Thermodynamics and Kinetics of Silicate Vaporization

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Phase Stability, Diffusion Kinetics, and their Applications
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Outline of Presentation

• Silicates are truly the ‘ubiquitous material’—found everywhere!
  – Natural systems: found in many minerals and rocks
  – Technology—coatings, structural ceramics

• Apply Knudsen Effusion Mass Spectrometry (KEMS) to study thermochemistry of silicates
  – KEMS allows measurement of equilibrium vapor pressures above condensed phase
  – Unique challenges
    • Complex vaporization behavior
    • Kinetic barriers to vaporization

• Examples
  – Geology: Thermochemistry of Olivine
  – Technology: Thermochemistry $Y_2O_3$-$SiO_2$ and $Yb_2O_3$-$SiO_2$ coating systems

• Vaporization kinetics of silicates
Over 90% of the Earth’s crust consists of silicate minerals
- Olivine \((\text{Fe}_x\text{Mg}_{1-x})_2\text{SiO}_4\) primary constituent of earth’s mantle

- Moon, Mars, Asteroids, Comets, Interplanetary dust particles and...

..Hot, rocky exoplanets (maybe!)


Silicates in Materials Science

- High-Temperature Materials: Silicate Coatings

- Silicon-based ceramics: combustion chambers, static parts in hot stage

- Protective coating against water vapor, condensed phase deposits
  - Rare earth (RE) silicates (RE$_2$O$_3$)$_n$(SiO$_2$)
Knudsen Effusion Mass Spectrometry (KEMS)

Knudsen Cell: Condensed Phase/Gas Equilibrium

Direct Molecular Beam from Effusate Into Mass Spectrometer

- Knudsen Cell: 1909
- Couple to mass Spectrometer: 1950s (Ingrahm et al.)
- Continuing valuable applications of these methods!
Standard Calibration Material: Au

- Temperature Measurement: very critical
- Use pyrometer (non-contact)
- At triple point: determine calibration constant

\[ P_M = \frac{SIT}{\sigma} \]

\[ I_{Au} = 552 \pm 12 \text{cps} \]
\[ S_{Au} = 2.94 \pm 0.07 \times 10^{13} \text{cps-K/atm} \]
\[ P_{Au} = 2.56 \times 10^{-8} \text{ atm at triple point} \]
Standard Calibration Material: Au
Heat of Vaporization Checks Temperature Calibration and Instrument Response

\[ \Delta_v H^o = -R^*(-41.162) = 342.20 \text{ kJ/mol} \]

Tables = 342 kJ/mol

\[ \Delta_G = \Delta_v H - T\Delta_v S = -RT \ln K_p = -RT \ln(P_M) \]

\[ \ln P_M = -\frac{\Delta_v H}{R} \left( \frac{1}{T} \right) + \frac{\Delta_v S}{R} \]

\( \ln P_M \) vs \( 1/T \) is a van’t Hoff plot with slope \( -\frac{\Delta_v H}{R} \)

Mass Spectrometer \( P_M = \frac{kIT}{\sigma} \)

\( P_M \) = partial pressure of \( M \);
\( k \) = instrument constant; \( I \) = ion intensity;
\( T \) = Absolute temperature;
\( \sigma \) = ionization cross section
Proceed to Oxide Solutions

- Partial pressures ↔ activities

- Complex vaporization and ionization behavior
  - \( \text{SiO}_2(s) = \text{SiO}_2(g) \)
    - \( \text{SiO}_2(g) + e^- \rightarrow \text{SiO}_2^+ + 2e^- \)
      - \( \rightarrow \text{SiO}^+ + \text{O} + 2e^- \)
  
  - \( \text{SiO}_2(s) = \text{SiO} (g) + \frac{1}{2} \text{O}_2(g) \)
    - \( \text{SiO}(g) + e^- \rightarrow \text{SiO}^+ + 2e^- \)
      - \( \rightarrow \text{Si}^+ + \text{O} + 2e^- \)

- Calculation of cross sections for molecules

- Vaporization may be kinetically limited

- Container Issues
  - Need inert container or container with known interactions: Mo, W, Pt, Ir
  - Silicates are very reactive!
Solutions: Measure Partial Thermodynamic Quantities

Olivine: FeO$_{1-\alpha}$(MgO)$_{1-\beta}$(SiO$_2$)$_{1-\gamma}$
Same Phase; Variable Stoichiometry

Pure Compound:
FeO(s) = Fe(g) + 1/2 O$_2$(g)

\[
K_p = \frac{P_{Fe}^o [P_{O_2}^o]^{1/2}}{a_{FeO}} = \frac{P_{Fe}^o [P_{O_2}^o]^{1/2}}{1}
\]

Solution:
FeO(solution, a < 1) = Fe(g) + 1/2 O$_2$(g)

\[
K_p = \frac{P_{Fe} [P_{O_2}^{o}]^{1/2}}{a_{FeO}}
\]

\[
a_{FeO} = \frac{P_{Fe} [P_{O_2}^{o}]^{1/2}}{P_{Fe}^o [P_{O_2}^o]^{1/2}}
\]

\[
\ln(a_{FeO}) \text{ vs } 1/T \quad \text{-- partial molar enthalpy}
\]
Procedure

- Ion intensity measurements of relevant species for:
  1. Pure compound
  2. Solution
- Best to have *in-situ* pure compound and solution

- BUT, for the highest temperature (>2000K), need to use one cell and change specimens. Assume constant calibration factor.
Example I—Natural Systems: Olivine

- \( \text{Mg}_2\text{SiO}_4 \) (Forsterite)-\( \text{Fe}_2\text{SiO}_4 \) (Fayalite)
- Primary Constituent of Earth’s Mantle
- Sources:
  - Pure form found on Hawaii Green Sand Beaches: Volcanic pipeline to Mantle
  - Mining debris
- Important in volcanism, meteorites, likely constituent of other planetary bodies
- Very reactive, particularly above melting. Use Ir cell.
Olivine – Starting Material and Characterization

93% forsterite and 7% fayalite, Fo$_{93}$Fa$_{7}$ - (Fe$_{0.07}$Mg$_{0.93}$)$_2$SiO$_4$

ICP-OES analysis of the as received olivine samples.

<table>
<thead>
<tr>
<th>Element</th>
<th>*Wt (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.0120(6)</td>
</tr>
<tr>
<td>Ca</td>
<td>0.035(2)</td>
</tr>
<tr>
<td>Co</td>
<td>0.0120(6)</td>
</tr>
<tr>
<td>Cr</td>
<td>0.052(3)</td>
</tr>
<tr>
<td>Fe</td>
<td>5.012(3)</td>
</tr>
<tr>
<td>Mg</td>
<td>30(2)</td>
</tr>
<tr>
<td>Mn</td>
<td>0.075(4)</td>
</tr>
<tr>
<td>Na</td>
<td>0.0080(4)</td>
</tr>
<tr>
<td>Ni</td>
<td>0.27(1)</td>
</tr>
<tr>
<td>Sc</td>
<td>0.0040(2)</td>
</tr>
<tr>
<td>Si</td>
<td>20(1)</td>
</tr>
</tbody>
</table>

*Uncertainties of the analyses are given in parentheses.

XRD pattern and Rietveld refinement of the as received olivine samples.

Phase content

- Forsterite – 87.7 ± 0.3%
- Enstatite – 7.1 ± 0.2%
- Silica – 0.84 ± 0.6%
- Sapphirine – 0.5 ± 0.1%
- Clinochlore – 3.9 ± 0.2%

Heating to > 1060°C removes impurities
Temperature dependence of ion intensity ratios of Mg\(^+\), Fe\(^+\), SiO\(^+\), O\(^+\) and O\(_2\)\(^+\) in the olivine sample.

Measurements show good agreement with the phase diagram calculated by Bowen and Shairer.


Fegley and Osborne, Practical Chemical Thermodynamics For Geoscientists, Elsevier 2013, Fig. 12-11.
Olivine—Solution of
$\text{Mg}_2\text{SiO}_4$ (Fosterite)-$\text{Fe}_2\text{SiO}_4$ (Fayalite)

- Composition of Interest: $\text{Fo}_{0.93}\text{Fa}_{0.07}$
- Activity gradient across olivine
- Work in two phase regions

- Excess $\text{SiO}_2$: Olivine + Pyroxene
- Excess $\text{MgO}$: Olivine + Magnesiowustite
Previous Data and Models of Olivine

• Thermodynamic measurements
  – Nafziger & Muan (1967); Kitayama & Katsura (1968)—from P(O₂) and stable phases
  – Sakawa et al. (1976): Equilibration method for a(FeO)
  – Plante et al. (1992): KEMS measurements of a(FeO)
  – Wood & Kleppa, Kojitani & Akaogi: Calorimetry
  – General agreement: a(FeO): Positive deviation from ideality

• Saxena et al. (1993): (Mg,Fe)₂SiO₄ Regular Solution Lo = 9000

• Decterov et al.: Sublattice

• Fabrichnaya (1998): (Mg,Fe)₂SiO₄ β and γ spinel; subregular solution with temperature dependent mixing parameters
## Thermodynamic Activities in Olivine – \((\text{Fe}_2\text{SiO}_4)_{0.07}(\text{Mg}_2\text{SiO}_4)_{0.93} + \text{MgO}\)

![Graph showing log(a) vs 1/T(K) for Olivine + MgO](image)

### Table: Thermodynamic Activities

<table>
<thead>
<tr>
<th>Component</th>
<th>x</th>
<th>a (1800K)</th>
<th>Compare to Ideality</th>
<th>(\Delta H_i (1700 – 1950))</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>0.62</td>
<td>0.353</td>
<td>(-)ve deviations</td>
<td>30.2 kJ/mol</td>
</tr>
<tr>
<td>“FeO”</td>
<td>0.047</td>
<td>0.081</td>
<td>(+)ve deviations</td>
<td>212.5 kJ/mol</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>0.33</td>
<td>0.046</td>
<td>(-)ve deviations</td>
<td>220.2 kJ/mol</td>
</tr>
</tbody>
</table>
## Thermodynamic Activities in Olivine – \((\text{Fe}_2\text{SiO}_4)_{0.07}(\text{Mg}_2\text{SiO}_4)_{0.93}\)

### Graph

![Graph showing log(a) vs. \(1/\text{T(K)} \times 10^4\) for MgO, FeO, and SiO\(_2\).](image)

### Table

<table>
<thead>
<tr>
<th>Component</th>
<th>(x)</th>
<th>(a) (1900K)</th>
<th>Compare to ideality</th>
<th>(\Delta H_i(1700 – 1950))</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>0.62</td>
<td>0.165</td>
<td>(-)ve deviation</td>
<td>-222.0 kJ/mol</td>
</tr>
<tr>
<td>“FeO”</td>
<td>0.047</td>
<td>0.053</td>
<td>(+)ve deviation</td>
<td>-55.2 kJ/mol</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>0.333</td>
<td>0.341</td>
<td>(+)ve deviation</td>
<td>116.2 kJ/mol</td>
</tr>
</tbody>
</table>
Comparison to Models (FactSage)

Olivine + 0.01 MgO

Olivine + 0.01 SiO2
Thermodynamics of Olivine: Lots to Do!

- Understand changes in activities on melting
- Compare partial molar enthalpies to total excess free energy
- Refine current models: our data suggests some components far from ideality
Example 2: Rare Earth Silicates
SiC and SiC based Composites for Heat Engines

- Strength retained to higher temperatures than metals
- Lighter weight
- Fiber Reinforced composites give some fracture toughness
- Protected by SiO$_2$ scale
  - Slow growing, good in pure oxygen
  - BUT…Attacked by basic molten salts; volatilized by water

SiC/SiC CMC HPBR Paralinear
(1100 °-1300°C, 6 atm; Robinson/Smialek 1998)
Si(OH)$_4$ volatility (Opila et al., 1998-2006)
Combine *Desirable Mechanical Properties of SiC with Chemical Inertness of Refractory Oxide*

- Lower activity of silica \( \Rightarrow \) less reaction

- Molten salt reaction
  - \( \text{Na}_2\text{O(s)} + \text{SiO}_2(s) = \text{Na}_2\text{O} \cdot x\text{SiO}_2 \)

- Water vapor enhanced volatilization
  - \( \text{SiC} + \frac{3}{2} \text{O}_2(g) = \text{SiO}_2 + \text{CO}(g) \)
  - \( \text{SiO}_2 + 2 \text{H}_2\text{O}(g) = \text{Si(OH)}_4(g) \)
  - \( P[\text{Si(OH)}_4] = K_a(\text{SiO}_2) [P(\text{H}_2\text{O})]^2 \)

\[
\begin{align*}
\text{H}_2\text{O}(g) & \rightarrow \text{Si(OH)}_4(g) \downarrow, \text{MOH}(g) \downarrow \\
\underline{\text{SiO}_2, \text{MO}} \\
\text{(Underline indicates in solution)}
\end{align*}
\]

Indirect evidence suggests that the SiO$_2$ thermodynamic activity is lower in the Y$_2$O$_3$-Y$_2$SiO$_5$ and Y$_2$SiO$_5$-Y$_2$Si$_2$O$_7$ regions. But there are no direct measurements!
Issues with Measuring $a(\text{SiO}_2)$ in RE Silicates

- Vapor pressure of SiO$_2$ too low to measure in temperature range of interest

- Need measurable signal for SiO$_2$—use reducing agent to make excess SiO(g). Tried several, selected Mo or Ta
  - For $a(\text{SiO}_2) > \sim 0.02$
    - $\text{Mo}(s) + 3\text{SiO}_2(\text{soln}) = 3\text{SiO(g)} + \text{MoO}_3(g)$
  - For $a(\text{SiO}_2) < \sim 0.02$
    - $2\text{Ta}(s) + 2\text{SiO}_2(\text{soln}) = 2\text{SiO(g)} + \text{TaO(g)} + \text{TaO}_2(g)$
  - Note reducing agent must not change solid phase composition
- Monosilicates + disilicates + Ta – leads to tantalates

- Need to account for non-equilibrium vaporization

- SiO overlaps with CO$_2$ (m/e = 44)
  - Use LN$_2$ cold finger for improved pumping
  - Shutter to distinguish vapor from cell and background
  - High resolution instrument (in our dreams…)
  - Gettering pump for CO$_2$
Monosilicate + Disilicate

$Y_2O_3\cdot SiO_2 + Y_2O_3\cdot 2SiO_2$

$Yb_2O_3\cdot SiO_2 + Yb_2O_3\cdot 2SiO_2$

THERMO-CALC (2010.08.10:09.24) :
DATABASE:USER
AC(O)=1, N=1, P=1.01325E5;
Work in Two Phase Region: Monosilicate + Disilicate

Three cells:
- Au (reference)
- $3\text{Mo} + \text{Y}_2\text{O}_3 \cdot 2\text{SiO}_2 + \text{Y}_2\text{O}_3 \cdot \text{SiO}_2$
- $3\text{Mo} + \text{SiO}_2$
- Mo as powder and cell material

$\text{Mo(s)} + 3\text{SiO}_2(\text{soln}) = 3\text{SiO(g)} + \text{MoO}_3(\text{g})$

- Compare cells 1 and 2

Note that cell is part of the thermodynamic system: Best way to overcome container issue!

$$K = \frac{[P(\text{SiO})]^3 P(\text{MoO}_3)}{[a(\text{SiO}_2)]^3}$$

$\text{Mo} + 3\text{SiO}_2 = 3\text{SiO} + \text{MoO}_3$

Cell 2: pure $\text{SiO}_2$

$$a(\text{SiO}_2) = 1 = \left(\frac{[P^o(\text{SiO})]^3 P^o(\text{MoO}_3)}{K}\right)^{0.33}$$

$\text{Mo} + 3\text{SiO}_2 = 3\text{SiO} + \text{MoO}_3$

Cell 3: $\text{SiO}_2$ in silicate

$$a(\text{SiO}_2) = \left(\frac{[P(\text{SiO})]^3 P(\text{MoO}_3)}{K}\right)^{0.33}$$

$$a(\text{SiO}_2) = \left(\frac{[I(\text{SiO})]^3 I(\text{MoO}_3)}{[I^o(\text{SiO})]^3 I^o(\text{MoO}_3)}\right)^{0.33}$$
Two Phase Mixture

<table>
<thead>
<tr>
<th></th>
<th>$a(\text{SiO}_2)$, 1650K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Y}_2\text{O}_3\cdot(\text{SiO}_2) + \text{Y}_2\text{O}_3\cdot2(\text{SiO}_2)$</td>
<td>0.281</td>
</tr>
<tr>
<td>$\text{Y}_2\text{O}_3\cdot(\text{SiO}_2) + \text{Yb}_2\text{O}_3\cdot2(\text{SiO}_2)$</td>
<td>0.194</td>
</tr>
</tbody>
</table>
XRD after KEMS Measurements of RE Monosilicates + Disilicates + Mo:

Yttrium monosilicate + disilicate + Mo

Ytterbium monosilicate + disilicate + Mo

<table>
<thead>
<tr>
<th>Phase</th>
<th>wt (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Y}_2\text{O}_3.(\text{SiO}_2) )</td>
<td>56</td>
</tr>
<tr>
<td>( \text{Y}_2\text{O}_3.2(\text{SiO}_2) )</td>
<td>36</td>
</tr>
<tr>
<td>Mo</td>
<td>8</td>
</tr>
</tbody>
</table>
Monosilicate $+$ RE$_2$O$_3$

$\text{Y}_2\text{O}_3$-$\text{SiO}_2$

$\text{Yb}_2\text{O}_3$-$\text{SiO}_2$

THERMO-CALC (2010.08.10:09.24) :
DATABASE:USER
AC(O)=1, N=1, P=1.01325E5;
Two cells:

- Au
- $3\text{Ta} + \text{Y}_2\text{O}_3 + \text{Y}_2\text{O}_3 \cdot \text{SiO}_2$
  
  - Ta as powder and cell material—cell is part of system

$2\text{Ta}(s) + 3\text{SiO}_2(\text{soln}) = 3\text{SiO}(g) + \text{TaO}(g) + \text{TaO}_2(g)$

- Using $P_{eq}(\text{SiO})$ and FactSage (free energy minimization)
- Correction for non-equilibrium vaporization
XRD after KEMS Measurements of RE Monosilicates + RE\textsubscript{2}O\textsubscript{3} + Ta:

Yttrium monosilicate + Y\textsubscript{2}O\textsubscript{3} + Ta

Ytterbium monosilicate + Yb\textsubscript{2}O\textsubscript{3} + Ta

<table>
<thead>
<tr>
<th>Phase</th>
<th>wt (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y\textsubscript{2}O\textsubscript{3}·(SiO\textsubscript{2})</td>
<td>41</td>
</tr>
<tr>
<td>Y\textsubscript{2}O\textsubscript{3}</td>
<td>49</td>
</tr>
<tr>
<td>Ta</td>
<td>4</td>
</tr>
<tr>
<td>Ta\textsubscript{3}Si</td>
<td>4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Phase</th>
<th>wt (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb\textsubscript{2}O\textsubscript{3}·(SiO\textsubscript{2})</td>
<td>24</td>
</tr>
<tr>
<td>Yb\textsubscript{2}O\textsubscript{3}</td>
<td>66</td>
</tr>
<tr>
<td>Ta</td>
<td>2</td>
</tr>
<tr>
<td>Ta\textsubscript{2}Si</td>
<td>2</td>
</tr>
</tbody>
</table>
\[ \Delta H_{(SiO_2, \ 1600 \ K)} = (5200.26) \cdot R \cdot 2.303 = 99.57 \text{ kJ/mol} \]

\[ \Delta H_{(SiO_2, \ 1600 \ K)} = (1412.60) \cdot R \cdot 2.303 = 27.05 \text{ kJ/mol} \]

\[
\begin{align*}
\text{RE}_2\text{O}_3(s, \ 1600 \ K) + \text{SiO}_2(s, \ 1600 \ K) &\rightarrow \text{RE}_2\text{SiO}_5(s, \ 1600 \ K) \\
\text{RE}_2\text{SiO}_5(s, \ 1600 \ K) &\rightarrow \text{RE}_2\text{SiO}_5(s, \ 298 \ K) \\
\text{RE}_2\text{O}_3(s, \ 298 \ K) &\rightarrow \text{RE}_2\text{O}_3(s, \ 1600 \ K) \\
\text{SiO}_2(s, \ 298 \ K) &\rightarrow \text{SiO}_2(s, \ 1600 \ K) \\
2 \text{ RE}(s, \ 298 \ K) + 3/2 \text{ O}_2(g, \ 298 \ K) &\rightarrow \text{RE}_2\text{O}_3(s, \ 298 \ K) \\
\text{Si}(s, \ 298 \ K) + \text{O}_2(g, \ 298 \ K) &\rightarrow \text{SiO}_2(s, \ 298 \ K) \\
2 \text{ RE}(s, \ 298 \ K) + \text{Si}(s, \ 298 \ K) + 5/2 \text{ O}_2(g, \ 298 \ K) &\rightarrow \text{RE}_2\text{SiO}_5(s, \ 298 \ K)
\end{align*}
\]

\[ \Delta \text{H}_f, \text{ RE silicate, } 298 \text{ K (kJ/mol)} \]

- KEMS: -2907 \pm 16
- Calorimetry*: -2868.54 \pm 5.34

\[ a(\text{SiO}_2), \ 1650 \text{ K} \]

- 0.000804
- 0.00298

Vaporization Coefficients

- Vapor Flux (mole/unit area-unit time) leaving a free surface into a vacuum: Described by Hertz-Knudsen-Langmuir (HKL) equation

\[ J(\text{max}) = \frac{P_{eq}}{\sqrt{2\pi MRT}} \]

- Measured flux—Modified by a factor \( \alpha \): Vaporization Coefficient

\[ J(\text{measured}) = \frac{\alpha P_{eq}}{\sqrt{2\pi MRT}} \]

- Metals: Generally unity; Oxides \( 10^{-1} \) to \( 10^{-5} \)

- Free surface vaporization = Langmuir vaporization

- Important parameter—relatively little expt’l or theoretical work since 1970s
  - True vapor flux in a deposition processes
  - High temperature material vaporization limit
  - True vapor flux in a geochemical/cosmochemical processes
What Leads to non-unity Vaporization Coefficients?

- Vaporization of silica
  - \( \text{SiO}_2(s) = \text{SiO}_2(g) \)
  - \( \text{SiO}_2(s) = \text{SiO}(g) + \frac{1}{2} \text{O}_2(g) \)
  - \( \text{SiO}_2(s) = \text{SiO}(g) + \text{O}(g) \)

- Complex process
  - Break apart \( \text{SiO}_4^{2-} \)
  - Adsorbed \( \text{SiO}_2(a), \text{SiO}(a), \text{O}_2(a), \text{O}(a) \)
  - Desorption to \( \text{SiO}_2(g), \text{SiO}(g), \text{O}_2(g), \text{O}(g) \)
  - Break O-O, Si-O bonds; make O=O double bond

- Expect a kinetic barrier \( \Rightarrow \) flux reduced from equilibrium
Measure 1798-1948K (1525-1675°C)
\[ \text{SiO}_2 \alpha \text{ (from total flux)} = (4.5 \pm 1.4) \times 10^{-3} \]
Importance of Vaporization Coefficient

• Calculate vapor pressures above a condensed phase oxide:
  – Modify by vaporization coefficient

• Thermodynamic measurements
  – Implicitly assume that $\alpha(A(g), \text{solution}) = \alpha(A(g), \text{pure component})$
  – $A(g)$—particular species

• Measurements of these until 1970s, then relatively little work

• Important parameter has major effect on vapor pressures
Summary

- Knudsen Effusion Mass Spectrometry
  - Powerful tool for thermodynamic measurements
  - In use for many years; but still very useful particularly for solutions
  - Procedures are system specific

- Example: Olivine
  - Challenge to find ‘inert’ cell material. Iridium probably the best
  - Treat as solid solution of ‘FeO’, MgO, SiO₂
  - The melting point of the olivine sample was determined by the ion intensity discontinuity to be 1805 °C
  - Compare to standards and derive thermodynamic activities in solid phase. Appears to be significant partial molar heats, deviations from ideality

- Example: Rare-earth silicates
  - The reduced SiO₂ activity in Rare-earth silicates should limit their reactivity with water vapor
  - Solid State rare earth oxides—activity of SiO₂
    - Need reducing agent to obtain a measurable signal for SiO(g), which in turn relates to activity of SiO₂. Reducing agent must not change solid phase composition.
    - Method and choice of reducing agent depends on particular silicate

- Vaporization Kinetics: Described by vaporization coefficient
Acknowledgements

• Helpful discussions with E. Opila (Formerly NASA Glenn now Univ of Virginia); B. Fegley (WUSTL)

• Multiple cell and sampling system improvements to mass spectrometer: E. Copland (formerly NASA Glenn; now CSIRO, Melbourne, Australia)

• XRD: R. Rogers (NASA Glenn)