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$_2$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

### 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 ((\text{Al}<em>x\text{Si}</em>{1-x})\text{O}_2)</td>
<td>quartzalbite</td>
<td>SiO₂, NaAlSi₃O₈</td>
<td></td>
</tr>
<tr>
<td>sheet silicates (phyllosilicates)</td>
<td>2:5 ≈ 4:10</td>
<td>((\text{Si}_2\text{O}_5)^{2-})</td>
<td>pyrophylite</td>
<td>Al₂Si₄O₁₀(OH)₂</td>
<td></td>
</tr>
<tr>
<td>single-chain silicates (inosilicates)</td>
<td>1:3 = 2:6</td>
<td>((\text{Si}_2\text{O}_3)^{2-}) or ((\text{Si}_2\text{O}_4)^{4-})</td>
<td>enstatite</td>
<td>Mg₂(SiO₄)₂ or Mg₂Si₂O₆</td>
<td></td>
</tr>
<tr>
<td>double-chain silicates (inosilicates)</td>
<td>4:11 = 8:22</td>
<td>((\text{Si}<em>4\text{O}</em>{10})^{12-})</td>
<td>tremolite</td>
<td>Ca₂Mg₃Si₄O₁₀(OH)₂</td>
<td></td>
</tr>
<tr>
<td>ring silicates (claysilicates)</td>
<td>1:3 = 6:18</td>
<td>((\text{Si}_2\text{O}_3)^{12-})</td>
<td>tourmaline</td>
<td>((\text{Na}_x\text{Ca}_y\text{Fe}_z\text{Mg},\text{Al})(\text{BO}_3)\text{Si}_3\text{O}_10\text{(OH)}_4)</td>
<td></td>
</tr>
<tr>
<td>isolated tetrahedral (island) silicates (notosilicates or orthosilicates)</td>
<td>1:4</td>
<td>((\text{Si}<em>4\text{O}</em>{10})^{6-})</td>
<td>forsterite</td>
<td>Mg₂SiO₄</td>
<td></td>
</tr>
<tr>
<td>paired tetrahedral silicates (sorosilicates)</td>
<td>2:7</td>
<td>((\text{Si}_2\text{O}_7)^{6-})</td>
<td>akermanite</td>
<td>Ca₂MgSi₂O₇</td>
<td></td>
</tr>
<tr>
<td>more complex silicates</td>
<td>1:4 and 2:7</td>
<td>((\text{Si}_2\text{O}_5)^{4-}) and ((\text{Si}_2\text{O}_7)^{6-})</td>
<td>vesuvianite</td>
<td>(\text{Ca}_{10}(\text{Mg},\text{Fe})_2\text{Al}_2(\text{Si}_2\text{O}_7)_2(\text{OH})_4)</td>
<td>(\text{Ca}_{10}(\text{Mg},\text{Fe})_2\text{Al}_2\text{Si}<em>3\text{O}</em>{10}\text{(OH)}_6)</td>
</tr>
</tbody>
</table>

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

MgO + SiO₂ = MgSiO₃

Base \hspace{1cm} Acid \hspace{1cm} 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**

**Thermodynamic Activity as Indicator of Stability?**

\[ a = \gamma \cdot C \]

<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>-282</td>
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<tr>
<td>Na₂O</td>
<td>0.89</td>
<td>1.15</td>
<td>-176</td>
</tr>
<tr>
<td>BaO</td>
<td>1.45</td>
<td>1.15</td>
<td>-127</td>
</tr>
<tr>
<td>SrO</td>
<td>1.59</td>
<td></td>
<td>-93.6</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>( \frac{1}{2} )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>( \frac{1}{2} )Nd₂O₃</td>
<td>2.71</td>
<td></td>
<td>-28.4</td>
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<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>( \frac{1}{2} )Sm₂O₃</td>
<td>2.78</td>
<td></td>
<td>-26.5</td>
</tr>
<tr>
<td>( \frac{1}{2} )Eu₂O₃</td>
<td>2.81</td>
<td></td>
<td>-22.1</td>
</tr>
<tr>
<td>( \frac{1}{2} )Gd₂O₃</td>
<td>2.85</td>
<td></td>
<td>-24.2</td>
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<tr>
<td>NiO</td>
<td>2.90</td>
<td></td>
<td>37.0</td>
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<tr>
<td>( \frac{1}{2} )Dy₂O₃</td>
<td>2.92</td>
<td></td>
<td>17.0</td>
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<tr>
<td>( \frac{1}{2} )Y₂O₃</td>
<td>2.94</td>
<td></td>
<td>-20.6</td>
</tr>
<tr>
<td>( \frac{1}{2} )Ho₂O₃</td>
<td>2.96</td>
<td></td>
<td>-16.7</td>
</tr>
<tr>
<td>( \frac{1}{2} )Er₂O₃</td>
<td>2.99</td>
<td></td>
<td>-15.9</td>
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<tr>
<td>( \frac{1}{2} )Tm₂O₃</td>
<td>3.02</td>
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<tr>
<td>( \frac{1}{2} )Yb₂O₃</td>
<td>3.05</td>
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<td>-13.2</td>
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<tr>
<td>( \frac{1}{2} )Lu₂O₃</td>
<td>3.07</td>
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<tr>
<td>ZnO</td>
<td>3.33</td>
<td></td>
<td>17.9</td>
</tr>
<tr>
<td>( \frac{1}{2} )Sc₂O₃</td>
<td>3.45</td>
<td></td>
<td>-0.6</td>
</tr>
<tr>
<td>( \frac{1}{2} )Fe₂O₃</td>
<td>4.65</td>
<td></td>
<td>26.7</td>
</tr>
<tr>
<td>( \frac{1}{2} )Zr₂O₃</td>
<td>4.76</td>
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<td>22.2</td>
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<tr>
<td>( \frac{1}{2} )Ga₂O₃</td>
<td>4.84</td>
<td></td>
<td>18.0</td>
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<tr>
<td>( \frac{1}{2} )Cr₂O₃</td>
<td>4.88</td>
<td></td>
<td>11.2</td>
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<tr>
<td>( \frac{1}{2} )Mn₂O₃</td>
<td>5.17</td>
<td></td>
<td>34.6</td>
</tr>
<tr>
<td>( \frac{1}{2} )Al₂O₃</td>
<td>5.60</td>
<td>0.605</td>
<td>11.0</td>
</tr>
<tr>
<td>( \frac{1}{2} )TiO₂</td>
<td>6.61</td>
<td></td>
<td>19.6</td>
</tr>
<tr>
<td>BeO</td>
<td>7.41</td>
<td></td>
<td>5.3</td>
</tr>
<tr>
<td>( \frac{1}{2} )GeO₂</td>
<td>7.55</td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>( \frac{1}{2} )WO₃</td>
<td>14.3</td>
<td></td>
<td>10.1</td>
</tr>
<tr>
<td>( \frac{1}{2} )MoO₃</td>
<td>14.6</td>
<td></td>
<td>3.3</td>
</tr>
<tr>
<td>( \frac{1}{2} )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

Activity
Pressure

\[M (s) = M (g)\]

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

\[a = \gamma \cdot C\]

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

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

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

Mass Spectrometer

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

\(P_M = \text{partial pressure of } M;\)

\(k = \text{instrument constant}; I = \text{ion intensity};\)

\(T = \text{Absolute temperature};\)

\(\sigma = \text{ionization cross section}\)

\[\text{Au(ℓ) = Au(g)}\]

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

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 \( \text{FeO}, \text{MgO}, \text{SiO}_2 \)
• 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

\[
\text{FeO}(s) = \text{Fe}(g) + \frac{1}{2} \text{O}_2(g)
\]

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

\[
\text{FeO(solute, } a < 1) = \text{Fe}(g) + \frac{1}{2} \text{O}_2(g)
\]

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

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

Exact approach depends on the system

RE-silicates - Reducing agent is used for to boost vaporization of $\text{SiO}_2$ 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

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>Wt (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample as received</td>
</tr>
<tr>
<td>Al</td>
<td>0.0120(6)</td>
</tr>
<tr>
<td>Ca</td>
<td>0.035(2)</td>
</tr>
<tr>
<td>Co</td>
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<tr>
<td>Cr</td>
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<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>
<tr>
<td>Mo</td>
<td>0</td>
</tr>
<tr>
<td>Ir</td>
<td>0</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 - \((\text{Fe}_x\text{Mg}_{1-x})_2\text{SiO}_4\)

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

\[\log(a_{\text{MgO}}) = \frac{P_M [P_{O_2}]^{1/2}}{P_M^0 [P_{O_2}^0]^{1/2}}\]

Fe, Mg or Si

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

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

Fe, Mg or Si

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

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

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

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

Y and Yb silicates
Need to be measured!

Key Parameters in Boundary Layer Limited Transport Modeling

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

- \( \nu = 0 \)  

- **Free Stream Gas Velocity**  

- **Combustion Gases**  

- **Si(OH)_4(g)**  

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

- \( v_\infty = \text{free stream velocity} \)  
- \( \rho_\infty = \text{free stream gas density} \)  
- \( L = \text{characteristic dimension} \)  
- \( \eta = \text{viscosity} \)  
- \( D_{\text{Si(OH)}} = \text{gas phase diffusivity of Si(OH)}_4 \)

- **Reduce a(\text{SiO}_2) \Rightarrow reduce recession.** Recession drives need for **coatings**
Indirect evidence suggests that the \( \text{SiO}_2 \) thermodynamic activity is lower in the \( \text{Y}_2\text{O}_3-\text{Y}_2\text{SiO}_5 \) and \( \text{Y}_2\text{SiO}_5-\text{Y}_2\text{Si}_2\text{O}_7 \) regions. But there are no direct measurements!
Issues with Measuring $a$(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 $a$(SiO$_2$) $< ~0.02$
    - $2$Ta(s) + $2$SiO$_2$(soln) = $2$SiO(g) + TaO(g) + TaO$_2$(g)
  - For $a$(SiO$_2$) $> ~0.02$
    - Mo(s) + $3$SiO$_2$(soln) = $3$SiO(g) + 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

1 – Monosilicate + RE₂O₃

Two cells:
- Au
- 3Ta + Y₂O₃ + Y₂O₃ · SiO₂

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

- Using \( P_{eq}(\text{SiO}) \) 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.
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$_3$.($\text{SiO}_2$) → RE$_2$O$_{3(s)}$(s, 1600 K) + SiO$_2$(s, 1600 K)

RE$_2$O$_{3(s)}$(s, 1600 K) + SiO$_2$(s, 1600 K) → RE$_2$SiO$_5$(s, 1600 K)

RE$_2$SiO$_5$(s, 298 K) → RE$_2$SiO$_5$(s, 1600 K)

SiO$_2$(s, 298 K) → SiO$_2$(s, 1600 K)

2 RE$_{(s, 298 K)}$ + 3/2 O$_{(2g, 298 K)}$ → RE$_2$O$_3$(s, 298 K)

Si$_{(s, 298 K)}$ + O$_2$(g, 298 K) → SiO$_2$(s, 298 K)

2 RE$_{(s, 298 K)}$ + Si$_{(s, 298 K)}$ + 5/2 O$_2$(g, 298 K) → RE$_2$SiO$_5$(s, 298 K)

ΔH$_1$ = measured in this work

ΔH$_2$ = H$_{1600 K}$ − H$_{298 K}$

ΔH$_3$

ΔH$_4$

ΔH$_5$

ΔH$_6$

ΔH$_7$ = ΔH$_f$.RE$_2$SiO$_5$,298 K

ΔH$_f$.RE silicate, 298 K (kJ/mol)

KEMS Calorimetry* Optical basicity** a(SiO$_2$), 1650 K

Y$_2$O$_3$.($\text{SiO}_2$) -2907 ± 16 -2868.54 ± 5.34 0.786 0.000804

Yb$_2$O$_3$.($\text{SiO}_2$) -2744 ± 11 -2774.75 ± 16.48 0.729 0.00298

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

Phase
$Y_2O_3.(SiO_2)$
$Y_2O_3.2(SiO_2)$
Mo

Phase
$Yb_2O_3.(SiO_2)$
$Yb_2O_3.2(SiO_2)$
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**

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

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

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