

# Natural glass alteration under a hyperalkaline condition for about 4000 years

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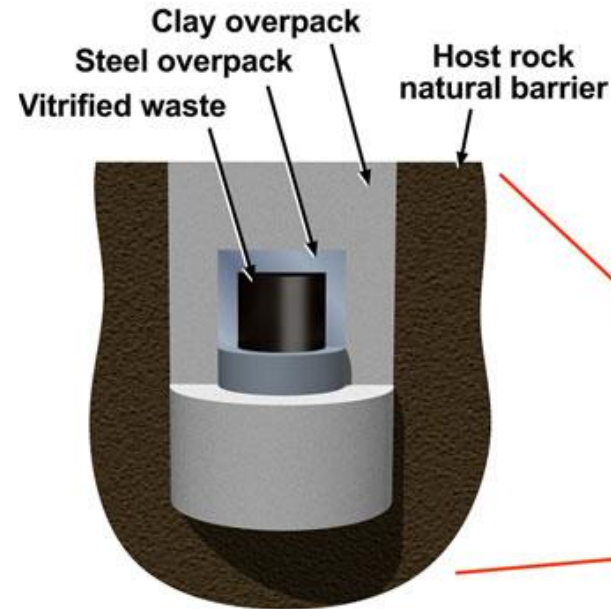


HOKKAIDO  
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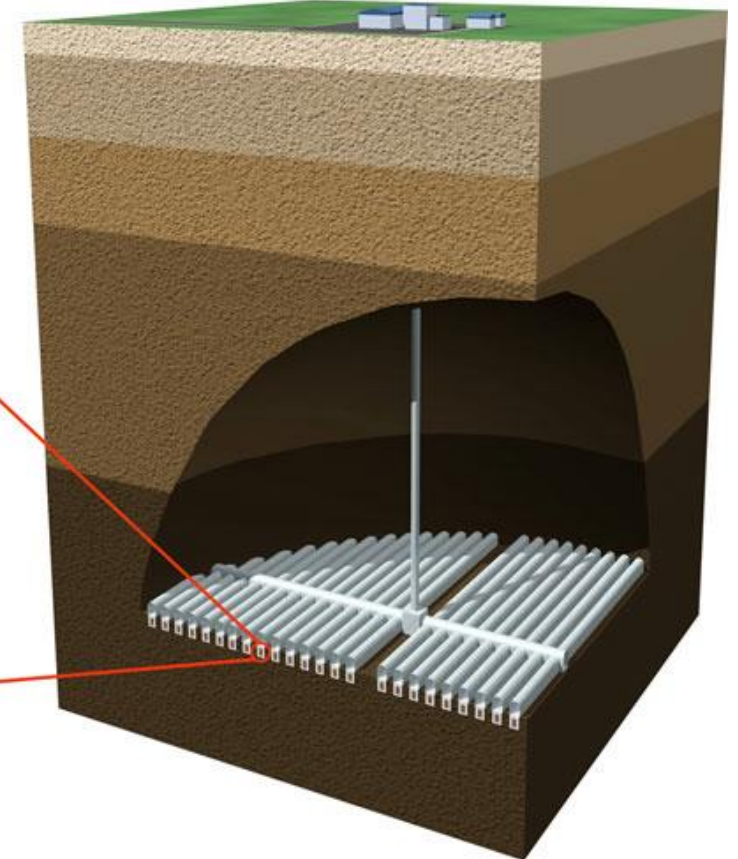
RWMC



Ancient glass (Zadar glass museum)

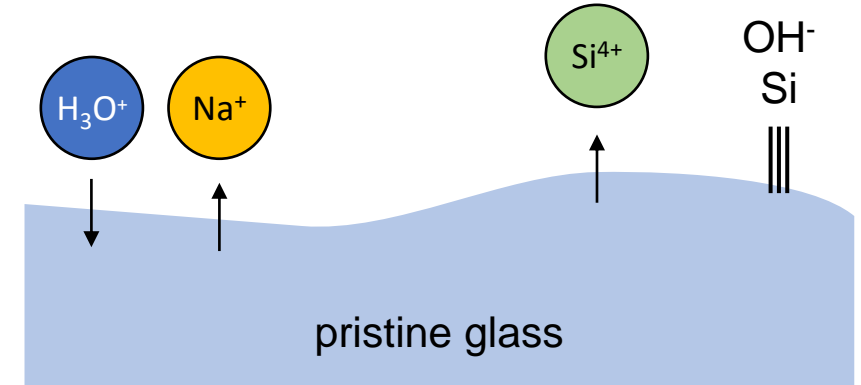
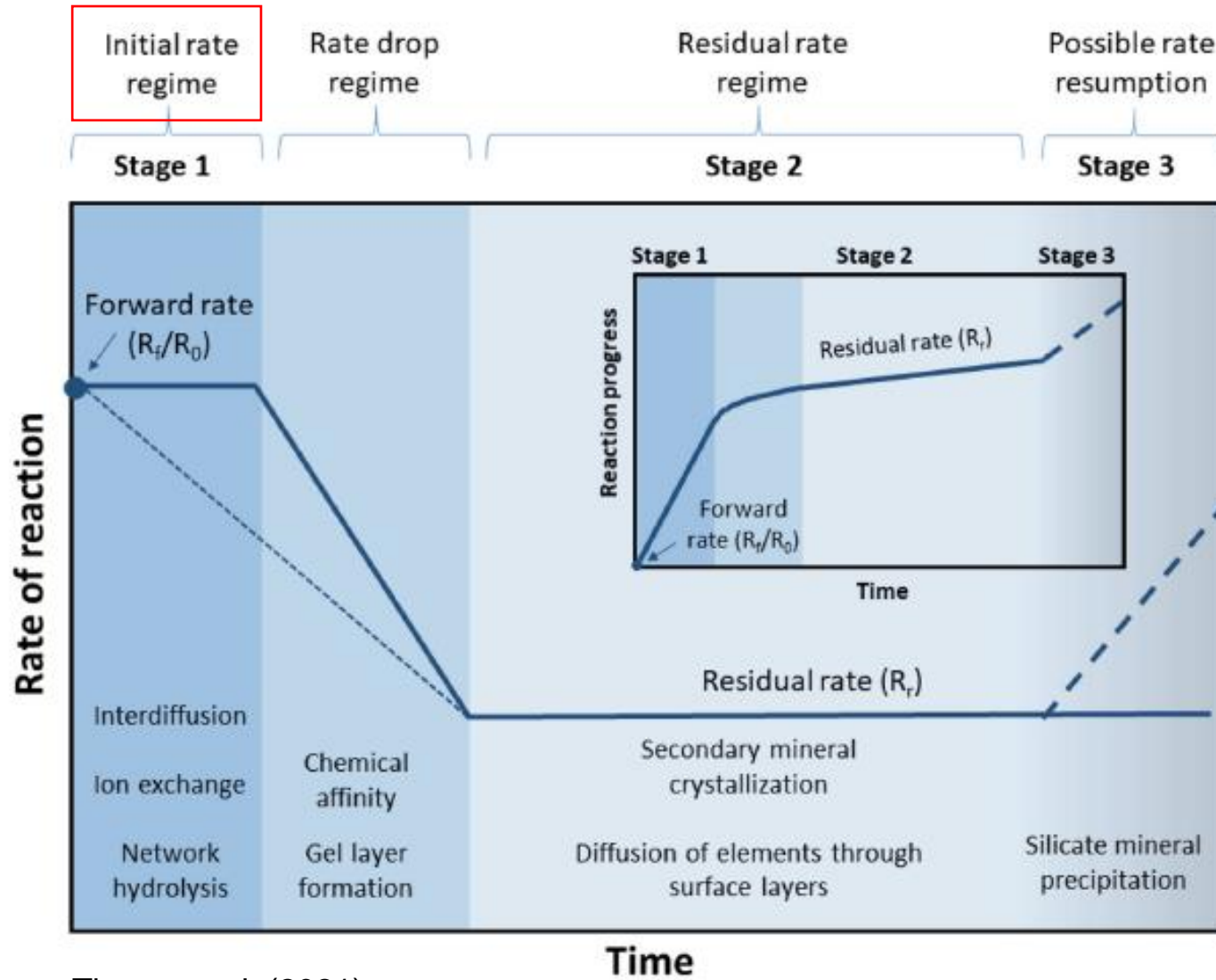


**Engineered Barrier**



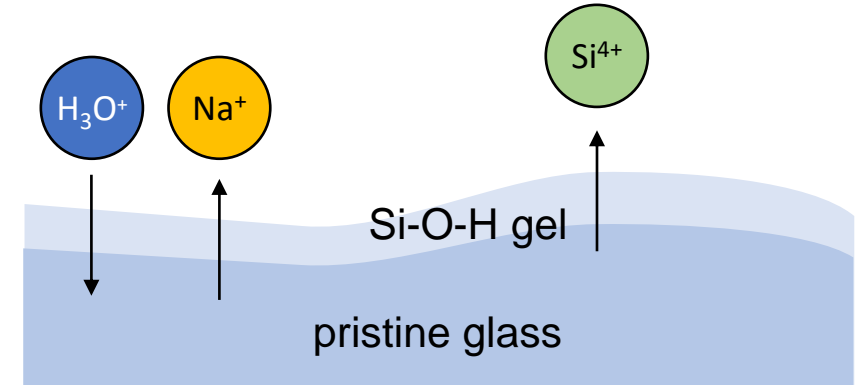
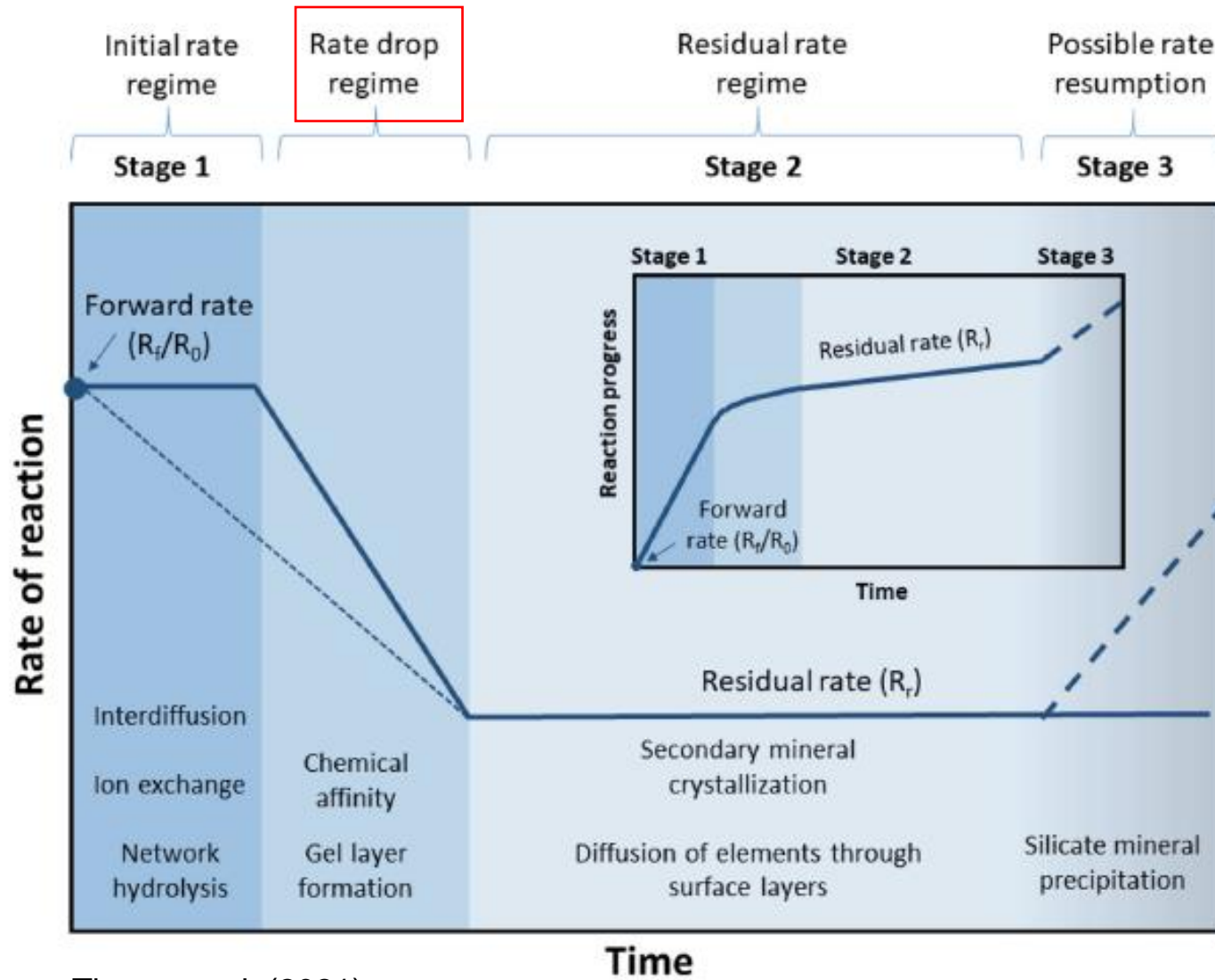
Thorpe et al. (2021)

- ☑ Fission products arising from spent fuel reprocessing are confined in borosilicate glasses, which are considered particularly durable.
- ☑ Glass alteration have been investigated in various experiments, modeling & natural analogues.



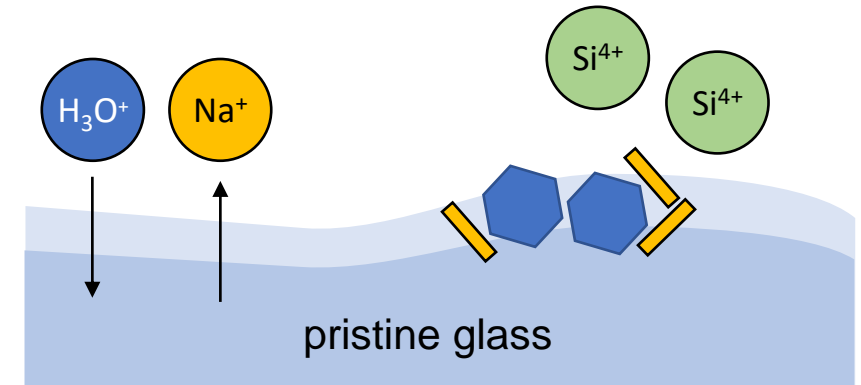
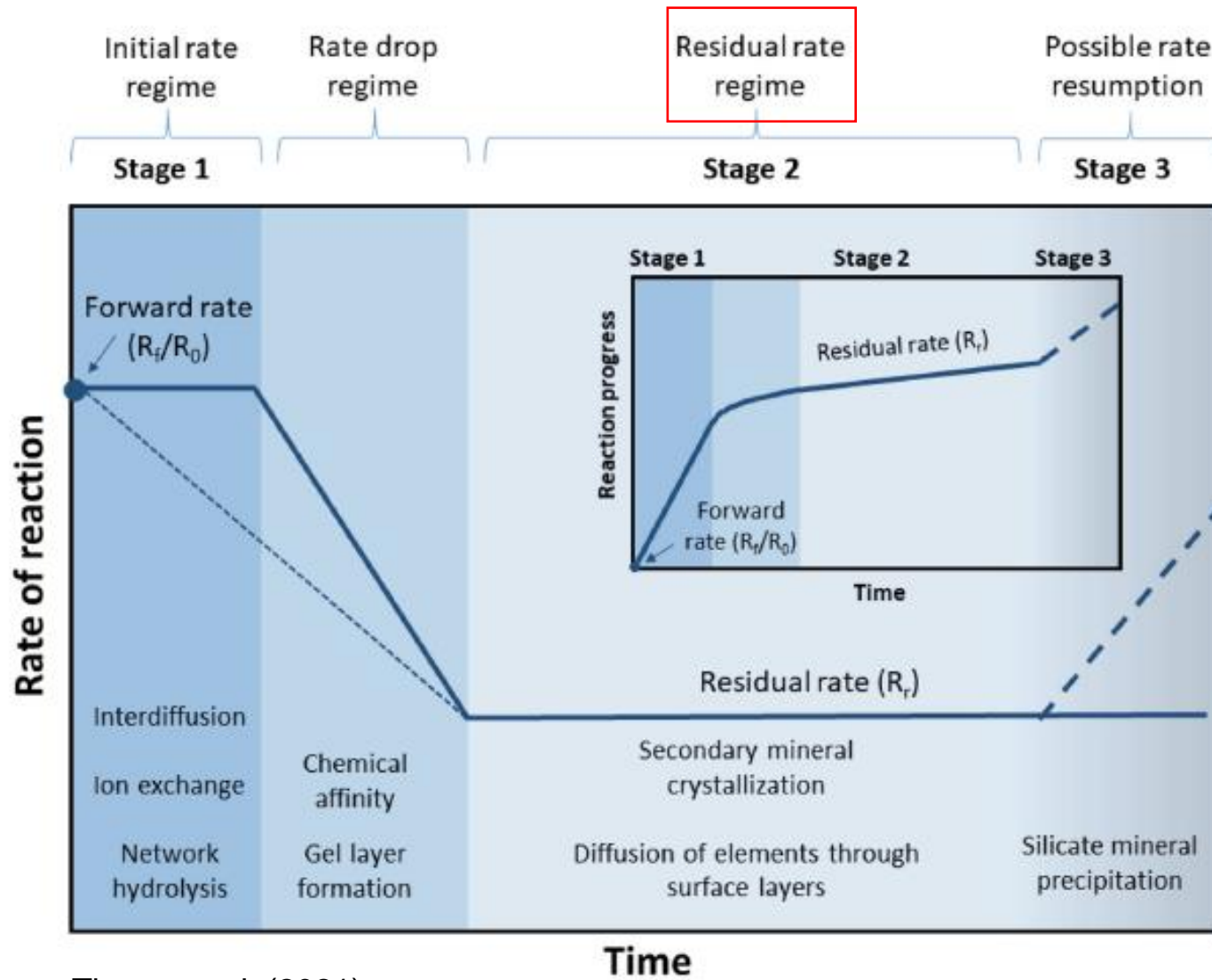
- ☑ Diffusion of  $H_3O^+$  into the glass
- ☑ Release of alkali ions (e.g.  $Na^+$ ,  $K^+$ )
- ☑ Si release & hydrolyzed surface

# Rates and Mechanisms of glass dissolution

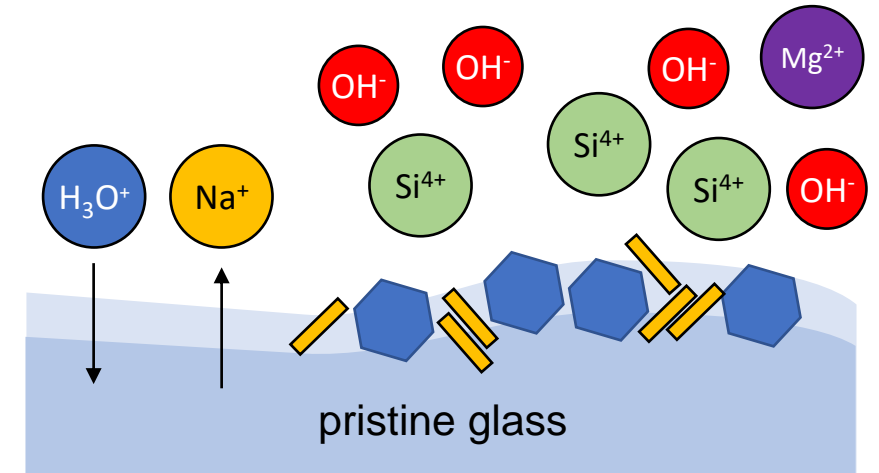
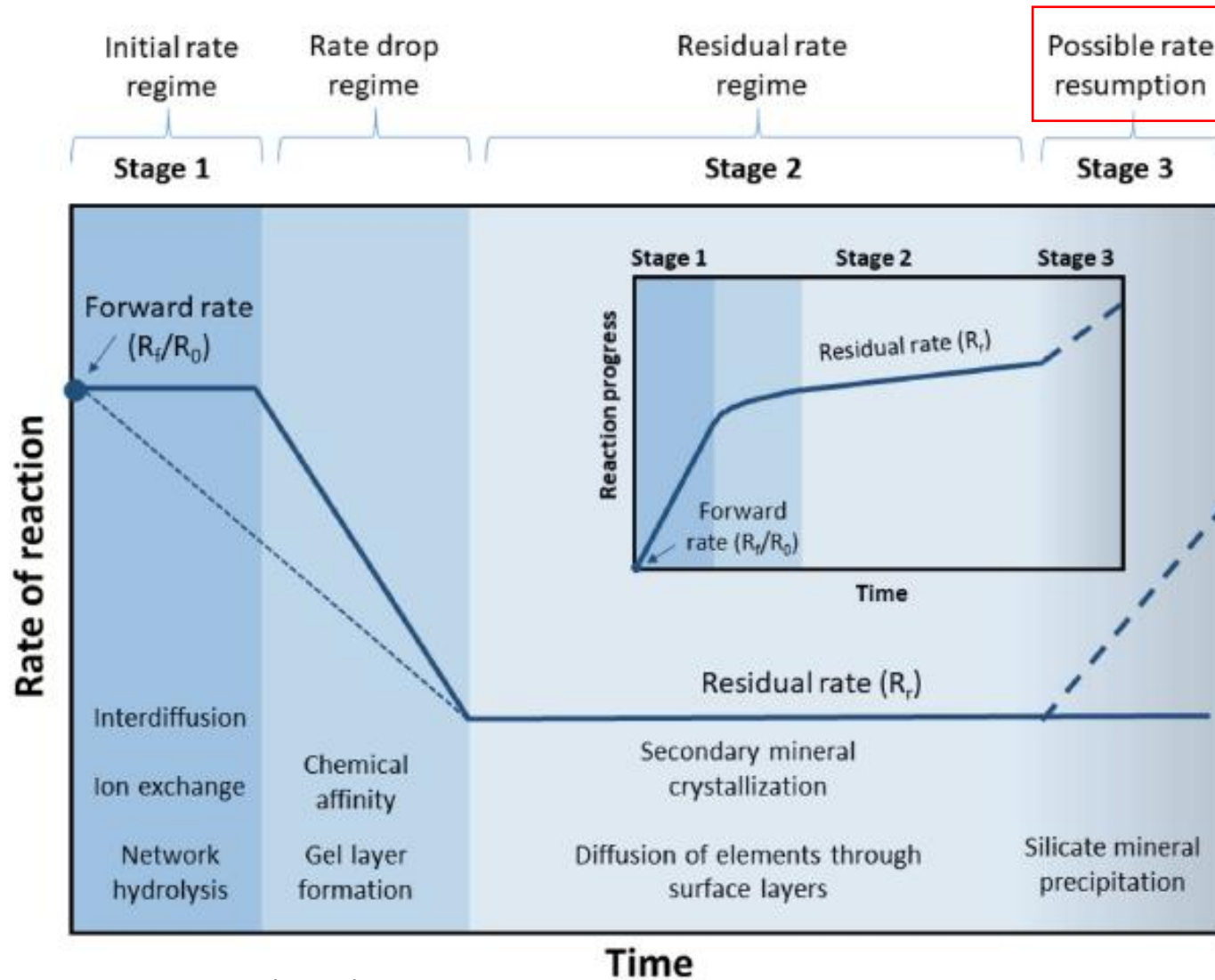


☑ The reaction front moves inwards

Thorpe et al. (2021)



☑ Corrosion products precipitate



☑ Possible water chemistry change?

Hyperalkaline fluids from cement materials may trigger Stage III

Possible rate resumption is problematic to predict long-term glass dissolution

Natural glass dissolution have been reported in seawater conditions (pH ~ 7 - 8)

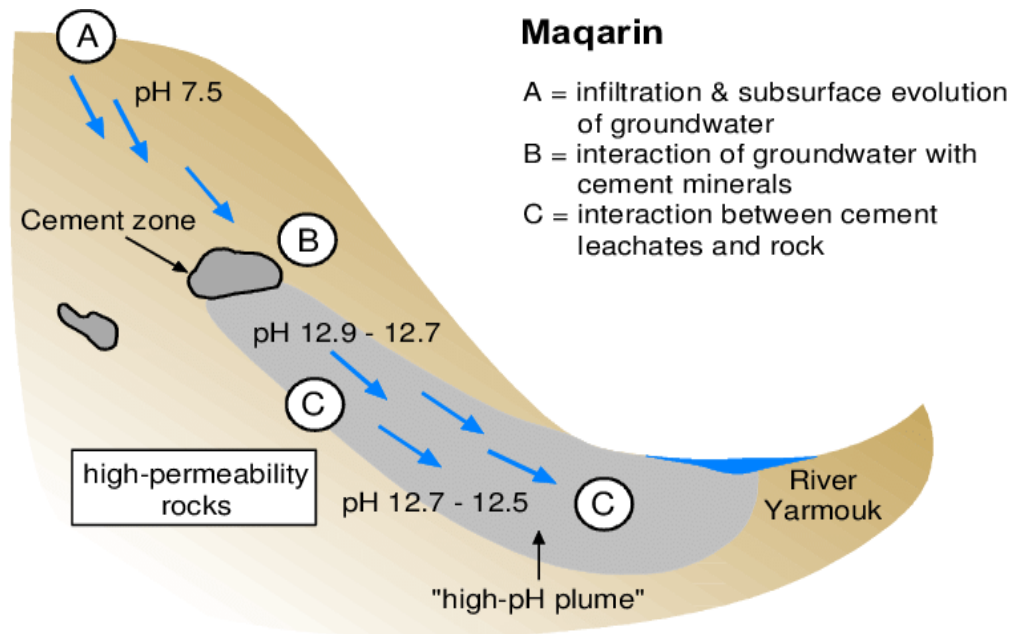
A few exceptions that achieve more alkaline conditions

① **Saline lakes ~ pH 9 - 10** (Savage et al. 2010)

\* $\text{Mg}(\text{OH})_2 + 2\text{H}^+ \rightleftharpoons \text{Mg}^{++} + 2\text{H}_2\text{O}$ : Brucite dissolution / precipitation equilibrium ~ pH 10.5

② **Maqarin natural analogue site in Jordan (natural cement production) pH > 12**

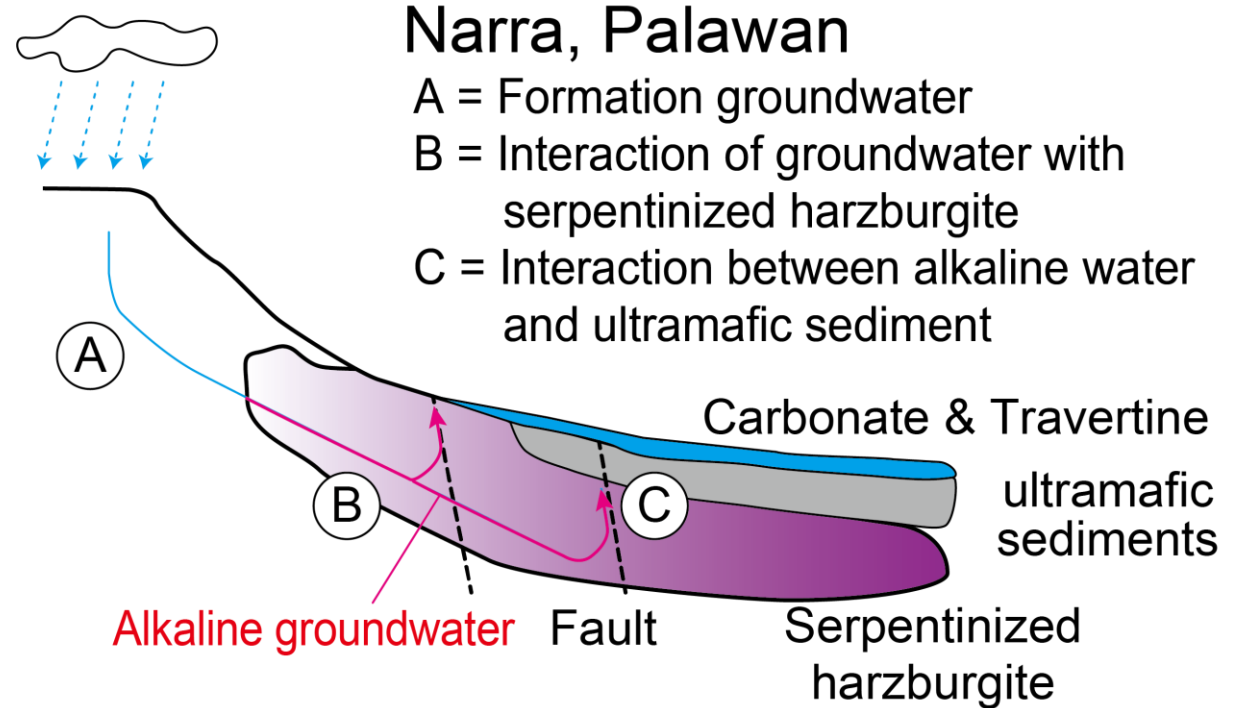
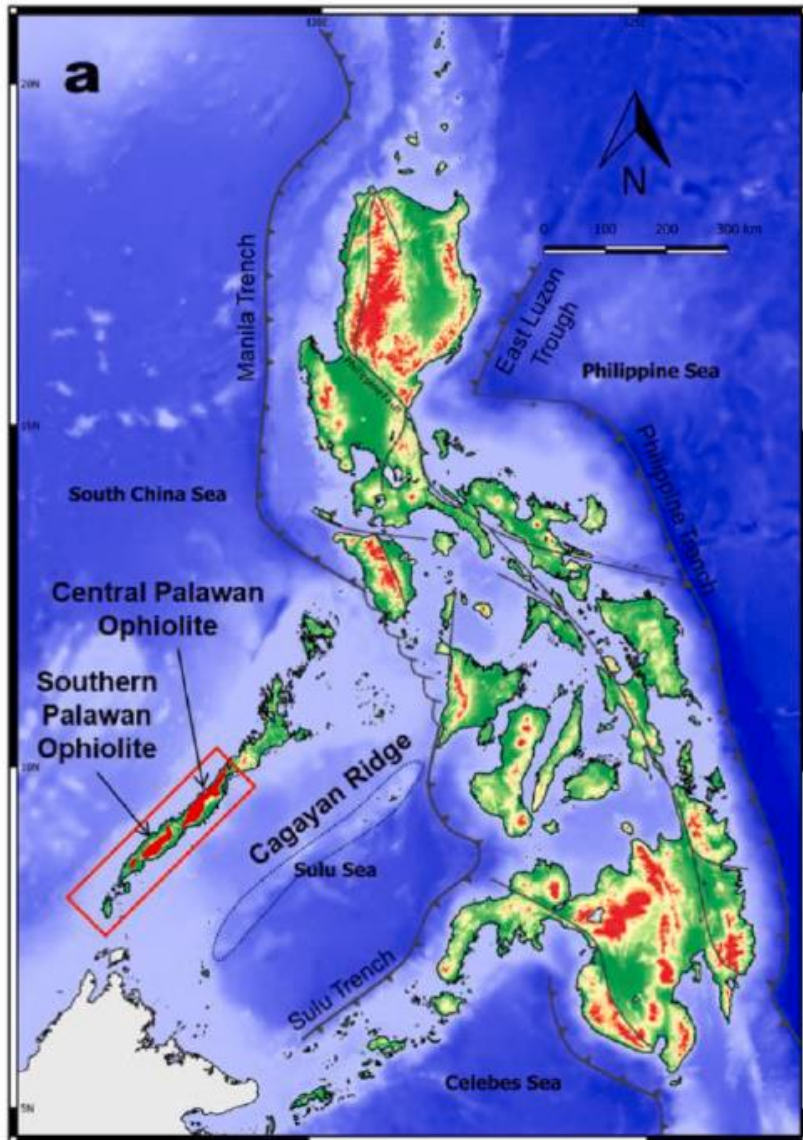
③ **Groundwater originated from ultramafic rocks (Ophiolite in Oman, the Philippines, etc.) pH > 11**



Alexander et al. (1998)



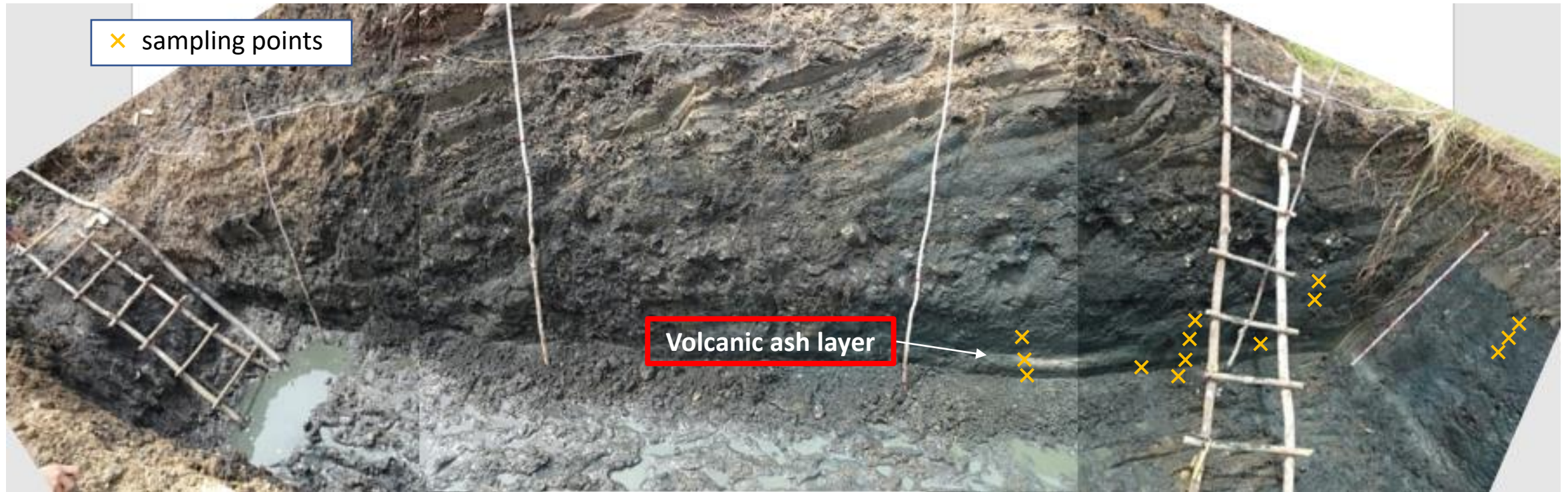
Pitty & Alexander (2011)



- △ Sediments aren't equivalent to bentonite
- ◎ Both solid and liquid samples are accessible
- ◎ pH ~ 11, ORP ~ -450 – -30 mV, Temp. ~ 30 – 40 °C
- ◎ Organic matters in sediments allow <sup>14</sup>C dating

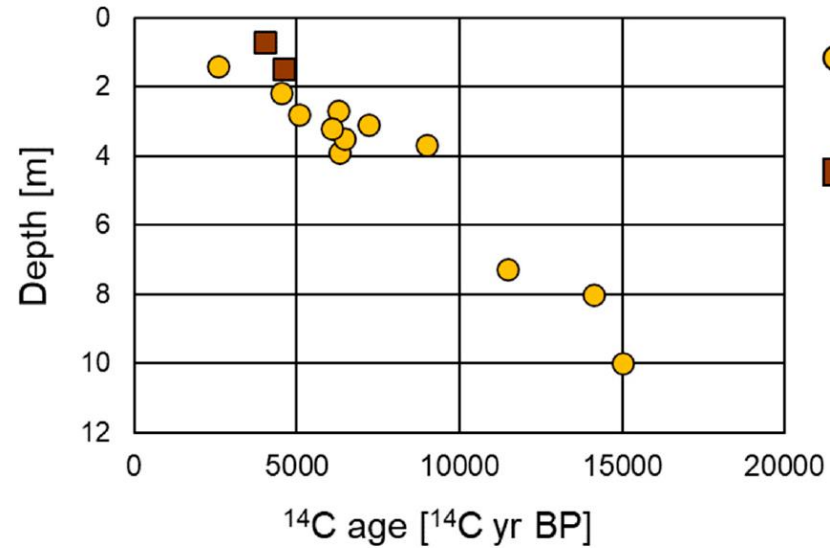
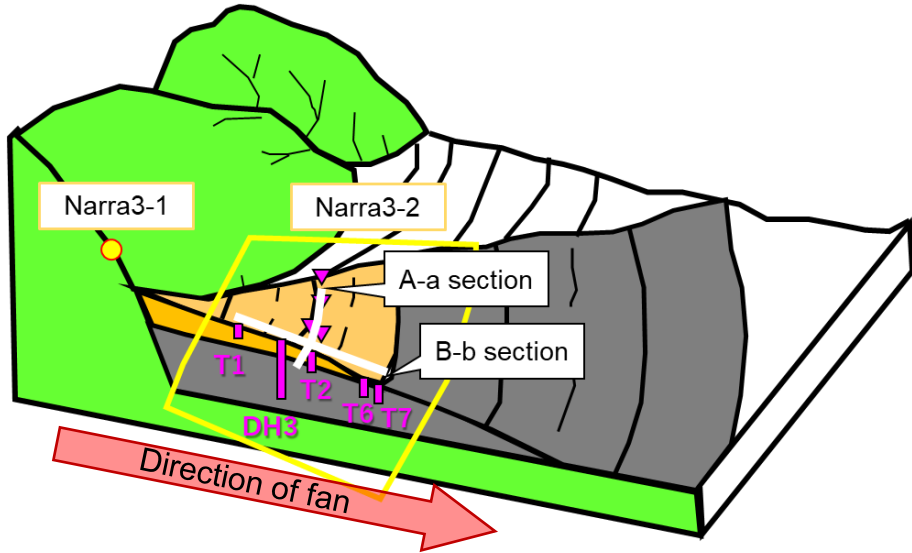
**NA study at Narra provides valuable implications to long-term reaction between clayey materials and alkaline fluids**

**In Narra, our main target was the clay alteration but...**



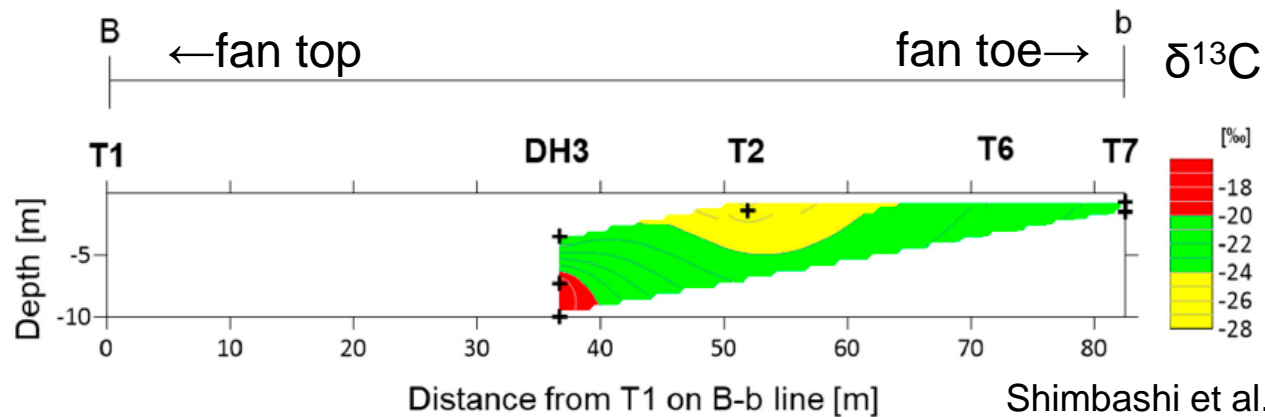
- ✓ To examine volcanic glass altered by interaction between alkaline groundwater
- ✓ To clarify the secondary minerals at glass surface
- ✓ To estimate dissolution rate in the long-term

Schematic topography of Narra 3-1 & 3-2



Shimbashi et al. (2020)

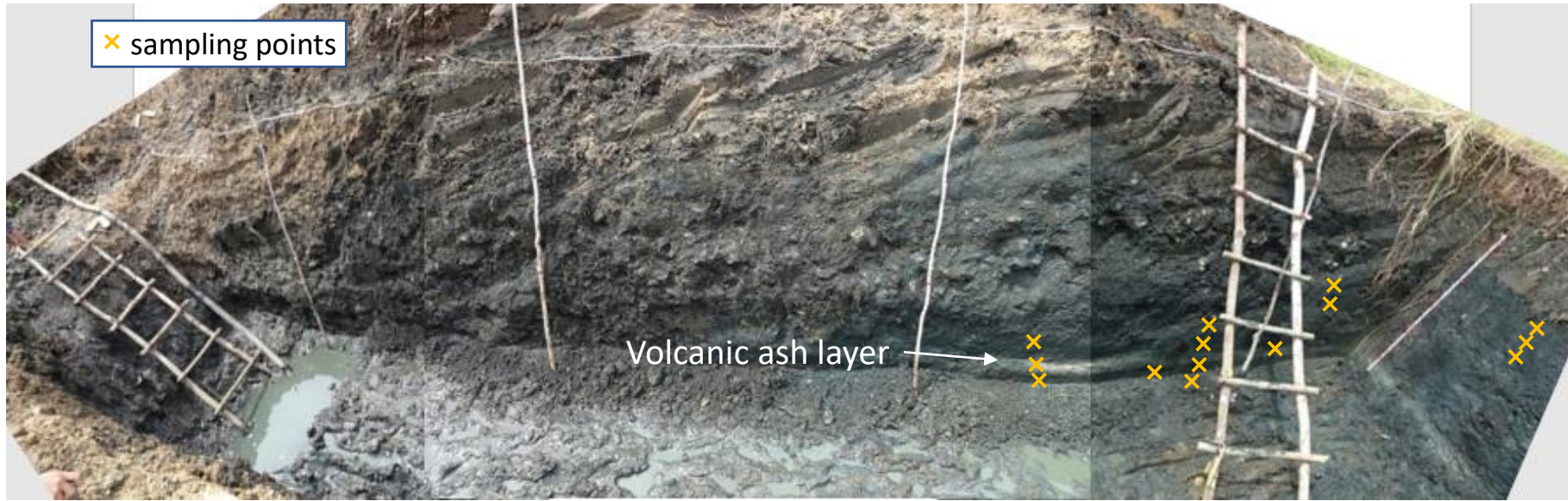
☑ Sediments deposited from 2000 to 15000 yrs ago



← Marine mud ~ -20‰  
 ← Freshwater sediments -25 to 22‰

Shimbashi et al. (2020)

☑ Environment migration from brackish to freshwater



Aqueous chemical species	Concentrations (ppm)
Temperature (°C)	27.7
pH	11.16
ORP (mV)	-141
Na <sup>+</sup>	49.1
K <sup>+</sup>	2.02
Mg <sup>2+</sup>	< 0.01
Fe <sup>(2+, 3+)</sup>	0.02
Al <sup>3+</sup>	0.18
Ca <sup>2+</sup>	26.8
Si <sup>4+</sup>	4.27
Cl <sup>-</sup>	28.6
SO <sub>4</sub> <sup>2-</sup>	0.63
HCO <sub>3</sub> <sup>-</sup>	8.9

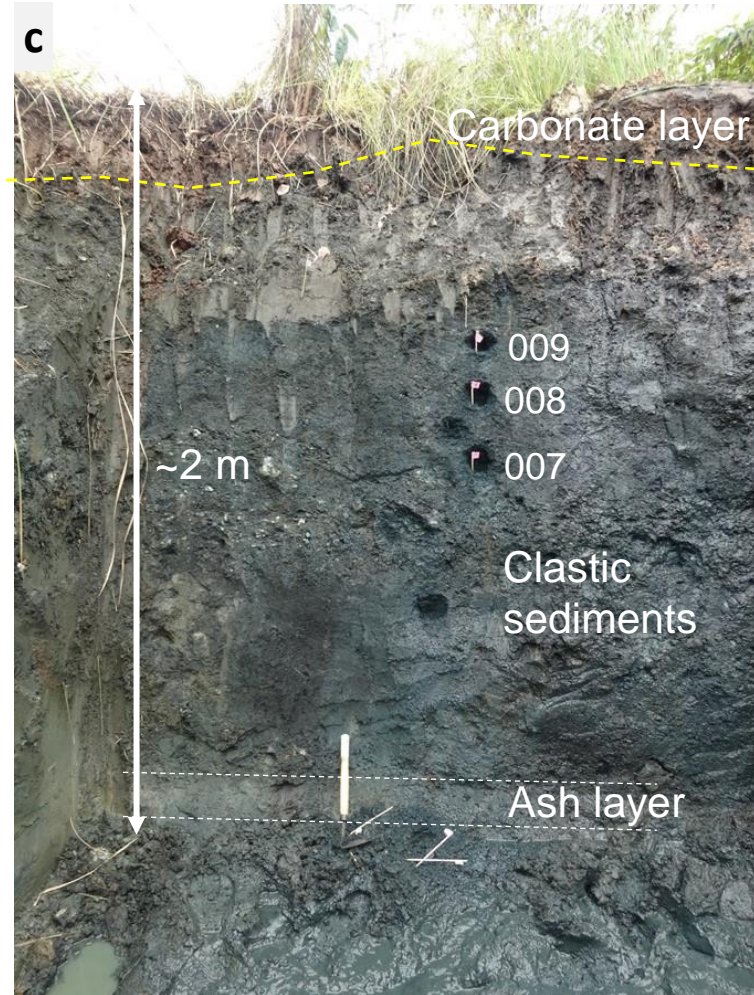
Data from Shimbashi et al. (2018)



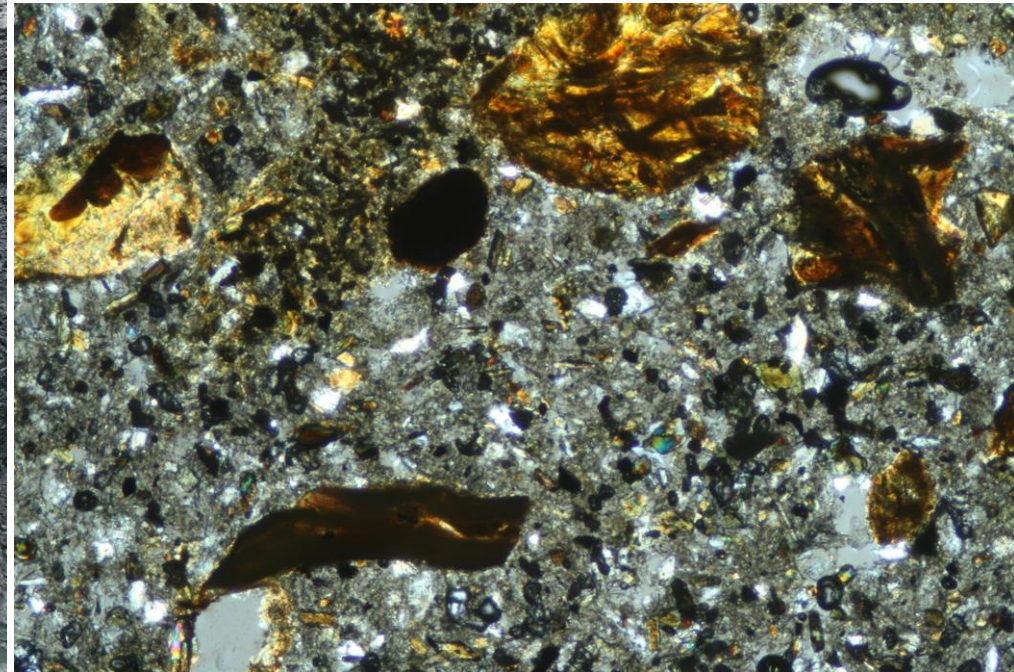
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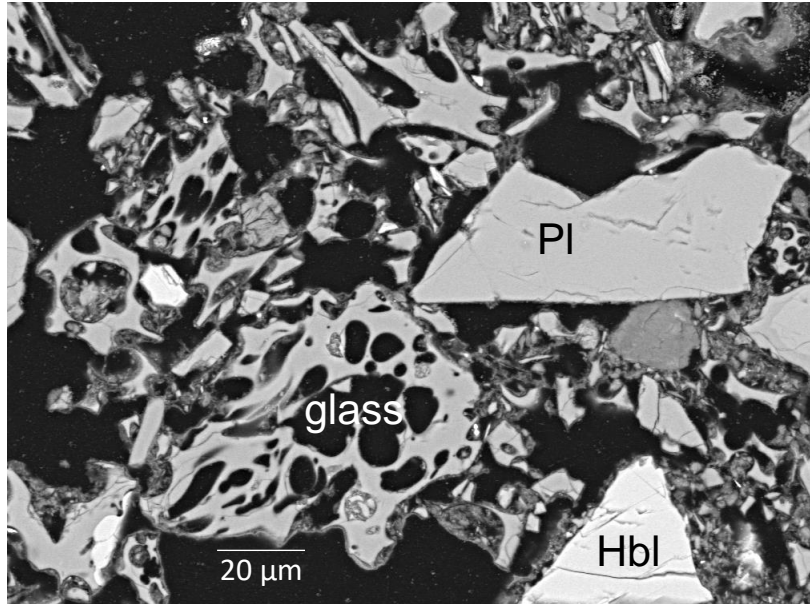
Data from Shimbashi et al. (2018)

# The volcanic ash layer containing glass



- Common minerals in the ash
- Quartz
  - Hornblende
  - Plagioclase
  - Volcanic glass
- Rhyolitic magma origin
- + Mixed with serpentinite lithics (yellowish ~ dark brown)

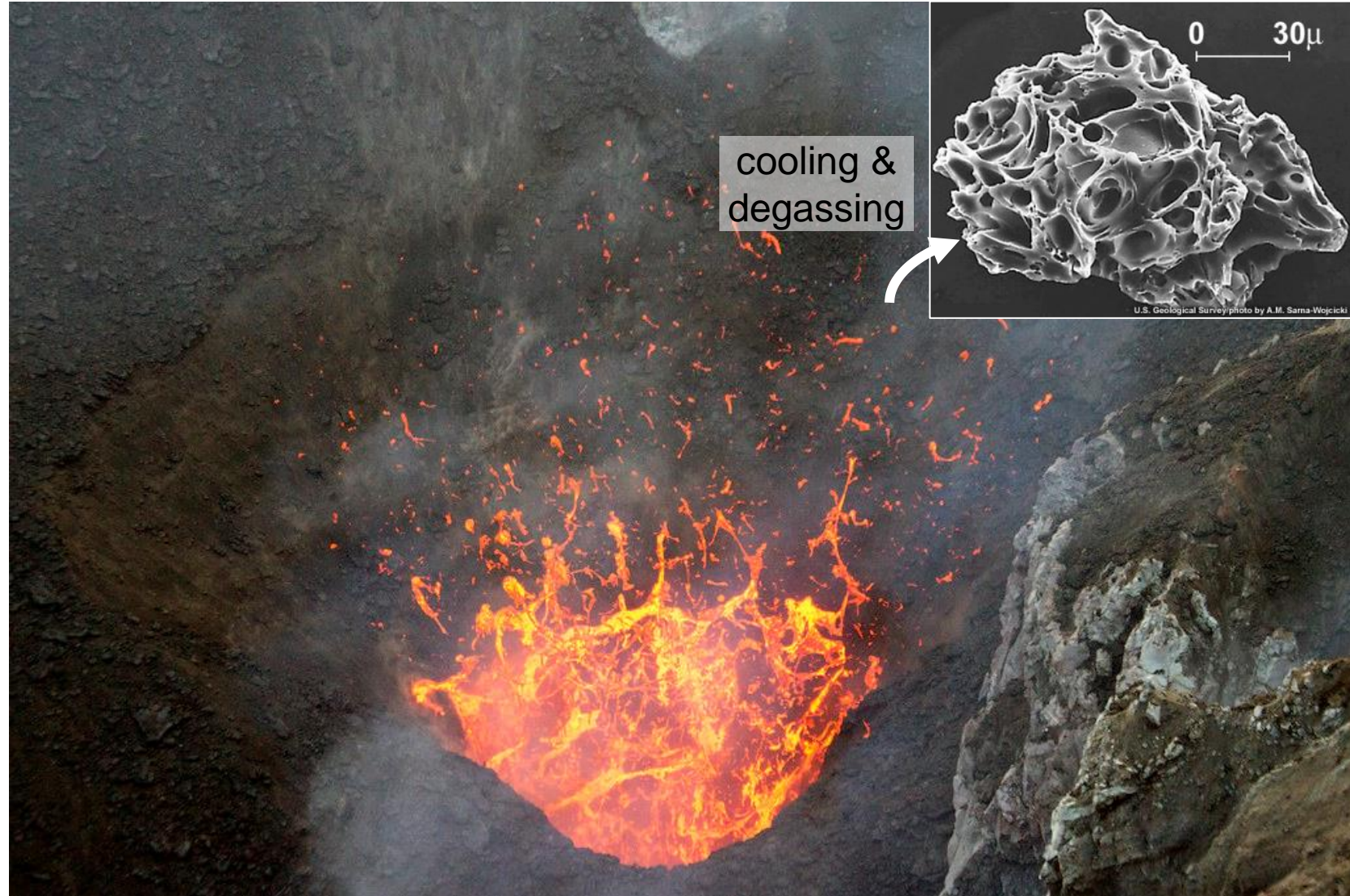




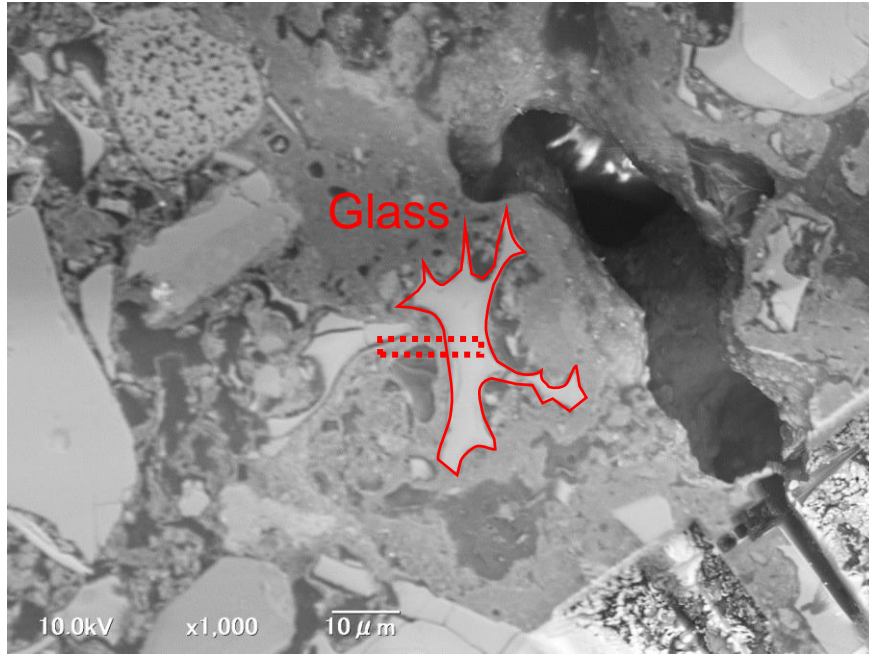
Pl: plagioclase, Hbl: hornblende, Qz: quartz

## Chemical composition (wt%)

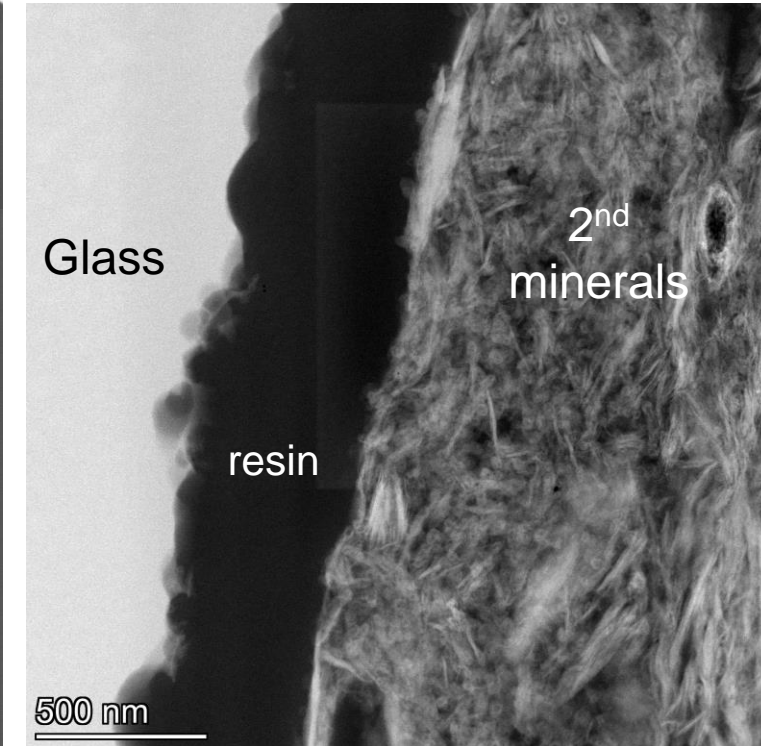
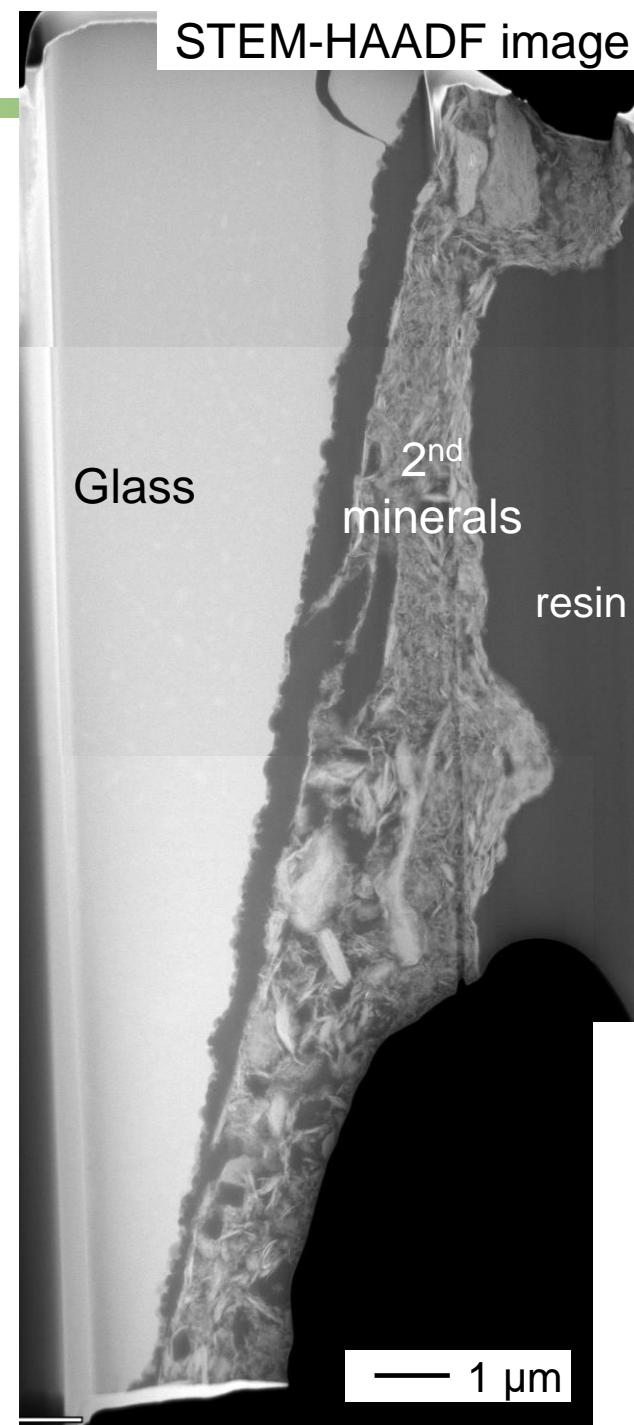
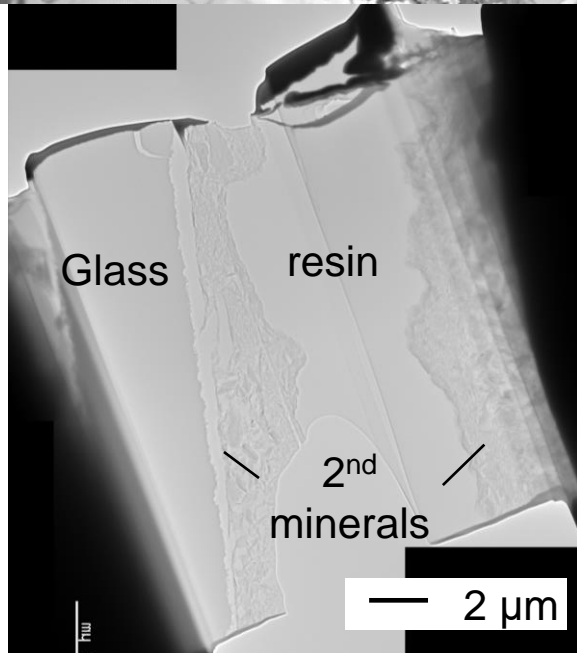
Na <sub>2</sub> O	2.62
MgO	0.19
Al <sub>2</sub> O <sub>3</sub>	13.86
SiO <sub>2</sub>	78.29
K <sub>2</sub> O	3.14
CaO	1.33
Fe <sub>2</sub> O <sub>3</sub>	0.58
total	100



# Micro-sampling of the glass surface

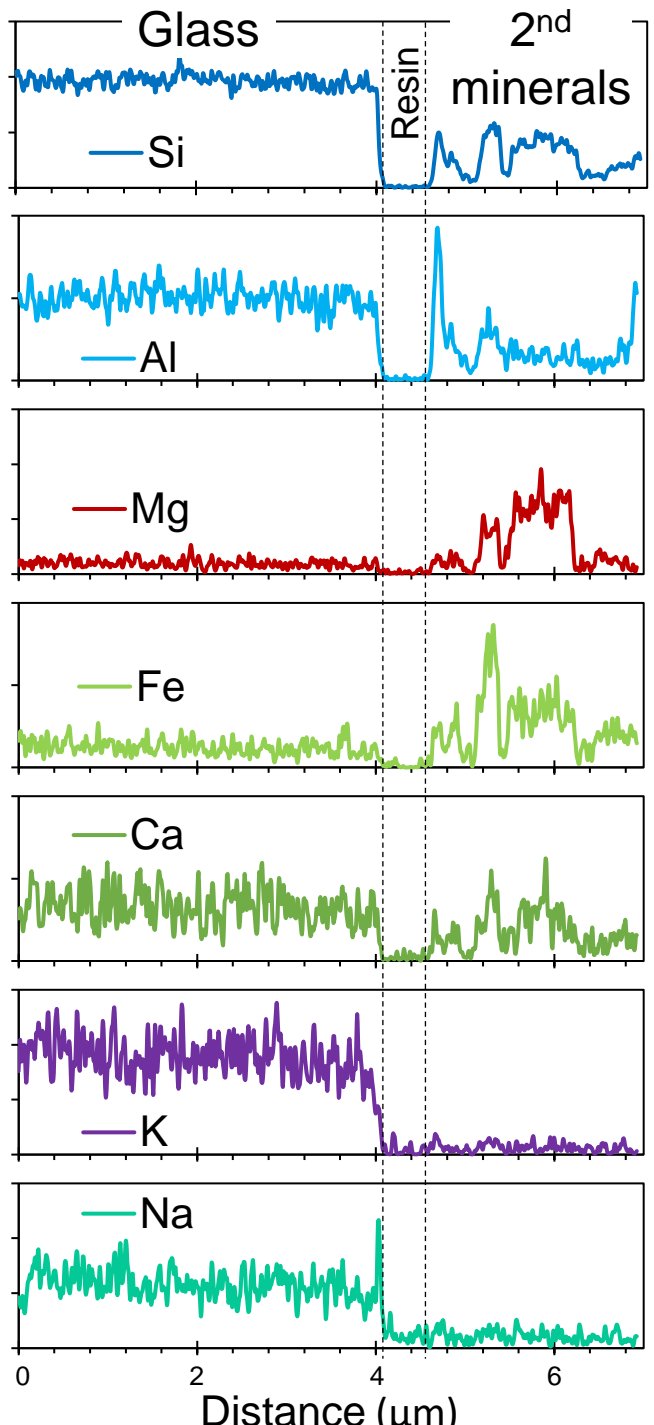
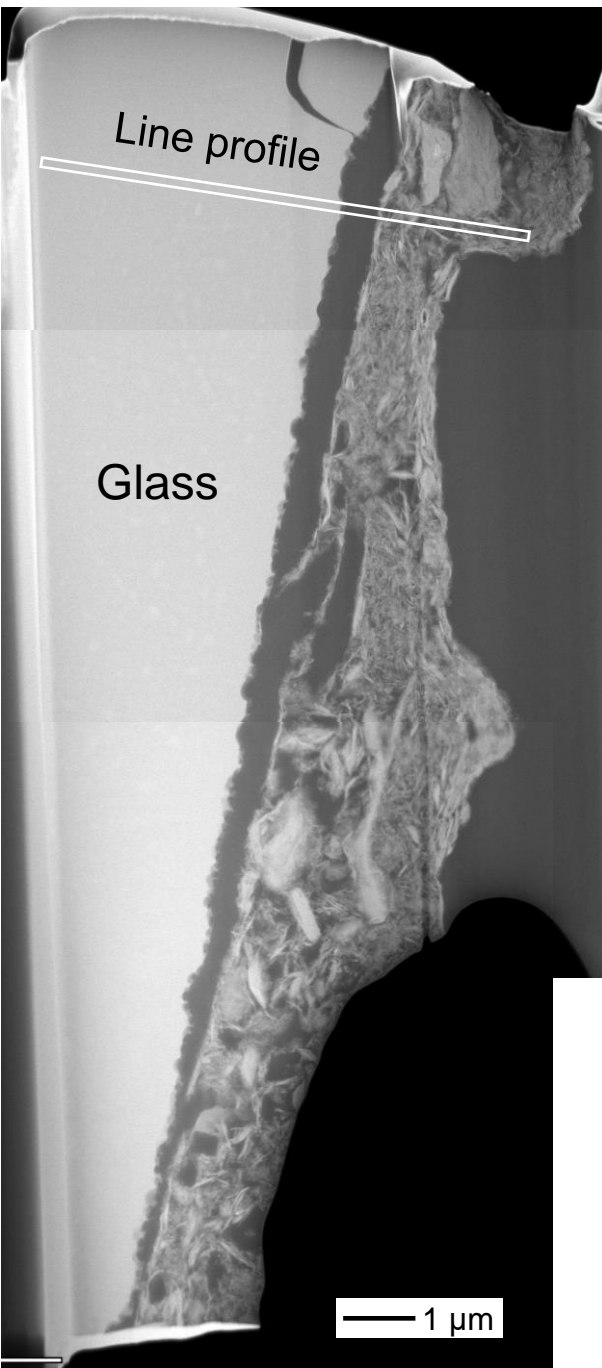


A thin foil (~ 150 nm thickness) prepared by FIB



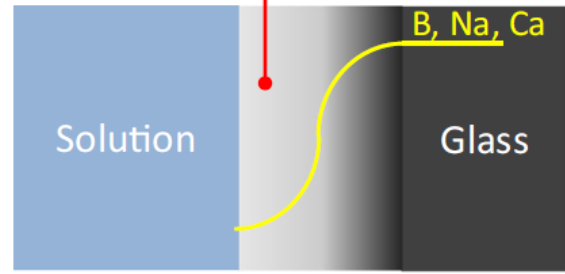
- ✓ Rough surface of the glass
- ✓ No gel-like layer
- ✓ Dense 2<sup>nd</sup> minerals formed at glass surface

# Elemental profiles



## Glass interface models in literatures

Material formed by inter-diffusion and in situ hydrolysis/condensation reactions

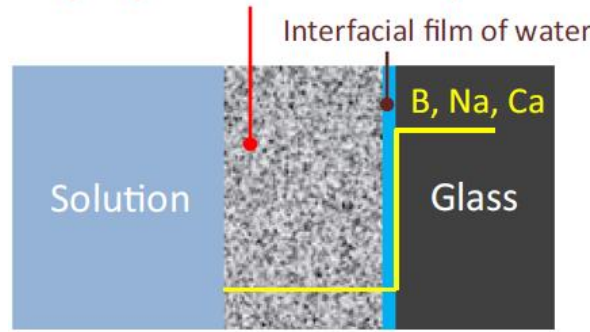


### Inter-diffusion model

- Profiles based on diffusion
- incongruent dissolution

e.g., Frugier et al. 2008

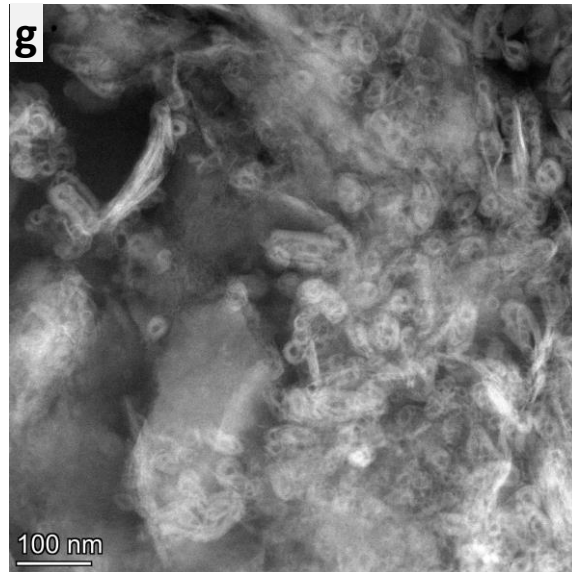
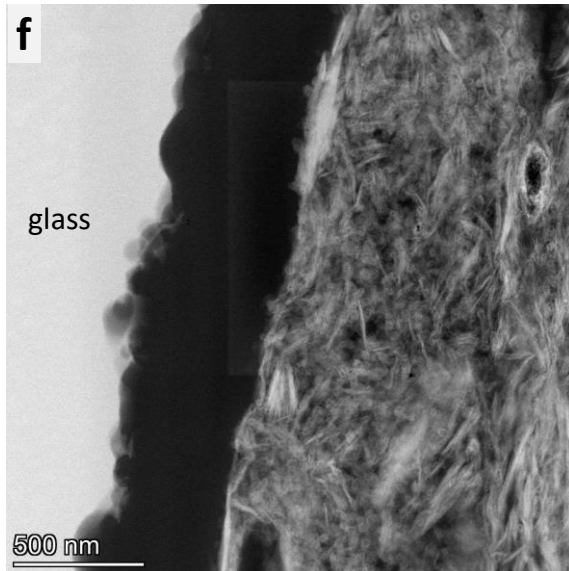
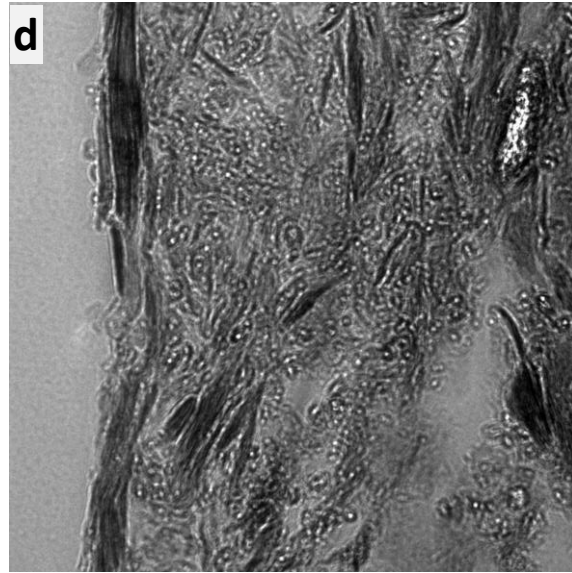
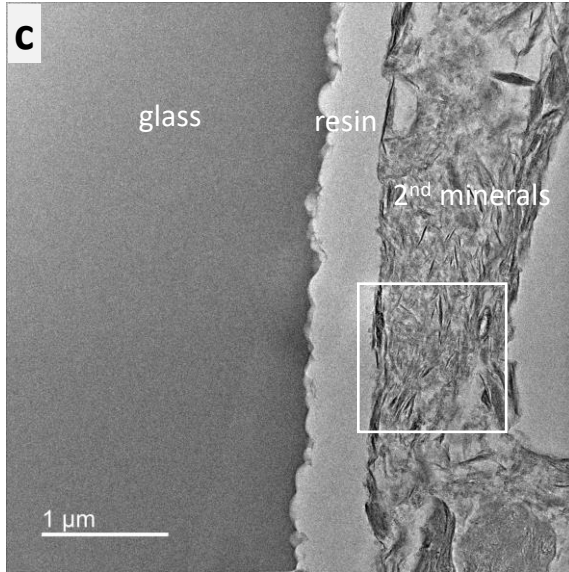
Material formed by congruent dissolution and precipitation of low soluble species



### Interface-coupled dissolution-precipitation model

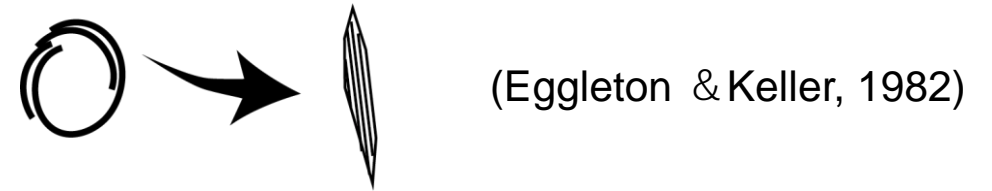
- Sharp boundary
- Congruent dissolution

e.g., Hellman et al. 2015



## Mixture of

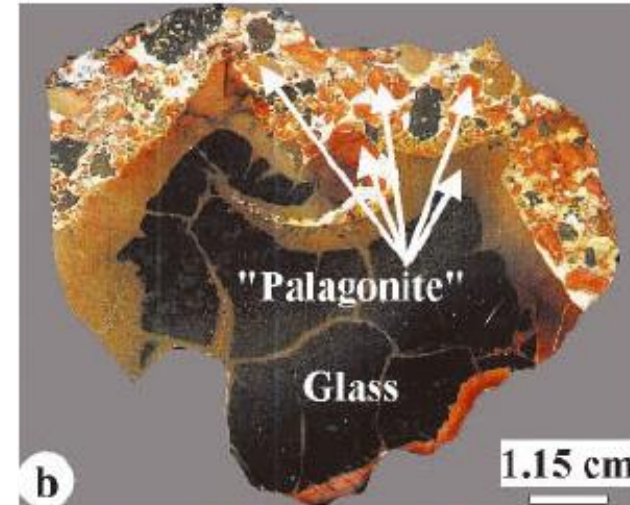
- Spherical, hollow particles ( $\sim 200 - 300 \text{ \AA}$ , Si & Al-rich)
- More crystalline smectites



2:1 clay layers bend to form 200 – 600  $\text{\AA}$  size, hollow particles

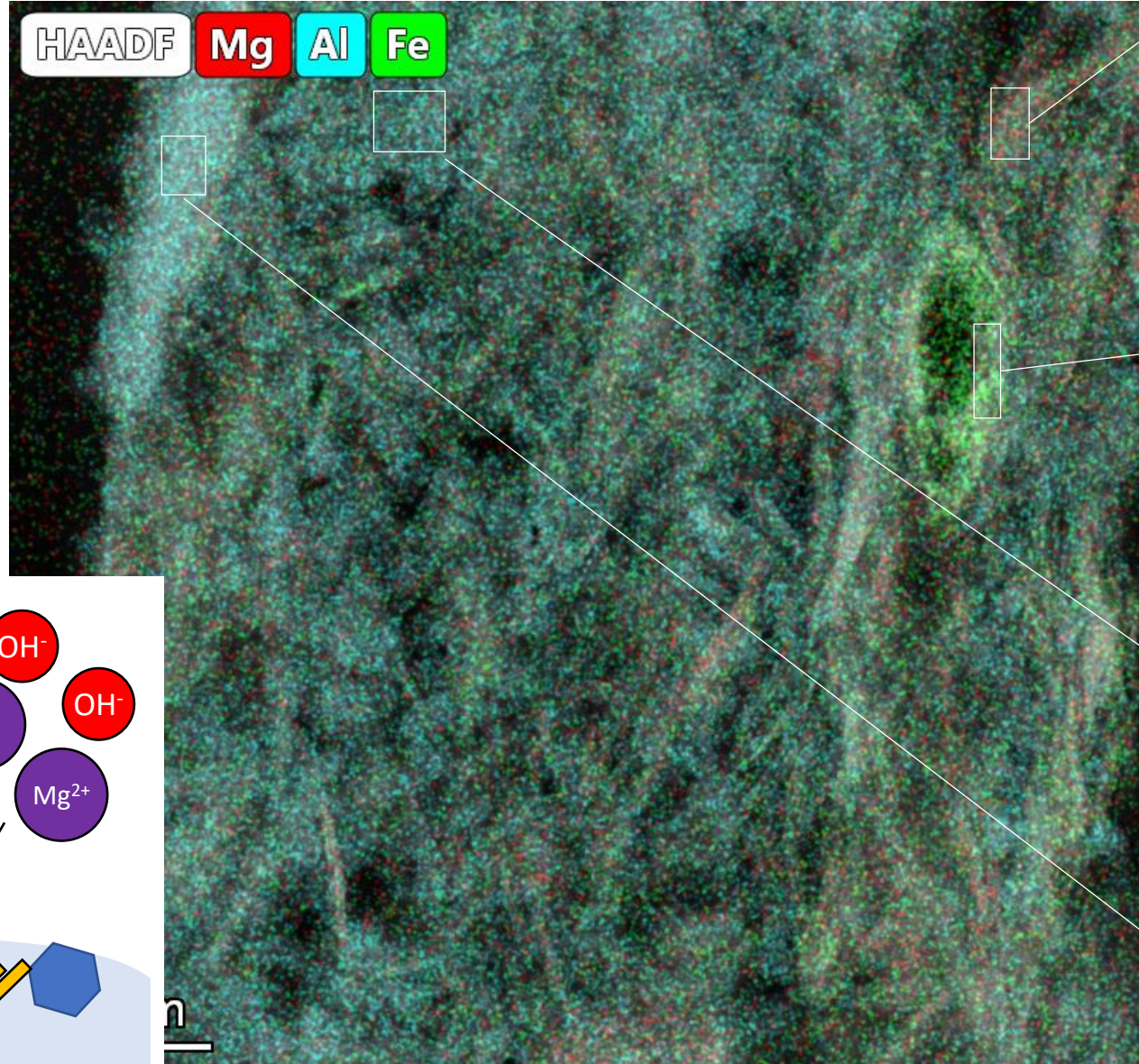
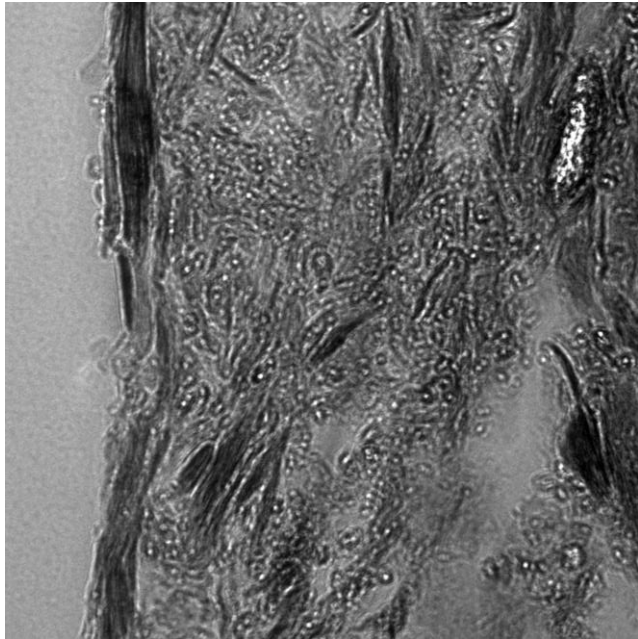
Platy crystals of dioctahedral smectite

## Similar to the "palagonite": altered products surrounding mafic glass



(Stroncik & Schmincke, 2001)

# Secondary minerals around glass surface

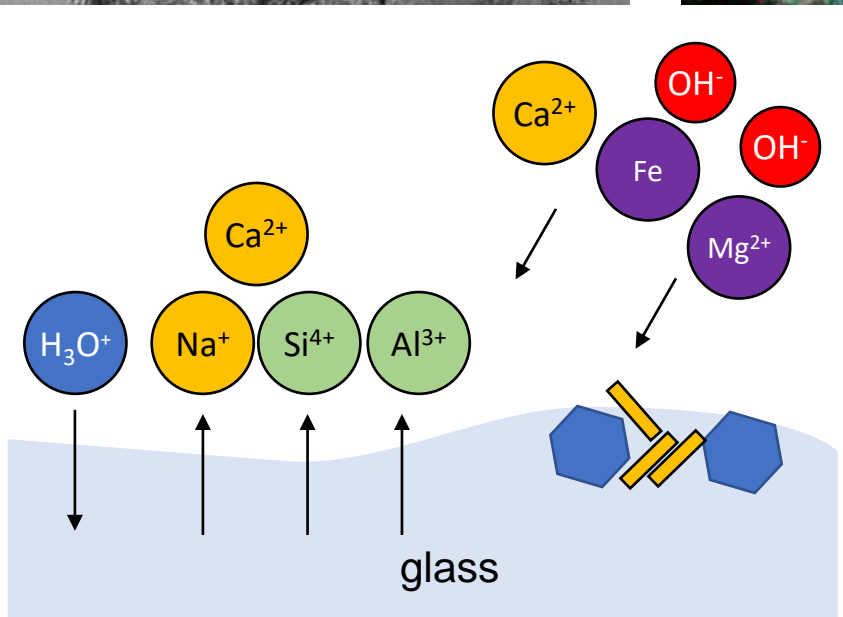


Saponite (Mg-rich)

Saponite (Fe-rich)

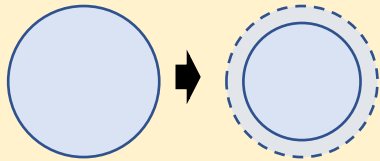
Spherical, hollow particles (Al-rich)

Montmorillonite (Al-rich, high-charge)

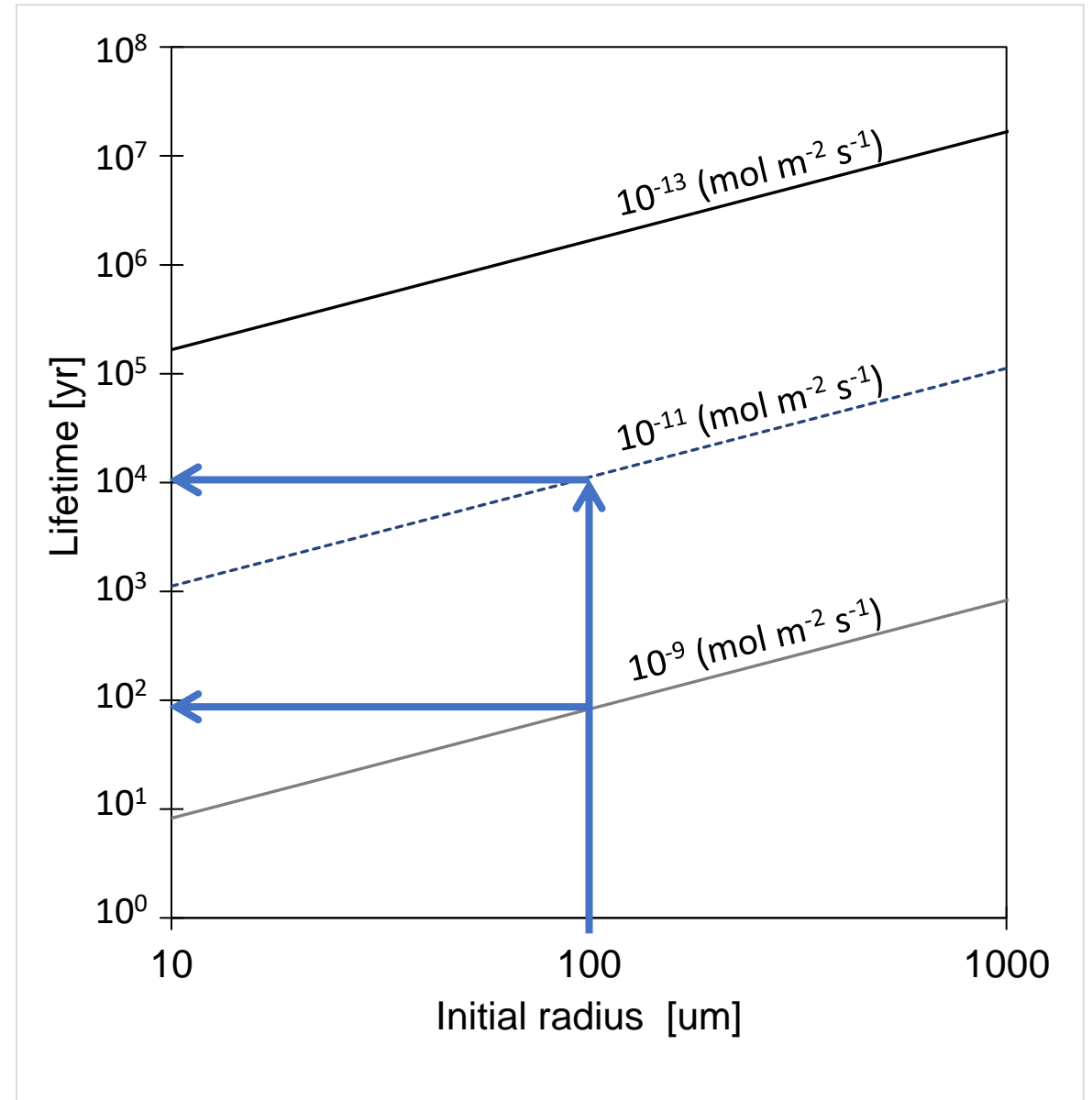


## Assumptions

- $\text{SiO}_2 = 78.29 \text{ wt}\%$   
     $\sim \text{Si}_{1.00} \text{Na}_{0.06} \text{Al}_{0.21} \text{K}_{0.05} \text{Ca}_{0.02} \text{O}_{2.39}$
- Glass density,  $\rho = 2.6 \text{ gcm}^{-3}$
- Molar volume,  $V_m = 29.3 \text{ cm}^3/\text{mol}$
- **Isometric dissolution of spherical grains**  
    (= Core shrink model)

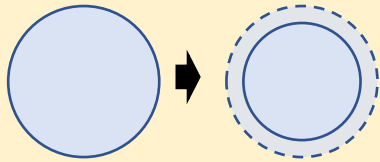


**Lifetime** = *radius* / ( $V_m \cdot r_{\text{geo}}$ ) (Lasaga, 1998)  
 $r_{\text{geo}}$  : the dissolution rate normalized by the geometric surface area.



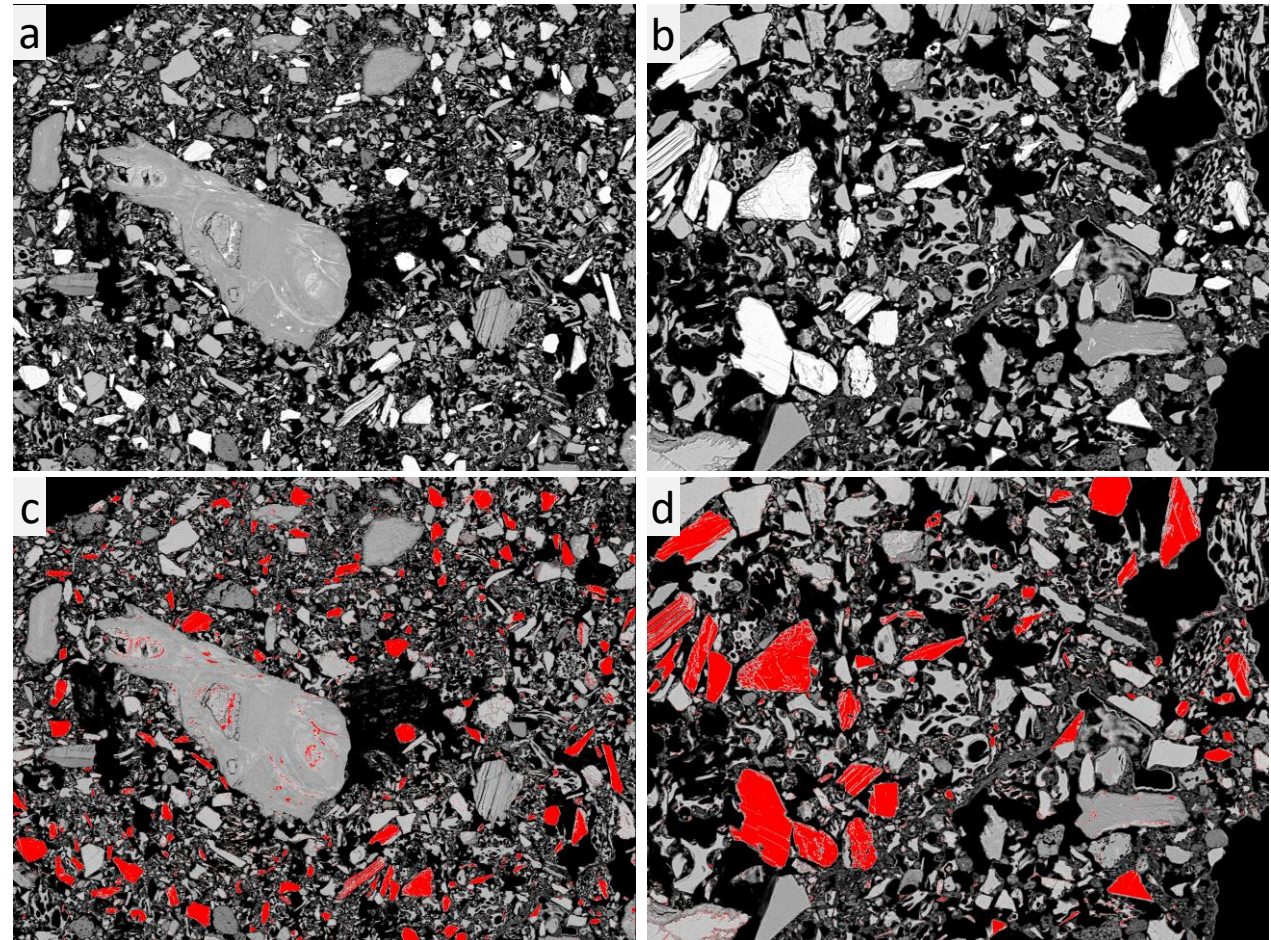
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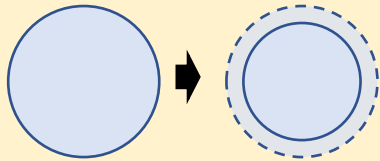
- **Lifetime of glass > depositional age**  
    from 3445 to 4516 yr
- **Initial grain size = ~ 40  $\mu\text{m}$  at maximum**



Grain size analysis using hornblende  
→ Radius ~37  $\mu\text{m}$  (max), ~ 9.7  $\mu\text{m}$  (median)

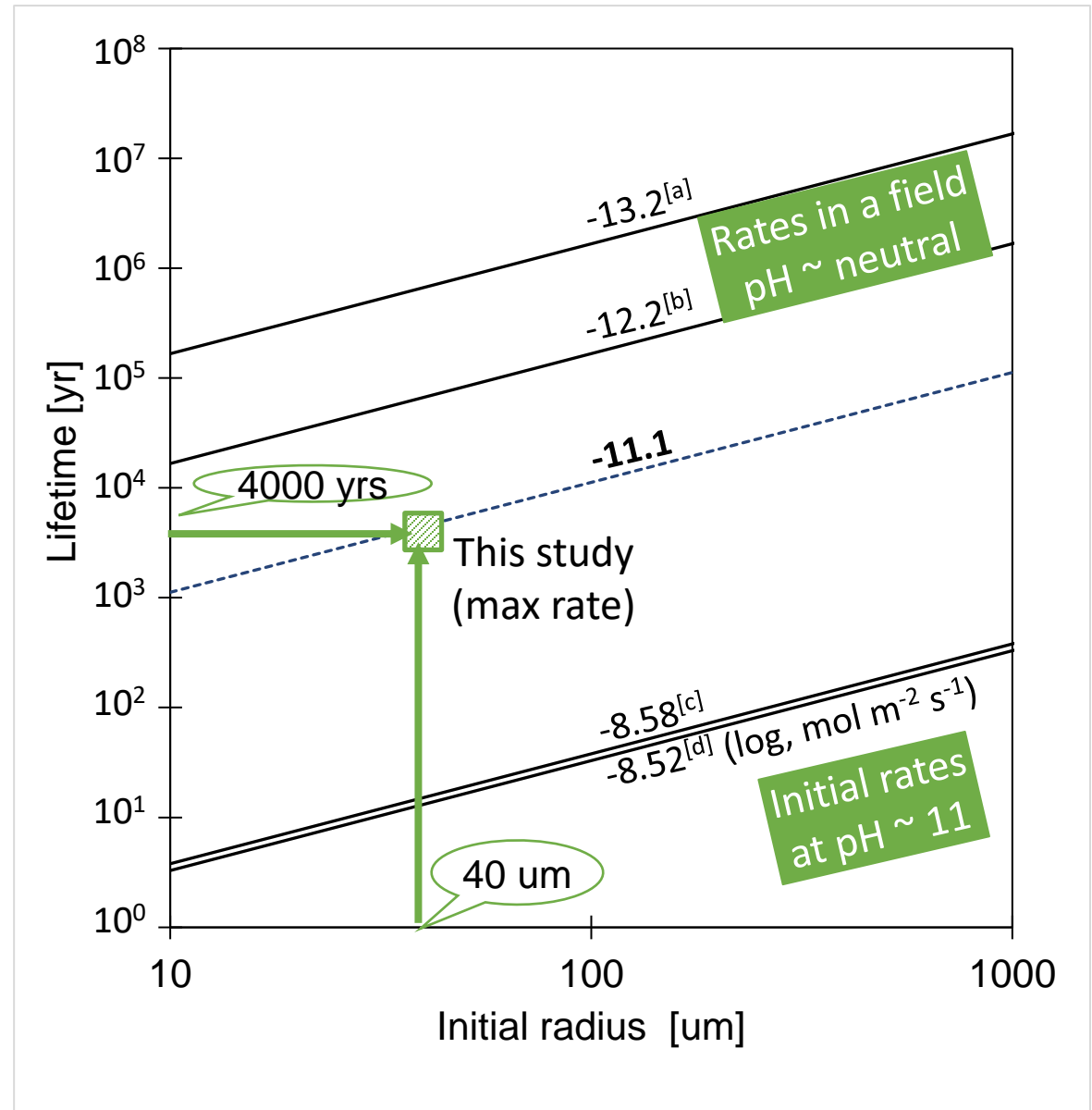
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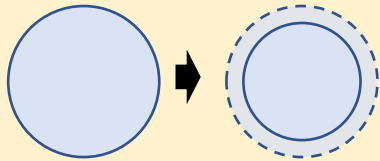
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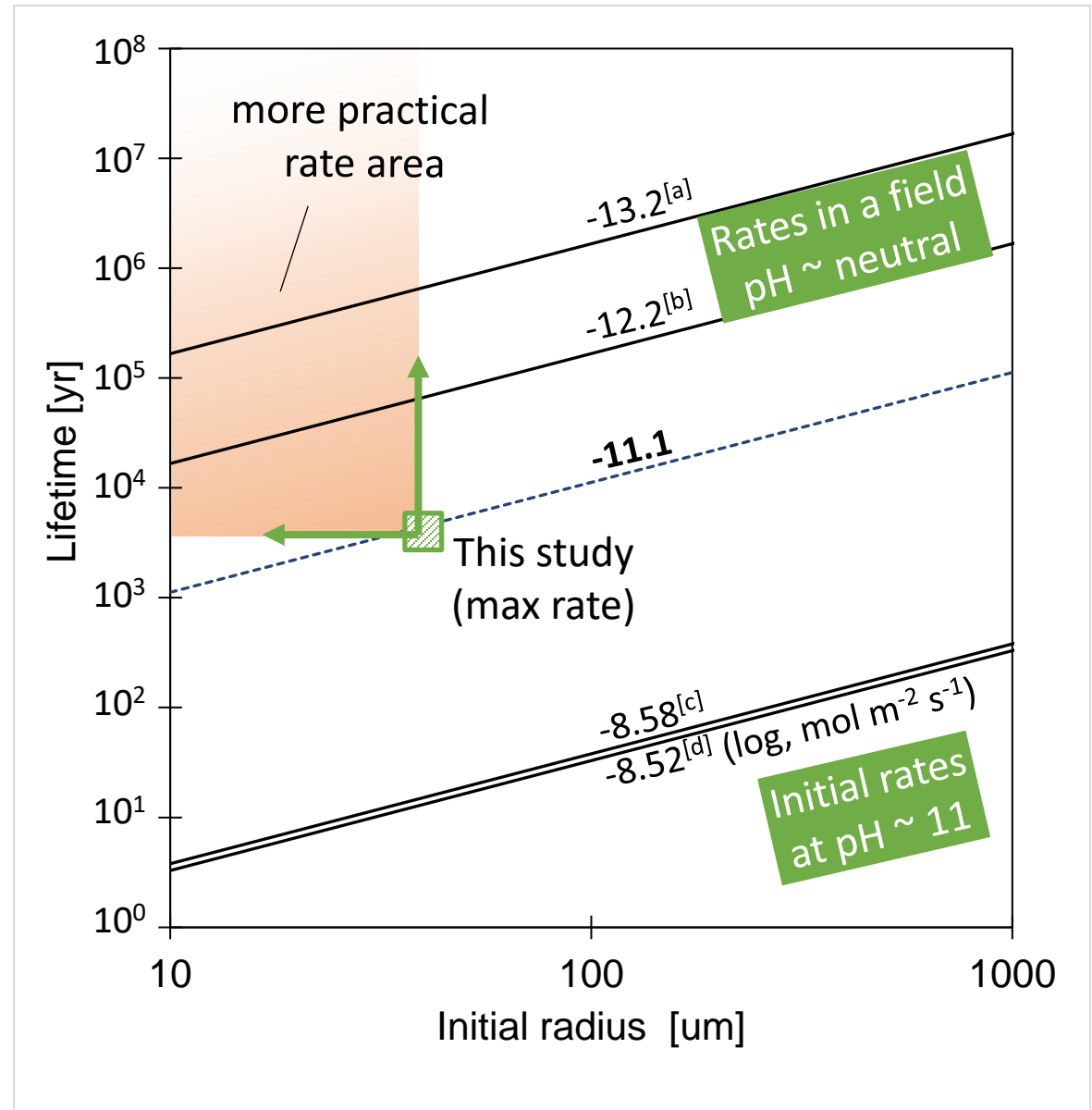
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# Summary

- 01** Narra site provides active alkaline alteration of clays and glass for about 2000 – 15000 yrs. Water chemistry of the alkaline seepage correspond to the low-alkali cement leachate.
- 02** Glass shards having bubble wall shape were found in the ultramafic sediment. Various smectite-like clays and amorphous hollow particles densely formed at the interface of the glass, indicating the supply of Mg and Fe surrounding sediments leads to formation of swelling clays rather than zeolites
- 03** Glass dissolution rate was slower 2.5 orders than initial rate in laboratory experiments. This slower rate may be resulted from secondary minerals' covering glass surface.

Thank to the participant of field survey at Narra

- Dr. Russell Alexander
- Prof. Caloy Arcilla
- Many graduates of our Lab.

And also you!



2015