Thermochemistry of Silicates

Gustavo Costa and Nathan Jacobson
NASA Glenn Research Center
Cleveland, OH

https://ntrs.nasa.gov/search.jsp?R=20150007887 2019-05-31T16:11:38+00:00Z
Outline of Presentation

• Silicates in Materials Science, Mineralogy, Geology and Planetary Science
  - Silicate Mineral Subclasses
  • Thermochemistry of Silicates
    - Stability of silicates in different environments and their acid-base chemistry
    - Partial thermodynamics quantities (activity): An indicator of reactivity
    - Thermodynamic activity in silicates
    - Methods to measure activity

• Thermochemistry of Olivine
• Thermochemistry of Rare earth Silicates
  - Results for Y$_2$O$_3$-SiO$_2$ and Yb$_2$O$_3$-SiO$_2$ systems
• Summary: Silicates
Silicates in Materials Science

Modern Solid-state Chemistry
- Mesoporous based Silicates Sensors: pH, metal cation and humidity
- Rare-Earth Silicates and Vitreous Silica:
  - Electronic devices: microwave, semiconductors, ferromagnetics, ferroelectrics, lasers and phosphors
  - High-Temperature Materials: refractory bricks and coatings

Coating applications:

Ceramics in non-moving parts:
- Combustor liners
- Exhaust nozzles
  Eventually moving parts!

Silicates in Geology, Mineralogy and Planetary Science

Ocurrence
- Over 90 % of the Earth’s crust consists of silicate minerals

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

..Hot, rocky exoplanets


# Silicate Mineral Subclasses

<table>
<thead>
<tr>
<th>Subclass</th>
<th>Si:O Ratio</th>
<th>Si Radical</th>
<th>Example</th>
<th>Mineral Formula</th>
<th>Arrangement of SiO₄ Tetrahedra</th>
</tr>
</thead>
<tbody>
<tr>
<td>framework silicates</td>
<td>1:2</td>
<td>SiO₂ or ((\text{Al}<em>{x}\text{Si}</em>{1-x})\text{O}_2)</td>
<td>quartz, albite</td>
<td>(\text{SiO}_2) Na((\text{AlSi}_3)\text{O}_9)</td>
<td>![Framework Silicate Diagram]</td>
</tr>
<tr>
<td>sheet silicates</td>
<td>2:5 = 4:10</td>
<td>((\text{SiO}<em>2)</em>{6}^{+})</td>
<td>pyrophyllite</td>
<td>(\text{Al}_2\text{Si}<em>5\text{O}</em>{10}(\text{OH})_2)</td>
<td>![Sheet Silicate Diagram]</td>
</tr>
<tr>
<td>single-chain silicates</td>
<td>1:3 = 2:6</td>
<td>((\text{SiO}<em>2)</em>{3}^{2-}) or ((\text{SiO}<em>2)</em>{4}^{4-})</td>
<td>enstatite</td>
<td>(\text{Mg}_2(\text{SiO}_3)_2) or (\text{Mg}_2\text{Si}_2\text{O}_6)</td>
<td>![Single-Chain Silicate Diagram]</td>
</tr>
<tr>
<td>double-chain silicates</td>
<td>4:11 = 8:22</td>
<td>((\text{SiO}<em>2)</em>{12}^{12-})</td>
<td>tremolite</td>
<td>(\text{Ca}_2\text{Mg}_2\text{Si}<em>5\text{O}</em>{22}(\text{OH})_2)</td>
<td>![Double-Chain Silicate Diagram]</td>
</tr>
<tr>
<td>ring silicates</td>
<td>1:3 = 6:18</td>
<td>((\text{SiO}<em>2)</em>{18}^{12-})</td>
<td>tourmaline</td>
<td>((\text{Na},\text{Ca})<em>x\text{Fe}^2_x\text{Mg}</em>{x}\text{Al}_{12-x}\text{Al}_2(\text{BO}<em>4)</em>{2}\text{Si}<em>2\text{O}</em>{16}(\text{OH})_4)</td>
<td>![Ring Silicate Diagram]</td>
</tr>
<tr>
<td>isolated tetrahedral</td>
<td>1:4</td>
<td>((\text{SiO}_2)_4^{4-})</td>
<td>forsterite</td>
<td>(\text{Mg}_2\text{Si}<em>4\text{O}</em>{8})</td>
<td>![Isolated Tetrahedral Diagram]</td>
</tr>
<tr>
<td>paired tetrahedral</td>
<td>2:7</td>
<td>((\text{SiO}_2)_7^{6-})</td>
<td>akermanite</td>
<td>(\text{Ca}_2\text{MgSi}_2\text{O}_7)</td>
<td>![Paired Tetrahedral Diagram]</td>
</tr>
<tr>
<td>more complex silicates</td>
<td>1:4 and 2:7</td>
<td>((\text{SiO}_2)_4^{4-}) or ((\text{SiO}_3)_7^{6-})</td>
<td>vesuvianite</td>
<td>(\text{Ca}_{10}(\text{Mg},\text{Fe})_2\text{Al}_2(\text{SiO}_3)_3(\text{Si}_2\text{O}_3)_2(\text{OH})<em>4) = (\text{Ca}</em>{16}(\text{Mg},\text{Fe})_2\text{Al}_2\text{Si}<em>2\text{O}</em>{14}(\text{OH})_8)</td>
<td>![Complex Silicate Diagram]</td>
</tr>
</tbody>
</table>

© 2011 Pearson Education, Inc.


- \((\text{Fe}^2_x\text{Mg}_{1-x})_2\text{SiO}_4\)
- Ortorrombic structure (*Pbnm*).
- Red – oxygen.
- Blue – A sites, silicon.
- Green – B sites, magnesium or iron.
Thermodynamics and Acid-Base Chemistry

```
MgO + SiO₂ = MgSiO₃
```

Base    Acid    Enstatite

Ionic Potential (z/r) and Acid-Base Scale

- z/r < 2 strongly basic
- 2 ≤ z/r < 4 basic
- 4 < z/r < 7 amphoteric
- z/r > acidic

Enthalpy of formation of orthosilicates vs. ionic potential (z/r) of divalent cations

```
\[ \gamma = a \cdot C \]
```

Thermodynamic Activity as Indicator of Stability?

Table 2. Acid-base scales for oxides

<table>
<thead>
<tr>
<th>Oxide</th>
<th>z/r of cation</th>
<th>Optical basicity</th>
<th>Enthalpy of solution (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₂O</td>
<td>0.66 ± 1.4²</td>
<td>1.8</td>
<td>- 282 ± 2</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.89 ± 1.15</td>
<td>1.7</td>
<td>- 176 ± 2</td>
</tr>
<tr>
<td>BaO</td>
<td>1.45 ± 1.15</td>
<td>1.8</td>
<td>- 127 ± 2</td>
</tr>
<tr>
<td>SrO</td>
<td>1.59 ± 1.15</td>
<td>1.8</td>
<td>- 93.6 ± 2</td>
</tr>
<tr>
<td>CaO</td>
<td>2.00 ± 1.0</td>
<td>1.8</td>
<td>- 58.0 ± 2</td>
</tr>
<tr>
<td>MnO</td>
<td>2.41 ± 1.0</td>
<td>1.8</td>
<td>- 5.4 ± 2</td>
</tr>
<tr>
<td>FeO</td>
<td>2.56 ± 1.0</td>
<td>1.8</td>
<td>- 16.0 ± 2</td>
</tr>
<tr>
<td>Y₂SiO₅</td>
<td>2.58 ± 1.0</td>
<td>1.8</td>
<td>- 42.6 ± 2</td>
</tr>
<tr>
<td>CoO</td>
<td>2.68 ± 1.0</td>
<td>1.8</td>
<td>- 23.0 ± 2</td>
</tr>
<tr>
<td>Y₂Al₂O₇</td>
<td>2.71 ± 1.0</td>
<td>1.8</td>
<td>- 28.4 ± 2</td>
</tr>
<tr>
<td>CuO</td>
<td>2.74 ± 1.0</td>
<td>1.8</td>
<td>- 33.0 ± 2</td>
</tr>
<tr>
<td>MgO</td>
<td>2.77 ± 0.76</td>
<td>1.8</td>
<td>- 4.8 ± 2</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.33 ± 1.0</td>
<td>1.8</td>
<td>- 17.0 ± 2</td>
</tr>
<tr>
<td>ScO₂</td>
<td>3.45 ± 1.0</td>
<td>1.8</td>
<td>- 16.7 ± 2</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>4.65 ± 1.0</td>
<td>1.8</td>
<td>- 15.9 ± 2</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>4.76 ± 1.0</td>
<td>1.8</td>
<td>- 15.7 ± 2</td>
</tr>
<tr>
<td>Ga₂O₃</td>
<td>4.84 ± 1.0</td>
<td>1.8</td>
<td>- 13.2 ± 2</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>4.88 ± 1.0</td>
<td>1.8</td>
<td>- 11.4 ± 2</td>
</tr>
<tr>
<td>Mn₂O₄</td>
<td>5.17 ± 1.0</td>
<td>1.8</td>
<td>- 17.9 ± 2</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.60 ± 0.605</td>
<td>1.8</td>
<td>- 13.4 ± 2</td>
</tr>
<tr>
<td>TiO₂</td>
<td>6.61 ± 1.0</td>
<td>1.8</td>
<td>- 11.1 ± 2</td>
</tr>
<tr>
<td>BeO</td>
<td>7.41 ± 1.0</td>
<td>1.8</td>
<td>- 9.3 ± 2</td>
</tr>
<tr>
<td>GeO₂</td>
<td>7.55 ± 1.0</td>
<td>1.8</td>
<td>- 7.0 ± 2</td>
</tr>
<tr>
<td>WO₃</td>
<td>14.3 ± 1.0</td>
<td>1.8</td>
<td>- 3.0 ± 2</td>
</tr>
<tr>
<td>MoO₃</td>
<td>14.6 ± 1.0</td>
<td>1.8</td>
<td>- 5.3 ± 2</td>
</tr>
<tr>
<td>SiO₂</td>
<td>15.4 ± 0.48</td>
<td>1.8</td>
<td>- 6.0 ± 2</td>
</tr>
</tbody>
</table>

www.nasa.gov
Partial Thermodynamics Quantities: Activity and Vapor Pressure Measurement

**Activity**

\[ \Delta_v G = \Delta_v H - T \Delta_v S = -RT \ln K_p = -RT \ln \left( \frac{P_M}{a_M} \right) \]

\[ a = \gamma \cdot C \]

\[ \gamma = \text{activity coefficient}; \ C = \text{concentration} \]

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

lnP_M vs 1/T is a van't Hoff plot with slope = \[ \frac{-\Delta_v H}{R} \]

**Pressure**

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

Tables = 342 kJ/mol

**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
Thermodynamic Activities

- Important solution parameters
- Quantify how vapor pressure is reduced due to solution formation
- Example: Olivine—can treat as solution of FeO, MgO, SiO₂
- Use data to calculate thermodynamic activity of each component
- Measure thermodynamic parameters for olivine solutions
  - e.g. ln a(FeO) vs 1/T slope is partial molar enthalpy
  - Input to codes to model:
    - Atmospheres of hot, rocky exoplanets
    - Vapor over lava

Solutions: \( A_{1-\alpha}B_{1-\beta}C_{1-\gamma} \)
Same Phase; Variable Stoichiometry

\[
\begin{align*}
FeO(s) &= Fe(g) + \frac{1}{2} O_2(g) \\
K_p &= \frac{P^o_{Fe} [P^o_{O_2} ]^{1/2}}{a_{FeO}} = \frac{P^o_{Fe} [P^o_{O_2} ]^{1/2}}{1} \\
K_p &= \frac{P^o_{Fe} [P^o_{O_2} ]^{1/2}}{a_{FeO}} \quad a_{FeO} = \frac{P^o_{Fe} [P^o_{O_2} ]^{1/2}}{P^o_{Fe} [P^o_{O_2} ]^{1/2}} \\
FeO(solution, a < 1) &= Fe(g) + \frac{1}{2} O_2(g)
\end{align*}
\]
Methods to measure silica activity

- Oxidation-reduction equilibrium using gas mixtures or electrochemical cells
- High temperature reaction calorimetry
- **Knudsen Effusion Mass Spectrometry**

Mass spectrometer: Intensity $\rightarrow$ Pressure $\rightarrow$ Activity

**Exact approach depends on the system**

- RE-silicates - Reducing agent is used for to boost vaporization of SiO$_2$ without changing solid composition
- Olivine – Single cell configuration is used to attain higher temperatures

Knudsen Effusion Mass Spectrometry (KEMS)

- 90° magnetic sector; non-magnetic ion source ion counting detector ⇒ no mass discrimination
- Cross axis electron impact ionizer
- Resistance heated cell; multiple Knudsen cell system
- Measurements to 2000°C, Pressure to 1 x 10^-10 bar

\[ p_i = k I_i^+ T / S_i \]

- \( p_i \) = pressure of component i
- \( k \) = instrument constant
- \( T \) = Temperature (K)
- \( S_i \) = ionization cross section

Intensity → Pressure → Activity

Use Multi-Cell Flange for a(SiO₂)

Design of E. Copland 2002

Olivine and Rare – Earth Silicates
Olivine - Results
Olivine – Starting Material and Characterization

93% forsterite and 7% fayalite, Fo$_{93}$Fa$_7$ - (Fe$_{0.7}$Mg$_{0.93}$)$_2$SiO$_4$

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%

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>5.01(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 patterns of the olivine samples: (A) as received, (B) after KEMS up to 2084 K in a Mo Knudsen cell (C) after KEMS up to 1850 K in a Mo Knudsen cell (D) after KEMS up 2079 K in an Ir Knudsen cell.

Chemical composition of the olivine powder samples Fo$_{93}$Fa$_7$ before and after KEMS up to 2084 K.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt (%)</th>
<th>Sample as received$^a$</th>
<th>After KEMS in a Mo cell</th>
<th>After KEMS in a Ir cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.0120(6)</td>
<td>0.016(6)</td>
<td>0.2(1)</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>0.035(2)</td>
<td>0.009(2)</td>
<td>0.04(2)</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>0.0120(6)</td>
<td>0.003(2)</td>
<td>0.004(3)</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>0.052(3)</td>
<td>0.035(4)</td>
<td>0.06(1)</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>5.01(3)</td>
<td>0.006(3)</td>
<td>0.93(3)</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>30(2)</td>
<td>35.0(1)</td>
<td>34(1)</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.075(4)</td>
<td>0.003(1)</td>
<td>0.031(3)</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>0.0080(4)</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.27(1)</td>
<td>0.005(3)</td>
<td>0.006(3)</td>
<td></td>
</tr>
<tr>
<td>Sc</td>
<td>0.0040(2)</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>20(1)</td>
<td>19.3(1)</td>
<td>21.8(8)</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>0</td>
<td>0.04(2)</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Ir</td>
<td>0</td>
<td>0</td>
<td>0.06(3)</td>
<td></td>
</tr>
</tbody>
</table>

Side view (cross-section) of the Mo Knudsen cell containing the olivine sample heat treated up to 2084 K.
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 Schairer.

Fegley and Osborne, “Practical Chemical Thermodynamics For Geoscientists,” Elsevier 2013, Fig. 12-11.

Temperature dependence of ion intensity ratios of Mg\(^{+}\), Fe\(^{+}\), SiO\(^{+}\), O\(^{+}\) and O\(_2\)^{+} in the olivine sample.

Thermodynamic Activities in Olivine - \((\text{Fe}_x\text{Mg}_{1-x})_2\text{SiO}_4\)

\[ \log(a_{\text{FeO}}) \]

\[ \log(a_{\text{SiO}}) \]

\[ \log(a_{\text{MgO}}) \]

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

\[ a_{\text{MO}} = \frac{P_M [P_{O_2}]^{1/2}}{P_M^{o} [P_{O_2}^{o}]^{1/2}} \]

\( \text{Fe, Mg or Si} \)

\( \text{MO}_{\text{solution, } a<1} = M(g) + 1/2O_2(g) \)

From FactSage or measured by KEMS
Rare earth Silicates
Low Reactivity of Rare earth Silicates

SiC + 3/2 O\textsubscript{2}(g) = SiO\textsubscript{2} + CO(g)

SiO\textsubscript{2} + 2 H\textsubscript{2}O(g) = Si(OH)\textsubscript{4}(g)

P[Si(OH)\textsubscript{4}] = K a SiO\textsubscript{2} [P(H\textsubscript{2}O)]\textsuperscript{2}

Y and Yb silicates Need to be measured!

SiC/SiC CMC HPBR Paralinear Weight Change
(1100 °-1300°C, 6 atm; Robinson/Smialek 1998)
Si(OH)\textsubscript{4} volatility (Opila et al., 1998-2006)

Key Parameters in Boundary Layer Limited Transport Modeling

- $\text{SiO}_2(\text{pure or in silicate soln}) + 2 \text{H}_2\text{O}(g) = \text{Si(OH)}_4(g)$

- Reduce $a(\text{SiO}_2)$ $\Rightarrow$ reduce recession. Recession drives need for coatings.
Indirect evidence suggests that the SiO₂ thermodynamic activity is lower in the Y₂O₃-Y₂SiO₅ and Y₂SiO₅-Y₂Si₂O₇ regions. But there are no direct measurements!
Issues with Measuring a(SiO₂) in RE Silicates

- Vapor pressure of SiO₂ too low to measure in temperature range of interest

- Need measurable signal for SiO₂—use reducing agent to make excess SiO(g). Tried several, selected Mo or Ta
  - For a(SiO₂) < ~0.02
    - 2Ta(s) + 2SiO₂(soln) = 2SiO(g) + TaO(g) + TaO₂(g)
  - For a(SiO₂) > ~0.02
    - Mo(s) + 3SiO₂(soln) = 3SiO(g) + MoO₃(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 CO₂ (m/e = 44)
  - Use LN₂ cold finger for improved pumping
  - Shutter to distinguish vapor from cell and background
  - Gettering pump for CO₂
Approaches use two phase regions

1 – Monosilicate + RE$_2$O$_3$

Two cells:
- Au
- 3Ta + Y$_2$O$_3$ + Y$_2$O$_3$ · SiO$_2$

2Ta(s) + 3SiO$_2$(soln) = 3SiO(g) + TaO(g) + TaO$_2$(g)

- Using $P_{eq}(\text{SiO})$ and FactSage (free energy minimization)
- Correction for non-equilibrium vaporization

2 – Monosilicate + Disilicate

Three cells:
- Au (reference)
- 3Mo + Y$_2$O$_3$ · 2SiO$_2$ + Y$_2$O$_3$ · SiO$_2$
- 3Mo + SiO$_2$

Mo(s) + 3SiO$_2$(soln) = 3SiO(g) + MoO$_3$(g)

- Compare cells 1 and 2
- Less data processing than with Ta
- Correction is not needed.
Monosilicate + RE$_2$O$_3$

Y$_2$O$_3$-SiO$_2$

Yb$_2$O$_3$-SiO$_2$

THERMO-CALC (2010.08.10:09.24): DATABASE:USER
AC(O)=1, N=1, P=1.01325E5;
XRD after KEMS Measurements of RE Monosilicates + RE$_2$O$_3$ + Ta:

Yttrium monosilicate + Y$_2$O$_3$ + Ta

<table>
<thead>
<tr>
<th>Phase</th>
<th>wt (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y$_2$O$_3$.SiO$_2$</td>
<td>41</td>
</tr>
<tr>
<td>Y$_2$O$_3$</td>
<td>49</td>
</tr>
<tr>
<td>Ta</td>
<td>4</td>
</tr>
<tr>
<td>Ta$_3$Si</td>
<td>4</td>
</tr>
</tbody>
</table>

Ytterbium monosilicate + Yb$_2$O$_3$ + Ta

<table>
<thead>
<tr>
<th>Phase</th>
<th>wt (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb$_2$O$_3$.SiO$_2$</td>
<td>24</td>
</tr>
<tr>
<td>Yb$_2$O$_3$</td>
<td>66</td>
</tr>
<tr>
<td>Ta</td>
<td>2</td>
</tr>
<tr>
<td>Ta$_2$Si</td>
<td>2</td>
</tr>
</tbody>
</table>
Raw Data—log (IT) vs 1/T
Cell (1): Au Reference  Cell (2): Ta + Y_2O_3 + MS

\[ \Delta_v H(Au\rightarrow1558K) = 342.6 \text{ kJ/mol} \]

Tabulated 346.3 kJ/mol
\[ \Delta H_{(SiO_2, 1600 \text{ K})} = (5200.26) \cdot R \cdot 2.303 = 99.57 \text{ kJ/mol} \]

**Yb_2O_3 + Yb_2O_3 \cdot (SiO_2)**

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

\[
\begin{align*}
\text{RE}_2O_3(s, 1600 \text{ K}) + SiO_2(s, 1600 \text{ K}) & \rightarrow \text{RE}_2SiO_5(s, 1600 \text{ K}) \\
\text{RE}_2SiO_5(s, 1600 \text{ K}) & \rightarrow \text{RE}_2SiO_5(s, 298 \text{ K}) \\
\text{RE}_2O_3(s, 298 \text{ K}) & \rightarrow \text{RE}_2O_3(s, 1600 \text{ K}) \\
SiO_2(s, 298 \text{ K}) & \rightarrow SiO_2(s, 1600 \text{ K}) \\
2 \text{RE}(s, 298 \text{ K}) + 3/2 O_2(g, 298 \text{ K}) & \rightarrow \text{RE}_2O_3(s, 298 \text{ K}) \\
Si(s, 298 \text{ K}) + O_2(g, 298 \text{ K}) & \rightarrow SiO_2(s, 298 \text{ K}) \\
2 \text{RE}(s, 298 \text{ K}) + Si(s, 298 \text{ K}) + 5/2 O_2(g, 298 \text{ K}) & \rightarrow \text{RE}_2SiO_5(s, 298 \text{ K}) \\
\end{align*}
\]

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

\[
\begin{array}{ccc}
\text{KEMS} & \text{Calorimetry*} & \text{Optical basicity**} \\
\text{Y}_2\text{O}_3 \cdot (\text{SiO}_2) & -2907 \pm 16 & -2868.54 \pm 5.34 & 0.786 \\
\text{Yb}_2\text{O}_3 \cdot (\text{SiO}_2) & -2744 \pm 11 & -2774.75 \pm 16.48 & 0.729 \\
\end{array}
\]

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

\[ 0.000804 \]

\[ 0.00298 \]

---

Monosilicate + Disilicate

\[ \text{Y}_2\text{O}_3\cdot\text{SiO}_2 + \text{Y}_2\text{O}_3\cdot2\text{SiO}_2 \]

THERMO-CALC (2010.08.10:09.24):
DATABASE: USER
AC(O)=1, N=1, P=1.01325E5;
XRD after KEMS Measurements of RE Monosilicates + Disilicates + Mo:

Yttrium monosilicate + disilicate + Mo

Ytterbium monosilicate + disilicate + Mo

Phase

Y$_2$O$_3$.SiO$_2$

Y$_2$O$_3$.2SiO$_2$

Mo

Phase

Yb$_2$O$_3$.SiO$_2$

Yb$_2$O$_3$.2SiO$_2$

Mo

wt (%)  
56  
36  
8
\[
Y_2O_3 \cdot (SiO_2) + Y_2O_3 \cdot 2(SiO_2)
\]

\[
Yb_2O_3 \cdot (SiO_2) + Yb_2O_3 \cdot 2(SiO_2)
\]

Optical basicity**

\[
\begin{align*}
Y_2O_3 \cdot (SiO_2) & \quad Y_2O_3 \cdot 2(SiO_2) \\
0.786 & \quad 0.699 \\
Yb_2O_3 \cdot (SiO_2) & \quad Yb_2O_3 \cdot 2(SiO_2) \\
0.729 & \quad 0.657
\end{align*}
\]

\[a(SiO_2), \ 1650 \ K\]

\[
\begin{array}{c}
0.281 \\
0.194
\end{array}
\]
Now Have the Needed Quantities for Modeling Recession

\[ Flux = 0.664 \left( \frac{v_\infty \rho_\infty L}{\eta} \right)^{0.5} \left( \frac{\eta}{D_{\text{Si(OH)4}} \rho_\infty} \right)^{0.33} \frac{D_{\text{Si(OH)4}}}{RTL} K a_{\text{SiO}_2} \left( P_{H_2O} \right)^2 \]

- \( T = 1300^\circ \text{C}; P = 10 \text{ bar}; P(H_2O) = 1 \text{ bar} \)
- \( v_\infty = 20 \text{ m/s} \)
- \( L = 10 \text{ cm} \)
- \( \eta = 5 \times 10^{-4} \text{ g/cm-s} \)
- \( \rho_\infty = 2.2 \times 10^{-3} \text{ g/cc} \)
- \( D_{\text{Si(OH)4}} = 0.19 \text{ cm}^2/\text{s} \)
- \( \log K = -2851.2/T - 3.5249 \) (Si(OH)\(_4\)(g) transpiration measurements)
- \( a(\text{SiO}_2) \) from activity measurements
Summary

• Fundamental understanding of thermodynamic is critical to models and structure-property relationships
  – Vapor pressure techniques—Knudsen effusion mass spectrometry
• Silicates are everywhere – from minerals to electronic materials to aircraft engines

Olivine

• Secondary phases of the olivine sample were removed at temperatures > 1060 °C.
• Mo and Re cell reacts with olivine sample. Ir must be used
• The main vapor species of the olivine sample are Mg\(^+\), O\(^+\), O\(_2\)\(^+\), SiO\(^+\) and Fe\(^+\) following this order of evaporation.
• The melting point of the olivine sample was determined by the ion intensity discontinuity to be 1805 °C.
• Temperature dependence of partial pressures of the species were determined and their activities. Next steps
• Vaporization coefficient measurements

Rare-Earth Silicates

• The reduced SiO\(_2\) activity in Rare-earth silicates should limit their reactivity with water vapor
• Solid State rare earth oxides—activity of SiO\(_2\)
  – Need reducing agent to obtain a measurable signal for SiO(g), which in turn relates to activity of SiO\(_2\). Reducing agent must not change solid phase composition.
  – Method and choice of reducing agent depends on particular silicate
• Thermodynamic data for gas phase hydroxides and solid candidate coating ⇒ recession modeling input data
Acknowledgements

• Helpful discussions with B. Opila (Formerly NASA Glenn now University of Virginia)

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

• XRD: R. Rogers (NASA Glenn)

• NASA/ORAU Post-doctoral Fellowship Program