Thermochemistry of Silicates

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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

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


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

..Hot, rocky exoplanets

### 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 SiO₄ Tetrahedra</th>
</tr>
</thead>
<tbody>
<tr>
<td>framework silicates (tectosilicates)</td>
<td>1:2</td>
<td>SiO₂ or ((Al_{1-x}Si_x)O_2)</td>
<td>quartz, albite</td>
<td>SiO₂</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Na₄(AlSi₃)O₉</td>
<td></td>
</tr>
<tr>
<td>sheet silicates (phyllosilicates)</td>
<td>2:5 = 4:10</td>
<td>(Si₂O₇)³⁻</td>
<td>pyrophyllite</td>
<td>Al₂Si₄O₁₀(OH)₂</td>
<td></td>
</tr>
<tr>
<td>single-chain silicates (inosilicates)</td>
<td>1:3 = 2:6</td>
<td>(SiO₂)²⁻ or (Si₂O₆)⁴⁻</td>
<td>enstatite</td>
<td>Mg₂(SiO₄)₂ or Mg₃Si₂O₆</td>
<td></td>
</tr>
<tr>
<td>double-chain silicates (inosilicates)</td>
<td>4:11 = 8:22</td>
<td>(Si₂O₇)¹²⁻</td>
<td>tremolite</td>
<td>Ca₂Mg₃Si₅O₁₈(OH)₂</td>
<td></td>
</tr>
<tr>
<td>ring silicates (closilicates)</td>
<td>1:3 = 6:18</td>
<td>(Si₂O₇)¹²⁻</td>
<td>tourmaline</td>
<td>(Na₁₋₁CaₓFeₓMgₓAl₁₋ₓLiₓAl₂(BO₃)₂Si₅O₁₈(OH)₄</td>
<td></td>
</tr>
<tr>
<td>isolated tetrahedral (isol) silicates (niosilicates or orthosilicates)</td>
<td>1:4</td>
<td>(SiO₄)⁴⁻</td>
<td>forsterite</td>
<td>Mg₂SiO₄</td>
<td></td>
</tr>
<tr>
<td>paired tetrahedral silicates (sorosilicates)</td>
<td>2:7</td>
<td>(SiO₂)⁶⁻</td>
<td>akermanite</td>
<td>Ca₃MgSi₂O₇</td>
<td></td>
</tr>
<tr>
<td>more complex silicates</td>
<td>1:4 and 2:7</td>
<td>(SiO₂)⁴⁻ or (SiO₂)⁶⁻</td>
<td>vesuvianite</td>
<td>CaₓMgₓ(FeₓMg₁₋ₓAl₁₋ₓLiₓAl₂(BO₃)₂Si₅O₁₈(OH)₄) = Caₓ(MgₓFeₓ)Al₂Si₅O₁₈(OH)₄</td>
<td></td>
</tr>
</tbody>
</table>

- (FeₓMg₁₋ₓ)₂SiO₄
- Ortorrombic structure (Pbmn).
- Red – oxygen.
- Blue – A sites, silicon.
- Green – B sites, magnesium or iron.
Thermodynamics and Acid-Base Chemistry

MgO + SiO$_2$ = MgSiO$_3$

**Base**  Acid  Enstatite

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

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

- $z/r < 2$ strongly basic
- $2 \leq z/r < 4$ basic
- $4 < z/r < 7$ amphoteric
- $z/r >$ acidic

**Thermodynamic Activity as Indicator of Stability?**

$$ a = \gamma \cdot C $$

**Table 2. Acid-base scales for oxides**

<table>
<thead>
<tr>
<th>Oxide $^{d}$</th>
<th>$z/r$ of cation</th>
<th>Optical basicity</th>
<th>Enthalpy of solution (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{K}_2\text{O}$</td>
<td>0.66$^{c}$</td>
<td>1.4$^{c}$</td>
<td>-282$^{d}$</td>
</tr>
<tr>
<td>$\text{Na}_2\text{O}$</td>
<td>0.89</td>
<td>1.15</td>
<td>-176</td>
</tr>
<tr>
<td>$\text{SrO}$</td>
<td>1.45</td>
<td>1.15</td>
<td>-127</td>
</tr>
<tr>
<td>$\text{BaO}$</td>
<td>1.59</td>
<td>-93.6</td>
<td>-59.2</td>
</tr>
<tr>
<td>$\text{CaO}$</td>
<td>2.00</td>
<td>1.0</td>
<td>-58.0</td>
</tr>
<tr>
<td>$\text{MgO}$</td>
<td>2.41</td>
<td>5.4</td>
<td>-23.5</td>
</tr>
<tr>
<td>$\text{FeO}$</td>
<td>2.56</td>
<td>16.0</td>
<td></td>
</tr>
<tr>
<td>$\text{MnO}_2$</td>
<td>2.58</td>
<td>-42.6</td>
<td></td>
</tr>
<tr>
<td>$\text{CoO}$</td>
<td>2.68</td>
<td>23.0</td>
<td></td>
</tr>
<tr>
<td>$\text{NiO}$</td>
<td>2.71</td>
<td>-28.4</td>
<td></td>
</tr>
<tr>
<td>$\text{FeO}_2$</td>
<td>2.74</td>
<td>33.0</td>
<td></td>
</tr>
<tr>
<td>$\text{MgO}$</td>
<td>2.77</td>
<td>0.76</td>
<td>-4.8</td>
</tr>
<tr>
<td>$\text{Sm}_2\text{O}_3$</td>
<td>2.78</td>
<td>-26.5</td>
<td></td>
</tr>
<tr>
<td>$\text{Eu}_2\text{O}_3$</td>
<td>2.81</td>
<td>-22.1</td>
<td></td>
</tr>
<tr>
<td>$\text{Gd}_2\text{O}_3$</td>
<td>2.85</td>
<td>-24.2</td>
<td></td>
</tr>
<tr>
<td>$\text{Nd}_2\text{O}_3$</td>
<td>2.90</td>
<td>37.0</td>
<td></td>
</tr>
<tr>
<td>$\text{ Dy}_2\text{O}_3$</td>
<td>2.92</td>
<td>-17.0</td>
<td></td>
</tr>
<tr>
<td>$\text{Y}_{2}\text{O}_3$</td>
<td>2.94</td>
<td>-20.6</td>
<td></td>
</tr>
<tr>
<td>$\text{Er}_2\text{O}_3$</td>
<td>2.98</td>
<td>-15.9</td>
<td></td>
</tr>
<tr>
<td>$\text{Tm}_2\text{O}_7$</td>
<td>3.02</td>
<td>-15.7</td>
<td></td>
</tr>
<tr>
<td>$\text{Yb}_2\text{O}_7$</td>
<td>3.05</td>
<td>-13.2</td>
<td></td>
</tr>
<tr>
<td>$\text{Lu}_2\text{O}_7$</td>
<td>3.07</td>
<td>-11.4</td>
<td></td>
</tr>
<tr>
<td>$\text{ZrO}_2$</td>
<td>3.33</td>
<td>17.9</td>
<td></td>
</tr>
<tr>
<td>$\text{Sc}_2\text{O}_3$</td>
<td>3.45</td>
<td>-0.6</td>
<td></td>
</tr>
<tr>
<td>$\text{Mg}_2\text{SiO}_4$</td>
<td>4.65</td>
<td>26.7</td>
<td></td>
</tr>
<tr>
<td>$\text{ZrO}_2$</td>
<td>4.76</td>
<td>22.2</td>
<td></td>
</tr>
<tr>
<td>$\text{Ga}_2\text{O}_3$</td>
<td>4.84</td>
<td>18.0</td>
<td></td>
</tr>
<tr>
<td>$\text{Cr}_2\text{O}_3$</td>
<td>4.88</td>
<td>11.2</td>
<td></td>
</tr>
<tr>
<td>$\text{Mn}_3\text{O}_5$</td>
<td>5.17</td>
<td>34.6</td>
<td></td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>5.60</td>
<td>0.605</td>
<td>11.0</td>
</tr>
<tr>
<td>$\text{TiO}_2$</td>
<td>6.61</td>
<td>10.8</td>
<td>19.6</td>
</tr>
<tr>
<td>$\text{BeO}$</td>
<td>7.41</td>
<td>14.4</td>
<td></td>
</tr>
<tr>
<td>$\text{GeO}_2$</td>
<td>7.55</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>$\text{WO}_3$</td>
<td>14.3</td>
<td>10.1</td>
<td></td>
</tr>
<tr>
<td>$\text{MoO}_3$</td>
<td>14.6</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>$\text{SiO}_2$</td>
<td>15.4</td>
<td>0.48</td>
<td>-1.8</td>
</tr>
</tbody>
</table>

A. Navrotsky, American Mineralogist, 79, 589-605, 1994..
Partial Thermodynamics Quantities: Activity and Vapor Pressure Measurement

Activity

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

Pressure

\[ a = \gamma \cdot C \]

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

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

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

Mass Spectrometer

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

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

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

Tables = 342 kJ/mol
Thermodynamic Activities

- Important solution parameters
- Quantify how vapor pressure is reduced due to solution formation
- Example: Olivine—can treat as solution of FeO, MgO, SiO$_2$
- Use data to calculate thermodynamic activity of each component
- Measure thermodynamic parameters for olivine solutions
  - e.g. $\ln a(\text{FeO})$ 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

$\text{FeO(s)} = \text{Fe(g)} + 1/2O_2(g)$

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

$K_p = \frac{P_{\text{Fe}}[P_{O_2}]}{a_{\text{FeO}}}$

$a_{\text{FeO}} = \frac{P_{\text{Fe}}[P_{O_2}]^{1/2}}{P_{\text{Fe}}^o[P_{O_2}^o]^{1/2}}$
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 $\rightarrow$ 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 $1 \times 10^{-10}$ 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

Use Multi-Cell Flange for a(SiO$_2$)

Olivine and Rare – Earth Silicates

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

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

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 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%
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>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>
</tr>
<tr>
<td>Ca</td>
<td>0.035(2)</td>
<td>0.009(2)</td>
<td>0.04(2)</td>
</tr>
<tr>
<td>Co</td>
<td>0.0120(6)</td>
<td>0.003(2)</td>
<td>0.004(3)</td>
</tr>
<tr>
<td>Cr</td>
<td>0.052(3)</td>
<td>0.035(4)</td>
<td>0.06(1)</td>
</tr>
<tr>
<td>Fe</td>
<td>5.01(3)</td>
<td>0.006(3)</td>
<td>0.93(3)</td>
</tr>
<tr>
<td>Mg</td>
<td>30(2)</td>
<td>35.0(1)</td>
<td>34(1)</td>
</tr>
<tr>
<td>Mn</td>
<td>0.075(4)</td>
<td>0.003(1)</td>
<td>0.031(3)</td>
</tr>
<tr>
<td>Na</td>
<td>0.0080(4)</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>
</tr>
<tr>
<td>Sc</td>
<td>0.0040(2)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Si</td>
<td>20(1)</td>
<td>19.3(1)</td>
<td>21.8(8)</td>
</tr>
<tr>
<td>Mo</td>
<td>0</td>
<td>0.04(2)</td>
<td>0</td>
</tr>
<tr>
<td>Ir</td>
<td>0</td>
<td>0</td>
<td>0.06(3)</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 - \((\text{Fe}_x\text{Mg}_{1-x})_2\text{SiO}_4\)

Fe, Mg or Si

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

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

\[ a_{MO} = \frac{P_M [P_{O_2}]^{1/2}}{P_M^0 [P_{O_2}^0]^{1/2}} \]

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

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

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

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

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)

- Reduce \( a(\text{SiO}_2) \) \( \Rightarrow \) reduce recession. Recession drives need for coatings

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

- \( v_\infty \) = free stream velocity \( \rho_\infty \) = free stream gas density \( L \) = characteristic dimension
- \( \eta \) = viscosity \( D_{\text{Si(OH)}_4} \) = gas phase diffusivity of \( \text{Si(OH)}_4 \)
Indirect evidence suggests that the SiO\textsubscript{2} thermodynamic activity is lower in the Y\textsubscript{2}O\textsubscript{3}-Y\textsubscript{2}SiO\textsubscript{5} and Y\textsubscript{2}SiO\textsubscript{5}-Y\textsubscript{2}Si\textsubscript{2}O\textsubscript{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 $a(\text{SiO}_2) < ~0.02$
    - $2\text{Ta}(s) + 2\text{SiO}_2(\text{soln}) = 2\text{SiO}(g) + \text{TaO}(g) + \text{TaO}_2(g)$
  - For $a(\text{SiO}_2) > ~0.02$
    - $\text{Mo}(s) + 3\text{SiO}_2(\text{soln}) = 3\text{SiO}(g) + \text{MoO}_3(g)$
  - 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 · SiO₂

2Ta(s) + 3SiO₂(soln) = 3SiO(g) + TaO(g) + TaO₂(g)

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

2 – Monosilicate + Disilicate

Three cells:
• Au (reference)
• 3Mo + Y₂O₃ · 2SiO₂ + Y₂O₃ · SiO₂
• 3Mo + SiO₂

Mo(s) + 3SiO₂(soln) = 3SiO(g) + MoO₃(g)

- Compare cells 1 and 2
- Less data processing than with Ta
- Correction is not needed.

$$K = \left[\frac{P(SiO)^3}{P(MoO_3)^n}\right]^{\frac{1}{a(SiO_2)}}$$

$$Mo + 3SiO_2 = 3SiO + MoO_3$$

$$a(SiO_2) = 1 - \frac{\left[\frac{P(SiO)^3}{P(MoO_3)^n}\right]}{K}$$

$$Mo + 3SiO_2 = 3SiO + MoO_3$$

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

Cell 2

Cell 3
Monosilicate + RE$_2$O$_3$

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

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

\[ \Delta_v H(\text{Au} \rightarrow 1558\text{K}) = 342.6 \text{ kJ/mol} \]

Tabulated 346.3 kJ/mol
Y\textsubscript{2}O\textsubscript{3} + Y\textsubscript{2}O\textsubscript{3}·(SiO\textsubscript{2})

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

Yb\textsubscript{2}O\textsubscript{3} + Yb\textsubscript{2}O\textsubscript{3}·(SiO\textsubscript{2})

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

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

\( \Delta H_1 = \text{measured in this work} \)

\( \Delta H_2 = H_{1600 \text{ K}} - H_{298 \text{ K}} \)

\( \Delta H_3 \)

\( \Delta H_4 \)

\( \Delta H_5 \)

\( \Delta H_6 \)

\( \Delta H_7 = \Delta H_{f, \text{RE}_2\text{SiO}_5, 298 \text{ K}} \)

\( \Delta H_{f, \text{RE silicate, 298 K}} \text{ (kJ/mol)} \)

<table>
<thead>
<tr>
<th>\text{RE}_2\text{O}_3·(SiO}_2)</th>
<th>\text{KEMS}</th>
<th>\text{Calorimetry*}</th>
<th>\text{Optical basicity**}</th>
<th>a(SiO}_2), 1650 \text{ K}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y\textsubscript{2}O\textsubscript{3}·(SiO\textsubscript{2})</td>
<td>-2907 ± 16</td>
<td>-2868.54 ± 5.34</td>
<td>0.786</td>
<td>0.000804</td>
</tr>
<tr>
<td>Yb\textsubscript{2}O\textsubscript{3}·(SiO\textsubscript{2})</td>
<td>-2744 ± 11</td>
<td>-2777.75 ±16.48</td>
<td>0.729</td>
<td>0.000298</td>
</tr>
</tbody>
</table>

*Liang et al. “Enthalpy of formation of rare-earth silicates Y\textsubscript{2}SiO\textsubscript{5} and Yb\textsubscript{2}SiO\textsubscript{5} and N-containing silicate Y\textsubscript{10}(SiO\textsubscript{4})\textsubscript{6}N\textsubscript{2},” J. Mater. Res. 14 [4], 1181-1185. **J. A. Duff, J. Phys. Chem. A 110, 13245 (2006)
Monosilicate + Disilicate

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

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

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

<table>
<thead>
<tr>
<th>Phase</th>
<th>wt (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Y}_2\text{O}_3.\text{(SiO}_2\text{)})</td>
<td>56</td>
</tr>
<tr>
<td>(\text{Yb}_2\text{O}_3.\text{2(SiO}_2\text{)})</td>
<td>36</td>
</tr>
<tr>
<td>Mo</td>
<td>8</td>
</tr>
</tbody>
</table>
\[ Y_2O_3 \cdot (SiO_2) + Y_2O_3 \cdot 2(SiO_2) \]

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

**Optical basicity**

<table>
<thead>
<tr>
<th>Compound</th>
<th>1650 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y_2O_3 \cdot (SiO_2)</td>
<td>0.786</td>
</tr>
<tr>
<td>Y_2O_3 \cdot 2(SiO_2)</td>
<td>0.699</td>
</tr>
<tr>
<td>Yb_2O_3 \cdot (SiO_2)</td>
<td>0.729</td>
</tr>
<tr>
<td>Yb_2O_3 \cdot 2(SiO_2)</td>
<td>0.657</td>
</tr>
</tbody>
</table>

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

- 0.281
- 0.194
Now Have the Needed Quantities for Modeling Recession

- \( T = 1300^\circ C; P = 10 \text{ bar}; P(H_2O) = 1 \text{ bar} \)
- \( v_\infty = 20 \text{ m/s} \)
- \( L = 10 \text{ cm} \)
- \( \eta = 5 \times 10^{-4} \text{ g/cm-s} \)
- \( \rho_\infty = 2.2 \times 10^{-3} \text{ g/cc} \)
- \( D_{Si(OH)_4} = 0.19 \text{ cm}^2/\text{s} \)
- \( \log K = -2851.2/T – 3.5249 \text{ (Si(OH)_4(g) transpiration measurements)} \)
- \( a(SiO_2) \text{ from activity measurements} \)

\[
Flux = 0.664 \left( \frac{v_\infty \rho_\infty L}{\eta} \right)^{0.5} \left( \frac{\eta}{D_{Si(OH)_4} \rho_\infty} \right)^{0.33} \frac{D_{Si(OH)_4}}{RTL} K a_{SiO_2} \left( P_{H_2O} \right)^2
\]
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

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• XRD: R. Rogers (NASA Glenn)

• NASA/ORAU Post-doctoral Fellowship Program