Extremely high alkalinity due to dissolution of mica-group silicate in the pelagic sediments of the Ulleung Basin (East Sea): stable Si isotopes evidence and reactive transport modelling

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Marine Silicate Alteration and Carbon Cycle

Recent studies have shown that marine silicate alteration, is able to regulate amounts of carbonic acid (H_2CO_3) in porewater through lithogenic silicate (LSi) dissolution and clay formation:

$$\text{Lithogenic silicate} + H^+ \rightarrow H_4SiO_4 + \text{Cations}$$

$$CO_3^{2-} + 2H^+ \leftrightarrow HCO_3^- + H^+ \leftrightarrow H_2CO_3$$

$$\text{Neoformed clay} + H^+ \leftarrow H_4SiO_4 + \text{Cations}$$

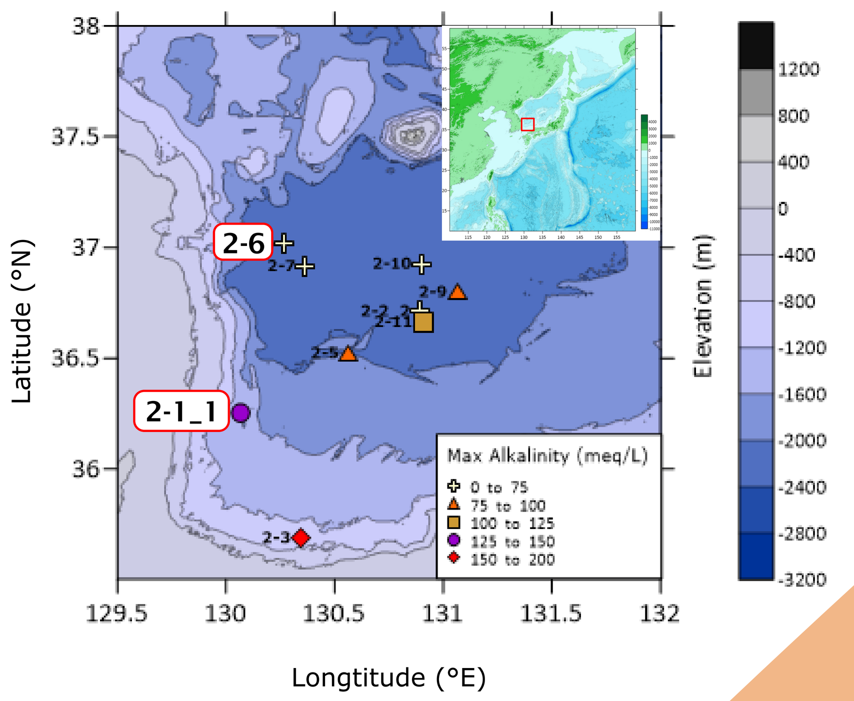
These processes are critical for global C and Si cycles since the amounts of H_2CO_3 affects partial pressure of CO_2 (pCO_2) in the ocean and potentially in the atmosphere. The rates of LSi dissolution and clay formation affect opal diagenesis (e.g., BSi dissolution and preservation in marine sediments). Though several studies have demonstrated the importance of marine silicate alteration, its current estimated rate remains highly uncertain (LSi dissolution: 5 – 20 T mol C yr⁻¹; Torres et al., 2020; clay formation: 0.5 – 10 T mol C yr⁻¹; Isson et al., 2020).

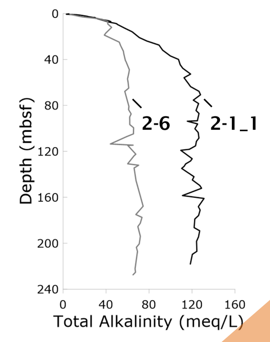
☆Research Question

What is the primary factor that controls the rates of LSi dissolution and clay formation?

(1)Reactant and product? (2) pH? (3) Something else?

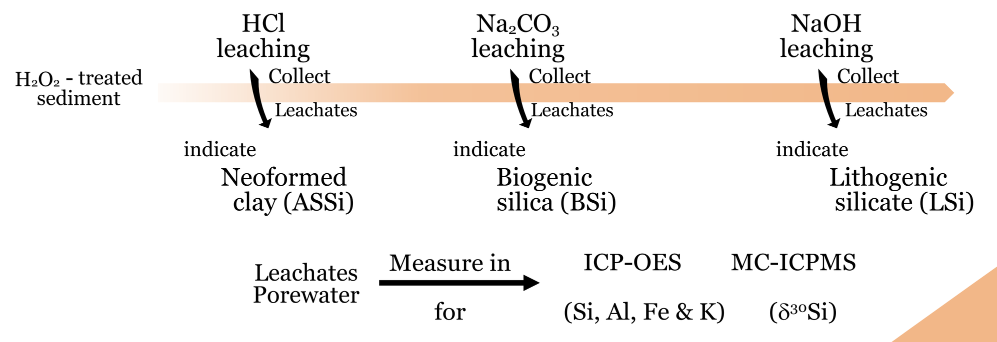
Study Area





Method

(A) Sequential leaching and Si isotope analysis



(B) Reactive transport simulation (Crunchflow)

Mineral: Mica, Smectite, Quartz, K-feldspar , Chlorite and SiO_2 (BSi)

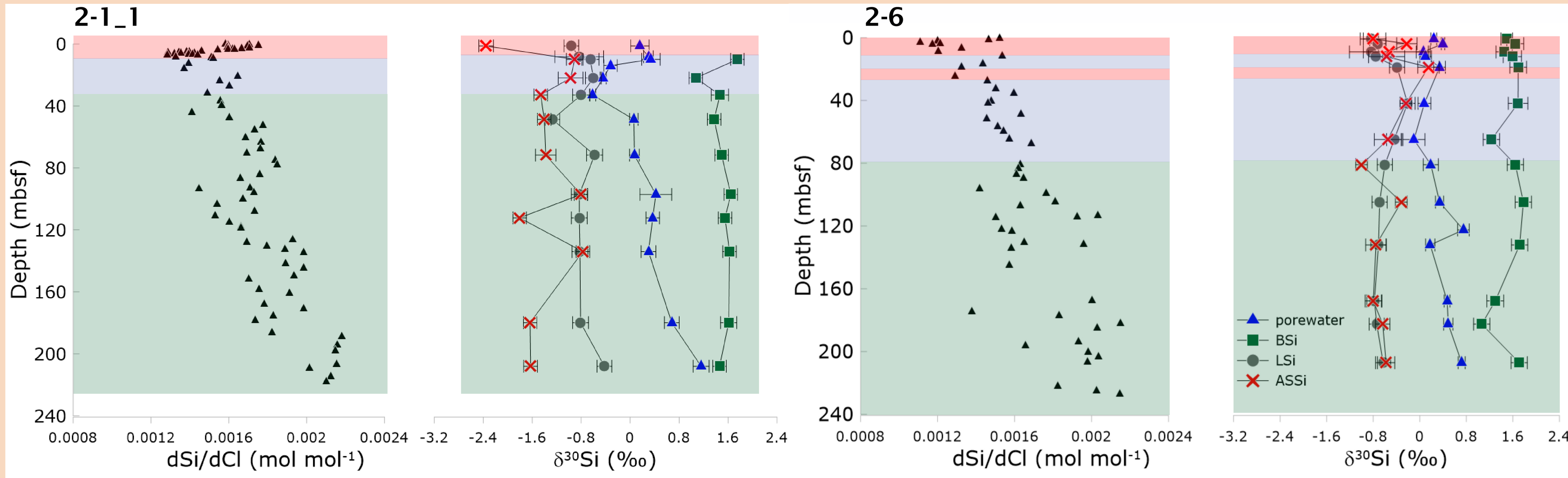
Microbial process:
Organic matter hydrolysis (OM hydrolysis)
Fermentation
Anaerobic oxidation of methane (AOM)
Methanogenesis
Sulfate reduction (SR)

Scenario
2-1_1
fit to measurement of 2-1_1
high OM hydrolysis
2-1_1 low
low OM hydrolysis

Interpretation

Zone	dSi	$\delta^{30}Si$ of porewater	Indicate
(red)	↓	↑	Clay formation
(blue)	↑	↓	LSi dissolution
(green)	↑	↑	BSi dissolution

Downcore marine silicate alteration



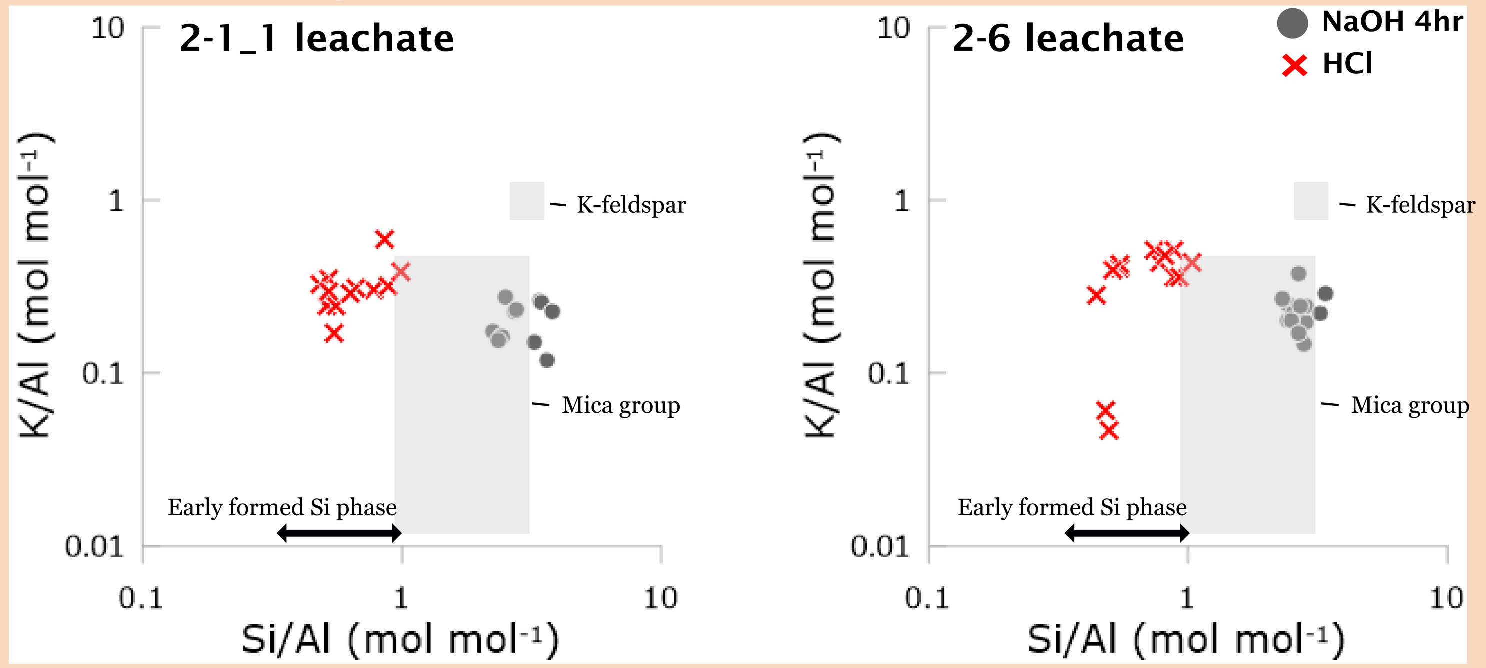
Mica-group silicate as the primary phase for lithogenic silicate dissolution

Simulation

LSi dissolution reactant:
phlogopite, vermiculite and albite

Clay formation product:
saponite and montmorillonite

Geochemistry



Take Home Message

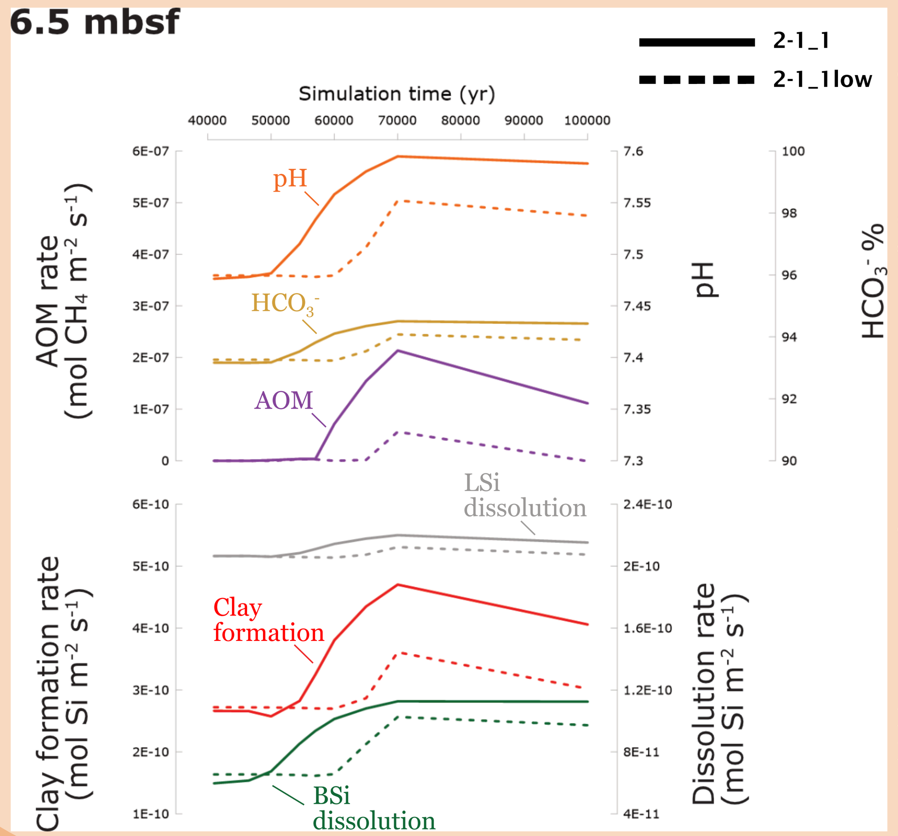
Primary factor affecting the rate of LSi dissolution and clay formation?

☆ **Microbial process**

Rate of marine silicate alteration controlled by microbial process

Surge in clay formation rate at shallow depth (zone)

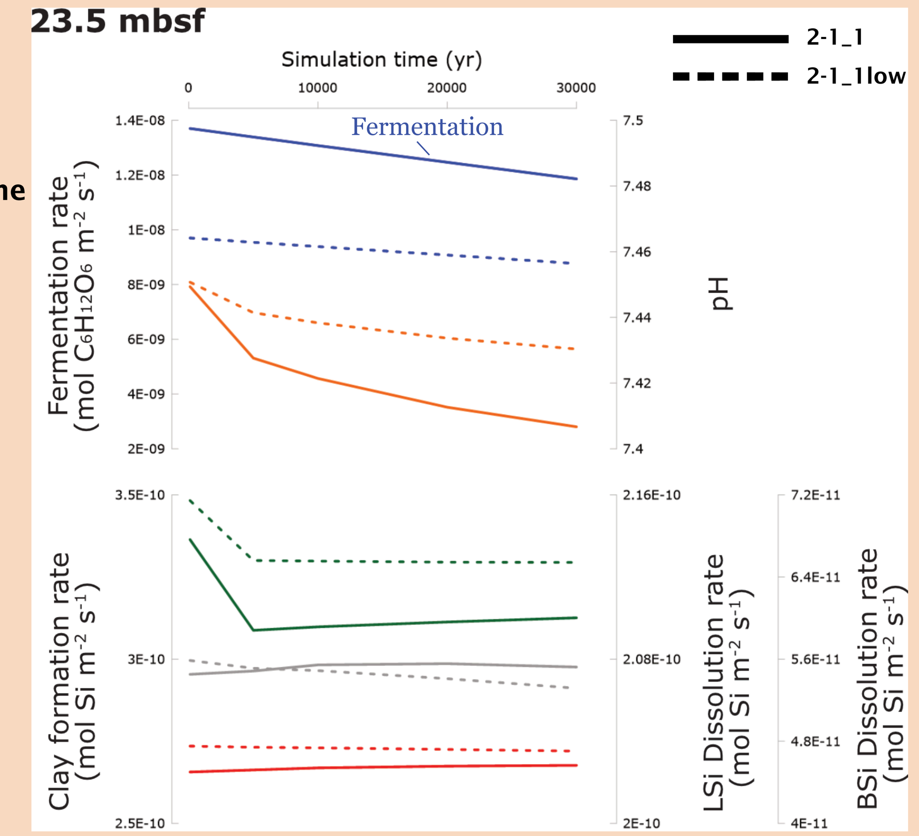
6.5 mbsf



Organic Matter hydrolysis
↓ control
Rate of Anaerobic oxidation of methane (AOM)+Sulfate Reduction (SR)
$CH_4 + SO_4^{2-} \rightarrow HS^- + HCO_3^- + H_2O$
↓ buffer
DIC and pH in porwater
$CO_3^{2-} + 2H^+ \leftrightarrow HCO_3^- + H^+ \leftrightarrow H_2CO_3$
↓ increase
Clay formation
$H_4SiO_4 + \text{Cations} \rightarrow \text{Neoformed clay} + H^+$
↓ increase
LSi and BSi dissolution
$\text{LSi} + H^+ \rightarrow H_4SiO_4 + \text{Cations}$
$\text{BSi} \rightarrow H_4SiO_4$

Alkalinity difference controlled by rates of clay formation (zone)

23.5 mbsf



Organic Matter hydrolysis
↓ control
Rate of Fermentation
$C_6H_{12}O_6 + 4H_2O \rightarrow 2CH_3COO^- + 4H_2 + 4H^+ + 2HCO_3^-$
↓ decrease/ increase
Clay formation and LSi dissolution
$H_4SiO_4 + \text{Cations} \rightarrow \text{Neoformed clay} + H^+$ (Major decrease)
$\text{LSi} + H^+ \rightarrow H_4SiO_4 + \text{Cations}$ (Minor promote)
↓ decrease
BSi dissolution
$\text{BSi} \rightarrow H_4SiO_4$

OM hydrolysis

Control → **Fermentation rate**; Control → **AOM + SR rate**

Fermentation rate: Decrease → **Smectite formation**; Increase → **Mica dissolution**

AOM + SR rate: Increase → **Smectite formation**

Smectite formation: Control → **Mica dissolution**; Control → **BSi dissolution**

Reference

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