THE BASICS OF GLASS SYNTHESIS (OXIDE GLASS) & IN-SITU VISUAL OBSERVATIONS OF GLASS MELTING PROCESSES

ICG Spring School Lloret del Mar, April 30th 2024

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Richard Pokorny – University of Chemistry and Technology Prague, Czechia
… with the fruitful help of Sophie Schuller!

CONTENTS

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01

WINDOW & WINDSHIELD: FLOAT GLASS PROCESS

Thermodynamics & Batch melting paths

FLOAT GLASS

GLASS QUALITY CHALLENGE

FLOAT FURNACE = FLAME-POWERED

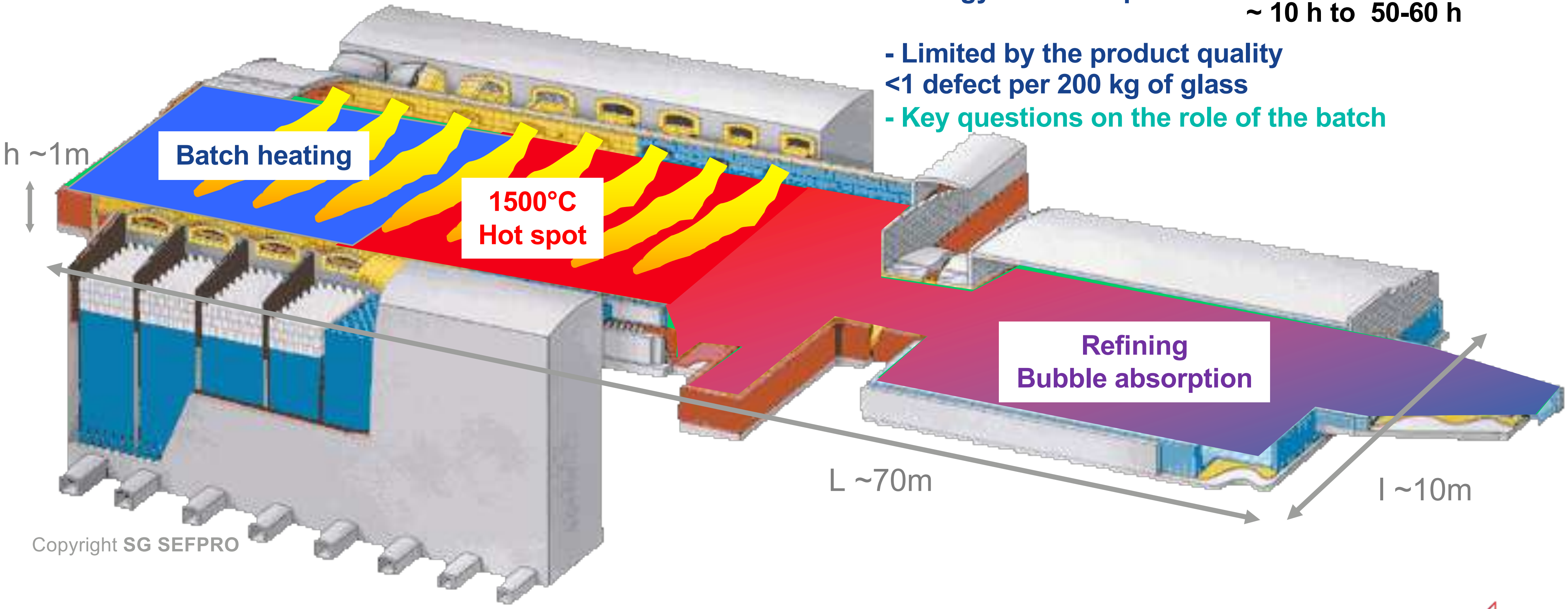
- Energy-intensive process

800 t/d

Residence time

~ 10 h to 50-60 h

- Limited by the product quality
<1 defect per 200 kg of glass
- Key questions on the role of the batch



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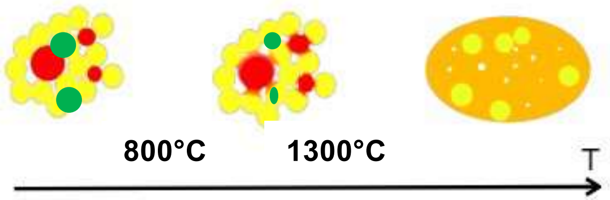
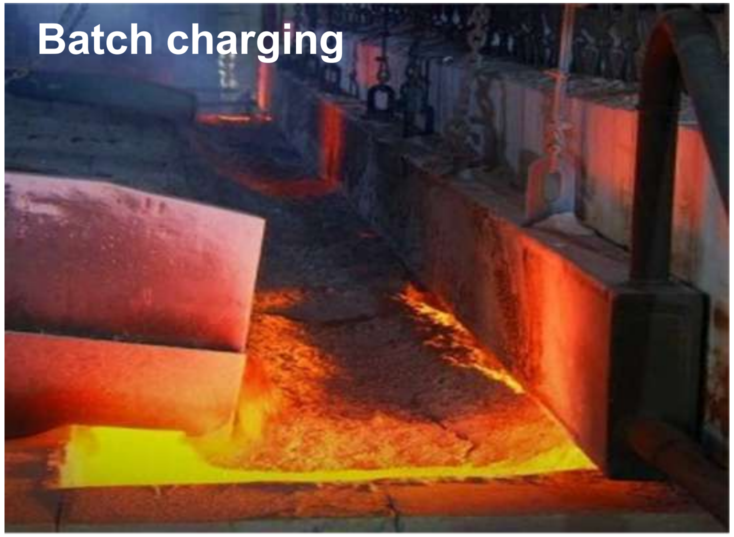
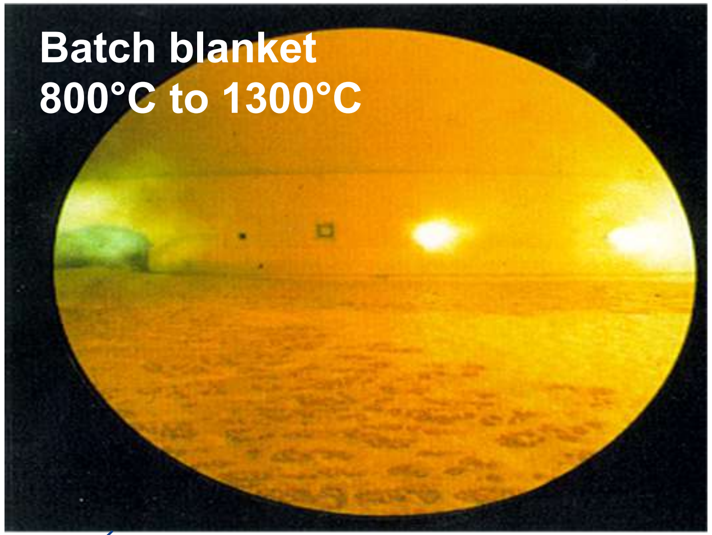
FLOAT GLASS

GLASS QUALITY CHALLENGE

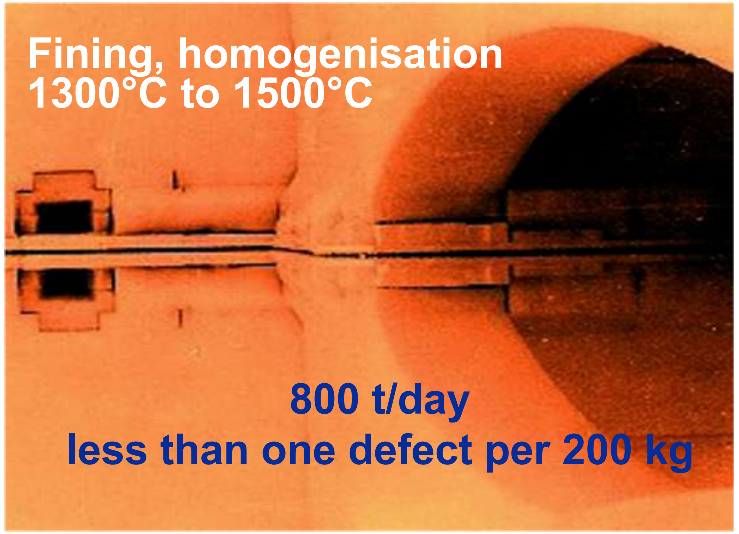




Batch charging

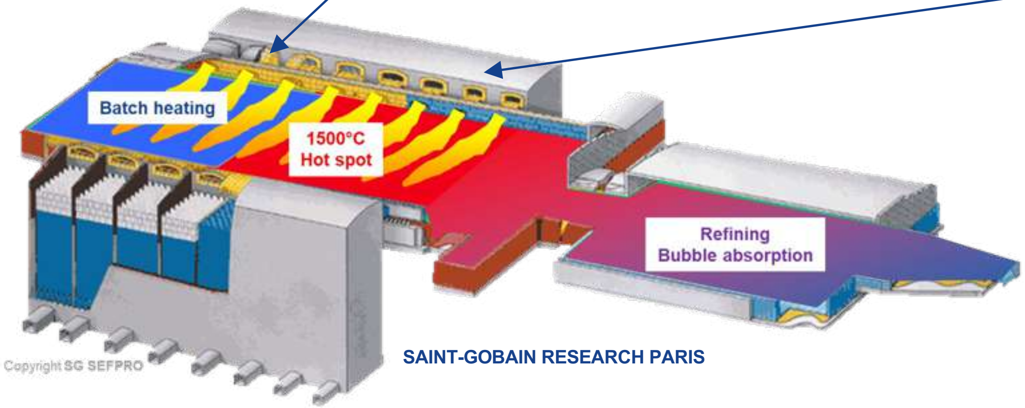


Batch blanket
800°C to 1300°C



Fining, homogenisation
1300°C to 1500°C

800 t/day
less than one defect per 200 kg



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THE SODA LIME SILICATE CASE

BATCH COMPOSITION

**Industrial batch : max 40% recycled glass (cullet)
+ Raw Materials**

Sand	Sodium carbonate	Calcium carbonate	Others	Glass	CO_2
SiO_2	Na_2CO_3	$CaCO_3$			
700 kg	250 kg	200 kg	50 kg	1000 kg	200 kg

SiO_2 + Carbonates + minor constituents ➔ **Silicate + ↑ CO_2**

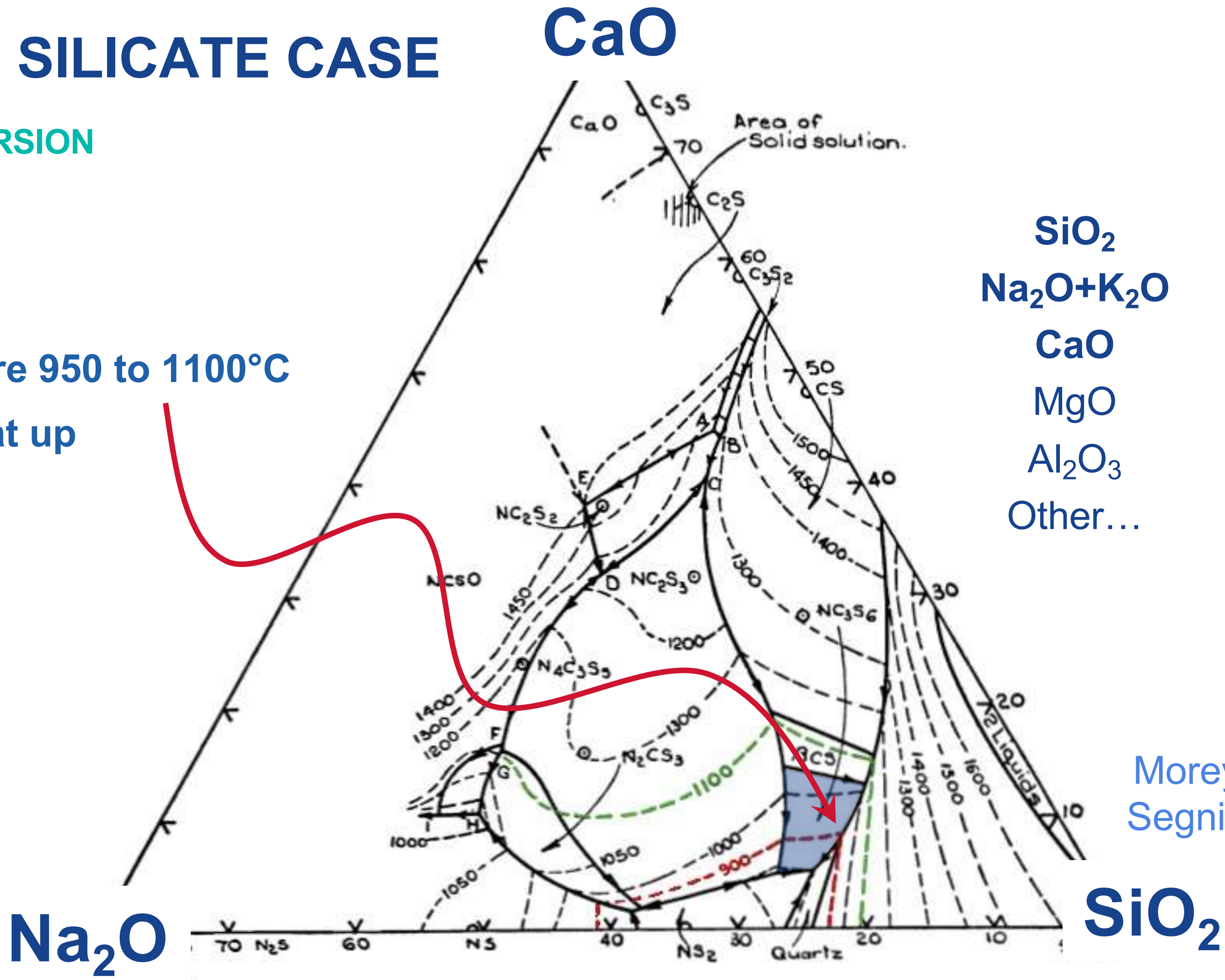
➔ Focus on the melting mechanisms (Fining part with the bubbles elimination. See Franck ☺)

THE SODA LIME SILICATE CASE

BATCH TO LIQUID CONVERSION

Liquidus temperature 950 to 1100°C

But necessity to heat up to 1500 - 1600°C



	wt%
SiO_2	**72**
Na_2O+K_2O	**14.5**
CaO	**10**
MgO	4
Al_2O_3	0.5
Other…	Fe_2O_3

Morey 1930
Segnit, 1953

THE SODA LIME SILICATE CASE

BATCH TO LIQUID CONVERSION

Batch « melting »

a chemical reaction

and not a purely physical process

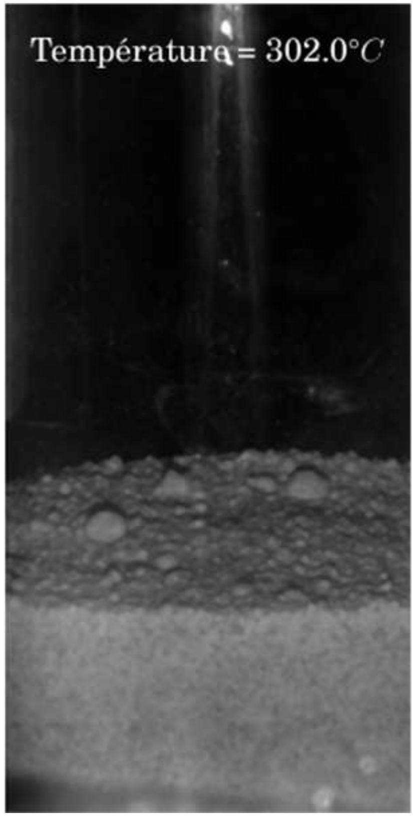
such as the term « melting »

could make one believe

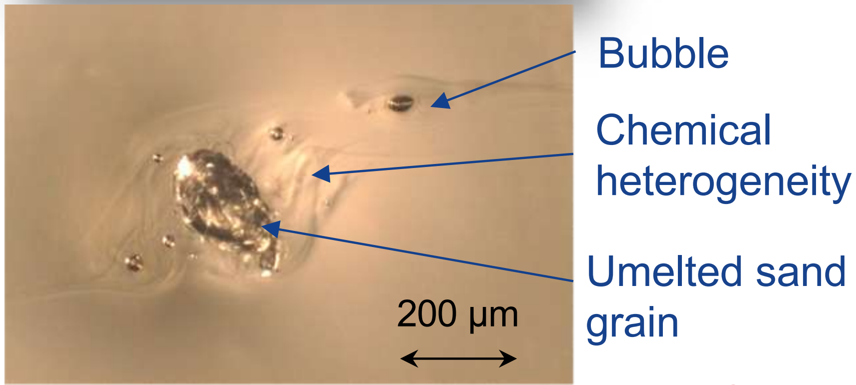
SiO_2 + Carbonates

⬇

Silicates + CO_2



Window glass video
70g batch
J. Meulemans & E. Janiaud Courtesy



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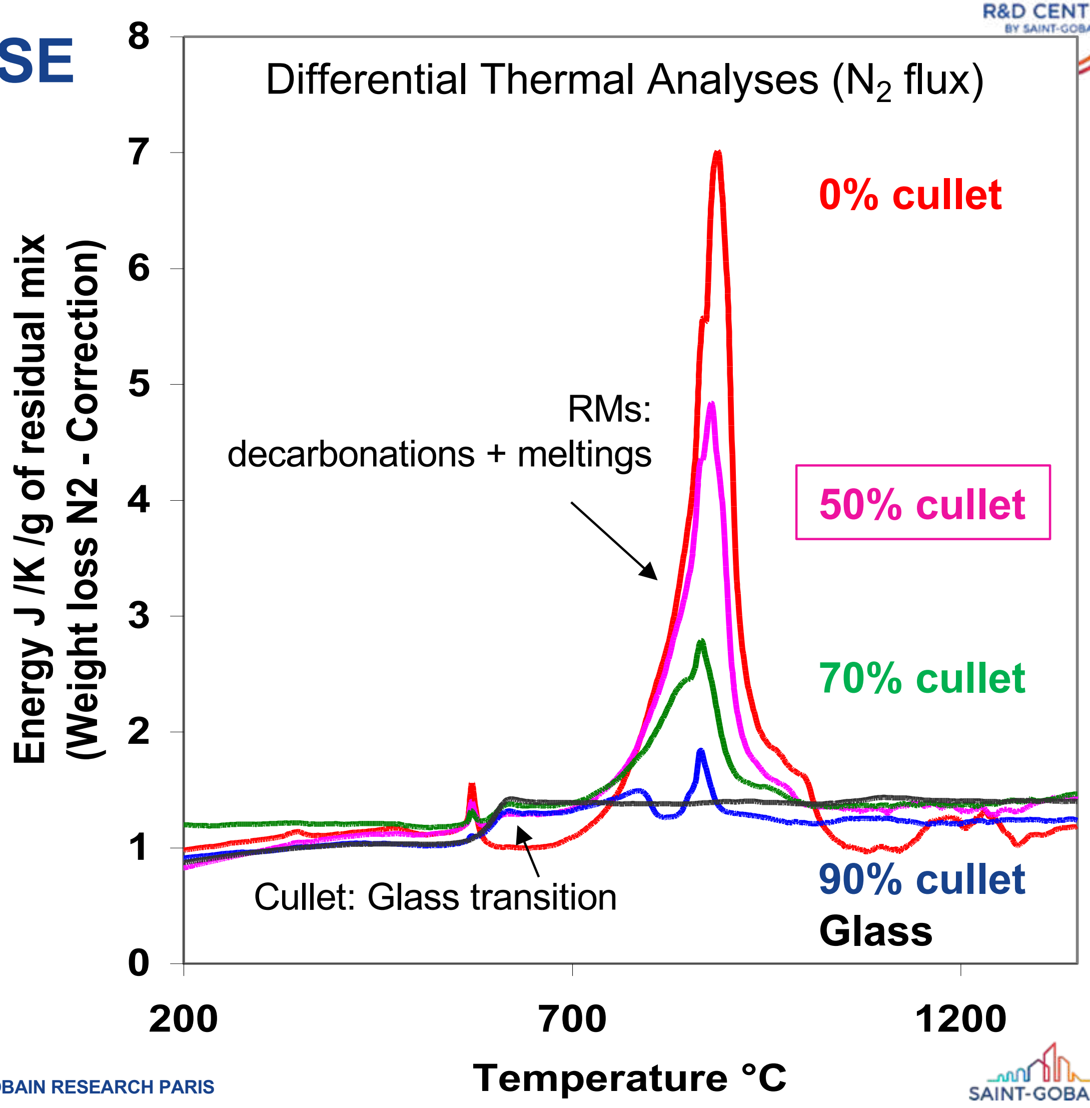
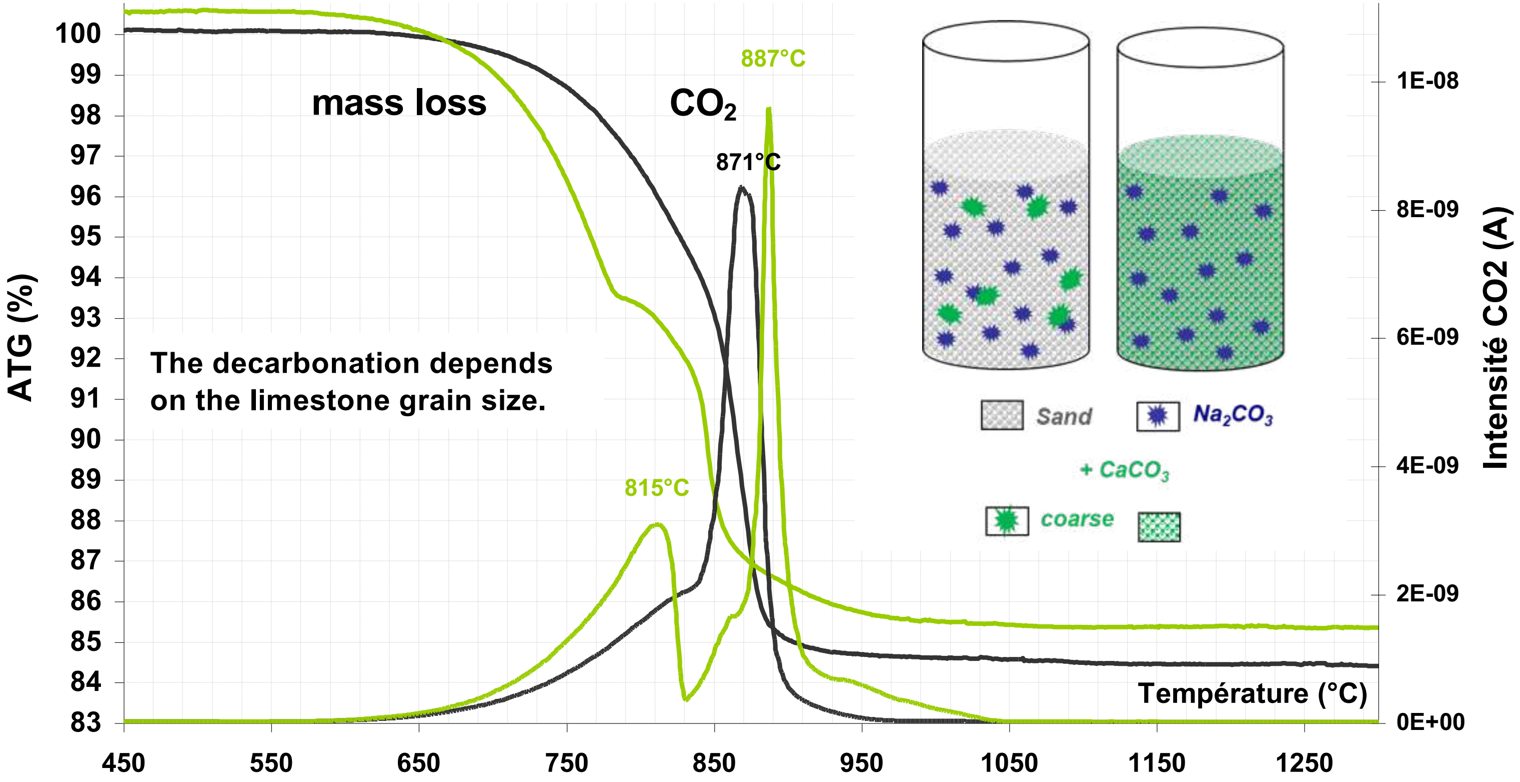


THE SODA LIME SILICATE CASE

INFLUENCE OF THE LIMESTONE GRAINSIZE

fine ➔ coarse limestone



The decarbonation depends on the limestone grain size.

Particle size impacts the melting kinetics.

➔ Modification of the nature of the interactions between the materials.

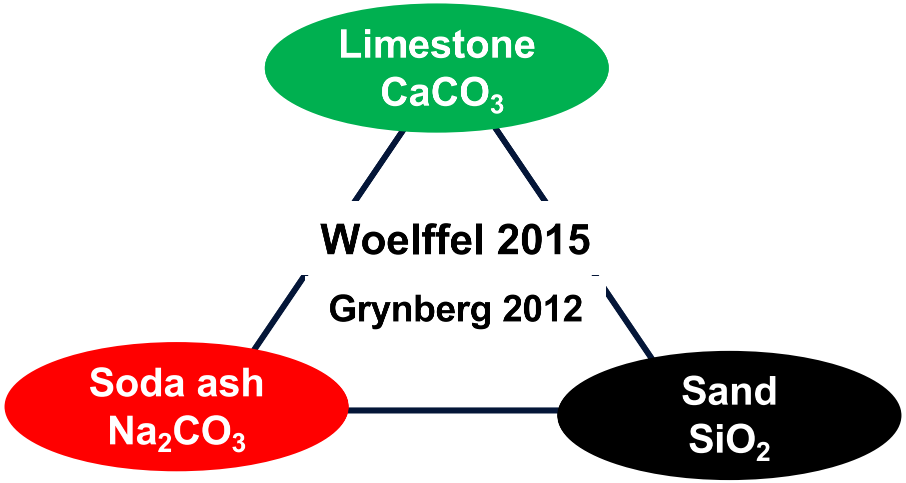
THE SODA LIME SILICATE CA

TERNARY STUDY

Simplification to the ternary

Multiple possible reaction paths

➔ Multiple possible intermediate products



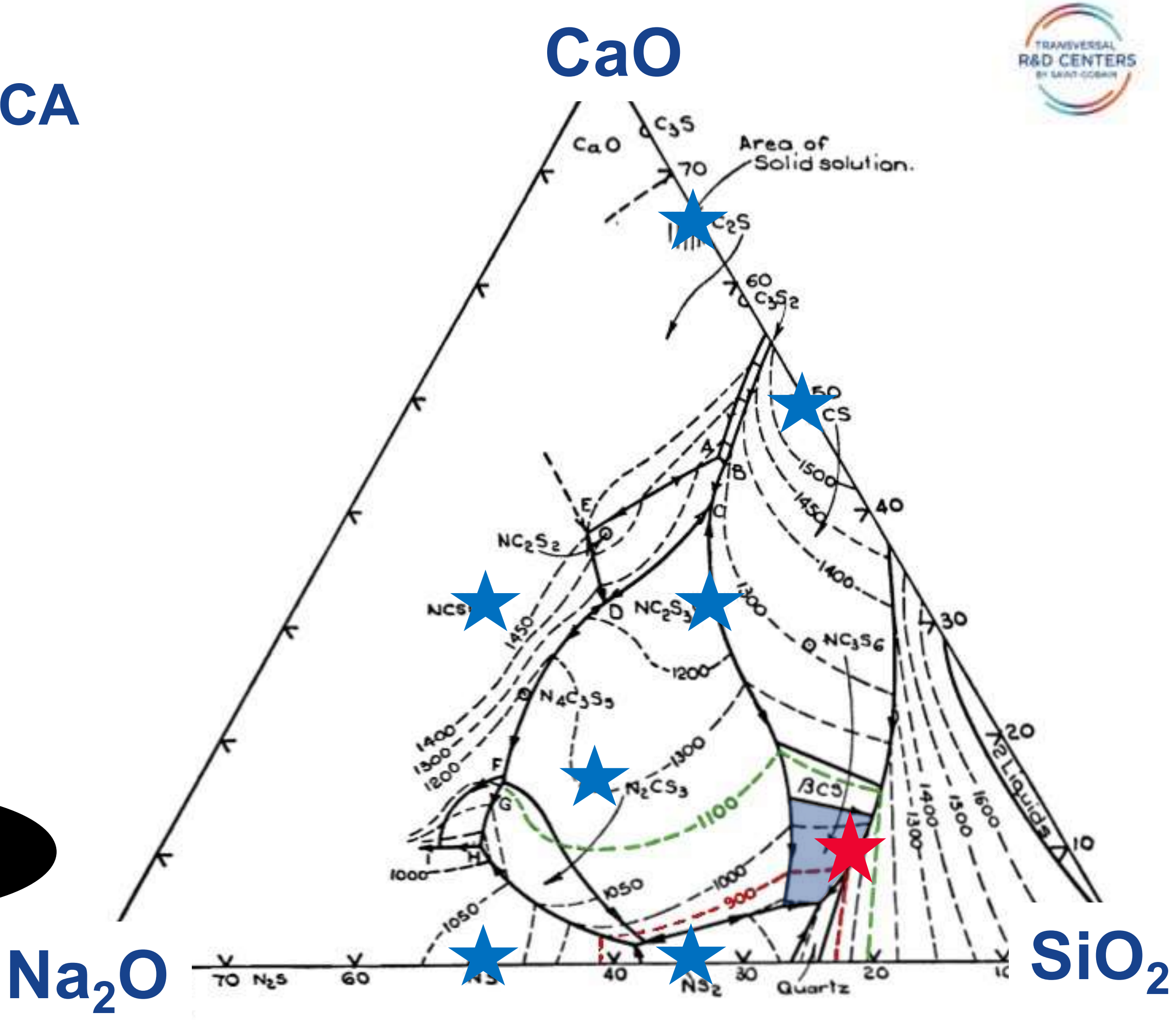
Limestone
$CaCO_3$

Woelffel 2015

Grynberg 2012

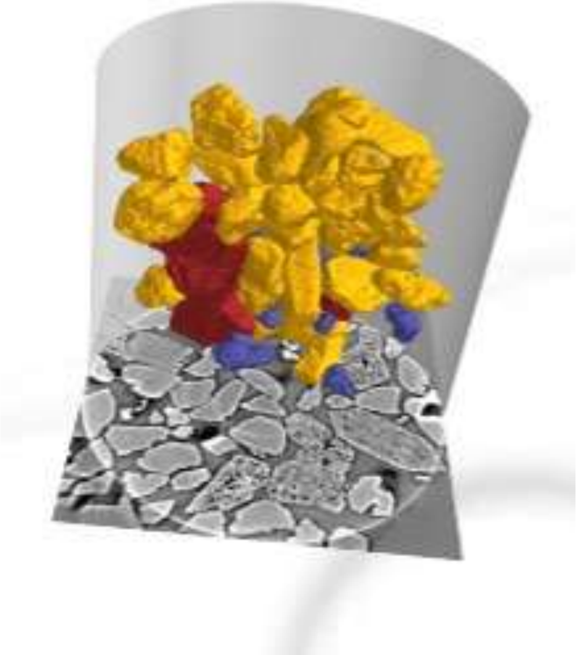
Soda ash
Na_2CO_3

Sand
SiO_2



THE SODA LIME SILICATE CASE

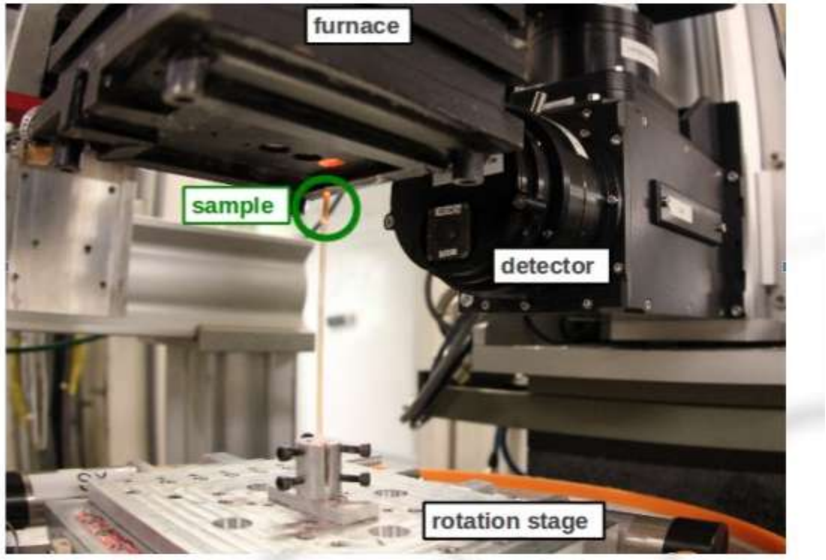
TERNARY STUDY



X-ray Tomography

Homogeneous heating
Image acquisition 1-5s
1µm pixel

ID19 ESRF beamline
Grenoble
France

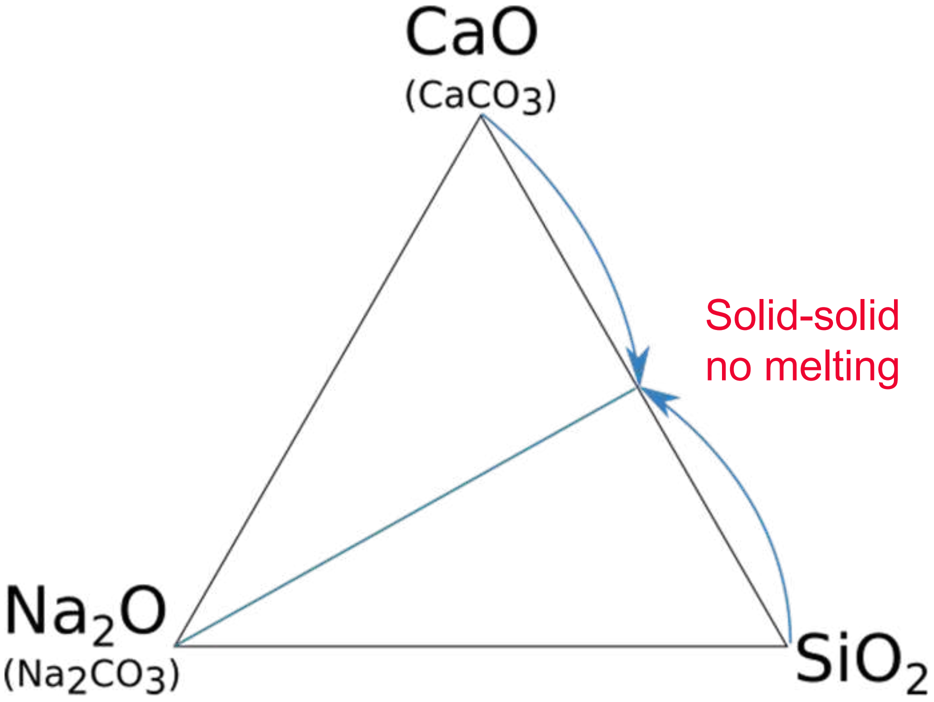


Ecole des Mines furnace
700-1500°C
[Limodin et al., 2009]

THE SODA LIME SILICATE CASE

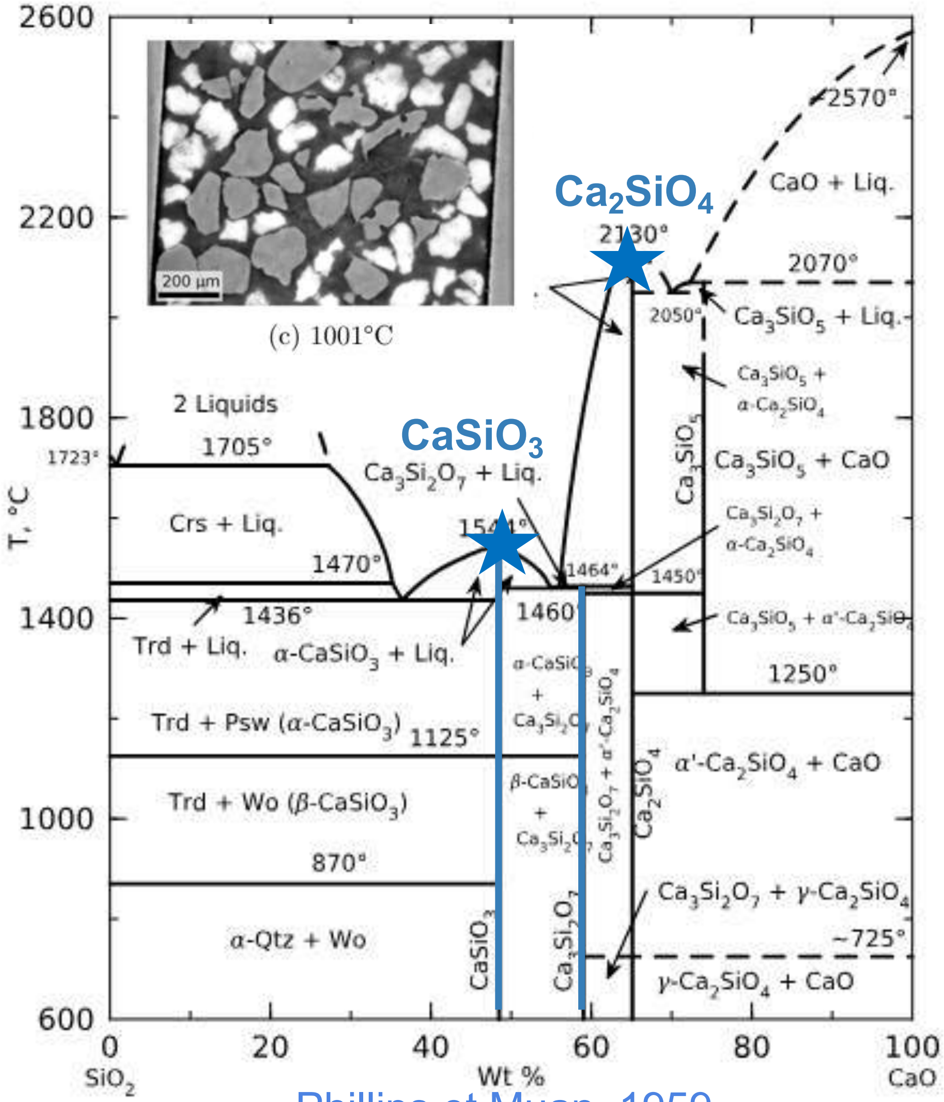
TERNARY STUDY

[1] $(SiO_2\text{-}CaO) + Na_2CO_3$: the impossible path



Solid-solid
no melting

Wilburn, F.W., et C.V. Thomasson. *Physics and Chemistry of Glasses* 2, nº 4 (août 1961): 126-31.

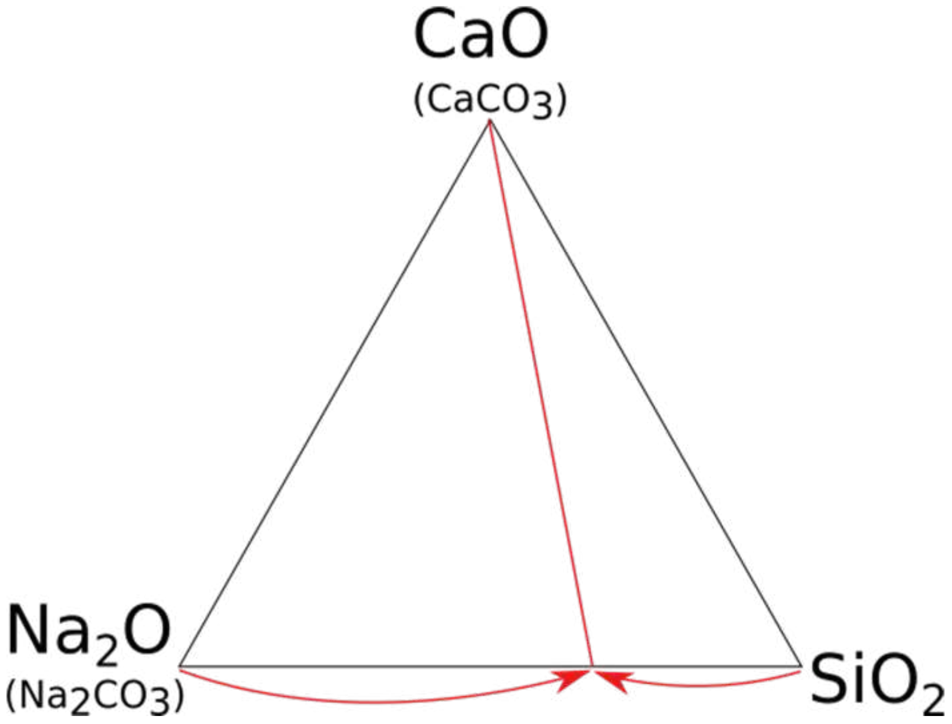


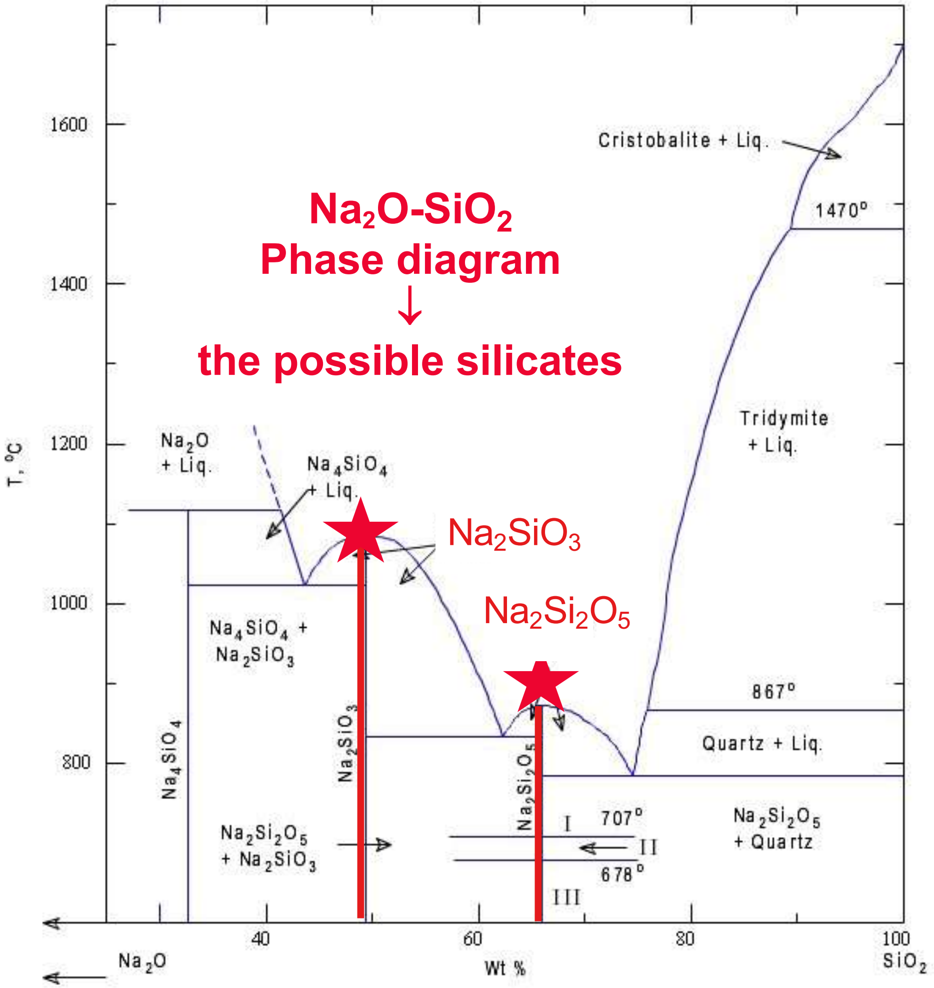
Phillips et Muan, 1959

THE SODA LIME SILICATE CASE

TERNARY STUDY

[2] Sodium silicate path: (Na_2CO_3 - SiO_2) + Ca-carriers





Na_2O-SiO_2
Phase diagram
↓
the possible silicates

Na_2SiO_3

$Na_2Si_2O_5$

[Kracek 1939]

THE SODA LIME SILICATE CASE

TERNARY STUDY

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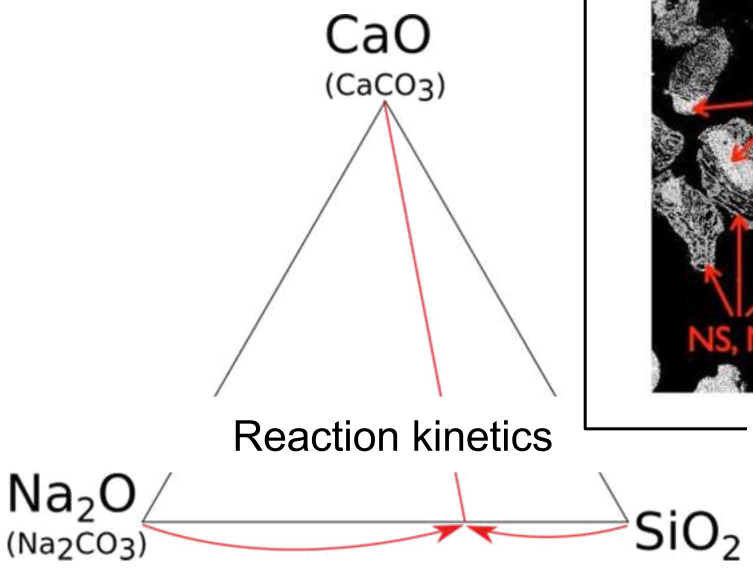
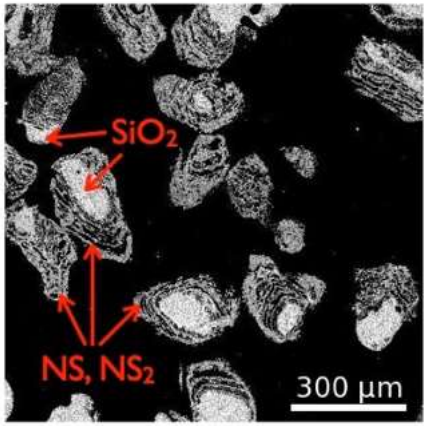


After Na_2CO_3 melting (860°C)

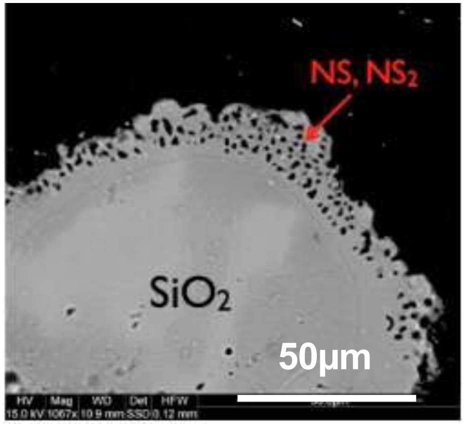
Reactive wetting



900°C 5min

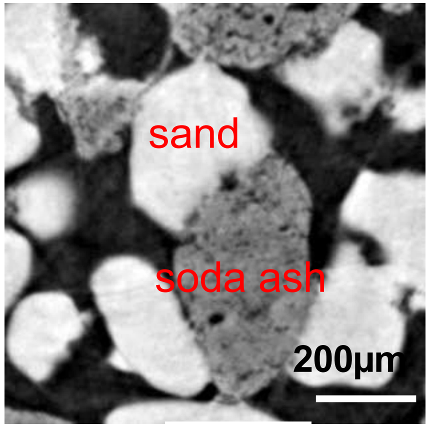
Before Na_2CO_3 melting

Vapor phase reaction



820°C 4h

Solid state diffusion



780°C

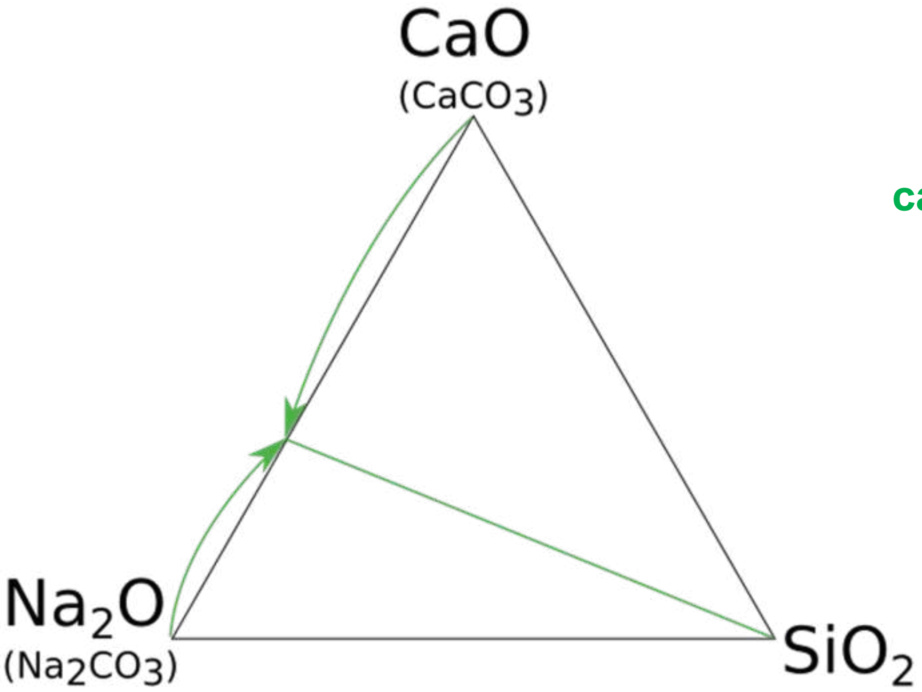
Dependance on the atmosphere (PCO_2, PO_2)

[Grynberg et al., 2015] IJAGS, [Gouillart et al., 2012] JACerS

THE SODA LIME SILICATE CASE

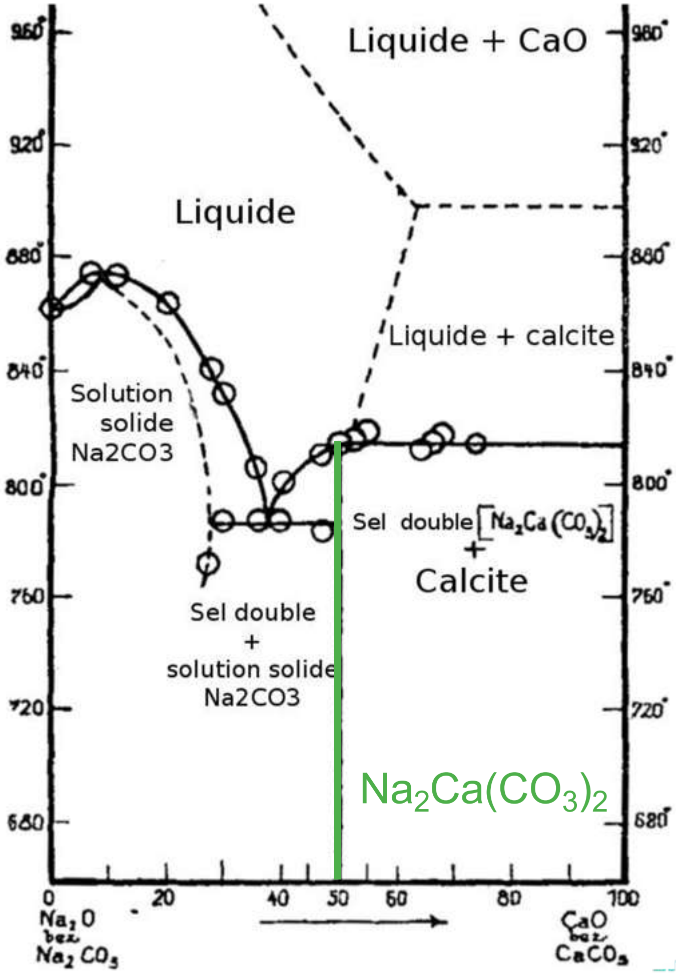
TERNARY STUDY

[3] The mix carbonate path: (Na_2CO_3 - $CaCO_3$) + SiO_2



Contact between carbonates ➔ mix carbonates

Even without CO_2



THE SODA LIME SILICATE CASE

TERNARY STUDY

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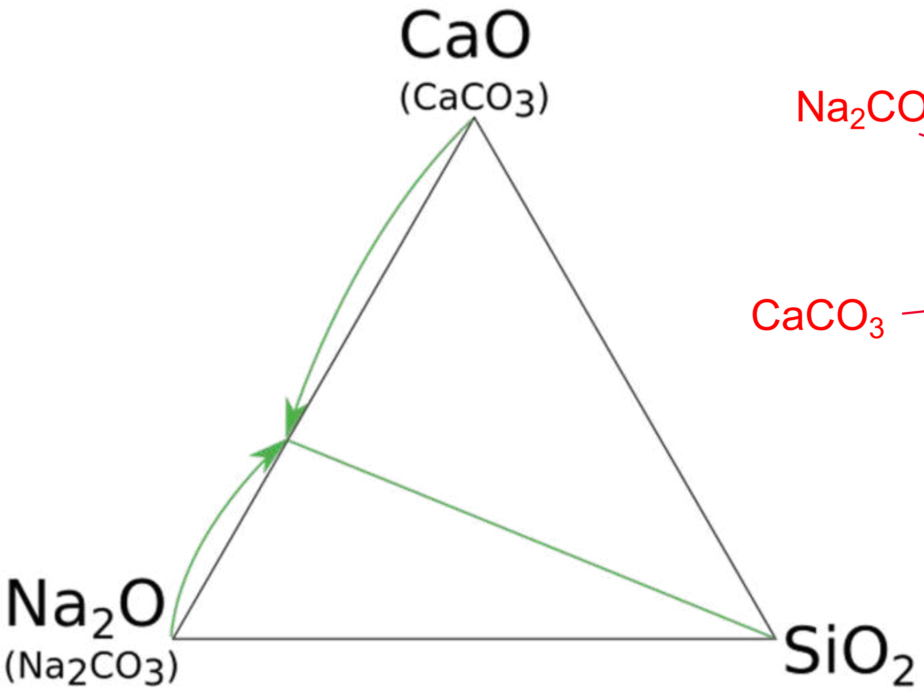
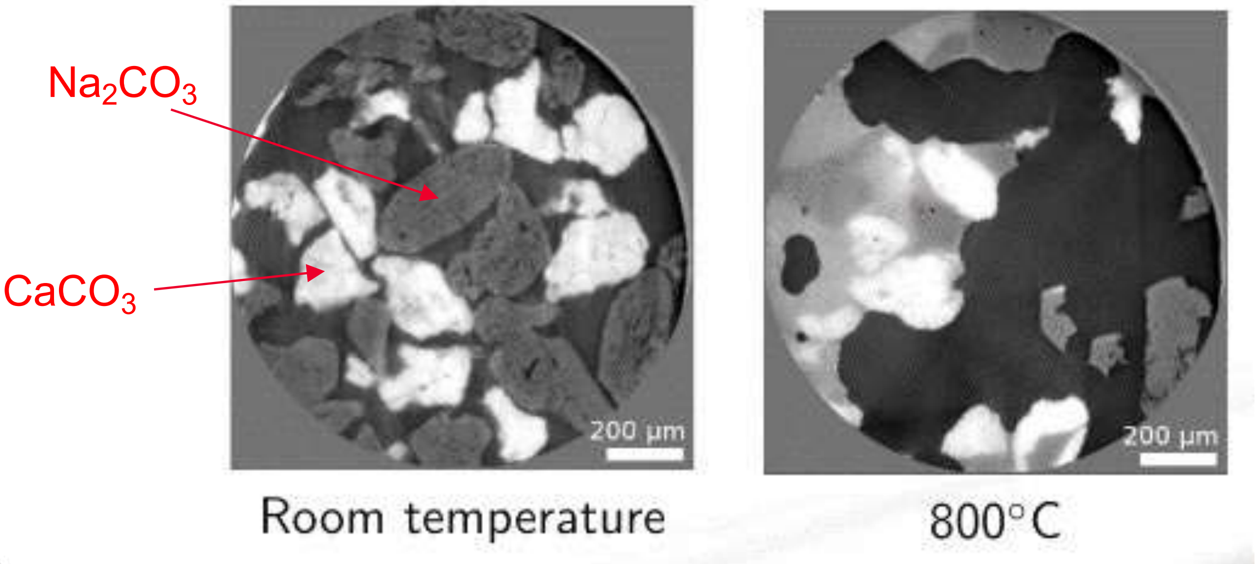


Formation of double carbonate is possible, with sufficient PCO_2



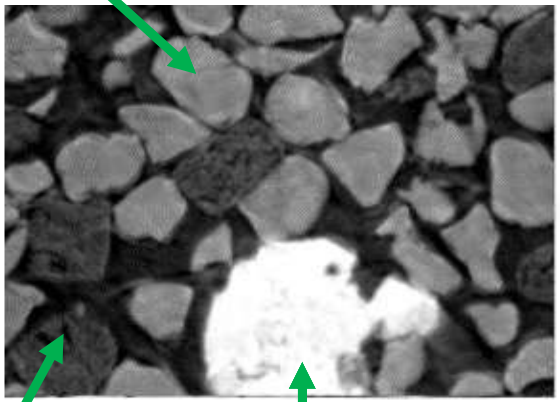
[Woelffel 2015]

THE SODA LIME SILICATE CASE

HOW THE FINAL QUALITY IS LINKED TO THE REACTION PATHS

Ternary mixture SiO_2, Na_2CO_3, $CaCO_3$

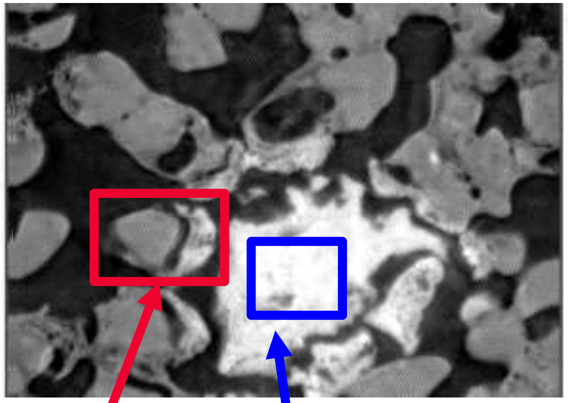
Fast heating at 900°C - 1 image in 1s every 6s



SiO_2

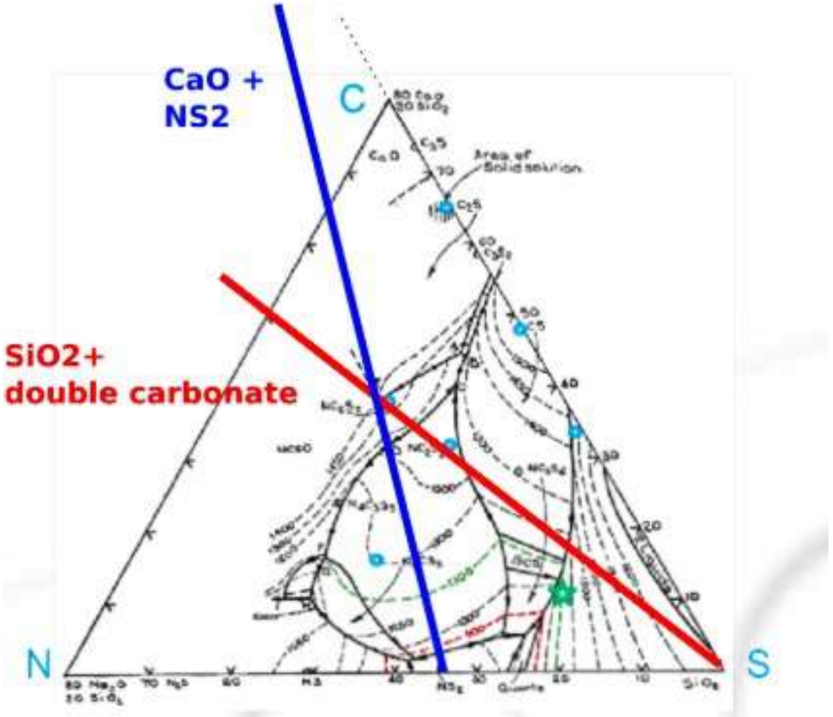
Na_2CO_3

$CaCO_3$



CaO

Double carbonate

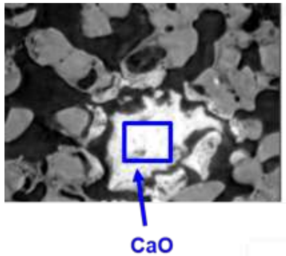


[Woelffel 2015]

Boundary : formation of double carbonate ←→ Core : formation of CaO

THE SODA LIME SILICATE CASE

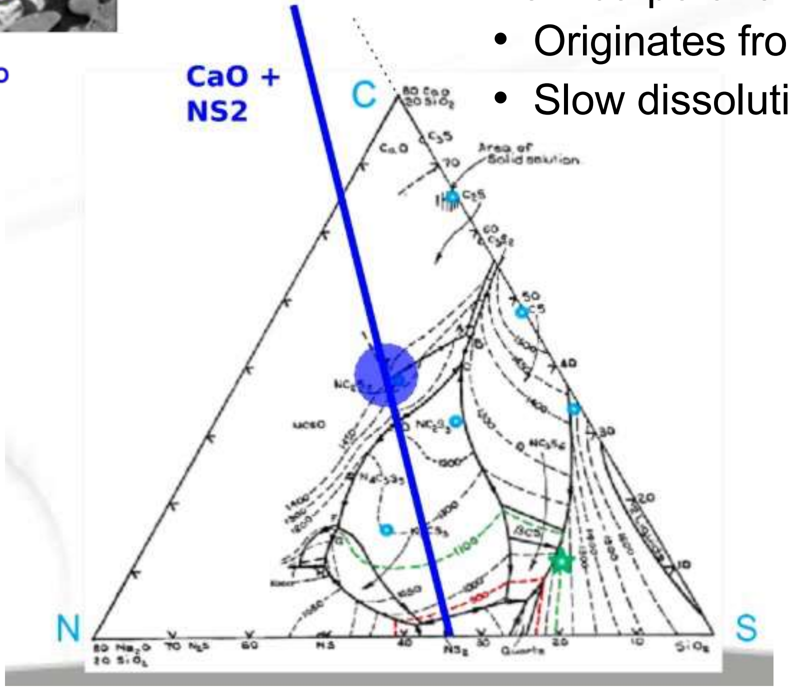
HOW THE FINAL QUALITY IS LINKED TO THE REACTION PATHS

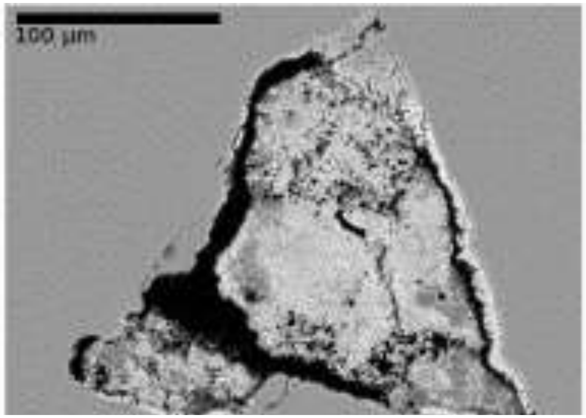


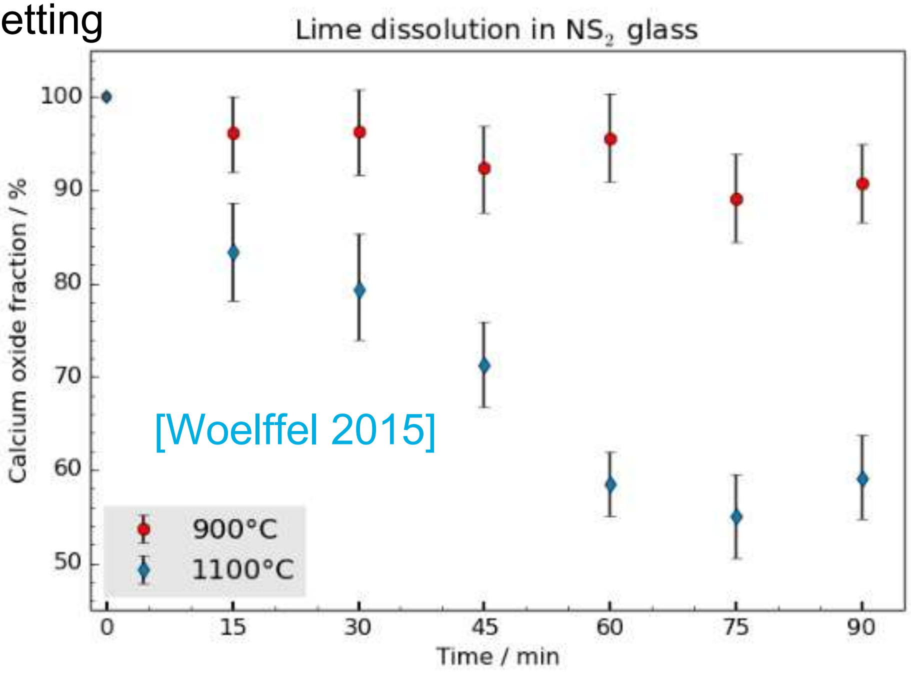
Core of CaO stays **unreacted** for a long time

➔ Delay in the formation of molten silicates

- Lime incorporation is slow
  - Originates from dewetting
  - Slow dissolution





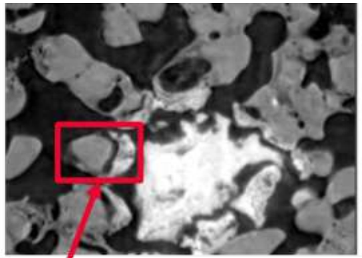


[Woelffel 2015]

THE SODA LIME SILICATE CASE

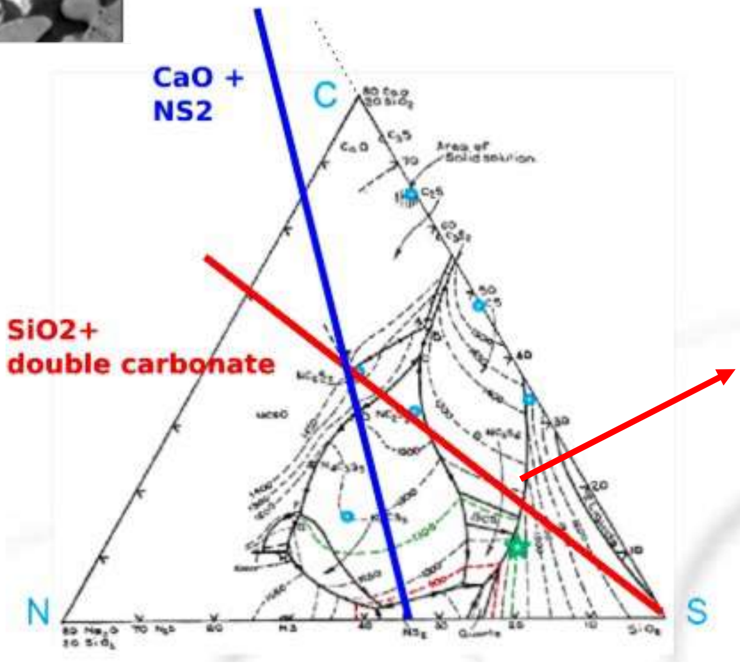
HOW THE FINAL QUALITY IS LINKED TO THE REACTION PATHS

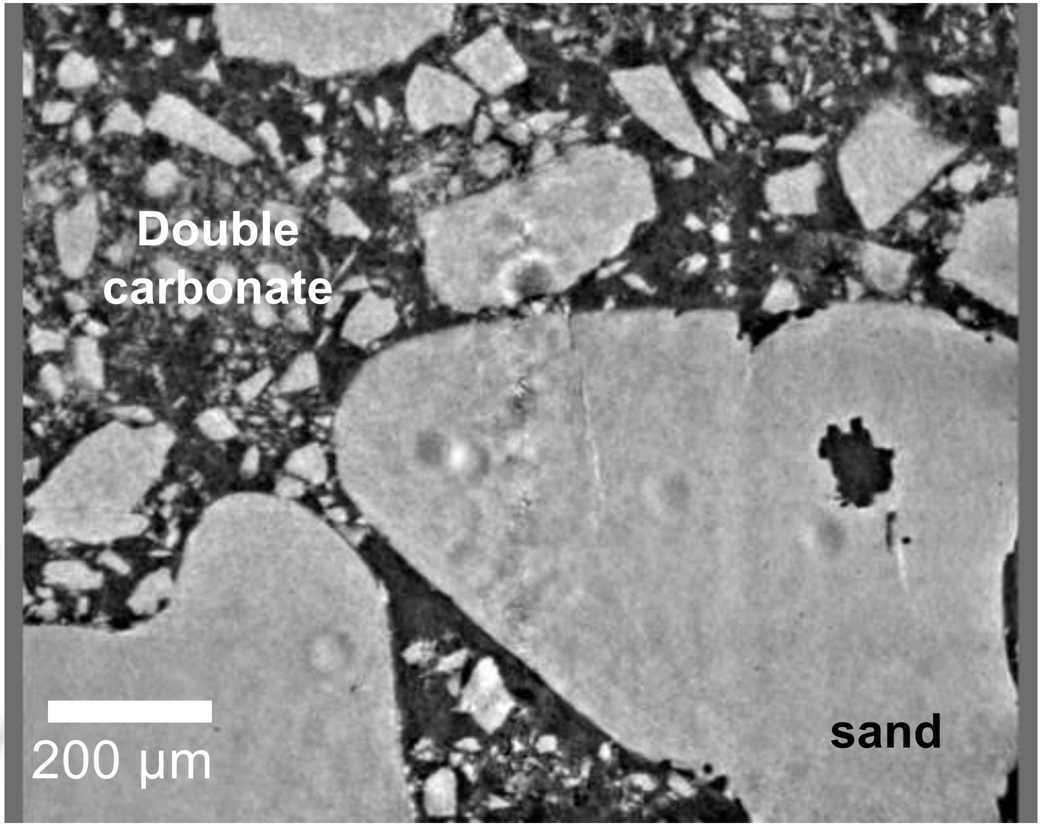
[Woelffel 2015]



Outer parts of the limestone grain react and convert into double carbonate

Double carbonate



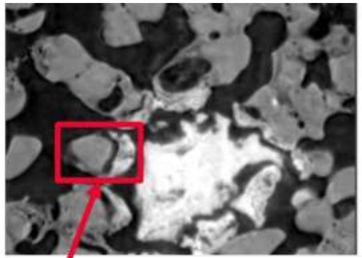


Sand + Eutectic mixte carbonate
Heating under CO_2 flux

THE SODA LIME SILICATE CASE

HOW THE FINAL QUALITY IS LINKED TO THE REACTION PATHS

[Woelffel 2015]



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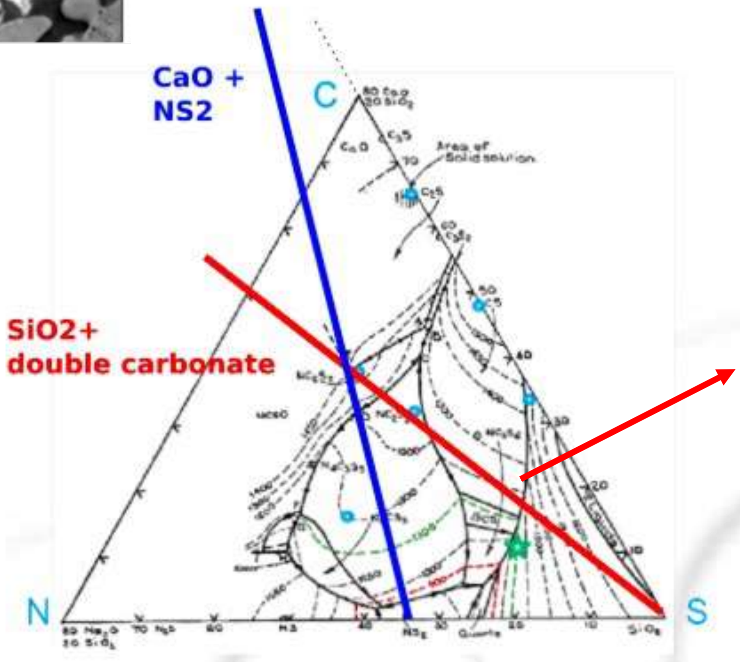
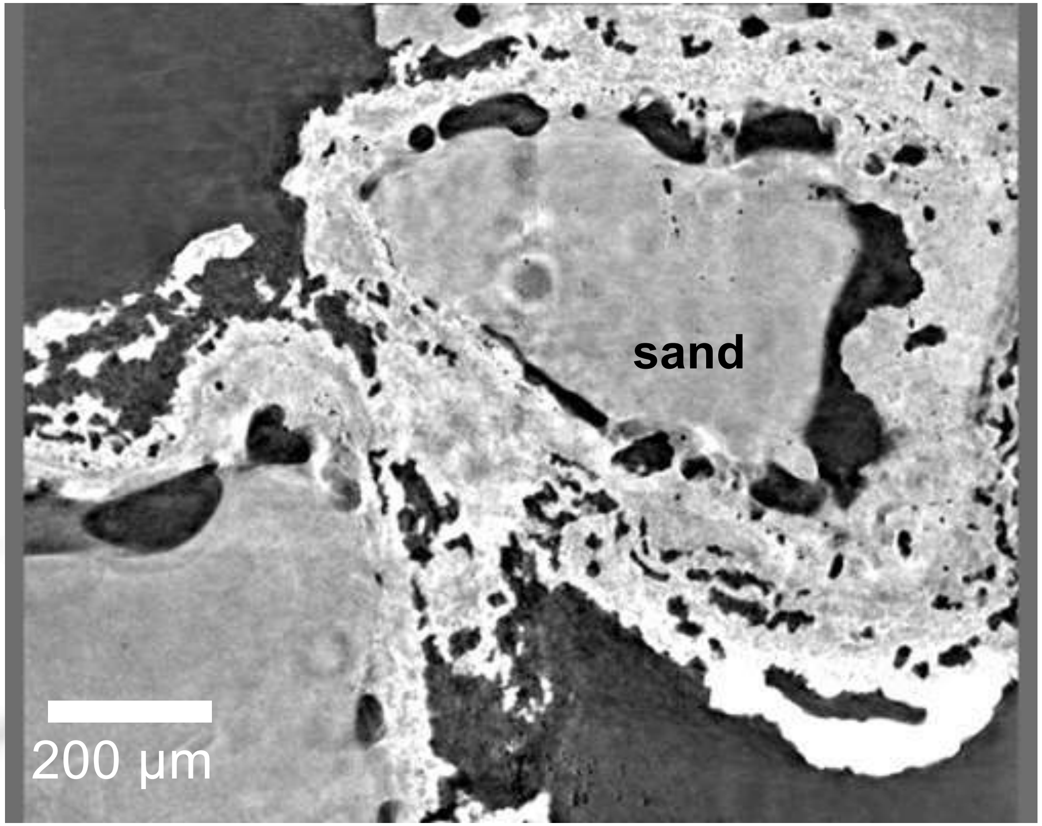




850°C $Na_2Si_2O_5$ (s) ➔ $Na_2Si_2O_5$ (l)

THE SODA LIME SILICATE CASE

KEY MESSAGES

Study at granular scale reveals complex physicochemical mechanisms

which allow integrating ± silica and limestone

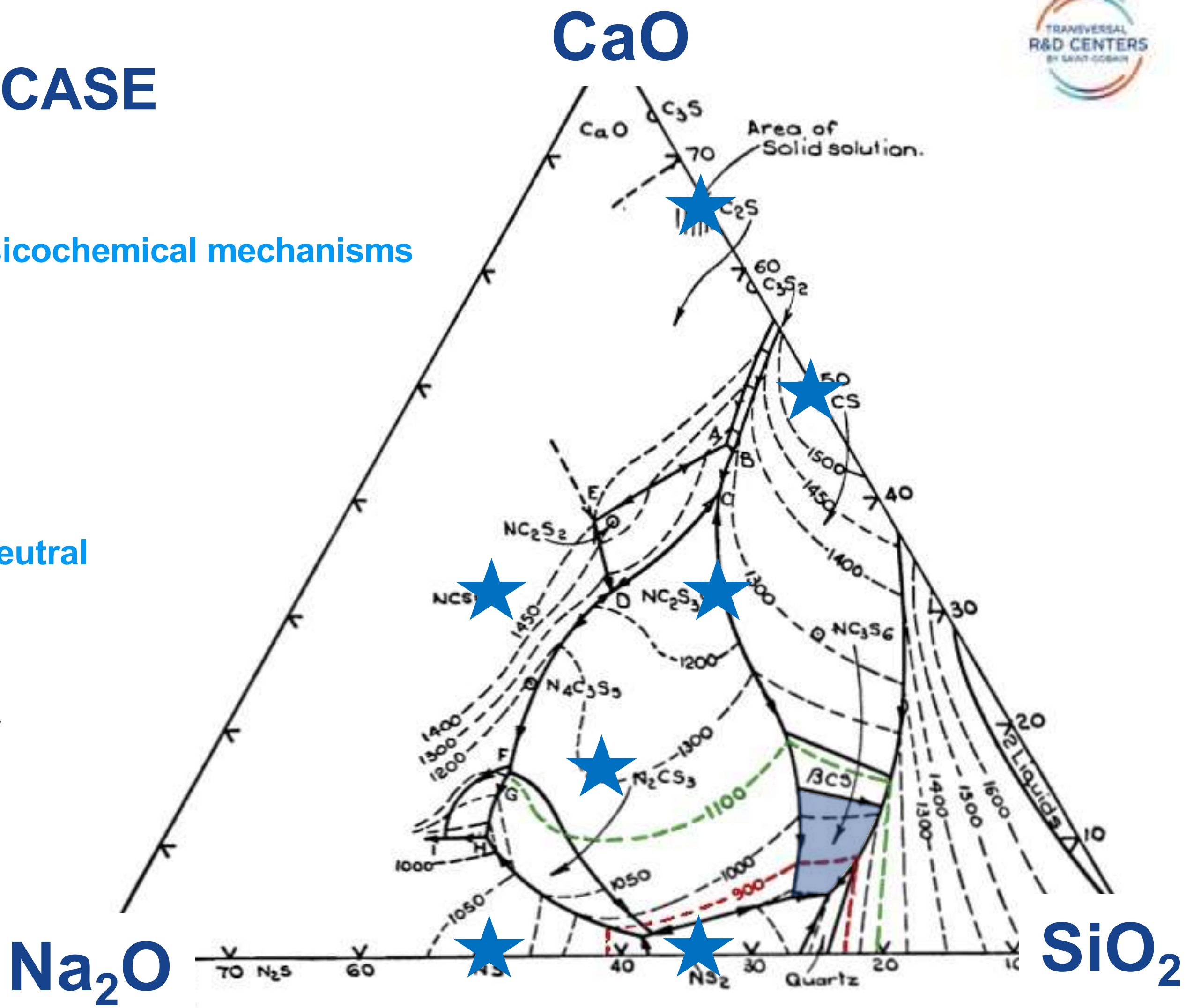
depending on the intermediate products

Events occuring at low temperature are not neutral

Important to favour the paths incorporating

- SiO_2 ➔ less grains to be digested
- CaO ➔ to avoid risk for heterogeneity

= Privilege the mixte carbonate path



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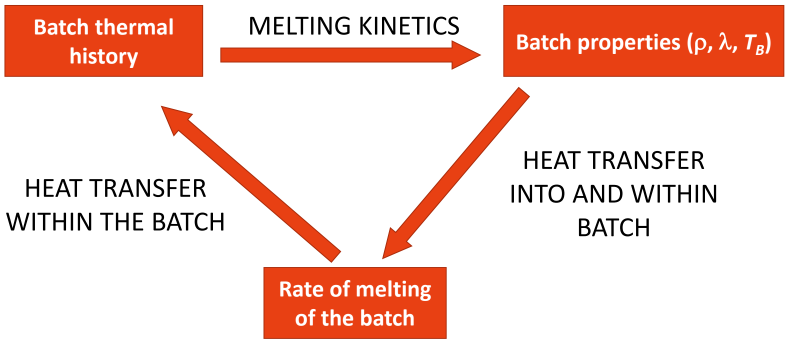
02

Modeling of batch melting

From the micro-scale to the macro-scale...

Mathematical models of batch melting

- ▶ Today, practically all new furnaces are developed with the help of mathematical models
- ▶ Detailed batch melting model couples the energy and mass balances with equations describing the conversion kinetics



Batch thermal history

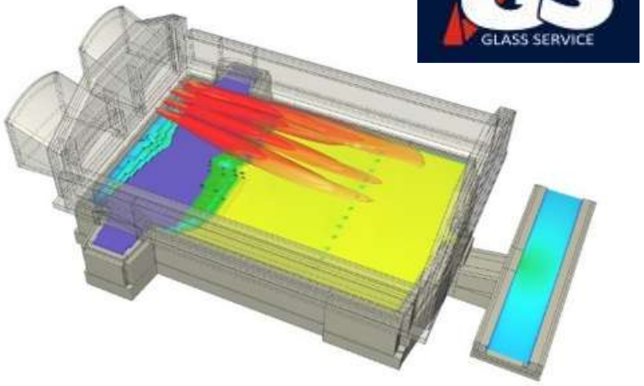
MELTING KINETICS

Batch properties (ρ, λ, T_B)

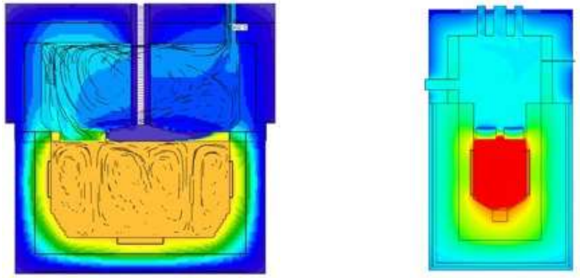
HEAT TRANSFER INTO AND WITHIN BATCH

Rate of melting of the batch

HEAT TRANSFER WITHIN THE BATCH



Regenerative end-port furnace for producing container glass



Abboud, A. W., Guillen, D. P., & Pokorny, R. (2020). Effect of cold cap coverage and emissivity on the plenum temperature in a pilot-scale waste vitrification melter. *International Journal of Applied Glass Science*, *11*(2), 357-368.

Mathematical models of batch melting

UCT PRAGUE

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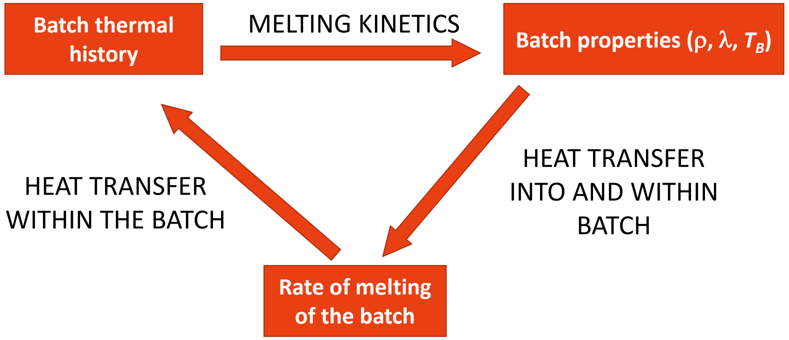
- Detailed batch melting model couples the energy and mass balances with equations describing the conversion kinetics



Batch thermal history

MELTING KINETICS

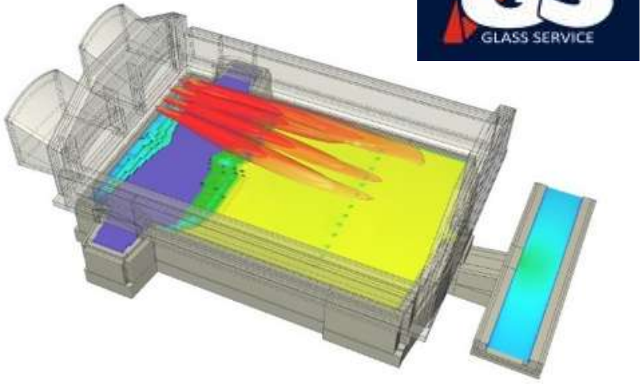
Batch properties (ρ, λ, T_B)

HEAT TRANSFER INTO AND WITHIN BATCH

Rate of melting of the batch

HEAT TRANSFER WITHIN THE BATCH

- While the general governing equations for the heat transfer and for the conversion kinetics are reasonably well understood, they are rarely coupled together
  - ☐ Without considering the batch thermal history, batch models are applicable only in a narrow range of conditions



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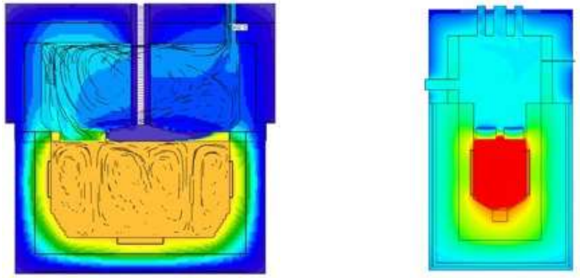

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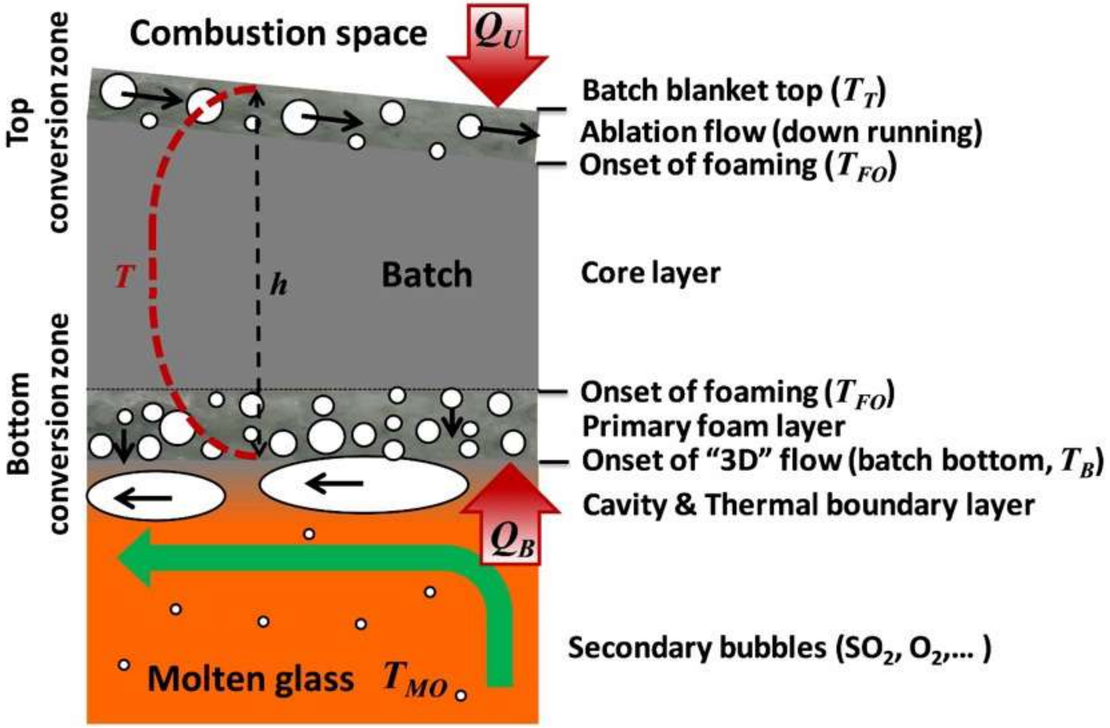
Analysis of kinetics of melting

UCT PRAGUE

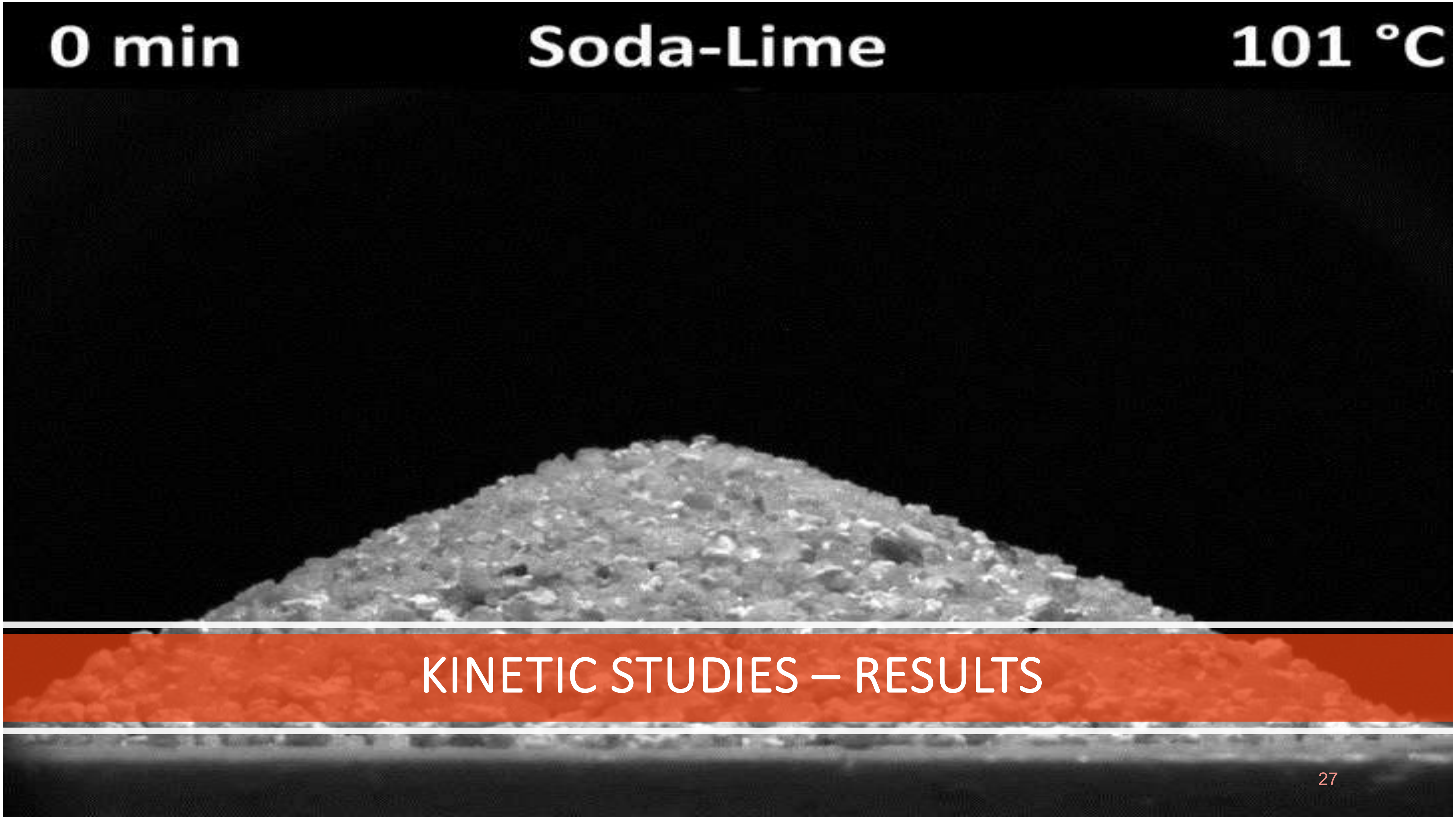
- ▶ Processes occurring during batch melting are numerous and complex
  - ☐ Batch reactions leading to the production of glass-forming melt
  - ☐ Evolution of primary foam, its growth and collapse
  - ☐ Dissolution of solid particles (silica)

- ▶ Measure the kinetics of silica dissolution (XRD), gas evolution (TGA & EGA), and foam formation (FET & EGA)

- ▶ Estimate the effect of the conversion kinetics on the rate of melting

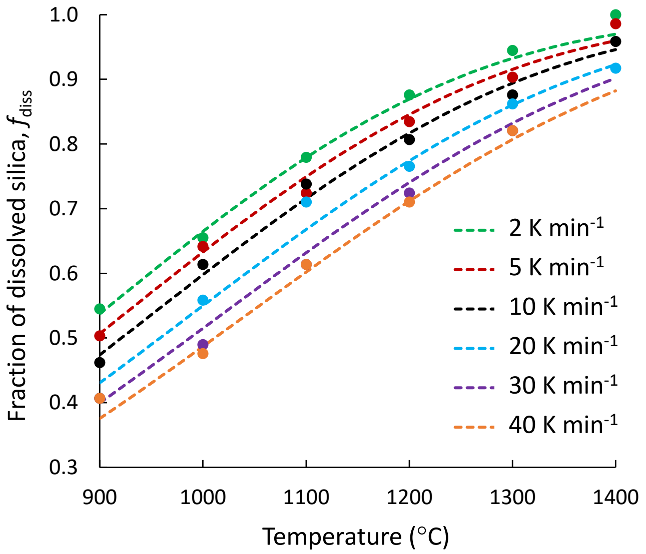


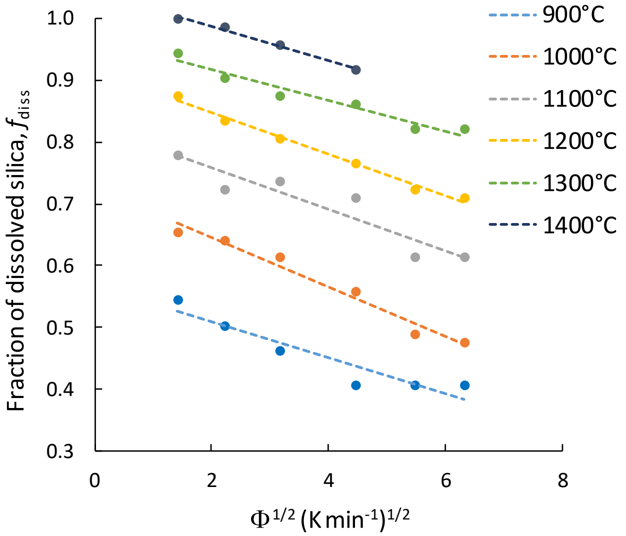
KINETIC STUDIES – RESULTS



Dissolution of silica (XRD) – Container glass

- Fraction of silica dissolved, f_{diss}, shifts to higher temperatures in response to faster heating
  - ☐ At a constant temperature, f_{diss} depends almost linearly on the square root of heating rate





Composition	
Sand	62.00
feldspar	13.49
Limestone	20.33
Soda ash	21.84
Na_2SO_4	0.391
Carbon	0.04
Total (g)	117.89

$$f_{diss} = 1 - \exp\left[-\left(\frac{T/T_0}{\left(1+\sqrt{\Phi/\Phi_f}\right)}\right)^{p_1}\right]$$

T	Temperature
Φ	Heating rate
T_0, Φ_f, p	Fitting parameters

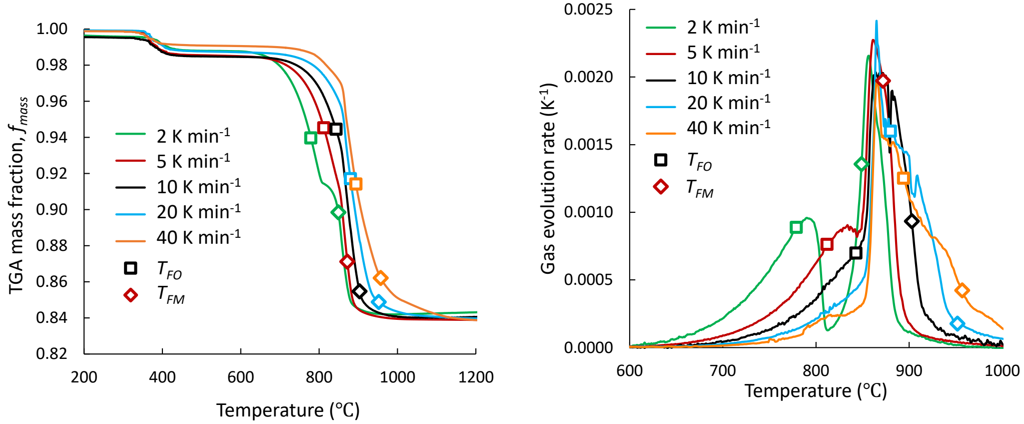
Gas Evolution (TGA and EGA)

- ▶ Limestone decrepitation ~400°C

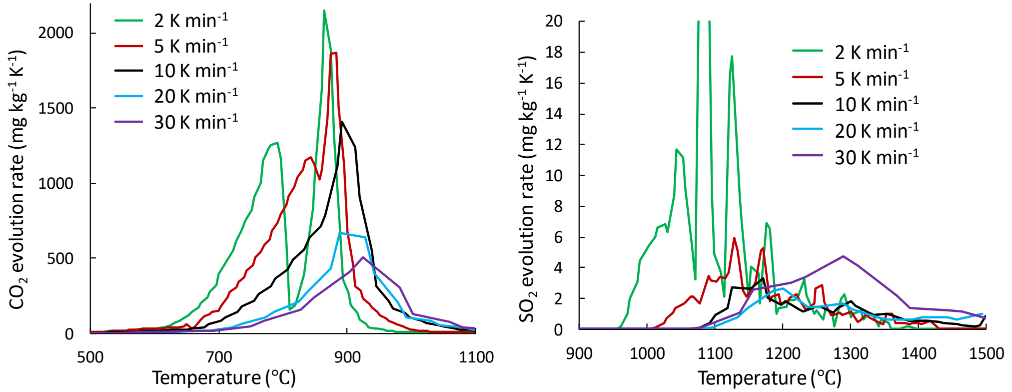
- ▶ CO_2 begins to evolve at ~600°C and continues up to ~1100°C
  - ☐ Two peaks visible at slower rates – first peak corresponds to decomposition of $CaCO_3$ and its reaction with solid silica sand, second peak occurs when melting soda considerably accelerates its reaction with silica
  - ☐ Decrease between the two peaks caused by the formation of double carbonate

- ▶ SO_2 is produced starting from 1000°C
  - ☐ $4CO + SO_4^{2-} \rightarrow S^{2-} + 4CO_2$
  - ☐ $S^{2-} + 3SO_4^{2-} \rightarrow 4SO_2 + 4O^{2-}$

TGA

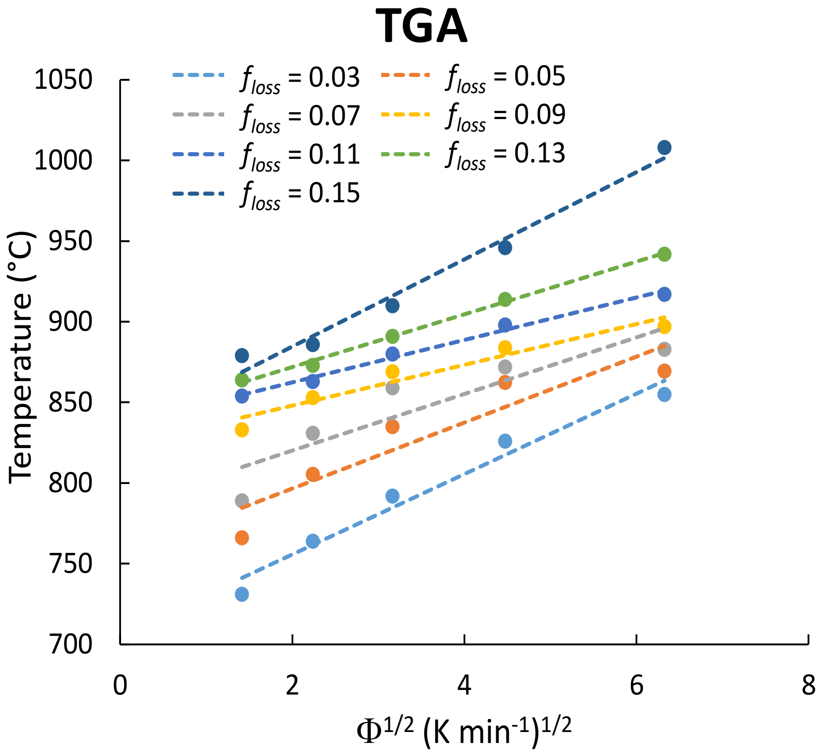


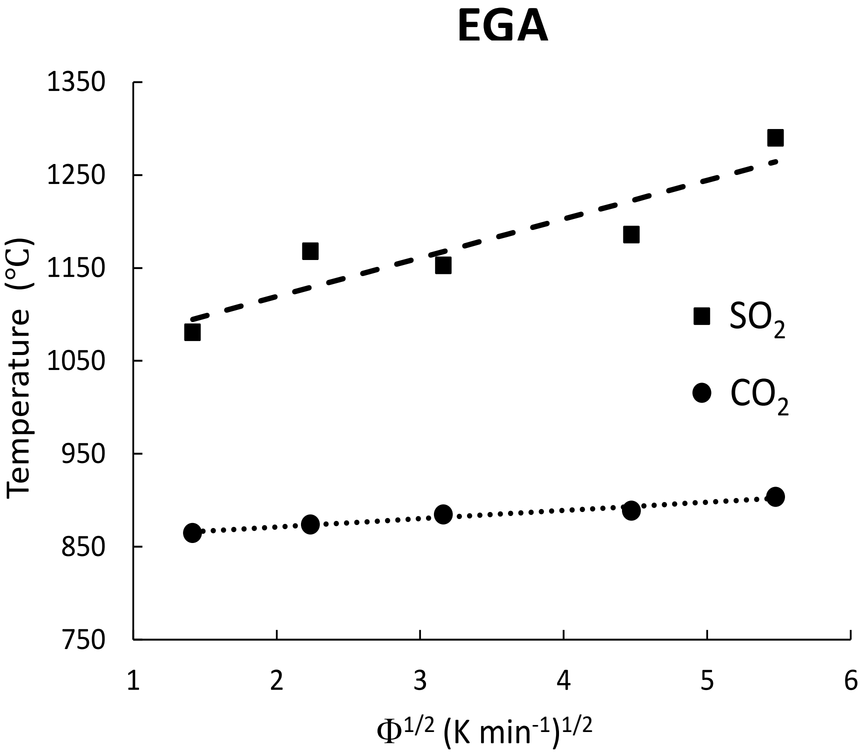
EGA



Gas Evolution (TGA and EGA)

- ▶ The gas evolving reactions shift to higher temperatures linearly with the square root of the heating rate – this dependence is nearly identical to that of silica dissolution

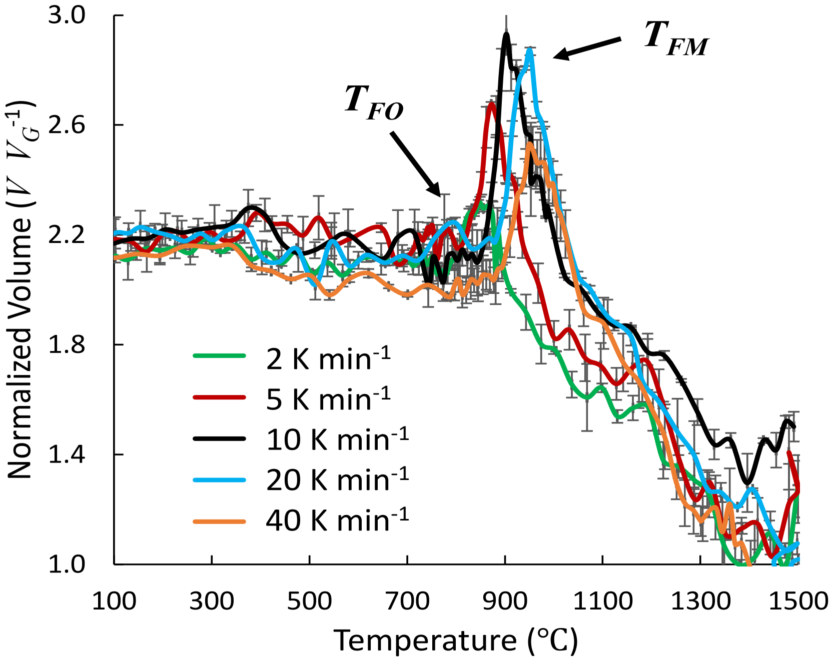


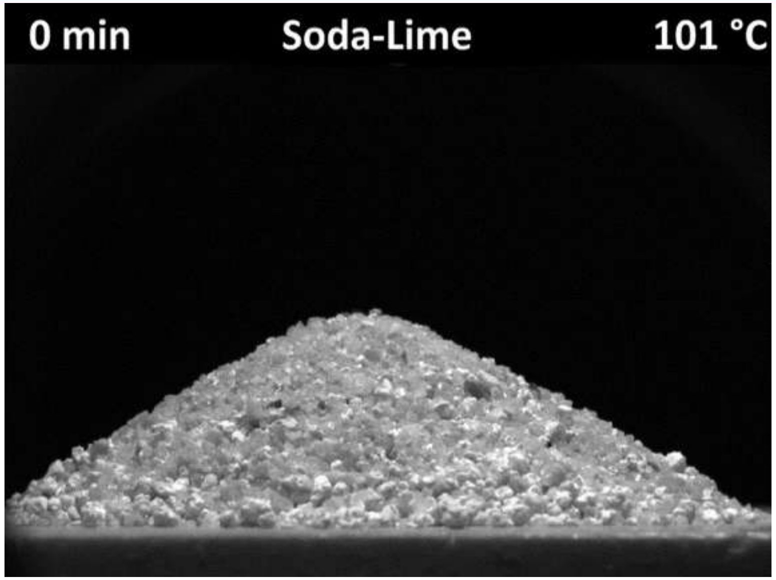


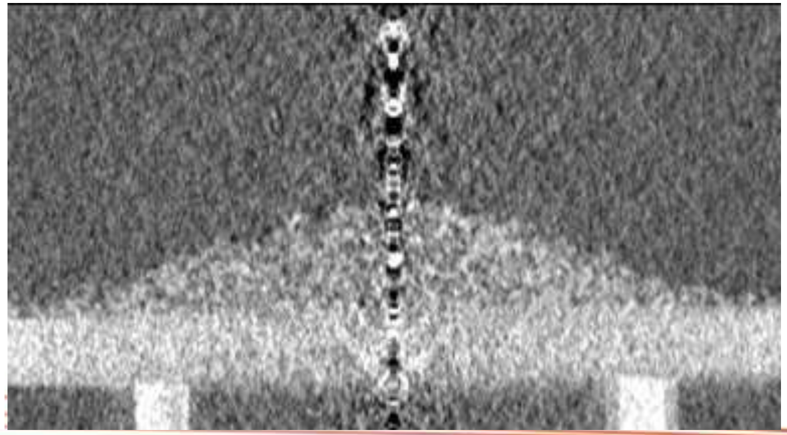
Volume expansion – Feed expansion test

UCT PRAGUE

- The feed volume shifts to higher temperatures in response to faster heating

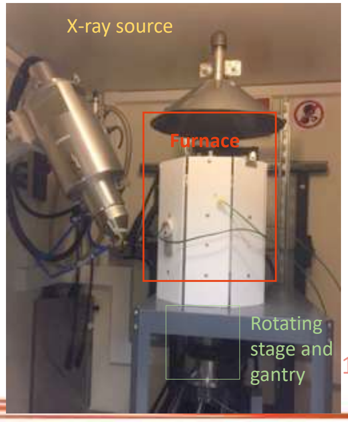






Observation furnace (visual)

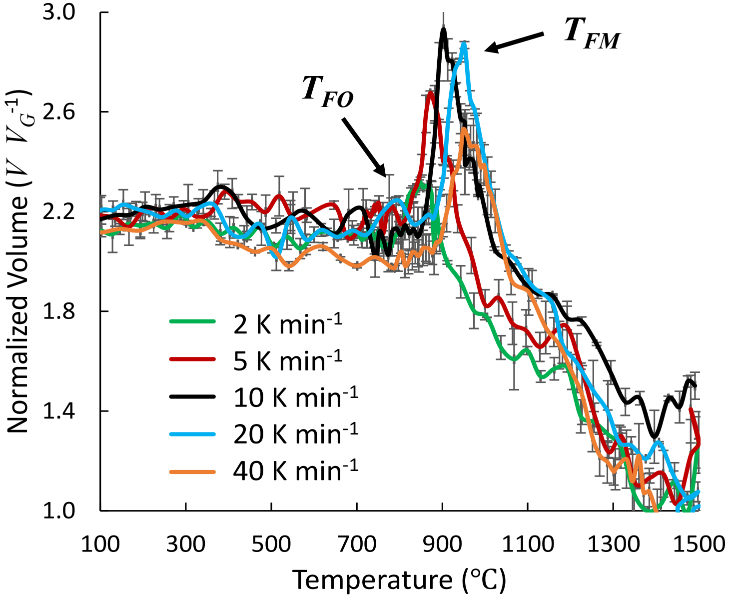
In-situ X-ray Furnace

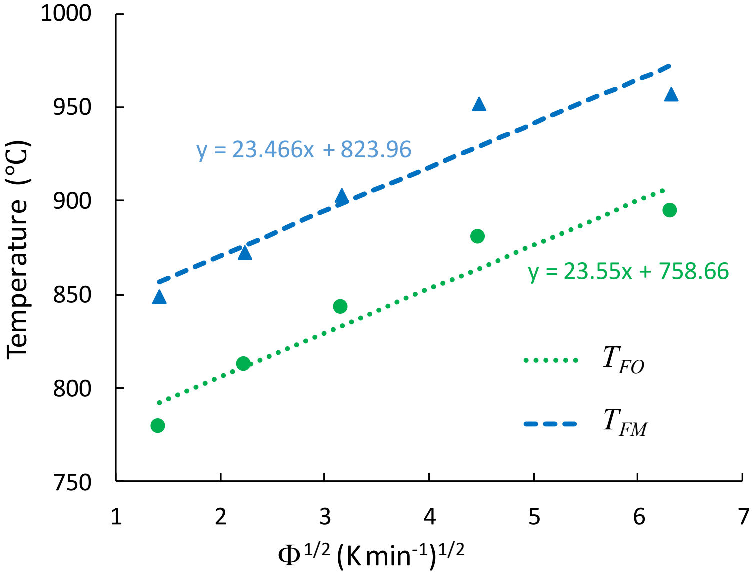


Volume expansion – Feed expansion test

UCT PRAGUE

- The foam onset and maximum temperatures increase with square root of heating rate
  - Similarly to temperatures at which a given f_{diss} and f_{loss} values are reached
  - This indicates that characteristic of foaming are also closely related to gas evolving reactions and to silica dissolution





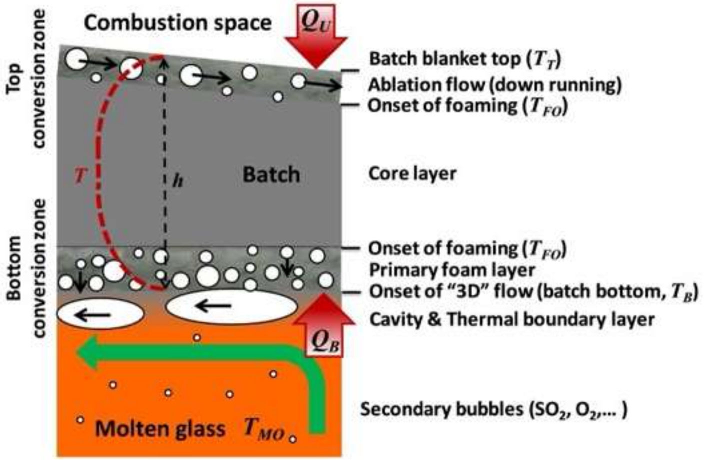
DISCUSION

Effects of kinetics on melting rate

- The melting rate depends on the heat flux to the batch from below and above

$$j_B = \xi_B (T_{MO} - T_B) \Delta H^{-1}$$

j is the melting rate [kg m^{-2}s^{-1}]
ΔH is the conversion heat [J kg^{-1}]
ξ is the heat transfer coefficient [W m^{-2}K^{-1}]
T_{MO} is the melter operating temperature [K]
T_B is the batch bottom temperature [K]



- Batch bottom temperature depends on thermal history
  - ☐ Characteristic temperatures increase with the square of root of heating rate $T_B = f(\Phi^{1/2})$

$$T_B = T_{B0}[1 + (\Phi/\Phi_B)^{1/2}]$$

- Within the batch blanket, heating rate increases with the square of melting rate, $\Phi \sim Cj^2$
  - ☐ Substituting, we find linear relation between batch bottom temperature and melting rate

$$T_B = T_{B0}[1 + Kj_B]$$

Effects of kinetics on melting rate

- The melting rate depends on the heat flux to the batch from below and above

$$j_B = \xi_B(T_{MO} - T_B)\Delta H^{-1} \longrightarrow j_B = \xi_B(T_M - T_{B0}[1 + Kj_B])\Delta H^{-1}$$

- Batch bottom temperature depends on thermal history
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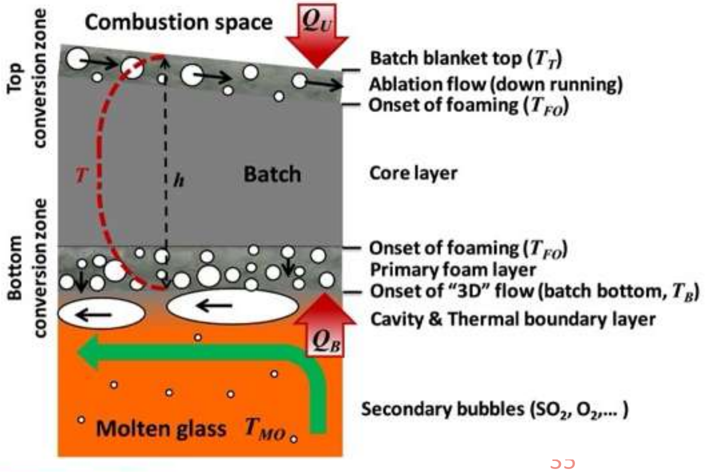

Effects of kinetics on melting rate

UCT PRAGUE

- The melting rate depends on the heat flux to the batch from below and above

$$j_B = \xi_B (T_{MO} - T_B) \Delta H^{-1} \longrightarrow j_B = \xi_B (T_M - T_{B0}[1 + K j_B]) \Delta H^{-1}$$

$$\longrightarrow j_B = \frac{\xi_B (T_M - T_{B0}) \Delta H^{-1}}{1 + \xi_B K T_{B0} \Delta H^{-1}}$$

- Batch bottom temperature depends on thermal history
  - ☐ Characteristic temperatures increase with the square of root of heating rate $T_B = \mathrm{f}(\Phi^{1/2})$

$$T_B = T_{B0}[1 + (\Phi/\Phi_B)^{1/2}]$$

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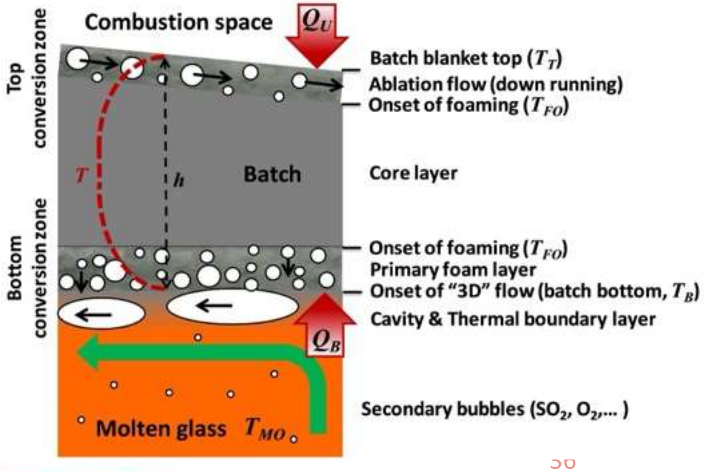


Effects of kinetics on melting rate

UCT PRAGUE

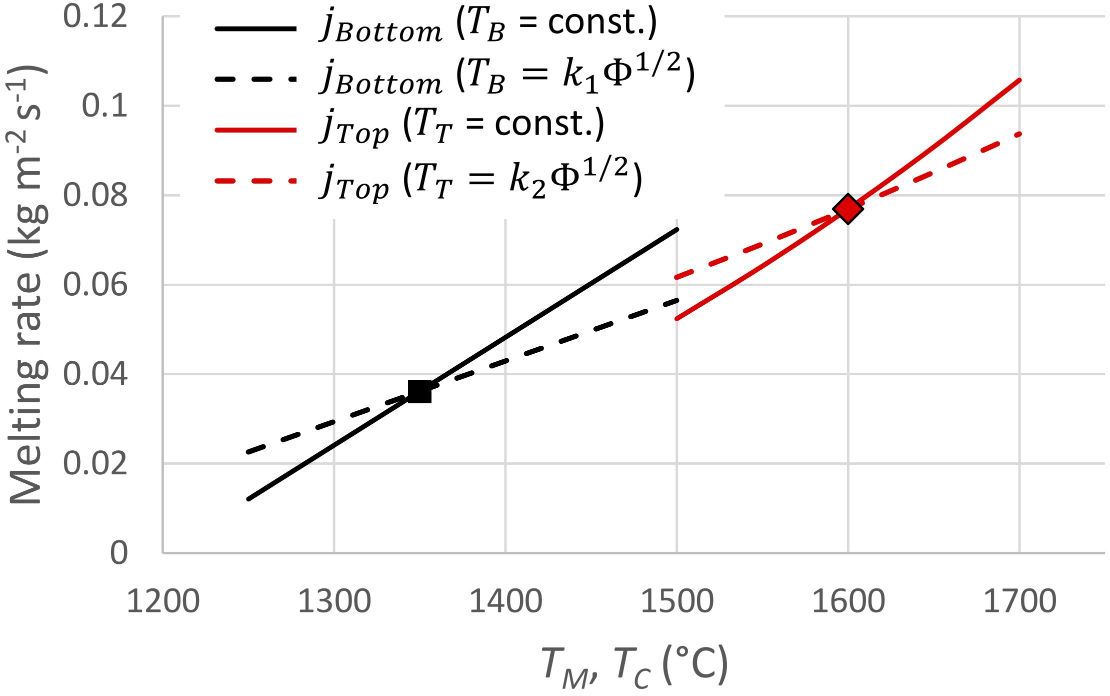
- Black dashed line
  - ☐ Considering conversion kinetics

$$j_B = \frac{\xi_B(T_M - T_{B0})\Delta H^{-1}}{1 + \xi_B K T_{B0} \Delta H^{-1}}$$

- Black solid line
  - ☐ Without conversion kinetics

$$j_B = \xi_B(T_{MO} - T_B)\Delta H^{-1}$$

- Melting rate affected less when effect of kinetics is considered



Detailed batch model

- Kinetic equation for silica dissolution
  - Sestak-Bergren

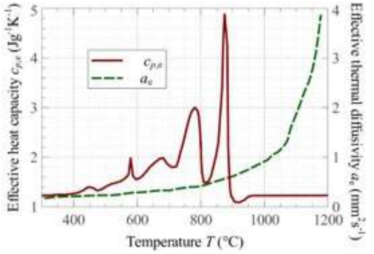
$$\frac{df_i}{dt} = A_i f_i^m (1 - f_i)^n \exp\left(-\frac{E_i}{RT}\right)$$

- Energy balance
  - Steady-state melting

$$j c_{p,\mathrm{e}} \frac{dT}{dx} + \frac{d}{dx}\left(\lambda \frac{dT}{dx}\right) = 0$$

- Equations for material properties, boundary conditions

Temperature-dependent material properties



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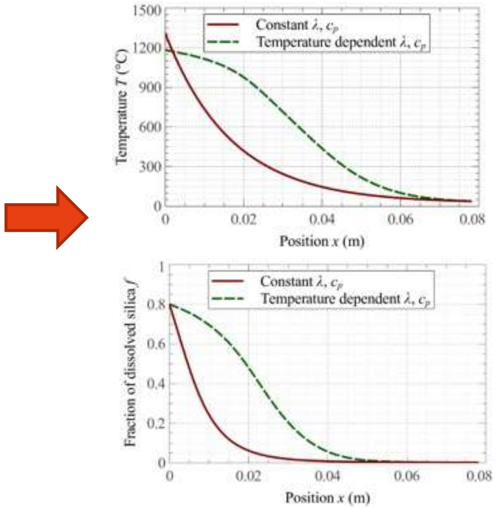
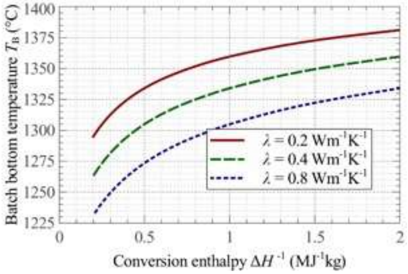
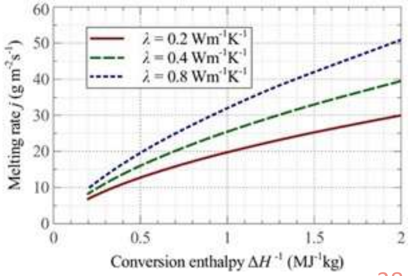


Effect of heat conductivity





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