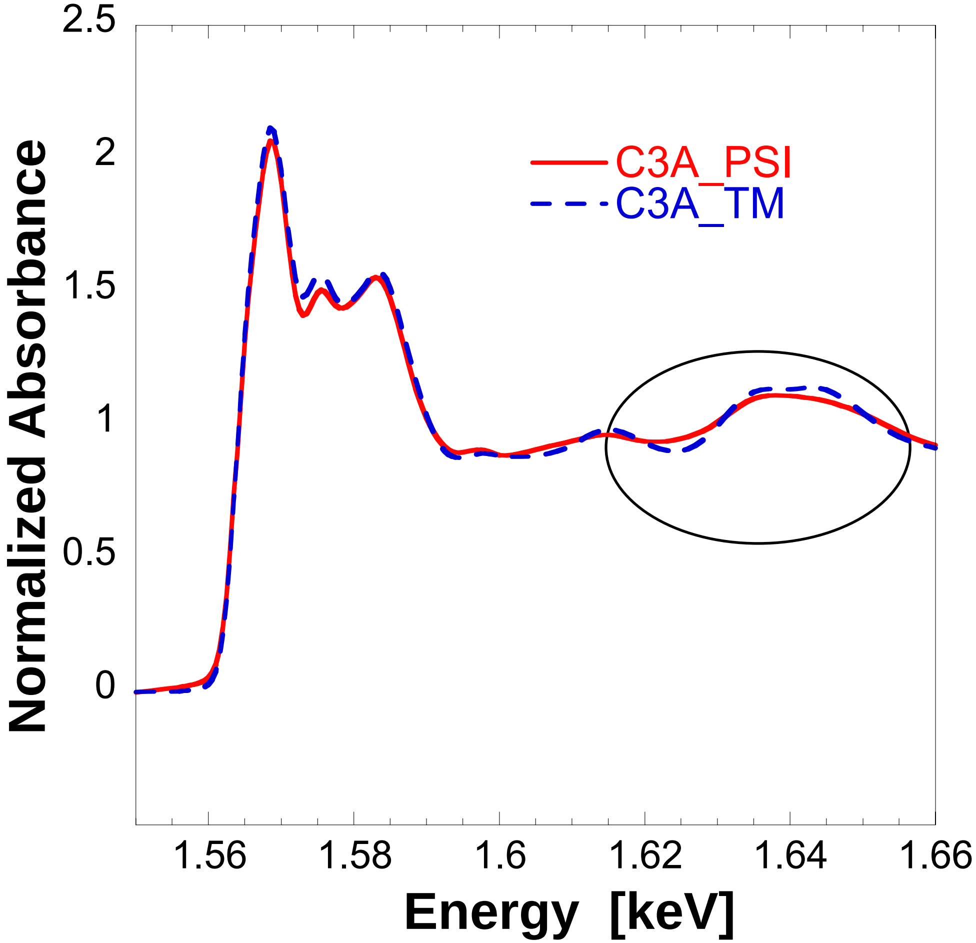
Reproducibility

Si-Hydrogarnet: -Two campaigns in June 2007 and April 2008 at the Lucia beamline@SLS



Variability in C_3A

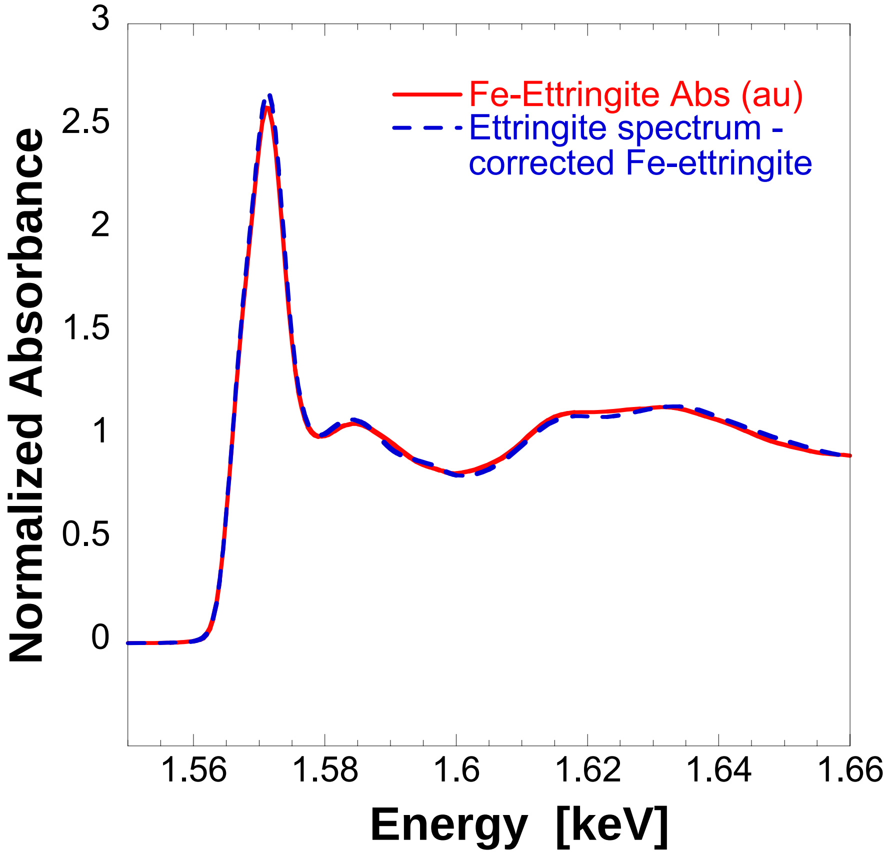
C_3A: - XANES data of C_3A prepared in different laboratories



Matschei et al. 2007

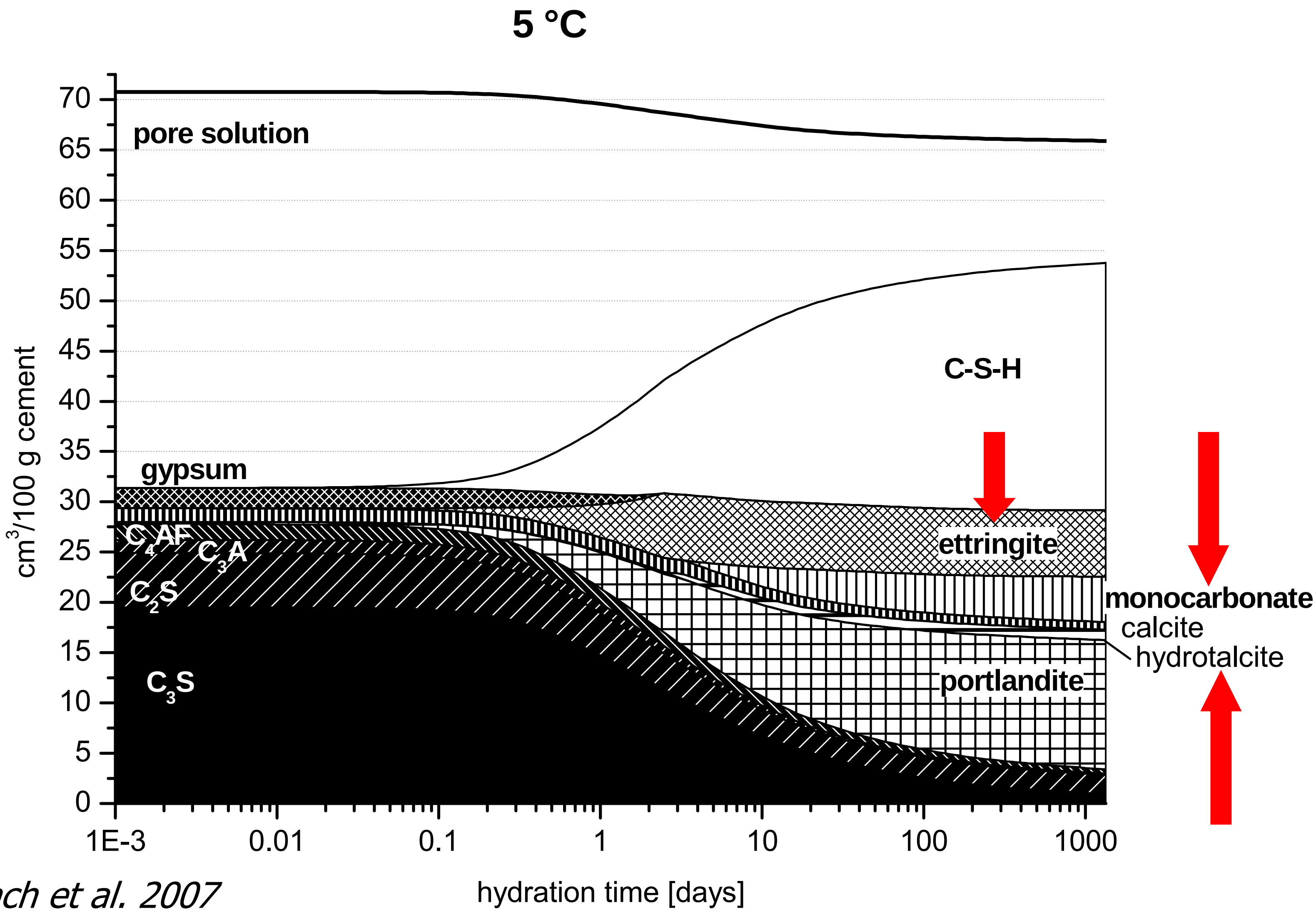
Consistency of AFt Spectra

Fe-ettringite: - Spectrum of Al/Fe-ettringite-ss
- Spectrum calculated based on ettringite



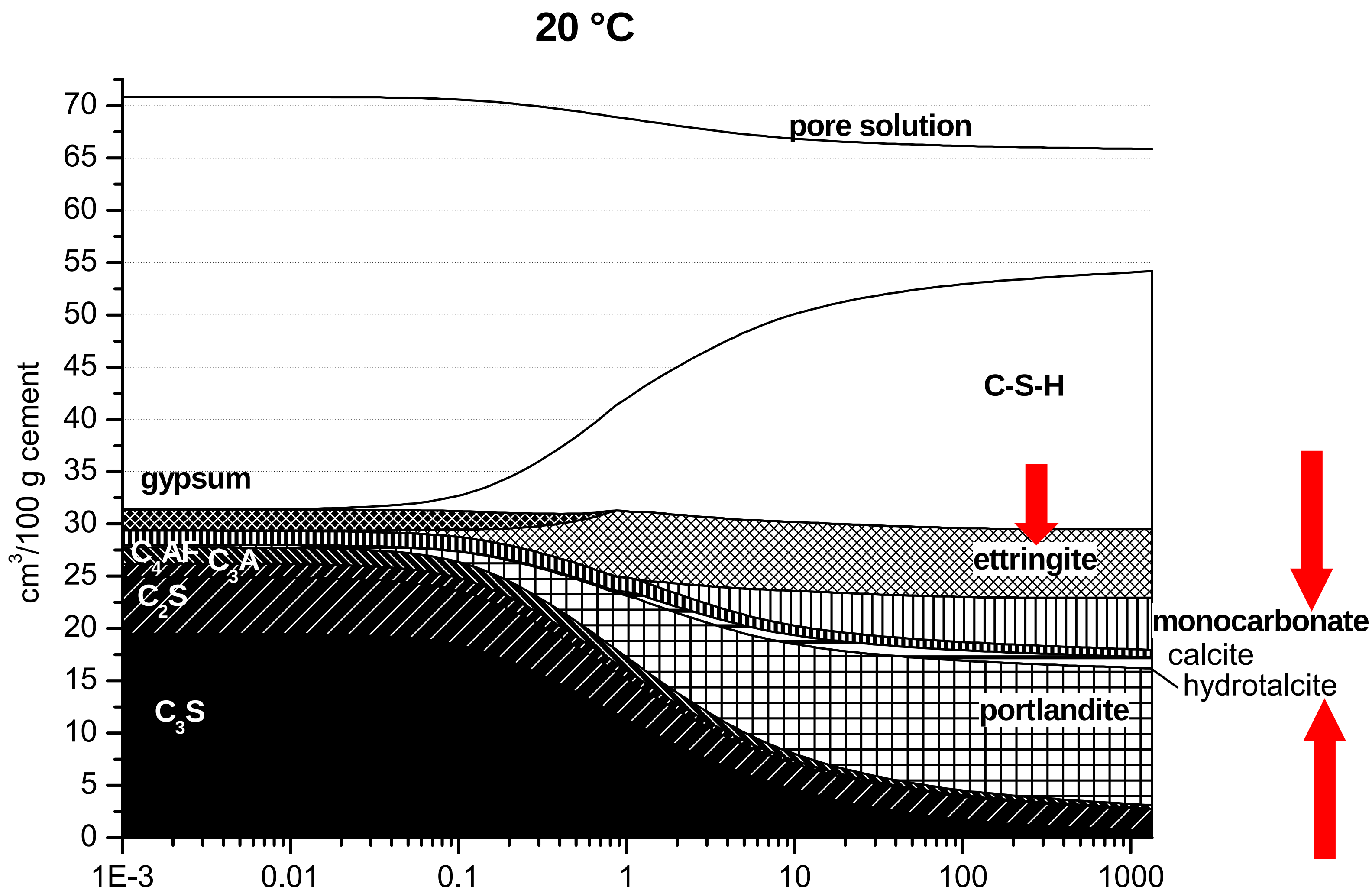
Aluminium speciation

HTS Modelling



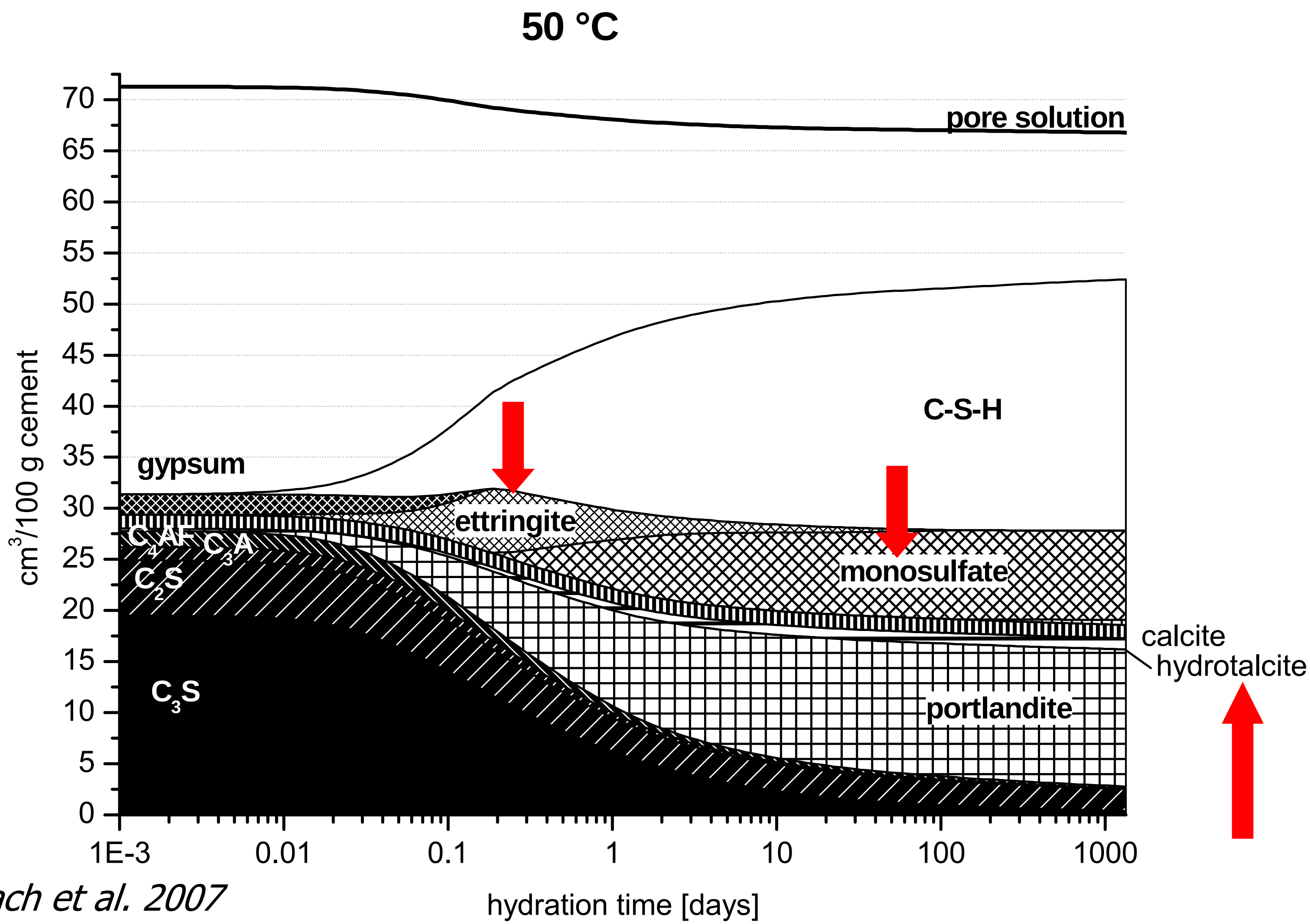
Lothenbach et al. 2007

HTS Modelling



Lothenbach et al. 2007

HTS Modelling

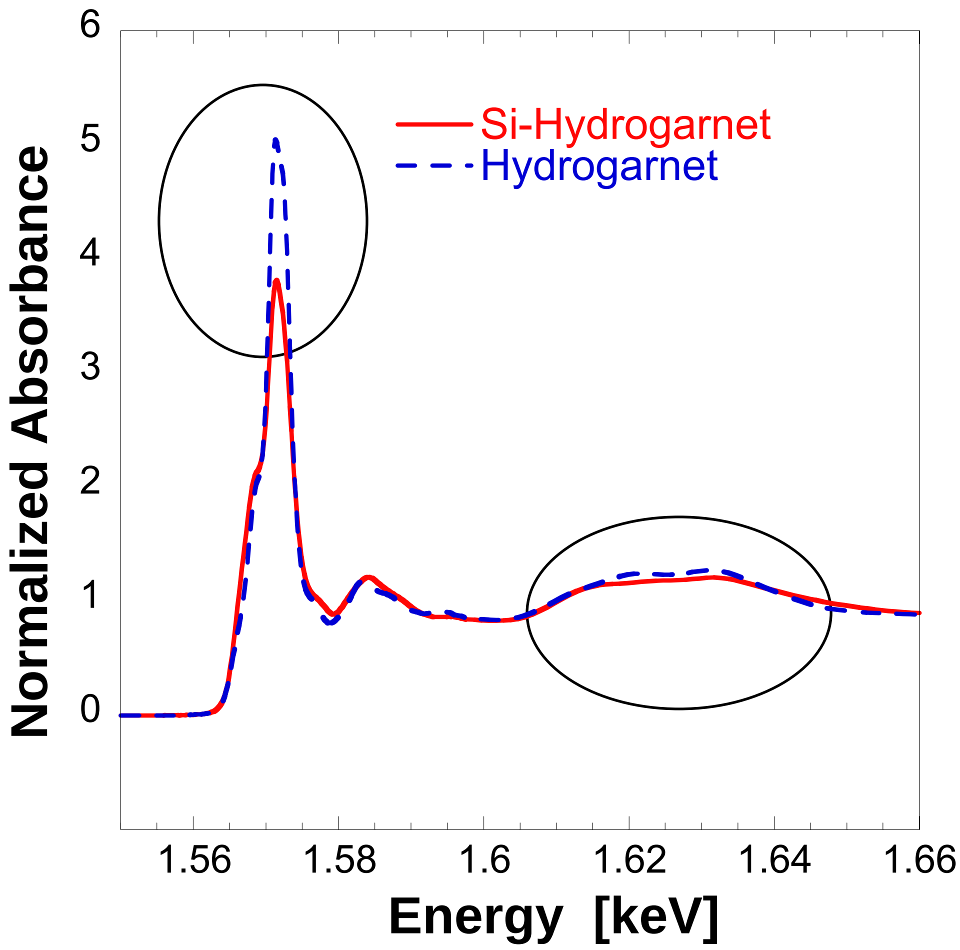


Lothenbach et al. 2007

References - Hydrogarnets

Si-hydrogarnet: C_3ASH_4

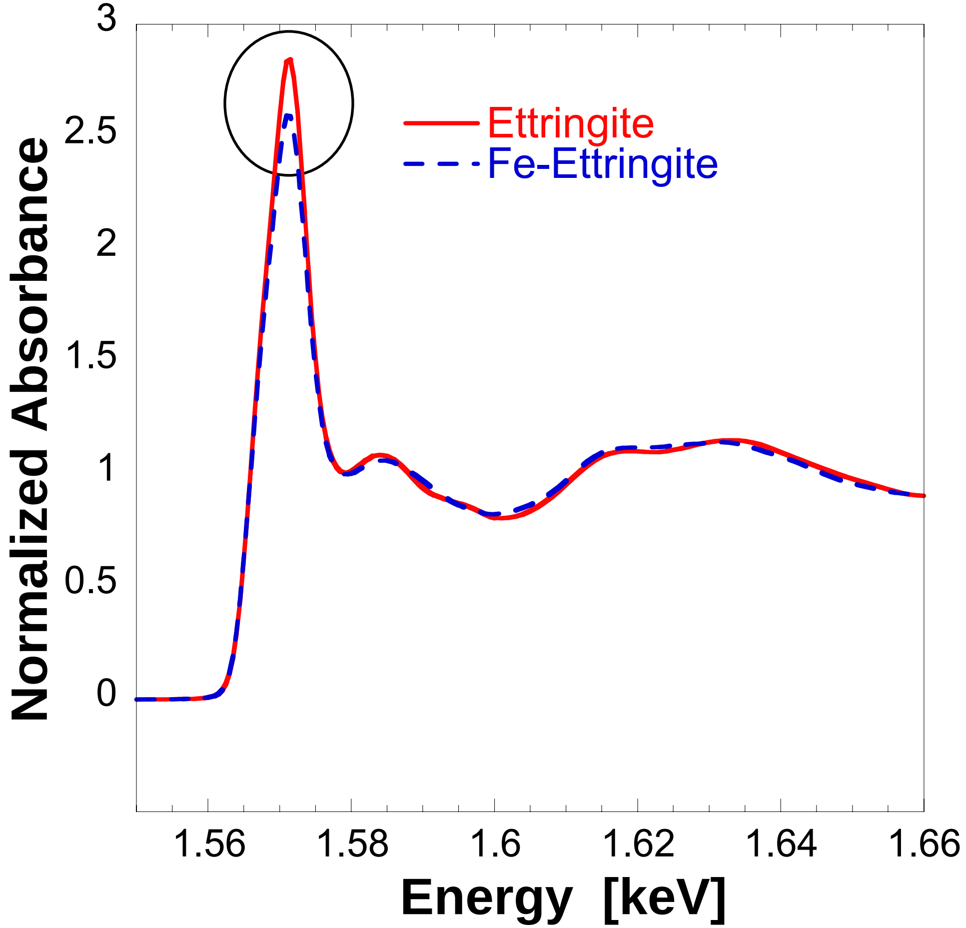
Hydrogarnet: C_3AH_6



References - Ettringite

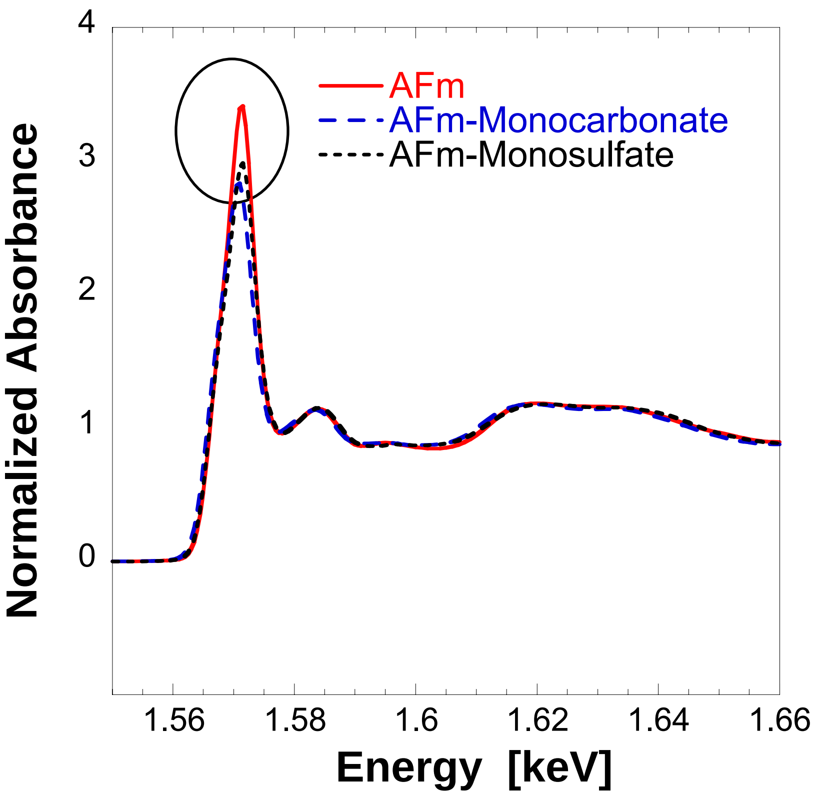
Ettringite: $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$

Al/Fe-Ettringite-ss: $Ca_6(Al/Fe)_2(SO_4)_3(OH)_{12}\cdot 26H_2O$



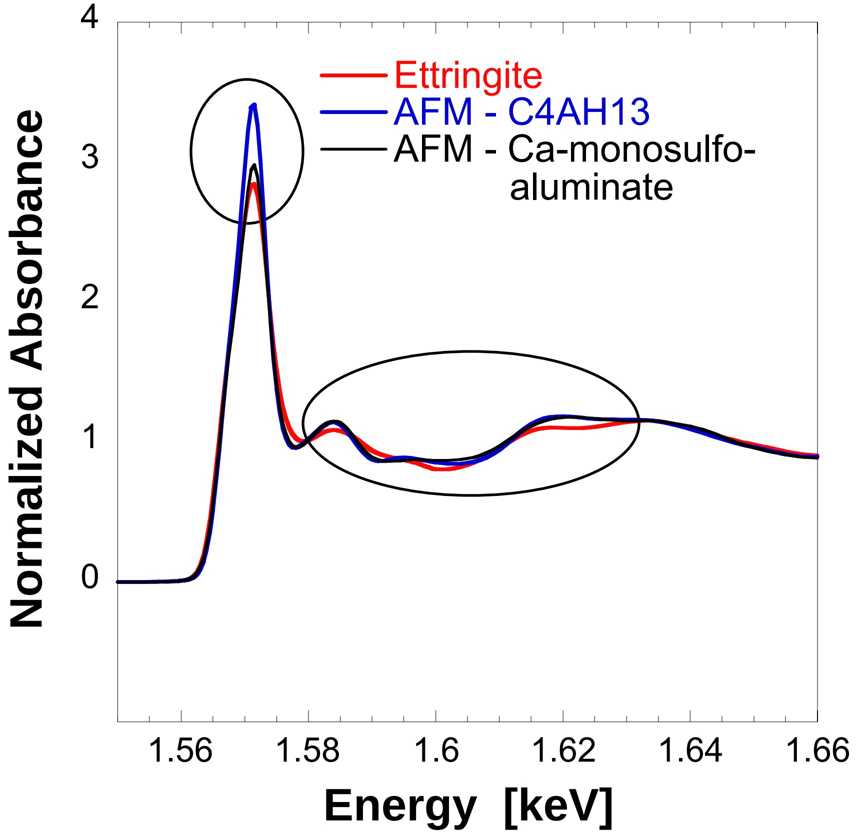
References - AFm-Phases

AFm - C_4AH_{13}:	$Ca_4Al_2(OH)_{14}\cdot 6H_2O$
AFm - Monocarbonate:	$Ca_4Al_2CO_3(OH)_{12}\cdot 5H_2O$
AFm - Monosulfate:	$Ca_4Al_2SO_4(OH)_{12}\cdot 6H_2O$

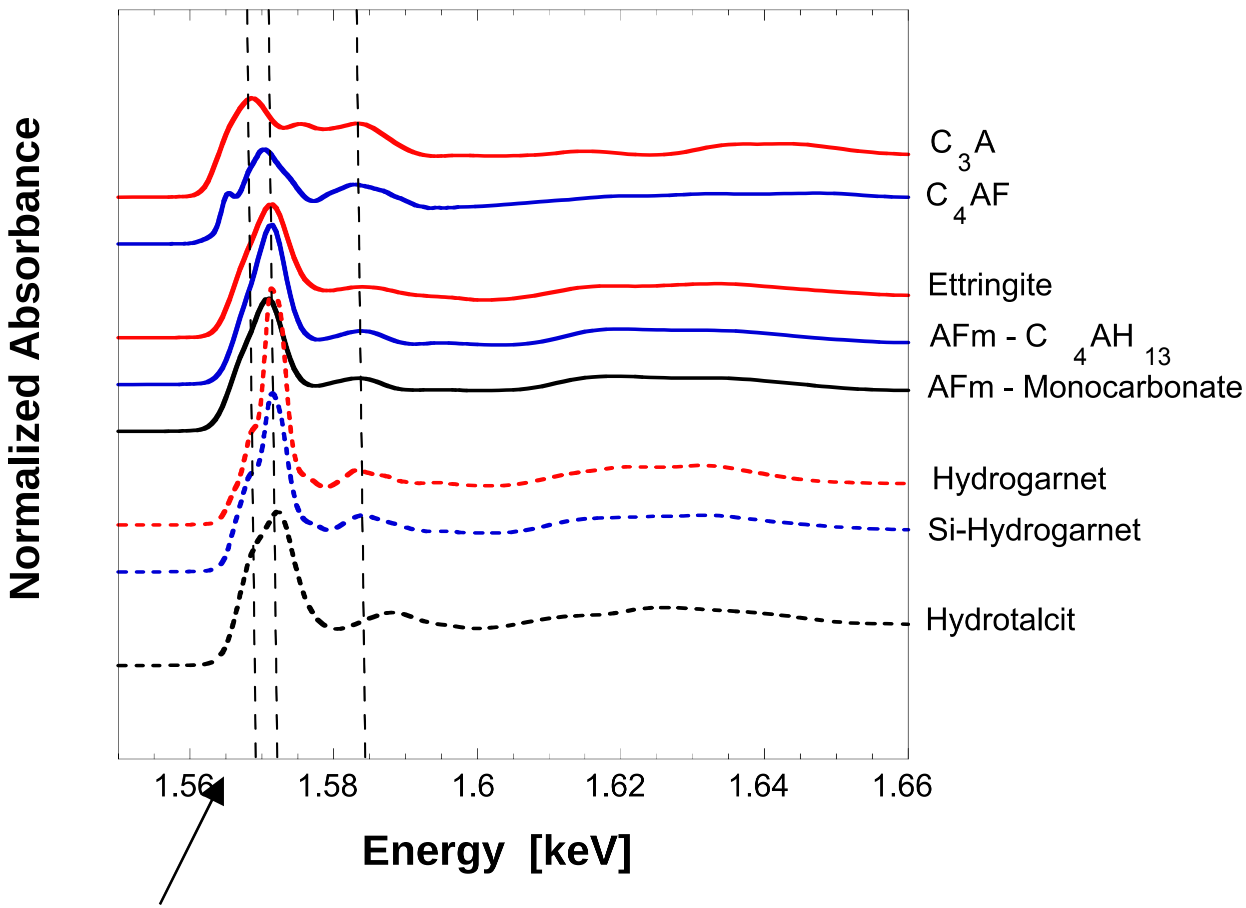


Ettringite - AFM-Phases - Comparison

Ettringite:	$Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$
AFm - C_4AH_{13}:	$Ca_4Al_2(OH)_{14}\cdot 6H_2O$
AFm - Monosulfate:	$Ca_4Al_2SO_4(OH)_{12}\cdot 6H_2O$

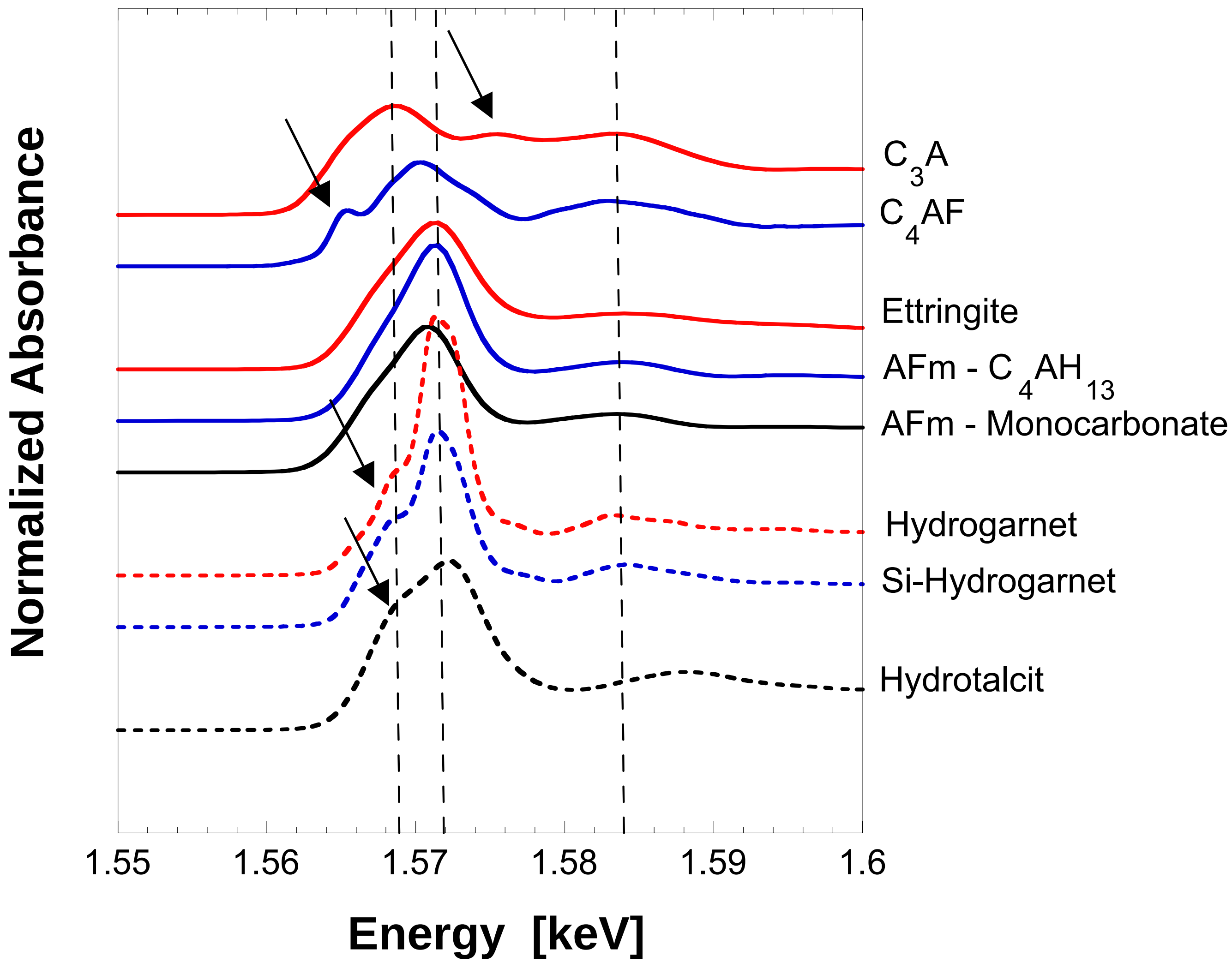


References - XANES data



⇒ Shift of 3 eV between clinker minerals and secondary phases

References - XANES data



Conclusions

Possible:

- Clinker minerals - AFt/AFm - Hydrogarnets - Hydrotalcite

Difficult:

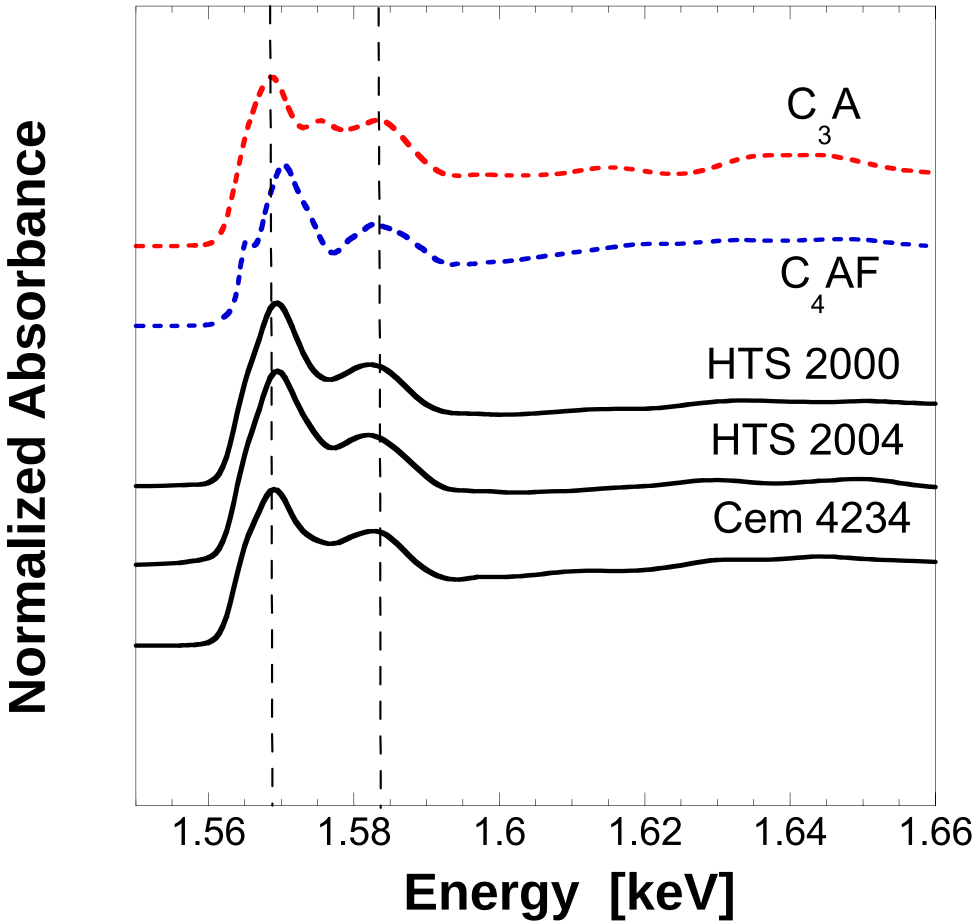
- AFm - C_4AH_{13} against AFm - Ca monocarbo/sulfoaluminates
- AFt (Ettringite) against AFm-type phases

Impossible:

- AFm - Ca monocarboaluminate and Ca monosulfoaluminate

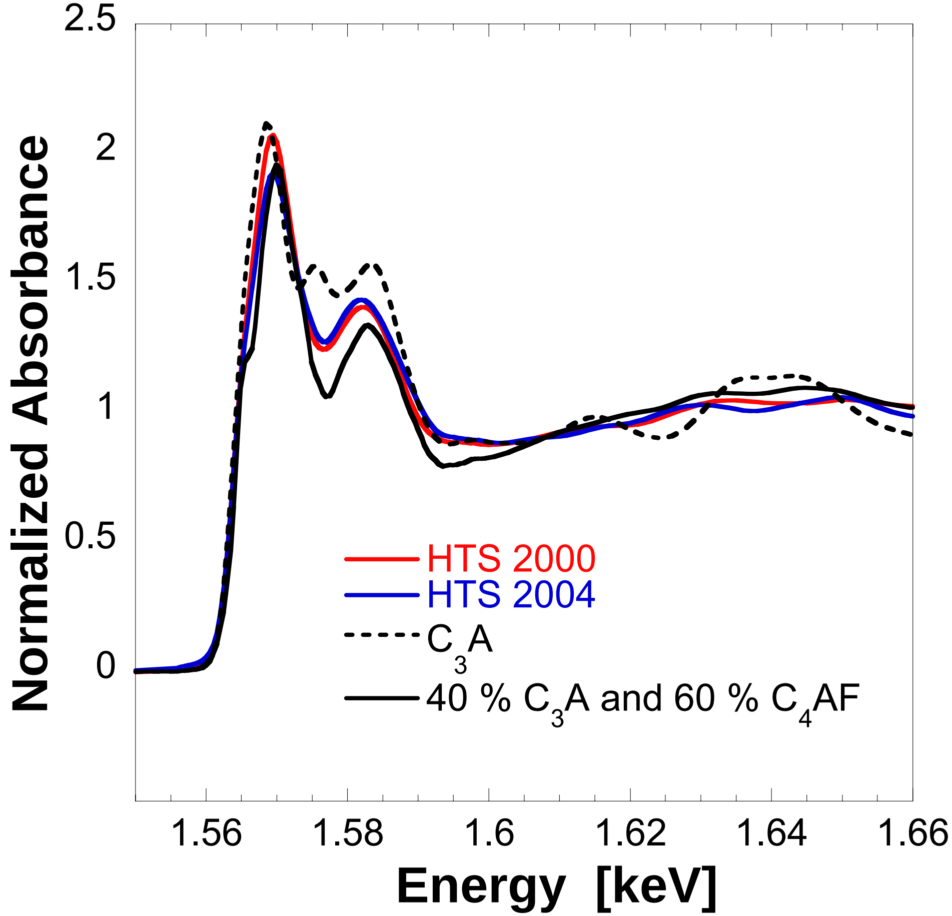
Clinkers

Cem 4234: - Portland cement *(Lothenbach et al. 2008)*
HTS 2000/2004: - Cem I 52.5 N HTS (Lafarge, France)

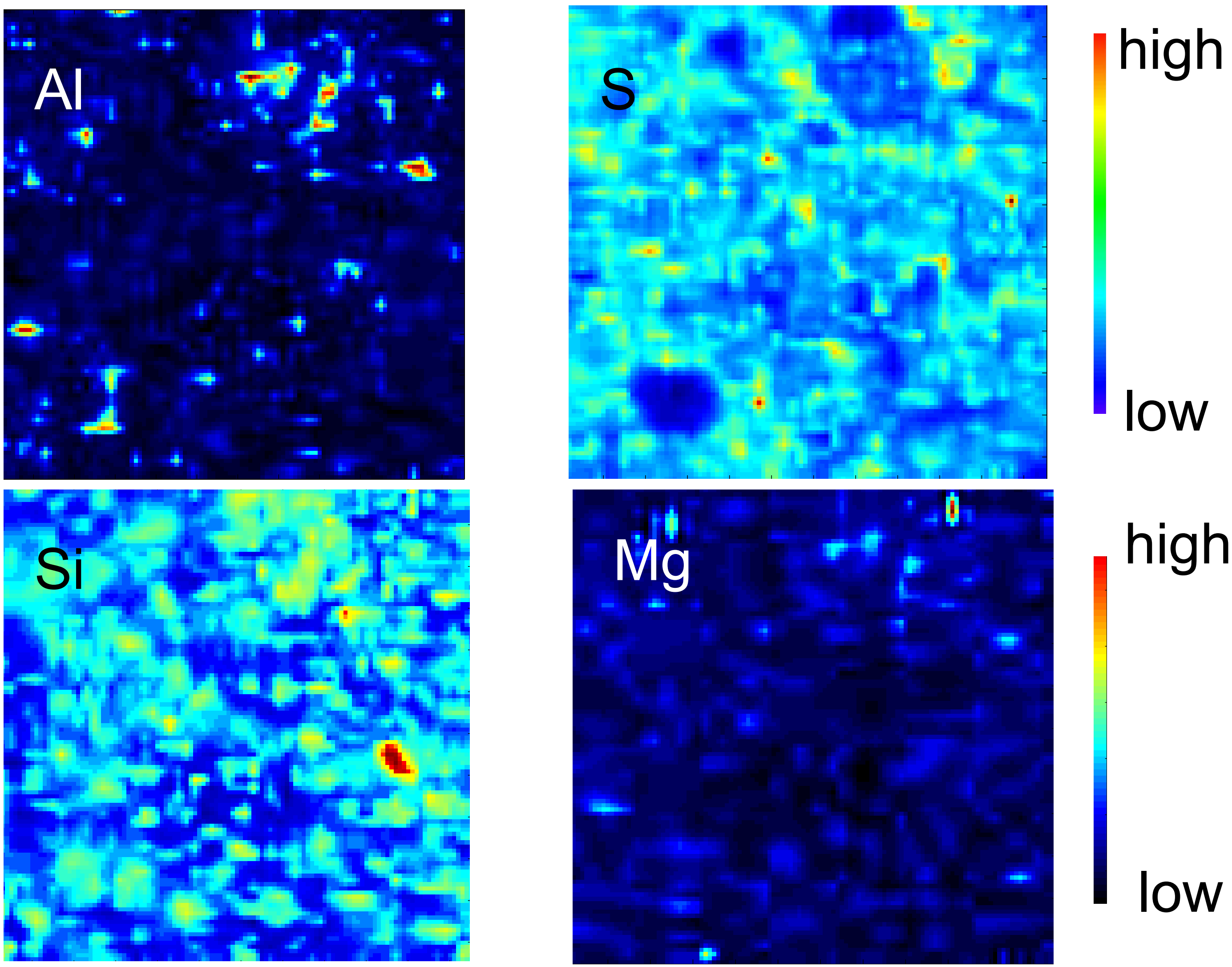


Clinkers

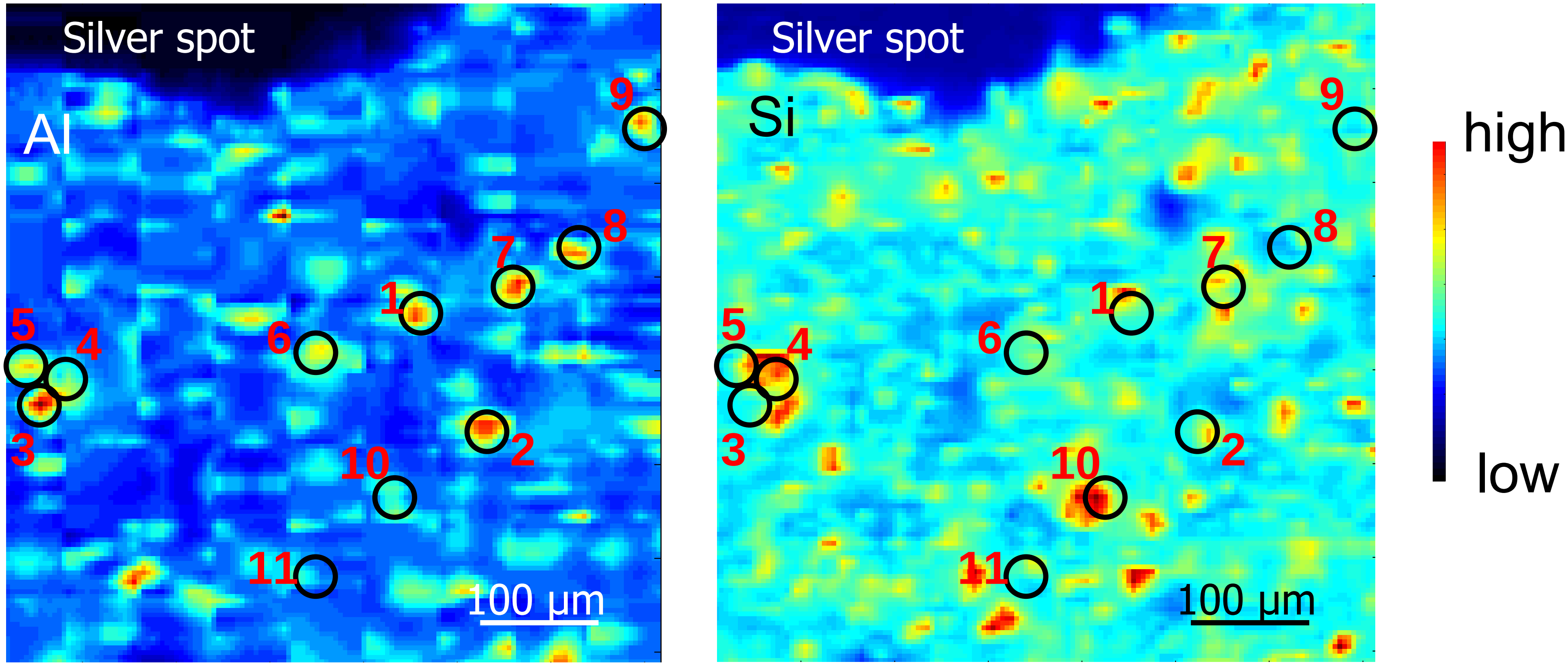
Linear combination: - 40 % C_3A and 60 % C_4AF based on chemical analyses



MicroXRF maps - Elemental distribution

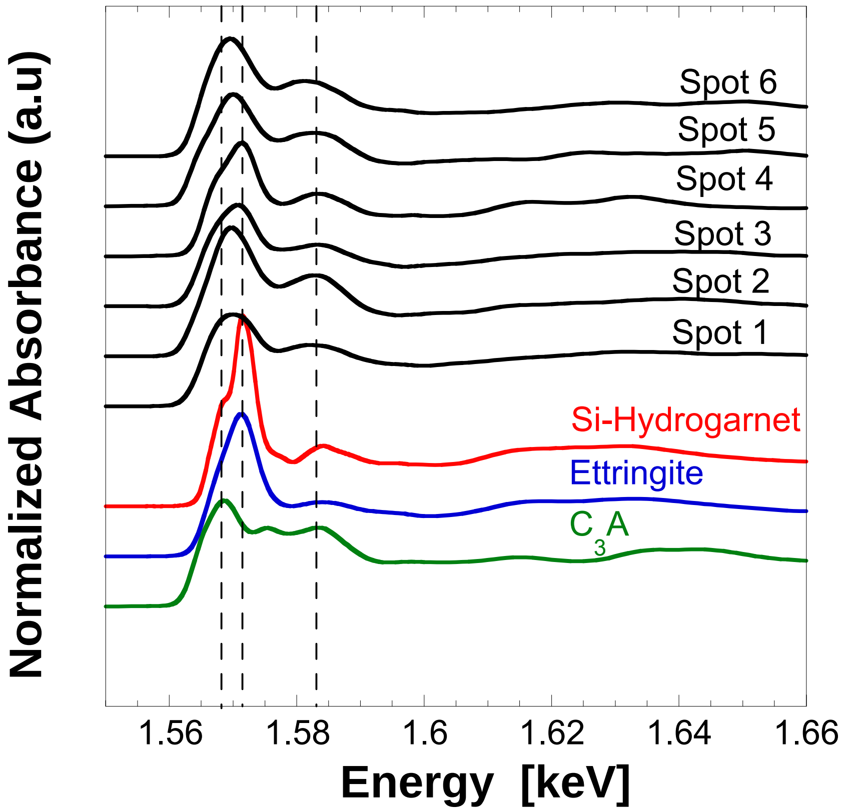


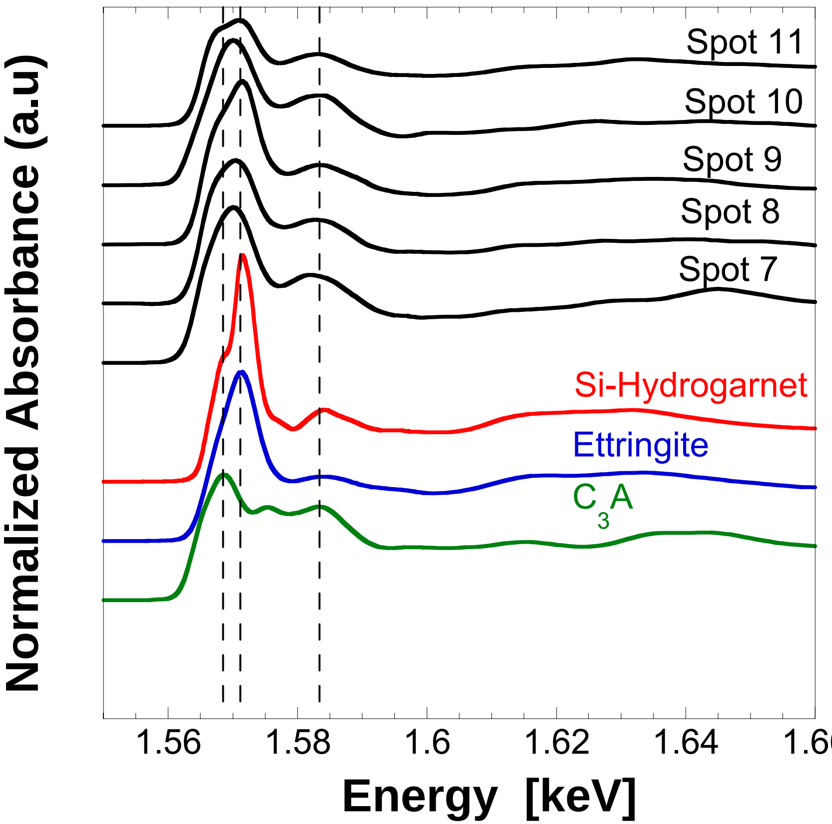
HTS 20° 28 d



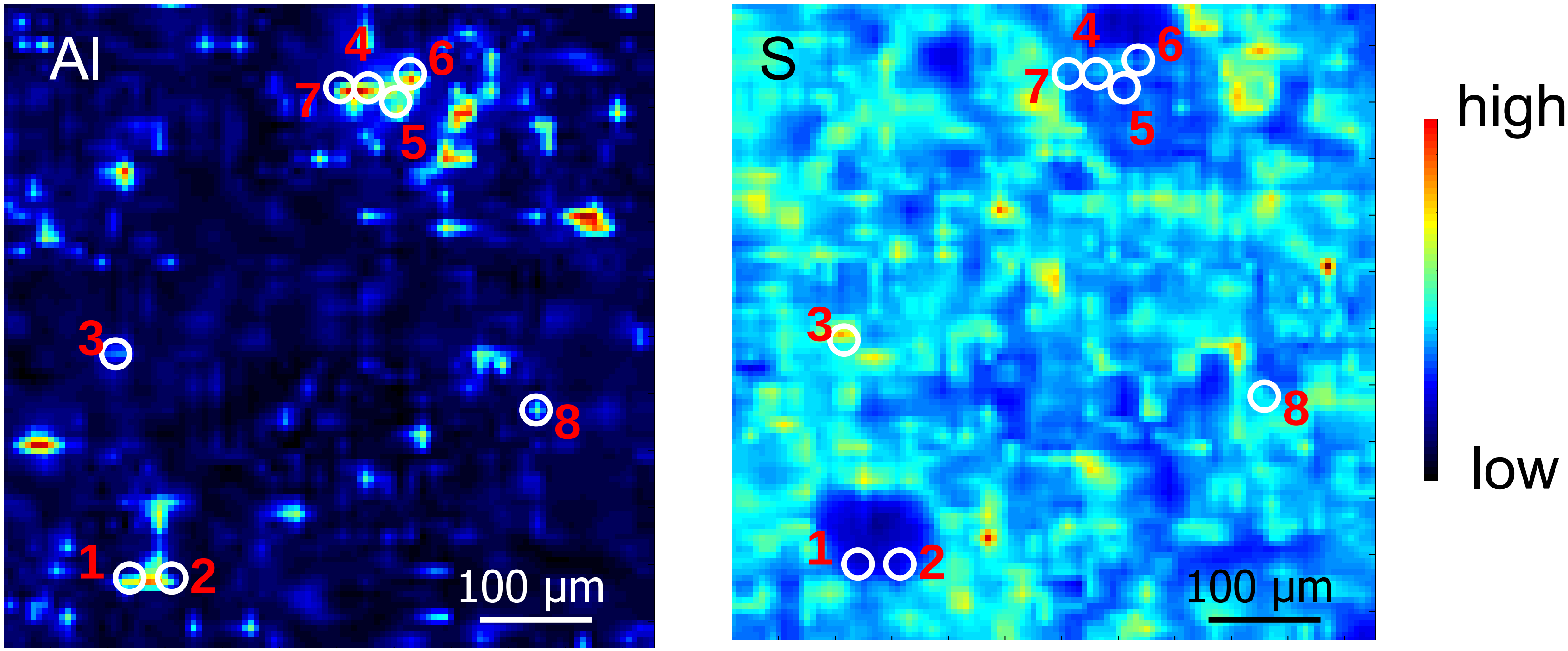
Spot 1: high Al, medium Si
Spot 2: high Al, medium Si
Spot 3: high Al, low Si
Spot 4: medium Al, high Si
Spot 5: high Al, medium Si
Spot 6: high Al, low Si
Spot 7: high Al, high Si
Spot 8: high Al, low Si
Spot 9: high Al, low Si
Spot 10: low Al, high Si
Spot 11: low Al, low Si

XANES HTS 20° 28d



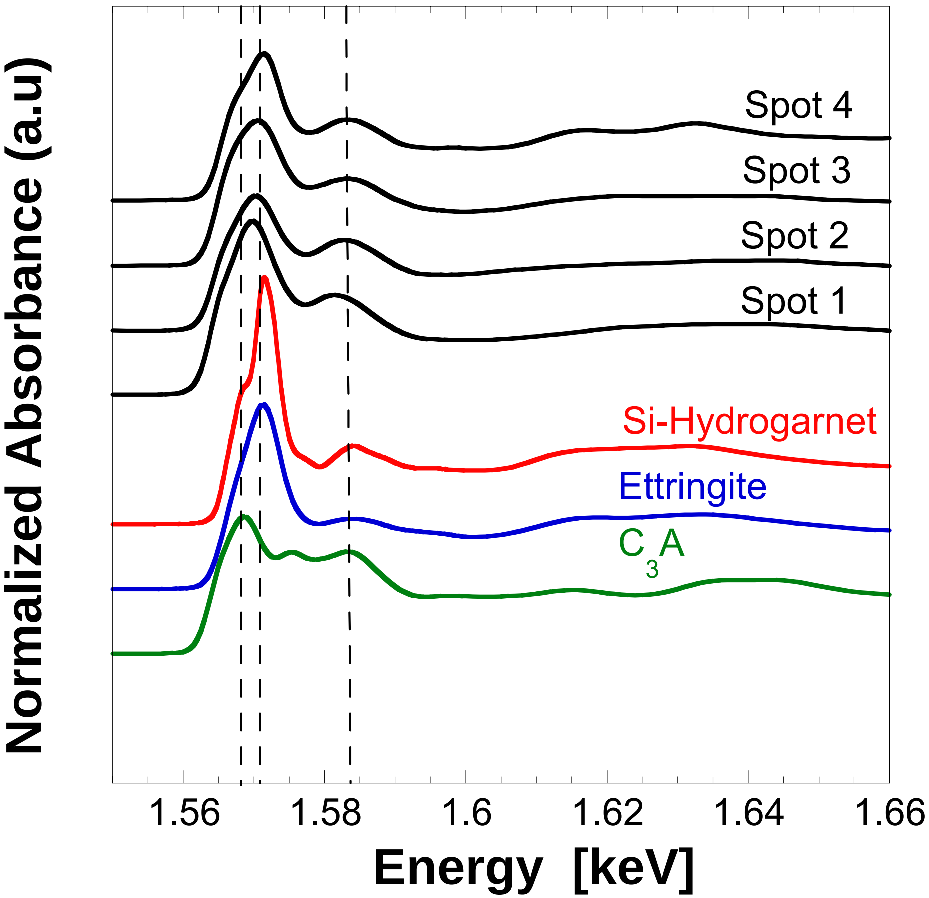


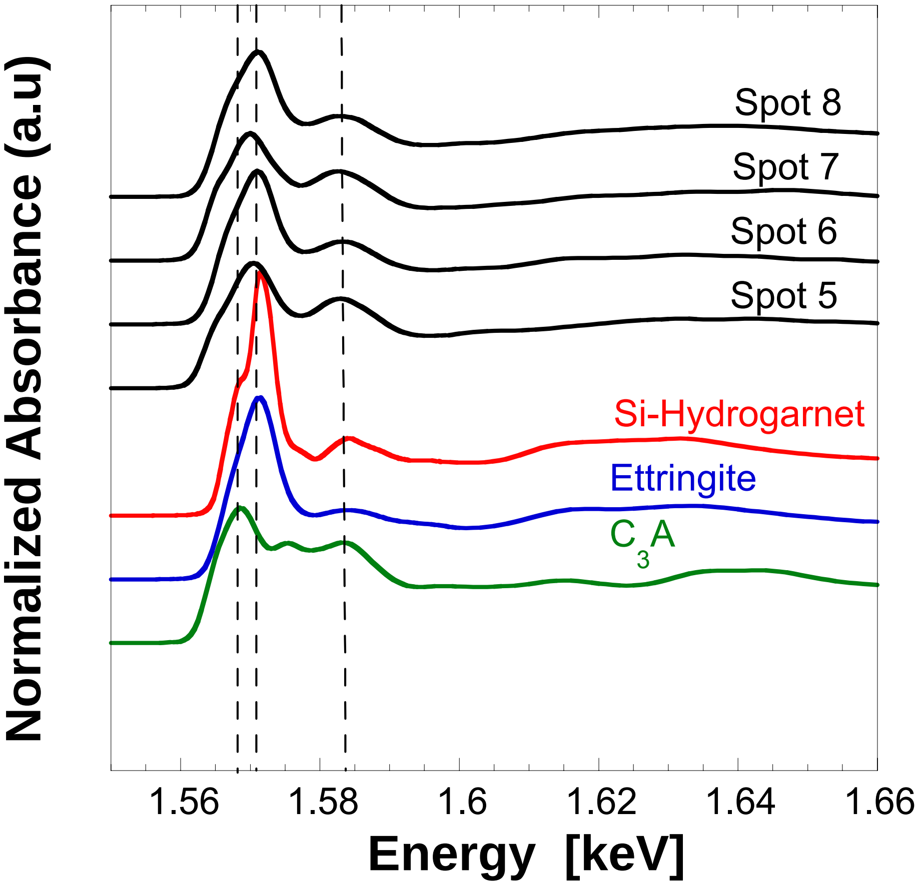
HTS 5° 28 d



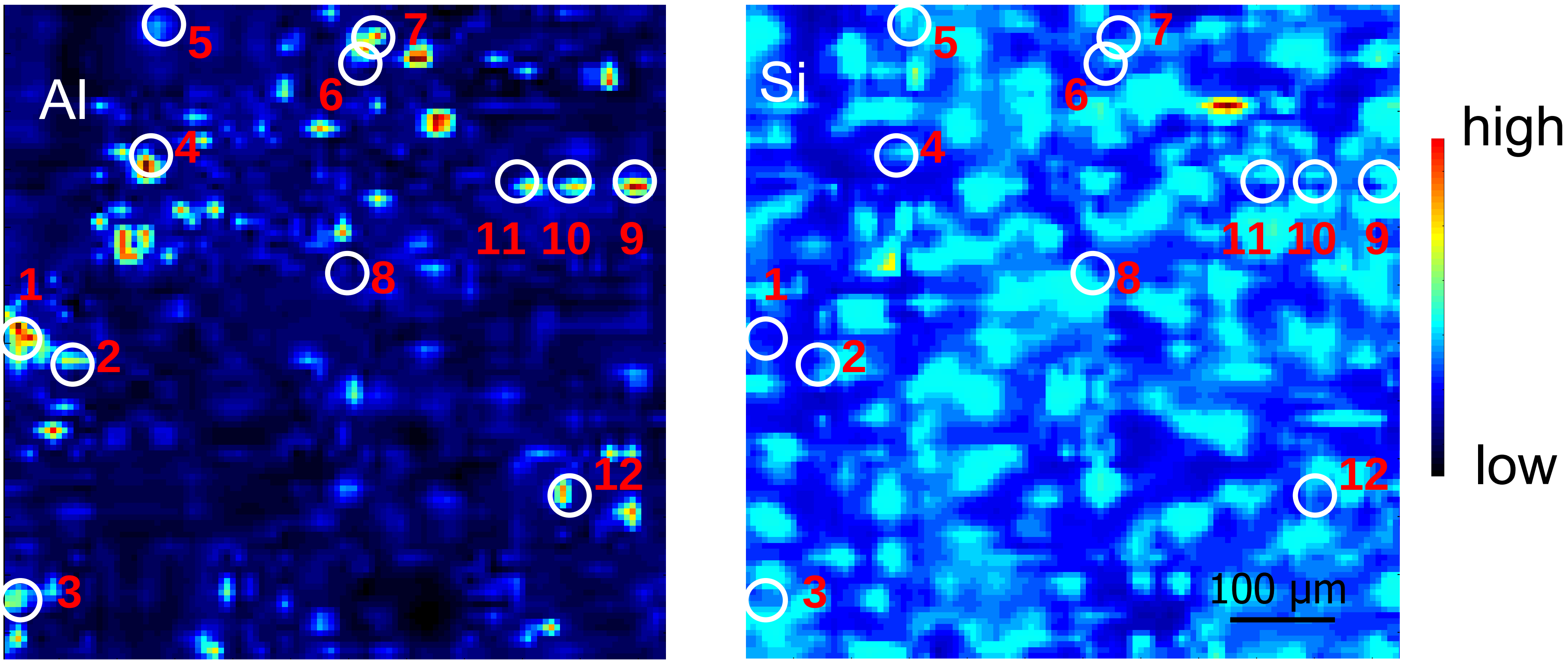
Spot 1: high Al, low S
Spot 2: medium Al, low S
Spot 3: low Al, high S
Spot 4: high Al, medium S
Spot 5: medium Al, low S
Spot 6: high Al, low S
Spot 7: high Al, low S
Spot 8: medium Al, medium S

XANES HTS 5° 28d





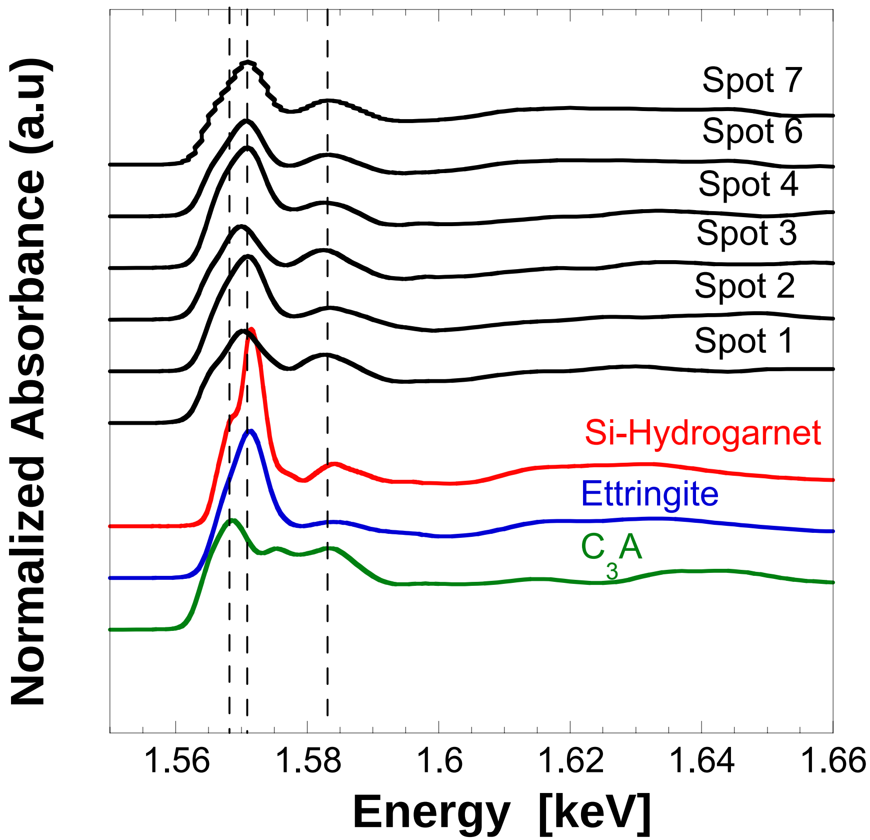
HTS 50° 28 d

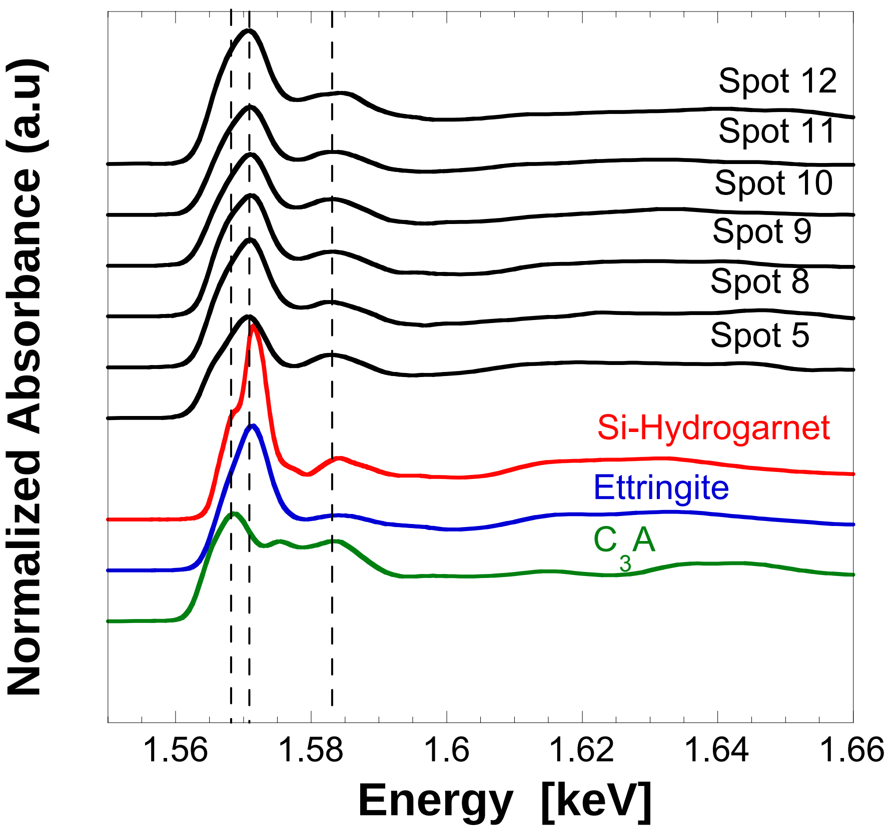


Spot 1: high Al, low Si
Spot 2: medium Al, medium Si
Spot 3: medium Al, low Si
Spot 4: high Al, medium Si
Spot 5: low Al, medium Si
Spot 6: medium Al, low Si

Spot 7: high Al, low Si
Spot 8: low Al, medium Si
Spot 9: high Al, medium Si
Spot 10: high Al, medium Si
Spot 11: high Al, medium Si
Spot 12: high Al, low Si

XANES HTS 50° 28d





Principal Components Analysis (PCA)

PCA

- Analyse a set of spectra to see if they can be represented as linear combination of a smaller number of spectra (abstract components)

$$\mathbf{D} = \mathbf{C} \times \mathbf{R}$$

$$(m \times r) \quad (m \times n) \quad (n \times r)$$

D: Data matrix which is factored into its components
C: Factor loading matrix
R: Factor-score matrix

Target transformation

- Determine which real reference can make up the abstract component
- SPOIL – number which measures the degree to which replacing an abstract component with the real reference would increase the fit error

SPOIL < 1.5: reference is an excellent candidate for a component
SPOIL 1.5 - 3: reference is a good candidate for a component
SPOIL 3 - 4.5: reference is a fair candidate for a component
SPOIL 4.5 - 6: reference is a poor candidate for a component

Principal Components Analysis

HTS 20° 28d

- 4-5 components (total of 11 XANES spectra - SPOIL < 4.5)
- C_3A/AFm(C_4AH_{13})/Ettringite/AFm-Monosulfate/Hydrotalcite/Si-Hydrogarnet

HTS 5° 28d

- 3 components (total of 8 XANES spectra SPOIL < 4.5)
- C_3A/AFm(C_4AH_{13})/Ettringite/AFm-Monosulfate/(AFm-Monocarbonate) Hydrotalcite/Si-Hydrogarnet

HTS 50° 28d

- 3 components (total of 12 XANES spectra – SPOIL < 4.5)
- C_3A/AFm(C_4AH_{13})/Ettringite/AFm-Monosulfate/(AFm-Monocarbonate) Hydrotalcite/Si-Hydrogarnet

Linear Combination

Aim:

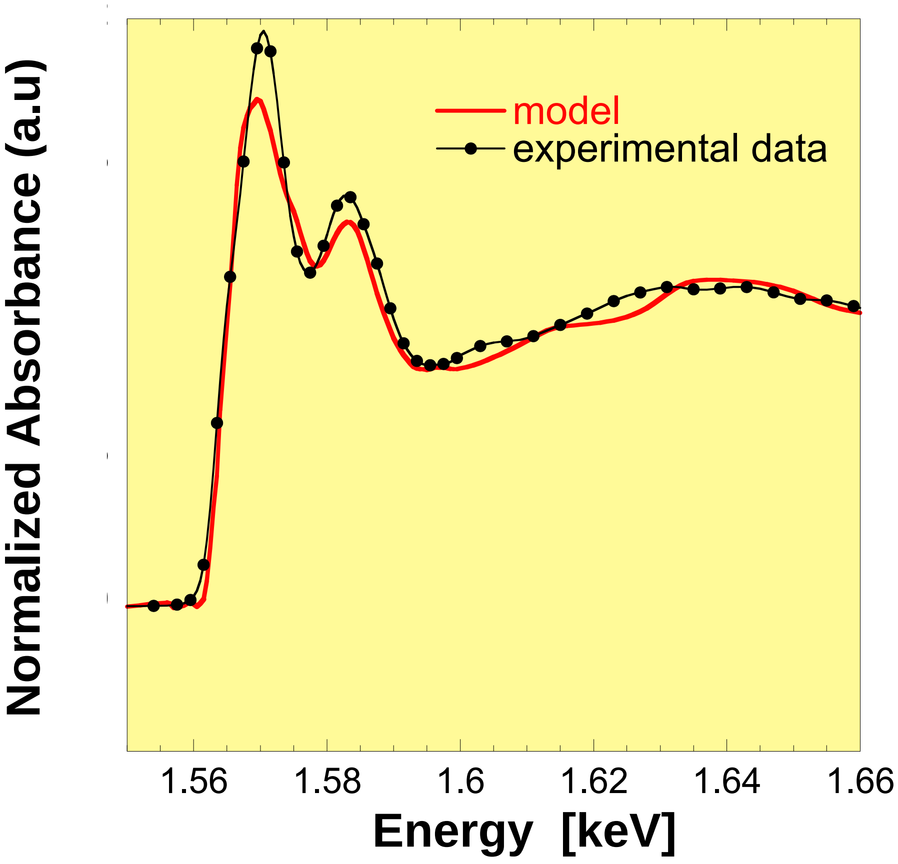
- XANES spectra as linear combination of reference spectra
- Minimum number of components according to PCA
- References selected based on the results from PCA/Target transformation

Procedure:

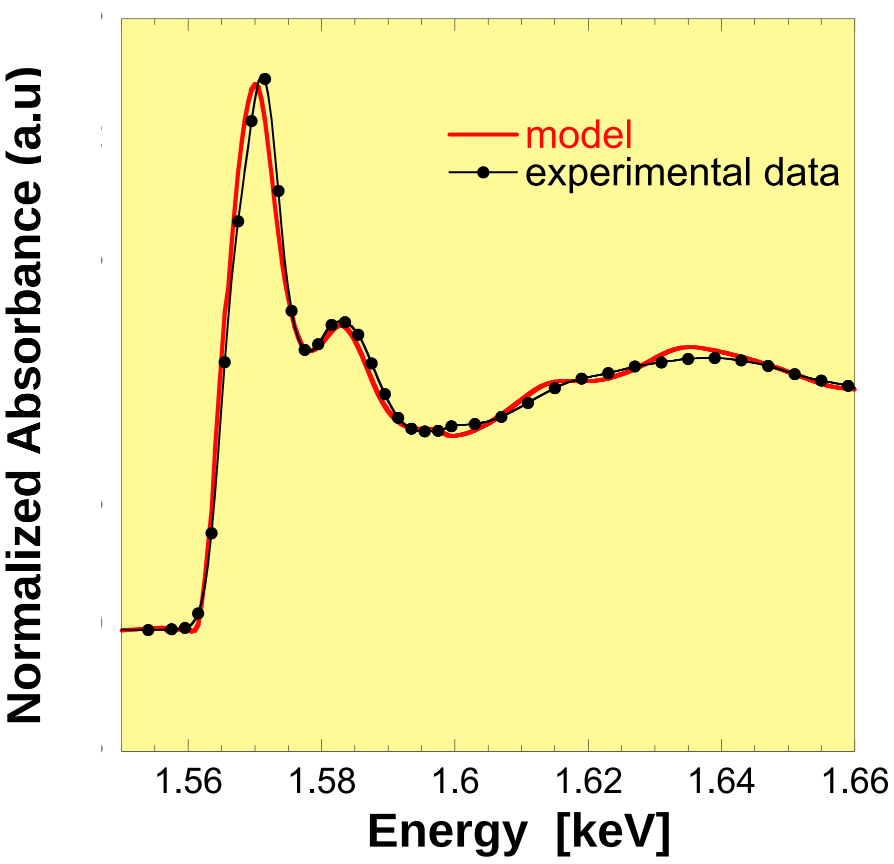
- Linear combination tool in Athena (Iffefit)
- Residual: $R = \dfrac{\sum(\text{data} - \text{fit})^2}{\sum(\text{data})^2} \times 100\%$
- Fit: excellent for $R \le 0.5$; fair for $R > 0.5$

HTS 5° 28 d

Spot 5 (R =0.67)



Spot 8 (R = 0.21)



Linear Combination HTS 5°

Spot	C_3A	C_4AF	Ettringite	AFm	Hydro-talcite	Res %
# 1	75 %			25 %		0.60
# 2	78 %		22 %			0.42
# 3	66 %		34 %			0.31
# 4	-	-		-		-
# 5	67 %	25 %		8 %		0.67
# 6	54 %		46 %			0.36
# 7	84 %		16 %			0.70
# 8	54 %		46 %			0.21

Linear Combination HTS 20°

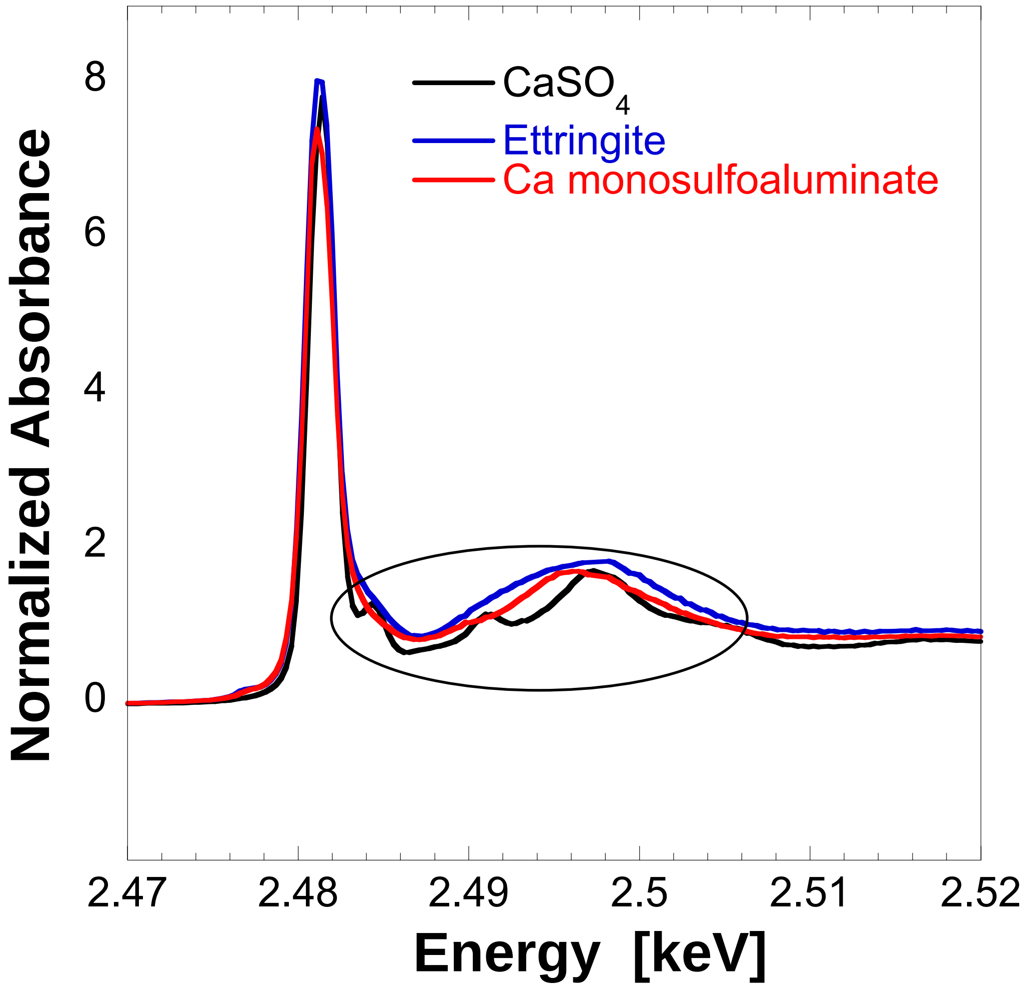
Spot	C_3A	C_4AF	Ettringite	AFm	Hydro-talcite	R
# 1	74 %		26 %			0.43
# 2	75 %		26 %			0.34
# 3	64 %		36 %			0.28
# 4	50 %		50 %			0.47
# 5	81 %		19 %			0.71
# 6	80 %		13 %	7 %		0.46
# 7	71 %		2%	27 %		0.65
# 8	68 %		23 %	9 %	0.2 %	0.32
# 9	51 %		26 %	11 %	12%	0.27
# 10	74 %		1 %	25 %		0.40
# 11	76 %		24 %			0.67

Linear Combination HTS 50°

Spot	C_3A	C_4AF	Ettringite	AFm	Hydro-talcite	R
# 1	66 %	29 %		5 %		0.75
# 2	56 %		44 %			0.36
# 3	71 %	24 %		5 %		0.77
# 4	54 %		38 %	8 %		0.27
# 5	60 %		40 %			0.40
# 6	55 %	33 %		12 %		1.0
# 7	57 %	27 %		16 %		0.91
# 8	50 %		48 %	2 %		0.32
# 9	54 %		46 %			0.39
# 10	66 %		34 %			0.44
# 11	65 %		35 %			0.81
# 12	60 %		32 %	8 %		0.41

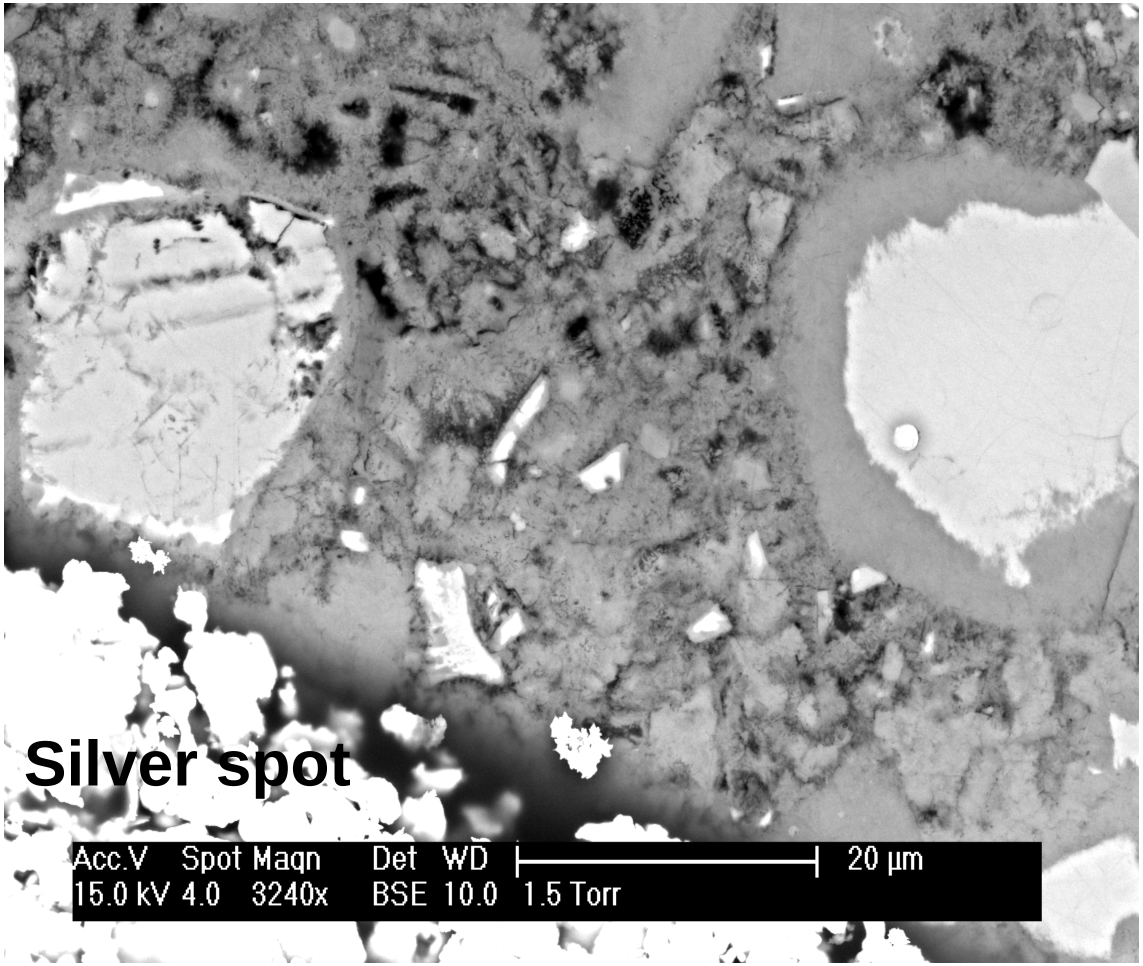
Sulfur speciation

Sulfur - References



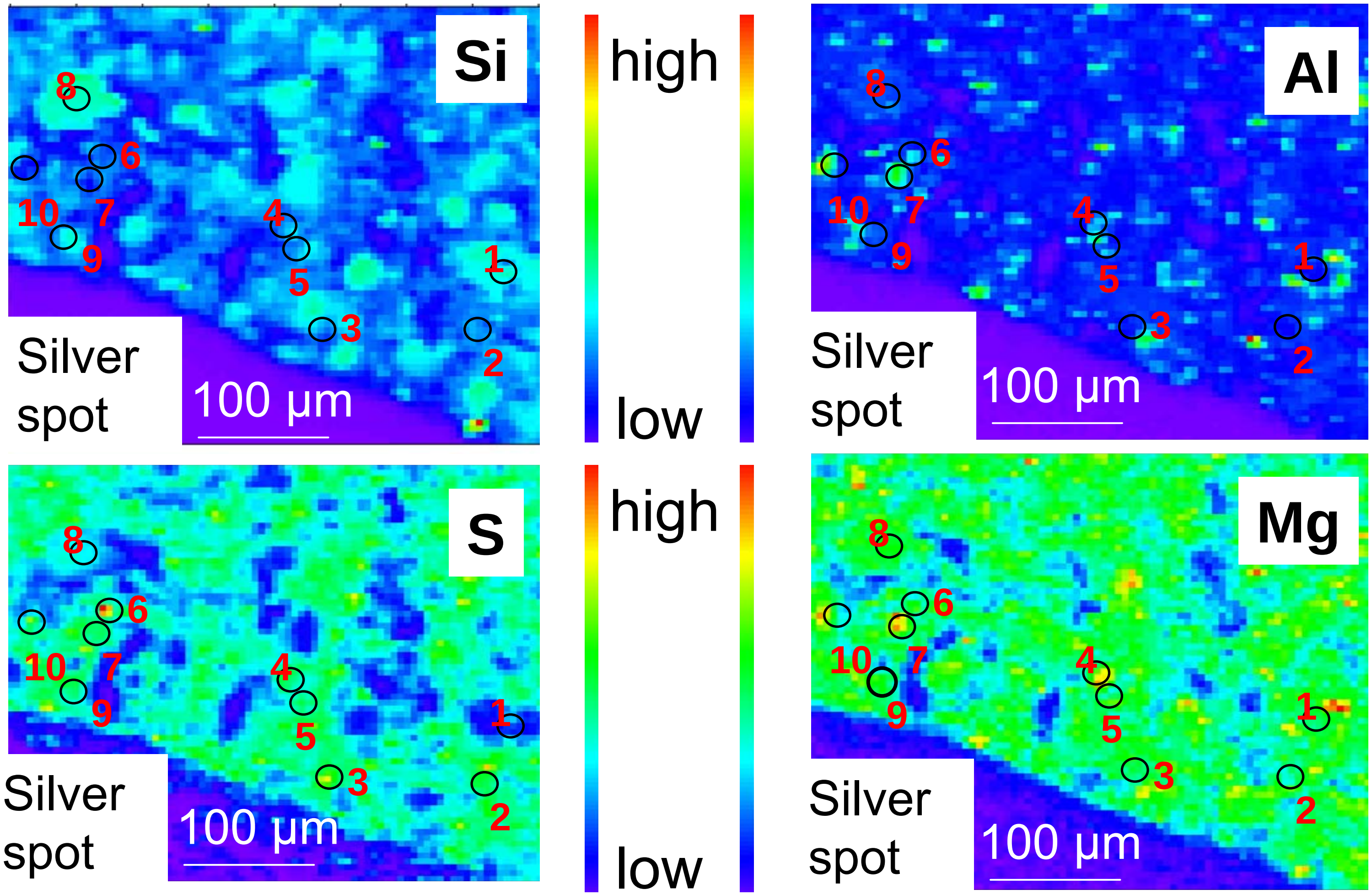
HCP Sample

HTS-50C : - HTS cement 2004 hydrated at 50° for 28 d

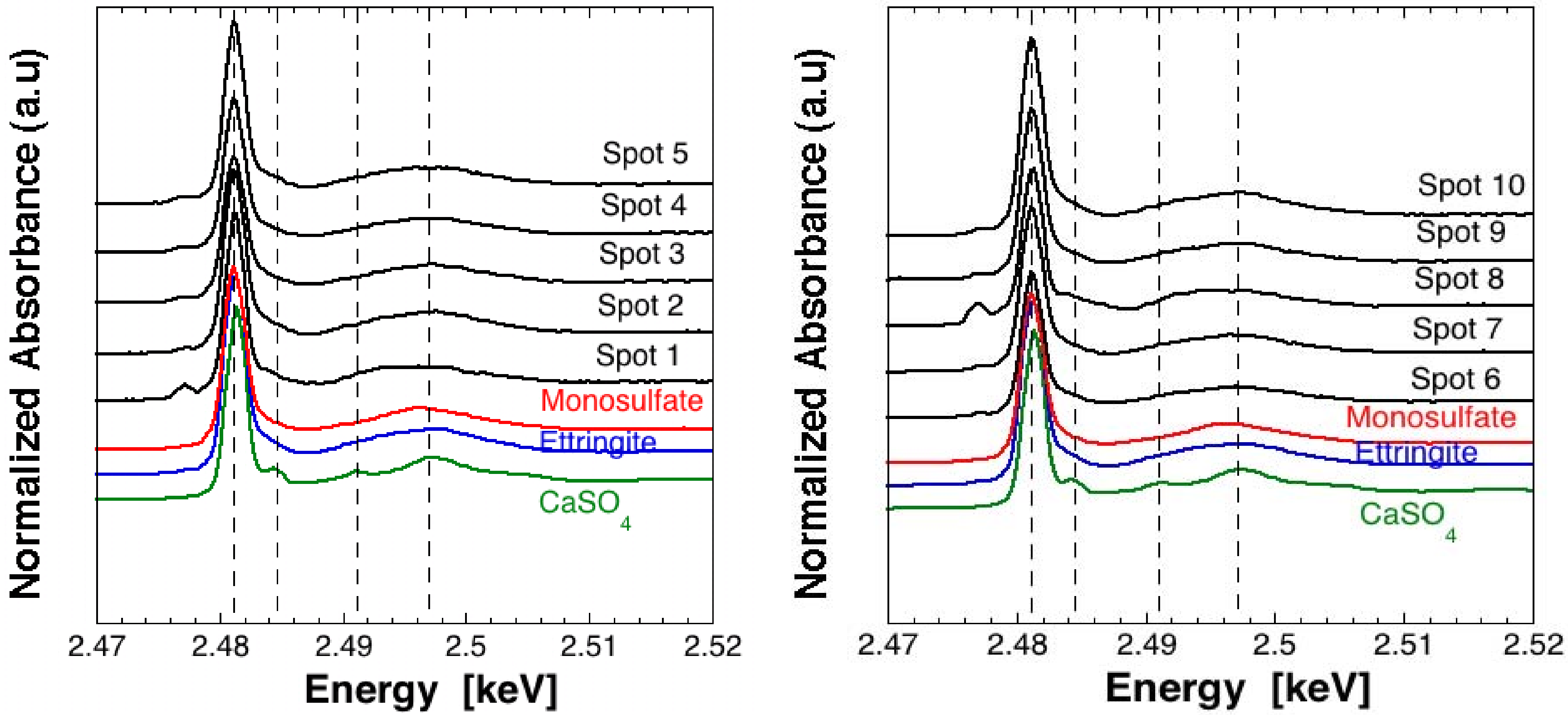


Ettringite
or
Monosulfate
Formation?

MicroXRF Maps

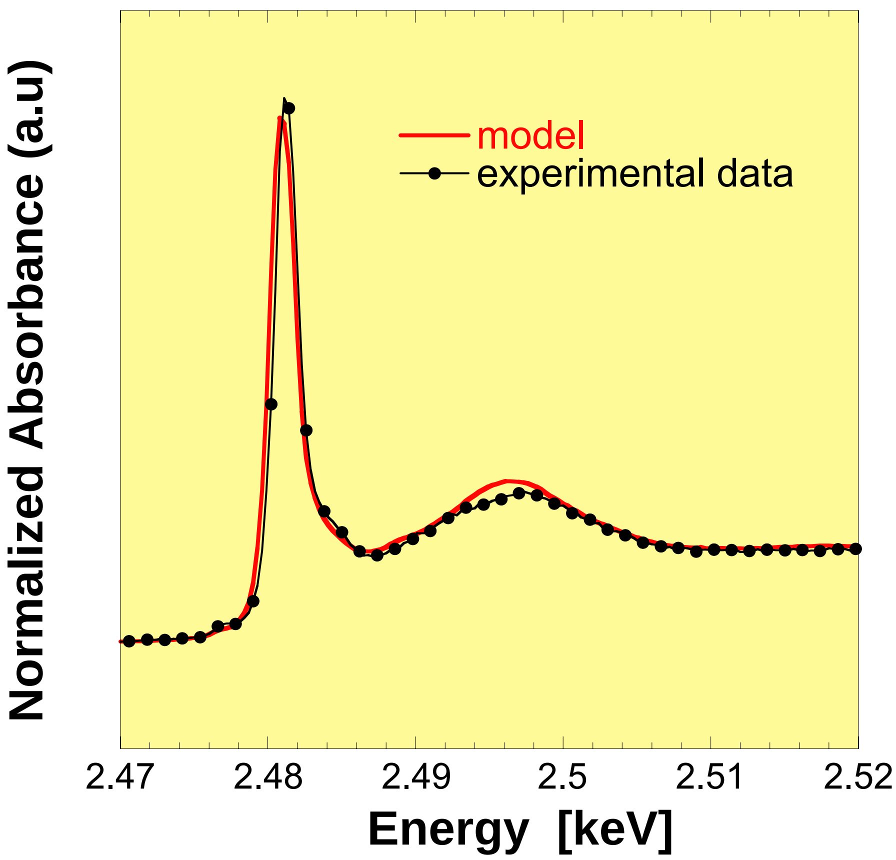


HTS 50° 28 d

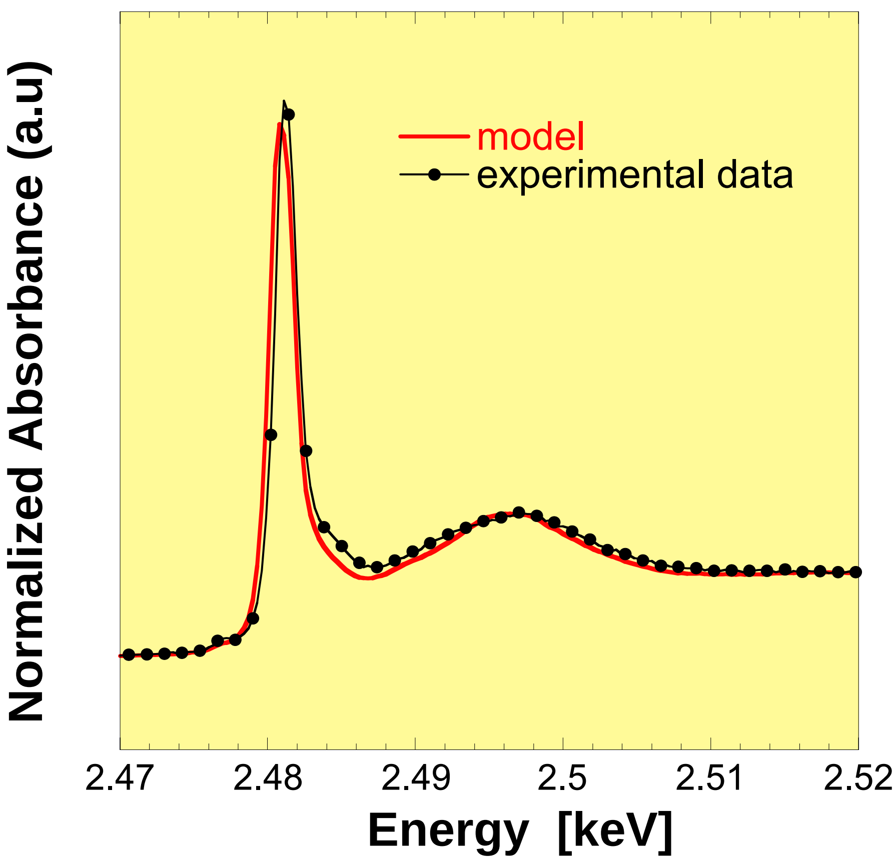

Normalized Absorbance (a.u)
Spot 5
Spot 4
Spot 3
Spot 2
Spot 1
Monosulfate
Ettringite
CaSO4
2.47
2.48
2.49
2.5
2.51
2.52
Energy [keV]
Normalized Absorbance (a.u)
Spot 10
Spot 9
Spot 8
Spot 7
Spot 6
Monosulfate
Ettringite
CaSO4
2.47
2.48
2.49
2.5
2.51
2.52
Energy [keV]

Linear combination

Spot 2 (R = 0.23)



Spot 6 (R = 0.33)



Linear Combination HTS 50°

Spot	$CaSO_4$	Ettringite	Monosulfate	Res %
# 1	32 %		68 %	0.76
# 2		38 %	62 %	0.23
# 3		14 %	86 %	0.36
# 4		24 %	76 %	0.37
# 5	16 %		84 %	0.37
# 6		39 %	61 %	0.33
# 7		33 %	67 %	0.34
# 8			100 %	1.3
# 9		38 %	62 %	0.46
# 10		35 %	65 %	0.33

Conclusions

Micro-spectroscopic approach to phase identification

- Allows cement phases to be identified with micro-scale resolution
- Requires good quality data (references, spectra from single spots) as single cement phases have to extracted from complex mixtures

Al speciation

- High content of C_3A at hot spots
- C_3A and ettringite as dominating Al species in cement paste hydrate for 28 days at 5°
- C_3A, ettringite and AFm phases present in cement paste hydrated for 28 days at 20° and 50°

S speciation

- Predominantely Ca monosulfoaluminate and some ettringite is observed in cement paste hydrated for 28 days at 50°
- Presence of Ca monosulfoaluminate consistent with thermodynamic modelling
- More sensitve with regards to distinction of ettringite and monosulfate

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Synthesis of references

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Thank you for your attention!