Chemical diffusion in silicate melts

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Joint Unit CNRS / Saint-Gobain

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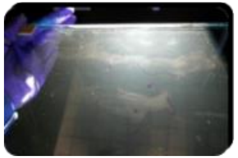
TRANSVERSAL R&D CENTERS BY SAINT-GOBAIN

500 staff working on industrial processes and materials for construction & industry: glass, mineral wools, gypsum, mortars, composites..

Improvement of glass products properties



2050 NET ZERO CARBON

Decarbonation of glass processes

Acknowledgements

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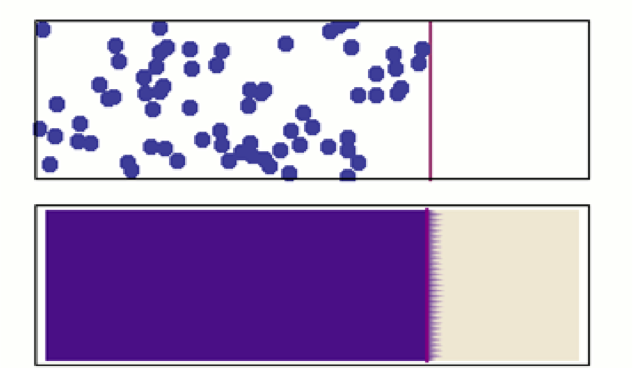
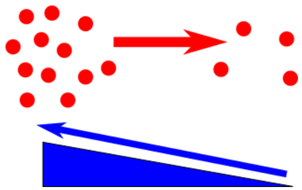
Collaborations: MAGI project, M. Toplis, M. Roskosz, L. Cormier, P. Simon, C. Bessada, E. Véron, M. Salanne, S. Schuller, H. Pablo, D. Vandembroucq.

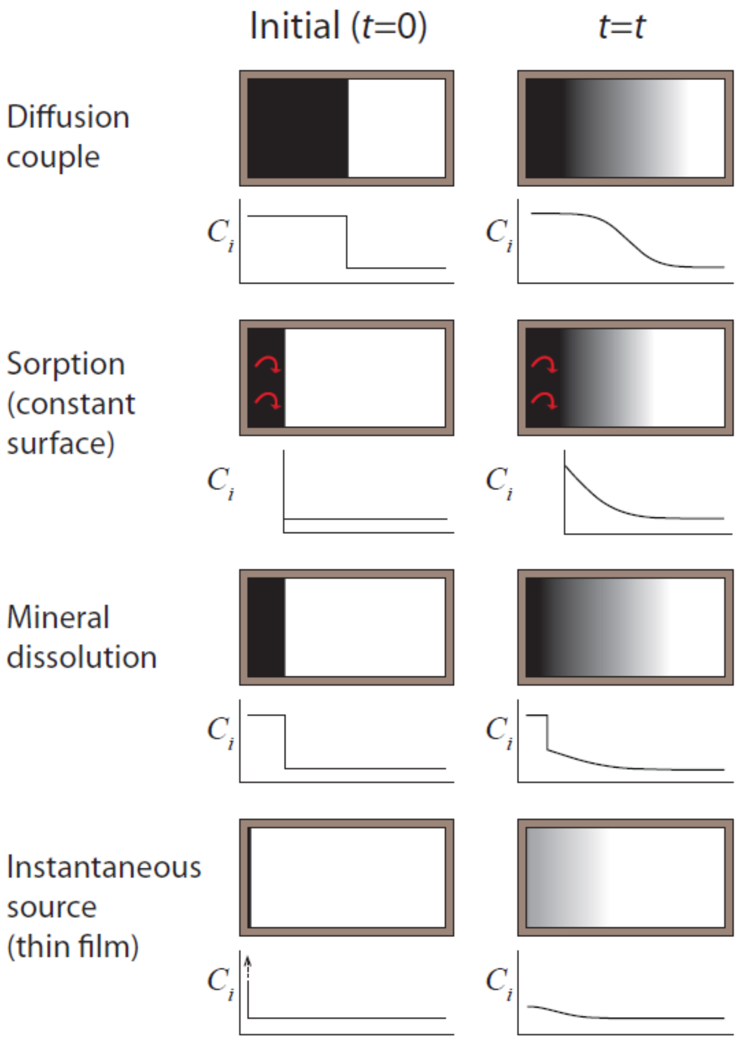
Chemical diffusion



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



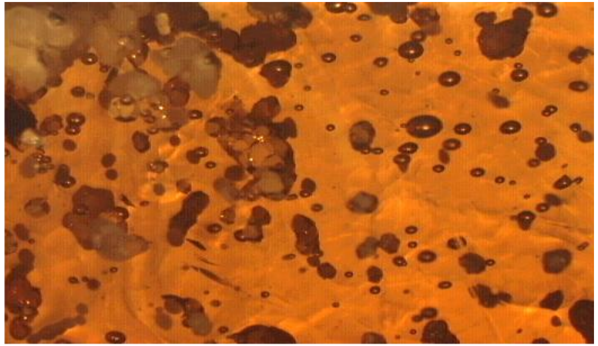
$$\frac{\partial C}{\partial t} = D\Delta C$$



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

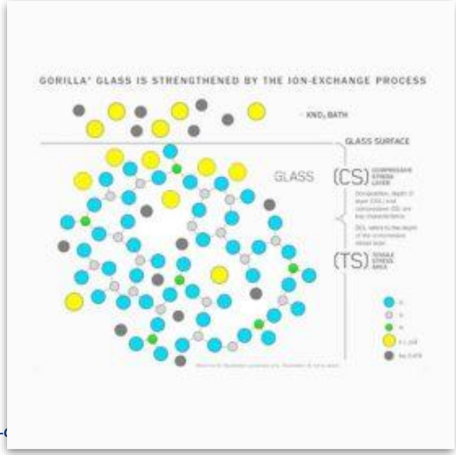
Glass melting: batch & stones



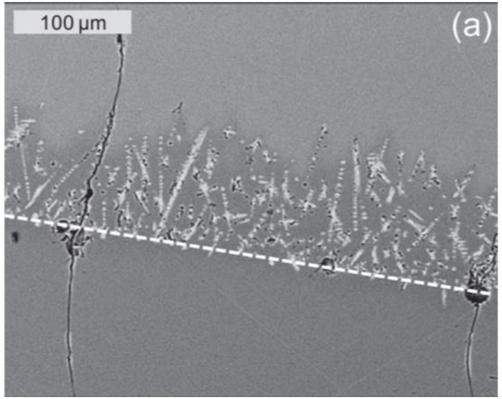
Refractory corrosion

Volatile diffusion & volcanic eruption

Ionic exchange (display)

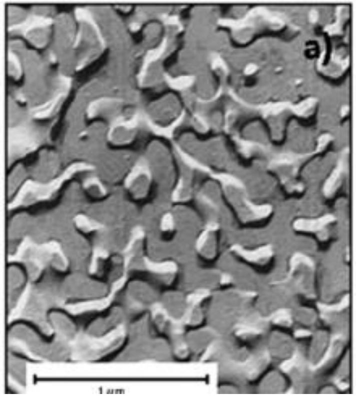


Crystallization



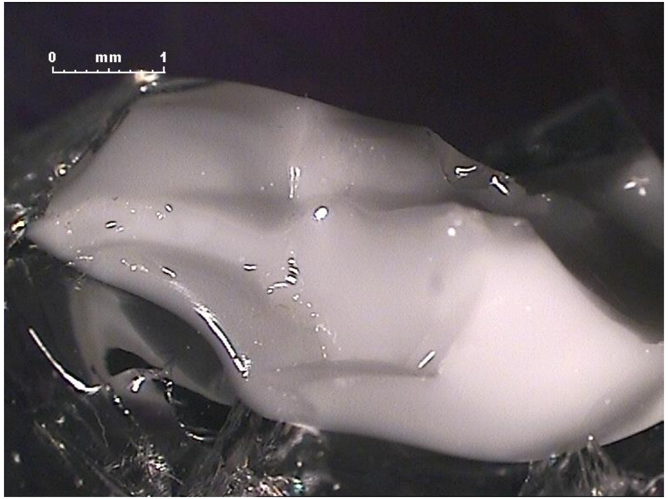
Pablo et al
JNCS 2019.

Phase separation



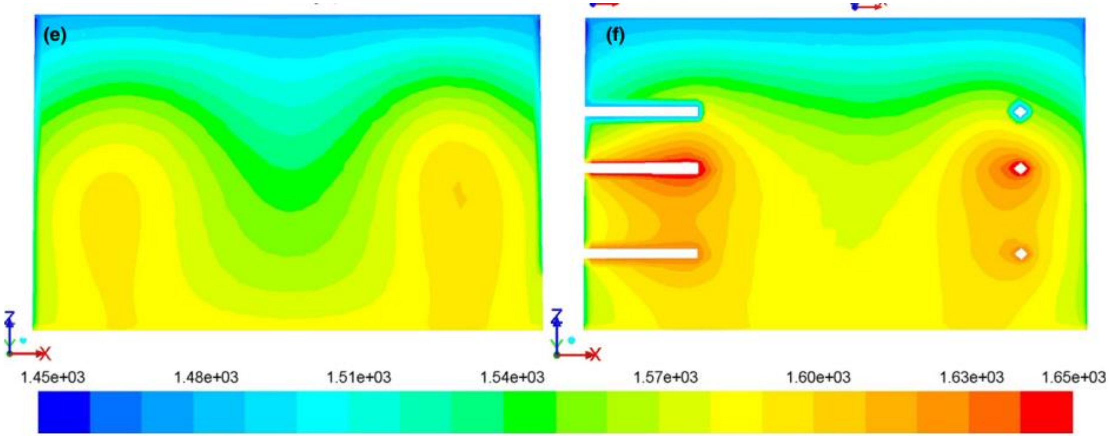
Why is diffusion important for sustainable glass?

More cullet → more impurities to dissolve



Courtesy of S. Di Pierro, SGR Paris

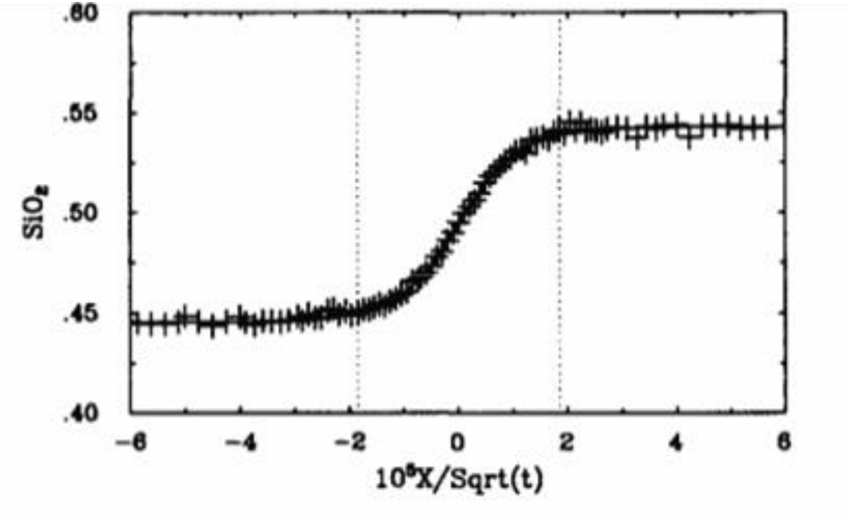
More corrosion of refractories with electric melting



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

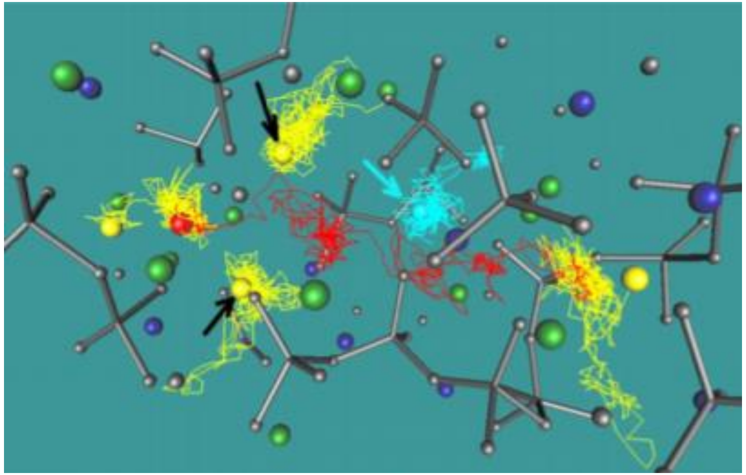
Measuring diffusion data

Concentration gradients (chemical concentrations, isotopes…)



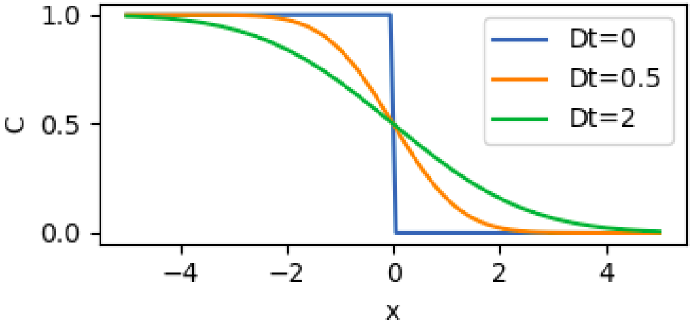
Liang, Yan, Frank M. Richter, and E. Bruce Watson. *Geochimica et Cosmochimica Acta* 60.24 (1996): 5021-5035.

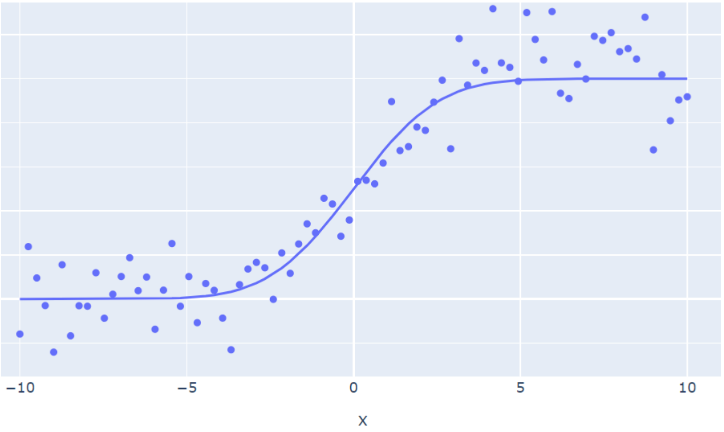
Analysis of trajectories in MD
Einstein formula (fluctuation-dissipation relation)



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

Fitting experimental diffusion profiles





Fit known parametric laws through noisy experimental points.

$$n(x,t) = n_0 \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right).$$

Importance of :

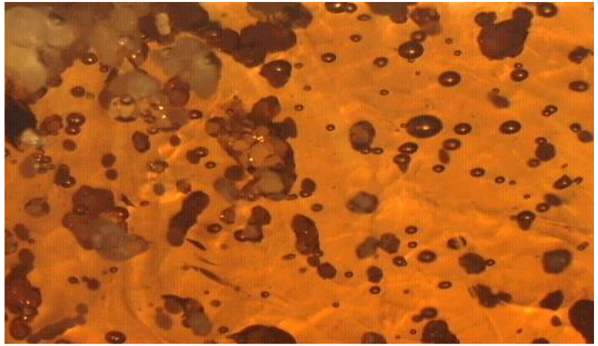
- spatial resolution and number of points
- experimental noise

Some orders of magnitudes

Diffusivity of gaseous molecules in air ? ~ 10^{-5} $m^2.s^{-1}$ (in 1s: l ~ a few mms)

Diffusivity of dissolved species in water ? ~ 10^{-9} $m^2.s^{-1}$

Diffusivity of Si in soda-lime silica melt at 1200°C : ~ 10^{-12} $m^2.s^{-1}$



in 1s: l ~ 1 micron

in 1 hour: l ~ 60 microns

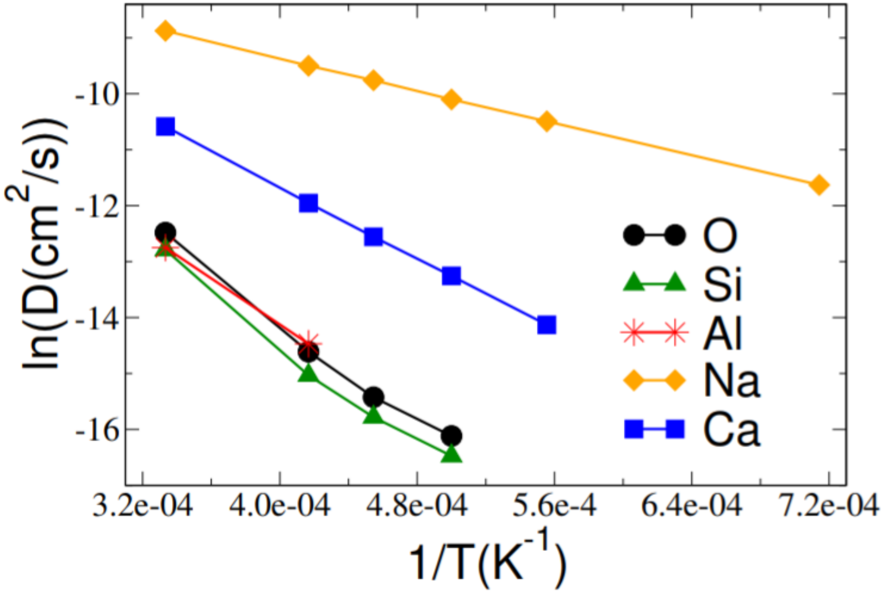
in 24 hours: l ~ 300 microns

Fortunately, convection can accelerate diffusion. **Peclet number** : Pe = Ul / D

Shrinking rate of particles ~ $Pe^{1/3}$ Assunção, M., M. Vynnycky, and K. M. Moroney. "On the dissolution of a solid spherical particle." *Physics of Fluids* 35.5 (2023).

Values of diffusivities in silicate melts - influence of species

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

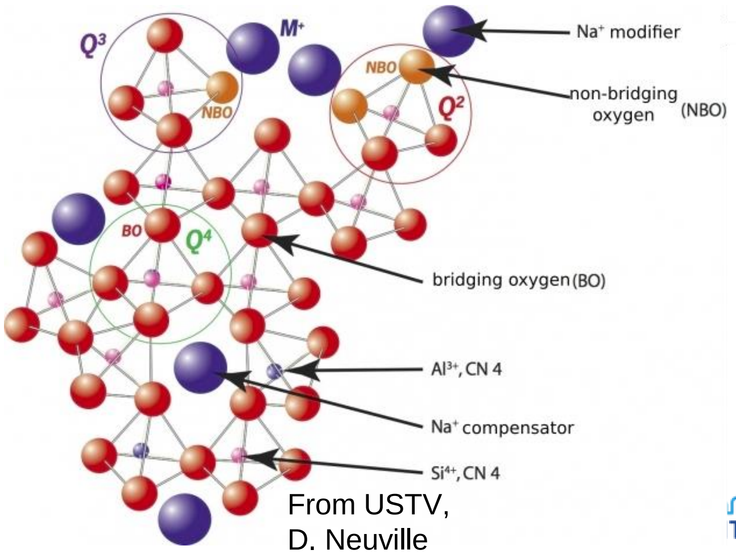


Col with Mathieu's Salanne's team: Serva, Alessandra, et al. "Structural and dynamic properties of soda–lime–silica in the liquid phase." *The Journal of Chemical Physics* 153.21 (2020): 214505.

D depends on **strength** and **number** of chemical bonds (i.e. on silicate structure)

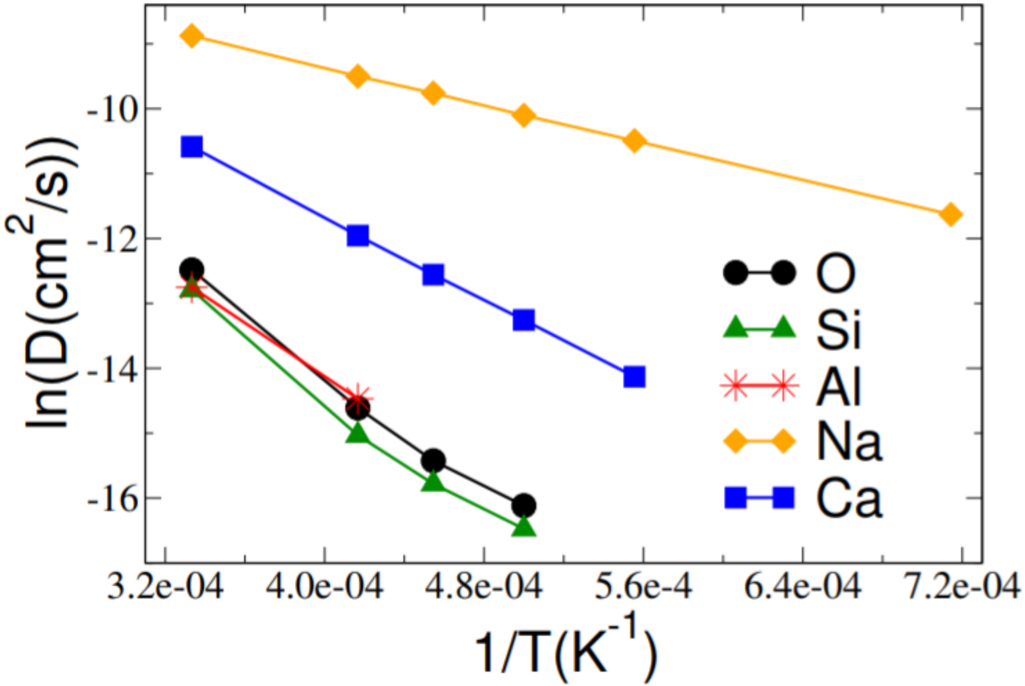
D(network modifiers) > D(network formers)

D(monovalent alkali ions) > D(divalent alkali-earth ions)



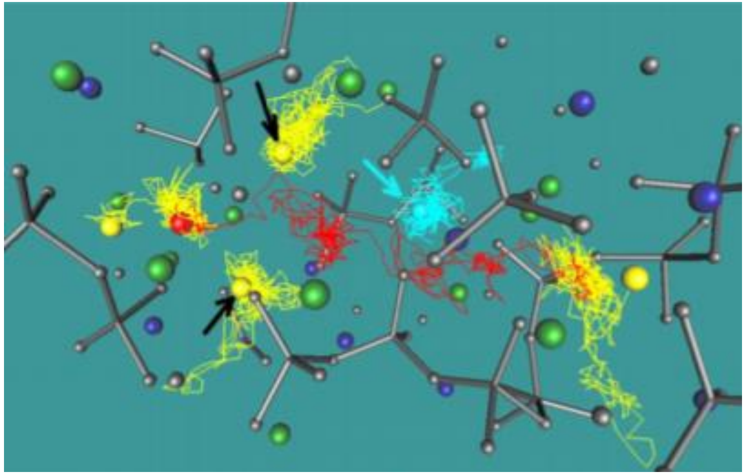
From USTV, D. Neuville

Values of diffusivities in silicate melts - influence of temperature



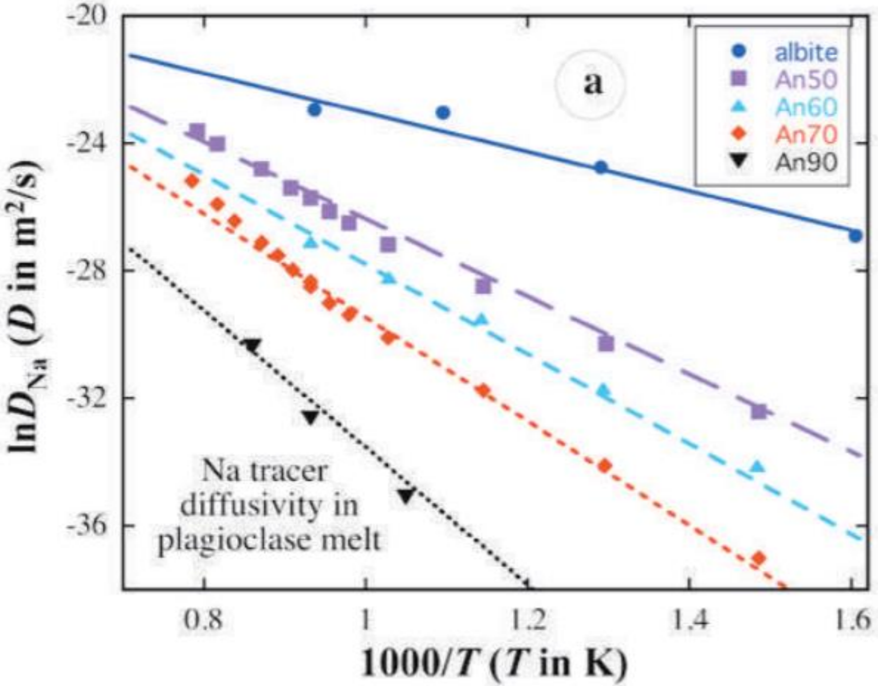
Serva, Alessandra, et al. "Structural and dynamic properties of soda–lime–silica in the liquid phase." *The Journal of Chemical Physics* 153.21 (2020): 214505. Coll. M. Salanne, MAGI project

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



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.

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

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

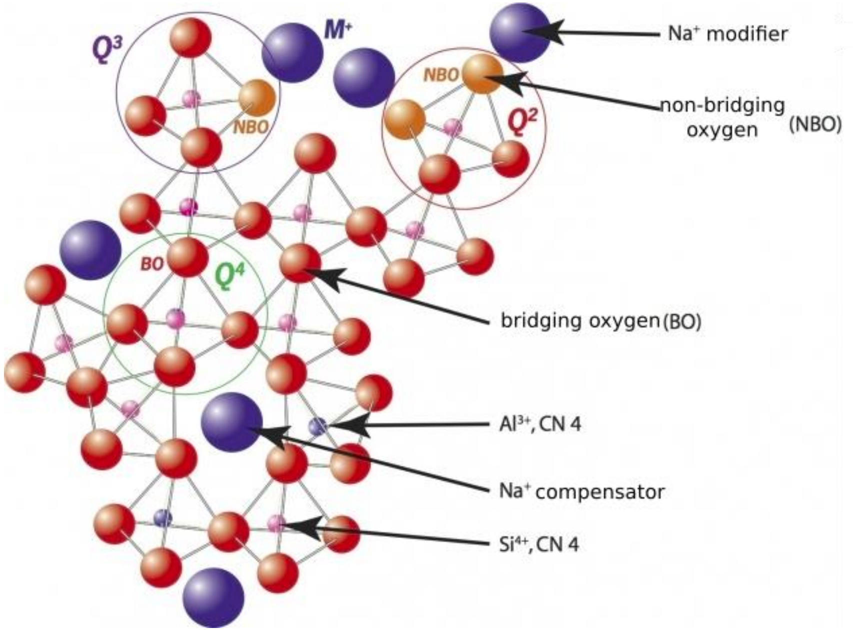
Viscous liquids: Stokes-Einstein and Eyring relation

→ network **formers**

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

η: viscosity

r: radius of particle

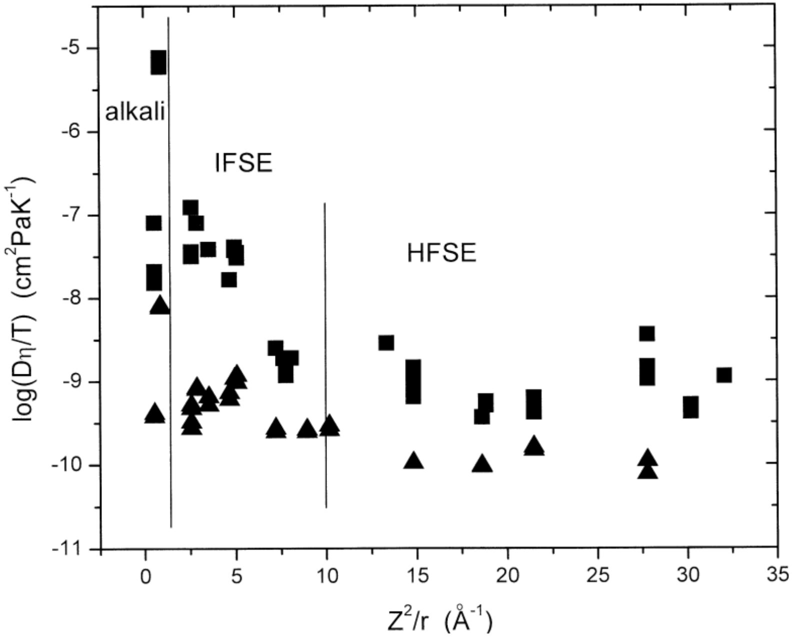


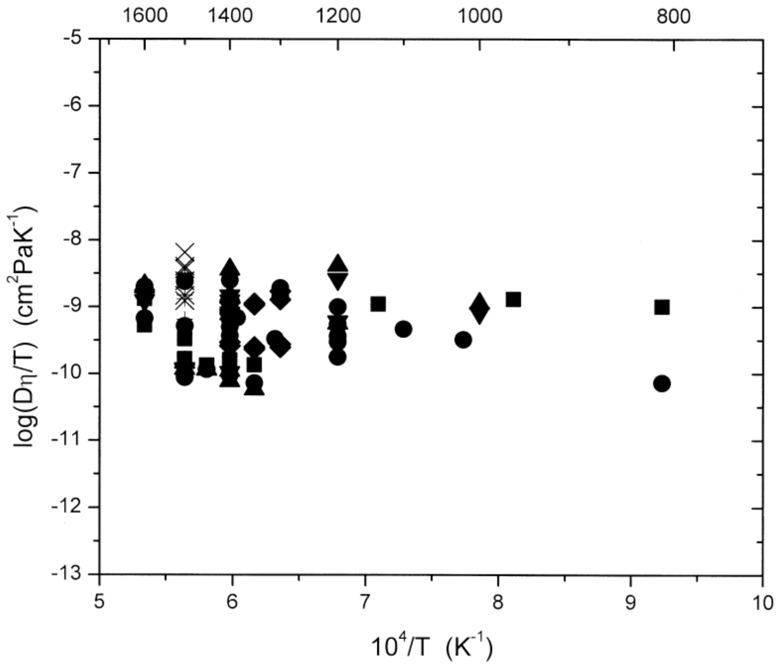
from USTV website
D. Neuville

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

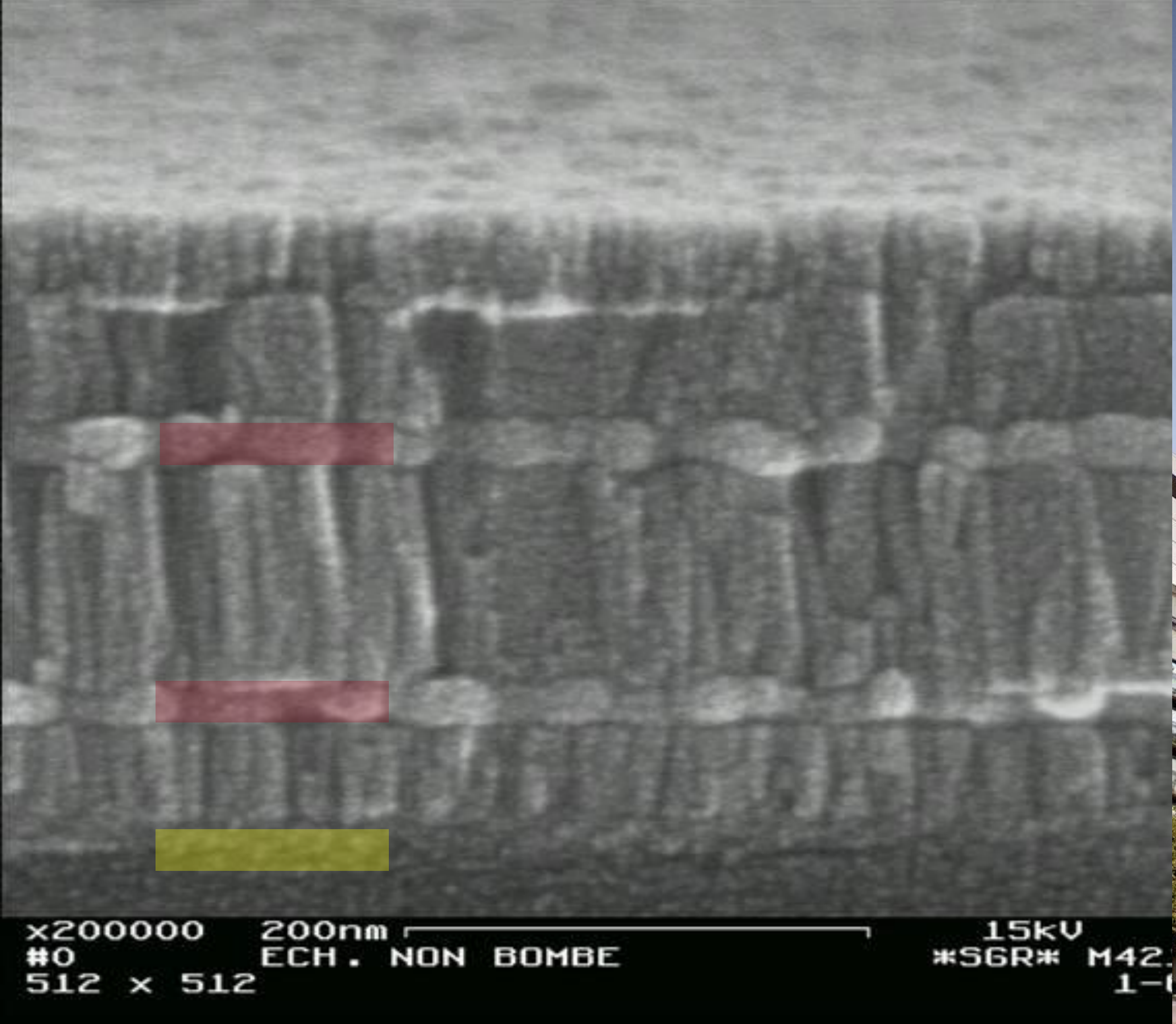
Relating diffusion and viscosity

Viscosity and diffusion





Empirical models relating viscosity and tracer diffusion in magmatic silicate melts, Mungall GCA 2002.


x200000 200nm 15kV
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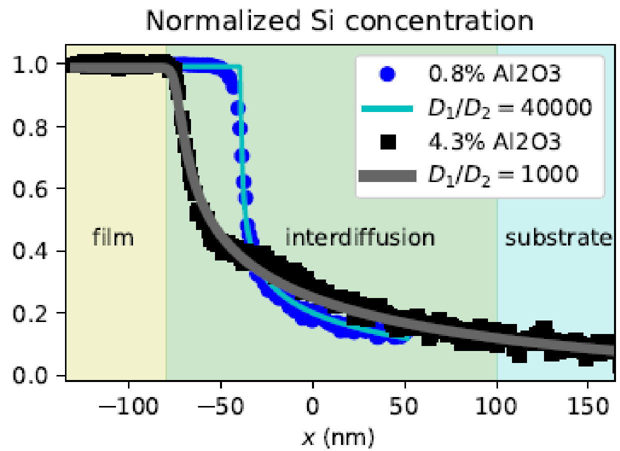
Diffusive dissolution of thin film and multicomponent effects



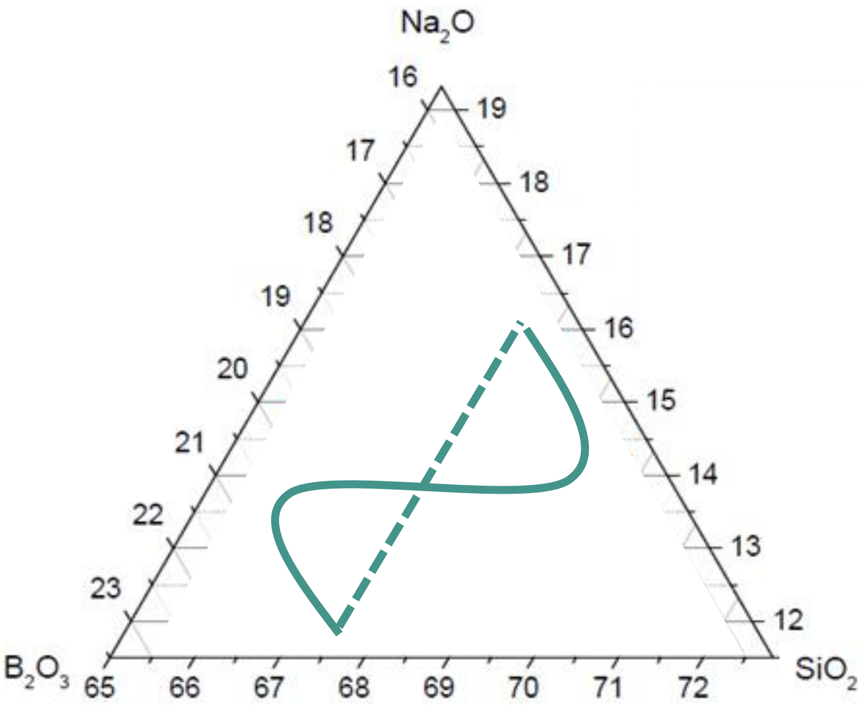
$$\frac{\partial C}{\partial t} = \nabla \cdot (D \nabla C)$$

D often considered constant, but sometimes this approximation cannot be used

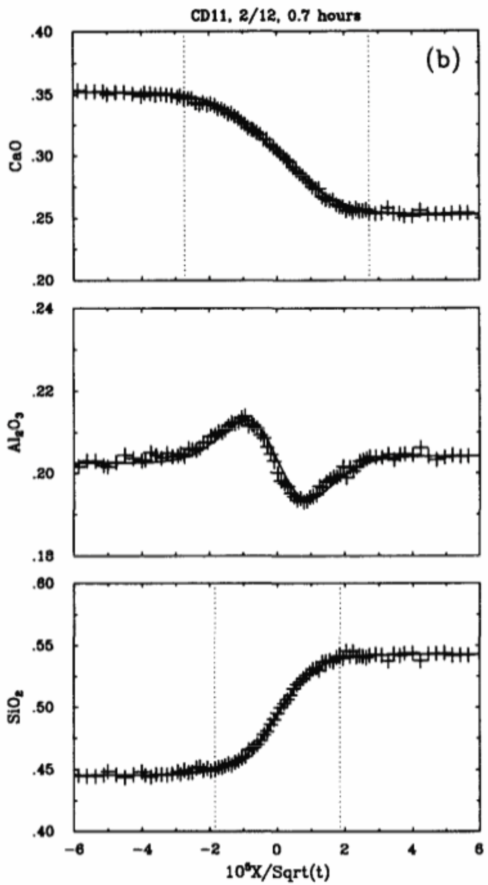
silica thin film	soda-lime glass
smaller D	larger D

PhD JT Fonné ; Fonné et al., JACS 2017, JACS2018
PhD S. Ben Khemis, coll. L Cormier, D. Vandembroucq

Multicomponent diffusion



From Pablo et al JNCS 2019,
coll. with the team of Sophie Schuller.



uphill diffusion

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

Diffusion matrix: how to describe multicomponent diffusion

$$\mathbf{j}_i(\mathbf{x}) = -\sum_k D_{ik} \nabla C_k(\mathbf{x})$$

$$\frac{\partial C_i}{\partial t} = \sum_k D_{ik} \Delta C_k(\mathbf{x})$$

$$\frac{\partial \mathbf{C}}{\partial t} = \mathbf{D} \Delta \mathbf{C}(\mathbf{x})$$

Measured in several ternary systems, mostly in geosciences [Liang et al., 1996], [Richter et al., 1998] : CaO/MgO − Al2O3 − SiO2.
Review by Y. Liang in 2010

Also used in multicomponent metallic alloys.

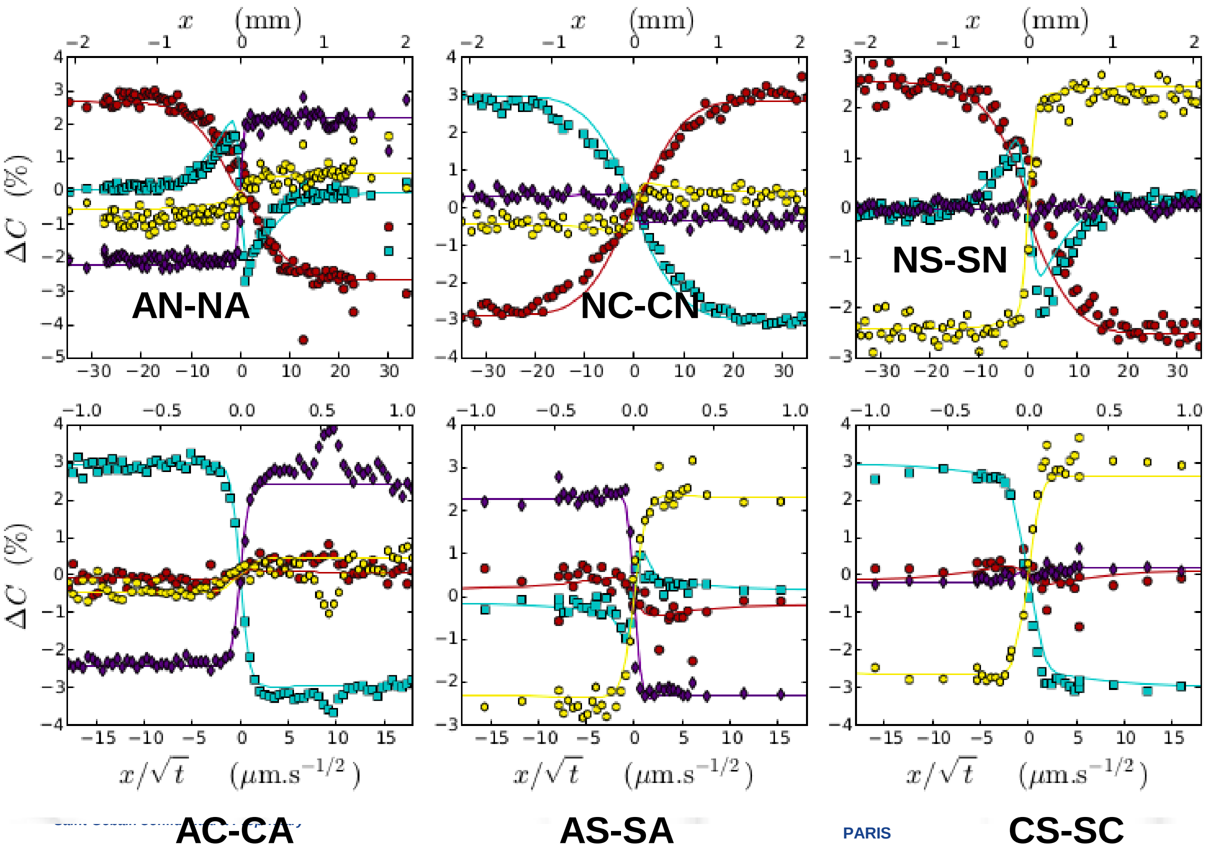
More rigorously: thermodynamic formulation with activity gradient (Onsager).

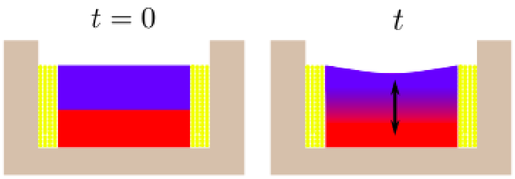
Few studies in industrial systems.

$$\frac{\partial}{\partial t}\begin{pmatrix} C_{\mathrm{Na}} \\ C_{\mathrm{Ca}} \\ C_{\mathrm{Al}} \\ C_{\mathrm{Si}} \end{pmatrix} = \begin{pmatrix} D_{\mathrm{Na,Na}} & D_{\mathrm{Na,Ca}} & D_{\mathrm{Na,Al}} & D_{\mathrm{Na,Si}} \\ D_{\mathrm{Ca,Na}} & D_{\mathrm{Ca,Ca}} & D_{\mathrm{Ca,Al}} & D_{\mathrm{Ca,Si}} \\ D_{\mathrm{Al,Na}} & D_{\mathrm{Al,Ca}} & D_{\mathrm{Al,Al}} & D_{\mathrm{Al,Si}} \\ D_{\mathrm{Si,Na}} & D_{\mathrm{Si,Ca}} & D_{\mathrm{Si,Al}} & D_{\mathrm{Si,Si}} \end{pmatrix} \Delta \begin{pmatrix} C_{\mathrm{Na}} \\ C_{\mathrm{Ca}} \\ C_{\mathrm{Al}} \\ C_{\mathrm{Si}} \end{pmatrix}$$

Example: multicomponent diffusion in a quaternary system

●Na_2O ■CaO ♦Al_2O_3 ●SiO_2 **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**

Multidiff: an open-source package for fitting multicomponent diffusion data

pythonhosted.org/multidiff/auto_examples/index.html

Présences site   Séminaires de 11h...   Livelink - Direction...

multidiff 0.1 documentation »

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Fitting multidiffusion profiles for three components

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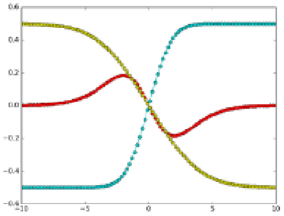
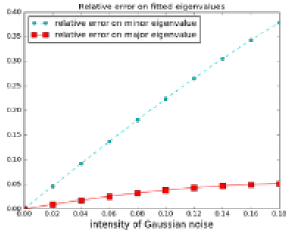
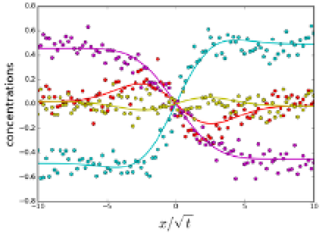
Examples



Fitting multidiffusion profiles for three components



Effect of measurement noise on accuracy of fit

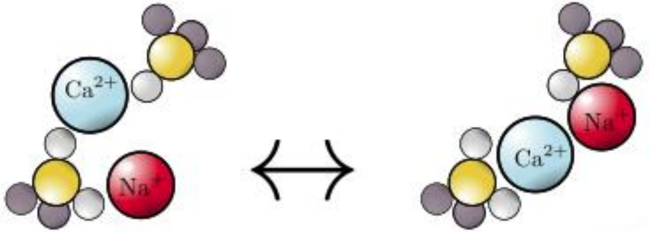


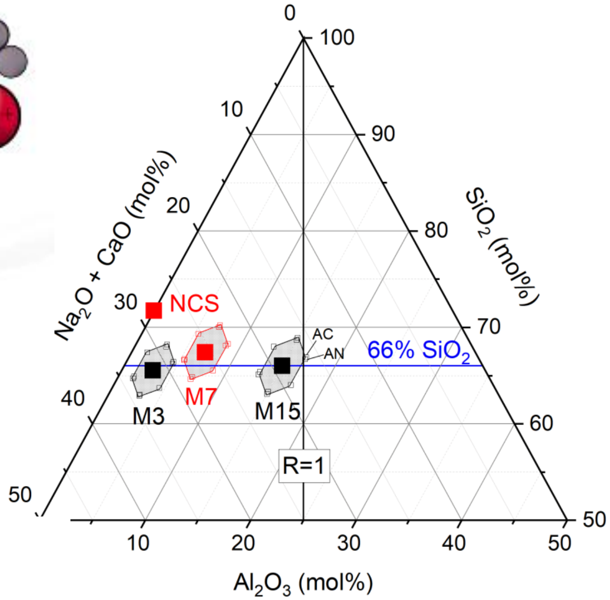
Effect of initialization on accuracy of fit

Dominant eigenvector

$$\Delta \begin{pmatrix} c_{Na_2O} \\ c_{CaO} \\ c_{Al_2O_3} \\ c_{SiO_2} \end{pmatrix} = \begin{pmatrix} 1 \\ -1 \\ 0 \\ 0 \end{pmatrix}$$

$$\frac{1}{2}Ca^{2+} \leftrightarrow Na^{+}$$

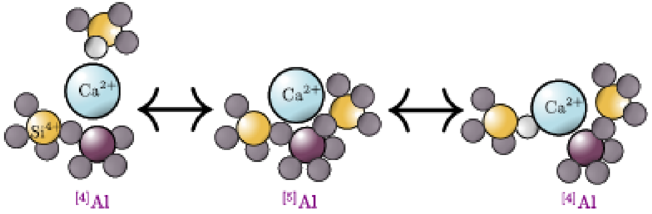




Other eigenvectors: involve network formers, smaller diffusivity value

Second eigenvector (52x less frequent)

$$Ca^{2+} \leftrightarrow 0.5Al^{3+} + 0.5Si^{4+}$$

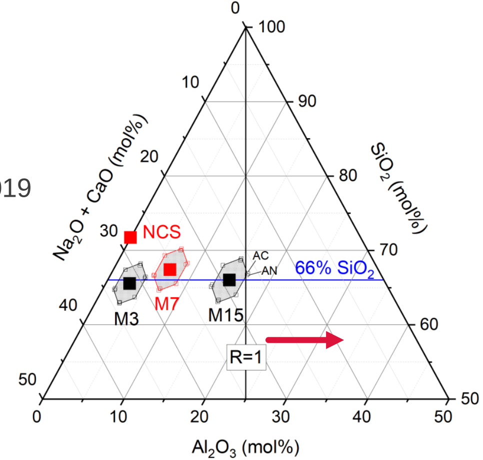


PhD M. Jacquemin, ANR MAGI, CEMHTI
P. Simon, C. Bessada, E. Burov

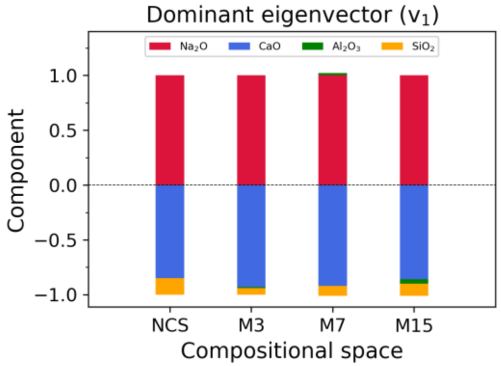
Diffusion pathways in Peralkaline compositions area

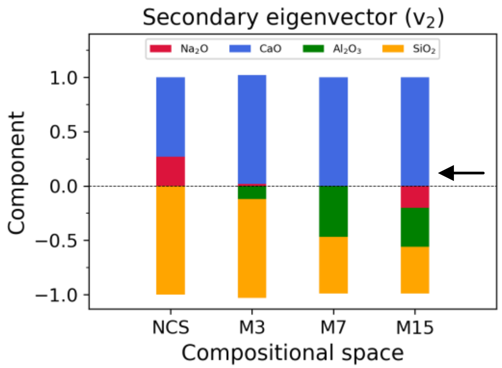
PhD Maxime Jacquemin, **MAGI project**

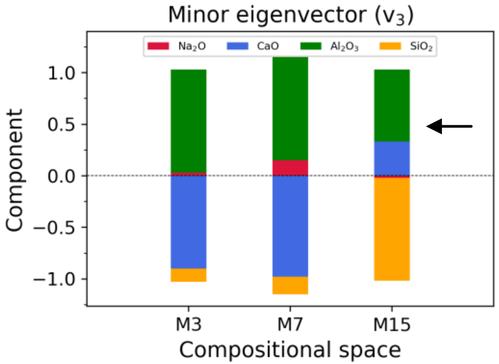
NCS : Trial&Spera, 1994
M7: Claireaux et al., *Geochim. Cosmochim. Acta* 2016, 2019



Eigenvectors $(\overrightarrow{v_i})$







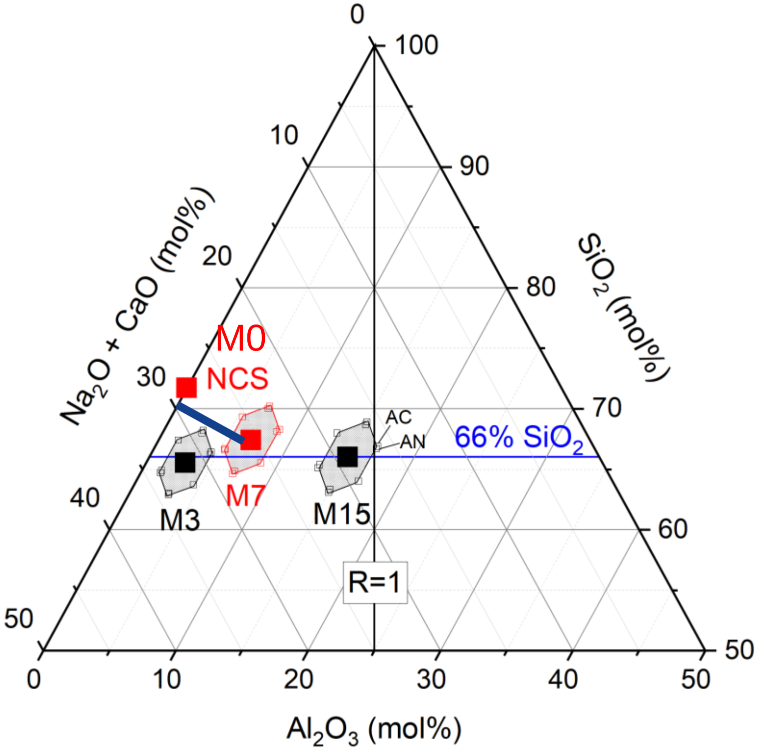
v_1 : Na ↔ Ca

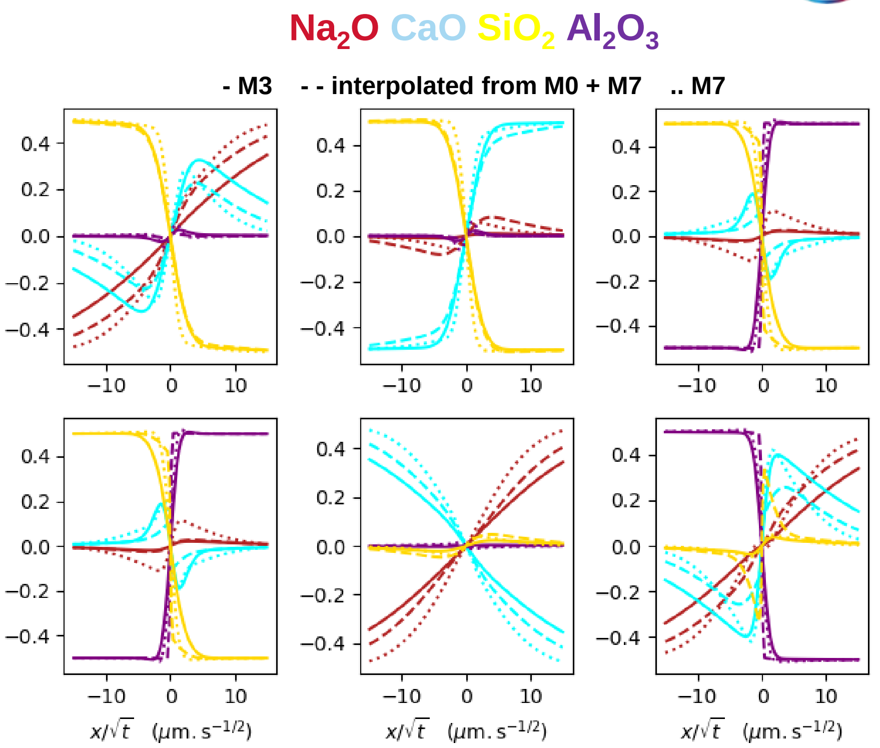
- **dominant vector is always Na <-> Ca**
- Independent of Al_2O_3 concentration and the structures role of Na and Ca

v_2 et v_3 : Formers ↔ Ca

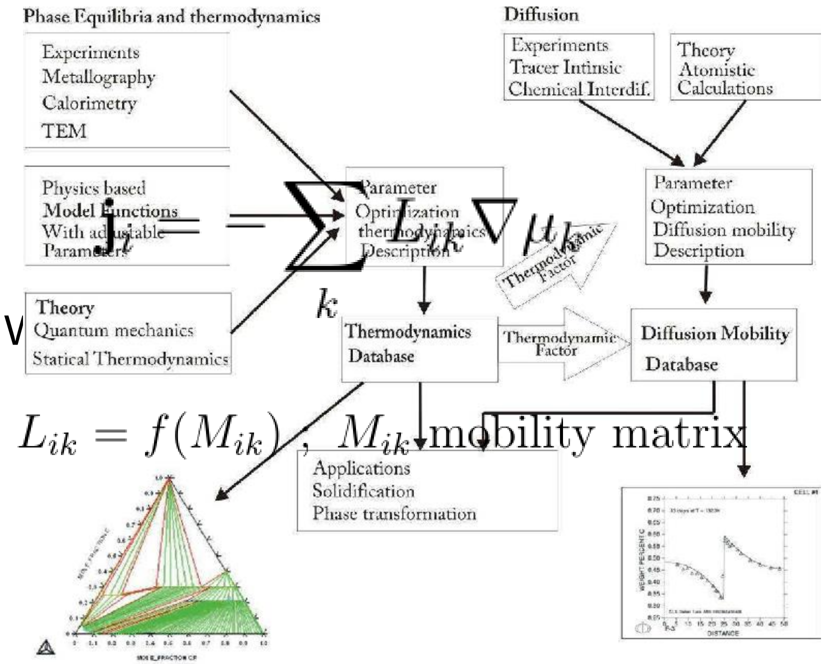
- Reaction evolution with Al_2O_3 concentration
- Al is associated to the Na or Ca near R=1

Can we interpolate diffusion matrices ?





Multicomponent diffusion and thermodynamics



$J_i = -\sum_k L_{ik} \nabla \mu_k$

V

$L_{ik} = f(M_{ik})$; M_{ik} mobility matrix

Hypothesis: model of mobility matrix M with composition.

In alloys (from Campbell et al. Acta Mat 2002, Development of a diffusion mobility database for Ni-base Superalloys)

$$M_{ki}^{L} = \delta_{ki} x_i M_i$$

$$M_i = \Theta_i \frac{1}{RT} \exp\left(\frac{\Delta Q_i^*}{RT}\right)$$

$$\Delta Q_i^* = \sum_j x_j Q_i^j + \sum_p \sum_{j>p} x_p x_j \sum_k A_i^{pj} (x_p - x_j)^k$$

Calphad method

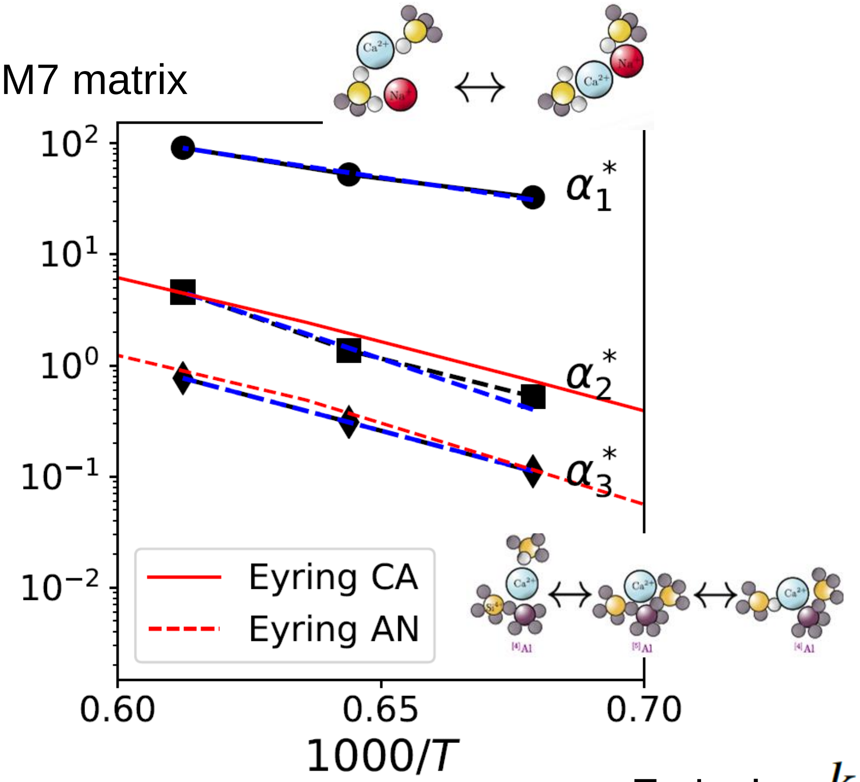
Work of Moelans & Blanpain in slags

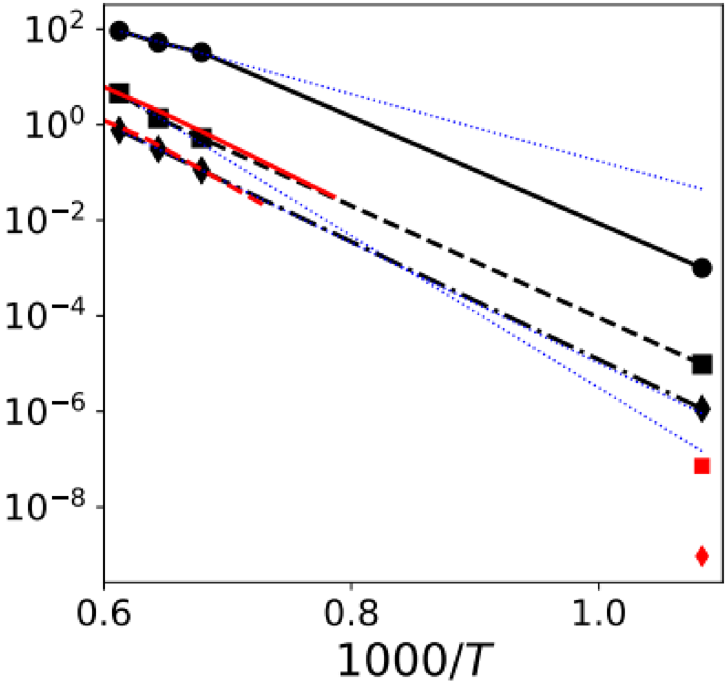
Heulens, J., Blanpain, B., & Moelans, N. (2011). A phase field model for isothermal crystallization of oxide melts. *Acta materialia*, *59*(5), 2156-2165.

Liu, J., Zou, J., Guo, M., & Moelans, N. (2016). Phase field simulation study of the dissolution behavior of Al_2O_3 into $CaO–Al_2O_3–SiO_2$ slags. *Computational Materials Science*, *119*, 9-18.

Energetics of multicomponent diffusion

M7 matrix

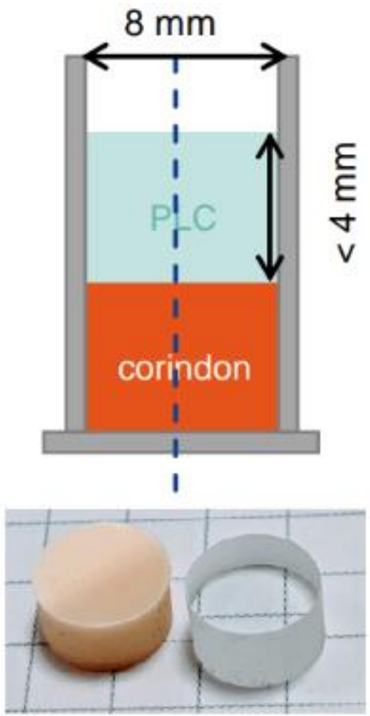


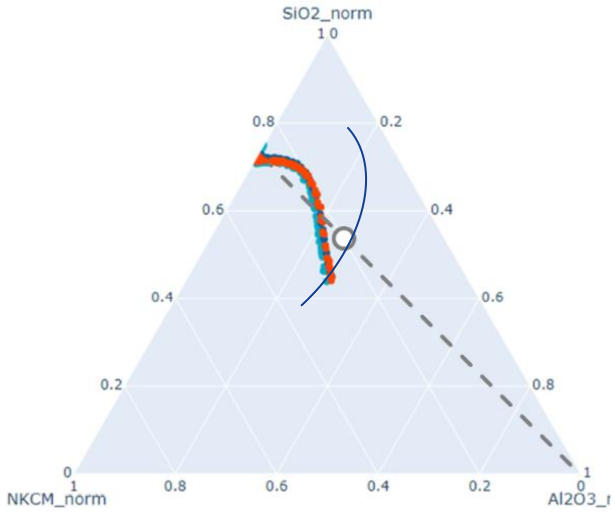


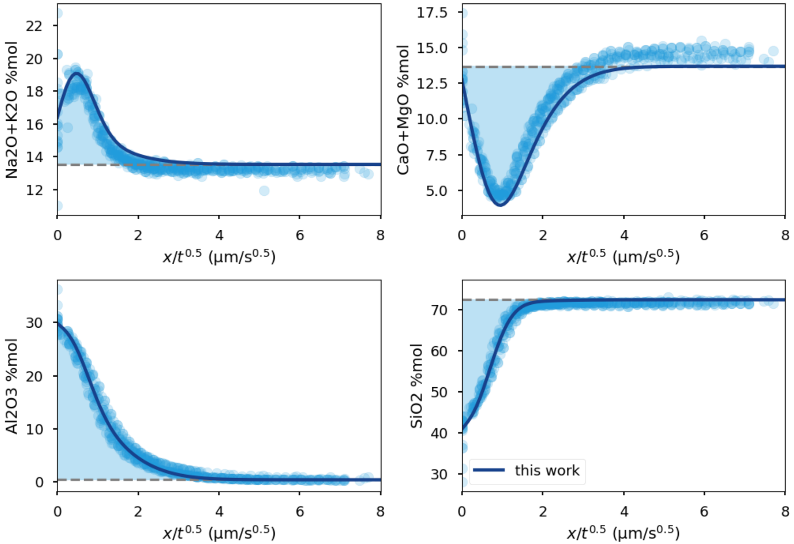
.Claireaux, Corinne, et al. "Influence of temperature on multicomponent diffusion in calcium and sodium aluminosilicate melts." *Journal of Non-Crystalline Solids* 505 (2019): 170-180.

Eyring's diffusivity $\frac{k_B T}{\eta d}$

Application: dissolution of Al_2O_3 refractories, PhD F. Yoshizawa







Dissolution mechanisms of minerals in silicate liquids of industrial interest, F. Yoshizawa

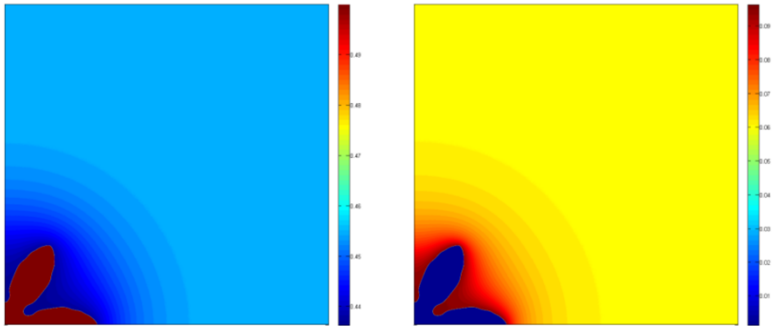
Alumina Dissolution into Silicate Slag, Zhang et al. JACS 2000;
Effects of melt viscosity and silica activity on the rate and mechanism of quartz dissolution in melts of the CMAS and CAS systems, Shaw 2004

Coll.Michael Toplis, Univ. Toulouse

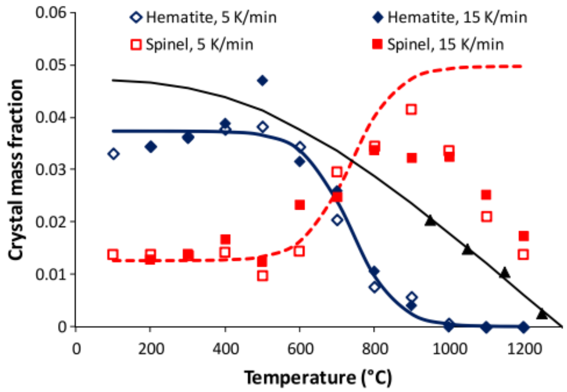
Applications: multiphysics modelling

How about batch dissolution rates?

Mostly phenomenological models… inspired by diffusion physics.



Heulens, J., Blanpain, B., & Moelans, N. (2011, January). Crystallization of CaO. SiO2 in a CaO-Al2O3-SiO2 Melt: Computer Simulations and In-situ Experiments.



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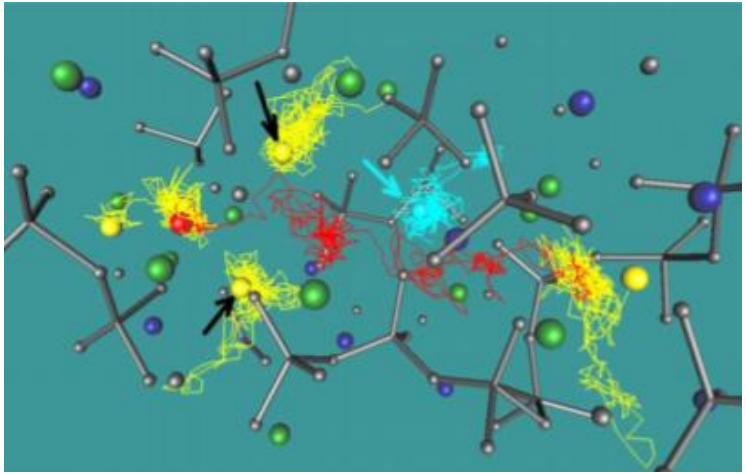
Ueda, N., Vernerová, M., Kloužek, J., Ferkl, P., Hrma, P., Yano, T., & Pokorný, R. (2021). Conversion kinetics of container glass batch melting. *Journal of the American Ceramic Society*, *104*(1), 34-44.

Conclusions

Diffusion is a microscopic phenomenon, with macroscopic consequences (corrosion of refractories for example).

The complex structure of silicate melts has strong consequences about diffusion:

- D(network formers) << D(modifiers)
- Strong multicomponent effects (couplings)



Diffusion is a thermally activated phenomenon.

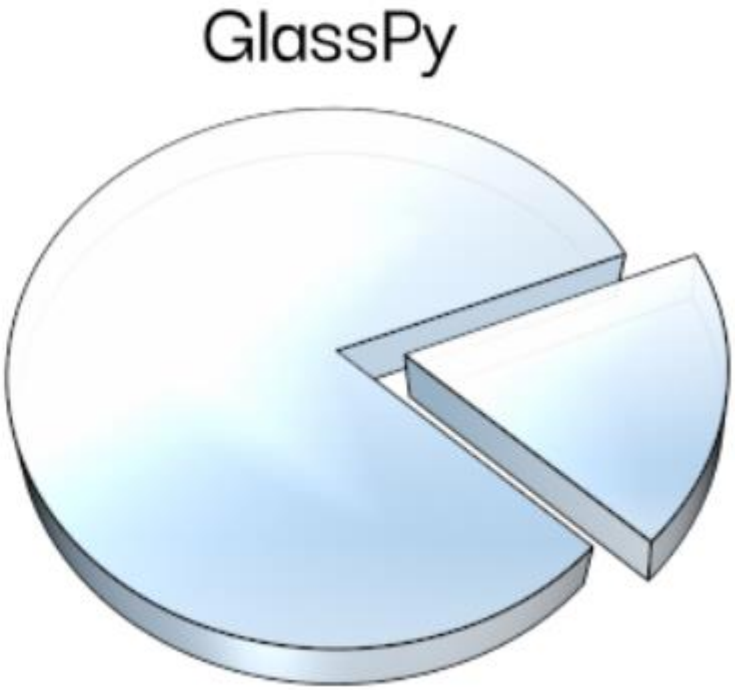
Perspectives

How to get & use more diffusion data?

Gather existing data from literature

Connection with thermodynamic models

Molecular dynamics and Green-Kubo formula



THANK YOU FOR YOUR ATTENTION!