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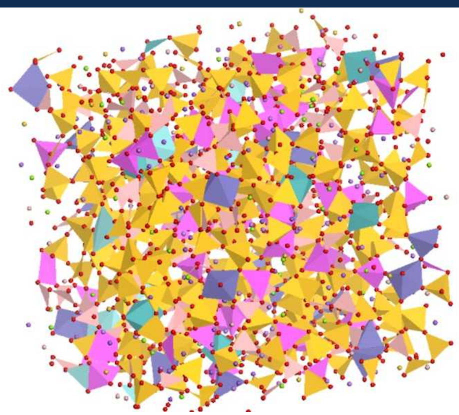

Nonlinear dynamics of aqueous dissolution of silicate glasses and its implications to glass waste form durability

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U.S. DEPARTMENT OF ENERGY | Nuclear Energy | NNSA National Nuclear Security Administration

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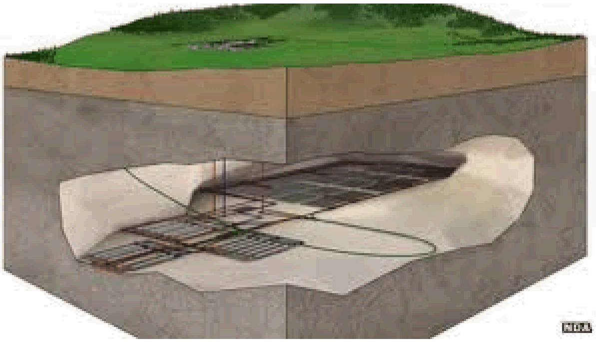
Multiple barrier system



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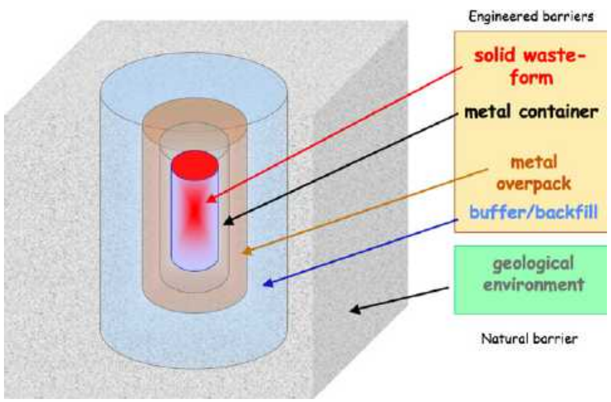
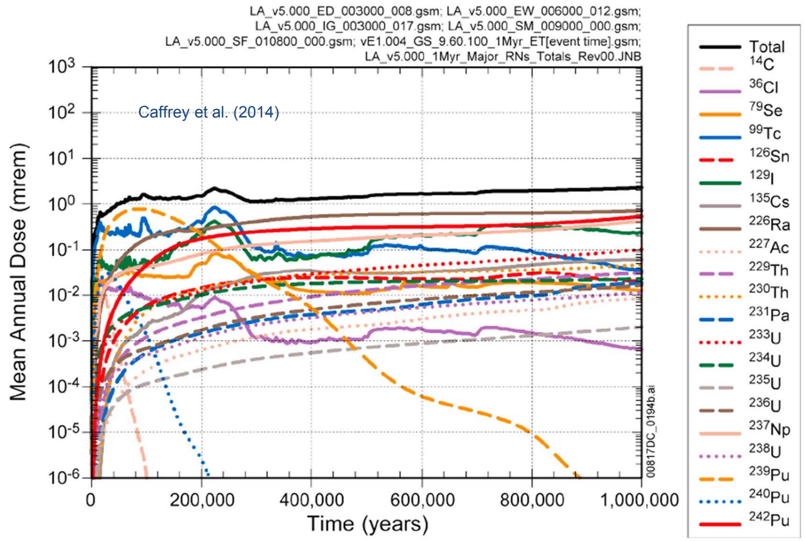
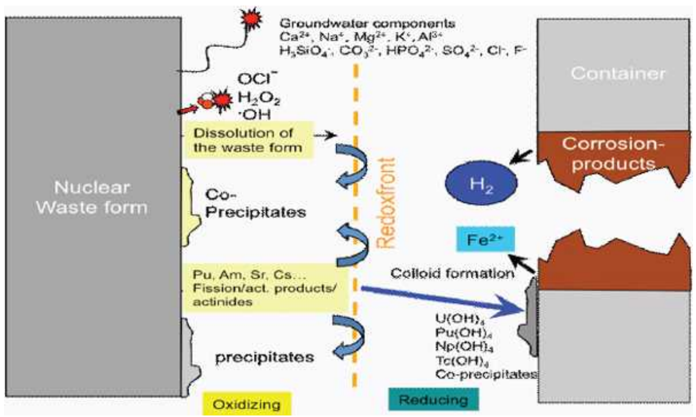
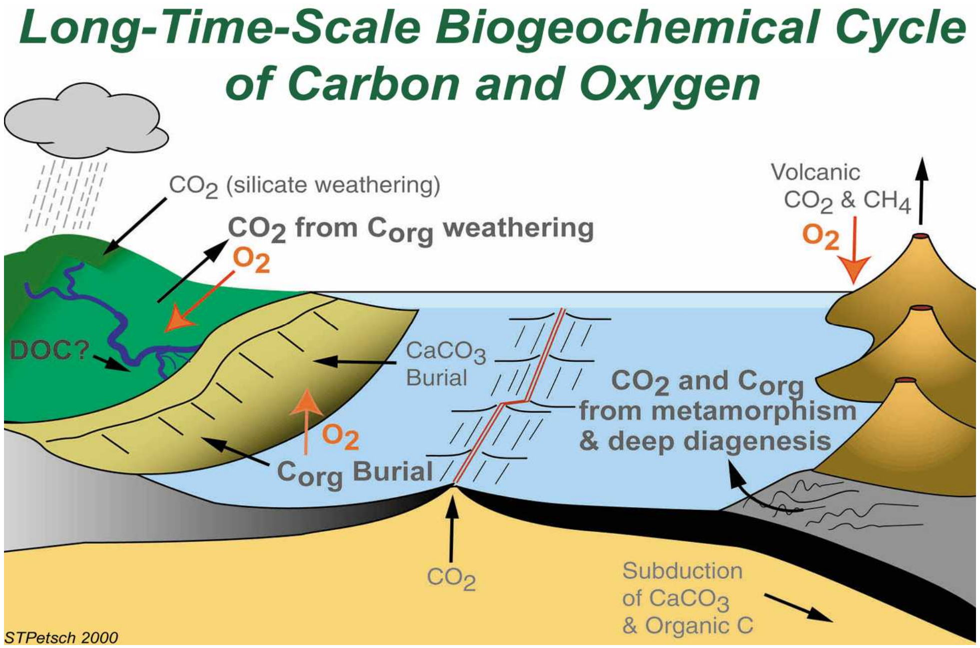






Chapman & Hooper (2012)

Silicate weathering & biogeochemical cycle

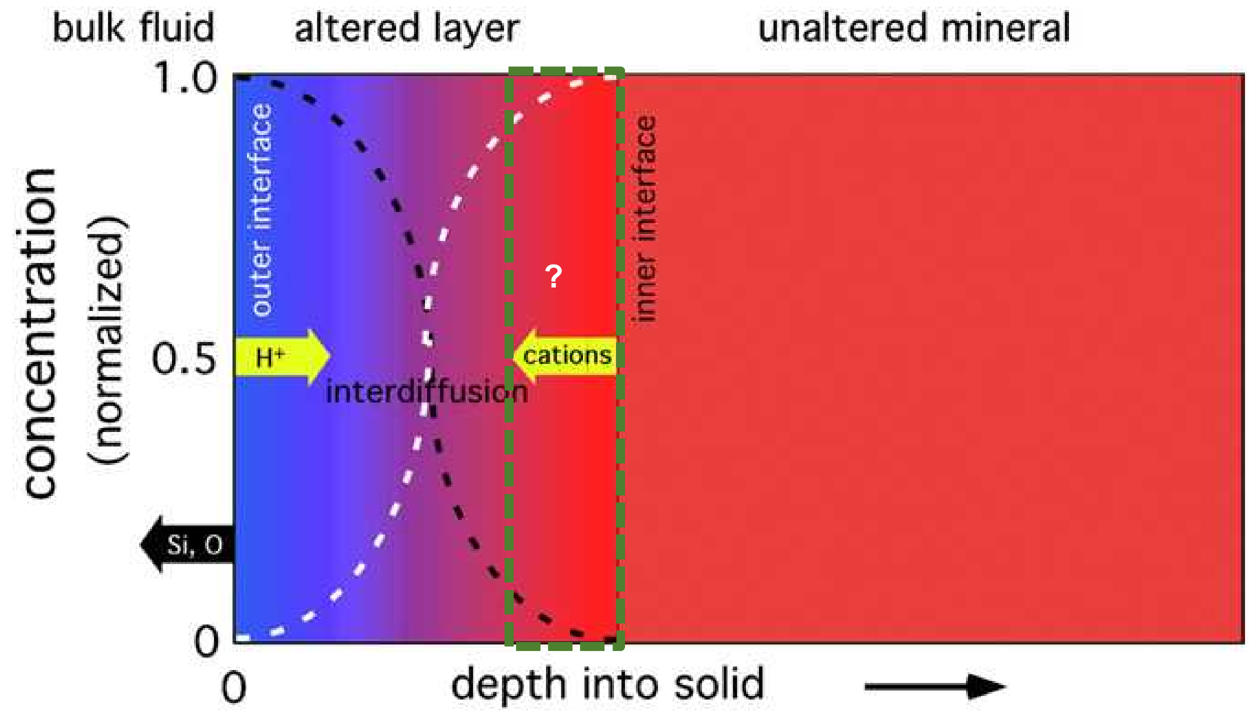


http://www.indiana.edu/~geol105b/1425chap8.htm

https://www.pinterest.com/pin/291397038360020104/

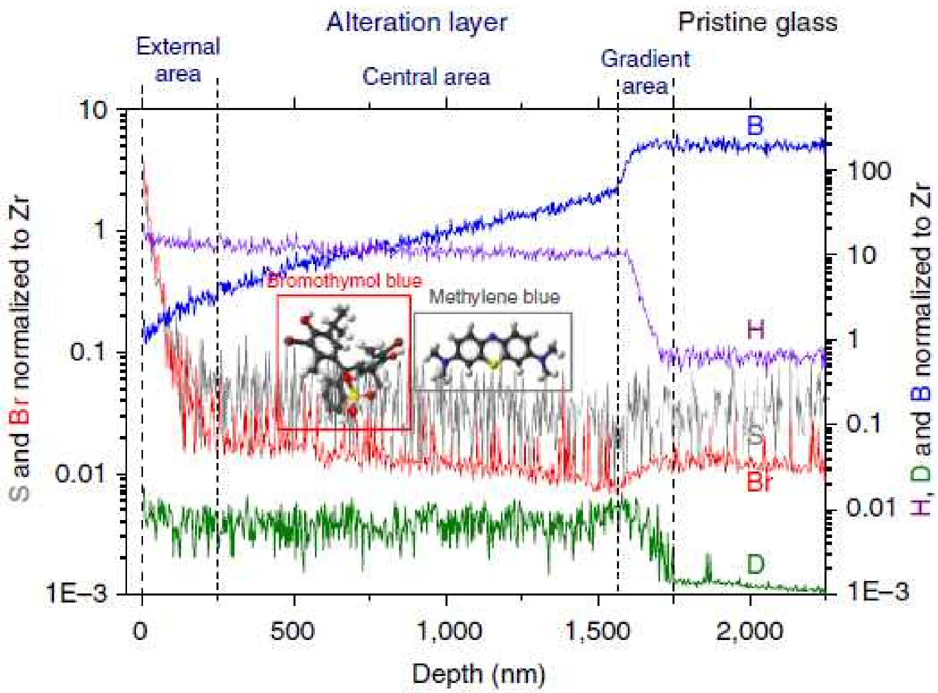
https://civil-engg-world.blogspot.com/2014/04/Residual-Soil-Laterites-Saprolites.html

Silicate glass dissolution: knowns & unknowns

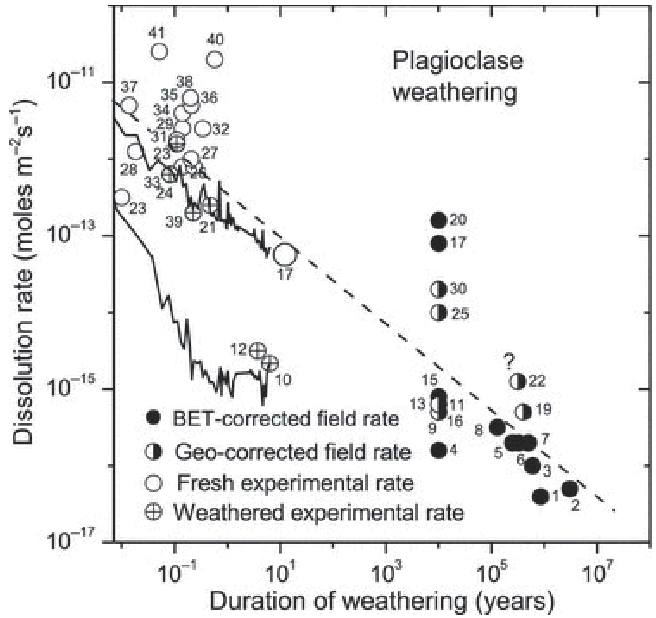


Hellmann et al. (2012)

Borosilicate dissolution: Surface layer formation in silica saturated solution

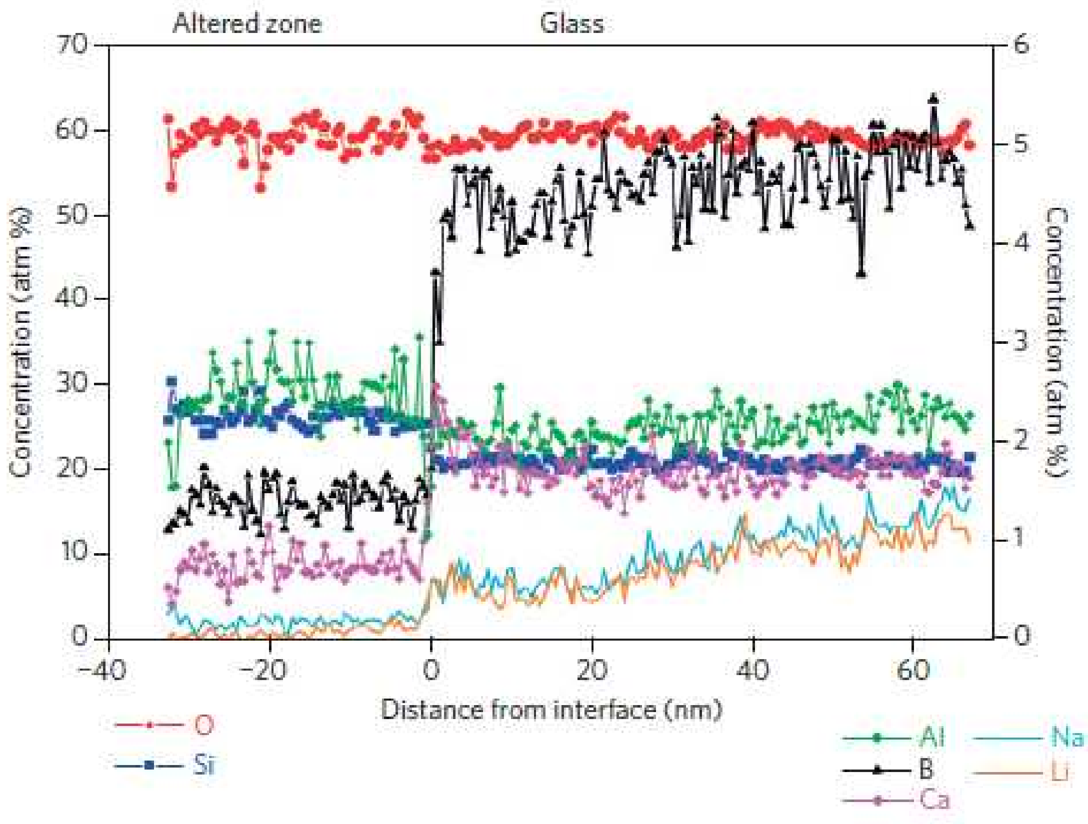


Gin et al. (2015)



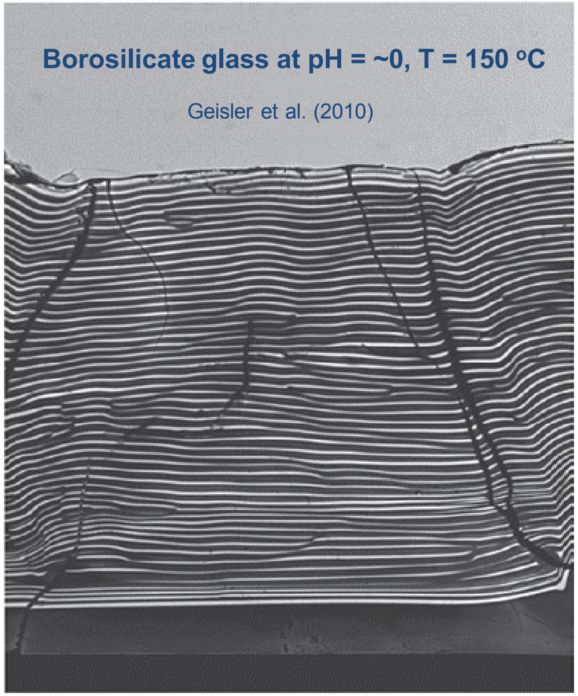
Brantley et al. (2011)

Borosilicate glass dissolution in deionized water at 50 °C



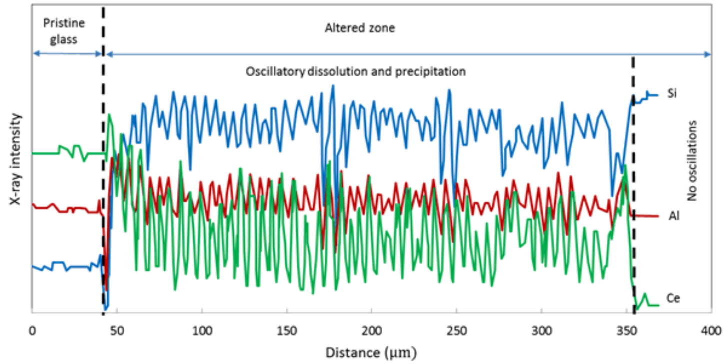
Hellmann et al. (2015)

Oscillatory dissolution/precipitation

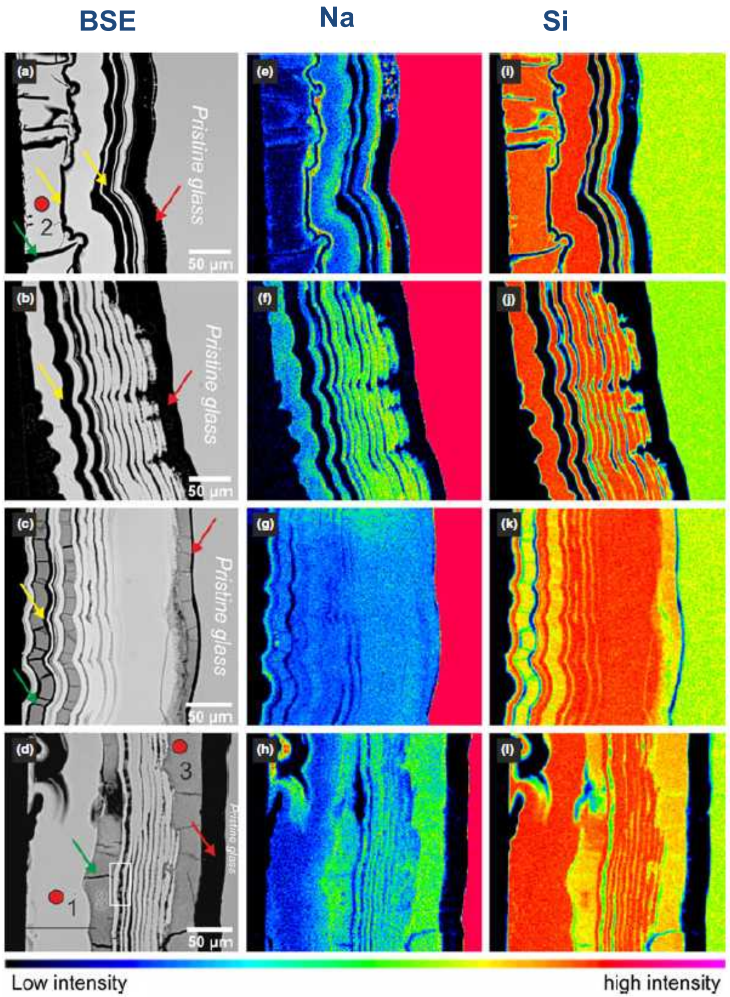


Borosilicate glass at pH = ~0, T = 150 °C

Geisler et al. (2010)



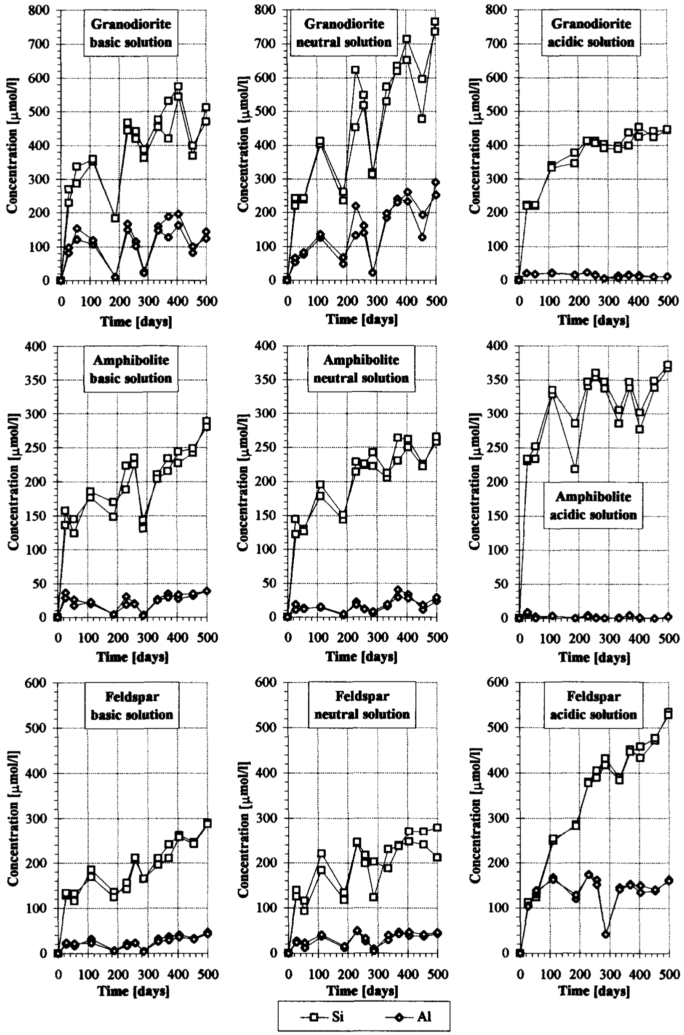
Geisler et al. (2010)



Borosilicate glass at initial pH = 2-12, T = 90 °C

Dohmen et al. (2013)

Oscillatory silicate mineral dissolution



Faimon. (1996)

Self-organization: Pattern arising from internal dynamics

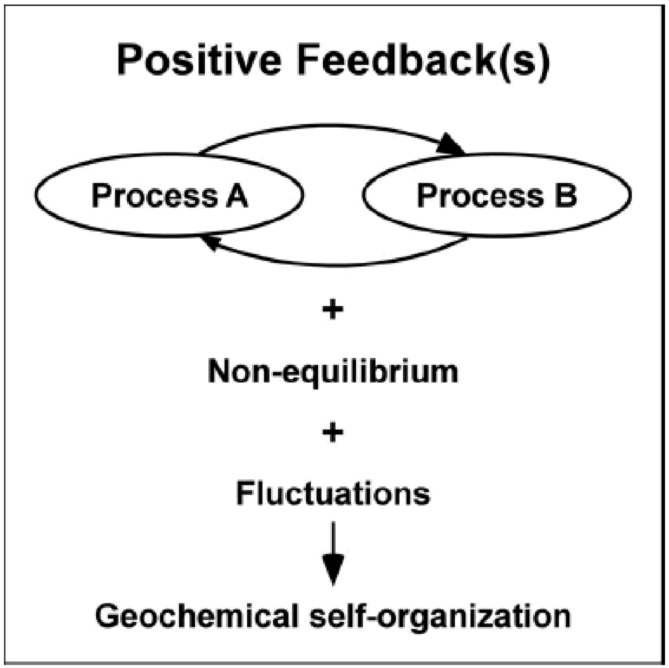
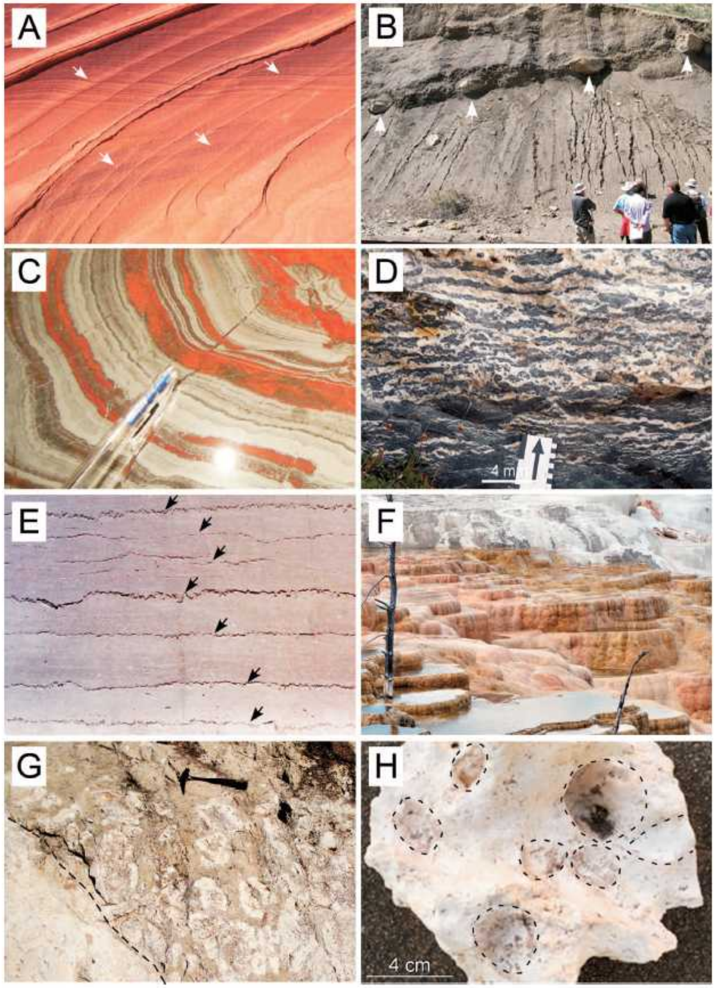
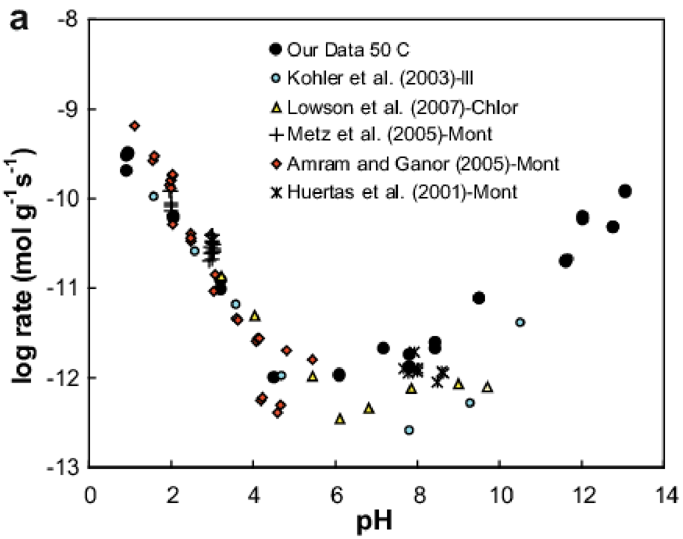


FIG. 1.—Necessary conditions for geochemical self-organization.

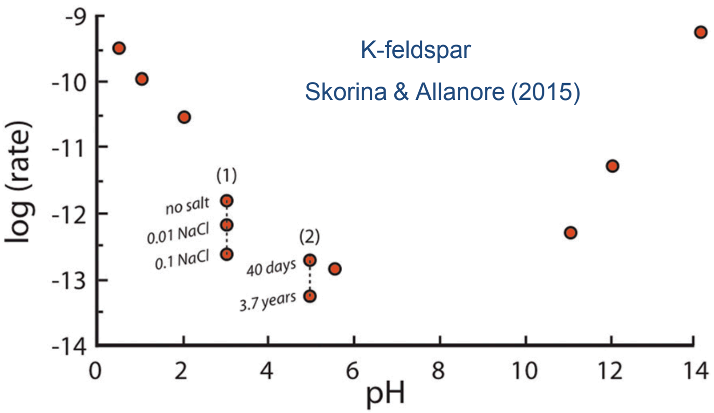
Wang & Budd. (2016)

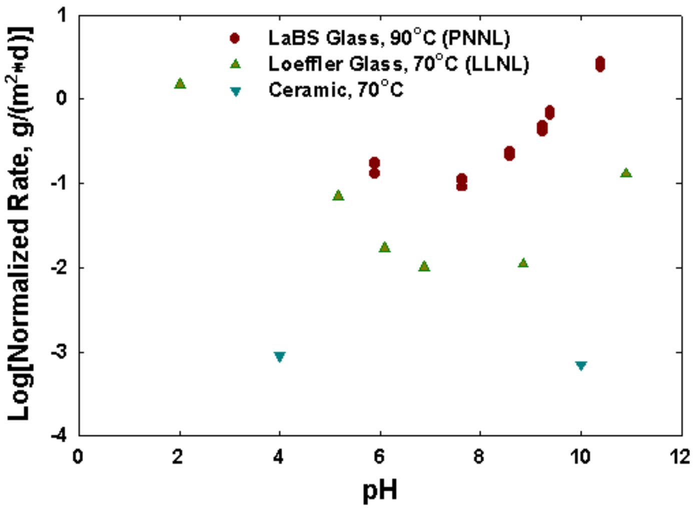


pH-dependent dissolution rate



Rozan et al. (2009)

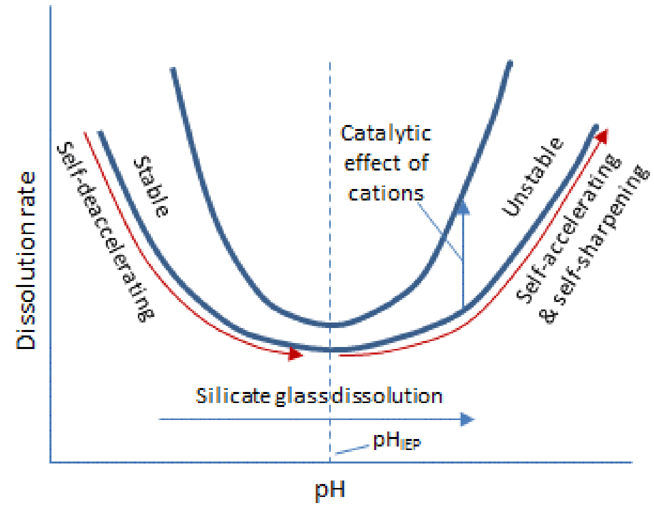




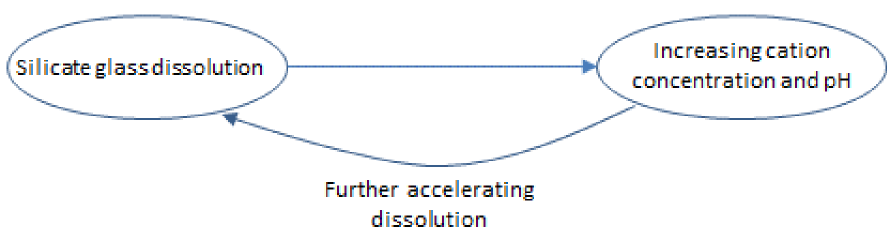
Strachan et al. . (2008)

Dissolution catalyzed by H^+ and OH^-

Positive feedback in silicate dissolution



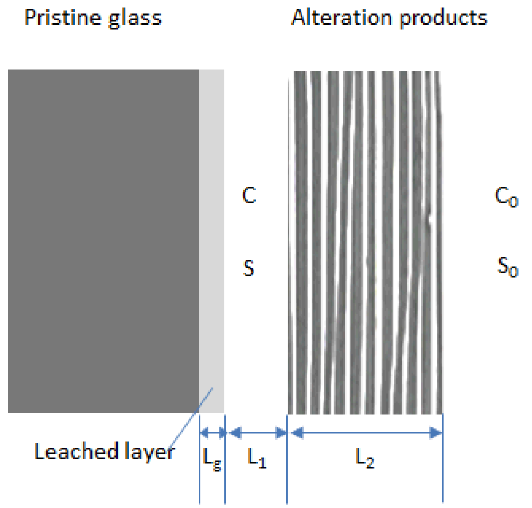
A



B

Wang et al. (2016)

Mathematical model



$$L_1 \frac{dC'}{dt} = \alpha k_d C_{\mathrm{IEP}} \left[1 + \beta \left(\frac{C'}{C_{\mathrm{IEP}}} \right)^n \right] (S_d^e - S') - \frac{D_c}{L_2} (C' - C_0)$$

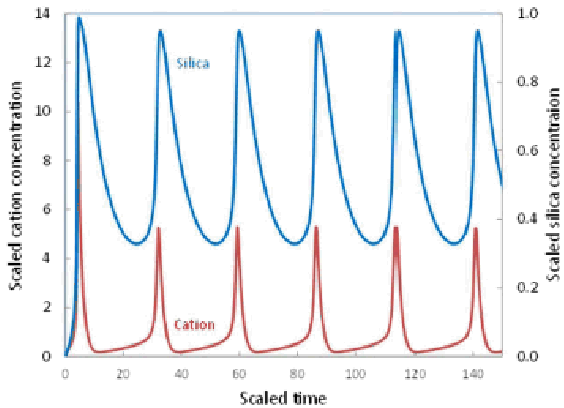
$$L_1 \frac{dS'}{dt} = \alpha k_d C_{\mathrm{IEP}} \left[1 + \beta \left(\frac{C'}{C_{\mathrm{IEP}}} \right)^n \right] (S_d^e - S') - \frac{D_s}{L_2} (S' - S_0) - k_p (S' - S_p^e)$$

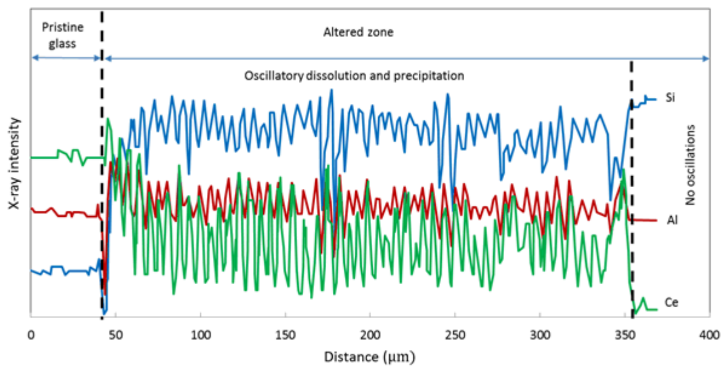
where

- C' – Cation concentration within the boundary layer
- C_0 – Cation concentration in the bulk solution (outside the altered zone)
- D_c – Diffusion coefficient of cations in the altered zone
- D_s – Diffusion coefficient of dissolved silica in the altered zone
- L_1 – Thickness of the boundary layer at the dissolution interface
- L_2 – Thickness of the altered zone
- k_d – Reaction rate constant for silicate material dissolution
- k_p – Reaction rate constant for silica mineral precipitation
- n – Order of silicate dissolution reaction with respect to cation
- S' – Silica concentration within the boundary layer
- S_0 – Silica concentration in the bulk solution
- S_d^e – Equilibrium silica concentration for material dissolution
- S_p^e – Equilibrium silica concentration for silica precipitation
- t – Time
- α – Molar ratio of cations (mainly Na^+) to Si^{4+} in the pristine silicate material
- β – Positive constant characterizing the catalytic effect of cations on silicate material dissolution

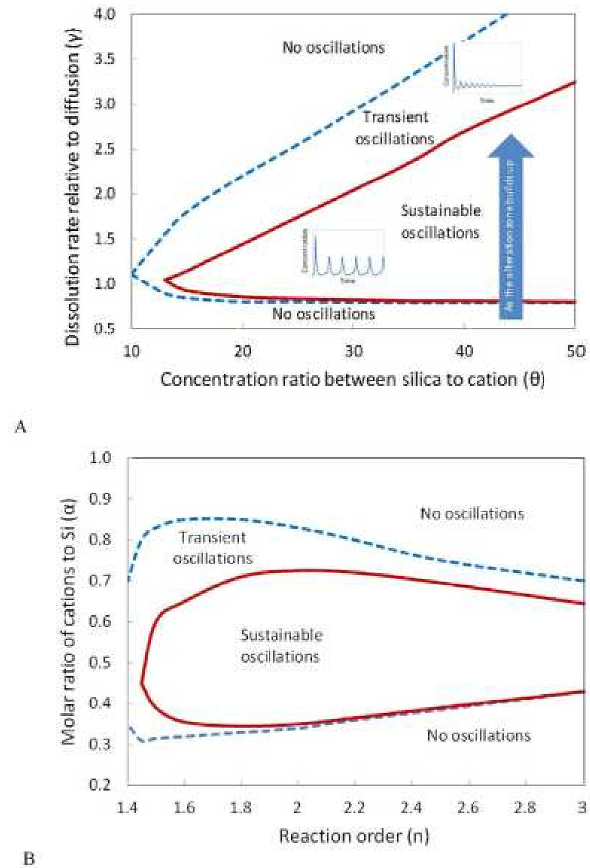
Wang et al., 2016, Scientific Reports

Nonlinear dynamics of silicate dissolution





Geisler et al. (2010)

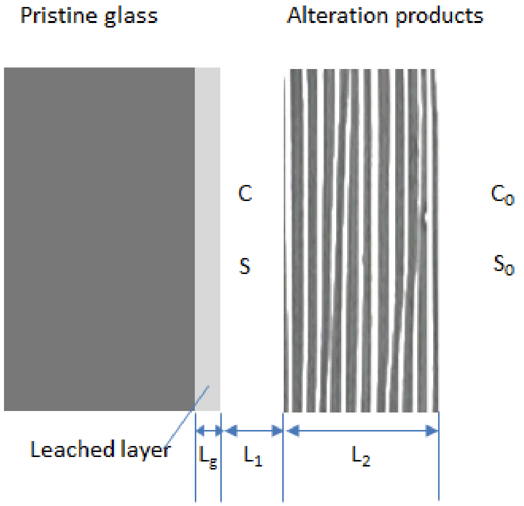


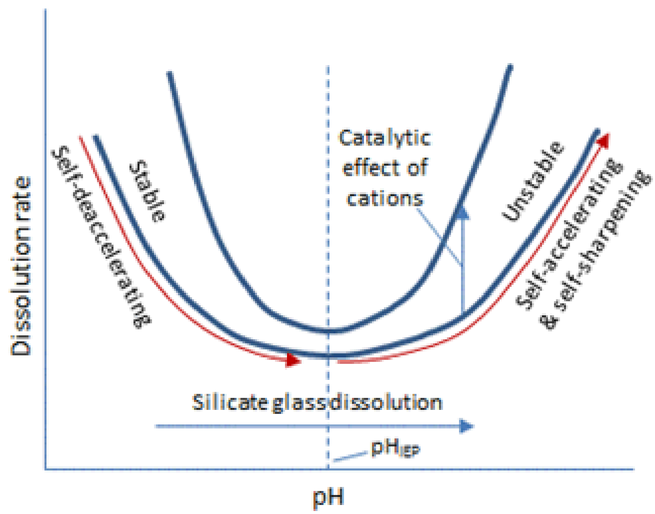
Wang et al., 2016, Scientific Reports

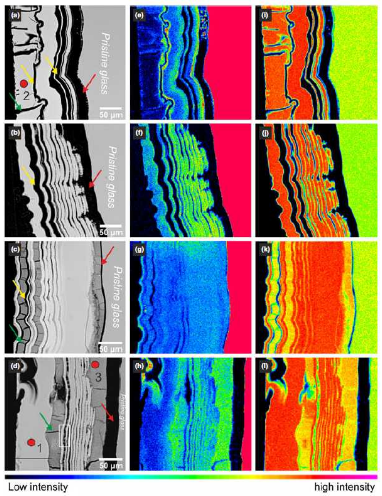
Predicted time scale: hours to years
Predicted spatial scale: sub-micron to tens of microns

Archeologic study of ancient Roman glass shows that each band might have formed over a year.

Self-sharpening & morphologic instability of a reaction front





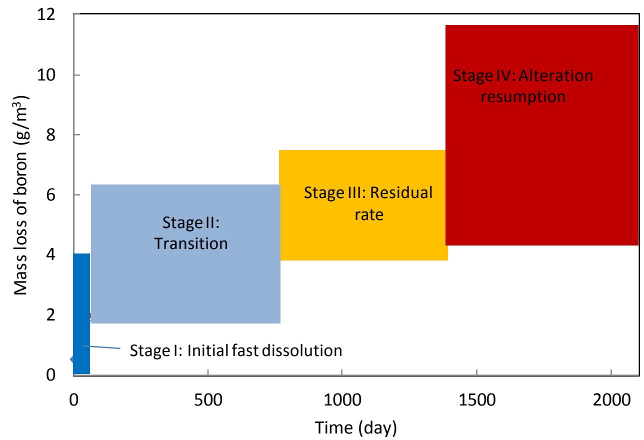


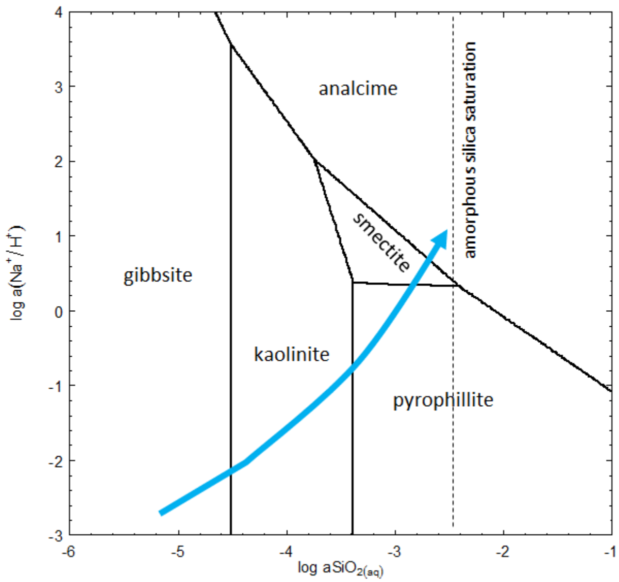
Dohmen et al. (2013)

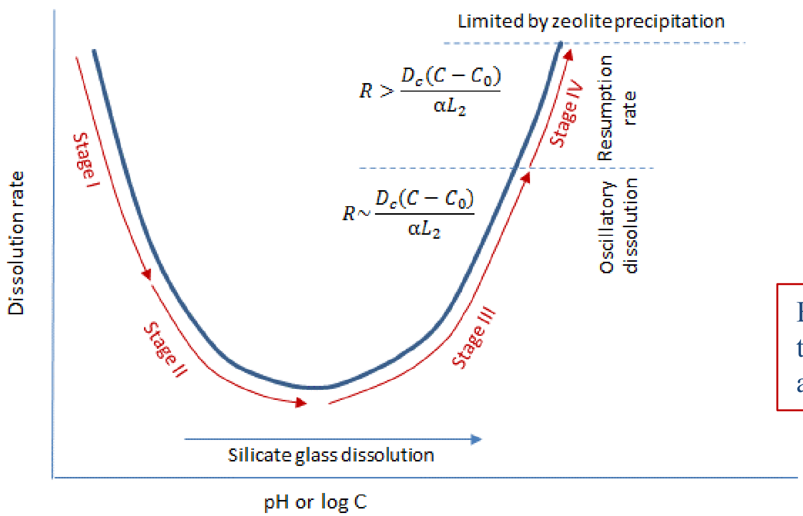
$$\frac{dL_g}{dt} \approx \frac{D_g}{L_g} - Rv_m = \frac{D_g}{L_g} - v_m k_d C_{\mathrm{IEP}}(S_d^e - S)\left[1 + \beta\left(\frac{D_g L_2}{C_{\mathrm{IEP}} L_g}\right)^n\right]$$

Morphologic instability arises from the same positive feedback.

Alteration resumption and zeolite formation

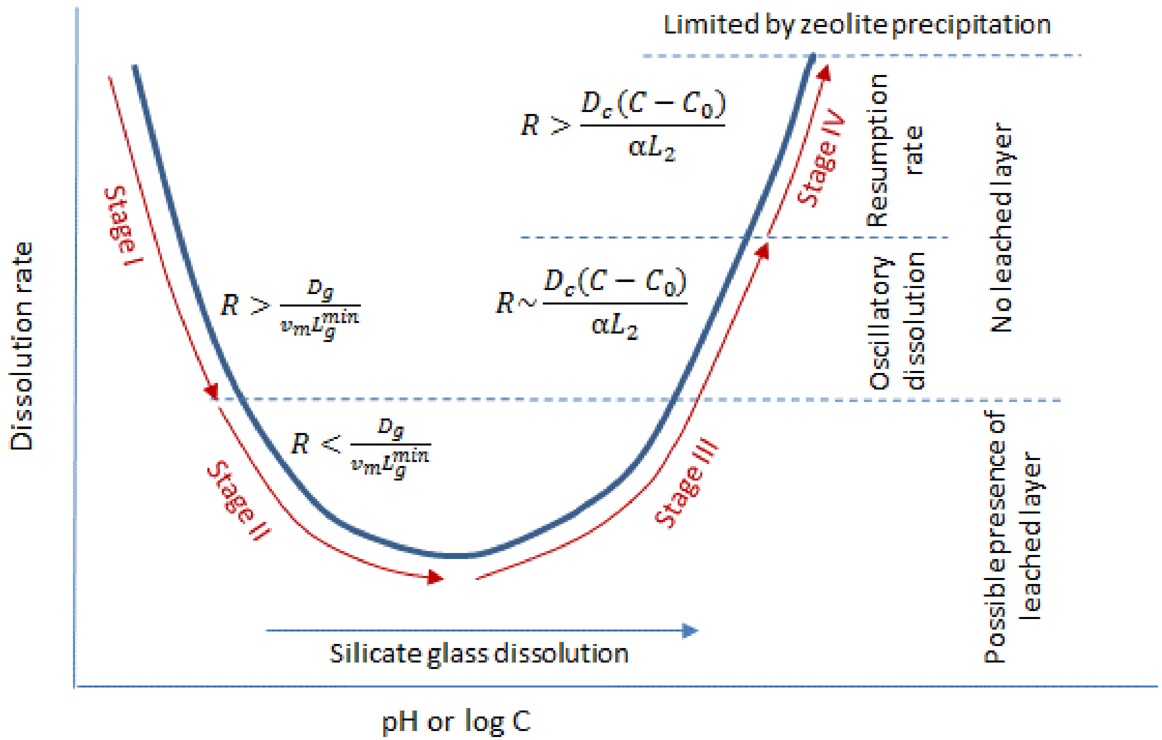






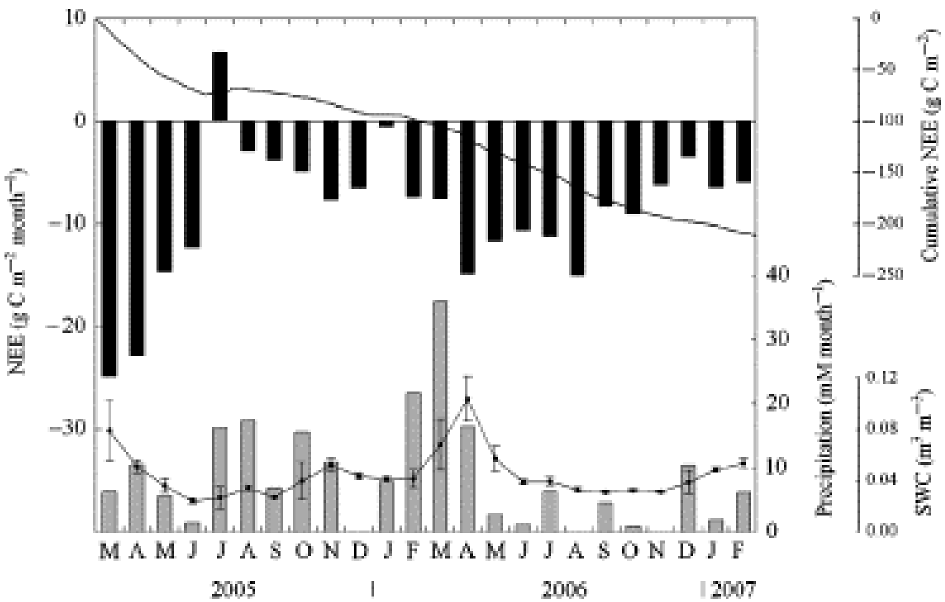
Eventually, the dissolution rate overtakes the mass exchange rate, leading to a “runaway” situation with a sharp increase in the cation concentration at the interface and therefore the dissolution rate.

Waste durability: Chemical composition and water chemistry



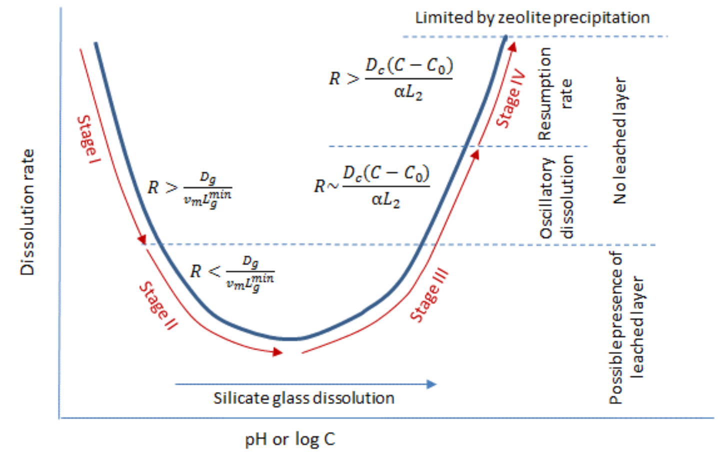
$$0.33\,Al^{3+} + 3.65\,Mg^{2+} + 3.67\,SiO_2(aq) + 4.66\,H_2O \rightarrow Mg_{3.65}Al_{0.33}Si_{3.67}O_{10}(OH)_2 + 7.32\,H^+$$

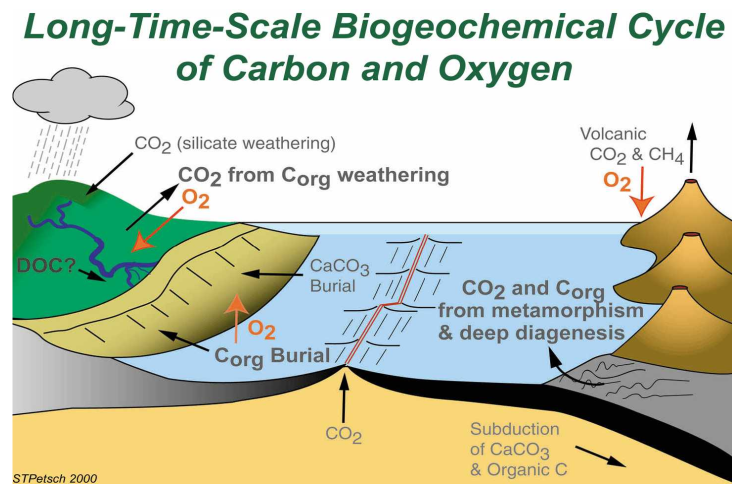
Implication to weathering



NEE: Net ecosystem CO_2 exchange

Wohlfahrt et al. (2002)





Concluding remarks

- Complex silicate material dissolution behaviors can emerge from a simple positive feedback between dissolution-induced cation release and cation-enhanced dissolution kinetics.
- This mechanism enables a systematic prediction of the occurrence of sharp dissolution fronts, oscillatory dissolution behaviors and multiple stages of glass dissolution.
- It provides a new perspective for predicting long-term silicate weathering rates in actual geochemical systems and developing durable silicate materials for various engineering applications.

Acknowledgements

- DOE-Spent Fuel Waste Science & Technology (SFWST)
- DOE-Energy Frontier Research Center (EFRC)