Chemical Imaging in Cementitious Systems

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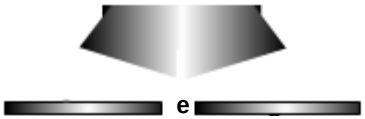
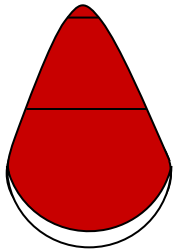
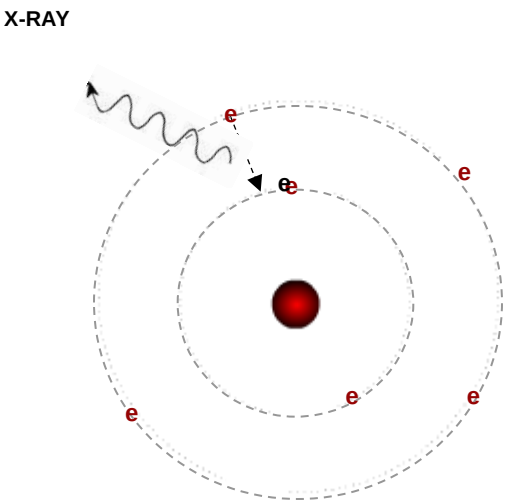
Characteristic X-rays in SEM

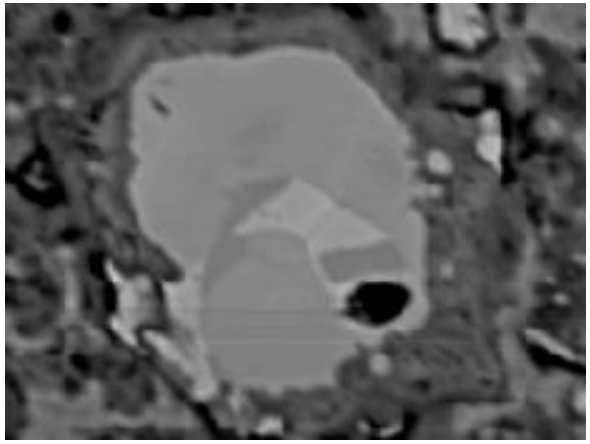




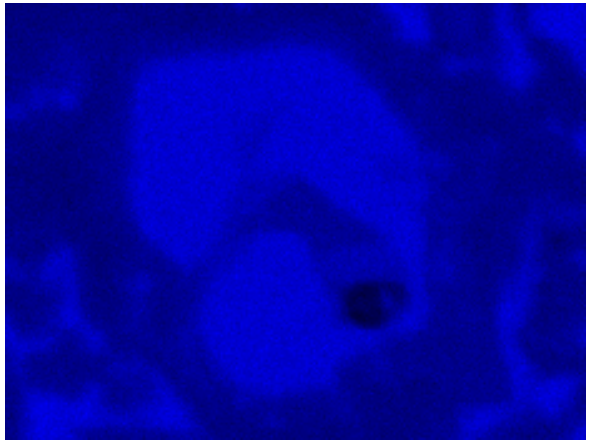


- The energy of the incident beam being high enough, some of the core electrons of the sample can be ejected.
- One electron from the upper layers will fill the resulting vacancy to decrease the atom's excitation .
- This relaxation generates a characteristic X-ray which energy corresponds to the diffrence between the level's energy of the considered electronic layers.
- This energies of these transitions are unique for each element and permit to identify them.

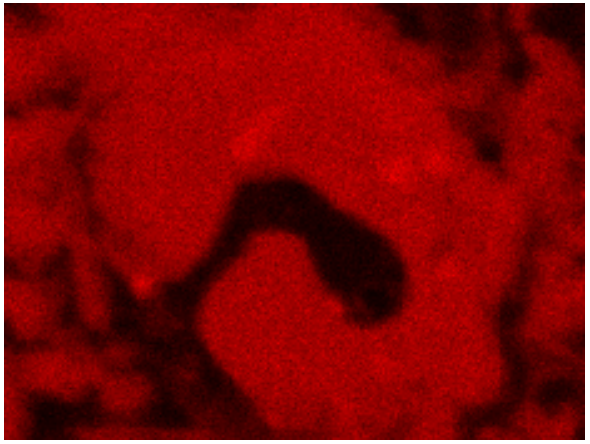
EDS chemical mapping



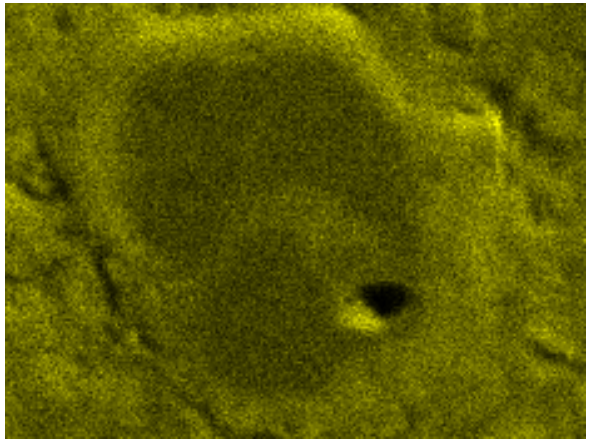
original image



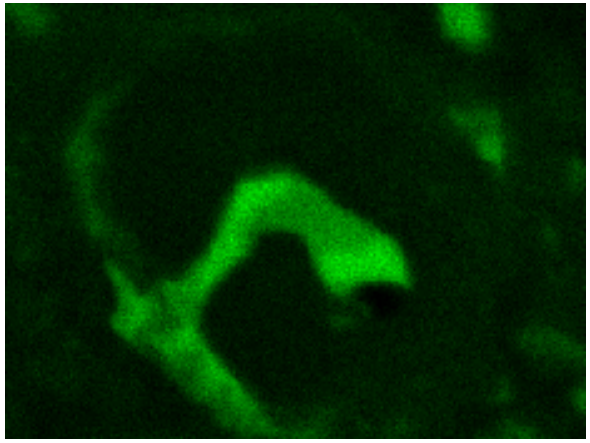
calcium mapping



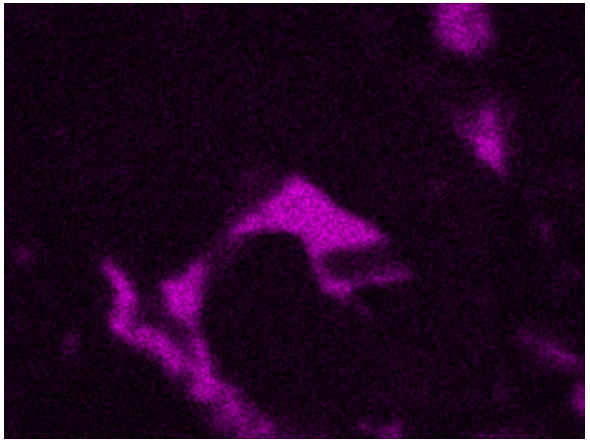
silicium mapping



oxygen image



aluminate mapping



iron mapping

New fast detector technology

- Acquisition time ~ 10X faster
- How to go beyond pretty pictures how to quantify:
  - Characterisation of Fly ashes – Thesis **Pawel Durdzinski**
    - CCR 73, 111-122 2015
    - CCR 78, 263-272 2015
  - Quantification of C-S-H composition – Thesis **John Rossen**
    - Submitted to Materials Characterisation

CHARACTERISATION OF FLY ASH

SCMs: most promising route to reducing CO_2 emissions

Very efficient solution: Less clinker in cement

+

Supplementary cementitious materials (SCM)


Limestone


Fly ash


Slag


Natural pozzolan

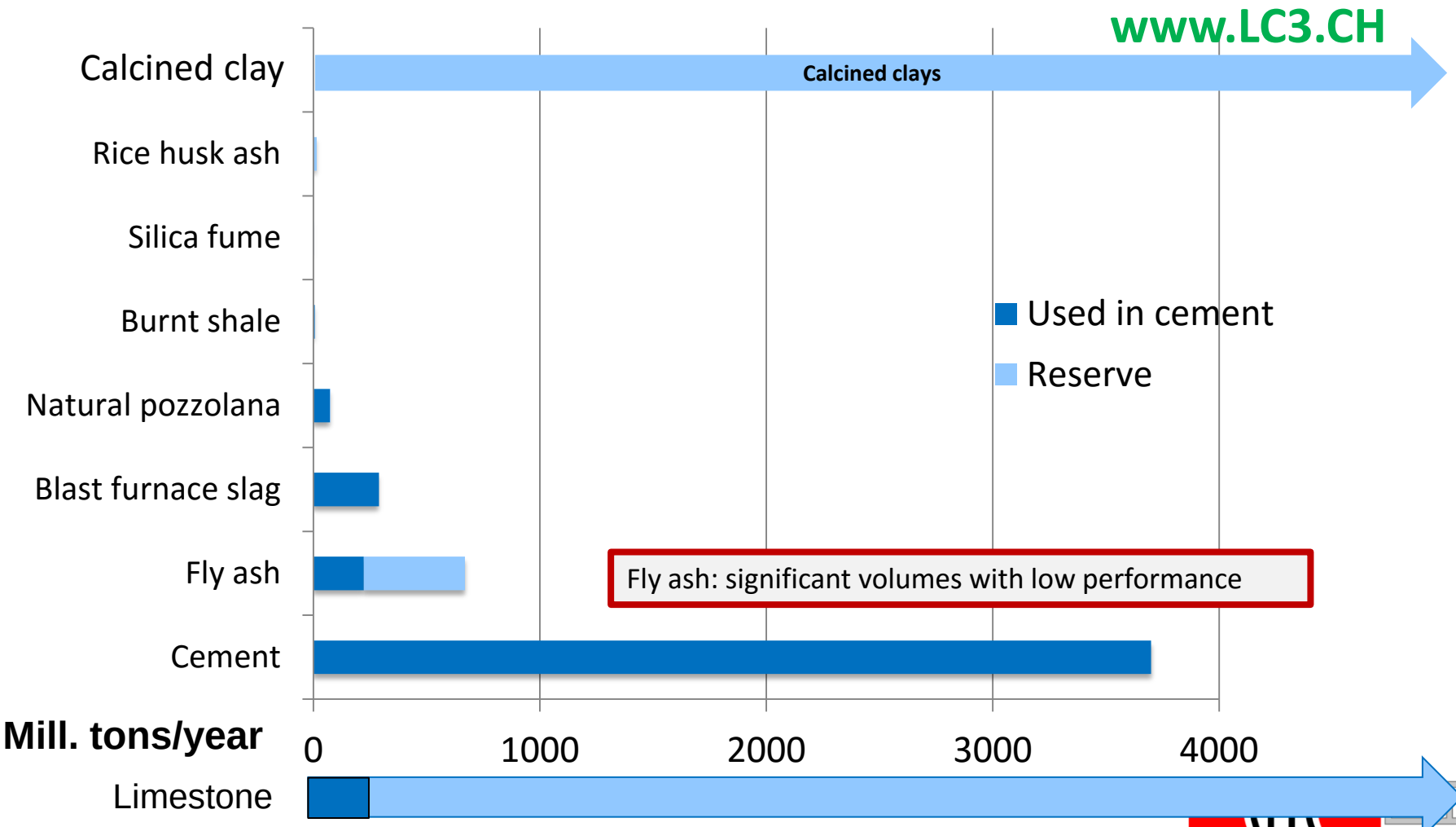

Calcined clay

Often by-products or wastes from other industries

Local availability very important!

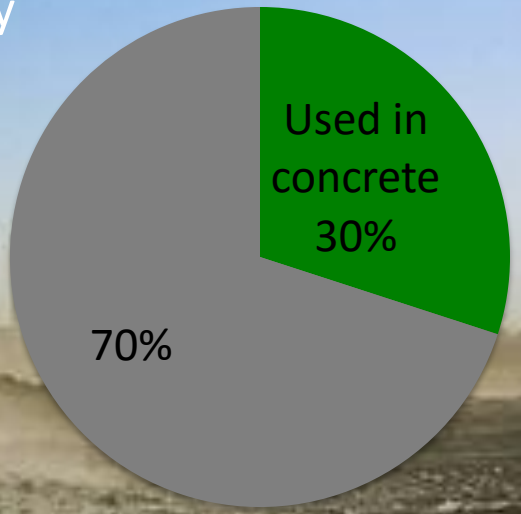
But supplies limited

Figures from ~2013



What does this mean for fly ash use?

- Production around 200 000 000 ton each year
- Limited use due to heterogeneity and variability

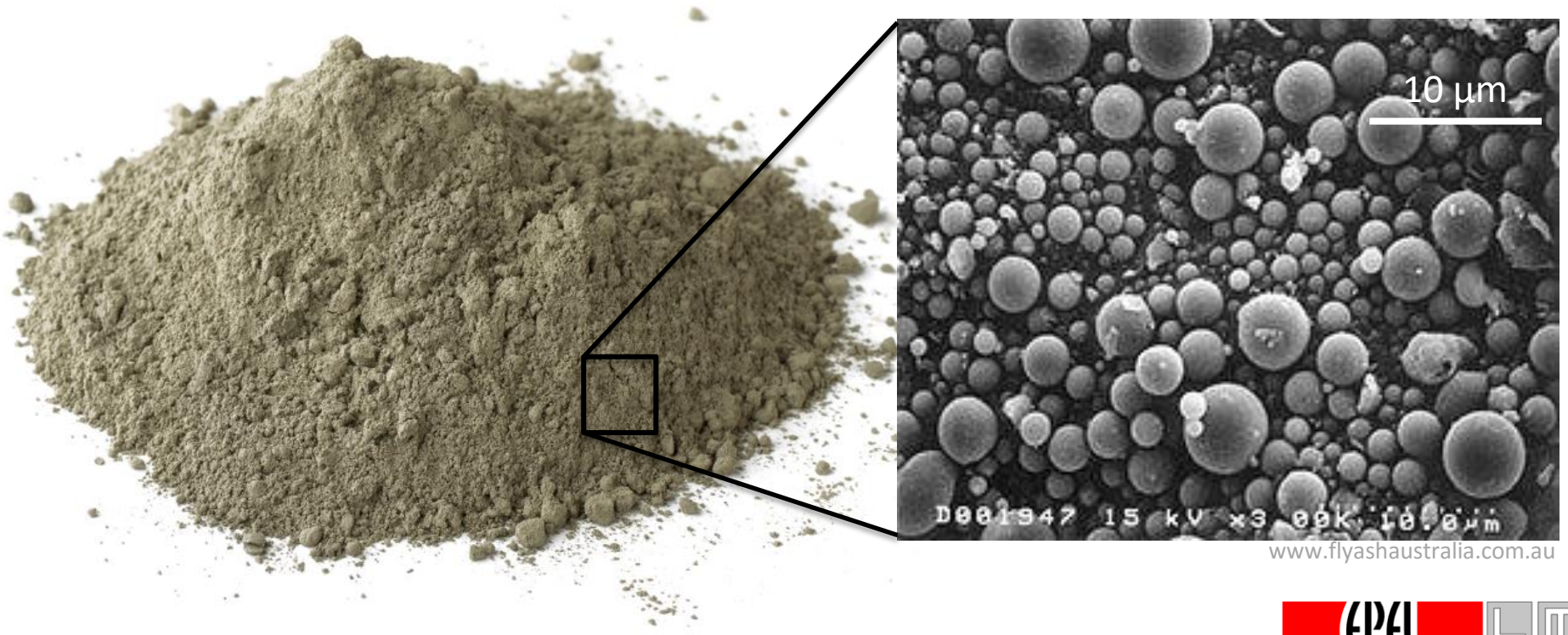


If 10% more of fly ashes can be used due to better qualification

18 000 000 ton/year less of ash landfilled

Fly ash

- By-product of coal combustion
  - Inorganic matter melts and solidifies as **glass** -> spherical particles
  - Crystalline phases: original and formed during cooling
  - Each burning particle - a single reactor -> heterogeneity



www.flyashaustralia.com.au

Current characterization techniques

Bulk chemical composition

X-Ray Fluorescence

Nutrition Facts

Serving Size 1 serving (55.9 g)

Amount per Serving	
Calories 99	Calories from Fat 34
	% Daily Value*
Total Fat 3.8g	**6%**
Saturated Fat 1.1g	**6%**
Omega-3 230mg	
Omega-6 190mg	
Trans Fat 0.0g	
Sodium 102mg	**4%**
Total Carbohydrates 16.5g	**5%**
Dietary Fiber 2.5g	**10%**
Sugars 10.2g	
Protein 3.5g	
Vitamin A 0%	Vitamin C 3%
Calcium 2%	Iron 12%

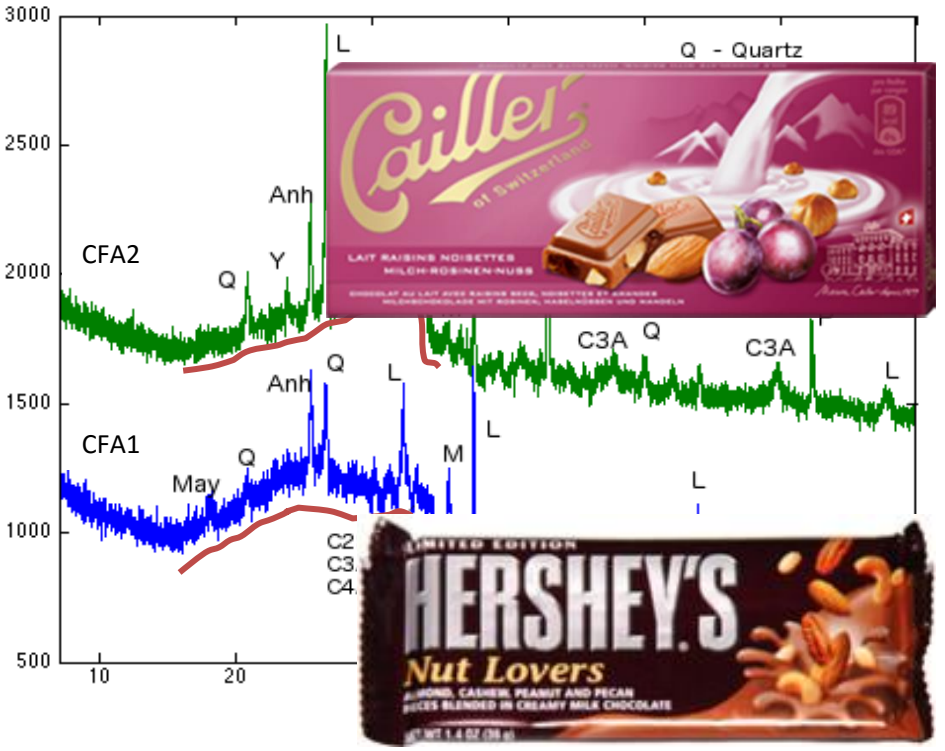
* Based on a 2000 calorie diet

others
CaO
SiO2
Al2O3

Two Ca-rich fly ashes used here seem similar

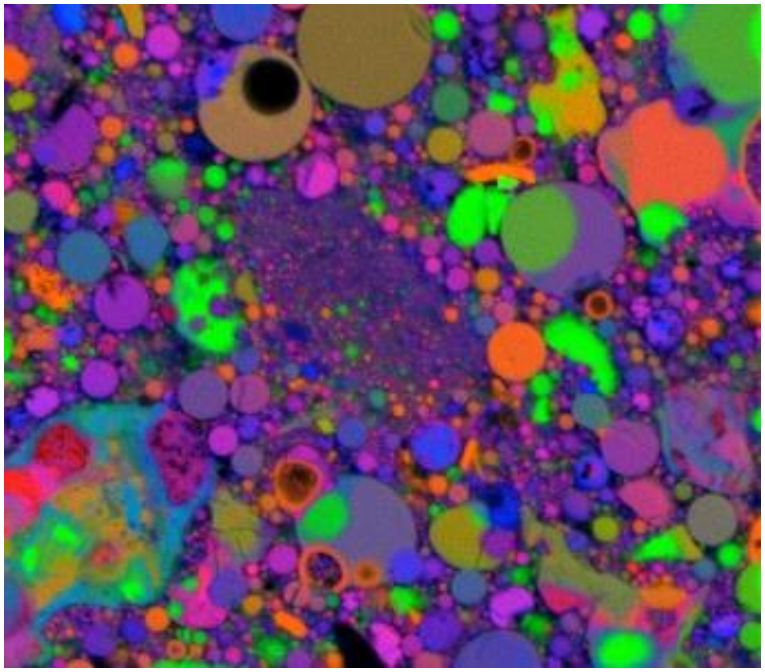
Phase composition

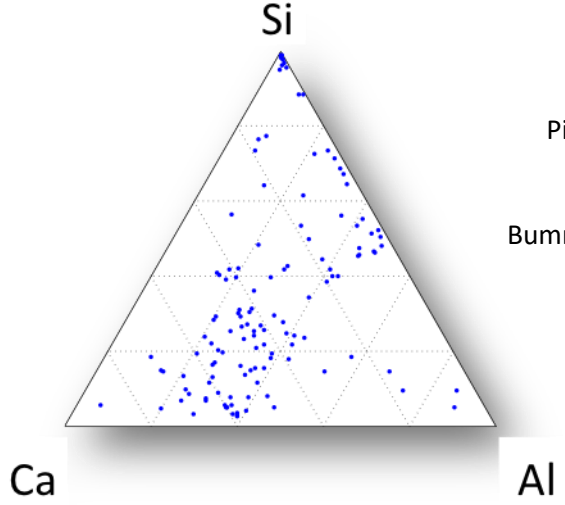
X-Ray Diffraction + Rietveld refinement



Crystalline phases. What about glass?

Scanning electron microscopy

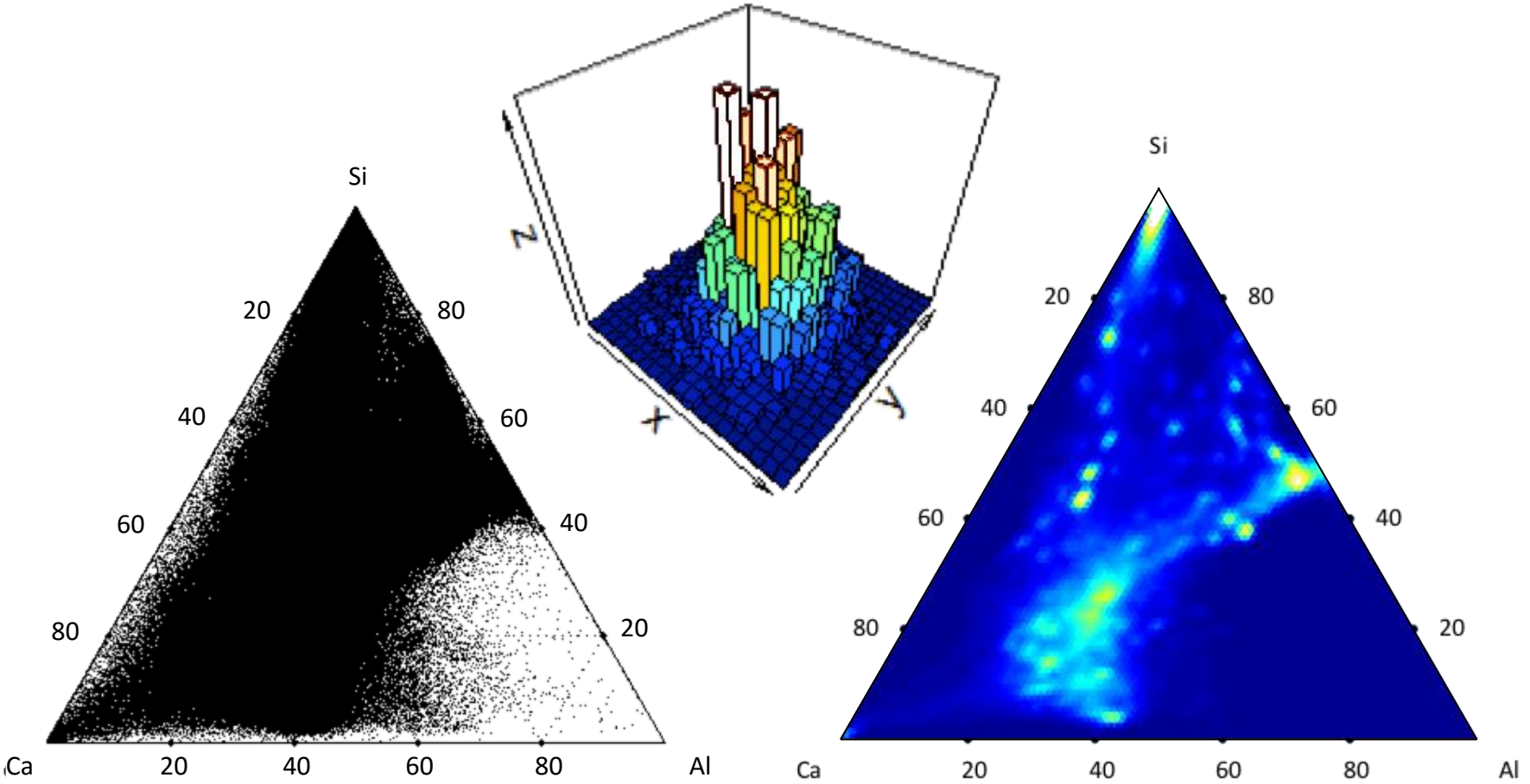




- EDS - full chemical information
- Heterogeneity → Scatter!
- Not enough information
- New detectors: mapping possible - more data

Stevenson et al., CCR 1984
Pietersen, Thesis TU Delft 1993
Kutchko and Kim, Fuel 2006
Johnson et al., Fuel 2010
Bumrongjaroen et al., WOCA 2011
Dhole et al., ACI Mater J 2013
…

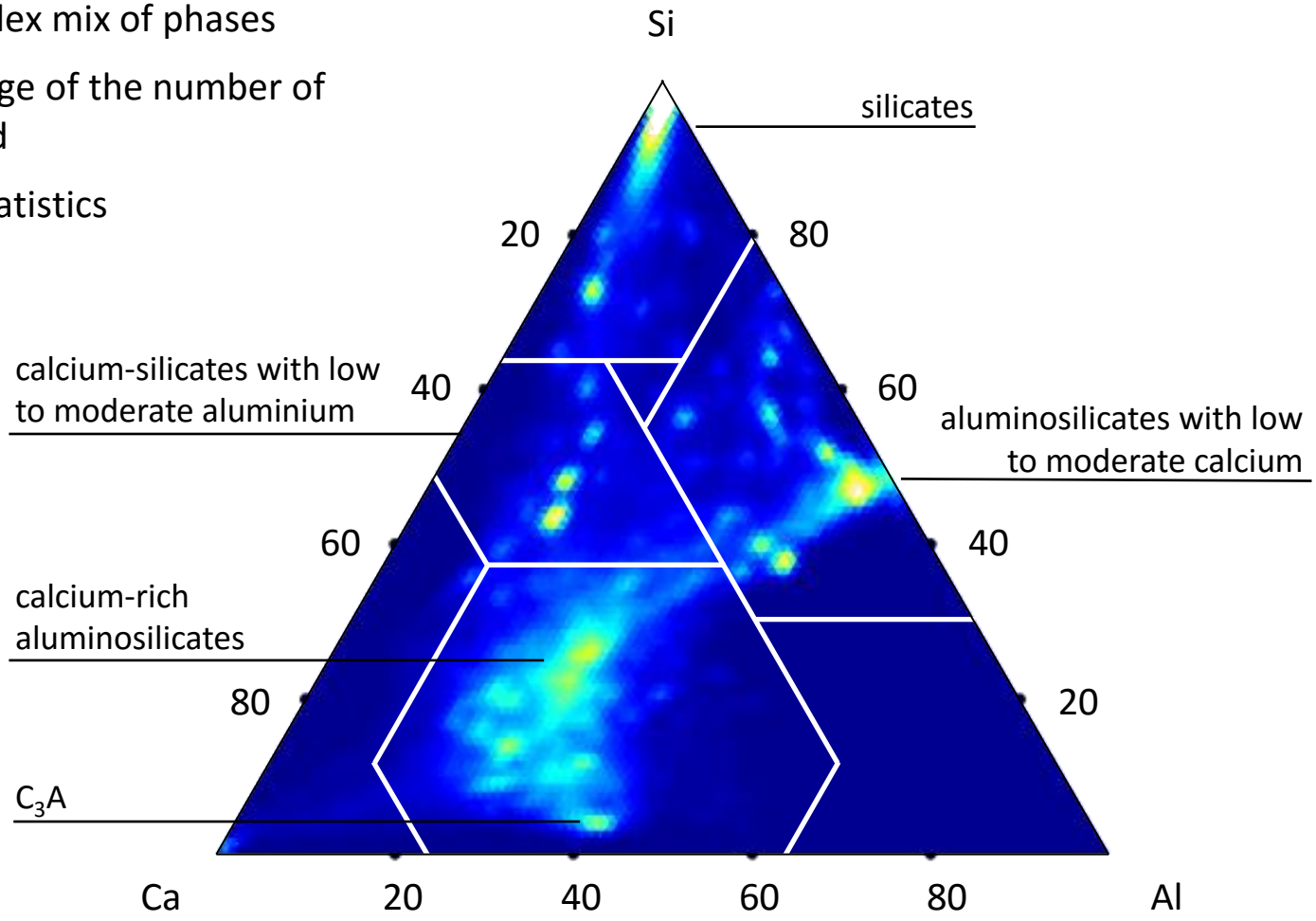
How to treat large scattered data sets?



Al-Si-Ca ternary plot → Al-Si-Ca ternary frequency plot

Detailed chemical composition of fly ash

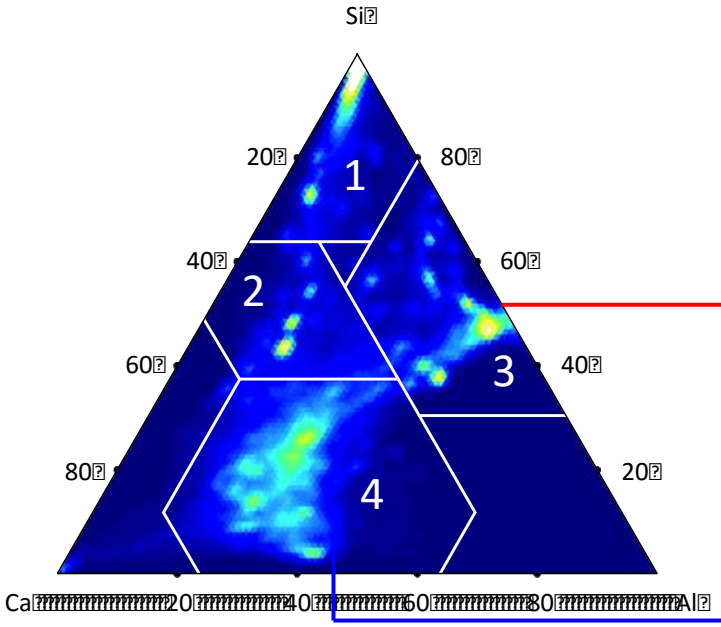
- Quick, visual and intuitive
- Insight into complex mix of phases
- No prior knowledge of the number of phases is required
- No “black box” statistics



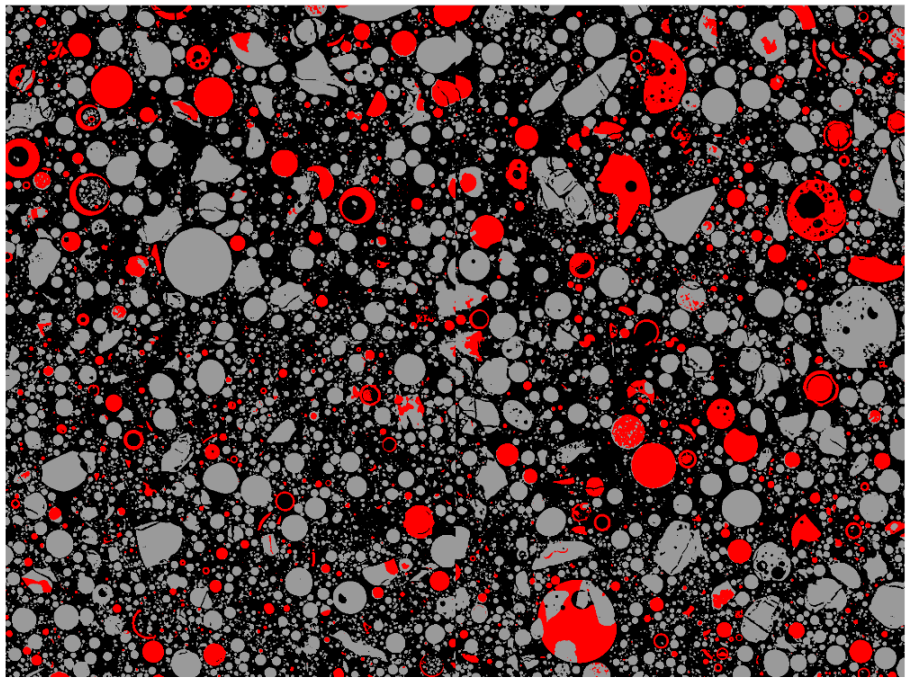
Durdziński et al., Cement and Concrete Research 73 (2015) 111-122

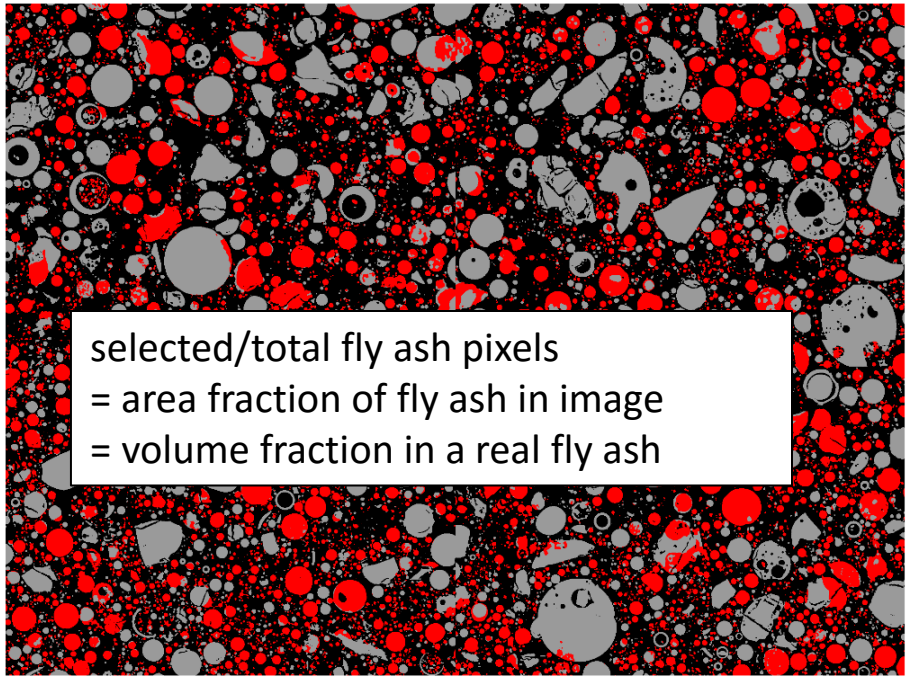
Detailed analysis

- Chemical composition and morphology of the identified populations

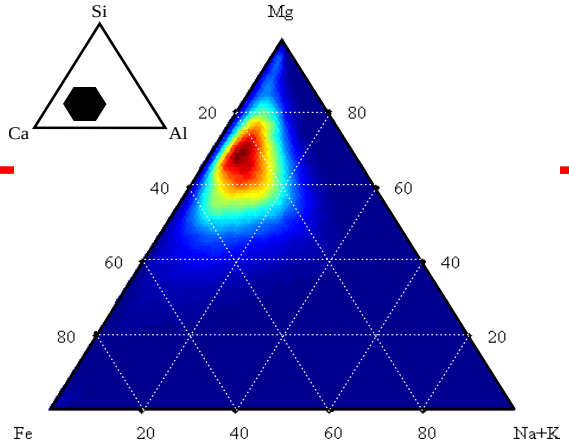


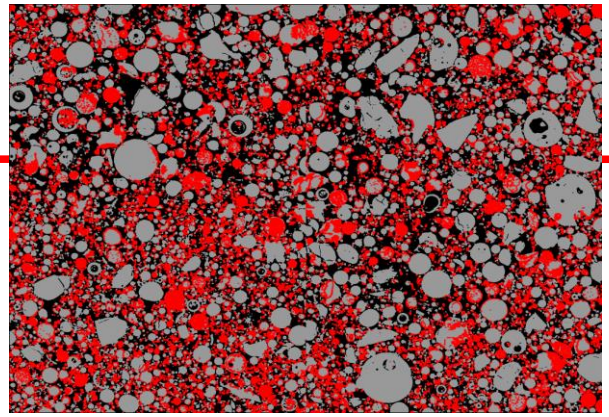
	1	2	3	4
Al	0.8	5.9	12.7	9.7
Si	30.1	15.0	15.7	7.1
Ca	1.2	11.3	3.5	16.6
Na+K	1.4	2.0	5.3	0.7
Mg	0.4	3.7	1.3	4.7
Fe	0.3	1.3	0.7	2.0
O and trace el.	65.8	60.8	60.8	59.1

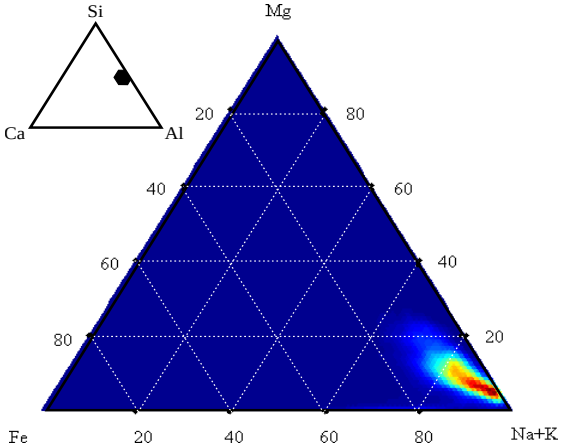


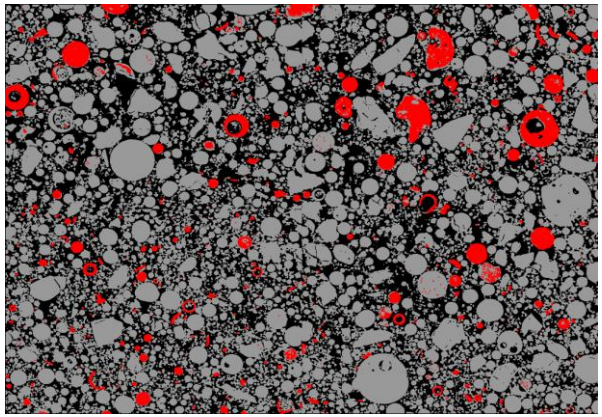


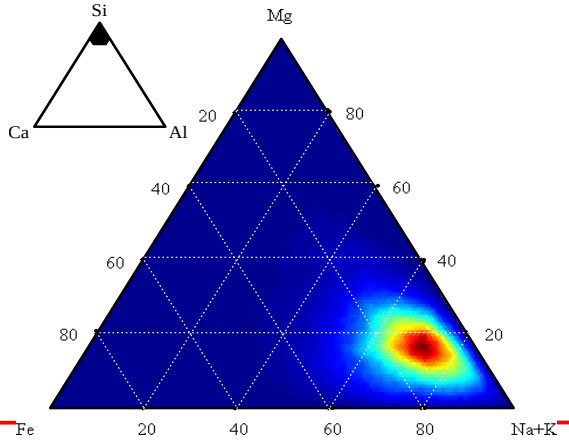
selected/total fly ash pixels
= area fraction of fly ash in image
= volume fraction in a real fly ash

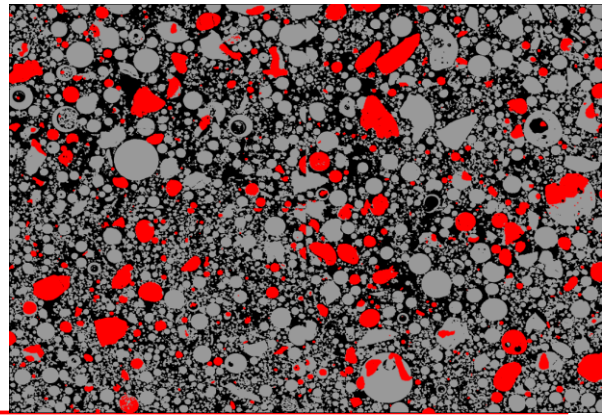




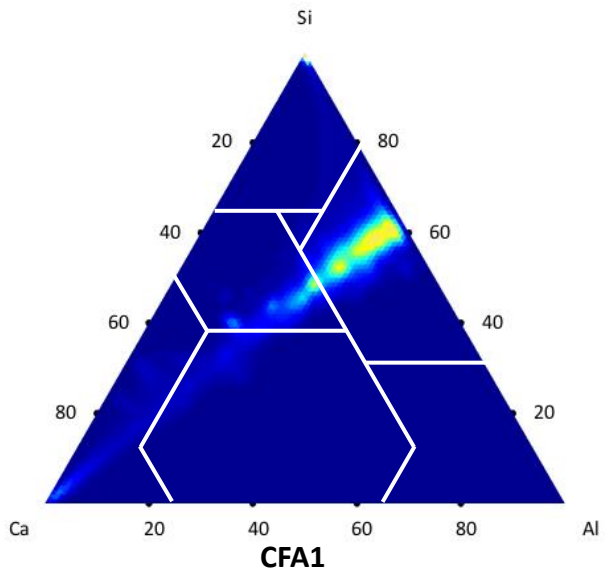




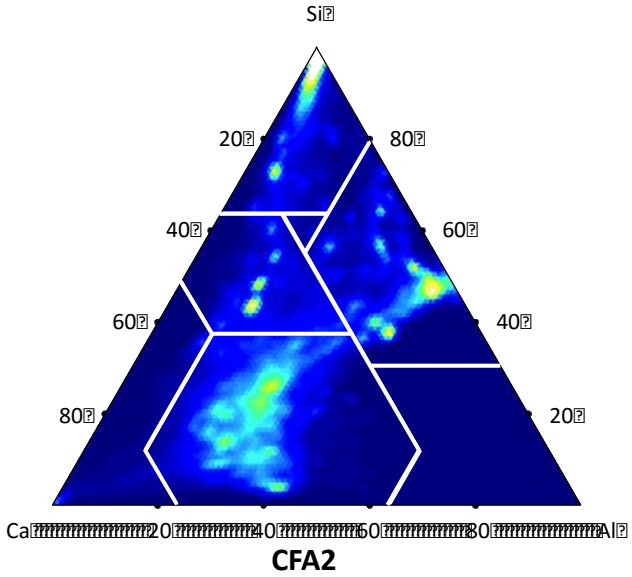




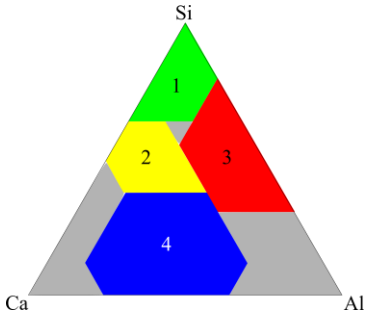
Quantification and comparison of fly ashes

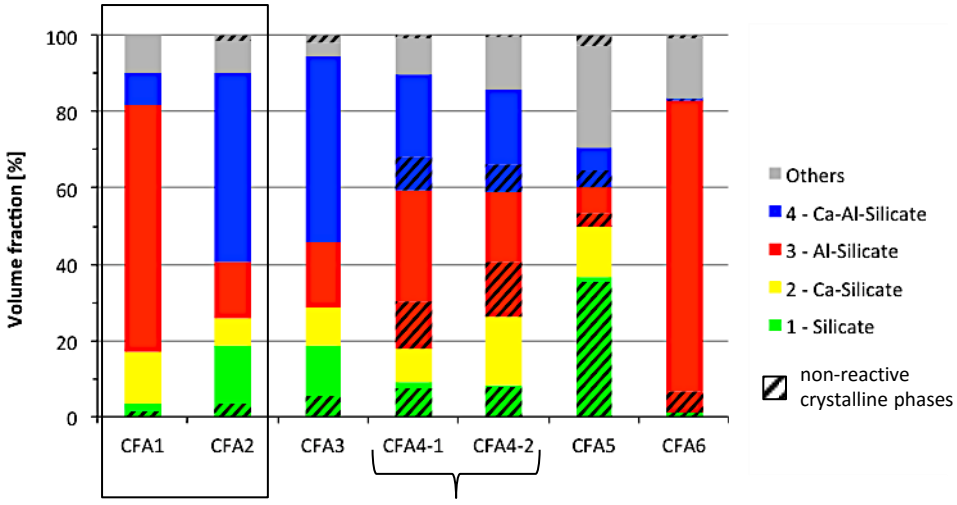


CFA1



CFA2





different batches from the same plant

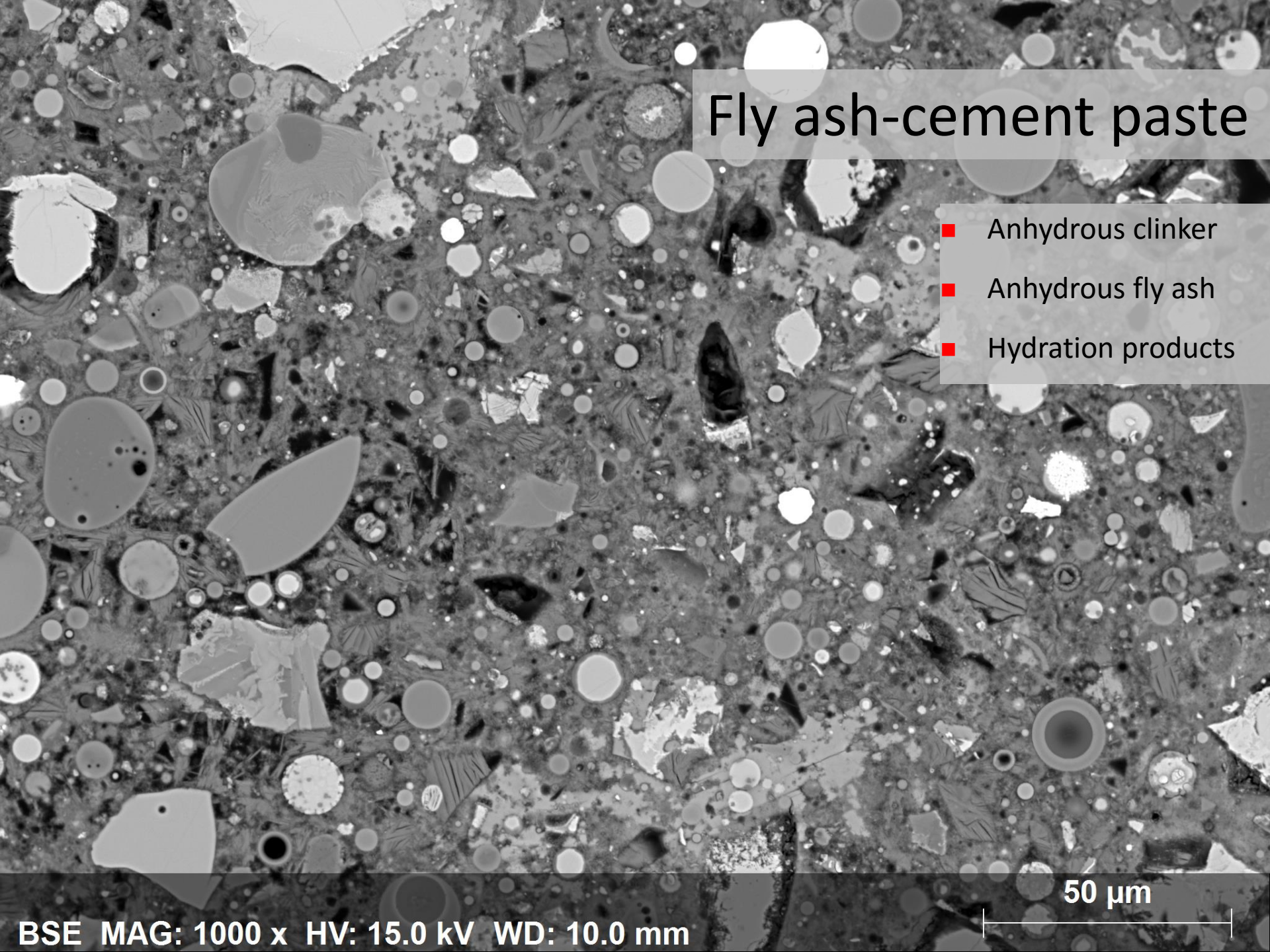
Other fly ashes for comparison

Very different phase composition CFA1 and CFA2

How does that impact the reaction?

Calcareous fly ash

REACTIVITY


Fly ash-cement paste
Anhydrous clinker
Anhydrous fly ash
Hydration products
50 µm
BSE MAG: 1000 x HV: 15.0 kV WD: 10.0 mm

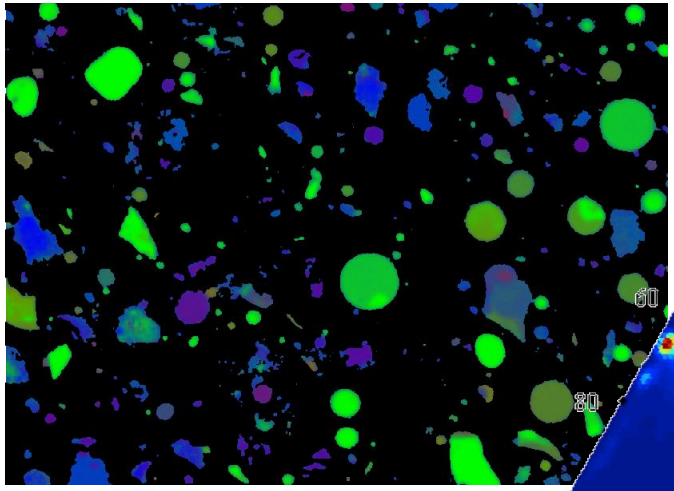
How much of the fly ash has reacted?

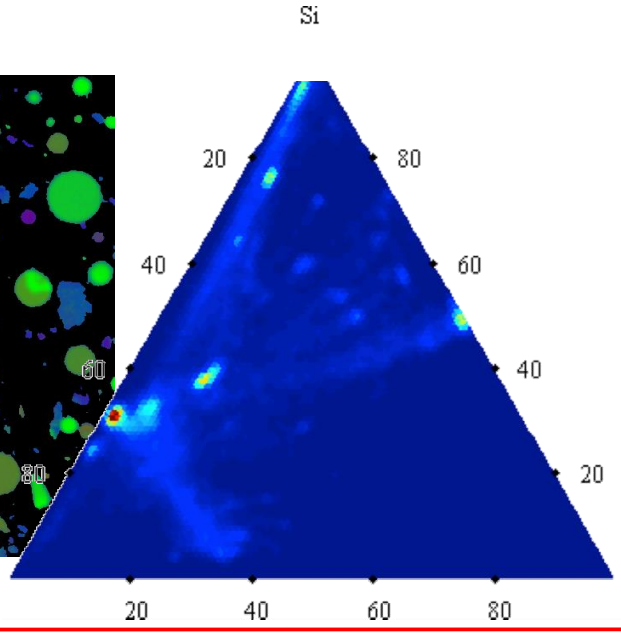
- Fly ash due to heterogeneity is probably the most difficult SCM to quantify
- Currently available techniques:
  - mostly fail
  - treat fly ash as a unique phase

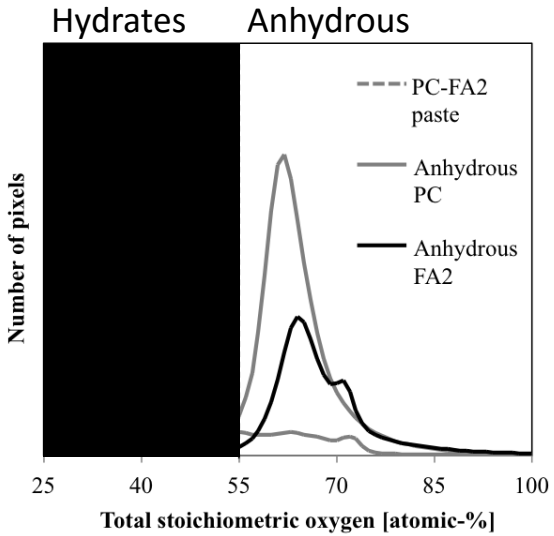
Hydrated fly ash-cement pastes

- Remove **interference from hydration products** - they contain water, which EDS does not measure
- Extract fly ash populations by the same Al-Si-Ca thresholds as for raw fly ash

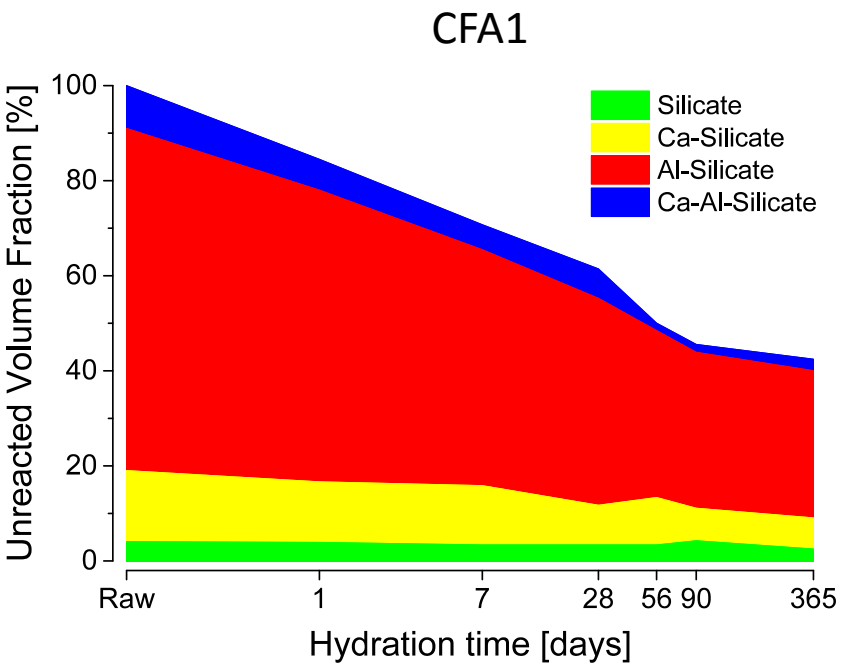
hydrates contain water → quantified total is lower → assume oxides → calculate oxygen → sum for all elements → histogram threshold → use as mask

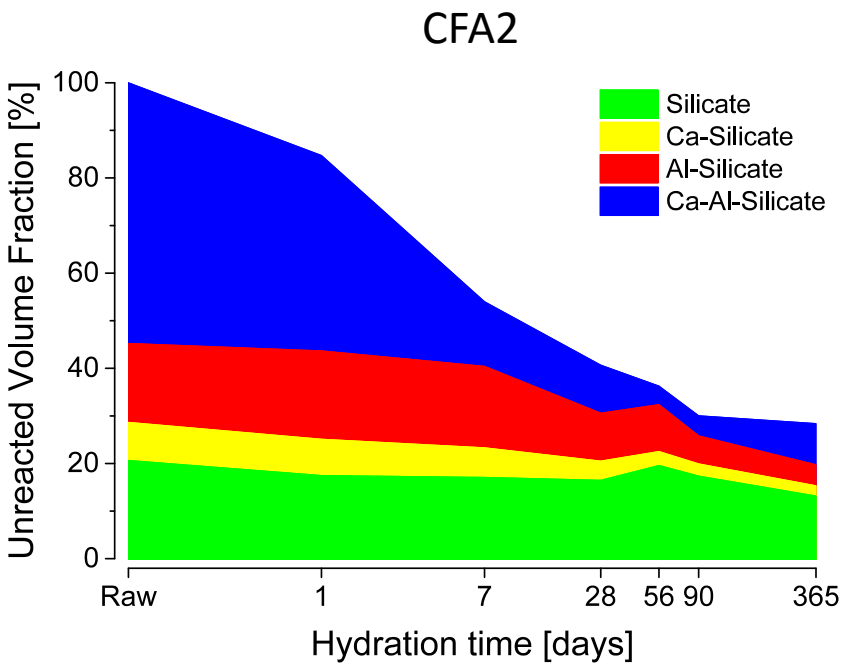






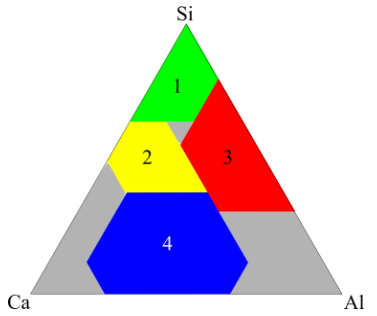
Consumption of fly ash populations in paste





The presented technique can track the reaction of individual fly ash components in cement paste.

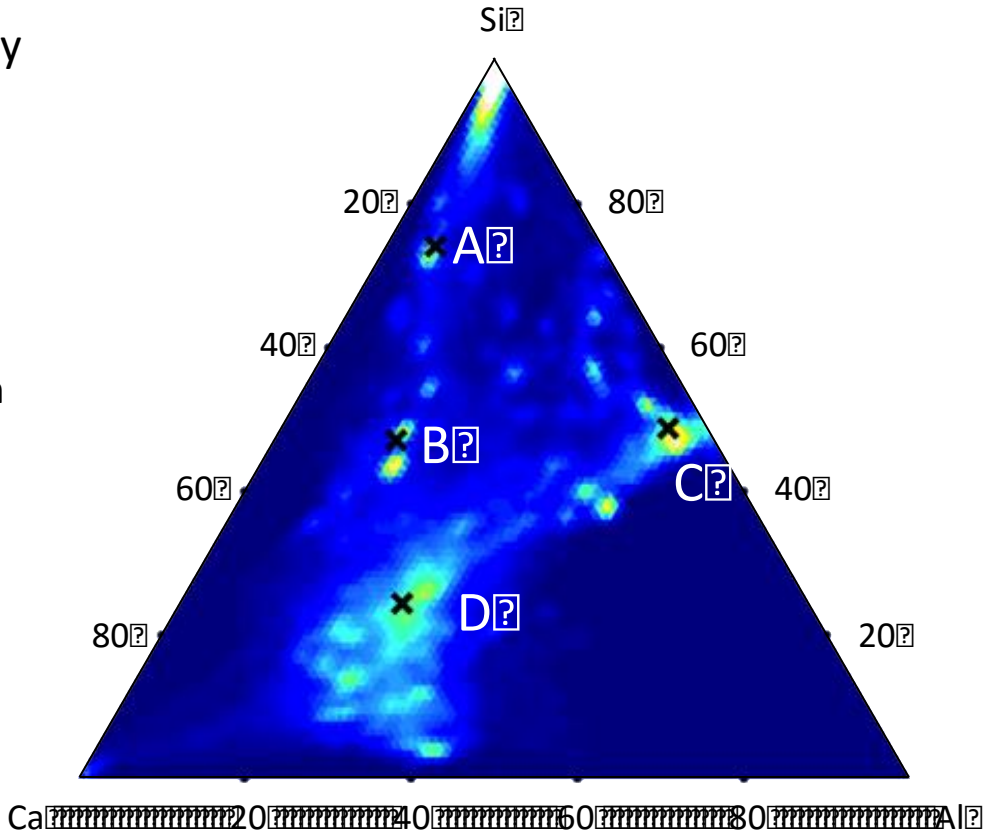
Important differences in reactivity of different glasses…
…why?



Model glasses

- Detailed analysis of fly ash reactivity

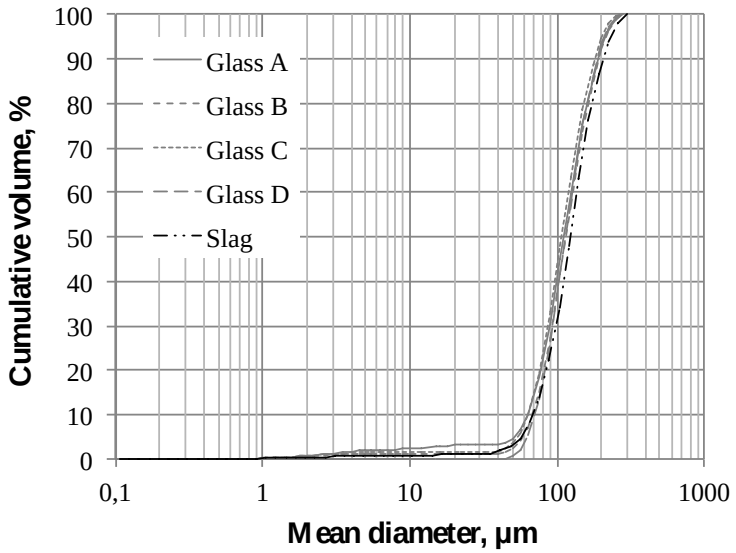
- 4 model glasses synthesized
  - Ca-Mg-Na-Alumino-Silicate
  - corresponding to those identified in **CFA2**



Processing of the glasses

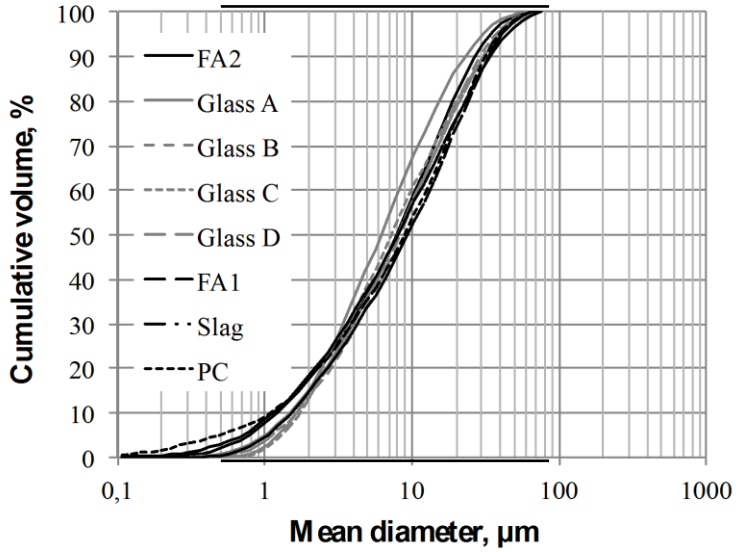
Dissolution experiment

- coarse grains - for a slower release of ions into solution



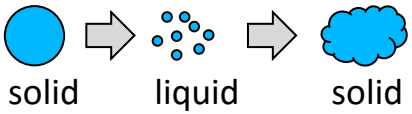
Hydration study in cement paste

- target the grain size distribution of the simulated fly ash CFA2



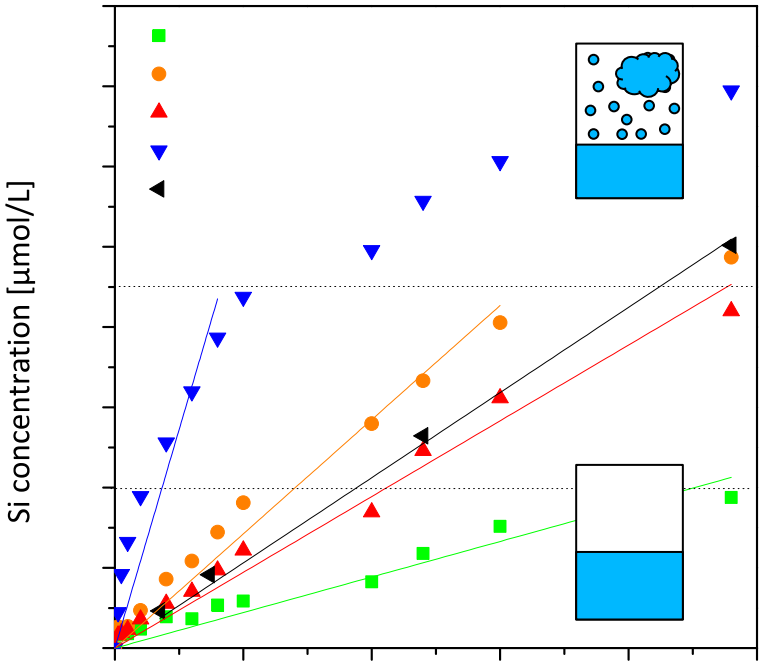
Dissolution experiment

Reaction in cement: **dissolution** + precipitation



Here a simplified system to look at the **dissolution** rate

- 250 mL NaOH pH 13 + 0.25 g glass at 20 °C
- measure the release of Si into the solution



Deceleration of the dissolution

- likely due to ions accumulating in solution - lower undersaturation
- precipitation may have removed Si from solution

Important difference between the glasses

Initial dissolution rates

- Normalized to Si content in glass
- Normalized to the specific surface area

Glass	A	B	C	D	Slag
Log dissolution rate [mol/m^2/s]	:8.17	:7.45	:7.57	:6.22	:7.25

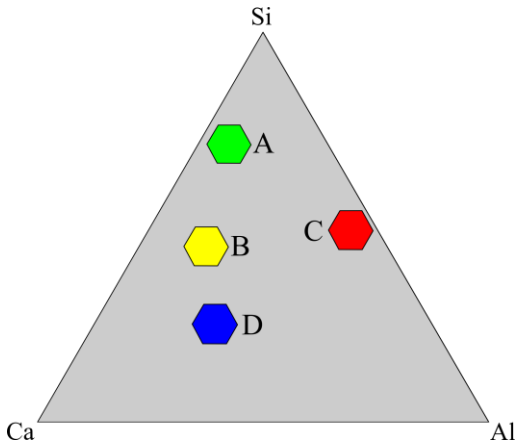
- Fly ash glasses may react at very different rates
  - The **maximum dissolution rate** seems related to the glass chemical composition
  - The **actual rate** will depend on other factors, notably the solution composition.

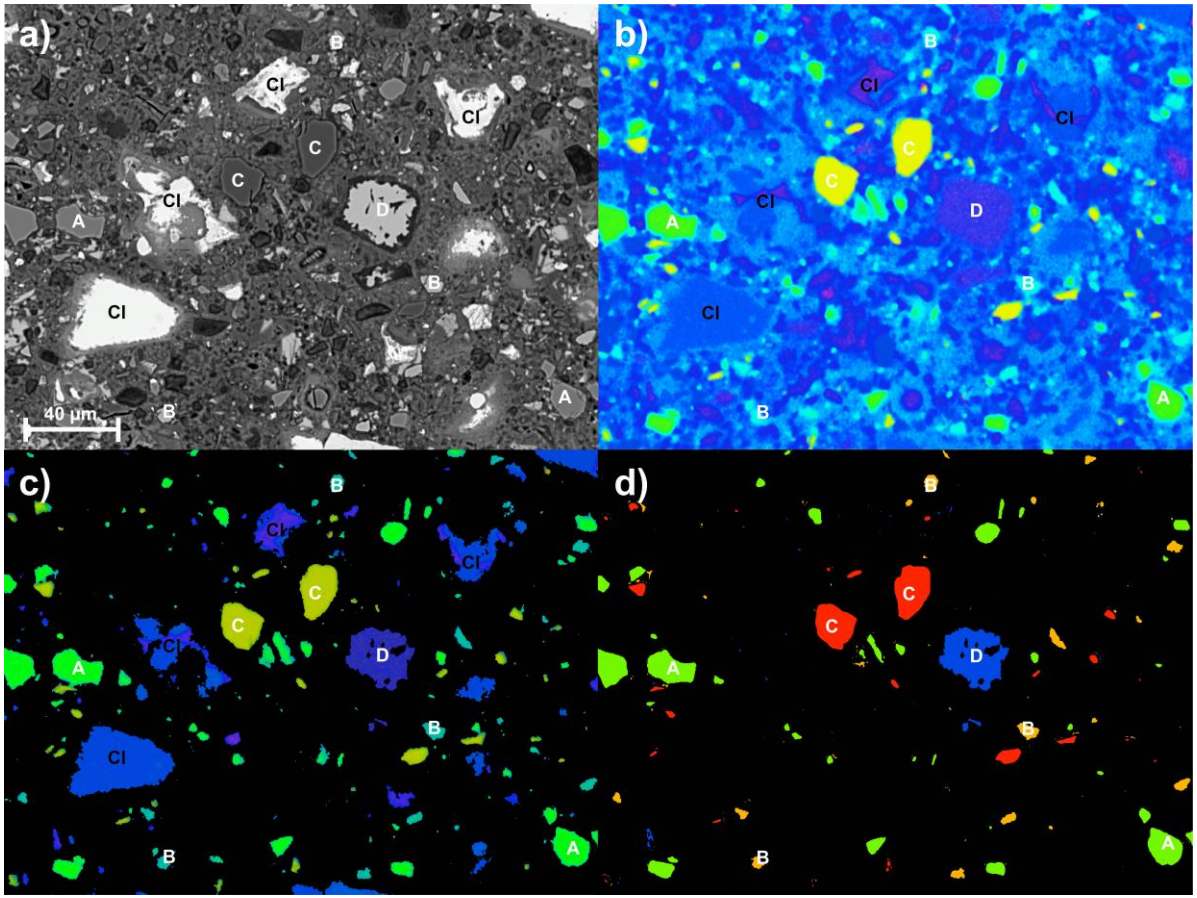
Glass-cement paste

55 wt.% PC + 45 wt.% glass:

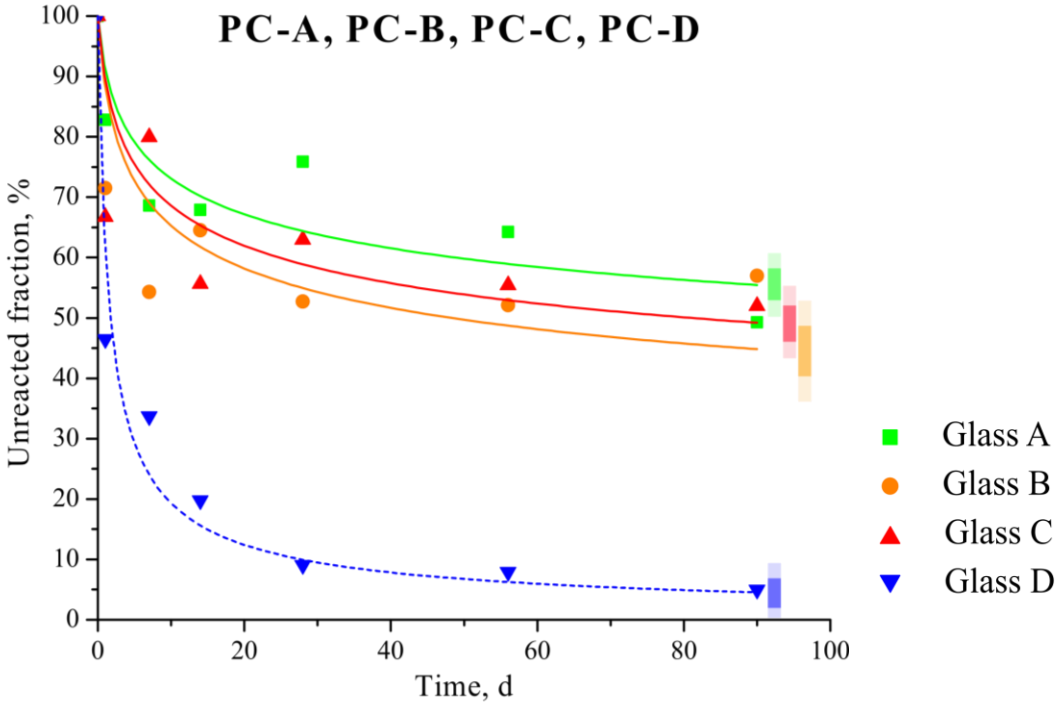
- A, B, C, D individually
- A+B+C+D = simulated CFA2
  (22% + 12% + 20% + 46%)

SEM-EDS image analysis used to track the reaction of the glasses





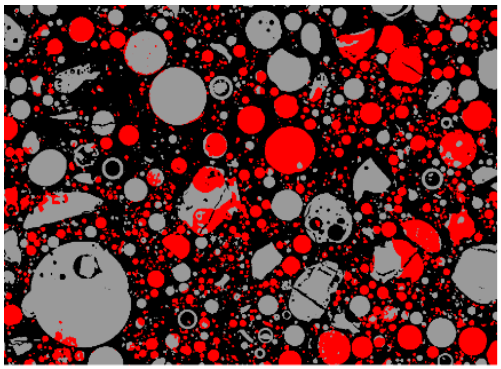
Glass-cement paste



intrinsic reactivity index

$$\frac{V}{V_0} = (1+t)^{-\kappa \frac{S}{V}}$$

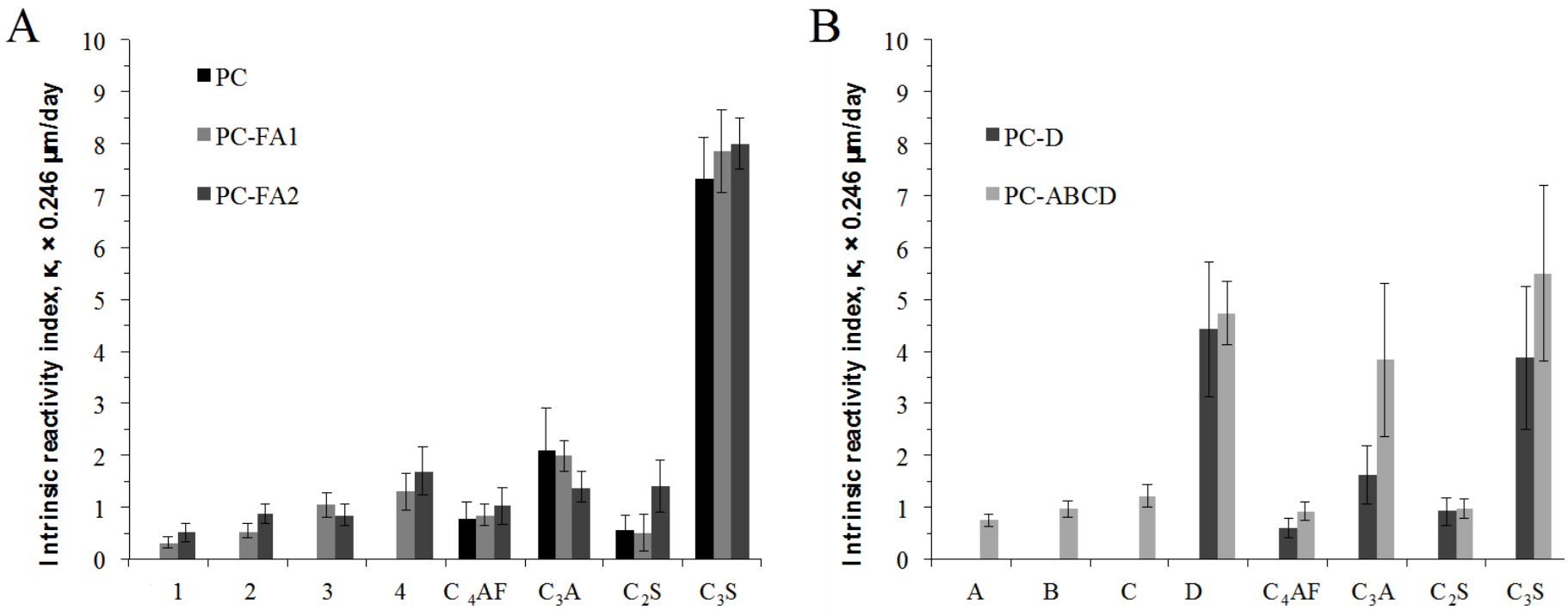
Surface/Volume effect of fineness



- Trends correspond to those measured in solution
- And to those of the populations in CFA2

Intrinsic reactivity index

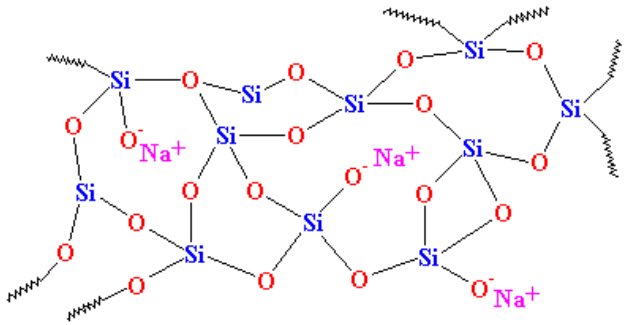
- Quantitative comparison of the reactivity of different cement components



Can we understand further what is behind glass reactivity?

Glass structure

- Glass chemical composition ➔ structure disorder ➔ intrinsic reactivity

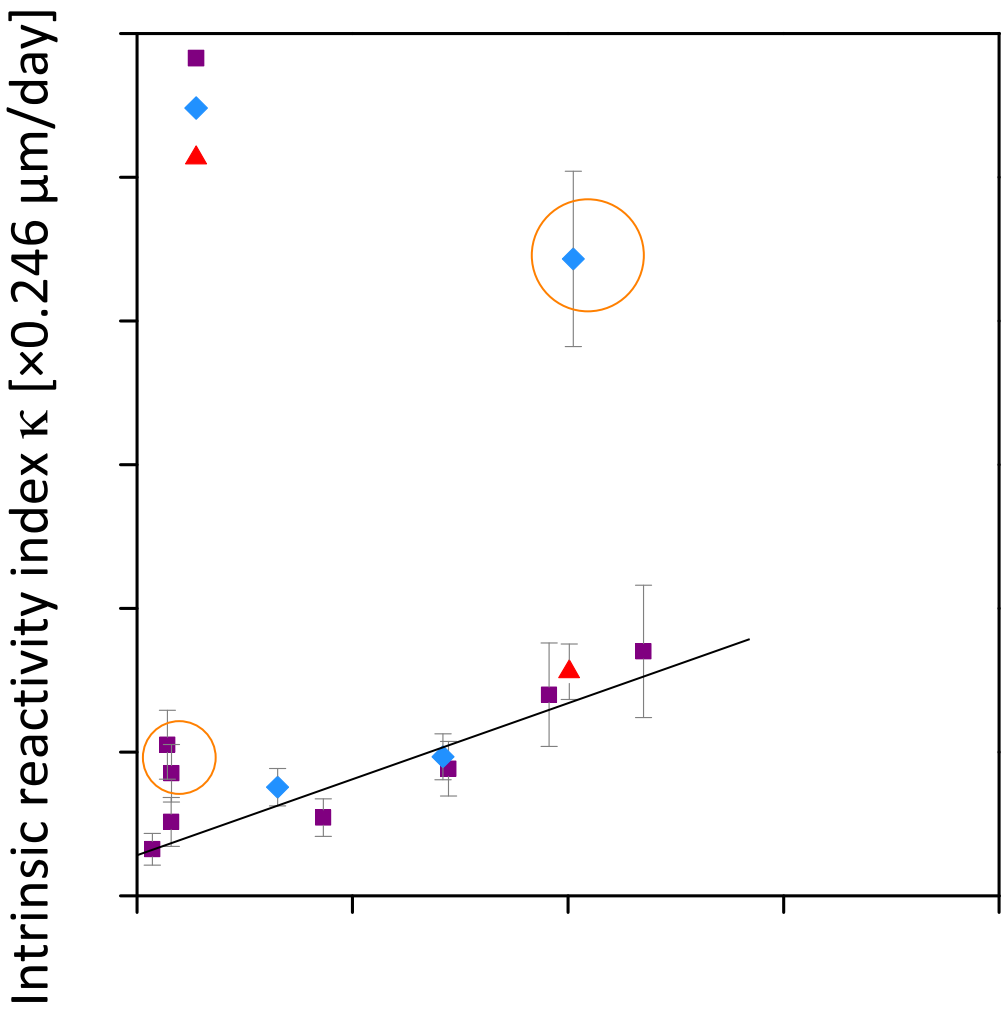


- NBO/T - ratio of non-bridging oxygens and tetrahedral ions
  - Na, K, Ca, Mg, Fe, Ti - modifiers - break the structure - create NBO
  - Si, Al - glass formers (T)

complete polymerization $0 < NBO/T < 4$ complete depolymerization

$$\frac{NBO}{T} = \frac{2(x_{CaO}+x_{MgO}+x_{Na_2O}+x_{K_2O}+x_{FeO}+2x_{TiO_2}-x_{Al_2O_3})}{x_{SiO_2}+2x_{Al_2O_3}}$$

Glass structure vs. reactivity



Chemical composition and **fineness** were the key factors to glass reactivity in the systems studied

Al can be a glass modifier - erroneous NBO/T, especially for Al-rich glasses

I this trend is verified for different glasses and systems

could be a basis for predictions of reactivity!

Durdziński et al., Cement and Concrete Research 78 (2015) 263-272

Conclusions – Fly Ash

- A novel method based on SEM-EDS:
  - can identify and quantify amorphous fly ash phases
  - is robust, intuitive and can be easily customized
  - opens new perspective for studies of composite cements - a generic and fundamental approach

- Reaction of fly ash glasses
  - was studied in detail in paste and on model glasses in alkaline solution
  - depends on their fineness and structure disorder (NBO/T) - mostly affected by chemical composition

- Further research is needed
  - Verify the link between glass composition and reactivity
  - Study a wider range of mix compositions
  - Link to the strength and durability

COMPOSITION OF C-S-H

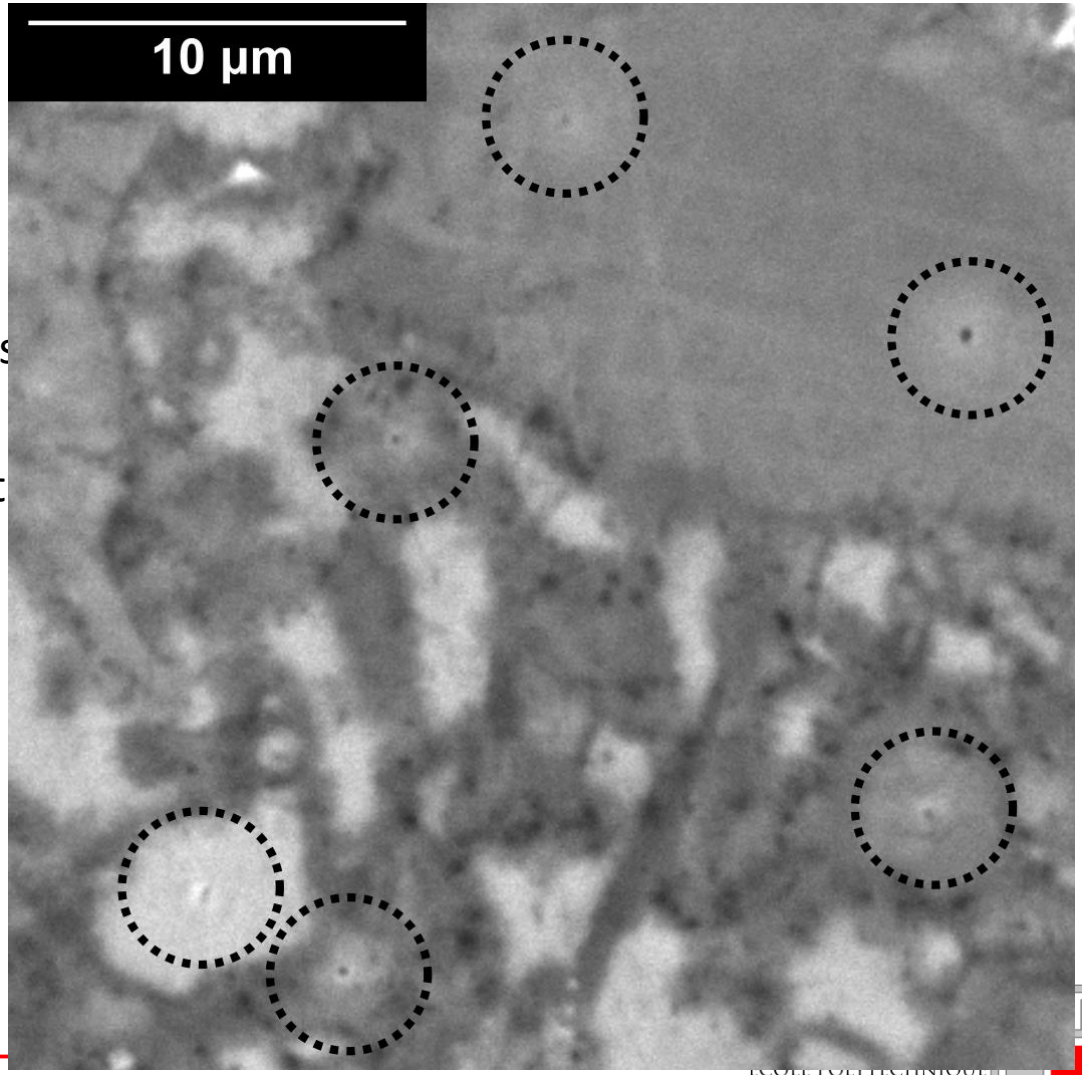
C-A-S-H

- Calcium silcate hydrate (C-S-H) containing aluminium
- Variable stoichiometry (Ca/Si, Al/Si)
- Part of the phase assemblage of cement paste

- Best = local microanalyses in polished sections by characteristic X-rays in an electron microscope (SEM-EDS or microprobe)
- SEM-EDS preferred because lower beam currents to limit beam damage and ability to observe the microstructure and choose points properly

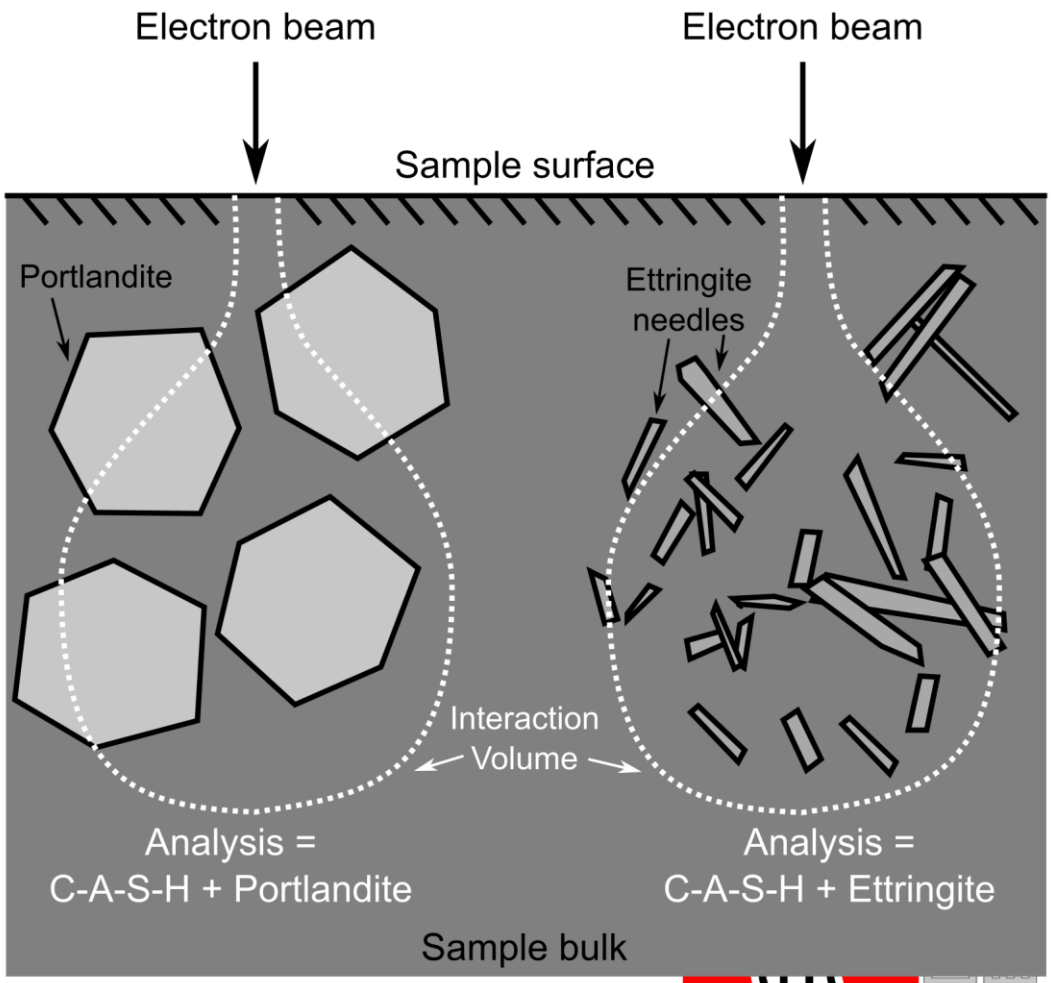
Hydrates are prone to beam damage

- Even after sample preparation (drying) there is significant amounts of bound water
- The markings indicated by a circle are damage in the hydrates after 3 seconds of exposure to a static electron beam at a current of 0.8 nA



And even when damage is under control, there is the problem of intermixing

- Each analysis contains a signal from several phases, due to the size of the interaction volume in bulk samples

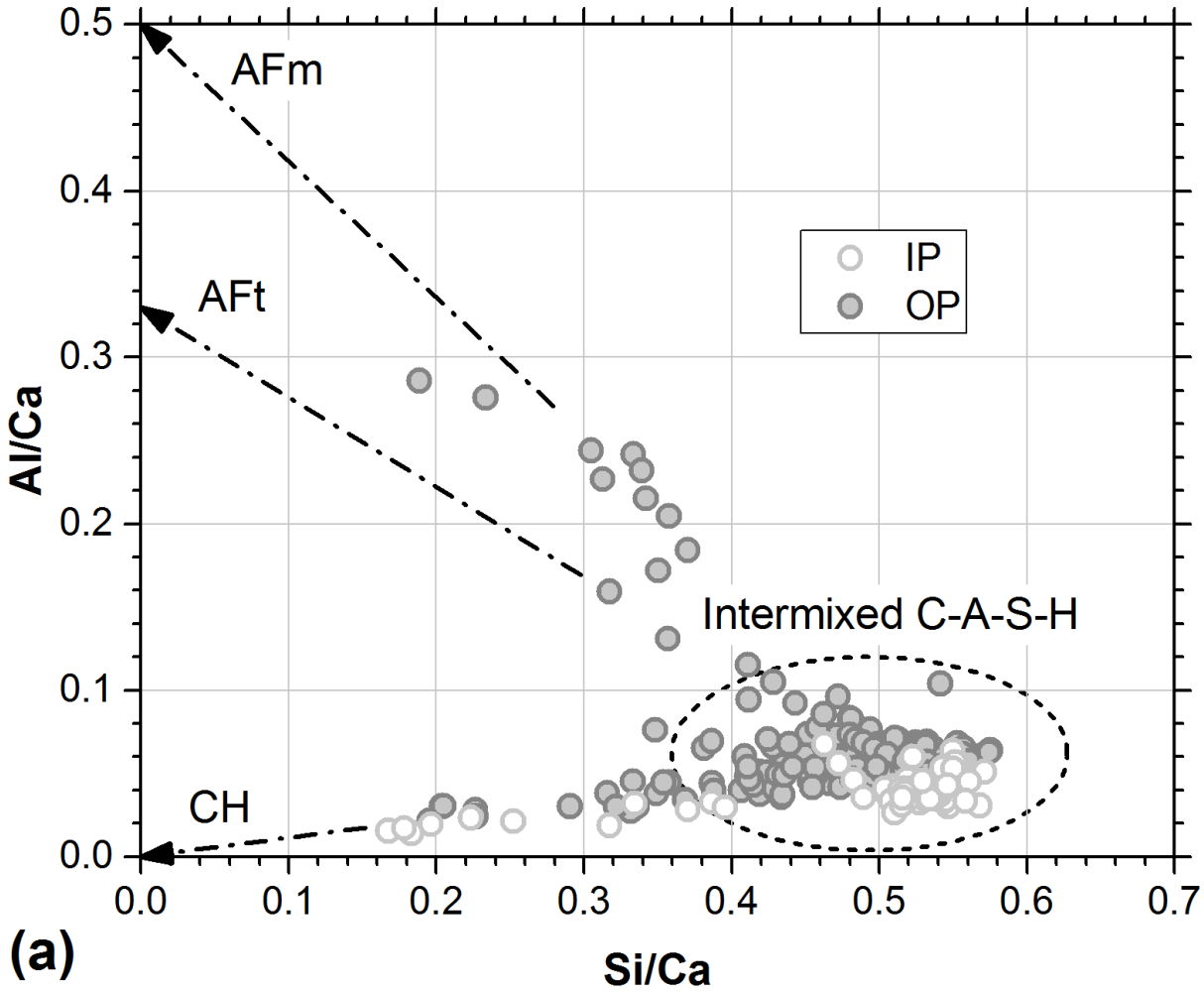


(c)

= C-A-S-H

How to find the composition of “pure” C-A-S-H?

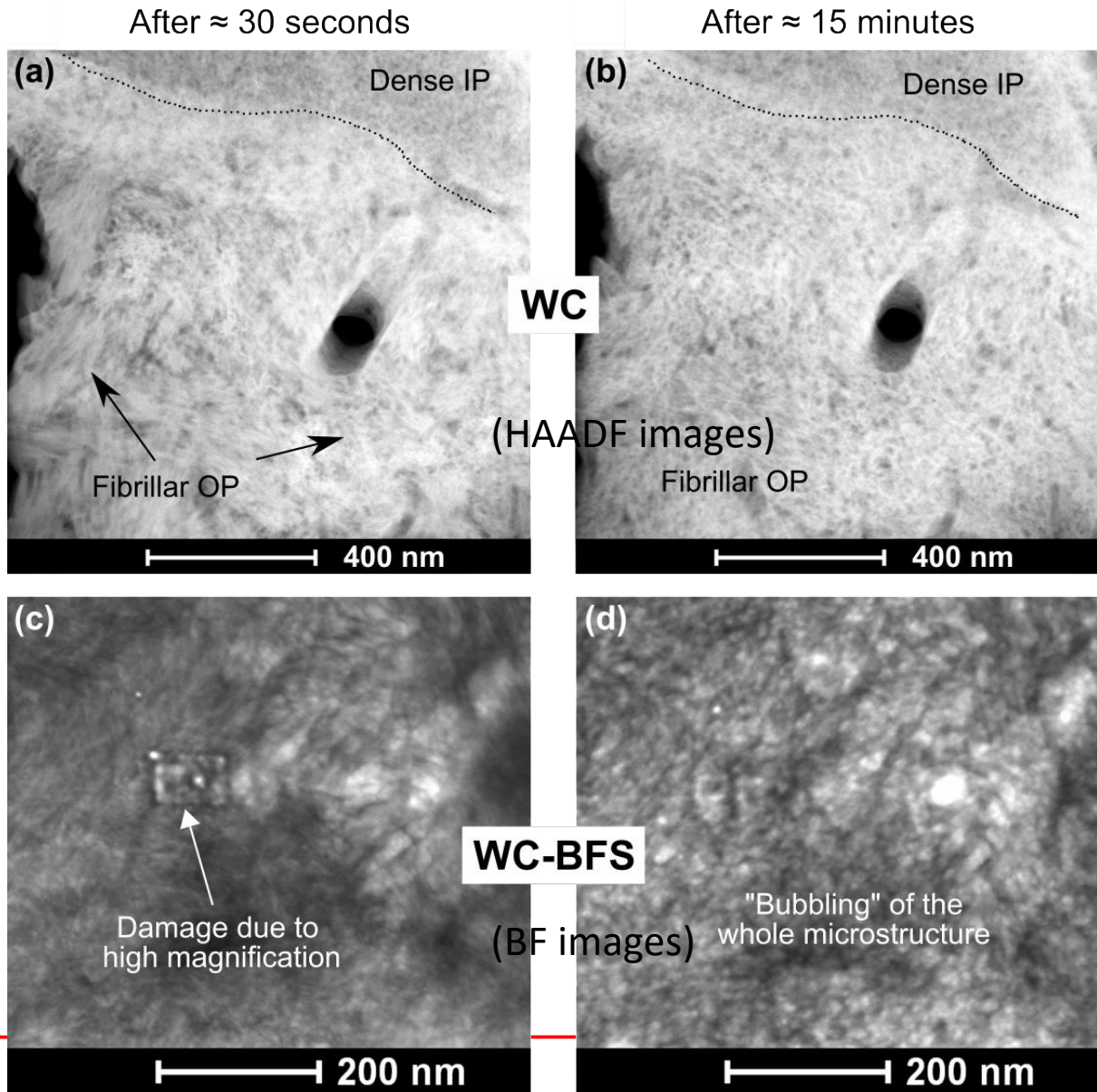
- Data treatment from Taylor 1987
- There is a cloud of points (intermixed C-A-S-H)
- How do we treat the data?



(a)

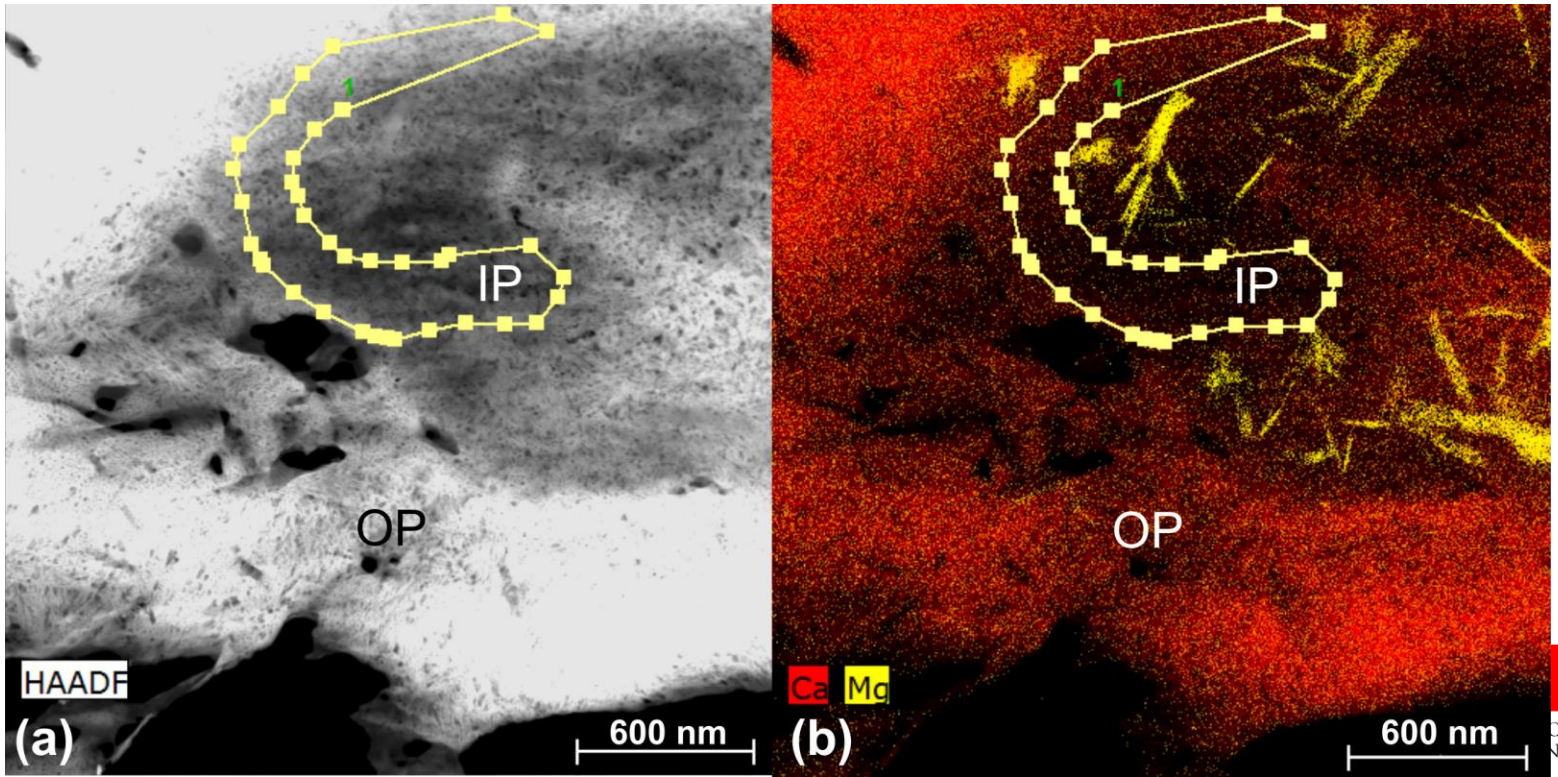
Comparison with TEM

- Damage occurs in the TEM
  - Bubbling of the C-A-S-H
  - Scanning mode helps to preserve the C-A-S-H much longer (such damage occurs after a minute in static beam TEM)
  - EDS is done using quantitative maps

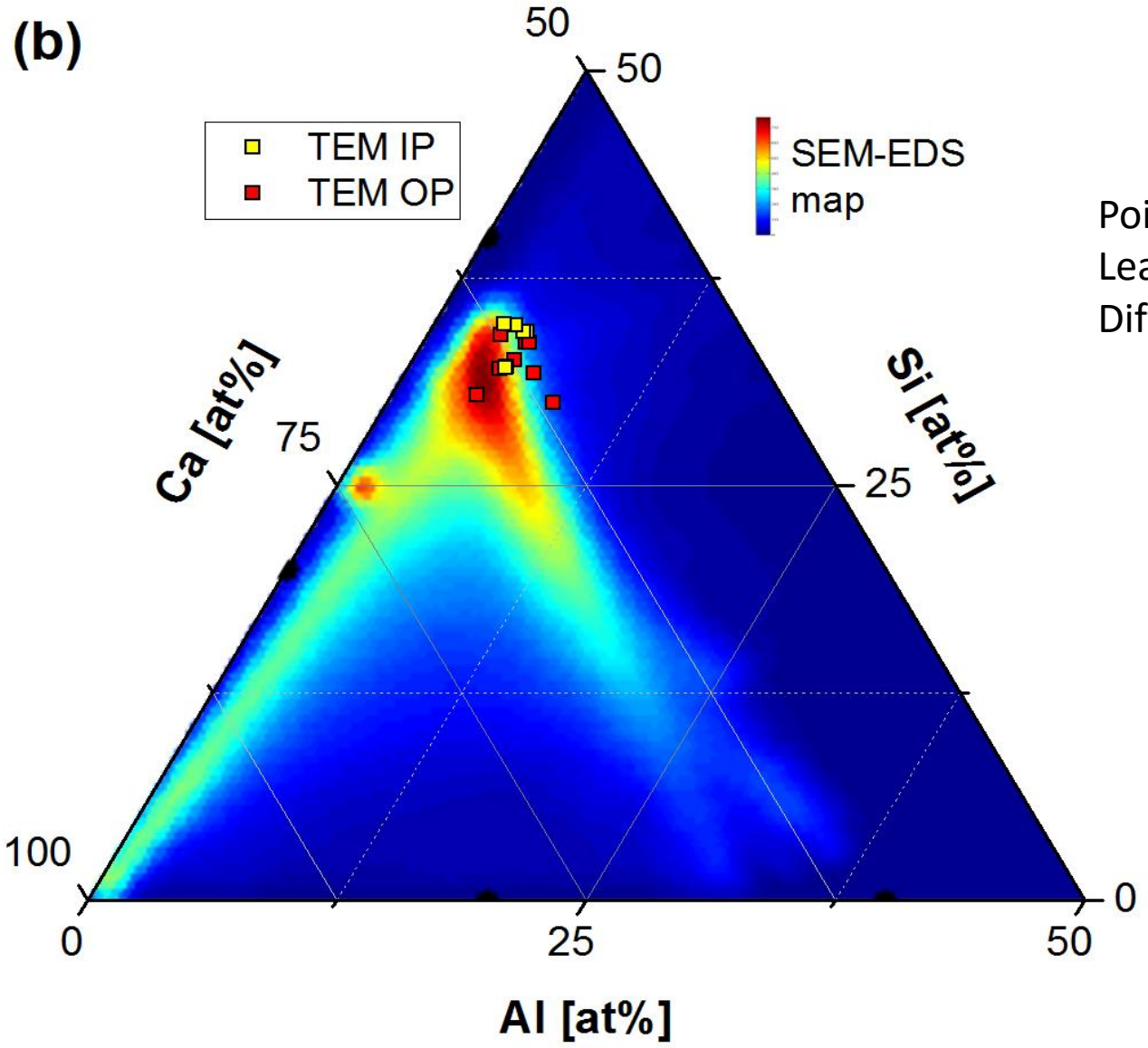


Comparison with TEM

- EDS quantification
  - Polygonal objects in regions devoid of other phases
  - Cliff-Lorimer quantification method standardless



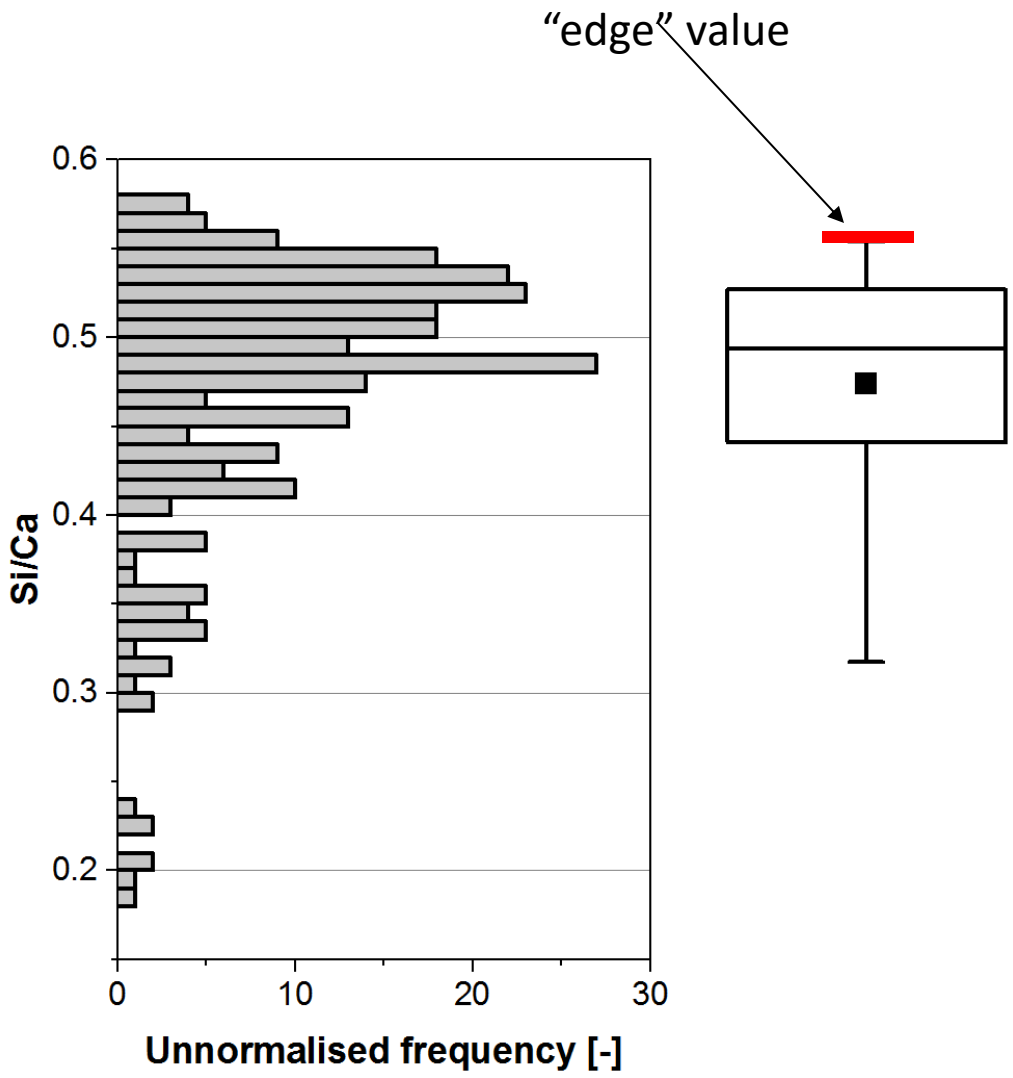
Does full mapping help to define C-S-H comp?



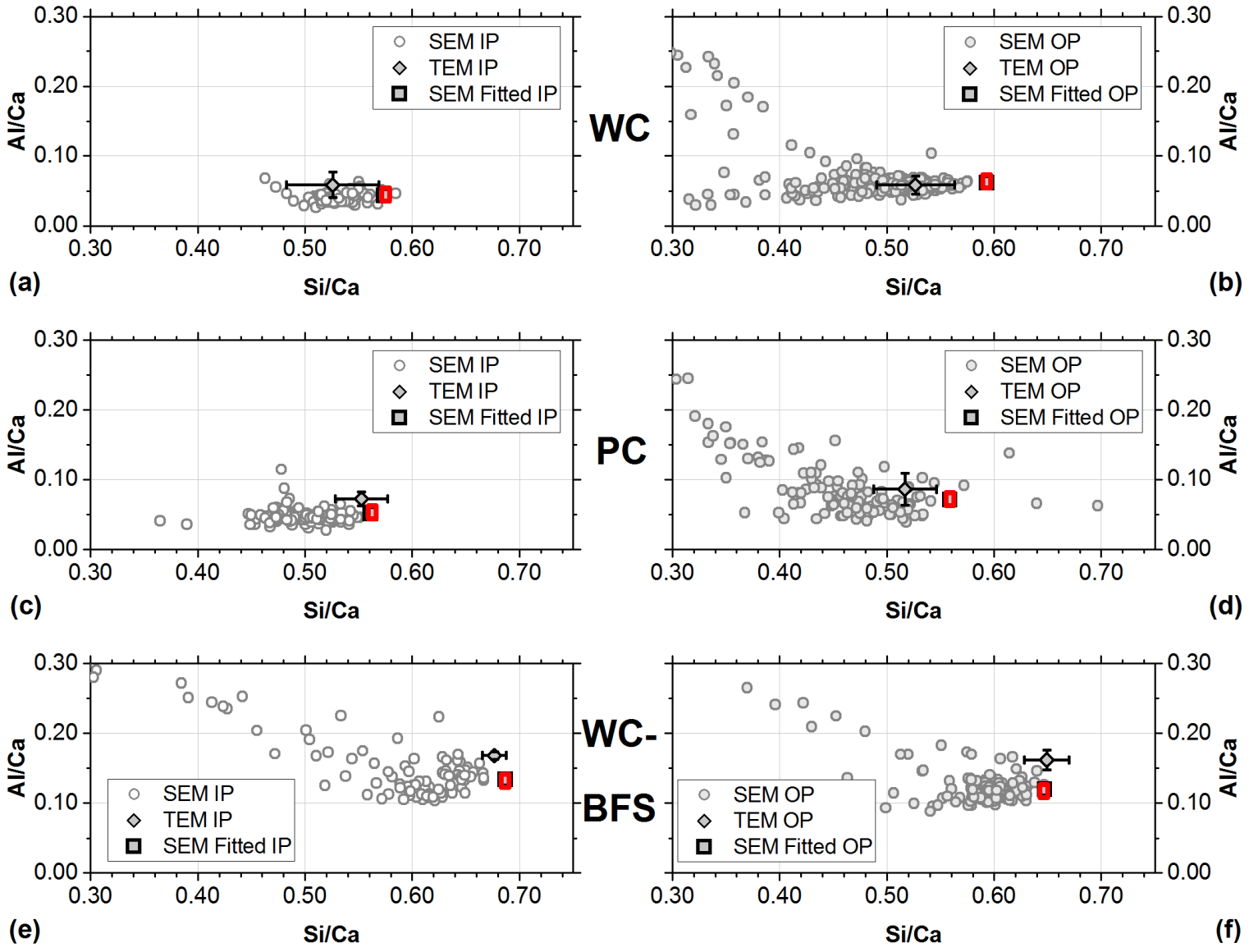
Points at edge,
Least intermixing
Difficult to define

Data representation

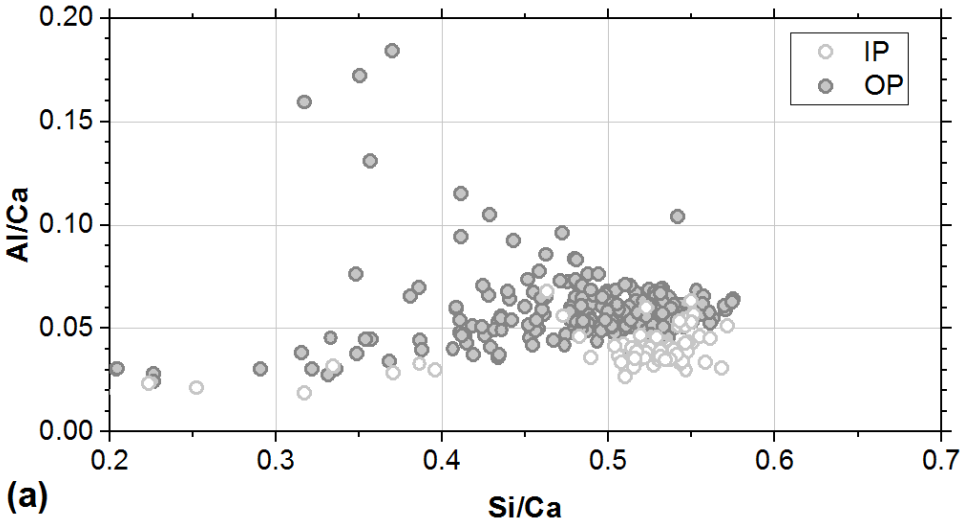
- To compare data without assuming any distribution, it is shown as box-plots
  - median value (-), the mean (■), the values at 25 and 75% (box edges) and the values at 5% and 95% (whiskers)

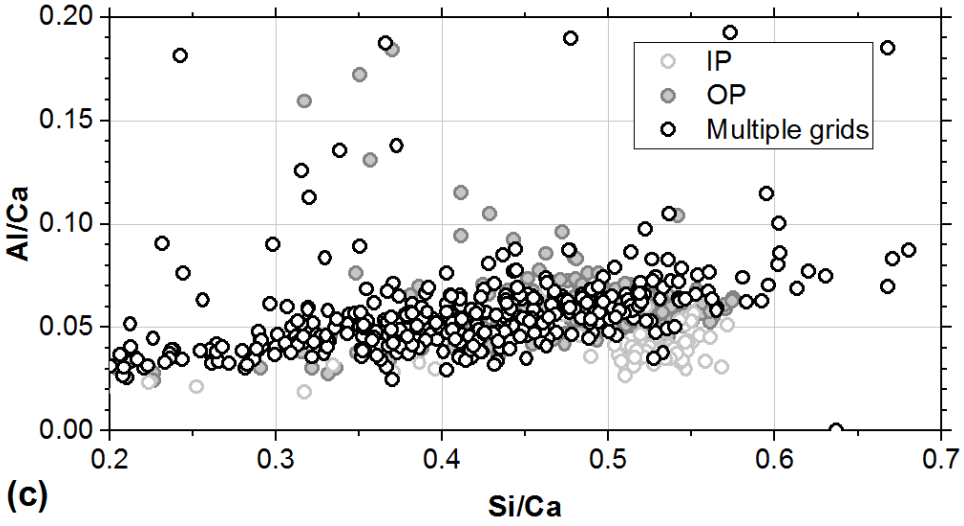


Seems to work well in most cases



Manual vs random choice of points





Conclusions C-S-H

- Analyses of C-S-H can be made with good accuracy in SEM
- Manual choice of points best
- Take Ca/Si at 95% of fitted distribution.

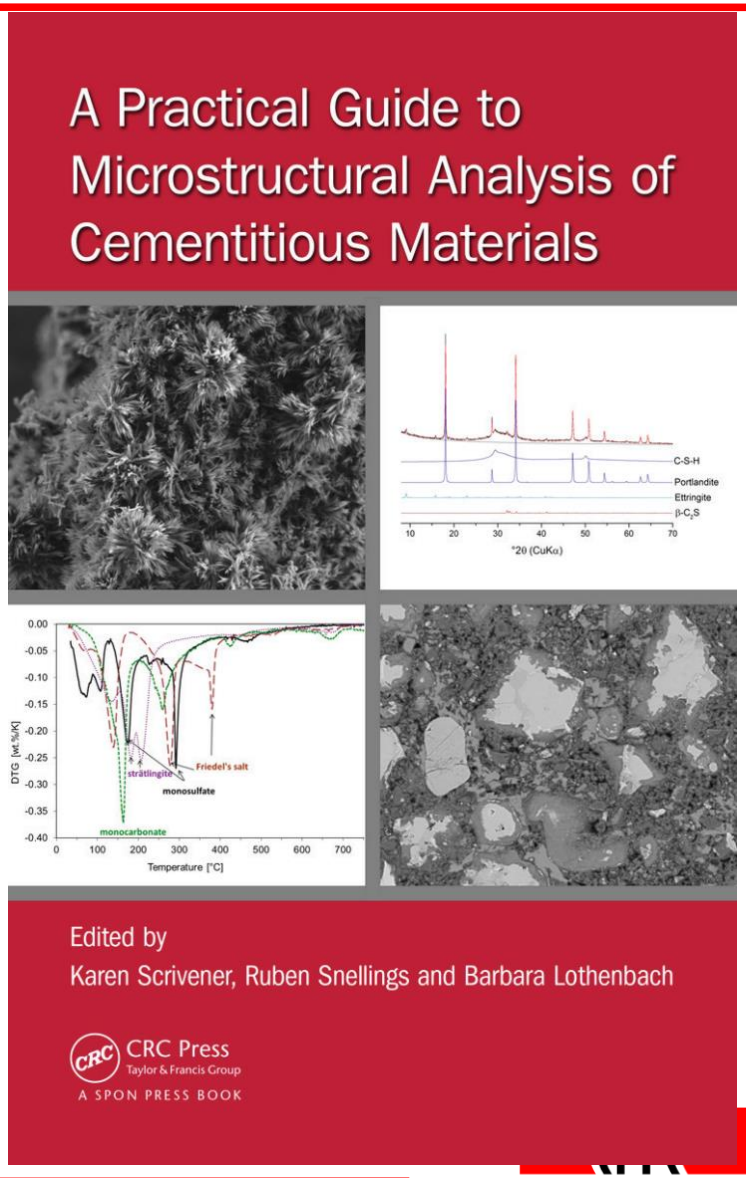

16th Euroseminar on Microscopy Applied to Building Materials
EMABM 2017
14-15-16-17 May 2017
Les Diablerets, Switzerland
emabm2017.epfl.ch

2nd International Conference on Calcined Clays for Sustainable Concrete

December 5th-7th, 2017
The Tryp Habana Libre Convention Center
Cuba

Microstructural analysis methods

- XRD
- Electron Microscopy - SEM/TEM
- Proton NMR
- MIP, TGA, etc




THANK YOU