Effect of Water Vapor on Fining Behavior and Properties of Soda Lime Silicate Glass Melts

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☐ A part of this research, supported by the New Glass Forum in 2024.

Background

Applications of bubble formation studies at our laboratory

- For carbon neutral, the fining process of hydrogen combustion in window glass melting.
- Modified glass melting using recycled glass cullet, e.g., PV glass waste.
- Other glasses melting, e.g., bottle glass, E-glass, aluminosilicate glass, new fining agent, composition dependence etc.

Purpose of this work

Better understanding basically:

- Bubble formation behavior using **in situ observation method under various water vapor partial pressures** at a university laboratory during melting process
- Properties of melt and glass prepared under various vapor partial pressures: **melt viscosity** and **residual OH concentration**

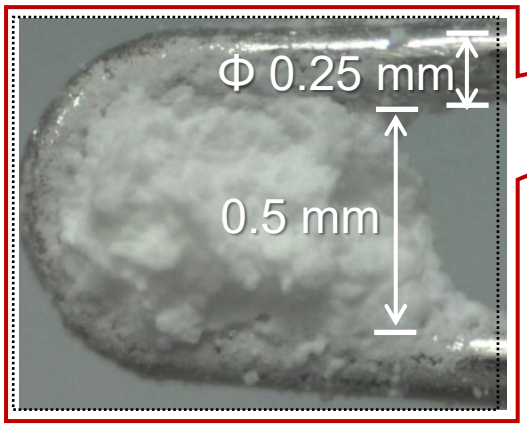
Outline

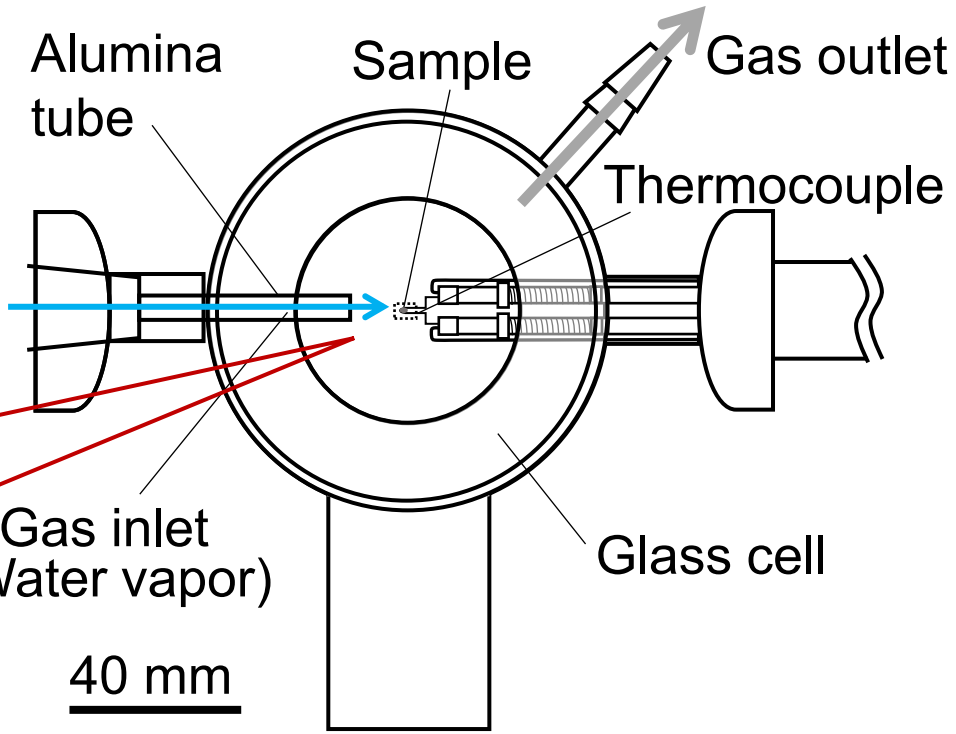
- Background and purpose
- **Hot thermocouple (HTC) method (in situ observation at high temperatures)**
- Bubble formation observation by crucible melting and quenching method
- Melt viscosity in crucible melting method
- Residual OH concentration in quenched glass

Experimental procedure

Sample composition (mol%)

- $15Na_2CO_3-10CaCO_3-75SiO_2$
- $12Na_2CO_3-10CaCO_3-75SiO_2$ $-3Na_2SO_4$



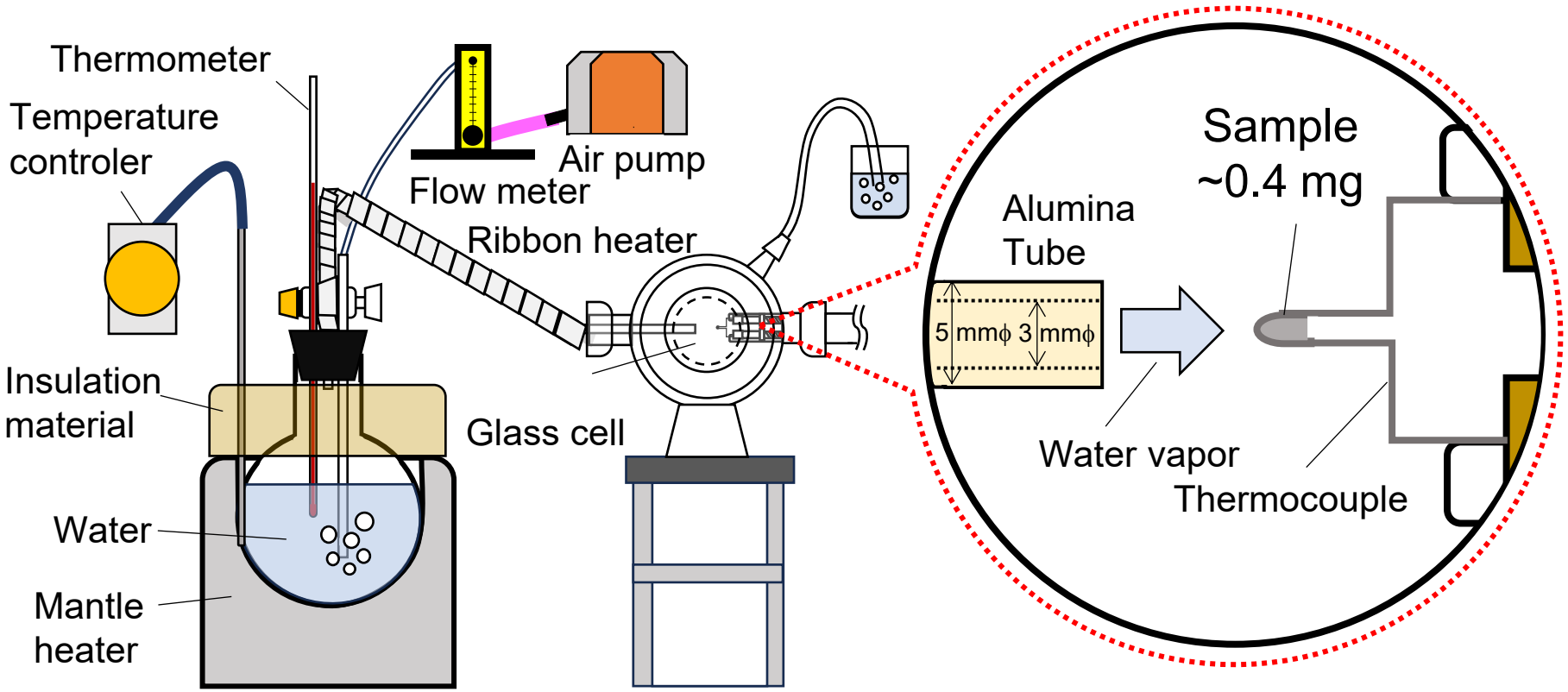


Hot-thermocouple cell

- Small sample amount (~0.4 mg)
- Direct observation through microscope
- Atmosphere control

Atmosphere control in HTC method

- Laboratory air P_{H_2O} = 2 kPa
- Water vapor (Simulated hydrogen combustion) P_{H_2O} = 98 kPa
  (90 vol% H_2O in H_2 100% atmosphere)

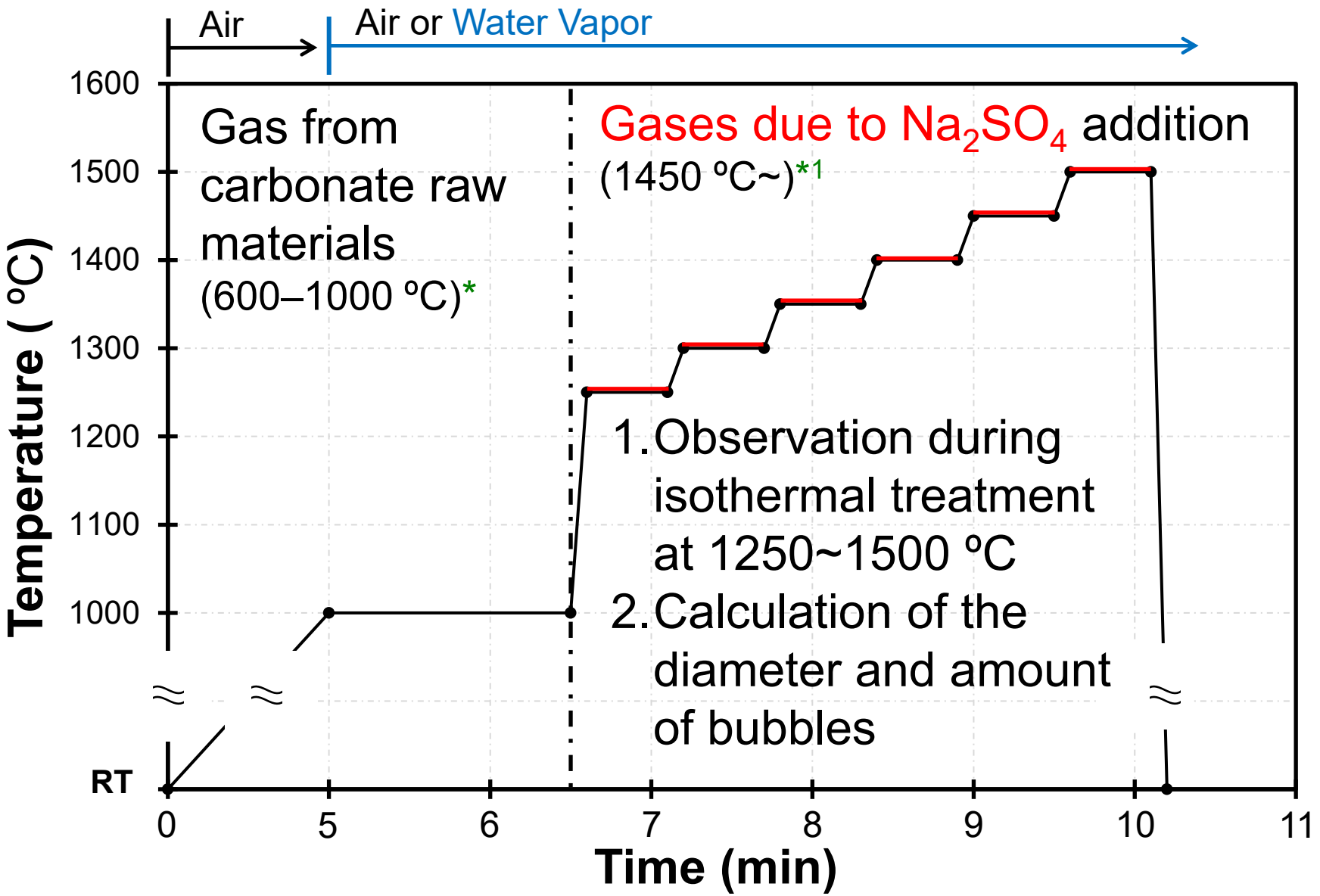


Hand-made setup of HTC method for high water paper partial pressure study, founded by the New Glass Forum

Heating schedule in HTC method

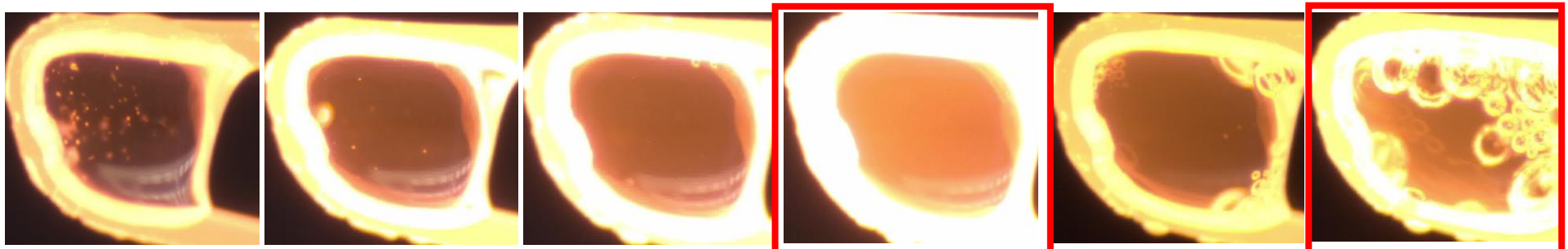
[Atmosphere]

* Mathieu Hubert, “Melting and Fining processes in industrial glass furnaces”, Celsian Glass & Solar, (2015).

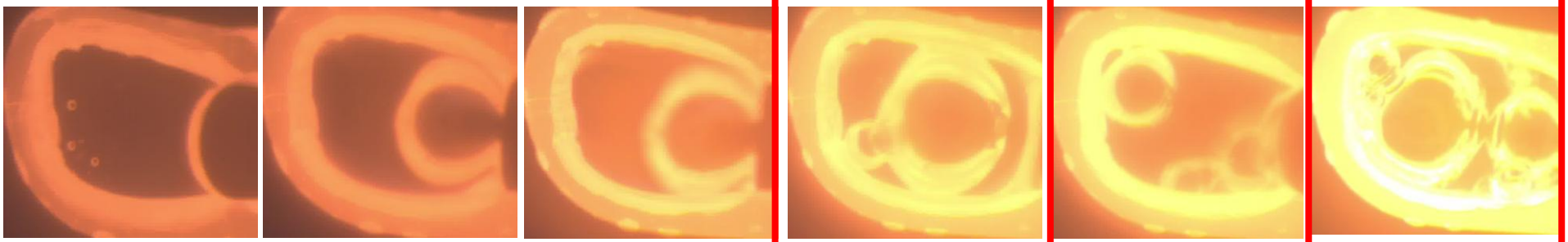


Snapshots at high temperatures

Air : P_{H_2O} =2 kPa



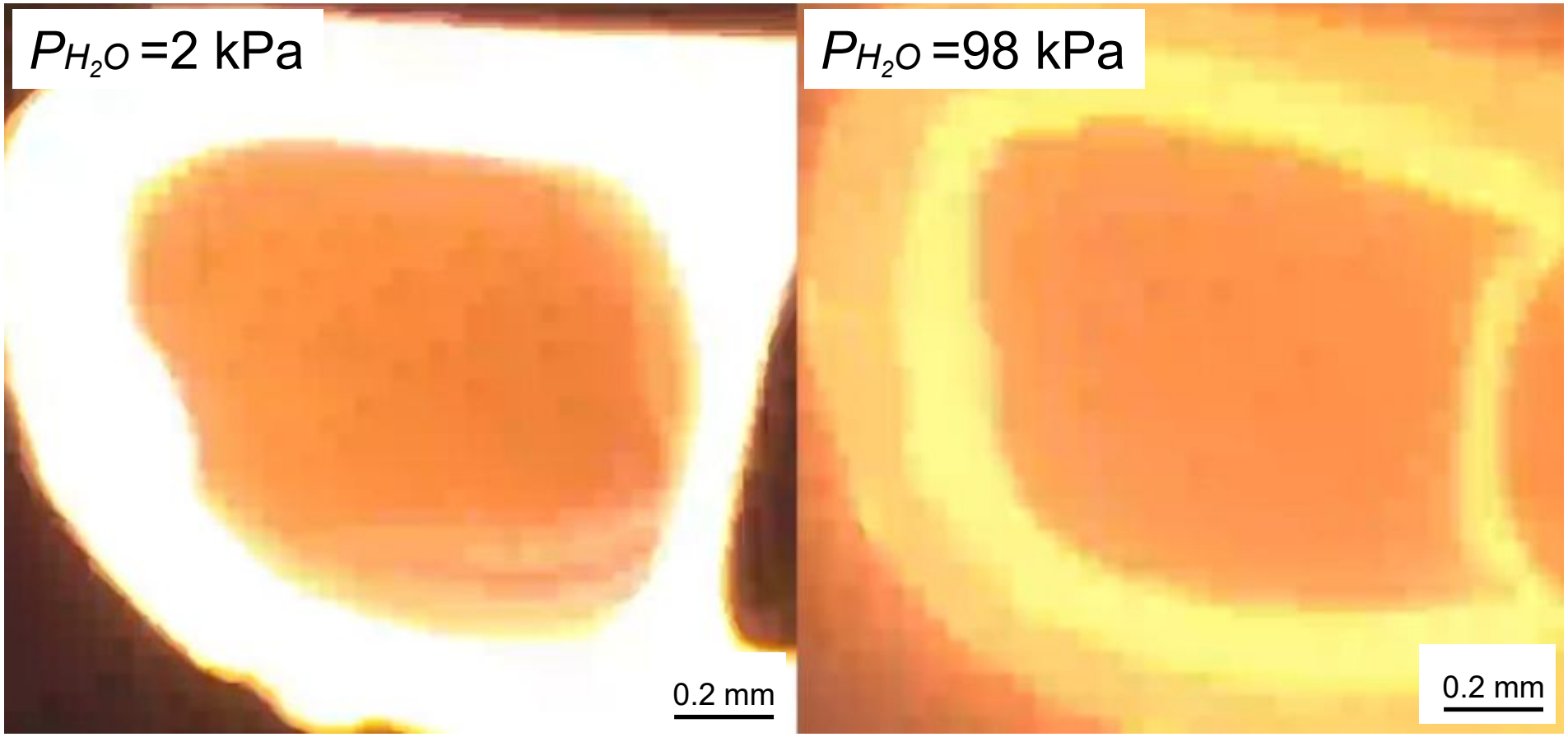
Water vapor : P_{H_2O} = 98 kPa



1250 1300 1350 1400 1450 1500

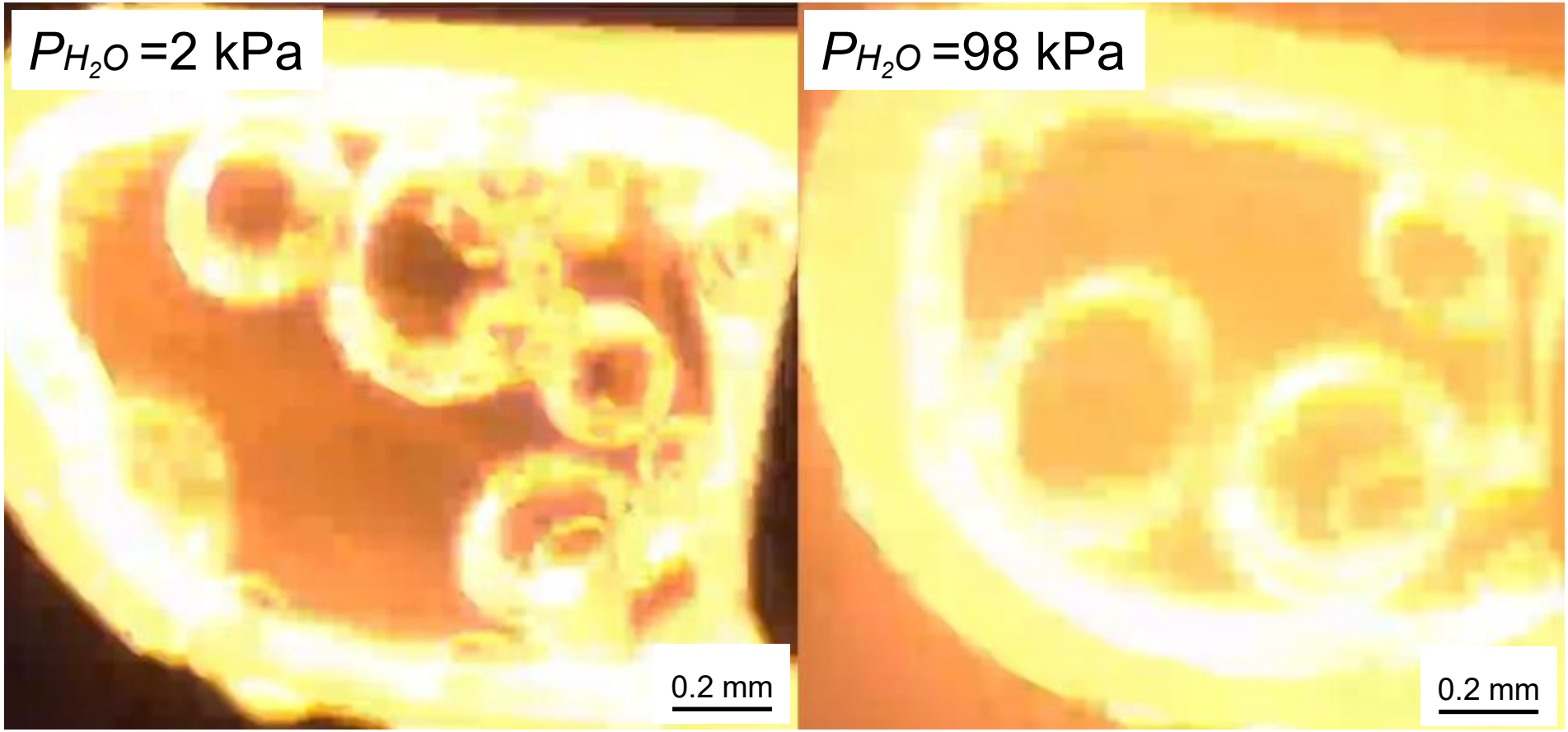
Temperature (ºC)

Video of bubble formation at 1400 ºC



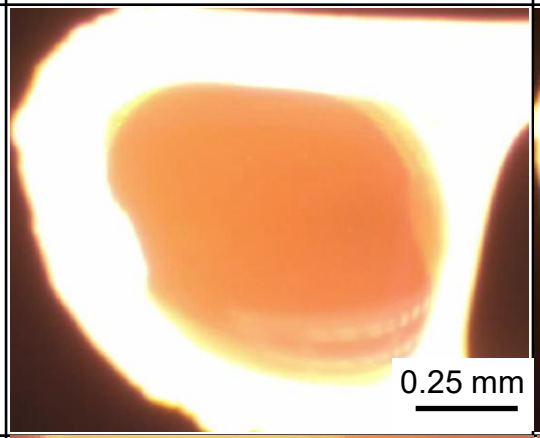
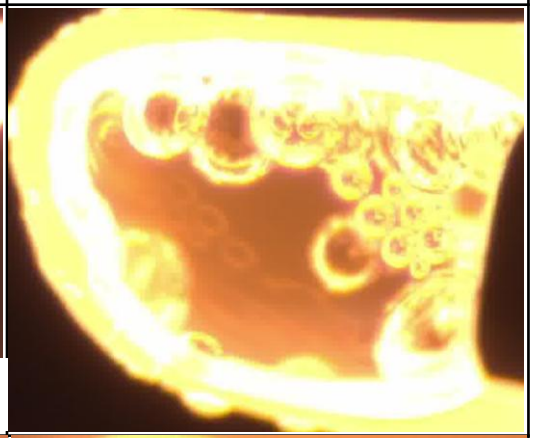
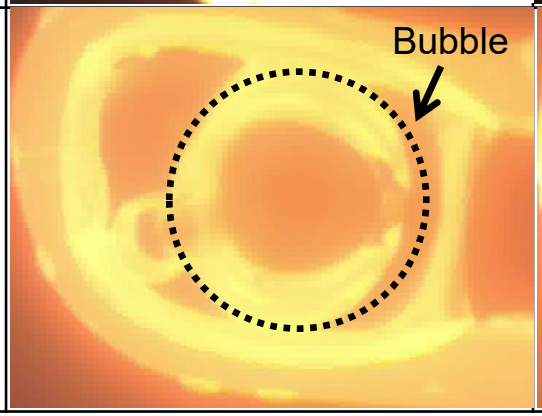
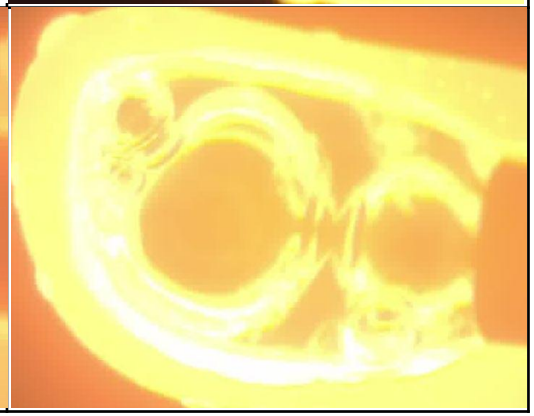
Only at P_{H_2O}=98 kPa, formation of SO_2 and O_2 due to Na_2SO_4 addition

Video of bubble formation at 1500 ºC



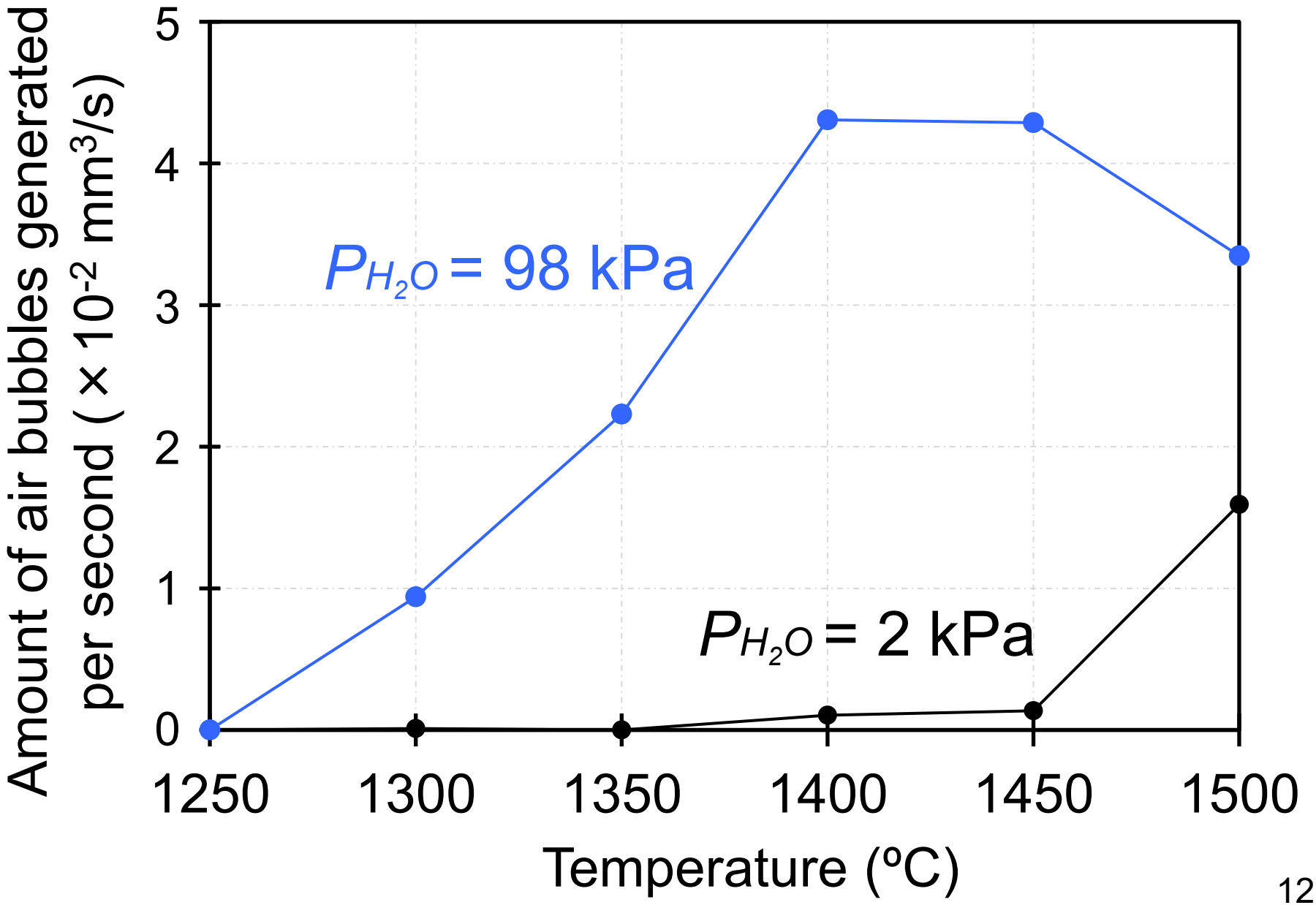
- Both at 2 kPa and 98 kPa for P_{H_2O}, the formation of SO_2 and O_2 due to Na_2SO_4 addition
- Larger bubbles at 98 kPa for P_{H_2O}.

Typical bubbles under various conditions

P_{H_2O}	Temperature (ºC)	
	1400	1500
2 kPa		
98 kPa		

Snapshots of bubbles at 1200–1500 ºC
→Calculation of formed bubble amount

Bubble amount versus temperature



Bubble Formation by Water Vapor

Main results obtained by the HTC method

Formation of SO_2 and O_2 gases at lower temperatures from 1300 ºC and higher temperatures

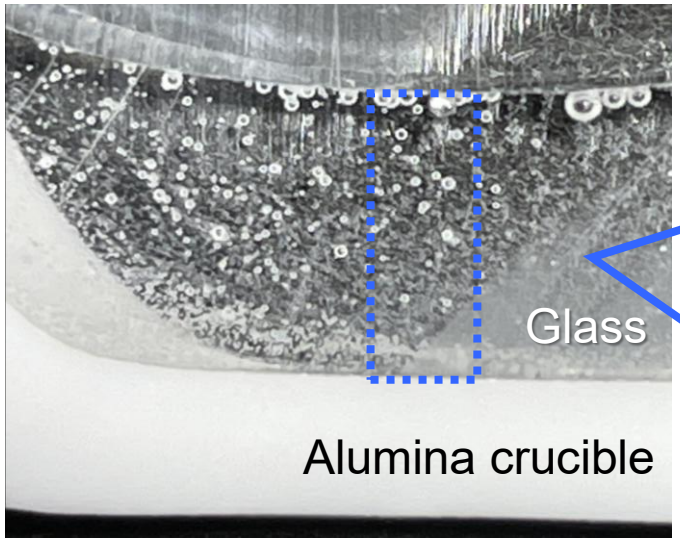
$$SO_4^{2-}(l) + H_2O(g) \Rightarrow SO_2(l, g) + \tfrac{1}{2}O_2(l, g) + 2OH^-(l)$$

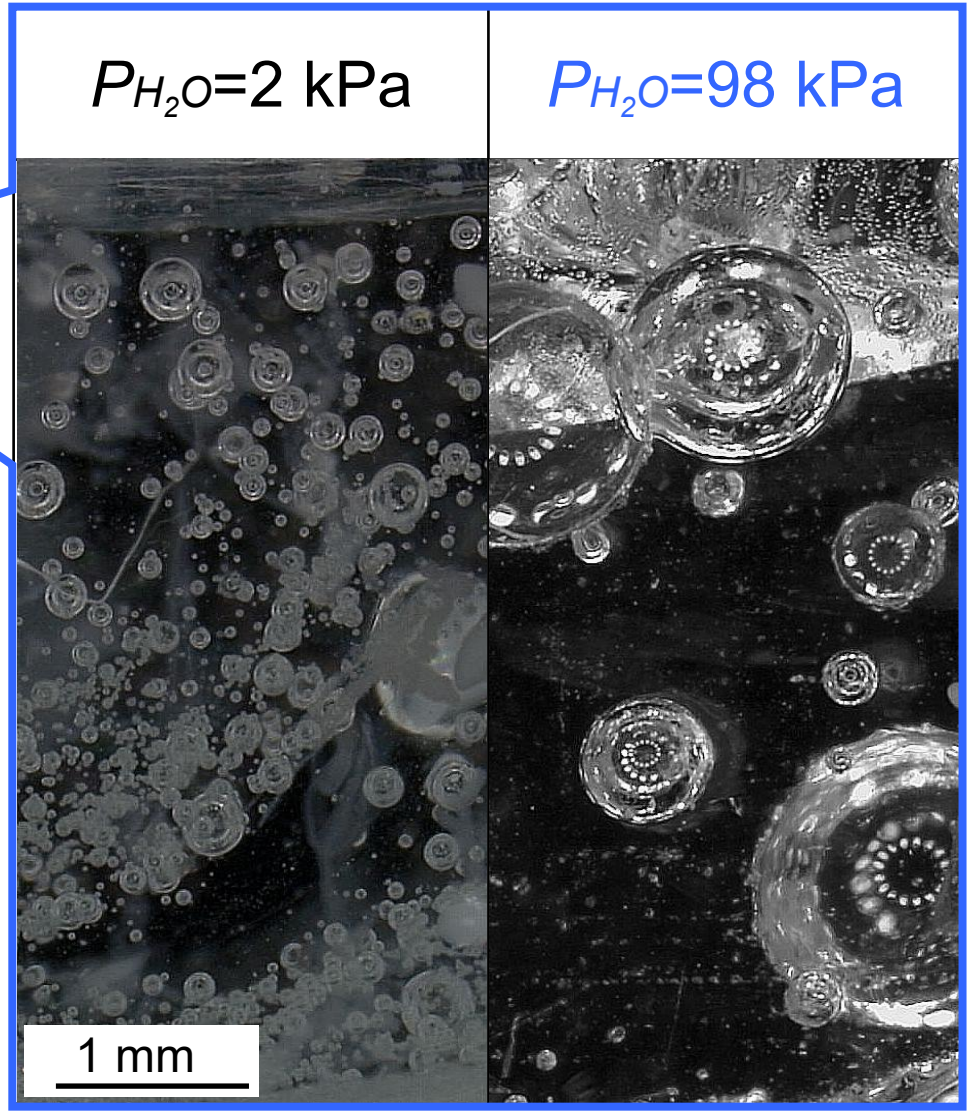
- MIROSLAVA HUJOVA, et al., Ceramics-Silikaty, 61 (2) (2017), 119-126.

Water vapor (Higher H_2O concentration)

The reaction occurs to the right side.

Crucible melting & quenching method*





Cross section

*The sample was melted at 1400 ºC **for 10 min** with water vapor partial pressures of 2 and 98 kPa and then cooled to room temperature.

Bubble Floating Rate @1400 ºC, 10min

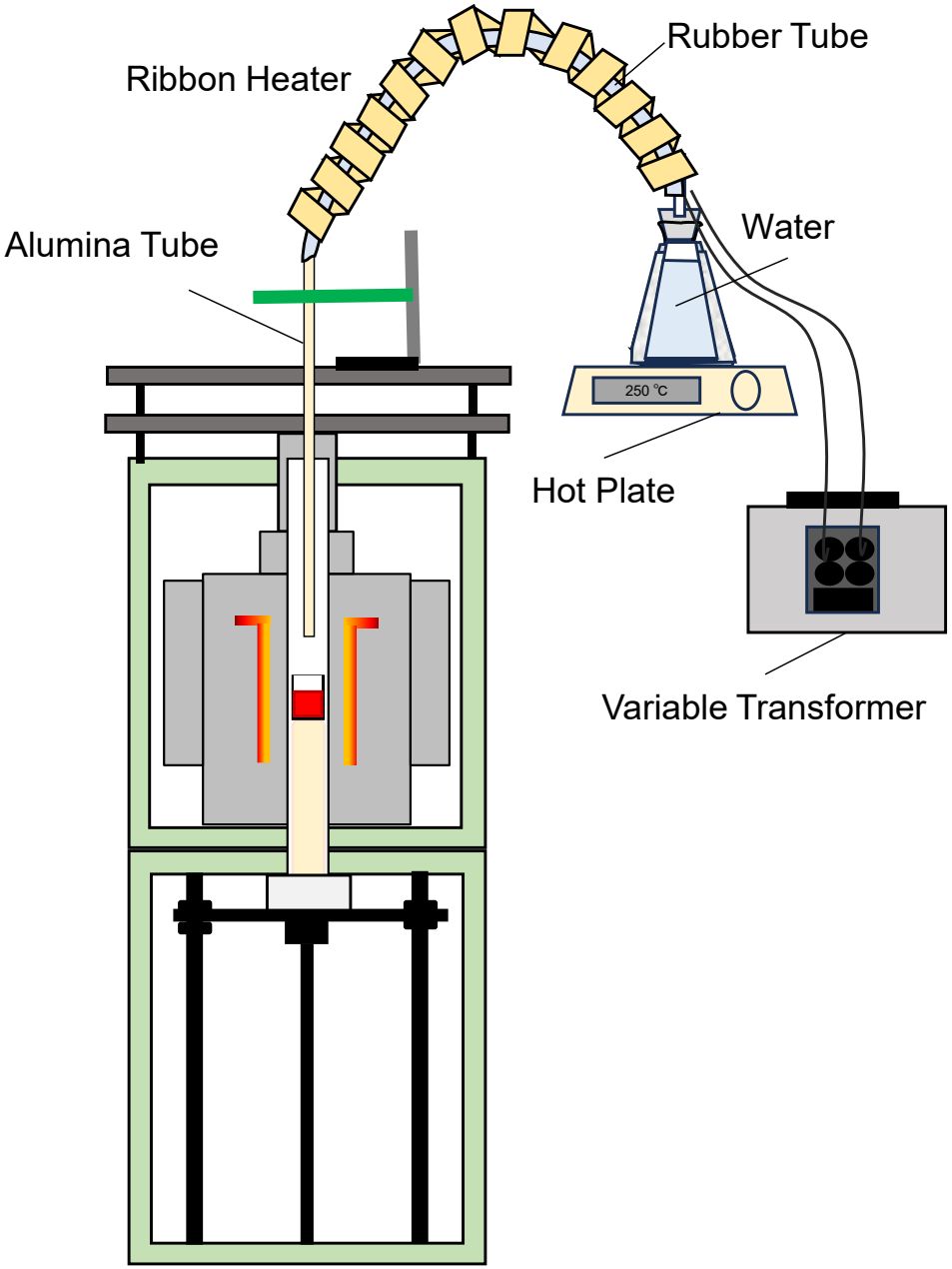
Calculation by Stokes' equation

$$V = \frac{2}{9} \cdot \frac{r^2 \, g(\rho_m - \rho_g)}{\eta}$$

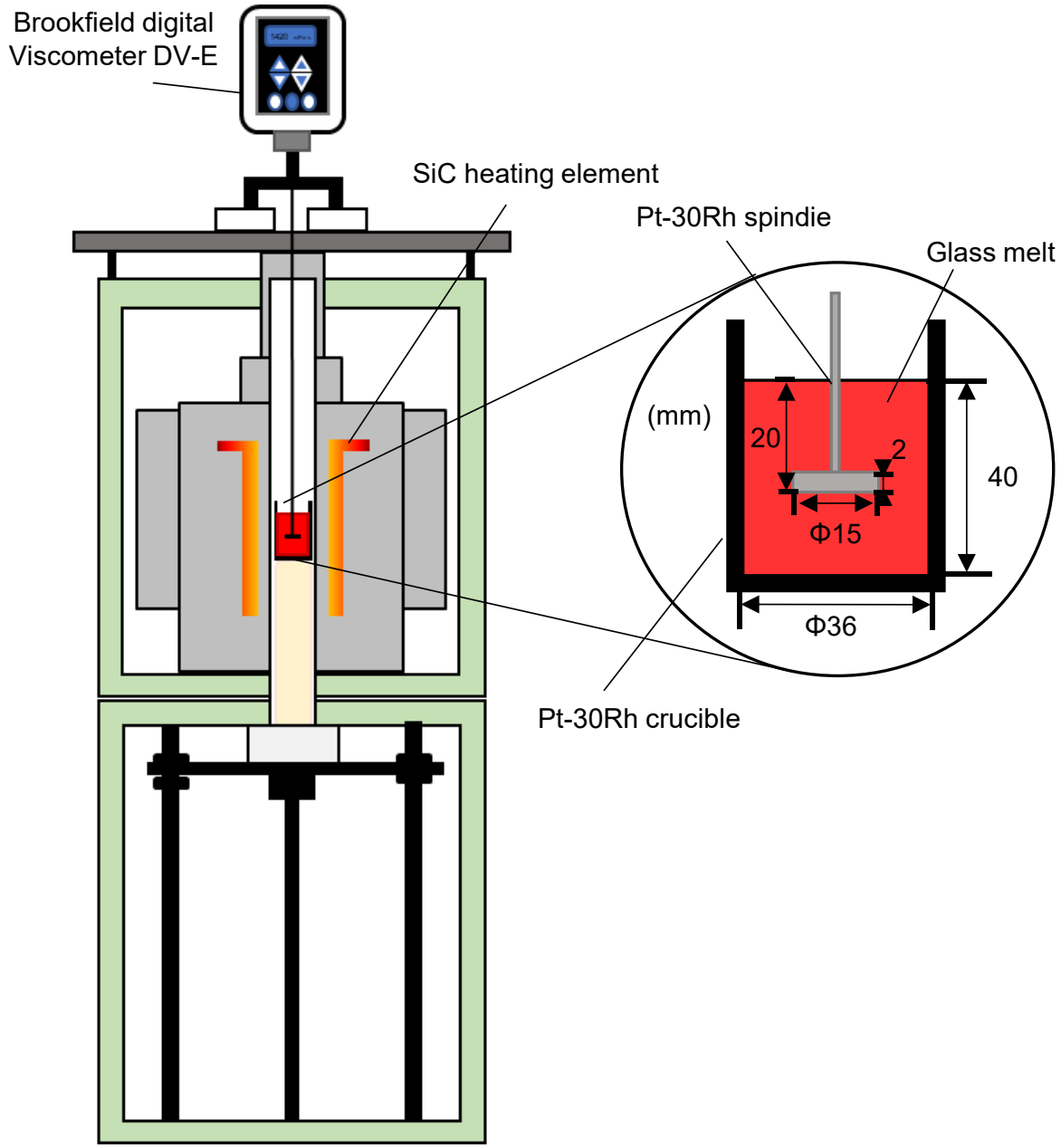
r: Bubble radius, g: gravitational acceleration,
ρ_m, ρ_g: melt and gas densities, η: melt viscosity

P_{H_2O} (kPa)	Average bubble diameter (mm)	Floating rate (mm/min)	Floating distance after 20 min (mm)
2	0.10	0.065	1.3
98	0.24	0.43	8.7

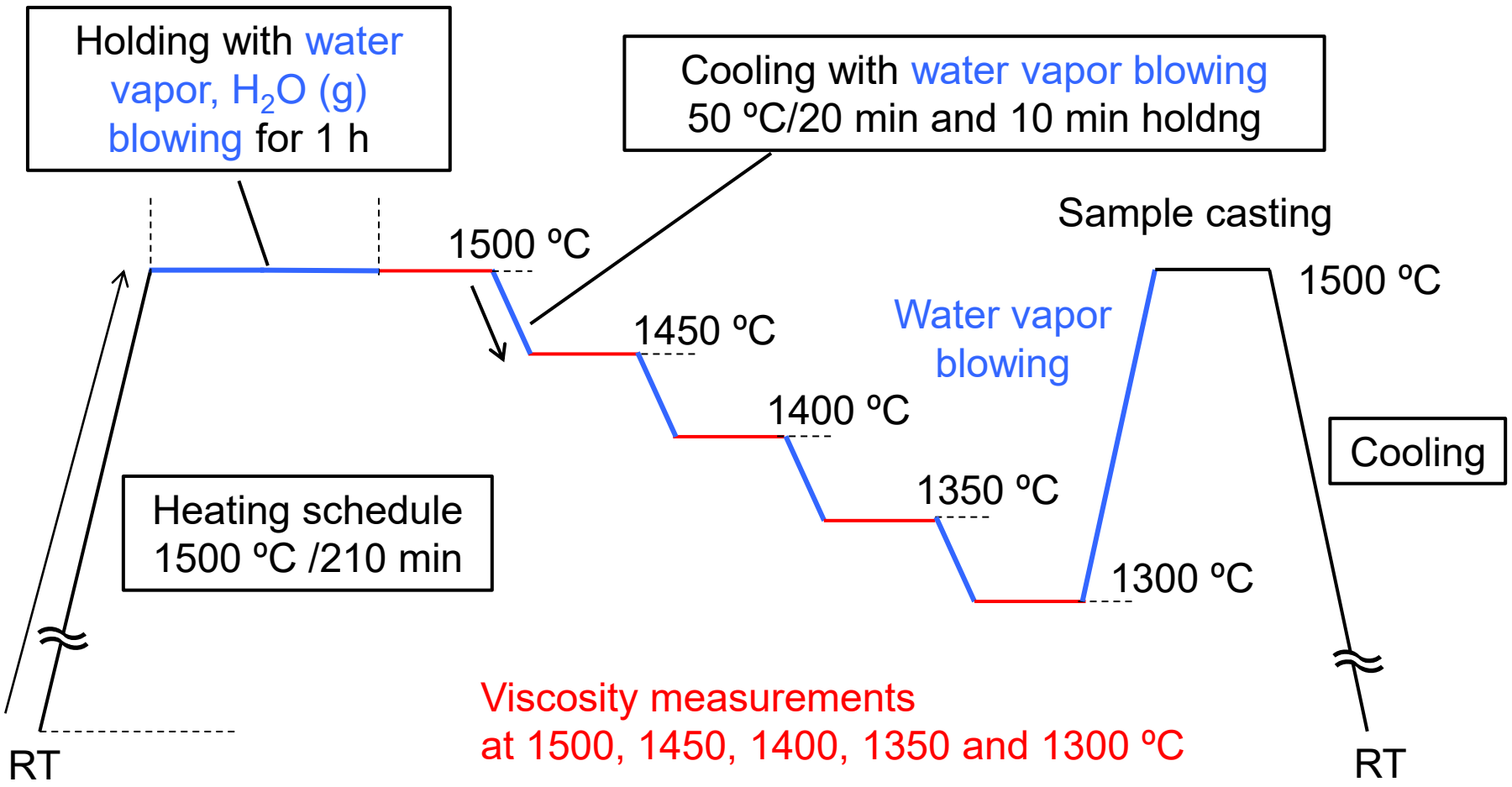
Water vapor control during crucible melting



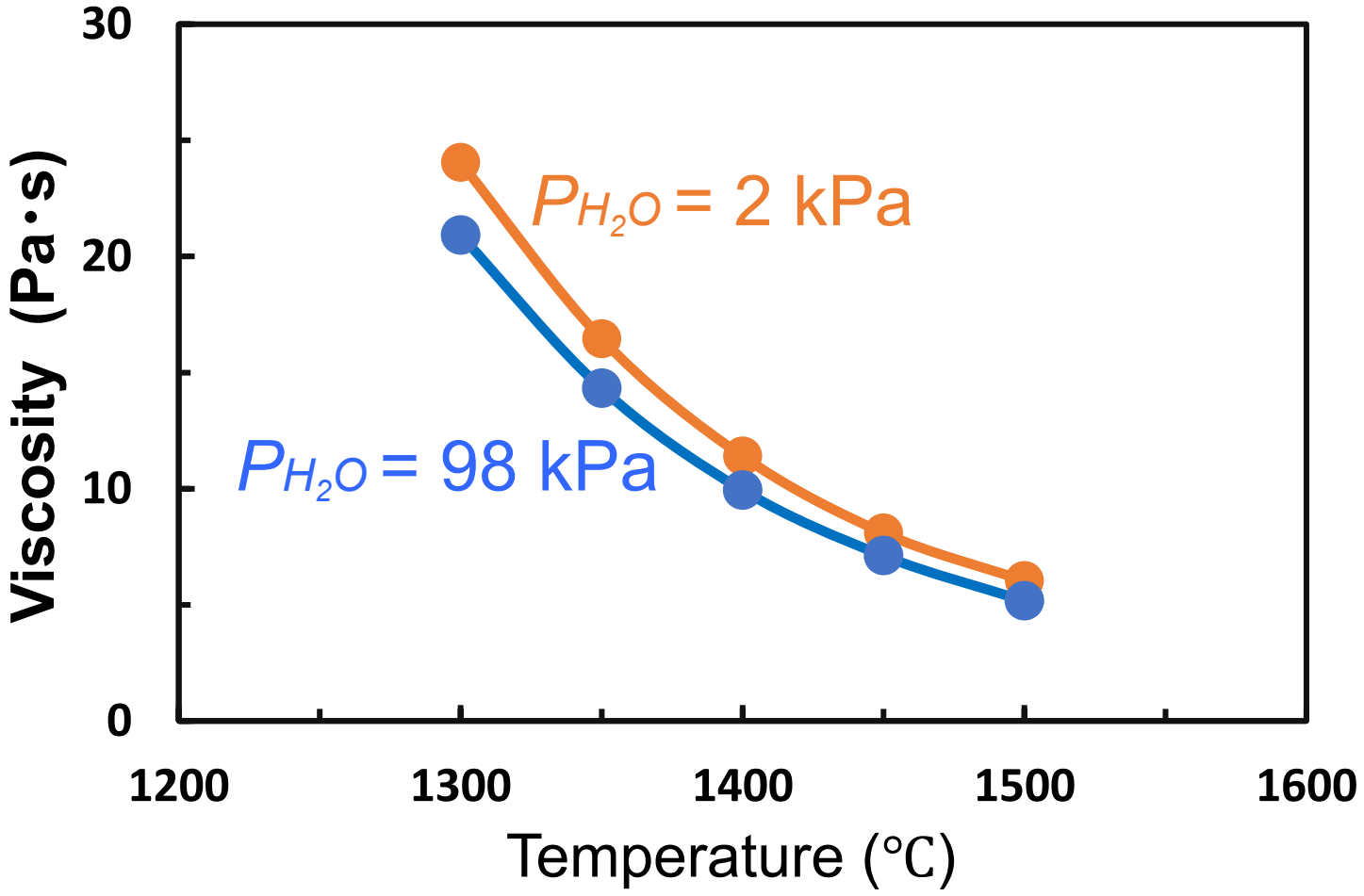
Schematic viscosity measurements



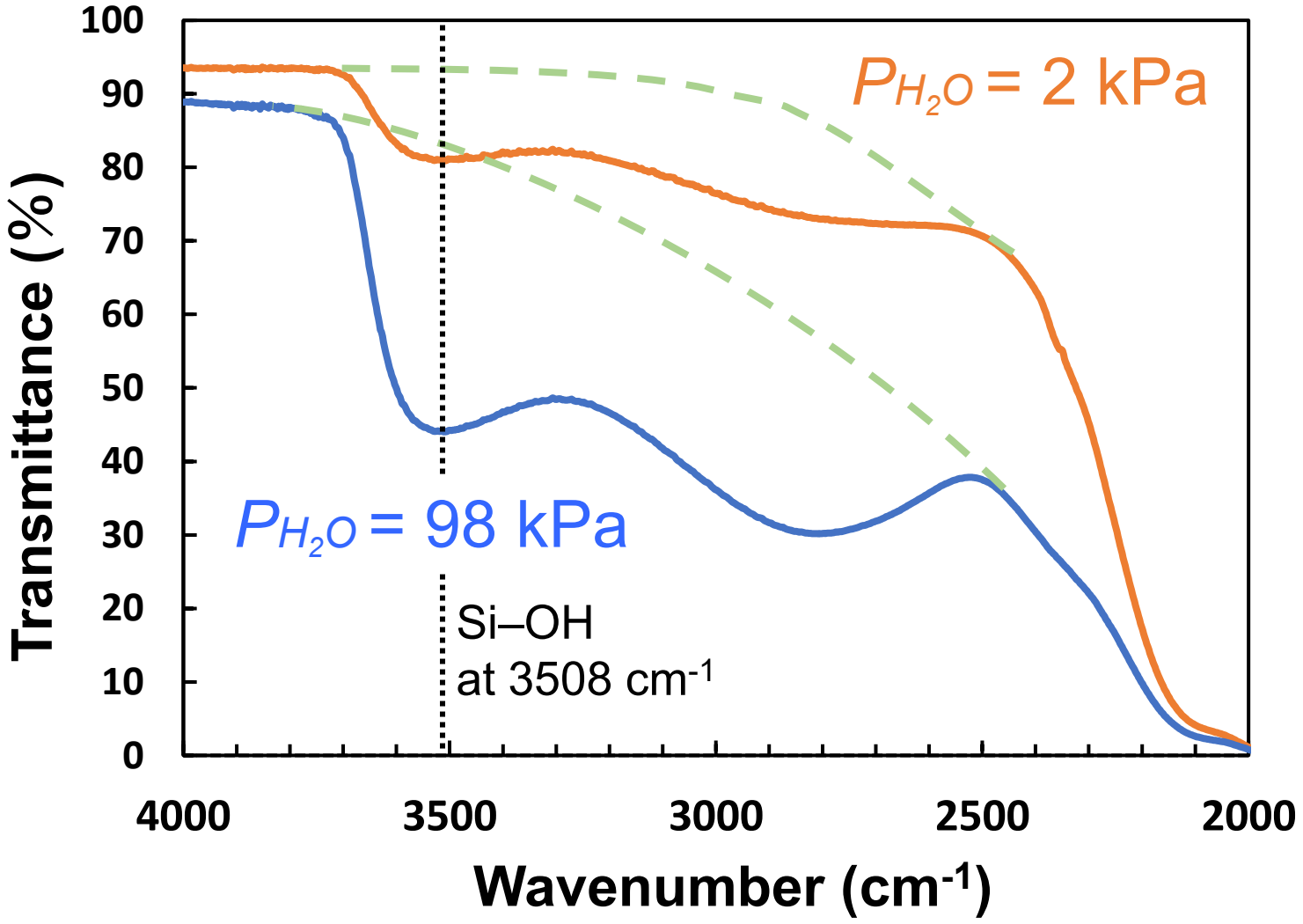
Temperature profile for viscosity measurements



Viscosity of soda lime glass melts



Infrared spectra of soda silicate glass



Calculation of OH concentration in glass

$A=-\log T \cdots (1)$

T: Transmittance
A: Absorbance
C: Water content (wt%)
t: Sample thickness
(0.10 cm)

$C=\beta_{OH} \cdot 18/\varepsilon \cdot d \cdots (2)^*$

ε: molar absorption coefficient * ,
43 ($mol^{-1} \cdot cm^{-1}$)
β_{OH}: Absorption coefficient, A/t (mm^{-1}) at 3508 cm^{-1}.
F_{OH}: OH molar weight, 18 (g•mol)
d: Glass density, 2.45 ($g \cdot cm^{-3}$)

* ε for a similar composition:
$14.6Na_2O–7.92CaO–1.3Al_2O_3–64SiO_2$

P_{H_2O} (kPa)	Absorbance (a. u.)	Water concentration (ppm)
2	0.061	104
98	0.273	467

*J.Paul Willams, 1976,CERAMIC BULLETIN Vol.55, pp.524-527

Conclusions

- Higher water vapor partial pressure promotes the bubble formation of SO_2 and O_2 at lower temperatures, e.g., 1300 ºC.
- Higher water vapor partial pressure results in higher bubble floating rate at a same temperature of 1500 ºC, compared to laboratory air atmosphere *at* P_{H_2O}=2 kPa.
- Under higher water vapor pressure melting soda lime glass melt shows ~14-16 % lower viscosity and contains higher OH concentration in glass state.

Thank you for your kind attention.