Thermochemistry of Silicates

Gustavo Costa and Nathan Jacobson
NASA Glenn Research Center
Cleveland, OH
gustavo.costa@nasa.gov
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 $Y_2O_3$-$SiO_2$ and $Yb_2O_3$-$SiO_2$ 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

Occurrence
- 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 2.6 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 SiO$_4$ Tetrahedra</th>
</tr>
</thead>
<tbody>
<tr>
<td>framework silicates (tectosilicates)</td>
<td>1:2</td>
<td>SiO$_4^-$</td>
<td>quartz</td>
<td>SiO$_2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Al$<em>x$Si$</em>{4-x}$)O$_2$</td>
<td>albite</td>
<td>Na(AlSi$_3$)O$_9$</td>
<td></td>
</tr>
<tr>
<td>sheet silicates (phyllosilicates)</td>
<td>2:5 = 4:10</td>
<td>Si$<em>4$O$</em>{10}^{5-}$</td>
<td>pyrophyllite</td>
<td>Al$_4$Si$_3$O$_9$(OH)$_2$</td>
<td></td>
</tr>
<tr>
<td>single-chain silicates (inosilicates)</td>
<td>1:3 = 2:6</td>
<td>SiO$_2$$^{2-}$ or SiO$_4$$^{4-}$</td>
<td>enstatite</td>
<td>Mg$_2$(SiO$_3$)$_2$ or Mg$_2$Si$_2$O$_6$</td>
<td></td>
</tr>
<tr>
<td>double-chain silicates (inosilicates)</td>
<td>4:11 = 8:22</td>
<td>Si$<em>4$O$</em>{10}^{12-}$</td>
<td>tremolite</td>
<td>Ca$_2$Mg$_3$Si$_4$O$_8$(OH)$_2$</td>
<td></td>
</tr>
<tr>
<td>ring silicates (claysilicates)</td>
<td>1:3 = 6:18</td>
<td>Si$<em>4$O$</em>{10}^{12-}$</td>
<td>tourmaline</td>
<td>(Na$<em>x$Ca$</em>{1-x}$Fe$_{1-x}$Mg,$Al$)$_3$Al$_2$(BO$_3$)$_2$Si$_3$O$_6$(OH)$_4$</td>
<td></td>
</tr>
<tr>
<td>isolated tetrahedral (island) silicates (n nosilicates or orthosilicates)</td>
<td>1:4</td>
<td>Si$<em>4$O$</em>{10}^{5-}$</td>
<td>forsterite</td>
<td>Mg$_2$Si$_2$O$_4$</td>
<td></td>
</tr>
<tr>
<td>paired tetrahedral silicates (sorosilicates)</td>
<td>2:7</td>
<td>Si$<em>4$O$</em>{10}^{6-}$</td>
<td>akermanite</td>
<td>Ca$_2$Mg$_2$Si$_2$O$_7$</td>
<td></td>
</tr>
<tr>
<td>more complex silicates</td>
<td>1:4 and 2:7</td>
<td>Si$<em>4$O$</em>{10}^{8-}$ or Si$<em>4$O$</em>{10}^{6-}$</td>
<td>vesuvianite</td>
<td>Ca$<em>{10}$(Mg$</em>{2,25}$Fe$_{0,75}$)$_2$Al$_2$(Si$_2$O$_5$)$_2$(Si$<em>3$O$<em>6$)(OH)$<em>4$ = Ca$</em>{10}$(Mg$</em>{2,25}$Fe$</em>{0,75}$)$_2$Al$_2$Si$_2$O$_7$(OH)$_4$</td>
<td></td>
</tr>
</tbody>
</table>


- (Fe$_x$Mg$_{1-x}$)$_2$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**

**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</td>
<td>1.4</td>
<td>-282₃</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.89</td>
<td>1.15</td>
<td>-176</td>
</tr>
<tr>
<td>SrO</td>
<td>1.59</td>
<td></td>
<td>-93.6</td>
</tr>
<tr>
<td>BaO</td>
<td>1.45</td>
<td>1.15</td>
<td>-127</td>
</tr>
<tr>
<td>CaO</td>
<td>2.00</td>
<td>1.0</td>
<td>-58.0</td>
</tr>
<tr>
<td>MnO</td>
<td>2.41</td>
<td></td>
<td>5.4</td>
</tr>
<tr>
<td>FeO</td>
<td>2.56</td>
<td></td>
<td>16.0</td>
</tr>
<tr>
<td>La₂O₃</td>
<td>2.58</td>
<td></td>
<td>-42.6</td>
</tr>
<tr>
<td>CoO</td>
<td>2.68</td>
<td></td>
<td>23.0</td>
</tr>
<tr>
<td>Nd₂O₃</td>
<td>2.71</td>
<td></td>
<td>-28.4</td>
</tr>
<tr>
<td>CuO</td>
<td>2.74</td>
<td></td>
<td>33.0</td>
</tr>
<tr>
<td>MgO</td>
<td>2.77</td>
<td>0.76</td>
<td>-4.8</td>
</tr>
<tr>
<td>Sm₂O₃</td>
<td>2.78</td>
<td></td>
<td>-26.5</td>
</tr>
<tr>
<td>Eu₂O₃</td>
<td>2.81</td>
<td></td>
<td>-22.1</td>
</tr>
<tr>
<td>Gd₂O₃</td>
<td>2.85</td>
<td></td>
<td>-24.2</td>
</tr>
<tr>
<td>NiO</td>
<td>2.90</td>
<td></td>
<td>37.0</td>
</tr>
<tr>
<td>Dy₂O₃</td>
<td>2.92</td>
<td></td>
<td>-17.0</td>
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<tr>
<td>Y₂O₃</td>
<td>2.94</td>
<td></td>
<td>-20.6</td>
</tr>
<tr>
<td>Ho₂O₃</td>
<td>2.96</td>
<td></td>
<td>-16.7</td>
</tr>
<tr>
<td>Er₂O₃</td>
<td>2.99</td>
<td></td>
<td>-15.9</td>
</tr>
<tr>
<td>Tm₂O₃</td>
<td>3.02</td>
<td></td>
<td>-15.7</td>
</tr>
<tr>
<td>Yb₂O₃</td>
<td>3.05</td>
<td></td>
<td>-13.2</td>
</tr>
<tr>
<td>Lu₂O₃</td>
<td>3.07</td>
<td></td>
<td>-11.44</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.33</td>
<td></td>
<td>17.9</td>
</tr>
<tr>
<td>Sc₂O₃</td>
<td>3.45</td>
<td>0.6</td>
<td>-18.8</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>4.65</td>
<td></td>
<td>26.7</td>
</tr>
<tr>
<td>Zr₂O₃</td>
<td>4.76</td>
<td></td>
<td>22.2</td>
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<tr>
<td>Ga₂O₃</td>
<td>4.84</td>
<td></td>
<td>18.0</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>4.88</td>
<td></td>
<td>11.2</td>
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<tr>
<td>Mn₂O₃</td>
<td>5.17</td>
<td></td>
<td>34.6</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.60</td>
<td>0.605</td>
<td>11.0</td>
</tr>
<tr>
<td>Ti₂O₃</td>
<td>6.61</td>
<td></td>
<td>19.6</td>
</tr>
<tr>
<td>BeO</td>
<td>7.41</td>
<td></td>
<td>14.4</td>
</tr>
<tr>
<td>GeO₂</td>
<td>7.55</td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>WO₃</td>
<td>14.3</td>
<td></td>
<td>10.1</td>
</tr>
<tr>
<td>MoO₃</td>
<td>14.6</td>
<td></td>
<td>3.3</td>
</tr>
<tr>
<td>SiO₂</td>
<td>15.4</td>
<td>0.48</td>
<td>-1.8</td>
</tr>
</tbody>
</table>
Partial Thermodynamics Quantities: Activity and Vapor Pressure Measurement

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

\[ a = \gamma \cdot C \]

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

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

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

Mass Spectrometer

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

\[ P_M = \text{partial pressure of } M; \]

\[ k = \text{instrument constant}; \ I = \text{ion intensity}; \]

\[ T = \text{Absolute temperature}; \]

\[ \sigma = \text{ionization cross section} \]

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

Tables = 342 kJ/mol

\[ \text{Black numbers = order data taken on 2-16-10} \]

\[ \text{Green numbers = order data taken on 2-17-10} \]
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-α}B_{1-β}C_{1-γ}**
Same Phase; Variable Stoichiometry

FeO(s) = Fe(g) + 1/2 O₂(g)

FeO(solution, a < 1) = Fe(g) + 1/2 O₂(g)

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

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

Exact approach depends on the system

RE-silicates - Reducing agent is used for to boost vaporization of SiO₂ 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

The intensity \( p_i \) of a component \( i \) is given by:

\[
p_i = k \frac{I_i T}{S_i}
\]

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

Olivine and Rare – Earth Silicates

Intensity → Pressure → Activity
Olivine - Results
Olivine – Starting Material and Characterization

93% forsterite and 7% fayalite, \( \text{Fo}_{93}\text{Fa}_{7} \) - \((\text{Fe}_{0.7}\text{Mg}_{0.93})_{2}\text{SiO}_{4}\)

**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>5.01(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.

**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%

**XRD pattern and Rietveld refinement of the as received olivine samples.**
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</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 Shairer.

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

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

\[ \text{Fe, Mg or Si} \]
\[ \text{MO}_{(\text{solution, } a<1)} = \text{M}_g + \frac{1}{2}\text{O}_2(g) \]

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

\[ a_{MO} = \frac{P_M [P_{O_2}]^{1/2}}{P^o_M [P^o_{O_2}]^{1/2}} \]

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

\[
\text{SiC} + \frac{3}{2} \text{O}_2(g) = \text{SiO}_2 + \text{CO}(g)
\]

\[
\text{SiO}_2 + 2 \text{H}_2\text{O}(g) = \text{Si(OH)}_4(g)
\]

\[
\text{P[Si(OH)_4]} = K \text{a SiO}_2 [\text{P(H}_2\text{O)}]^2
\]

Y and Yb silicates
Need to be measured!

Key Parameters in Boundary Layer Limited Transport Modeling

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

\[
\text{Flux} = 0.664 \left( \frac{v_x \rho_\infty L}{\eta} \right)^{0.5} \left( \frac{\eta}{D_{\text{Si(OH)}_4} \rho_\infty} \right)^{0.33} \frac{D_{\text{Si(OH)}_4} P_{\text{Si(OH)}_4}}{RTL} = 0.664 \left( \frac{v_x \rho_\infty L}{\eta} \right)^{0.5} \left( \frac{\eta}{D_{\text{Si(OH)}_4} \rho_\infty} \right)^{0.33} \frac{D_{\text{Si(OH)}_4} P_{\text{Si(OH)}_4}}{RTL} \]

\( v_\infty \) = free stream velocity \( \rho_\infty \) = free stream gas density \( L \) = characteristic dimension

\( \eta \) = viscosity \( D_{\text{Si(OH)}_4} \) = gas phase diffusivity of \( \text{Si(OH)}_4 \)

- Reduce \( a(\text{SiO}_2) \) \( \Rightarrow \) reduce recession. Recession drives need for coatings
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 $a(\text{SiO}_2) < \sim 0.02$
    - $2\text{Ta}(s) + 2\text{SiO}_2(\text{soln}) = 2\text{SiO}(g) + \text{TaO}(g) + \text{TaO}_2(g)$
  - For $a(\text{SiO}_2) > \sim 0.02$
    - $\text{Mo}(s) + 3\text{SiO}_2(\text{soln}) = 3\text{SiO}(g) + \text{MoO}_3(g)$
  - 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
  - Gettering pump for CO$_2$
Approaches use two phase regions

Cells are part of the system

1 – Monosilicate + RE₂O₃

Two cells:
- Au
- 3Ta + Y₂O₃ + Y₂O₃ \cdot SiO₂

2Ta(s) + 3\overline{SiO₂}(soln) = 3SiO(g) + TaO(g) + TaO₂(g)

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

\[ K = \left[ \frac{P(SiO)^3 \cdot P(MoO_3)}{a(SiO_2)^3} \right]^{0.33} \]

Mo + 3SiO₂ = 3SiO + MoO₃

\[ a(SiO_2) = \left[ \frac{P(SiO)^3 \cdot P(MoO_3)}{K} \right]^{0.33} \]

Mo + 3SiO₂ = 3SiO + MoO₃

\[ a(SiO_2) = \left[ \frac{I(SiO)^3 \cdot I(MoO_3)}{I'(SiO)^3 \cdot I''(MoO_3)} \right]^{0.33} \]

2 – Monosilicate + Disilicate

Three cells:
- Au (reference)
- 3Mo + Y₂O₃ \cdot 2SiO₂ + Y₂O₃ \cdot SiO₂
- 3Mo + SiO₂

Mo(s) + 3\overline{SiO₂}(soln) = 3SiO(g) + MoO₃(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 + Y₂O₃ + MS

ΔᵥH(Au→1558K) = 342.6 kJ/mol

Tabulated 346.3 kJ/mol
**Y_{2}O_{3} + Y_{2}O_{3} \cdot (SiO_{2})**

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

**Yb_{2}O_{3} + Yb_{2}O_{3} \cdot (SiO_{2})**

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

\[
\begin{align*}
RE_{2}O_{3}(s, 1600 \, K) + SiO_{2}(s, 1600 \, K) & \rightarrow RE_{2}SiO_{5}(s, 1600 \, K) \\
RE_{2}SiO_{5}(s, 1600 \, K) & \rightarrow RE_{2}SiO_{5}(s, 298 \, K) \\
RE_{2}O_{3}(s, 298 \, K) & \rightarrow RE_{2}O_{3}(s, 1600 \, K) \\
SiO_{2}(s, 298 \, K) & \rightarrow SiO_{2}(s, 1600 \, K) \\
2 \, RE(s, 298 \, K) + 3/2 \, O_{2}(g, 298 \, K) & \rightarrow RE_{2}O_{3}(s, 298 \, K) \\
Si(s, 298 \, K) + O_{2}(g, 298 \, K) & \rightarrow SiO_{2}(s, 298 \, K) \\
2 \, RE(s, 298 \, K) + Si(s, 298 \, K) + 5/2 \, O_{2}(g, 298 \, K) & \rightarrow RE_{2}SiO_{5}(s, 298 \, K) \\
\end{align*}
\]

**Optical basicity**

<table>
<thead>
<tr>
<th>RE silicate, 298 K (kJ/mol)</th>
<th>KEMS</th>
<th>Calorimetry*</th>
<th>Optical basicity**</th>
<th>a(SiO_{2}), 1650 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y_{2}O_{3} \cdot (SiO_{2})</td>
<td>-2907 ± 16</td>
<td>-2868.54 ± 5.34</td>
<td>0.786</td>
<td>0.000804</td>
</tr>
<tr>
<td>Yb_{2}O_{3} \cdot (SiO_{2})</td>
<td>-2744 ± 11</td>
<td>-2777.75 ± 16.48</td>
<td>0.729</td>
<td>0.00298</td>
</tr>
</tbody>
</table>

Monosilicate + Disilicate

\[ \text{Y}_2\text{O}_3-\text{SiO}_2 + \text{Y}_2\text{O}_3-2\text{SiO}_2 \]

\[ \text{Yb}_2\text{O}_3-\text{SiO}_2 + \text{Yb}_2\text{O}_3-2\text{SiO}_2 \]

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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

<table>
<thead>
<tr>
<th>Phase</th>
<th>wt (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Y_2O_3.(SiO_2) )</td>
<td></td>
</tr>
<tr>
<td>( Y_2O_3.2(SiO_2) )</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td></td>
</tr>
</tbody>
</table>
\[ Y_2O_3.(SiO_2) + Y_2O_3.2(SiO_2) \]

- Optical basicity**
  - \( Y_2O_3.(SiO_2) \)
    - 0.786
  - \( Yb_2O_3.(SiO_2) \)
    - 0.729
  - \( Y_2O_3.2(SiO_2) \)
    - 0.699
  - \( Yb_2O_3.2(SiO_2) \)
    - 0.657

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

- \( a(SiO_2), 1650 \, K \)
  - 0.281
  - 0.194
Now Have the Needed Quantities for Modeling Recession

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

\[
\text{Flux} = 0.664 \left( \frac{v_\infty \rho_\infty L}{\eta} \right)^{0.5} \left( \frac{\eta}{D_{\text{Si(OH)}_4} \rho_\infty} \right)^{0.33} \frac{D_{\text{Si(OH)}_4}}{RTL} K a_{\text{SiO}_2} (P_{\text{H}_2\text{O}})^2
\]
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)

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