Solution controlled dissolution: dissolution kinetics of synthetic slag glasses

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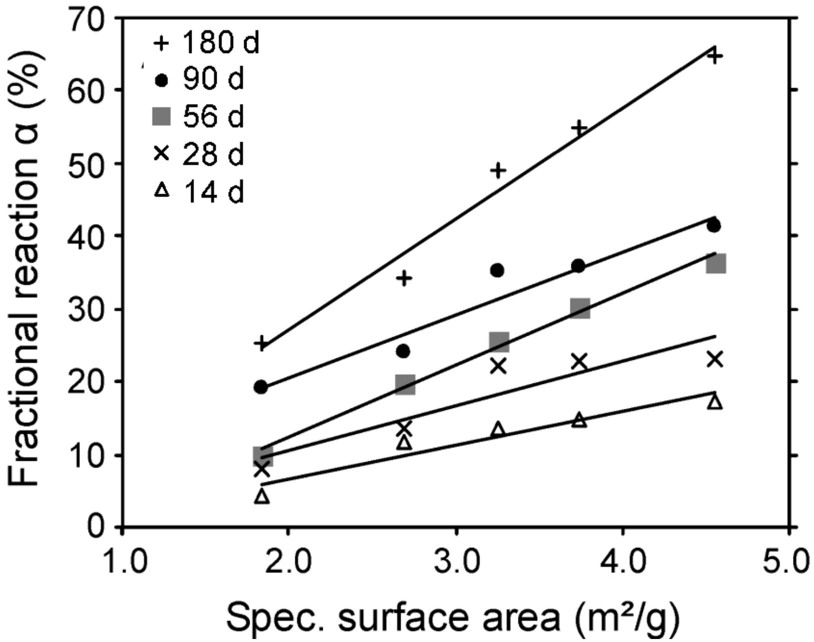
Introduction

- What determines the pozzolanic reactivity of a material?
  - Some data….



Consumption of CH by quartz samples of different fineness (CH: Q = 1:1, 40 °C, w:s 1:1)

Introduction

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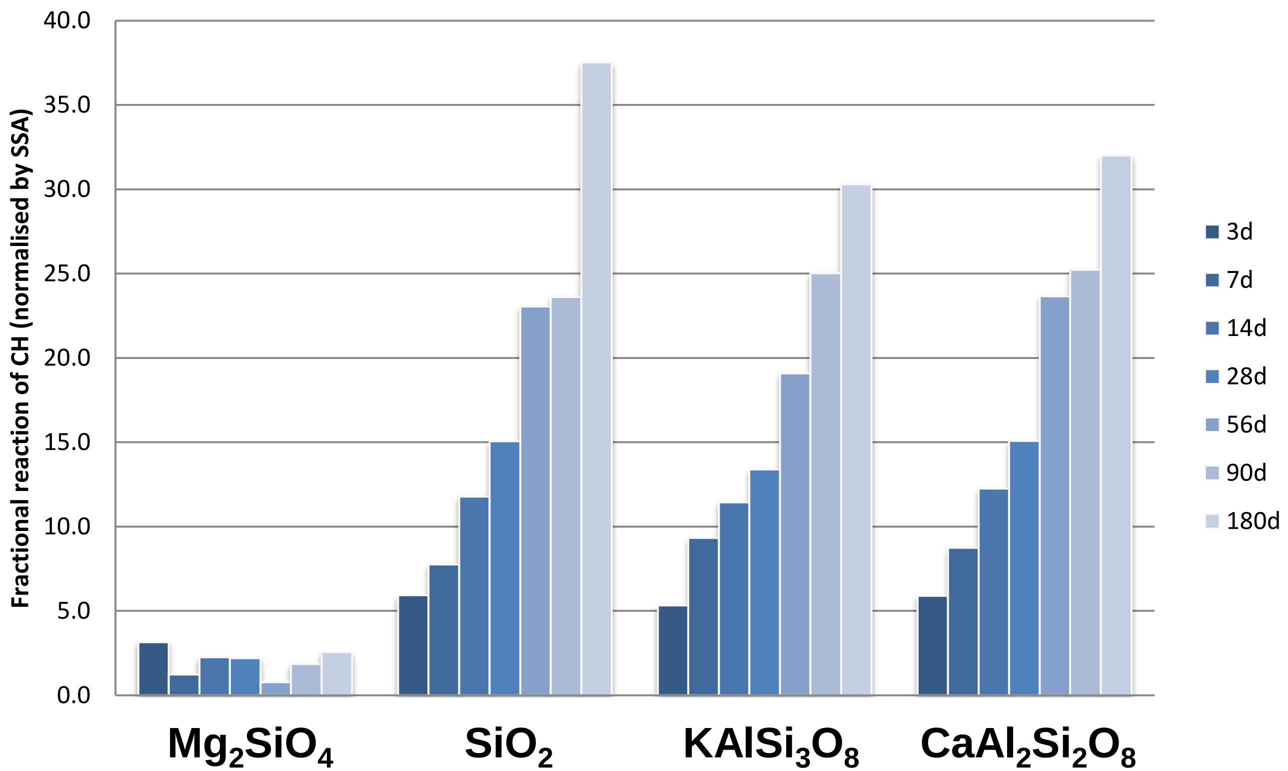
  - Some data….



Consumption of CH by pure mineral standards
(CH: M = 1:1, 40 °C, w:s 1:1)

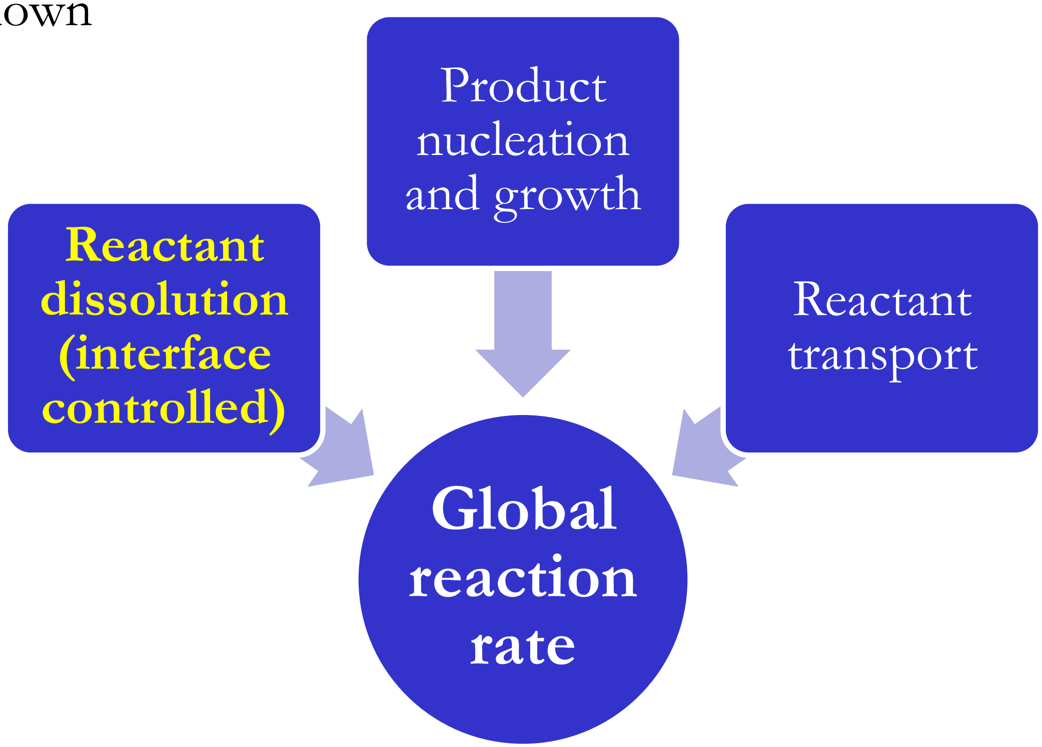
Rate controlling mechanisms

$$\underset{\textbf{1, 4}}{SCM} + \underset{\textbf{2}}{water} \ (+X^{m+}) \xrightarrow{\text{pH, T}} \underset{\textbf{3}}{hydration\ products}$$

1. Interface dissolution
2. Water availability
3. Space filling of reaction products
4. Diffusion through leached layer or reaction product layer

Rate controlling mechanisms

- Dissolution and precipitation processes are simultaneous
- Rate control depends on properties of reactants and hydration products
  - e.g. Alite hydration: rate control of main reaction by N & G
  - Reaction mechanisms and rates of glassy phases in solutions largely unknown



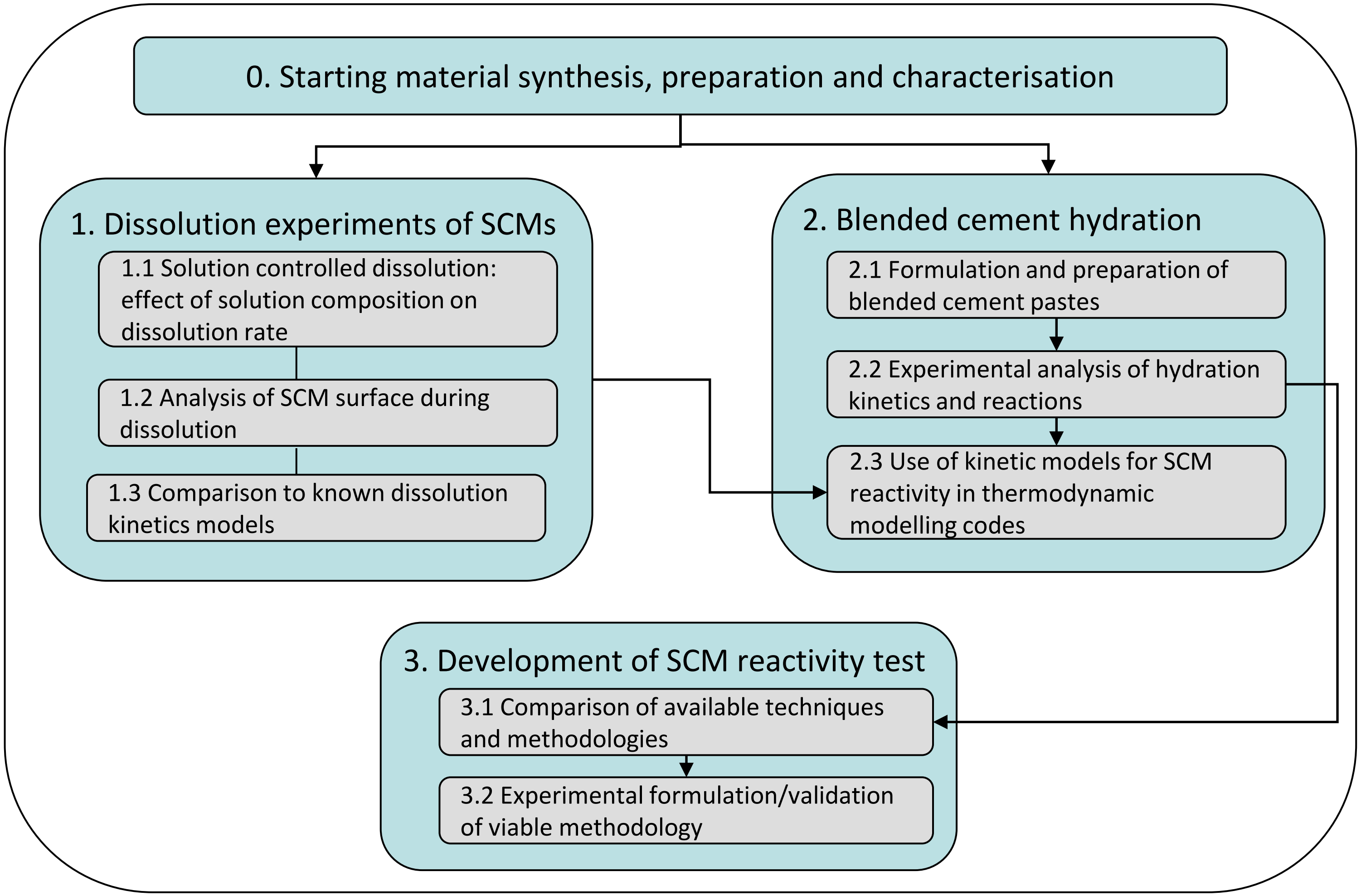
Lines of research

- Can SCM dissolution rates be directly related to reactivity?
  - Assuming that:
    - Water/space is available
    - Dissolution occurs far-from-equilibrium
    - Diffusion of reactants is not rate-controlling

- Control of SCM composition on reactivity/dissolution rates
  - Variation of polymerization degree (Ca/Al+Si) and Al/Si of synthetic glasses

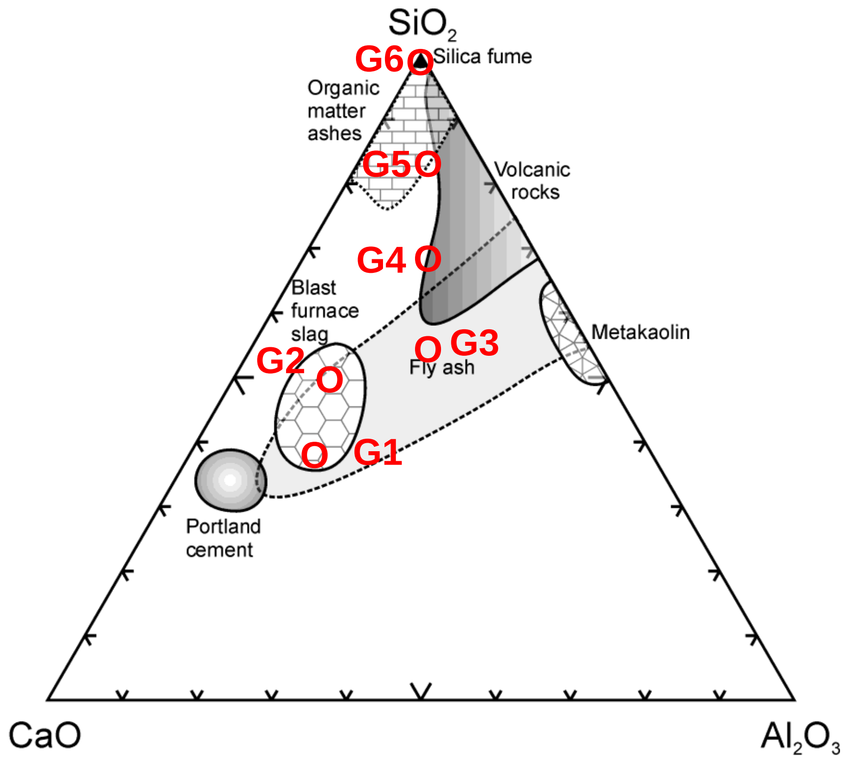
- Control of solution composition on SCM reactivity
  - Al-inhibition
  - Ca, Si activity
  - Solution saturation

Experimental scheme



Materials

- Synthetic glasses (CaO-SiO_2-Al_2O_3)



- SCM-types: BFS, FA, natural pozzolans, SF

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Glass synthesis and preparation

Glass synthesis

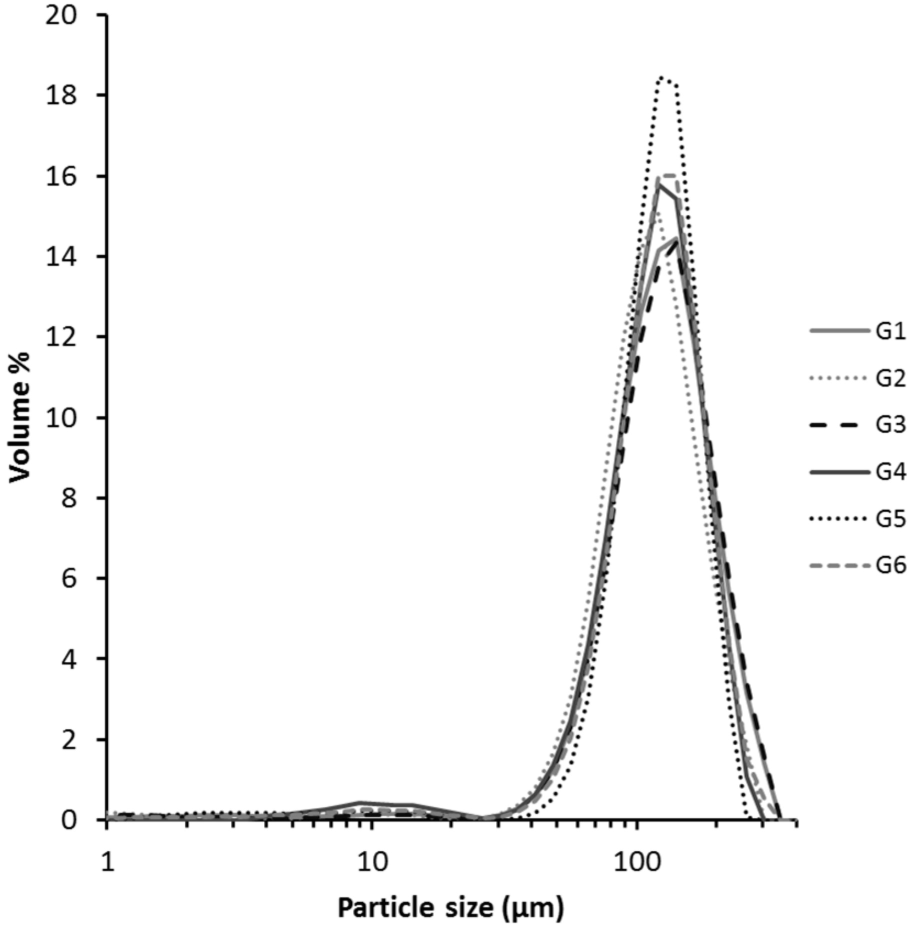
- Mixing of reagent-grade $CaCO_3$, Al_2O_3 and SiO_2 in ethanol suspension in a ball mill for 4h
- Pelletising of evaporated powders
- Firing at 1600 C for 4h
- Distilled water quench
- Drying at 60 C

Sample preparation for dissolution experiments

- Hand grinding + dry sieving of 50-125 μm fraction
- 5 cycles of ultrasonic cleaning in aceton and water
- Drying at 60 C

Glass synthesis

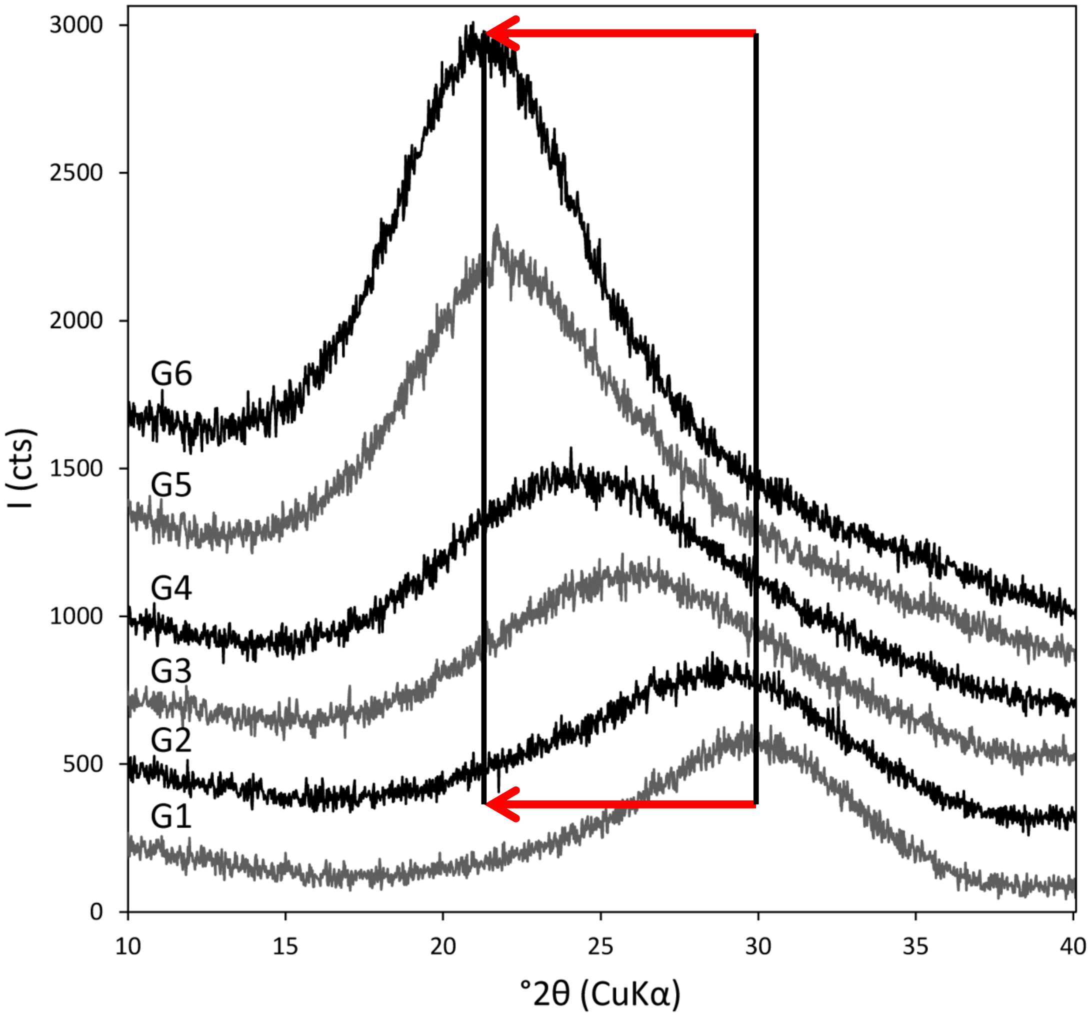
- Glass characterisation: PSD, BET



Glass type		Chemical composition (wt%)			BET	Grain size
		CaO	Al_2O_3	SiO_2	(m^2/g)	d_{50} (µm)
G1	BFS	43.0	19.0	38.0	0.0091	114.7
G2	BFS	36.0	16.0	48.0	0.0151	107.2
G3	FA	20.0	37.0	43.0	0.1004	116.0
G4	FA	15.0	27.0	58.0	0.0501	113.2
G5	NP	6.5	11.5	82.0	0.0548	115.2
G6	SF	0.0	0.0	100.0	0.0440	107.1

Glass synthesis

- Glass characterisation: XRD



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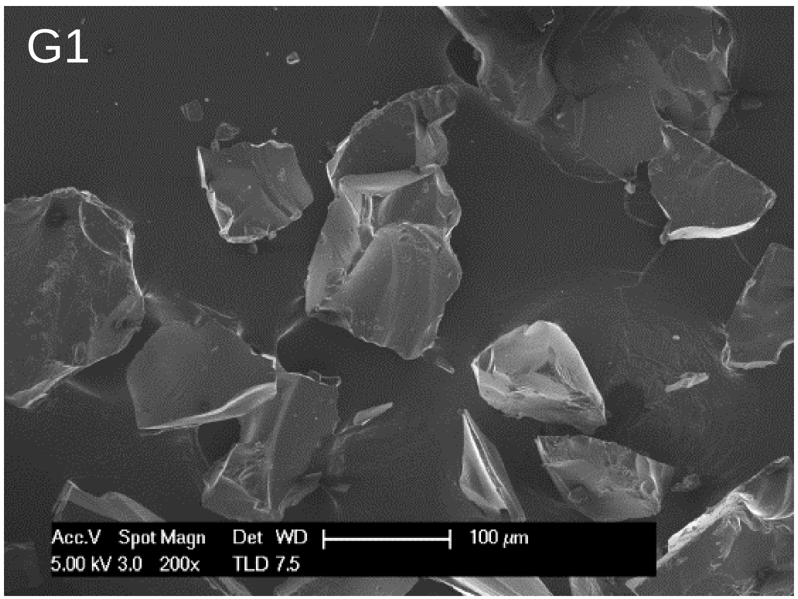
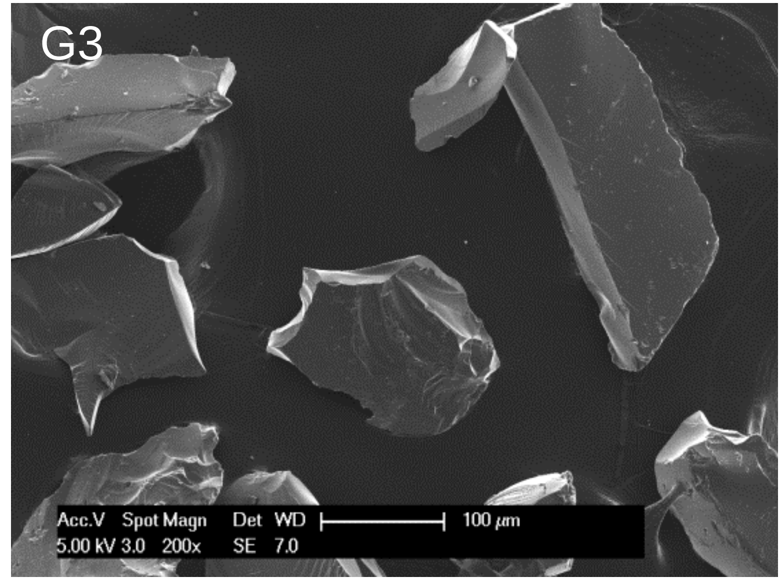
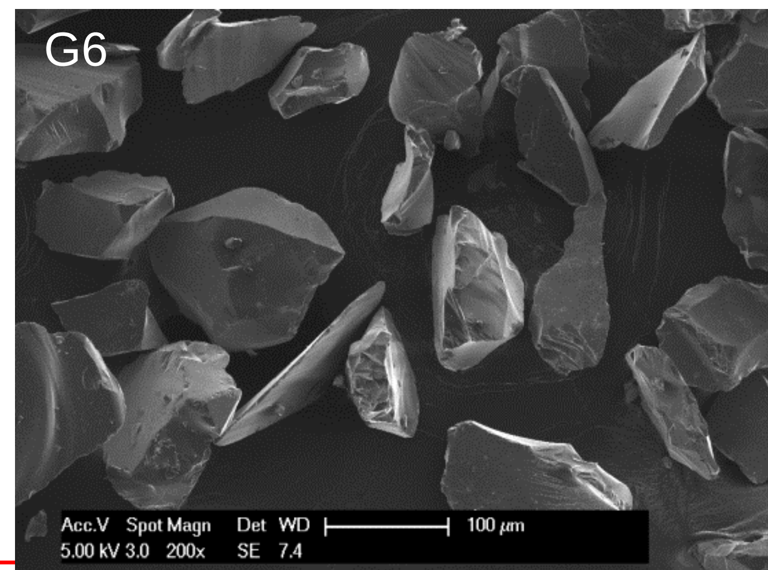
Glass synthesis

- Glass characterisation
  - SEM

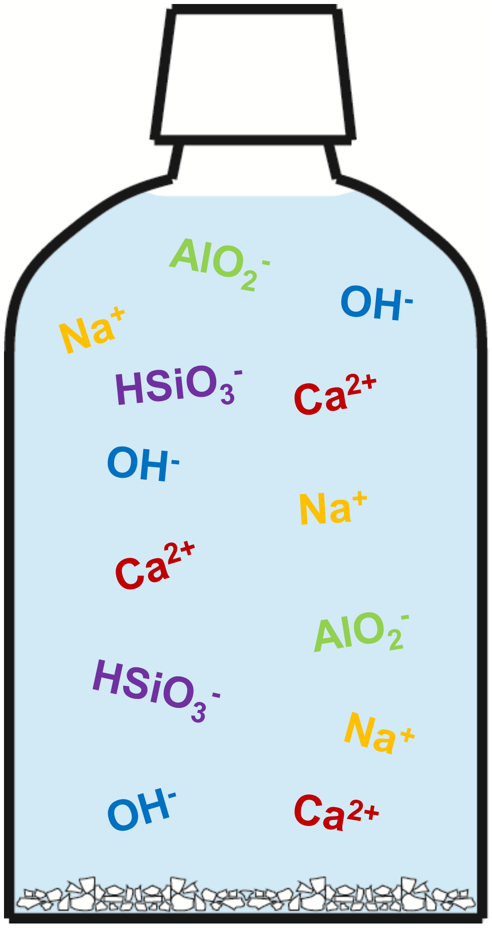






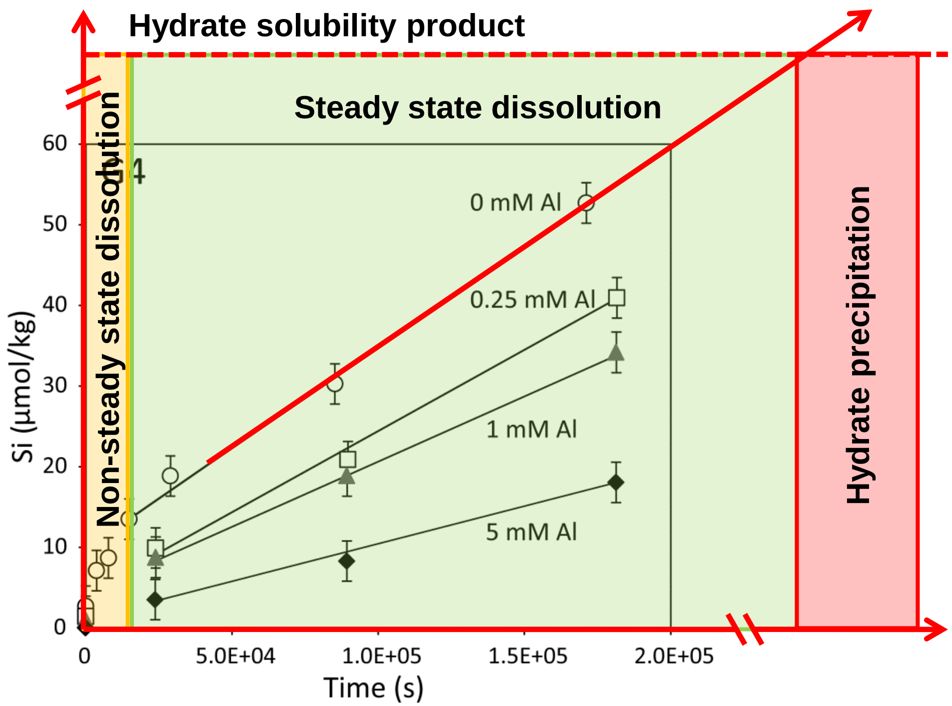
Dissolution experiments

- Experimental setup
  - Batch reactor: closed system
    - Fixed T (20 C)
    - Glass SA to solution volume: SA/V = 0.1-1 cm^{-1}
  - Extended time before hydrate precipitation
  - Sampling at selected time intervals
  - Variable solution concentrations (pH, solutes,…)
- Solution preparation
  - Ultrapure H_2O, reagent grade solutes
  - Boiling and N_2 purging of H_2O to remove CO_2
  - pH 13 + variable concentrations of Al, Ca, Si, SO_4,…



Dissolution experiments

- ICP-OES measurement of release of glass components
  - Matrix matched standards, concentrations down to 2-3 μM measurable
- Dissolution rate calculation



- Glass dissolution rates calculated from linear increase in indicator element concentration (X) over time (t) during steady state regime
- $r_{+,X} = \frac{d(X)}{\Delta t} \nu_X / (m\ A\ V_{soln})$
- ν_X is the mole fraction of the indicator element in the glass

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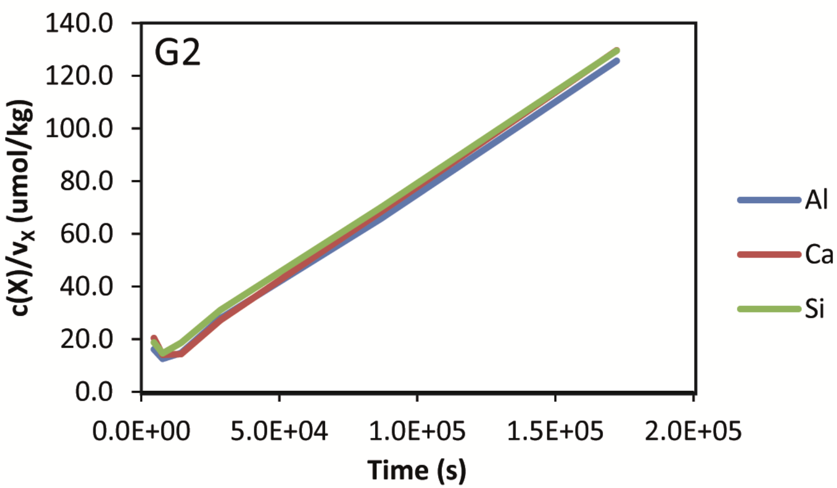
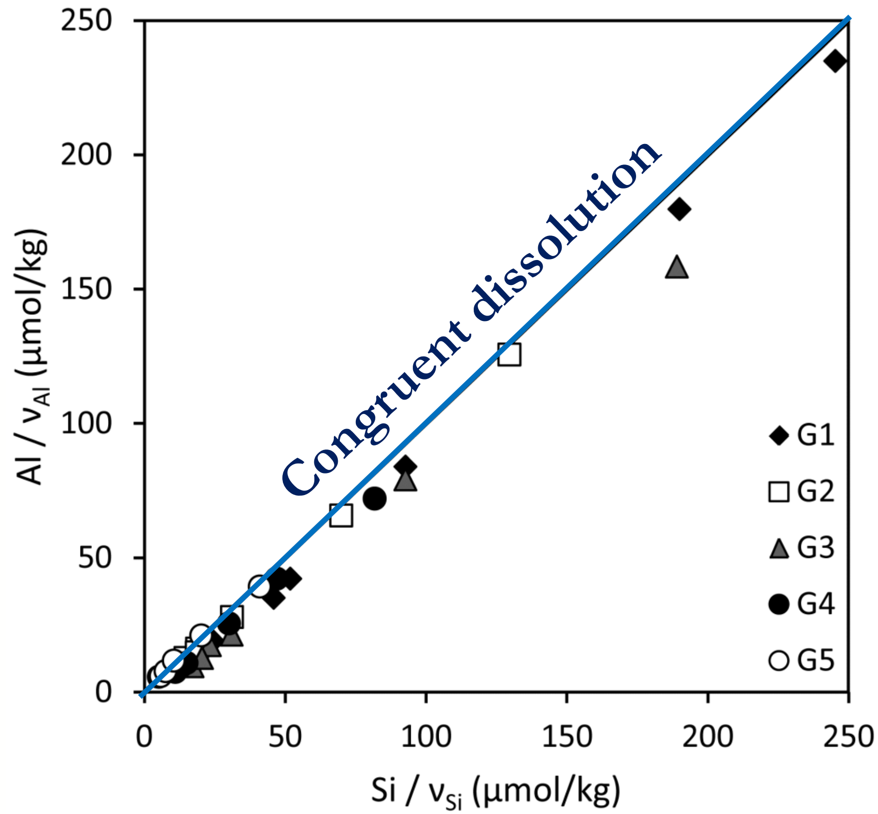
Dissolution experiments

Incongruent or congruent dissolution?

- **Initial non-steady state dissolution** appears to be **congruent**
- **Steady state dissolution** of the glasses is **congruent**, no indication for preferential leaching of glass components
- Si, Al (and Ca) can be used as indicator elements for dissolution rate calculations





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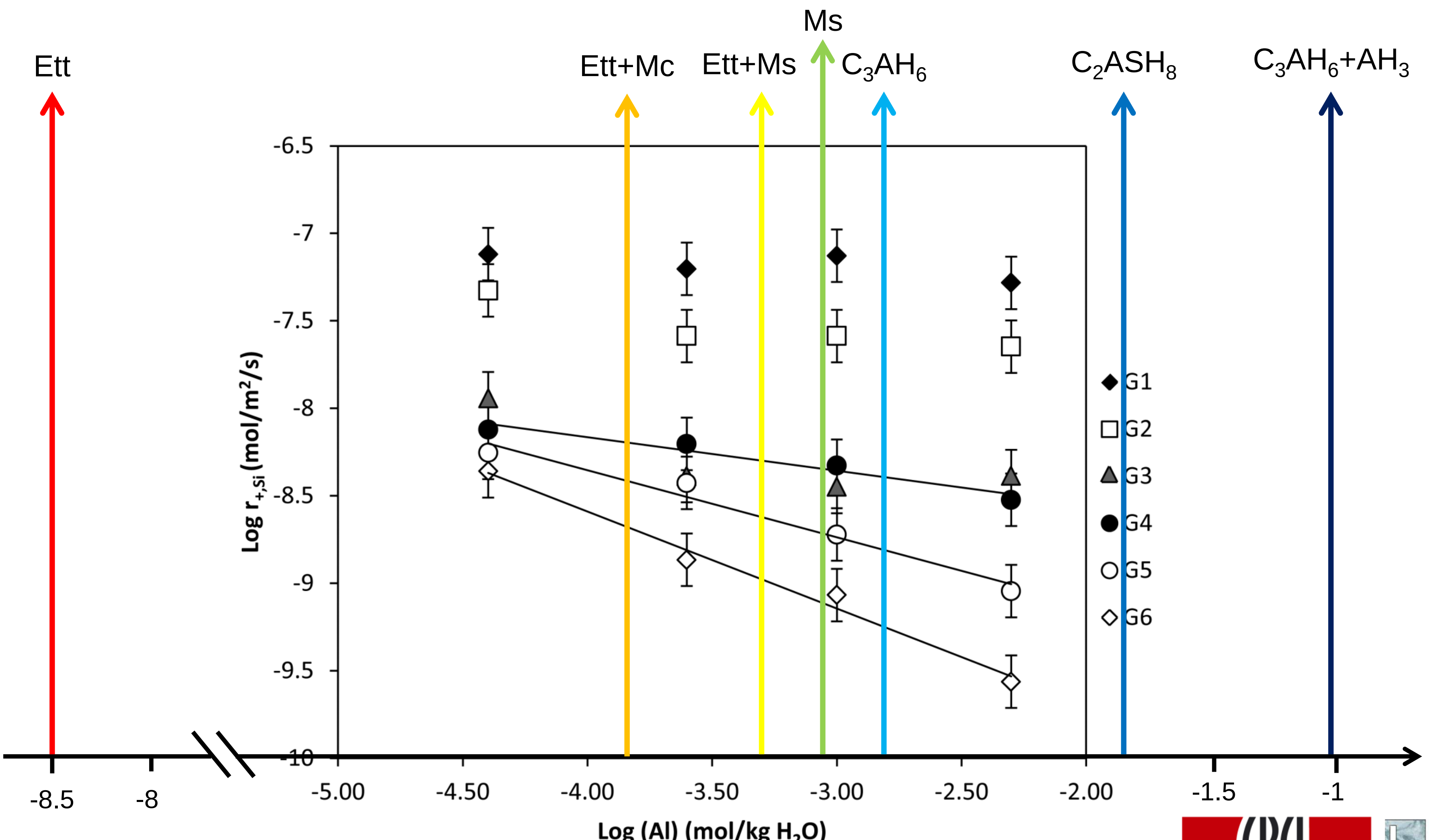
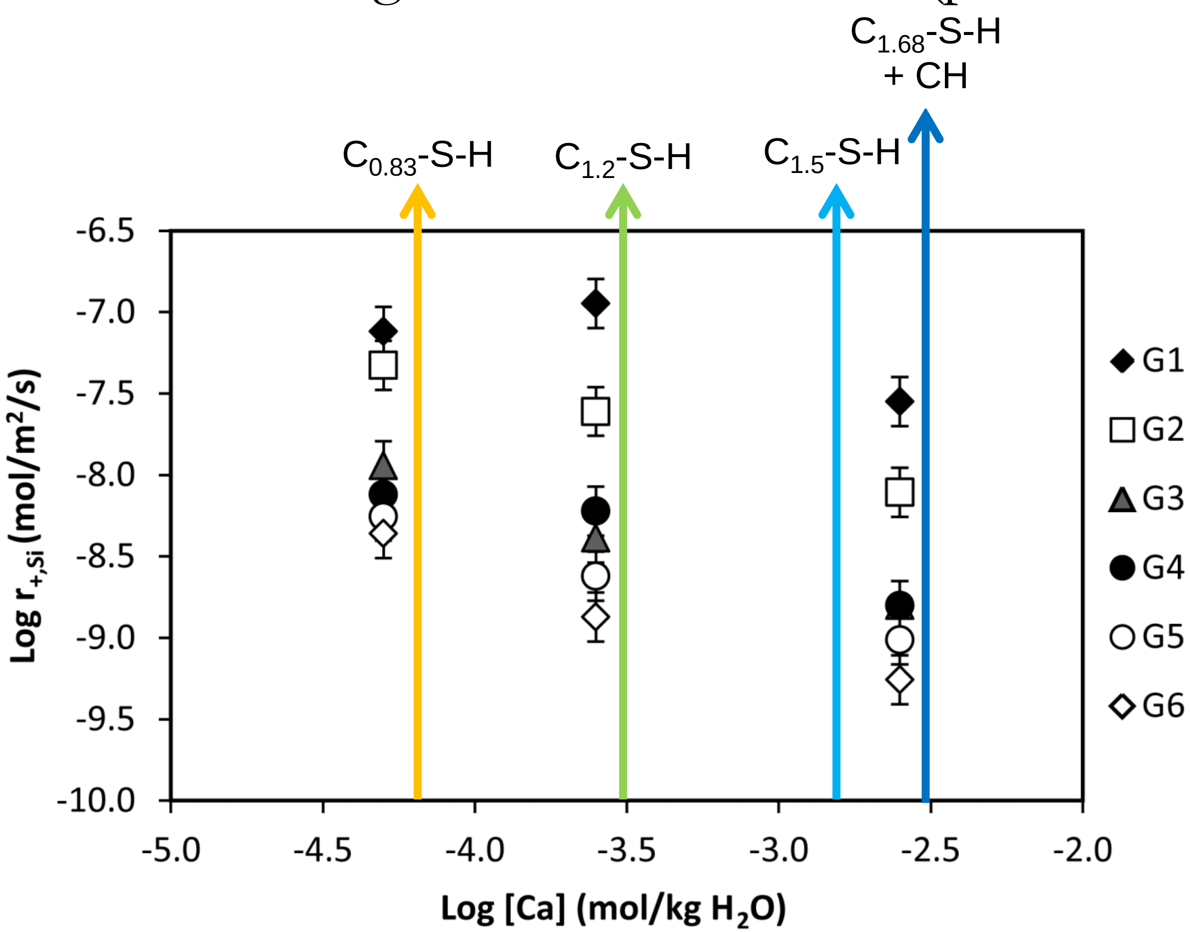
Dissolution experiments

- Effect of Al on glass dissolution rates (pH 13, NaOH)



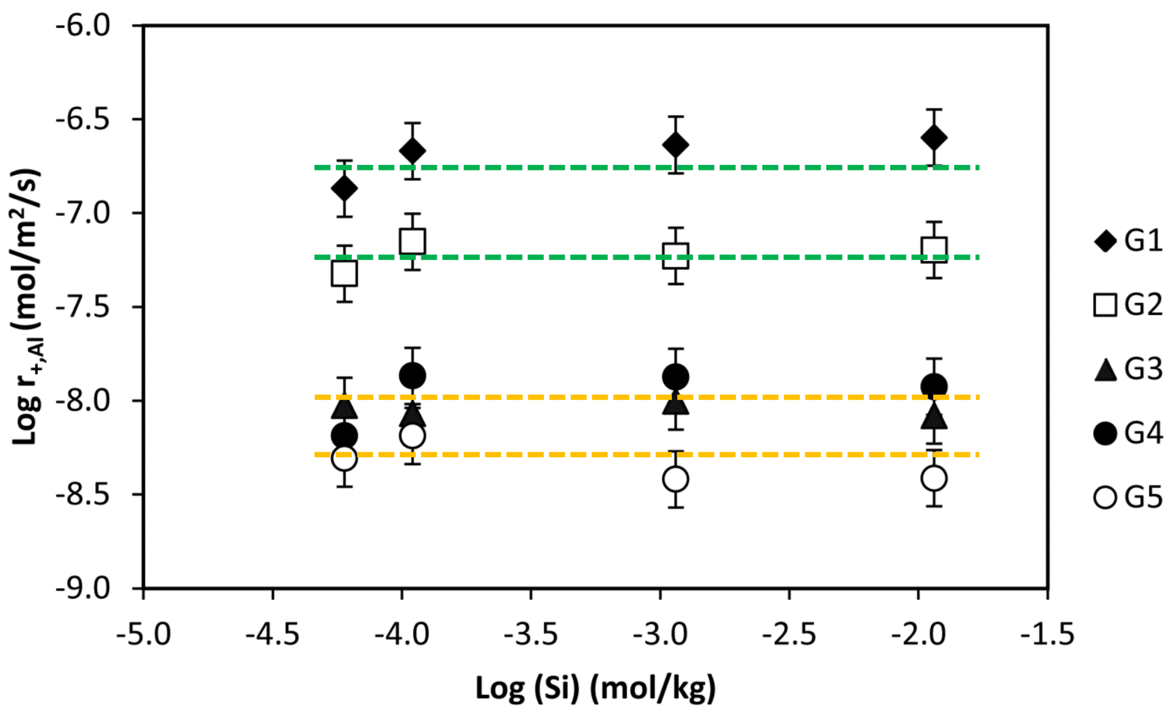
Dissolution experiments

- Effect of Ca on glass dissolution rates (pH 13, NaOH)



Dissolution experiments

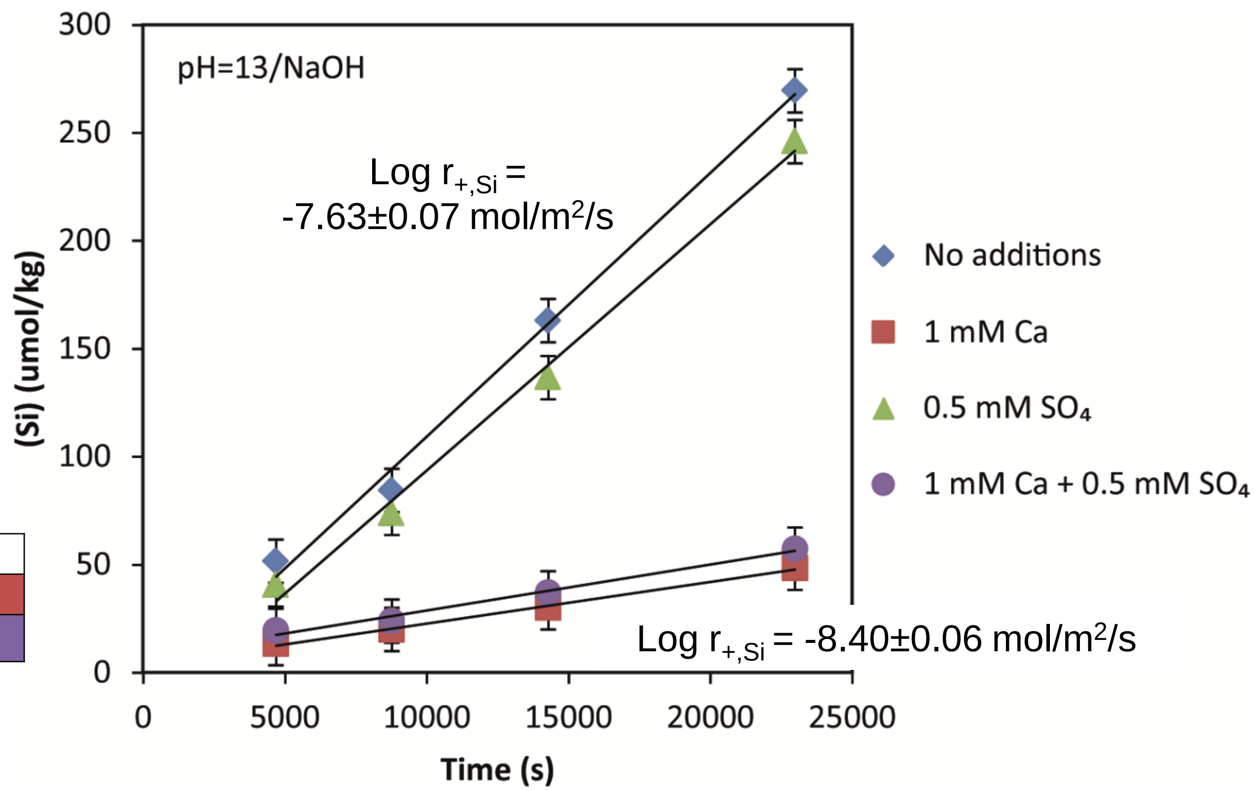
- Effect of Si on glass dissolution rates (pH 13, NaOH)
  - No retardation due to increase in Si concentrations



Dissolution experiments

- Effect of solution composition on MK dissolution rate
  - 1 mM Ca strongly decreases dissolution rates
  - 0.5 mM SO_4 does not affect MK dissolution rates

pH 13/NaOH	-	1 mM Ca
-	A	B
0.5 mM SO_4	C	D



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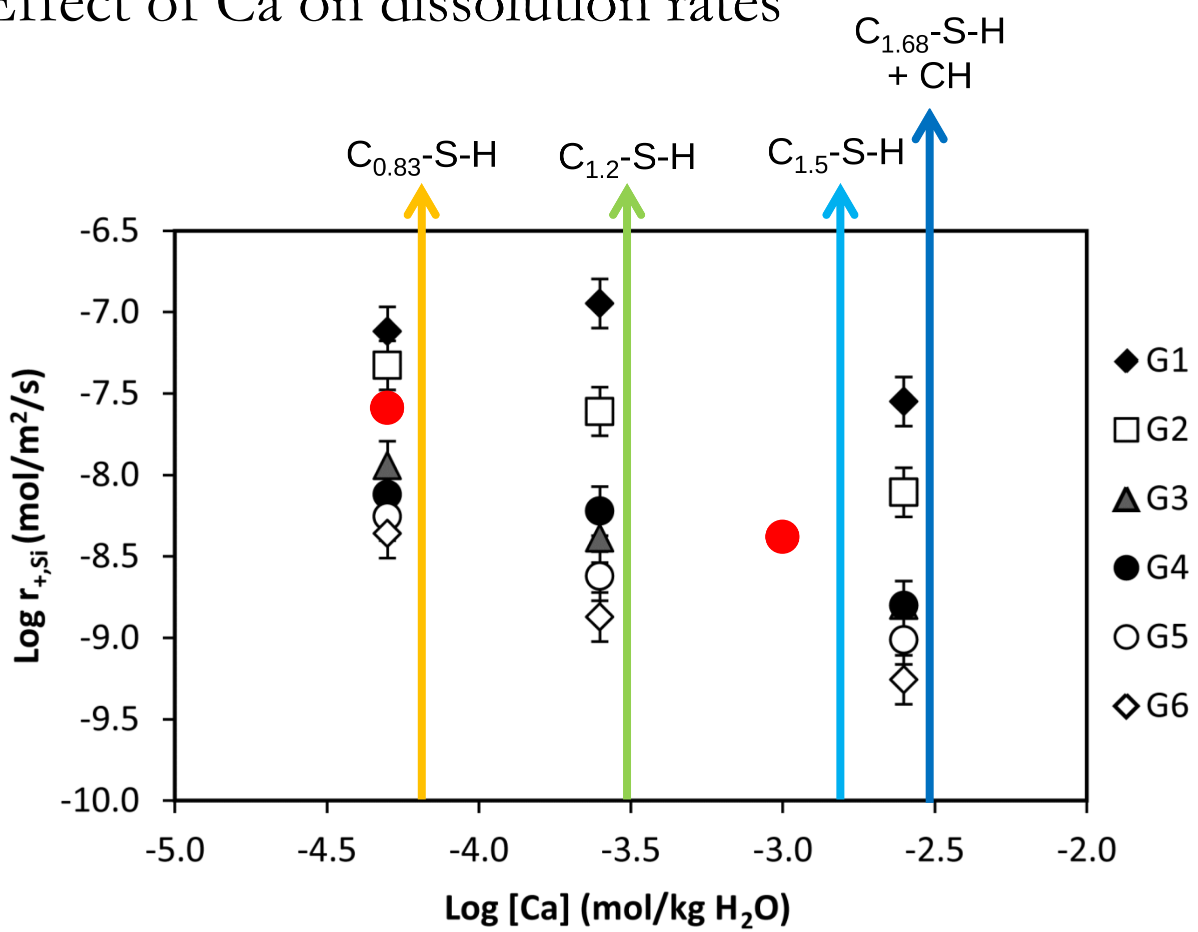
Dissolution experiments

- Effect of Ca on dissolution rates



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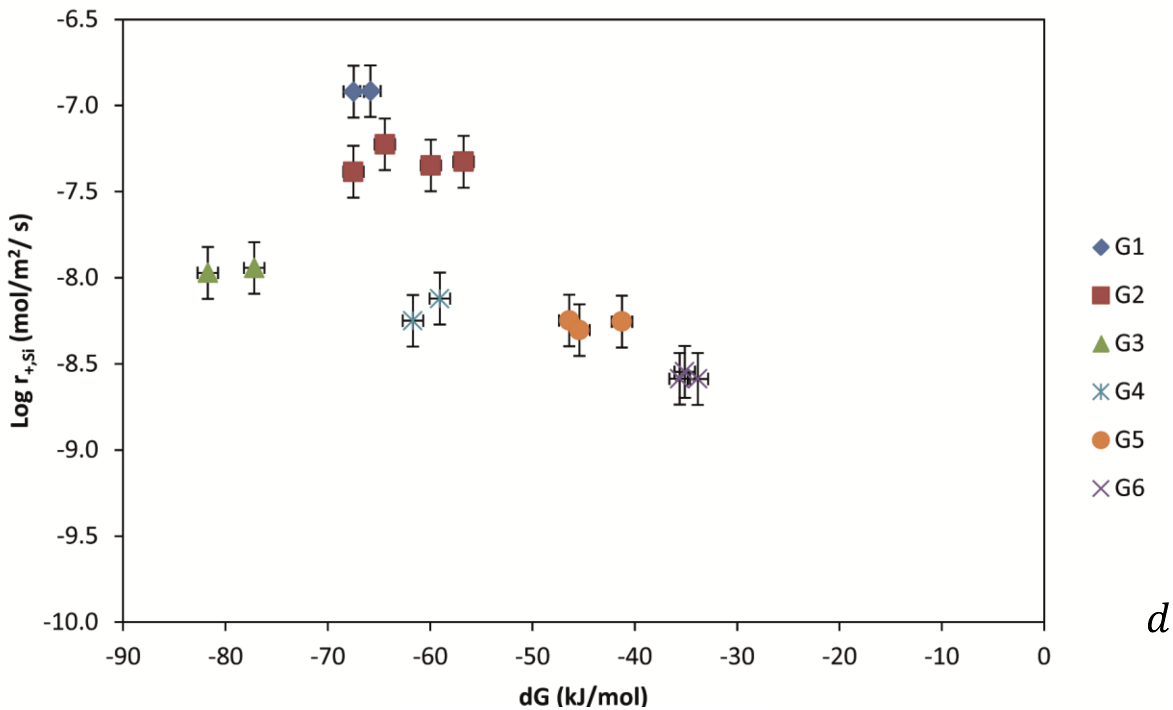
Dissolution experiments

- Effect of chemical affinity: solution saturation
  - At large undersaturations dissolution rates of glasses are not dependent of chemical affinity
  - Precipitation of hydrates should occur before the solutions leave the high undersaturation regime (towards the glass phase)



$$dG = RTln\left(\frac{IAP}{K_{sp}}\right)$$

undersaturation

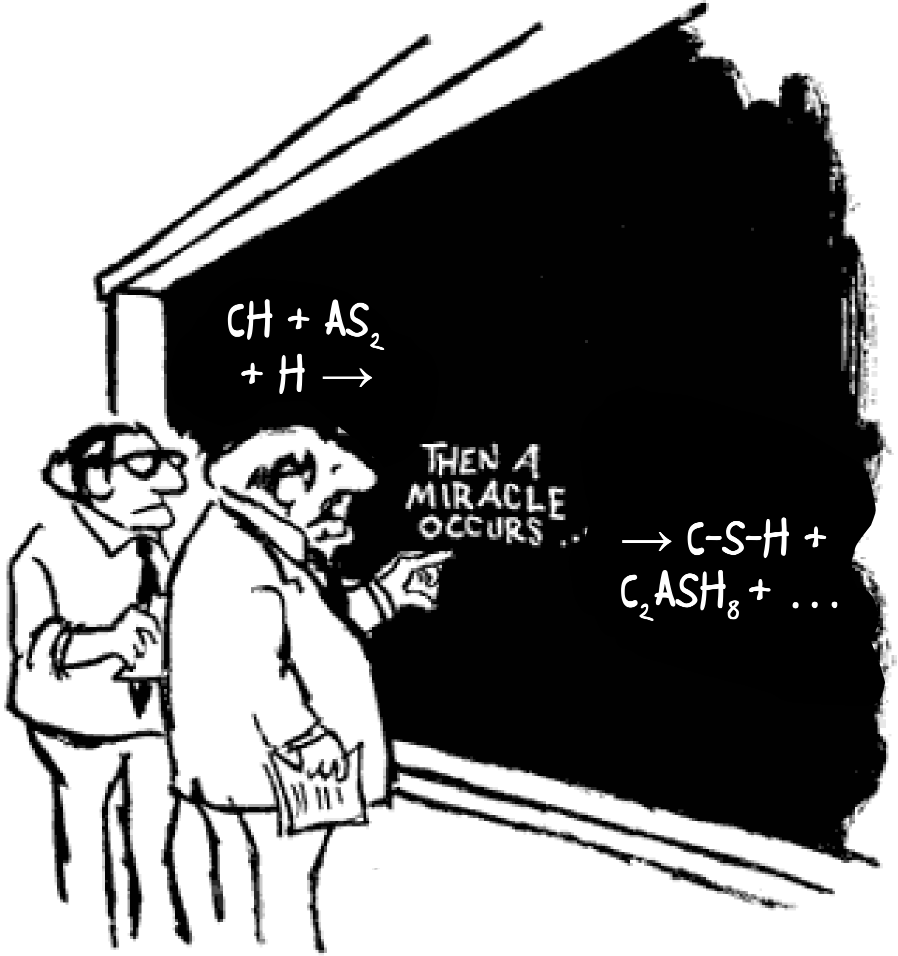
Conclusions

- C-A-S glass synthesis was successful using preblending, firing at 1600 C and water quenching

- Dissolution rates can be calculated from batch reactors at low SA/V ratios, avoiding hydrate precipitation, a wide range of parameters can be tested

- Dissolution rate experiments show that at pH 13:
  - Glass dissolution is congruent
  - Al and Ca in solution inhibit glass dissolution
  - Si and SO_4 in solution do not affect dissolution rates

Thank you for your attention!



"I think you should be more explicit here in step two."