Vitesse d’

ration des raux

s

Eric H. Oelkers

GET/Université Paul Sabatier, Toulouse, FRANCE

Science Institute,University of Iceland, ICELAND

Earth Sciences, University College London, UK

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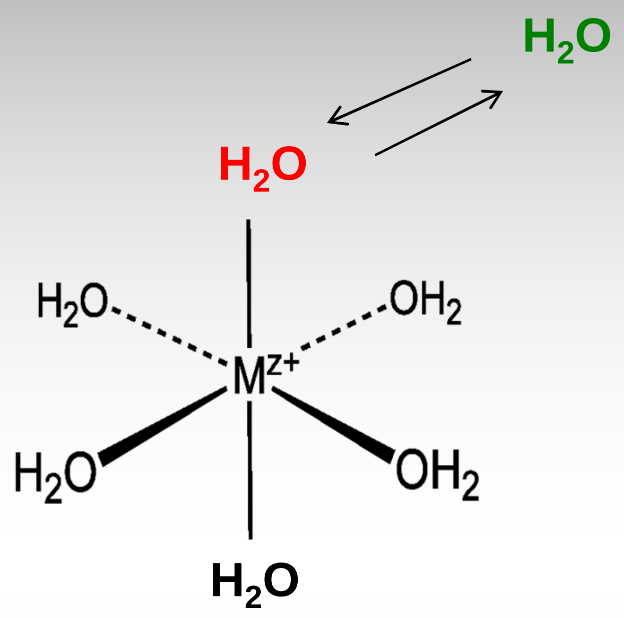
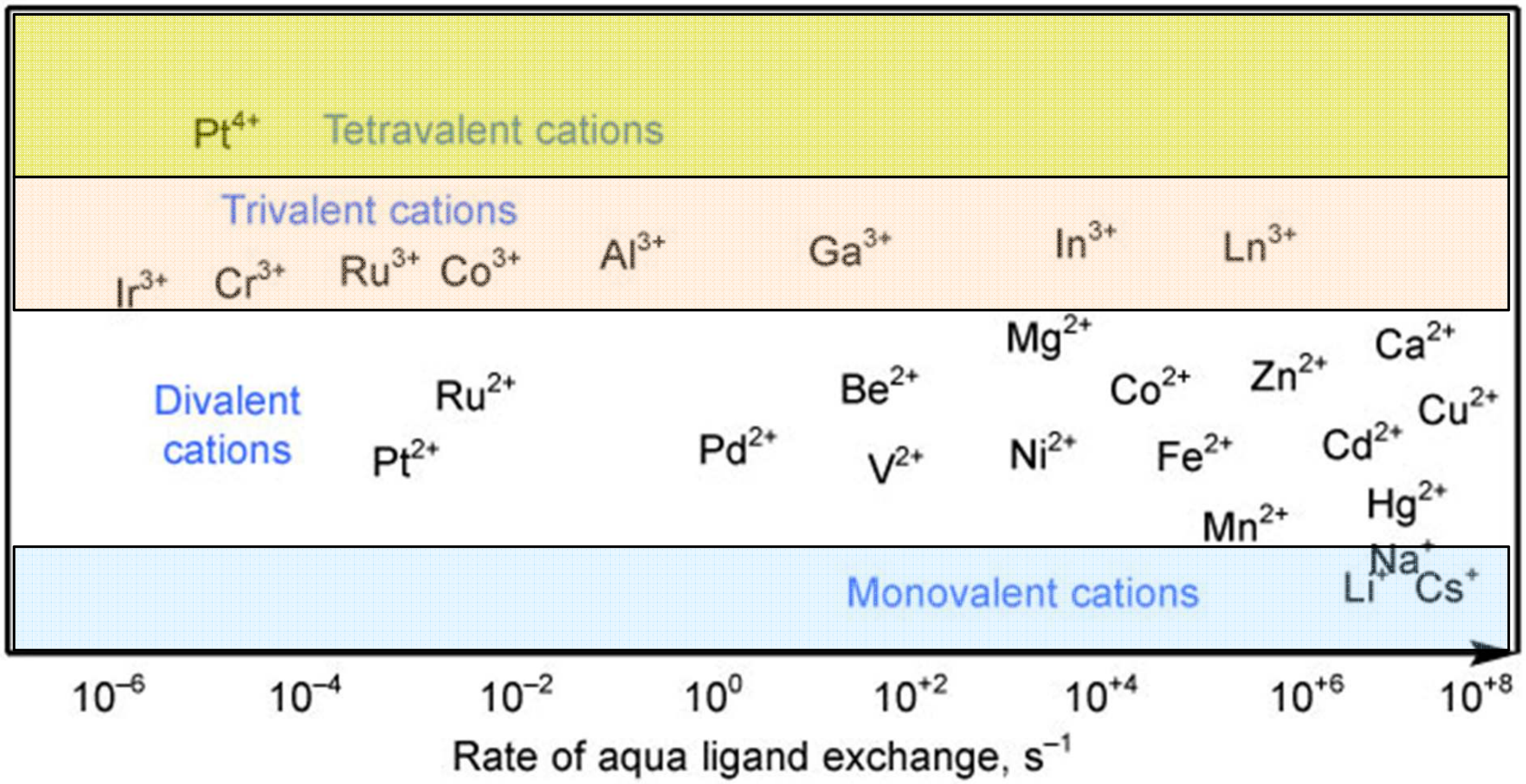
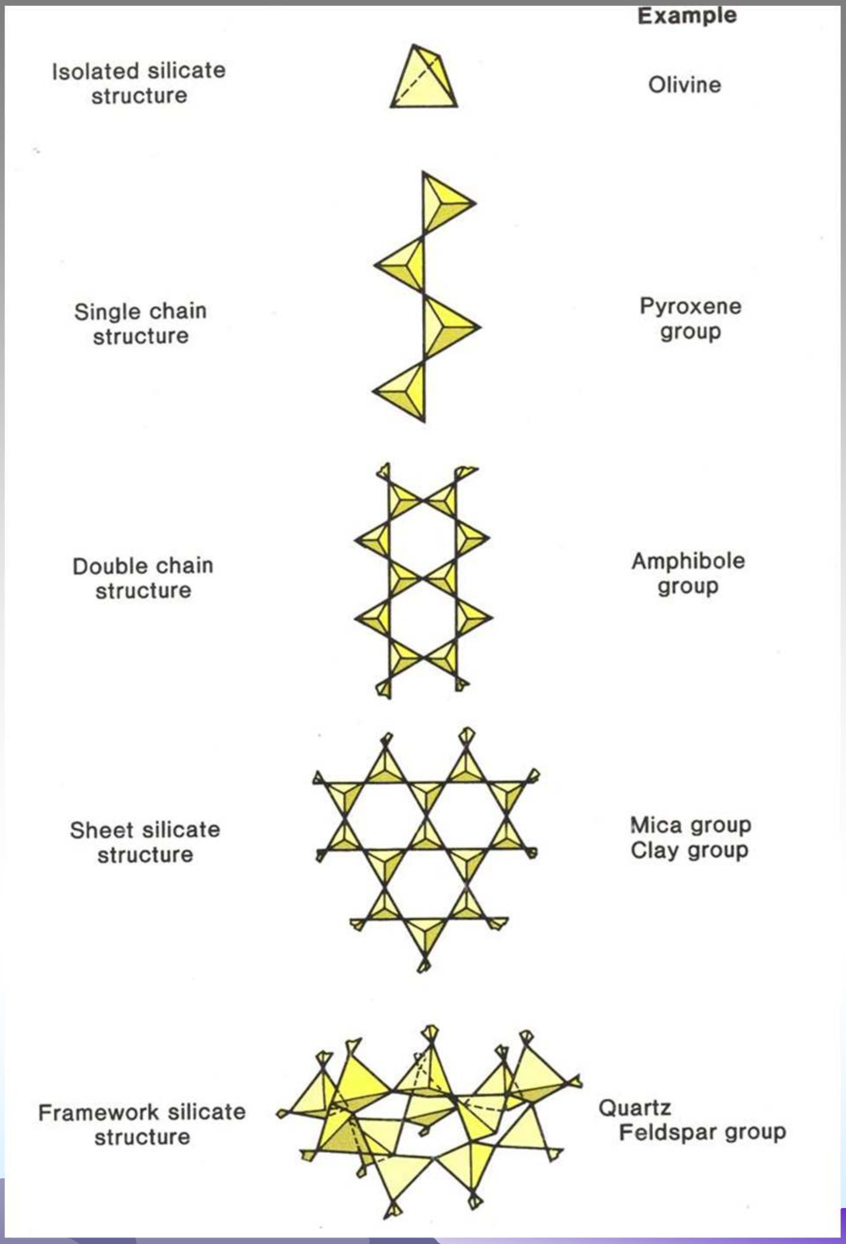
Metal-water- exchange rates



Metal-oxygen exchange rates vary by orders of magnitude



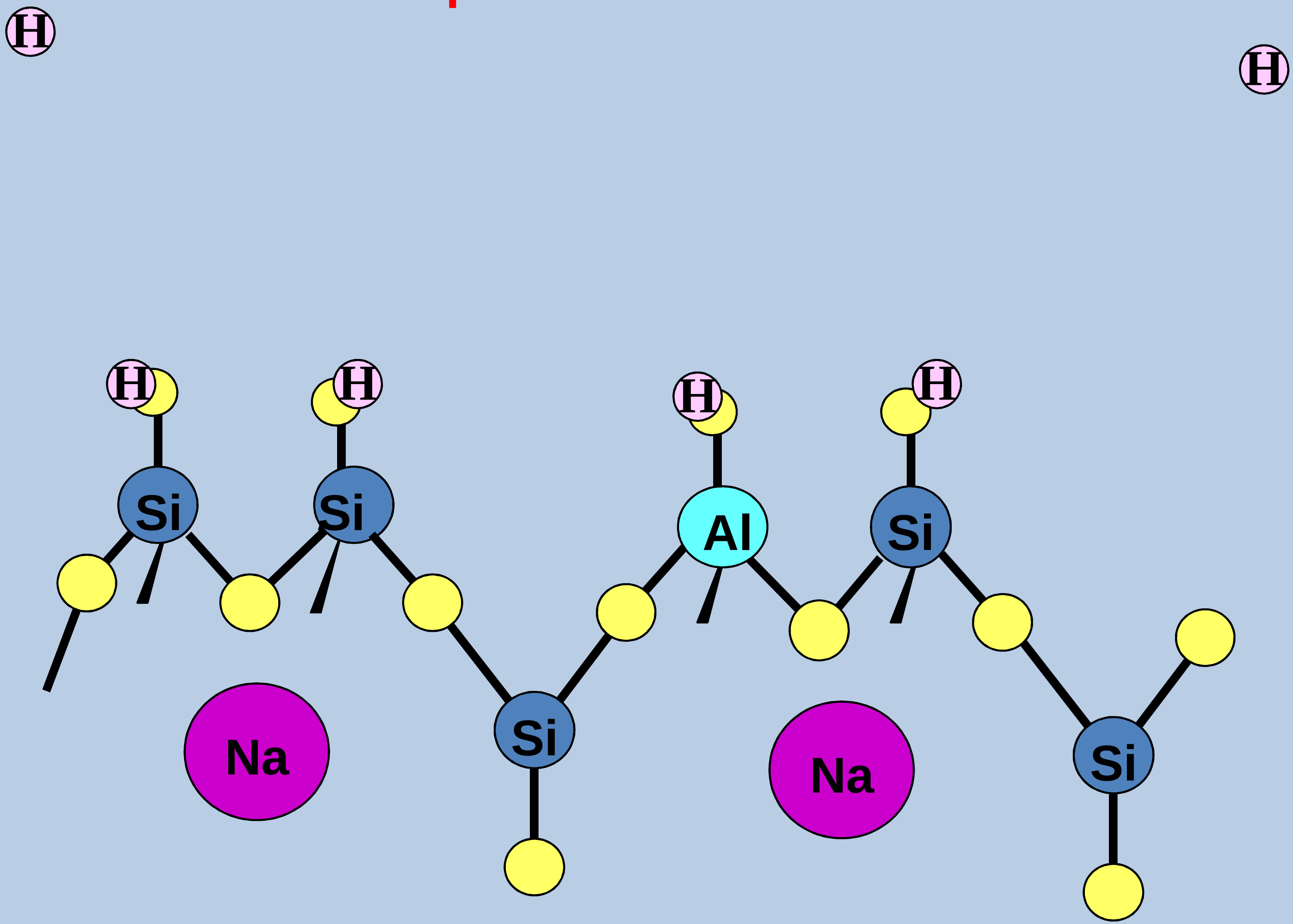
Silicate minerals have a wealth of structures to help deduce dissolution mechanisms…



Mechanisms for Multi-oxide Mineral Dissolution

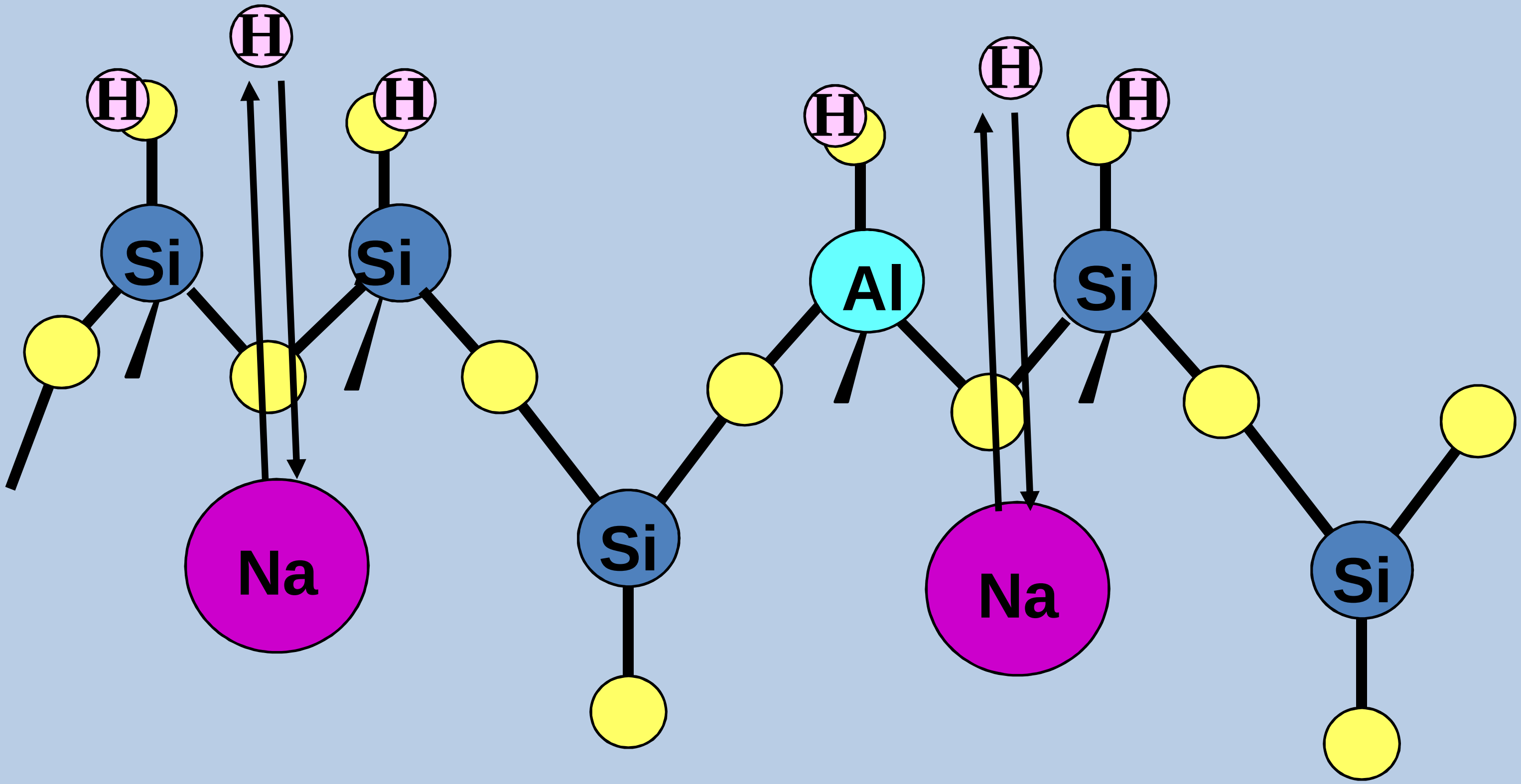
Reaction	Alkali-Feldspar	Anorthite	Muscovite	Enstatite	Wollas-tonite	Forsterite	Basaltic Glass
Alkali metal -H exchange	Step 1	↓	Step 1	↓	↓	↓	Step 1
Ca-H exchange reaction	↓	Step 1	↓	↓	Step 1	↓	Step 2
Mg-H exchange reaction	↓	↓	↓	Step 1	↓	Mineral Destroyed	Step 3
Tetrahedral Al-H exchange reaction	Step 2	Mineral Destroyed	Step 2	↓	↓		Step 4
Breaking Si-O bonds[1]	Mineral Destroyed		Mineral Destroyed	Mineral Destroyed	Mineral Destroyed		Solid Destroyed

Alkali Feldspar dissolution mechanism



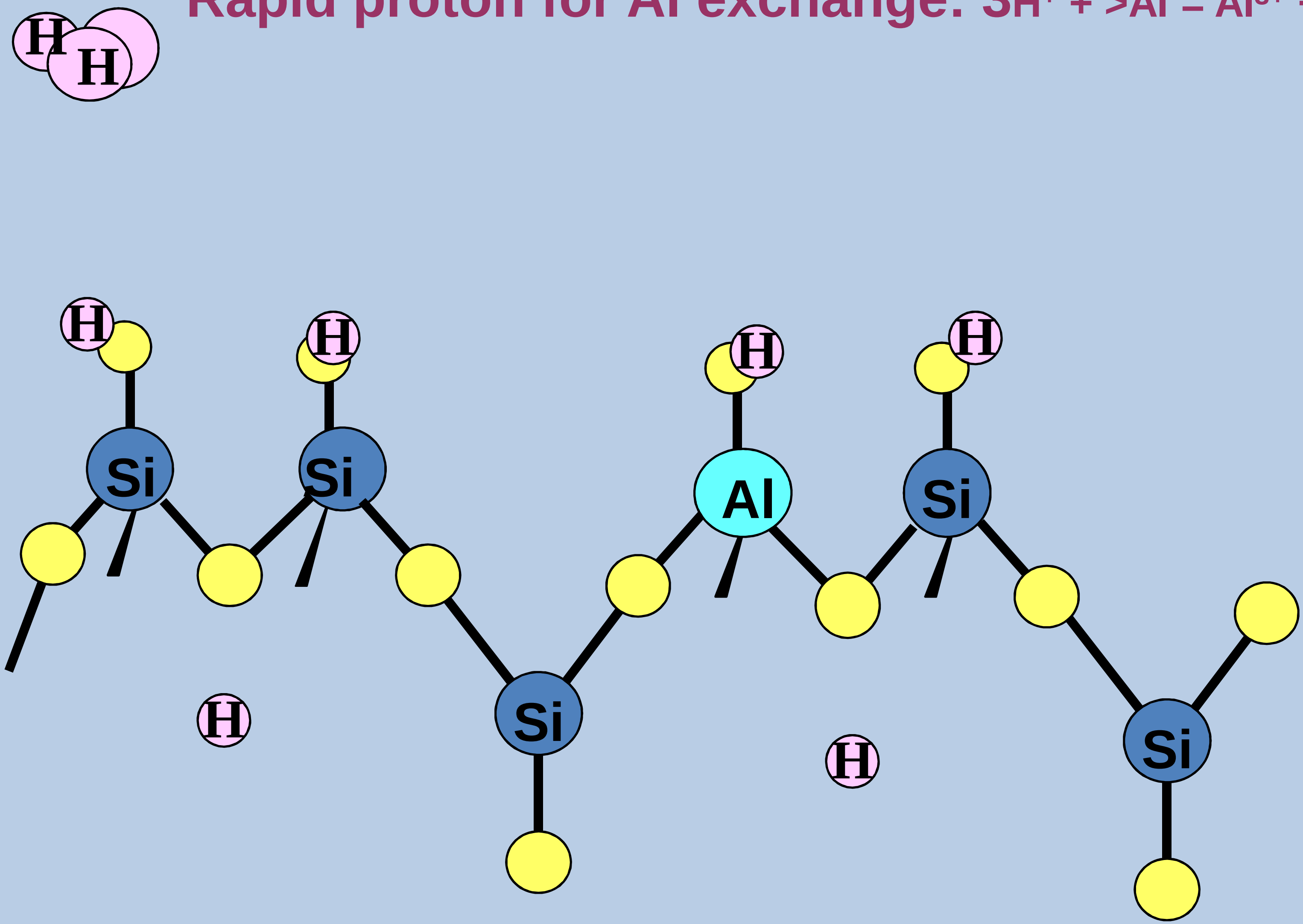
Alkali Feldspar dissolution mechanism

Rapid Na/H exchange: H^{+} + >Na = Na^{+} + >H



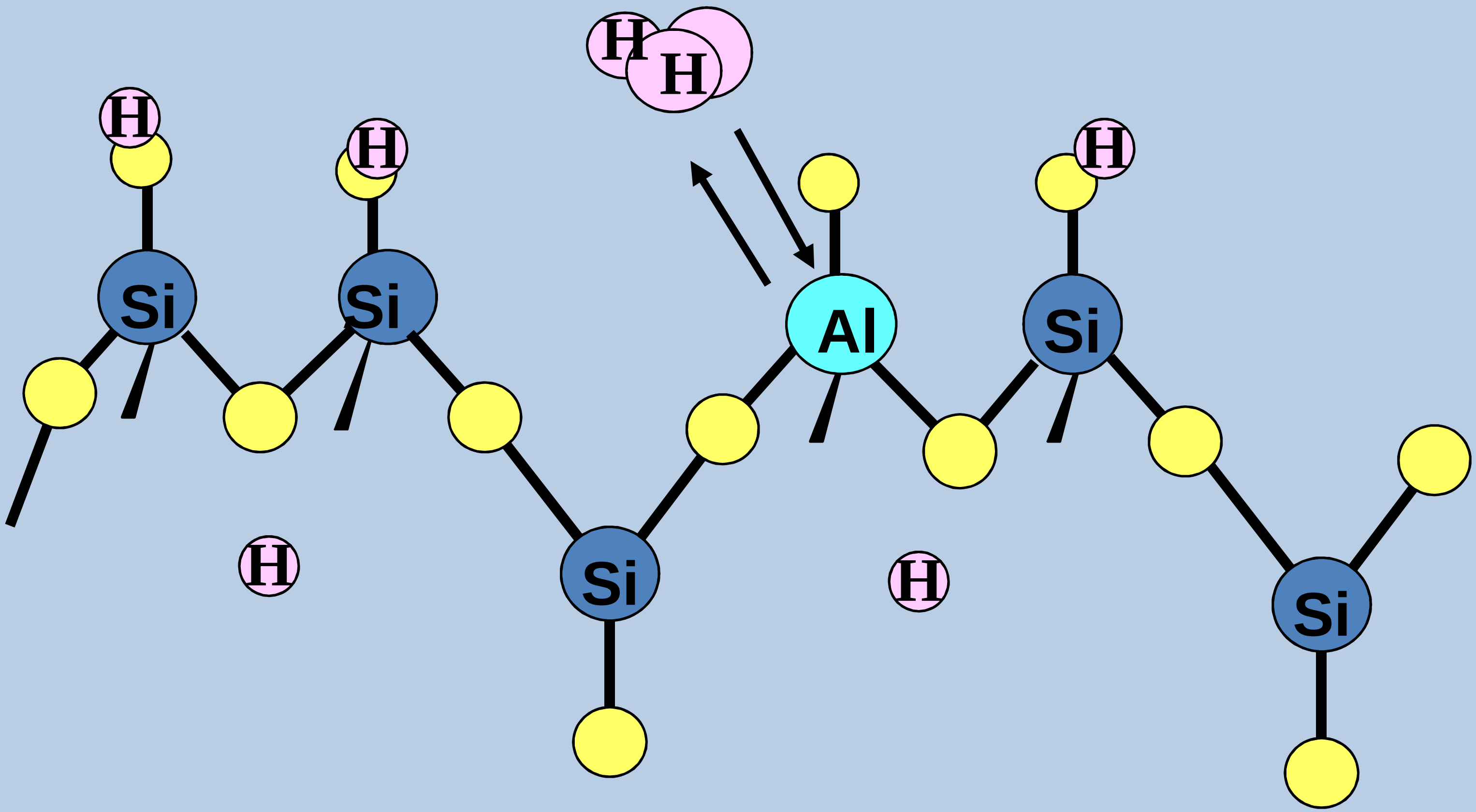
Alkali-felspar dissolution mechanism

Rapid proton for Al exchange: $3H^{+} + >Al = Al^{3+} + >H_3$

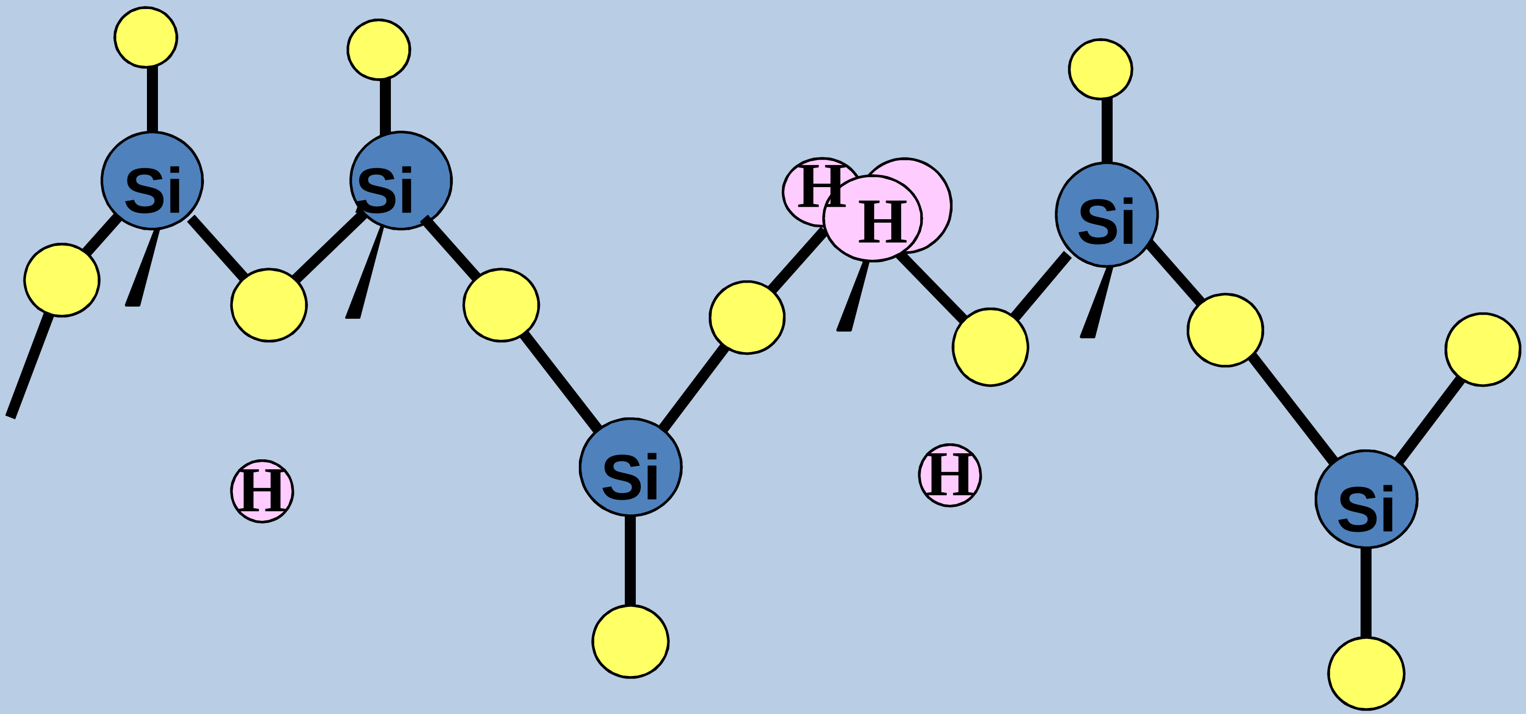


Alkali-feldspar dissolution mechanism

Rapid proton for Al exchange

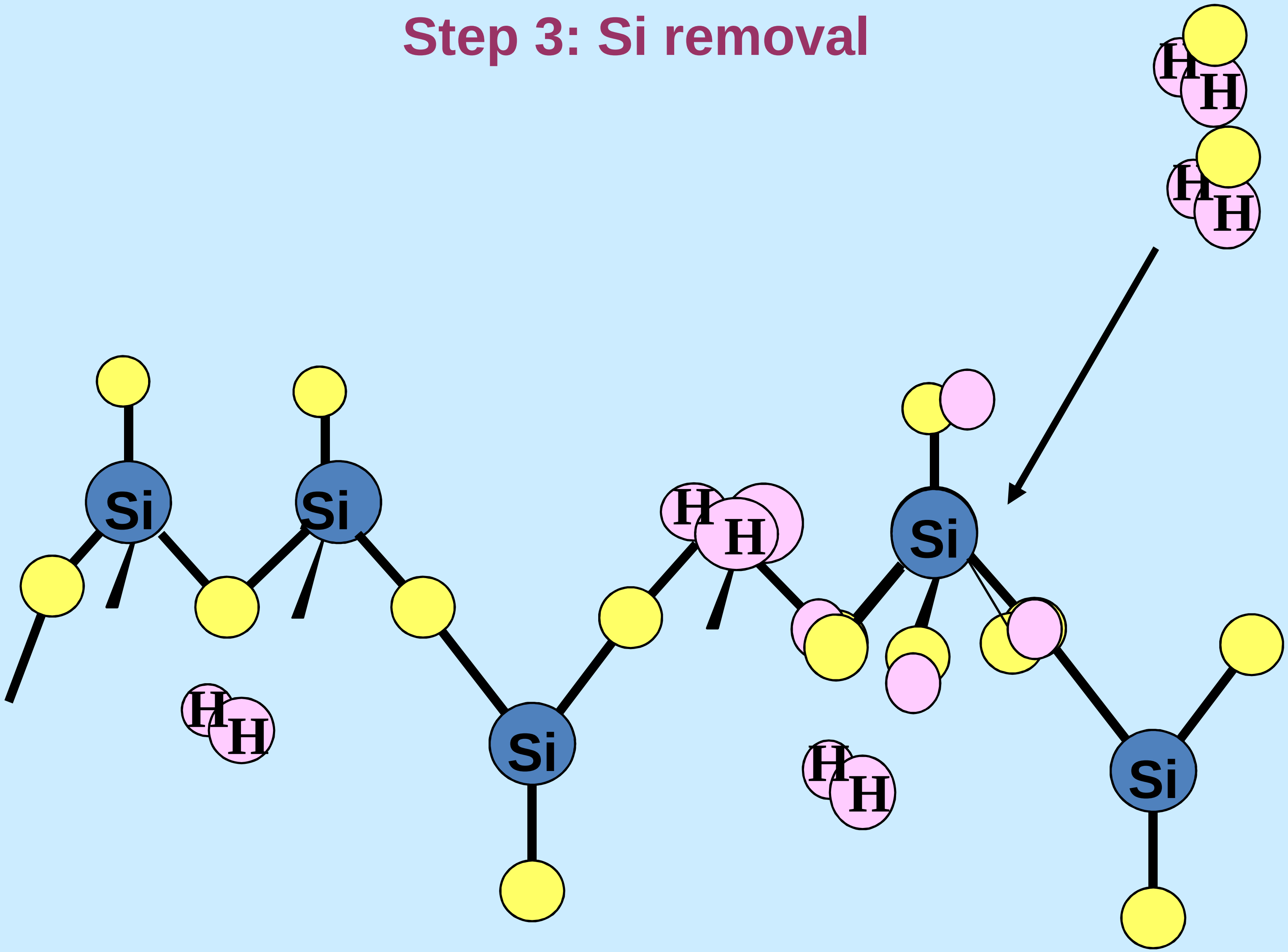


The albite surface in acidic pH solutions



Alkali feldspar Dissolution Mechanism:

Step 3: Si removal



Transition State Theory

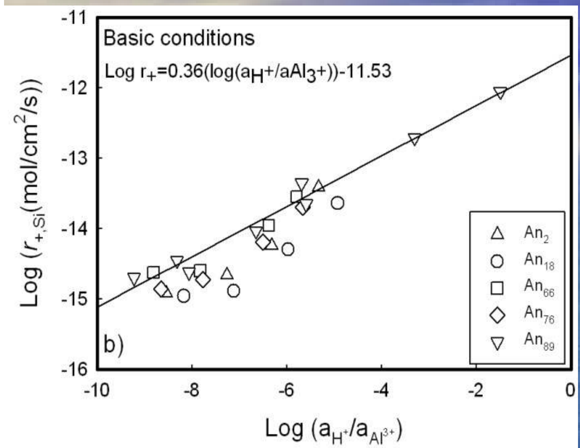
Forward dissolution rate is proportional to activated site concentration

$$\boldsymbol{r} = \mathbf{k}\,[\mathbf{A}^+] = \mathbf{k} \quad K\left(a^{z}_{\mathrm{H}^+}/a_{\mathrm{M}^{z+}}\right)^{n} \quad (1\text{-}\exp(A^*/\sigma RT))$$

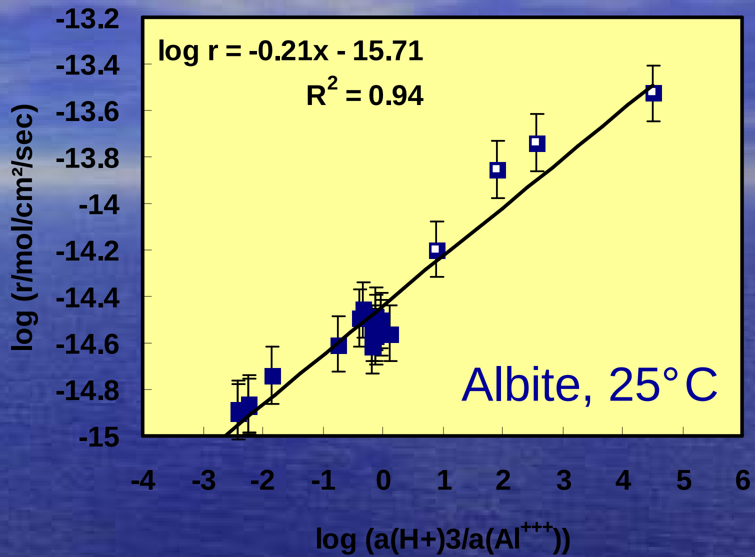
So for the alkali feldspars far from equilibrium….

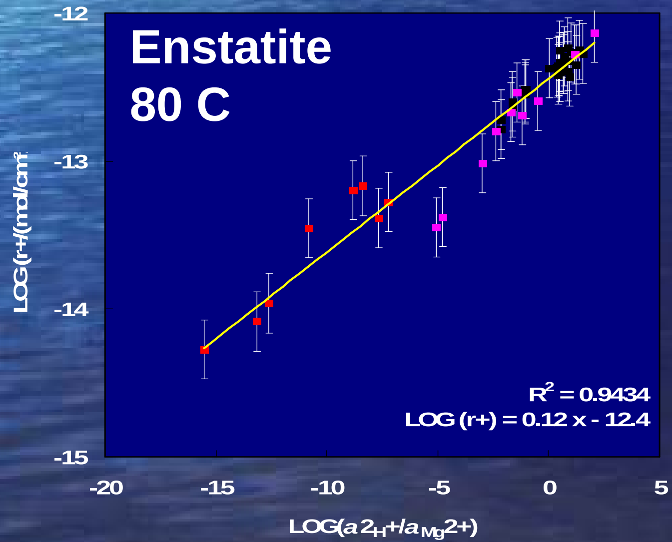
$$\boldsymbol{r} = \mathbf{k'} \; K\left(a^{3}_{\mathrm{H}^+}/a_{Al^{3+}}\right)^{n}$$

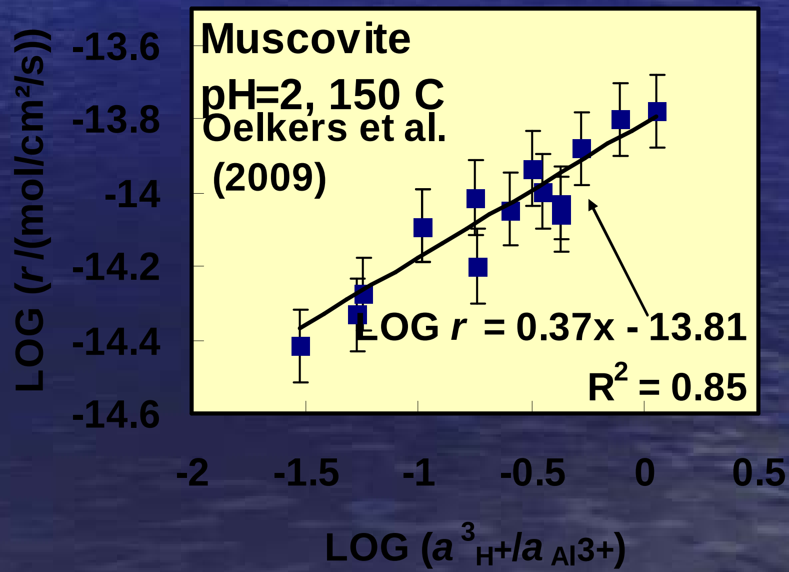
Multi-oxide dissolution rates versus ($a^n_{H^+}/a_{M^{n+}}$) in non-complexing systems



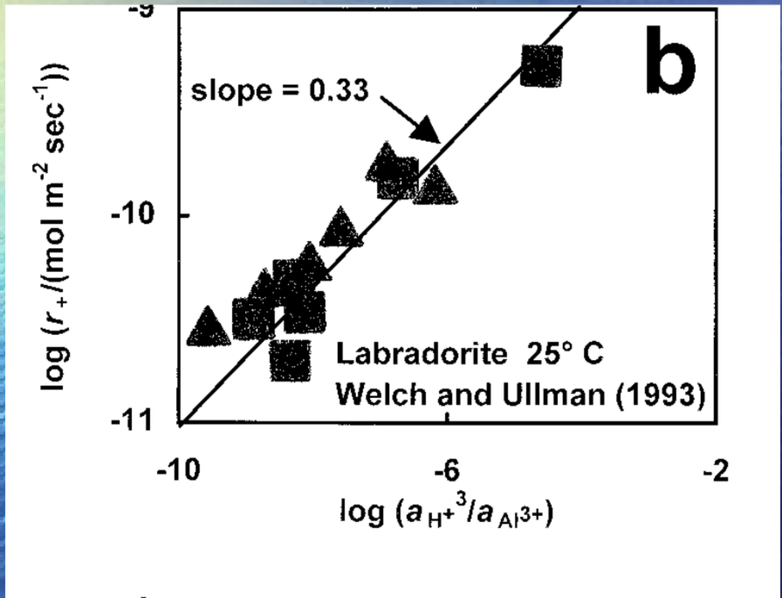
Plagiocalse at 25 C Gudbrandsson et al, 2014)



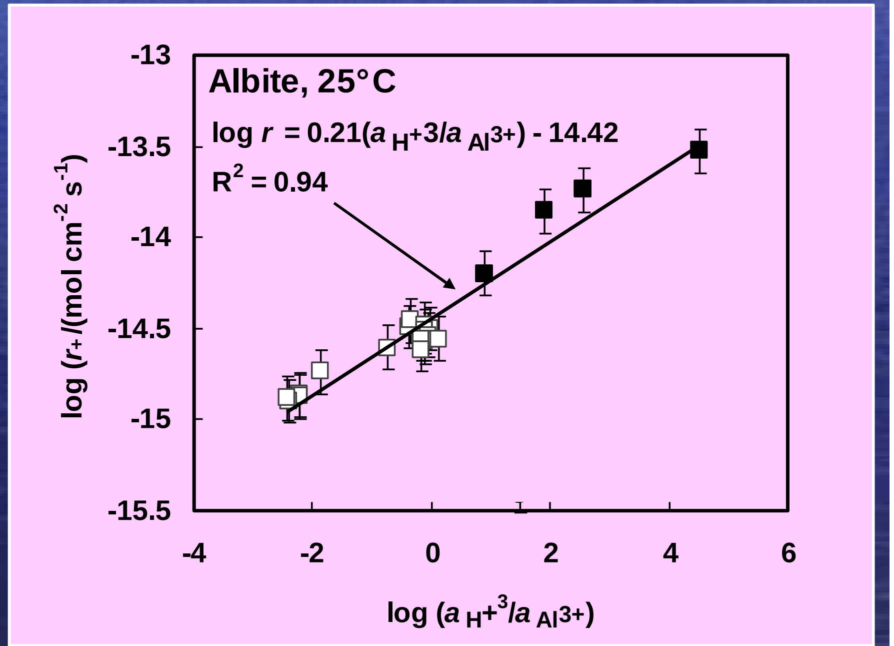




This also takes account of the effect of other ligands

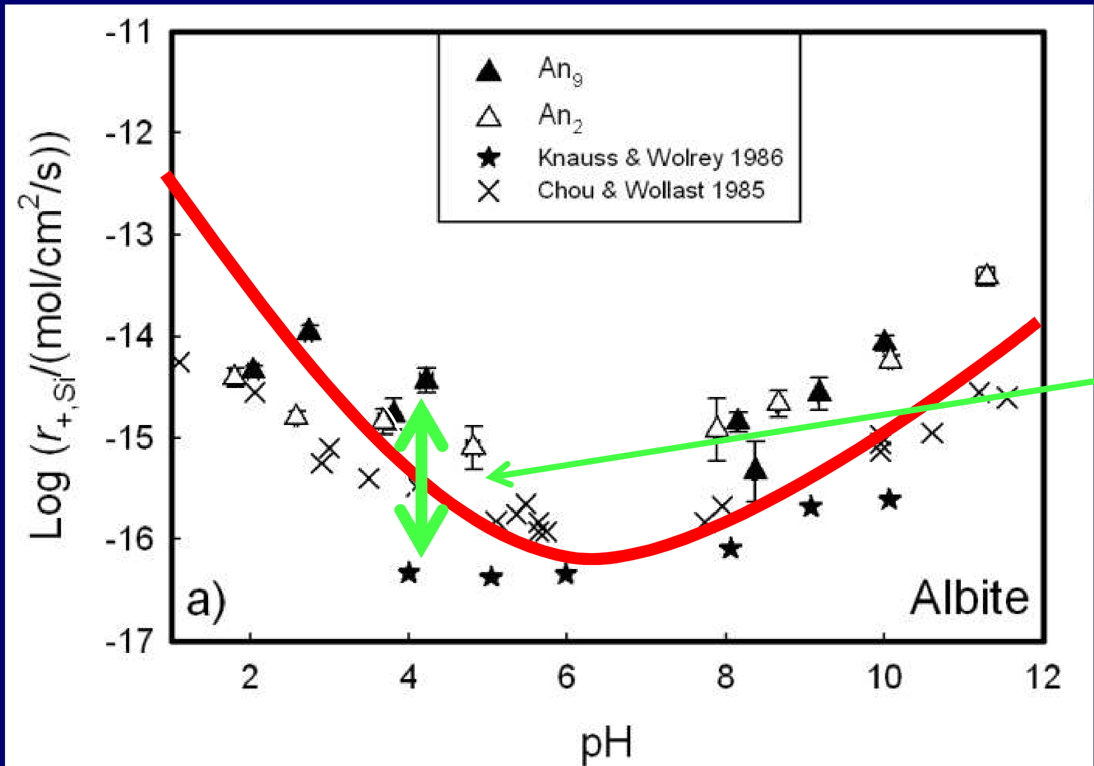


Organic ligands (Oelkers and Schott, 1998)



Flouride (Harouiya and Oelkers, 2004)

Albite dissolution rates as a function of pH



~2 orders of magnitude scatter

Gudbrandsson et al. (2014)

Sources of ‘Data Scatter’

- Degree of order of Al-Si framework (Zhang and Luttge, 2007, 2009)

- Grain size (Fischer et al (2012)

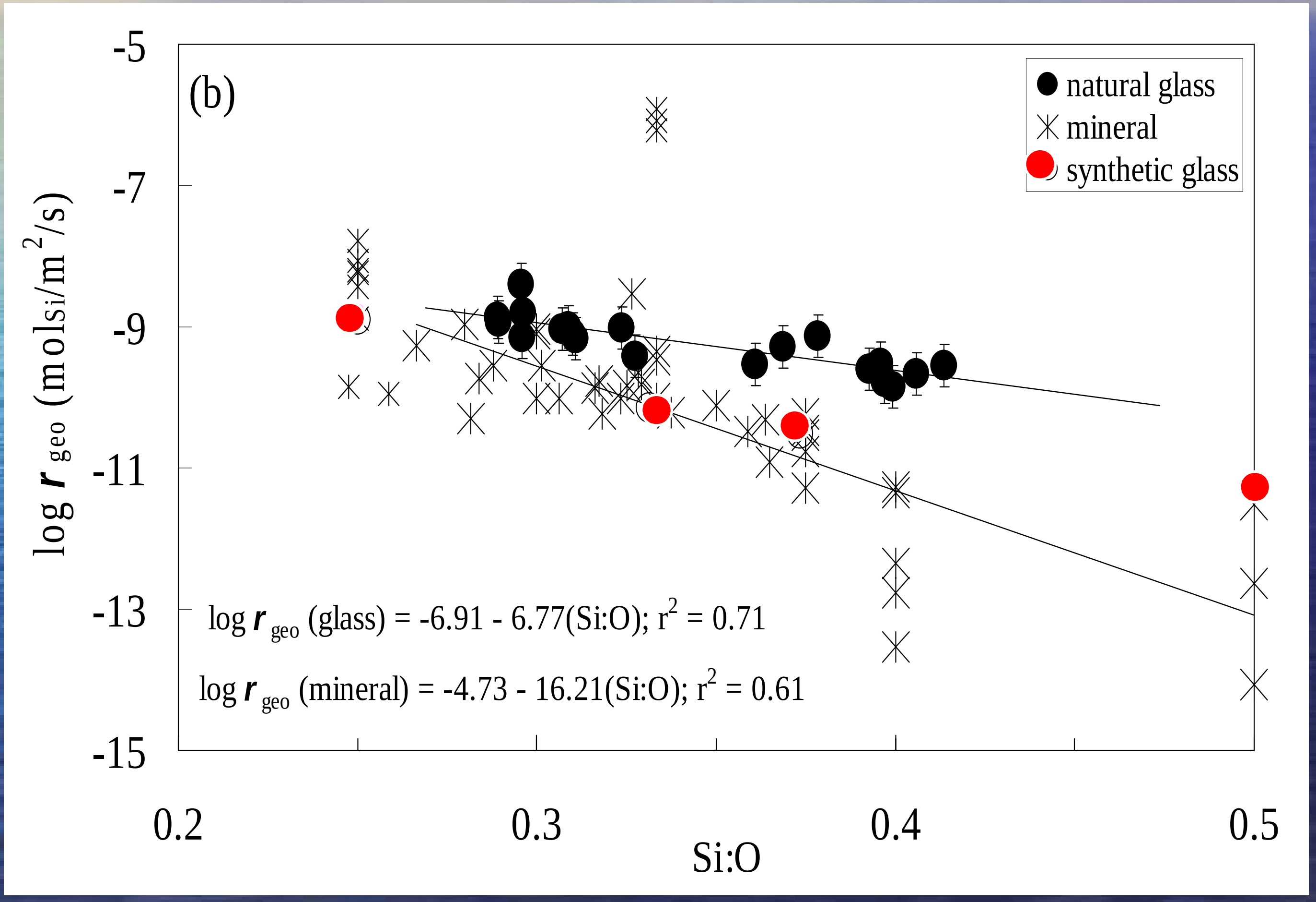
- Sample preparation (Beig and Luttge (2006)

- Small compostional differences/exsoltuion textures (Holdren and Spyer, 1985)

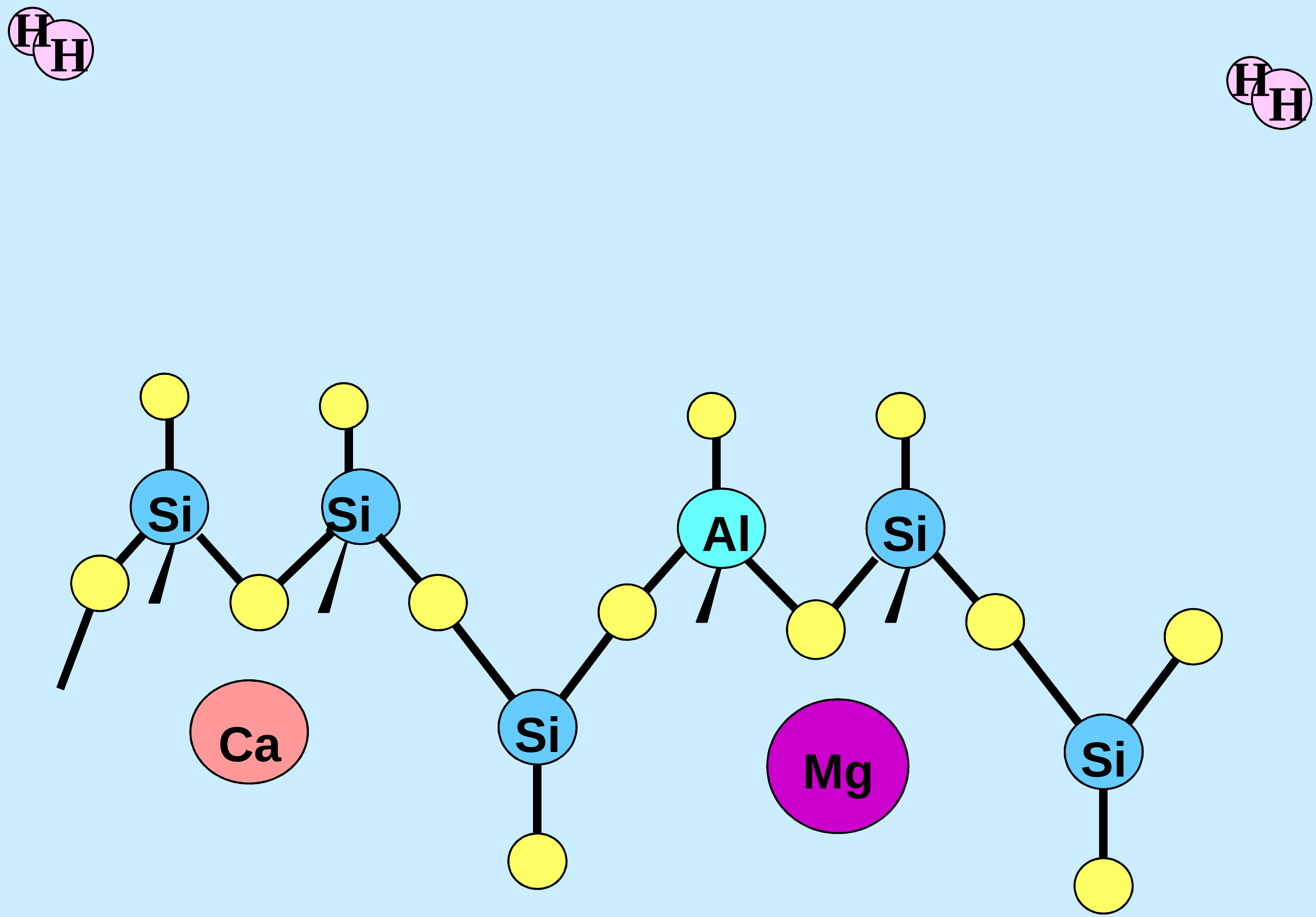
- Differences in reactive surface area among samples (Gautier et al., 2000)

- Loss of reactive surface area with time (Kohler et al., 2005)

Comparison of glass versus mineral dissolution rates (25 C pH 4) (Wolff-Bosenbach et al., 2006)

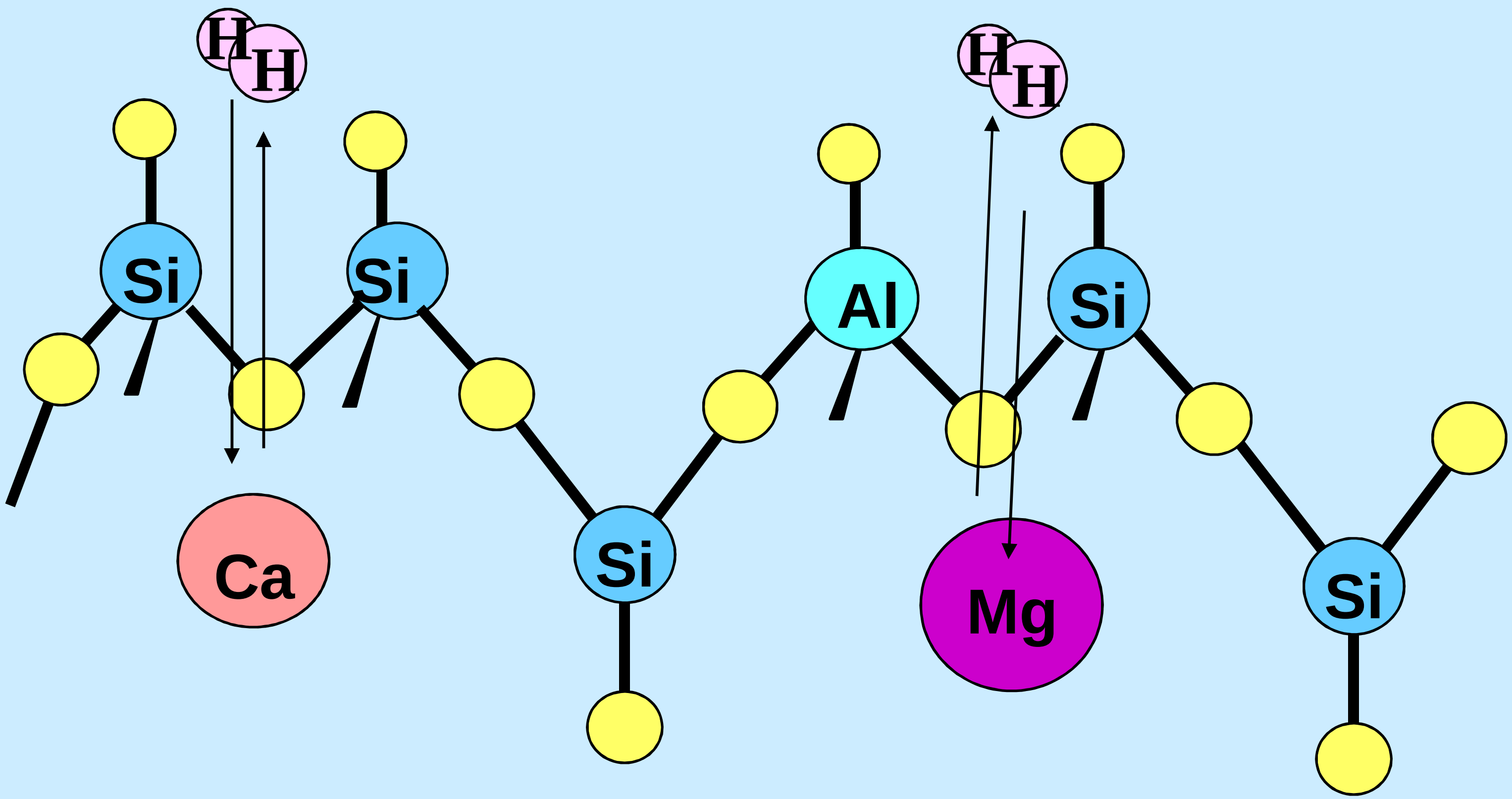


Basaltic Glass Dissolution Mechanism



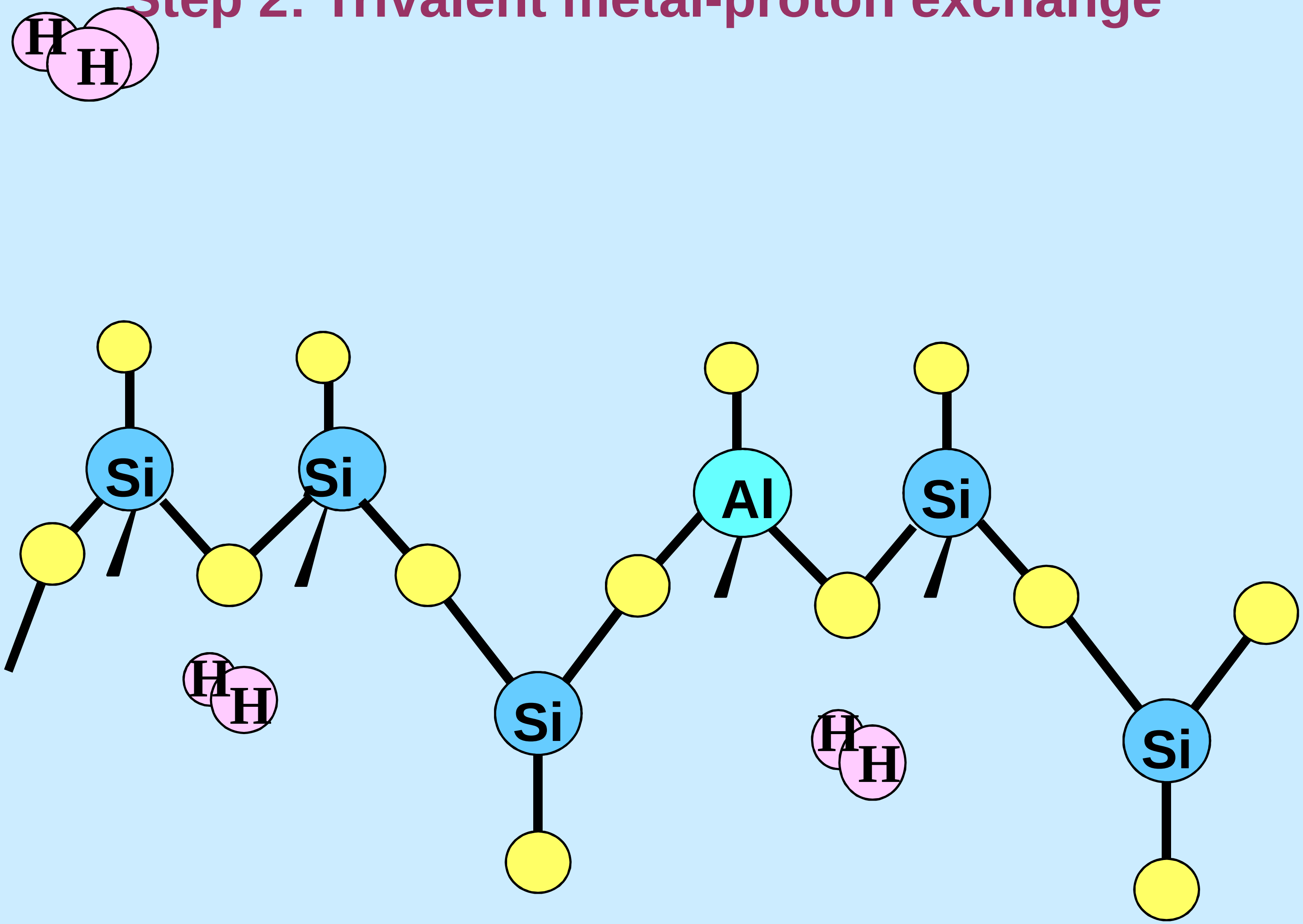
Basaltic Glass Dissolution Mechanism

Step 1: Mono/divalent metal exchange



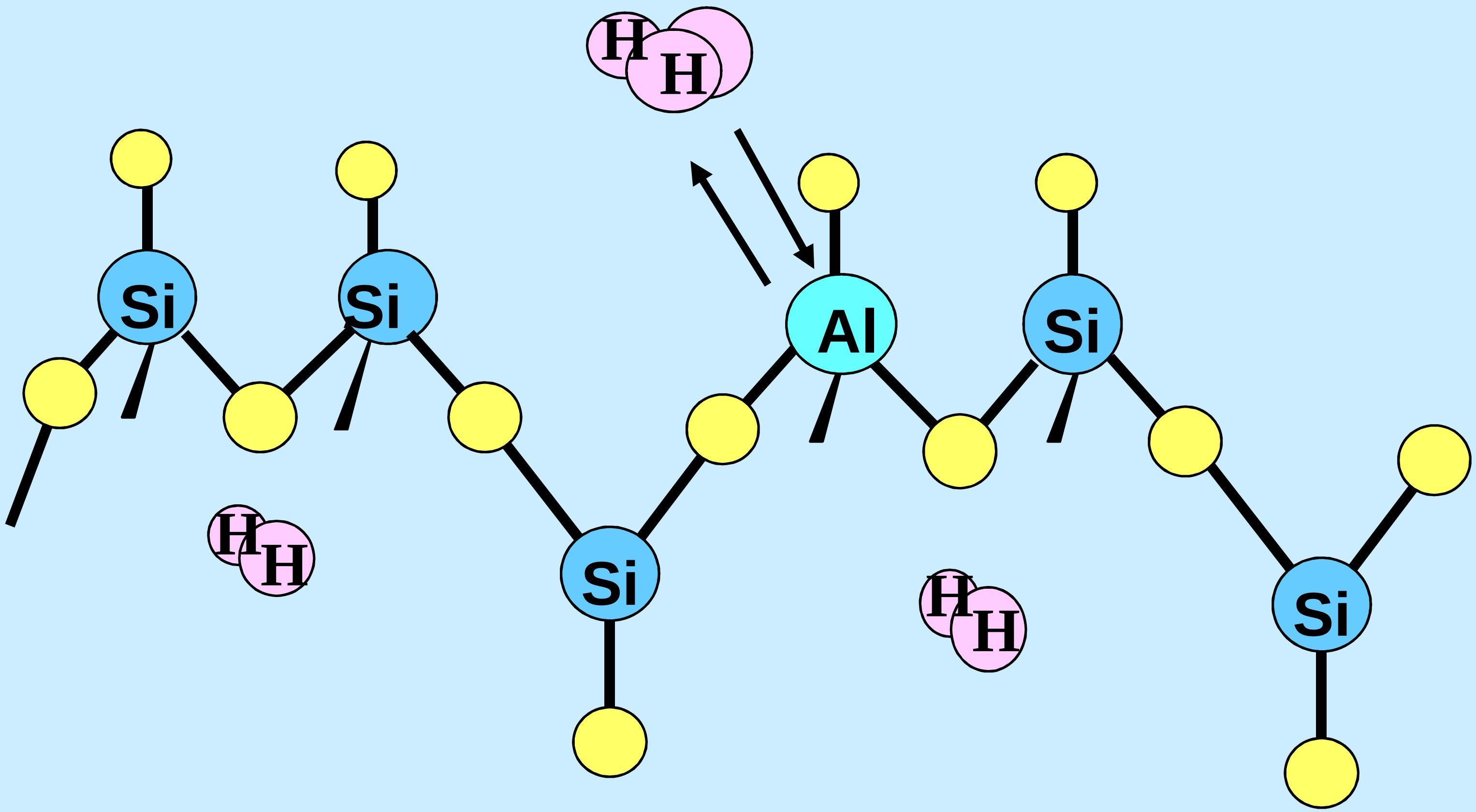
Basaltic Glass Dissolution Mechanism:

Step 2: Trivalent metal-proton exchange



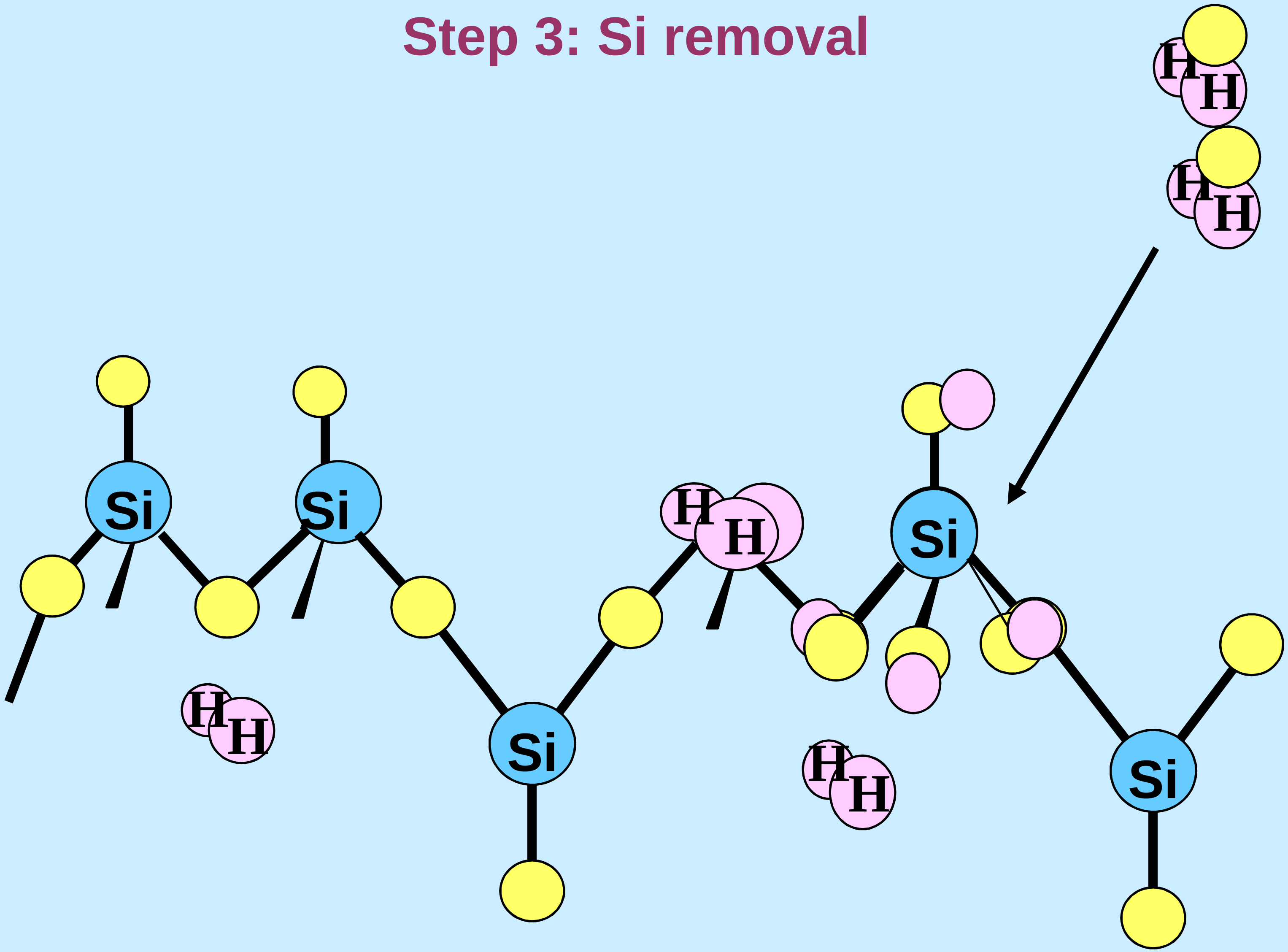
Basaltic Glass Dissolution Mechanism:

Step 2: Trivalent metal-proton exchange



Basaltic Glass Dissolution Mechanism:

Step 3: Si removal



Basaltic Glass Dissolution Rate Equation

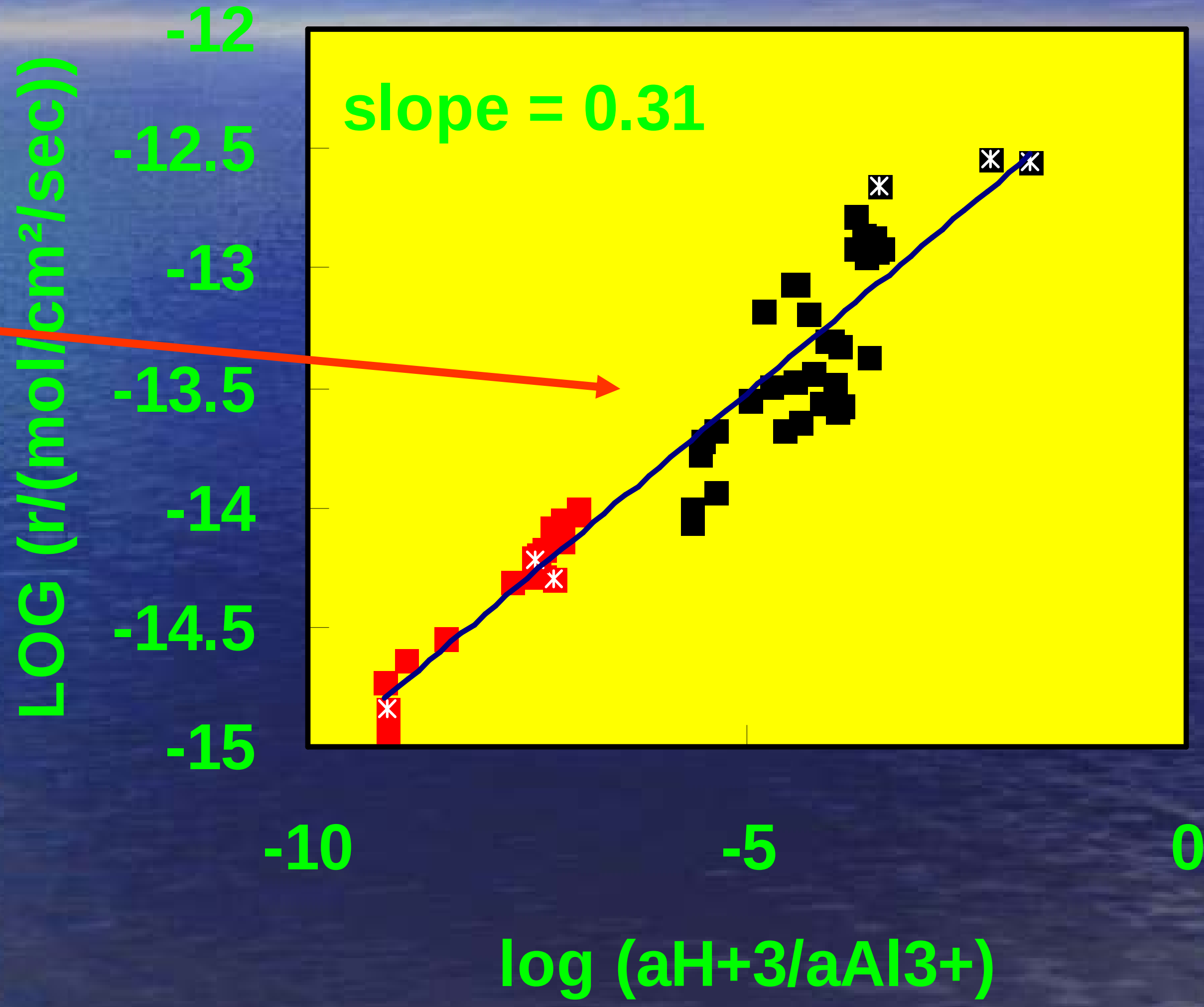
$$r = ks\left(\frac{a^{3}_{\mathrm{H}^{+}}}{a_{\mathrm{Al}^{3+}}}\right)^{1/3}\left(1 - exp\left(A^{*}/RT\right)\right)$$

Aqueous Activity Ratio

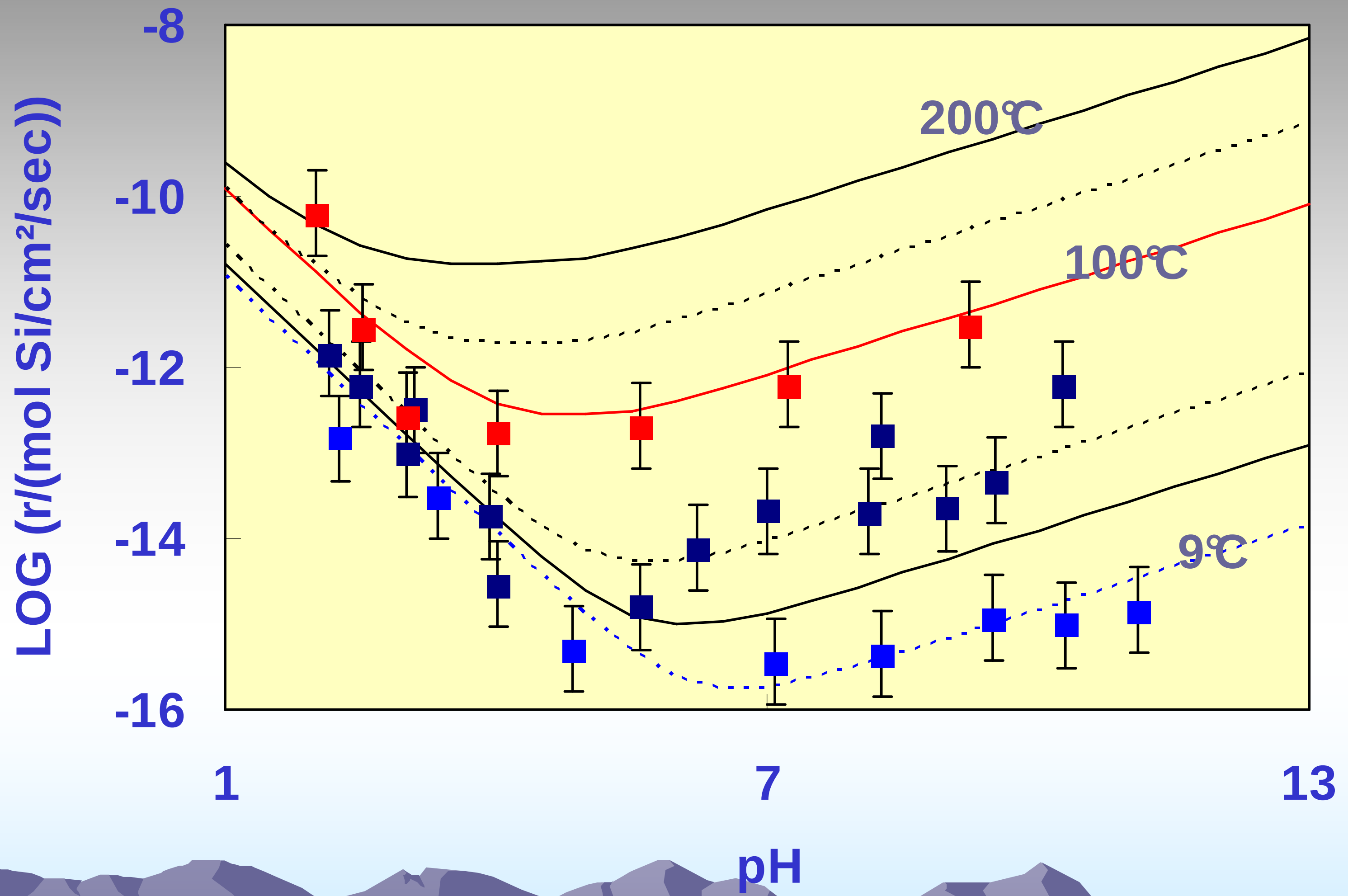
Chemical Affinity of Al-Si-Fe surface layer normalized to 1 Si

Variation of measured Basaltic Glass Dissolution rates with ($a_{H^+}/a_{Al^{+3}}$) (Oelkers and Gislason, 2001)

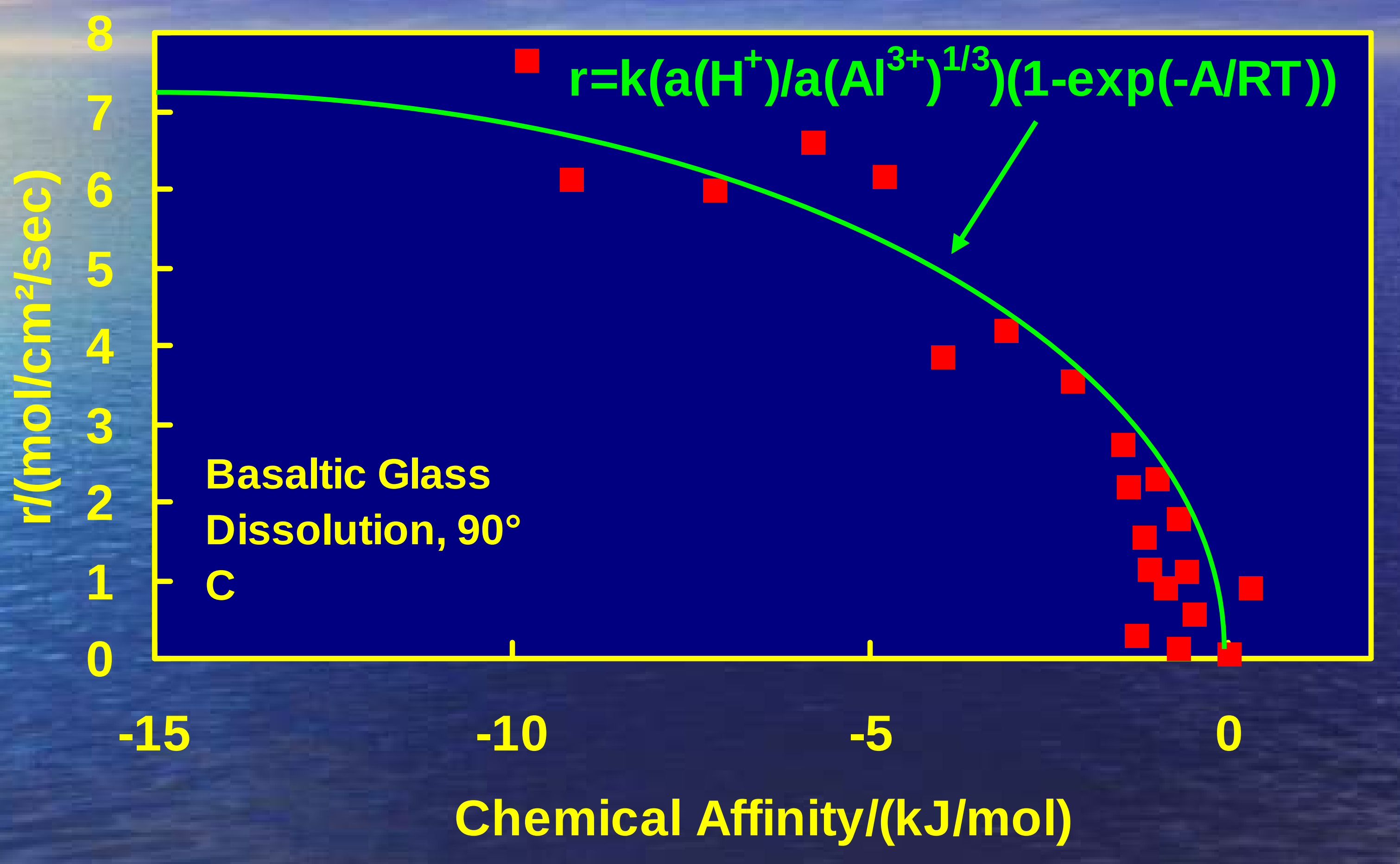
A single regression curve is found for all data at both acidic and basic pH



Measured basaltic glass dissolution rates as a function of pH



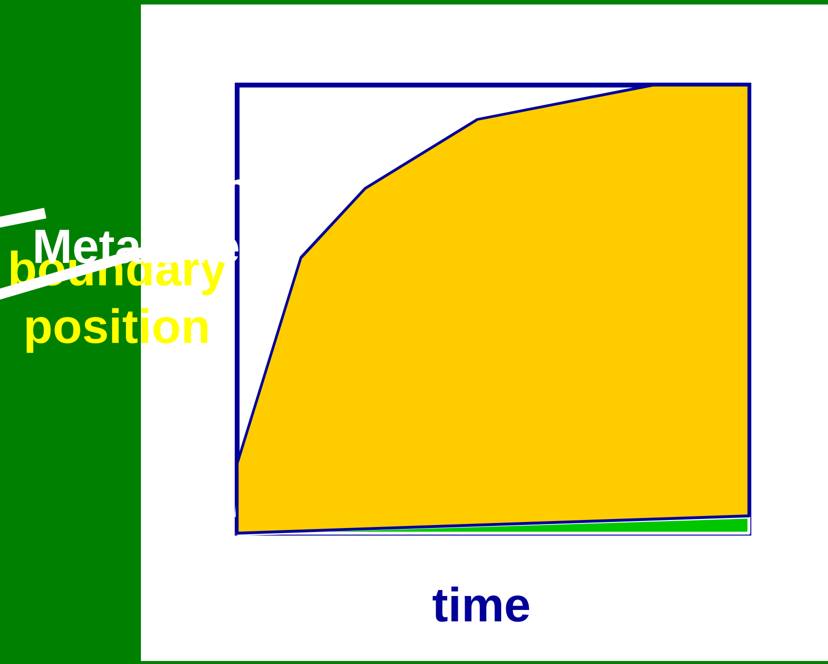
Variation of basaltic glass dissolution rates with chemical affinity of leached layer (after Daux et al., 1998)



Evolution of leached layers

Case 1: $r_{diffusion} \sim r_{dissoltuion}$

Case 2: $r_{diffusion} \gg r_{dissolution}$

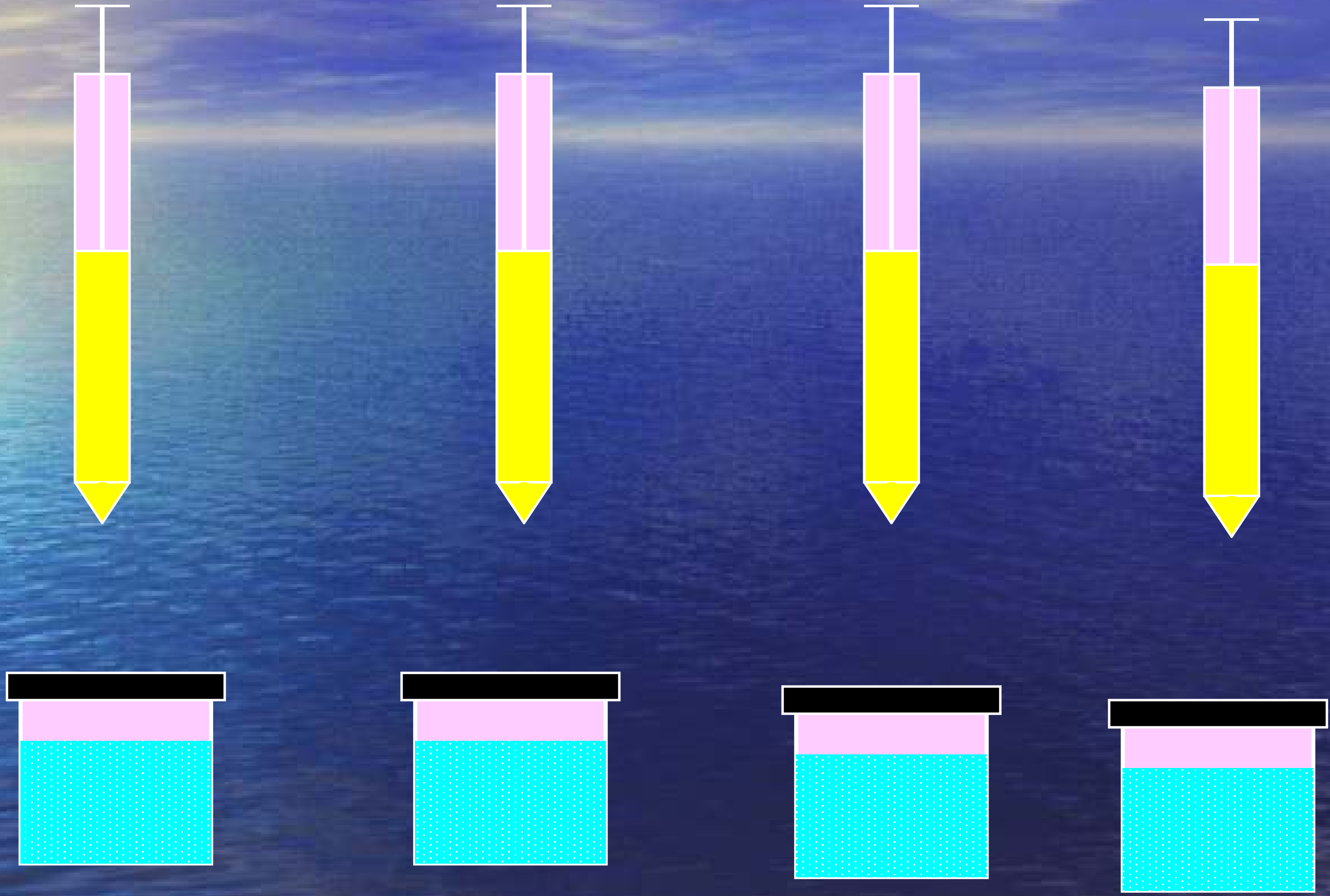


Leached layer grows continuously with time; never reaches a constant thickness

Meta

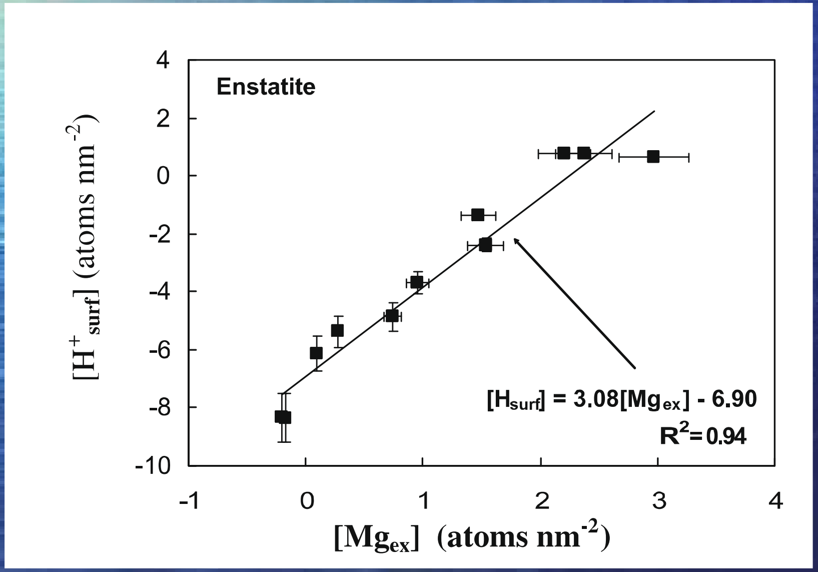
metals

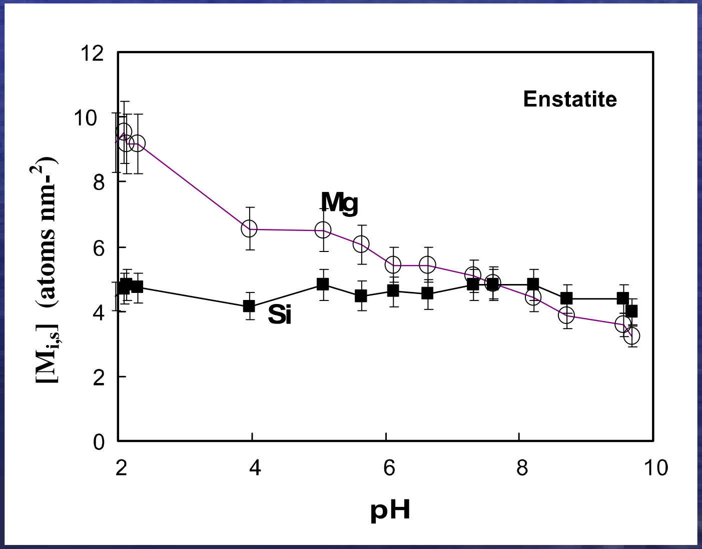
How we did titrations



Titrations illustrate the proton for metal exchange and how this reaction varies with pH

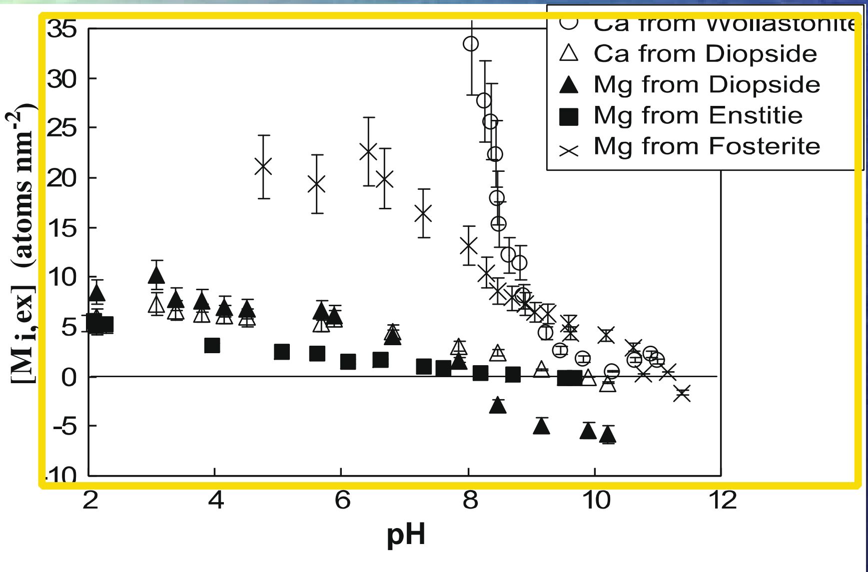
Example Enstatite ($MgSiO_3$, Oelkers et al., 2009)

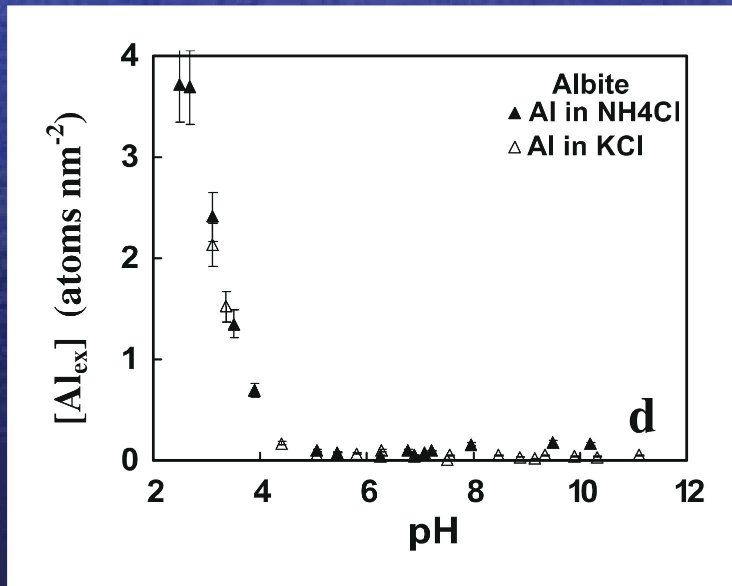




$>Mg + 3H^+ = >H_3^+ + Mg^{2+}$

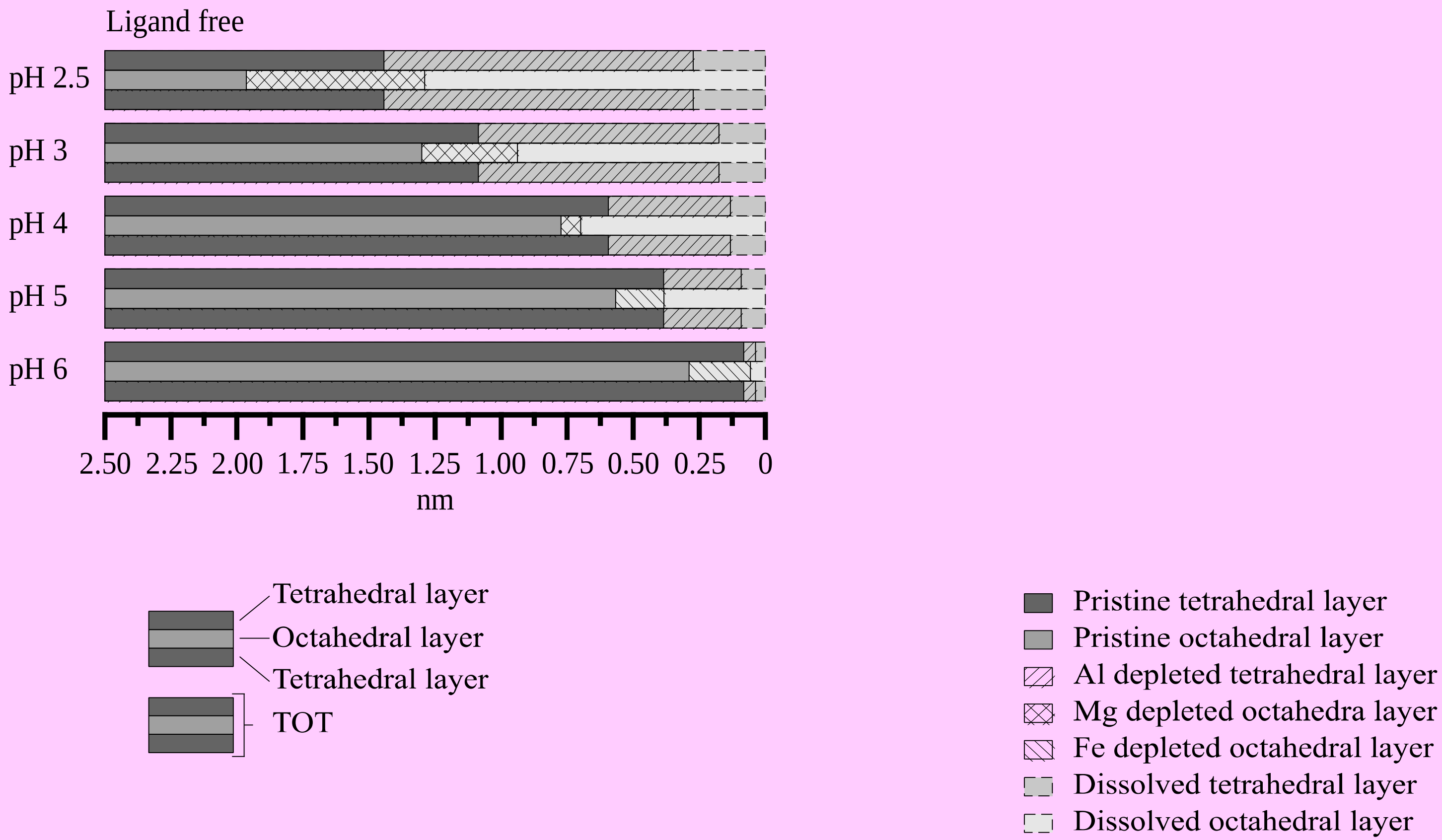
The above dissolution mechanisms explain ‘dissolution’ but not surface compostion and at times release rates of other elements…





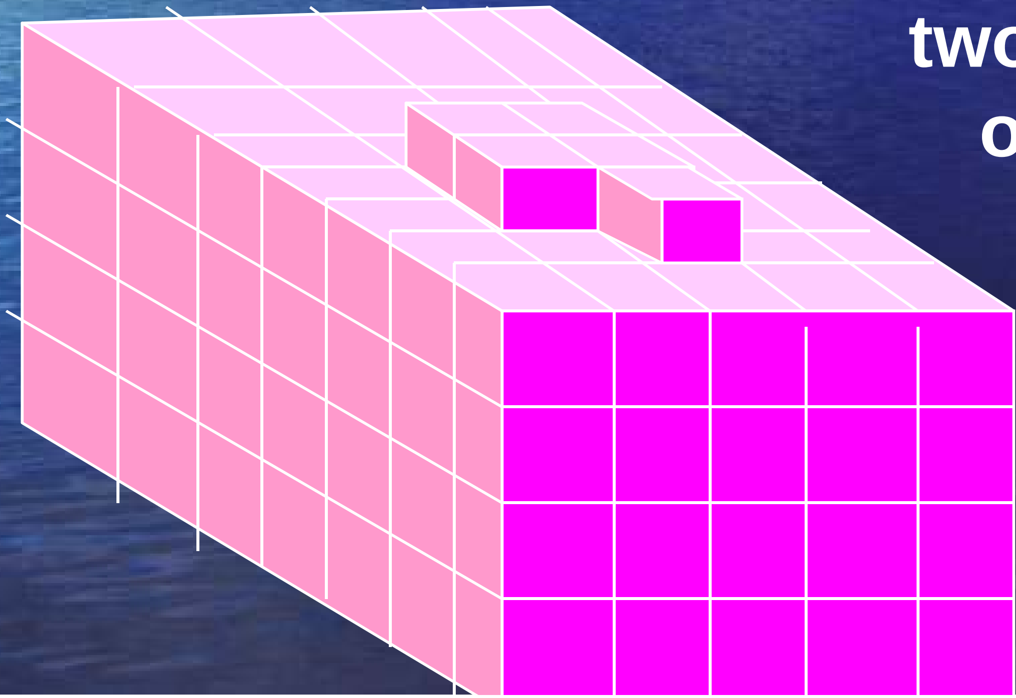
Excess metals released during 20 minute titrations from various minerals (Oelkers et al, 2009)

Biotite near surface as a function of pH (Bray et al. 2014)



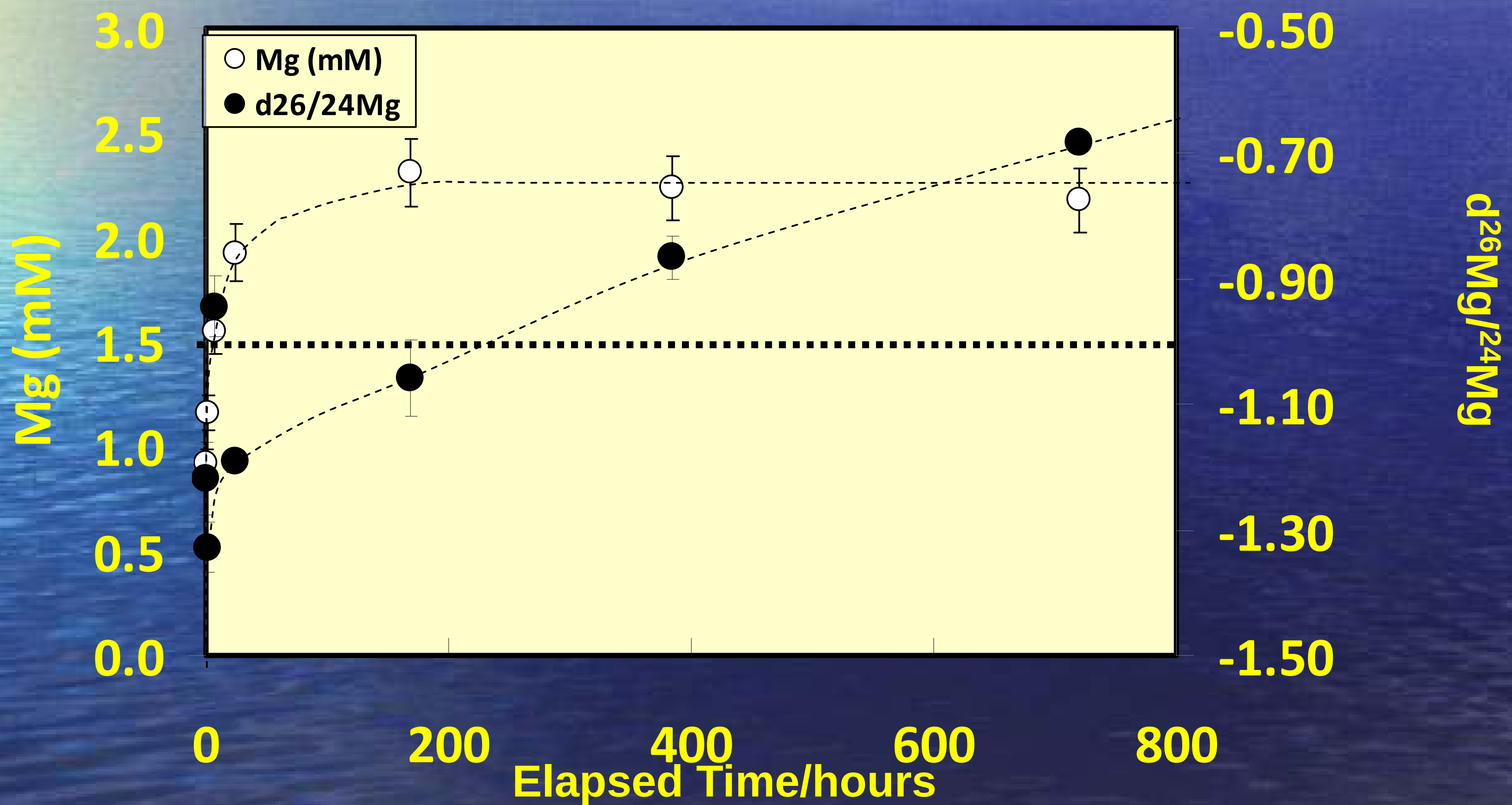
The degree to which metals are depleted on the near surface depends on fluid composition, notably pH

Law of micro-reversibility



Equilibrium is the two-way transfer of material…

New Challenges: Defining element exchange using stable isotopes: Fluid Mg evolution during 25 C hydromagnesite dissolution and equilibrium (Oelkers et al., 2014)



Summary:

- **Rate mechanisms for multi-oxide minerals and glasses can be deduced from relative metal-water exchange rates**
- **These mechanisms provide robust equations for prediction dissolution rates**
- **Second order effects can lead to +/- 2 orders of magnitude uncertainty**
- **Faster metal exchange reactions lead to surface depletion zones that depend on fluid composition**
- **But the exchange reactions still continue at 'equilibrium' consistent with dynamic equilibrium**

Vitesse d’ ration des raux s

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GET/Université Paul Sabatier, Toulouse, FRANCE

Science Institute,University of Iceland, ICELAND

Earth Sciences, University College London, UK

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Major elements/minerals...

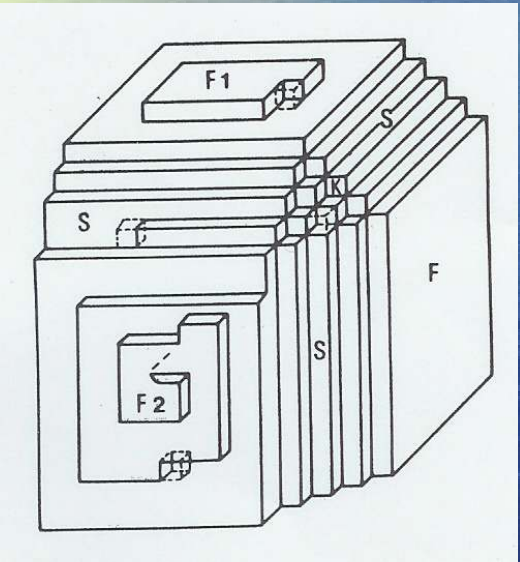
Over the past 16 years in Toulouse alone we have the dissolution rates of more than 40 rock forming minerals as a function of temperature and solution composition in bulk/mixed-flow reactors.

Minerals/glasses include:

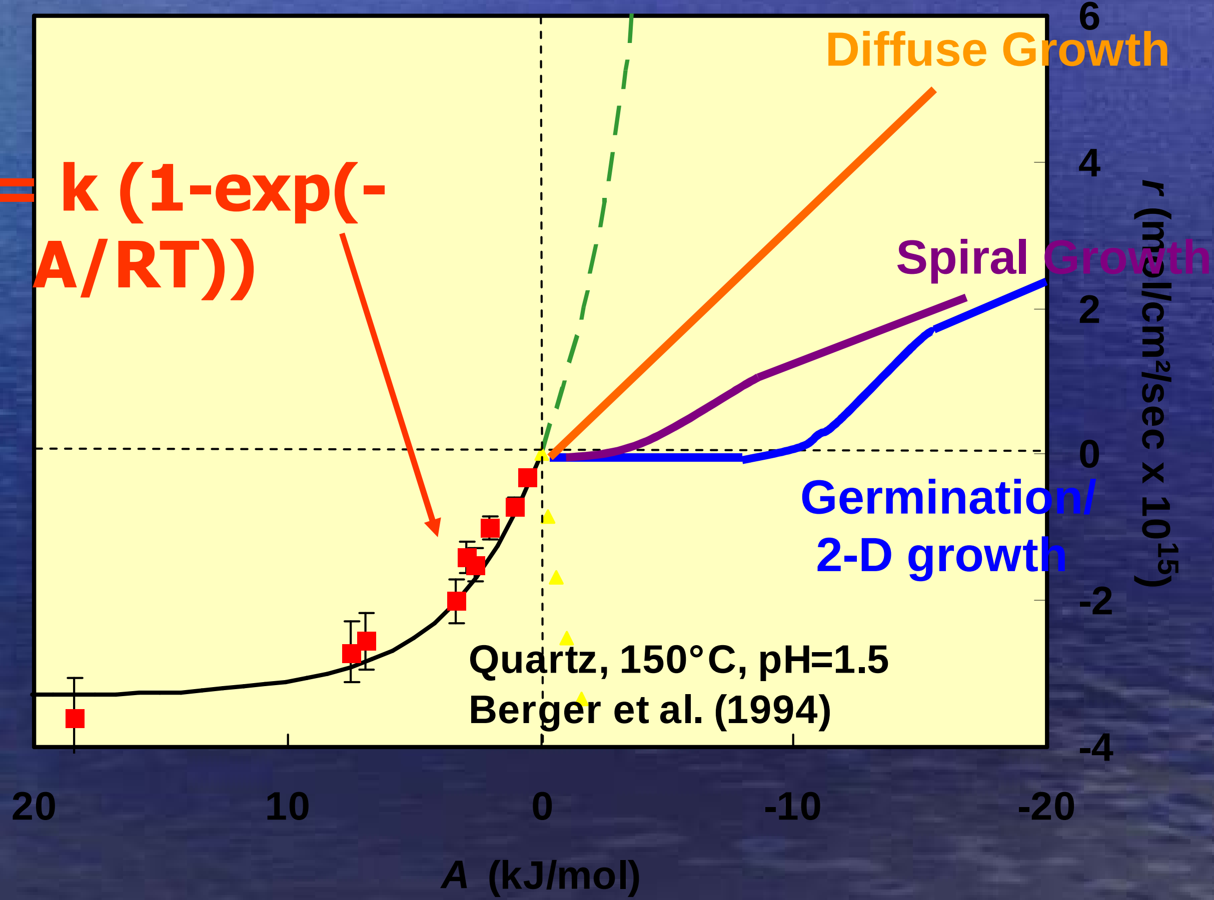
Oxides: Quartz, moganite, hematite,
FRAMEWORK SILICATES: albite, K-feldspars, anorthite, kyanite
SHEET SILICATES/CLAYS: kaolinite, talc, muscovite, illite, talc, tremolite, serpentine
CHAIN SILICATES: diopside, forsterite, hornblende, enstatite, wollastonite,
CARBONATES: calcite, dolomite, magnesite, dawsonite,
PHOSPHATES: apatite, monazite, rhabdophane, struvite
GLASS: basaltic, rholytic
MISCELLANEOUS: halite

These rates are currently being incorporated into a computer enabled database to allow their use in geochemical modeling calculations

Precipitation rates What do we know?



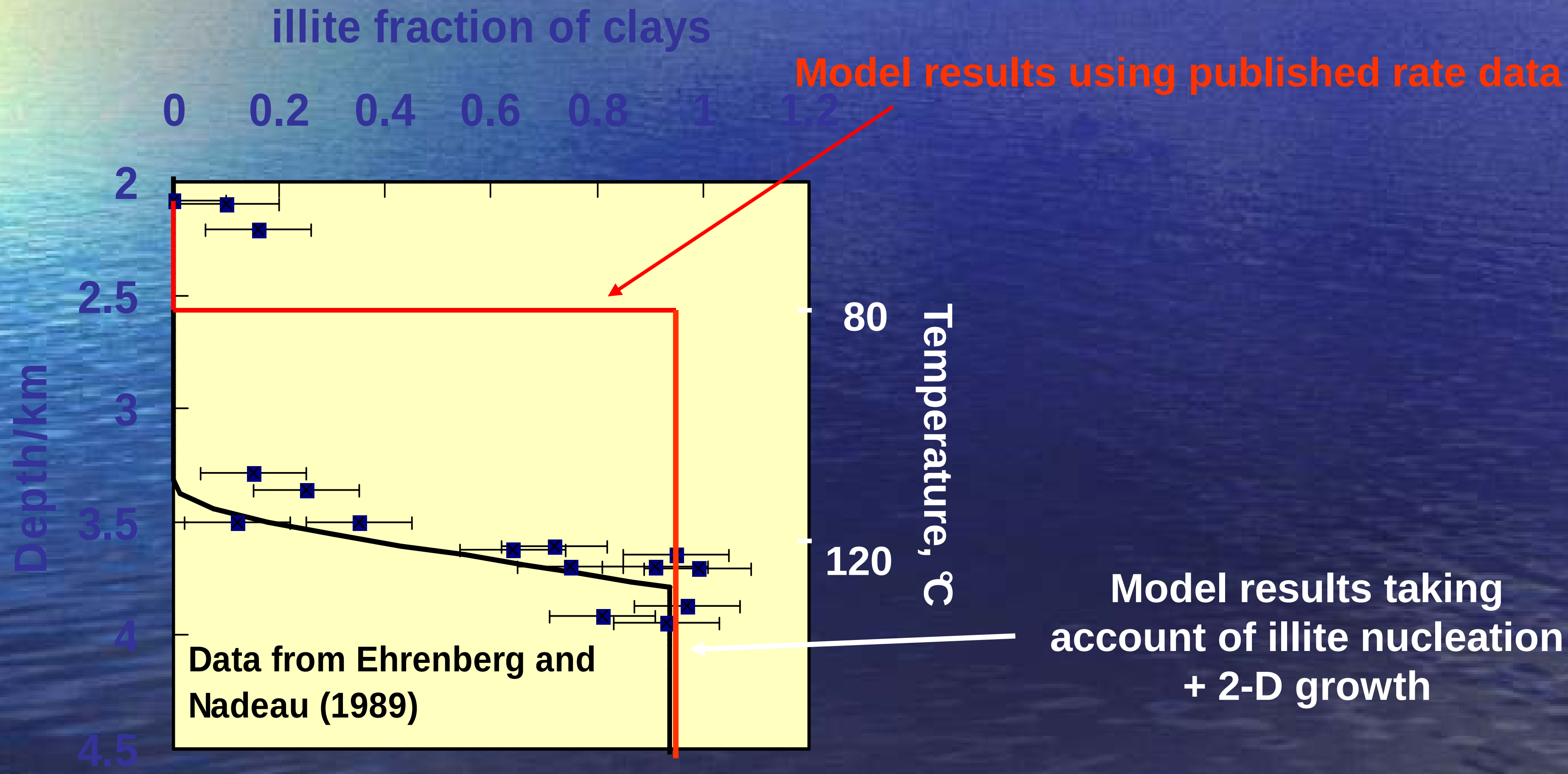
$r = k\,(1-\exp(-A/RT))$



Example: Modeling of illite formation in Garn formation (Oelkers et al., in prep.)

$$Al_2Si_2O_5(OH)_4 + KAlSi_3O_8 = KAl_3Si_3O_{10}(OH)_2 + 2SiO_2 + H_2O$$

kaolinite K-spar Illite quartz



Summary

- General model describing dissolution rates and mechanisms developed/parameterized for all major minerals/glasses
- In geosciences its currently unclear how this can be extended to nucleation/growth

General Silicate Dissolution Mechanism:

Basic Assumptions

1) Metals removed via proton exchange reactions

2) Partially liberated metals are removed faster than fully attached metals

3) At any given pH and Temperature metals are removed in same relative order in all silicates

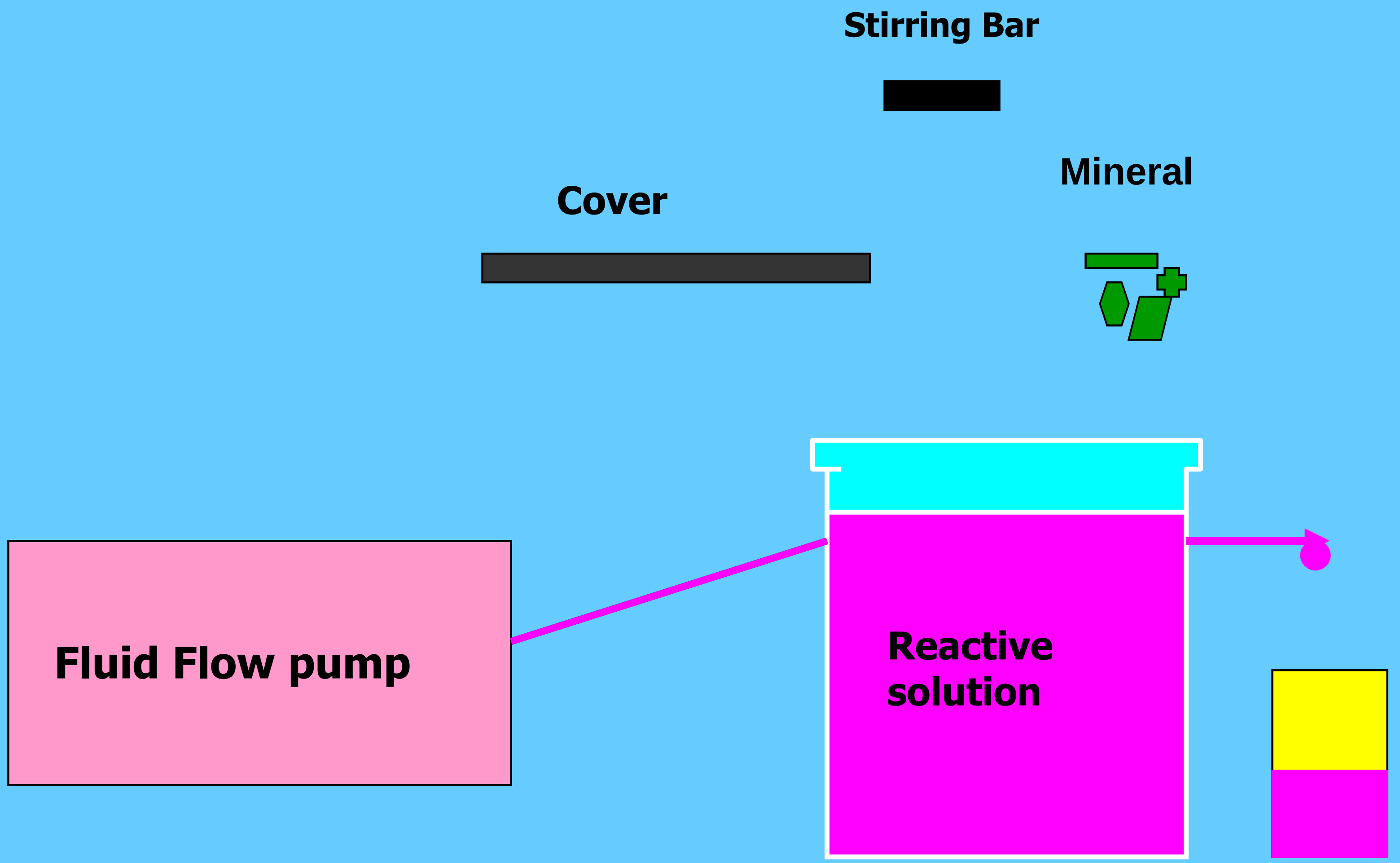
Basaltic Glass
(from Vatuajokull Iceland)

$SiAl_{0.36}Ti_{0.03}Fe(III)_{0.02}$

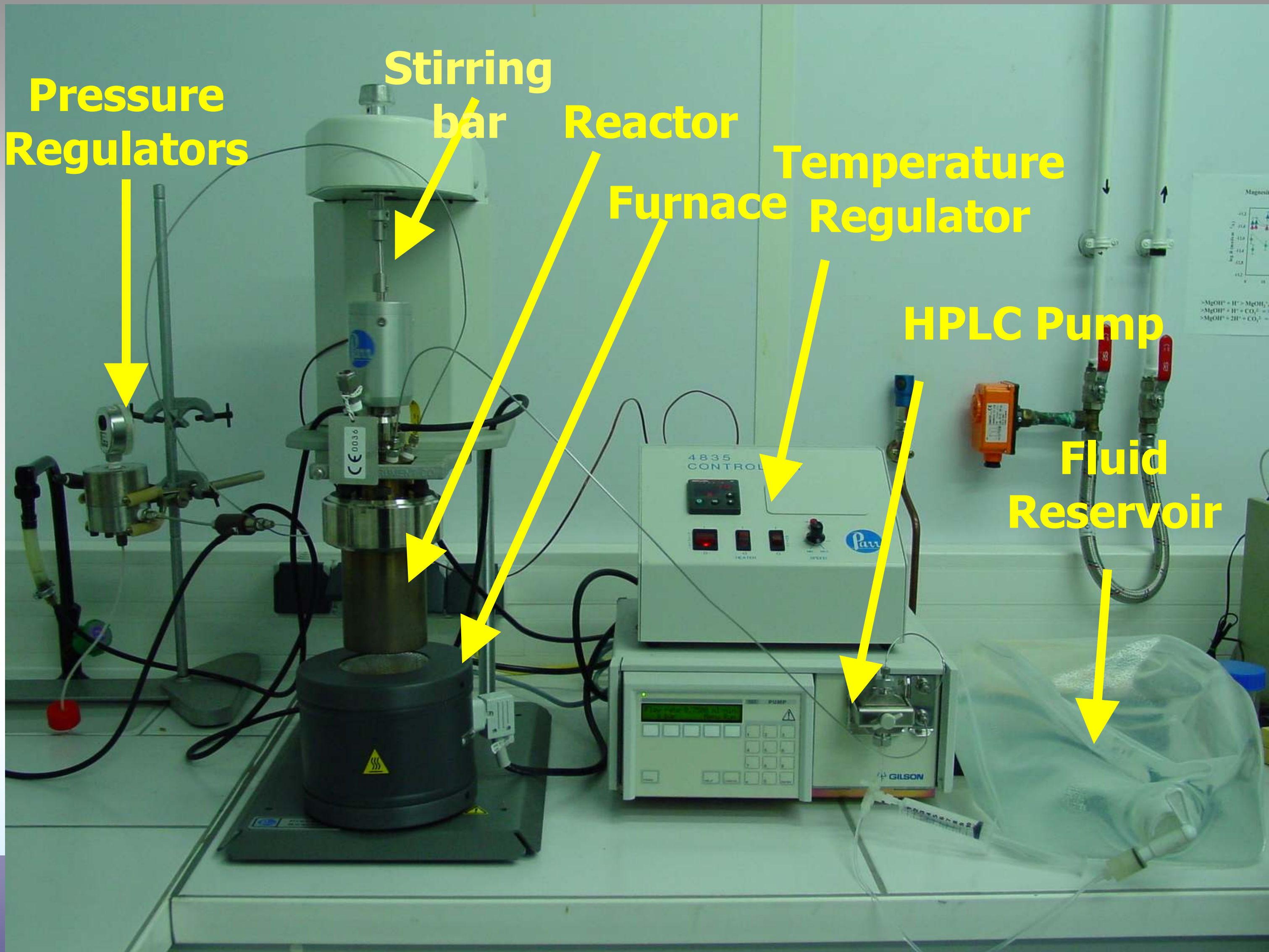
$Ca_{0.30}Mg_{0.25}Fe(II)_{0.15}Na_{0.04}$

$O_{3.35}$

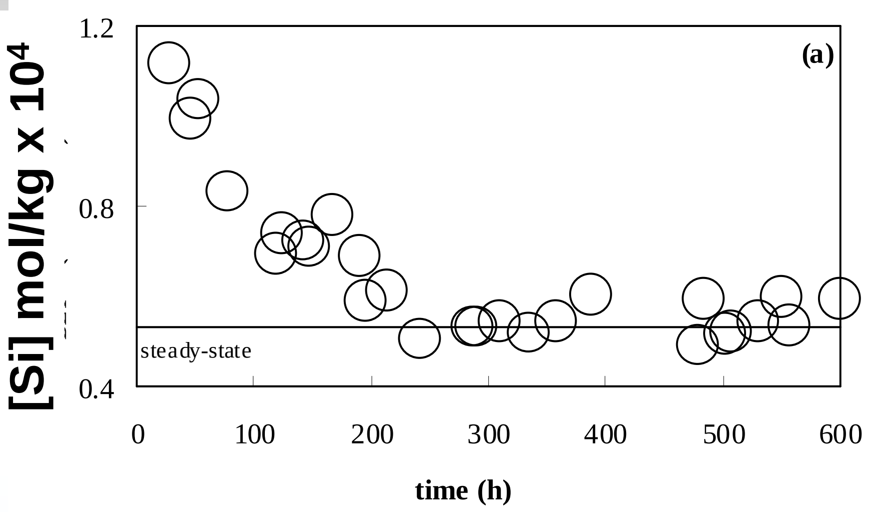
Open System reactor experiments:

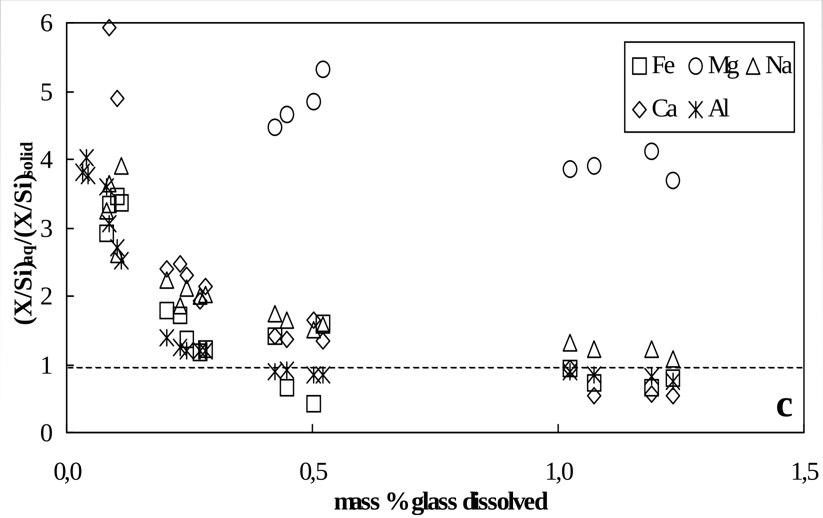


High Temperature Open system reactors



Typical fluid evolution during glass dissolution experiment





Mathematical Necessities 1: Thermodynamics

Metal-proton exchange reaction:

$$M< + z\,H^{+} = M^{z+} + H_{z}<$$

Metal in near surface site

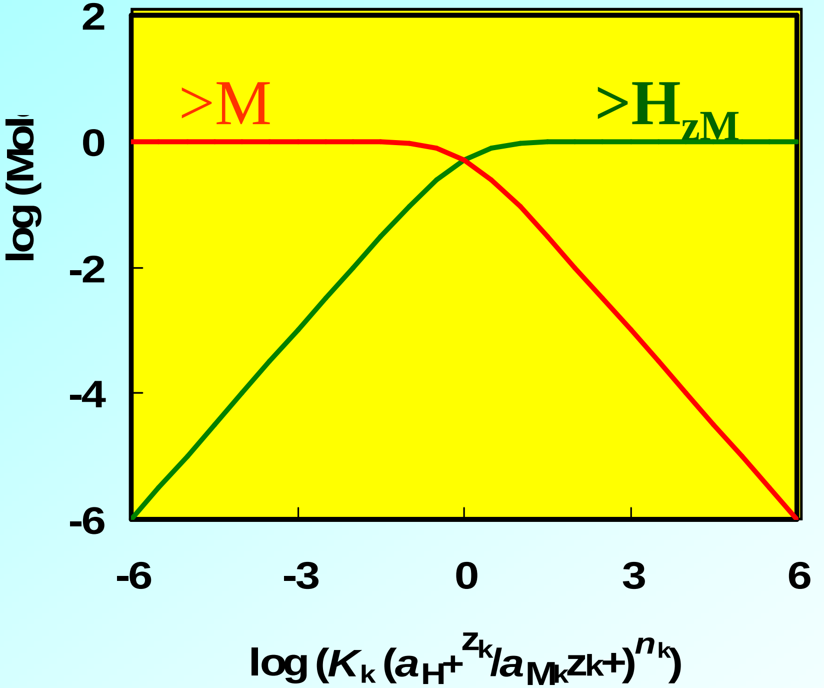
Protons in near surface site

which implies….

$$[H_{z}<] = \frac{K\left(a^{z}_{H^{+}} \big/ a_{M^{z+}}\right)}{1 + K\left(a^{z}_{H^{+}} \big/ a_{M^{z+}}\right)}$$

Equilibrium constant for exchange reaction

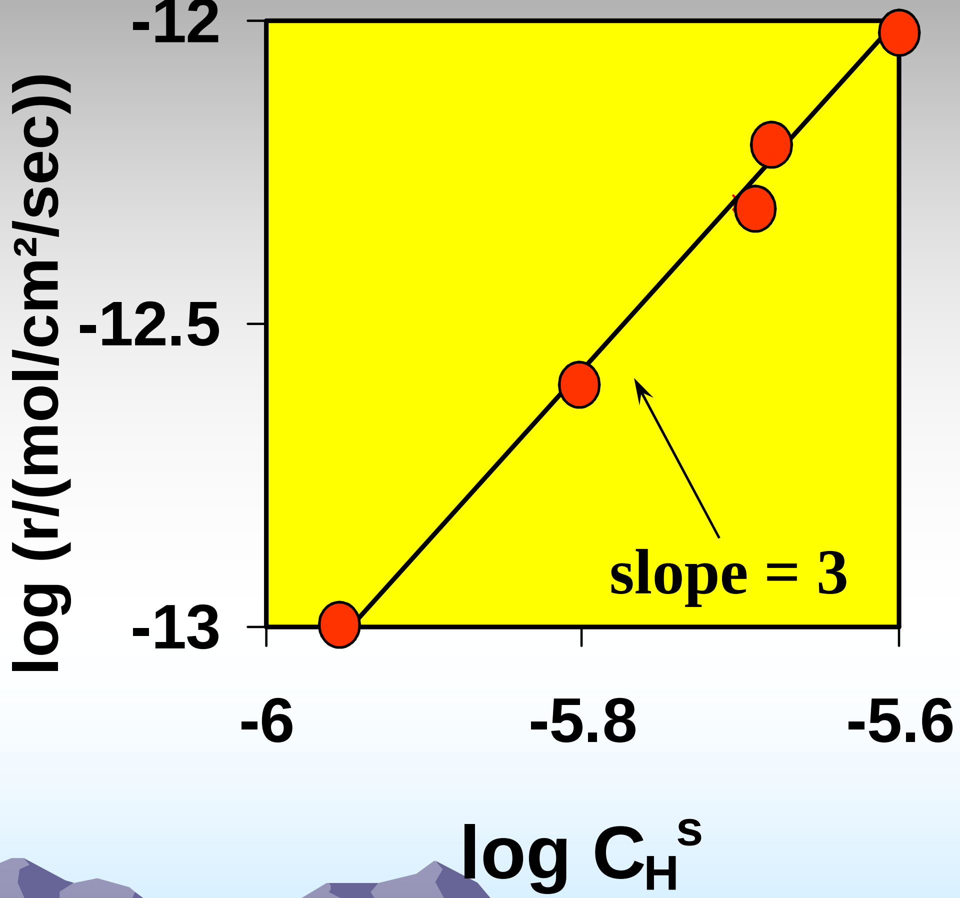
Surface Speciation as a function of aqueous concentration



Al_2O_3 dissolution (after Furrer and Stumm, 1986)

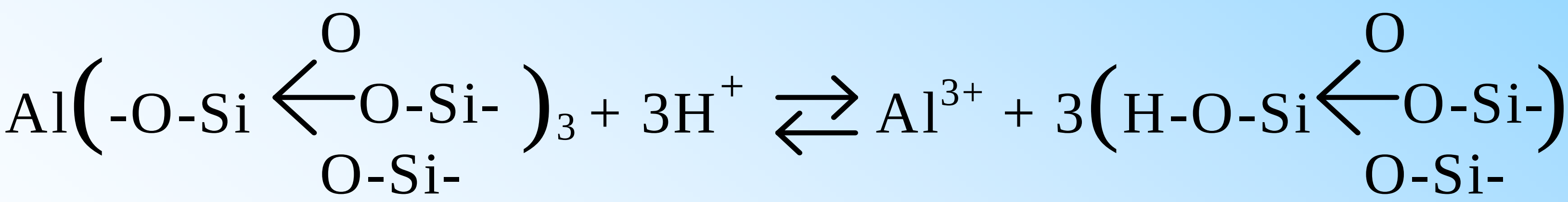
$$3H^+ + 1.5\ Al_2O_3 = Al^{3+} + 1.5\ H_2O$$

- Rate proportional to protonated precursor complex
- Overall reaction a metal for proton exchange reaction



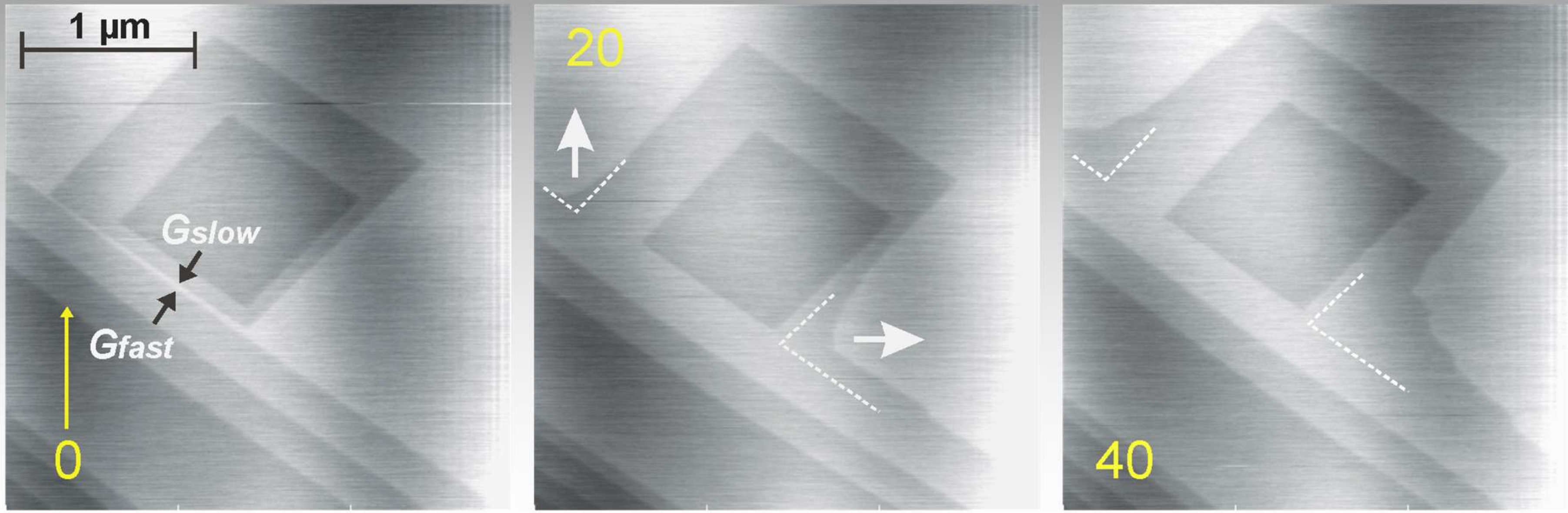
What are partially detached metals?

Example of albite aluminosilicate framework dissolution:



calcite dissolution

pH 5.6, room temp.

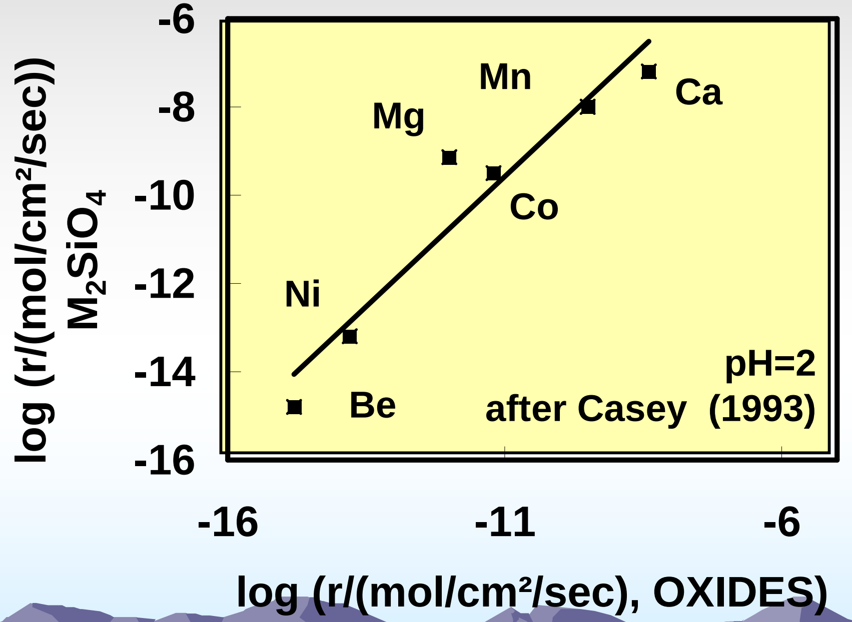


Jordan and Rammensee (1998)

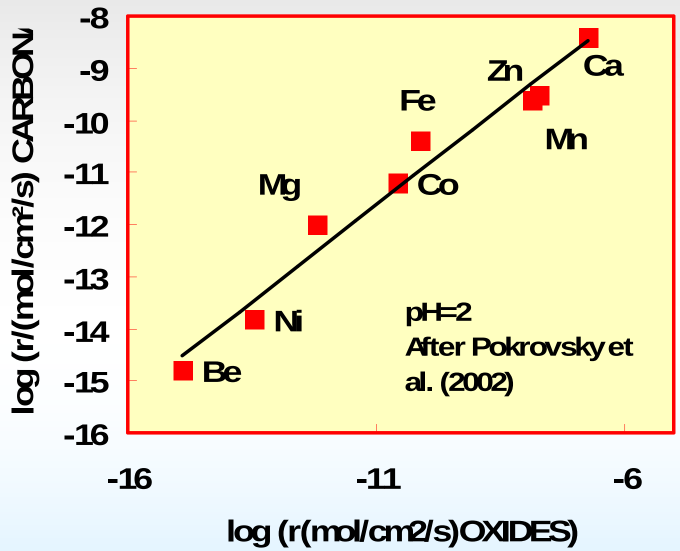
T=24°C, pure H_2O

Relative metal-oxygen bond breaking rate same in all minerals

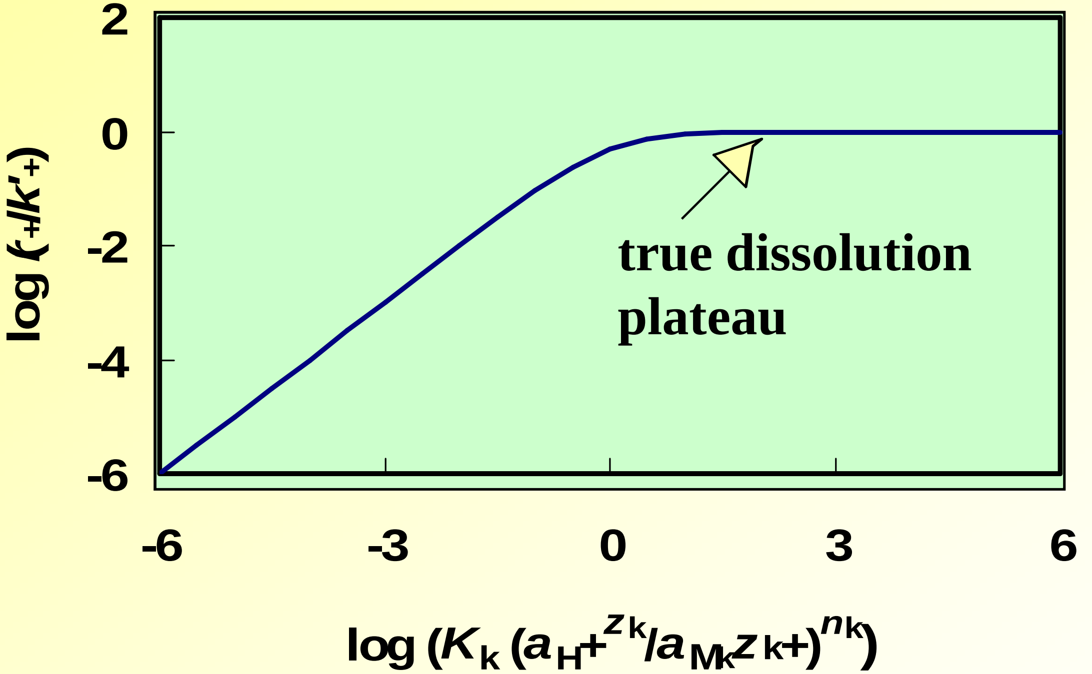
Olivines



Carbonates



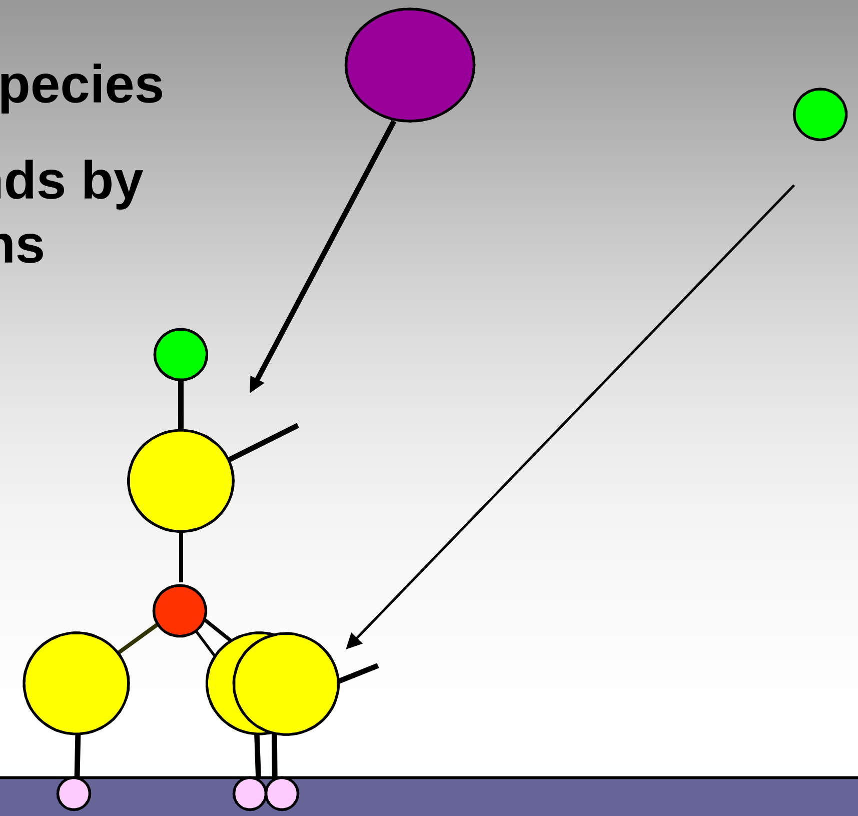
Normalized 'far from equilibrium' dissolution rate as a function of aqueous solution composition



Activated Complex Formation/Generalized Surface Coordination Model

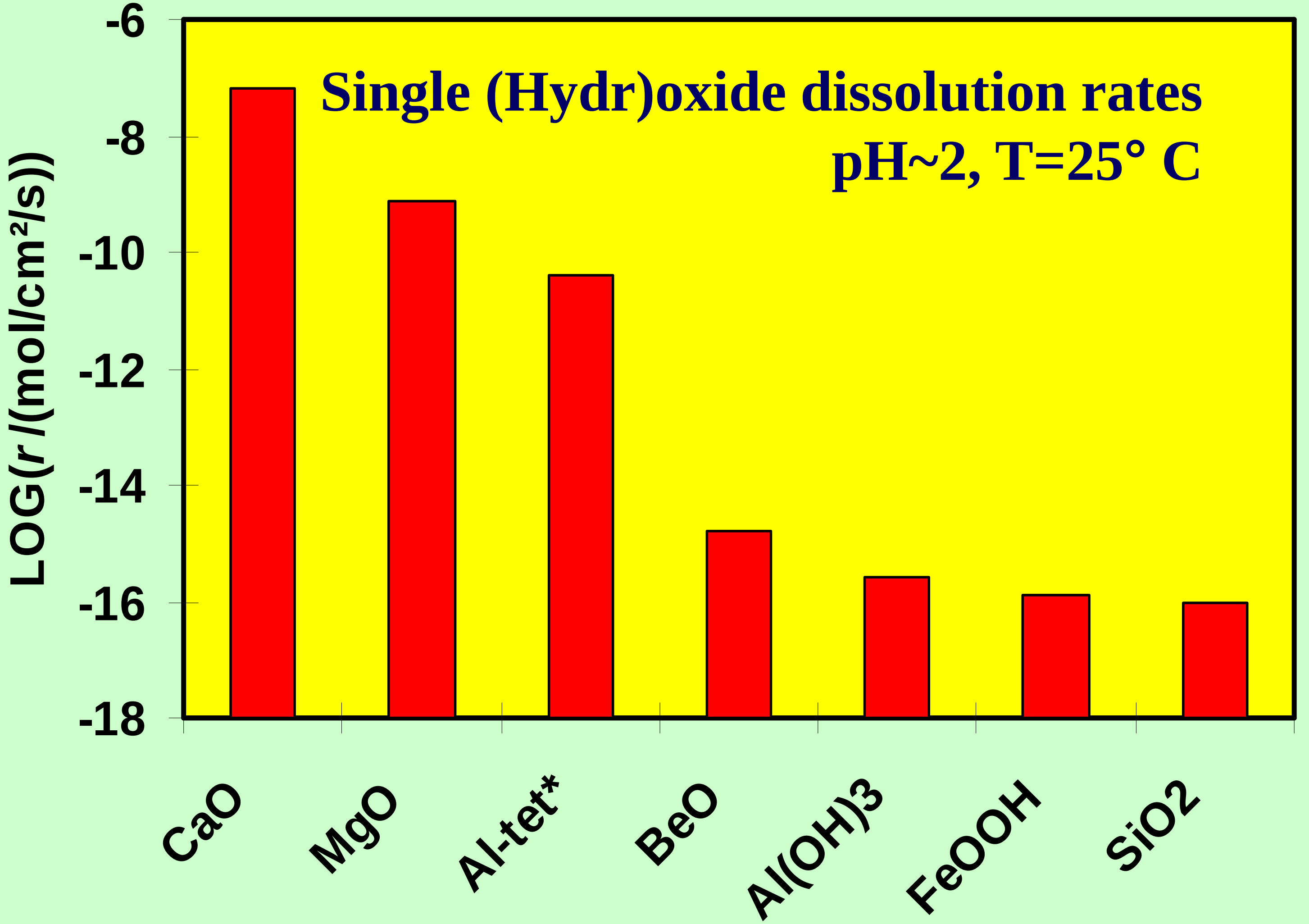
1) Sorption of aqueous species

2) Breaking bridging bonds by removal of adjacent atoms



Single-oxide Mineral Dissolution:

Metal-Oxygen bonds break at very different rates



Example: Al_2O_3 dissolution (after Furrer and Stumm, 1986)