Kinetic Paths, Metastable States & Ferrite Nucleation: The Impact of the “Semiconductor Condition”

Reid F. Cooper
Department of Geological Sciences
Brown University

Acknowledgements: Glen Cook, John Fanselow, Donald Smith, Rebecca Everman, Claire Pettersen

Foundation:

7th Santa Fe Conference on Rock Magnetism; 23 June 2006
Phenomena of Interest—and Questions

• Stability of transition-metal cation-bearing glasses or melts as a function of cation valence.

• Kinetic mechanisms of oxidation 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.

• The big question: applicability to issues in paleomagnetism?
Ionic/Covalent Melts and Glasses: Flexible Network

**long-range order** (fully polymerized “molecular” crystal, e.g., SiO₂ polymorphs)

**amorphous**: short-range order (fully polymerized “continuous random network”—Zachariasen [1932])

**amorphous**: partially polymerized “continuous random network?”
### Polymerization Indices

<table>
<thead>
<tr>
<th>MC</th>
<th>NBO</th>
<th>O/T</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.33</td>
<td>2</td>
<td>3.0 - 3.5 Chains, rings, and pyrosilicate ions</td>
</tr>
<tr>
<td>0.50</td>
<td>4</td>
<td>4.0 Orthosilicate ions</td>
</tr>
</tbody>
</table>

- **MC/O**: network-modifying cations / total O\(^{2-}\)
- **NBO/T**: non-bridging O\(^{2-}\) tetrahedral cations
- **O/T**: total O\(^{2-}\) tetrahedral cations
Tracer Diffusion & MC/O v. NBO/T: Henderson et al. (1985)

Cation diffusion behavior correlates well with polymerization as described by the MC/O index.

- Log $D_{i,1573K}$ v. (NBO/T)
- Log $Q_D$ v. (NBO/T)
- Log $D_{i,1573K}$ v. (MC/O)

Fig. 6. Variation in diffusivity (1300°C) of eight cations in six
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?

Thermodynamic (landscape) branch for an ideal gas—PV = RT
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 have order and be persistent.

The old future’s gone…
—John Gorka
And what is a large excursion in a thermodynamic potential?
How about erupting Fe$^{2+}$-bearing magma onto the floor of the ocean…

Huge, rapid excursions in temperature, in pressure, in oxygen fugacity, in water fugacity … many, many metastable branches are possibilities…

Sinton and Detrick (1992)
Perfit et al. (1994)

Gorda Ridge pillow lava
©MBARI 2002
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: \[
\dot{j}_i = -\frac{c_i D_i}{RT} \frac{d\eta_i}{d\xi} = -\frac{c_i D_i}{RT} \left( \frac{d\mu_i}{d\xi} + z_i F \frac{d\varphi}{d\xi} \right)
\]

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

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

\(j_o^2\) (\(c_{O_2}D_{O_2}\)) largest

\(j_{O^2-}\) (\(c_{O^2-}D_{O^2-}\)) \(\gg\) (\(c_{h^+}D_{h^+}\)) \(\gg\) (\(c_{O_2}D_{O_2}\))

→ rate-limited by electronic conductivity

\(j_{h^+}\) (\(c_{h^+}D_{h^+}\)) \(\gg\) (\(c_{M^{2+}}D_{M^{2+}}\)) \(\gg\)

\([c_{O^2-}D_{O^2-}]\) or (\(c_{O_2}D_{O_2}\))

→ rate-limited by modifier-cation diffusion

Independent (parallel) kinetic responses: “different paths on the thermodynamic landscape”

‡anhydrous conditions
**Experimental Approach 1**

**Compositions:** Fe$^{2+}$-doped MAS (enstatite-cordierite-liquid divariant [cotectic]); 20 mol% subt. FeO for MgO; glass specimens

**Polish:** flat surface (<30 nm RMS roughness)

**Anneal:** 700°C; 24h; between QFM and QIF

**Oxidize in air:** 710-770°C; 12-144h

**Analysis:** Rutherford Back-scattering Spectrometry (RBS); Transmission Electron Microscopy (TEM)
Experimental Approach 2:
RBS—Billiards Physics

$\alpha \equiv {}^4\text{He}^+$

homogeneous alloy

alloy thin film

Chu et al. (1978)
RBS: Annealed, Unoxidized Fe-MAS Glass

Uniform chemical composition with depth—to a depth of 2-3 μm

Standardless technique! Simulation approach is based on knowing nuclear-scattering & electron-stopping cross-sections, which are compiled.
Morphology is only possible for kinetic Mode III: material oxidizes by outward diffusion of Fe$^{2+}$ and Mg$^{2+}$ creating a continuous oxide film that covers the aluminosilicate glass beneath.

- Large Fe and Mg signal at the very surface
- Fe depletion beneath the surface
- Energy shift of Si edge: shift matches FWHM of Fe surface peak
- No change in O edge
Internal Oxidation of Fe-MAS Supercooled Liquid

formation of nm-scale ferrite at internal interface

Oxidized 770°C; 24h; air
conventional TEM

S: continuous, polycrystalline crystalline surface layer; \((\text{Mg,Fe})_3\text{O}_4 + \text{MgO}\)

D: 1 – 5 nm diameter precipitates of \((\text{Mg,Fe})_3\text{O}_4\)
Kinetics of the Oxidation Reaction

- (Areal density)$^2$ v. time: parabolic, diffusion-limited kinetics

\[ \frac{d(\Delta \xi)}{dt} = k'/\Delta \xi \quad \text{or} \quad (\Delta \xi)^2 = 2k't \]
where \( k' \propto \overline{D} \bullet (\Delta G/RT) \)

- Single activation energy for process, regardless which “layer” is measured
Reaction Analysis: Oxidation of Fe-MAS Glass: Phenomenological

\[
(Mg,Fe)_3O_4 + MgO \rightarrow (Mg,Fe)_3O_4
\]

\[
\begin{array}{c}
\text{Surface Layer} \\
\text{Depleted Glass} \\
\text{Unoxidized Glass}
\end{array}
\]

Reactions:

at \( \xi = 0 \):
\[
(Mg_{1-y}Fe_y)^{2+} = 2h^+ + (Mg_{1-y}Fe_y)^x_{Me \text{ (surface)}}
\]

at \( \xi = \xi'' \):
\[
2h^+ + \lambda (Mg_{1-x}Fe_x)Al_{p}Si_{q}O_{s} = MgFe_2O_4 + \psi MgAl_{\lambda_p/\psi}Si_{\lambda_q/\psi}O_{(\lambda_x-4)/\psi} + (Mg_{1-y}Fe_y)^{2+}
\]

\[
\lambda = (2+y)/x \quad ; \quad \psi = \lambda - 4
\]
Kinetic Analysis: Oxidation of Fe-MAS Glass: Phenomenological

1. Flux Equations (Fick-Einstein):

\[ j_{Me^{2+}} = \frac{-c_{Me^{2+}} \cdot D_{Me^{2+}}}{RT} \frac{d\eta_{Me^{2+}}}{d\xi} = \frac{-c_{Me^{2+}} \cdot D_{Me^{2+}}}{RT} \left( \frac{d\mu_{Me^{2+}}}{d\xi} + 2F \frac{d\phi}{d\xi} \right) \]  \hspace{1cm} (1A)

\[ j_{h^{\ast}} = \frac{-c_{h^{\ast}} \cdot D_{h^{\ast}}}{RT} \frac{d\eta_{h^{\ast}}}{d\xi} = \frac{-c_{h^{\ast}} \cdot D_{h^{\ast}}}{RT} \left( \frac{d\mu_{h^{\ast}}}{d\xi} + F \frac{d\phi}{d\xi} \right) \]  \hspace{1cm} (1B)

2. Continuity—Charge Neutrality (fluxes are coupled):

\[ \sum_{i} z_{i} j_{i} = 0 = 2j_{Me^{2+}} + j_{h^{\ast}} \]  or  \[ 2j_{Me^{2+}} = -j_{h^{\ast}} \]  \hspace{1cm} (2)

3. Plug Eqs. (1) into (2); solve for $Fd\phi$ in terms of $d\mu_{Me^{2+}}$:

Constraint (Mode III): \( (c_{h^{\ast}} \cdot D_{h^{\ast}}) \gg (c_{Me^{2+}} \cdot D_{Me^{2+}}) \)

leads to: \[ d\eta_{h^{\ast}} = 0 \]  \hspace{1cm} (3)

Semiconductor Condition: the large transport coefficient makes it impossible to sustain an electrochemical potential gradient for $h^{\ast}$!
Kinetic Analysis: Oxidation of Fe-MAS Glass: Phenomenological (continued)

4. Employ definitions of oxidation and ionization; leads to:

\[
j_{\text{Me}^{2+}} = \frac{c_{\text{Me}^{2+}} D_{\text{Me}^{2+}}}{2RT} \frac{d \mu_{O_2}}{d \xi}
\]  

(4)

A chemical potential gradient in oxygen can generate, as the dominant kinetic response, a cation flux with little or no motion of an oxygen species.

5. Growth of Depleted Zone (\(\Delta \xi = 0\) to \(\xi''\)):

\[
d(\Delta \xi)/dt = j_{\text{Me}^{2+}} \cdot \lambda \cdot V_m
\]  

(5)

6. Plug (4) into (5); separate variable and integrate:

\[
\xi = 0 \text{ to } \xi = \xi'': \quad \Delta \xi^2 = 2k't
\]

\[
k' = \frac{1}{2} \frac{X_{\text{Me}^{2+}}}{\bar{D}_{\text{Me}^{2+}}} \lambda \ln \left( \frac{a_0}{a_{O_2}^{\xi''}} \right)
\]

\[
a_0 = 0.21(\text{air}); \quad a_{O_2}^{\xi''} \approx \text{FMQ}
\]
Fe$^{2+,3+}$: How Low Can You Go?‡

**Critical:** value of \((c_h \cdot D_{h^+})\)

\[ B_h = \frac{D_{h^+}}{kT} \cdot \frac{L^2}{kT} \cdot \exp(-2\alpha L) \cdot \exp\left(-\frac{W}{kT}\right) \]

hole mobility is a function of concentration!!

0.19 at% Fe$^{2+,3+}$

⇒ change-over to Mode I or II only at distinctly low \(c_{Fe}\) and low \(T\)

0.04 at% Fe$^{2+,3+}$

‡and retain semiconductor condition, that is!
Melt Oxidation: "Isothermal Undercooling"

Experimental Approach 3: AeroAcoustic Levitation (AAL)

Weber et al., RSI, 65 (1994)

**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.
Basalt Oxidation: Microstructure (transmitted light)

- Two reaction fronts visible based on crystallization.
- Leisegang Bands beyond internal crystalline front.

1400±25°C: Ar 30 s + air 5s

Cooper et al., Science, 274, 1173 (1996)
Specimen: glass prepared from nepheline-normative olivine basalt (Columbia River Plateau)

Data (dots) show constant composition with depth.

Oxygen “peak” related to non-Rutherford resonance with 2.5 MeV $\alpha$-particles.

Standardless chemical technique! Simulation based on knowing nuclear-scattering electron-stopping cross-sections, which are compiled. Input: XRF data (below).

<table>
<thead>
<tr>
<th>Oxide</th>
<th>SiO$_2$</th>
<th>TiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>FeO</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>P$_2$O$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td>43.69</td>
<td>2.7</td>
<td>14.29</td>
<td>12.22</td>
<td>0.19</td>
<td>9.54</td>
<td>11.35</td>
<td>3.34</td>
<td>1.09</td>
<td>0.72</td>
</tr>
<tr>
<td>mol%</td>
<td>45.92</td>
<td>2.13</td>
<td>8.85</td>
<td>10.74</td>
<td>0.17</td>
<td>14.95</td>
<td>12.78</td>
<td>3.4</td>
<td>0.73</td>
<td>0.32</td>
</tr>
</tbody>
</table>

(a) XRF; (b) calculated
RBS: Oxidation of Liquid Basalt

- Oxidation in Ar\textsuperscript{(g)} (a\textsubscript{O2}~\textasciitilde10\textsuperscript{-6}) mobilizes Fe\textsuperscript{2+}, which diffuses to the free surface.

- Oxidation in air (a\textsubscript{O2}=0.21) mobilizes both Fe\textsuperscript{2+} and Ca\textsuperscript{2+}.

\textbf{Columbia River flood basalt}
\textbf{CO\textsubscript{2} laser; 1400±25\textdegree{C}}

\rightarrow \textit{unequivocal proof of Mode III oxidation}
Reaction Dynamic: Oxidation of Liquid Basalt in Air

Two reaction fronts move through liquid simultaneously: deepest reaction results in magnetite nucleation; following reaction sees magnetite transformed to hematite. *Relative transport coefficients of Fe$^{2+}$ and Ca$^{2+}$ revealed!*

Surface oxides produce multicolored, metallic patina—as seen on fresh basalt.
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!
Surface Phases—Oxidized Basaltic Glass (550°C; 100h; air)

SEI image <24h after completion of experiment:
Partial coverage of surface with phases having lateral scale ~0.2μm; additional phase with scale ~0.5μm: XRD reveals former to be MgO & CaO, latter to be nepheline.

SEI image—same specimen after 4 months in humid air at ~20°C:
Partial vitrification of MgO & CaO; large crystals of nepheline form—oxidation continues via out-diffusion of Na⁺.
Mode III Oxidation in Nature (?)

- Specular surface patina and near-surface nucleation and crystallization of fresh basalt flows (e.g., Dutton, 1884)
- Surface reflectance of, and hematite formation on Martian basalts, soils (Minitti et al., 2002; 2004)
- Desert varnish formation (e.g., McKeown and Post, 2001)

Internal Oxidation (perhaps Mode III) in Nature (?)

- Magnetic mineral spatial distribution, grain size and (related) magnetic remanence strength in MORBs (e.g., Zhou et al., 2000)
Crystalline Solids: Chemical activity (fugacity) is manifest physically in the distribution of point defects

Example: p-type, rocksalt-structure oxide \( \text{Me}_{1-\delta} \text{O} \) (e.g., \( \text{Ni}_{1-\delta} \text{O} \))

RXN: \( 3\text{Me}^x_{\text{Me}} + \frac{1}{2} \text{O}_2(g) = V''_{\text{Me}} + 2\text{Me}^\bullet_{\text{Me}} + \text{MeO} \)

MA: \( [V''_{\text{Me}}][h^\bullet]^2 \propto f_{O_2}^{1/2} \)

CN: \( 2[V''_{\text{Me}}] = [h^\bullet] \)

CN→MA: \( [V''_{\text{Me}}], [h^\bullet] \propto f_{O_2}^{1/6} \)

Ni\(_{1-\delta}\)O @ 1000°C:

- \( \text{O}_2(g) \)
- \( \text{Me}^\bullet_{\text{Me}} \)
- \( \text{Me}^{2+} \)
- \( \text{Me}^\bullet_{\text{Me}} \)
- \( \text{Me}^{2+} \)

An equivalent for the amorphous state?

V\(_{\text{Me}}''\) ≡ cation vacancy (of charge –2) in the oxide
Me\(_{\text{Me}}^\bullet\) ≡ Me\({}^3+\) sitting in structure where Me\(_{2}^{2+}\) should be —which is the ‘identity’ of an electron hole, i.e., h\(^\bullet\)
Paradigm for Understanding Kinetics

**Crystalline Solids:**

Crystal $\equiv$ Lattice + Basis

Basis $\equiv$ solid solution of atoms/ions ("regular elements") and point defects ("irregular elements"); apply solution thermodynamics to the basis

Chemical Dynamics are wrought by the motion of the irregular elements in response to a chemical-potential-gradient driving force

**Amorphous State?**

"Point defects" are not defined. Apply solution thermodynamics to structural elements of the glass/melt: highly mobile minority elements may be key to chemical dynamics.

Reactions:

at $\xi = 0$:

$$\frac{1}{2} O_2(g) + 4\text{SiOFe}_{0.5} + 2\text{SiO(Ca}_\varepsilon\text{Mg}_f)_{0.5} \rightarrow 6\text{SiOFe}_{0.33} + e\text{CaO} + f\text{MgO}$$

at $\xi = \xi^*$:

$$6\text{SiOFe}_{0.33} + x\text{SiONa} + 4\text{SiO(Ca}_a\text{Mg}_b)_{0.5} \rightarrow (2 - x)\text{NaFeO}_2 + (2x - 2)\text{SiONa}$$

$$+3x\text{SiOFe}_{0.33} + (4 - 2x)\text{SiOSi}$$

$$+2\text{SiO(Ca}_c\text{Mg}_d)_{0.5} + 2\text{SiO(Ca}_\varepsilon\text{Mg}_f)_{0.5}$$

where

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

$$2\text{SiOFe}_{0.5} \equiv \text{Fe}^{2+}; \quad \text{NaFeO}_2 \equiv \text{network-forming Fe}^{3+}$$
Redox Diffusion Dynamics in Semiconducting Silicate Melts

Polaron formation/consumption

\[ \text{rxn: } 4\text{SiOM}_{0.5} + \text{SiOSi} + \frac{1}{2}\text{O}_2(g) = 6\text{SiOM}_{0.33} \]

\[ 2\text{SiOM}_{0.5} \equiv \text{modifier Fe}^{2+} \]

\[ 3\text{SiOM}_{0.33} \equiv \text{modifier Fe}^{3+} \equiv h^* \]

Polaron/modifier-cation migration

\[ \text{rxn: } 2\text{SiOM}_{0.5} + 6\text{SiOM}_{0.33} = 6\text{SiOM}_{0.33} + 2\text{SiOM}_{0.5} \]
Melt Structure & the Metastable Branch

Given the dynamic oxidation response of Fe$^{2+}$-doped MgO-Al$_2$O$_3$-SiO$_2$ glass (domination/rate-limitation by chemical diffusion of Mg$^{2+}$ and Fe$^{2+}$) and basalt liquids/glasses (rate-limitation by Ca$^{2+}$?) specific structural questions that can be explored include:

1. Can the addition of larger alkaline earth oxides so prop-open the structure as to allow molecular O$_2$ diffusion to dominate the reaction?

2. Can chemical diffusion of Me$^{2+}$ of different sizes allow the applicability of percolation theory (MRN model) to be explored via dynamic structural change? And is this change a potential part of metastable branch persistence?
**MRN: Percolation of Modifier Oxides**

With increased concentration of modifier oxides, does the *continuous-random-network* structure model of Zachariassen (1932) evolve to one where modifiers form percolative channels in the structure?

**Modified Random Network (MRN) Model:**


Percolation: Threshold Behavior  
(Zallen, 1983)

For identically sized, but distinguishable-by-type (e.g., color or conductivity [here]), spheres, three-dimensional percolation of the minor component occurs when its volume fraction exceeds 16%, regardless of the packing geometry.

Partial molar volume threshold for percolation of modifier oxides in a silicate melt?
Experimental Approach 4: Philosophical

- Oxidize Fe$^{2+}$-doped alkaline earth aluminosilicate containing a substantial quantity of CaO ($\bar{V}_{\text{CaO}} \sim 1.5\bar{V}_{\text{MgO}}$) in two different environments on either side of Fe$_3$O$_4$:Fe$_2$O$_3$ (“MH”) oxygen activity buffer.
  \[ a_{\text{O}_2} > \text{MH will provide two reaction fronts...} \]

- Apply diffraction, microscopy and ion-backscattering spectroscopy techniques to discern the mechanism, morphology and kinetics of oxidation for the different oxidation conditions.
  \[ \rightarrow \text{Cation diffusion mechanism will result in lowering of volume fraction of modifiers in oxidized glass. Above percolation threshold, discrete oxide particle formation on the surface is favored; below percolation threshold, continuous oxide film on surface is favored.} \]
**Experimental Approach 5: Practical**

Fe-CMAS Glass ("JE"):

\textit{MC/O: 0.143}

\textit{Volume Fraction Modifiers: 0.166}‡

<table>
<thead>
<tr>
<th>Oxide</th>
<th>mol%</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>63.2</td>
<td>59.2</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>8.2</td>
<td>13.0</td>
</tr>
<tr>
<td>CaO</td>
<td>10.1</td>
<td>8.8</td>
</tr>
<tr>
<td>MgO</td>
<td>9.6</td>
<td>6.0</td>
</tr>
<tr>
<td>FeO</td>
<td>6.7</td>
<td>7.5</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>2.2</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Oxidation: \( T = 750^\circ \text{C} \text{ or } 755^\circ \text{C} \text{ (~}T_g\text{) ; } 1h \leq t_{soak} \leq 200h \)

1. Argon ("UHP" grade): \( p_{O_2} \approx 1 \times 10^{-6} \)
2. Dry Air ("zero" grade): \( p_{O_2} = 0.21 \)

Analysis: 1. Surface X-ray Diffraction (XRD)
2. Optical Microscopy
3. Transmission Electron Microscopy (TEM; HEED)
4. Rutherford Backscattering Spectroscopy (RBS)

‡Lange and Carmichael (1987)
**RBS: Oxidized Fe-CMAS ("JE") Glass**

argon; 750°C; ~20h

- **Argon**: no mobilization of Ca\(^{2+}\); tilting Si edge—partial coverage of (precipitates on) surface with Fe-Mg oxides.

air; 755°C; 25h

- **Air**: mobilization of Ca\(^{2+}\), but not to free surface; shifted Si edge—continuous oxide film on surface.
Oxidation Kinetics: Fe-CMAS ("JE")

- **Argon**: internal oxidation, formation of ferrite through mobilization of Mg$^{2+}$ and Fe$^{2+}$. Discrete surface ppts.

**Oxidized residual glass**: \[ \sum V_{MeO} = 0.12 \]

- **Air**: ferrite to $\gamma$-hematite transformation via mobilization of Ca$^{2+}$. Continuous surface film.

**Oxidized residual glass**: \[ \sum V_{MeO} = 0.10 \]

→ **Modifier Percolation Limit ~10 vol%**
Mineral Reactions and nm-Scale Ferrite

Oxidation of olivine produces nm-scale ppts. of almost pure magnetite and pure amorphous silica within a matrix of pure forsterite.

Other Fe^{2+}-bearing minerals—opx, cpx—can be expected to behave similarly.

Dislocations in olivine “decorated” by internal oxidation

Wu & Kohlstedt, JACerS, 71 (1988)
Absolutely! (Particularly “alternative-view” ones like these!) It is the energetics behind the diagrams that are critical: thus, paying homage to disconnects between equilibrium and reality—and paying attention to texture—helps discern the kinetic mechanism in reactions.
Big $\Delta G$? Many, Many Possibilities!  Kinetic Path is Key

With a very small $\Delta G$, one reaction is possible: the equilibrium one shown on the phase diagram.

With a large $\Delta G$, many reactions are possible (shown for $X_{\text{Sn}}^\text{eu}$ liquid): kinetics dictates what is seen, NOT equilibrium thermodynamics.
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: $h^\bullet$ or $e^\prime$) 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. Oxidation of basaltic (and analog) liquids & glasses sees non-equilibrium ferrites forming at an internal reaction front. By so removing Fe$^{2+}$ from the melt/glass, the kinetics for continued reaction can possibly be affected (depending on temperature and the presence of other transition-metal species).

4. Dynamic oxidation experiments provides evidence for a number of structure/chemistry relationships in amorphous aluminosilicates, the most significant kinetically, perhaps, being the applicability of percolation theory.

5. In a crystallizing magma, the slower oxidation of Fe$^{2+}$-bearing minerals—to the point of ferrite nucleation—could produce remanence carriers that are particularly resistant temporally.

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

General:
H. Schmalzried, *Solid State Reactions (2nd Ed.),* Verlag Chemie, Weinheim, FRG (1981). (This is a research monograph that is of distinct usefulness in understanding kinetics in ionic solids & minerals. It is not an “easy read”—every word counts—but it rewards the interested with great insight.)

Internal Oxidation (crystalline solutions)


Internal Oxidation (silicate glasses & melts)


Internal Oxidation (silicate glasses & melts; continued)


Internal Reduction (crystalline solutions)

Internal Reduction (silicate glasses & melts)

Non-Equilibrium Thermodynamics—Philosophy
Slides held in reserve...
**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; MoSi$_2$ 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:CO$_2$ in range 240:1 (QIF–2) to 1750:1 (QIF–4); 200 cm$^3$min$^{-1}$
- Active measurement of $a_{O_2}$ (YSZ sensor)
- Free-fall quench

### Original Melt Compositions

<table>
<thead>
<tr>
<th>Oxide</th>
<th>FeMAS wt%</th>
<th>FeMAS mol%</th>
<th>FeCMAS wt%</th>
<th>FeCMAS mol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>59.2</td>
<td>59.2</td>
<td>59.2</td>
<td>63.3</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>15.5</td>
<td>9.1</td>
<td>13.0</td>
<td>8.2</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>2.1</td>
<td>0.8</td>
<td>5.5</td>
<td>2.2</td>
</tr>
<tr>
<td>FeO</td>
<td>5.6</td>
<td>4.7</td>
<td>7.5</td>
<td>6.7</td>
</tr>
<tr>
<td>MgO</td>
<td>17.4</td>
<td>25.9</td>
<td>6.0</td>
<td>9.6</td>
</tr>
<tr>
<td>CaO</td>
<td>0.1</td>
<td>0.1</td>
<td>8.8</td>
<td>10.1</td>
</tr>
<tr>
<td>Fe$<em>{2+}$/Fe$</em>{total}$</td>
<td>0.75</td>
<td></td>
<td>0.60</td>
<td></td>
</tr>
<tr>
<td>NBO/T</td>
<td>0.53</td>
<td></td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td>MC/O</td>
<td>0.18</td>
<td></td>
<td>0.17</td>
<td></td>
</tr>
</tbody>
</table>

FeMAS; 1400°C; 0.5h; QIF–2
Fe-MAS Reduction Results:
Kinetics

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

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

**Internal: $\xi = \xi' \ to \ \xi''$**
- $T = 1380^\circ \text{C}; \ p_{O_2} \approx 10^{-13} \ \text{atm}; \ t = 1.0 \ \text{h}$
- Zero-loss (scattering contrast) image: dark phase is Fe\(^{\circ}\); HEED: bcc-Fe
- Size distribution is relatively uniform
- “String-of-pearls” morphology consistent with MRN model for unreacted melt.
Reduction Kinetics: Polymerization Model

- **Reaction at Free Surface, $\xi'$:**

  \[
  2\text{SiOMg}_{0.5} + 6\text{SiOFe}_{0.33} \rightleftharpoons \text{MgO} + 2\text{SiOSi} + 4\text{SiOFe}_{0.5} + \frac{1}{2} \text{O}_2(g) \\
  = 2\text{SiOMg}_{0.5} + 4\text{SiOFe}_{0.5} + \text{SiOSi} + \frac{1}{2} \text{O}_2(g)
  \]
  *polymerization decreases: MC/O goes from 3/8 to 3/7*

- **Reaction at Internal Reduction Front, $\xi''$:**

  \[
  2\text{SiOMg}_{0.5} + 6\text{SiOFe}_{0.5} \rightleftharpoons \text{Fe}^0 + 6\text{SiOFe}_{0.33} + 2\text{SiOMg}_{0.5}
  \]
  *polymerization increases: MC/O goes from 4/8 to 3/8*
Band Structure Definitions

General:

Point Defects; Ionic Solids

donor defect states

acceptor defect states

Mg$_{Mg}^x$ + 2Fe$_{Mg}^x$ + $\frac{1}{2}$O$_2$(g) = V$_{Mg}''$ + 2Fe$_{Mg}^*$ + MgO

Fe$_{Mg}^*$ ≡ h$^*$

(Mg,Fe)O
Metal: Metal-Oxide Equilibria: *Ellingham Diagram*

- $\Delta G^\circ$: pure metal + pure $O_2 = $ pure oxide
- all reactions calculated for 1 mole of $O_2$ so as to discern relative oxidation potentials of the pure metals
  → formulated this way, lines passing through plot origin are loci of constant oxygen activity
- no kinetics information
Metal:Metal-Oxide Equilibria at Arbitrary Activity

e.g., Reaction of molten Sn with a Na₂O-CaO aluminosilicate melt: *Almost infinite driving force for oxidation of metal and reduction of silicate melt:*

**Sn:SnO:**
\[ \Delta G_{\text{Sn:SnO}} = \Delta G^0_{\text{Sn:SnO}} + RT \ln \frac{a_{\text{SnO}}^2}{a_{\text{Sn}}^2 p_{O_2}} \]

at interface, \( a_{\text{Sn}} \sim 1 \) and \( a_{\text{SnO}} \sim 0 \): *Ellingham line rotates CW*

**Na:Na₂O:**
\[ \Delta G_{\text{Na:Na}_2\text{O}} = \Delta G^0_{\text{Na:Na}_2\text{O}} + RT \ln \frac{a_{\text{Na}_2\text{O}}^2}{a_{\text{Na}}^4 p_{O_2}} \]

at interface, \( a_{\text{Na}} \sim 0 \) and \( a_{\text{Na}_2\text{O}} \sim 0.1 \): *Ellingham line rotates CCW*