Aqueous dissolution rate of nuclear waste glasses as a function of environmental parameters

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3rd Summer School on nuclear and industrial glasses for energy transition

3rd Sumglass 2023, in Nimes, September 25-29, 2023

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Micro-Channel as a New Tool to Investigate Glass Dissolution Kinetics

2nd SumGLASS 2013

Yaohiro INAGAKI
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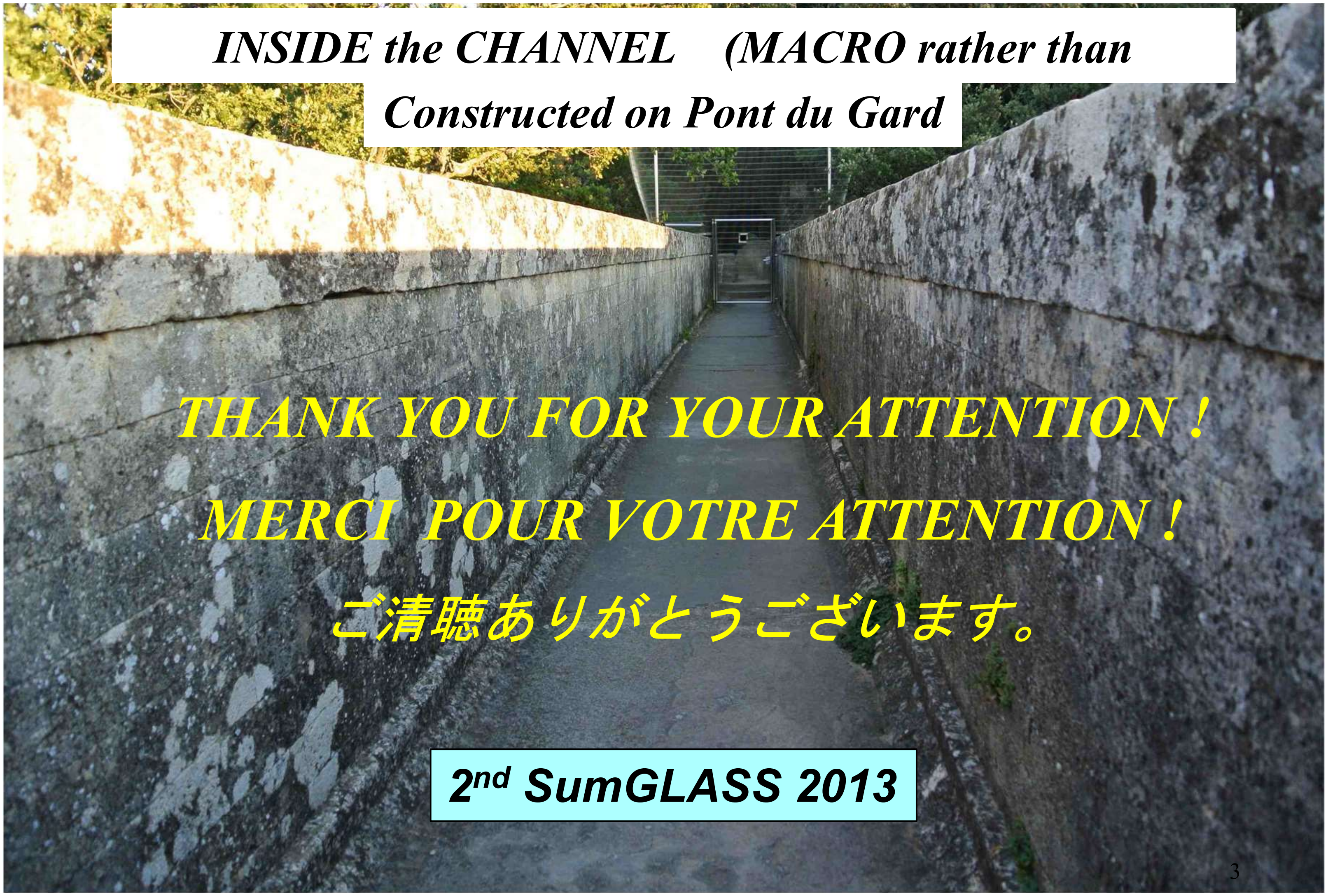
Fukuoka, Japan

2nd International Summer School on Nuclear Glass Wasteform
SumGLASS 2013, at the site of Pont du Gard, September 26, 2013


INSIDE the CHANNEL (MACRO rather than
Constructed on Pont du Gard
THANK YOU FOR YOUR ATTENTION !
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ご清聴ありがとうございます。
2nd SumGLASS 2013

Need for evaluation of glass dissolution kinetics

Assessment of HLW glass performance in long-term geological disposal with reliability requires;

(1) Reliable modeling based on scientific principles with sound understanding of reaction mechanism.

(2) Parameterization of mechanistic models to determine glass dissol. (alteration) rate as a function of environmental parameters.

Dissolution rate = function (C_i, pH, temp, time, ...)

We need
"Reliable evaluation of glass dissolution kinetics"

"Kinetic evaluation"= evaluation of reaction rate as a function of parameters based on reaction mechanism

How to evaluate glass dissolution kinetics ?

Experimental studies

Atomistic simulation studies

How to evaluate glass dissolution kinetics ?

Experimental studies

Atomistic simulation studies

Evaluation of the long-term dissolution kinetics

Modeling the long-term dissolution
for the geological disposal with reliability

How to evaluate glass dissolution kinetics ?

Experimental studies

<u>Dissolution tests</u>
- *Measure. of dissolution rate*
- *Analysis of alteration layers*

Atomistic simulation studies

Evaluation of the long-term dissolution kinetics

Modeling the long-term dissolution
for the geological disposal with reliability

How to evaluate glass dissolution kinetics ?

Experimental studies

Atomistic simulation studies

Dissolution tests

- Measure. of dissolution rate

- Analysis of alteration layers

Dissolution rate changes by environmental conditions such as solution composition, pH, temp, time, etc.

Evaluation of the long-term dissolution kinetics

Modeling the long-term dissolution for the geological disposal with reliability

How to evaluate glass dissolution kinetics ?

Experimental studies

Atomistic simulation studies

<u>Dissolution tests</u>
- *Measure. of dissolution rate*
- *Analysis of alteration layers*

Dissolution rate changes by environmental conditions such as solution composition, pH, temp, time, etc.

Needs for precise, consistent and systematic data as a function of environmental parameters

Evaluation of the long-term dissolution kinetics

Modeling the long-term dissolution for the geological disposal with reliability

Need for precise measurement of dissolution rate

Evaluation of Glass Dissolution Kinetics

Dissolution rate = function (C_i, pH, temp, time,….)

- ***Sound understanding of reaction mechanism***
- ***Parameterization of mechanistic models***

Only a few data on glass dissolution rate available to the kinetic evaluation

Need for much more experimental data on glass dissolution rate with mechanism measured precisely, consistently, systematically as a function of environmental parameters

Test methods for measuring dissolution rate

<u>Standard Test Methods for Durability of HLW glass</u>

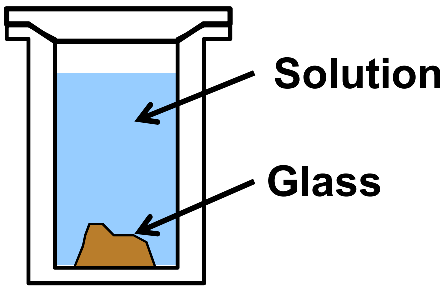
- ***MCC-1: Static leach test***
- ***MCC-2: Static, High-Temperature leach test***
- ***MCC-3: Agitated Powder leach test***
- ***MCC-4: Low-flow-rate leach test***
- ***MCC-5: Soxhlet leach test***
- ***PCT: Product consistency test***
- ***SPFT: Single-Pass Flow-Through test***

. . . . VHT, ASTM, ISO, etc.

Unsuitable for measurement of dissolution rate as a function of various environmental parameters

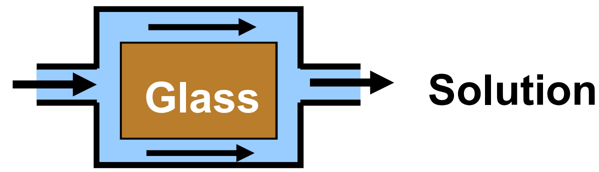
Types of test methods for measuring dissolution rate

Static Test



- Simple apparatus & operation
- High S/V ratio (powdered glass)
- Precise solution measurement
- Solution conditions ***Uncontrolled*** (pH, composition, etc)

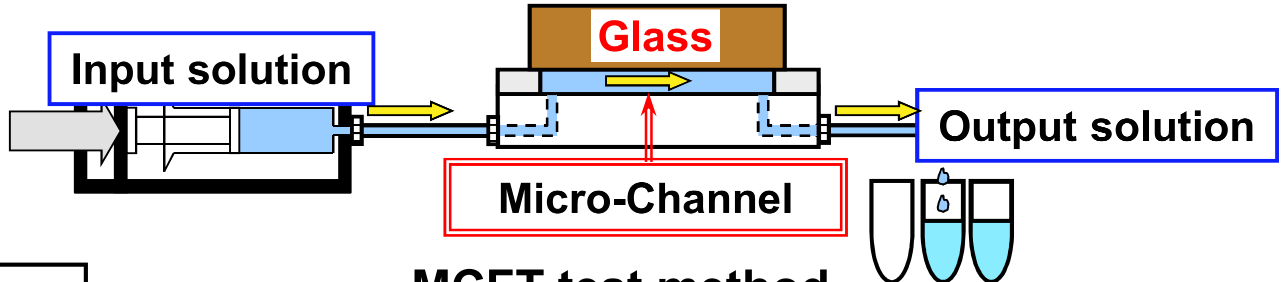
Flow-Through Test



- ***Controlled*** const. solution condition
- Intricate apparatus & operation
- Usually low S/V ratio
- Large experimental errors

"Flow-through test" is suitable for measurement of dissolution rate as a function of environmental parameters, however, we should improve / develop test method for precise measurement.

Features of Micro-Channel Flow-Through test method



MCFT test method

Features

- ***Flow-through method provides,***
  - *well-controlled constant solution conditions (pH, C_i, etc.).*
- ***Use of coupon shaped glass specimen provides,***
  - *precise determination of reaction surface area, flow rate,*
  - *direct / totally quantitative analyses of reacted glass surface.*
- ***Use of micro-channel reactor provides,***
  - *high S/V ratio leading to precise measurement of solution by ICP-MS.*

Precise measurement of glass dissolution rate as a function of environmental parameters

Environmental parameters under disposal conditions

Modeling HLW glass performance in geological disposal requires

"Evaluation of dissolution kinetics under disposal conditions".

Major environmental parameters to be considered

- ***Temp : a fundamental parameter of kinetics, varies with the site & period.***
- ***pH : affects glass dissolution rate with mechanism, and varies with disposal site and period.***
- ***Si : a major glass constituent, major element dissolved in ground water affecting glass dissolution rate, and the concentration varies with the site and period.***

 # Reaction time: Form & growth of surface alteration layers

"Reliable & precise data of glass dissolution as a function of Temp, pH and Si concentration.

Initial dissolution rate, r_0, as a function of pH & temp

Definition of glass dissolution rate

Normalized dissolution rate of element *i*

$$NR_i \ [\mathrm{g/m^2/d}] \equiv \frac{dNL_i}{dt} = \frac{C_i}{\Delta t} \frac{1}{f_i} \frac{V}{S}$$

C_i : Conc. of element ***i*** in output solution at each sampling

Δt : Each sampling period

f_i : Mass fraction of element ***i*** in original glass

V : Output solution volume at each sampling

S : Geometric glass surface area in contact with solution

Glass dissolution rate, *r*

$$r \equiv NR_{Si} \ [\mathrm{g/m^2/d}]$$

Initial dissolution rate, r_0, in 1st-order dissolution rate law

$$r = r_0 (1 - Q/K) + r_{residual} = r_0 (1 - C_{Si}/C_{sat}) + r_{residual}$$

$$r_0 \equiv NR_{Si} \text{ at } C_{Si} \simeq 0$$

Glass specimens used for MCFT test

***ISG**: International Simple Glass*

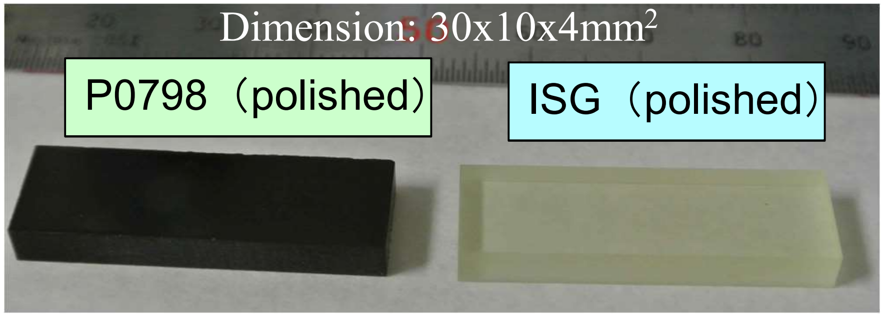
ISG	SiO_2	B_2O_3	Na_2O	Al_2O_3	CaO	ZrO_2	Others
wt%	56.2	17.3	12.2	6.1	5.0	3.3	-

***P0798**: Japanese reference glass*

*P0798**	SiO_2	B_2O_3	Na_2O	Al_2O_3	CaO	ZrO_2	Others**
wt%	46.6	14.2	10.0	5.0	3.0	1.5	19.7

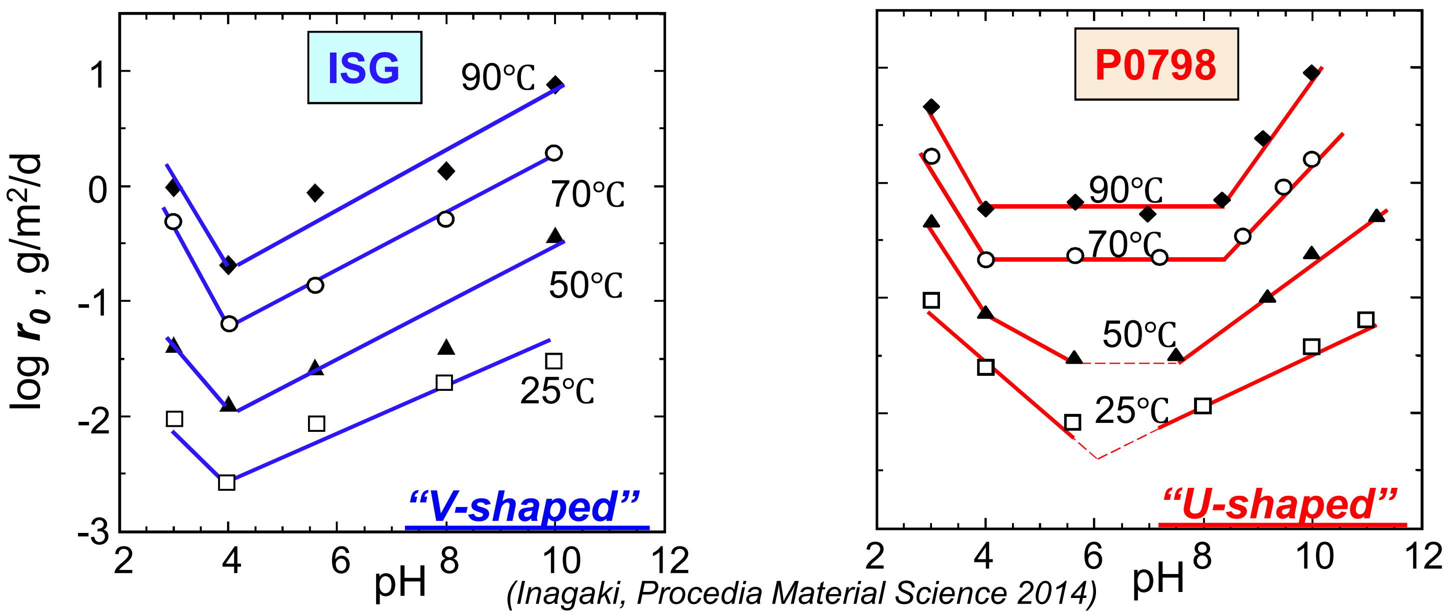
*P0798 has a composition ***close to French SON68***

**Others: Li_2O, ZnO, Fe_2O_3, MoO_3, CeO_2, Nd_2O_3, Cs_2O, etc., total 28 elements



Test results: Initial dissolution rate, r_0 (pH, temp)

Initial dissolution rate, r_0, as a function of pH and temp by MCFT
ISG vs P0798

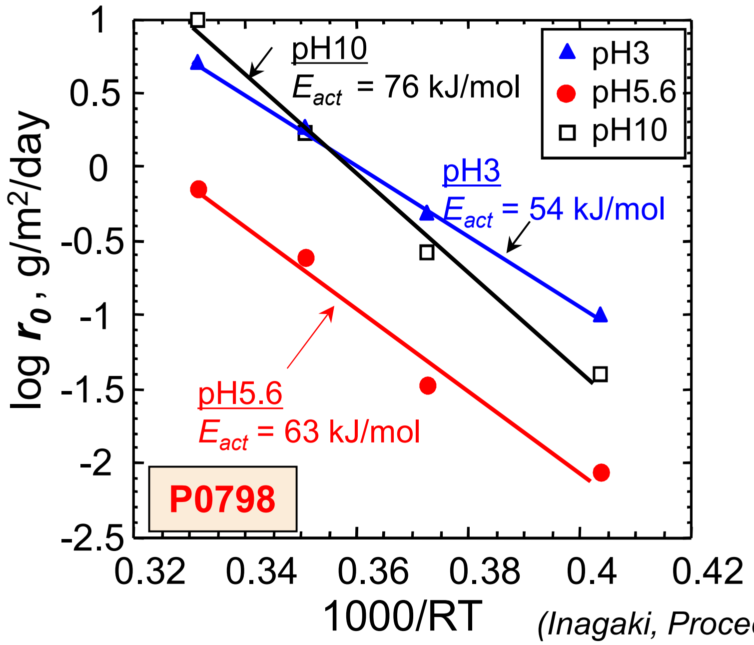


(Inagaki, Procedia Material Science 2014)

ISG ⇨ "V-shaped" pH dependence at the bottom pH4
P0798 ⇨ "U-shaped" pH dependence at the bottom pH6

Test results: Initial dissolution rate, r_0 (pH, temp)

Activation energy E_{act} of r_0 as a function of pH by MCFT
ISG vs P0798



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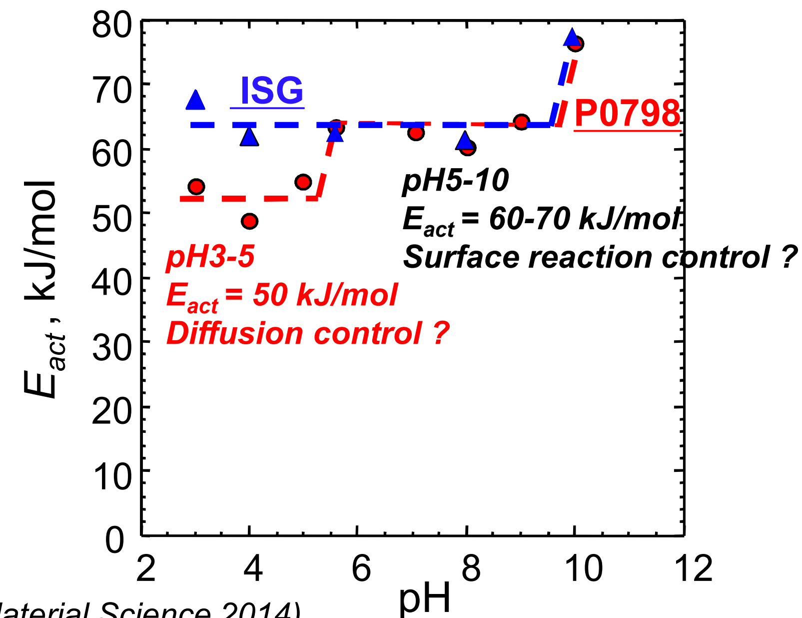
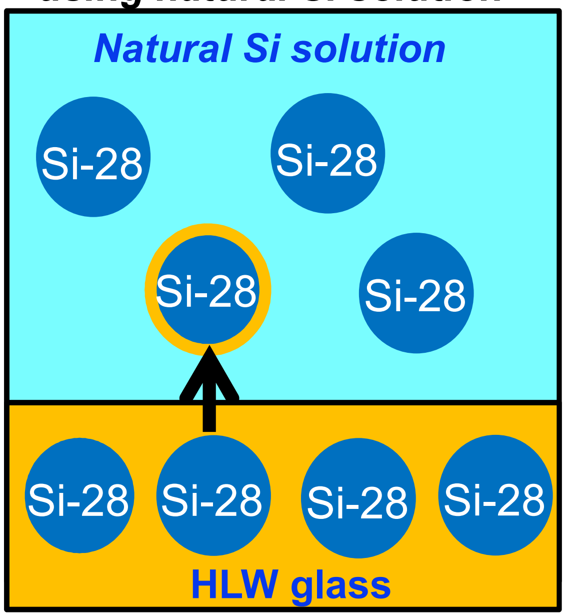


A certain difference in E_{act} between P0798 and ISG at acidic pH
The dissolution mechanism changes with pH and glass composition

Glass dissolution rate as a function of C_{Si}: Test method

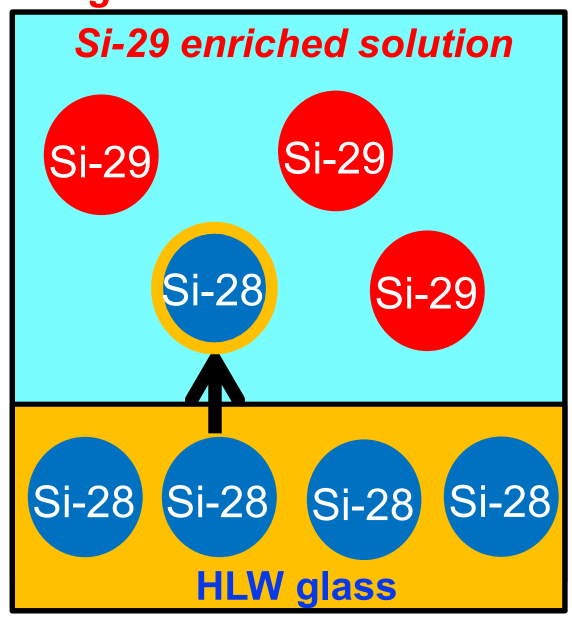
How to measure ? → MCFT test by using Si isotopes

Conventional test
using natural Si solution



Impossible to distinguish Si dissolved from glass into solution

Present test
using Si-29 enriched solution



Possible to distinguish Si-28 dissolved from glass into solution

Test method: Isotopic ratio of Si used for the test

Isotopic ratio of natural Si and Si-29 enriched SiO_2 [at %]

	Si-28	**Si-29**	**Si-30**
Natural Si	**92.22**	4.69	3.09
Si-29 enriched SiO_2 (Isoflex USA)	0.14	**99.21**	0.65

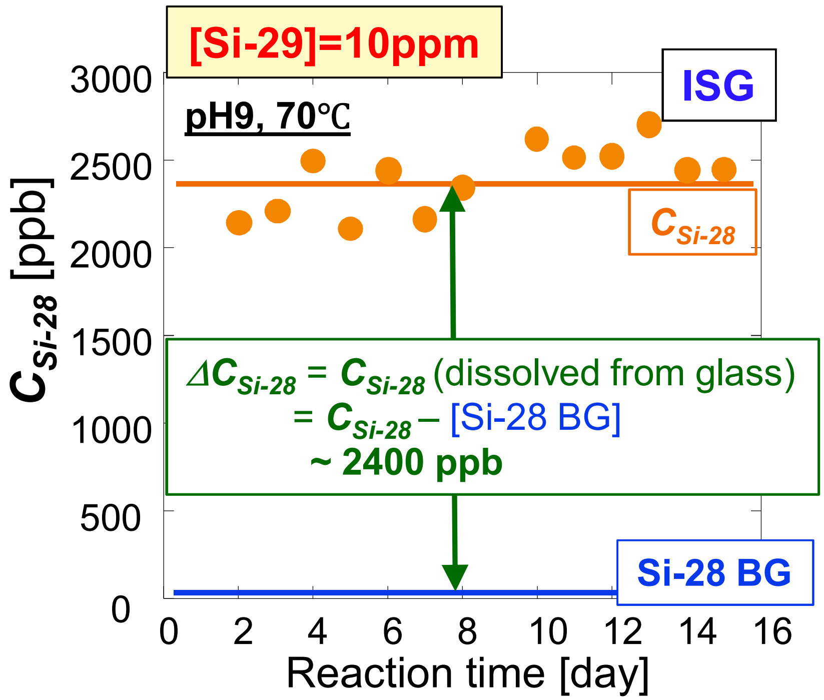
Isotopic ratio of Si for glass and test solution [at %]

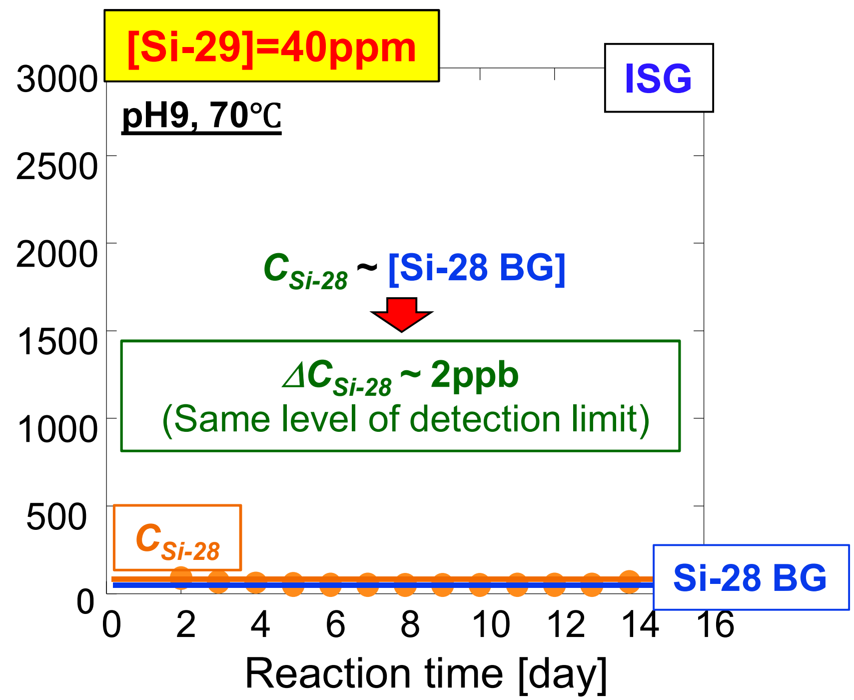
	Si-28	**Si-29**
Glass (P0798, ISG) （**Natural Si**）	**92.22**	4.69
Test solution containing Si (Si-29 enriched)	0.14	**99.21**

Concentration of Si-28 dissolved from glass into solution can be measured to determine the glass dissolution rate.

Test results: Glass dissolution rate, r (C_{Si})

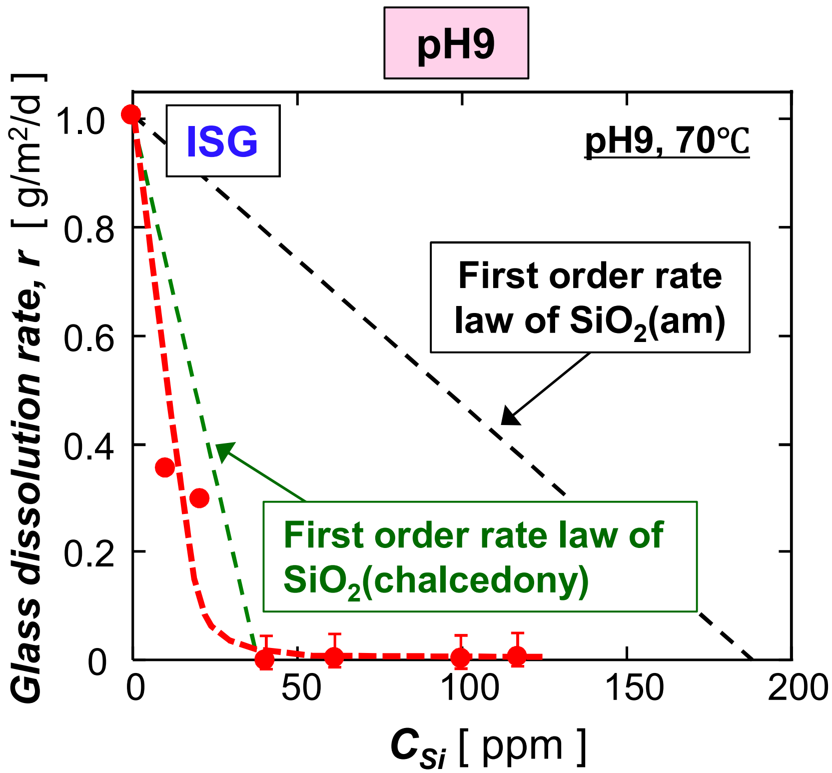
***Si-28* concentration in output solution measured for determination of *glass dissolution rate* at pH9**





(Inagaki, GOMD 2022)

Test results: Glass dissolution rate, r (C_{Si}) at pH9



(Inagaki, GOMD 2022)

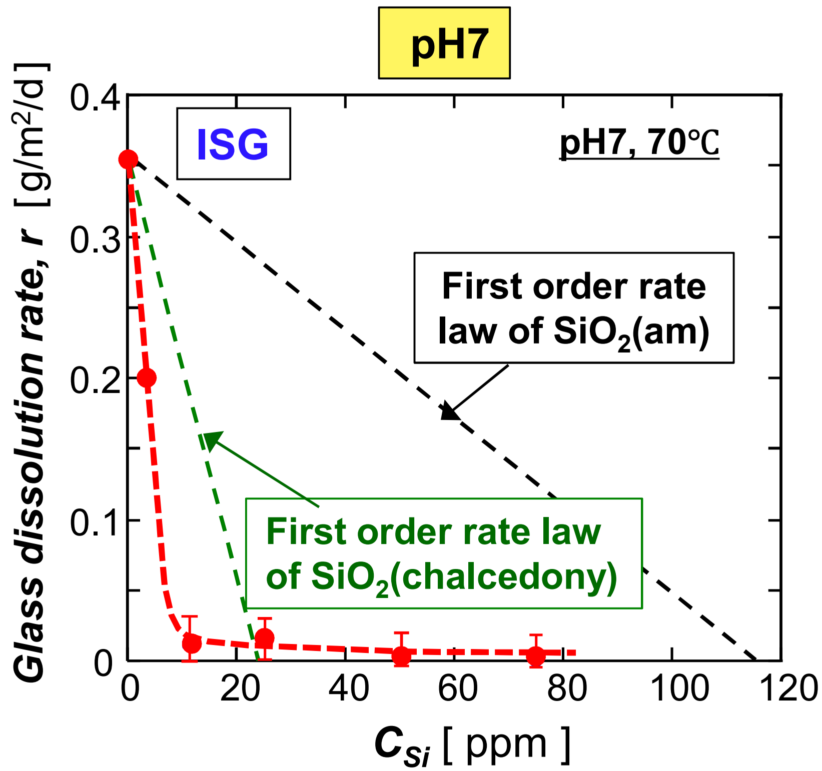
Glass dissolution rate at pH9:

- ***Decreases drastically with C_{Si}.***
- ***Far from the first order rate law of SiO_2(am).***
- ***Near that of SiO_2 (chalcedony).***
- ***But the shape differs from the first order rate law.***

⇓ ***suggests***

- ***Not controlled by a simple surface reaction of SiO_2,***
- ***Formation of surface alteration layer can affect the dissolution rate even in the early stage of dissolution.***

Test results: Glass dissolution rate, r (C_{Si}) at pH7



(Inagaki, GOMD 2022)

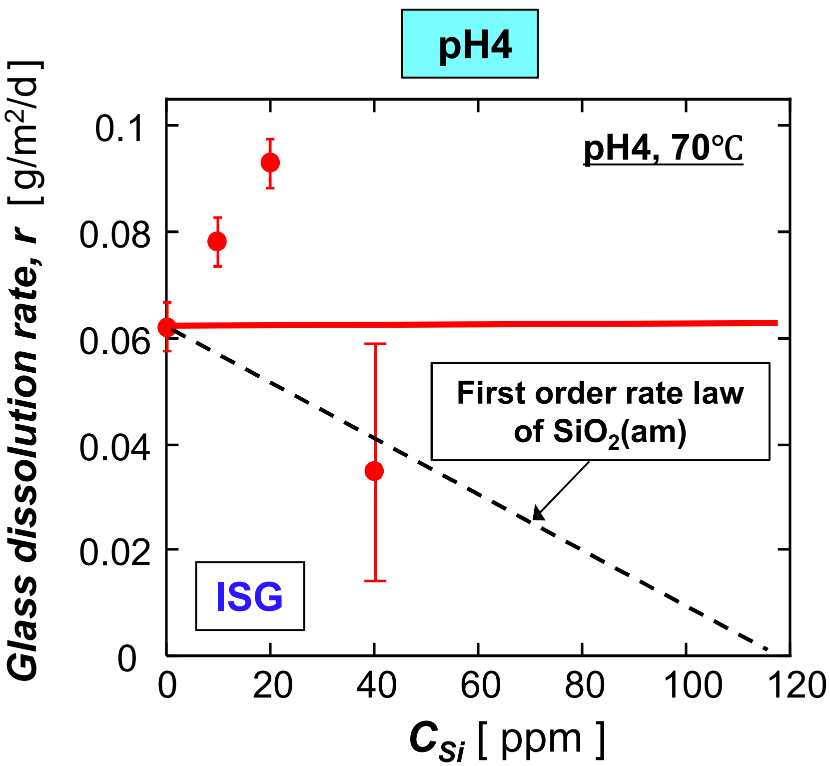
Glass dissolution rate at pH7:

- *Similar behavior as at pH9.*
- *Decreases drastically with C_{Si}.*
- *Far from the first order rate law of SiO_2(am).*
- *The shape differs from the first order rate law.*

suggests

- *Not controlled by a simple surface reaction,*
- *Formation of surface alteration layer can affect the dissolution rate even in the early stage of dissolution.*

Test results: Glass dissolution rate, r (C_{Si}) at pH4



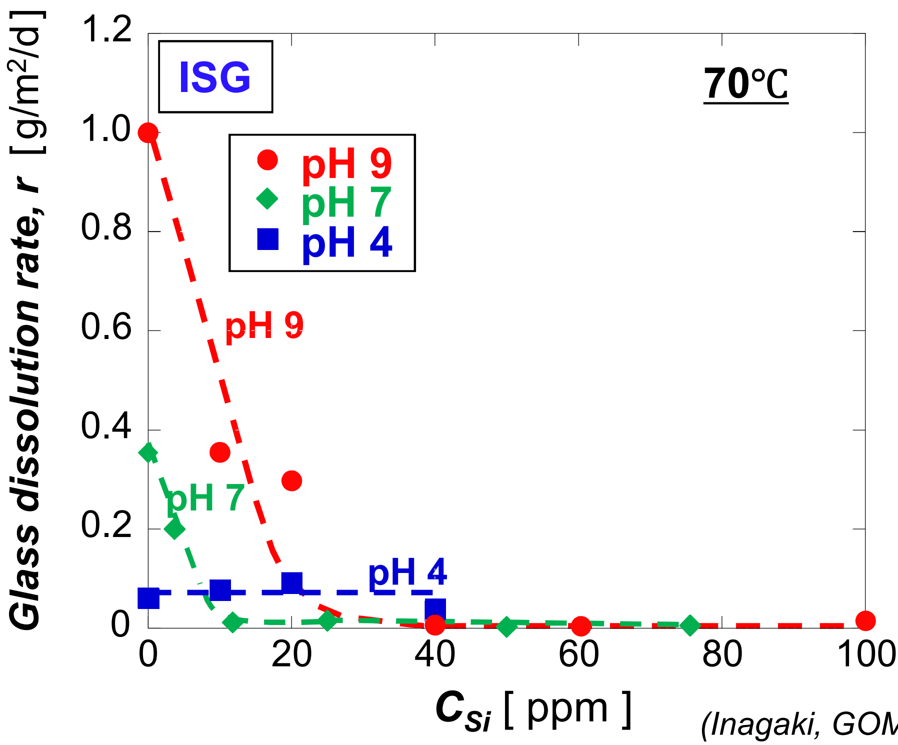
(Inagaki, GOMD 2022)

Glass dissolution rate at pH4:

- ***Quite different behavior from that at pH7,9.***
- ***Slightly increases with C_{Si},***
- ***Or not affected by C_{Si}.***

- ***Controlled by a different mechanism from that at pH7,9.***
- ***Different surface alteration layer may form at pH4,***
- ***causing the different dissolution mechanism.***

Test results: Glass dissolution rate, r (C_{Si} , pH)



(Inagaki, GOMD 2022)

Effects of C_{Si}

Glass dissolution rate, r :

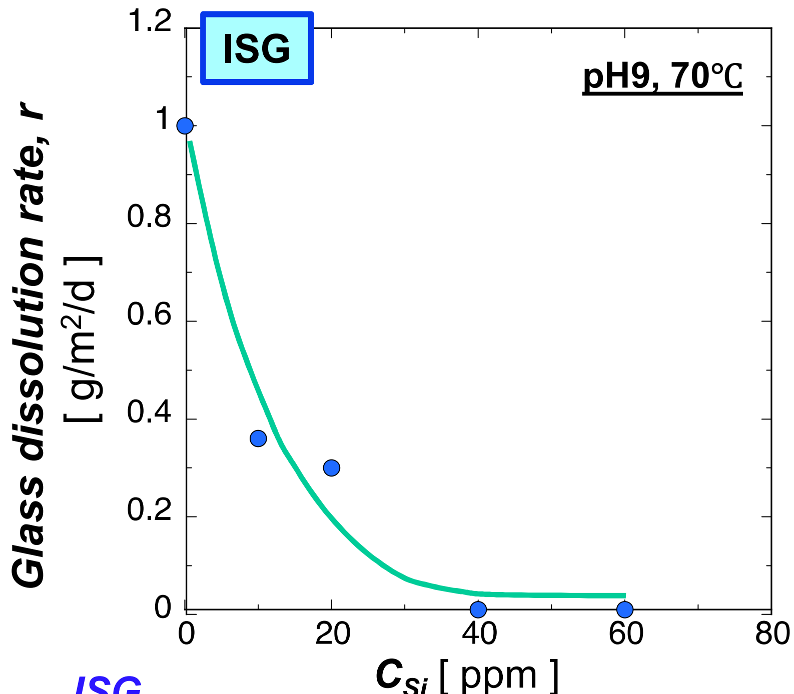
at pH9, pH7

- Decreases drastically with C_{Si} .

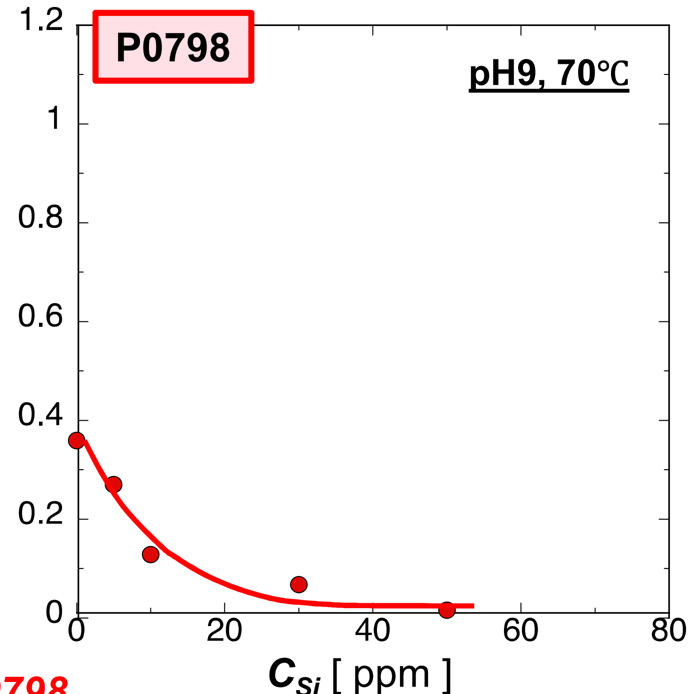
at pH4

- Not affected by C_{Si} .

Test results: Effect of glass type on r (C_{Si}) at pH9



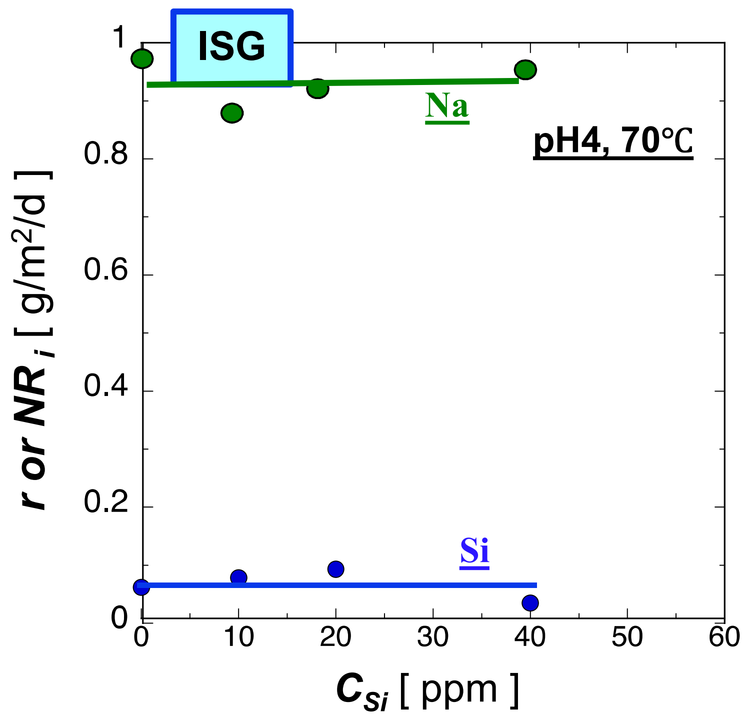
ISG,
non-linear relation between r vs C_{Si}



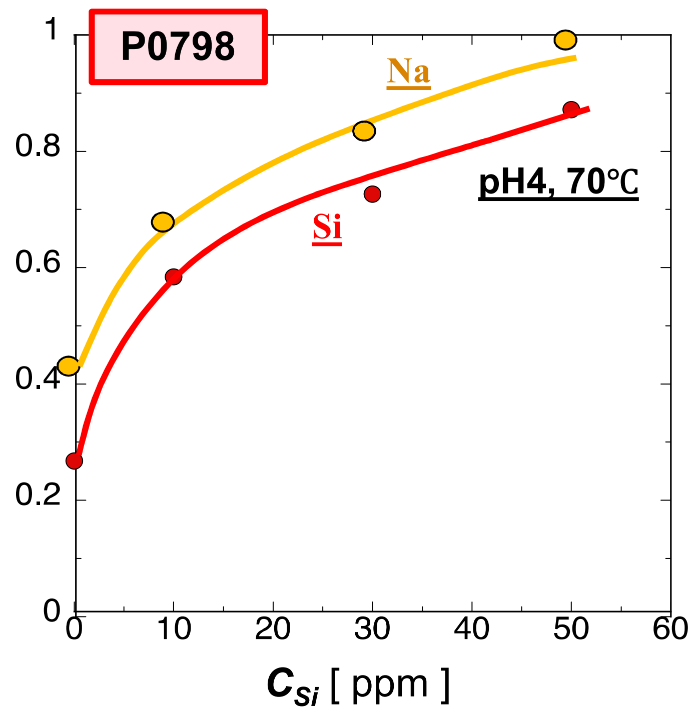
P0798,
non-linear relation between r vs C_{Si}

The similar rate controlling mechanism at pH9, 70°C between ISG and P0798

Test results: Effect of glass type on r (C_{Si}) at pH4



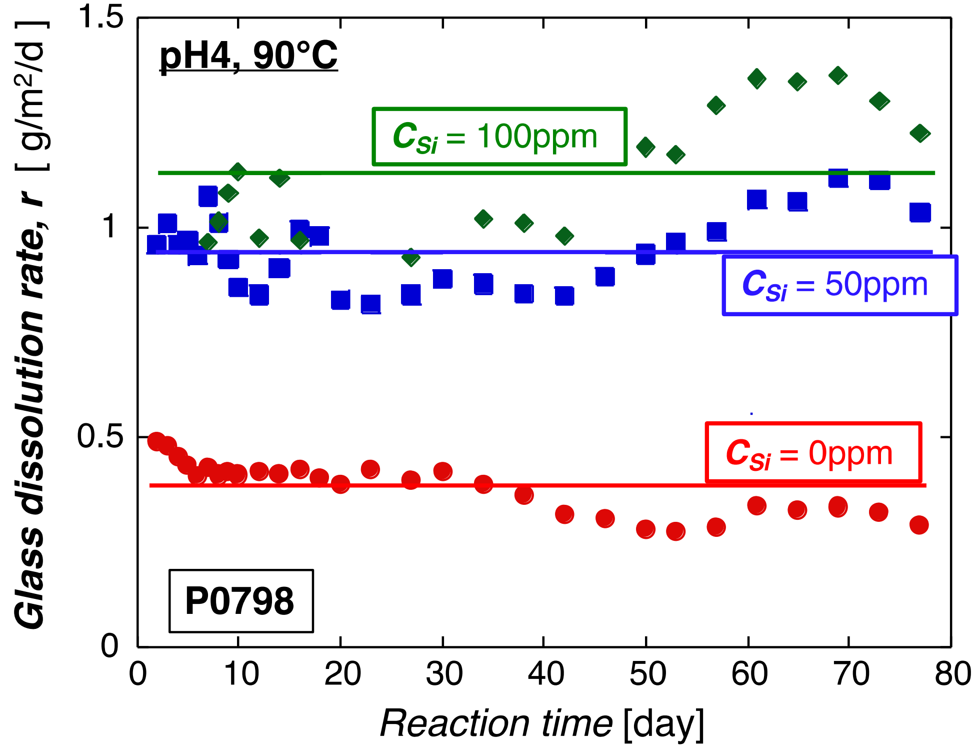
ISG: No C_{Si} dependency



P0798: Increases slightly with C_{Si}

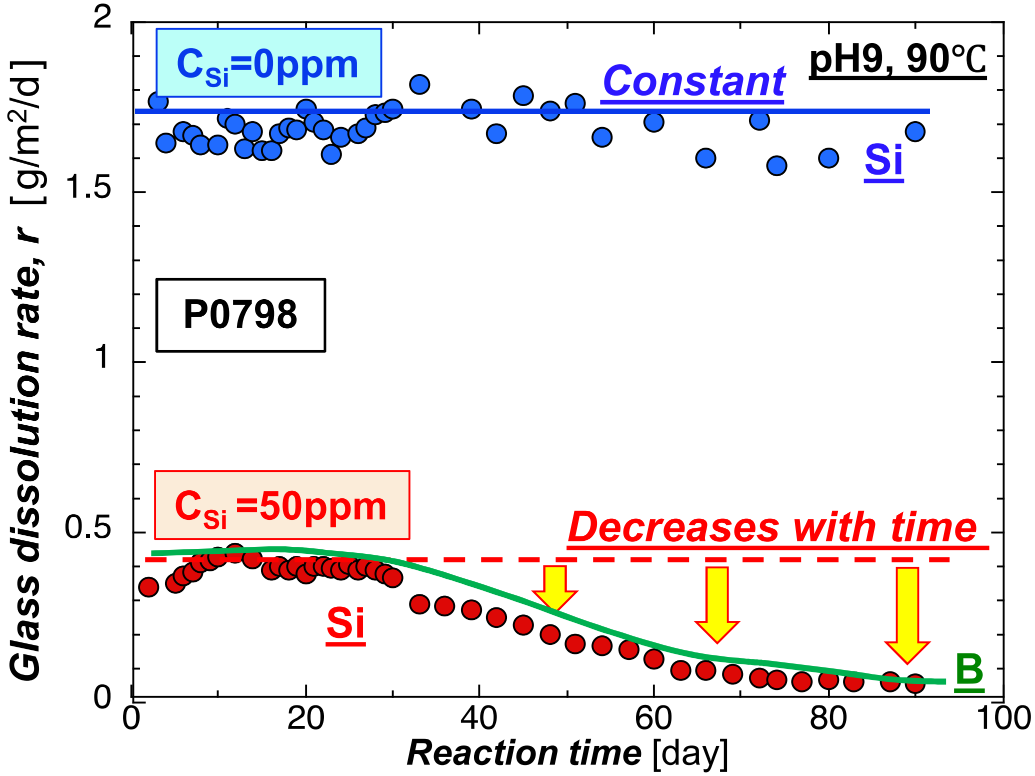
- The glass dissolution rate for P0798 increases with C_{Si} at pH4 ?
- The data is correct ?

Re-test results: Dissolution rate of P0798, r (C_{Si}) at pH4



At pH4,
- Glass dissolution rate for P0798 increases with the Si concentration.
- How is the mechanism to explain the increase in r with C_{Si} ?

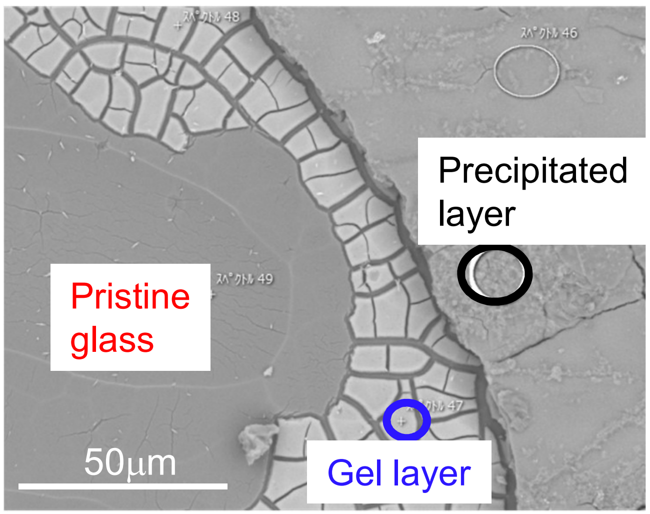
Test results: Effect of C_{Si} on r (t) at pH9, 90°C



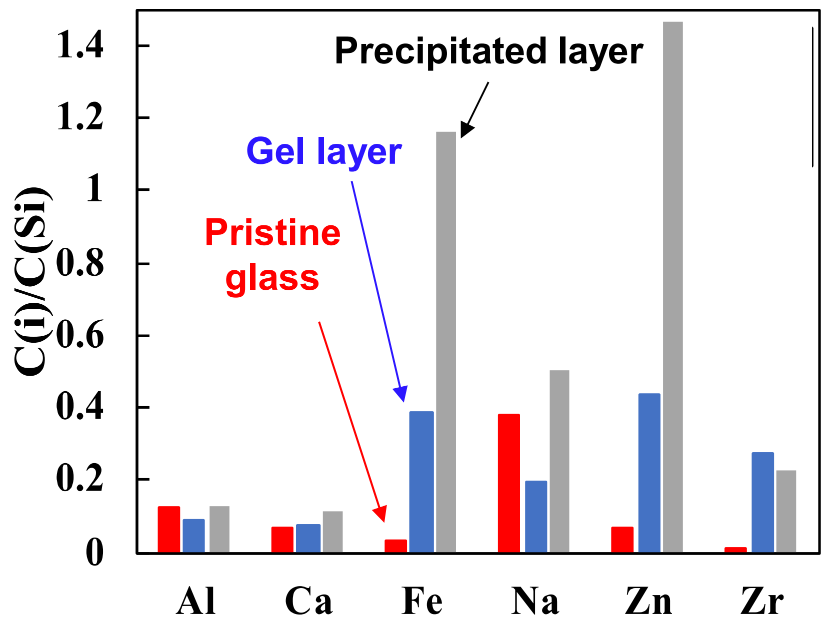
- At [Si] = 50ppm, r decreases with time after 30days.
- Effects of formation & growth of protective surface layer ?

SEM-EDX Analysis of altered surface layers(C_{Si} = 0)

[Si]=0ppm, pH9, 90℃, 90days
→ *Constant r with time*



Relative atomic ratio to Si by EDX



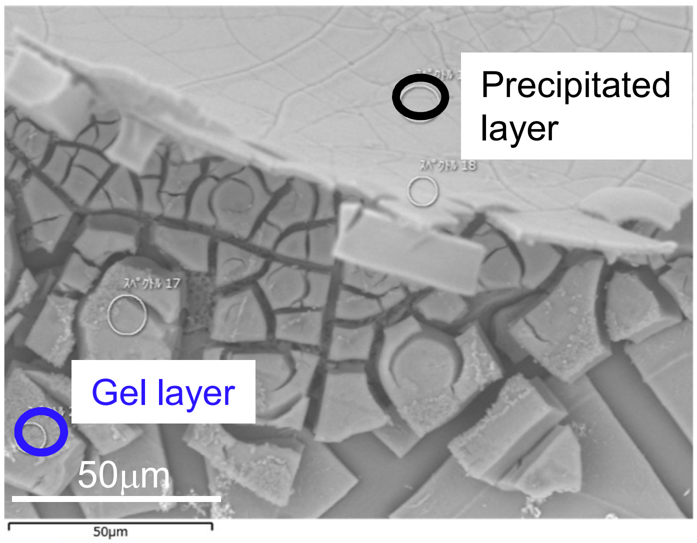
In case of [Si] = 0ppm

Insoluble elements, such as Fe, Zn, concentrated in the layers

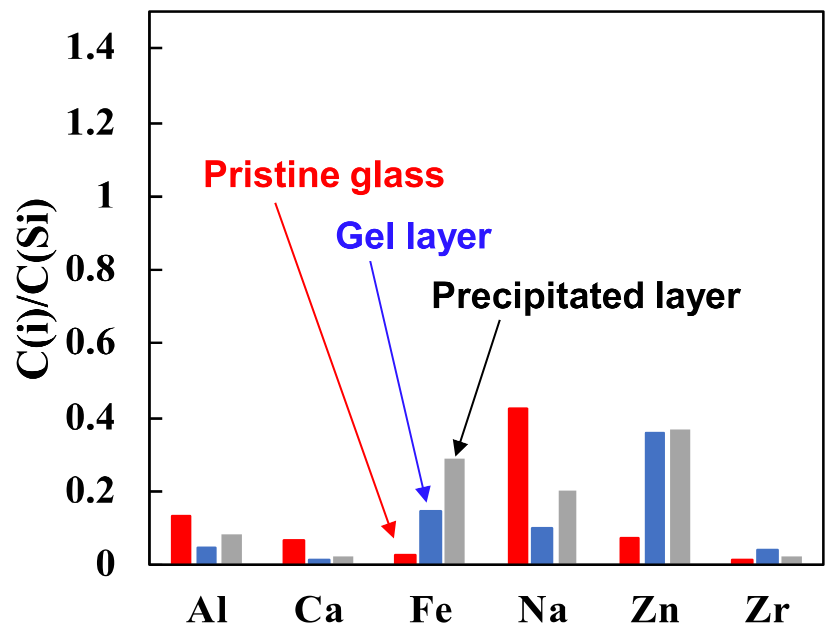
→ ***Layers rich in soluble elements form to be not protective***

SEM-EDX Analysis of altered surface layers (C_{Si} = 50ppm)

[Si]=50ppm, pH9, 90℃, 90days
→ *Decrease in r with time*



Relative atomic ratio to Si by EDX



In case of [Si]=50ppm

Concentration of Si is high in the layers

→ ***Si-rich layers from and grow to be protective***

Summary, Conclusions or Proposal ? (1)

- *An assessment of the long-term waste glass performance requires reliable modeling of the glass dissolution rate based on scientific principles.*

- *For the reliable modeling, we need reliable evaluation of the glass dissolution kinetics.*

- *The only way to complete the reliable kinetic evaluation is a high-level integration of experimental & simulation studies with consistency.*

- *The experimental study should provide the precise, consistent & systematic data on glass dissolution rate as a function of environmental parameters for the reliable kinetic evaluation.*

Summary, Conclusions or Proposal ? (2)

- ***We measured the glass dissolution rate as a function of environmental parameters, and the results show followings,***

- ***The dissolution rate changes depending on environmental parameters complicatedly rather than we had expected.***

- ***The dissolution rate with mechanism is suggested to be affected by types & properties of the alteration layers, which can change sensitively by environmental parameters.***

- ***Consequently, we need much more experimental data on the glass dissolution rate & alteration layers measured precisely, consistently & systematically as a function of environmental parameters for the reliable kinetic evaluation.***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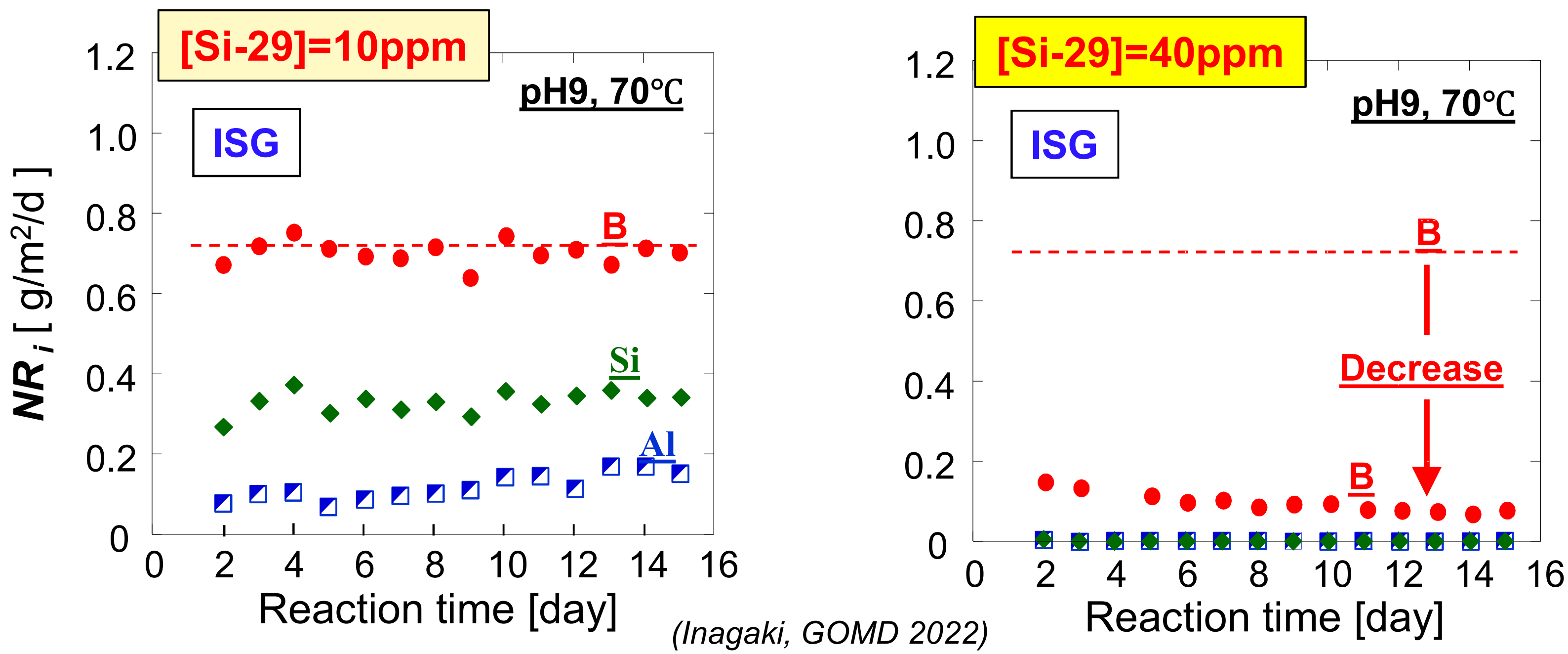
Arenes de Nimes,
An excellent stone vessel with large size, suitable for static test ?

Extra Files

Test results: Effects of C_{Si} on Boron dissolution at pH9



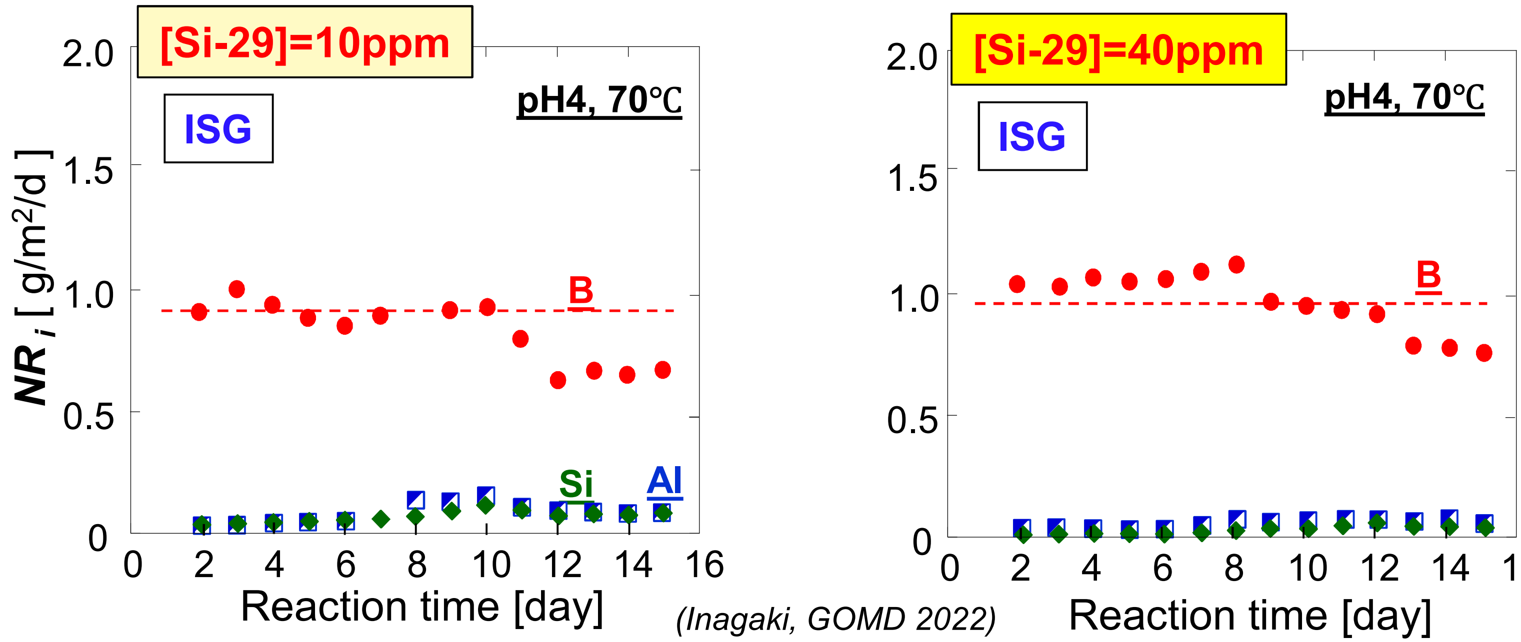
(Inagaki, GOMD 2022)

***At pH9*, Increase in C_{Si} ,**

- causes remarkable decrease in NR(B) as well as Si & Al.

- suggested to enhance the protective surface layer formation.

Test results: Effects of C_{Si} on Boron dissolution at pH4



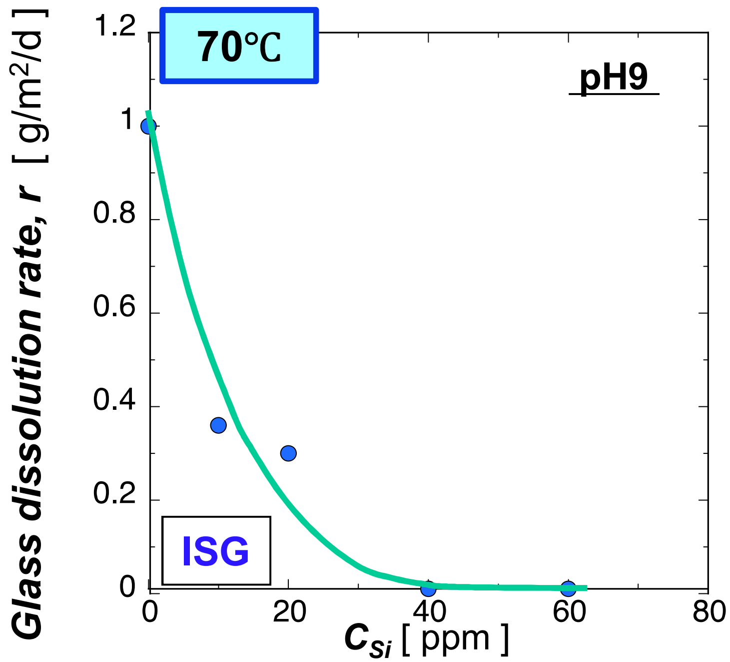
(Inagaki, GOMD 2022)

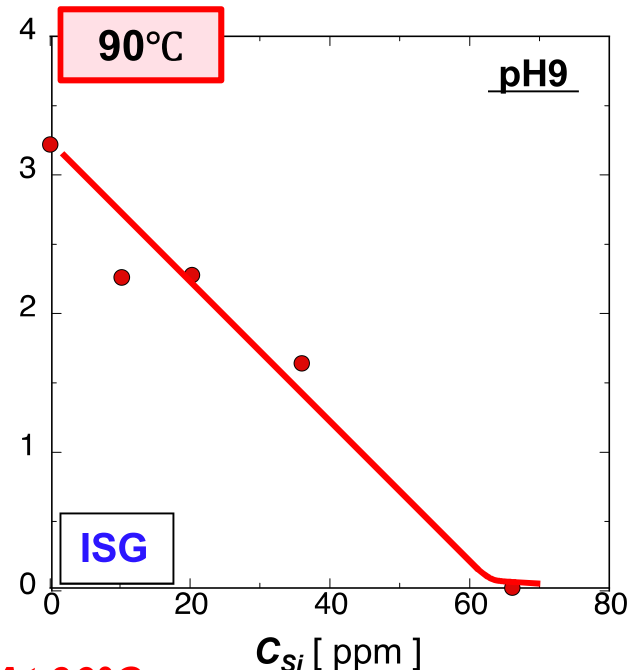
***At pH4*, Increase in C_{Si}**

- ***has no effects on NR(B) as well as Si & Al,***
- ***has no effects on the protective surface layer formation.***

Effects of C_{Si} on glass dissolution change depending on pH

Test results: Effect of temp on r (C_{Si}) at pH9





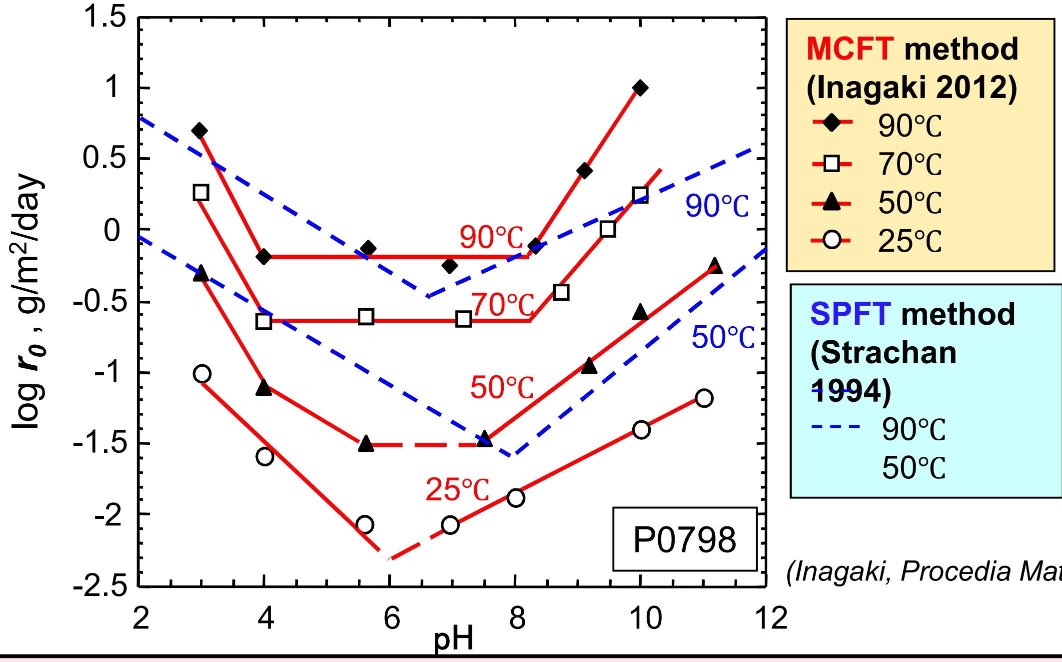
At 70°C,
non-linear relation between r and C_{Si}

At 90°C,
a good linear relation between r vs C_{Si}

The dissolution mechanism may change by temp at pH9 ?

Test results: Initial dissolution rate, r_0 (pH, temp)

Initial dissolution rate, r_0, as a function of pH and temp (P0798)
MCFT vs SPFT



(Inagaki, Procedia Materials Science 2014)

A certain difference between MCFT and SPFT
By MCFT ⇨ "U-shaped" pH dependence
By SPFT ⇨ "V-shaped" pH dependence