TRANSVERSAL R&D CENTERS BY SAINT-GOBAIN

High-temperature liquids in the glass and ceramic industry- some challenges

Emmanuelle Gouillart
Scientific director of Saint-Gobain Research Paris

Ekaterina Burov, Cyril Condolf, Eric Janiaud, Cécile Jousseaume, Johann Meulemans, Adrien Stoliaroff

TRANSVERSAL R&D CENTERS BY SAINT-GOBAIN

GLASS AT SAINT-GOBAIN

Glass
for the construction and mobility markets

Glass wool
for the construction and technical insulation markets

Glass veil and technical textiles
for the construction and industrial markets

Glass-ceramic solutions
for cooking and fireplaces applications

Other applications (not SG) : bioglass, sealing glass, optical fibers, ….

Saint-Gobain Confidential & Proprietary SAINT-GOBAIN RESEARCH PARIS

Glass families & glass production

Glass family	Key components	Common applications and uses
Soda lime	Na_2O-CaO-SiO_2	Flat glass (window), tableware Container glass (bottle and jars)
Borosilicate	Na_2O-B_2O_3-SiO_2	Headlights, Laboratory and cooking ustensils materials and tubing
Speciality glass	Na_2O-CaO-B_2O_3-SiO_2	Construction materials such as glass wool for insulation and glass fiber for reinforcement
	MgO-Al_2O_3-SiO_2	Glass fibers for reinforcement
	Al_2O_3-CaO-B_2O_3-BaO-SiO_2	Substrate glass for displays (LCD, computer, mobile phone)

Source: Renewable and Sustainable Energy Reviews 155 (2022) 11885

SAINT-GOBAIN

https://www.varzene.com/en/vmagazine/Developments-in-Glass-Mold-industry

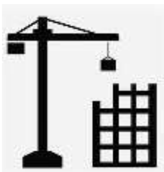

http://washingtonglassschool.com/float-glass-fun-facts

Impact environnemental de la construction

Quelle est la part de la construction (bâtiments) dans nos émissions de CO_2 ?

40%

12 % construction

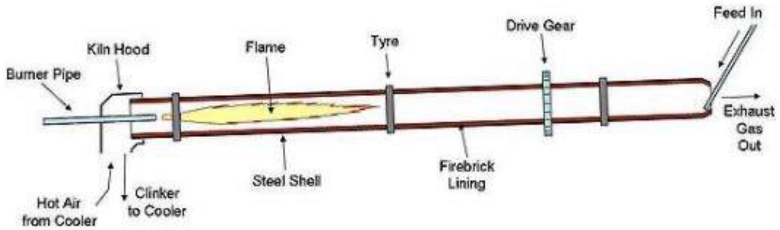
Avant tout: béton et armature métallique

Verre: 0.2% des émissions
100 millions de tonnes CO_2 /an

SAINT-GOBAIN

SAINT-GOBAIN

HIGH-TEMPERATURE PROCESSES



0.9 kg CO2 / kg cement

1.8 kg CO2 / kg steel

0.6-0.8 kg CO2 / kg glass

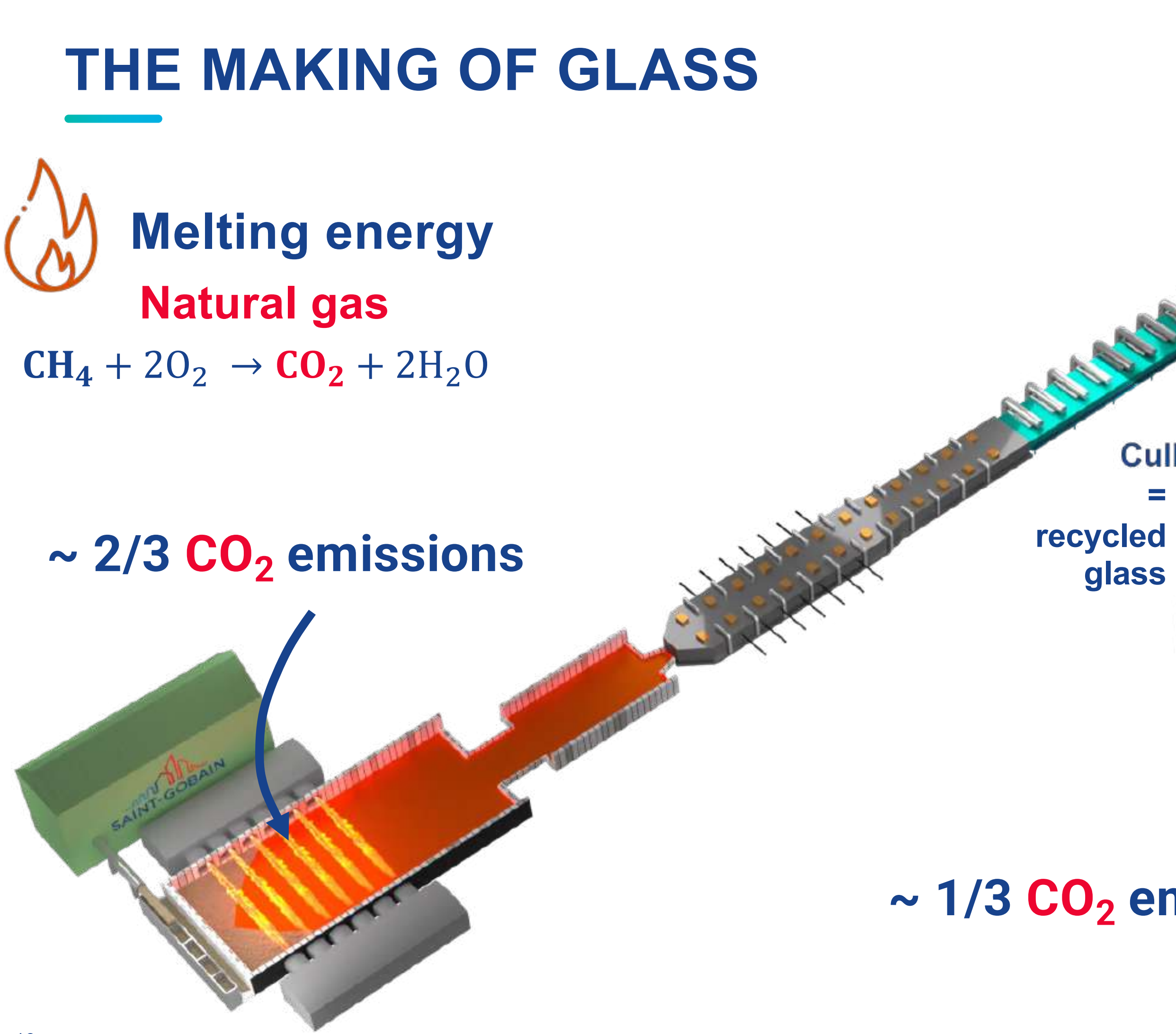
THE MAKING OF GLASS

Melting energy

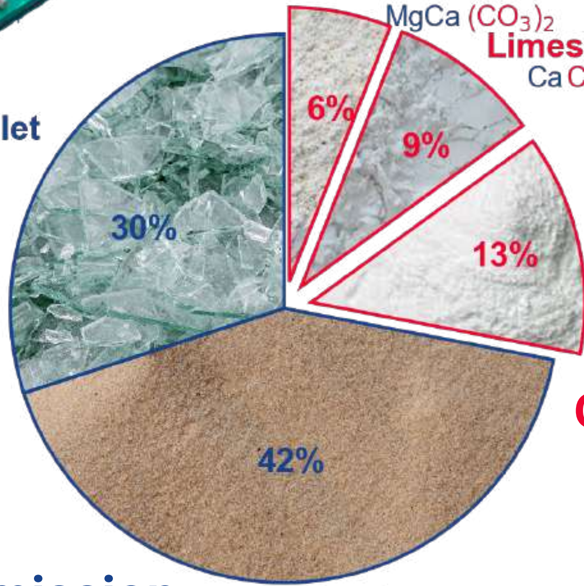
Natural gas

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

~ 2/3 CO_2 emissions



Raw material batch



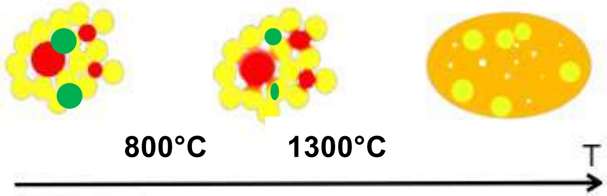
~ 1/3 CO_2 emission

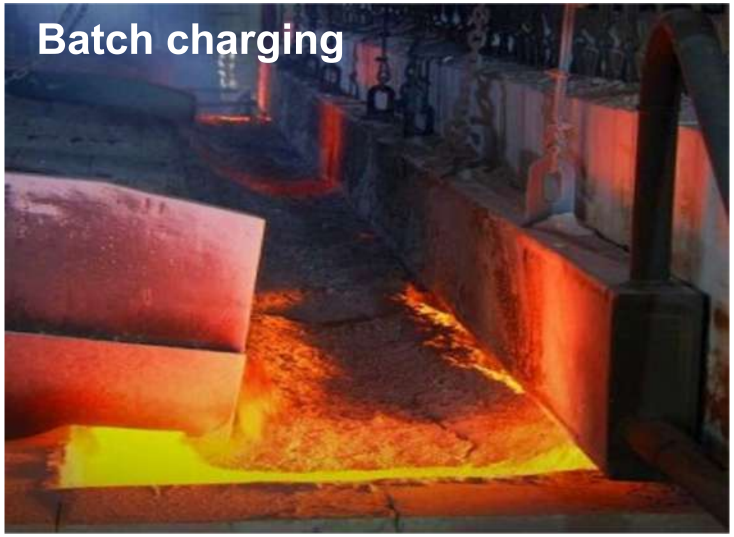

1/3

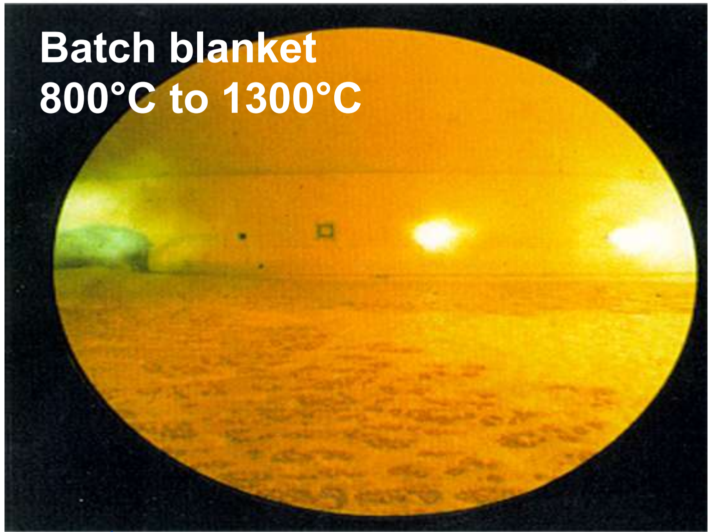

2/3

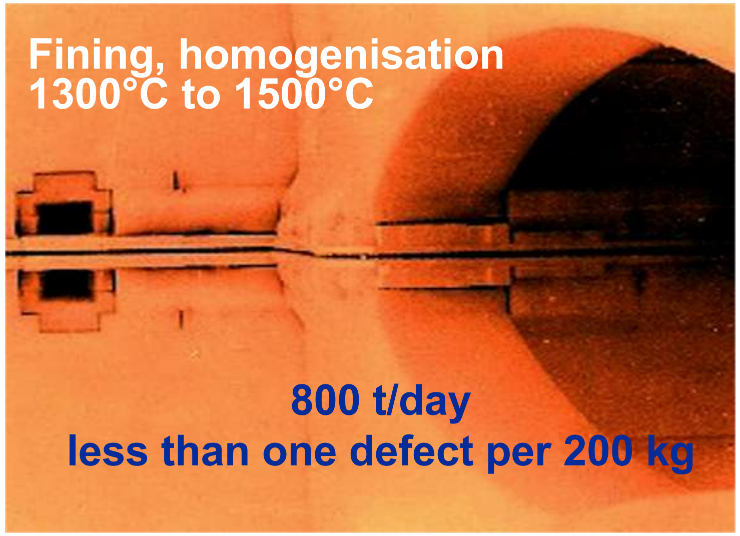
FLOAT GLASS

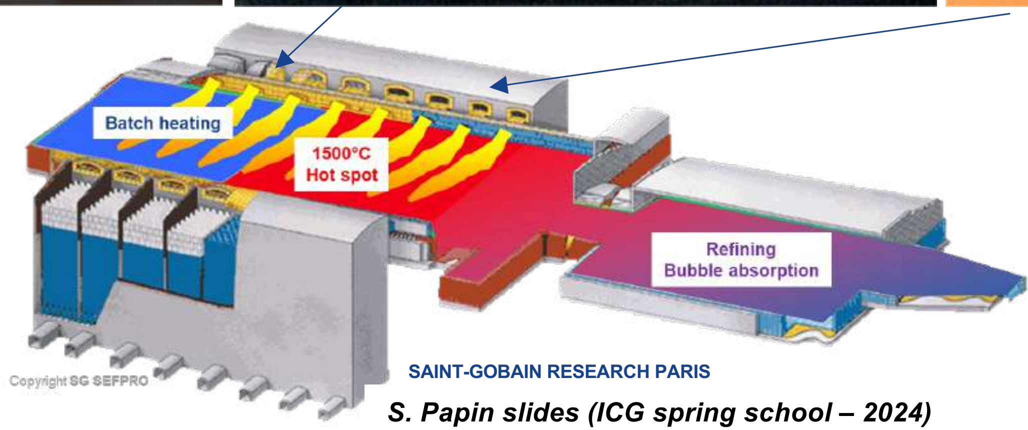
GLASS QUALITY CHALLENGE











SAINT-GOBAIN RESEARCH PARIS

S. Papin slides (ICG spring school – 2024)

ALTERNATIVE RAW MATERIALS

Decarbonate glass raw materials

Limestone substitution with wollastonite in India

- ✓ Up to 80% replacement :9kt CO_2 savings per year

Challenges:

- ✓ Different reaction paths & enthalpies
- ✓ Impurities

More cullet

Impurities are more problematic for flat glass than bottle glass

Collecting construction cullet is less mature

ALTERNATIVE WAYS OF HEATING

Electrical heating

Verallia + Fives project in Cognac 180 t/d

Challenges: higher refractory corrosion

Removing bubbles can be an issue

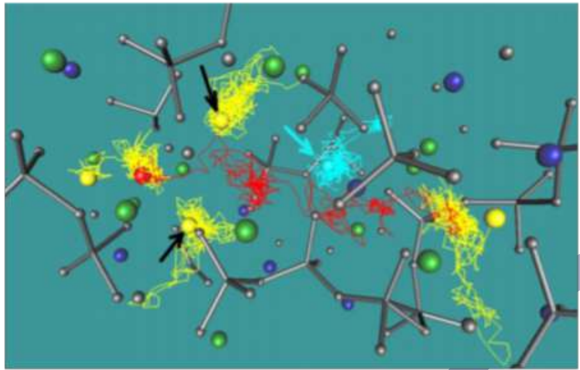
Hydrogen hybrid combustion

Hydrogen combustion flames, Herzogenrath

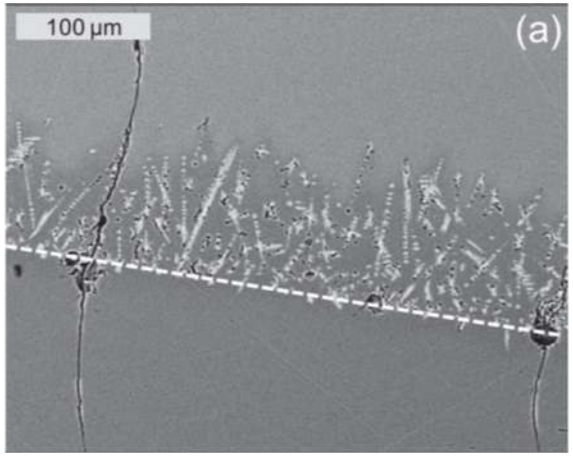
World's 1st glass production with 30% hydrogen

- ✓ Trial in Herzogenrath, Germany in March 2023
- ✓ More water in molten glass

PROPERTIES OF HIGH-TEMPERATURE LIQUIDS



Structure



Kinetic / transport properties: viscosity, diffusivity, electrical conductivity

Thermodynamical properties: **liquidus**, enthalpy, phase separation

Einstein relations

$$D_i = M_i k T \gamma_i$$

mobility $$M_i = v/F$$

The diffusion of different kinds of species can be investigated through different physical quantities.

Charged particles: Nerst-Einstein relation

→ network **modifiers**

$$D = \frac{\mu_q k T}{q}$$

q: charge of ions

Viscous liquids: Stokes-Einstein and Eyring relation

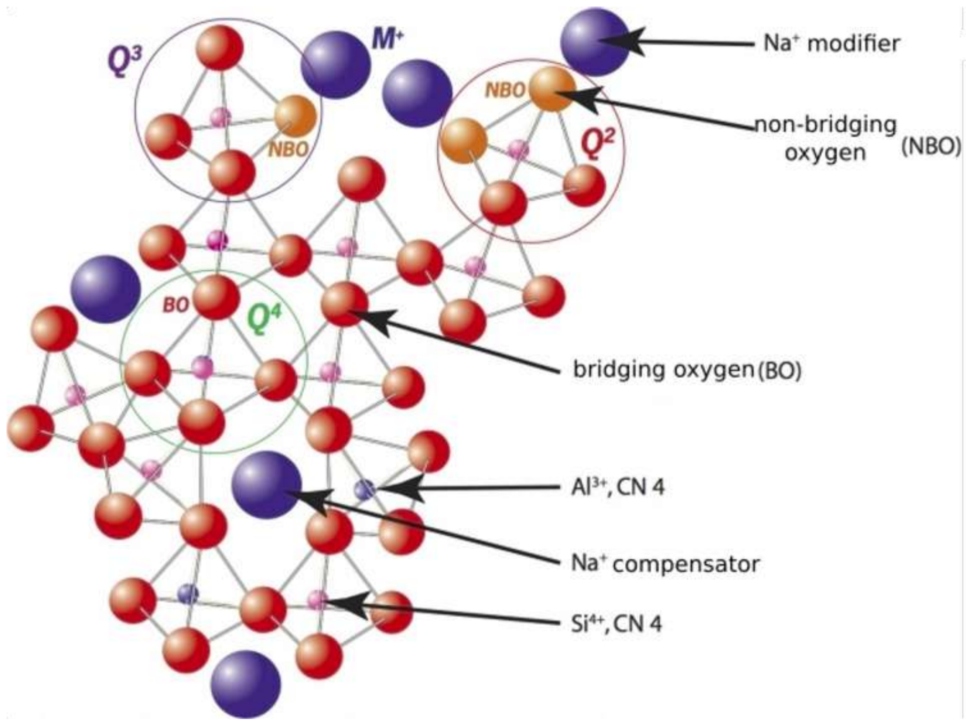
→ network **formers**

$$D = \frac{k_B T}{6\pi\,\eta\,r}. \qquad D = \frac{kT}{2\eta r}$$

η: viscosity

r: radius of particle

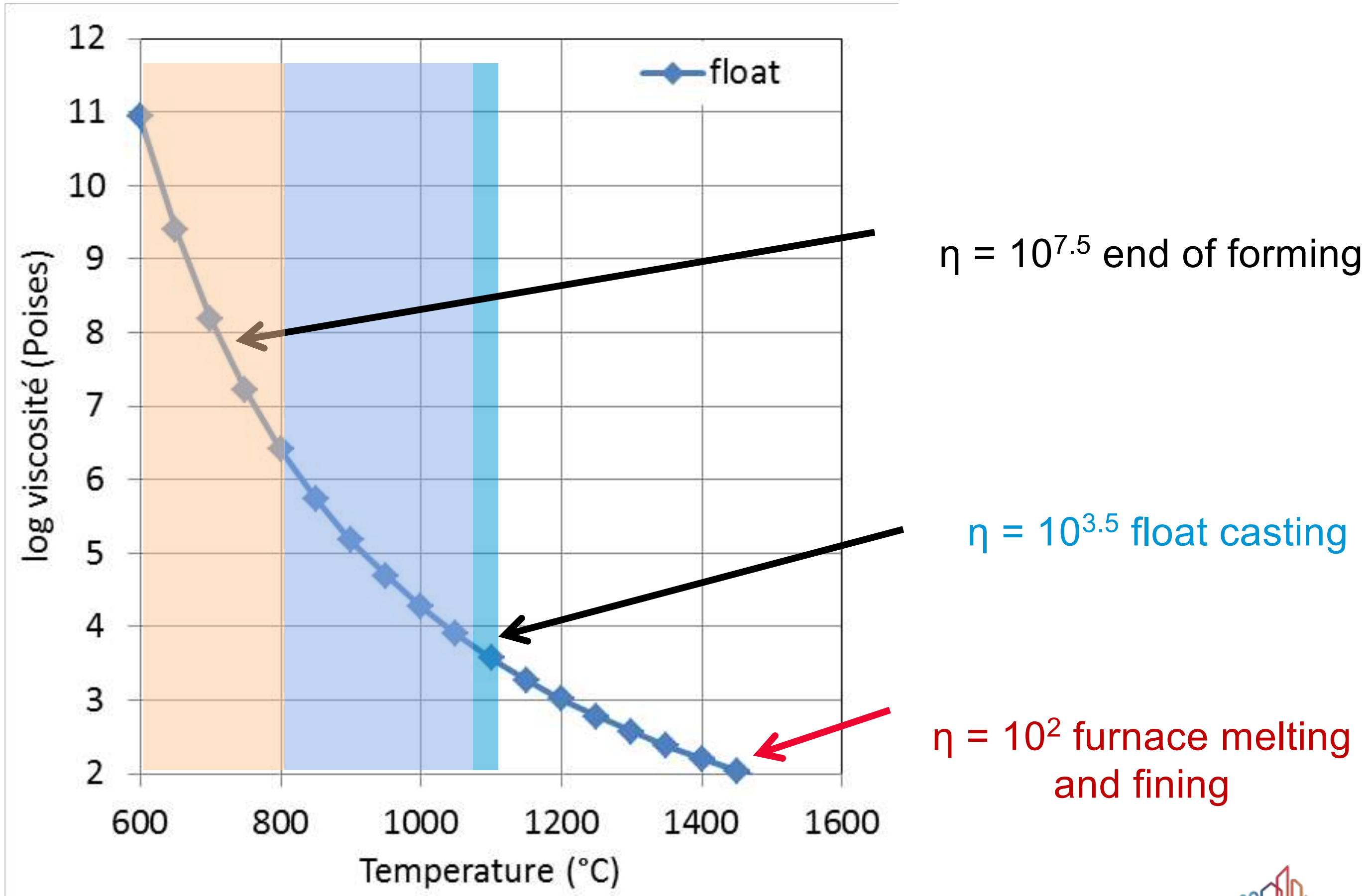
https://en.wikipedia.org/wiki/Fluctuation-dissipation_theorem



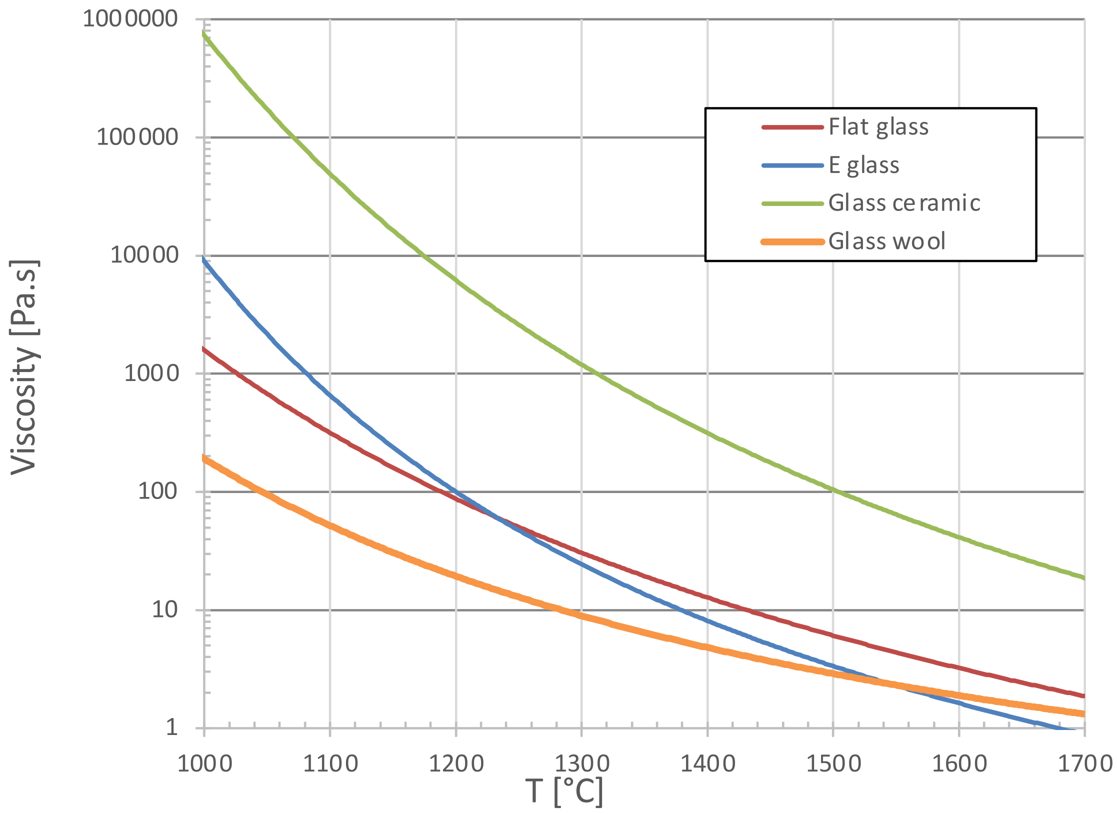
from USTV website
D. Neuville

VISCOSITY VARIATIONS DURING THE PROCESS

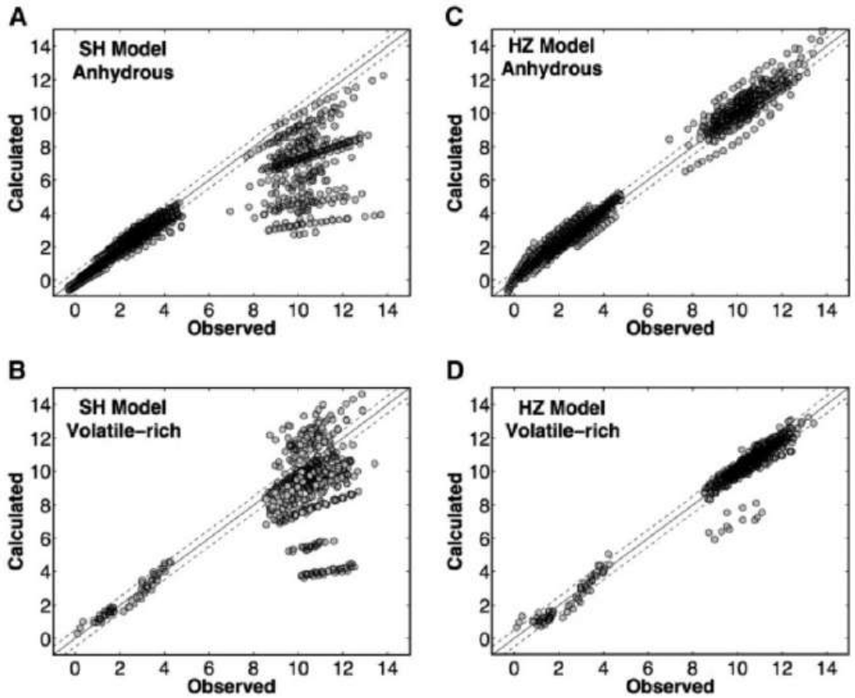
	dynamic Viscosity (Pa.s)	dynamic Viscosity (Poises)
Gas	10^{-5}	10^{-4}
Water, mercury Olive oil	10^{-3} $1.5\ 10^{-3}$ 10^{-1}	10^{-2} $1.5\ 10^{-2}$ 1
Motor Oil	1	10^{1}
Honey	10	10^{2}

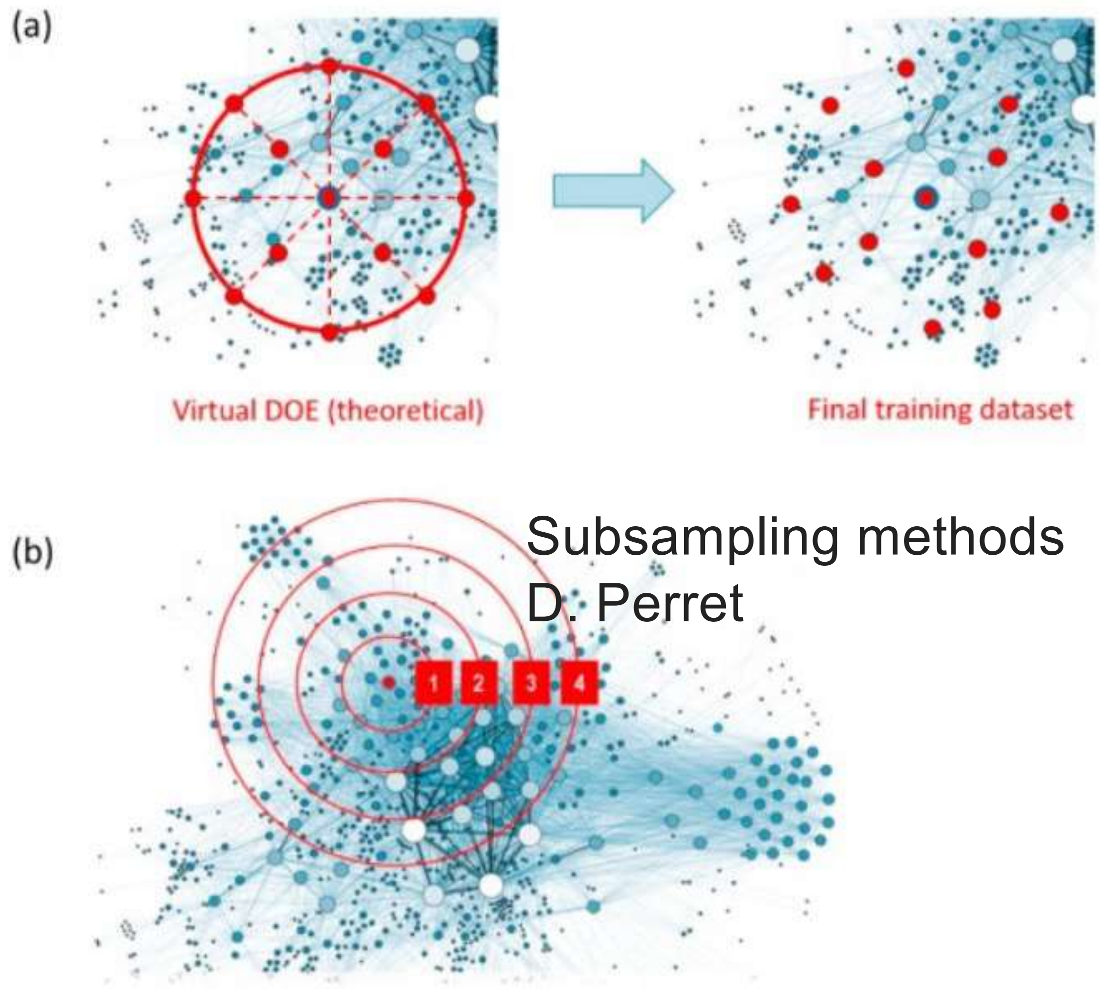


GLASS VISCOSITY



EMPIRICAL VISCOSITY MODELS

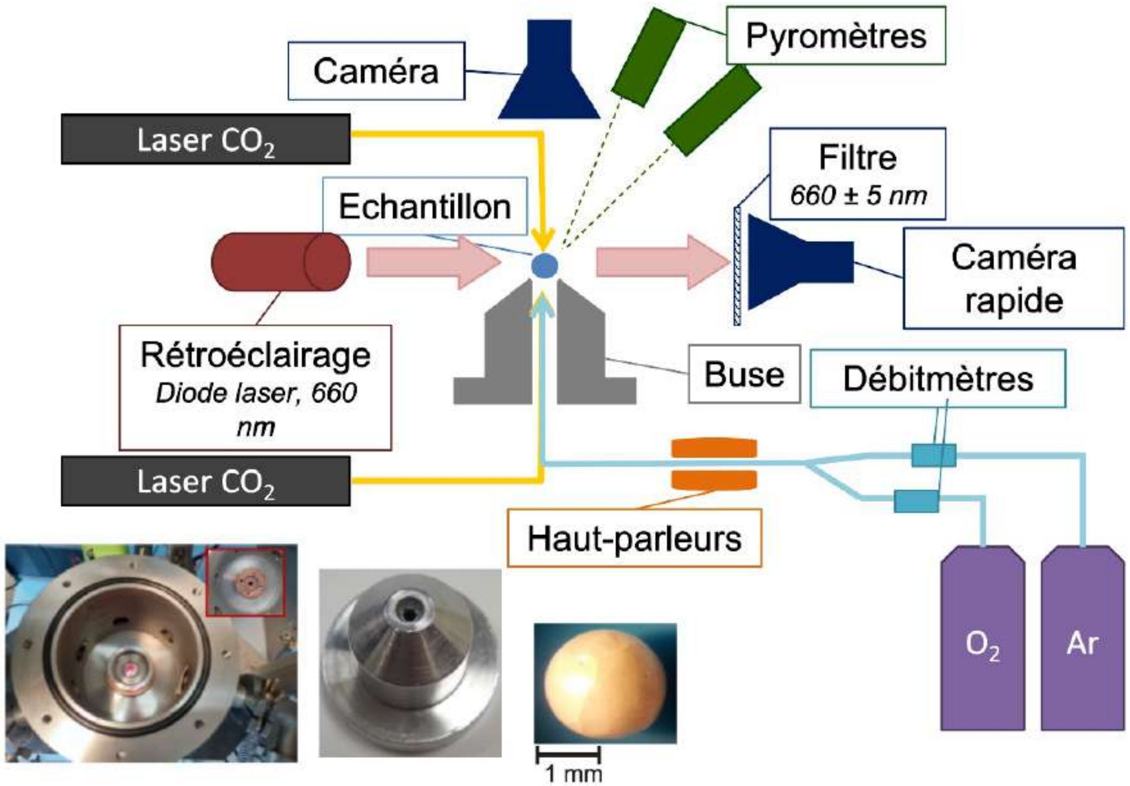


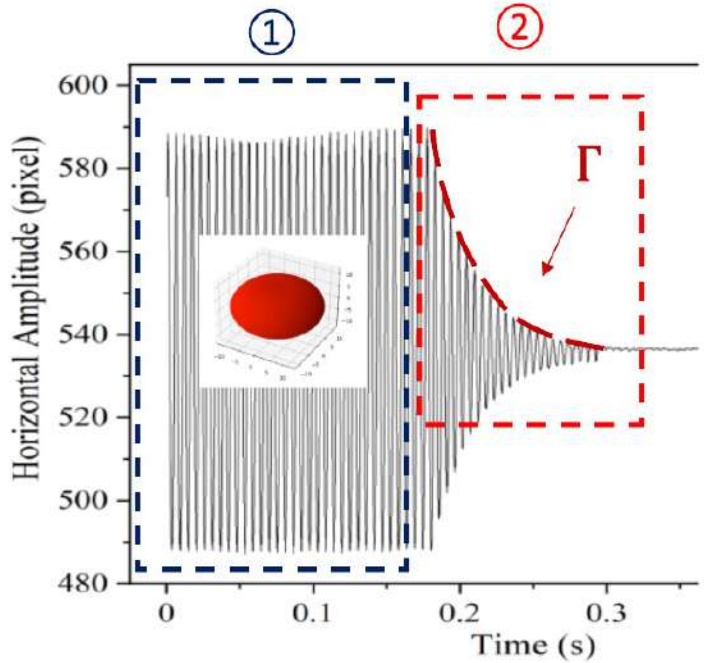


Subsampling methods
D. Perret

Parametric models of composition
Priven, Fluegel, Giordano…

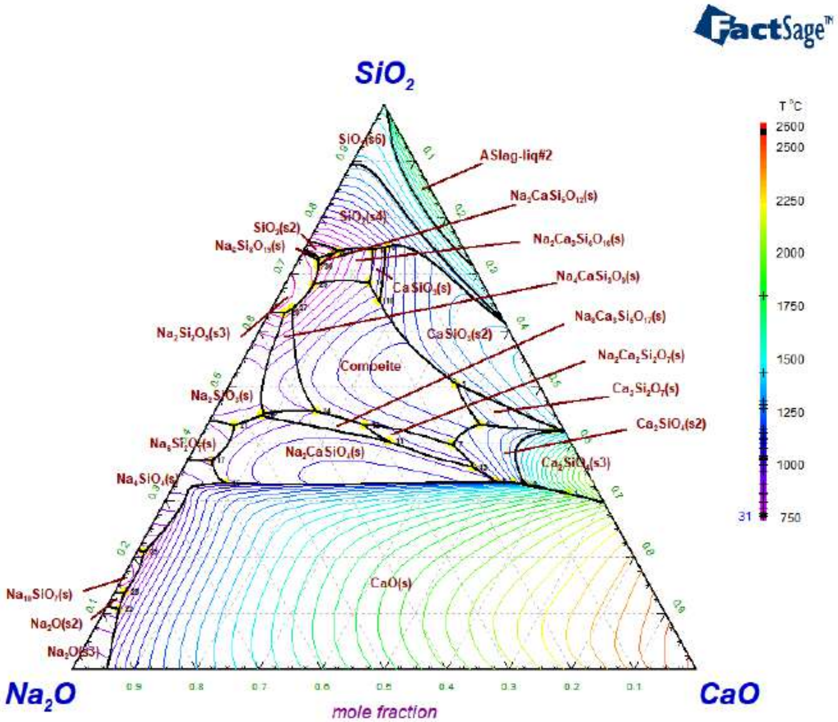
ADVANCED MEASUREMENTS OF VISCOSITY - CEMHTI

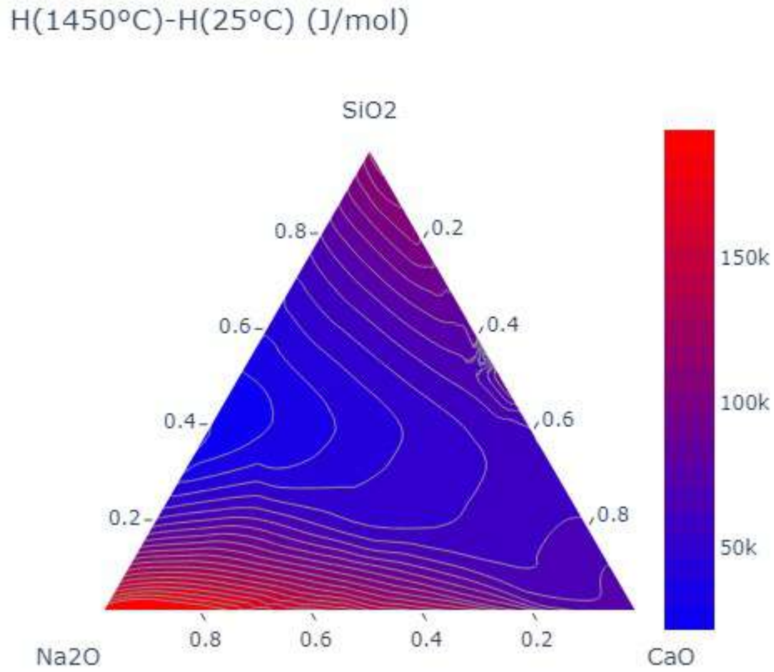




THERMODYNAMIC PROPERTIES OF MELT

T LIQUIDUS AND ENTHALPY

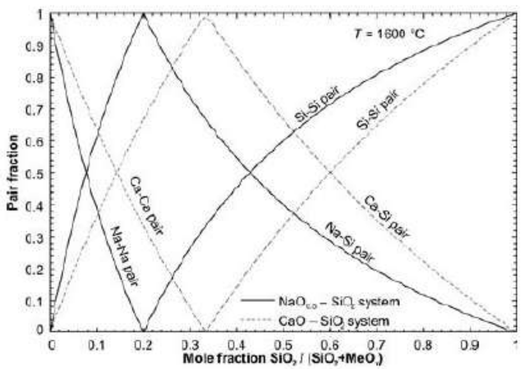




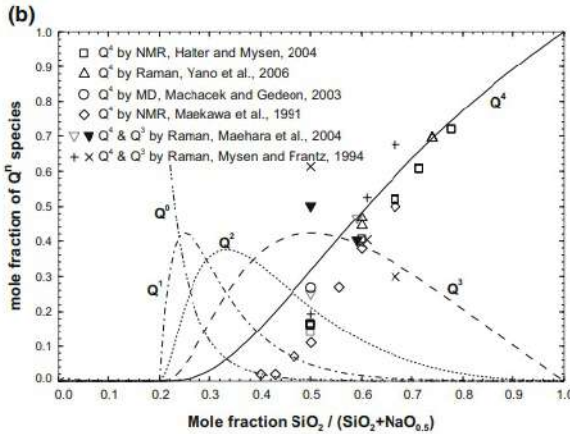
PHYSICAL PROPERTIES OF MELT

VISCOSITY

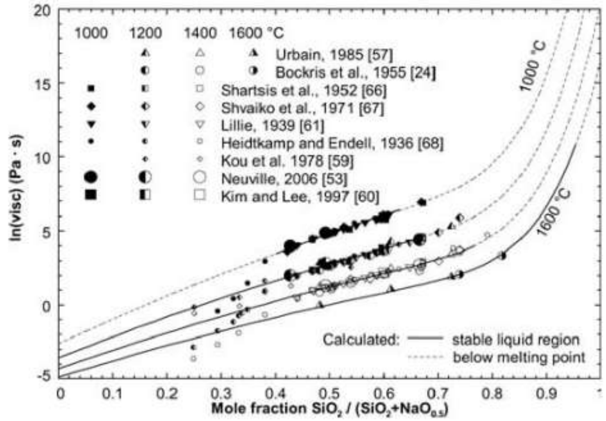
Calculated pair fractions Na-Si, Na-Na and Si-Si at equilibrium



Q^n species (silicon atoms having 0, 1, 2, 3, or 4 bridging oxygens)



Viscosity model = f(pair fractions)

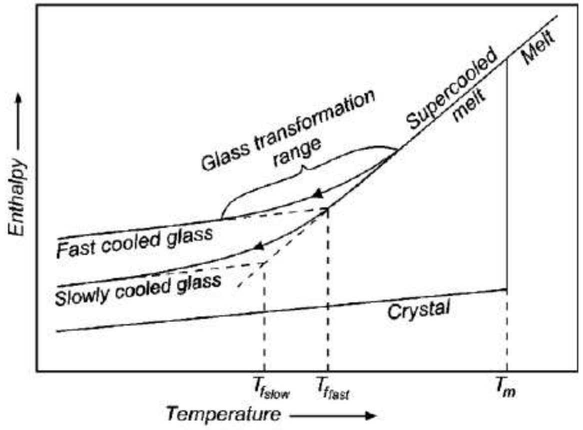


A. N. Grundy et al. A model to calculate the viscosity of silicate melts Part I Part I: Viscosity of binary SiO2-MeOx systems (Me = Na, K, Ca, Mg, Al) International Journal of Materials Research, vol. 99, no. 11, 2008, pp. 1185-1194.

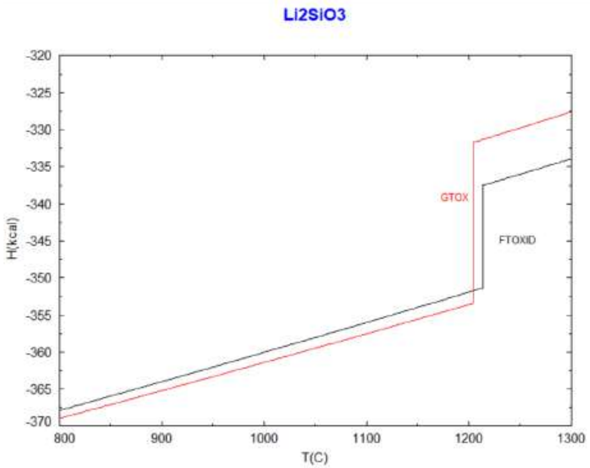
OUR NEEDS

IMPROVE THERMODYNAMIC DATABASES

Cullet

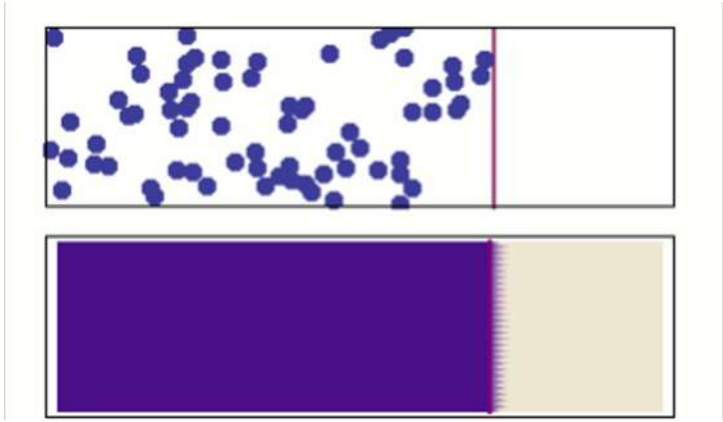


Addition of elements in oxide database : Se (PV glass), ZrO_2 (contained in refractories)…

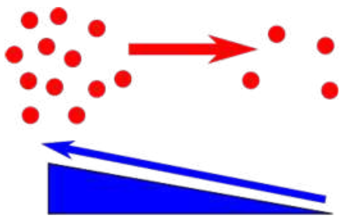


Raw materials

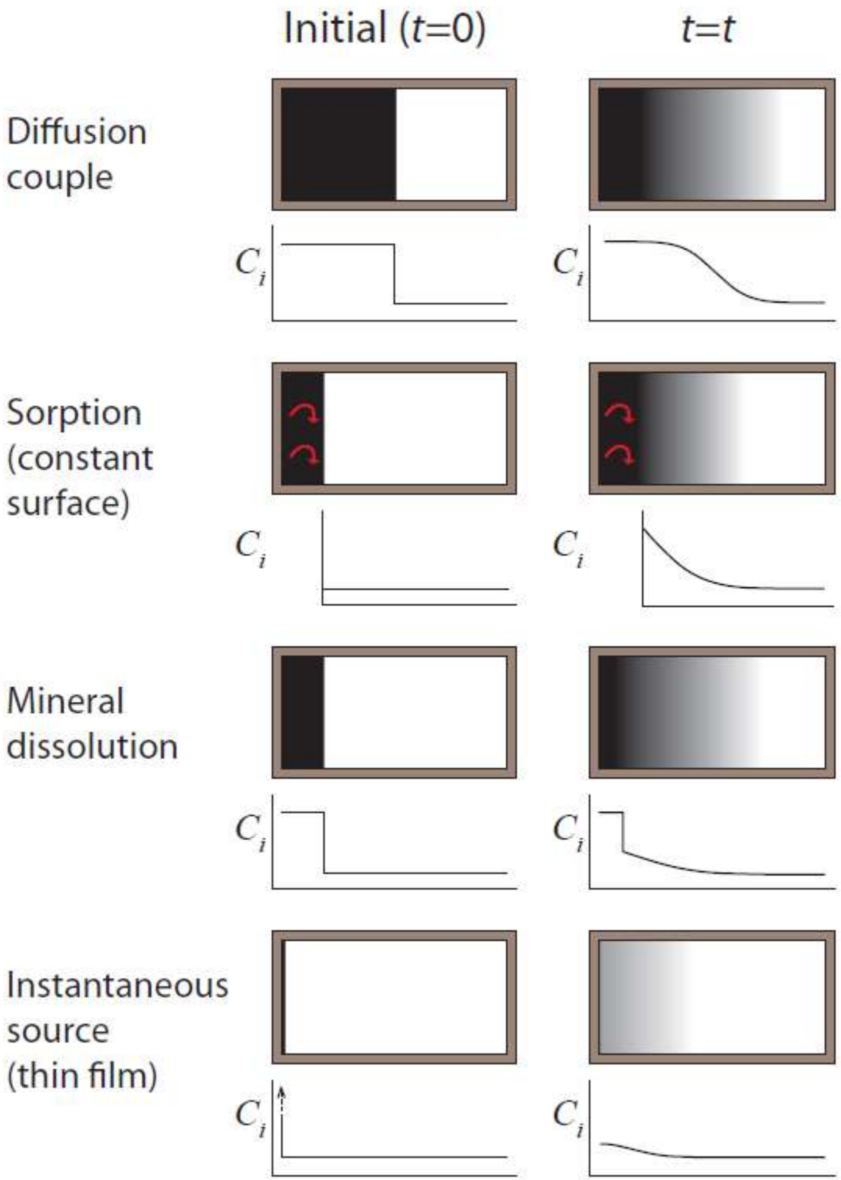
Chemical diffusion



$$\mathbf{j} = -D\nabla C$$



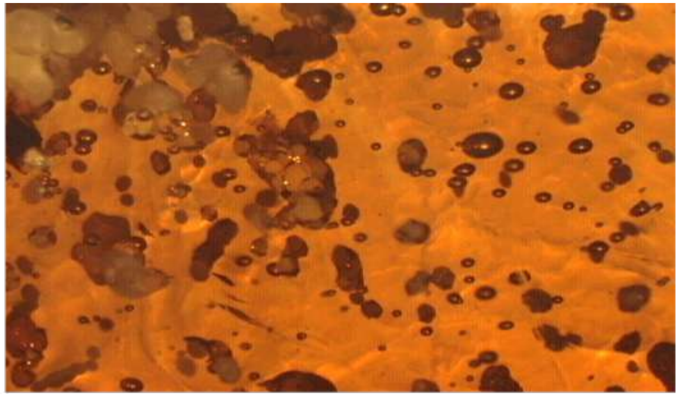
$$\frac{\partial C}{\partial t} = D\Delta C$$



Zhang, Y., & Gan, T. (2022). Diffusion in melts and magmas. *Reviews in Mineralogy and Geochemistry*, *87*(1), 283-337.

Consequences and applications of molecular diffusion in silicate melts

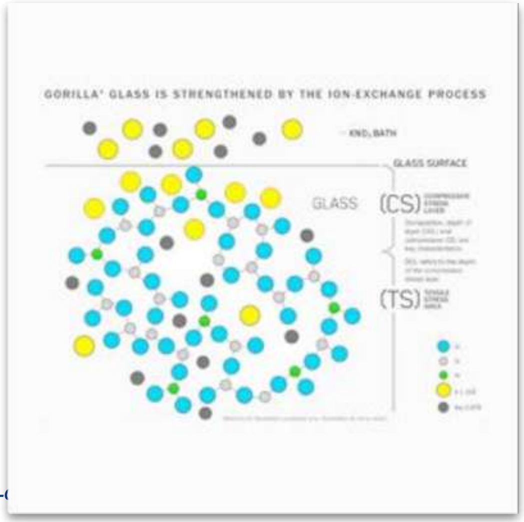
Glass melting: batch & stones



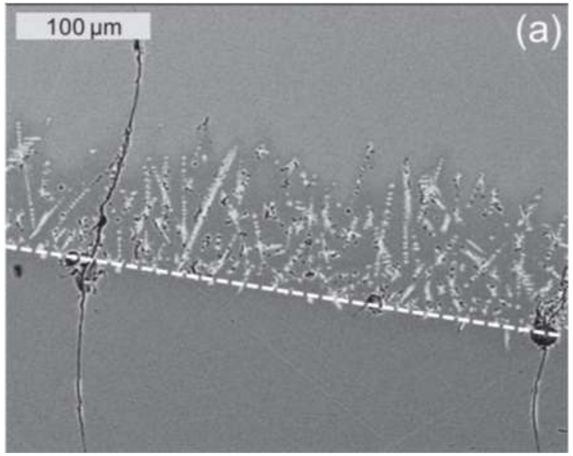
Refractory corrosion

Volatile diffusion & volcanic eruption

Ionic exchange (display)

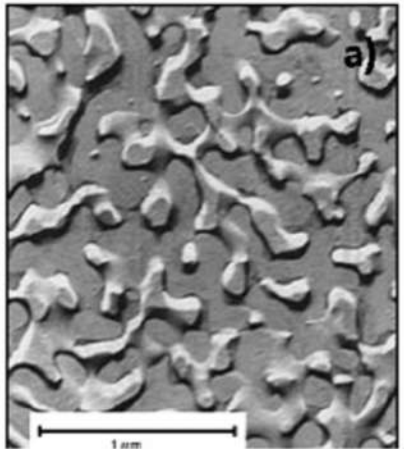


Crystallization



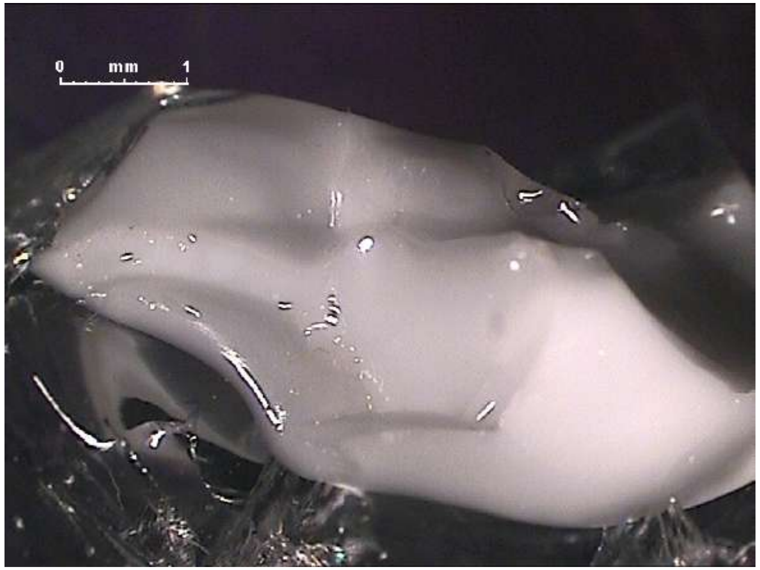
Pablo et al
JNCS 2019.

Phase separation



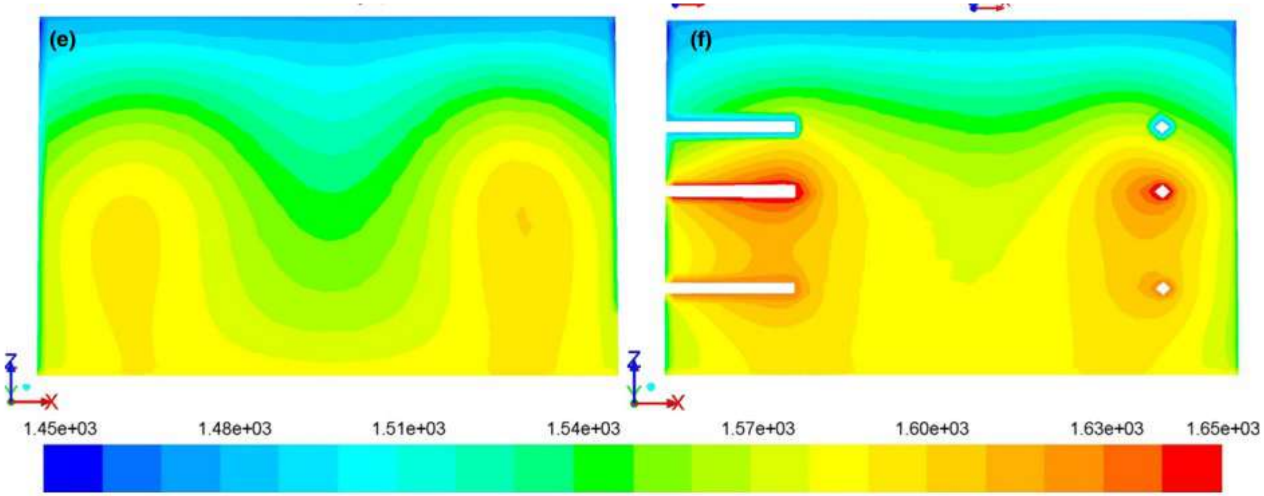
Why is diffusion important for sustainable glass?

More cullet → more impurities to dissolve



Courtesy of S. Di Pierro, SGR Paris

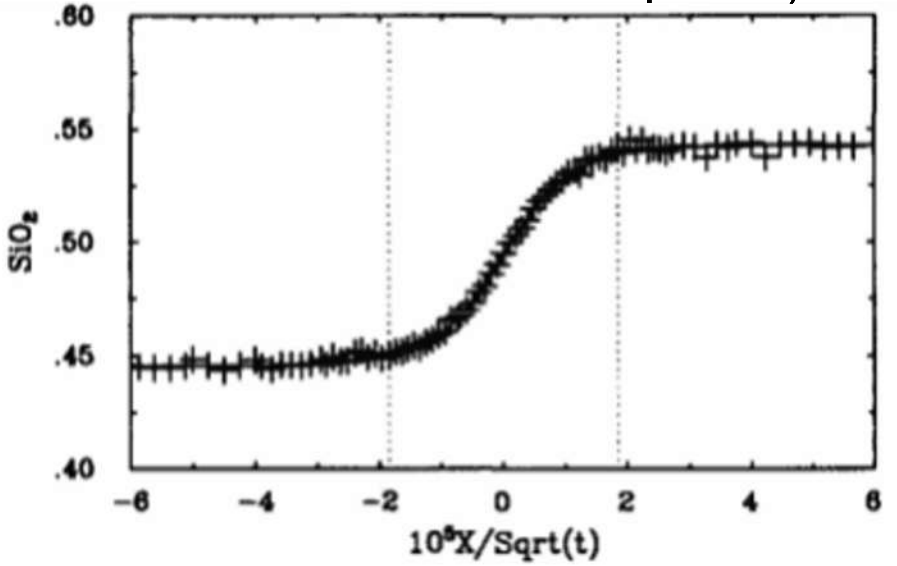
More corrosion of refractories with electric melting



Li, Hailong, et al. "3D simulation of borosilicate glass all-electric melting furnaces." *Journal of the American Ceramic Society* 97.1 (2014): 141-149.

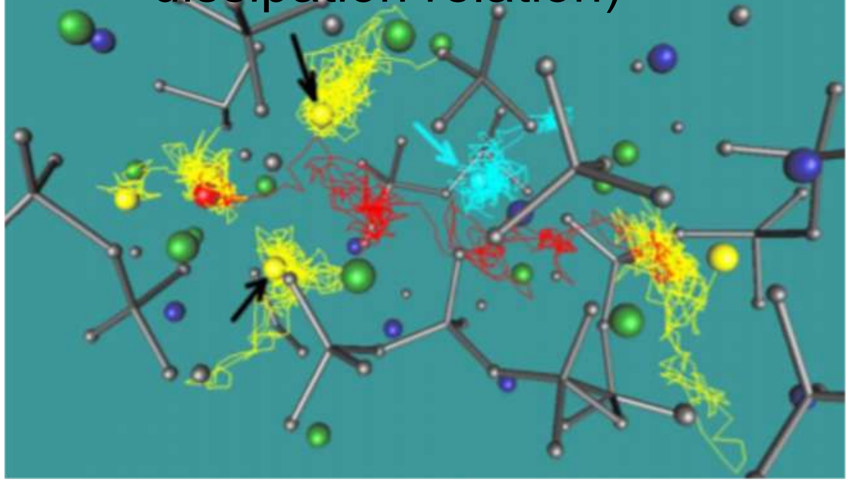
Measuring diffusion data

Concentration gradients (chemical concentrations, isotopes…)



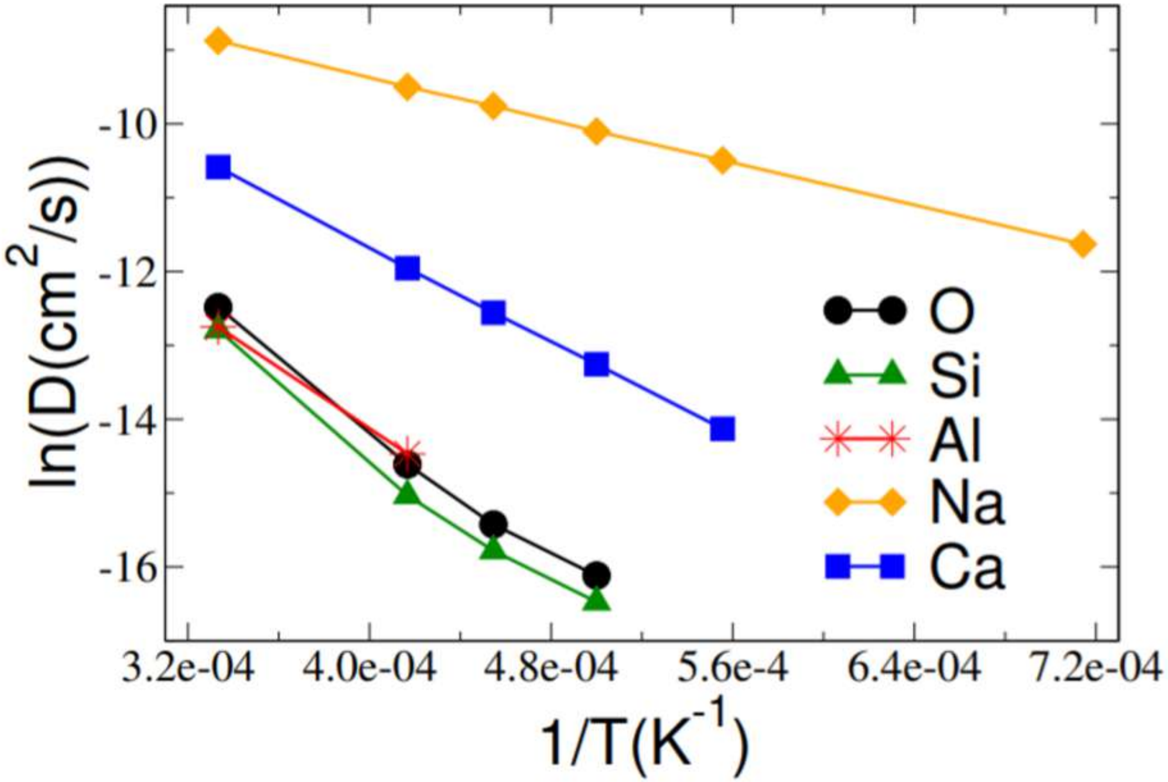
Liang, Yan, Frank M. Richter, and E. Bruce Watson. *Geochimica et Cosmochimica Acta* 60.24 (1996): 5021-5035.

Analysis of trajectories in MD Einstein formula (fluctuation-dissipation relation)



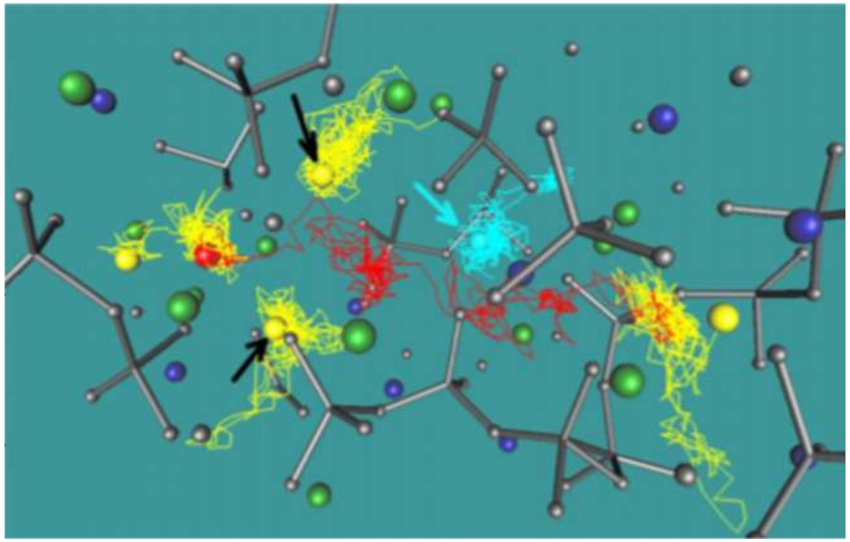
Tilocca, Antonio. *The Journal of chemical physics* 133.1 (2010): 014701.

Values of diffusivities in silicate melts - influence of temperature



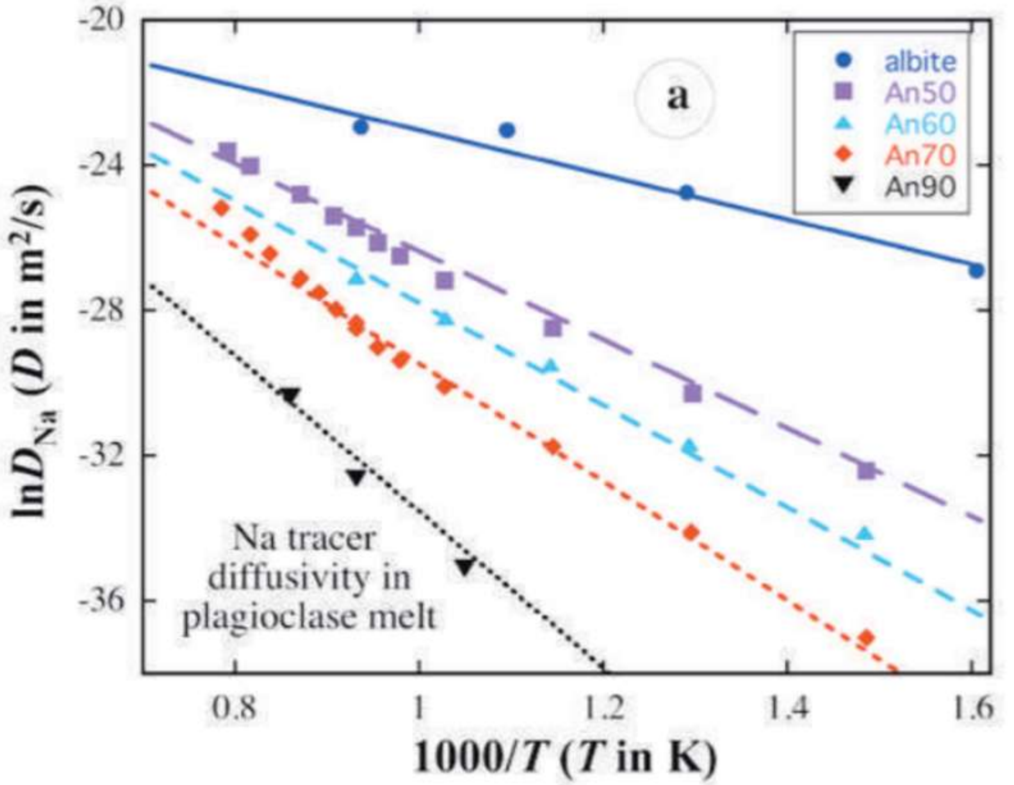
Serva, Alessandra, et al. "Structural and dynamic properties of soda–lime–silica in the liquid phase." *The Journal of Chemical Physics* 153.21 (2020): 214505. Coll. M. Salanne, MAGI project

Arrhenian behaviour
Activation energy related to chemical bonds



Tilocca, Antonio. *The Journal of chemical physics* 133.1 (2010): 014701.

Values of diffusivities in silicate melts - influence of composition



$$D_{\text{Na TD}}^{\text{plag melt}} = \exp\left[-16.87 + 5.318X_{\text{An}} - \frac{(6158 + 5769X_{\text{An}} + 12480X_{\text{An}}^2)}{T}\right]$$

Self-diffusion of sodium in various silicate melts

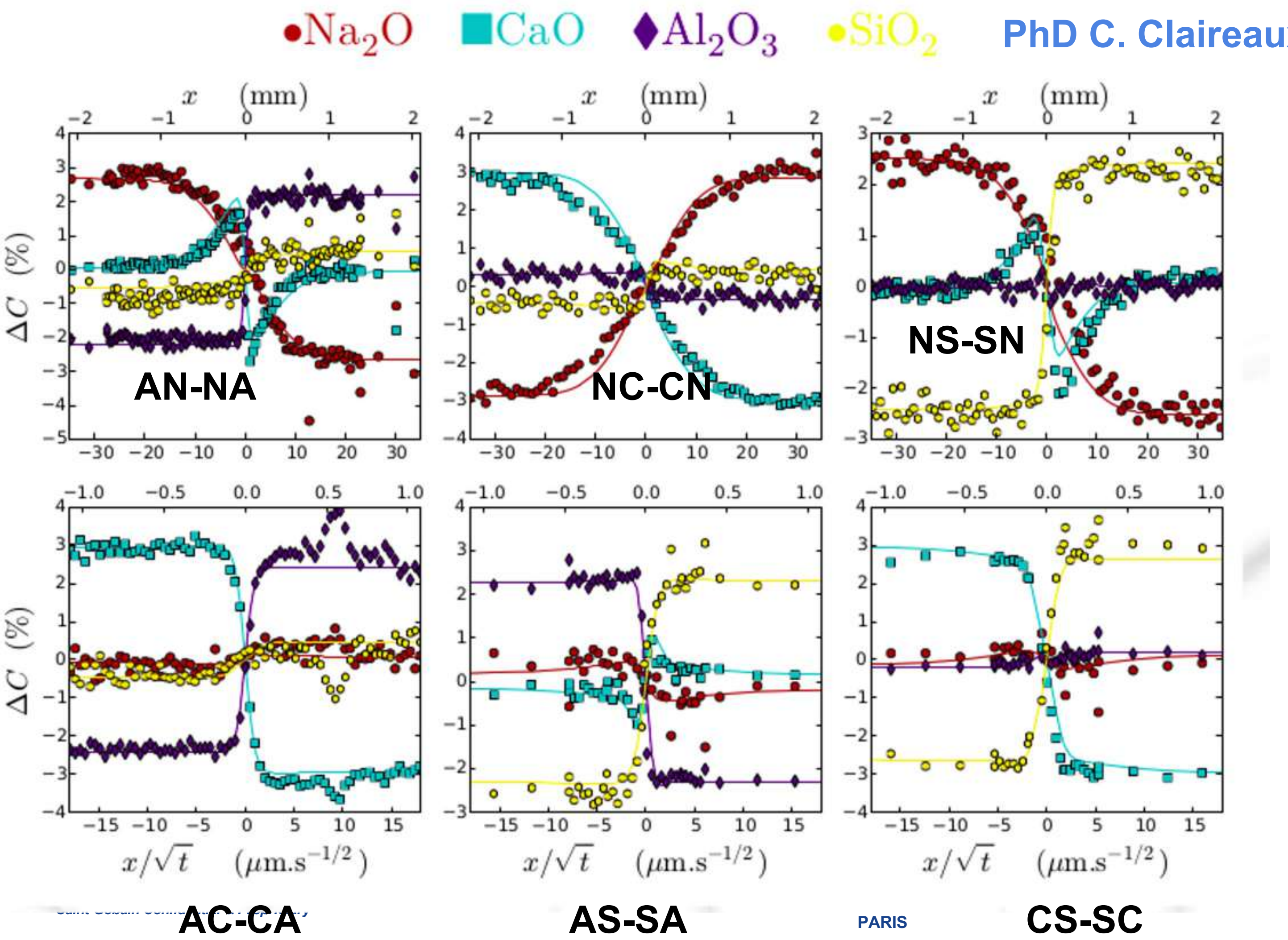
Zhang, Y., Ni, H., & Chen, Y. (2010). Diffusion data in silicate melts. *Reviews in Mineralogy and Geochemistry*, *72*(1), 311-408.

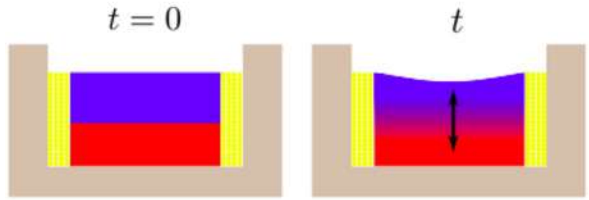
More sodium → larger D of sodium.

Qualitative trend: D increases when viscosity decreases.

Example: multicomponent diffusion in a quaternary system

PhD C. Claireaux





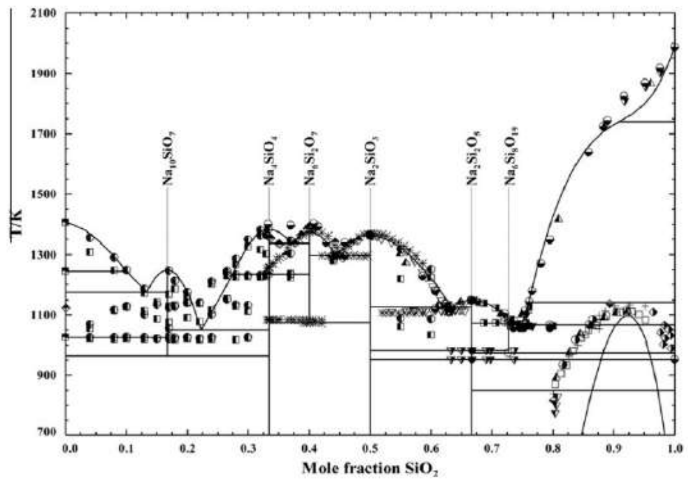
6 diffusion-couple experiments

Claireaux, Corinne, et al. "Atomic mobility in calcium and sodium aluminosilicate melts at 1200 C." *Geochimica et Cosmochimica Acta* 192 (2016): 235-247.

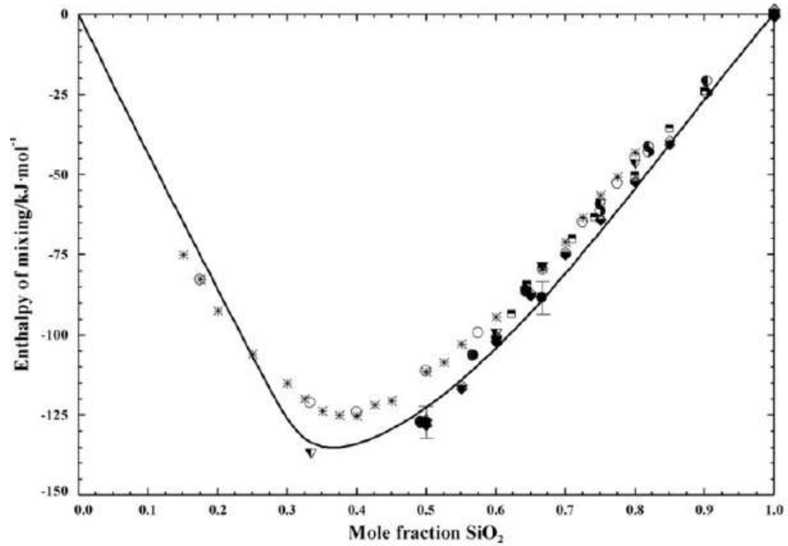
multidiff open-source code: diffusion matrix, **eigenvalues & eigenvectors**

THERMODYNAMIC DATABASE OF OXIDE SYSTEM

FTOXID DATABASE (CRCT MONTREAL)



Calculated (Na_2O + SiO_2)
phase diagram

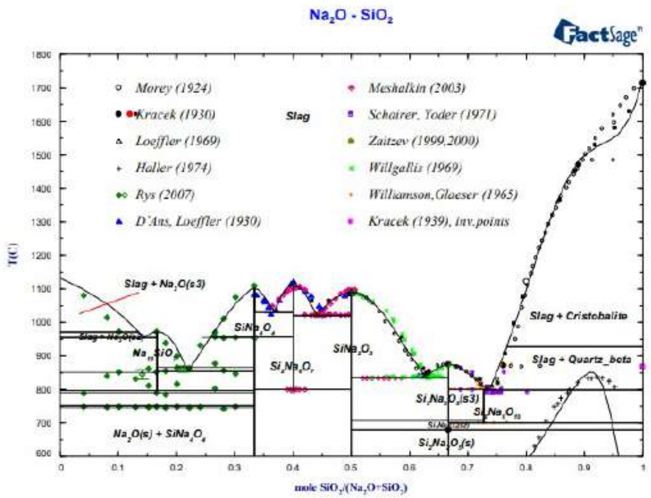


Calculated enthalpy of mixing in the (Na_2O + SiO_2)
system at 1450 K

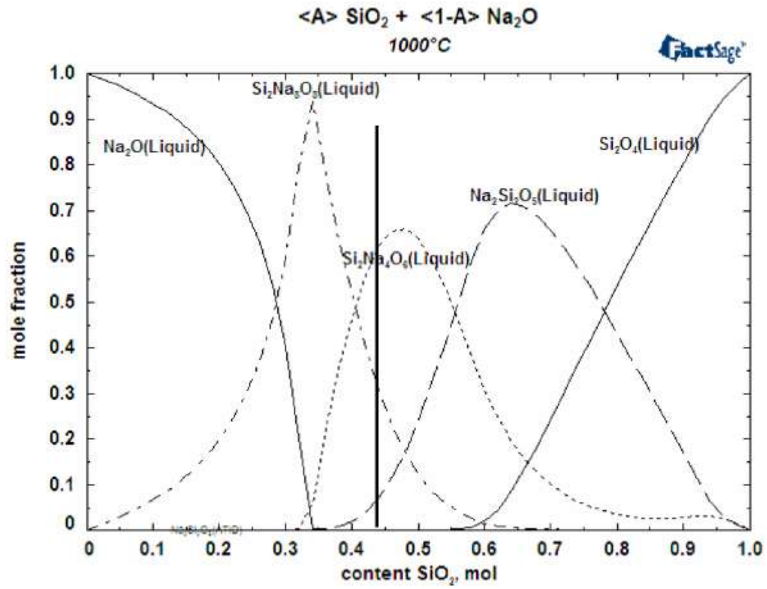
G. Lambotte, P. Chartrand / J. Chem. Thermodynamics 43 (2011) 1678–1699

THERMODYNAMIC DATABASE OF OXIDE SYSTEM

OTHER DATABASE : GTOX (GTT TECHNOLOGIES)



Calculated (Na_2O + SiO_2) phase diagram



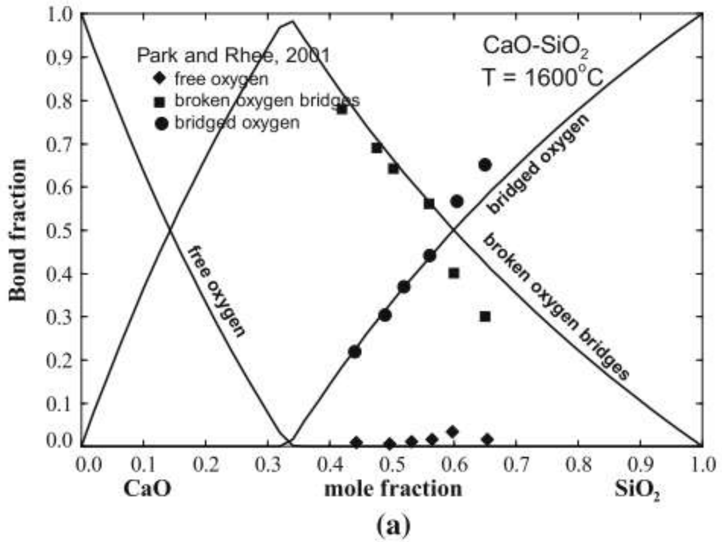
Calculated structure of the Na_2O-SiO_2 liquid at 1000°C (mole fractions of associate species)

E. Yazhenskikh, 2005. Development of a new database for thermodynamic modelling of the system Na_2O-K_2O-Al_2O_3-SiO_2. Fakültat für Georessourcen und Materialtechnik, RWTH, Aachen, Germany,

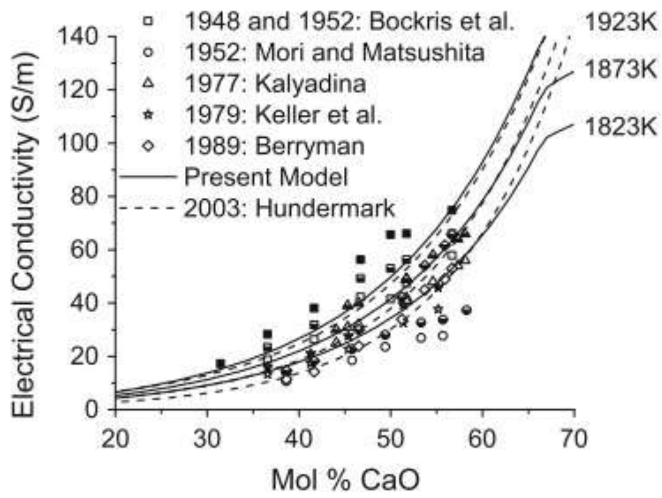
OUR NEEDS

OTHER STRUCTURAL MODELS

Bond fractions for $CaO-SiO_2$ slag at 1600°C (FTOxid database)



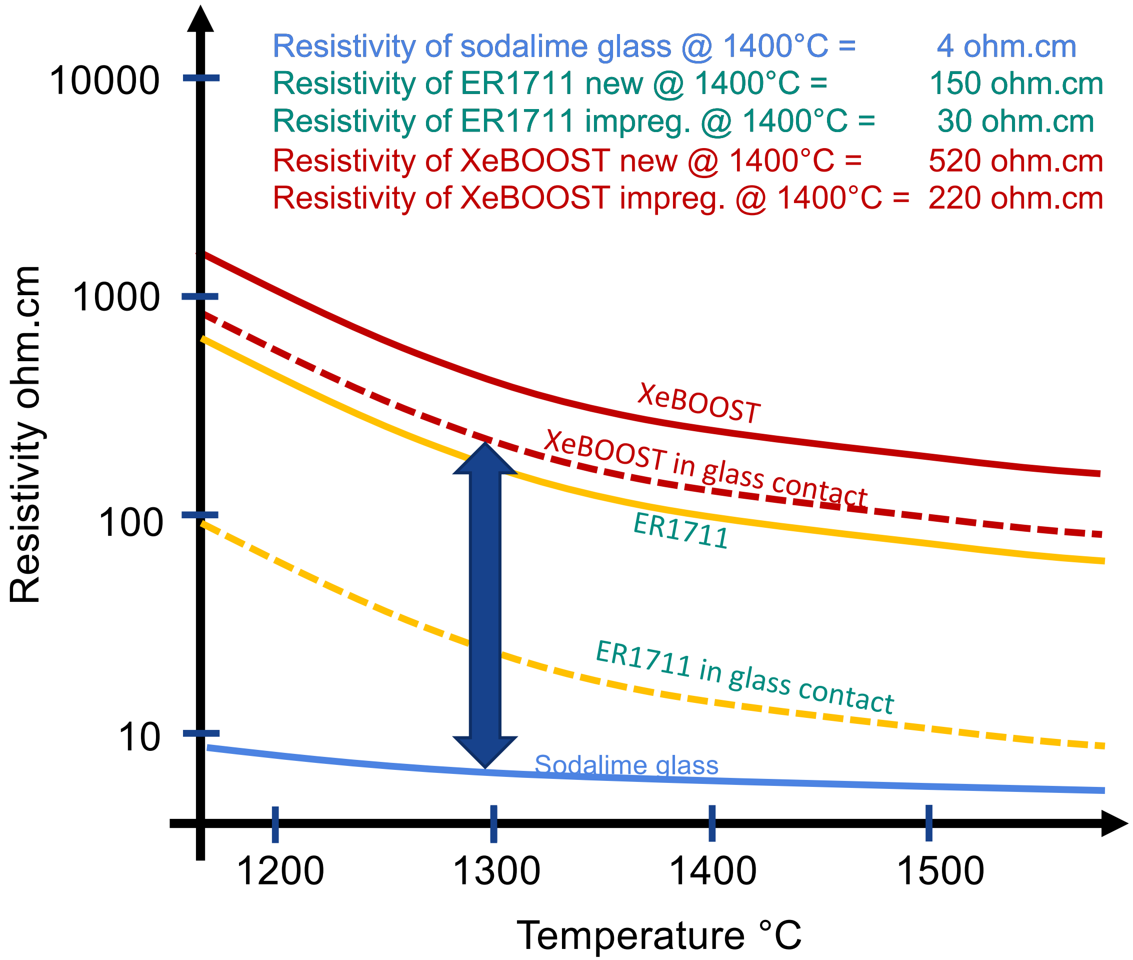
Electrical conductivity of $CaO-SiO_2$ slag at 1650°C

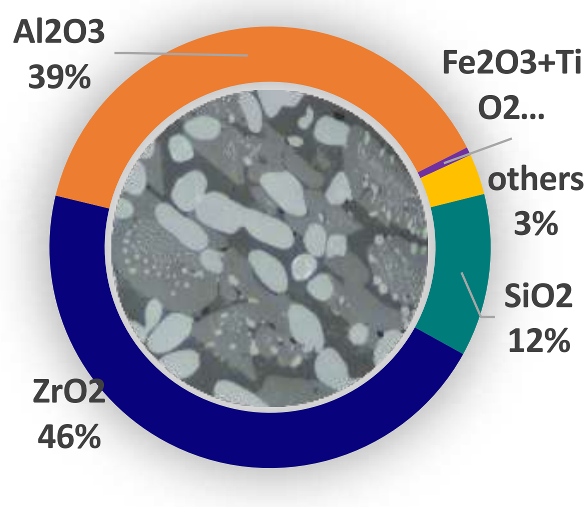


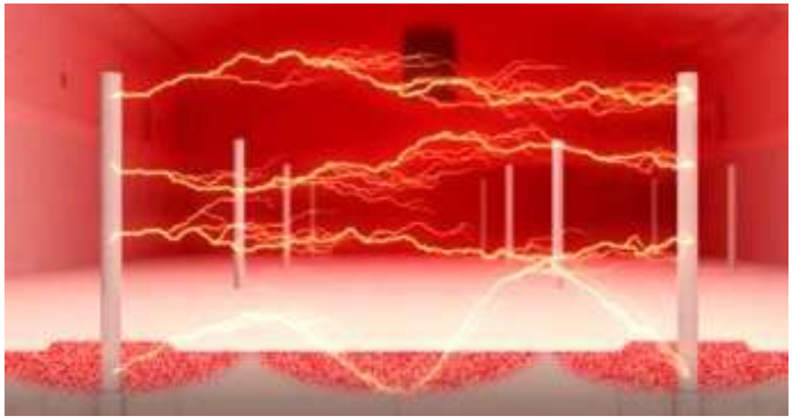
Thibodeau, E. and I.-H. Jung. A Structural Electrical Conductivity Model for Oxide Melts. Metallurgical and Materials Transactions B. 2015, 47(1), 355-383.

ELECTRICAL RESISTIVITY

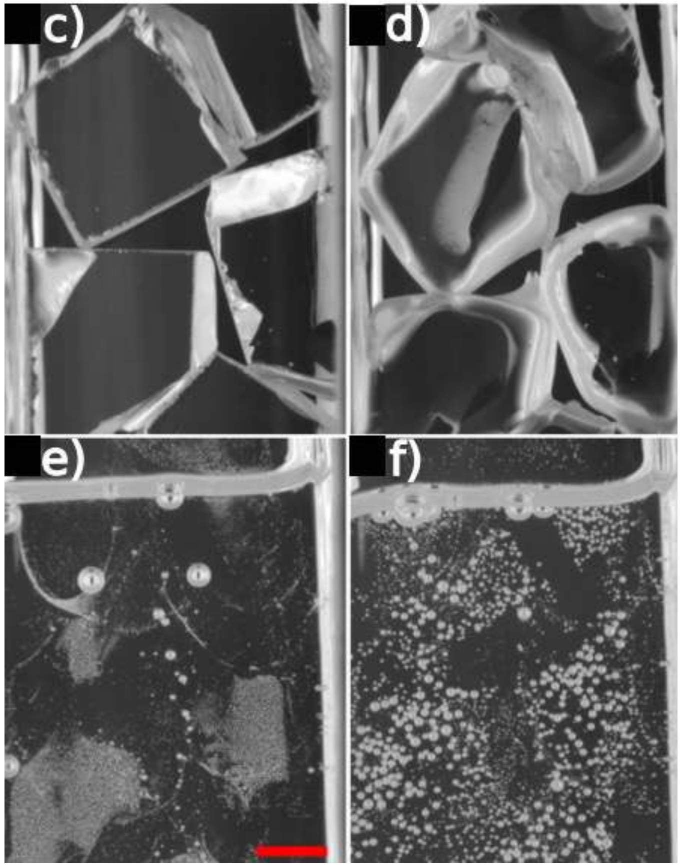
- **Sodalime glass and AZS with sodium infiltration**



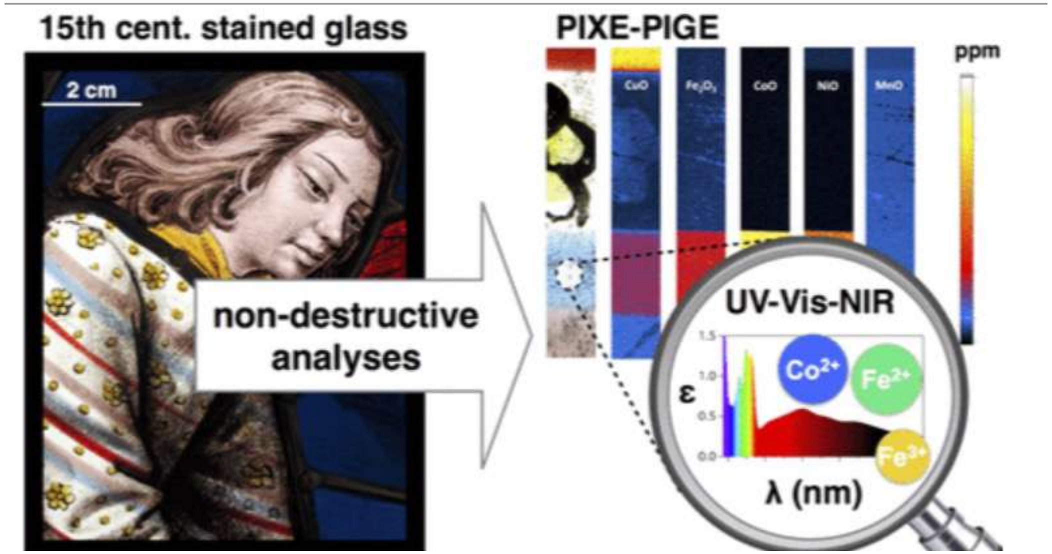




Redox: glass color and fining



Boloré, D., & Pigeonneau, F. (2018). *JACerS*, *101*(5)



Hunault, Myrtille OJY, et al. "Nondestructive redox quantification reveals glassmaking of rare French gothic stained glasses." *Analytical chemistry* 89.11 (2017): 6277-6284.

Conclusions

High-temperature properties of silicate liquids are strongly correlated to structure

Lots of non-linear and non-monotonous effects → prediction is hard without physics-informed models

Development of advanced models and smart design of experiments


THANK YOU FOR YOUR ATTENTION!