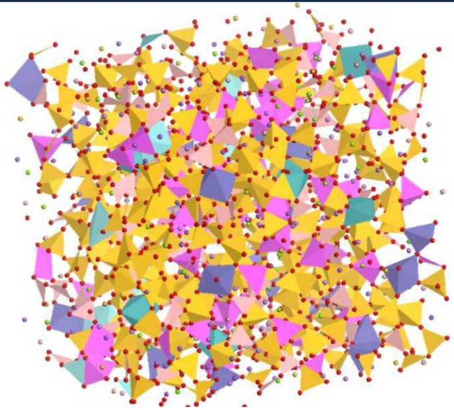
SAND2019-3083C



Nonlinear dynamics of aqueous dissolution of silicate materials

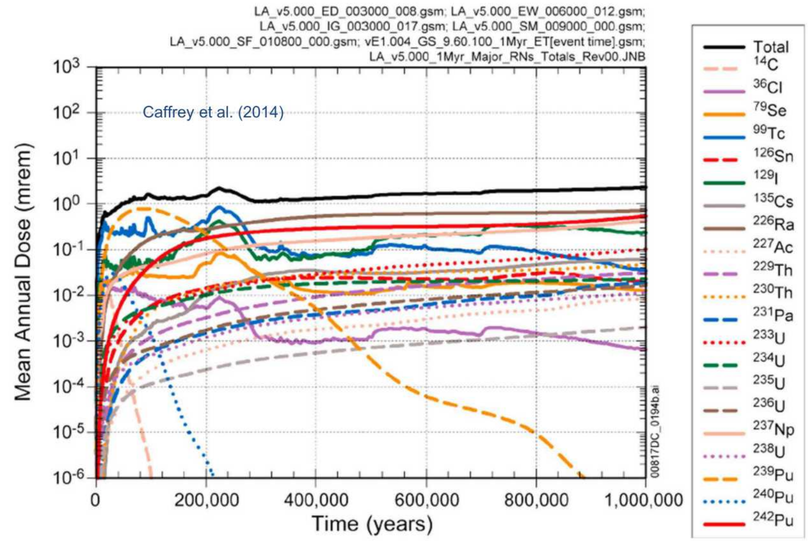
Yifeng Wang, Carlos F. Jove-Colon and Kristopher L. Kuhlman

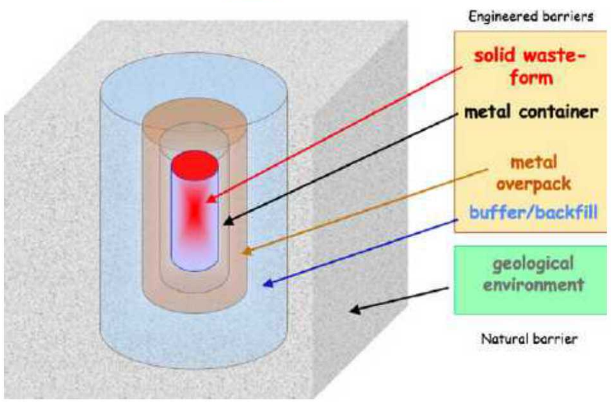
Sandia National Laboratories, P. O. Box 5800, Albuquerque, New Mexico 87185-0779, USA

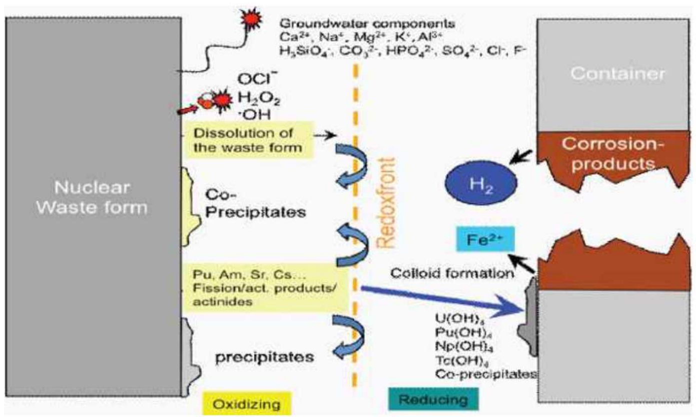
IHLRWMC, April, 2019

Multiple barrier system

http://www.bbc.com/news/uk-england-cumbria-21161367

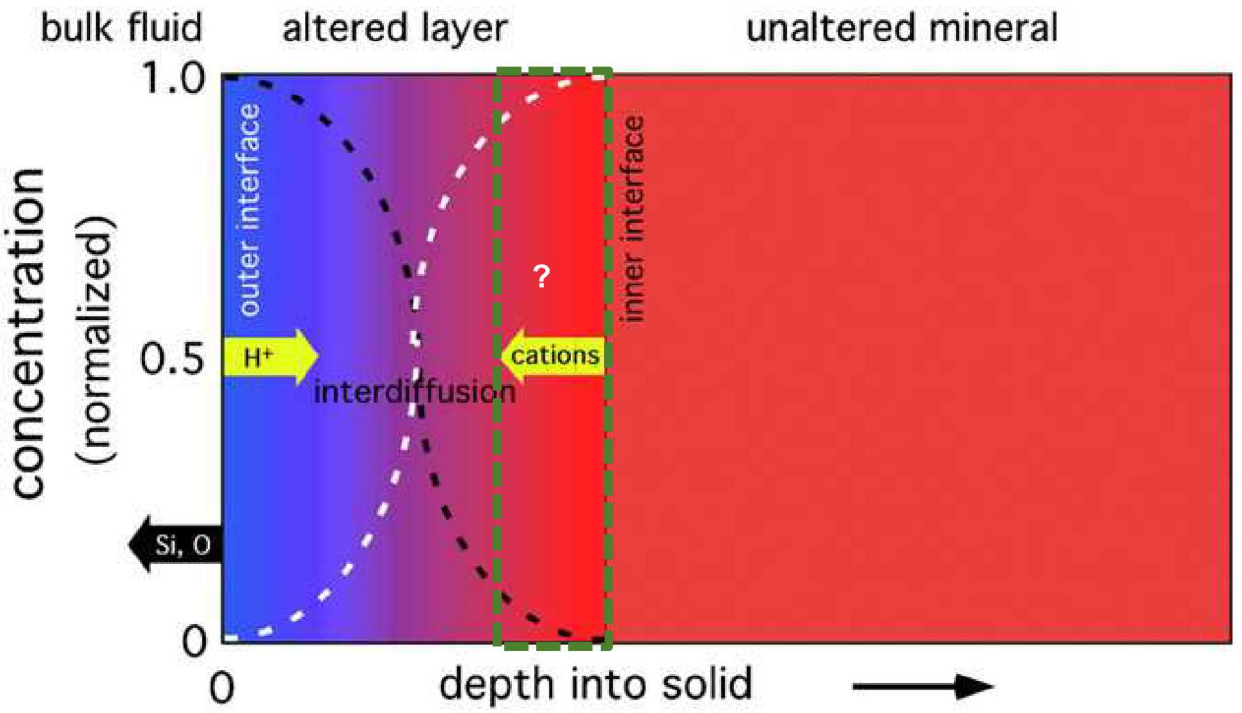






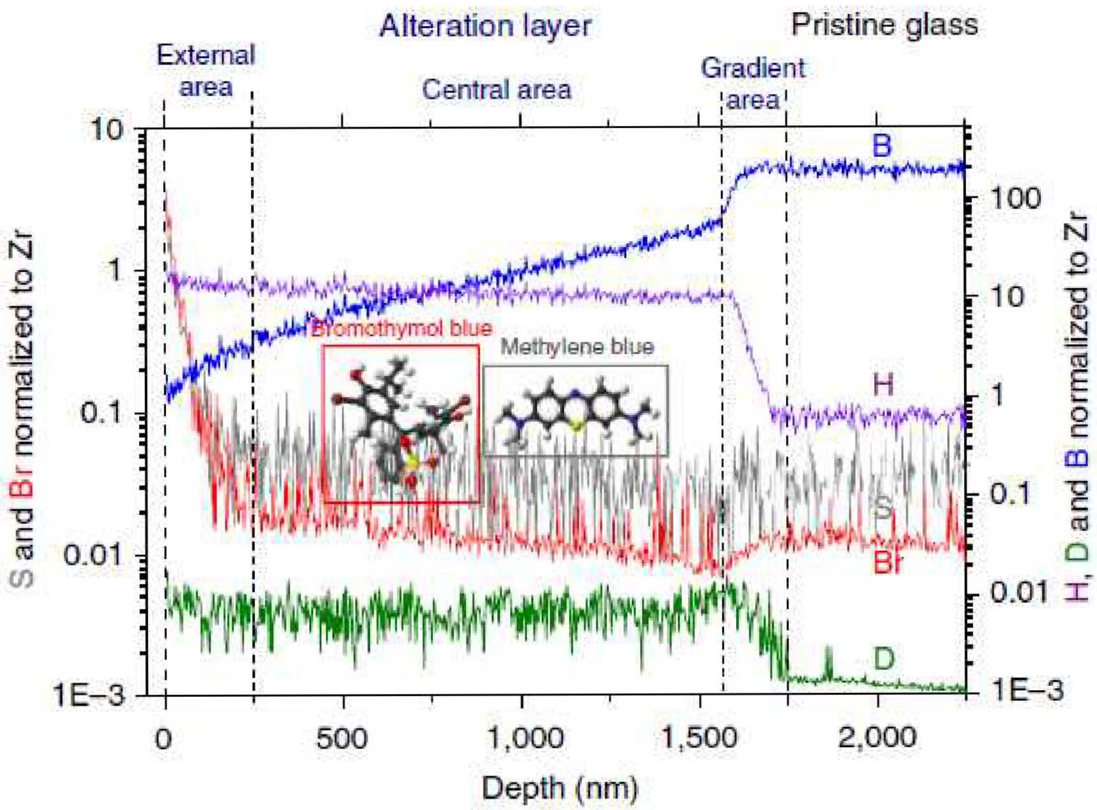
Chapman & Hooper (2012)

Silicate glass dissolution: knowns & unknowns



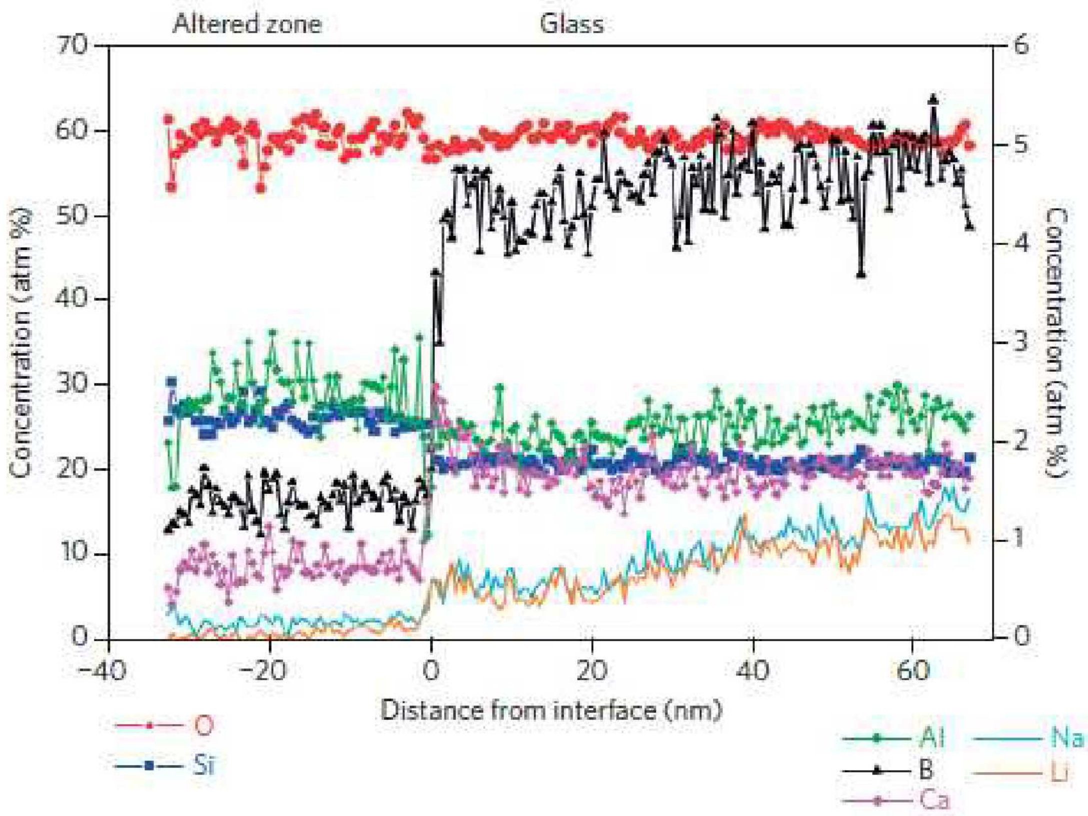
Hellmann et al. (2012)

Borosilicate dissolution: Surface layer formation in silica saturated solution



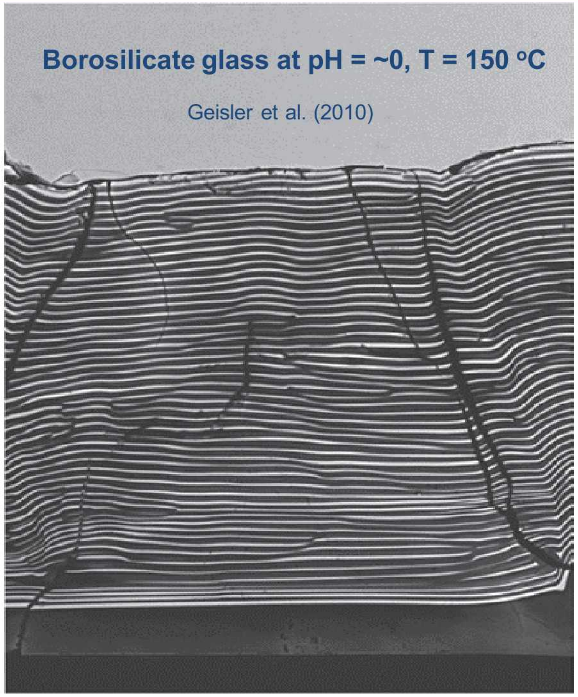
Gin et al. (2015)

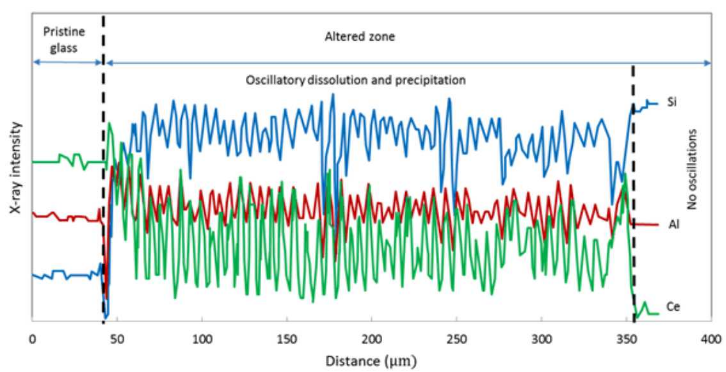
Borosilicate glass dissolution in deionized water at 50 ^oC



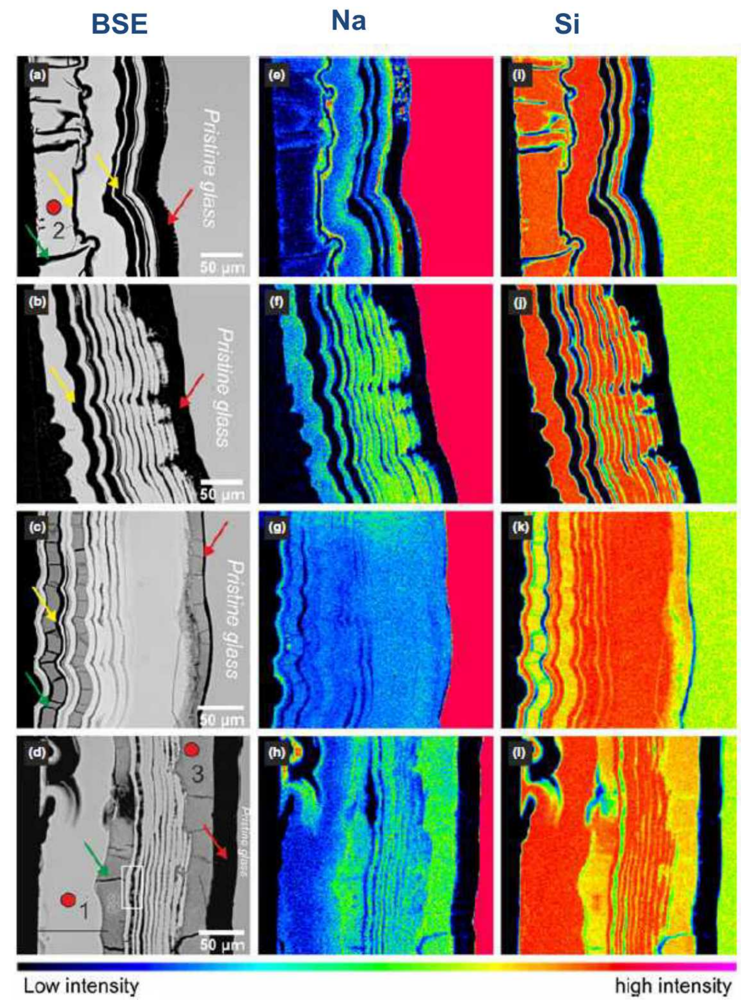
Hellmann et al. (2015)

Oscillatory dissolution/precipitation





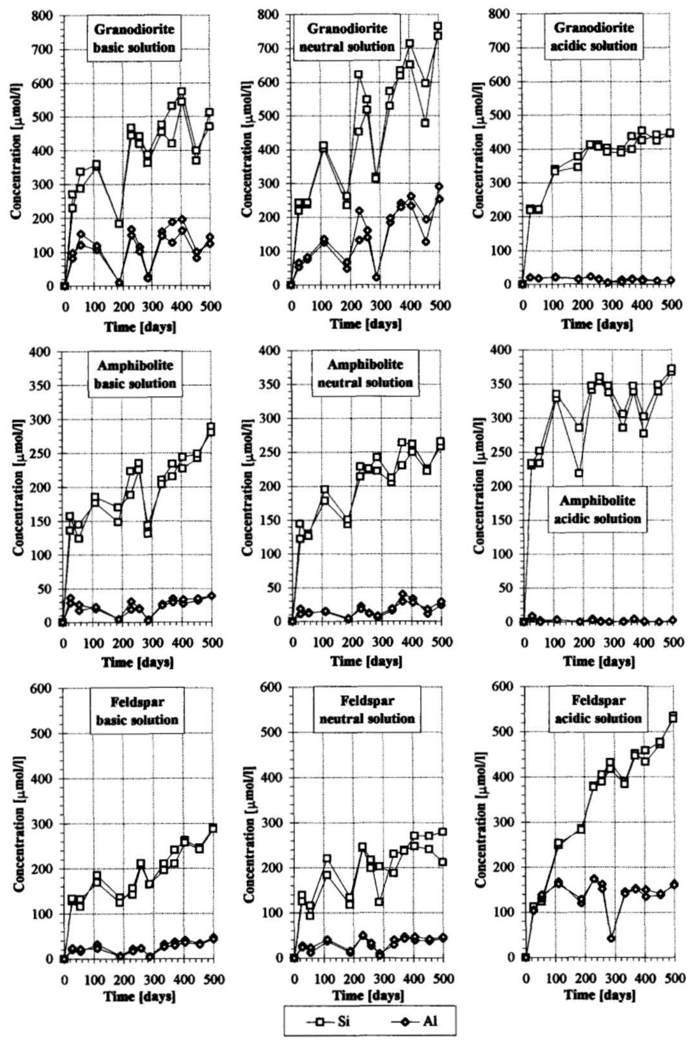
Geisler et al. (2010)



Borosilicate glass at initial pH = 2-12, T = 90 ^{o}C

Dohmen et al. (2013)

Oscillatory silicate mineral dissolution



Faimon. (1996)

Self-organization: Pattern arising from internal dynamics

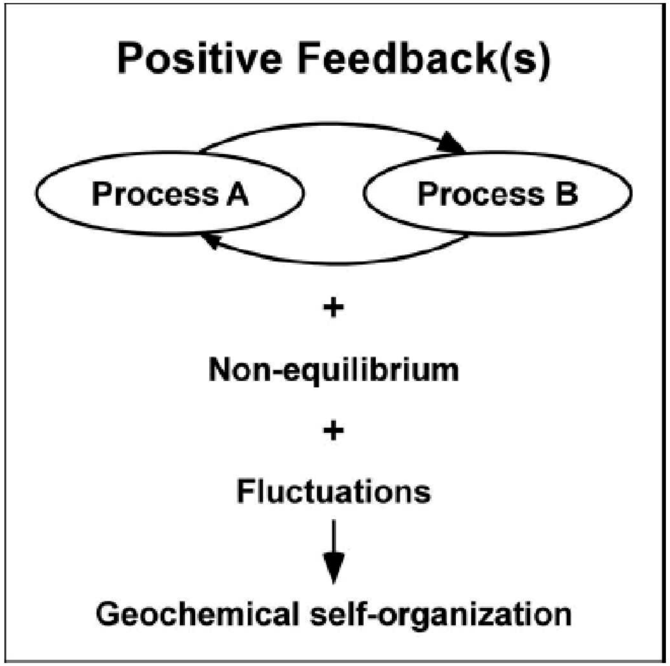
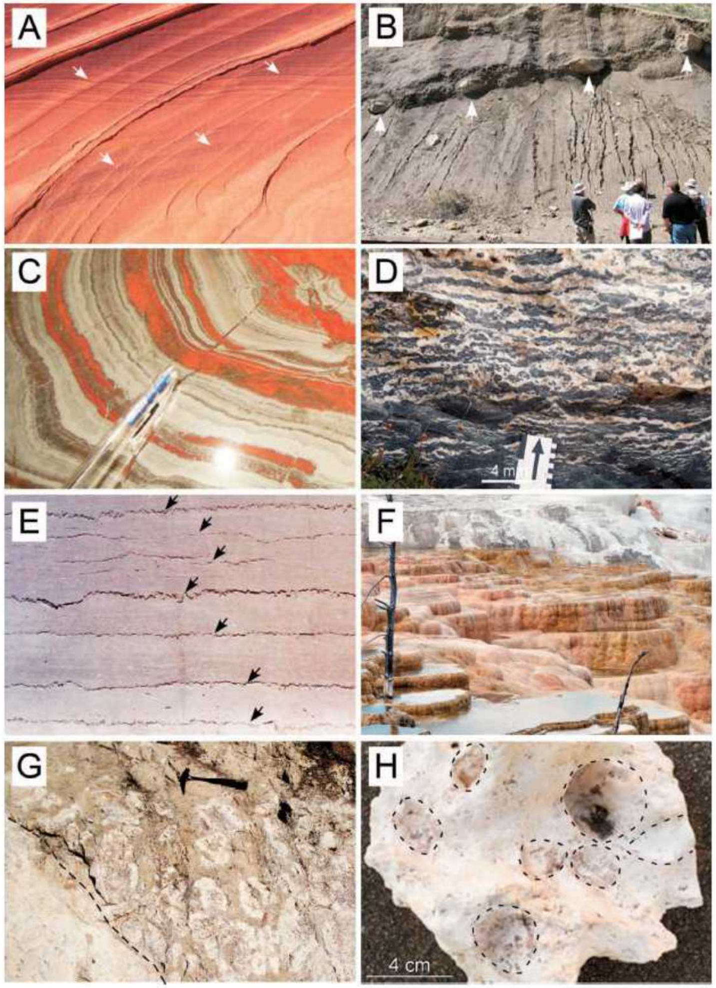
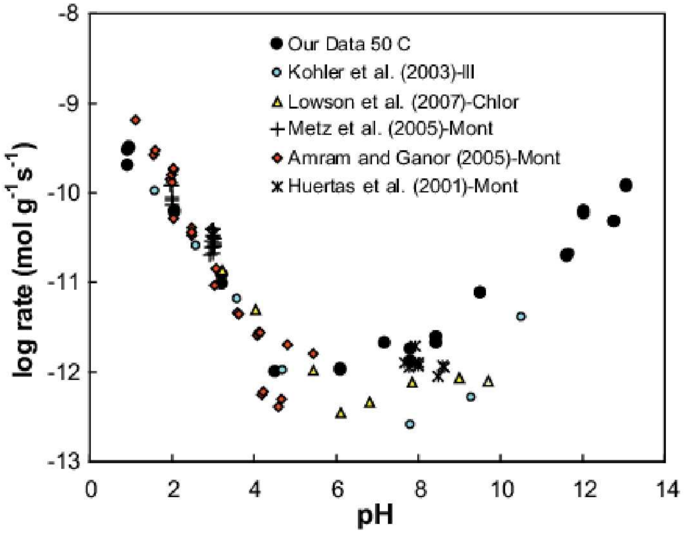


FIG. 1.—Necessary conditions for geochemical self-organization.

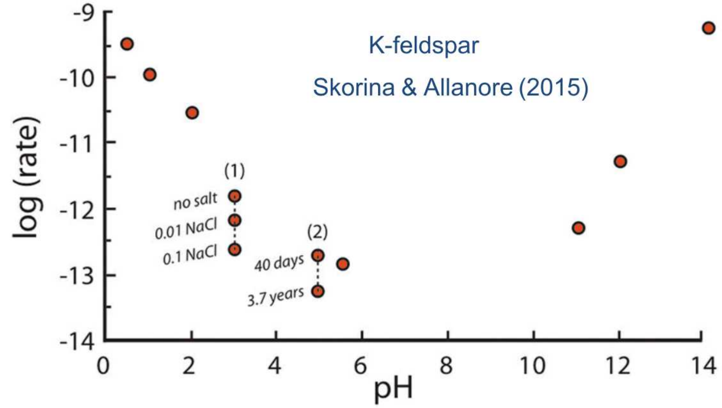
Wang & Budd. (2016)

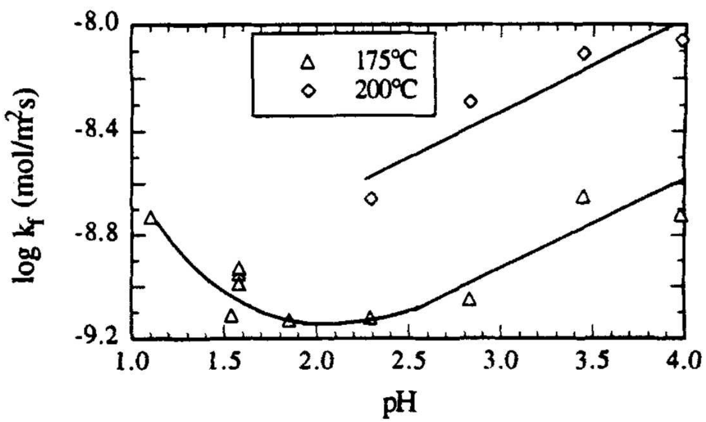


pH-dependent dissolution: Catalyzed by H+ and OH-

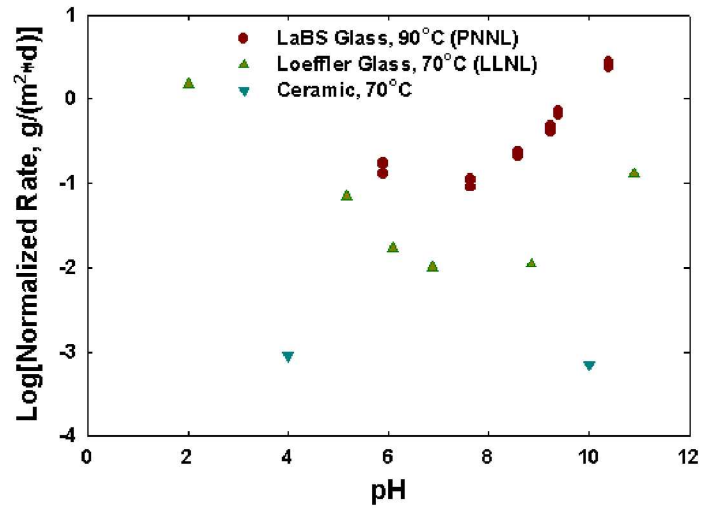


Rozan et al. (2009)



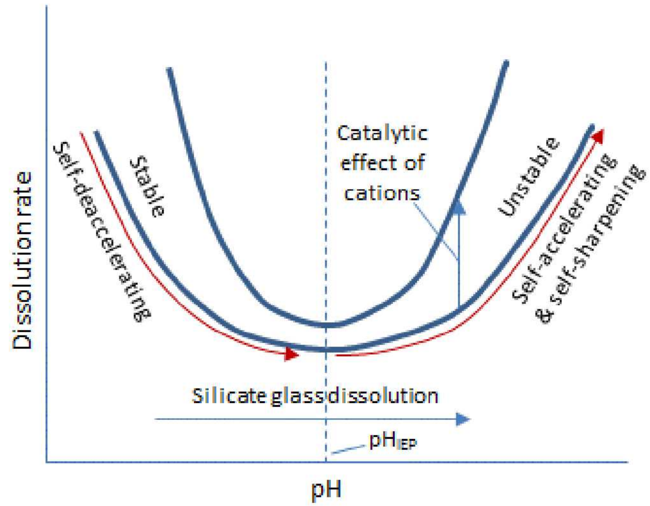


Quartz (Worley et al., 1996)



Strachan et al. . (2008)

Positive feedback in silicate dissolution



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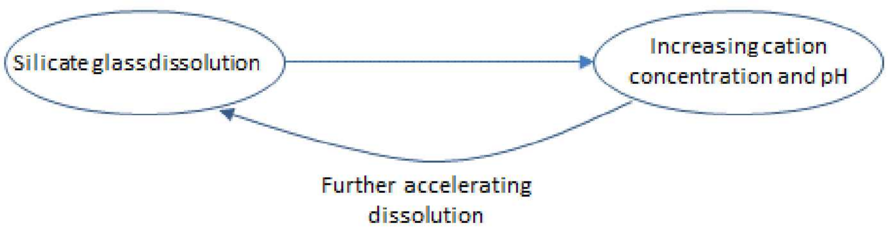
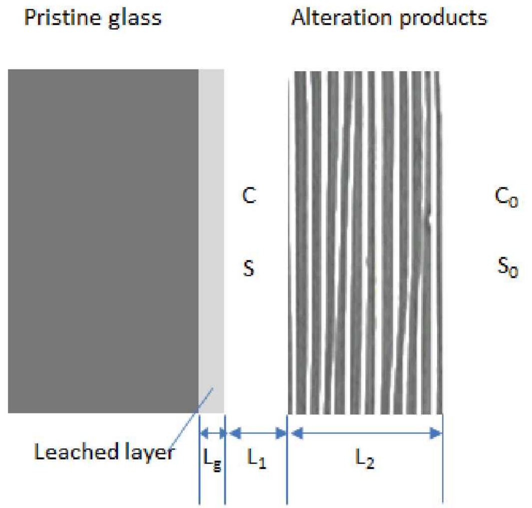


B

Wang et al. (2016)

Mathematical model



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

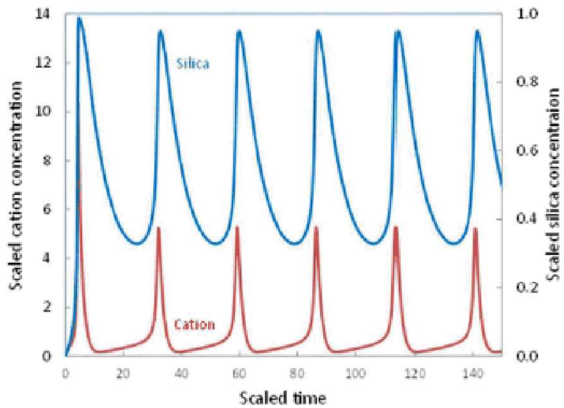
$$L_1\frac{dS'}{dt} = \alpha k_d C_{\mathrm{IEP}}\left[1+\beta\left(\frac{C'}{C_{\mathrm{IEP}}}\right)^n\right](S_d^e - S') - \frac{D_s}{L_2}(S' - S_0) - k_p(S' - S_p^e)$$

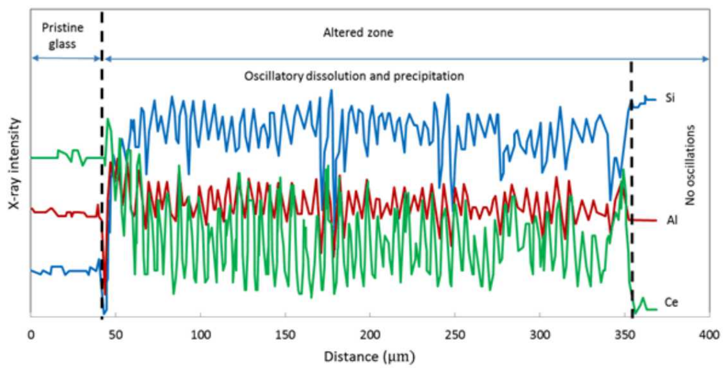
where

- 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

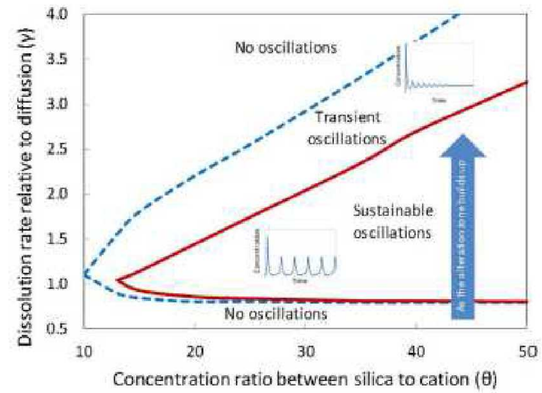
Wang et al., 2016, Scientific Reports

Nonlinear dynamics of silicate dissolution





Geisler et al. (2010)



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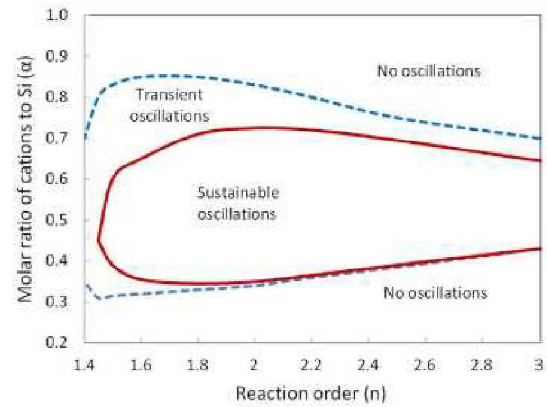


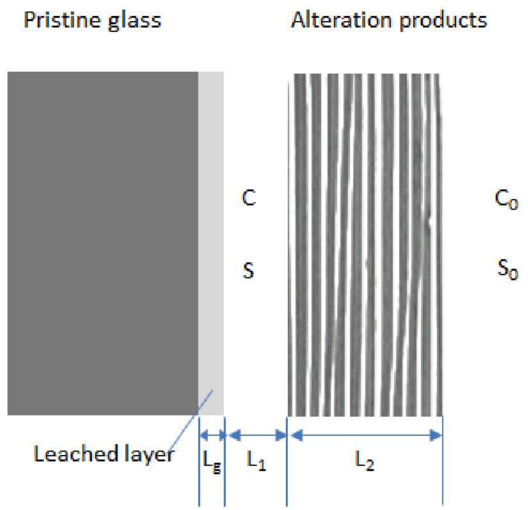
B

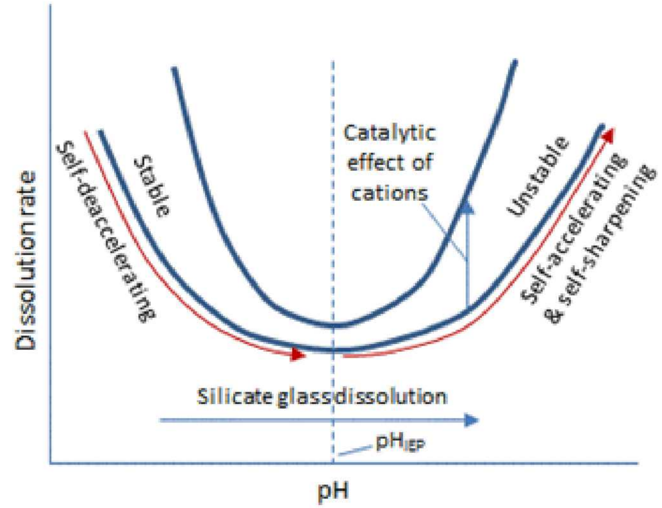
Predicted time scale: hours to years
Predicted spatial scale: sub-micron to tens of microns

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

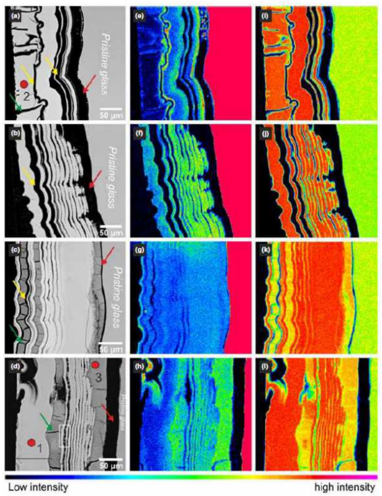
Wang et al., 2016, Scientific Reports

Self-sharpening & morphologic instability of a reaction front

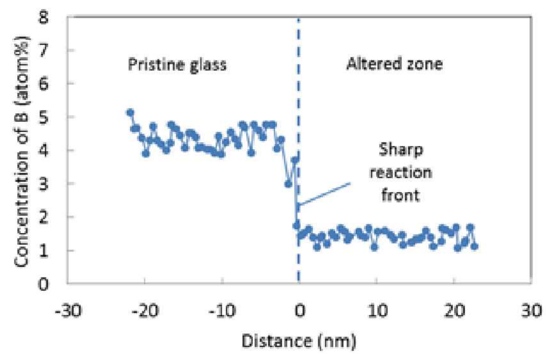




$$\frac{dL_g}{dt} \approx \frac{D_g}{L_g} - Rv_m = \frac{D_g}{L_g} - v_m k_d C_{\mathrm{IEP}}(S_d^e - S)\left[1 + \beta\left(\frac{D_g L_2}{C_{\mathrm{IEP}} L_g}\right)^n\right]$$

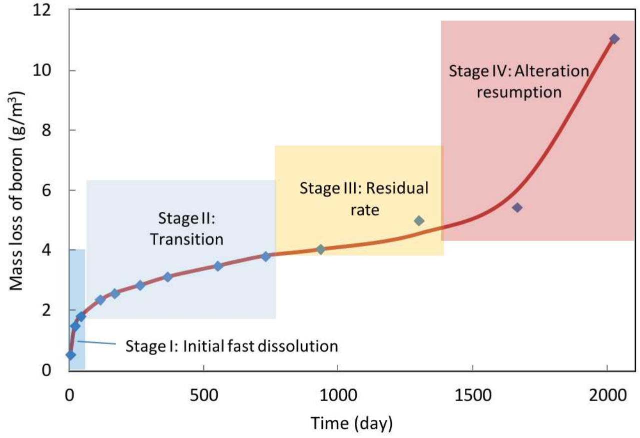


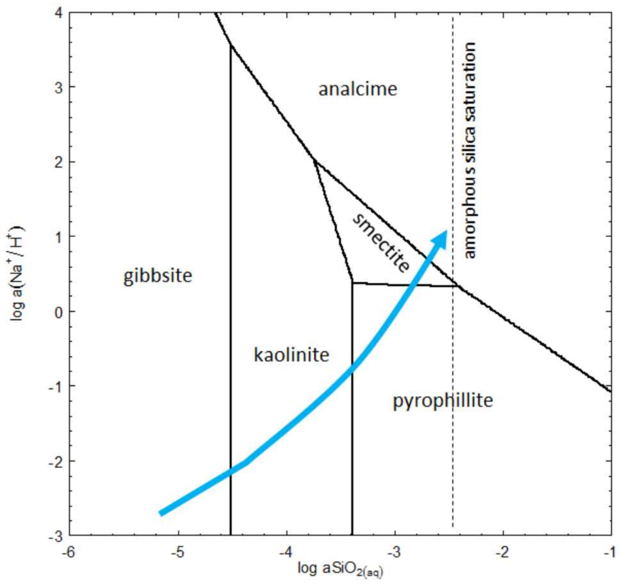
Dohmen et al. (2013)

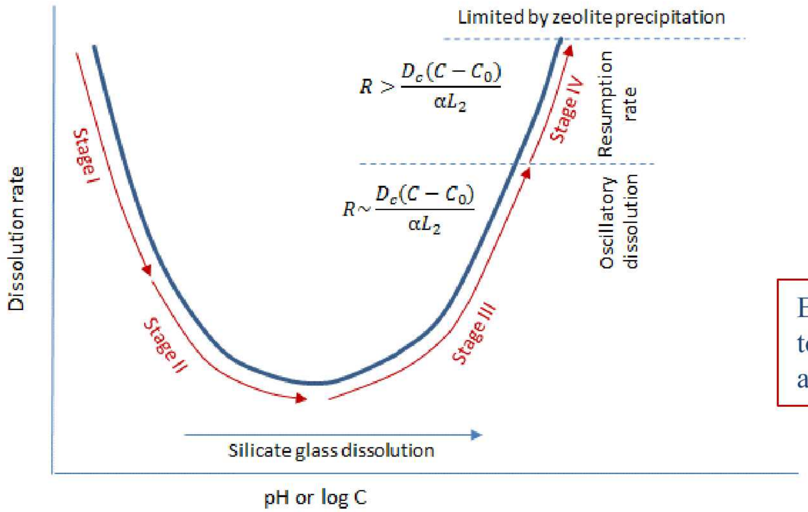


Hellmann et al. (2015)

Alteration resumption and zeolite formation

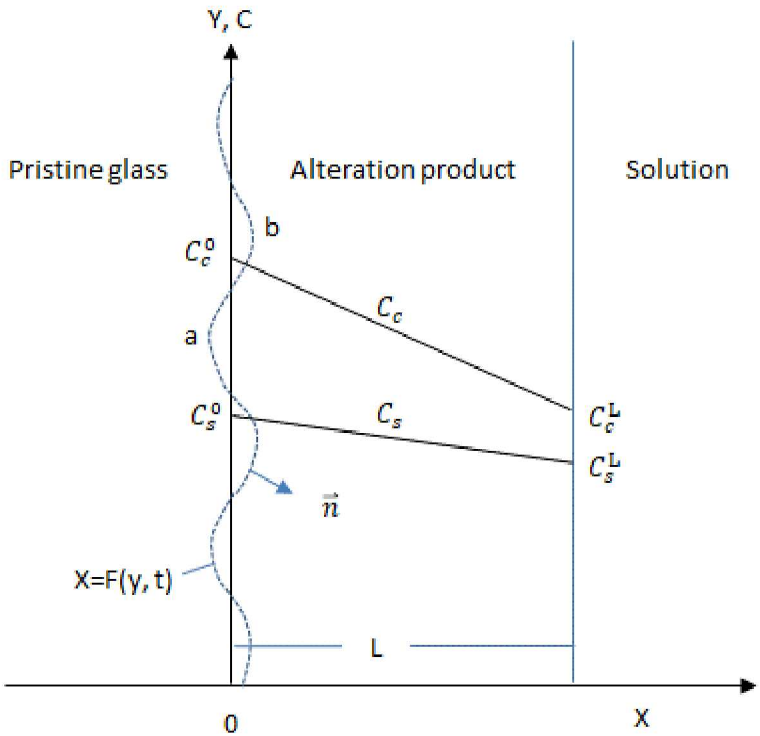






Eventually, the dissolution rate overtakes the mass exchange rate, leading to a "runaway" situation with a sharp increase in the cation concentration at the interface and therefore the dissolution rate.

Morphological evolution of dissolution front



Wang et al. (2018)

For $F(Y, t) < X < L$:

$$\frac{\partial C_s}{\partial t} = D_s \nabla^2 C_s$$

$$\frac{\partial C_c}{\partial t} = D_c \nabla^2 C_c$$

At $X = F(Y, t)$:

$$\alpha_s R = -D_s \vec{\nabla} C_s \cdot \vec{n}$$

$$\alpha_c R = -D_c \vec{\nabla} C_c \cdot \vec{n}$$

$$R = k\left[1 + \beta\left(\frac{C_c}{C_{IEP}}\right)^m\right](C_s^e - C_s)$$

$$C_s^e = C_s^e(\infty)(1 + \Gamma \mathrm{K})$$

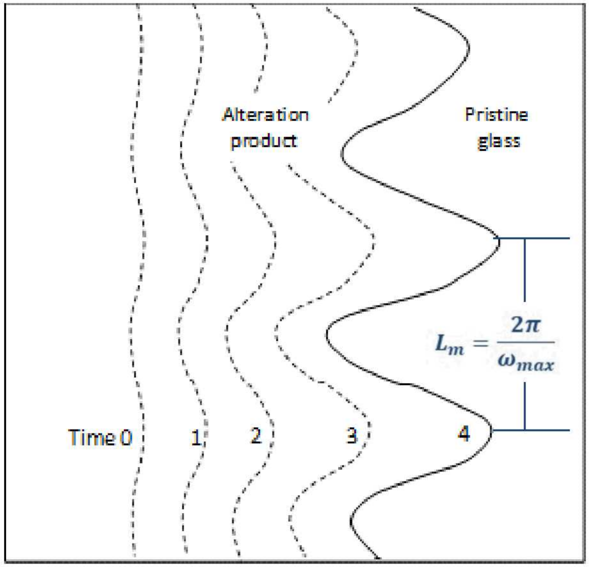
$$\mathrm{K} = -\frac{\partial^2 F}{\partial Y^2} \Big/ \left[1 + \left(\frac{\partial F}{\partial Y}\right)^2\right]^{3/2}$$

$$\vec{n} = \left(1, -\frac{\partial F}{\partial Y}\right)^T \Big/ \left[1 + \left(\frac{\partial F}{\partial Y}\right)^2\right]^{1/2}$$

$$\rho \frac{\partial F}{\partial t} = \bar{R} - R\left[1 + \left(\frac{\partial F}{\partial Y}\right)^2\right]^{1/2}$$

$$\bar{R} = k\left[1 + \beta\left(\frac{\bar{C}_c}{C_{IEP}}\right)^m\right][C_s^e(\infty) - \bar{C}_s]$$

Morphological instability analysis



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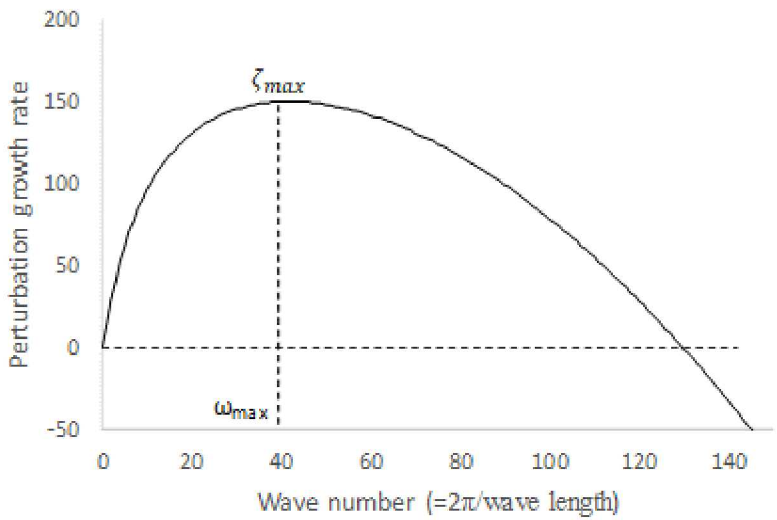
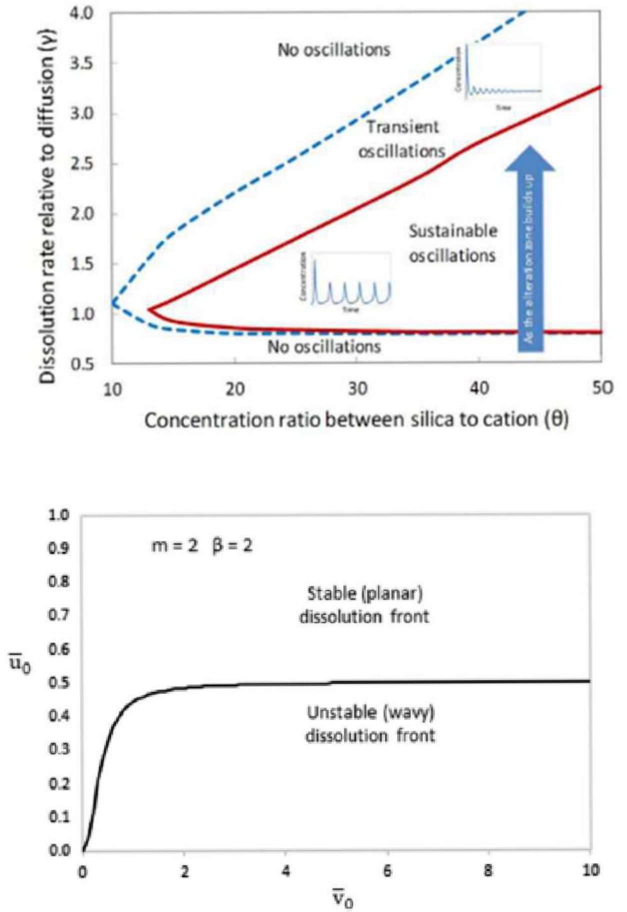


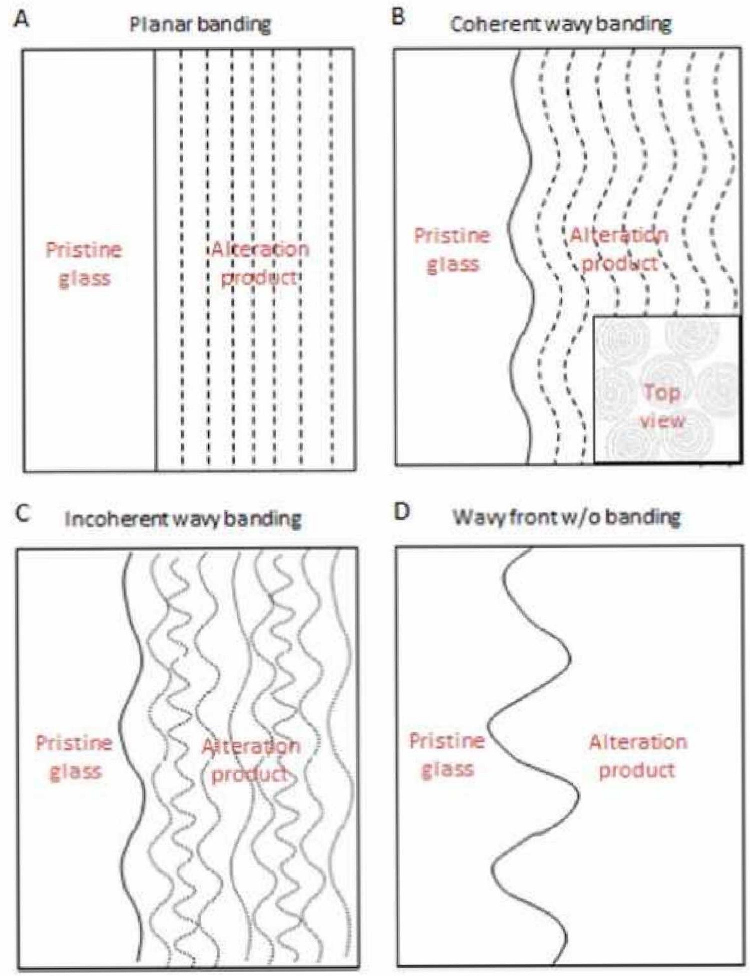
B

$$\delta f = \hat{f} e^{\zeta\tau} \cos(\omega y)$$

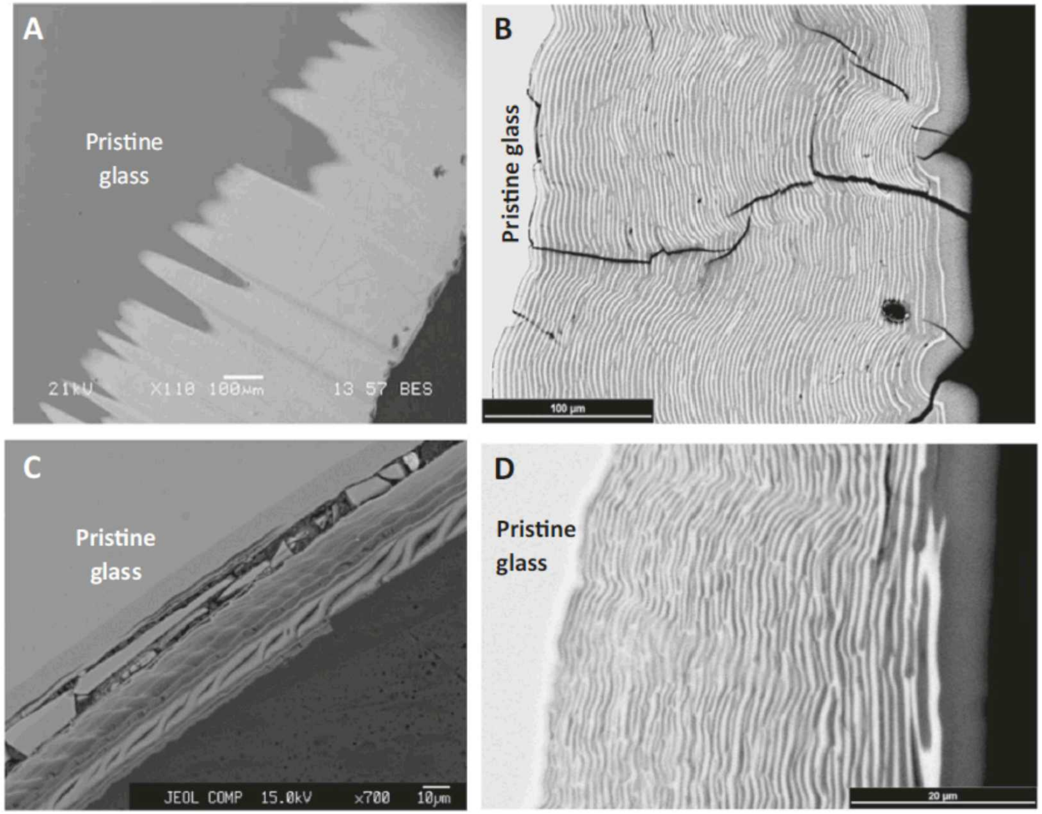
$$\zeta = \frac{\omega^3 \gamma \frac{\partial \bar{r}}{\partial \bar{u}}\Big|_{s=0} - \omega \frac{d\bar{r}}{ds}\Big|_{s=0}}{\omega + a_c \theta \eta \frac{\partial \bar{r}}{\partial \bar{v}}\Big|_{s=0} + a_s \theta \frac{\partial \bar{r}}{\partial \bar{u}}\Big|_{s=0}}$$

Corrosion product textures: Predictions

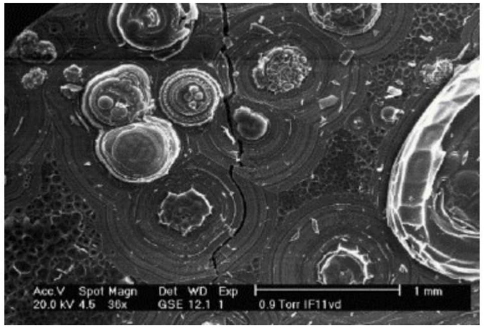




Corrosion product textures: Observations



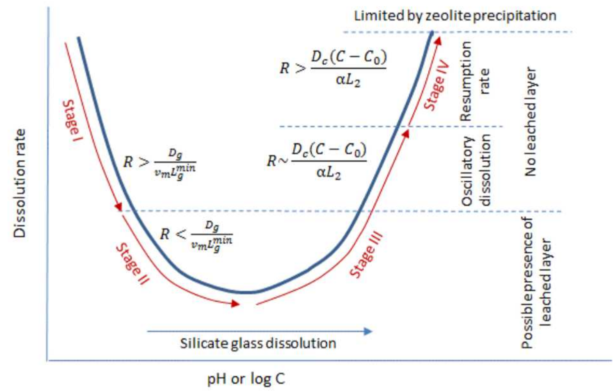
Wang et al. (2018)



Roman glass from seabed
Dal Bianco et al. (2004)

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, multiple stages of glass dissolution and morphological instability.
- 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

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