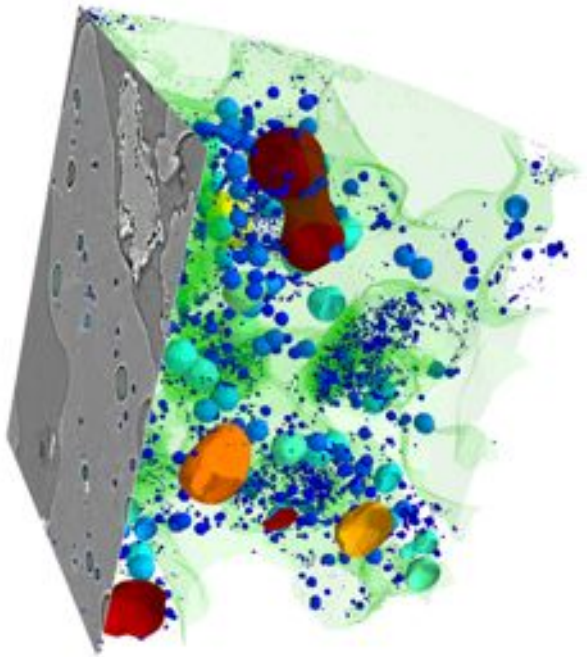
Journées USTV/GDR Verres, Baccarat 2014

Early melting reactivity stages, soda-lime glass heterogeneities content



William Woelffel[1]

Chopinet M-H.[1], Toplis M. J.[2], Boller E.[3], Gouillart E[1], Véron E[4]

[1] Surface du Verre et Interfaces, CNRS/Saint-Gobain, Aubervilliers, France

[2] IRAP, Observatoire Midi Pyrénées, Toulouse, France

[3] ID19, European Synchrotron Radiation Facility, Grenoble, France

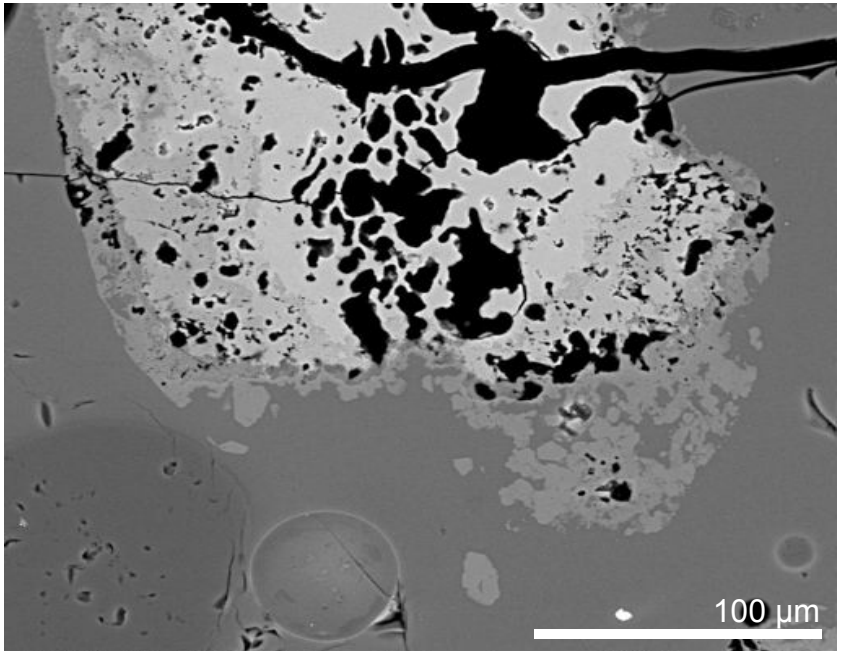
[4] CEMHTI, CNRS, Orléans, France

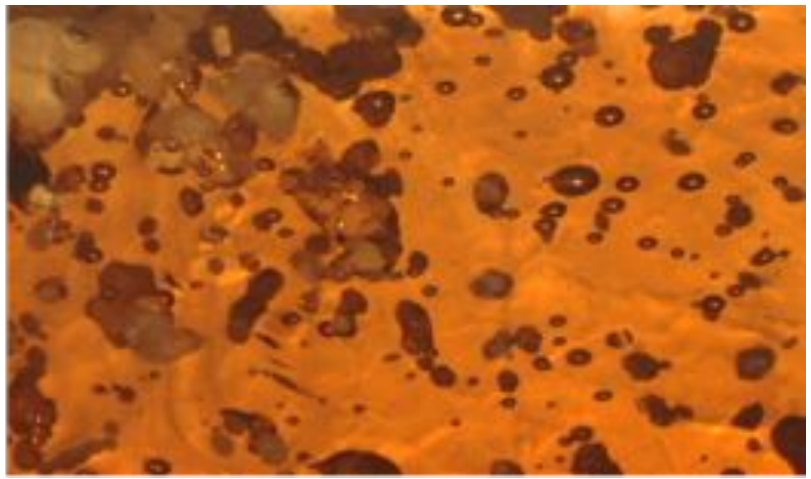
cnrs advancing the frontiers

SAINT-GOBAIN

What's the matter with soda-lime batch melting?

- Heating a glass batch to its liquidus temperature yields **poor results**
  - **Unmolten** grains
  - **Inhomogeneous** glass
  - Numerous **bubbles**
- Contrary to Na_2CO_3, $CaCO_3$ does not **melt** nor **react fully** and completely at low temperature

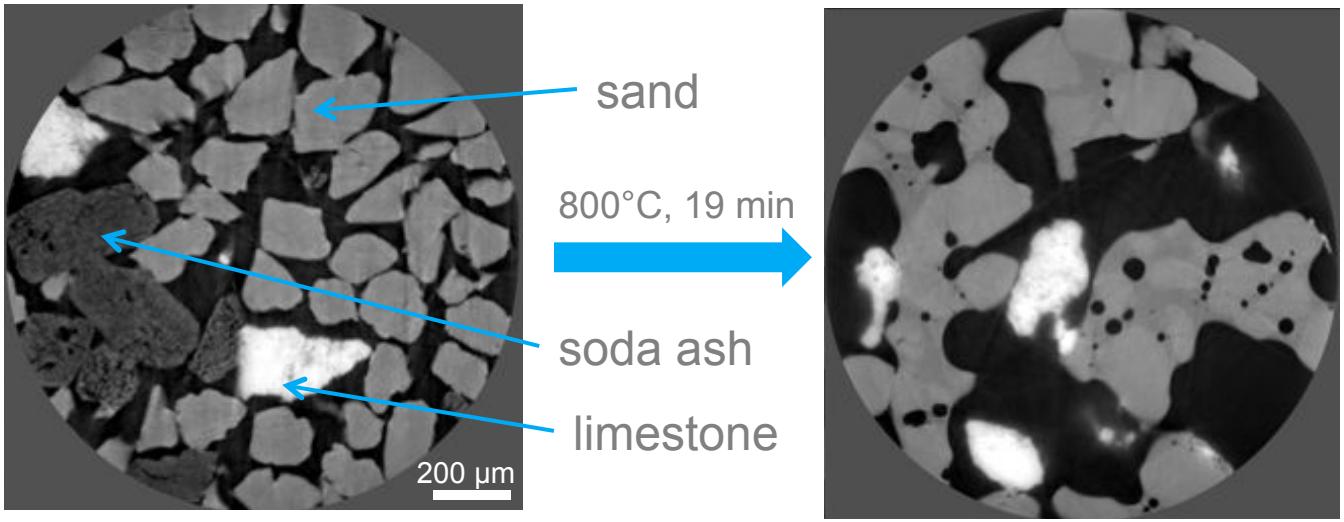




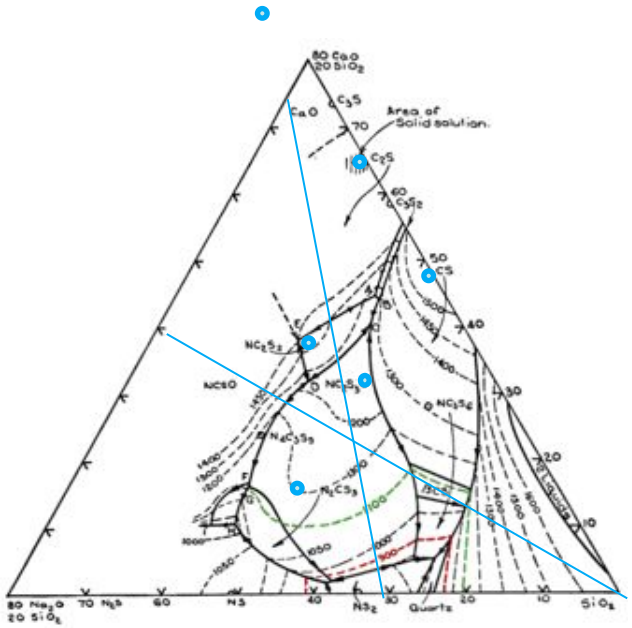
From carbonates to glass

- From a **polyphasic**, heterogeneous, granular state to a **homogeneous** glass:
  - **Granular** stacking & forces
  - Chemical **reactions**
  - **Deeply entangled**

- Ultrafast *in situ* tomography on ID19, ESRF, France



From carbonates to glass



- Two [1] pseudo-binary reaction axes
  1. NS_2-C as observed by SEM
  2. NC-S the mixed carbonate route

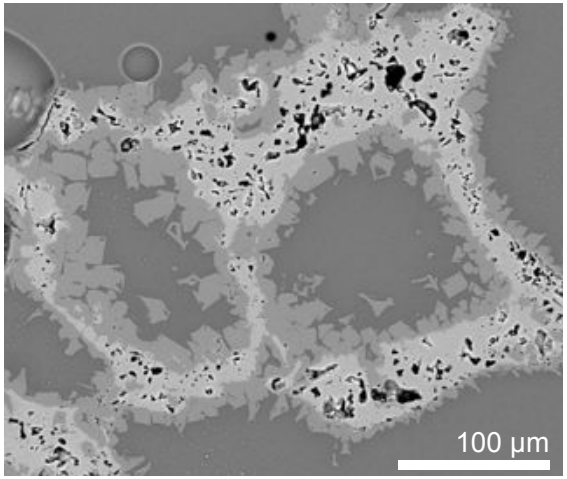
- Axis 1: NS_2-C
  - Quick reaction between silica and sodium carbonate
  - Slow, boundary- or diffusion-controlled reactions between calcium oxide-based compounds and a glassy liquid

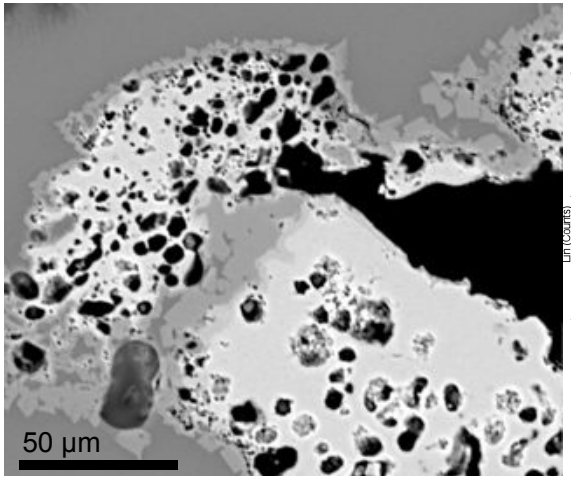
- Axis 2: NC-S
  - Formation of liquid and/or solid mixed carbonates at low T
  - Quick consumption by reaction with silica [2]

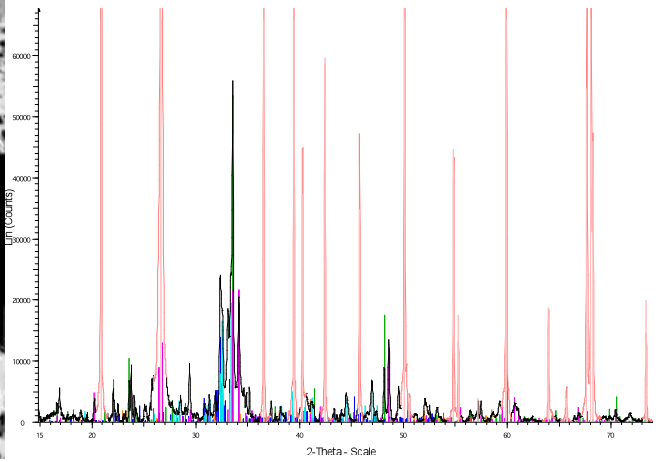
[1] Wilburn, F.W. & Thomasson C.V. *Phys. Chem. Glasses* 2, n°4 (1961)
[2] Cable, M. & D. Martlew. *Glastech. Ber.* 61, nº 2 (1988): 31-35.

From carbonates to glass

- Calcium carbonate reacts to form a series of intermediate compounds
  - CaO, CS, C_2S, NC_2S_2, N_2CS_3, NC_2S_3, NCS_2 in SEM/EDX
  - Observed as **shell compounds** around Ca-based grains surrounded by a nearly **homogeneous glass**
  - Detected as **crystals** in XRD experiments & reported by [1] & [2]





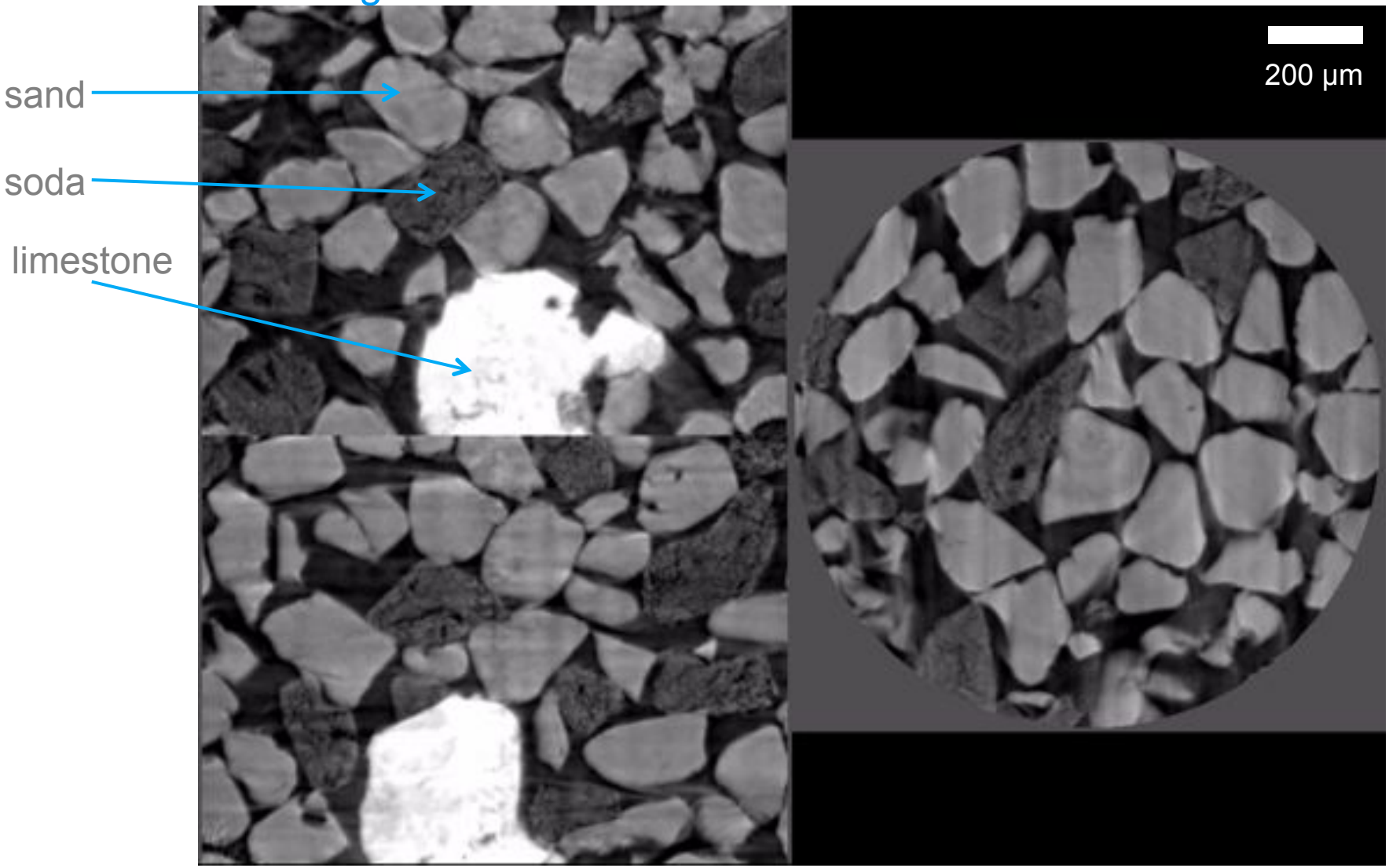


[1] Dolan, M. D. & Misture, S. T. *Glass Tech.* 45, 140–147 (2004).

[2] Tsujimura, T., Tanaka C., & Sakamoto O. *Glass Tech.: Euro. J.of Glass Sc. and Tech. Part A* 53, nº 5 (2012): 202-210.

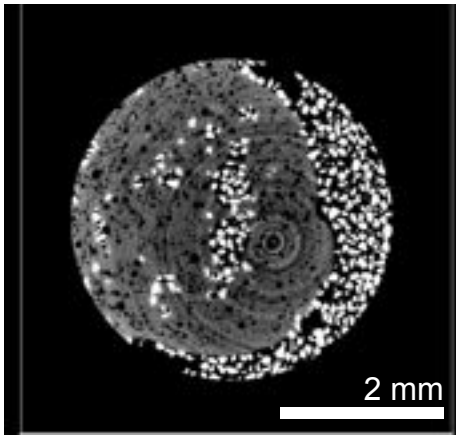
Life of a calcium carbonate grain

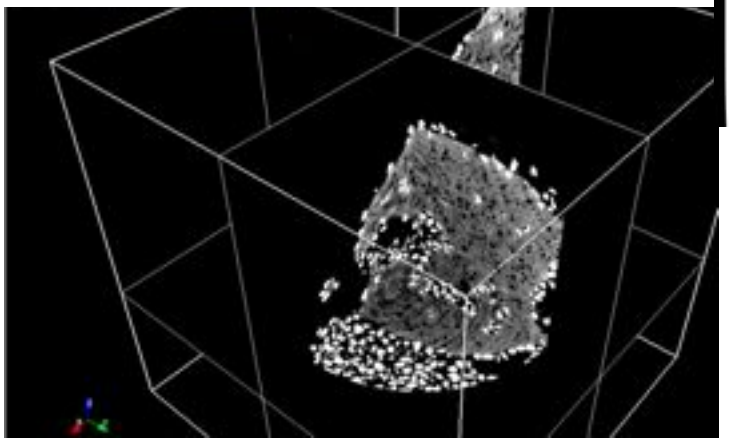
- Wetting leads to C_2S grains + shell ternary silicates
- Poor wetting leads to calcination

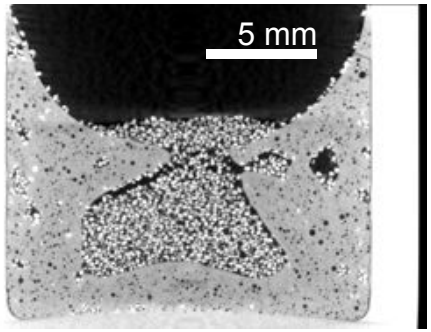


Life of a calcium carbonate grain

- Unreacted $CaCO_3$ form **CaO**, which isn't nice
  - CO_2 emissions **prevent wetting**
  - Lime has **poor wetting** behavior



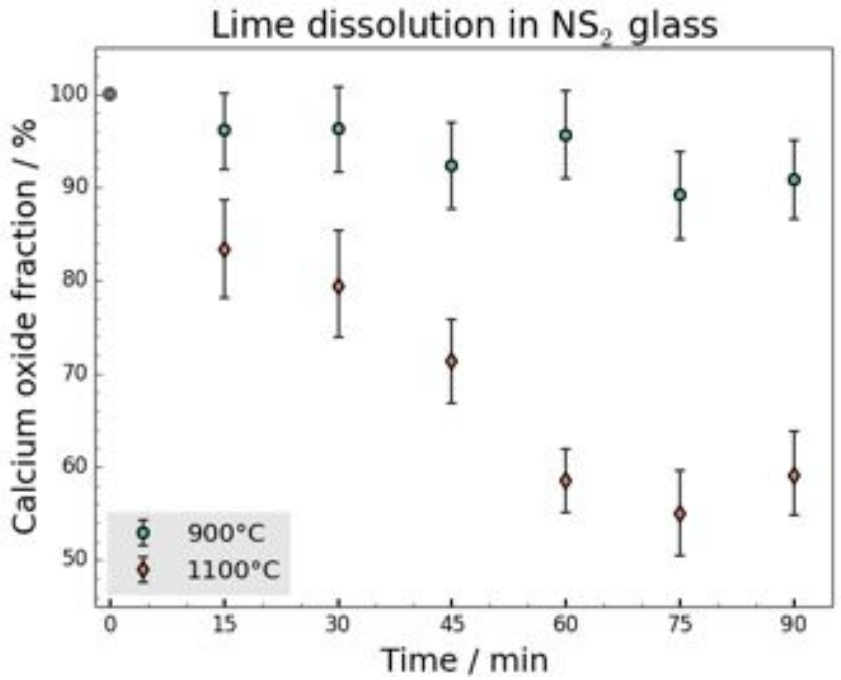




- Lime dissolution at low temperature is slow
  - Sieved NS_2 (< 250 µm) + CaO (200 -250 µm)
  - Alumina crucibles, static temperature
  - *Ex situ* tomography

Life of a calcium carbonate grain

- Lime is to be avoided
  - Slow dissolution making CaO unavailable for SiO_2 network depolymerization
  - Glass segregation at lab scale [1]

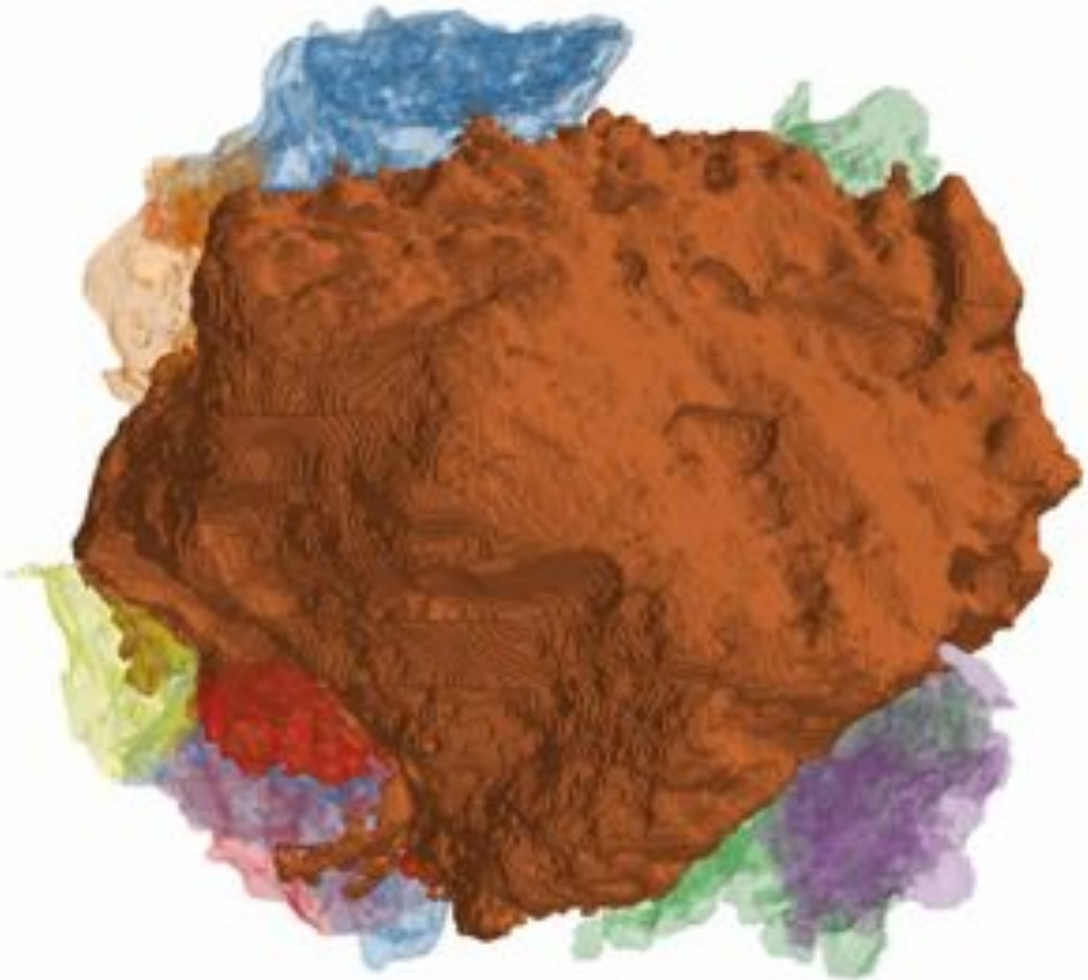


- But how?

[1] Chopinet, M.H., E. Gouillart, S. Papin, & M.J. Toplis. *Glass Tech.-Eur. J. of Glass Sc. and Tech. Part A* 51, nº 3 (2010): 116-22.

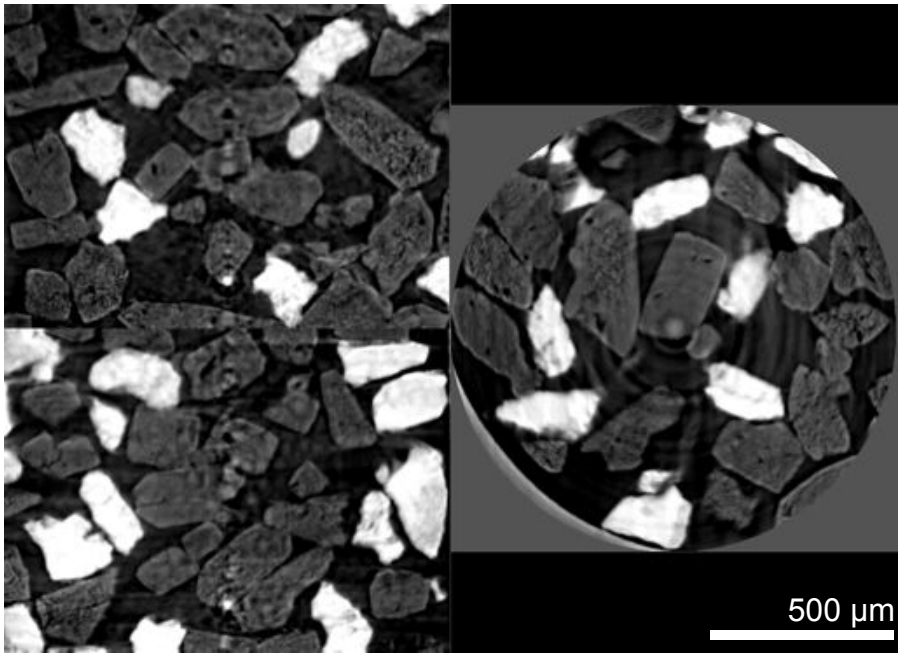
Life of a calcium carbonate grain

- Munching depth detection

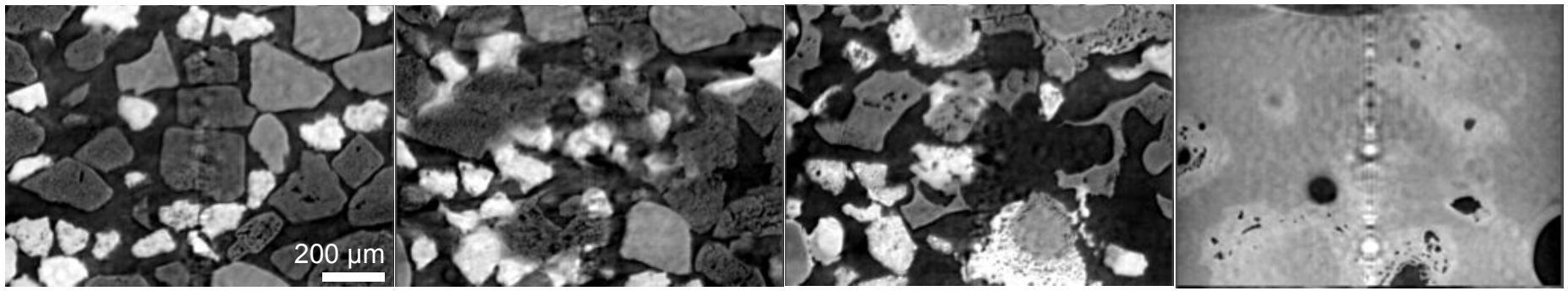


Life of a calcium carbonate grain

- Mixed carbonate formation: observed in the absence of silica



- Quick reaction with silica, forming refractory Ca & Na silicates



Conclusion

- **Tomography has become a valuable link in the glass melting investigation chain**
  - Reveals mechanisms
  - Enhances the understanding of local chemical interactions
  - Fuel for thought

- **Tomography & image processing : towards quantitative measurements**
  - Already used for SiO_2-Na_2CO_3 system (Gouillart *et al.*, J. Am. Cer. Soc. 2012)

- **Lime is an unproductive chemical path**
  - Size threshold effect: XRD
  - Chemistry?

Thank you for your attention