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 (Al₆Si₄O₁₄)O₂⁻</td>
<td>quartz</td>
<td>SiO₂</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>albite</td>
<td>Na(AlSi₃)O₈</td>
<td></td>
</tr>
<tr>
<td>sheet silicates (phyllosilicates)</td>
<td>2:5 ~ 4:10</td>
<td>(Si₂O₅)⁴⁻</td>
<td>pyrophyllite</td>
<td>Al₄Si₄O₁₀(OH)₂</td>
<td></td>
</tr>
<tr>
<td>single-chain silicates (inosilicates)</td>
<td>1:3 ~ 2:6</td>
<td>(SiO₂)²⁻ or (Si₂O₅)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>(Si₂O₅)₁²⁻</td>
<td>tremolite</td>
<td>Ca₂Mg₃Si₄O₁₂(OH)₂</td>
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</tr>
<tr>
<td>ring silicates (closilicates)</td>
<td>1:3 ~ 6:18</td>
<td>(Si₂O₅)₁²⁻</td>
<td>tourmaline</td>
<td>(NaₓCaₓFeₓMgₓAlₓLiₓ)₂Al₂(BO₃)₂Si₄O₁₂(OH)₄</td>
<td></td>
</tr>
<tr>
<td>isolated tetrahedral (island) silicates</td>
<td>1:4</td>
<td>(SiO₄)⁴⁻</td>
<td>forsterite</td>
<td>Mg₂SiO₄</td>
<td></td>
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<tr>
<td>paired tetrahedral silicates (sorosilicates)</td>
<td>2:7</td>
<td>(Si₂O₇)⁶⁻</td>
<td>akermanite</td>
<td>Ca₉Mg₅Si₇O₂₂</td>
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<tr>
<td>more complex silicates</td>
<td>1:4 and 2:7</td>
<td>(SiO₄)⁴⁻ and (Si₂O₅)⁴⁻</td>
<td>vesuvianite</td>
<td>Ca₁₀(AlₓMgₓFeₓ)₄Si₄O₁₆(OH)₄ = Ca₁₀/₄(AlₓMgₓFeₓ)₄Al₂Si₄O₁₂(OH)₄</td>
<td></td>
</tr>
</tbody>
</table>

- (FeₓMg₁₋ₓ)₂SiO₄
- Ortorrombic structure (\(Pbnm\)).
- Red – oxygen.
- Blue – A sites, silicon.
- Green – B sites, magnesium or iron.

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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>B</th>
<th>C</th>
<th>D</th>
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</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>
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<tr>
<td>BaO</td>
<td>1.45</td>
<td>1.15</td>
<td>-127</td>
<td>-67.9</td>
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<tr>
<td>SrO</td>
<td>1.59</td>
<td></td>
<td>-93.6</td>
<td>-59.2</td>
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<tr>
<td>CaO</td>
<td>2.00</td>
<td>1.0</td>
<td>-58.0</td>
<td>-23.5</td>
<td>-37.1</td>
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<tr>
<td>MnO</td>
<td>2.41</td>
<td></td>
<td>5.4</td>
<td></td>
<td></td>
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<tr>
<td>FeO</td>
<td>2.56</td>
<td></td>
<td>16.0</td>
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<tr>
<td>V₂O₅</td>
<td>3.58</td>
<td></td>
<td>-42.6</td>
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<tr>
<td>CoO</td>
<td>2.68</td>
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<td>23.0</td>
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<td>-20.6</td>
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<td>V₂NiO₃</td>
<td>2.71</td>
<td></td>
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<td>CuO</td>
<td>2.74</td>
<td></td>
<td>33.0</td>
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<td>11.1</td>
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<tr>
<td>MgO</td>
<td>2.77</td>
<td>0.76</td>
<td>-4.8</td>
<td>-25.9</td>
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<tr>
<td>V₂SmO₃</td>
<td>2.78</td>
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<tr>
<td>V₂EuO₃</td>
<td>2.81</td>
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<td>-24.2</td>
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<tr>
<td>V₂GdO₃</td>
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<td>NiO</td>
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<tr>
<td>V₂DyO₃</td>
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<td>V₂Y₂O₃</td>
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<td>V₂H₂O₃</td>
<td>2.96</td>
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<tr>
<td>V₂ErO₃</td>
<td>2.99</td>
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<td>V₂TmO₃</td>
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<td>V₂YbO₃</td>
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<td>V₂ScO₃</td>
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<td>17.9</td>
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<tr>
<td>V₂FeO₃</td>
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<td>22.2</td>
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<tr>
<td>V₂GaO₃</td>
<td>4.84</td>
<td></td>
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<tr>
<td>V₂CrO₃</td>
<td>4.88</td>
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<tr>
<td>V₂Mn₂O₅</td>
<td>5.17</td>
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<td>34.6</td>
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<td>V₂Al₂O₅</td>
<td>5.60</td>
<td>0.605</td>
<td>11.0</td>
<td>30.0</td>
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<td>V₂TiO₂</td>
<td>6.61</td>
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<td>10.8</td>
<td>19.6</td>
<td>5.3</td>
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<td>BeO</td>
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<td>14.4</td>
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<td>V₂GeO₂</td>
<td>7.55</td>
<td></td>
<td>1.0</td>
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<tr>
<td>V₂WO₃</td>
<td>14.3</td>
<td></td>
<td></td>
<td></td>
<td>10.1</td>
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<tr>
<td>V₂MoO₃</td>
<td>14.6</td>
<td></td>
<td></td>
<td></td>
<td>3.3</td>
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<tr>
<td>V₂SiO₂</td>
<td>15.4</td>
<td>0.48</td>
<td>-1.8</td>
<td>-6.0</td>
<td></td>
</tr>
</tbody>
</table>

Thermodynamic Activity as Indicator of Stability?

\[ a = \gamma \cdot C \]

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

$$\Delta_v G = \Delta_v H - T\Delta_v S = -RT \ln K_p = -RT \ln(P_M / a_M)$$

$$a = \gamma \cdot C$$

$$\gamma = \text{activity coefficient}; C = \text{concentration}$$

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

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

Mass Spectrometer

$$P_M = \frac{kIT}{\sigma}$$

$$P_M = \text{partial pressure of } M;$$

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

$$T = \text{Absolute temperature};$$

$$\sigma = \text{ionization cross section}$$

$$\Delta_v H^o = \frac{-R \cdot 41.162}{41.162} = 342.20 \text{ kJ/mol}$$

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, 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

FeO(s) = Fe(g) + 1/2 O₂(g)

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

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

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

$$K_p = \frac{P_{Fe}^o [P_{O_2}^o]^{1/2}}{a_{FeO}}$$
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 \( \Rightarrow \) 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 \( a(\text{SiO}_2) \)

Design of E. Copland 2002

Olivine and Rare – Earth Silicates

Intensity \( \rightarrow \) Pressure \( \rightarrow \) Activity

www.nasa.gov
Olivine - Results
Oliven – 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>
<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>
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</tr>
<tr>
<td>Si</td>
<td>20(1)</td>
<td>19.3(1)</td>
<td>21.8(8)</td>
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<tr>
<td>Mo</td>
<td>0</td>
<td>0.04(2)</td>
<td>0</td>
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</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.
Complete van’t Hoff Plot

Interesting discontinuity at melting

Temperature dependence of ion intensity ratios of Mg$^+$, Fe$^+$, SiO$^+$, O$^+$ and O$_2^+$ in the olivine sample.

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

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

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

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

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

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

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

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

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

Y and Yb silicates
Need to be measured!

Key Parameters in Boundary Layer Limited Transport Modeling

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

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

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

- \( v_x \) = free stream velocity  \( \rho_x \) = 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 $a(\text{SiO}_2) < ~0.02$
    - $2\text{Ta}(s) + 2\text{SiO}_2(\text{soln}) = 2\text{SiO}(g) + \text{TaO}(g) + \text{TaO}_2(g)$
  - 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

1 – Monosilicate + RE\textsubscript{2}O\textsubscript{3}

Two cells:
- Au
- \(3\text{Ta} + \text{Y}_{2}\text{O}_3 + \text{Y}_2\text{O}_3 \cdot \text{SiO}_2\)

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

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

2 – Monosilicate + Disilicate

Three cells:
- Au (reference)
- \(3\text{Mo} + \text{Y}_2\text{O}_3 \cdot 2\text{SiO}_2 + \text{Y}_2\text{O}_3 \cdot \text{SiO}_2\)
- \(3\text{Mo} + \text{SiO}_2\)

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

- 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

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

<table>
<thead>
<tr>
<th>Phase</th>
<th>wt (%)</th>
<th>Phase</th>
<th>wt (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y$_2$O$_3$.SiO$_2$</td>
<td>41</td>
<td>Yb$_2$O$_3$.SiO$_2$</td>
<td>24</td>
</tr>
<tr>
<td>Y$_2$O$_3$</td>
<td>49</td>
<td>Yb$_2$O$_3$</td>
<td>66</td>
</tr>
<tr>
<td>Ta</td>
<td>4</td>
<td>Ta</td>
<td>2</td>
</tr>
<tr>
<td>Ta$_3$Si</td>
<td>4</td>
<td>Ta$_2$Si</td>
<td>2</td>
</tr>
</tbody>
</table>

Table: Crystallographic data for the phases present in the samples.
Raw Data—log (IT) vs 1/T

Cell (1): Au Reference  
Cell (2): Ta + Y$_2$O$_3$ + MS

Δ$_v$H(Au--1558K) = 342.6 kJ/mol

Tabulated 346.3 kJ/mol
\[
\Delta H_{\text{SiO}_2, 1600 \text{ K}} = (5200.26) \cdot R \cdot 2.303 = 99.57 \text{ kJ/mol}
\]

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

<table>
<thead>
<tr>
<th>(\text{Y}_2\text{O}_3 \cdot \text{SiO}_2)</th>
<th>KEMS</th>
<th>Calorimetry*</th>
<th>Optical basicity**</th>
<th>(a(\text{SiO}_2), 1650 \text{ K})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-2907 \pm 16)</td>
<td>(-2868.54 \pm 5.34)</td>
<td>0.786</td>
<td>0.000804</td>
<td></td>
</tr>
<tr>
<td>(\text{Yb}_2\text{O}_3 \cdot \text{SiO}_2)</td>
<td>(-2744 \pm 11)</td>
<td>(-2774.75 \pm 16.48)</td>
<td>0.729</td>
<td>0.00298</td>
</tr>
</tbody>
</table>

Monosilicate + Disilicate

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

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

**Diagram Details:**
- **Temperature (Kelvin):** 1600 to 2800
- **Mole Fraction SiO$_2$:** 0 to 1

**Thermocalc Parameters:**
- Time: 2010.08.10:09.24
- Database: User
- AC(O)=1, N=1, P=1.01325E5

**Chemical Reactions:**
- $\text{Y}_2\text{O}_3\text{-SiO}_2 + \text{Y}_2\text{O}_3\text{-2SiO}_2$
- $\text{Yb}_2\text{O}_3\text{-SiO}_2 + \text{Yb}_2\text{O}_3\text{-2SiO}_2$
XRD after KEMS Measurements of RE Monosilicates + Disilicates + Mo:

Yttrium monosilicate + disilicate + Mo

<table>
<thead>
<tr>
<th>Phase</th>
<th>wt (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y₂O₃.(SiO₂)</td>
<td></td>
</tr>
<tr>
<td>Y₂O₃.2(SiO₂)</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td></td>
</tr>
</tbody>
</table>

Ytterbium monosilicate + disilicate + Mo

<table>
<thead>
<tr>
<th>Phase</th>
<th>wt (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb₂O₃.(SiO₂)</td>
<td>56</td>
</tr>
<tr>
<td>Yb₂O₃.2(SiO₂)</td>
<td>36</td>
</tr>
<tr>
<td>Mo</td>
<td>8</td>
</tr>
</tbody>
</table>
\[ \text{Optical basicity}^* \]

\[
\begin{array}{c|c|c}
Y_2O_3 \cdot (SiO_2) & Y_2O_3 \cdot 2(SiO_2) & a(SiO_2), 1650 K \\
0.786 & 0.699 & 0.281 \\
Yb_2O_3 \cdot (SiO_2) & Yb_2O_3 \cdot 2(SiO_2) & 0.194 \\
0.729 & 0.657 & \\
\end{array}
\]
Now Have the Needed Quantities for Modeling Recession

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

Flux $= 0.664 \left( \frac{v_\infty \rho_\infty L}{\eta} \right)^{0.5} \left( \frac{\eta}{D_{Si(OH)_4} \rho_\infty} \right)^{0.33} \frac{D_{Si(OH)_4}}{RTL} K a_{SiO_2} (P_{H_2O})^2$
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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• XRD: R. Rogers (NASA Glenn)

• NASA/ORAU Post-doctoral Fellowship Program