Silicate Melts & Glasses: Chemical Diffusion, Nucleation & Crystallization, Interrelated

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Phenomena of Interest—and Questions

• Stability of transition-metal cation-bearing glasses or melts as a function of cation valence and the consequent relationship between melt structure and liquidus phase.

• Kinetic mechanisms of oxidation and reduction in these systems.

• Texture or ”Reaction Morphology”—the spatial distribution of elements and phases that result from a reaction—as evidence of the mechanism(s) dominating the reaction.

  → Interrelated: cf. Wagner/Schmalzried Theory of Oxidation

• Discerning the role(s) kinetic mechanisms play in in establishing a “persistent” metastability.
Thermodynamics of Nucleation: $|\Delta_{\text{rxn}} G| > 0$

The general model of nucleation is well studied and well understood: with a driving potential $|\Delta_{\text{rxn}} G| > 0$ and sufficient thermal energy, transformations will occur at rates that can be predicted.

**But does the magnitude of $\Delta_{\text{rxn}} G$ have an effect?**

General expectation for silicate glass-ceramics: liquidus phase forms

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Fahrenheit (1724)
Volmer & Weber (1926)
Turnbull (1952)
Big $\Delta_{\text{rxn}}G$? Many, Many Possibilities! Kinetic Path is Key

With a very small $\Delta_{\text{rxn}}G$, one reaction is possible: the equilibrium one shown on the phase diagram.

With a large $\Delta_{\text{rxn}}G$, many reactions are possible (shown for $X_{\text{Sn}}^{\text{eu}}$ liquid): kinetics often dictates what is seen, not (necessarily) equilibrium thermodynamics.
Eg.: Large Undercooling in MgO-SiO$_2$: Forsterite Glass-Ceramics

Hypoeutectic melt composition experiences both metastable liquid-phase immiscibility and nucleation of metastable Mg$_2$SiO$_4$
Thermodynamic Landscape and Prigogine’s Bifurcations

Small perturbations from equilibrium can be easily understood and analyzed: the system is constrained to the “thermodynamic branch.” But what of large perturbations?

Figure 30 Bifurcation diagram showing how a state variable $X$ is affected when the control parameter $\lambda$ varies. A unique solution $(a)$, the thermodynamic branch, loses its stability at $\lambda_c$. At this value of the control parameter new branches of solutions $(b_1, b_2)$, which are stable in the example shown, are generated.

Figure 31 Mechanical illustration of the phenomenon of bifurcation.

Thermodynamic (landscape) branch for an ideal gas—PV = RT
Thermodynamic Landscape and Prigogine’s Bifurcations

The old future’s gone… —John Gorka

Pushing the system beyond a certain state opens up a variety of possibilities—branches of metastability.

1. The branch that is accessed is a function of kinetics.
2. Branches can produce order, with potential persistence.

The old future’s gone… —John Gorka
Cation Roles: Network Former or Network Modifier

Structural Role of Iron Cations in Aluminosilicate Melts/Glasses

Fe$^{2+}$ -- network modifier

Fe$^{3+}$ -- network modifier:
  \[ \text{Fe}^{3+}:\text{Fe}^{2+} < 1:2 \]
  -- mixed modifier/former:
  \[ 1:2 \leq \text{Fe}^{3+}:\text{Fe}^{2+} \leq 1:1 \]
  -- network former:
  \[ \text{Fe}^{3+}:\text{Fe}^{2+} > 1:1 \]

→ Alkali cations act more aggressively to stabilize Fe$^{3+}$ as a network former than do alkaline earth cations

Paul (1990)

\[ \text{CN IV} \Rightarrow \text{CN VI} \]

\[ \begin{align*}
\frac{r_{\text{Fe}^{2+}}}{r_{\text{O}^{2-}}} &= 0.53 \\
\frac{r_{\text{Fe}^{3+}}}{r_{\text{O}^{2-}}} &= 0.45 \\
\Rightarrow \text{CN} &= \text{VI} \\
\Rightarrow \text{CN} &= \text{IV} ?
\end{align*} \]
Oxidation State and Liquidus Surface

Roeder & Osborn, Am. J. Sci., 264 (1966): M-F-S @ 40 wt% CaAl$_2$Si$_2$O$_8$
Redox Dynamics in Silicate Melts: Chemical Diffusion of an Oxygen Species?

1 & 2: Dunn (1982)
3: Yinnon & Cooper (1980)
4: Muehlenbachs & Kushiro (1974)
7: Doremus (1960)
8-11: Dunn (1983)

Oxygen diffusion “remains one of the less well understood aspects of transport in silicate melts.”

--S. Chakraborty, RiMG 32 (1995)
“Modes” of Dynamic Oxidation†

Given the Fick-Einstein Relationship: \[ j_i = -\frac{c_i D_i \frac{d\eta_i}{d\xi}}{RT} = -\frac{c_i D_i}{RT} \left( \frac{d\mu_i}{d\xi} + z_i F \frac{d\phi}{d\xi} \right) \]

Fe\(^{2+}\)-bearing melt/glass

Relative Transport Coefficients dictate the kinetic response! E.g.:

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- I
  - (c\(_{O_2}D_{O_2}\)) largest
  - e.g.,
    - (c\(_{O_2^2-D_{O_2^-}}\)) \gg (c\(_{h\cdot D_{h\cdot}}\)) \gg (c\(_{O_2 D_{O_2}}\))
    - \(\rightarrow\) rate-limited by electronic conductivity

- II
  - (c\(_{h\cdot D_{h\cdot}}\)) \gg (c\(_{M^{2+}D_{M^{2+}}}\)) \gg
    - \([c\(_{O_2^2-D_{O_2^-}}\) or (c\(_{O_2 D_{O_2}}\)])
    - \(\rightarrow\) rate-limited by modifier-cation diffusion

- III
  - independent (parallel) kinetic responses: “different paths on the thermodynamic landscape”

†anhydrous conditions
Melt Oxidation: “Isothermal Undercooling”

Roeder & Osborn, Am. J. Sci., 264 (1966): M-F-S @ 40 wt% CaAl$_2$Si$_2$O$_8$
Experimental Approach: AeroAcoustic Levitation (AAL)

![Diagram of AAL setup]

**FIG. 1.** Schematic of the aero-acoustic levitator. A, levitated specimen; B, gas flow tube and heater; C, translation stage; D, flow control system; E, acoustic transducers (three axis); F, diode laser specimen illuminator (3 axis); G, specimen position detector (3 axis); H, video camera; J, vacuum chuck; K, laser beam heating.

Weber et al., RSI, 65 (1994)
Oxidation of Basalt Liquid
Columbia River Flood Basalt; Aero-Acoustic Levitation

- Oxidation in Ar(g) \((a_{O_2} \approx 10^{-6})\) mobilizes Fe\(^{2+}\), which diffuses to the free surface.
- Oxidation in air \((a_{O_2} = 0.21)\) mobilizes both Fe\(^{2+}\) and Ca\(^{2+}\).

\(\rightarrow\) data are **unequivocal proof that oxidation is accomplished & rate-limited by chemical diffusion of divalent network modifier cations!**
Basaltic Glass near $T_g$: Fe$^{3+}$ Stabilized as Network Former

- Surface: discontinuous ppts of lime & periclase (+minor nepheline)
- Na$^+$ from depth stabilizes Fe$^{3+}$ as network former: *no ferrite formation*!

Reactions:

at $\xi = 0$:

$$\frac{1}{2} O_2(g) + 4SiOFe_{0.5} + 2SiO(Ca_{\xi}Mg_{f})_{0.5} \rightarrow 6SiOFe_{0.33} + eCaO + fMgO$$

at $\xi = \xi^*$:

$$6SiOFe_{0.33} + xSiONa + 4SiO(Ca_{\xi}Mg_{b})_{0.5} \rightarrow (2 - x)NaFeO_2 + (2x - 2)SiONa$$

$$+ 3xSiOFe_{0.33} + (4 - 2x)SiOSi$$

$$+ 2SiO(Ca_{\xi}Mg_{d})_{0.5} + 2SiO(Ca_{\xi}Mg_{f})_{0.5}$$

where

$$3SiOFe_{0.33} = h^*; \quad 2SiO(Ca,Mg)_{0.5} = (Ca,Mg)^{2+}; \quad SiONa = Na^+;$$

$$2SiOFe_{0.5} = Fe^{2+}; \quad NaFeO_2 = \text{network-forming Fe}^{3+}$$
**Dynamic Reduction: The Mirror Image?**

**Mechanism:**
Oxygen ablates (chemically) from free surface; creates excess cations, which diffuse inwards and are charge-compensated by outward motion of $h^*$.

**Motivation:**
Thermokinetics responsible for distribution (concentric, periodic precipitation) of metal in primitive chondrules

Semarkona LL3.0; Bourot-Denise et al. (2001)
Experimental Approach

- Original material: bulk oxide glasses prepared conventionally (Fe-soaked Pt crucibles); initial $a_{O_2} \sim$ FMQ
- Reaction Vessel: vertical tube furnace; MoSi₂ resistance elements; alumina muffle
- 2–3mm cube sectioned; suspended in wire cage (Fe, Mo, Pt)
- Temperature range: 1350-1450°C ($>$ silicate melt liquidus; $<$ $T_{m,Fe}$)
- Dynamic gas mixing CO:CO₂ in range 240:1 (QIF–2) to 1750:1 (QIF–4); 200 cm³min⁻¹
- Active measurement of $a_{O_2}$ (YSZ sensor)
- Free-fall quench
Fe-MAS Reduction Results: Kinetics

$T = 1380^\circ C; \ p_{O_2} \approx 10^{-13} \ atm; \ t = 0.5 \ h$
Fe-MAS Reduction Results: Microstructures

**Free Surface**

- Secondary Electron Image
- \( T = 1380^\circ C; p_{O_2} \approx 10^{-13} \text{ atm}; t = 1.0 \text{ h} \)
- Pure bcc-Fe crystals: most demonstrating (111) with truncations being traces of \{100\}
- Vapor-phase transport important in coarsening

**Internal: \( \xi = \xi' \text{ to } \xi'' \)**

- \( T = 1380^\circ C; p_{O_2} \approx 10^{-13} \text{ atm}; t = 1.0 \text{ h} \)
- Zero-loss (scattering contrast) image: dark phase is Fe\(^0\); HEED: bcc-Fe
- Size distribution is relatively uniform
- “String-of-pearls” morphology consistent with Modified Random Network (MRN) model for unreacted melt.
Reduction Kinetics: Polymerization Model following Hess (1980)

→ **Diffusion-limited reaction**

→ **Rate matching that of tracer diffusion of small divalent network modifier**

**Reaction at Free Surface, \( \xi' \):**

\[
2\text{SiOMg}_{0.5} + 6\text{SiOFe}_{0.33} = \text{MgO} + 2\text{SiOSi} + 4\text{SiOFe}_{0.5} + \frac{1}{2}\text{O}_2(g)
\]

\[
= 2\text{SiOMg}_{0.5} + 4\text{SiOFe}_{0.5} + \text{SiOSi} + \frac{1}{2}\text{O}_2(g)
\]

*polymerization decreases: MC/O goes from 3/8 to 3/7*

**Reaction at Internal Reduction Front, \( \xi'' \):**

\[
2\text{SiOMg}_{0.5} + 6\text{SiOFe}_{0.5} = \text{Fe}^0 + 6\text{SiOFe}_{0.33} + 2\text{SiOMg}_{0.5}
\]

*polymerization increases: MC/O goes from 4/8 to 3/8*
Liquid Metal-Silicate Reactions: Spatial Control of Melt Structure

NCS Melt on Liquid Sn°

1100 ≥ T(°C) ≥ 600
1.5 ≤ t (min) ≤ 15

← Reaction Morphology
Experimental Apparatus and Specimen Assembly
Dynamic Reduction in the Float-Glass Reaction

Controlling the activity of Sn through use of an exothermic alloying with Au allows the dynamic to be manipulated, and allows, too, moving the temperature much higher.

Can creative co-design of silicate & metal melts allow creation of surface regions with unique properties?

Dynamic involves simultaneous reduction and solution-formation reactions: that these can occur at different rates allows "structural" gradients.
Approach: Glass-Ceramic-Forming Silicate Melt & Multiply Oxidizable Metal Alloy

Spinel Glass-Ceramic Compositions

<table>
<thead>
<tr>
<th></th>
<th>MA§</th>
<th>Zn-MA§</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>oxide</td>
<td></td>
</tr>
<tr>
<td></td>
<td>wt. %</td>
<td>mol. %</td>
</tr>
<tr>
<td>SiO₂</td>
<td>62.36</td>
<td>67.19</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>27.45</td>
<td>17.43</td>
</tr>
<tr>
<td>MgO</td>
<td>8.53</td>
<td>15.30</td>
</tr>
<tr>
<td>CaO</td>
<td>0.06</td>
<td>0.07</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.030</td>
<td>0.012</td>
</tr>
<tr>
<td>MnO</td>
<td>0.006</td>
<td>0.005</td>
</tr>
<tr>
<td>ZnO</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Na₂O</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>O²⁻</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
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| ΔºG₅SnO  > | ΔºG₅Cu₂O  |

Liquid Bronze Float Alloy: Cu-36at% Sn
Reduction and Mobilization of Ionic Si (1): Rapid Incorporation and “Release” of Cu$^{+,2+}$
Reduction and Mobilization of Ionic Si (2):  
*Including Redox Couples involving Sn^{2+,4+} & Zn^{+,2+}*  

Reduction/solution reaction clearly involves mobilization of ionic Si and Zn out of the silicate melt; transport coefficient consistent with Si^{2+}.

**Table: ZnMAS Composition (wt% and mol%)**

<table>
<thead>
<tr>
<th>Oxide</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>ZnO</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td>61.33</td>
<td>27.01</td>
<td>0.14</td>
<td>1.80</td>
<td>0.01</td>
<td>8.43</td>
<td>0.06</td>
<td>0.47</td>
</tr>
<tr>
<td>mol%</td>
<td>66.86</td>
<td>17.35</td>
<td>0.06</td>
<td>1.45</td>
<td>0.01</td>
<td>13.70</td>
<td>0.07</td>
<td>0.50</td>
</tr>
</tbody>
</table>
Reaction Dynamics: Zn-MAS on Cu-36at% Sn

Reaction dynamic couples \( \text{Sn}^{2+,4+} \) mobility with that of \( \text{Si}^{2+} \) and \( \text{Zn}^{+,2+} \); the latter results in Leisegang Bands at “depth.”

XES Map for Sn
1297°C; ½ h

500 μm
Summary/Conclusions

1. Dynamic oxidation or reduction of a transition-metal-cation-bearing ionic melt or glass does not *a priori* require the diffusive motion of an oxygen species: rapidly moving electronic species (polarons: h⁺ or e’) decouple the motions of cations from anions and other cations such that a variety of *kinetically parallel* responses are possible.

2. Kinetic parallel responses allow a reacting system to “explore” a variety of paths on the thermodynamic “landscape,” which can lead to spatial & temporally persistent, metastable states.
Summary/Conclusions (continued)

3. Dynamic redox experiments provide evidence for a number of structure/chemistry/dynamics relationships in amorphous aluminosilicates; these can perhaps be exploited for engineering purposes. Such exploitation essentially involves designing the thermodynamic landscape via chemistry: in the float process, we can design chemically both the glass-melt and the alloy float medium, affecting both the driving force and the transport coefficient(s).

4. Solution models emphasizing polymerization seem a fruitful approach to describing a “point-defect” thermodynamics in the amorphous state. Prediction in dynamics becomes possible.

Fe-MAS; 1380°C; 10 min; a_{O2} = 10^{-13}