Multicomponent diffusion in silicate melts

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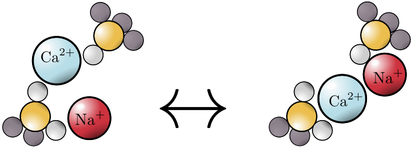
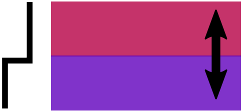
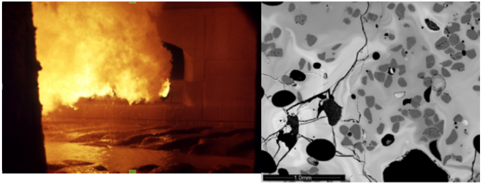




heterogeneous system
concentration gradient

chemical diffusion

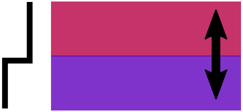
How to predict diffusive exchanges in heterogeneous systems ?



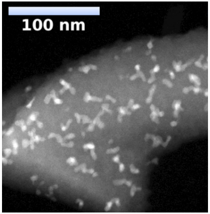
glass melting


refractory corrosion

heterogeneous system
concentration gradient



chemical diffusion



Dargaud 2011

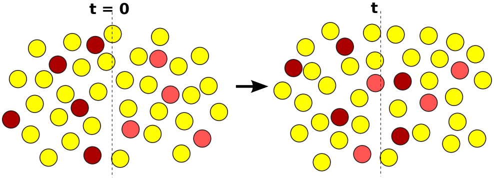
crystallization
phase separation


thin films on glass substrate

How to predict diffusive exchanges in heterogeneous systems ?

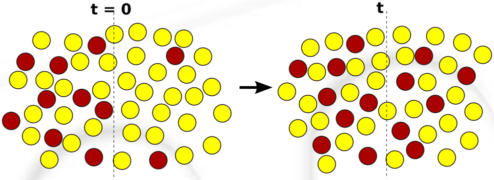
Different configurations for diffusion

Isotopic diffusion : marked tracer



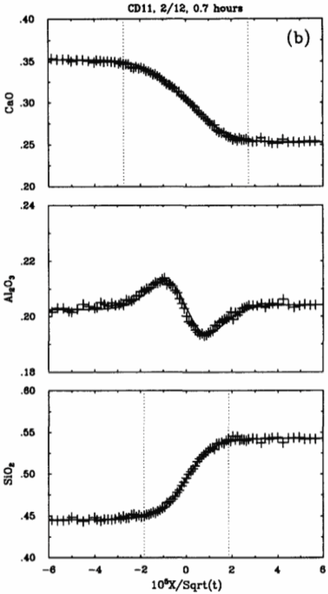
[Jambon and Carron, 1976, Richter et al., 1999]

Chemical diffusion : gradient of chemical concentration



[Trial and Spera, 1994, Chakraborty et al., 1995a, Liang et al., 1996]

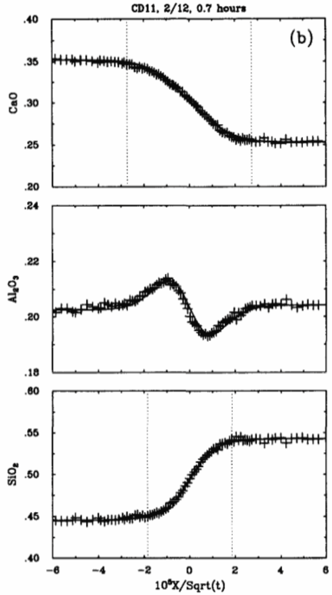
Interdiffusion effects : uphill diffusion



← [Liang et al., 1996]

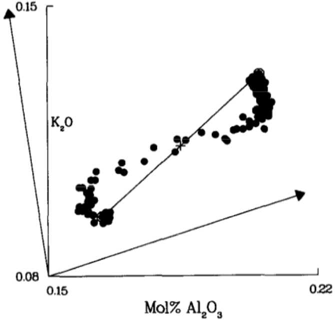
uphill diffusion

Interdiffusion effects : uphill diffusion



← [Liang et al., 1996]

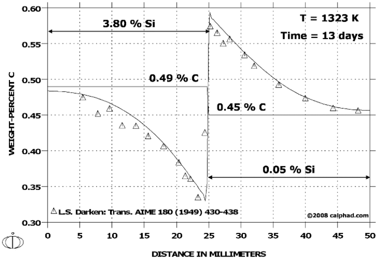
uphill diffusion



[Chakraborty et al., 1995b]

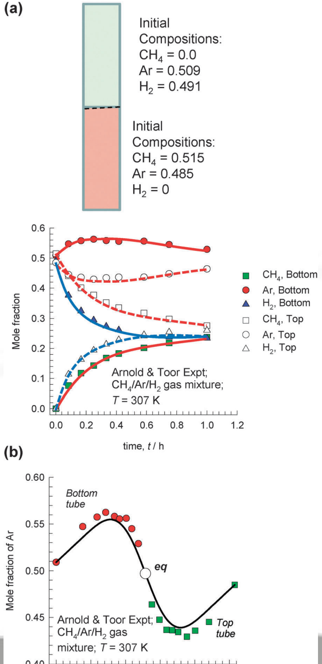
non-straight diffusion paths

Uphill diffusion in various materials

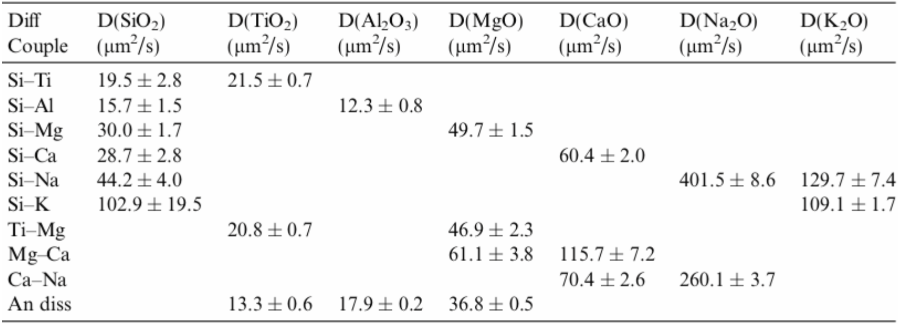


Darken, Fe-Si-C alloy

[Krishna2015]



Interdiffusion effects



Diff Couple	$D(SiO_2)$ ($\mu m^2/s$)	$D(TiO_2)$ ($\mu m^2/s$)	$D(Al_2O_3)$ ($\mu m^2/s$)	$D(MgO)$ ($\mu m^2/s$)	$D(CaO)$ ($\mu m^2/s$)	$D(Na_2O)$ ($\mu m^2/s$)	$D(K_2O)$ ($\mu m^2/s$)
Si–Ti	19.5 ± 2.8	21.5 ± 0.7					
Si–Al	15.7 ± 1.5		12.3 ± 0.8				
Si–Mg	30.0 ± 1.7			49.7 ± 1.5			
Si–Ca	28.7 ± 2.8				60.4 ± 2.0		
Si–Na	44.2 ± 4.0					401.5 ± 8.6	129.7 ± 7.4
Si–K	102.9 ± 19.5						109.1 ± 1.7
Ti–Mg		20.8 ± 0.7		46.9 ± 2.3			
Mg–Ca				61.1 ± 3.8	115.7 ± 7.2		
Ca–Na					70.4 ± 2.6	260.1 ± 3.7	
An diss		13.3 ± 0.6	17.9 ± 0.2	36.8 ± 0.5			

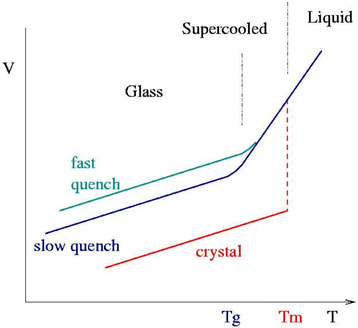
[Guo and Zhang, 2016]

Effective binary diffusion coefficient (EBDC) depends on counter-diffusing species.

Viscous liquids quenched into amorphous solids

Glass transition and viscosity

Avoiding crystallization



Glass transition and viscosity

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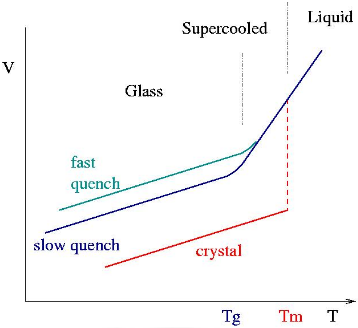
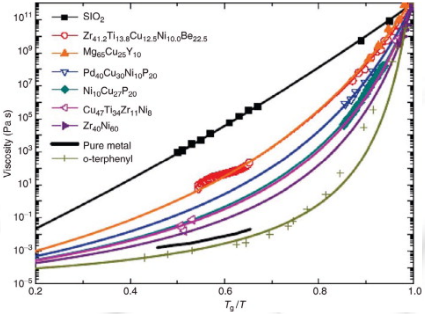
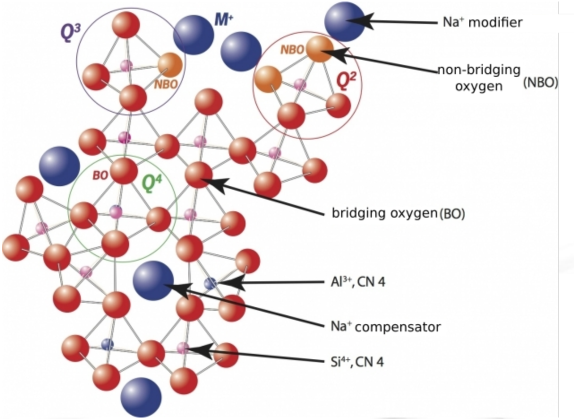


Avoiding rearrangements :
fast quenching rates or
low mobilities



Silicate glasses are strong network-forming glasses : easy to process
Downside : low mobility, high viscosity

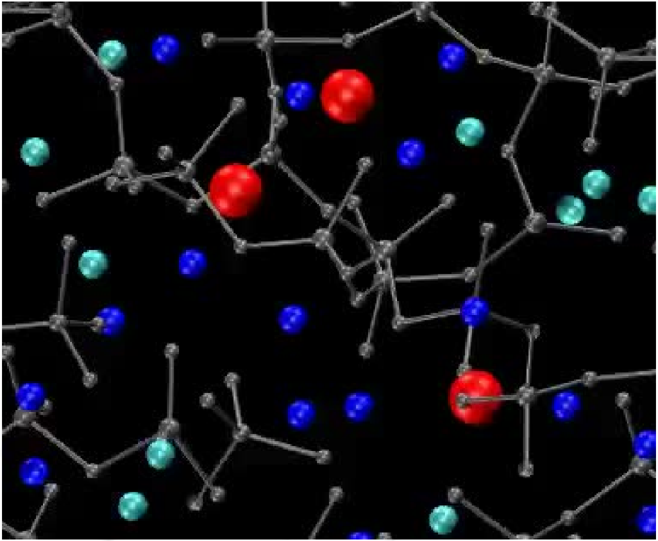
Composition and structure of silicate glasses



Polymerized network of tetrahedra

- Network formers : Si, Al, (B, P, ...)
- Network modifiers (or compensators) : Na, Ca, (K, Mg, ...)

Diffusion and reorganizations of silicate network



`https://www.youtube.com/watch?v=SOUIMspT4jw`, A. Tilocca

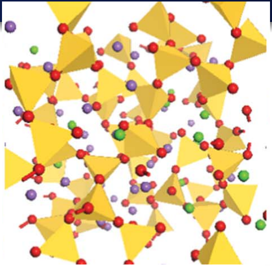
Diffusion matrix formalism

Fick's law

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

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

Diffusion matrix formalism



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Diffusion matrix

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

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

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

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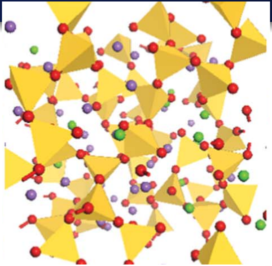

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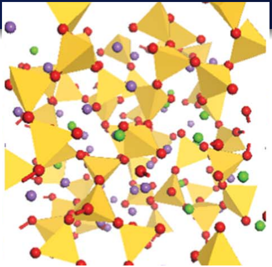

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Measured in several ternary systems, mostly in geosciences [Liang et al., 1996], [Richter et al., 1998] : $\mathrm{CaO/MgO} - \mathrm{Al_2O_3} - \mathrm{SiO_2}$

Also used in multicomponent metallic alloys

$$\mathbf{j}_i = -C_i M_i \nabla \mu_i = -\sum_j C_i M_i \frac{\partial \mu_i}{\partial C_j}\frac{\partial C_j}{\partial x}$$

Questions

What are the diffusion matrices in systems of industrial interest ?

- $Na_2O - CaO - SiO_2$ (NCS, W. Woelffel)
- $Na_2O - Al_2O_3 - SiO_2$ (NAS, V. Pukhkaya)
- $Na_2O - CaO - Al_2O_3 - SiO_2$ (NCAS, C. Claireaux)
- $Na_2O - CaO - Al_2O_3 - SiO_2 - ZrO_2$ (NCASZ, M. Ficheux)
- $Na_2O - B_2O_3 - SiO_2$ (NBS, H. Pablo)

How do diffusion matrices depend on composition & temperature ?

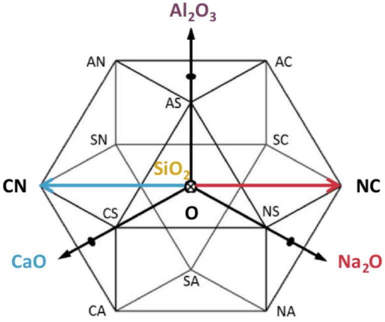
Can we predict them ?

Can we use diffusion matrices for thin films as well ?

Principle of multidiffusion experiments

[Claireaux et al., 2016] : quaternary system $\mathrm{CaO{-}Na_2O{-}Al_2O_3{-}SiO_2}$

Diffusion couples centered on $64.5\%\mathrm{SiO_2}, 13.3\%\mathrm{Na_2O}, 10.8\%\mathrm{CaO}, 11.33\%\mathrm{Al_2O_3}$



12 different compositions

$\Delta \pm 2.5\%$

A lot of diffusion experiments !

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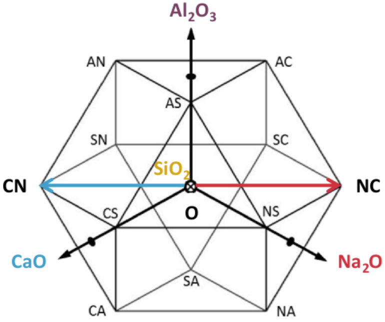

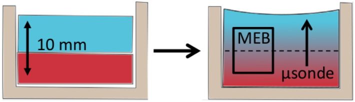

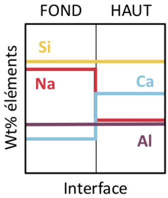

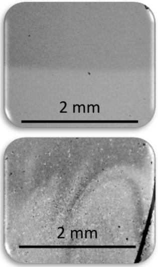

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$\Delta \pm 2.5\%$

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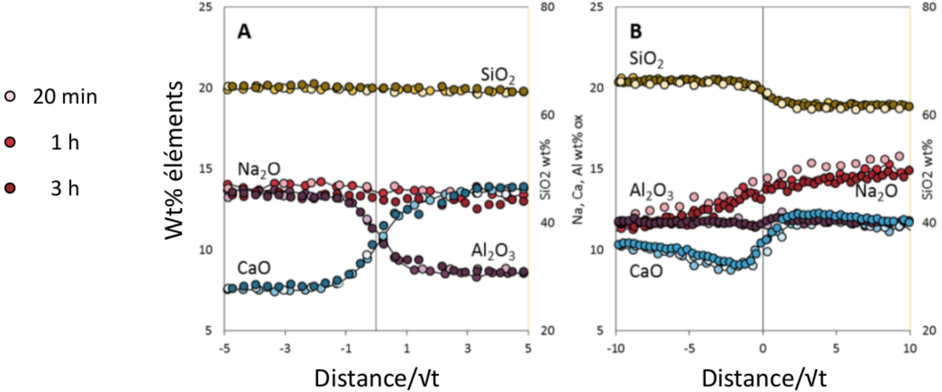
Typical diffusion profiles

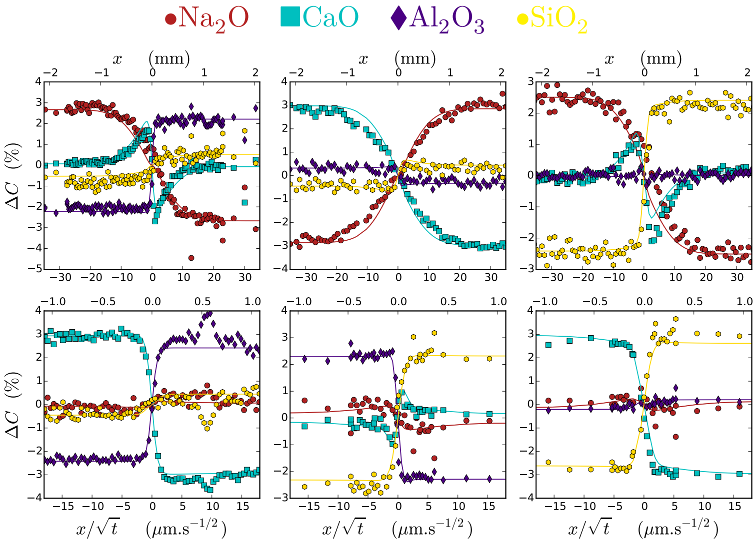
Electron microprobe profiles



Good rescaling by $\sqrt{t}$

$$C(x,t) = f\left(\frac{x}{\sqrt(t)}\right)$$

NCAS system at 1200°C

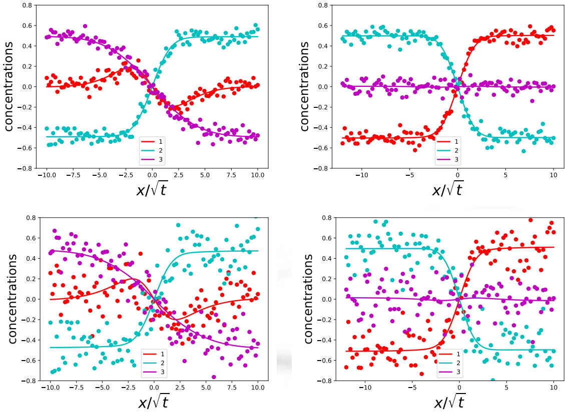


[Claireaux et al., 2016] GCA, Claireaux JNCS 2018

Python package to fit and simulate diffusion profiles : `multidiff`.

Estimation of diffusion matrix

Estimating the best diffusion matrix so that generated theoretical diffusion profiles fit optimally experimental diffusion profiles.



low noise

more noise

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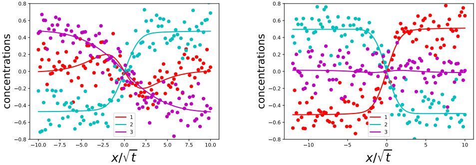
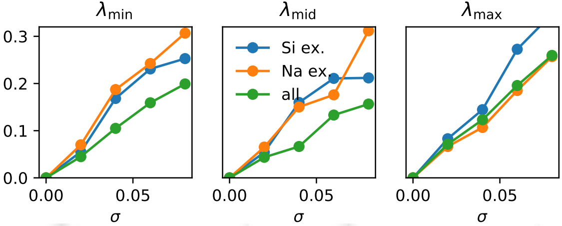


more noise

The more experiments (and data points), the better !

Relative error on eigenvalues vs. intensity of noise



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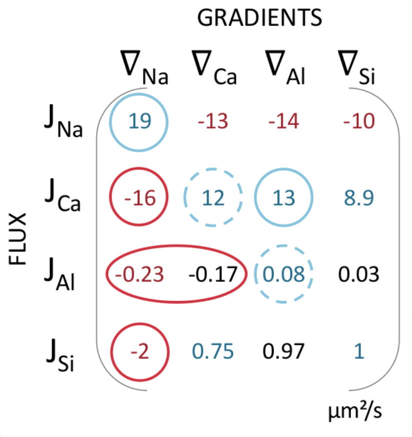

GRADIENTS

FLUX

$$\begin{array}{c|cccc} & \nabla_{Na} & \nabla_{Ca} & \nabla_{Al} & \nabla_{Si} \\ \hline J_{Na} & 19 & -13 & -14 & -10 \\ J_{Ca} & -16 & 12 & 13 & 8.9 \\ J_{Al} & -0.23 & -0.17 & 0.08 & 0.03 \\ J_{Si} & -2 & 0.75 & 0.97 & 1 \end{array}$$

µm²/s

- Not symmetric
- Large off-diagonal terms

The matrix can be used to compute the evolution of **any** diffusion couple (in the domain of interest).

Diffusion matrix formalism

Let us define

$$\mathbf{D} = \mathbf{P}\mathbf{L}\mathbf{P}^{-1},$$

with

$$\mathbf{L} = \begin{pmatrix} \lambda_1 & \cdots & \cdots \\ \vdots & \ddots & \cdots \\ \vdots & \vdots & \lambda_{n-1} \end{pmatrix}$$

the diagonal matrix of **eigenvalues** λ_i, and $\mathbf{P} = (\mathbf{v}_1, \dots, \mathbf{v}_{n-1})$ is the block matrix of the **eigenvectors** $\mathbf{v}_i : \mathbf{L}\mathbf{v}_i = \lambda_i \mathbf{v}_i$

With $\tilde{\mathbf{C}} = \mathbf{P}^{-1}\mathbf{C}$ and $\tilde{\Delta \mathbf{C}} = \mathbf{P}^{-1}\Delta\mathbf{C}$,

$$\frac{\partial \tilde{\mathbf{C}}}{\partial t} = \mathbf{L}\nabla^2 \tilde{\mathbf{C}}$$

$$\tilde{C}_i(x,t) = \tilde{\Delta C_i} \operatorname{erf}\left(\frac{x}{\sqrt{2\lambda_i t}}\right).$$

Diffusion matrix formalism

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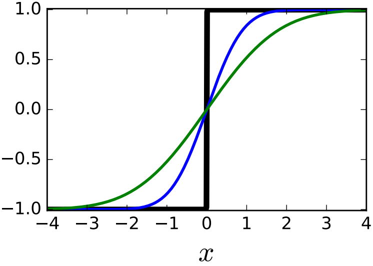
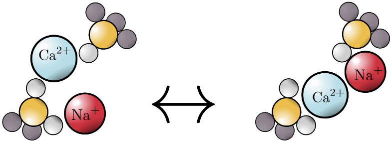


Diffusion eigenvectors at 1200° C

Dominant eigenvector, $\lambda_1 \simeq 30.10^{-12}\mathrm{m}^2.\mathrm{s}^{-1}$

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



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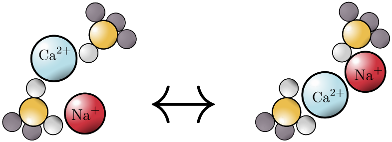
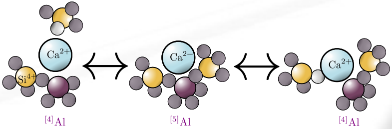


Second eigenvector (52x less frequent)

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



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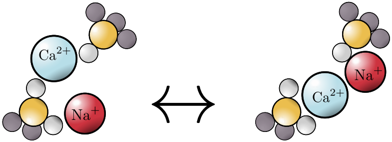

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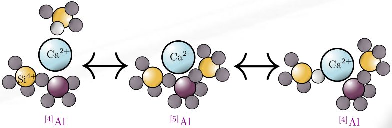
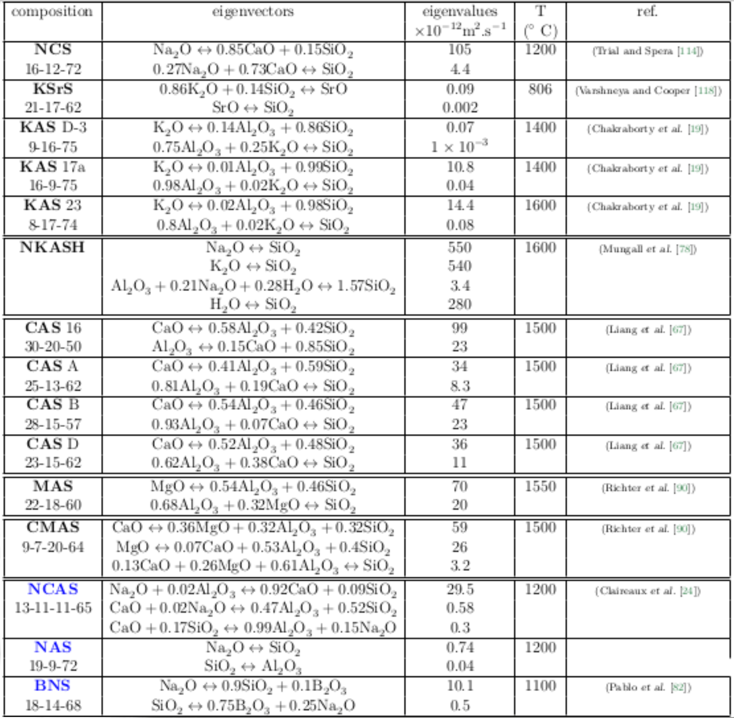
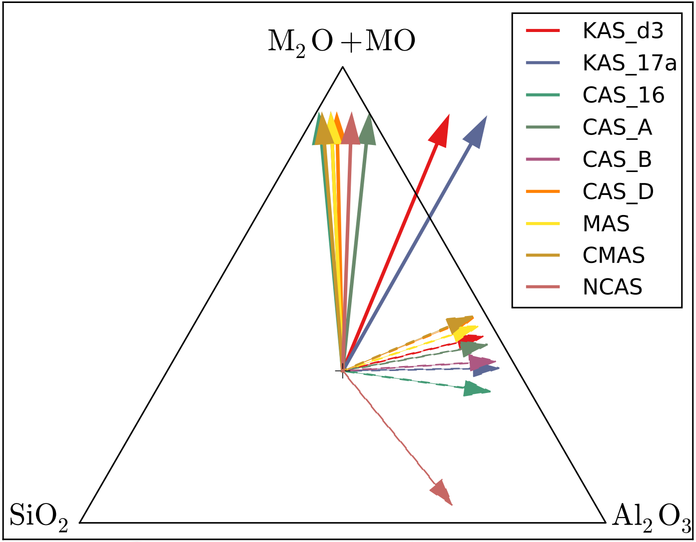


Third eigenvector (155x less frequent)

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

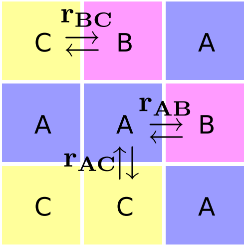


composition	eigenvectors	eigenvalues $\times 10^{-12} m^2.s^{-1}$	T (° C)	ref.
NCS	$Na_2O \leftrightarrow 0.85CaO + 0.15SiO_2$	105	1200	(Trial and Spera [114])
16-12-72	$0.27Na_2O + 0.73CaO \leftrightarrow SiO_2$	4.4		
KSrS	$0.86K_2O + 0.14SiO_2 \leftrightarrow SrO$	0.09	806	(Varshneya and Cooper [118])
21-17-62	$SrO \leftrightarrow SiO_2$	0.002		
KAS D-3	$K_2O \leftrightarrow 0.14Al_2O_3 + 0.86SiO_2$	0.07	1400	(Chakraborty *et al.* [19])
9-16-75	$0.75Al_2O_3 + 0.25K_2O \leftrightarrow SiO_2$	1×10^{-3}		
KAS 17a	$K_2O \leftrightarrow 0.01Al_2O_3 + 0.99SiO_2$	10.8	1400	(Chakraborty *et al.* [19])
16-9-75	$0.98Al_2O_3 + 0.02K_2O \leftrightarrow SiO_2$	0.04		
KAS 23	$K_2O \leftrightarrow 0.02Al_2O_3 + 0.98SiO_2$	14.4	1600	(Chakraborty *et al.* [19])
8-17-74	$0.8Al_2O_3 + 0.02K_2O \leftrightarrow SiO_2$	0.08		
NKASH	$Na_2O \leftrightarrow SiO_2$	550	1600	(Mungall *et al.* [78])
	$K_2O \leftrightarrow SiO_2$	540		
	$Al_2O_3 + 0.21Na_2O + 0.28H_2O \leftrightarrow 1.57SiO_2$	3.4		
	$H_2O \leftrightarrow SiO_2$	280		
CAS 16	$CaO \leftrightarrow 0.58Al_2O_3 + 0.42SiO_2$	99	1500	(Liang *et al.* [67])
30-20-50	$Al_2O_3 \leftrightarrow 0.15CaO + 0.85SiO_2$	23		
CAS A	$CaO \leftrightarrow 0.41Al_2O_3 + 0.59SiO_2$	34	1500	(Liang *et al.* [67])
25-13-62	$0.81Al_2O_3 + 0.19CaO \leftrightarrow SiO_2$	8.3		
CAS B	$CaO \leftrightarrow 0.54Al_2O_3 + 0.46SiO_2$	47	1500	(Liang *et al.* [67])
28-15-57	$0.93Al_2O_3 + 0.07CaO \leftrightarrow SiO_2$	23		
CAS D	$CaO \leftrightarrow 0.52Al_2O_3 + 0.48SiO_2$	36	1500	(Liang *et al.* [67])
23-15-62	$0.62Al_2O_3 + 0.38CaO \leftrightarrow SiO_2$	11		
MAS	$MgO \leftrightarrow 0.54Al_2O_3 + 0.46SiO_2$	70	1550	(Richter *et al.* [90])
22-18-60	$0.68Al_2O_3 + 0.32MgO \leftrightarrow SiO_2$	20		
CMAS	$CaO \leftrightarrow 0.36MgO + 0.32Al_2O_3 + 0.32SiO_2$	59	1500	(Richter *et al.* [90])
9-7-20-64	$MgO \leftrightarrow 0.07CaO + 0.53Al_2O_3 + 0.4SiO_2$	26		
	$0.13CaO + 0.26MgO + 0.61Al_2O_3 \leftrightarrow SiO_2$	3.2		
NCAS	$Na_2O + 0.02Al_2O_3 \leftrightarrow 0.92CaO + 0.09SiO_2$	29.5	1200	(Claireaux *et al.* [24])
13-11-11-65	$CaO + 0.02Na_2O \leftrightarrow 0.47Al_2O_3 + 0.52SiO_2$	0.58		
	$CaO + 0.17SiO_2 \leftrightarrow 0.99Al_2O_3 + 0.15Na_2O$	0.3		
NAS	$Na_2O \leftrightarrow SiO_2$	0.74	1200	
19-9-72	$SiO_2 \leftrightarrow Al_2O_3$	0.04		
BNS	$Na_2O \leftrightarrow 0.9SiO_2 + 0.1B_2O_3$	10.1	1100	(Pablo *et al.* [82])
18-14-68	$SiO_2 \leftrightarrow 0.75B_2O_3 + 0.25Na_2O$	0.5		


M_2O+MO
SiO_2
Al_2O_3
KAS_d3
KAS_17a
CAS_16
CAS_A
CAS_B
CAS_D
MAS
CMAS
NCAS

A toy model for multicomponent diffusion

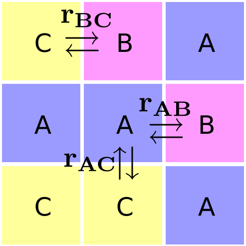
Random exchange of neighbors with fixed probability r_{AB}

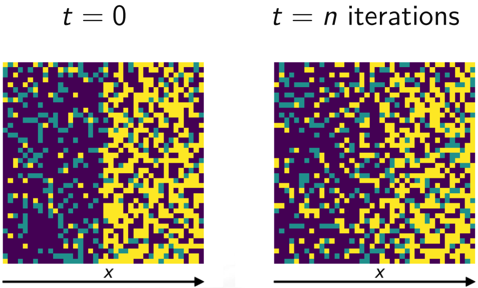


Coll. with B. Seoane

A toy model for multicomponent diffusion

Random exchange of neighbors with fixed probability r_{AB}

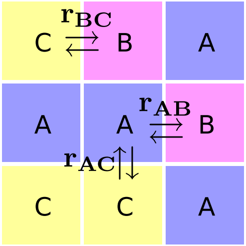


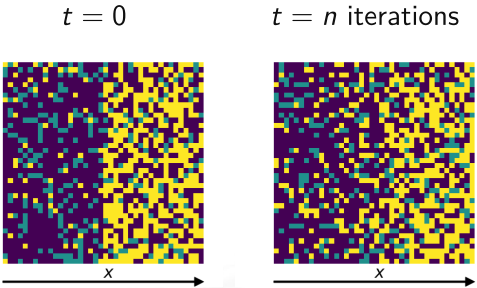


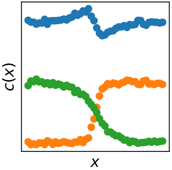
Coll. with B. Seoane

A toy model for multicomponent diffusion

Random exchange of neighbors with fixed probability r_{AB}



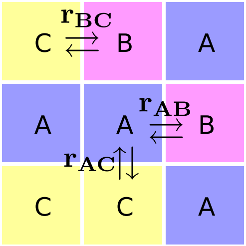


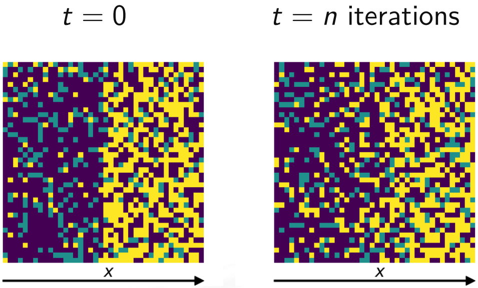


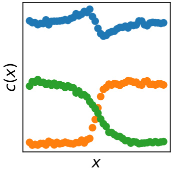
Coll. with B. Seoane

A toy model for multicomponent diffusion

Random exchange of neighbors with fixed probability r_{AB}







Compute diffusion matrix from exchange rates r_{ij}

$$\mathbf{D} = \frac{1}{3}\begin{pmatrix} (1-c_2)r_{13} + c_2 r_{12} & c_1(r_{13} - r_{12}) \\ c_2(r_{23} - r_{12}) & (1-c_1)r_{23} + c_1 r_{12} \end{pmatrix}$$

Coll. with B. Seoane

A different view on microscopic dynamics

composition	eigenvectors	eigenvalues $\times 10^{-12} \mathrm{m}^2.\mathrm{s}^{-1}$	T (° C)
NCS 16-12-72	$Na_2O \leftrightarrow 0.85CaO + 0.15SiO_2$ $0.27Na_2O + 0.73CaO \leftrightarrow SiO_2$	105 4.4	1200
NCAS 13-11-11-65	$Na_2O + 0.02Al_2O_3 \leftrightarrow 0.92CaO + 0.09SiO_2$ $CaO + 0.02Na_2O \leftrightarrow 0.47Al_2O_3 + 0.52SiO_2$ $CaO + 0.17SiO_2 \leftrightarrow 0.99Al_2O_3 + 0.15Na_2O$	29.5 0.58 0.3	1200
BNS 18-14-68	$Na_2O \leftrightarrow 0.9SiO_2 + 0.1B_2O_3$ $SiO_2 \leftrightarrow 0.75B_2O_3 + 0.25Na_2O$	10.1 0.5	1100

A different view on microscopic dynamics

composition	eigenvectors	eigenvalues $\times 10^{-12} \mathrm{m}^2.\mathrm{s}^{-1}$	T (° C)
NCS	$\mathrm{Na_2O} \leftrightarrow 0.85\mathrm{CaO} + 0.15\mathrm{SiO_2}$	105	1200
16-12-72	$0.27\mathrm{Na_2O} + 0.73\mathrm{CaO} \leftrightarrow \mathrm{SiO_2}$	4.4	
NCAS	$\mathrm{Na_2O} + 0.02\mathrm{Al_2O_3} \leftrightarrow 0.92\mathrm{CaO} + 0.09\mathrm{SiO_2}$	29.5	1200
13-11-11-65	$\mathrm{CaO} + 0.02\mathrm{Na_2O} \leftrightarrow 0.47\mathrm{Al_2O_3} + 0.52\mathrm{SiO_2}$	0.58	
	$\mathrm{CaO} + 0.17\mathrm{SiO_2} \leftrightarrow 0.99\mathrm{Al_2O_3} + 0.15\mathrm{Na_2O}$	0.3	
BNS	$\mathrm{Na_2O} \leftrightarrow 0.9\mathrm{SiO_2} + 0.1\mathrm{B_2O_3}$	10.1	1100
18-14-68	$\mathrm{SiO_2} \leftrightarrow 0.75\mathrm{B_2O_3} + 0.25\mathrm{Na_2O}$	0.5	

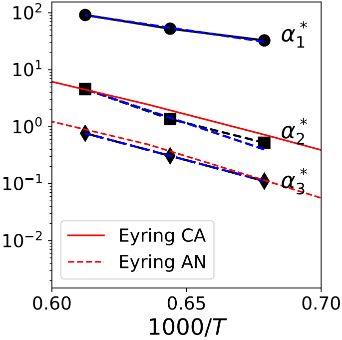
composition	exchange rates		
NCS	$r_{NC} = 3.2$	$r_{NS} = 1.3$	$r_{CS} = 0$
NCAS	$r_{NC} = 1$	$r_{NA} = 0.4$	$r_{NS} = 0.4$
	$r_{CA} = 0$	$r_{CS} = 0$	$r_{AS} = 0$
BNS	$r_{BN} = 0.2$	$r_{BS} = 0$	$r_{NS} = 0.2$

Stoechiometry of diffusion eigenvectors related to

- binary exchange rates
- ... but also oxide concentrations

Energetics of diffusion matrices

NCAS melts, temperature dependence of eigenvalues

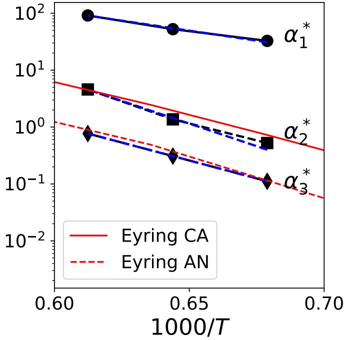


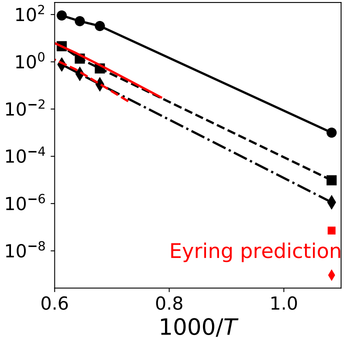
High-temperature :

- Arrhenian behavior
- Eyring relation OK

Energetics of diffusion matrices

NCAS melts, temperature dependence of eigenvalues





High-temperature :

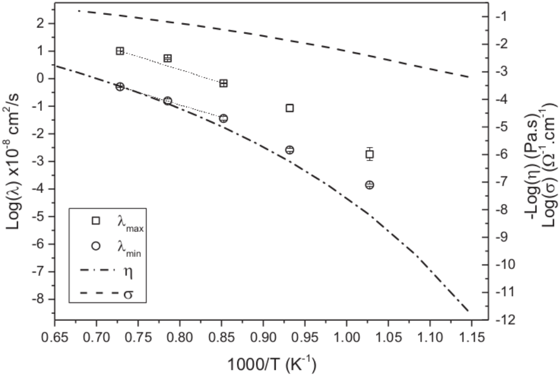
- Arrhenian behavior
- Eyring relation OK

Close to T_g

- Still Arrhenian
- Breakdown of Eyring relation

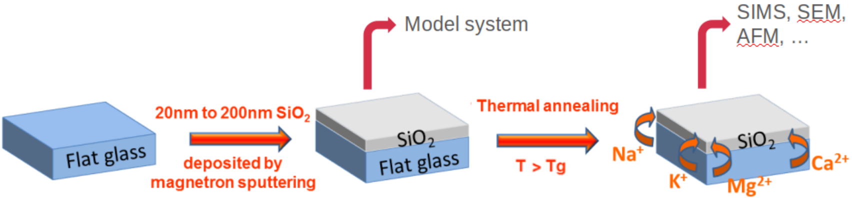
Energetics of diffusion matrices

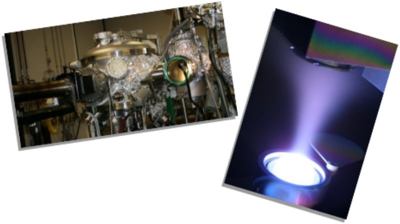
Same behavior observed in sodium borosilicate composition [Pablo et al., 2017]



Arrhenian + breakdown of Eyring relation close to T_g

Annealing of PVD-sputtered silica layers on soda-lime substrate (Planiclear)



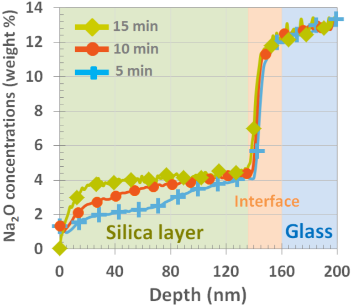


Pure and Al-doped silica thin films

Uptake of alkali ions in silica layers

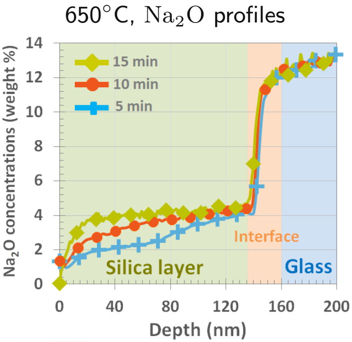
Exchange between protons and alkali ions

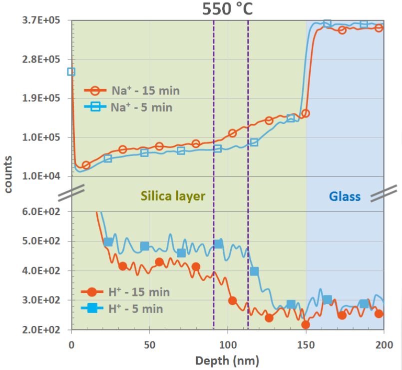
650°C, $\mathrm{Na_2O}$ profiles



Uptake of alkali ions in silica layers

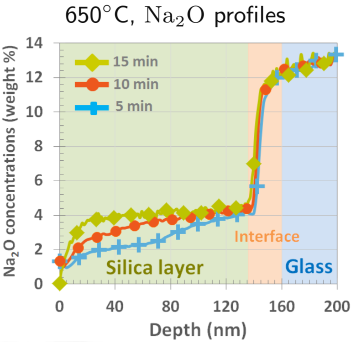
Exchange between protons and alkali ions

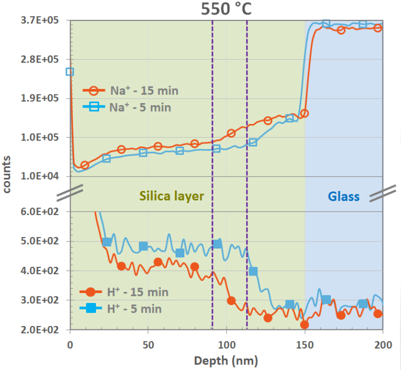




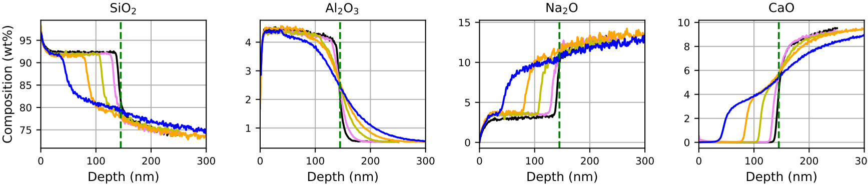
Uptake of alkali ions in silica layers

Exchange between protons and alkali ions


650°C, Na_2O profiles

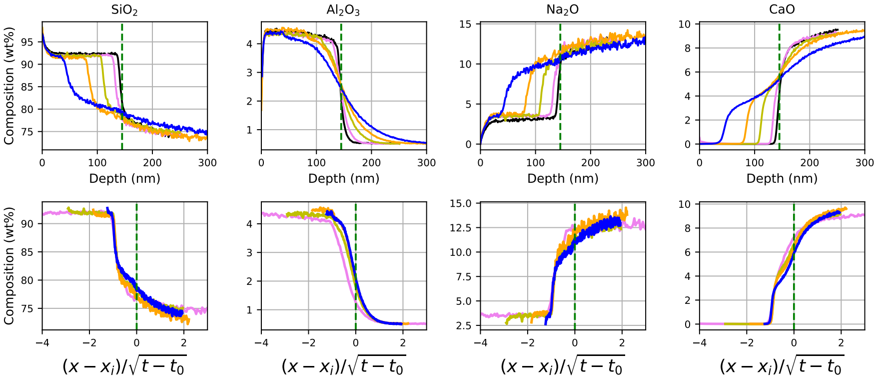

550 °C

Diffusive dissolution of thin film and multicomponent effects



Fonné et al., JACS 2017, JACS2018

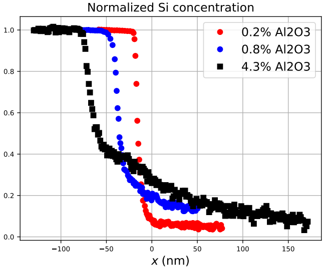
Diffusive dissolution of thin film and multicomponent effects



- Diffusion distance of Al smaller than for Si
- Na coupled to Si, Ca to both Si and Al.
- Can we use the bulk diffusion matrix to explain these results ?

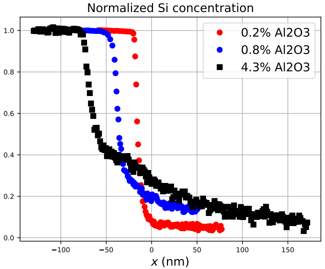
Fonné et al., JACS 2017, JACS2018

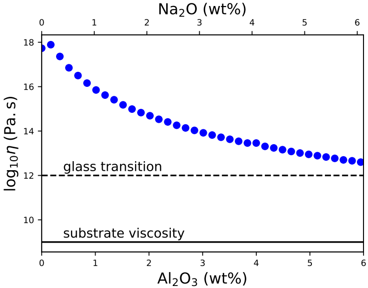
Fitting asymmetric diffusion profiles



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

Fitting asymmetric diffusion profiles





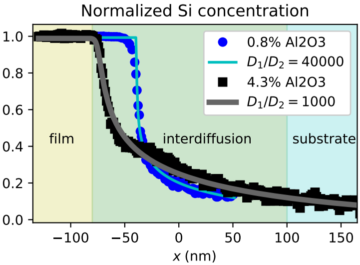
High Si diffusivity (& viscosity) ratio between substrate and film

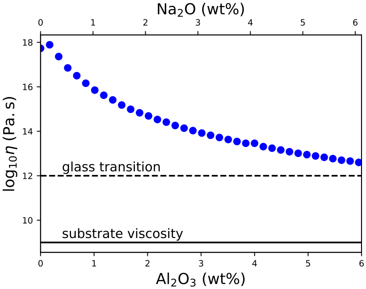
Using Crank's model to fit profiles :

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

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

Fitting asymmetric diffusion profiles


Normalized Si concentration

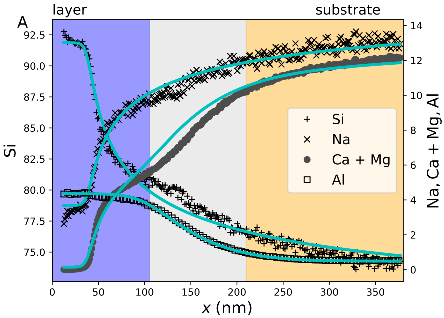


High Si diffusivity (& viscosity) ratio between substrate and film
Using Crank's model to fit profiles :

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

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

Multicomponent diffusion consistent between bulk and thin films

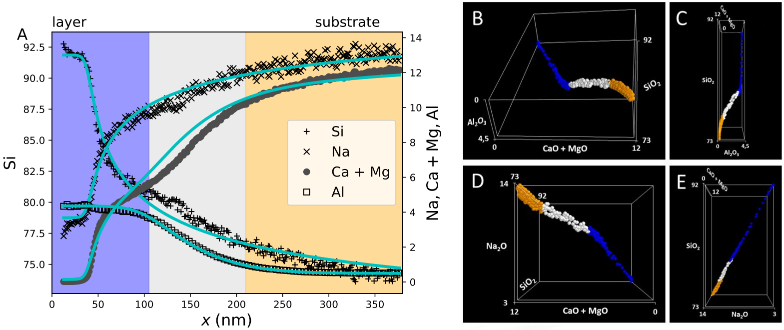


$$\frac{1}{2}\mathrm{Na_2O} + \frac{1}{2}\mathrm{CaO} \leftrightarrow \mathrm{SiO_2}.$$

$$\mathrm{CaO} \leftrightarrow \mathrm{Al_2O_3}$$

Fonné et al., JACS 2017, JACS2018

Multicomponent diffusion consistent between bulk and thin films

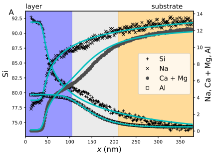


$$\frac{1}{2}\mathrm{Na_2O} + \frac{1}{2}\mathrm{CaO} \leftrightarrow \mathrm{SiO_2}.$$

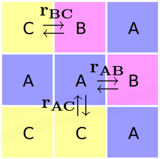
$$\mathrm{CaO} \leftrightarrow \mathrm{Al_2O_3}$$

Fonné et al., JACS 2017, JACS2018

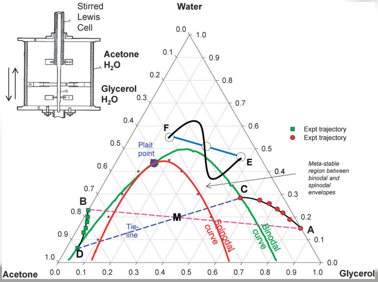
Conclusions



- Diffusion matrices : a powerful tool to predict diffusive exchanges (useful outside of geochemistry !)



- Diffusion matrix coefficients are related to concentration and local mobility (exchange rates).
  Link with structure ?

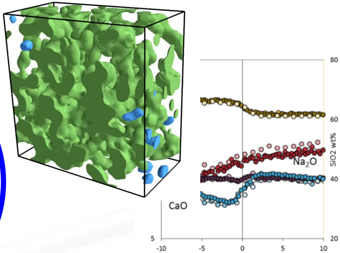


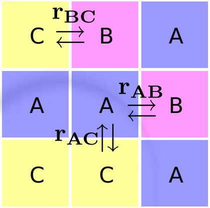
- **Link with phase separation, crystallization, oxidation-reduction, ... ?**

Conclusions

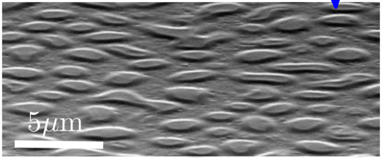
Industrial systems & questions

Controlled experiments





Physics models



Materials properties and design

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Conclusions

- Diffusion matrices : a powerful tool (useful outside of geochemistry !)
- Multicomponent effects modeled on bulk and thin films
- Contrast of transport properties have to be modeled
- Exchanges with atmosphere cannot be neglected for thin films, role of water and Al content