



DE LA RECHERCHE À L'INDUSTRIE

# Mechanism of O<sub>2</sub> bubble formation in borosilicate melts

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Luiz F.P. Pereira,\* Annabelle Laplace, Franck Pigeonneau

## ➤ HOW DO BUBBLES BEHAVE IN NUCLEAR GLASS MELTS ?

- Nucleation type ?
- Main growth mechanism ?
- Bubble density decay ?
- Is bubble behaviour function of temperature ?
- How do bubbles behave with time ?
- Influence of insoluble crystals ?

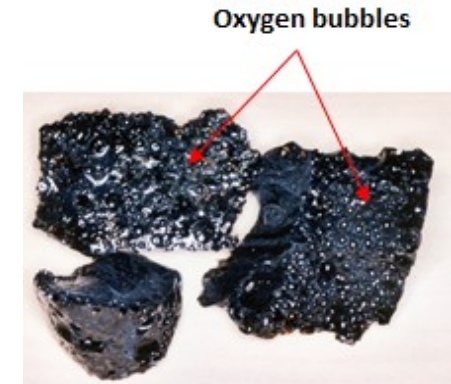


Fig. 1: Example of bubbled glass

**PhD goal : Fundamental comprehension of O<sub>2</sub> bubble formation linked to redox reaction.**

## ➤ Nuclear glass = Glass matrix + nuclear waste



- The waste may contain multivalent elements: Fe, Ce, Cr ...
- Redox reaction might happen :
  - $\text{Ce}^{4+} + \frac{1}{2} \text{O}^{2-} \rightleftharpoons \text{Ce}^{3+} + \frac{1}{4} \text{O}_{2(g)}$
  - $T_{\text{HL}} \approx \text{O}_{2 \text{ HL}}$
  - Ce speciation and/or PO<sub>2</sub> give clues about O<sub>2</sub> production

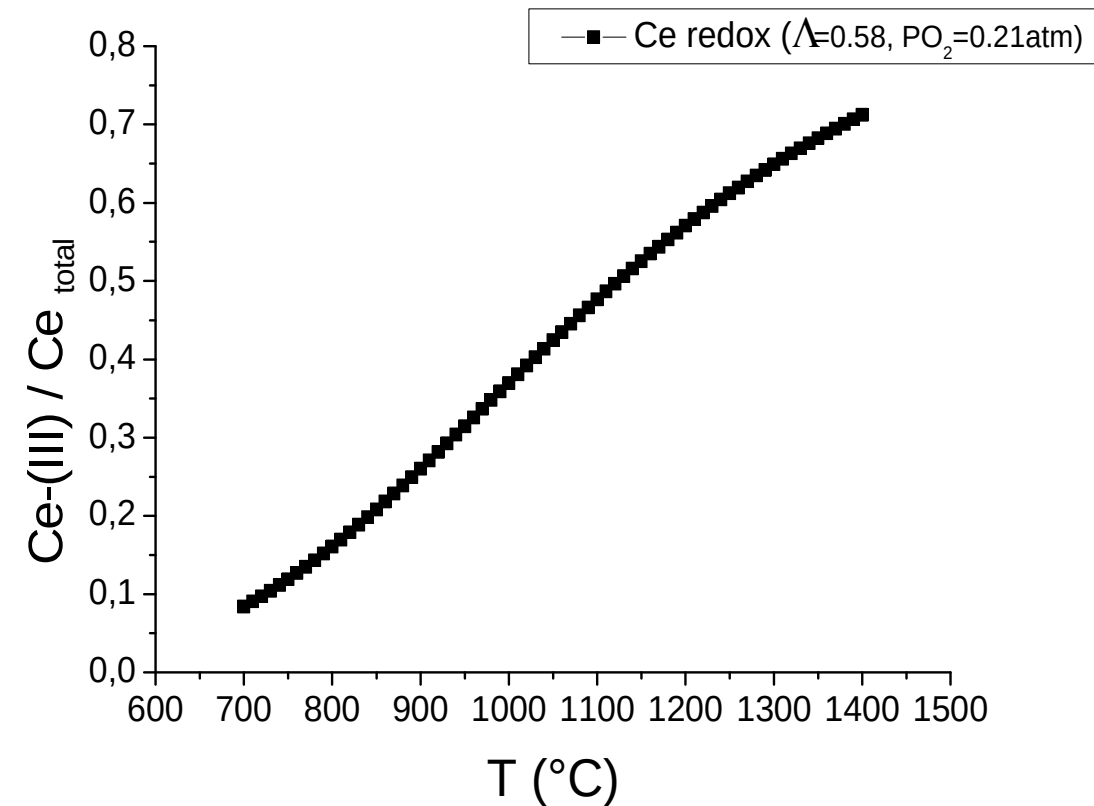
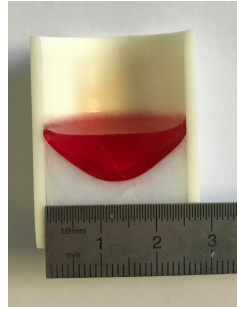


Fig. 2: Ce redox evolution with temperature for fixed PO<sub>2</sub>. Pinet *et al.*<sup>1</sup>

1) Pinet et al., Modeling the redox equilibrium of the Ce<sup>4+</sup>/Ce<sup>3+</sup> couple in silicate glass by voltammetry. *JNCS*, 352, 5382-5390 (2006).

## ➤ Glass synthesis :

- Borosilicate glass powder +  $\text{CeO}_2$
- Temperature (800-1100 °C) and duration
  - e.g. 1100°C (20, 30, 40, 60, 120min)
- With and without cerium
- Different granulometries



## ➤ Sample preparation :

- Cutting
- Polish



## ➤ Optical microscope :

- Mapping
- Reconstruction a cross-section



## ➤ Image treatment :

- Bubble number density ( $N_b$ )
- Bubble diameter ( $d_{\text{mean}}$ )
- Occupied bubble area (A%)



## ➤ Data treatment :

- Bubble size distribution (histograms)
- 2D  $\rightarrow$  3D conversion
- Statistic plots (QQ plots)



## ➤ Characterisations :

- Viscosity ( $\eta$ )
- Density ( $\rho$ )
- Surface tension ( $\sigma$ )
- XANES
- Gas bubble composition by mass spectroscopy
- Laser granulometry

## ➤ Experiment at 800 °C :

- Borosilicate glass powder with and without CeO<sub>2</sub>
  - Glass powder (250 < glass < 500 μm)
  - Apparent density: 50% of bulk glass

## ➤ What have we seen ?

- Large air package in both cases
- Entrapped air as microbubbles (well dispersed)
  - Bubble number density and size distribution

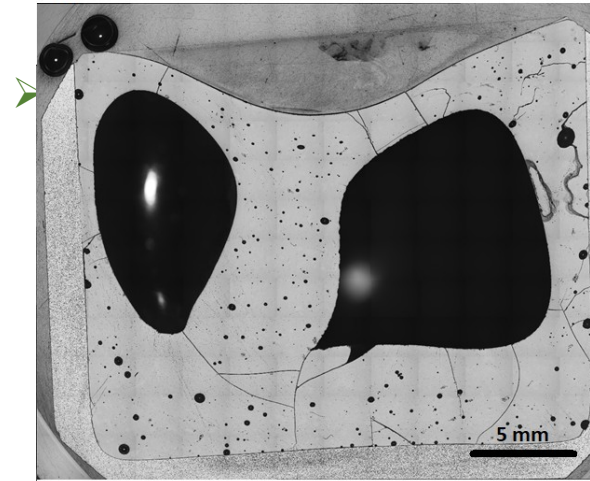
## ➤ Melting mechanism ?

- Air percolation towards unmelted regions (large air package)
- Remaining trapped air (microbubbles)

## ➤ Bubble gas composition :

- N<sub>2</sub> rich in the beginning (70 vol%)

a) 800 °C 20min with Ce



800 °C 20min without Ce

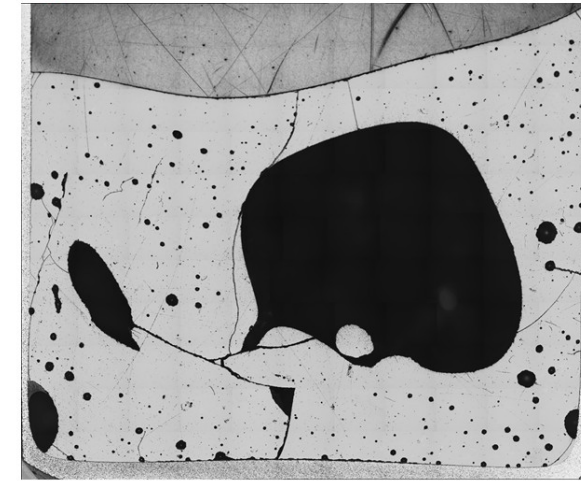


Fig. 3: Optical microscope images of glass a) 800 °C 20min with Ce b) 800 °C 20min without Ce

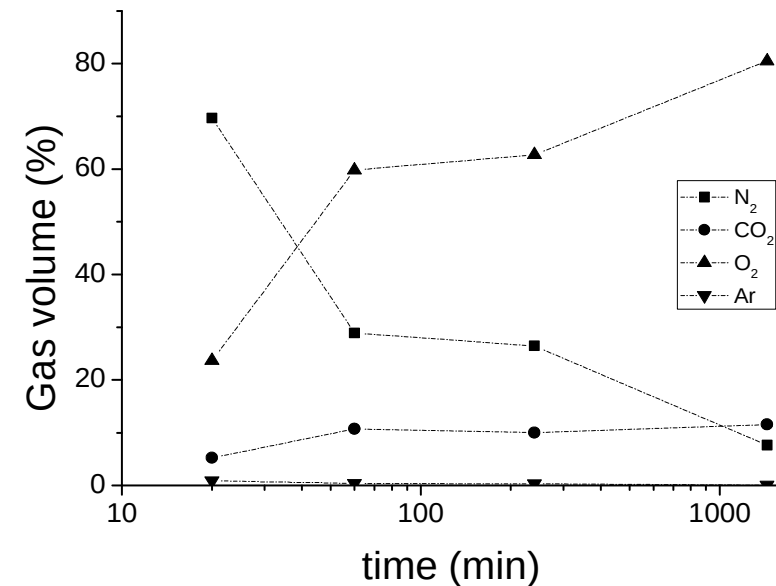
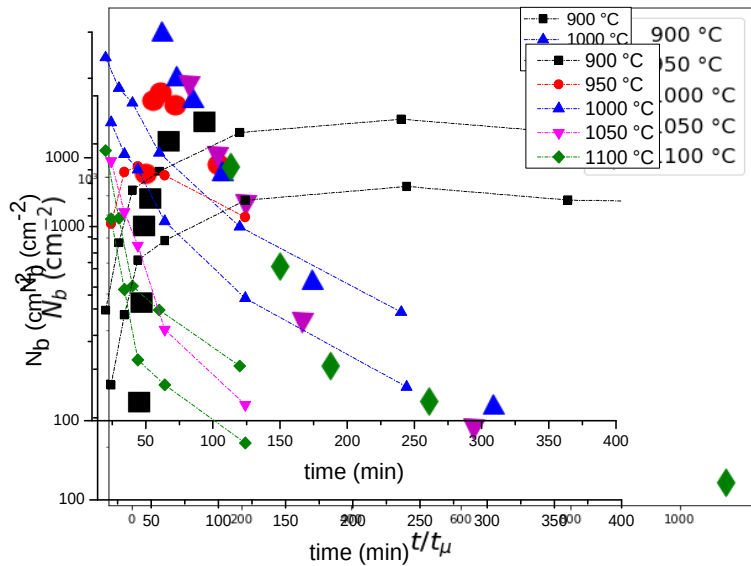


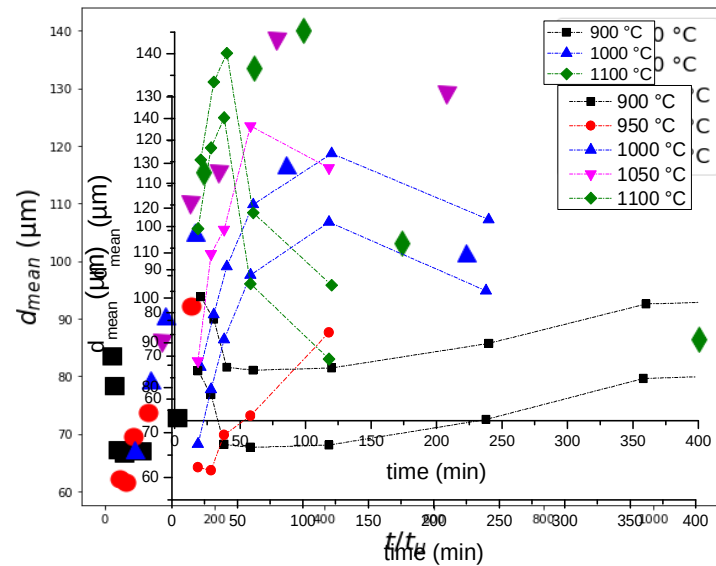
Fig. 4: Bubble gas composition for samples synthesised at 900 °C

## ➤ Bubble behaviour in the molten glass :

- Bubble number density ( $N_b$ )



- Bubbles mean diameter ( $d_{\text{mean}}$ )



- Bubble occupied area ( $A\%$ )

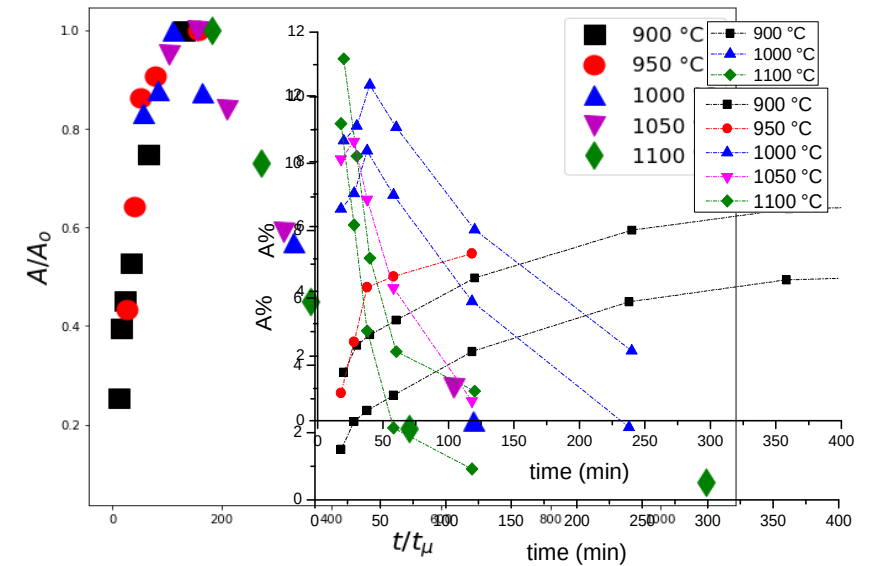


Fig. 7: Normalized results of  $N_b$ ,  $d_{\text{mean}}$ ,  $A$  in terms of  $1/\eta$ .

evolution are fundamentally the same,  
regardless of temperature

## ➤ Conclusions and insights :

- Bubble “nucleation” from pre-existing air trapped bubbles
- The mechanisms that govern bubble evolution are essentially the same, regardless of temperature

## ➤ Perspectives :

- Numerical model – mathematical prediction
- Influence of crystals in bubble formation in the same system (ongoing)
- Camera *in-situ* observation
- Bubbles linked to crystallisation



▶ **THANK YOU FOR YOUR ATTENTION**

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