Diffusion and phase separation in silicate melts – physics problems inspired by glass industry

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Basic research inspired by Saint-Gobain’s products and processes
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Viscous liquids quenched into amorphous solids
Glass transition and viscosity

Avoiding rearrangements:
fast quenching rates or
low mobilities

Silicate glasses are strong network-forming glasses: good glass-forming ability
**Downside**: low mobility, high viscosity
**Origin**: polymerization of (alumino)-silicate network
Glass transition and viscosity

Avoiding rearrangements: fast quenching rates or low mobilities

Silicate glasses are strong network-forming glasses: good glass-forming ability

**Downside**: low mobility, high viscosity

**Origin**: polymerization of (alumino)-silicate network
1. Diffusion couplings in silicate melts

2. Morphology of phase separation
Outline

1 Diffusion couplings in silicate melts

2 Morphology of phase separation
How to predict diffusive exchanges in heterogeneous systems?
How to predict diffusive exchanges in heterogeneous systems?
Interdiffusion effects: uphill diffusion

[Liang et al., 1996]
Interdiffusion effects: uphill diffusion

[Liag et al., 1996]

**uphill diffusion**

<table>
<thead>
<tr>
<th>Diff Couple</th>
<th>$D(\text{SiO}_2)$ ($\mu$m$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si–Ti</td>
<td>19.5 ± 2.8</td>
</tr>
<tr>
<td>Si–Al</td>
<td>15.7 ± 1.5</td>
</tr>
<tr>
<td>Si–Mg</td>
<td>30.0 ± 1.7</td>
</tr>
<tr>
<td>Si–Ca</td>
<td>28.7 ± 2.8</td>
</tr>
<tr>
<td>Si–Na</td>
<td>44.2 ± 4.0</td>
</tr>
<tr>
<td>Si–K</td>
<td>102.9 ± 19.5</td>
</tr>
<tr>
<td>Ti–Mg</td>
<td></td>
</tr>
<tr>
<td>Mg–Ca</td>
<td></td>
</tr>
<tr>
<td>Ca–Na</td>
<td></td>
</tr>
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<td>An diss</td>
<td></td>
</tr>
</tbody>
</table>

[Guo and Zhang, 2016]

Diffusion coefficient depends on counter-diffusing species
Diffusion and reorganizations of silicate network

https://www.youtube.com/watch?v=SQUIMspT4jw

A. Tilocca
Fick’s law

\[ j = -D \nabla C \]

\[ \frac{\partial C}{\partial t} = D \Delta C \]
Diffusion matrix formalism

Fick’s law

\[ j = -D \nabla C \]
\[ \frac{\partial C}{\partial t} = D \Delta C \]

Diffusion matrix

\[ j_i(x) = -\sum_k D_{ik} \nabla C_k(x) \]

\[ \frac{\partial}{\partial t} \begin{pmatrix} C_{Na} \\ C_{Ca} \\ C_{Al} \\ C_{Si} \end{pmatrix} = \begin{pmatrix} D_{Na,Na} & D_{Na,Ca} & D_{Na,Al} & D_{Na,Si} \\ D_{Ca,Na} & D_{Ca,Ca} & D_{Ca,Al} & D_{Ca,Si} \\ D_{Al,Na} & D_{Al,Ca} & D_{Al,Al} & D_{Al,Si} \\ D_{Si,Na} & D_{Si,Ca} & D_{Si,Al} & D_{Si,Si} \end{pmatrix} \Delta \begin{pmatrix} C_{Na} \\ C_{Ca} \\ C_{Al} \\ C_{Si} \end{pmatrix} \]
**Diffusion matrix formalism**

**Fick’s law**

\[
\mathbf{j} = -D \nabla \mathbf{C}
\]

\[
\frac{\partial \mathbf{C}}{\partial t} = D \Delta \mathbf{C}
\]

**Diffusion matrix**

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

\[
\begin{pmatrix}
C_{Na} \\
C_{Ca} \\
C_{Al} \\
C_{Si}
\end{pmatrix}
= 
\begin{pmatrix}
D_{Na,Na} & D_{Na,Ca} & D_{Na,Al} & D_{Na,Si} \\
D_{Ca,Na} & D_{Ca,Ca} & D_{Ca,Al} & D_{Ca,Si} \\
D_{Al,Na} & D_{Al,Ca} & D_{Al,Al} & D_{Al,Si} \\
D_{Si,Na} & D_{Si,Ca} & D_{Si,Al} & D_{Si,Si}
\end{pmatrix}
\Delta
\begin{pmatrix}
C_{Na} \\
C_{Ca} \\
C_{Al} \\
C_{Si}
\end{pmatrix}
\]
Diffusion matrix formalism

Fick’s law

\[ \mathbf{j} = -D \nabla C \]
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Diffusion matrix

\[ \frac{\partial}{\partial t} \begin{pmatrix} C_{\text{Na}} \\ C_{\text{Ca}} \\ C_{\text{Al}} \\ C_{\text{Si}} \end{pmatrix} = \begin{pmatrix} D_{\text{Na},\text{Na}} & D_{\text{Na},\text{Ca}} & D_{\text{Na},\text{Al}} & D_{\text{Na},\text{Si}} \\ D_{\text{Ca},\text{Na}} & D_{\text{Ca},\text{Ca}} & D_{\text{Ca},\text{Al}} & D_{\text{Ca},\text{Si}} \\ D_{\text{Al},\text{Na}} & D_{\text{Al},\text{Ca}} & D_{\text{Al},\text{Al}} & D_{\text{Al},\text{Si}} \\ D_{\text{Si},\text{Na}} & D_{\text{Si},\text{Ca}} & D_{\text{Si},\text{Al}} & D_{\text{Si},\text{Si}} \end{pmatrix} \Delta \begin{pmatrix} C_{\text{Na}} \\ C_{\text{Ca}} \\ C_{\text{Al}} \\ C_{\text{Si}} \end{pmatrix} \]

Measured in several ternary systems, mostly in geosciences [Liang et al., 1996], [Richter et al., 1998]: CaO/MgO – Al₂O₃ – SiO₂

Also used in multicomponent metallic alloys
Questions

What are the diffusion matrices in systems of industrial interest?

- $\text{Na}_2\text{O} – \text{CaO} – \text{SiO}_2$ (NCS, W. Woelffel)
- $\text{Na}_2\text{O} – \text{Al}_2\text{O}_3 – \text{SiO}_2$ (NAS, V. Pukhkaya)
- $\text{Na}_2\text{O} – \text{CaO} – \text{Al}_2\text{O}_3 – \text{SiO}_2$ (NCAS, C. Claireaux)
- $\text{Na}_2\text{O} – \text{CaO} – \text{Al}_2\text{O}_3 – \text{SiO}_2 – \text{ZrO}_2$ (NCASZ, M. Ficheux)
- $\text{Na}_2\text{O} – \text{B}_2\text{O}_3 – \text{SiO}_2$ (NBS, H. Pablo)
Questions

What are the diffusion matrices in systems of industrial interest?

- $\text{Na}_2\text{O} - \text{CaO} - \text{SiO}_2$ (NCS, W. Woelffel)
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- $\text{Na}_2\text{O} - \text{CaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{ZrO}_2$ (NCASZ, M. Ficheux)
- $\text{Na}_2\text{O} - \text{B}_2\text{O}_3 - \text{SiO}_2$ (NBS, H. Pablo)

Large number of experiments

How do diffusion matrices depend on composition & temperature? Can we predict them?
NCAS system at 1200°C

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

Python package to fit and simulate diffusion profiles: \texttt{multidiff}
Diffusion eigenvectors at $1200^\circ$ C

Dominant eigenvector

\[ \frac{1}{2} \text{Ca}^{2+} \leftrightarrow \text{Na}^+ \]
Diffusion eigenvectors at 1200° C

**Dominant eigenvector**

\[ \frac{1}{2} \text{Ca}^{2+} \leftrightarrow \text{Na}^+ \]

**Second eigenvector (52x less frequent)**

\[ \text{Ca}^{2+} \leftrightarrow 0.5\text{Al}^{3+} + 0.5\text{Si}^{4+} \]
Diffusion eigenvectors at 1200° C

**Dominant eigenvector**

\[
\frac{1}{2} \text{Ca}^{2+} \leftrightarrow \text{Na}^+
\]

**Second eigenvector** (52x less frequent)

\[
\text{Ca}^{2+} \leftrightarrow 0.5\text{Al}^{3+} + 0.5\text{Si}^{4+}
\]

**Third eigenvector** (155x less frequent)

\[
\text{Al}^{3+} \leftrightarrow 0.5\text{Ca}^{2+} + 0.5\text{Si}^{4+}
\]
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 $r_{AB}$

t = 0
t = n iterations

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Random exchange of neighbors with fixed probability $r_{AB}$

$t = 0$

$t = n$ iterations

Coll. with B. Seoane
A toy model for multicomponent diffusion

Random exchange of neighbors with fixed probability $r_{AB}$

$D = \frac{1}{3} \begin{pmatrix} (1 - c_2)r_{13} + c_2r_{12} & c_1(r_{13} - r_{12}) \\ c_2(r_{23} - r_{12}) & (1 - c_1)r_{23} + c_1r_{12} \end{pmatrix}$

Coll. with B. Seoane
A toy model for multicomponent diffusion

Random exchange of neighbors with fixed probability $r_{AB}$

$t = 0$  
$t = n$ iterations

Analytical form of diffusion matrix from rates $r_{ij}$

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

<table>
<thead>
<tr>
<th>composition</th>
<th>exchange rates</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCS</td>
<td>$r_{NC} = 3.2$, $r_{NS} = 1.3$, $r_{CS} = 0$</td>
</tr>
<tr>
<td>NCAS</td>
<td>$r_{NC} = 1$, $r_{NA} = 0.4$, $r_{NS} = 0.4$; $r_{CA} = 0$, $r_{CS} = 0$, $r_{AS} = 0$</td>
</tr>
<tr>
<td>BNS</td>
<td>$r_{BN} = 0.2$, $r_{BS} = 0$, $r_{NS} = 0.2$</td>
</tr>
</tbody>
</table>

← experiments

Coll. with B. Seoane
Annealing of PVD-sputtered silica layers on soda-lime substrate (Planiclear)

Flat glass → 20nm to 200nm SiO₂ deposited by magnetron sputtering → Pure and Al-doped silica thin films
Diffusive dissolution of thin film and multicomponent effects

Al-doped SiO$_2$ thin film on glass, different annealing times at 650° C

SIMS profiles

PhD JT Fonné; Fonné et al., JACS 2017, JACS2018
**Diffusive dissolution of thin film and multicomponent effects**

**Al-doped SiO$_2$ thin film on glass, different annealing times at 650° C**

**SIMS profiles**

- **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?**

PhD JT Fonné; Fonné et al., JACS 2017, JACS2018
Fitting asymmetric diffusion profiles

Normalized Si concentration

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:

\[ D_{Si} = D_0 \exp(-\beta C_{Si}) \]

Fitted values of \( \beta \) consistent with Eyring’s law and viscosity model.
High Si diffusivity (& viscosity) ratio between substrate and film
Using Crank’s model to fit profiles:

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

Fitted values of $\beta$ consistent with Eyring’s law and viscosity model
Use bulk eigenvectors to fit profiles
1. Diffusion couplings in silicate melts

2. Morphology of phase separation
Principles of phase separation

- Stable
- Unstable
- Nucleation & growth
- Spinodal decomposition
Principles of phase separation

Microstructure coarsening: decrease interfacial energy
Porous membranes: Vycor

Suzuki et al. 2008

Super-hydrophobic porous films

Aytug et al. 2013

Dargaud et al. 2012

Model materials for crack propagation

Dalmas et al. 2008

Nuclear waste glasses

Dargaud et al. 2012

Aytug et al. 2013

Glass ceramics

Martineau et al. 2010

Glass ceramics

Microstructure of basaltic magmas

Veksler et al. 2007

Luminescent glass

Chenu et al. 2014
Cahn-Hilliard equation

https://www.youtube.com/watch?v=sysya3Lo78Y

Fabio Garofalo
A classical topic of statistical physics

Cahn-Hilliard equation
https://www.youtube.com/watch?v=sysya3Lo78Y
Fabio Garofalo

Dynamic scaling

Is it the same microstructure?
Coarsening mechanisms

- diffusion

\[ \ell(t) \sim \left( \frac{\gamma D \Omega}{kT} t \right)^{\frac{1}{3}} \]

Regime observed in borosilicates

Laplace pressure: \[ \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \]

\[ \ell(t) \sim \frac{\gamma}{\eta} t \]

Dalmas et al. 2007

Wheaton et al. 2007
The system: barium borosilicates

Liquid-liquid phase separation
Different compositions separating into the same phases: different volume fractions.
The system: barium borosilicates

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Liquid-liquid phase separation
Different compositions separating into the same phases:
different volume fractions.

[Bouttes et al., 2015], Acta Mat. 92
In-situ tomography on ID19 beamline, ESRF
Acquisition parameters

Furnace: 600 – 1400° (isothermal)
Time resolution: 5-20 s for 3-D image
Spatial resolution: 1 µm
1 image: 1000x1000x500 pixels
In-situ tomography on ID19 beamline, ESRF

**Acquisition parameters**

Furnace: 600 – 1400° (isothermal)
Time resolution: 5-20 s for 3-D image
Spatial resolution: 1 µm
1 image: 1000x1000x500 pixels
Coarsening: $\phi \leq 0.5$ case, $1200^\circ C$

box size: $400 \ \mu m$, barium-rich phase represented
Only the less viscous phase breaks up

Barium-rich phase (less viscous) : liquid bridge breaks up

34 min  36 min  37 min  39 min

40 μm
Only the less viscous phase breaks up

Barium-rich phase (less viscous) : liquid bridge breaks up

Silica-rich phase (more viscous) : loop is filled in

Break-up : strong shear preferentially in more fluid phase

\[ \frac{\eta_{\text{viscous}}}{\eta_{\text{fluid}}} > 10^4 \]
Evolution of characteristic length

\[ \ell = \frac{\nu}{S} \]

- Linear evolution with time
- Coarsening rate increases with temperature
Coarsening rate vs. temperature

\[ \dot{l}(t) \approx \frac{\gamma}{\eta_v} \]

[Bouttes et al., 2015], Acta Mat. 92
Dynamic scaling: self-similarity of microstructure

Curvatures

\[ H = \frac{\kappa_1 + \kappa_2}{2} \]

\[ K = \kappa_1 \kappa_2 \]
Dynamic scaling: self-similarity of microstructure

Curvatures

\[ H = \frac{\kappa_1 + \kappa_2}{2} \]

\[ K = \kappa_1 \kappa_2 \]

[Bouttes et al., 2014], PRL 112
Towards local statistics of break-ups
Coarsening and fragmentation, 1200° C
Break-up and fragmentation
Break-up and fragmentation

Only the barium-rich phase breaks up in domains
A broad distribution of domain sizes

Histogram of domain sizes

\[ n_V \propto l^{-5/3} \]

Different fragmentation times ⇒ different domain sizes

[Bouttes et al., 2014] PRL, [Bouttes et al., 2016] PRL
A broad distribution of domain sizes

Histogram of domain sizes

![Histogram of domain sizes](image)

\[ n_V \propto \ell^{-5/3} \]

Viscous phase: long thin bridges

Fluid phase: rounded ends

Different fragmentation times \( \Rightarrow \) different domain sizes

[Bouttes et al., 2014] PRL, [Bouttes et al., 2016] PRL
Coupling between diffusion and hydrodynamic transport

Nanotomography, C. Brillatz, FOV 100 µm
Coupling between diffusion and hydrodynamic transport

Nanotomography, C. Brillatz, FOV 100 µm
Perspectives: towards smaller scales

Coupling between diffusion and hydrodynamic transport

Nanotomography, C. Brillat, FOV 100 µm
Perspectives: towards smaller scales

Coupling between diffusion and hydrodynamic transport

Nanotomography, C. Brillatz, FOV 100 \( \mu \text{m} \)

Phase separation in silicate thin films

- Droplet size depends on film thickness
- Interaction with substrate

PhD JT Fonné, B Bouteille
Morphology evolution: beyond the simplistic picture

Importance of **hydrodynamic** effects and **viscosity contrast**

In situ and 3-D imaging needed
Conclusions

- Industrial systems & questions
  - Controlled experiments, tools development
  - Microscopic understanding
  - Materials properties and design

Materials properties and design

Microscopic understanding
Bibliography I

Fragmentation and limits to dynamical scaling in viscous coarsening: An interrupted in situ x-ray tomographic study.

Topological symmetry breaking in viscous coarsening.

Hydrodynamic coarsening in phase-separated silicate melts.

Multicomponent diffusion in ternary silicate melts in the system $K_2O-Al_2O_3-SiO_2$: I. experimental measurements.

Multicomponent diffusion in ternary silicate melts in the system $K_2O-Al_2O_3-SiO_2$: II. mechanisms, systematics, and geological applications.

Atomic mobility in calcium and sodium aluminosilicate melts at 1200 c.

Multicomponent diffusion in silicate melts: $SiO_2$–$TiO_2$–$Al_2O_3$–$MgO$–$CaO$–$Na_2O$–$K_2O$ system.
Diffusion of Na, K, Rb and Cs in glasses of albite and orthoclase composition.

Diffusion in silicate melts: I. self diffusion in CaO − Al$_2$O$_3$ − SiO$_2$ at 1500° C and 1 GPa.

In situ and real-time 3-d microtomography investigation of dendritic solidification in an al–10wt.% cu alloy.

Quantitative x-ray tomography.

Isotope fractionation by diffusion in molten oxides.

Multicomponent diffusion and convection in molten MgO − Al$_2$O$_3$ − SiO$_2$.

Measuring the multicomponent diffusion matrix: Experimental design and data analysis for silicate melts.
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
Different configurations for diffusion

**Isotopic diffusion**: marked tracer

\[ t = 0 \]

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

**Chemical diffusion**: gradient of chemical concentration

\[ t = 0 \]

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