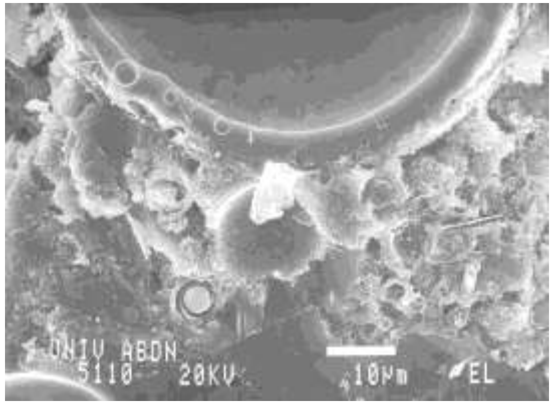
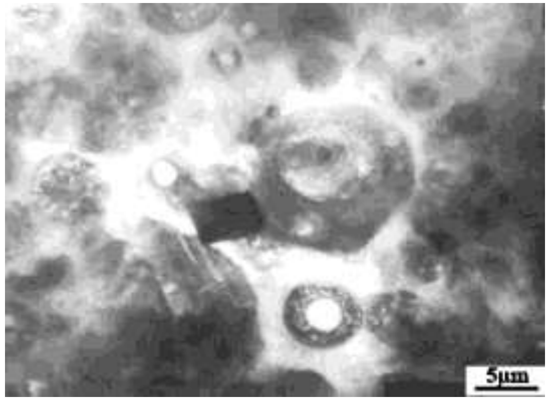
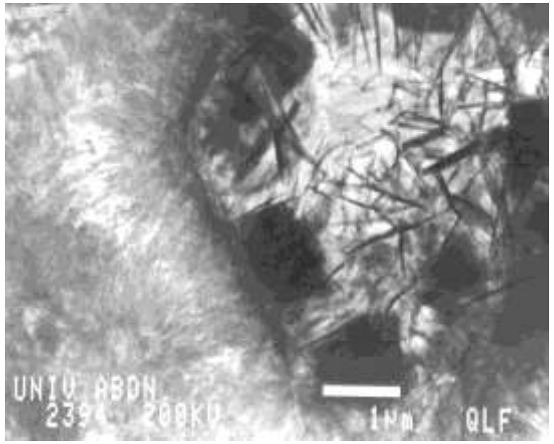
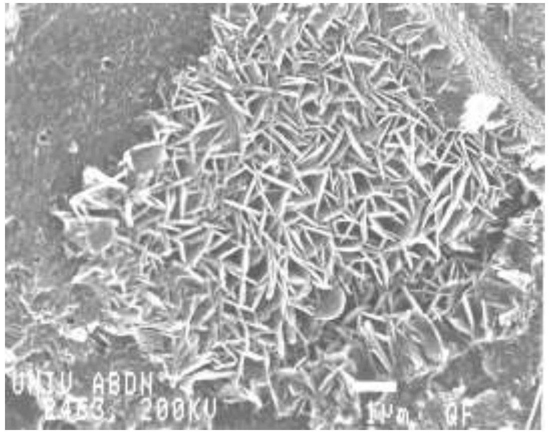
Early Stage Dissolution Characteristics of aluminosilicate glasses
– a basis for SCM reactivity

Katrina C Newlands and Donald E Macphee









Department of Chemistry, University of Aberdeen
Meston Walk, Old Aberdeen AB24 3UE
Scotland, UK
d.e.macphee@abdn.ac.uk

UNIVERSITY OF ABERDEEN

nanocem

58º Congresso Brasileiro do Concrete

11-14th October, 2016

Cement Chemistry @ Aberdeen

Prof HFW Taylor

Prof FP Glasser

Phase equilibria applicable to:
- radioactive waste management
- novel cement systems
- SCM reactivity
- cement/concrete durability
- kiln chemistry and modelling
- CO_2 sequestration

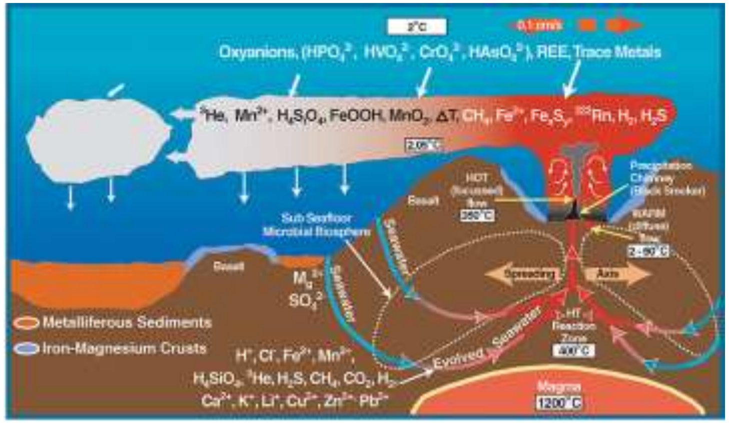
Prof FP Glasser	**Chemistry**
Prof DE Macphee	**Chemistry**
Dr MS Imbabi	**Engineering**
Dr Angel Cuesta Ciscar	Chemistry
Dr Marcus Campbell Bannerman	Engineering

Photocatalytic concretes:
- modified TiO_2
- catalyst selectivity
- catalyst-cement composites

Concretes and Building Envelopes:
- thermal flux optimisation
    - microstructure control
    - block/unit design
    - PCMs in concrete

Why is glass reactivity important?

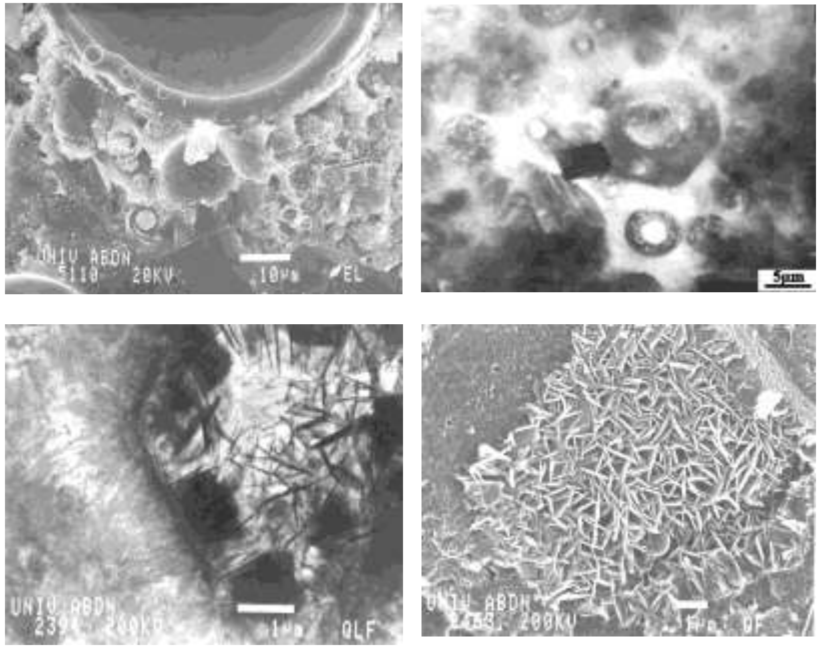
Glasses in concrete technology

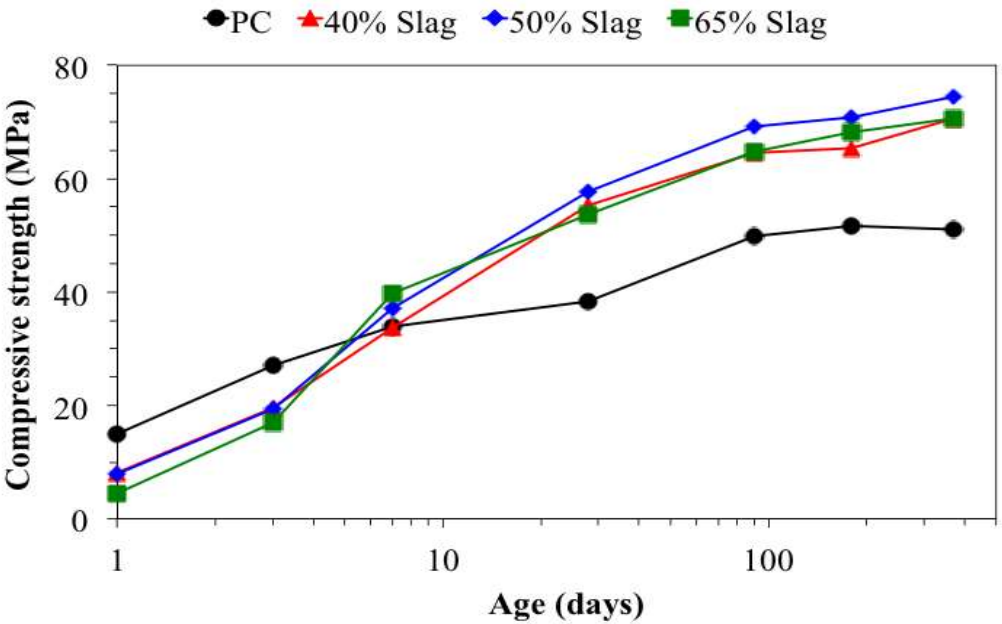


Glasses in geochemistry

Glasses in waste management

Glasses in concrete technology





- **SCMs** have an important role in the development of sustainable, low CO_2, cements
  - dilution of OPC content
  - contribution to space filling, strength development and durability

- But slow early strength development presents a practical limitation

- Unknown hydration rates limit their level of substitution, e.g. BFS, PFA

- Need more fundamental understanding of glass reactivity

Dubovoy, V.S., *et al*, ASTM Special Technical Publication pp. 29-48, (1986)
Also:
K. Luke and F. P. Glasser, *Cem. Concr. Res.*, 17, (2), 273–282, (1987)
V. Kocaba, *et al*, *Cem. Concr. Res.*, 42, (3), 511–525, (2012).

The ‘structure’ of aluminosilicate glass

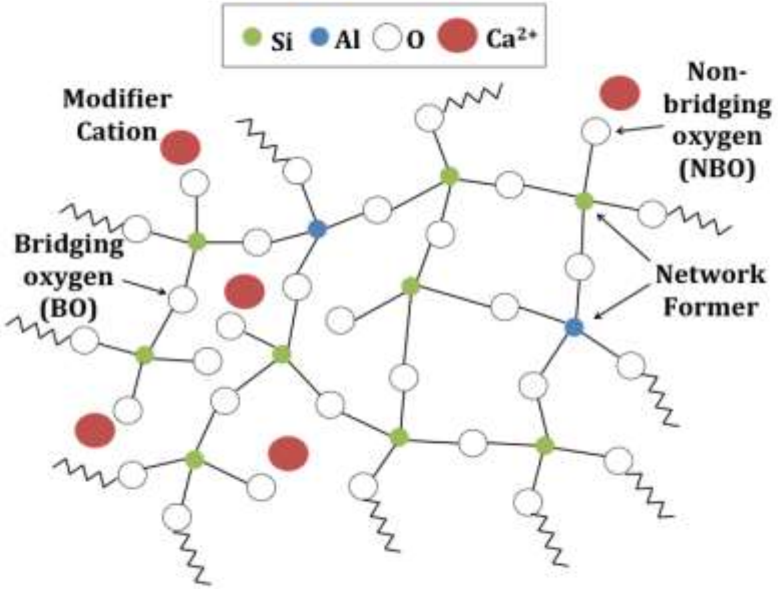
Reactivity linked to:

- Physical properties (e.g. fineness/surface area, amorphous content)
- Chemical properties (e.g. composition (glass and activator), structure)

Several hydraulic indices (HI) have been defined →

S. C. Pal, *et al*, Cem. *Concr. Res.*, 33, (9), 1481–1486, (2003).

$$\frac{\text{structure modifying (e.g. CaO)}}{\text{structure forming constituents (e.g. } SiO_2 \text{ and } Al_2O_3\text{)}}$$



Structure

- a heterogeneously *polymerised network* of silicate and aluminate *tetrahedral*
- partially disrupted through network modifiers at *non-bridging oxygens* (NBOs) – an electrostatic interaction
- NBOs – sites for attack by polar solvents, e.g. aqueous activators

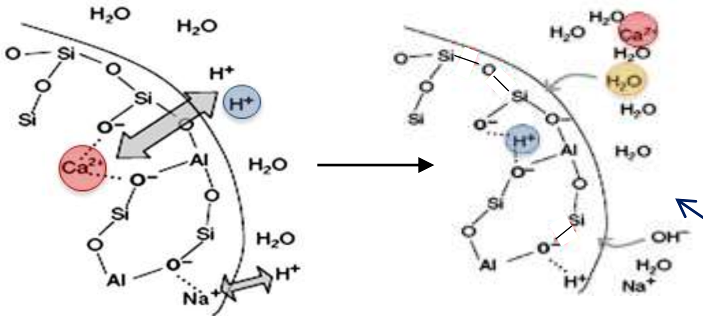
$$\frac{NBO}{T} = \frac{2[Ca] - [Al]}{[Si] + [Al]}$$

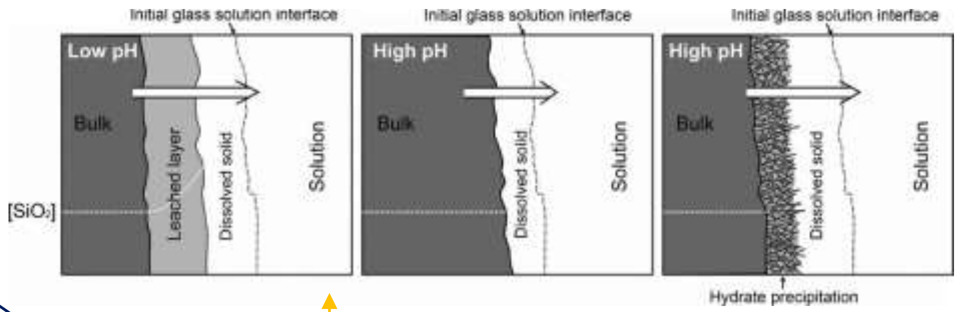
- an indicator of the state of aluminosilicate depolymerisation correlated with reactivity (and the HI)

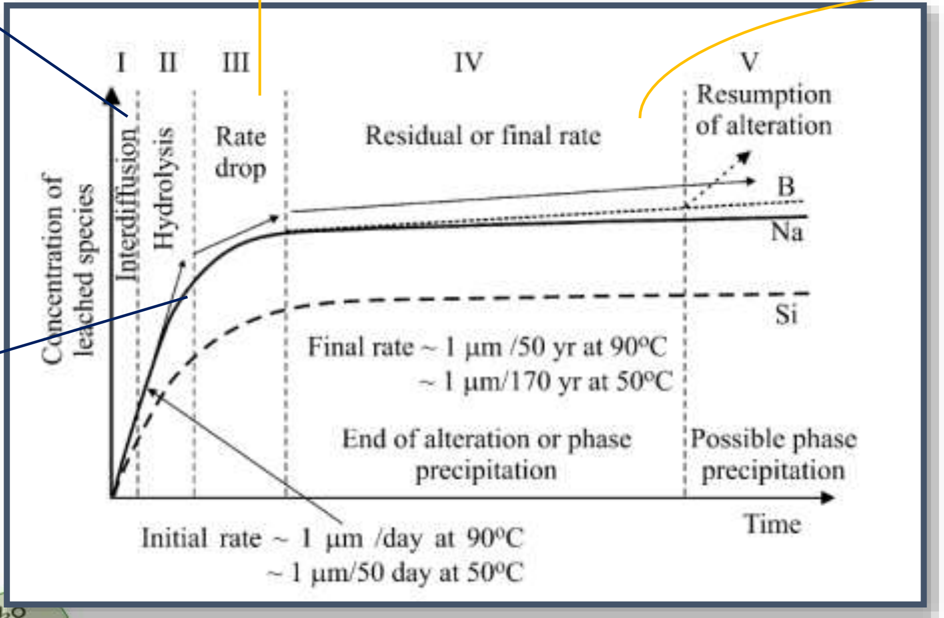
Moesgaard, M. and Yue, Y.Z., J Non-Cryst. Solids, 355, 867-73, (2009)
Moesgaard, M. *et al.*, Chem. Mats., 22, 4471-83, (2010)
Moesgaard, M. *et al.*, Cem. Concr. Res., 41, 359-64, (2011)

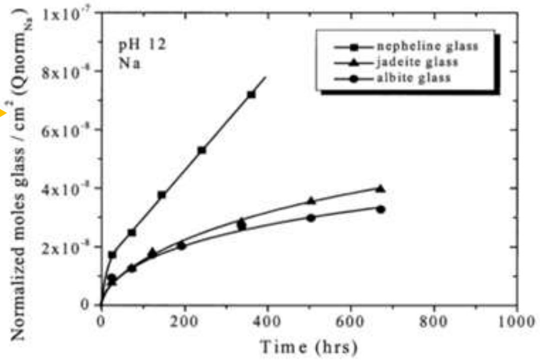
Factors conditioning glass corrosion/dissolution rates

pH 7-10



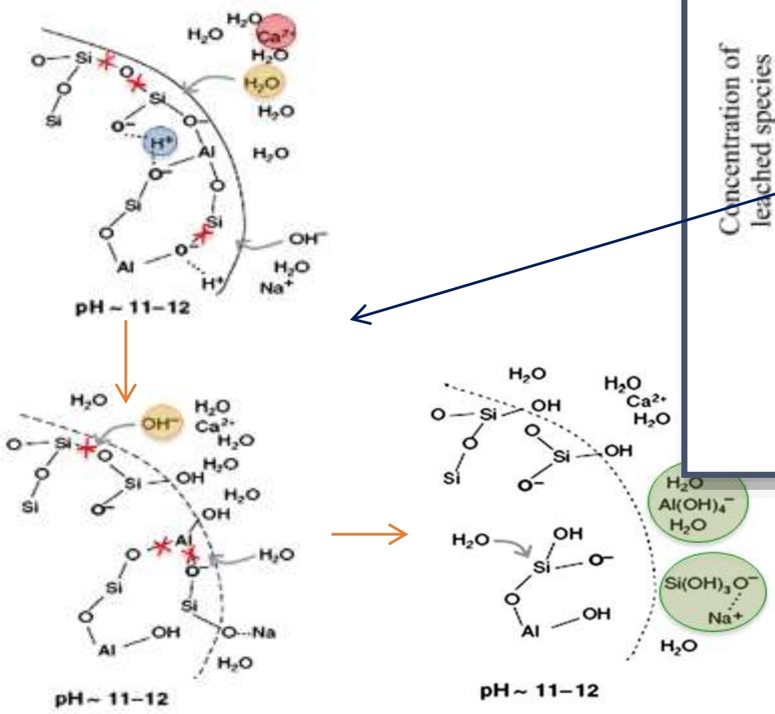






- What controls steady state dissolution rate (K_{diss})?
- What happens in the early ages of hydration?

pH > 11



Hamilton, J.P. *et al*. (2001). *Geochimica et Cosmochimica Acta*, 65, 3683-3702
Bourcier, W. L. (1993). *MRS Proceedings*, 333, 1-14
Casey, W.H.(2008). *Nature Materials*, 7, 930-932
Snellings, R., (2014), *J. Amer. Ceram. Soc.*, 1–12

Aims and Objectives

Aims

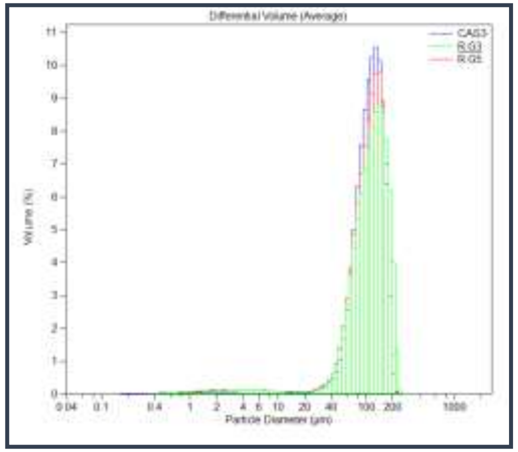
- Study the *early stage* relations between reaction rate of SCMs and their:
  - Composition
  - Local environment

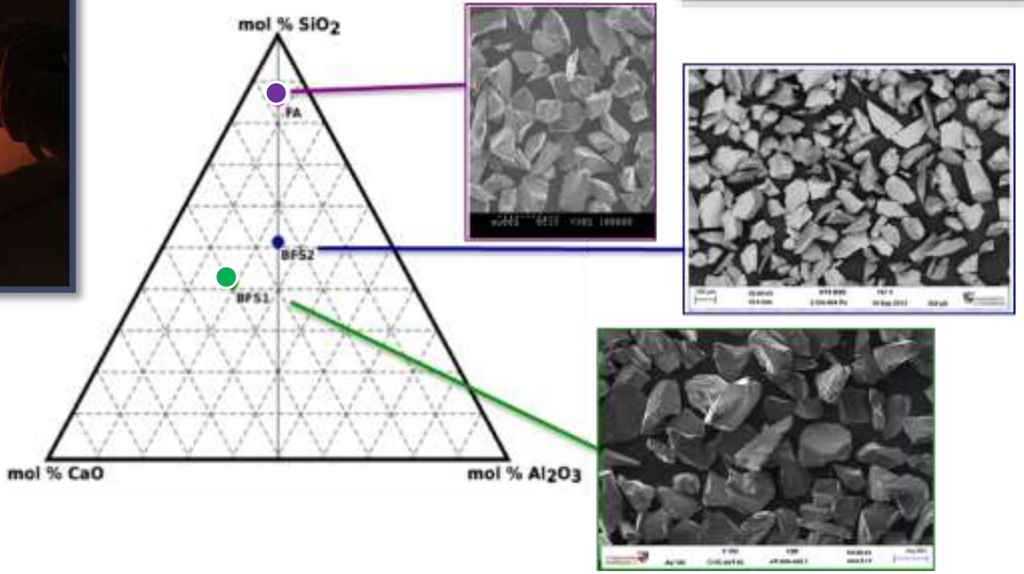
- Assimilate trends in relation to current models for glass dissolution
- **Identify implications for SCM reactivity in cementitious systems**

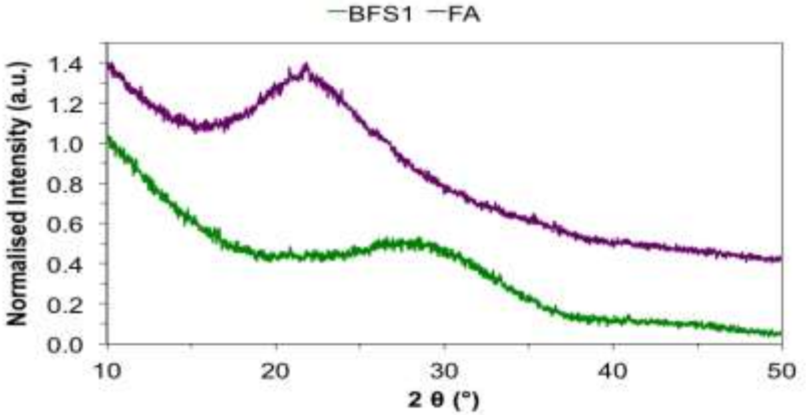
Objectives

- Synthesise glasses with a composition indicative of a *blastfurnace slag-like and a fly ash*-like glass
- Assess stability in various activator solutions: **H_2O** (pH 7), **1mM** and **0.1M NaOH** and **KOH** (pH 11 and 13) under conditions expected to limit precipitation solids(l/s=10000)
- Correlate aqueous and solid composition changes with time
- Undertake solid surface characterisation where possible

Glass synthesis and characterisation







	Chemical Composition (mol%)							
Glass	SiO_2	Al_2O_3	CaO	Grain Size (µm)	SSA (m^2/g)	NBO/T	Al-O-Si	Si-O-Si
BFS1	41.98±1.03	17.37±1.75	40.66±0.34	110.7 ± 38.39	0.042	0.61	3.30	0.69
FA	85.24±3.32	7.21±1.75	7.55±1.47	110.9 ± 42.97	0.124	0.007	0.68	3.32

Reactor set-up and analytical overview

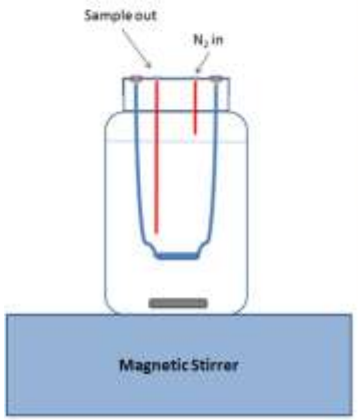
w/s ratio 10,000 - chosen **to avoid precipitating products**

Synthetic glass (1 mm) + Activator solution

H_2O, 1mM and 0.1M NaOH, 1mM and 0.1M KOH, $Ca(OH)_2$.

Test system

- Solids analyses (Periodic sampling consistent with solution analyses)
  - Raman/IR spectroscopy → Surface hydroxylation
  - XPS
  - SEM/EDX
  - TOF-SIMS
  - AFM
  - XRD → Mineralogy
  - XPS, SEM/EDX, TOF-SIMS →
    - surface elemental composition
    - depth profiling
- Solution analyses (Periodic sampling (5 mins to 3 hours))
  - MP-AES
  - ICP-OES

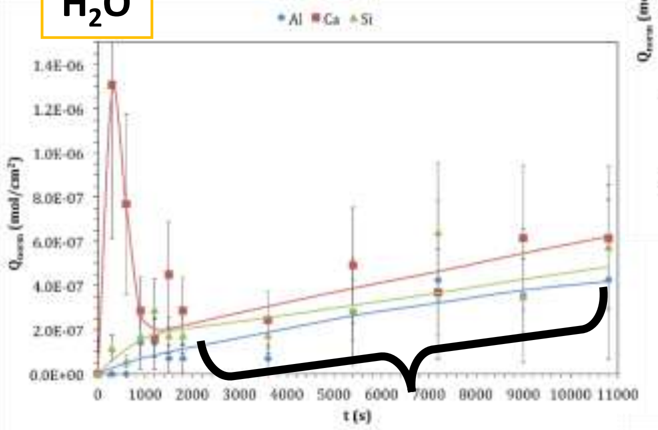


Dissolution Profiles

$Q_x = (C_x V_{soln})/(SSA.m)$

BFS1

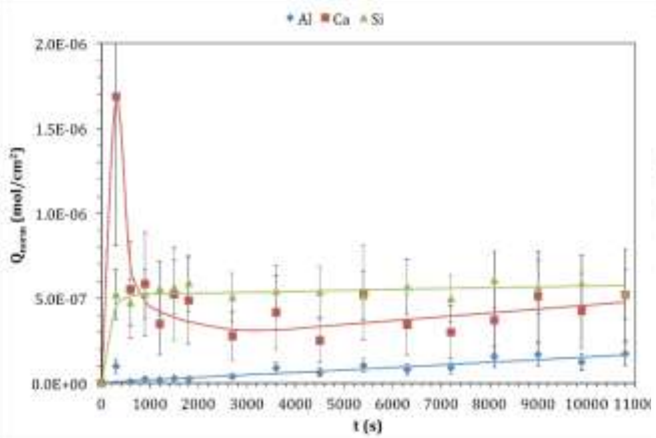
H_2O



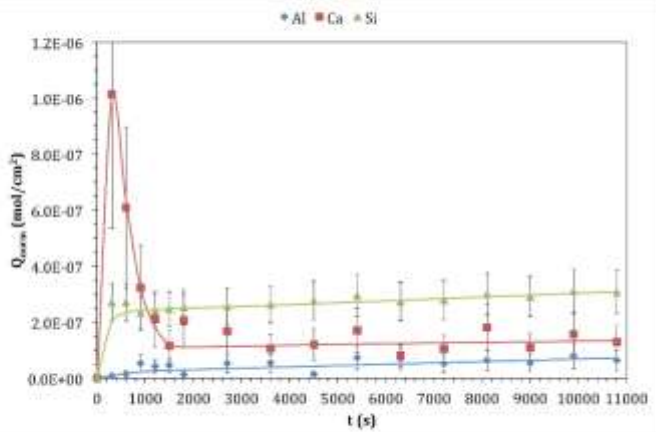
Steady-state
dissolution regime
from which K_{dis} is
calculated

$K_{dis} = Q_x/t$

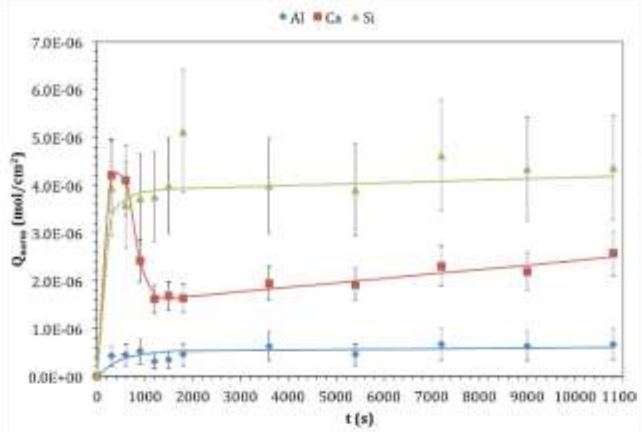
1mM NaOH



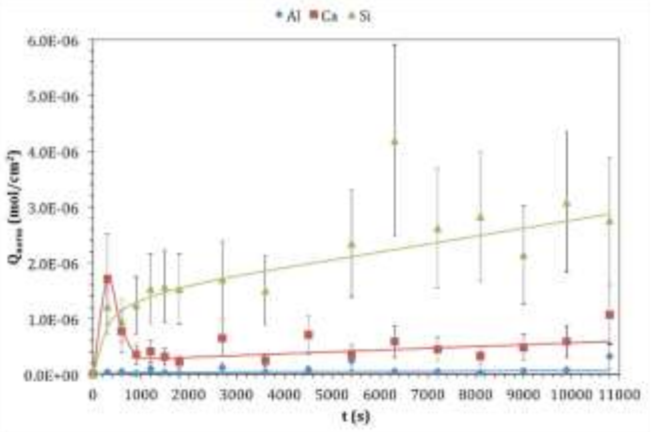
1mM KOH



0.1M NaOH

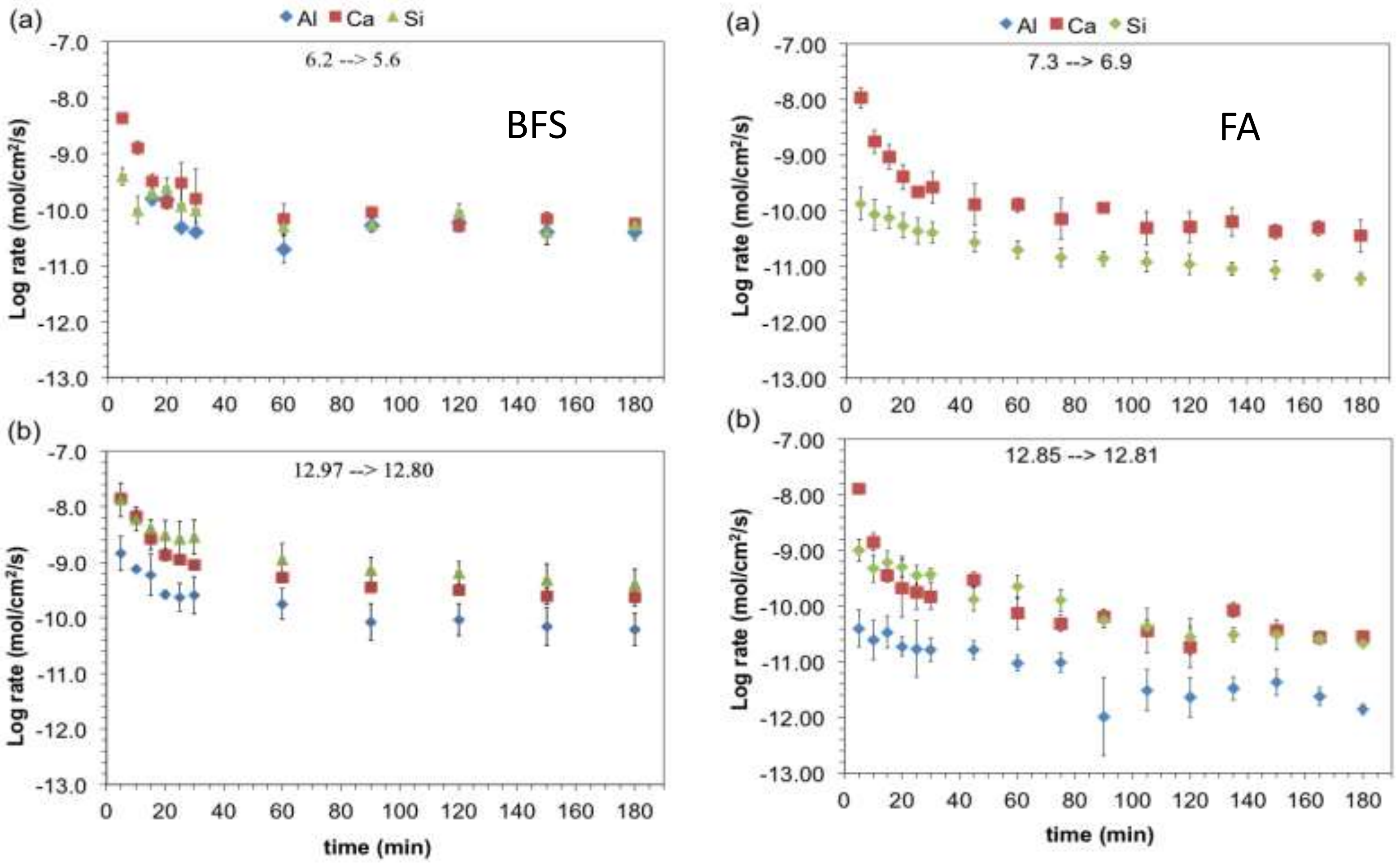


0.1M KOH



Hamilton, J. P. *et al.* (2001). *Geochimica et Cosmochimica Acta*, 65, 3683-3702

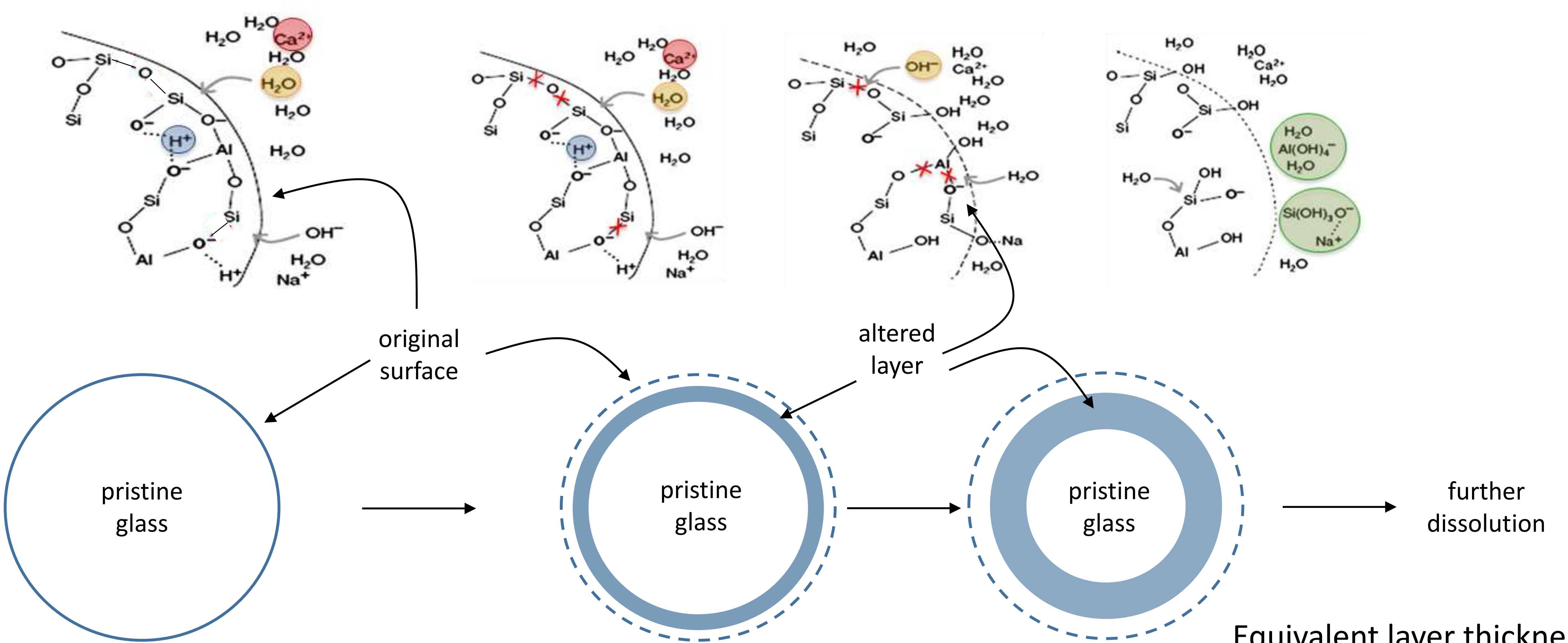
Dissolution Profiles - Normalised elemental fluxes $Q_{norm} = (C_x V_{soln})/(SSA.m.x)$; $rate = Q_{norm}/t$



Exposure to (a) H_2O and (b) 0.1M NaOH; pH changes during the experiment are indicated

- The release rates of matrix ions to solution increases with activator pH. *Increased pH enhances network hydrolysis*
- The preferential release of Ca over Si and Al is reduced at the higher pH. *Aluminosilicate network solubility becomes more prominant, reducing the impact of ion exchange/diffusion.*
- Higher Si and Al release rates were observed in BFS1 than in the FA glass. *BFS glass has a higher NBO/T ratio* ⟶ *higher state of depolymerisation*
- The FA glass also showed relatively higher Ca release rates in water initially
- A change in the rate of Si and Al release from the FA glass arises in alkaline conditions after about 80 minutes and about 30 minutes in BFS
- All solutions show a reduction in activator pH

Solid phase - Layer formation



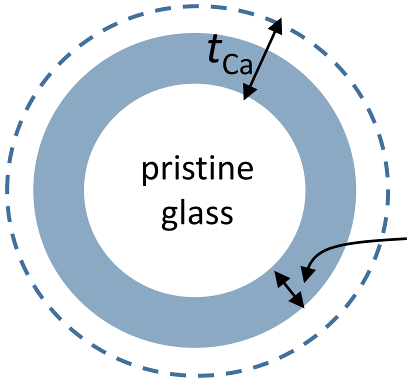
‘Mass balance’ approach allows reaction front characteristics to be modelled → Solution composition as a measure of lost glass volume →

Equivalent layer thickness

$$t_i = \frac{c_i V}{x_i M \rho S A}$$

e.g. Frugier, P, *et al*, *J. Nucl. Mater.*, 380, 8-21, 2008.

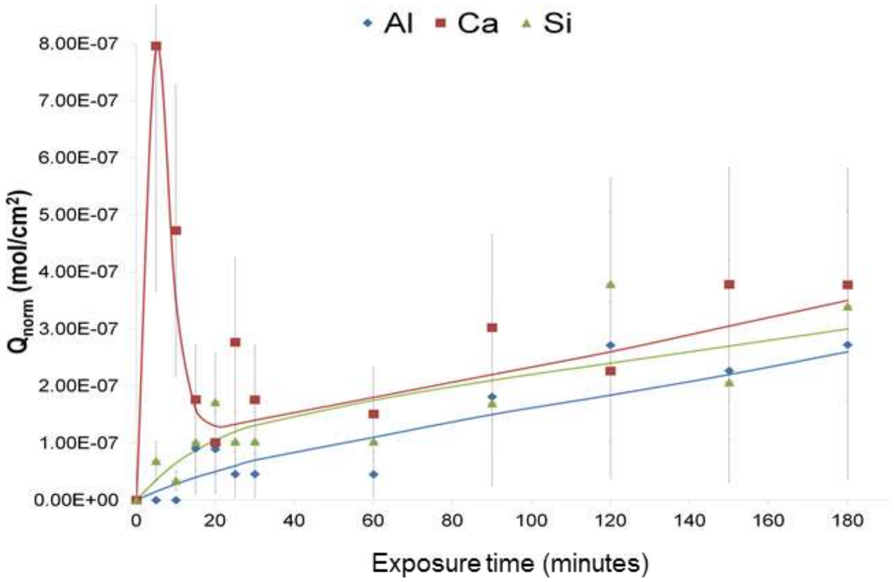
Layer formation and equivalent thickness



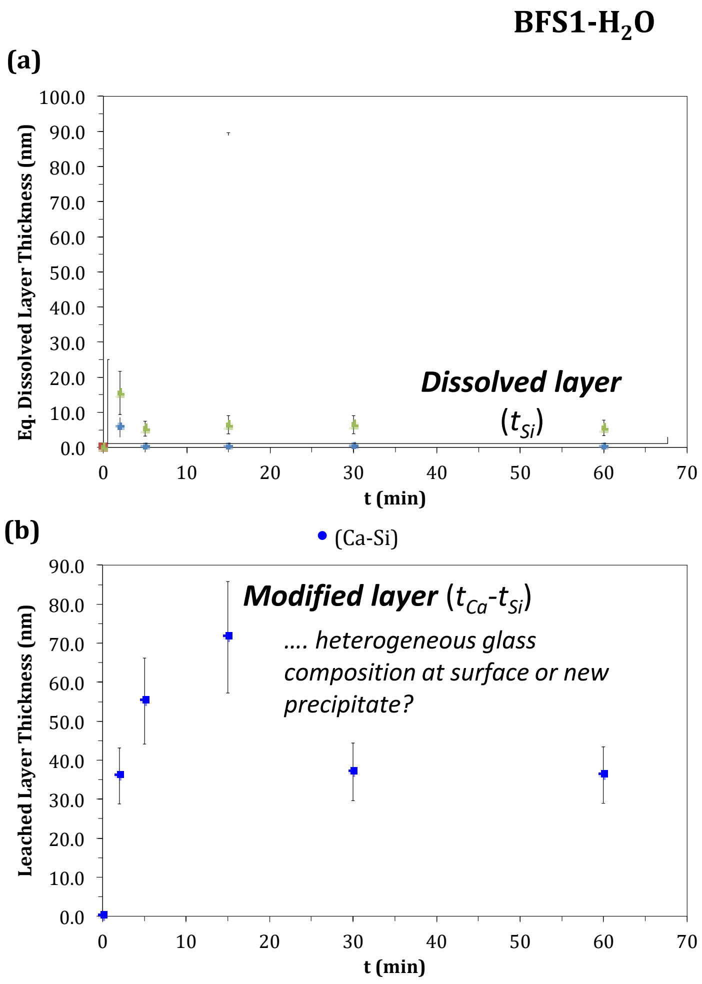
$t_{\text{dissolved layer}}$ = t calculated for a network ion, e.g. Si

$t_{\text{altered layer}} = t_{Ca} - t_{\text{dissolved layer}}$

$$t_i = \frac{c_i V}{x_i M \rho S A}$$



BFS1-H$_2$O



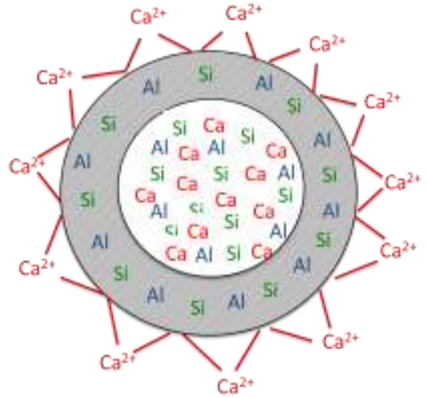
Dissolved layer (t_{Si})

Modified layer (t_{Ca}-t_{Si})

…. heterogeneous glass composition at surface or new precipitate?

Calculated dissolved layer thickness at 30 minutes is less than at 2 minutes!

- Calculation influenced by
  - i. heterogeneity in glass composition
  - ii. changing composition/solubility of the glass due to surface modifications/precipitation (also influencing K_{dis})

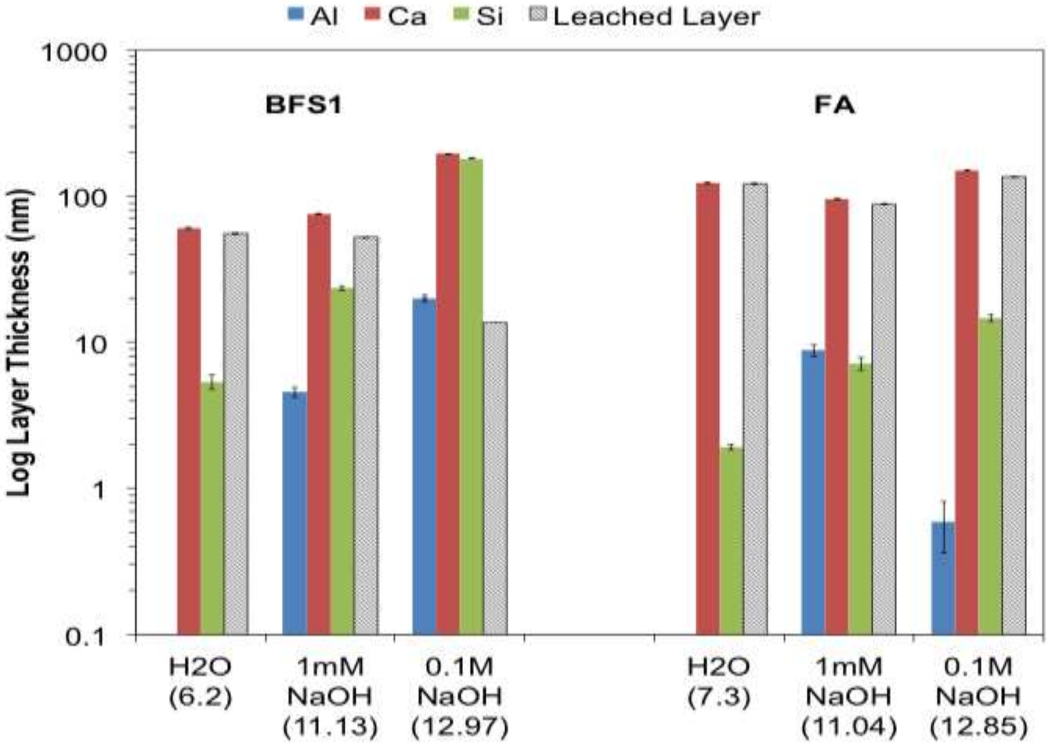


- **Only early stage data used for reference**

Casey, W. H., *et al*, *Geochimica et Cosmochimica Acta*, *53*, 821–832(1989).

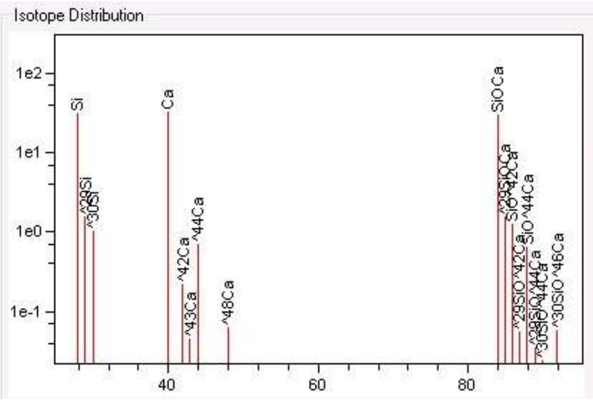
Equivalent dissolved layer thickness

- 5 min solution data

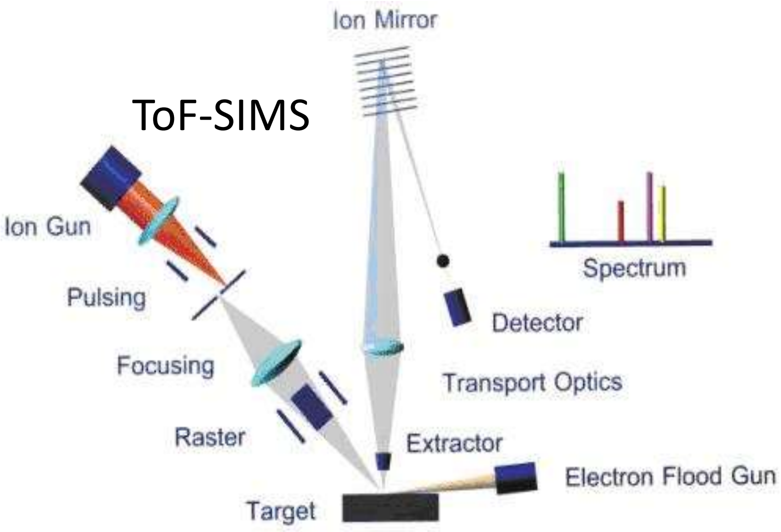


- Dissolved layer thickness greatest in alkaline solution
- Decrease in leached layer thickness with increasing alkalinity for BFS
- Higher leached layer thickness in FA attributed to exposure of internal porosity

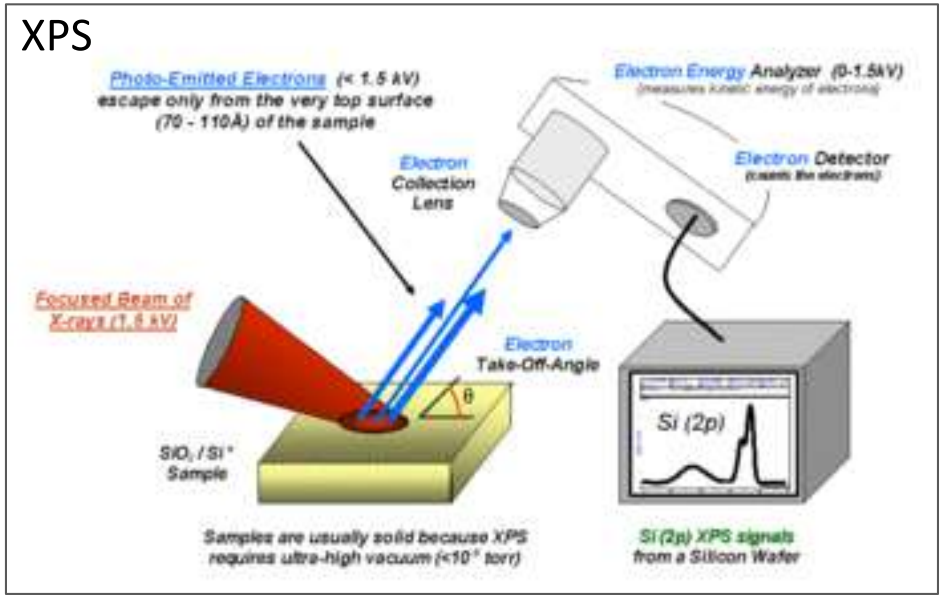
Solid surface analysis



ToF-SIMS

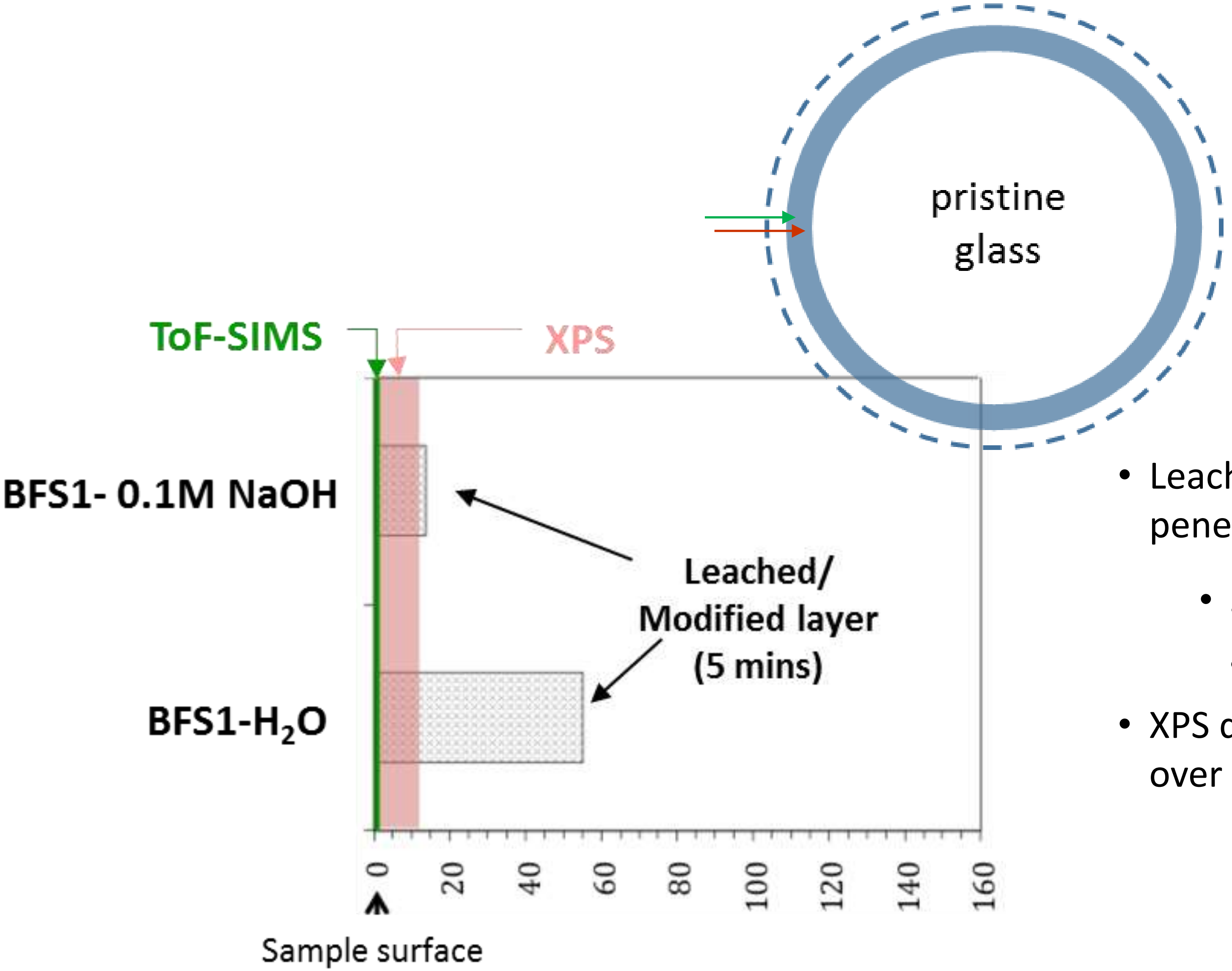


XPS



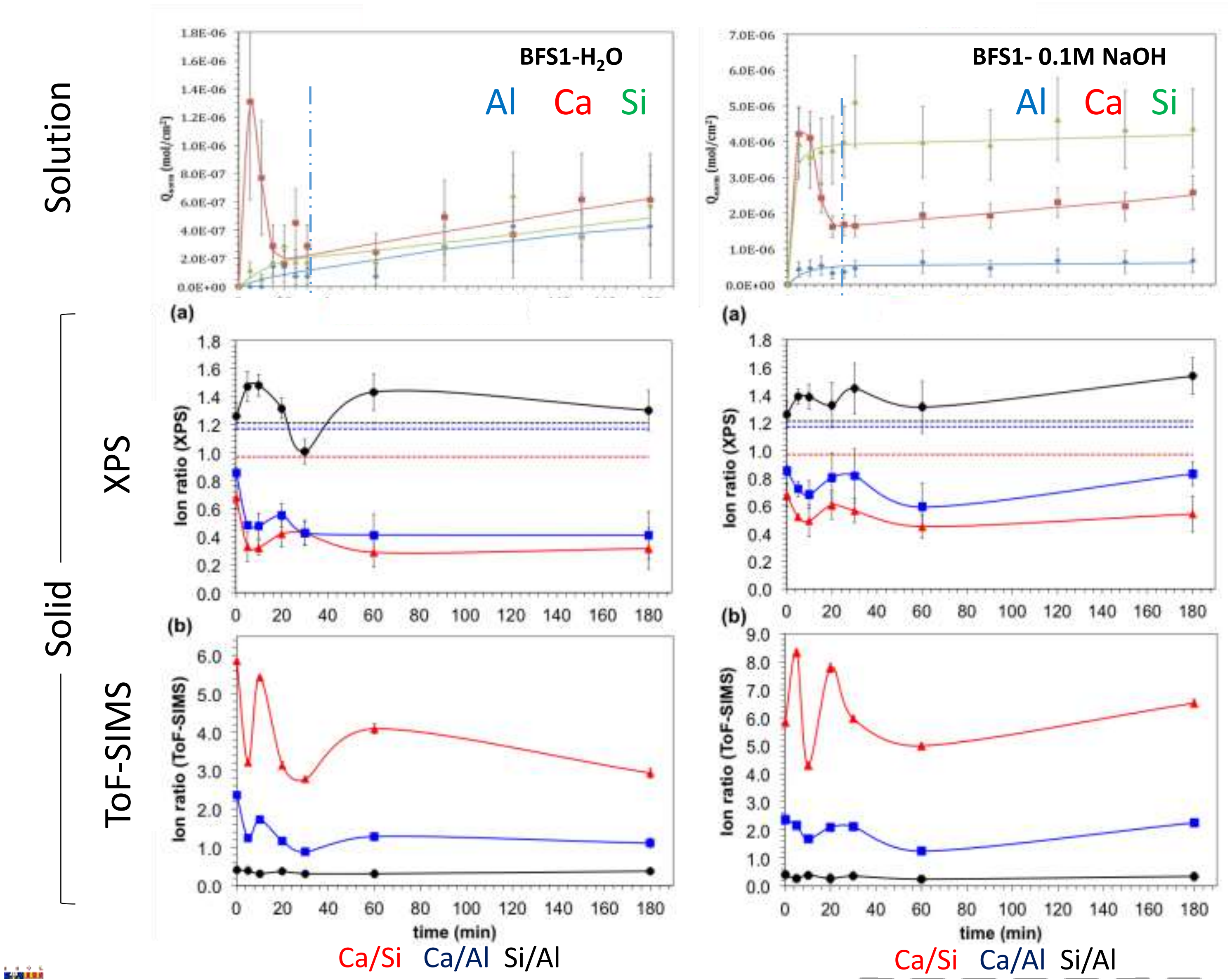
Penetration depth (nm)	**~ 1.5**	**6 - 10**
Data reported as	Elemental ratios from counts (^{23}Na, ^{27}Al, ^{28}Si and ^{40}Ca) as a percentage of the total secondary ions emitted	Ratios of peak areas corresponding to Si 2p, Al 2p, Ca 2p3/2, Na 1s, C 1s and O 1s

Solid surface analysis - scale



- Leached/modified layer thickness at 5 mins > penetration depths for XPS/ToF SIMS
  - Surface analysis does not include pristine glass
- XPS data represent an average composition over the ToF-SIMS region and the XPS region

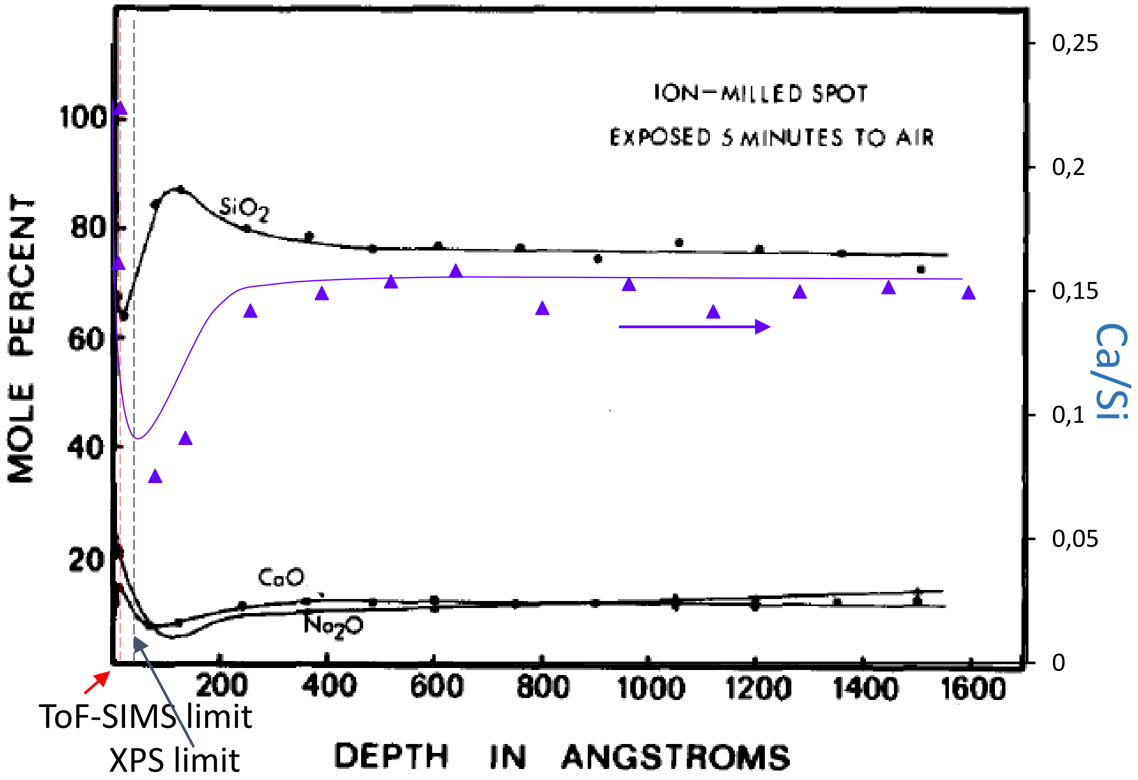
Surface analysis of solids – ion ratios relative to pristine glass (BFS)



- Solution data indicate an immediate release of Ca on exposure to activator (initial 'wash off')
- Ca/Si and Ca/Al depleted across the underlying, XPS region (Si elevated)
- Surface Ca/Si and Ca/Al (ToF-SIMS) significantly elevated initially and reduce only slowly (in the first 20-30 minutes)
- Resorption of Ca (5-30 minutes) indicated by solution data not clearly supported by ToF-SIMS data.
- Combined XPS and ToF-SIMS data are consistent with Ca migration to the particle surface **prior to experimentation**.

Surface analysis of solids – pre-hydration?

Surface compositional profile (AES-ion milling) of a typical soda-lime-silica glass after 5 minutes exposure to air at room temperature



- **Initial Ca release observed by solution analyses likely to be attributable to a surface accumulation prior to activator exposure**

Hench, L. L., & Clark, D. E. (1978). *Journal of Non-Crystalline Solids*, *28*, 83–105.

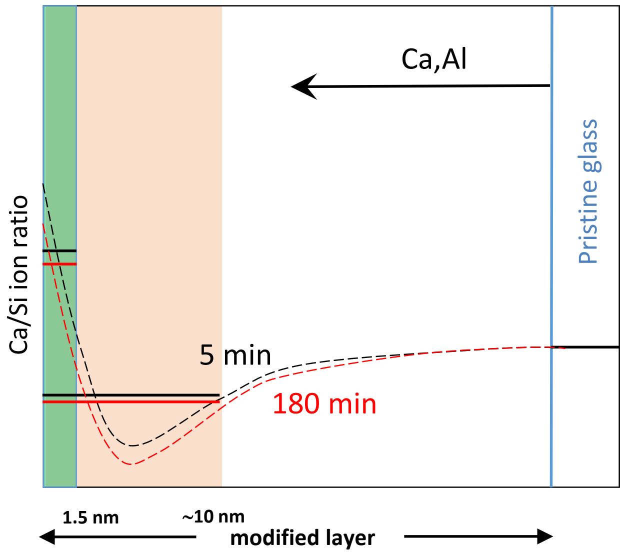
Surface analysis of solids – ion distribution after exposure (BFS)

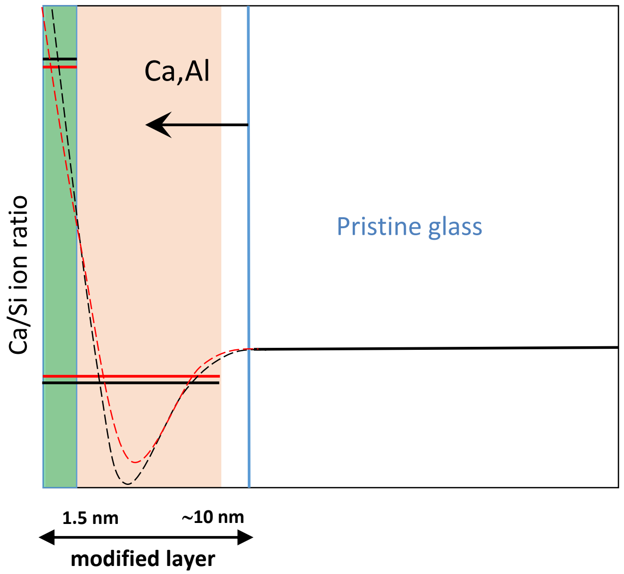
BFS1- H_2O

	Time	Ca/Si	Ca/Al	Si/Al
	0	0.97	1.17	1.21
XPS	5	0.33	0.46	1.47
ToF-SIMS	5	3.2	1.3	0.35
XPS	20	0.42	0.55	1.32
ToF-SIMS	20	3.2	1.2	0.35
XPS	180	0.3	0.42	1.3
ToF-SIMS	180	2.9	1.2	0.35

BFS1- 0.1 M NaOH

	Time	Ca/Si	Ca/Al	Si/Al
	0	0.97	1.17	1.21
XPS	5	0.52	0.72	1.4
ToF-SIMS	5	8.3	2.2	0.3
XPS	20	0.6	0.8	1.33
ToF-SIMS	20	7.7	2.1	0.3
XPS	180	0.55	0.85	1.54
ToF-SIMS	180	6.4	2.3	0.38



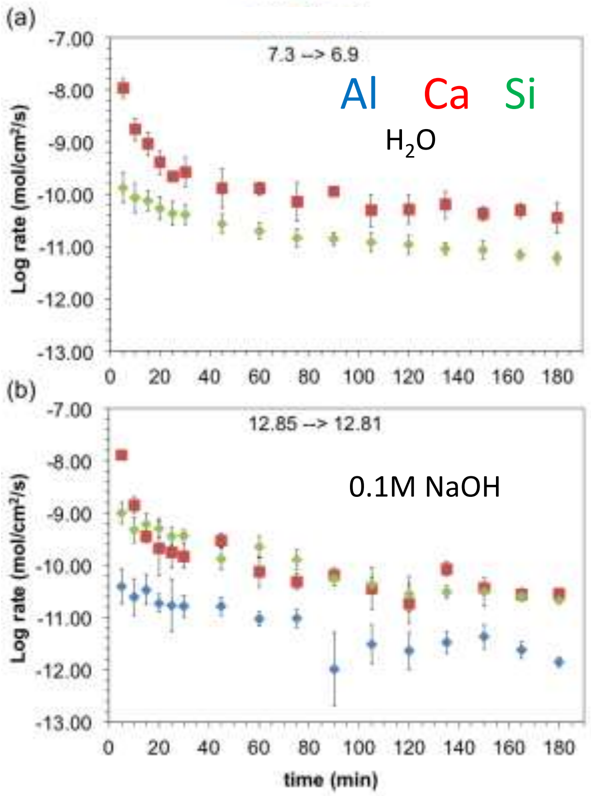


Possible compositional profile with depth in near surface region of the dissolving glass (e.g. Ca/Si) after 5 minutes exposure to activator

- Average compositions by ToF-SIMS and XPS indicated over respective penetration depths
- This imposes ratio distributions to satisfy averages over different length scales.
- Ca/Si, Ca/Al and Si/Al ratios collectively indicate a concentration of Ca at the surface and an excess of Si in the sub-surface
- Results are consistent with Ca and Al migration to the surface and/or precipitation of a new phase
- Although only semi-quantitative, the compositional profile is similar at 5 and 180 mins in water….
- …..but different in NaOH

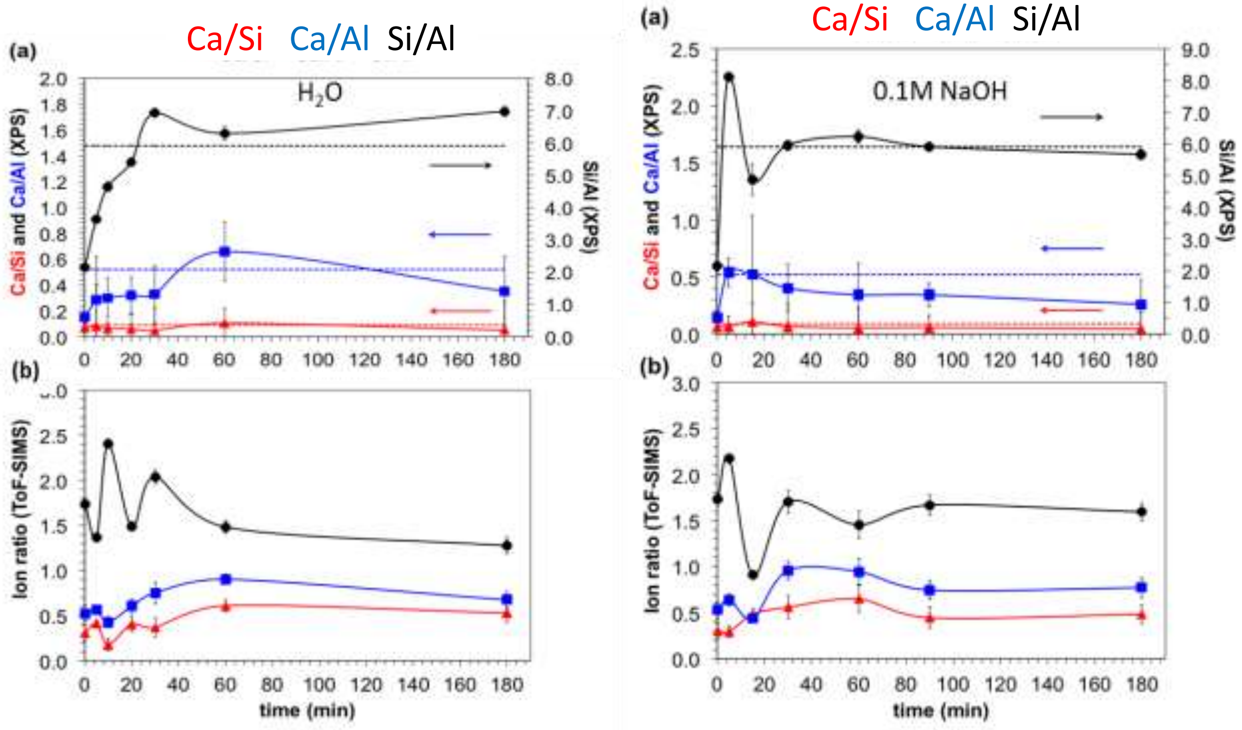
Surface analysis of solids – ion ratios relative to pristine glass (FA)

Solution



Normalised elemental fluxes ($mol/cm^2/s$) over time for FA

Solid



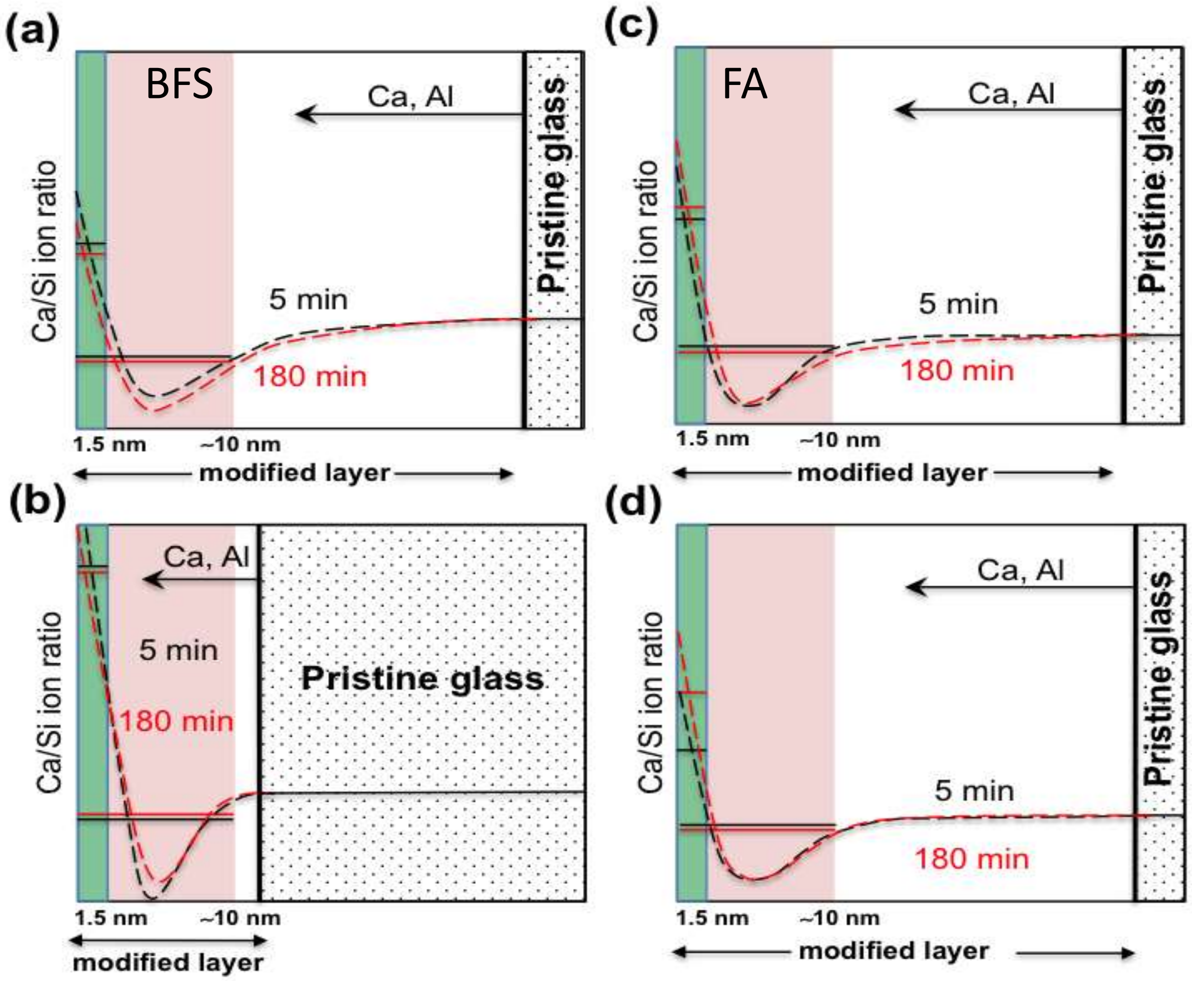
Ion ratio plots for FA. Data are from XPS (a) and ToF-SIMS (b) analysis. Dashed lines across the graph represent the relevant ratios in the pristine glass.

- Solution data indicated an immediate preferential release of Ca on exposure to activator but less significantly than with BFS
- Initial XPS data give Ca/Al and Ca/Si lower than that for the pristine glass, indicating Si and Al enrichment – particularly in water.
- ToF-SIMS indicates a slight increase with time, suggesting a response to the re-adsorption of Ca indicated from solution data

Surface analysis of solids – ion distribution after exposure

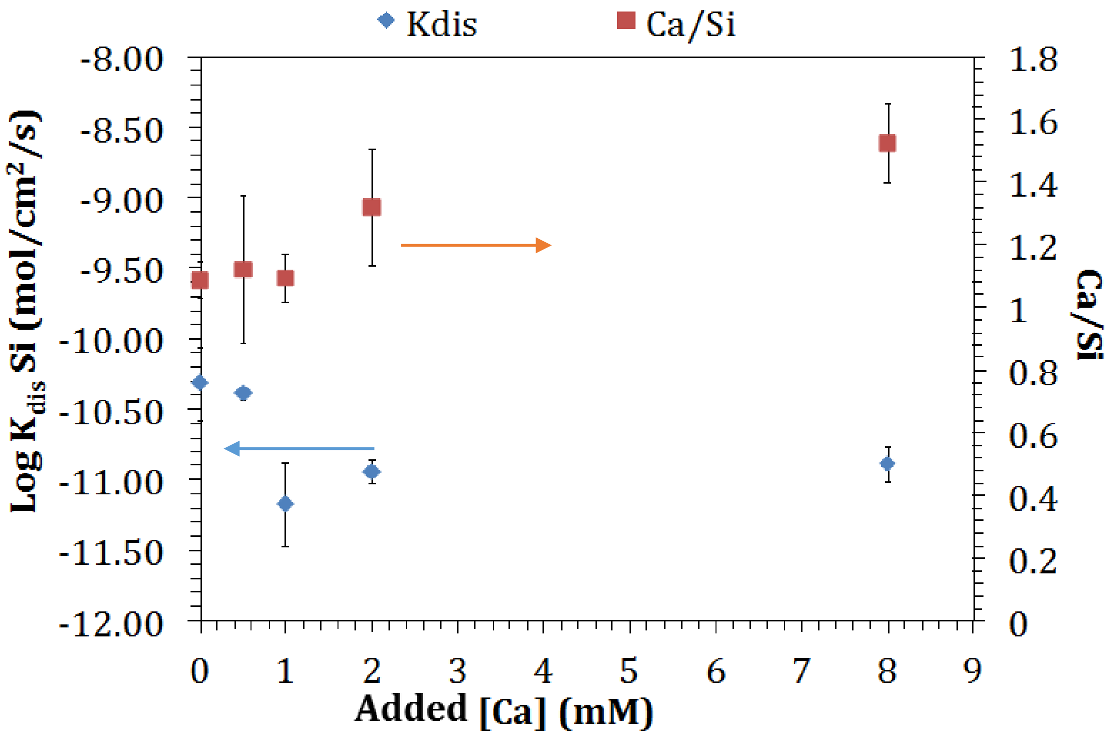
H_2O

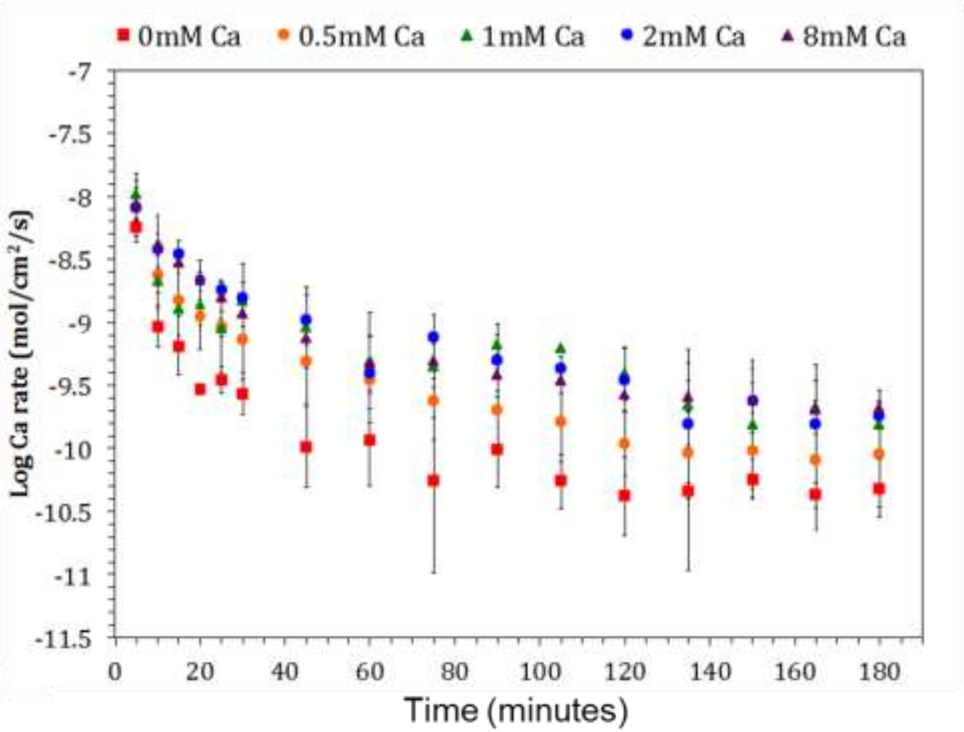
0.1M NaOH



- In general, similar profiles are obtained for FA glasses as were obtained for BFS. Note the different modified layer thickness in BFS compared with FA
- The semi-quantitative data suggest a possible reduction in the near surface gradient for FA than is observed in BFS, especially in NaOH
- This would be consistent with the reduced Ca content of FA and the consequent reduction in its influence associated with a surface ‘wash off’ effect
- This was less evident with BFS because of the more significant accumulation of Ca in the near surface of the BFS glass

Influence of added Ca to the solution on glass dissolution rate (BFS-H_2O)



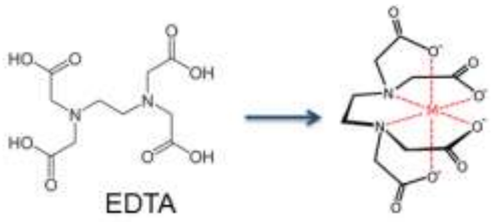


- Silicate dissolution rates are lowered as added [Ca] is increased; solubility of glass or influence of a passivating layer?
- Ca release rates *increase* on increase in added [Ca] – formation of C-(A)-S-H with increasing Ca/Si?
- EDS/SEM suggests Ca enrichment in near surface layer (up to 1 µm)

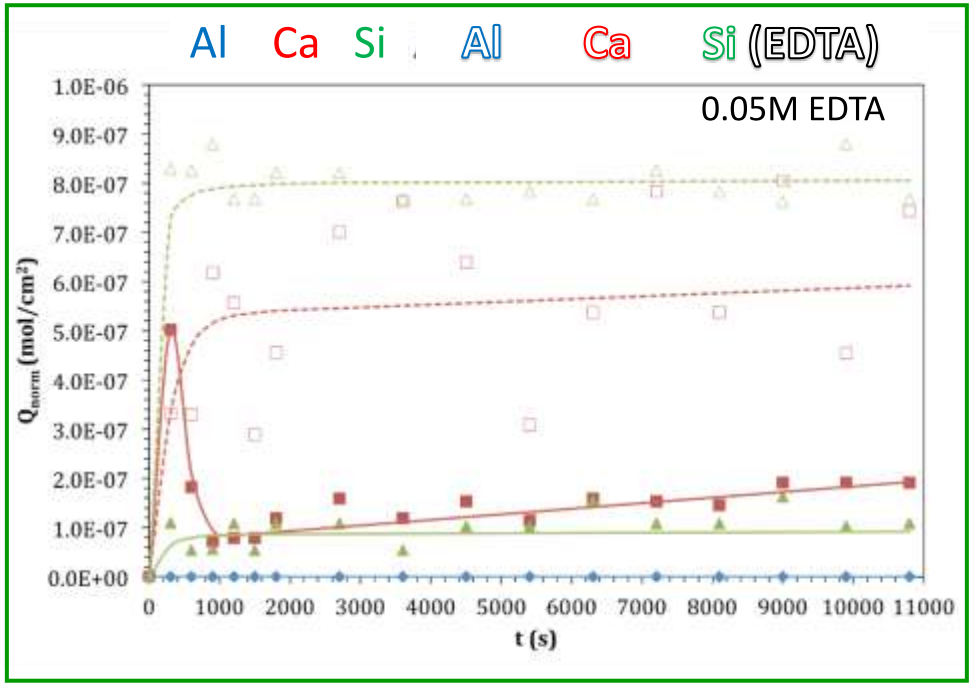
[1] Chave, T. *et al.* (2011). *Geochim. Cosmochim. Ac.*, 75, 4125-4139
[2] Utton, C.A. *et al.* (2013). *J. Nucl. Mater.*, 435, 112-122

Inhibiting Ca re-integration on the surface

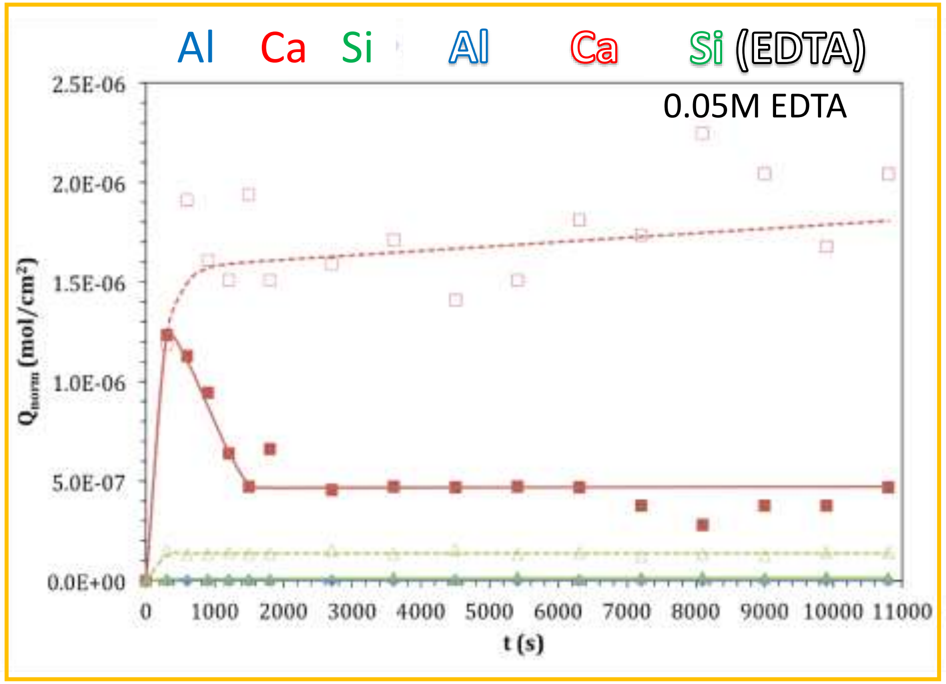
Ethylenediaminetetra-acetic acid (**EDTA**) is a powerful chelating agent forming a stable 1:1 complex with Ca



BFS1



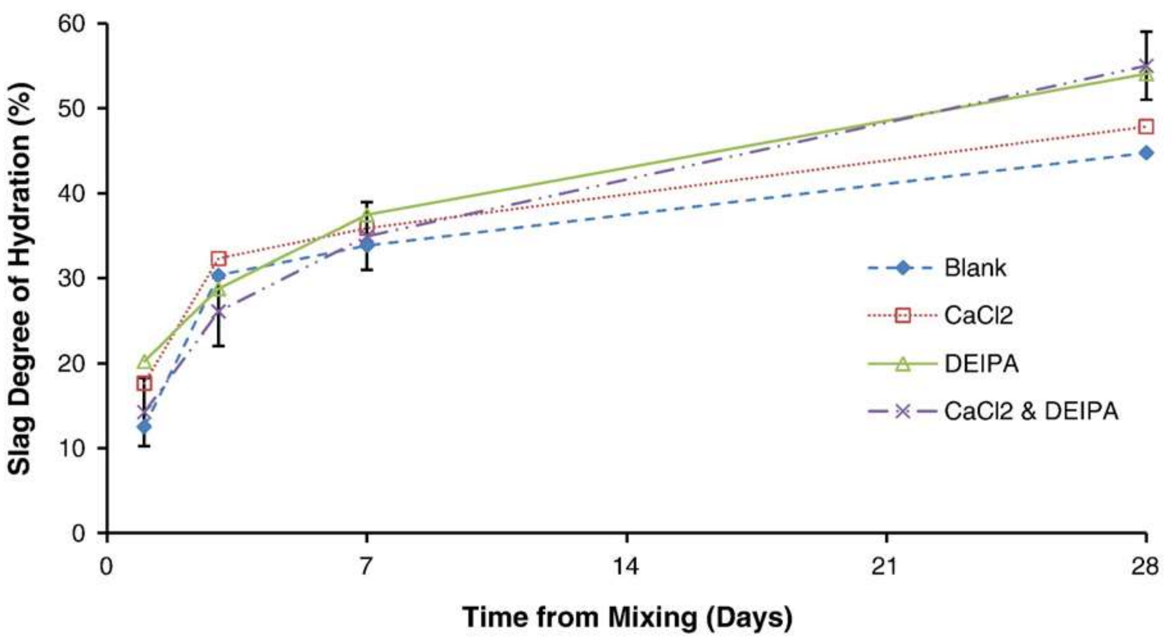
FA

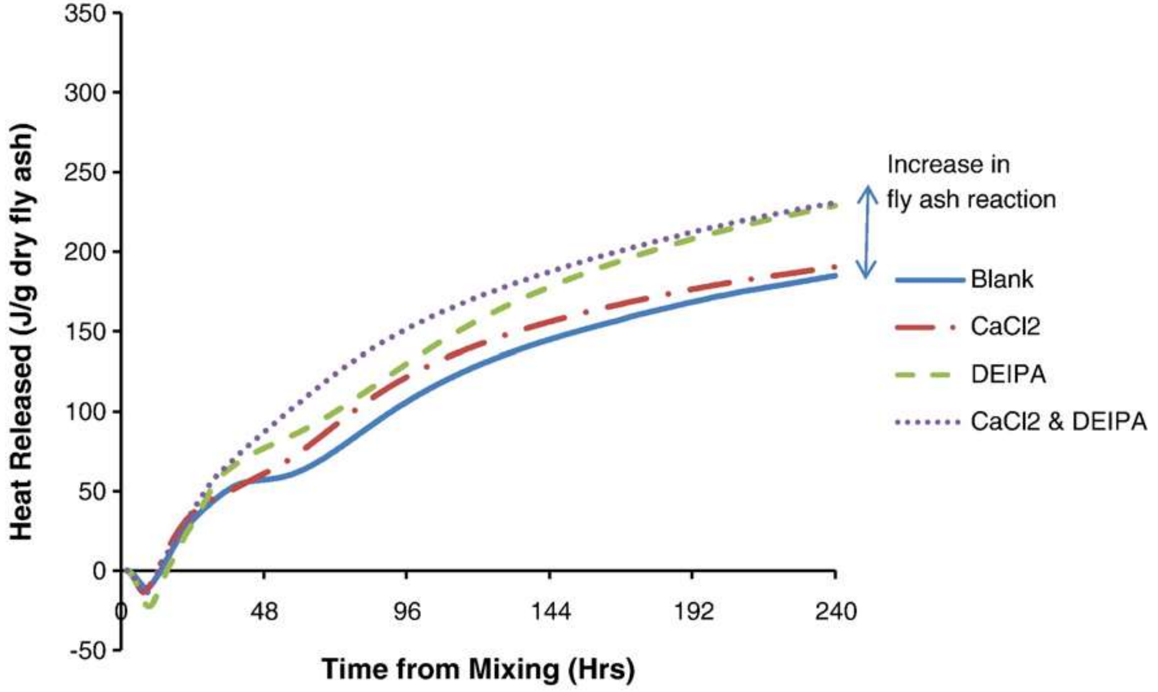


- No re-adsorption of Ca observed
- Si outputs are higher compared to solutions with no EDTA
  - inhibition of a passivating layer forming on the glass surface which favours Si release to solution
- Al retained in the solid phase (perhaps as gibbsite – pH 8)

Practical validation?

- the use of chemical activators (e.g.$CaCl_2$,diethanol-isopropanolamine (DEIPA) and other Ca salts) in blended cement systems

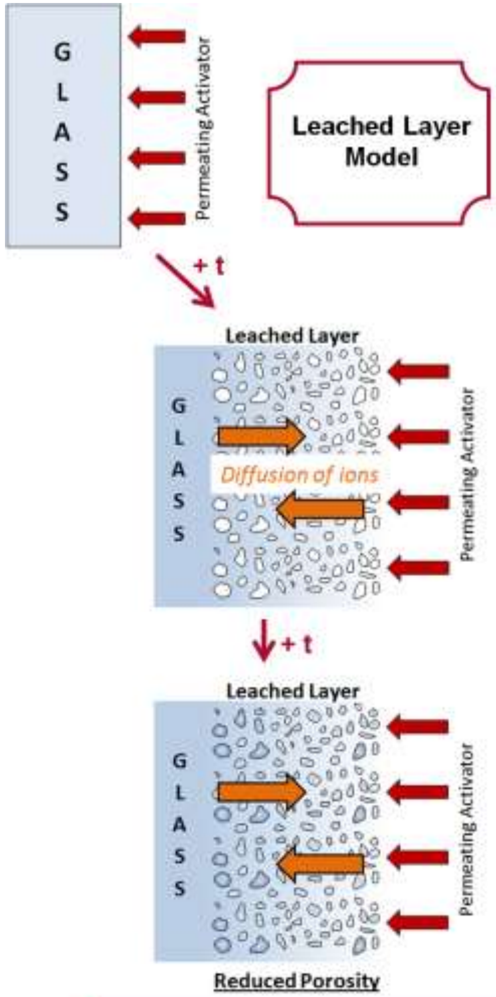




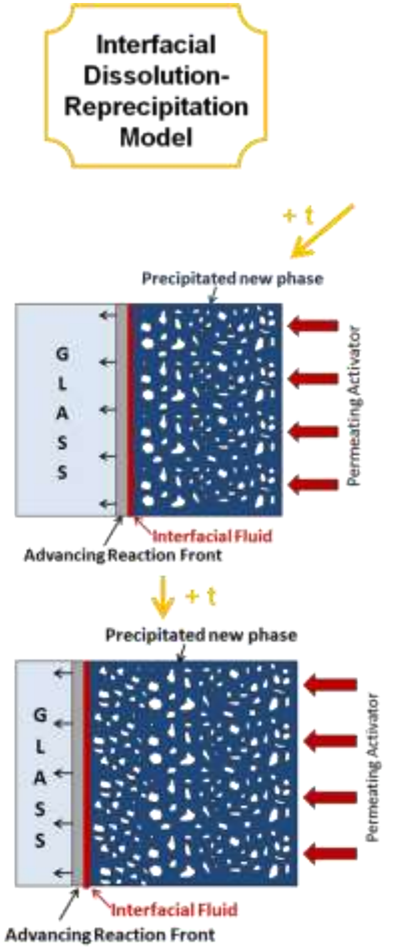
- same principle as EDTA – solubilising additives for Ca
- in these studies it’s hard to differentiate the effects of SCMs from those of cement
- the simplified system in our study would suggest that the inhibition of Ca re-adsorption on the glass surface results in a higher rate of glass dissolution

[1] Riding, K. *et al.* (2010). *Cement Concrete Res.*, 40, 935-946
[2] Bellmann, F. *et al.* (2009). *Cement Concrete Res.*, 39, 644-650
[3] Pacewska, B. et al. (2008). *J. Therm. Anal Calorim.*, 93, 769-776

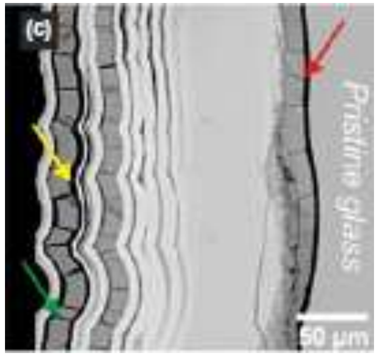
Dissolution Models



- Non-stoichiometric release of modifier cations leading to the formation of a chemically altered leached layer
- Kinetics is diffusion-controlled



- Congruent dissolution occurs at a single reaction front in a thin fluid film in contact with the pristine glass
- Kinetics is interface-controlled



Sodium borosilicate glass
90^{o}C/168 hours/pH 10

Dohmen, L., *et al*, *Int J App Glass Sci*, *4*(4), 357–370, (2013)

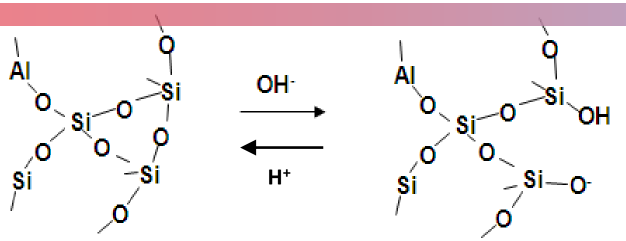
Influence of *local* chemistry on species reactivity

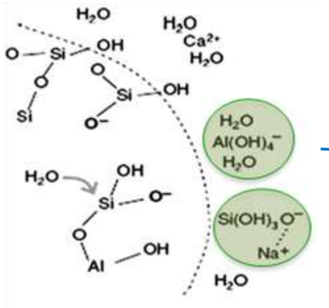
← *more acid*

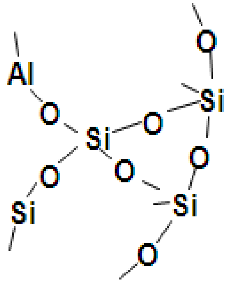
← *re-polymerisation*

network hydrolysis/dissolution →

more alkaline →



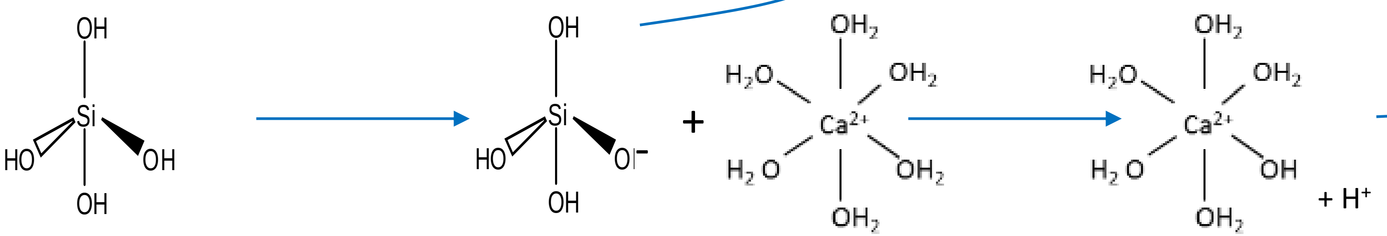


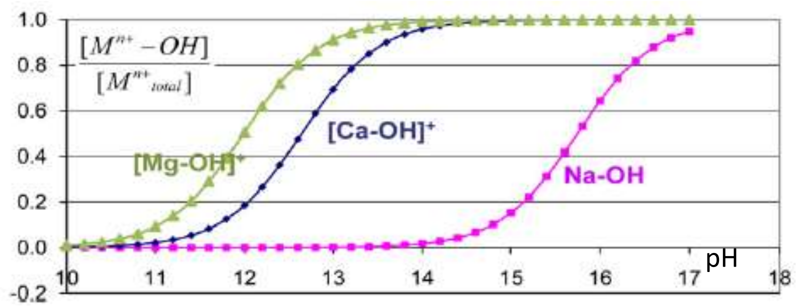


passivation

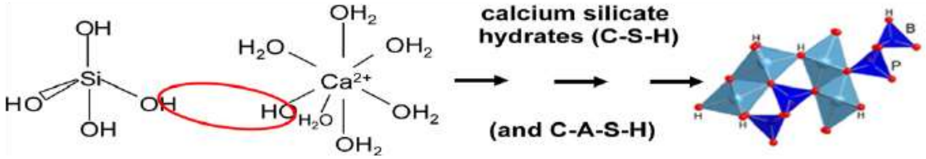
condensation

+ H^+ (matrix dissolution)





increasing silicate deprotonation with pH → surface adsorption of Ca → deprotonation of $Ca_{(aq)}$ at high pH →

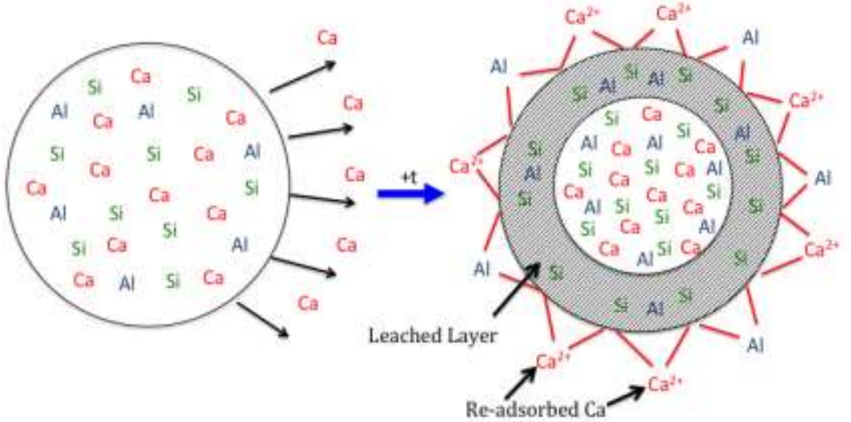


covalently bonded hydrate

Sharp, J. H., *et al*, (2010), *Adv Cem Res*, *22*(4), 195–202.
Gartner EM and Macphee, DE, (2011), *C&CR.*, 41, 736-49
Nicoleau, L., *et al*, (2014), *Cem. Concr. Res.*, *59*, 118–138.

Glass alteration - Summary

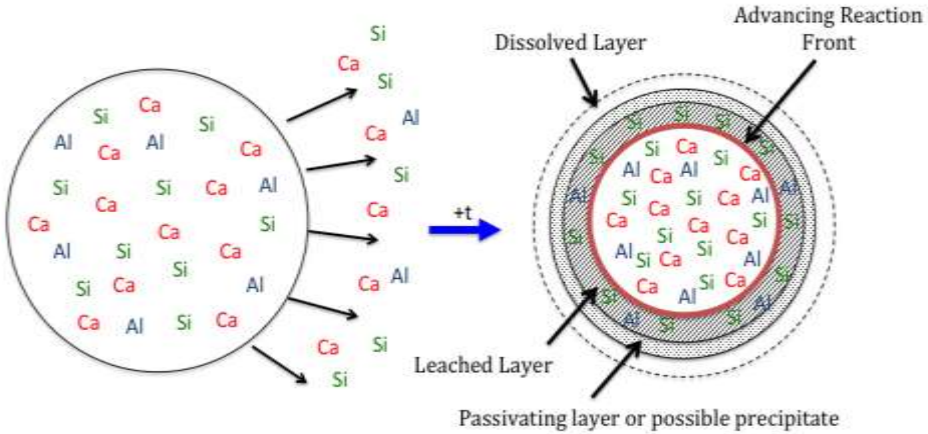
Near-neutral pH



- ion-exchange reactions override glass network dissolution, favouring the formation of a leached layer.
- The relatively low solubility of glass forming elements releases insufficient ion concentrations to precipitate new phases.
- surface re-structuring, possibly involving condensation of a partially hydrolysed Al-O-Si network, to provide surface binding sites for the adsorption of hydrated Ca^{2+} - reduction in aqueous Ca concentration

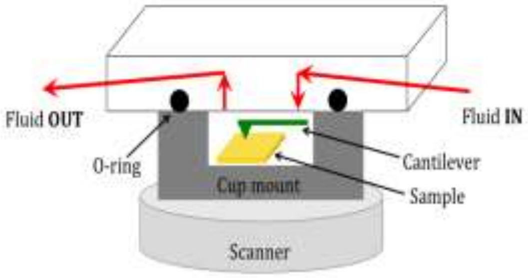
v.s.

Alkaline pH

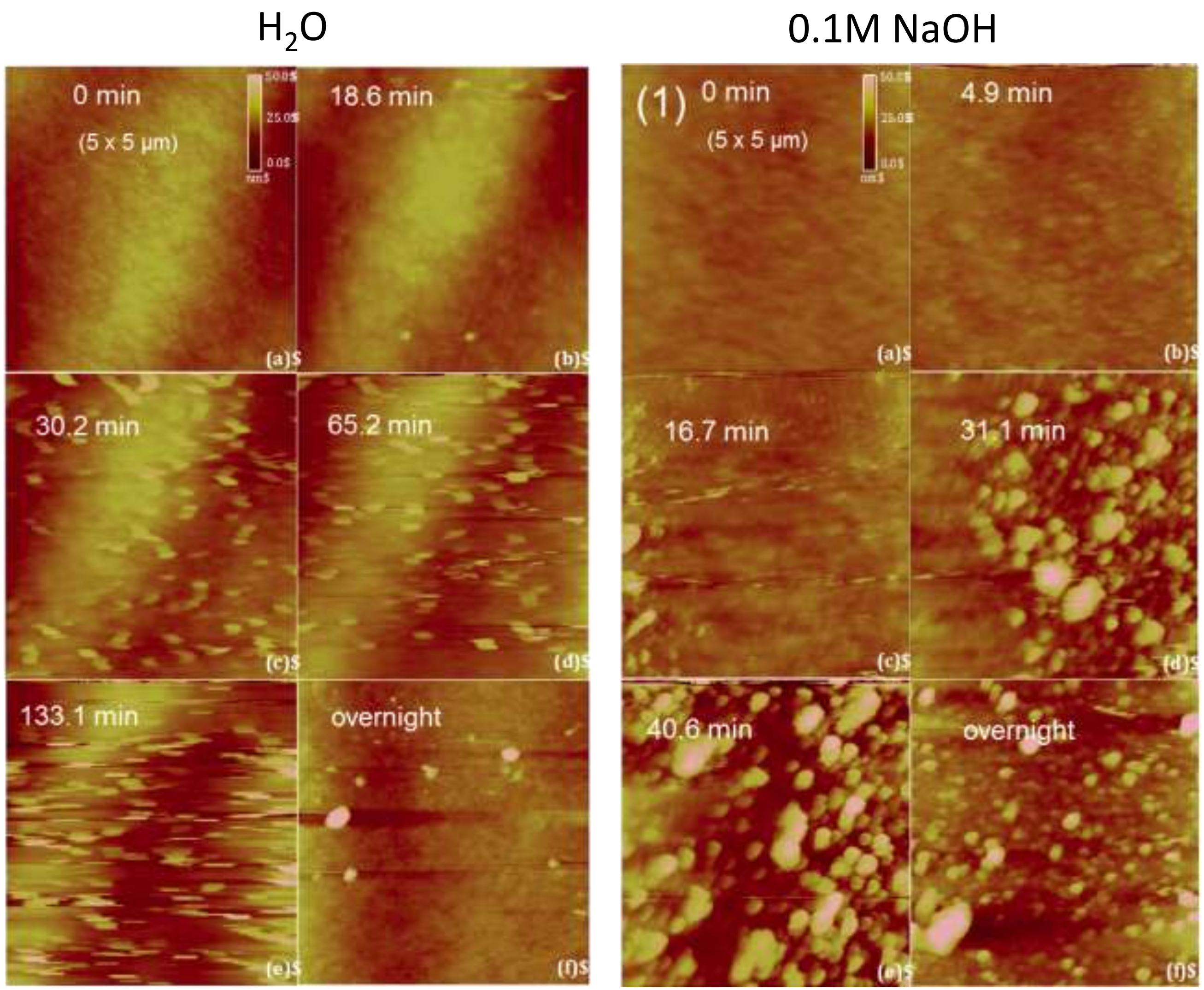


- network dissolution is increased with hydrolysis and ion-exchange processes occurring simultaneously, resulting in enhanced Si outputs to solution.
- At pH > 11 deprotonation of the hydrated Ca^{2+} enables it to coordinate with hydrolysed Si and Al species initialising condensation reactions by which precipitation of low Ca/Si C-(A)-S-H gels may occur.
- TOF-SIMS analyses indicate Al and Ca enrichment on the surface, which could be explained by the surface precipitation of a C-A-S-H phase or the modification of a silicate-rich surface by Al and Ca.

Significance to other surface characteristics - AFM studies



	Water	0.1M NaOH
Particle size (mm)	3 x 4 x 0.3	3 x 3 x 0.5
Exposure Time (m)	139	43.9

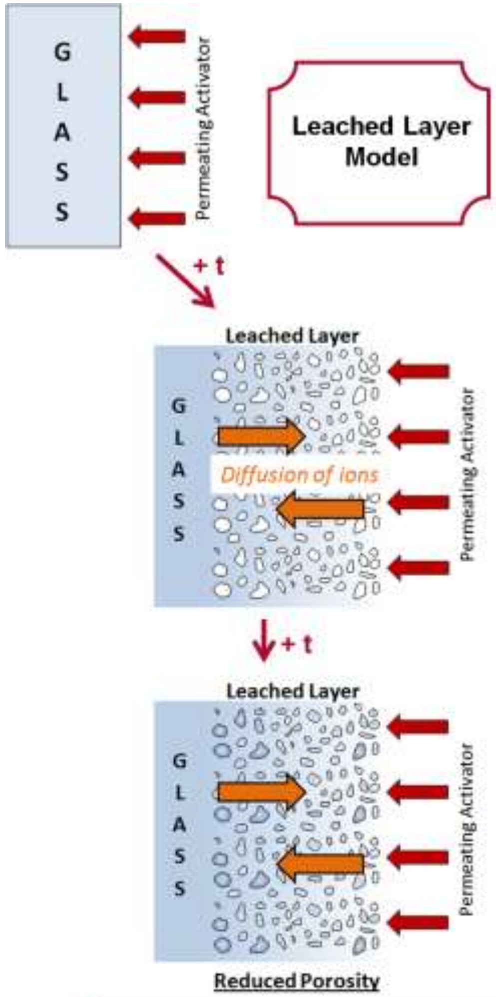

H_2O

0.1M NaOH

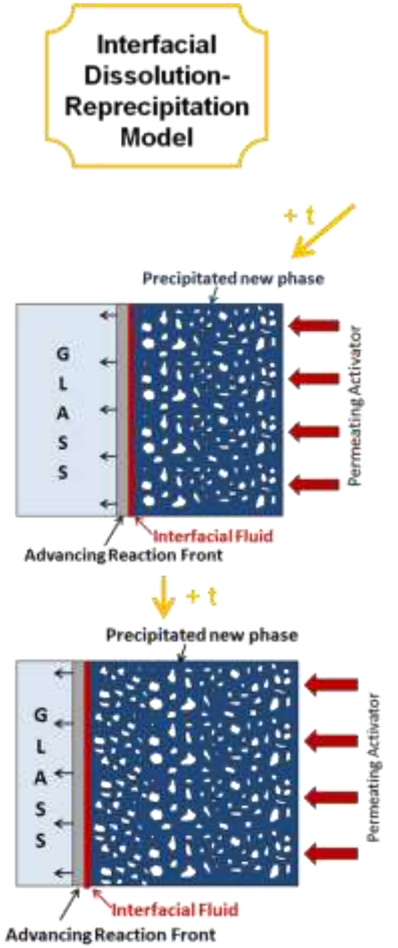
In-situ AFM height images obtained in contact mode from ground particulate BFS1 exposure to H_2O and 0.1M NaOH for various times

- Appearance of streaking and ‘particles’
- May be due to tip dragging of soft material
- Less streaking at longer ages → material hardening and becoming more firmly attached to the surface
- Effects appear more quickly with alkaline activator

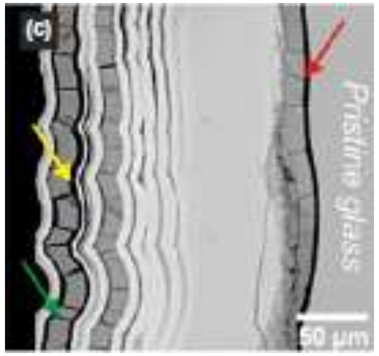
Dissolution Models



- Non-stoichiometric release of modifier cations leading to the formation of a chemically altered leached layer
- Kinetics is diffusion-controlled



- Congruent dissolution occurs at a single reaction front in a thin fluid film in contact with the pristine glass
- Kinetics is interface-controlled



Sodium borosilicate glass
90^oC/168 hours/pH 10

Dohmen, L., *et al*, *Int J App Glass Sci*, *4*(4), 357–370, (2013)

Conclusions

- Aluminosilicate glass dissolution profiles showed initial Ca concentration maxima in the first 30 min of exposure to the activating solution
- A subsequent reduction in Ca concentration suggests Ca-reincorporation in the reacting surface
- Surface specific analysis indicates Ca and Al enrichment at the surface, suggesting the formation of a Ca-modified aluminosilicate layer
- Differing chemistries are thought to be responsible for the Ca and Al re-integration on the reacting surface depending on the pH of the solution
  - near-neutral conditions favour Ca re-adsorption and surface condensation reactions
  - alkaline solutions favour Ca-reintegration via covalently bound phases
- AFM indicates the formation of an initially soft surface layer as well as particulate precipitates of nanometre dimensions from very early exposure times. A stiffening of the surface layer is evident with time in water, supporting a dissolution-reprecipitation mechanism for SCM reactivity.

Conclusions

- Dissolution rates are lowered when Ca concentrations in the activating solution are increased, supporting the concept of a Ca-modified passivating layer.
- Ca reabsorption is suppressed in the presence of EDTA leading to higher aqueous silicate release rate – higher glass dissolution rates.
- The short-term dissolution behaviour may account for the hydration behaviour of BFS in blended cements/concretes occurring over longer timescales

Acknowledgements

Andrew and Christine Putnis, University of Münster — AFM with reaction cell
Jørgen Skibsted, Morten Foss, John Hansen, Aarhus University — XPS, TOF-SIMS, NMR
Karen Scrivener, EPFL — DSC
NANOCEM

Thank you for your attention.

Kings College, Old Aberdeen