Glass formation followed by in-situ tomography

E. Gouillart

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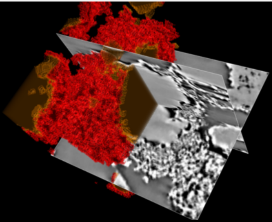

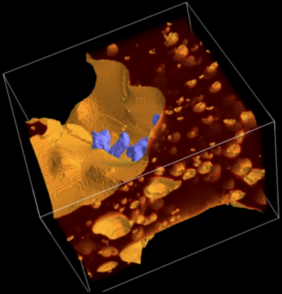

Collaborations

Glass
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D. Dalmas
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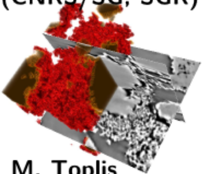

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Tomography acquisition
E. Boller
(ID 19)
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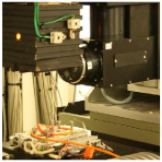

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P. Lhuissier
(Simap)

Reconstruction
S. Roux
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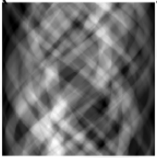
(ESPCI)
M. Mézard
(LPTMS Orsay)



H. Talbot
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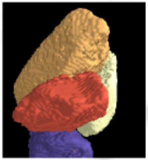
Image processing
H. Talbot
(ESIEE)
L. Moisan
(Paris V)



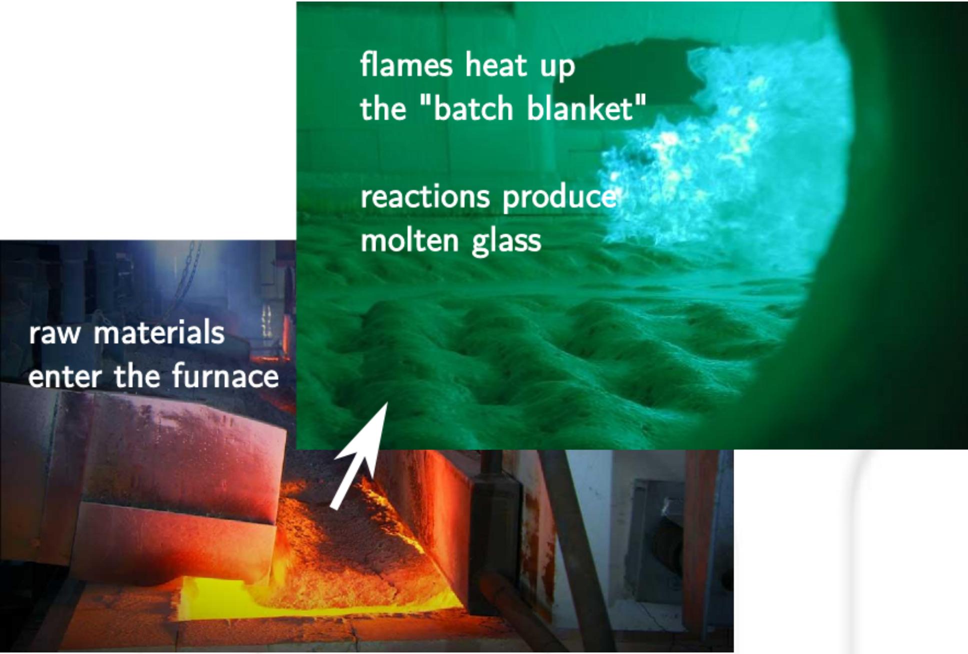
G. Varoquaux
(INRIA Saclay)

ANR project EDDAM (MATEIS, INSA Lyon)

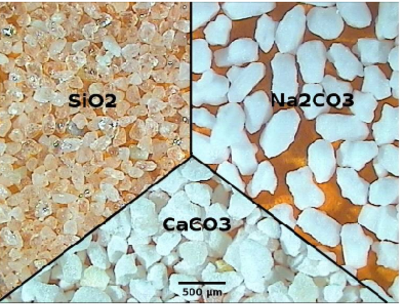
1. Why study glass formation ?
2. In-situ tomography
3. Reactions in the $Na_2CO_3 - SiO_2$ system
4. Evolution of calcium carbonate

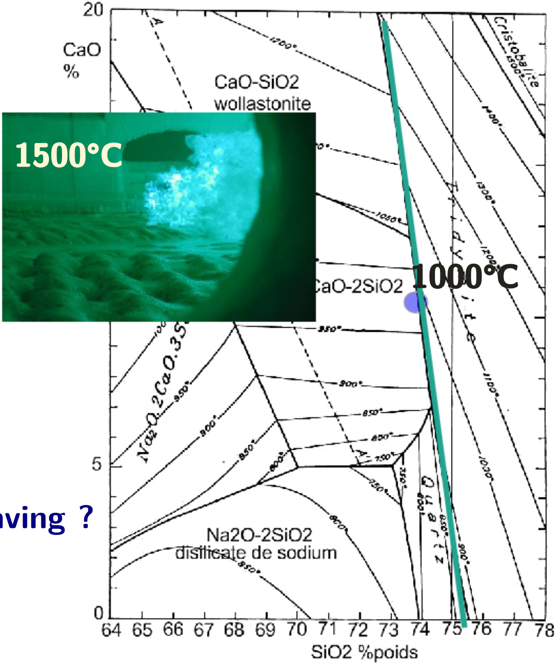
Outline

1. Why study glass formation ?
2. In-situ tomography
3. Reactions in the $Na_2CO_3 - SiO_2$ system
4. Evolution of calcium carbonate


flames heat up
the "batch blanket"
reactions produce
molten glass
raw materials
enter the furnace

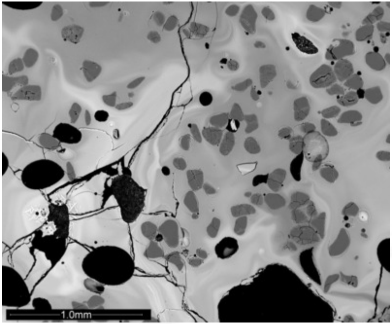
Coarse raw materials
-> slow kinetics





A lot of room for energy saving ?

Producing homogeneous glass is difficult

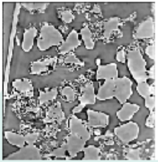


Defects

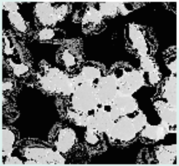
- Unmolten grains, bubble, chemical gradients...
- How are they related to the grain sizes, the temperature path, etc. ?

Tools for studying glass batch melting in SGR

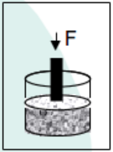
in-situ X-ray tomography



SEM imaging

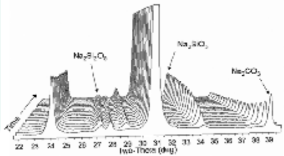


TMA

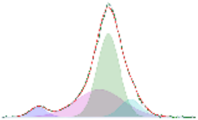


Literature:
TGA
in-situ XRD
in-situ NMR

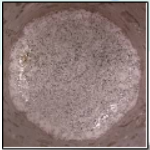
X-ray diffraction



Raman spectroscopy

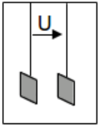


Static melting

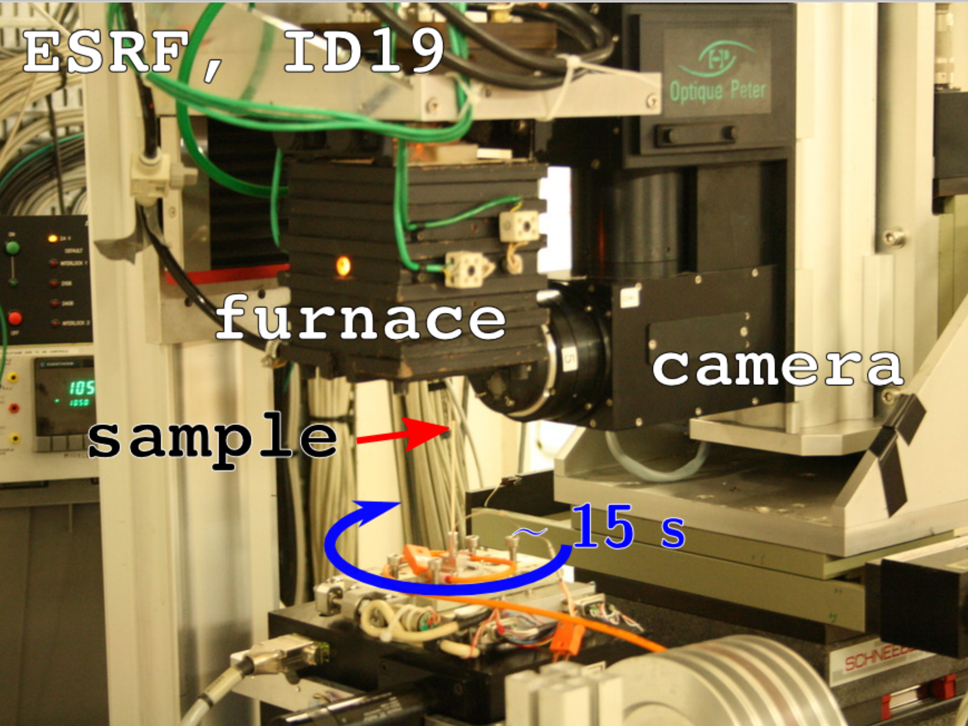


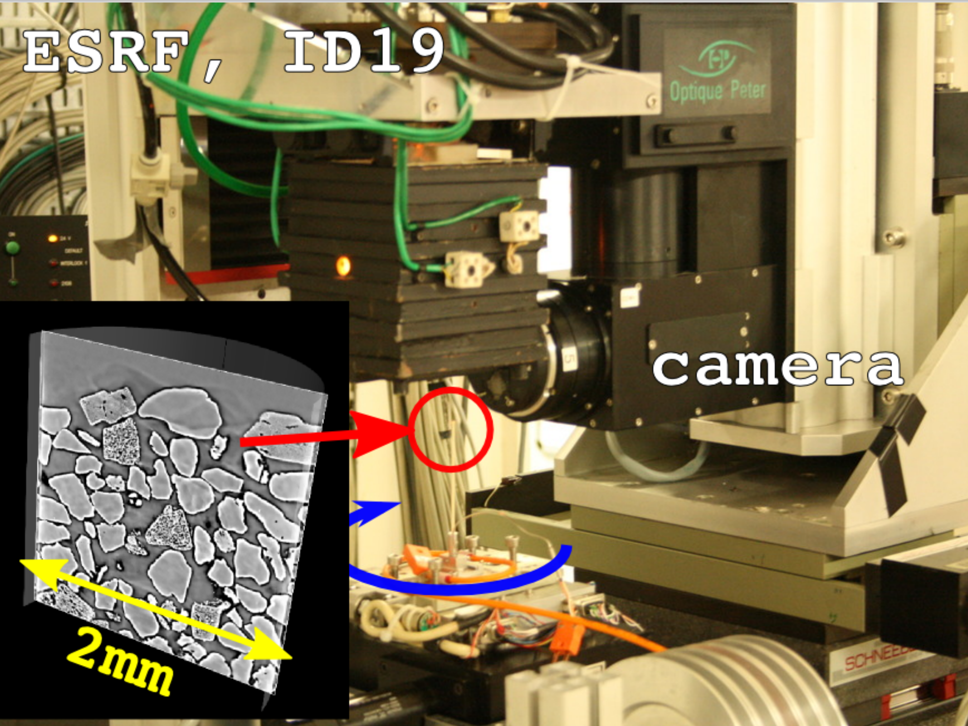
Thermal analyses: TGA/TDA, DSC

Electrical conductivity



Outline

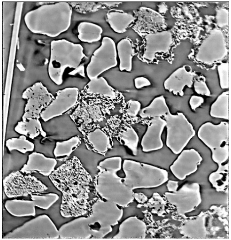

ESRF, ID19
Optique Peter
furnace
camera
sample
~15 s


ESRF, ID19
Optique Peter
camera
2mm

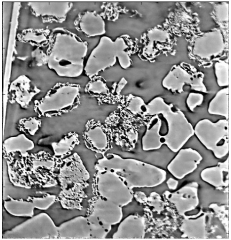
Reactive melting of glass raw materials

http://www.youtube.com/watch?v=pPyG_fEee_o

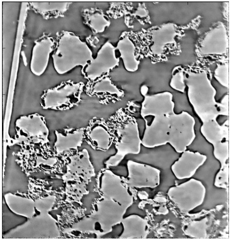
Visualizing glass melting from the inside



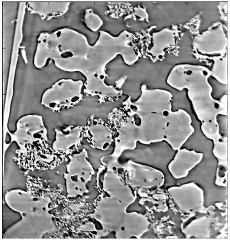
$T = 760^\circ$ C



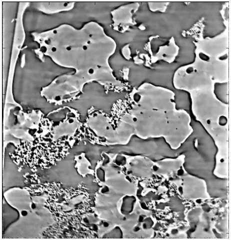
$T = 799^\circ$ C



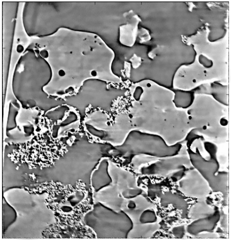
$T = 820^\circ$ C



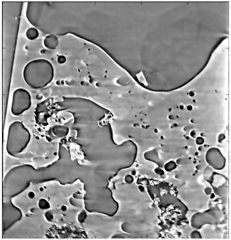
$T = 835^\circ$ C



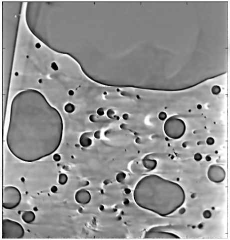
$T = 850^\circ$ C



$T = 860^\circ$ C

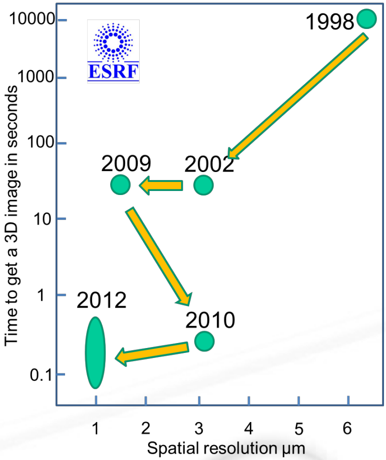


$T = 877^\circ$ C



$T = 920^\circ$ C

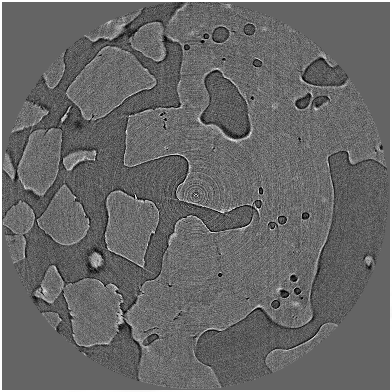
Faster and faster imaging !



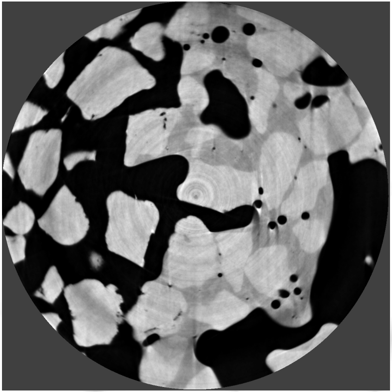
Courtesy Luc Salvo

$\Rightarrow$ huge amounts of (noisy) data to process... $O(100\mathrm{Gb})$ for one experiment

Absorption and phase contrast

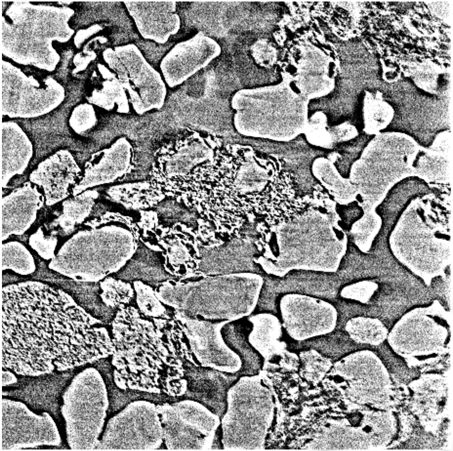


Absorption reconstruction



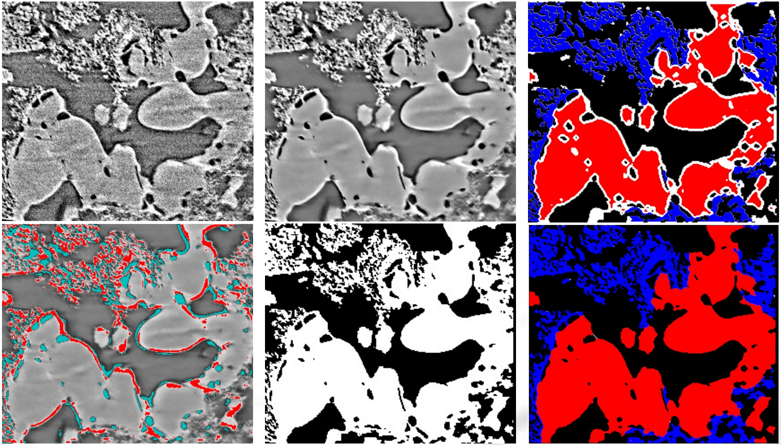
Phase reconstruction (Paganin algorithm, single distance)

Datasets and issues



- In-situ images : speed vs. quality tradeoff. Noisy images, poor contrast, artifacts...
- Huge datasets : $O(1)$ Go / image $\times$ # images in timeseries.
- Complicated system : what information do we want ?

Quantitative image processing



- Denoising
- Segmentation of the phases
- Tracking objects, measuring contacts statistics...

Outline

1. Why study glass formation ?
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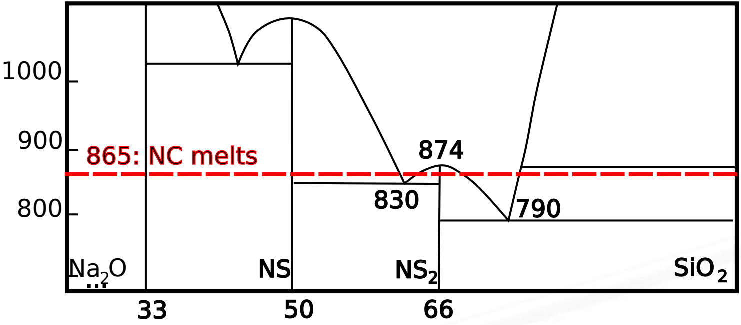
3. **Reactions in the $Na_2CO_3 - SiO_2$ system**
4. Evolution of calcium carbonate

The $Na_2O - SiO_2$ system



- Starting from Na_2CO_3 and not from Na_2O : where/how does the system enter the phase diagram ?
  - $T < 865°$ C : solid-state reactions (Turner, Wilburn, ...)

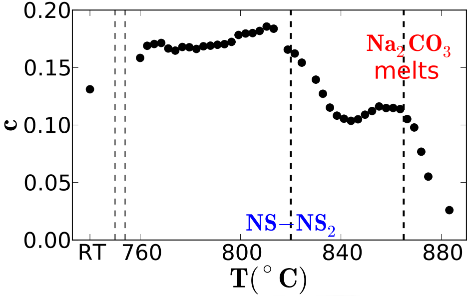
$$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2$$

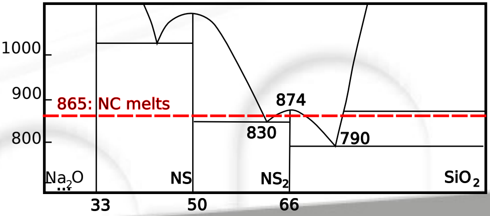
$$Na_2SiO_3 + SiO_2 \rightarrow Na_2Si_2O_5$$

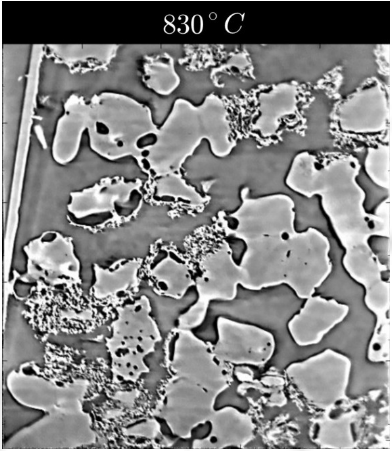
  - $T \geq 865°$ C : reactions between molten Na_2CO_3 and SiO_2.

Both transformations mechanisms of Na_2CO_3 can be observed
Reaction in solid and liquid state

Volume fraction of sodium carbonate + crystalline silicates
ternary batch, 5 $K.min^{-1}$ ramp







[Gouillart et al., JACS 2012]

Both transformations mechanisms of Na_2CO_3 can be observed

Reaction in solid and liquid state

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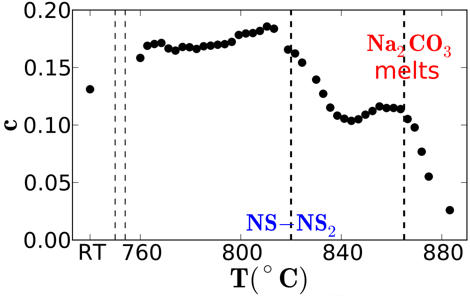
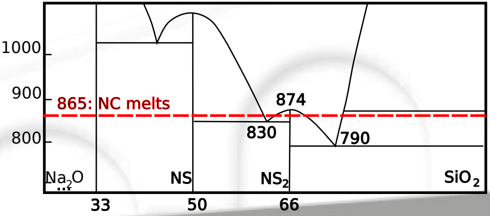
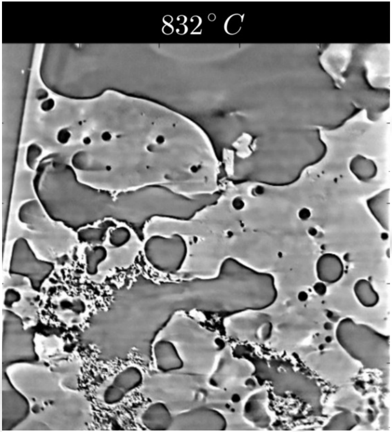


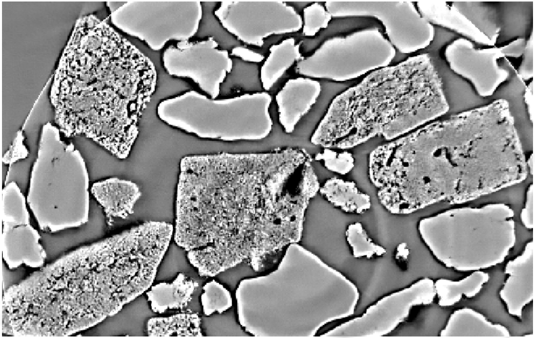




[Gouillart et al., JACS 2012]

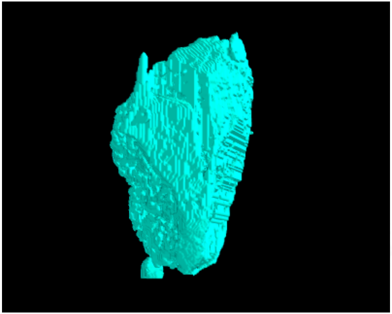
Porous grains with a large specific area

Novacarb sodium carbonate

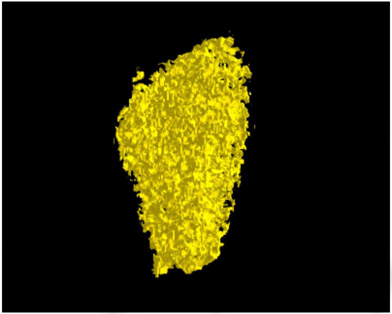


Porous grains with a large specific area

Novacarb sodium carbonate



grain



open porosity

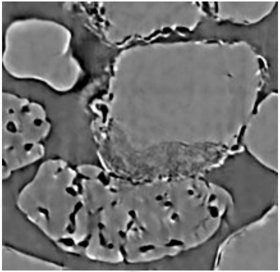
A very reactive system in the solid-state

Formation of crystalline silicates :

$$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2 \quad \text{metasilicate NS}$$

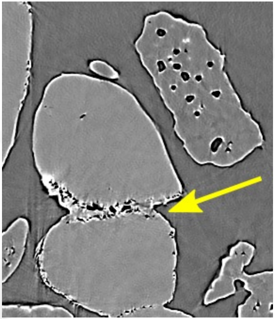
$$Na_2SiO_3 + SiO_2 \rightarrow Na_2Si_2O_5 \quad \text{disilicate } NS_2$$

Solid-state reaction at interspecies contacts



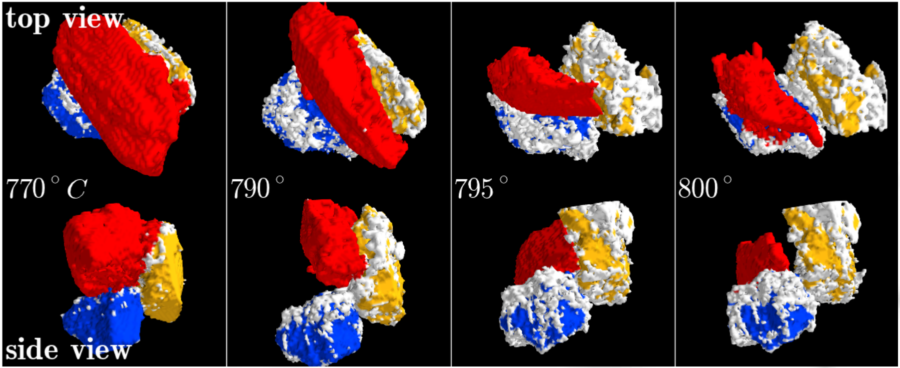
36% Na_2CO_3, 74% SiO_2, 760 °C

Reaction without contact ? ?



36% Na_2CO_3, 74% SiO_2, 730 °C

Tracking individual grains to learn reaction paths

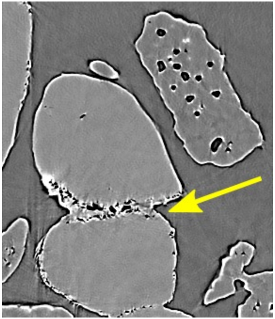


Sodium carbonate, blue and yellow : two sand grains, white : sodium silicates

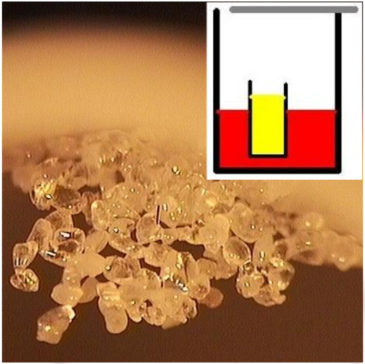
⇒ sodium carbonate is extremely reactive and mobile : **"semi-local" process**

Reaction in vapor phase

Reaction without contact ? ?

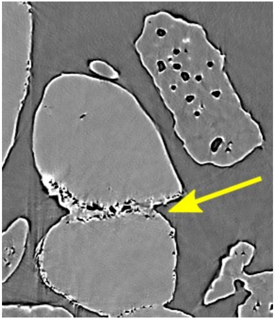


Yes ! !

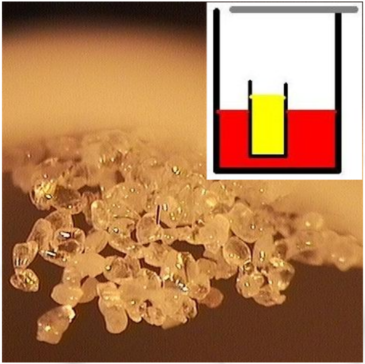


Reaction in vapor phase

Reaction without contact ? ?



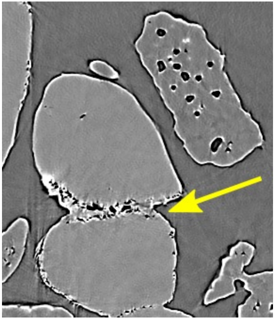
Yes ! !



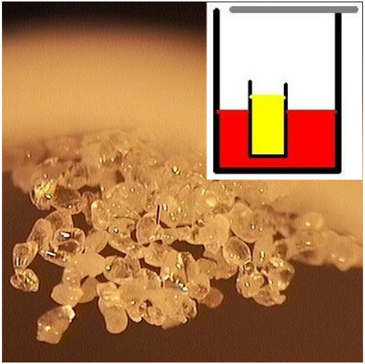
$$Na_2CO_3 \rightarrow "Na_2O" + CO_2 \quad K \ll 1 \; (10^{-7})$$

Reaction in vapor phase

Reaction without contact ? ?



Yes ! !



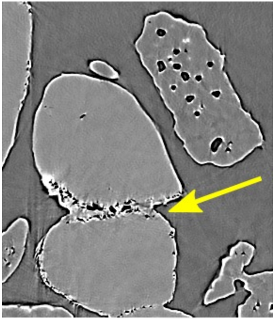
$$Na_2CO_3 \rightarrow Na_2O + CO_2$$

Na_2O reacts with silica surface

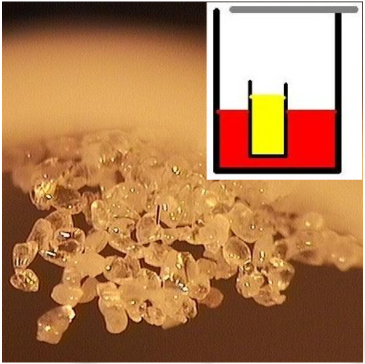
$$Na_2O + SiO_2 \rightarrow Na_2SiO_3$$

Reaction in vapor phase

Reaction without contact ? ?



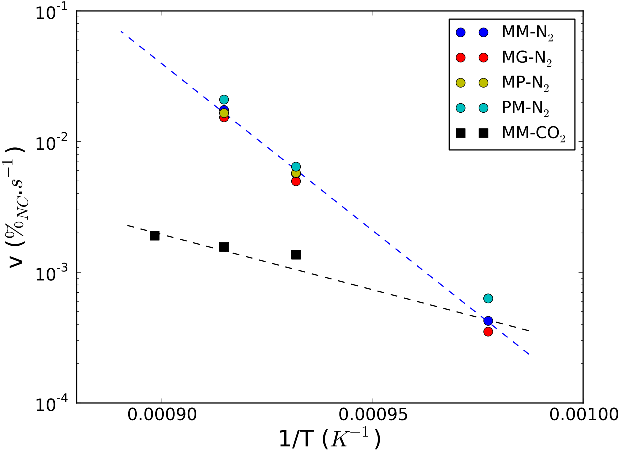
Yes ! !



$$Na_2CO_3 \rightarrow Na_2O + CO_2$$

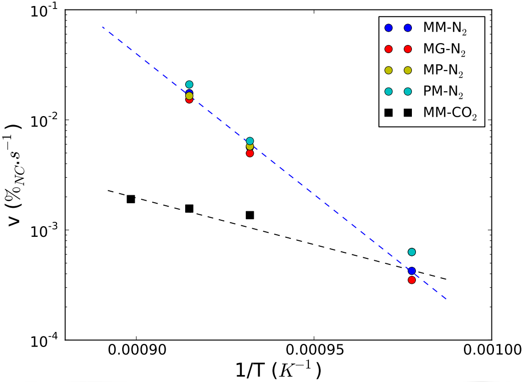
decomposition depends on CO_2 partial pressure

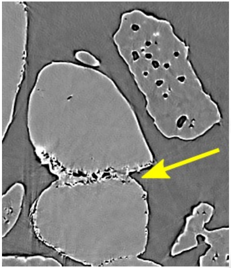
2 different reaction mechanims, depending on the atmosphere



Kinetics of Na_2CO_3 transformation measured by TGA
coll. N. Ferruaud, C. Cazako, S. Papin

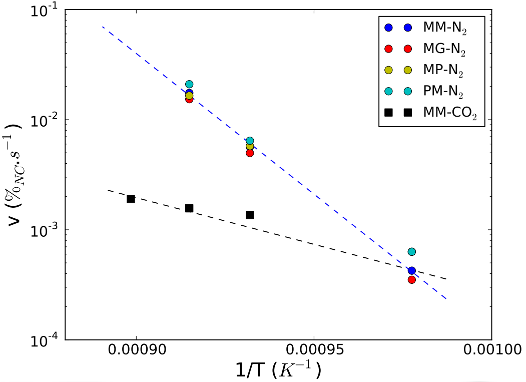
2 different reaction mechanims, depending on the atmosphere

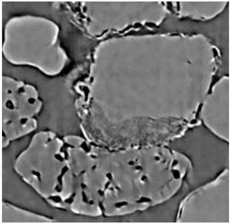




low CO_2 partial pressure : vapor-phase reactions are favored
Small samples in tomography $\rightarrow$ CO_2 is easily removed.

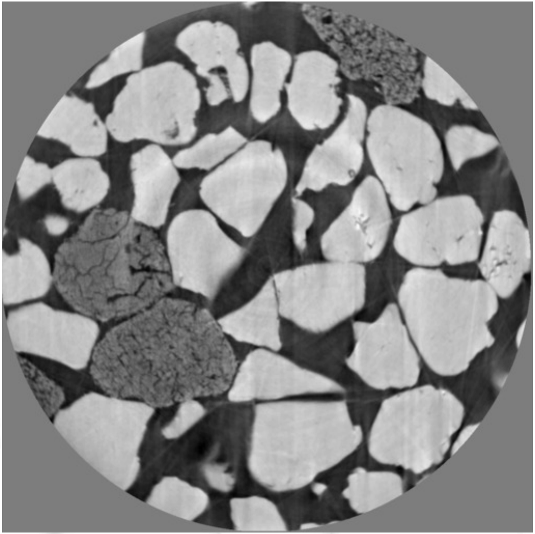
2 different reaction mechanims, depending on the atmosphere





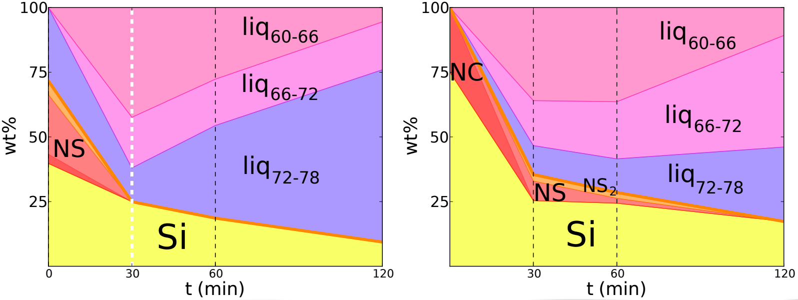
high CO_2 partial pressure : Na_2CO_3 decomposes only when in contact with silica.

Solid-state reactions



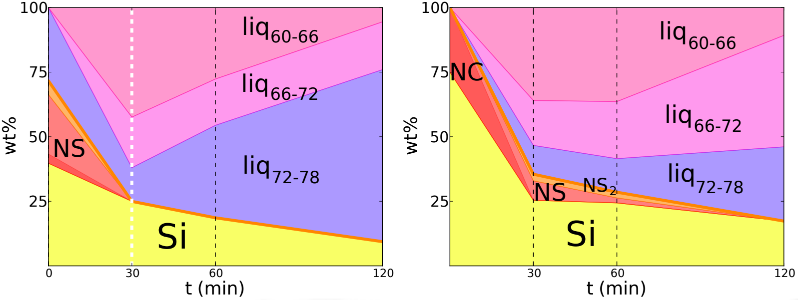
800° C, 4× speed-up (scans of 2s every 6s)

Raman + XRD → chemical / crystalline composition of the system



4-h plateau at 820° C — direct melting at 900° C

Raman + XRD → chemical / crystalline composition of the system

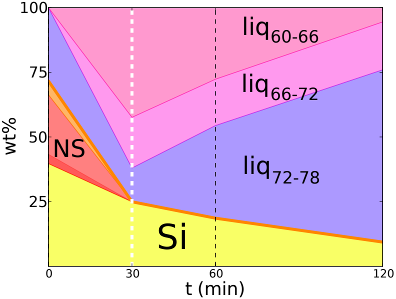


4-h plateau at 820° C

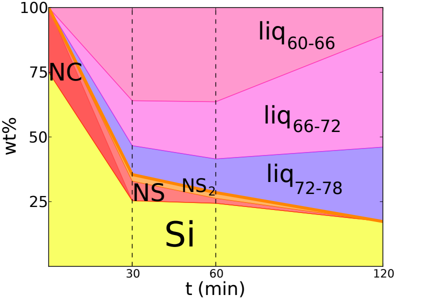
direct melting at 900° C

Better homogeneity when solid-state reactions have been favored.

Raman + XRD → chemical / crystalline composition of the system



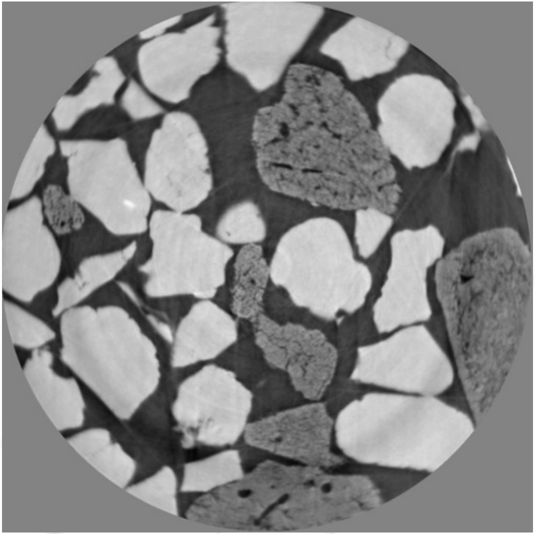
4-h plateau at 820° C



direct melting at 900° C

Better homogeneity when solid-state reactions have been favored.
Can it be explained by the spatial distribution of sodium silicates ?

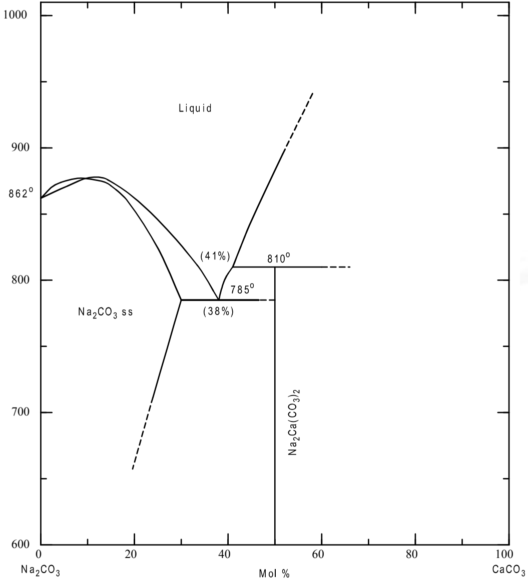
Reactions above the melting point of Na_2CO_3



900° C, 4× speed-up (scans of 1s every 6s)

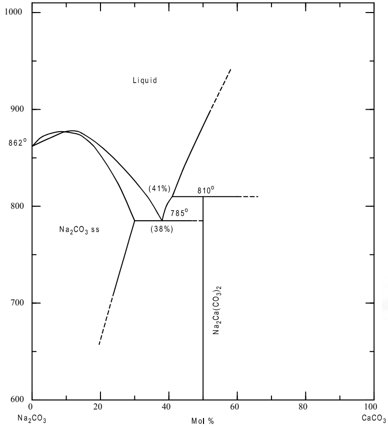
Outline

The $Na_2CO_3 - CaCO_3$ system



Kracek

The $Na_2CO_3 - CaCO_3$ system



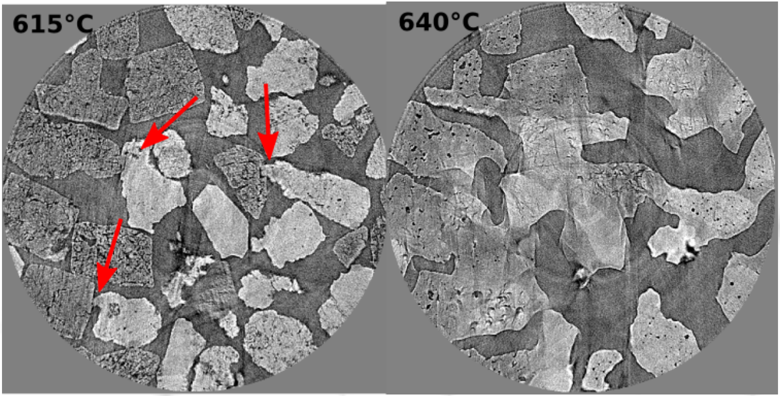
Kracek

- Possible formation of a double carbonate
- Also possible : calcination of $CaCO_3$

Solid-state reactions between the two carbonates

Coll. S. Papin (SGR), G. Matzen, E. Véron (CEMHTI)

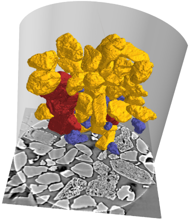
- Mixture of the two carbonates (50/50) : significant reaction



Evolution of calcium carbonate in a ternary batch

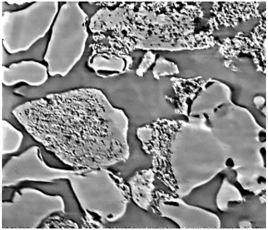
Two very different reaction paths

- depending on contacts with sodium carbonate

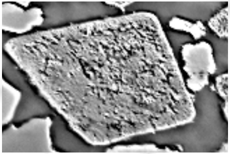


Ternary batch 75% SiO_2 13% Na_2CO_3 12% $CaCO_3$: < 1 one contact with Na_2CO_3 for $CaCO_3$ grains (monodisperse grains)

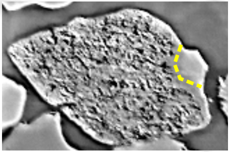
Double carbonate path : contacts Na_2CO_3 - $CaCO_3$ $\rightarrow$ formation of a crystalline double carbonate.



760 °C

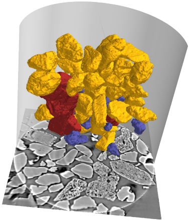


25 °C



760 °C

Evolution of calcium carbonate in a ternary batch

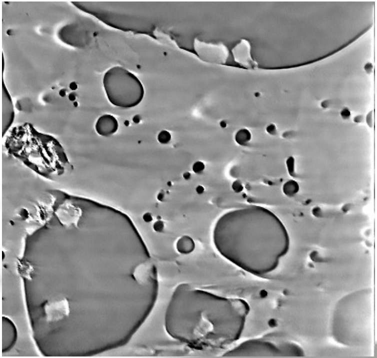


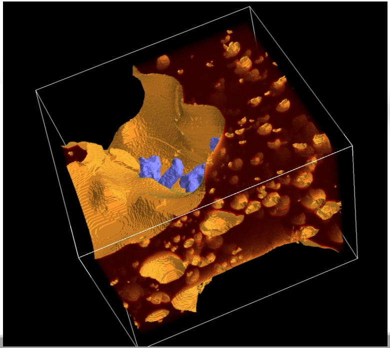
Two very different reaction paths

- depending on contacts with sodium carbonate

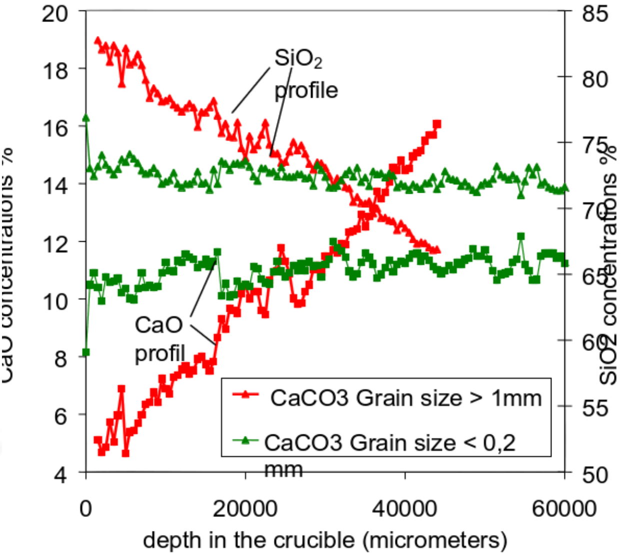
Calcination path : no contacts with Na_2CO_3

$CaCO_3 \rightarrow CaO + CO_2$ formation of refractory calcium oxide





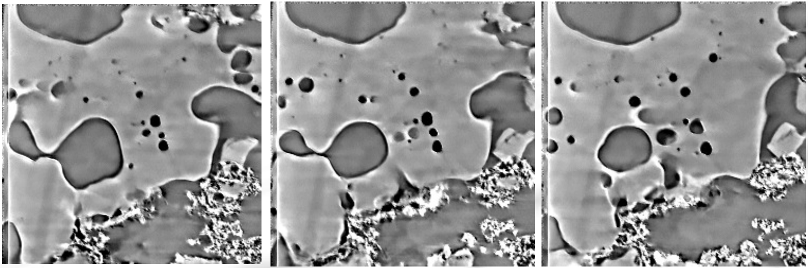
A clue for explaining chemical segregation ?



[Chopinet et al., Glass. Tech. 2010]

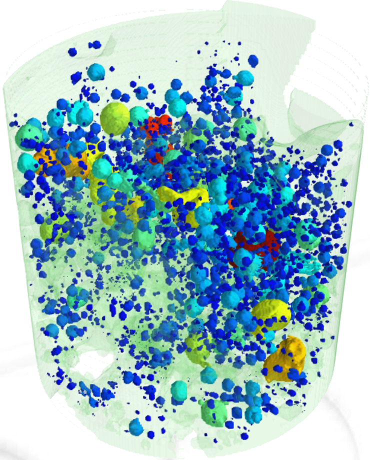
Bubbles

Bubbles are created as a result of the production of melts and the deconnexion of the granular network : open pores between grains are closed down by the melts.



Bubbles

⇒ the initial distribution of bubble sizes is partially determined by the geometry of the granular packing

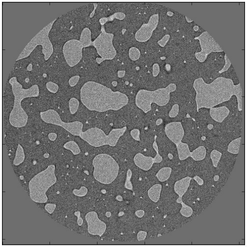


Need for faster acquisitions to follow bubbles creation and evolution.

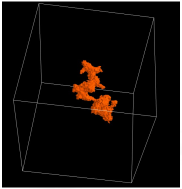
Domain coarsening in phase-separating glasses

PhD of David Bouttes

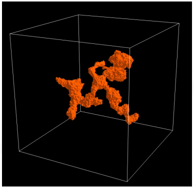
- Barium-borosilicate glass
- Phase-separation in liquid state (1000 - 1400° C)



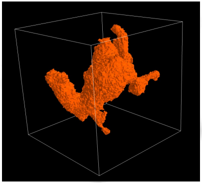
ID19



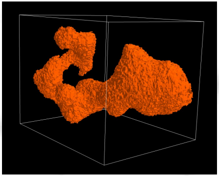
$t = 17$ min



$t = 25$ min



$t = 42$ min



$t = 65$ min

Evolution of the shape of the domains

- Hydrodynamical regime

Conclusions

- **In-situ tomography : a great technique for studying glass melting**
  - Quantitative data on transformations
  - Rich source of inspiration
  - Needs to be coupled with other techniques
- **The technique is still developing**
  - Towards faster and faster imaging
  - Challenging data processing
- **Could in-situ tomography be used to study other systems in glass science ?**

Thank you for your attention !