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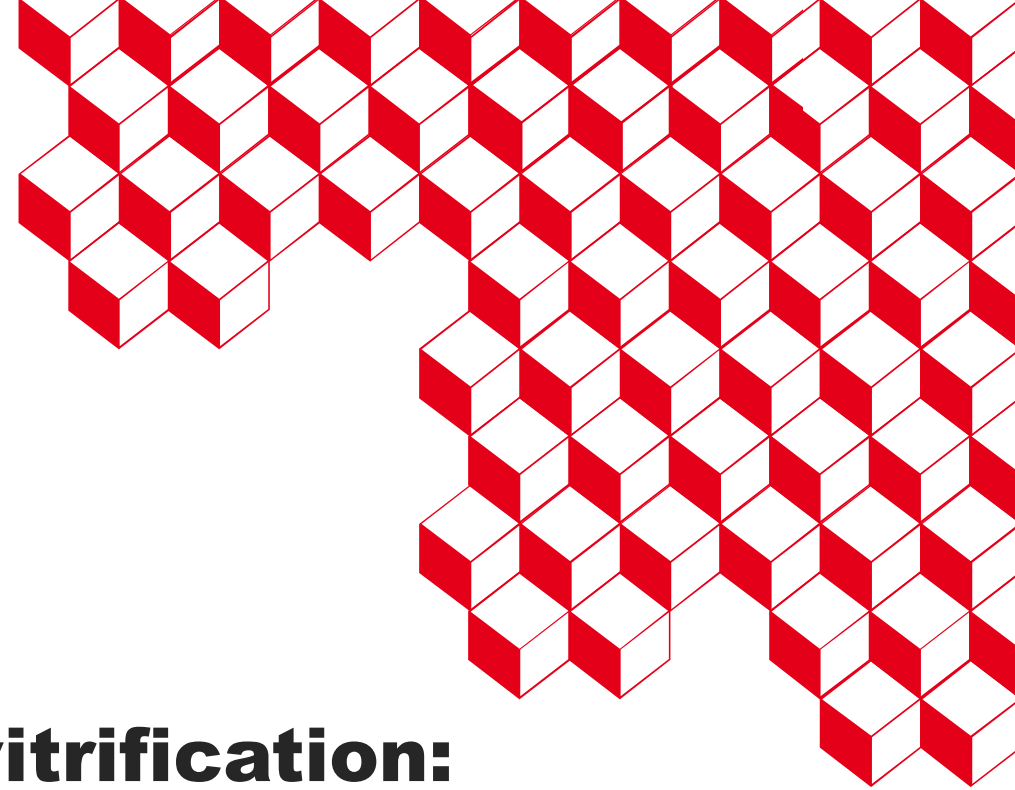
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Modeling of liquid nuclear waste vitrification: focus on the chemical processes

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V. Benavent¹, M. Delaunay¹, E. Sauvage¹

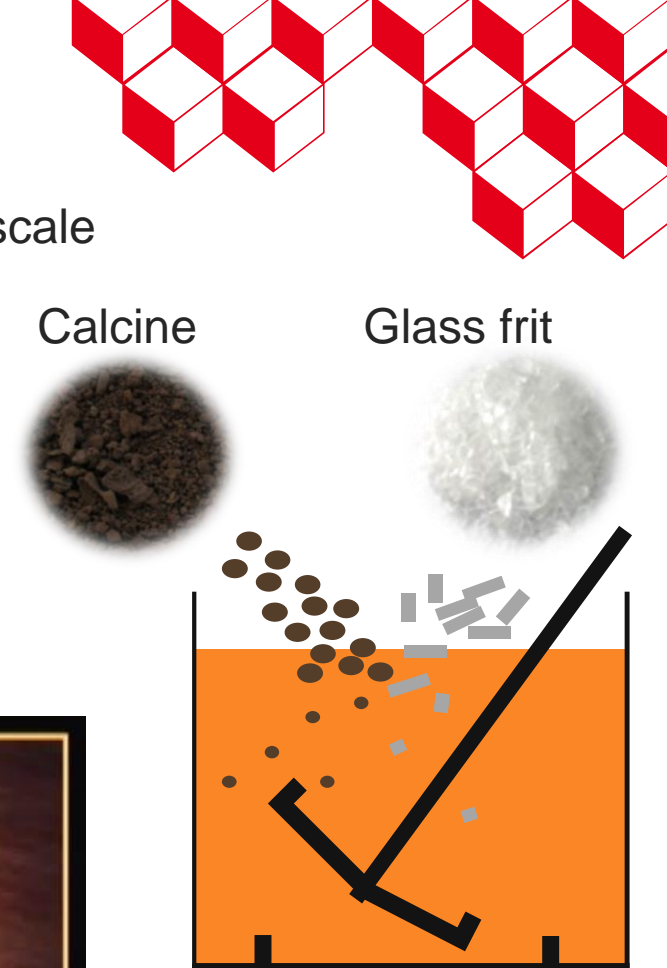
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Context: Vitrification process of nuclear waste

- High-level nuclear waste: processing in glass, stable and sustainable at the atomic scale
- Vitrification process in France:
 - **Nitric solution** of nuclear fission and actinide product
 - **Calcination** (around 450 °C) of nitric solution with calcination additive
 - **Addition of calcine and glass frit** in the vitrification melter (cold crucible or induction heated metal melter)
 - Element **dissolution** into the vitreous network (around 20 weight % in the glass)
 - Melting and strengthening of the glass into metallic container for storage

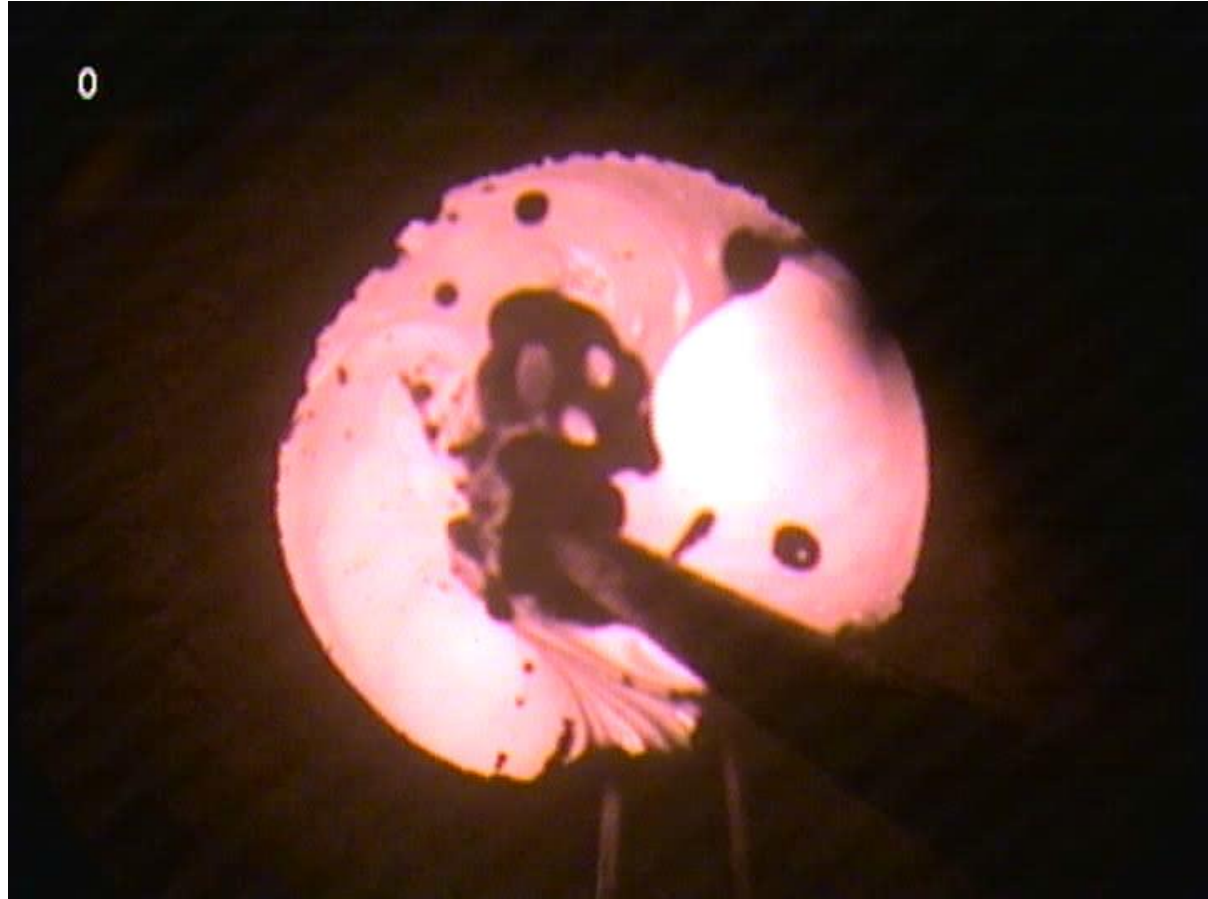


→ Vitrification process by « solid feeding »

Context: Vitrification process of nuclear waste

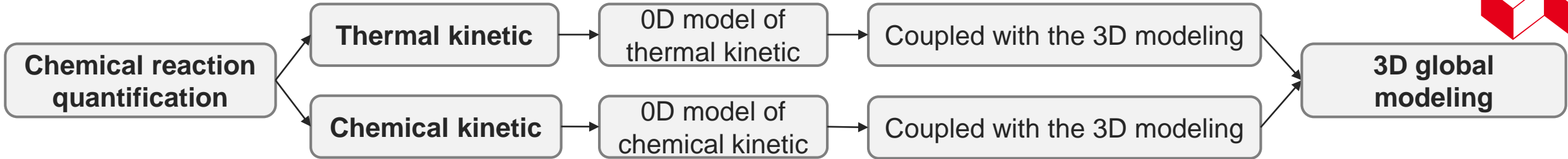
- Other way of vitrification: **liquid radioactive waste directly added at the surface of vitrification melter**
 - No calcination step
 - No calcination additive
 - Production cost reduction

→ Vitrification process
by « liquid feeding »



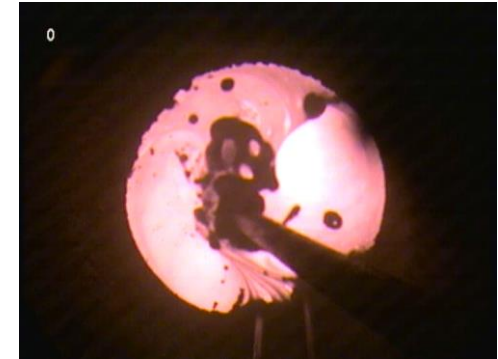
Vitrification by liquid feeding in cold crucible (CEA, Marcoule)

Context: Modelisation of vitrification



Objective: liquid feeding

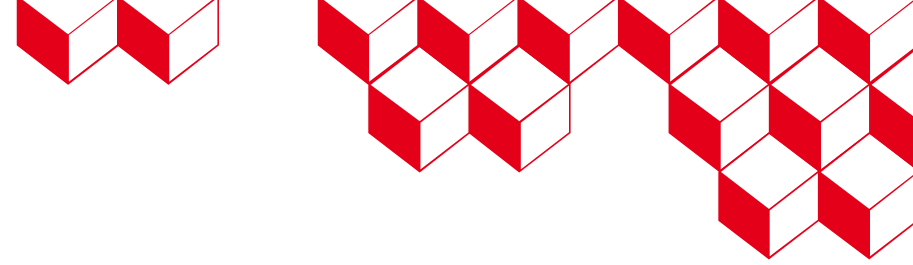
- Modeling liquid radioactive waste vitrification and coupling to the 3D model
- Predict and optimise vitrification process by liquid feeding



- Study of **chemical and thermal kinetics** occurring during the elaboration of nuclear glass by **liquid feeding**
 - Characterisation of the **chemical reactions** between glass frit and the liquid solution
 - Determination of **chemical kinetic of the liquid dissolution** in glass frit
 - Study of the **thermal flow evolution** related to the chemical reactions between precursors
- **Coupling** to the numerical simulation (3D modeling)



- 1. Characterize the chemical reactions between liquid and glass frit in temperature**
- 2. Determine the dissolution kinetic of the liquid in the glass frit**
- 3. Determine the thermal flow evolution related to the chemical reactions between precursors**



- 1. Characterize the chemical reactions between liquid and glass frit in temperature**
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Strategy

1. Characterize the chemical reactions between liquid and glass frit in temperature

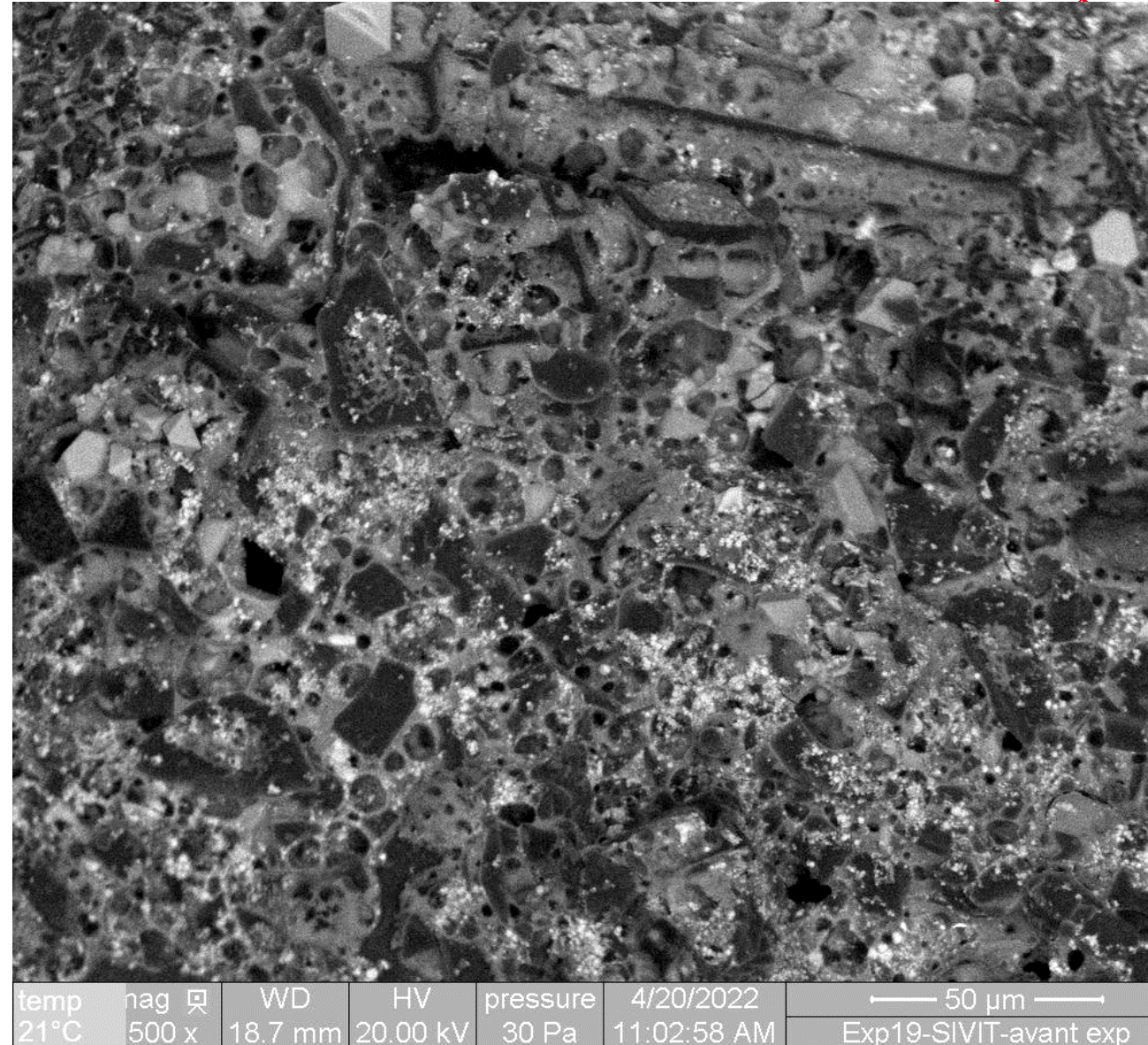
Starting material

- **Liquid waste of UOX type** (without Al and platinoid) + **glass frit**
- Glass frit/glass ratio (F/G) of 0,76 → **waste rate**
- **Liquid solution dried**, not decomposed (100% of nitrates)

- **In situ high temperature experiments** at the ESEM
(Environmental Scanning Electron Microscope)
- Study of **microstructure** and **identification of intermediate compounds** (ESEM)
- **Characterization** of compounds by XRD analysis (X-ray diffraction), phase transformation in temperature
- Correlation of results in order to **identify phase(s) proxy of chemical reaction kinetic**

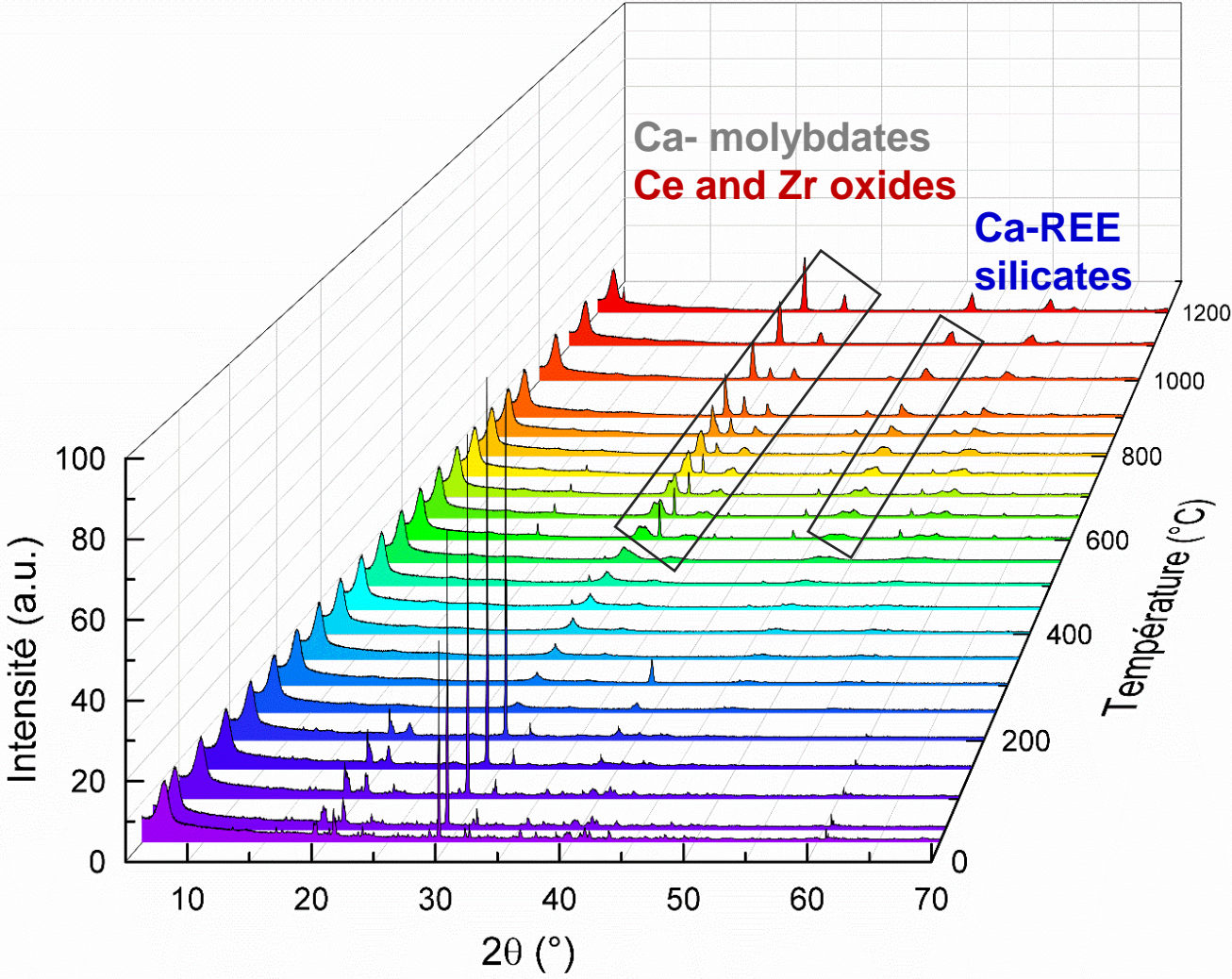
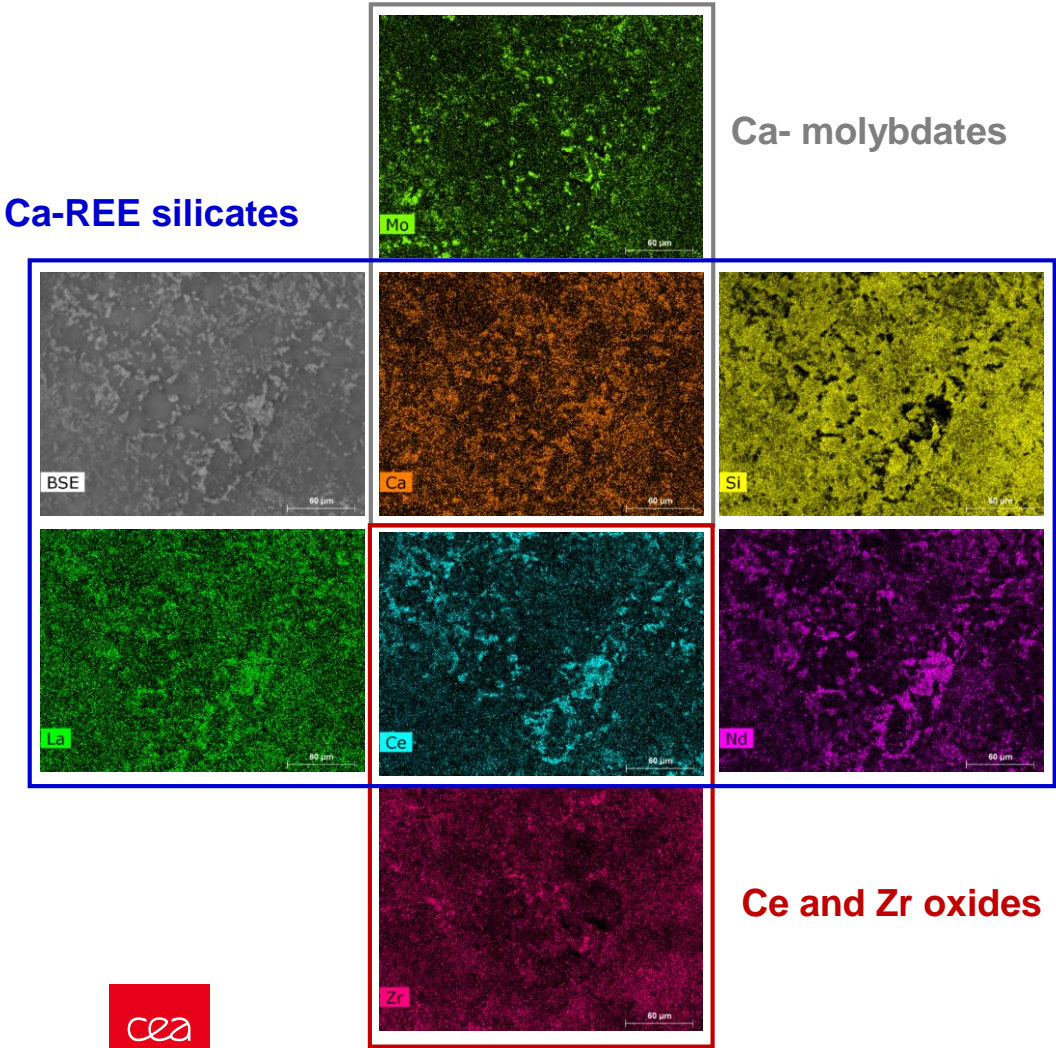
In situ high temperature experiments

- Transformation steps:
 - 185 – 235°C: Na- nitrates melting
 - 240 – 295°C: Na- nitrates melting
 - 450 – 485°C: nitrate decomposition
 - 600 – 630 °C: glass softening, formation of intermediate compounds
 - >730°C: moving glass, decrease of its viscosity; dissolution of intermediate compounds
 - 1000°C: liquid glass + intermediate compounds



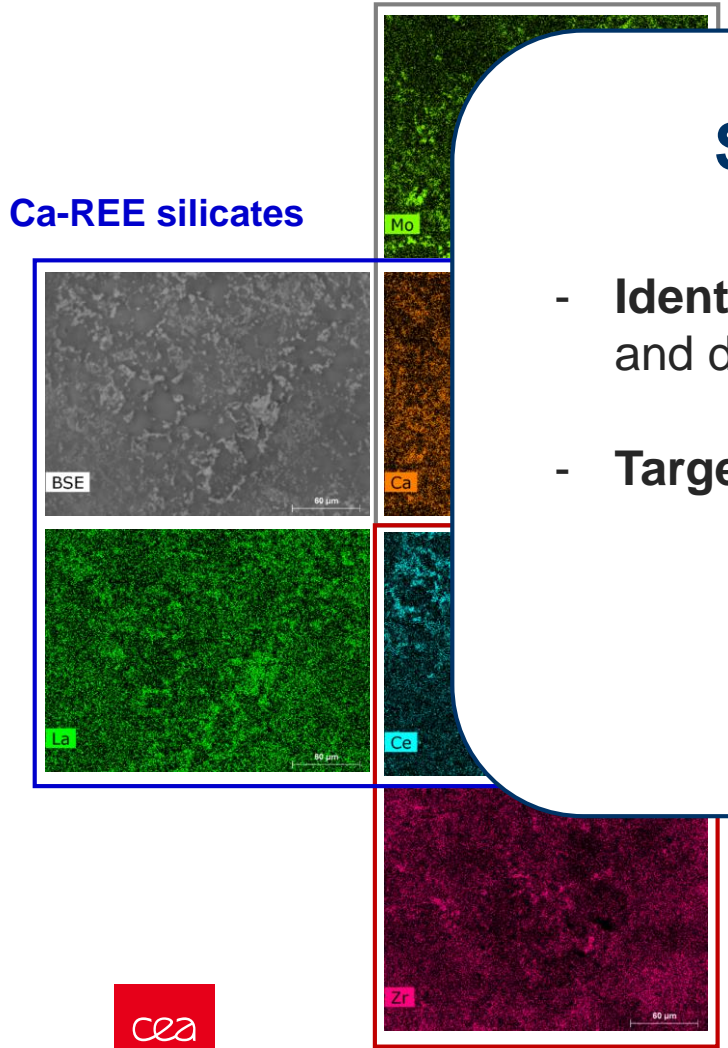
In situ high temperature experiments

- Identification of secondary phases:



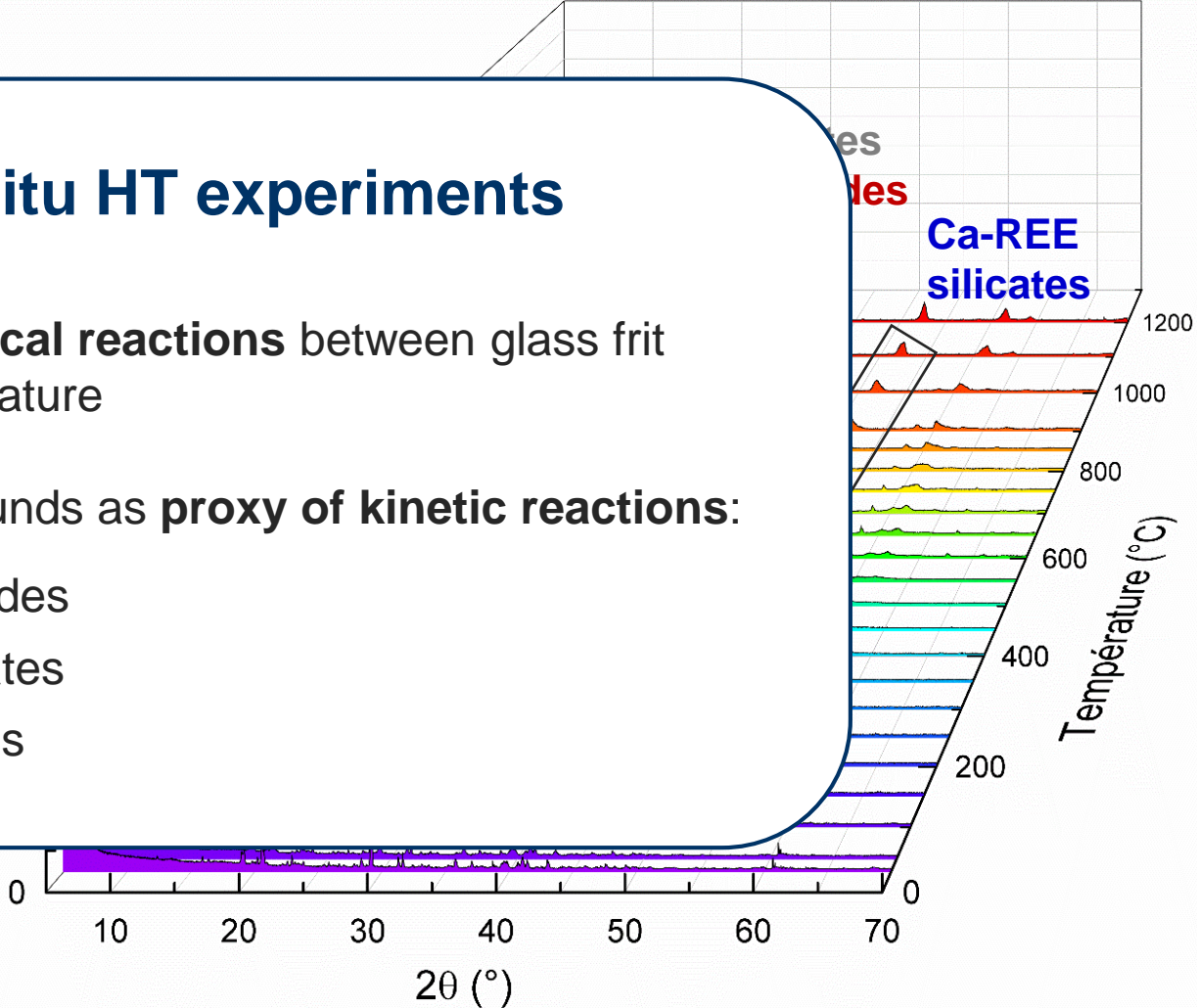
In situ high temperature experiments

- Identification of secondary phases:



Summary of in situ HT experiments

- Identification of the chemical reactions between glass frit and dried solution in temperature
- Target intermediate compounds as proxy of kinetic reactions:
 - Ce and Zr oxides
 - Ca-REE silicates
 - Ca molybdates





1. Characterize the chemical reactions between liquid and glass frit in temperature
- 2. Determine the dissolution kinetic of the liquid in the glass frit**
3. Determine the thermal flow evolution related to the chemical reactions between precursors

Strategy

2. Determine the dissolution kinetic of the liquid in the glass frit

Noyes-Witney equation (1897):

$$C_i(t) = C_{is} \left(1 - e^{-\frac{t}{\tau_i}}\right)$$

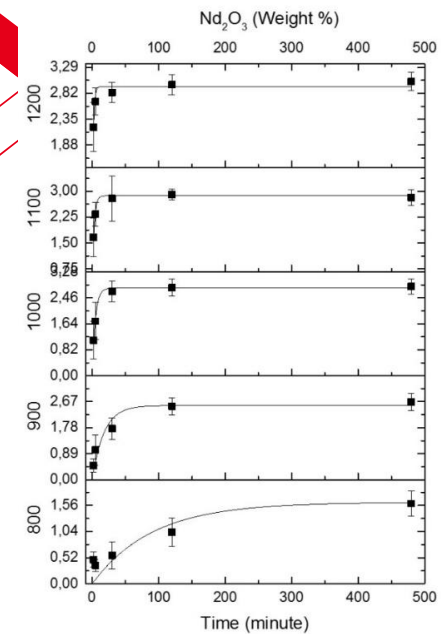
Evolution of element concentration in the glass



Dissolution of the dried solution

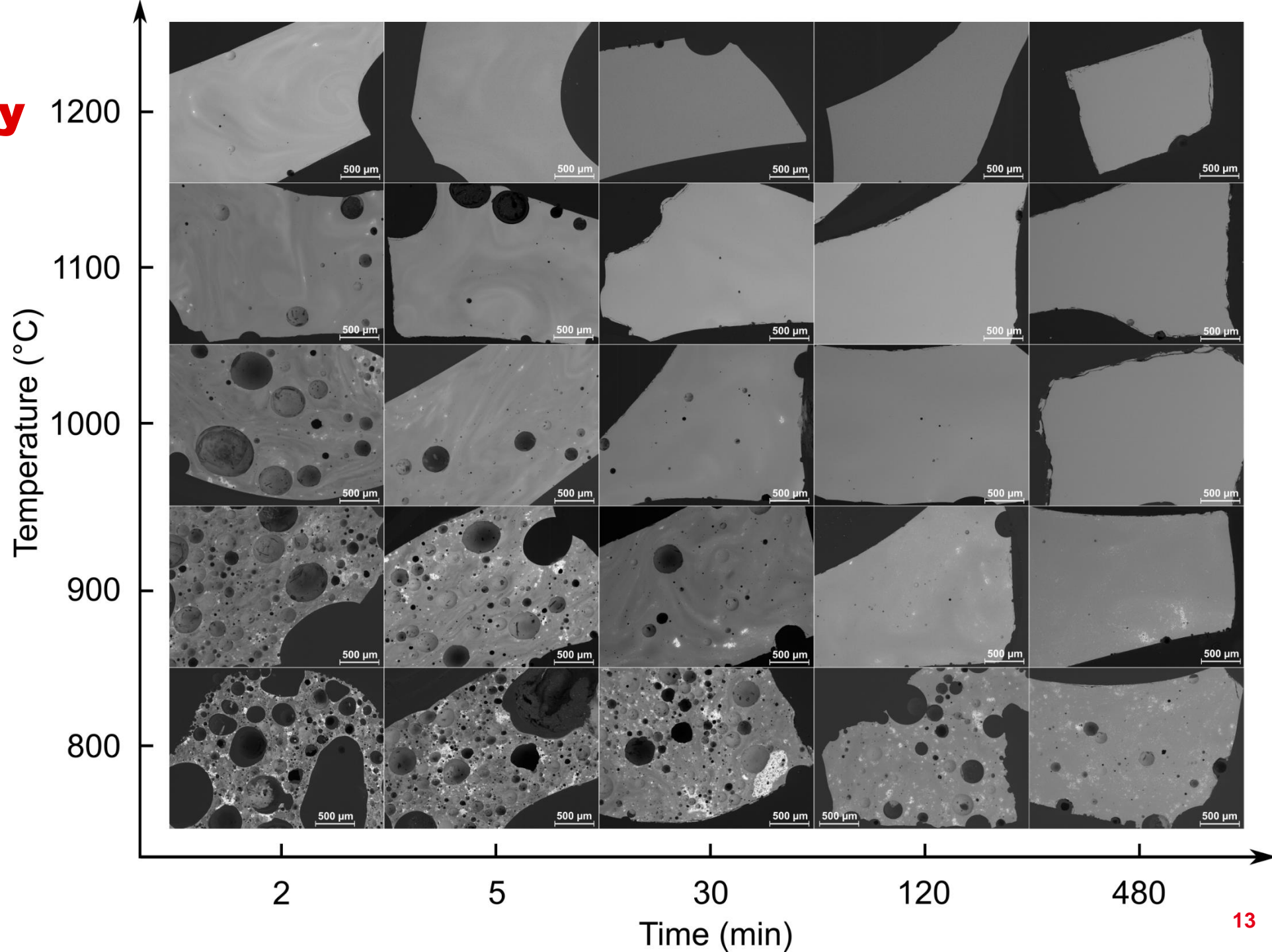


- Experiments in furnace for thermal treatment (25 samples):
 - Crushing of the dried solution and mixing with glass frit powder (F/G of 0,76)
 - Experiments at 800 to 1200°C and during 2-5-30-120-480 min
- Characterization of samples:
 - Study of microstructure and phase identification (SEM)
 - Methodology to analyse glass composition (SEM)
- Parameterization of concentration evolution



HT experiments, glass morphology

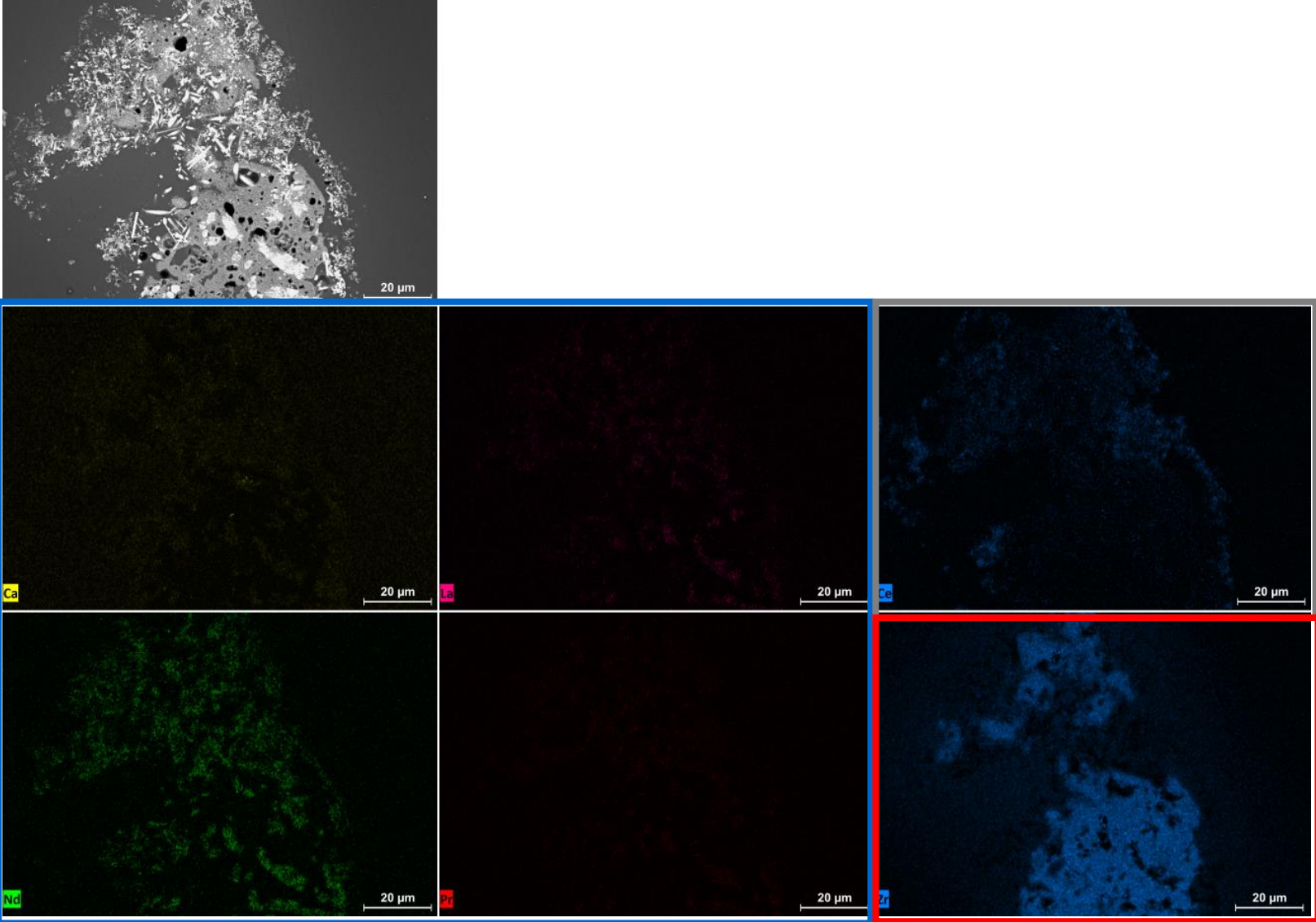
- 800 - 1200 °C and 2 - 480 min, 25 samples
- Evolution of glass morphology
- Secondary phases
- Observation of **secondary phase dissolution** in the glass frit
- **Homogeneous glass at 1200 °C**



Identification of secondary phases

- Chemical mapping:

900 °C – 30 min



Ca-REE- silicate

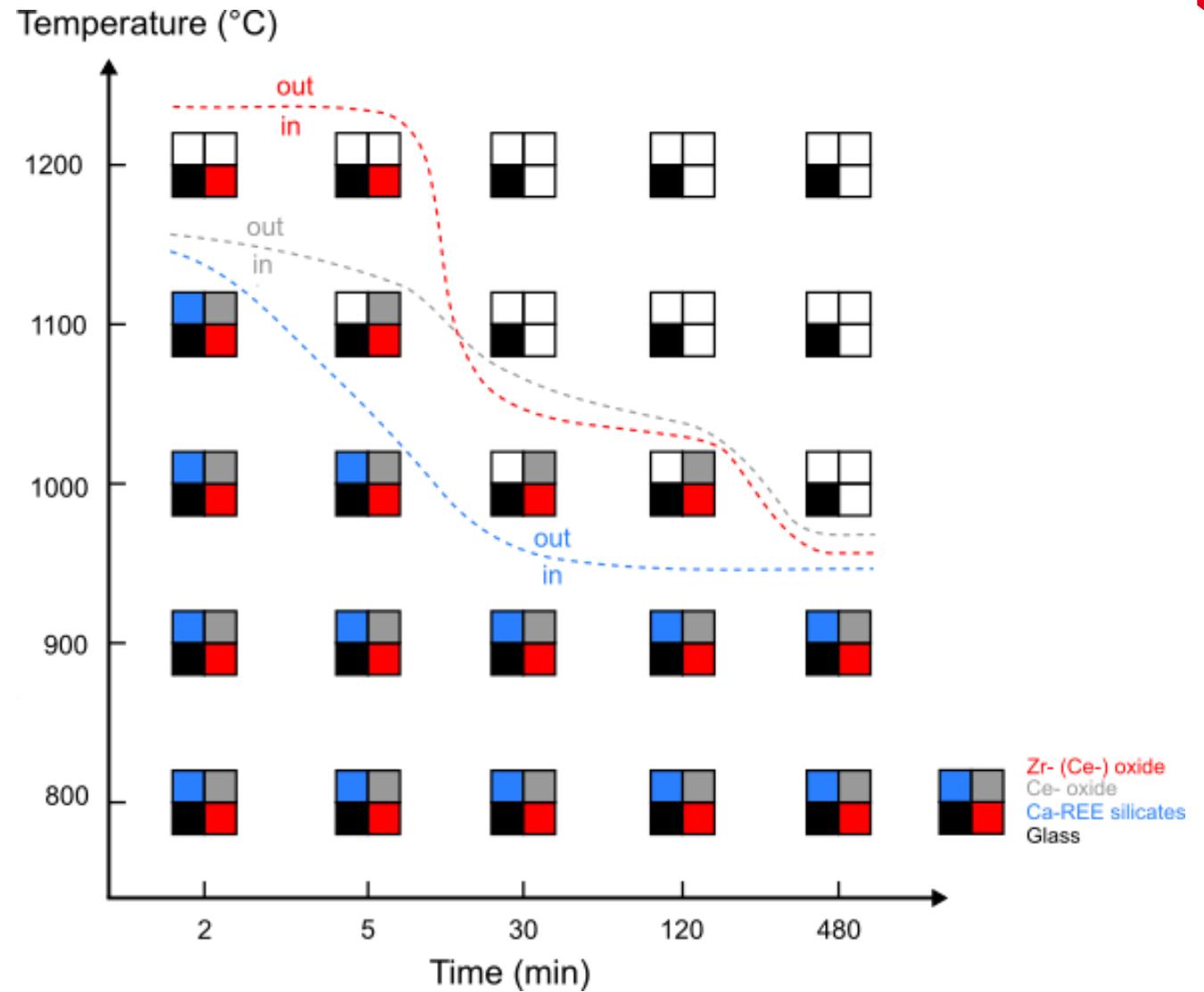
Ce- oxide

Zr- oxide



Identification of secondary phases

- Phase diagram: phase evolution in function of time and temperature
- Phase dissolution order:
 - Silicates de TR et Ca (between 1000 and 1100°C)
 - Ce- Oxide (1100 °C)
 - Zr- (Ce-?) Oxide (1200 °C)



Chemical modeling

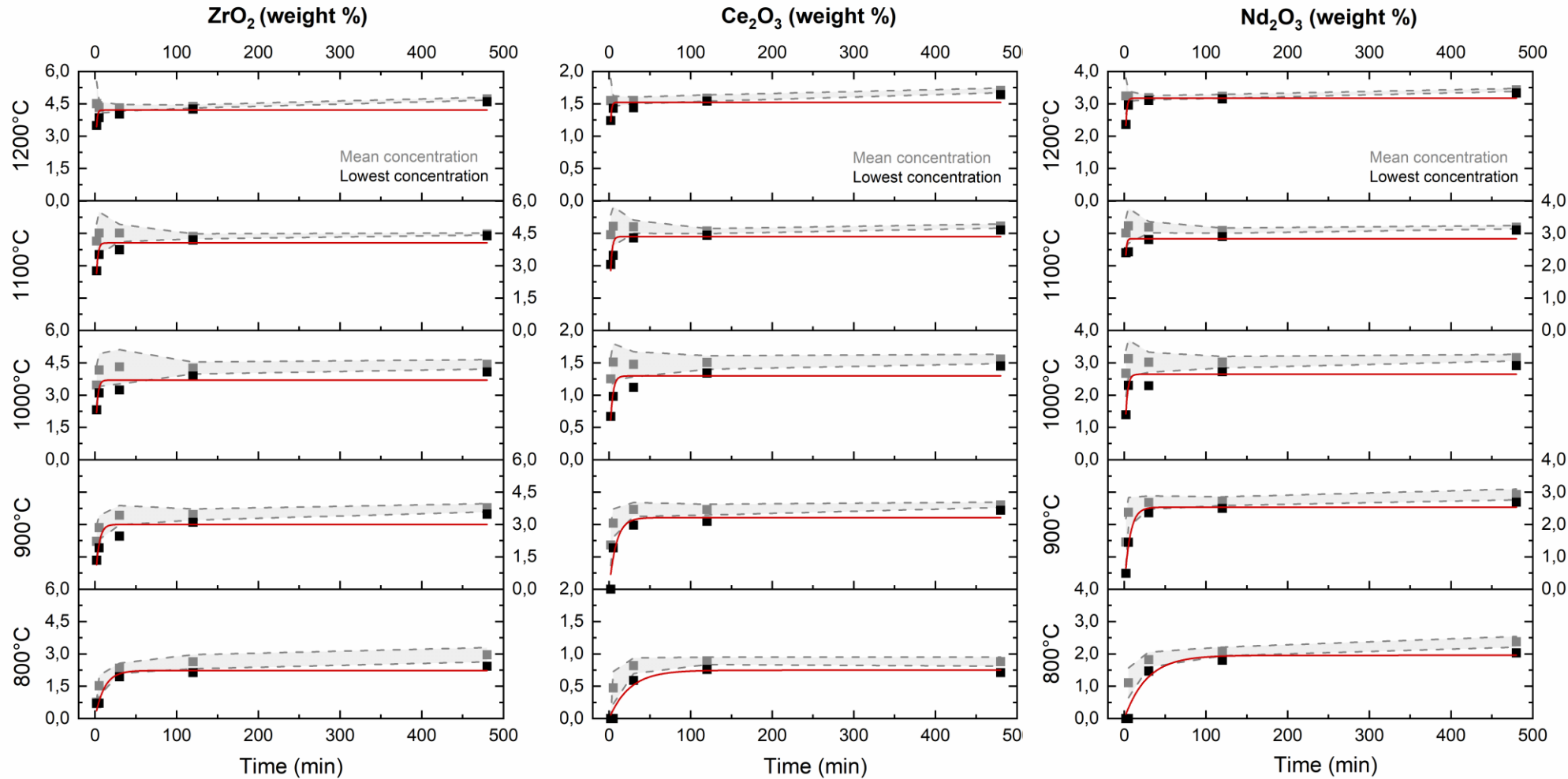
- Calibration and parameterization of element dissolution in the glass (Zr, Mo, Ce, La, Nd and Pr)

$$C_i(t) = C_{is} \left(1 - e^{-\frac{t}{\tau_i}} \right)$$

- Parameterization based on the lowest concentration to describe the **lowest kinetics of the secondary phase dissolution**



C_s (saturation concentration) and **τ** (saturation time) at each temperature

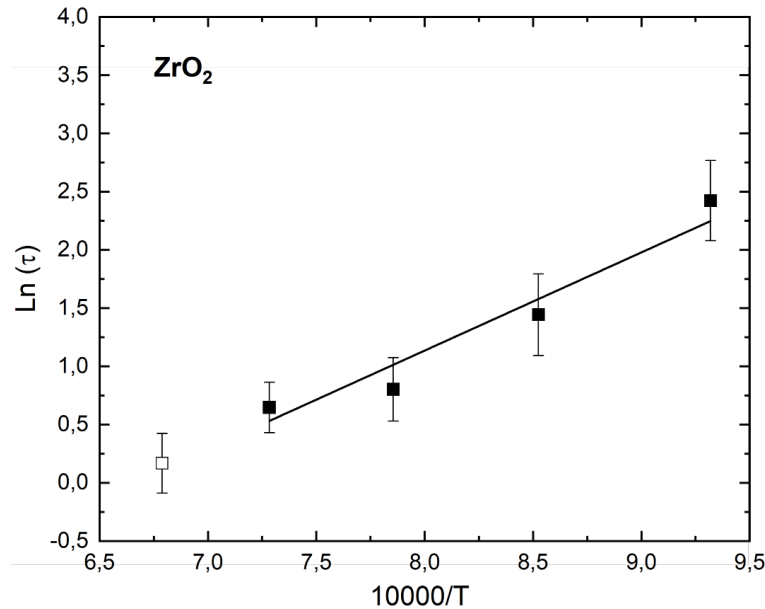


Chemical modeling

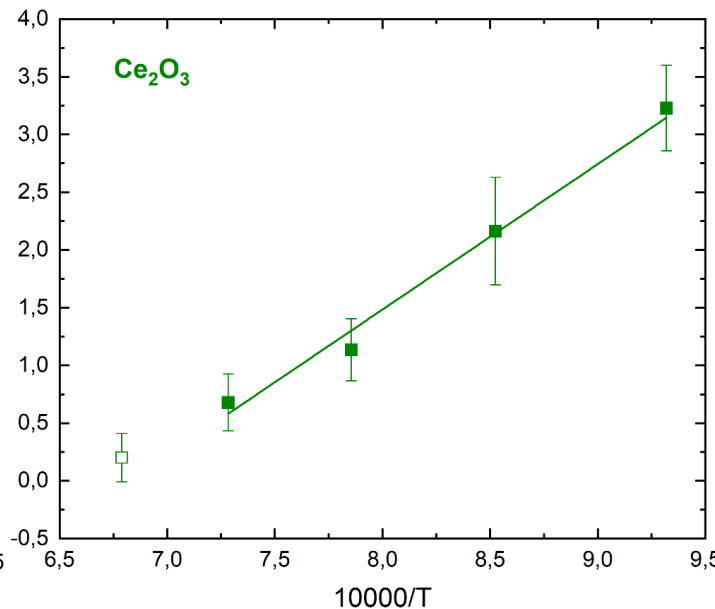
- Calibration and parameterization of element dissolution in the glass (Zr, Mo, Ce, La, Nd and Pr)

$$C_i(t) = C_{is} \left(1 - e^{-\frac{t}{\tau_i}}\right)$$

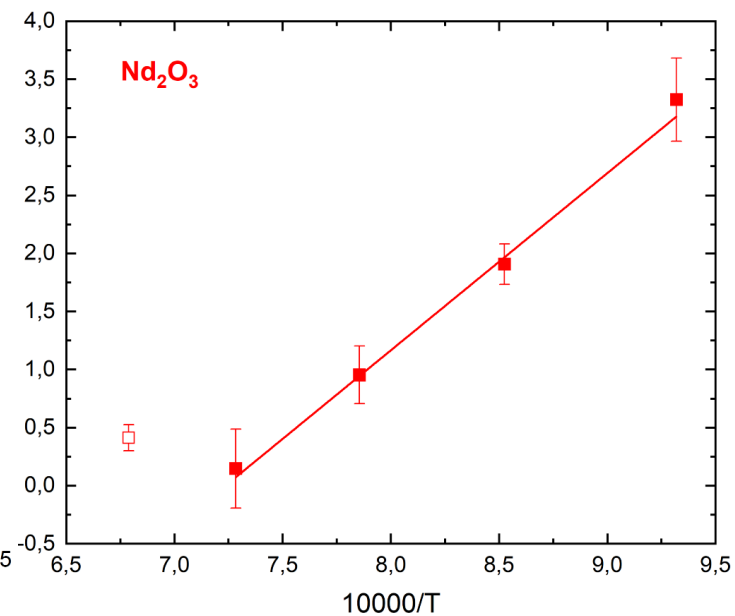
$$\tau = \frac{Ea}{A e^{RT}}$$



$$Ea (\text{ZrO}_2) = 70,08 \text{ kJ.mol}^{-1}$$



$$Ea (\text{Ce}_2\text{O}_3) = 104,72 \text{ kJ.mol}^{-1}$$

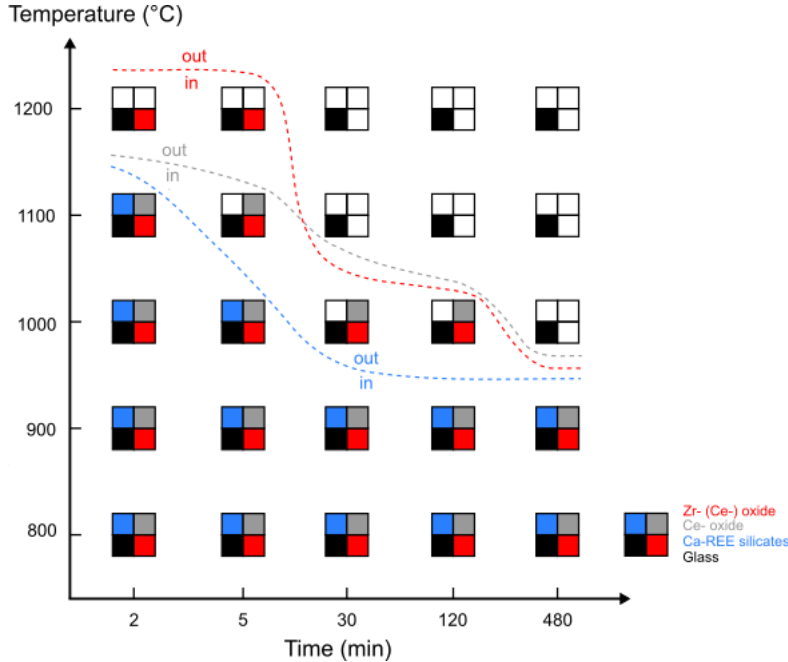
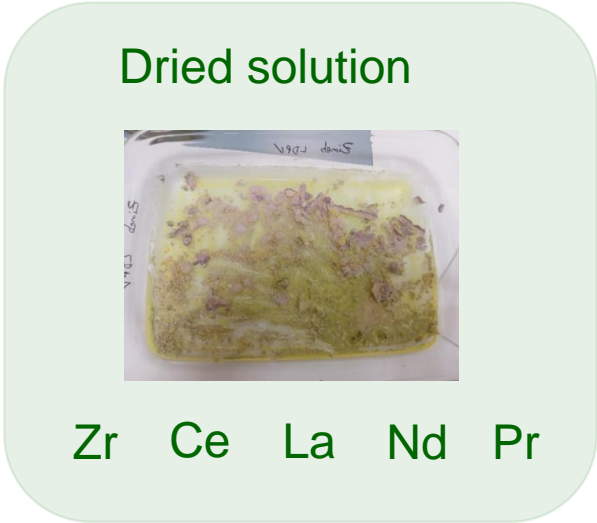


$$Ea (\text{Nd}_2\text{O}_3) = 126,80 \text{ kJ.mol}^{-1}$$

Ea (activation energy) and **A** (pre-exponential factor)

Chemical modeling

- Sum up: dried solution dissolution and secondary phase formation processes



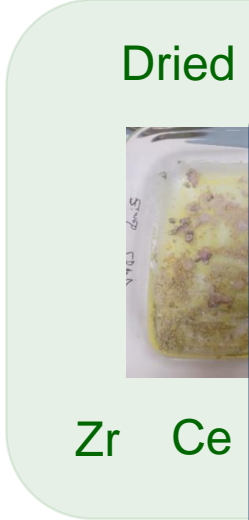
Zr- (Ce-) oxide and Ce- oxide
 Phases inherited from the solution
 → **Dissolution in the glass**

Ca – REE- silicates
 Intermediate compounds
 Dissolution of the dried solution in the glass frit and element diffusion
 → **Formation – dissolution**



Chemical modeling

- Sum up: dried solution dissolution and secondary phase formation processes

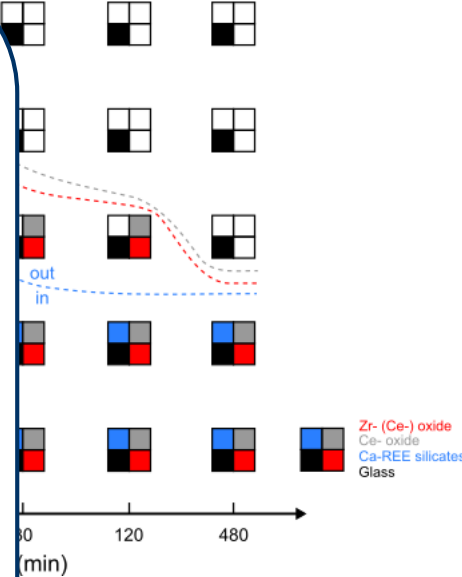


Summary HT experiments

- Determination of the **dried solution dissolution** in glass frit
- Determination of the processes of **secondary phase formation**
- **Methodology valid** in the liquid feeding system

→ **Determination of thermodynamic and kinetic parameters**

Temperature (°C)



Zr- (Ce-) oxide and

Phases inherited from the solution

→ **Dissolution in the glass**

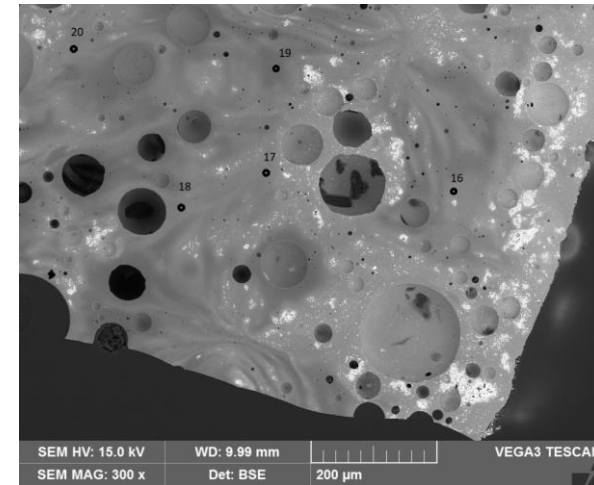
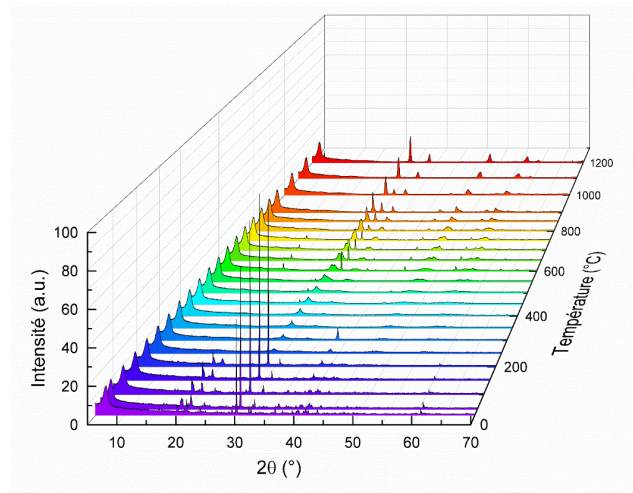
Dissolution of the dried solution in the glass frit and element diffusion

→ **Formation – dissolution**



Conclusion and perspectives

- ▶ Acquire the chemical parameters for the modeling of vitrification process in cold crucible by liquid feeding
 - ▶ In situ high temperature experiments (ESEM and XRD): **Target of kinetic reaction of tracer** in the liquid feeding system (Ce and Zr oxides and Ca-REE silicates)
 - ▶ Thermal treatment experiments (800-1200°C, 2-480 min), study of the **glass composition evolution** to determine **dissolution kinetic of the dried solution**
 - **Methodology valid** in the liquid feeding system
 - **Calibration** and parameterisation of the dissolution kinetic
 - ▶ Modeling of the thermal kinetics based on the denitration reaction (work in progress)
- ➡ **To an implementation of the parameters in a global 3D modeling of the elaboration of nuclear glass by liquid feeding in cold crucible**



- ▶ Change of scale: experiments at intermediate scale by direct liquid feeding (addition of the liquid directly at the surface of the glass melt with a mechanical agitator)

A grayscale micrograph of a cell, likely a yeast or similar microorganism. The cell is roughly circular and contains a large, dark, centrally located nucleus. The cytoplasm is filled with various organelles, including numerous small, dark, spherical granules and larger, lighter-colored vesicles or vacuoles. The cell membrane is clearly visible, and the overall appearance is that of a complex, multi-organellar structure.

Thank you



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Le 23 mars 2023