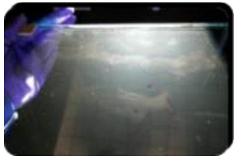
Modeling chemical diffusion in silicate melts

Emmanuelle Gouillart, Ekaterina Burov
Saint-Gobain Research Paris
Joint Unit CNRS / Saint-Gobain

Saint-Gobain Research Paris

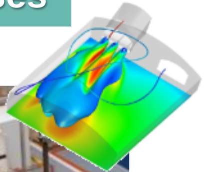
500 staff working on industrial processes and materials for construction & industry: glass, mineral wools, gypsum, mortars, composites..

Improvement of glass products properties



2050 NET ZERO CARBON

Decarbonation of glass processes



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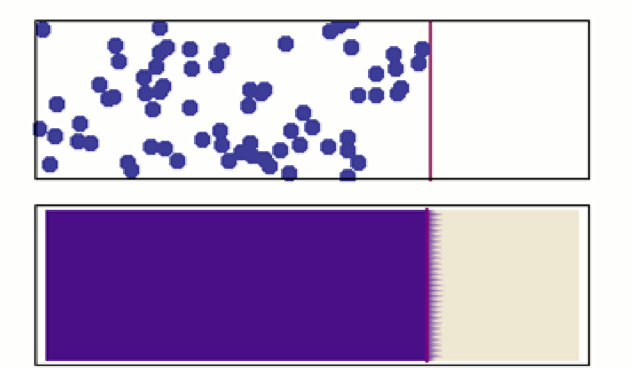
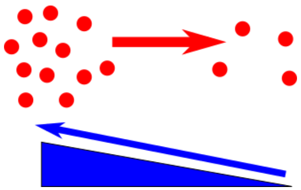
PhD Students: W. Woelffel, C. Claireaux, M. Ficheux, M. Jacquemin, S. Ben Khemis, B. Bouteille, JT Fonné, F. Yoshizawa

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

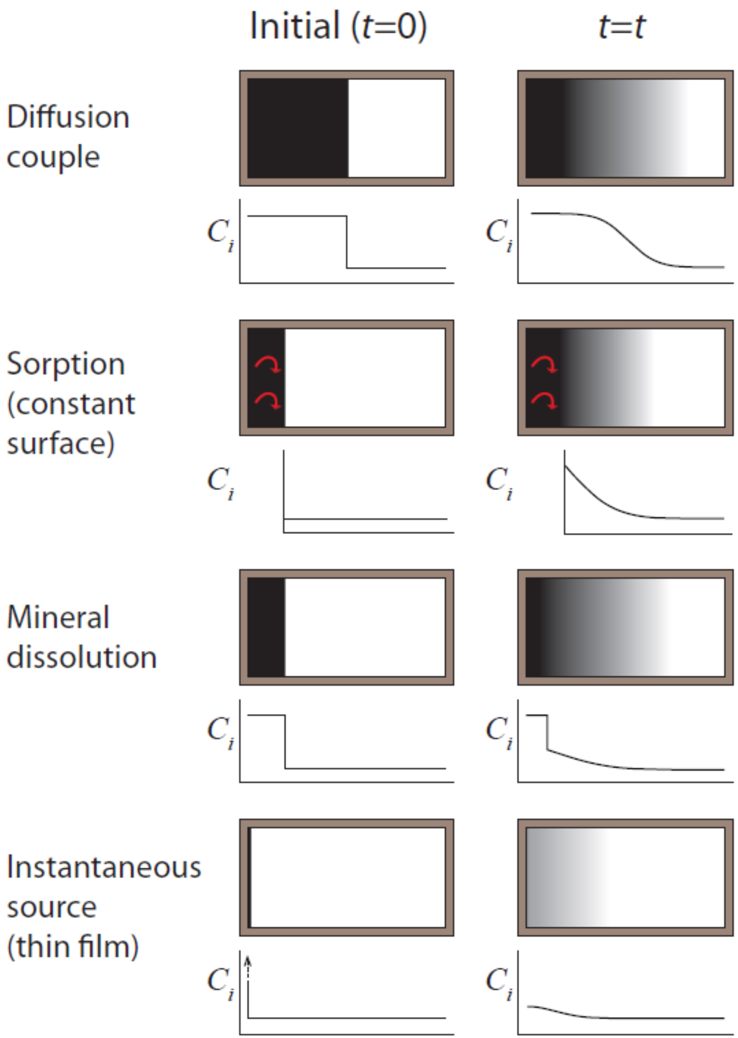


$$\mathbf{j} = -D\nabla C$$



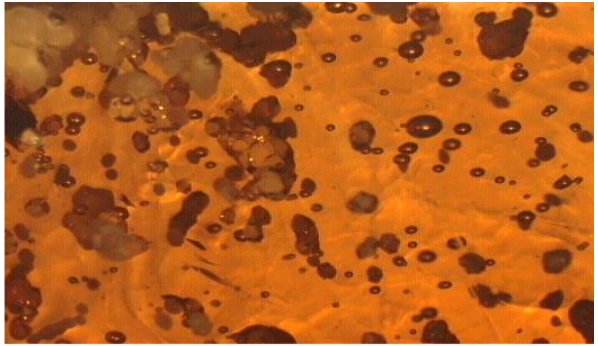
$$\frac{\partial C}{\partial t} = D\Delta C$$

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

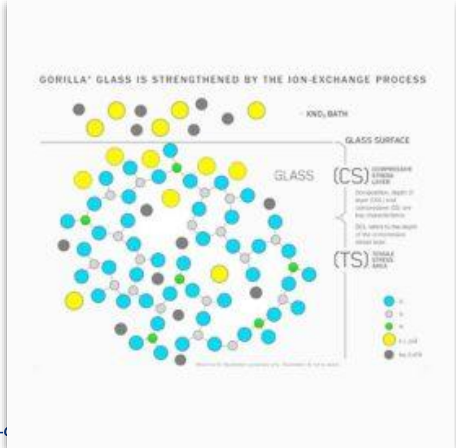
Glass melting: batch & stones



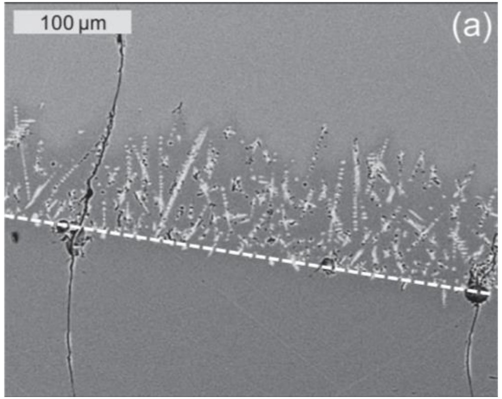
Refractory corrosion

Volatile diffusion & volcanic eruption

Ionic exchange (display)

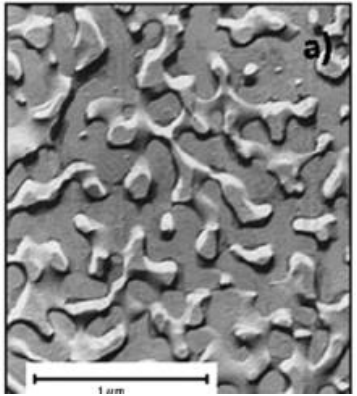


Crystallization



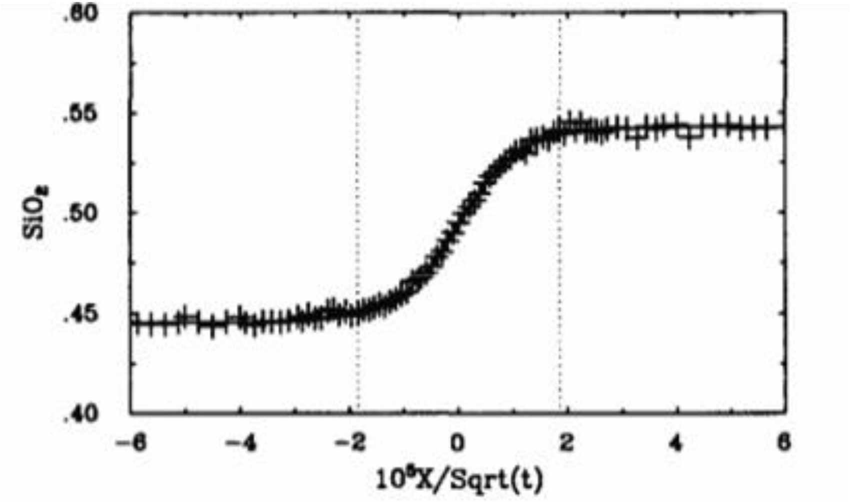
Pablo et al JNCS 2019.

Phase separation



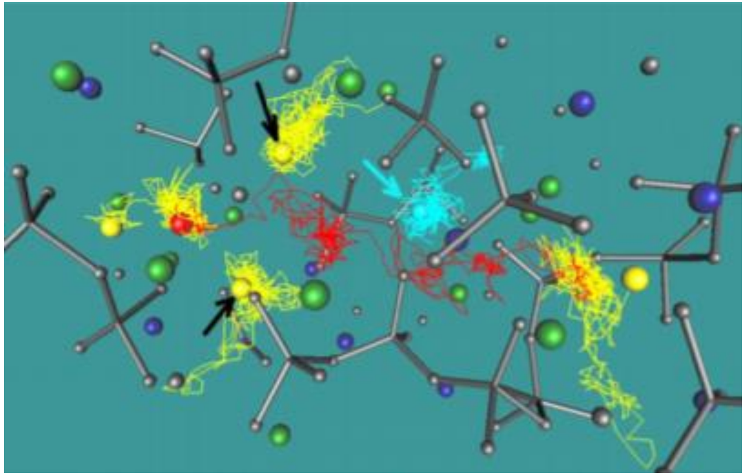
Measuring diffusion data

Concentration gradients (chemical concentrations, isotopes…)



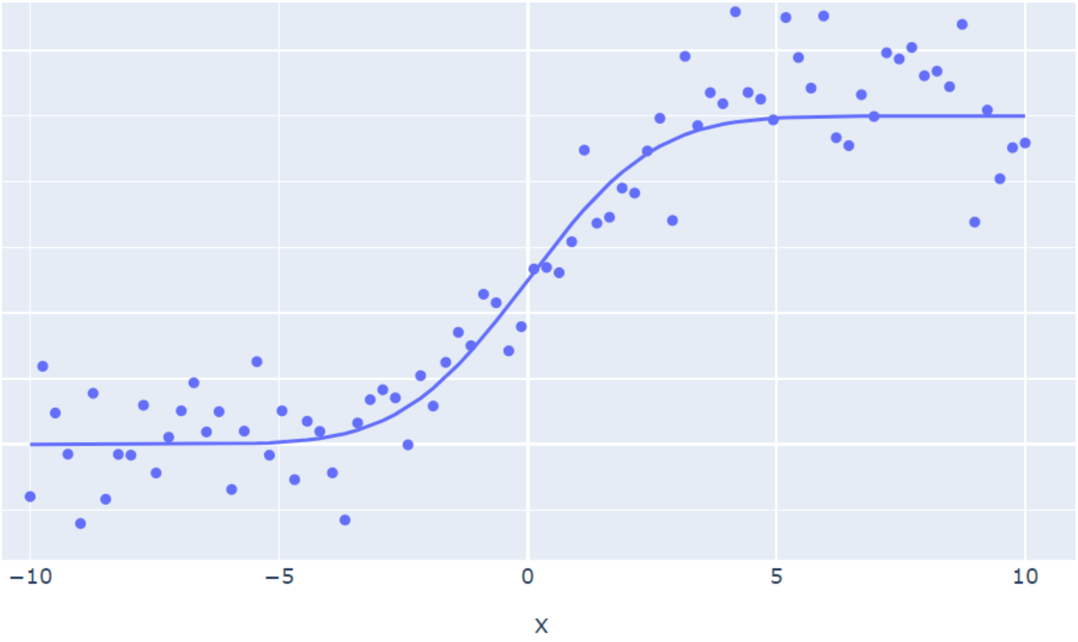
Liang, Yan, Frank M. Richter, and E. Bruce Watson. *Geochimica et Cosmochimica Acta* 60.24 (1996): 5021-5035.

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

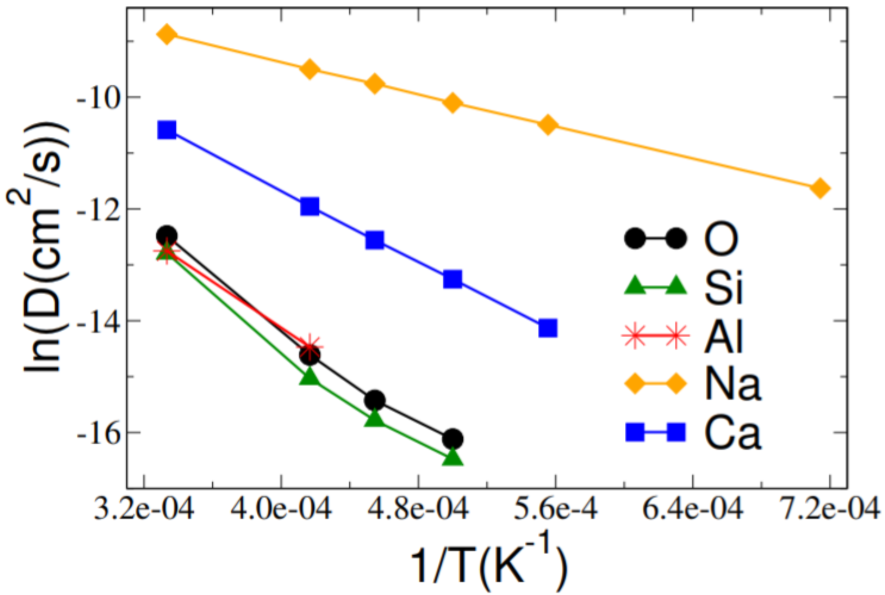
Values of diffusivities in silicate melts - influence of species

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

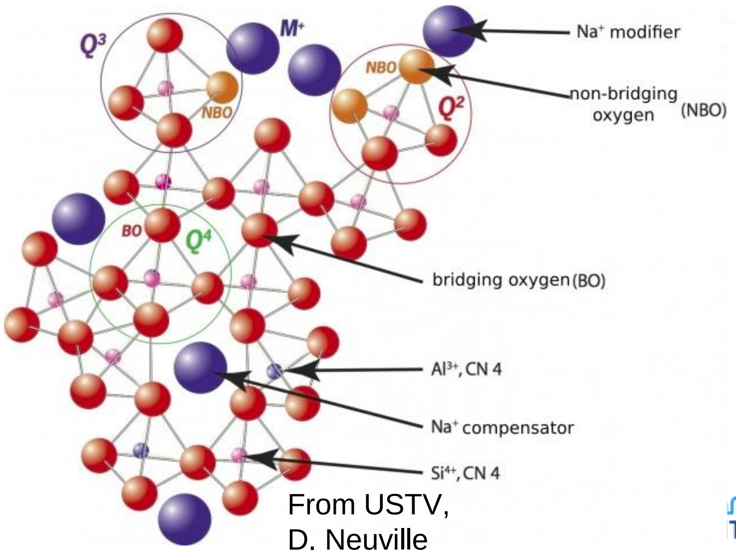
D depends on **strength** and **number** of chemical bonds (i.e. on silicate structure)

D(network modifiers) > D(network formers)

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

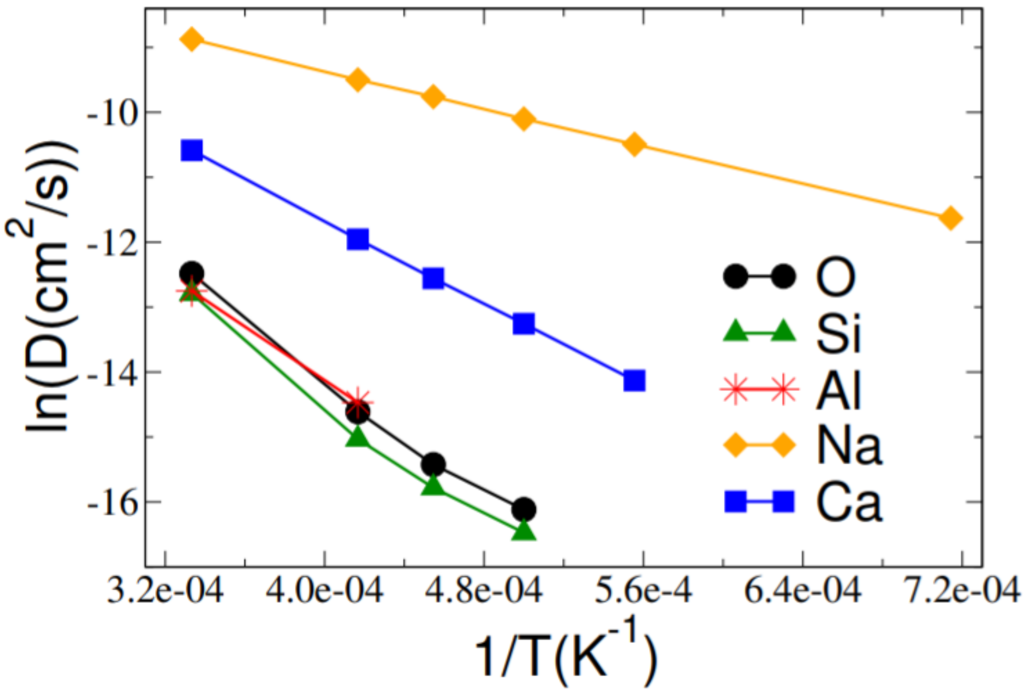


Col with Mathieu's Salanne's team: Serva, Alessandra, et al. "Structural and dynamic properties of soda–lime–silica in the liquid phase." *The Journal of Chemical Physics* 153.21 (2020): 214505.



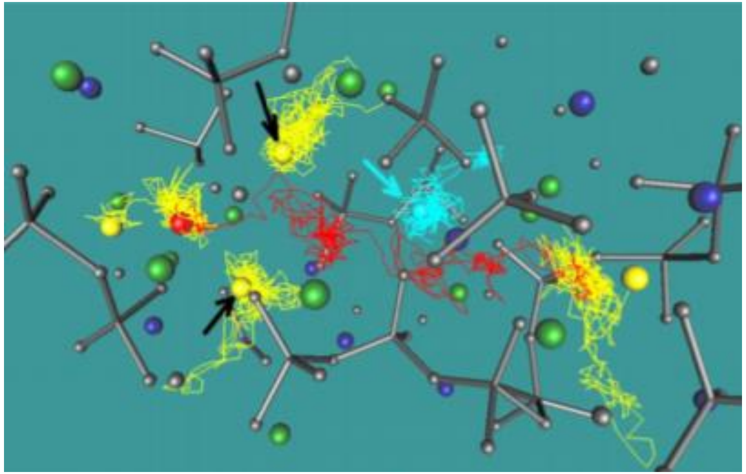
From USTV, D. Neuville

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

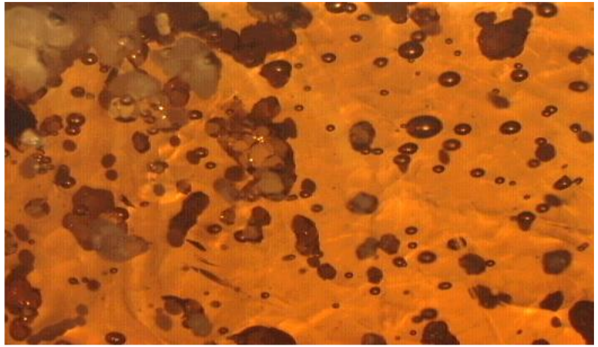
Arrhenian behaviour
Activation energy related to chemical bonds



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

Some orders of magnitudes

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** : Ul / D

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

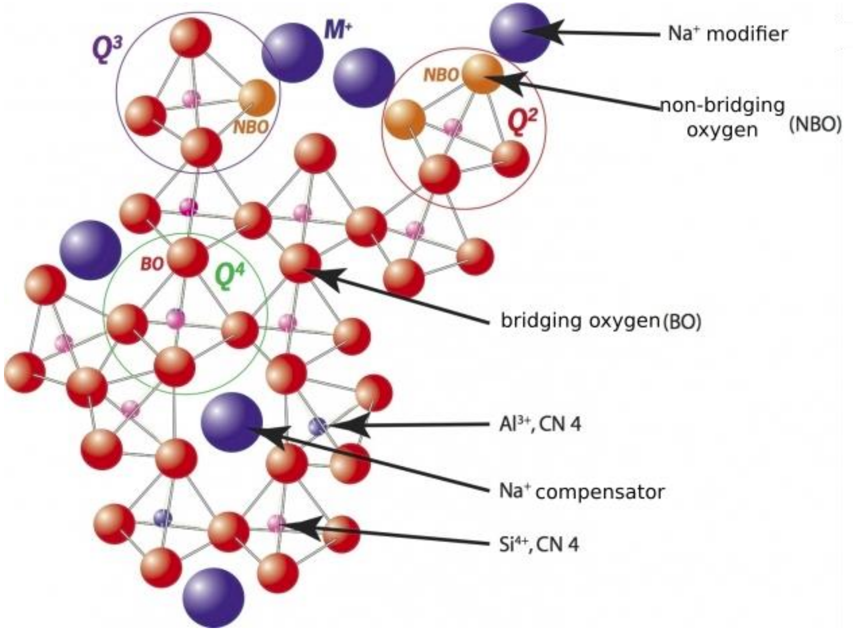
Viscous liquids: Stokes-Einstein and Eyring relation
→ network **formers**

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

$$D = \frac{kT}{2\eta r}$$

η: viscosity

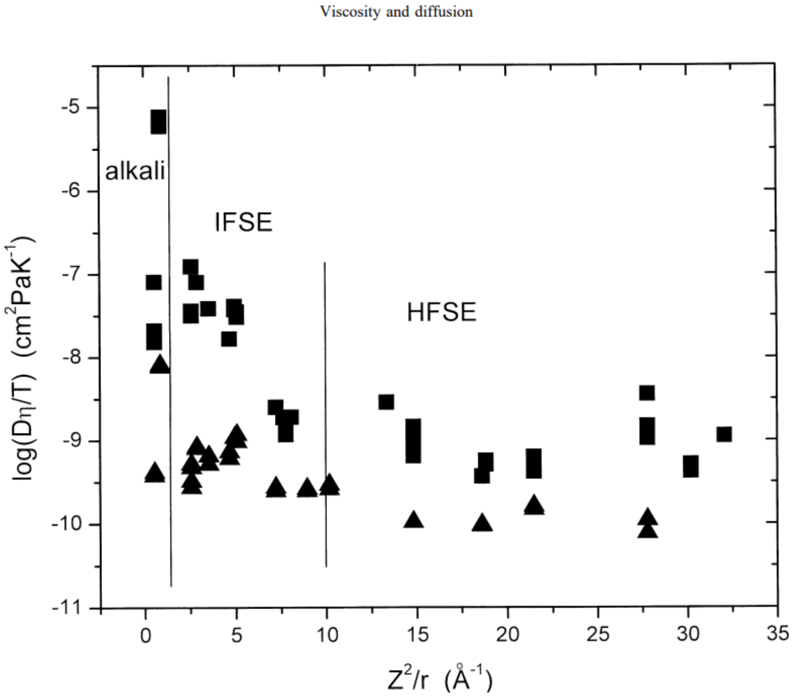
r: radius of particle

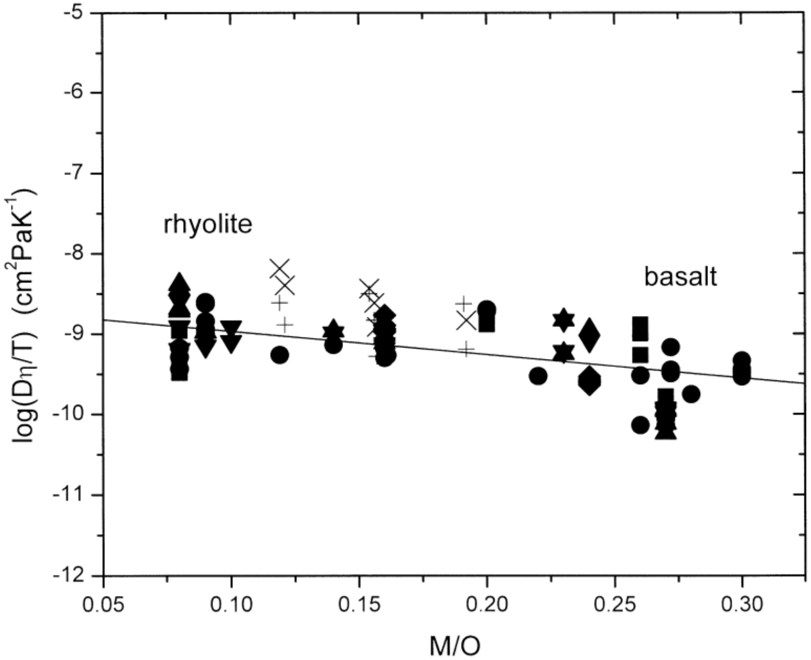


from USTV website
D. Neuville

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

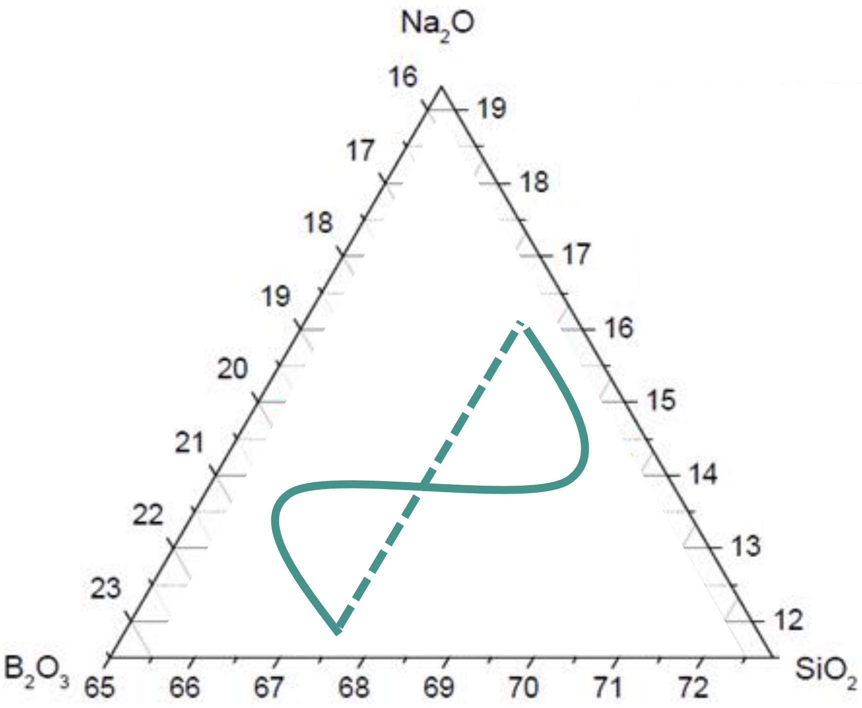
Relating diffusion and viscosity



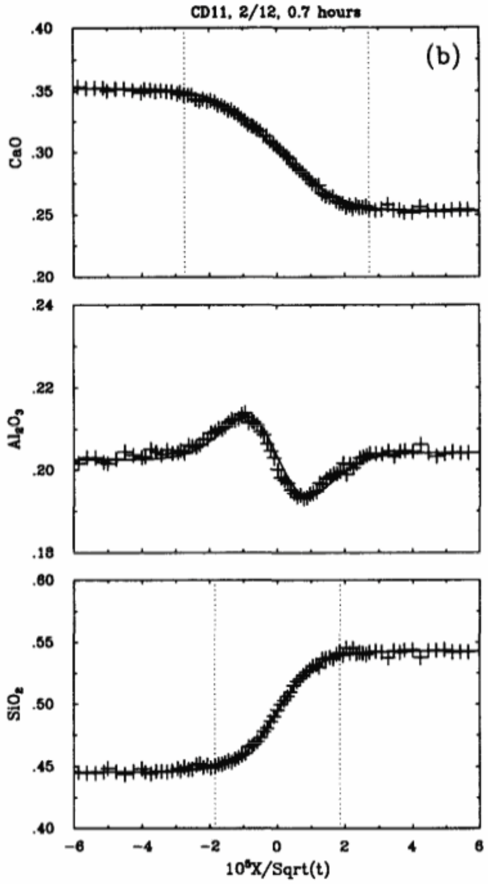


Empirical models relating viscosity and tracer diffusion in magmatic silicate melts, Mungall GCA 2002.

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

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

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

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

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

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

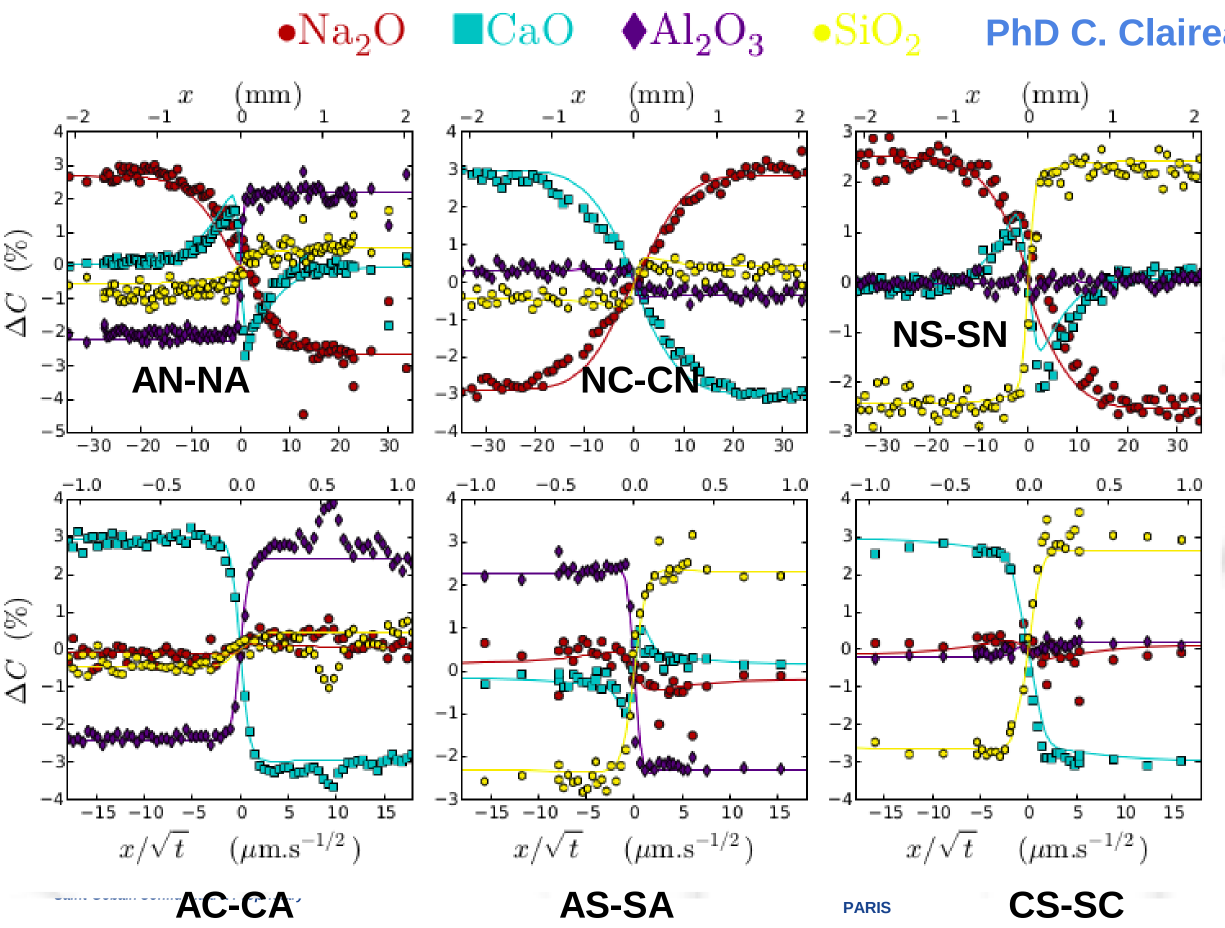
Also used in multicomponent metallic alloys.

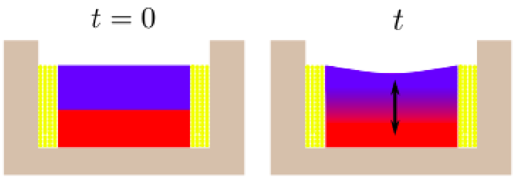
More rigorously: thermodynamic formulation with activity gradient (Onsager).

Few studies in industrial systems.

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**

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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Installation

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Fitting multidiffusion profiles for three components

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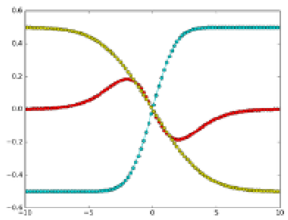
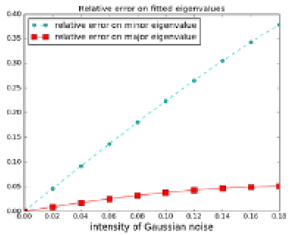
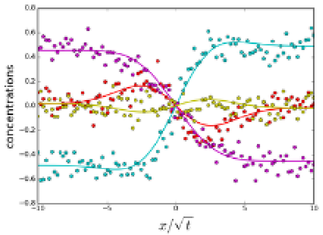
Examples



Fitting multidiffusion profiles for three components



Effect of measurement noise on accuracy of fit

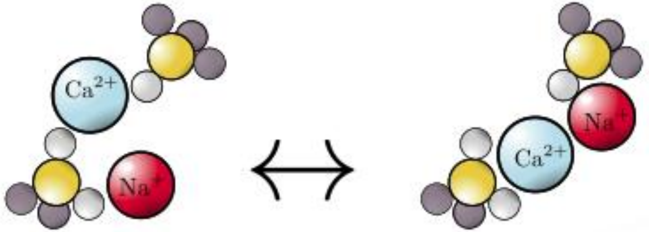


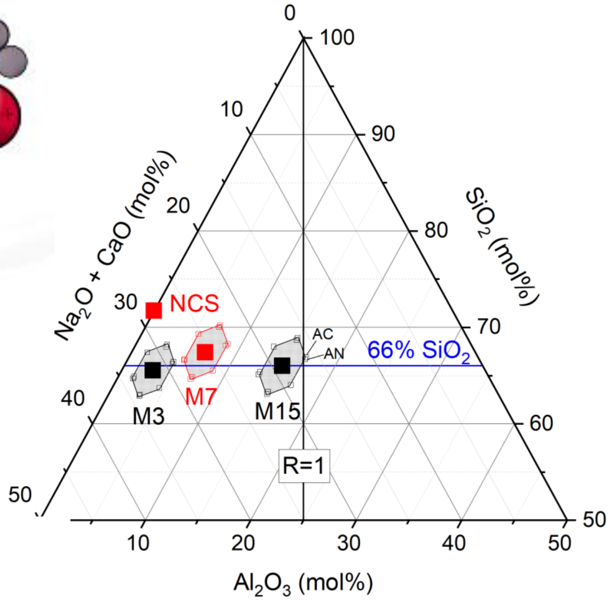
Effect of initialization on accuracy of fit

Dominant eigenvector

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

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

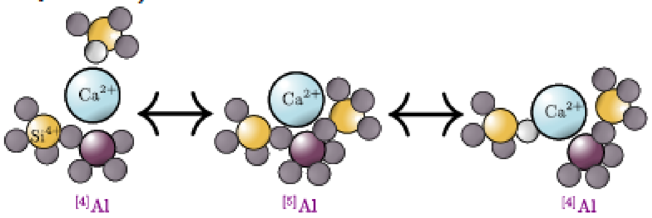




Other eigenvectors: involve network formers, smaller diffusivity value

Second eigenvector (52x less frequent)

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

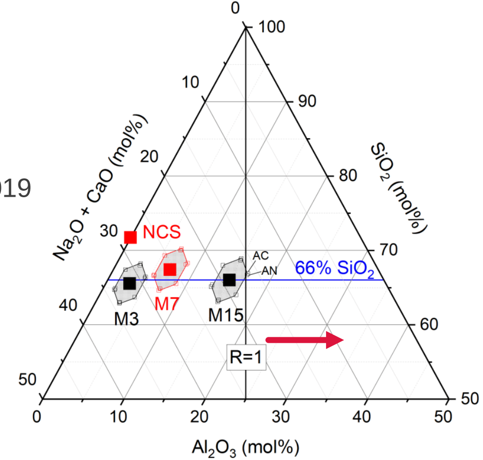


PhD M. Jacquemin, ANR MAGI, CEMHTI
P. Simon, C. Bessada, E. Burov

Diffusion pathways in Peralkaline compositions area

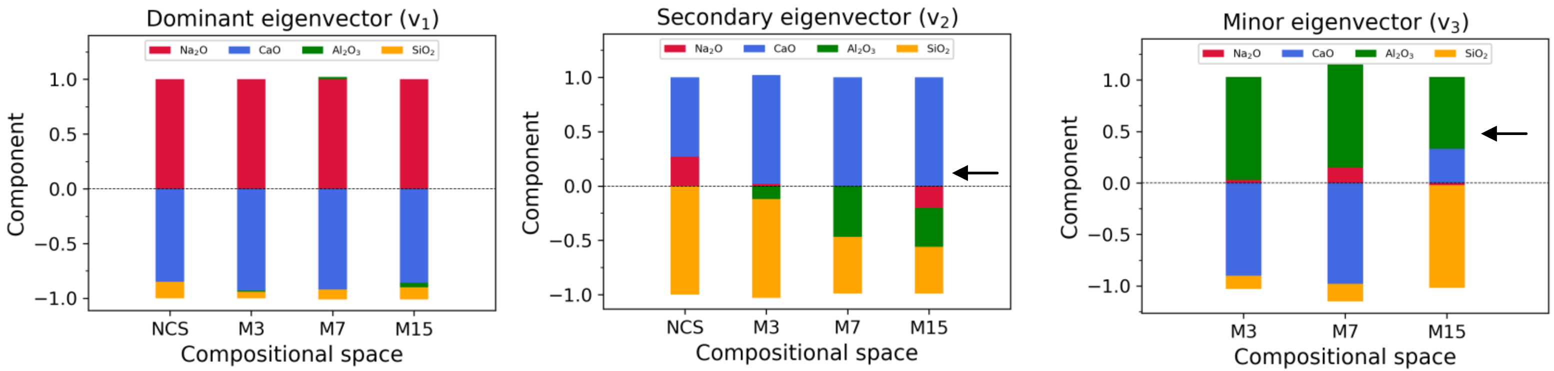
PhD Maxime Jacquemin, **MAGI project**

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



Eigenvectors $(\vec{v_i})$

Na_2O CaO Al_2O_3 SiO_2



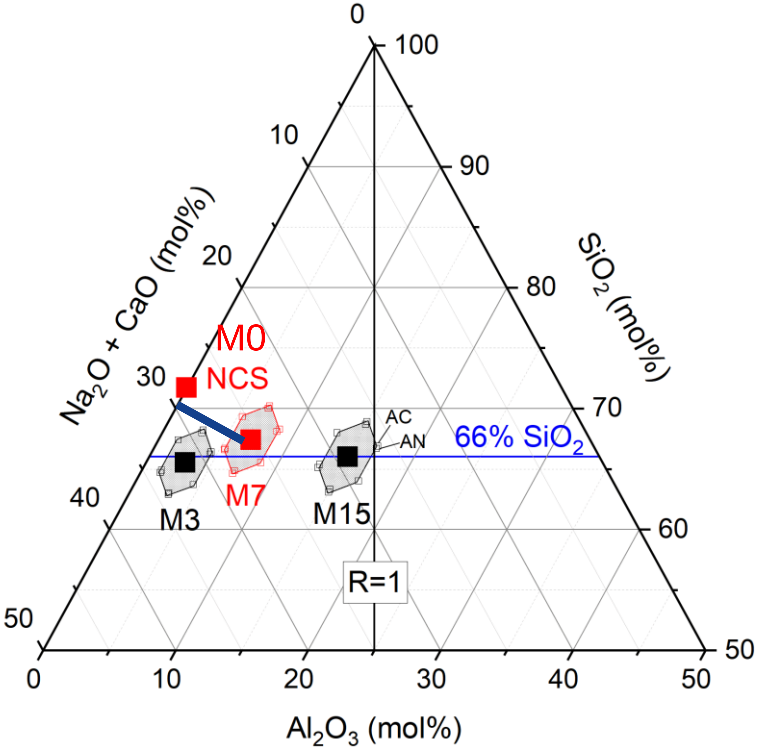
v_1 : Na ↔ Ca

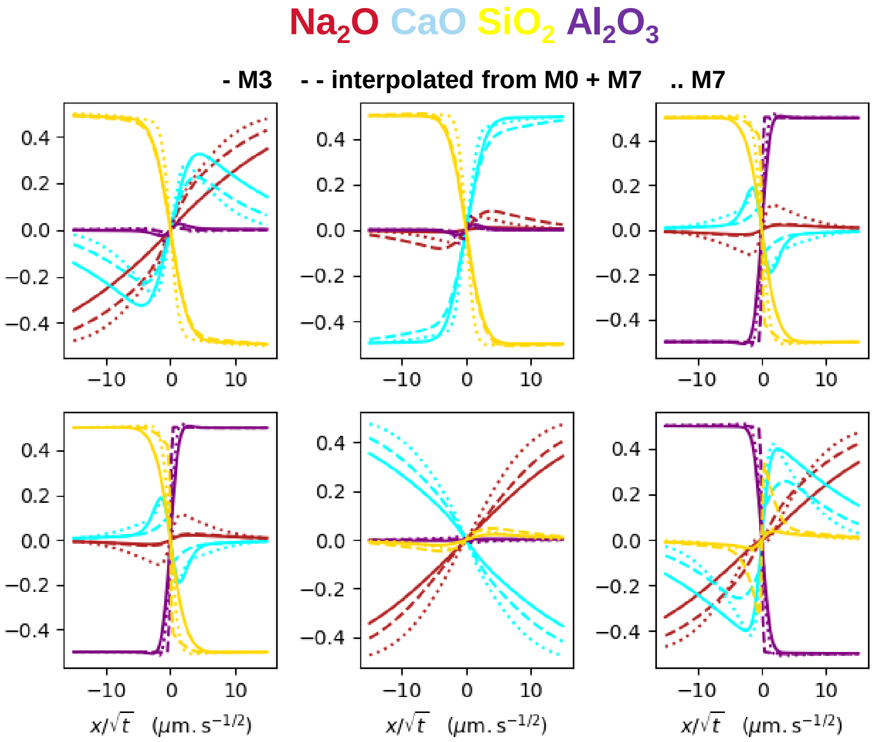
v_2 et v_3 : Formers ↔ Ca

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

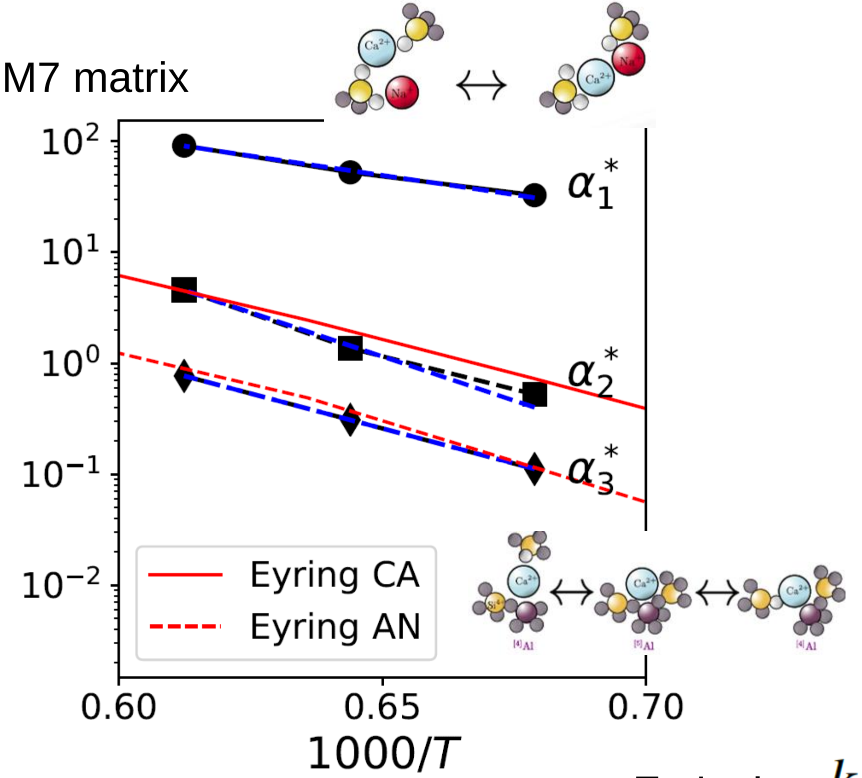
- Reaction evolution with Al_2O_3 concentration
- Al is associated to the Na or Ca near R=1

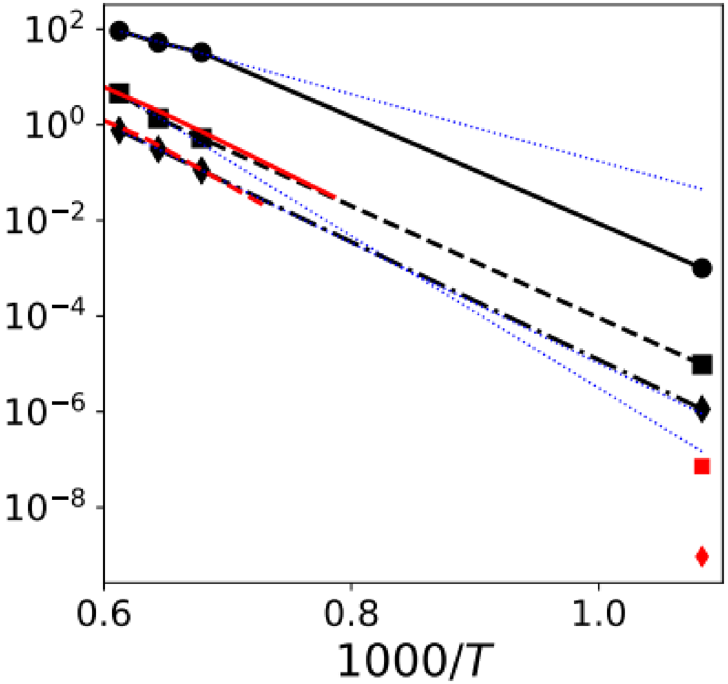
Can we interpolate diffusion matrices ?





Energetics of multicomponent diffusion

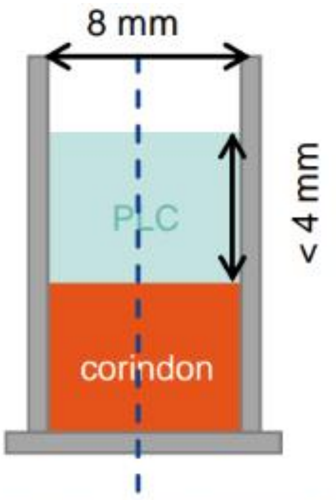


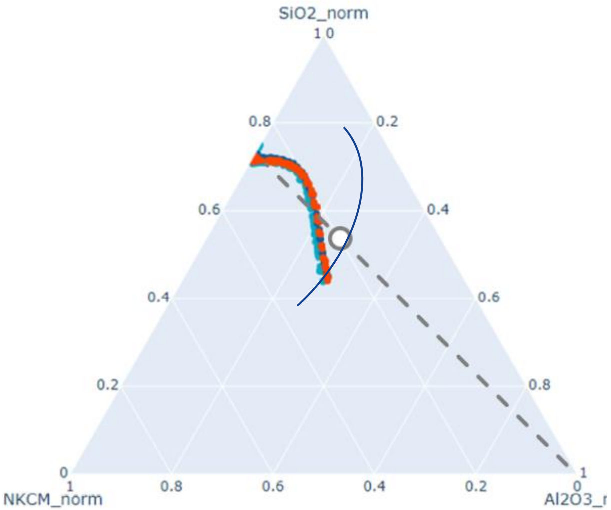


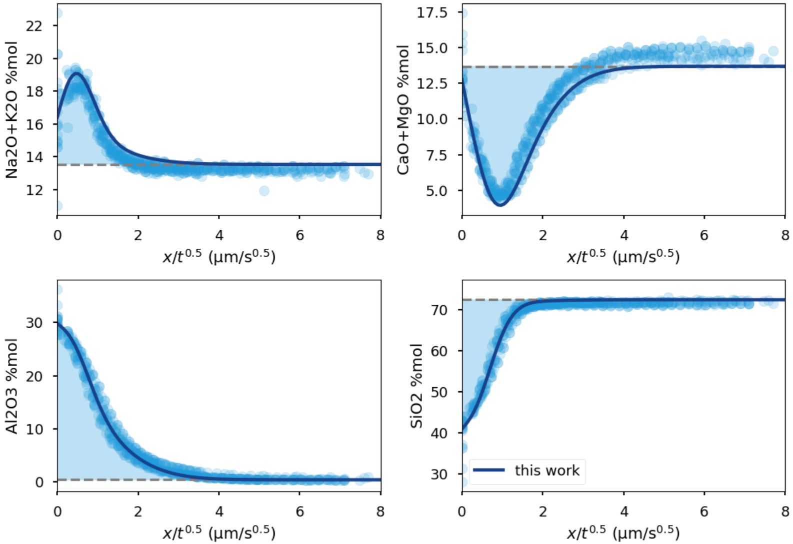
.Claireaux, Corinne, et al. "Influence of temperature on multicomponent diffusion in calcium and sodium aluminosilicate melts." *Journal of Non-Crystalline Solids* 505 (2019): 170-180.

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

Application: dissolution of Al_2O_3 refractories, PhD F. Yoshizawa



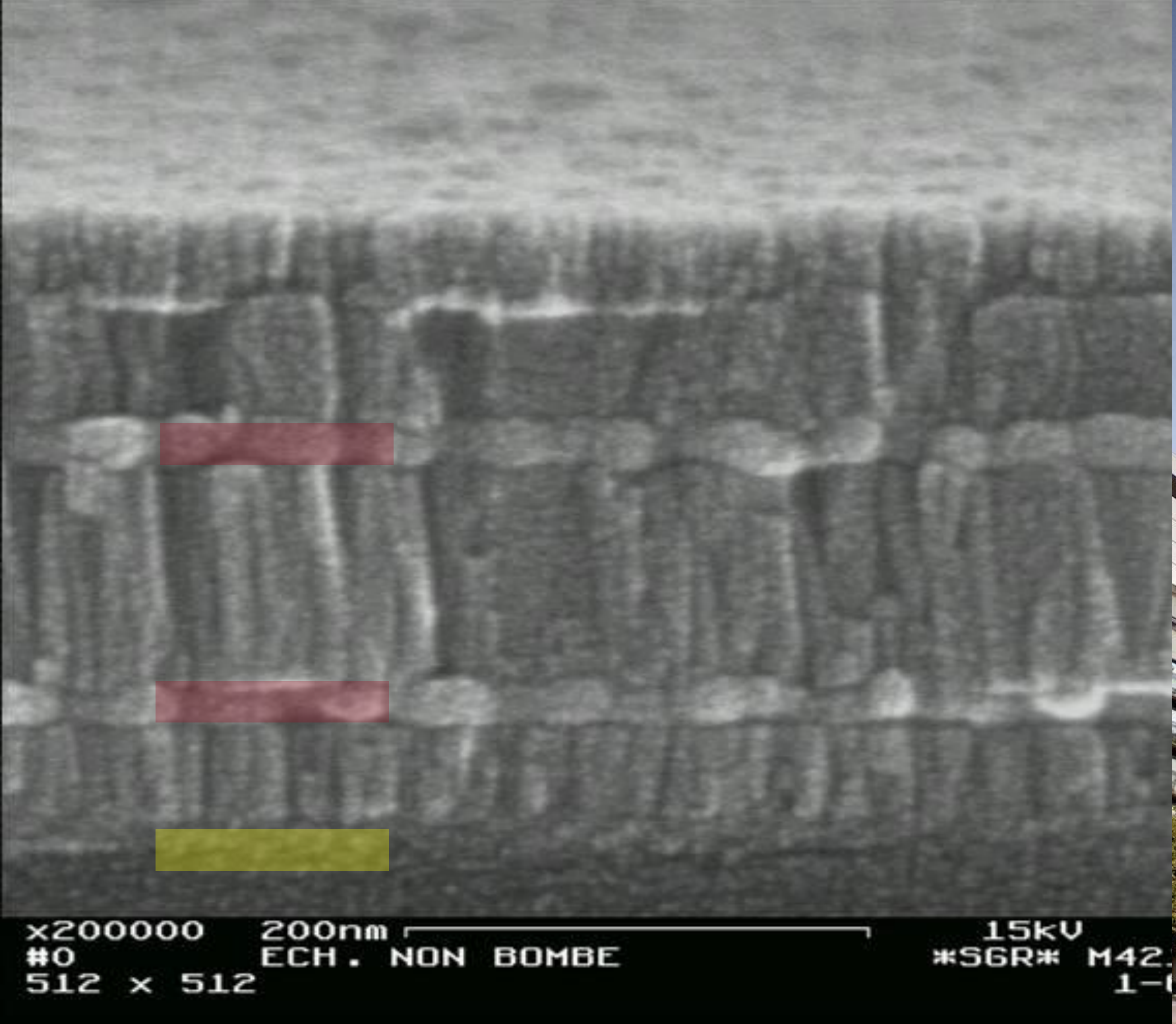




Dissolution mechanisms of minerals in silicate liquids of industrial interest, F. Yoshizawa

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


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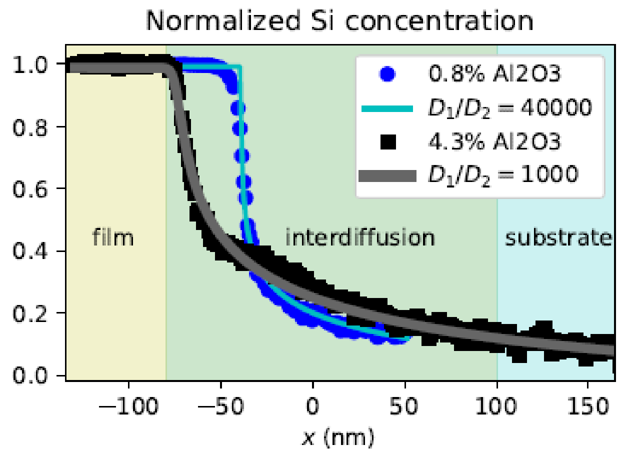
Diffusive dissolution of thin film and multicomponent effects



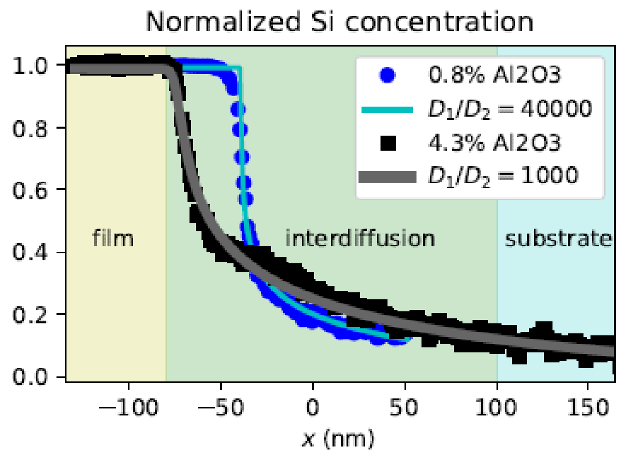
$$\frac{\partial C}{\partial t} = \nabla \cdot (D \nabla C)$$

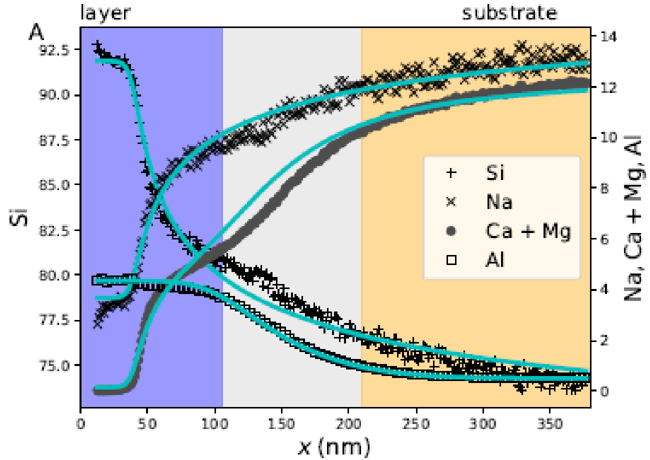
D often considered constant, but sometimes this approximation cannot be used

smaller D larger D

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

Diffusive dissolution of thin film and multicomponent effects





High Si diffusivity (& viscosity) ratio between substrate and film

Using Crank's model to fit profiles :

$$D_{\mathrm{Si}} = D_0 \exp(-\beta C_{\mathrm{Si}})$$

Fitted values of β consistent with Eyring's law and viscosity model

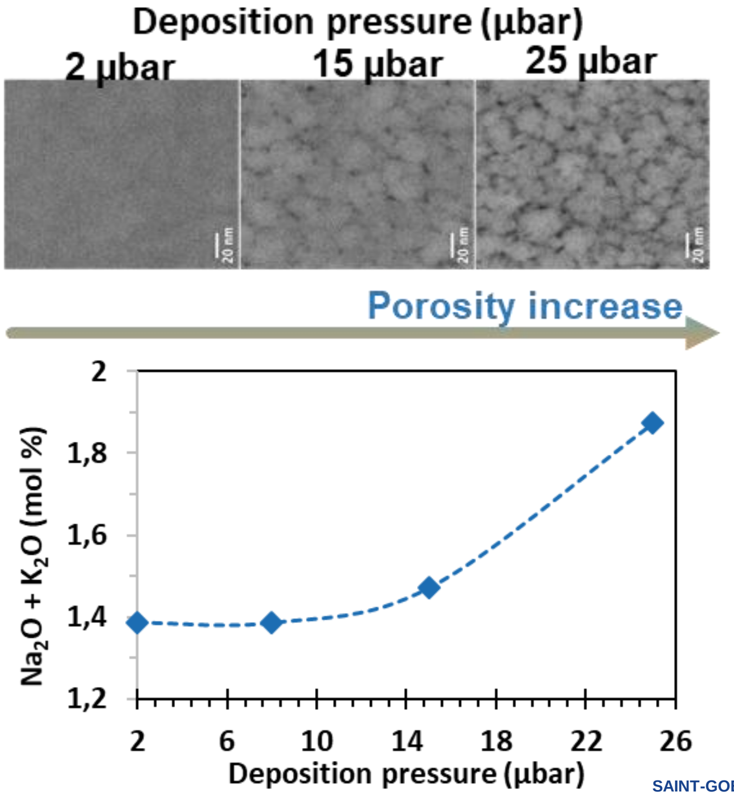
Use bulk eigenvectors to fit profiles

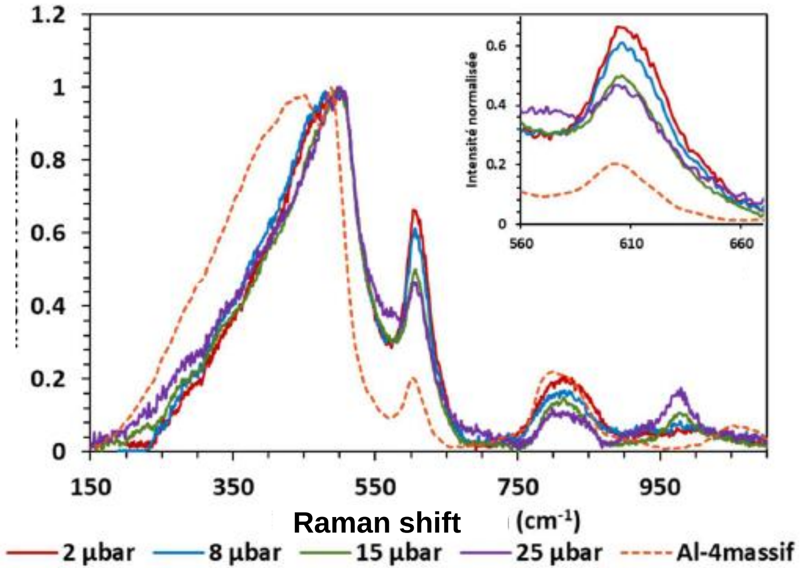
PhD JT Fonné ; Fonné et al., JACS 2017, JACS2018 PhD S. Ben Khemis, coll. L Cormier

Diffusion and structure of thin films, PhD Sirine Ben Khemis

Silica thin films with different sputtering conditions

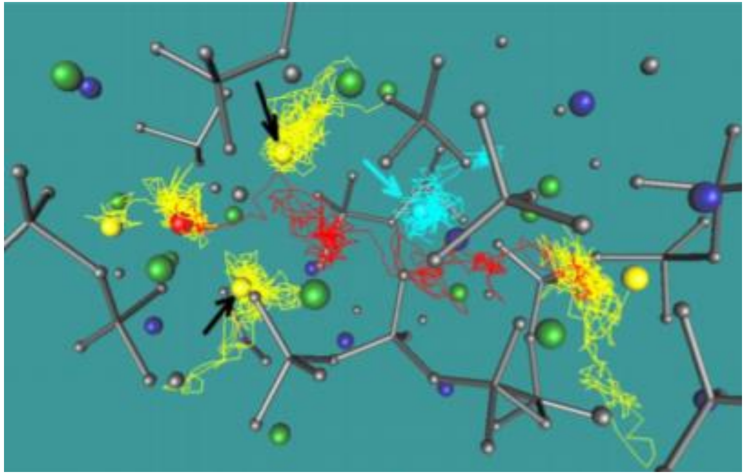
MAGI project, L. Cormier (IMPMC), E. Burov (SVI)





Khemis, S. Ben, et al. "Structural analysis of sputtered amorphous silica thin films: A Raman spectroscopy investigation." *Thin Solid Films* 733 (2021): 138811.

Conclusions



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

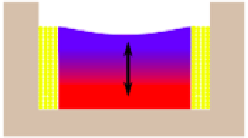
The complex structure of silicate melts has strong consequences about diffusion:

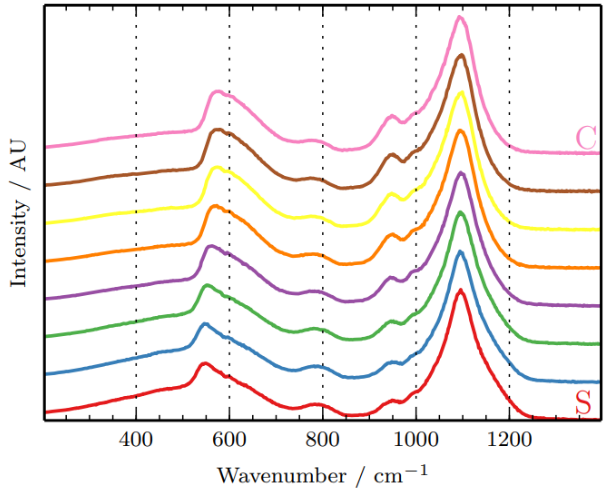
- D(network formers) << D(modifiers)
- Strong multicomponent effects (couplings)

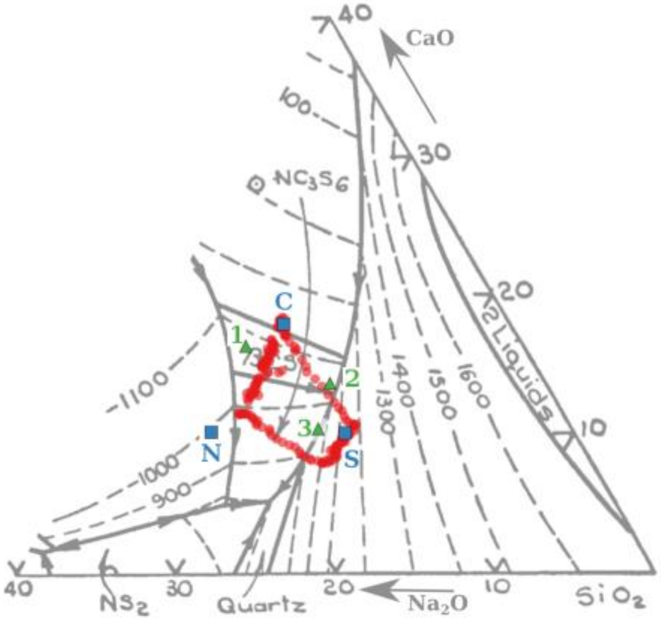
Diffusion is a thermally activated phenomenon.


THANK YOU FOR YOUR ATTENTION!

Diffusion profiles as a tool for materials informatics



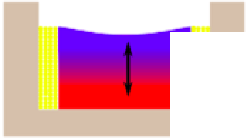




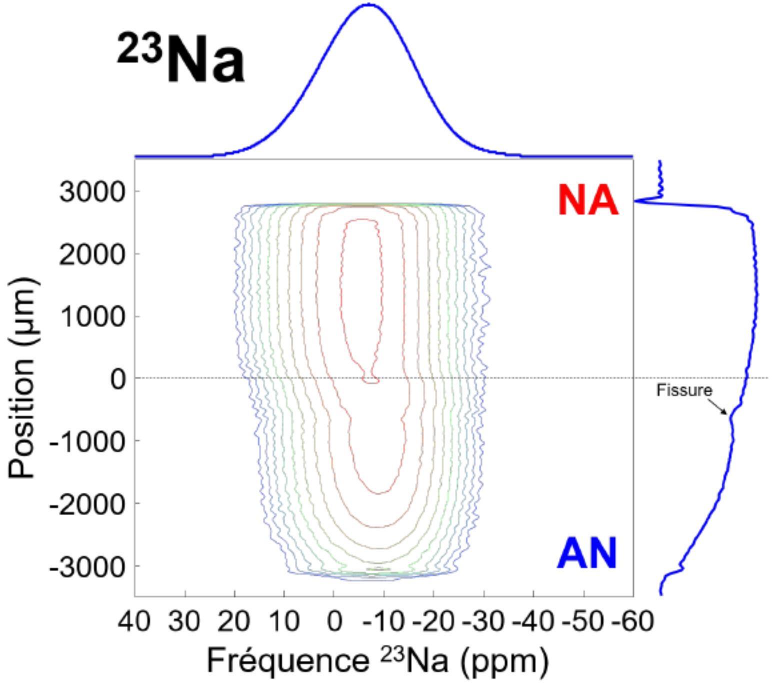
Woelffel, William, et al. "Analysis of soda-lime glasses using non-negative matrix factor deconvolution of Raman spectra." *Journal of Non-Crystalline Solids* 428 (2015): 121-131.

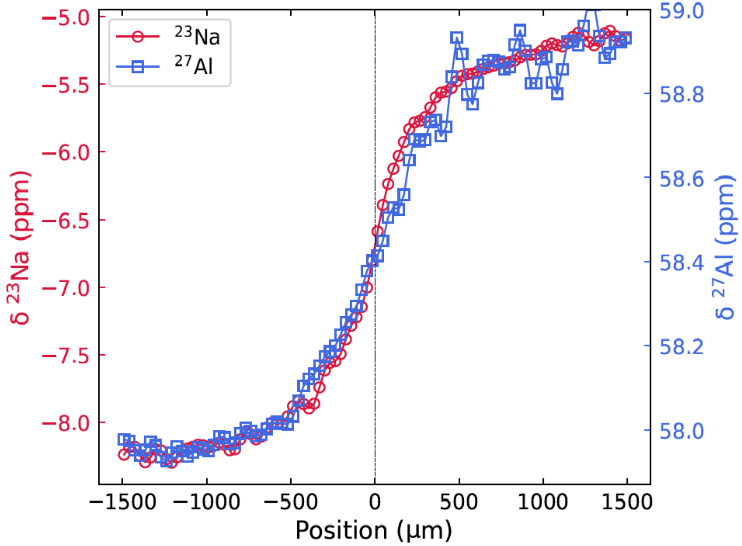
400 different composiitions with EMPA and Raman data
PCA analysis to reduce dimensionality of Raman data
Model to estimate composition from Raman spectrum in NCS

Diffusion profiles as a tool for materials informatics



NMR





Sarou-Kanian, Vincent, et al. "Metabolite localization in living drosophila using high resolution magic angle spinning NMR." *Scientific reports* 5.1 (2015): 1-5.

Coll. CEMHTI, C. Bessada, P. Simon, V. Sarou-Kanian, Pierre Florian, César Leroy, Laura Piveteau, Franck Fayon & Dominique Massiot