

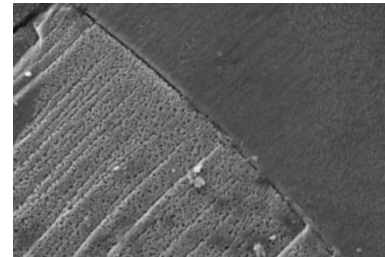
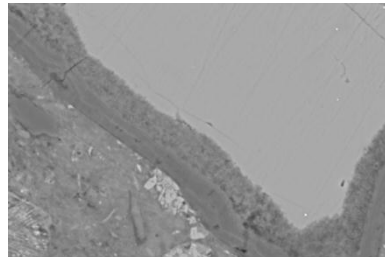
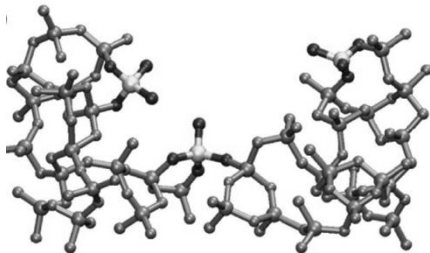
# Dissolution theories for cementitious binders

## A case for the interface

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Laboratory of Construction Materials

EPFL



# Outline

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- Introduction
- Rate controlling mechanisms
- Dissolution kinetics
- Implications for performance and durability
- Conclusions and perspectives

# Introduction

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- Cementitious binder?
  - **Glue** binding solid materials (through solid-solid grain boundaries that remain attractive in  $\text{H}_2\text{O}$ )
  - **Filler** of empty space between particles
- Activation of (alumino-)silicates:
  - Blended cement environment:
    - pH: 13 – 13.5
    - C-(A)-S-H products
  - Alkali activation
    - pH  $\gg$  14
    - Product assemblage depend on material composition and activator

# Why studying kinetics?

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## Hydration/reaction kinetics

Availability of reactive species

Reaction product formation

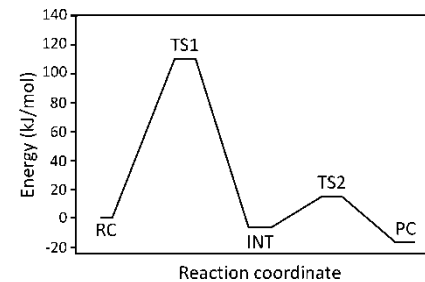
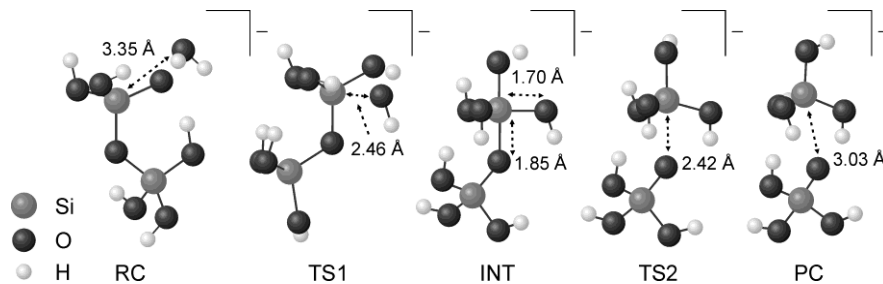
Distribution of products: microstructure

Strength development, heat generation

Porosity, permeability: durability

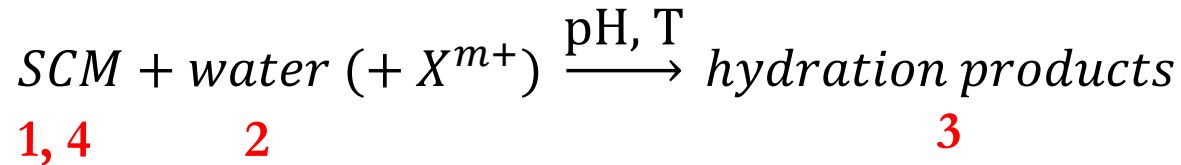
# Reaction kinetics in cementitious binders

- Chemical and microstructural processes are complex and interdependent
- Difficult to resolve individual mechanisms or parameters that determine kinetics
- Fundamental approach: hydration as series of coupled processes (flow chart approach)
  - Breaking down problem to study kinetics of individual mechanistic steps
  - Foundation for understanding interactions among coupled phenomena
  - Kinetics are often controlled by one significantly slower step



# Rate controlling mechanisms

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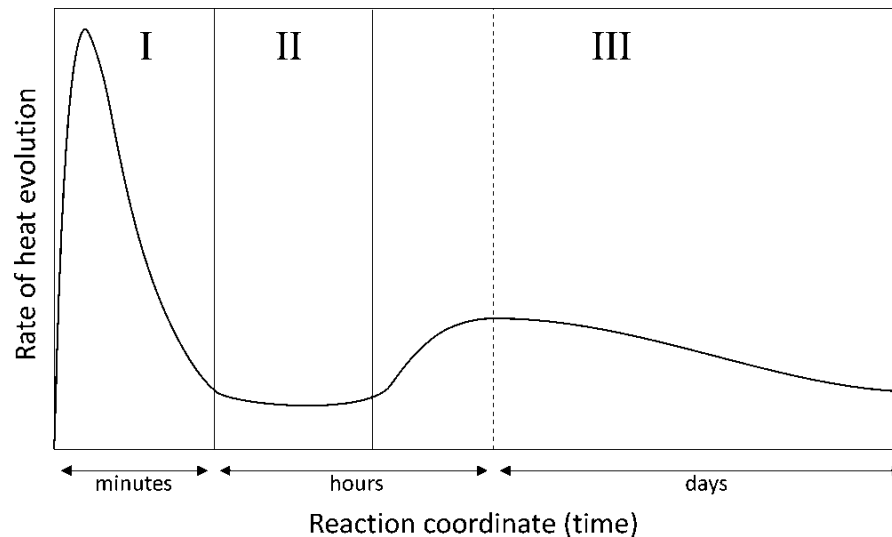


1. Surface dissolution control
2. Water availability
3. Space filling of reaction products
4. Diffusion through leached layer or reaction product layer

# Rate controlling mechanisms

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- Changes in reaction environment:
  - Solution composition (pH,  $[H_2O]$ , solution saturation)
  - Availability of growth space
  - Leached layer/reaction product layer development
- Changes in rate controlling mechanism at different stages

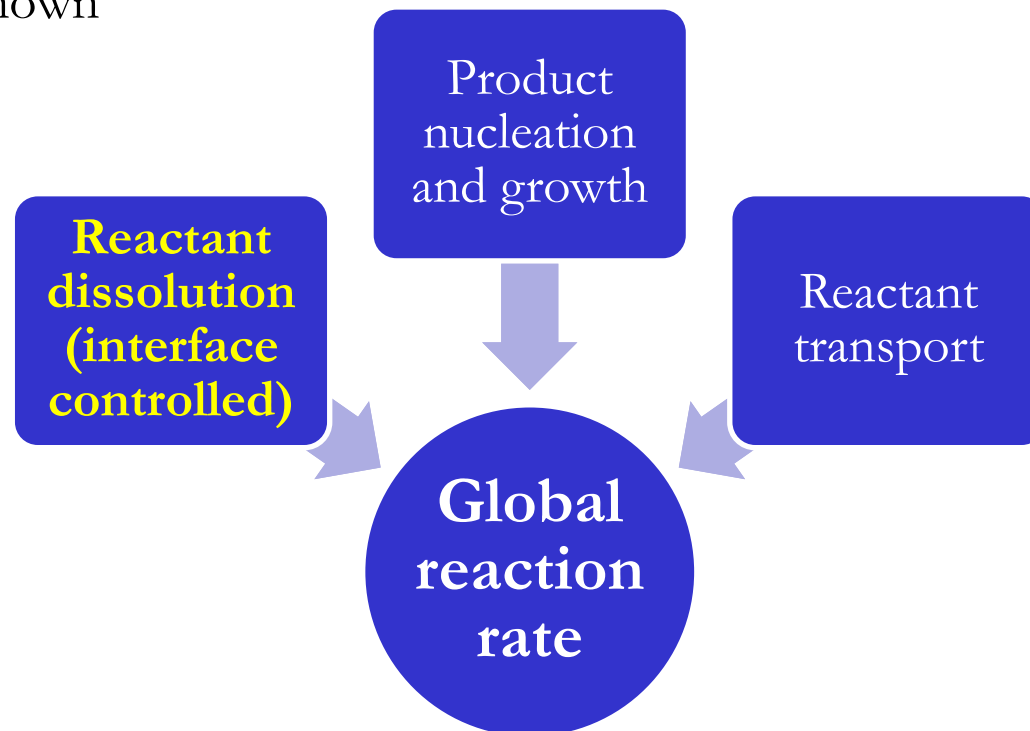


[Snellings et al., 2012]

# Rate controlling mechanisms

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- 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





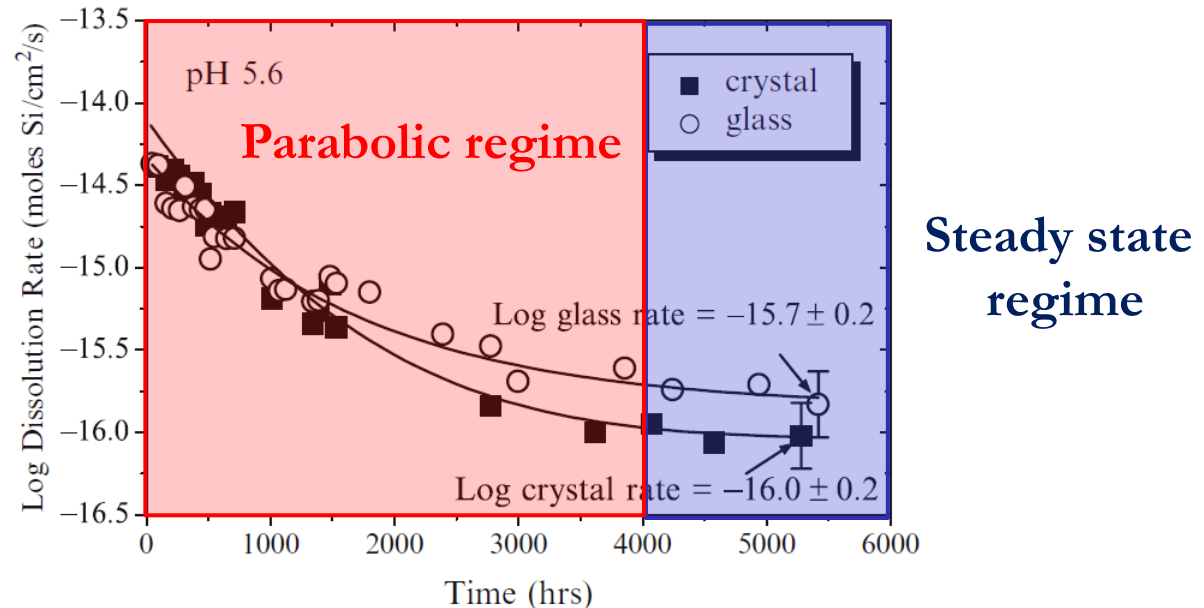
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# Theories for dissolution kinetics

# Dissolution

## ■ Dissolution rate measurements

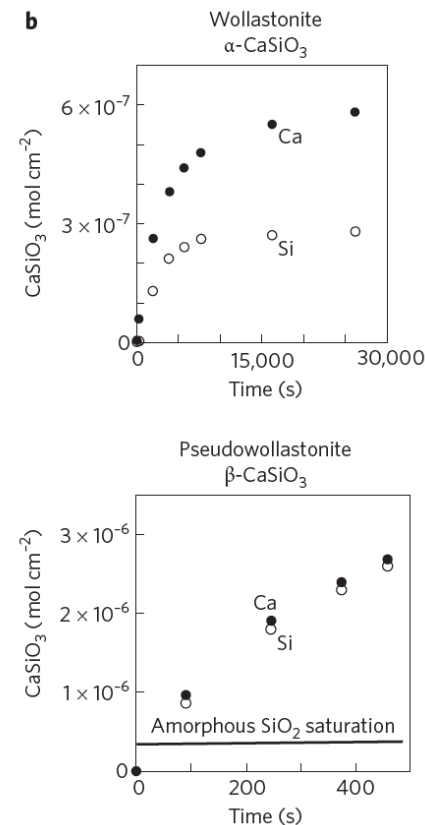
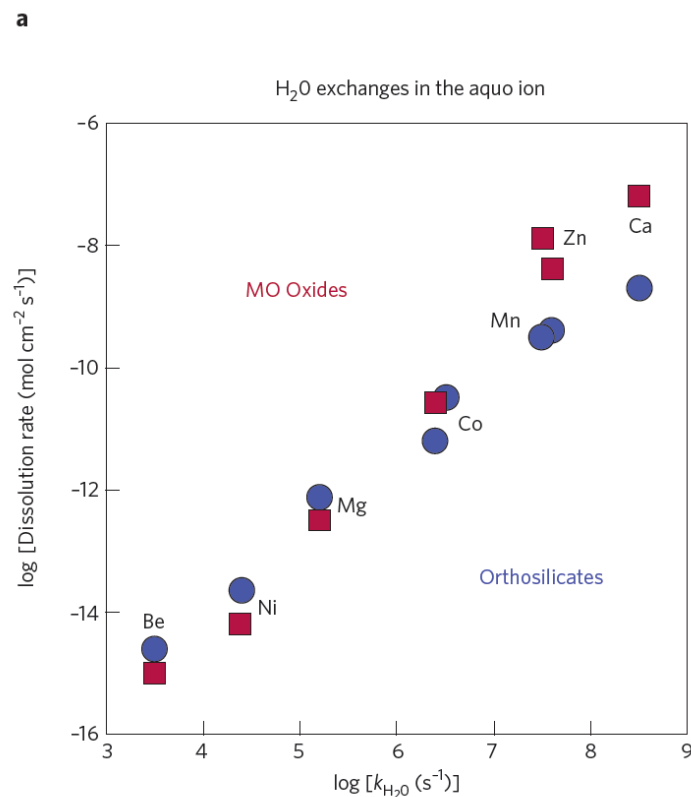
- In bulk: increase in concentration of solutes through time, solid mass loss
- Rates are normalised to the total surface area (BET measurements or geometric calculation)
- Initial *parabolic* kinetics followed by steady state rate (reported)



[Hamilton et al., 2000]

# Reactivity trends for mineral and glass dissolution

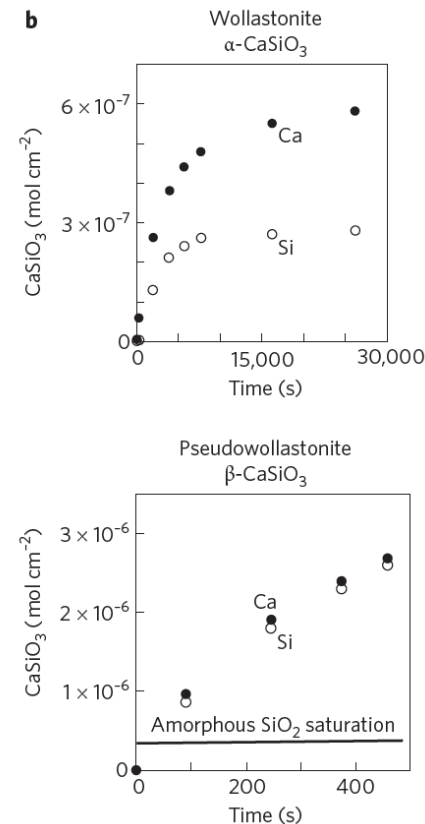
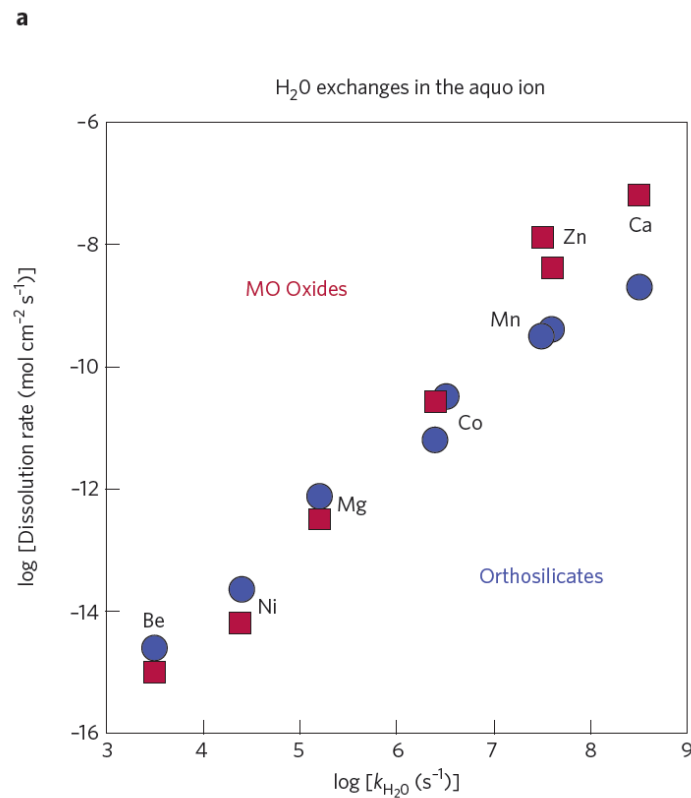
- Congruent dissolution:
  - Dissolution rates of MO oxides and orthosilicates scale with rate of exchange of inner sphere  $\text{H}_2\text{O}$  ( $k_{\text{H}_2\text{O}}$ ) from the ion in solution



[Casey & Westrich, 1992; Ohlin et al. 2010]

# Reactivity trends for mineral and glass dissolution

- Incongruent (nonstoichiometric) dissolution:
  - Preferential leaching of elements from the surface
  - Leached surface layer of sparingly soluble components

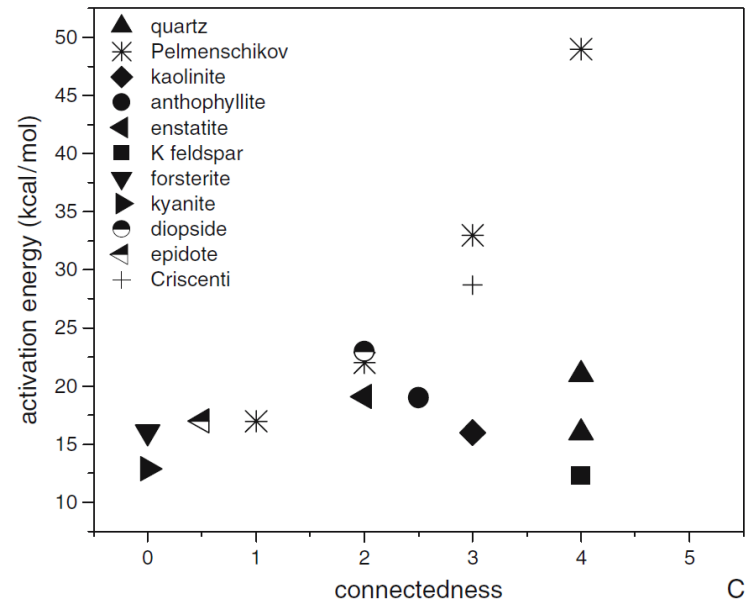
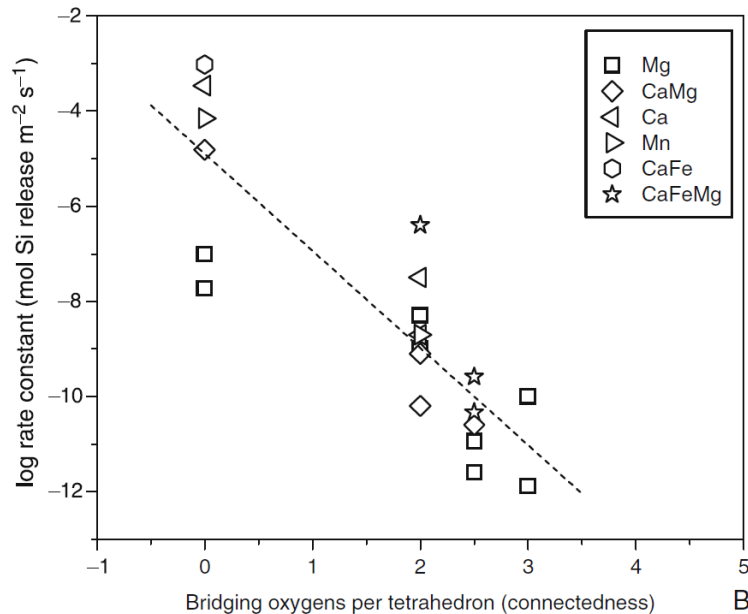


[Casey & Westrich, 1992; Ohlin et al. 2010]

# Reactivity trends for mineral and glass dissolution

## ■ Polymer connectivity

- Silicate network: the higher the connectivity, the lower the dissolution rate
- Ab initio calculations indicate rate control of Q2 detachment

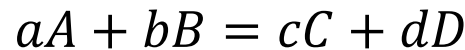


[Brantley et al., 2004; Brantley, 2008]

# Surface dissolution control: driving force

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- Saturation state of a solution with respect to a crystalline or amorphous solid



$$\Delta G = \Delta G^0 + RT \ln \left( \frac{[C]^c [D]^d}{[A]^a [B]^b} \right)$$

Q = reaction quotient

At equilibrium:  $\Delta G = 0$   $K_{sp} = \left( \frac{[C]^c [D]^d}{[A]^a [B]^b} \right)_{eq}$

$$\Delta G^0 = -RT \ln K_{sp}$$

In general:  $\Delta G = -RT \ln K_{sp} + RT \ln Q = RT \ln \frac{Q}{K_{sp}}$

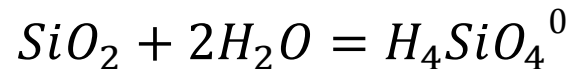
# Surface dissolution control: saturation state

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- Saturation state  $\sigma$

$$\sigma = \left( \frac{\Delta G}{RT} \right) = \ln \left( \frac{Q}{K_{sp}} \right)$$

- $\sigma < 0$  for dissolution
- e.g. dissolution of amorphous silica

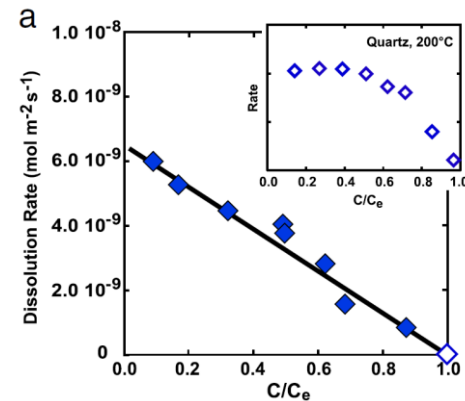
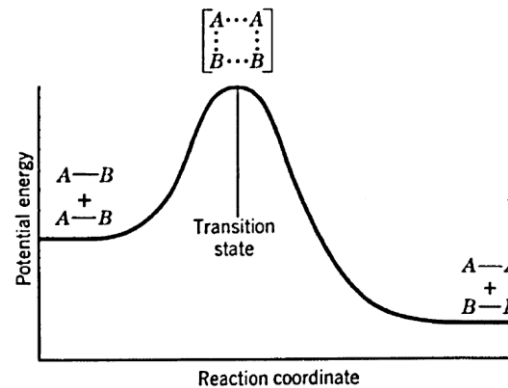


$$\sigma = \ln \left( \frac{Q}{K_{sp}} \right) = \ln \left( \frac{[\text{H}_4\text{SiO}_4^0]}{K_{sp}} \right)$$

# Surface dissolution control: linear rate law

- Linear dependence of dissolution rate on driving force

$$r_{diss} = k_+ \left\{ 1 - \exp\left(\frac{\Delta G}{RT}\right) \right\} = k_+ \left\{ 1 - \left(\frac{Q}{K_{sp}}\right) \right\}$$



- Assumptions:

- One single, slow rate controlling step (first order reaction)
- Based on bulk dissolution studies/empirical rate laws
- Surface defects do not play a role

[Rimstidt & Barnes, 1980; Lasaga, 1981; Aagaard & Helgeson, 1982  
Icenhower et al., 2004; Dove et al., 2008]



# Surface dissolution control: exponential rate laws

## ■ Problems:

- Non-linear dependence: introduction of reaction orders  $n$

1) dissolution plateau at high degree of undersaturation

$$r_{diss} = k_+ \left\{ 1 - \exp\left(\frac{n\Delta G}{RT}\right) \right\} = k_+ \left\{ 1 - \left(\frac{Q}{K_{sp}}\right)^n \right\}$$

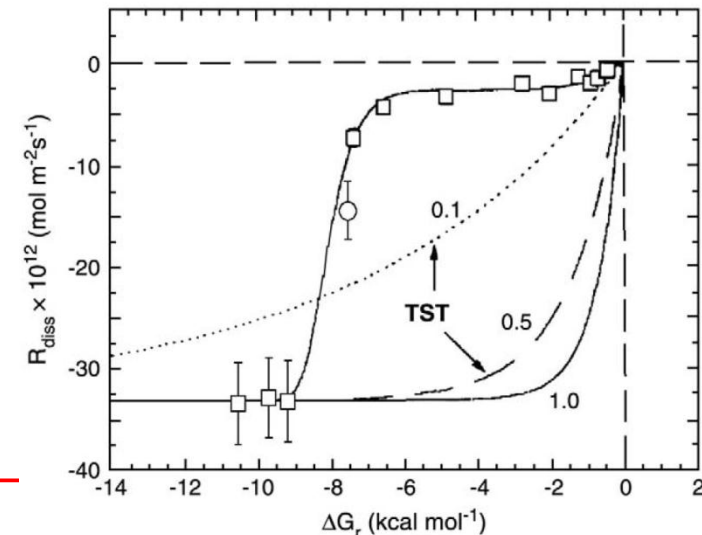
[Dove & Crerar, 1990; Nagy & Lasaga, 1992]

2) exponential dependence on driving force

$$r_{diss} = k_+ \left\{ 1 - \exp\left(\frac{\Delta G}{RT}\right) \right\}^n = k_+ \left\{ 1 - \left(\frac{Q}{K_{sp}}\right) \right\}^n$$

- Wide variation in reaction orders
  - Contradictions in rate law applicability
- Control of **surface defects** on dissolution

[Burch et al., 1993; Schott & Oelkers, 1995]



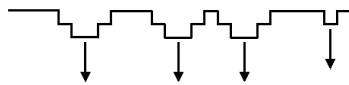
# Surface dissolution control: mechanistic description

- Mechanistic description of **congruent** dissolution and growth

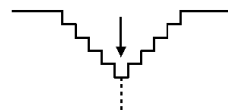
[Cabrera et al., 1954; Lasaga & Lüttge, 2001; Dove et al., 2005]

- **Depending on solution composition dissolution occurs:**

- 1) At pre-existing surface steps (Q2 species at surface)
- 2) At dislocation defects intersecting the surface (crystals)
- 3) Homogeneously across the surface (or at impurities)



Step nucleation at plain surface



Step propagation from dislocation defect



Step retreat

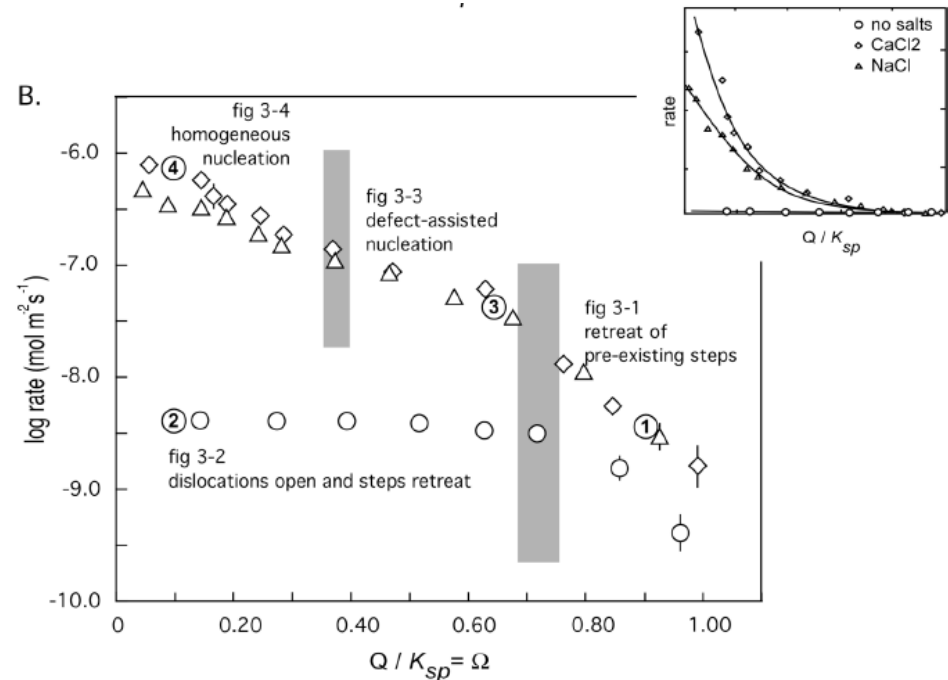
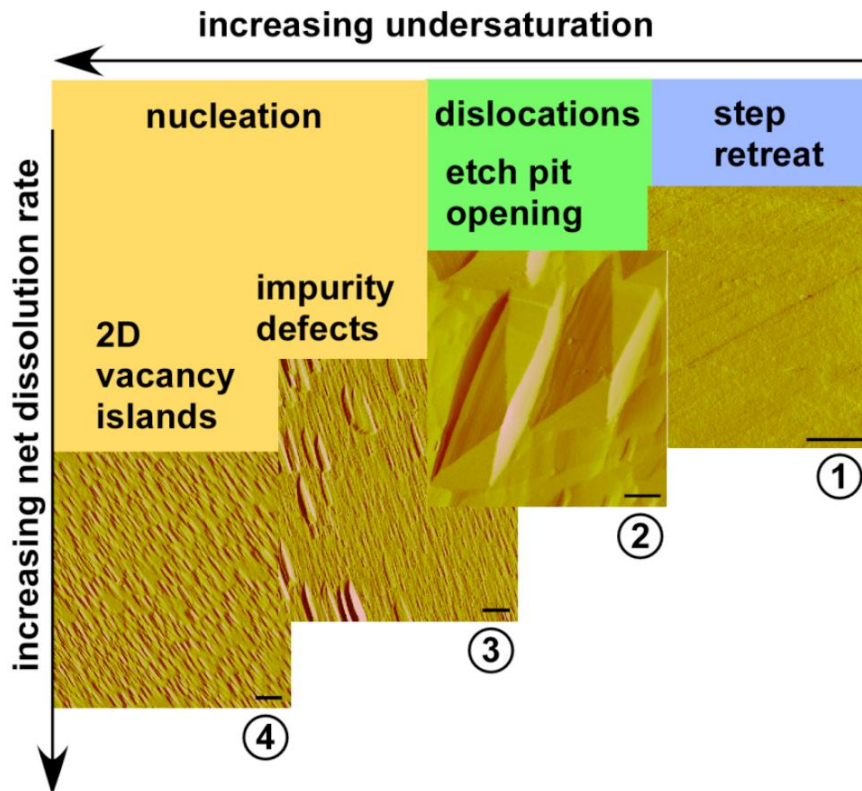
- **Parameters:**

- Temperature  $T$  (K)
- Saturation state  $\sigma$
- Step edge energy  $\alpha$  (mJ/m<sup>2</sup>)
- Step kinetic coefficient  $\beta$  (cm/s)

[Development of theory in Dove et al., 2005]

# Surface dissolution control: mechanistic description

- Quartz dissolution mechanism depends on  $\sigma$ ,  $T$ , salt concentration, presence of adsorbate species, compositional impurities

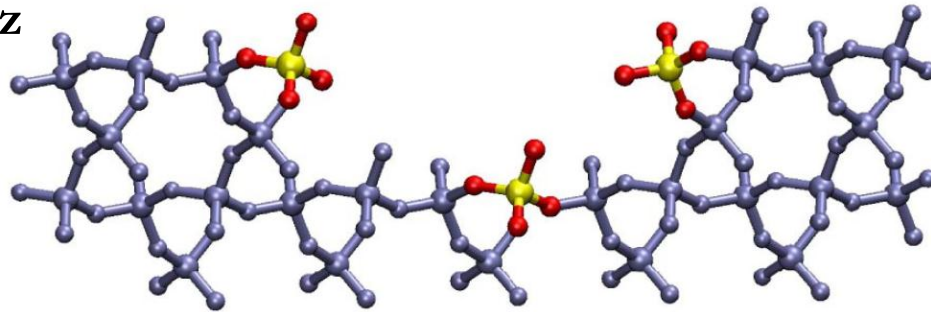


[Brickmore et al., 2006; Dove et al., 2007]

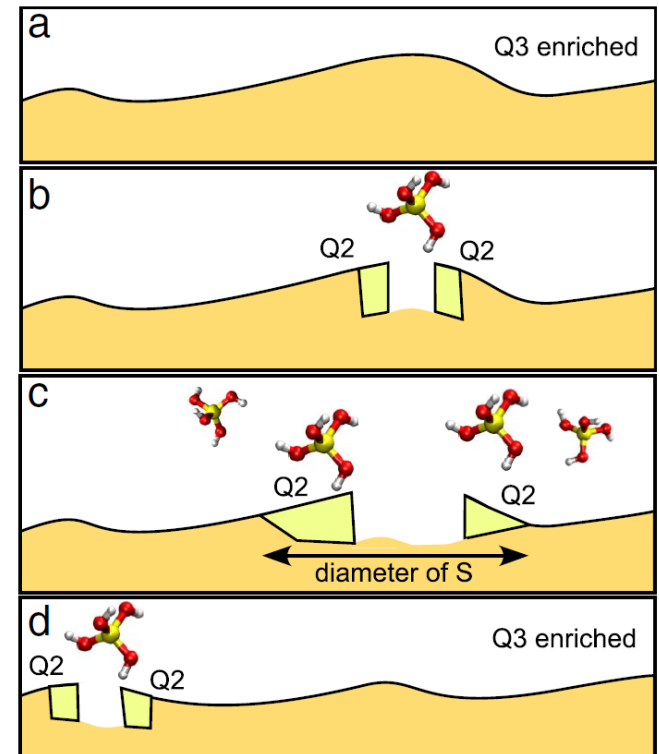
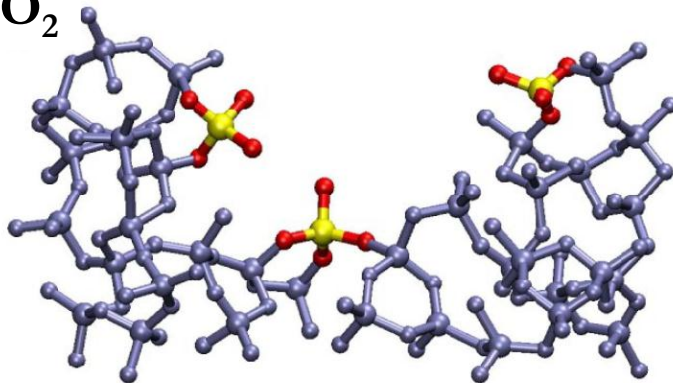
# Surface dissolution control: crystal vs. amorphous

- Step retreat = Q2 detachment, surface pitting = Q3 detachment
- Dissolution rate of amorphous phases is usually higher due to:
  - Lower interfacial energy
  - Greater strain on Si-O-Si bonds

Quartz



Amorphous SiO<sub>2</sub>

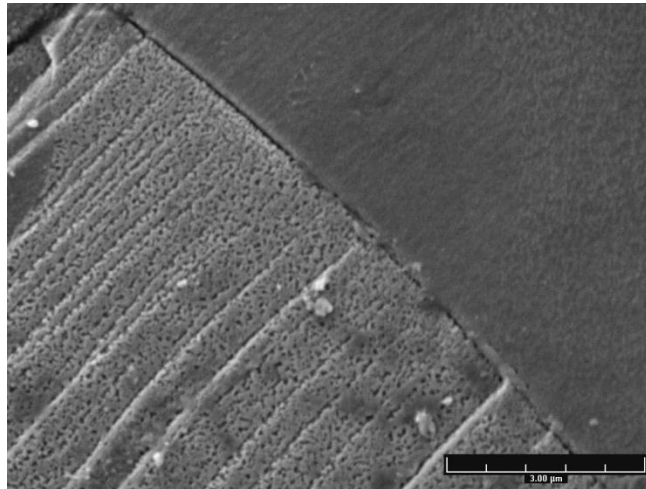


[Dove et al., 2008]

# Surface dissolution control: surface morphology

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- Total dissolution is the combined sum of:
  - Step retreat velocity (depends on saturation state)
  - Nucleation of steps (formation of etch pits)
- Increasing the surface roughness (#steps) will increase initial dissolution rate:
  - Chemical etching (in acid, or at high undersaturation)
  - Grinding (creation of damaged, roughened layer)



C<sub>3</sub>S dissolution  
at high undersaturation

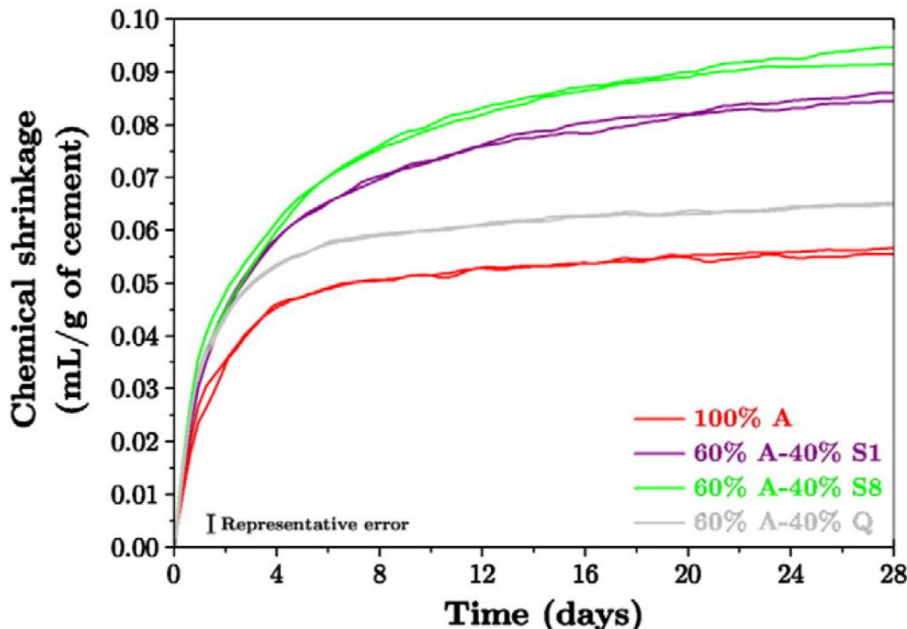
[Juilland et al., 2010]

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# Other rate controlling processes

# Water availability

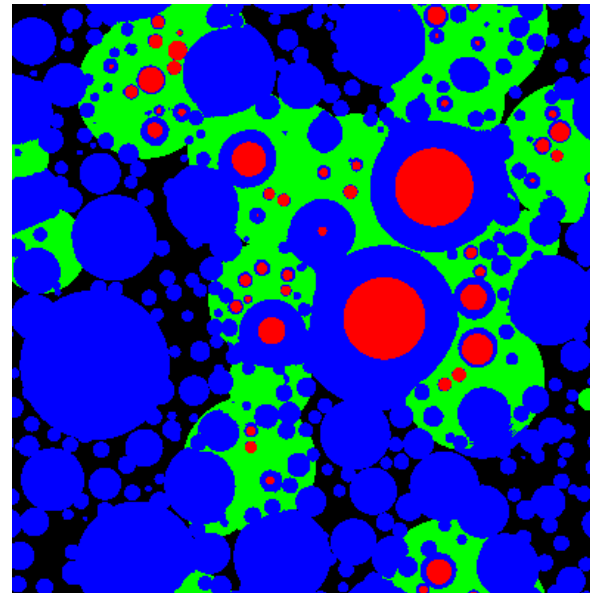
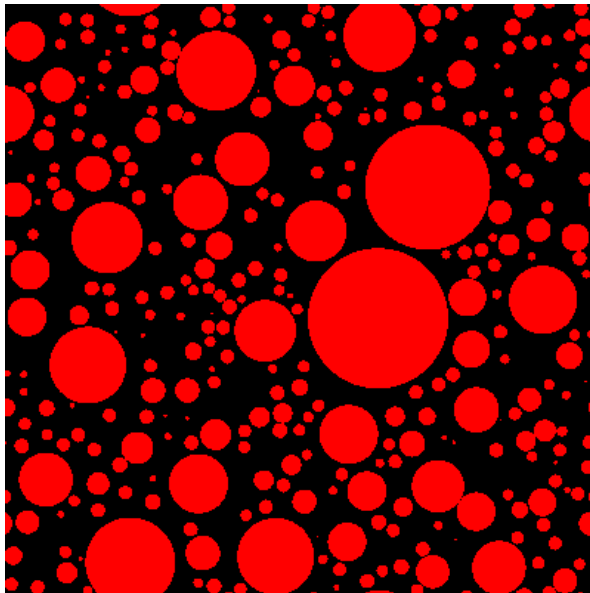
- Important in practice when low w/b ratios are used (high-performance applications)
- Consumption of water in hydration reactions
- Chemical shrinkage:  $V_{\text{hydration products}} < V_{\text{reactants}}$
- Formation of gas filled porosity/decrease in RH
  - E.g. alite hydration stops when  $\text{RH} < 80\%$  [Flatt et al., 2011]



# Space filling by hydration products

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- Main hydration period in Portland cement is controlled by nucleation and growth of products
- Eventual impingement of reaction products leads to growth deceleration



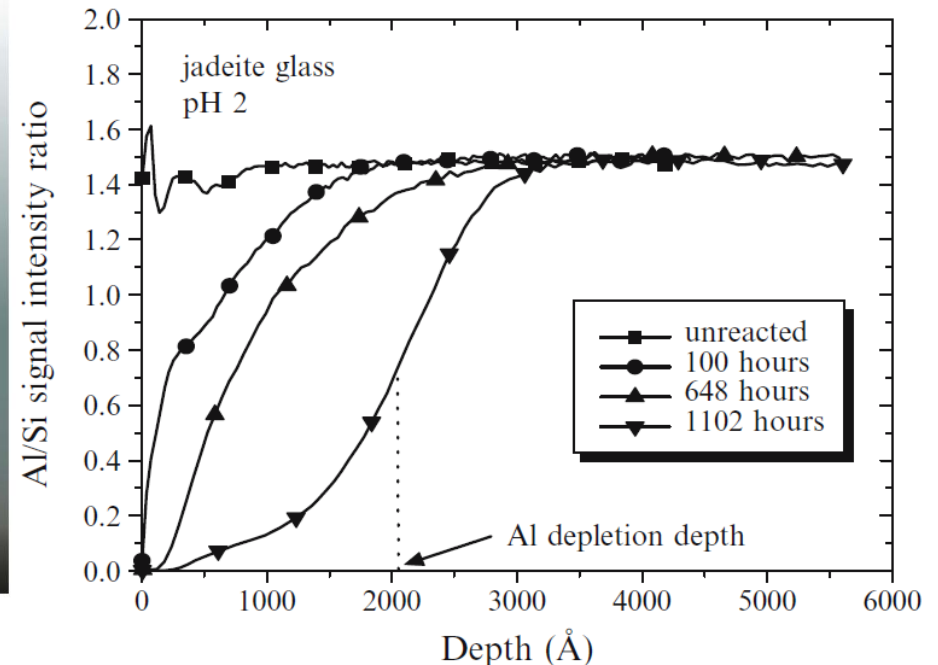
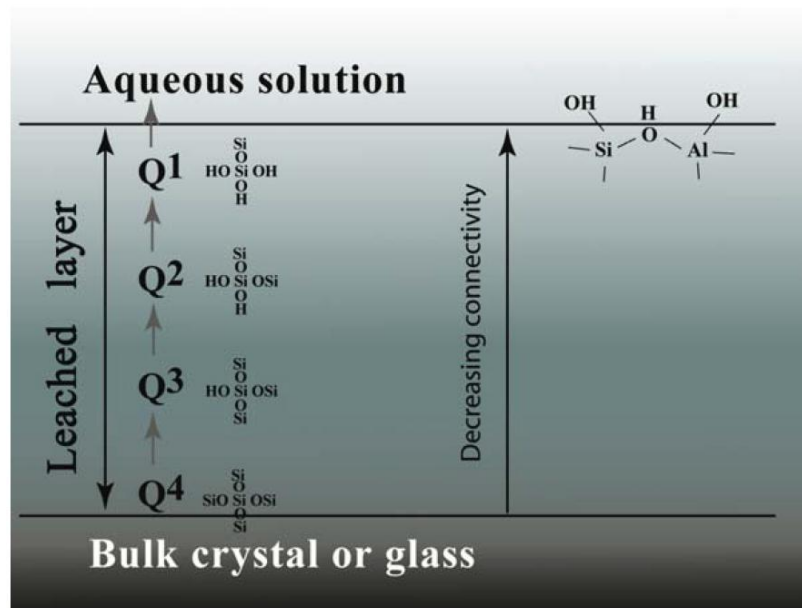
Hydration of polydisperse distribution of alite particles  
modelled using  $\mu ic$  [Bishnoi, 2009]



# Transport through leached/reaction product layer

## 1. Initial stage:

- Incongruent dissolution leads to formation of leached/passivated layer
- Congruent dissolution is reached when diffusion rate of leached cations and Si release rate equalize

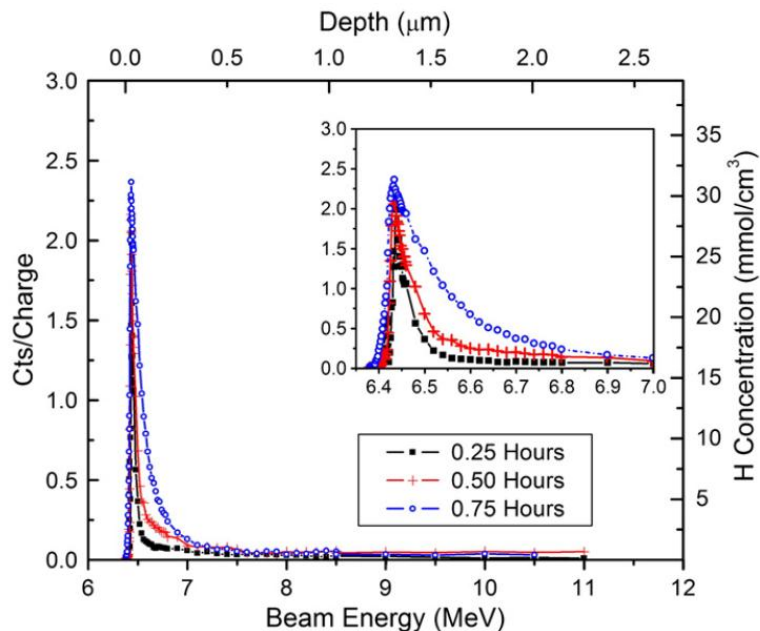


[Tsomaia et al., 2003]

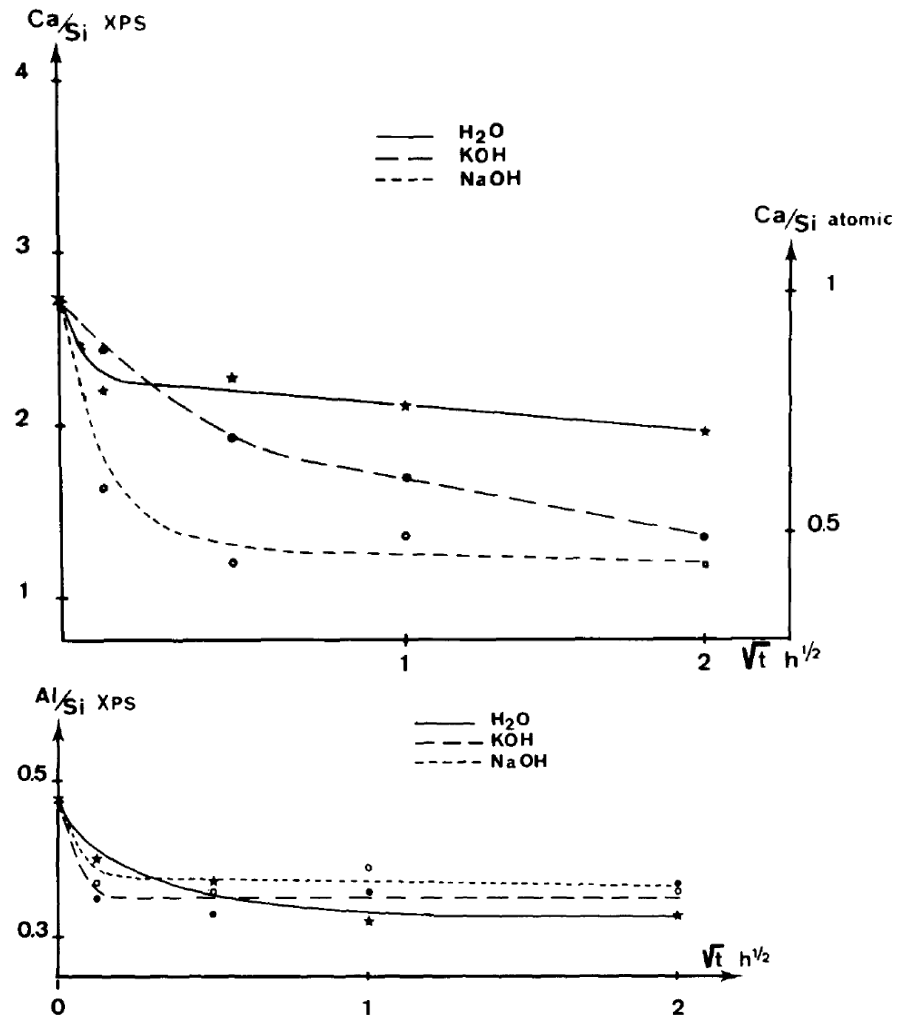
[Hamilton et al., 2001]

# Diffusion through leached/reaction product layer

- XPS BFS depth profiles:
  - Surface leaching
  - Precipitation of products
  
- Alite H concentration profiles through time



[Schweitzer et al., 2007]

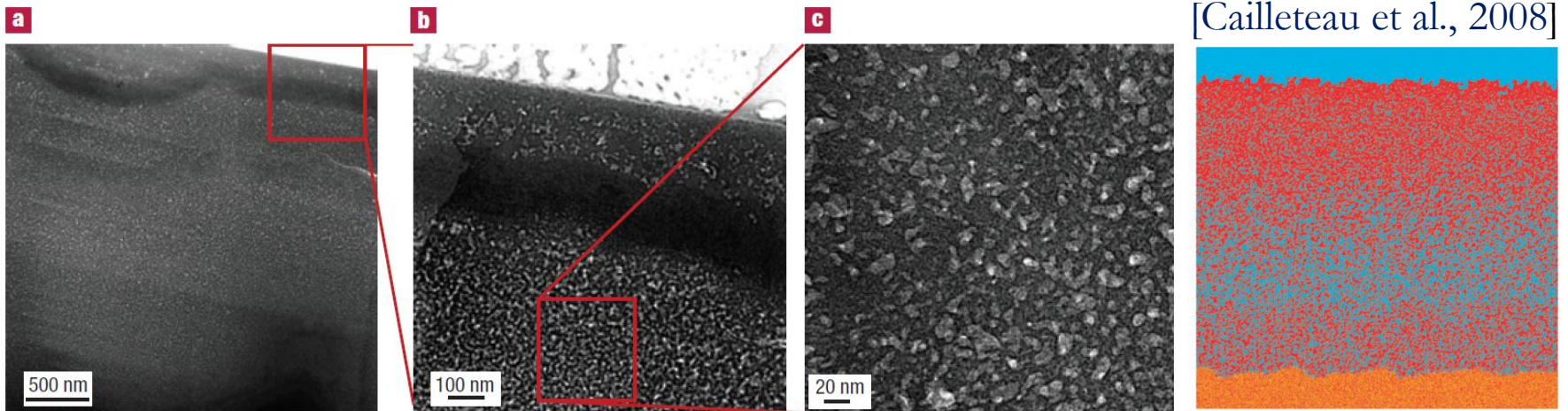


[Regourd et al., 1983]

# Diffusion through leached/reaction product layer

## 2. Deceleration stage:

- Reconstruction and condensation of leached layer during corrosion of Ca-Na-B glass corrosion



- Dense and loose BFS hydration products in 30 yr old concrete

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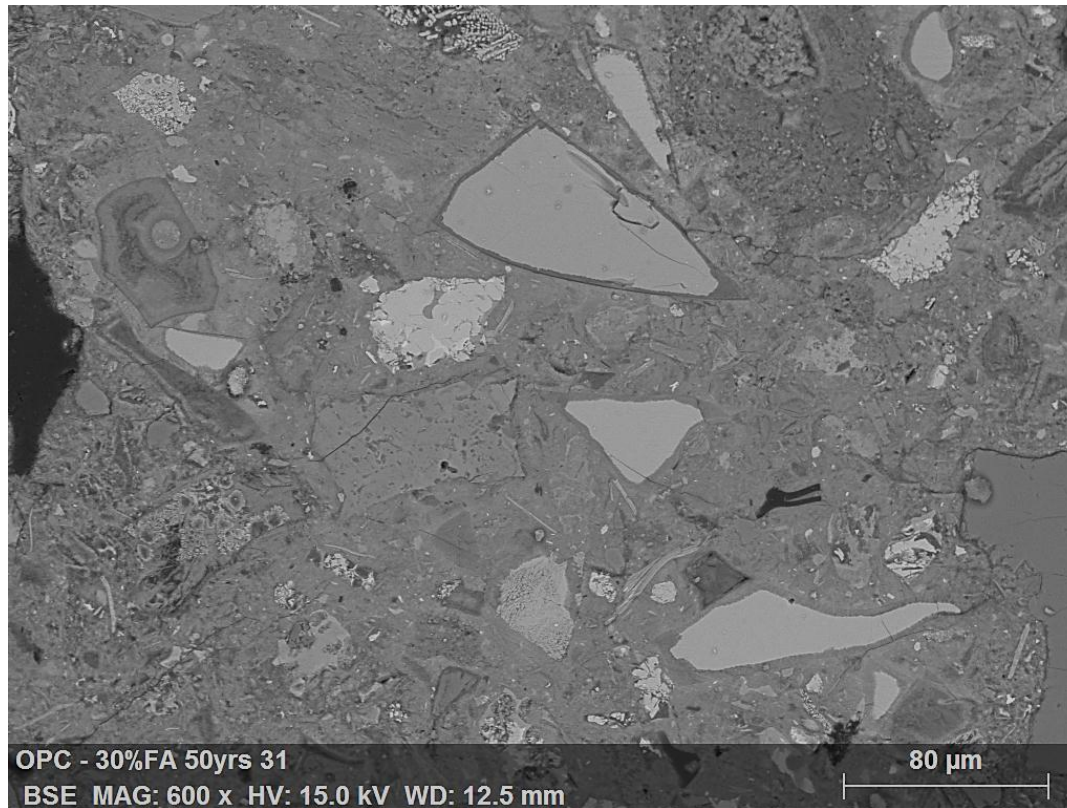
# Implications for Performance & Durability

# Implications for performance and durability

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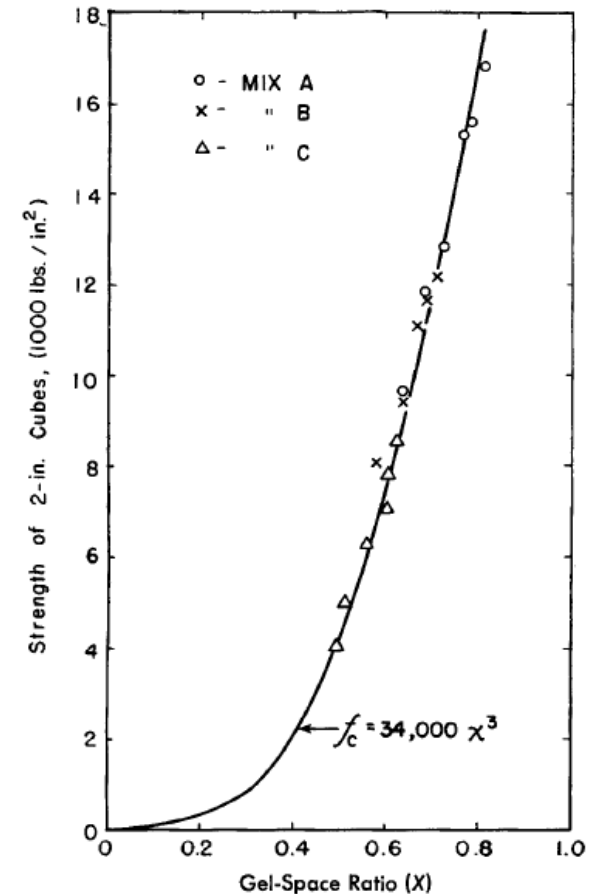
- Linking kinetics and bulk mechanical properties:

Do we really need the microstructure (complex)?



# Does microstructure matter?

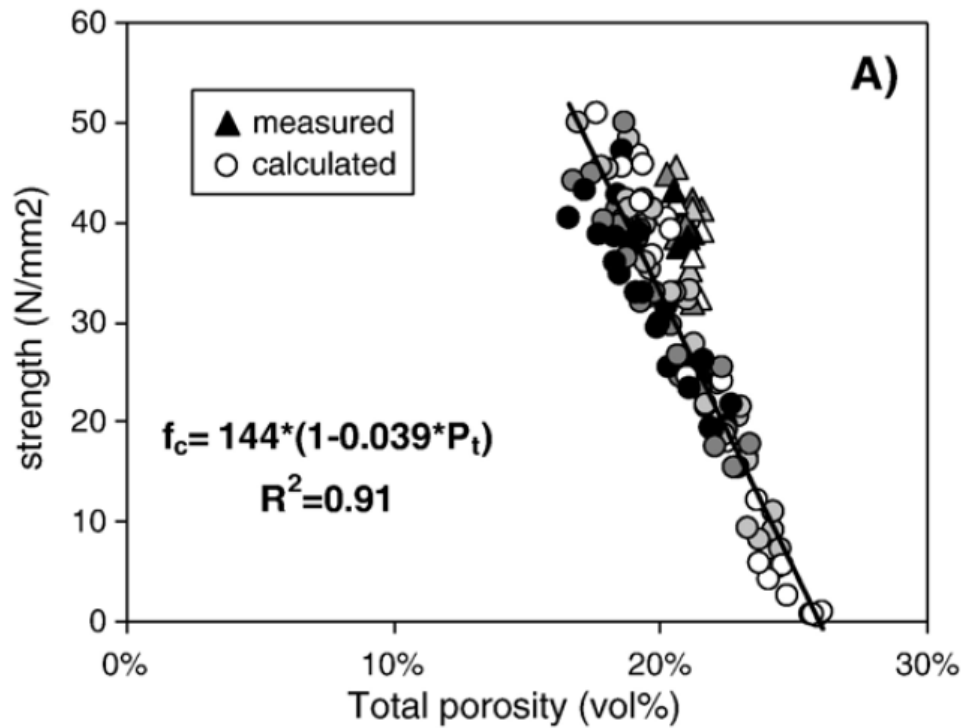
- Powers' model
  - $X = 1 - \text{porosity}$
  - Same relation as found in numerous other rocks
  - Dependence only on amount, not on size or location
  - Calibration needed at 3 days compressive strength
  - Relationship varies for different systems



[Powers, 1958]

# Does microstructure matter?

- Thermodynamic modelling
  - Mass balance equations, thermodynamics indicate phase assemblage
  - Product properties need to be known (composition, solubility, density)



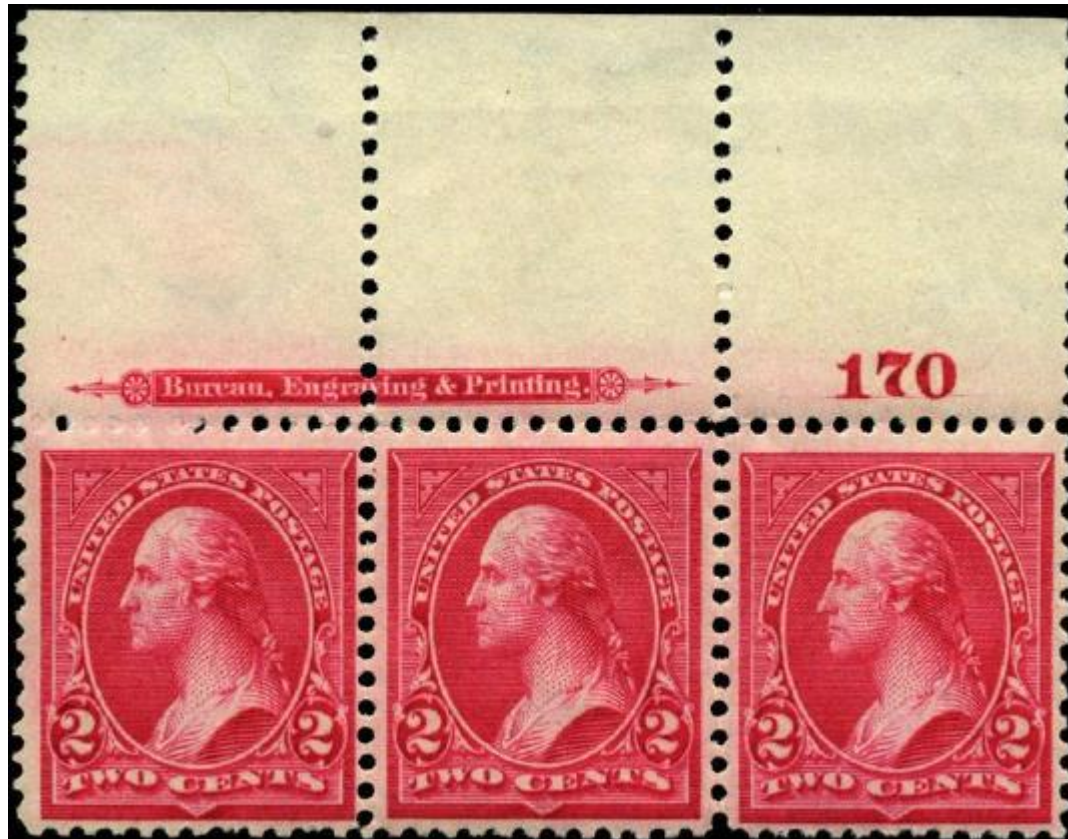
Broad correlation between total porosity (measured and calculated) and strength.

[Lothenbach et al., 2008]

# Microstructure does matter

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- Distribution of porosity-cracking behaviour



\*After C. Dunant



# Implications for bulk properties

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- Linking kinetics – microstructure – mechanics: many question marks remain...
  - Dissolution and reaction kinetics (how to measure degree of reaction?)
  - Reaction product properties: composition, density
  - Microstructural development: homogeneous or heterogeneous nucleation, nucleation density, growth (isotropic, planar, linear) behaviour, condensation,...
- Numerical modelling can help:
  - To model interactions between simultaneous processes, taking into account large numbers of factors and data
  - To compare, test and develop experiments and hypotheses

Available programs: CemHyd3D, HyMoStruc, Hydratica,  $\mu$ ic

# Conclusions and perspectives

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- Dissolution theories describe rate dependency on:

- Saturation state
- Solution composition (pH, electrolytes,...)
- Phase composition
- Surface morphology

↳ Modelling global weathering processes, nutrient release,...

- Extension of databases to synthetic phases/glass

↳ Engineering of material reactivity, availability of reactive species

# Conclusions and perspectives

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- Key to mechanistic understanding is **isolating and analysing** the individual constitutive steps in hydration
  - e.g. insights into mineral dissolution kinetics
- (Long term) scientific effort should focus on:
  - Building and expanding of quantitative databases (reactant dissolution rates, product properties, microstructure development)
  - Application of new and improved analytical techniques to capture elusive parameters
  - Integration of experimental data in numerical models using improved process equations

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**Thank you for your attention!**