Thermodynamics and Kinetics of Silicate Vaporization

Nathan S. Jacobson
Gustavo C. C. Costa
NASA Glenn Research Center

MS&T 2015

Phase Stability, Diffusion Kinetics, and their Applications
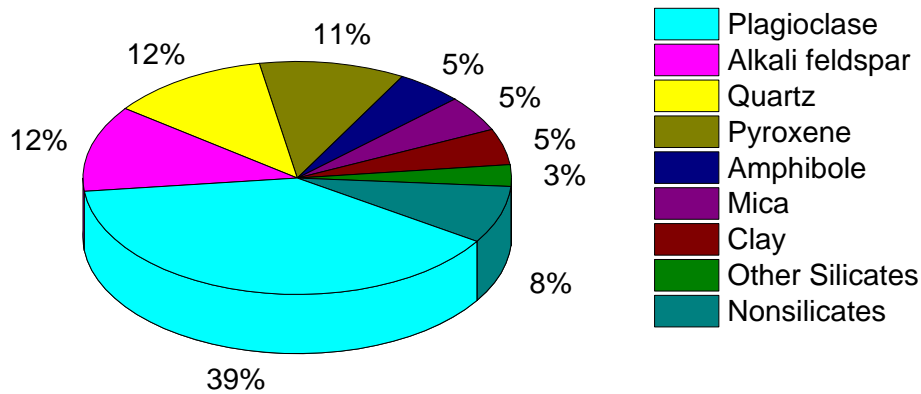
October 7, 2015

Columbus, Ohio

Outline of Presentation

- Silicates are truly the 'ubiquitous material'—found everywhere!
  - Natural systems: found in many minerals and rocks
  - Technology—coatings, structural ceramics

- Apply Knudsen Effusion Mass Spectrometry (KEMS) to study thermochemistry of silicates
  - KEMS allows measurement of equilibrium vapor pressures above condensed phase
  - Unique challenges
    - Complex vaporization behavior
    - Kinetic barriers to vaporization

- Examples
  - Geology: Thermochemistry of Olivine
  - Technology: Thermochemistry Y_2O_3-SiO_2 and Yb_2O_3-SiO_2 coating systems

- Vaporization kinetics of silicates

Silicates in Geology, Mineralogy and Planetary Science

- Over 90% of the Earth's crust consists of silicate minerals
  - Olivine $(Fe_xMg_{1-x})_2SiO_4$ primary constituent of earth's mantle

Pie chart:
- Plagioclase — 39%
- Alkali feldspar — 12%
- Quartz — 12%
- Pyroxene — 11%
- Amphibole — 5%
- Mica — 5%
- Clay — 5%
- Other Silicates — 3%
- Nonsilicates — 8%

D. Perkins, Mineralogy, 3, Prentice Hall, 2011.

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

..Hot, rocky exoplanets (maybe!)

G. E. Brown, Rev. Mineral. Geochem., 5, 275-381, 1980. M. T. DeAngelis etal., Am. Mineral., 97, 653-656, 2012.
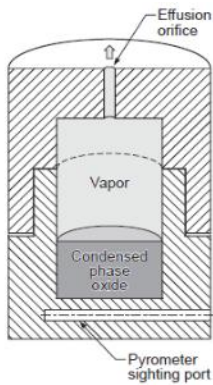
Silicates in Materials Science

- High-Temperature Materials: Silicate Coatings
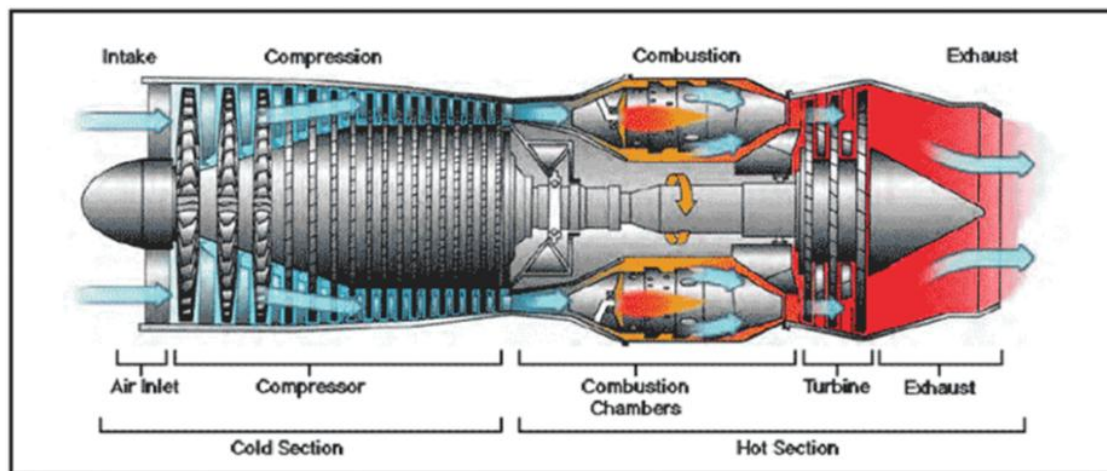
- Silicon-based ceramics: combustion chambers, static parts in hot stage

- Protective coating against water vapor, condensed phase deposits
  - Rare earth (RE) silicates $(RE_2O_3).n(SiO_2)$

Knudsen Effusion Mass Spectrometry (KEMS)

**Knudsen Cell:
Condensed Phase/Gas
Equilibrium**

**Direct Molecular Beam from
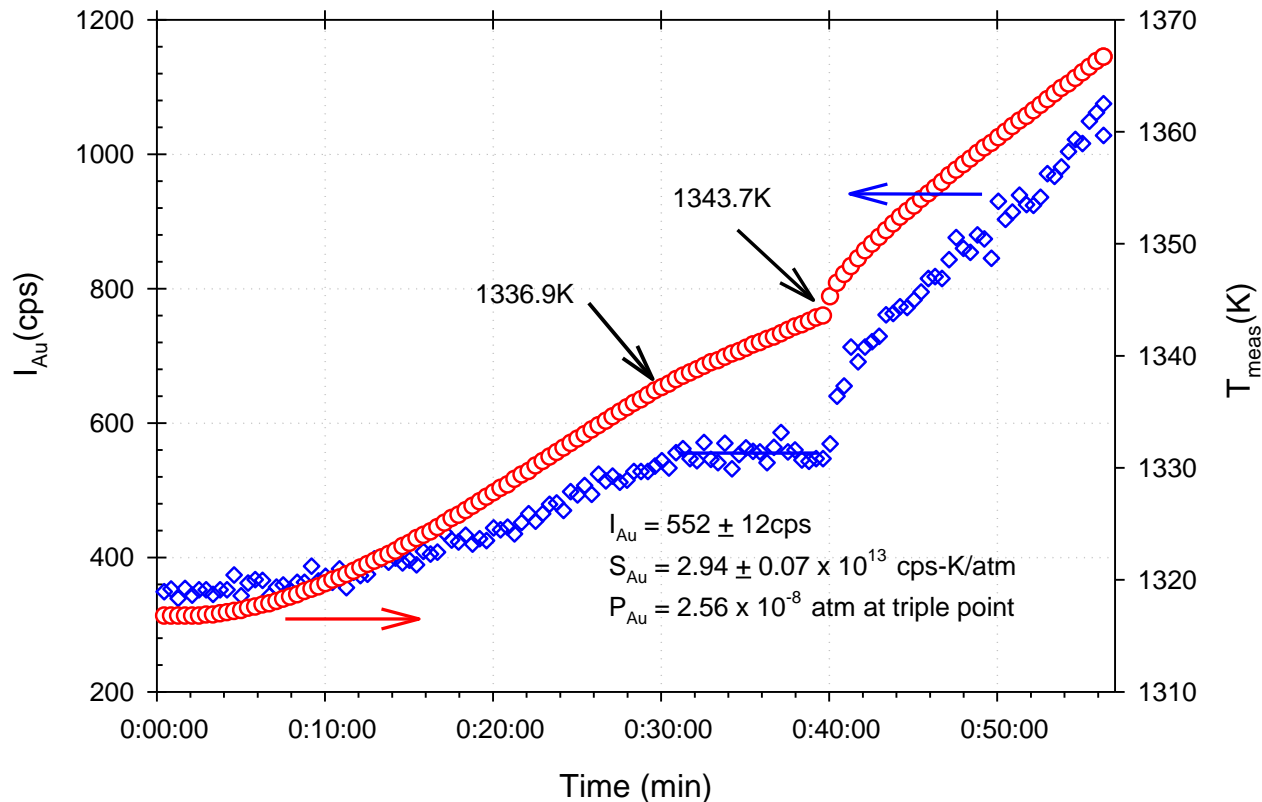Effusate
Into Mass Spectrometer**
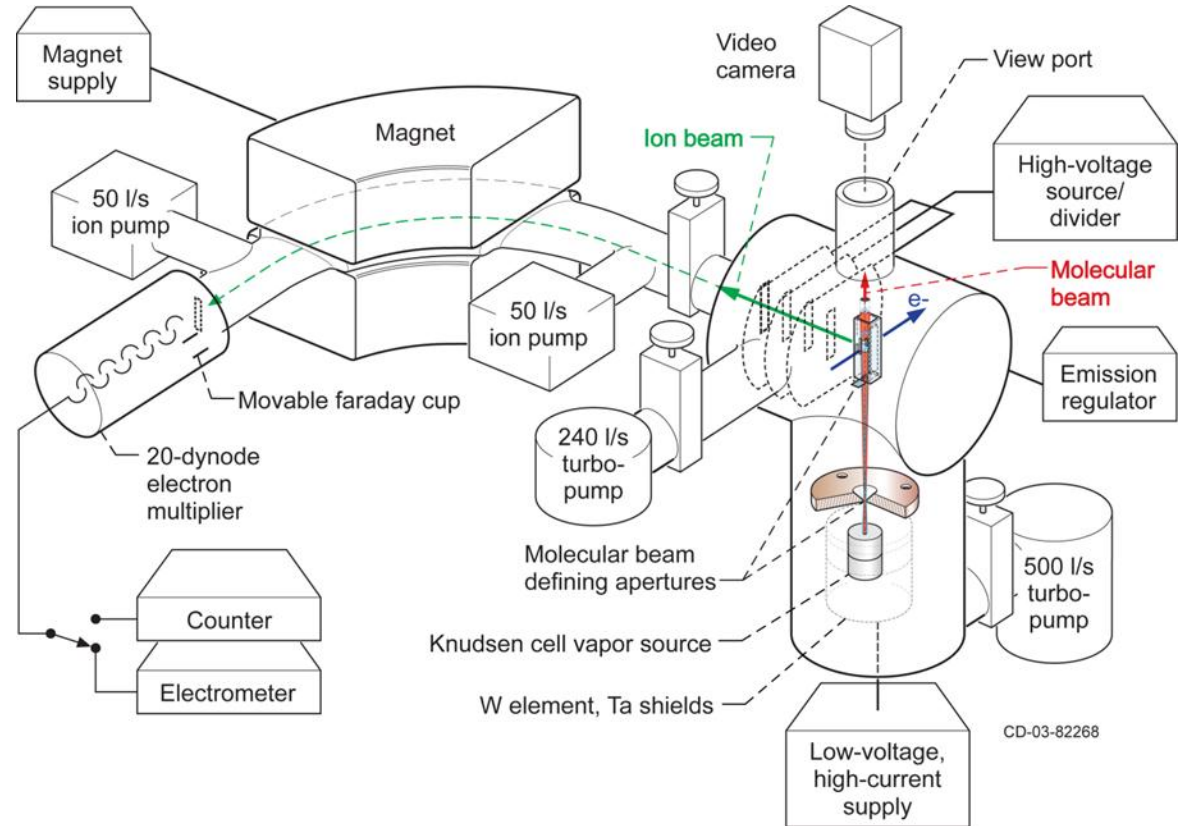
- Knudsen Cell: 1909
- Couple to mass Spectrometer: 1950s (Ingrahm et al.)
- Continuing valuable applications of these methods!

Standard Calibration Material: Au

- Temperature Measurement: very critical
- Use pyrometer (non-contact)
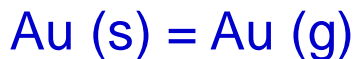- At triple point: determine calibration constant

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

$I_{Au} = 552 \pm 12\,cps$

$S_{Au} = 2.94 \pm 0.07 \times 10^{13}\ cps\text{-}K/atm$

$P_{Au} = 2.56 \times 10^{-8}\ atm$ at triple point

1343.7K

1336.9K

Standard Calibration Material: Au
Heat of Vaporization Checks Temperature Calibration and Instrument Response

$$\Delta_V H^o = -R*(-41.162) = 342.20 \text{ kJ/mol}$$

Au (s) = Au (g)

Tables = 342 kJ/mol

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

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

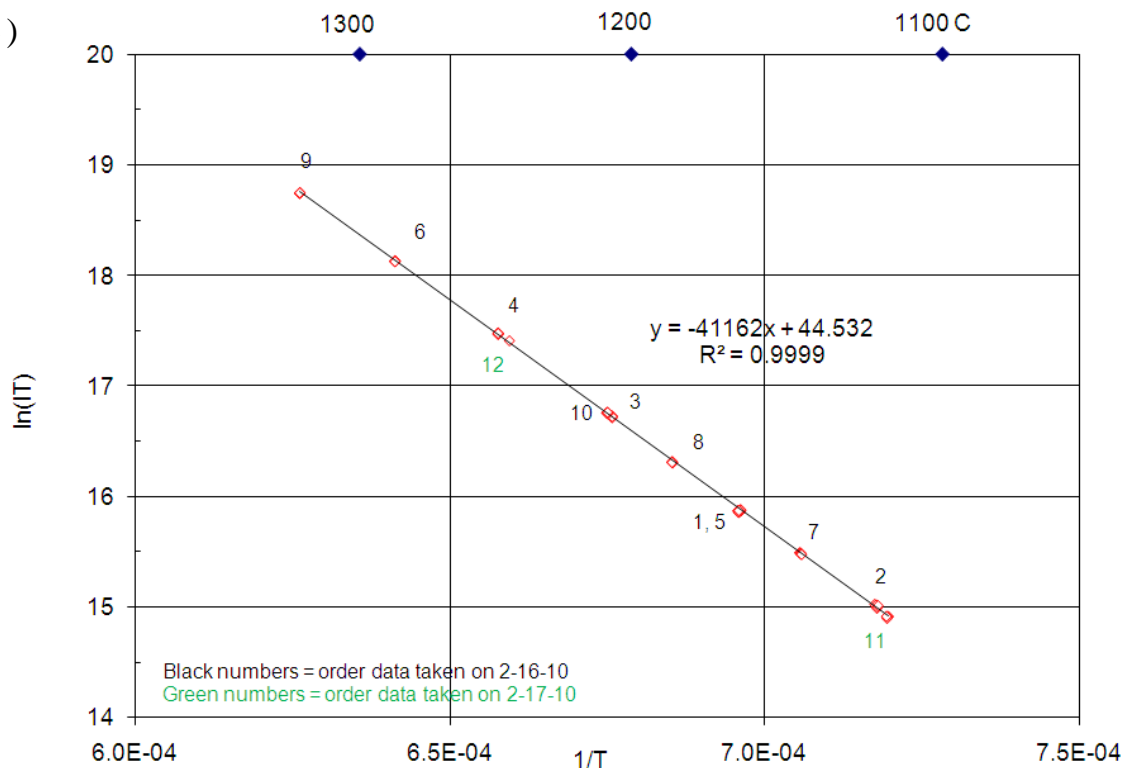$\ln P_M$ vs $1/T$ is a van't Hoff plot with slope $= \dfrac{-\Delta_v H}{R}$

$$\text{Mass Spectrometer} \quad P_M = \frac{kIT}{\sigma}$$

P_M = partial pressure of M;

k = instrument constant; I = ion intenisty;

T = Absolute temperature;

σ = ionization cross section

y = -41162x + 44.532
R² = 0.9999

Black numbers = order data taken on 2-16-10
Green numbers = order data taken on 2-17-10

Proceed to Oxide Solutions

- Partial pressures $\leftrightarrow$ activities

- Complex vaporization and ionization behavior
  - $SiO_2(s) = SiO_2(g)$
    - $SiO_2(g) + e^- \rightarrow SiO_2^+ + 2e^-$
      $$\rightarrow SiO^+ + O + 2e^-$$

  - $SiO_2(s) = SiO(g) + \frac{1}{2} O_2(g)$
    - $SiO(g) + e^- \rightarrow SiO^+ + 2e^-$
      $$\rightarrow Si^+ + O + 2e^-$$

- Calculation of cross sections for molecules

- Vaporization may be kinetically limited

- Container Issues
  - Need inert container or container with known interactions: Mo, W, Pt, Ir
  - Silicates are very reactive!
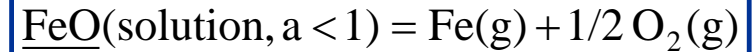
Solutions: Measure Partial Themodynamic Quantities

Olivine: $FeO_{1-\alpha}(MgO)_{1-\beta}(SiO_2)_{1-\gamma}$
Same Phase; Variable Stoichiometry

Pure Compound:

$$FeO(s) = Fe(g) + 1/2\,O_2(g)$$
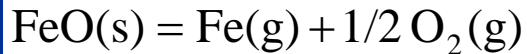
$$K_p = \frac{P_{Fe}^o[P_{O_2}^o]^{1/2}}{a_{FeO}} = \frac{P_{Fe}^o[P_{O_2}^o]^{1/2}}{1}$$

Solution:

$$\underline{FeO}(solution, a < 1) = Fe(g) + 1/2\,O_2(g)$$

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

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

$\ln(a_{FeO})$ vs $1/T$ – – partial molar enthalpy

Procedure

- Ion intensity measurements of relevant species for:
    1. Pure compound
    2. Solution
- Best to have *in-situ* pure compound and solution
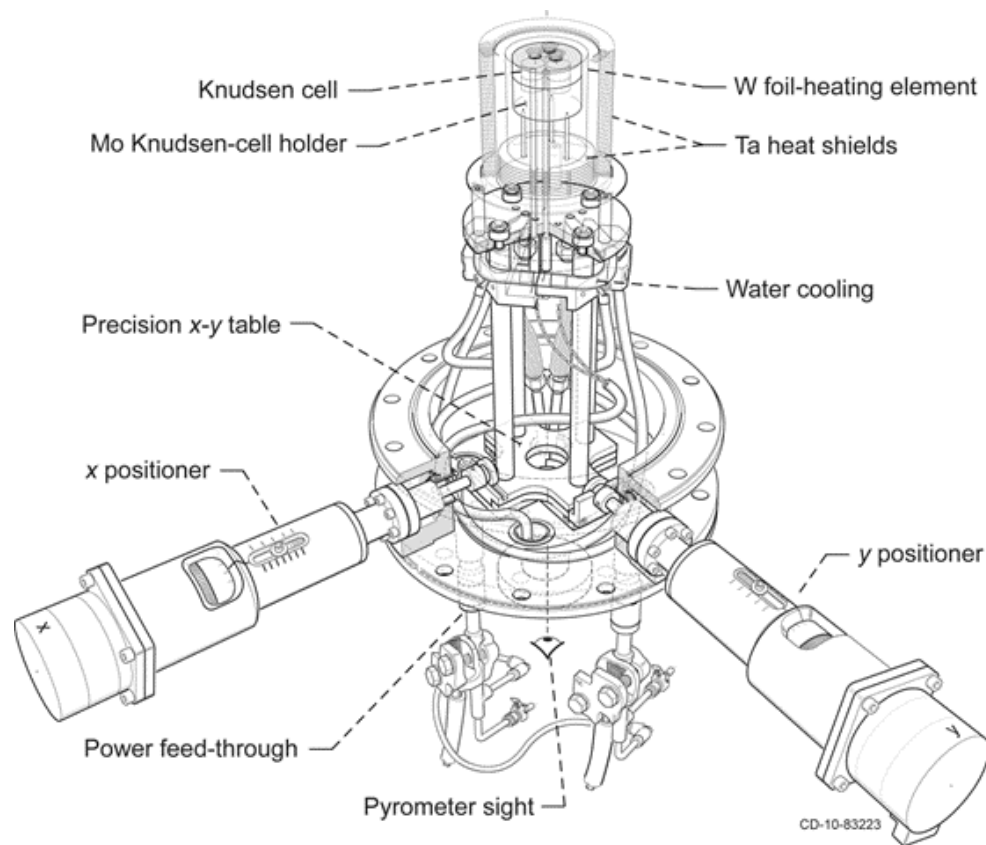
- BUT, for the highest temperature (>2000K), need to use one cell and change specimens. Assume constant calibration factor.

Example I—Natural Systems: Olivine

- Mg_2SiO_4 (Forsterite)-Fe_2SiO_4 (Fayalite)
- Primary Constituent of Earth's Mantle
- Sources:
  – Pure form found on Hawaii Green Sand Beaches: Volcanic pipeline to Mantle
 – Mining debris

- Important in volcanism, meteorites, likely constituent of other planetary bodies

- Very reactive, particularly above melting. Use Ir cell.

Olivine – Starting Material and Characterization

93% forsterite and 7% fayalite, $Fo_{93}Fa_7$ - $(Fe_{0.07}Mg_{0.93})_2SiO_4$

ICP-OES analysis of the as received olivine samples.

forsterite	87.68 %
enstatite	7.08 %
Silica	0.84 %
Sapphirine	0.45 %
Clinochlore	3.94 %
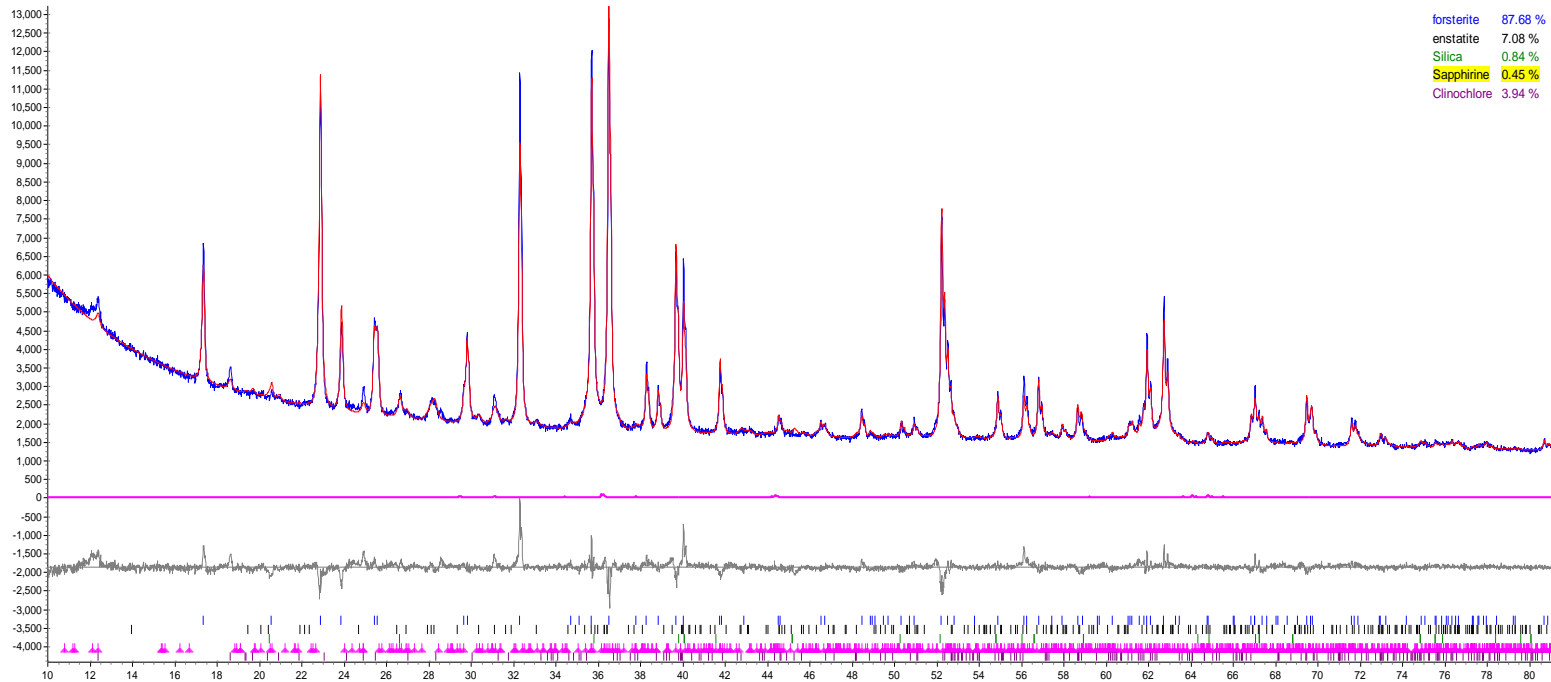
| Element	*Wt (%)
Al	0.0120(6)
Ca	0.035(2)
Co	0.0120(6)
Cr	0.052(3)
Fe	5.01(3)
Mg	30(2)
Mn	0.075(4)
Na	0.0080(4)
Ni	0.27(1)
Sc	0.0040(2)
Si	20(1)

*Uncertainties of the analyses are given in parentheses.

XRD pattern and Rietveld refinement of the as received olivine samples.
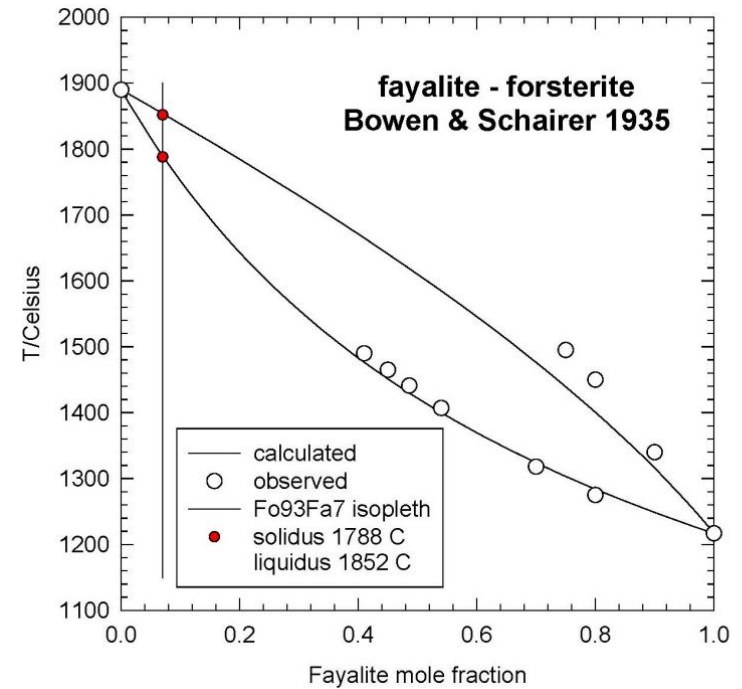
Phase content
- Forsterite – 87.7 ± 0.3%
- Enstatite – 7.1 ± 0.2%
- Silica – 0.84 ± 0.6%
- Sapphirine – 0.5 ± 0.1%
- Clinochlore – 3.9 ± 0.2%

Heating to > 1060°C removes impurities

Complete van't Hoff Plot
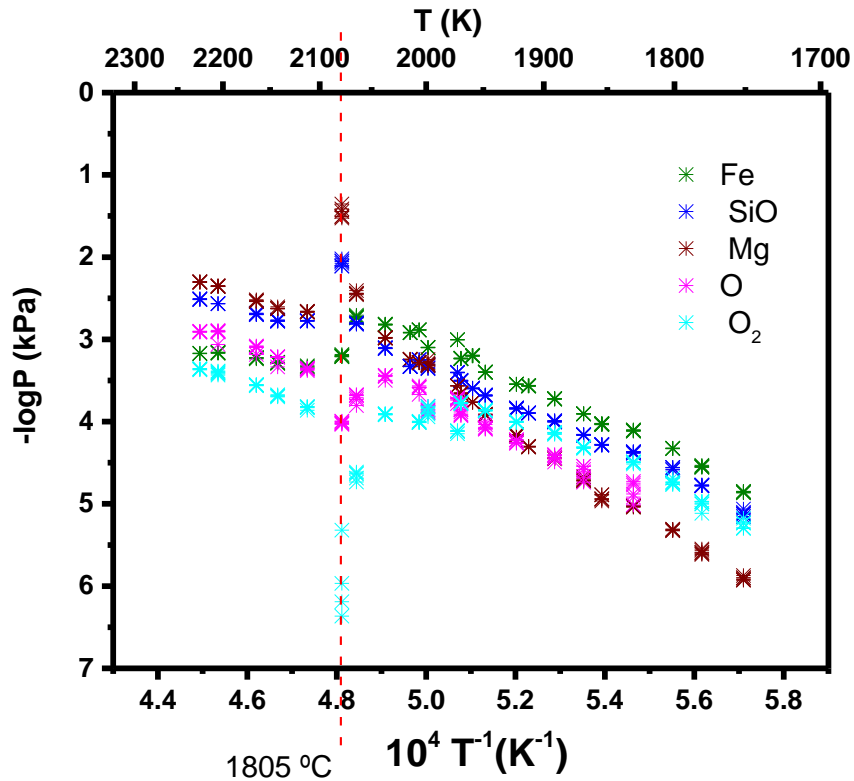
Temperature dependence of ion intensity ratios of Mg^+, Fe^+, SiO^+, O^+ and O_2^+ in the olivine sample.

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.

Bowen and Schairer, Am. J. Sci. 29, 151-171 (1935).

Olivine—Solution of
Mg_2SiO_4 (Fosterite)-Fe_2SiO_4 (Fayalite)
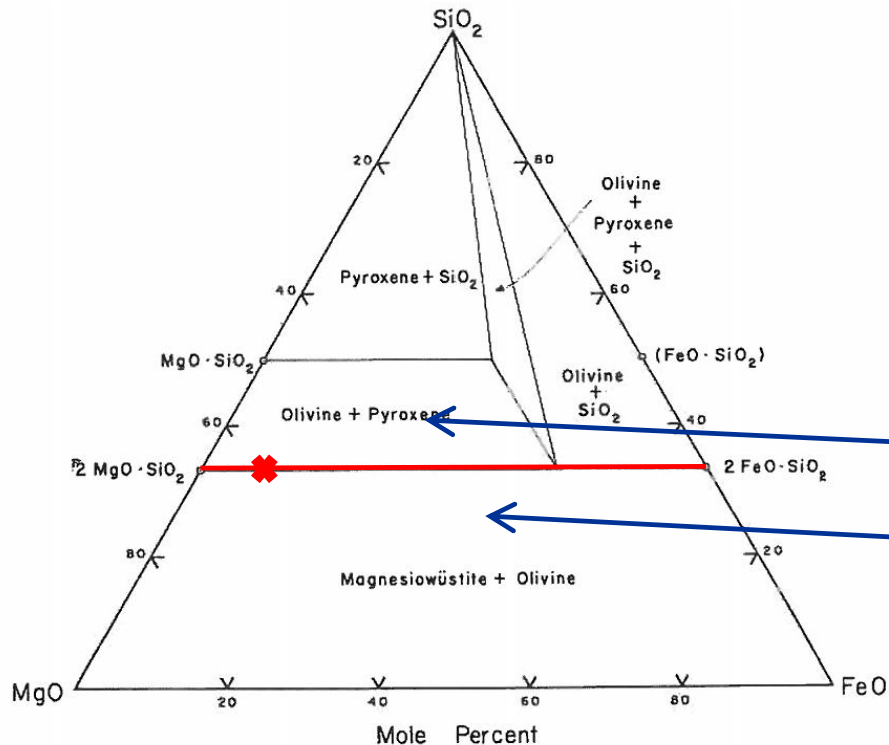
- Composition of Interest: $Fo_{0.93}Fa_{0.07}$

- Activity gradient across olivine

- Work in two phase regions

Excess SiO_2: Olivine + Pyroxene

Excess MgO: Olivine + Magnesiowustite

Previous Data and Models of Olivine

- Thermodynamic measurements
  - Nafziger & Muan (1967); Kitayama & Katsura (1968)—from $P(O_2)$ and stable phases
  - Sakawa et al. (1976): Equilibration method for a(FeO)
  - Plante et al. (1992): KEMS measurements of a(FeO)
  - Wood & Kleppa, Kojitani & Akaogi: Calorimetry
  - General agreement: a(FeO): Positive deviation from ideality

- Saxena et al. (1993): $(Mg,Fe)_2SiO_4$ Regular Solution Lo = 9000

- Decterov et al.: Sublattice

- Fabrichnaya (1998): $(Mg,Fe)_2SiO_4$ β and γ spinel; subregular solution with temperature dependent mixing parameters
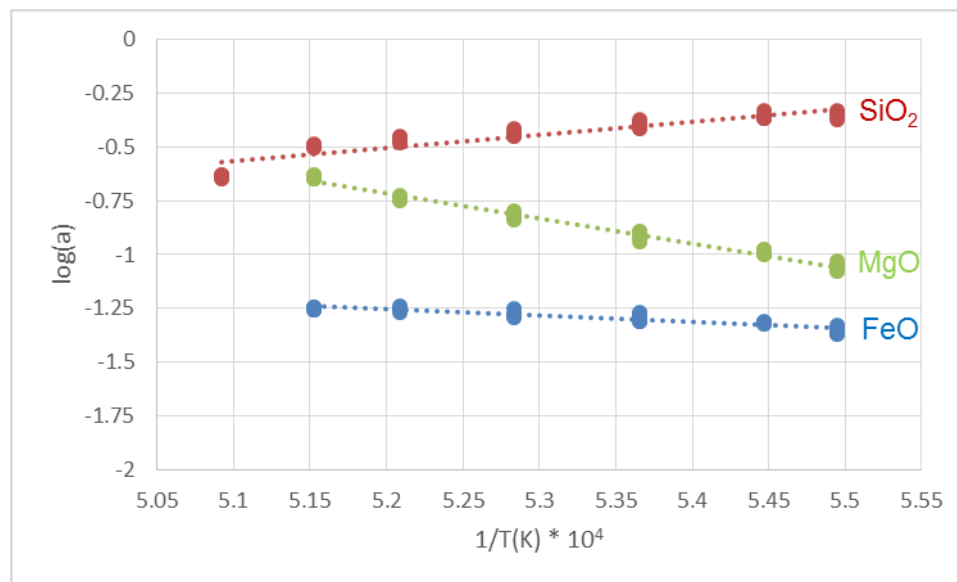
Thermodynamic Activities in Olivine – $(Fe_2SiO_4)_{0.07}(Mg_2SiO_4)_{0.93}$+ MgO

Olivine + MgO
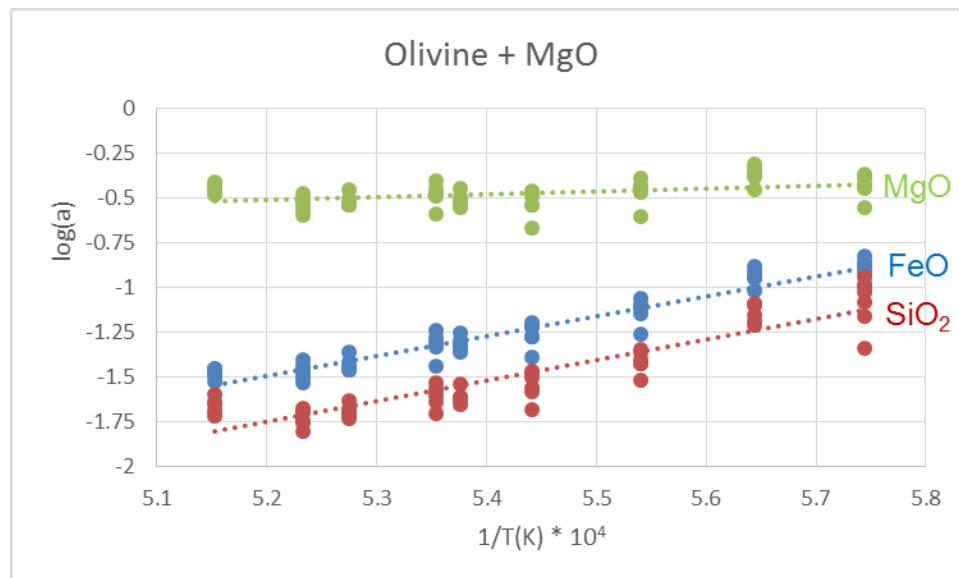
| Component	x	a (1800K)	Compare to Ideality	$\Delta \overline{H_i}(1700-1950)$	
MgO	0.62	0.353	(-)ve deviations	30.2 kJ/mol	
"FeO"	0.047	0.081	(+)ve deviations	212.5 kJ/mol	Consistent with literature
SiO_2	0.33	0.046	(-)ve deviations	220.2 kJ/mol	

Thermodynamic Activities in Olivine – $(Fe_2SiO_4)_{0.07}(Mg_2SiO_4)_{0.93}$

Component	x	a (1900K)	Compare to ideality	$\Delta\overline{H}_i(1700-1950)$	
MgO	0.62	0.165	(-)ve deviation	-222.0 kJ/mol	
"FeO"	0.047	0.053	(+)ve deviation	-55.2 kJ/mol	Consistent with literature
SiO$_2$	0.333	0.341	(+)ve deviation	116.2 kJ/mol	

Comparison to Models (FactSage)
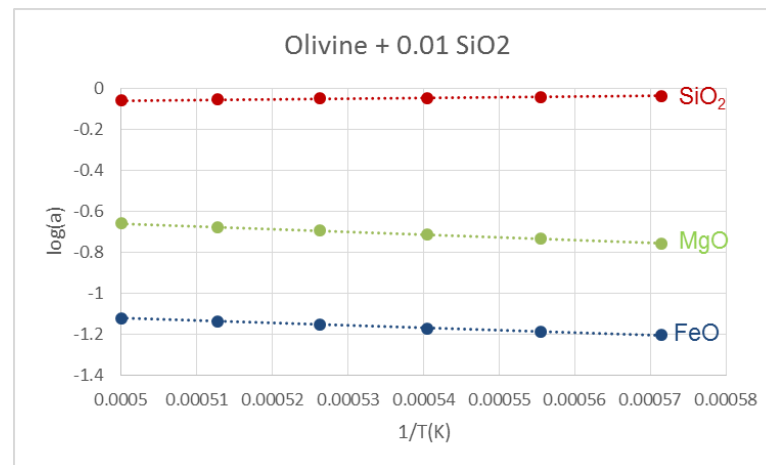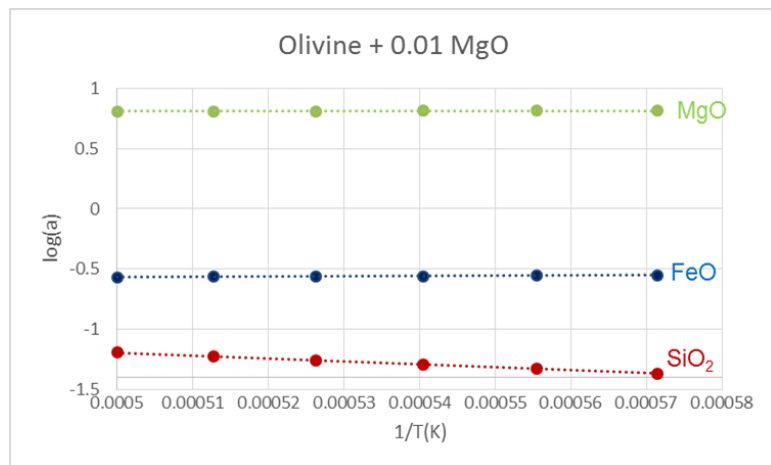
Thermodynamics of Olivine: Lots to Do!

- Understand changes in activities on melting

- Compare partial molar enthalpies to total excess free energy

- Refine current models: our data suggests some components far from ideality

Example 2: Rare Earth Silicates

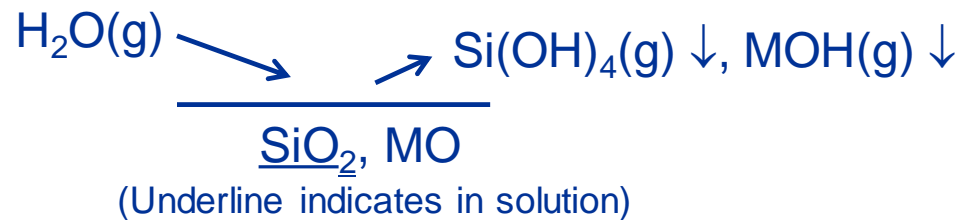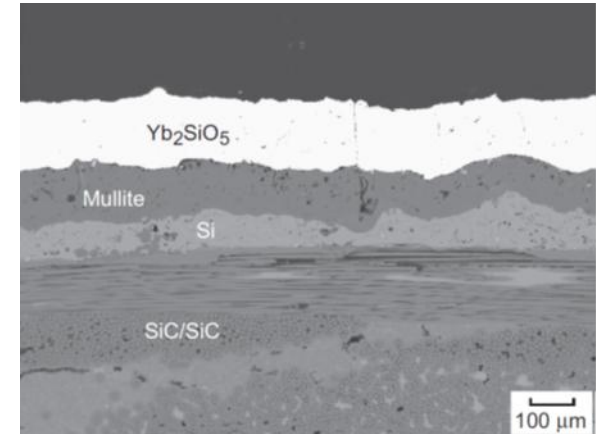# SiC and SiC based Composites for Heat Engines

- Strength retained to higher temperatures than metals

- Lighter weight

- Fiber Reinforced composites give some fracture toughness

- Protected by SiO_2 scale

  - Slow growing, good in pure oxygen

  - BUT…Attacked by basic molten salts; volatilized by water
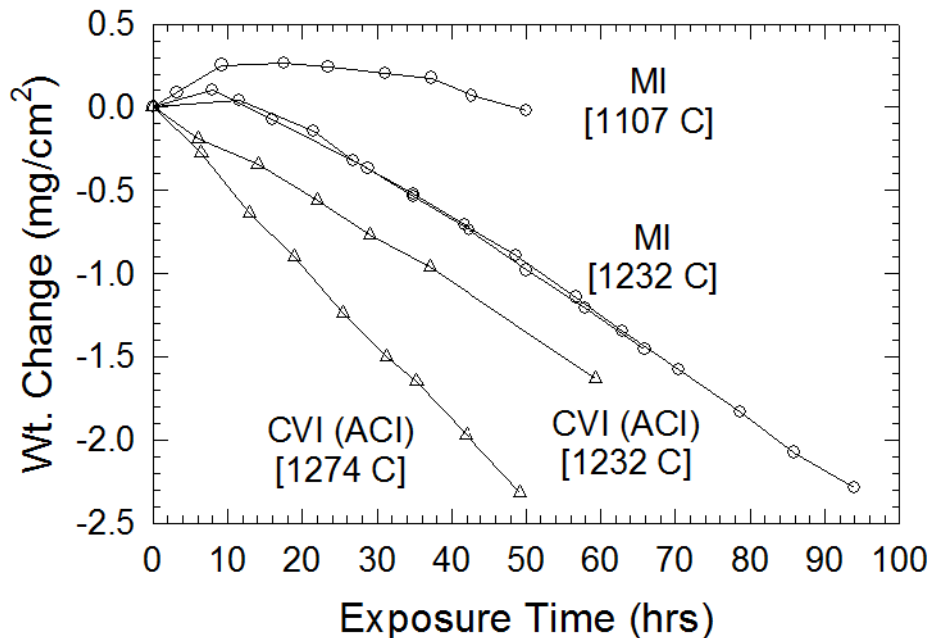
SiC/SiC CMC HPBR Paralinear
(1100 °-1300°C, 6 atm; Robinson/Smialek 1998)
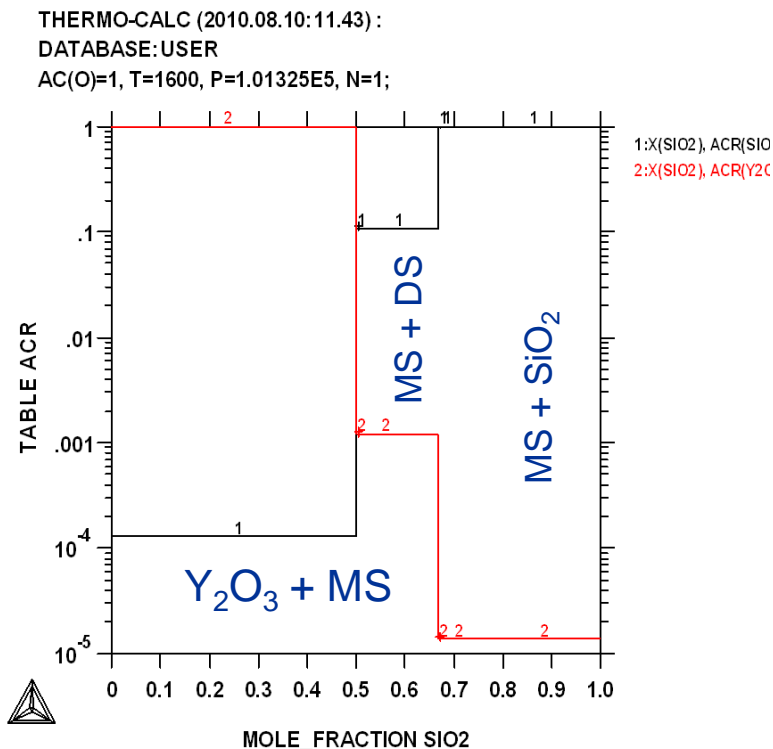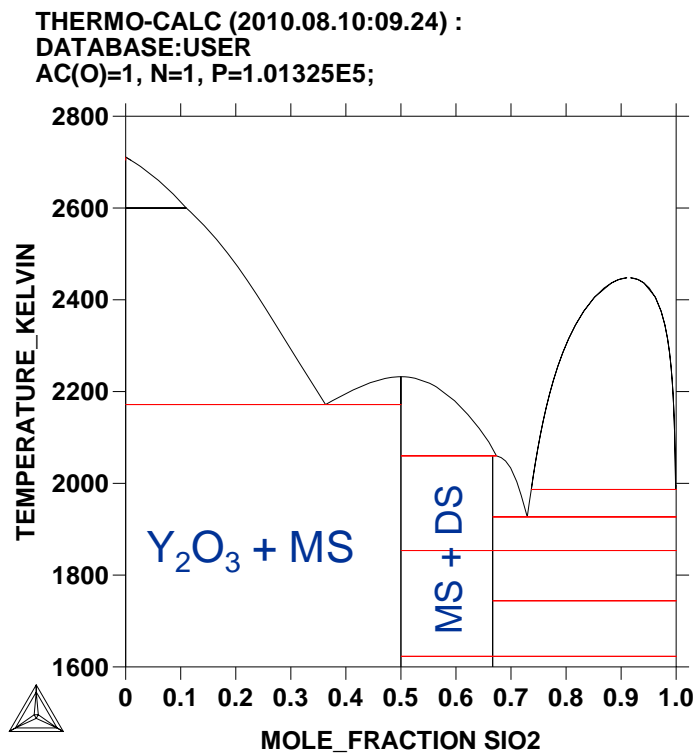$Si(OH)_4$ volatility (Opila et al., 1998-2006)

Combine *Desirable Mechanical Properties of SiC with Chemical Inertness of Refractory Oxide*

- Lower activity of silica $\Rightarrow$ less reaction

- Molten salt reaction
  - $Na_2O(s) + SiO_2(s) = Na_2O \cdot xSiO_2$

- Water vapor enhanced volatilization
  - $SiC + 3/2\ O_2(g) = SiO_2 + CO(g)$
    $\underline{SiO_2} + 2\ H_2O(g) = Si(OH)_4(g)$
  - $P[Si(OH)_4] = K\ a(SiO_2)\ [P(H_2O)]^2$

$$H_2O(g) \searrow \nearrow Si(OH)_4(g) \downarrow, MOH(g) \downarrow$$
$$\underline{SiO_2}, MO$$

(Underline indicates in solution)

Meschter et al., Annu Rev Mater Res 43, 559 (2013)
N. S. Jacobson, J Am Ceram Soc 97, 1959 (2014)

Rare Earth Silicates: Good CTE Match to SiC
Calculated Y_2O_3-SiO_2 Phase Diagram

Indirect evidence suggests that the SiO_2 thermodynamic activity is lower in the Y_2O_3-Y_2SiO_5 and Y_2SiO_5-$Y_2Si_2O_7$ regions
But there are no direct measurements!

Fabrichnaya-Seifert Database

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 $a(SiO_2) > \sim 0.02$
    - $Mo(s) + 3\underline{SiO_2}(soln) = 3SiO(g) + MoO_3(g)$
  - For $a(SiO_2) < \sim 0.02$
    - $2Ta(s) + 2\underline{SiO_2}(soln) = 2SiO(g) + TaO(g) + TaO_2(g)$
  - Note reducing agent must <u>not</u> 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
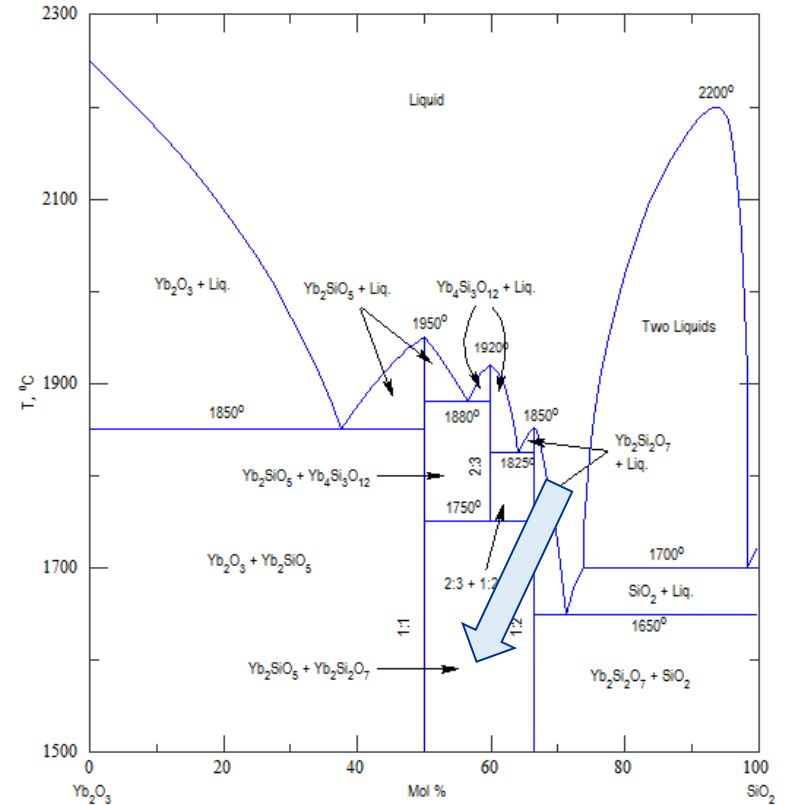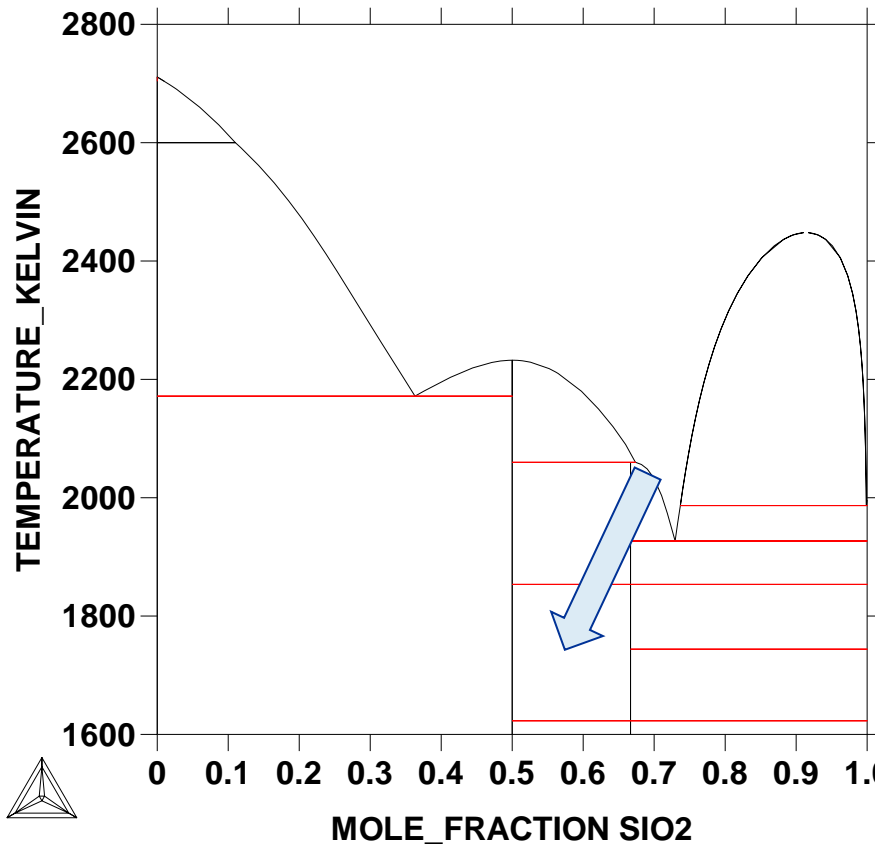 - High resolution instrument (in our dreams…)
  - Gettering pump for CO_2

Monosilicate + Disilicate

Y_2O_3-SiO_2 + Y_2O_3-$2SiO_2$

THERMO-CALC (2010.08.10:09.24) :
DATABASE:USER
AC(O)=1, N=1, P=1.01325E5;

Yb_2O_3-SiO_2 + Yb_2O_3-$2SiO_2$

Work in Two Phase Region:
Monosilicate + Disilicate

Three cells:

- Au (reference)

- $3Mo + Y_2O_3 \cdot 2SiO_2 + Y_2O_3 \cdot SiO_2$

- $3Mo + SiO_2$

- Mo as powder and cell material
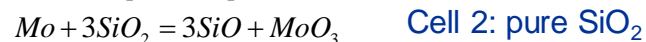
$Mo(s) + 3\underline{SiO_2}(soln) = 3SiO(g) + MoO_3(g)$
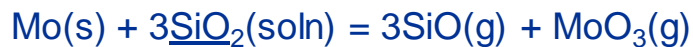
- Compare cells 1 and 2

Note that cell is part of the thermodynamic system: Best way to overcome container issue!

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

$Mo + 3SiO_2 = 3SiO + MoO_3$ Cell 2: pure SiO_2

$$a(SiO_2) = 1 = \left\{ \frac{[P^o(SiO)]^3 P^o(MoO_3)}{K} \right\}^{0.33}$$

$Mo + 3\underline{SiO_2} = 3SiO + MoO_3$ Cell 3: SiO_2 in silicate
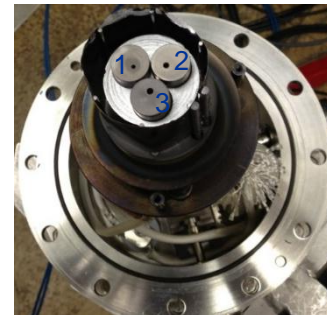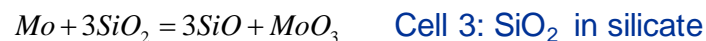
$$a(SiO_2) = \left\{ \frac{[P(SiO)]^3 P(MoO_3)}{K} \right\}^{0.33}$$

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

$Y_2O_3.(SiO_2) + Y_2O_3.2(SiO_2)$

$Yb_2O_3.(SiO_2) + Yb_2O_3.2(SiO_2)$
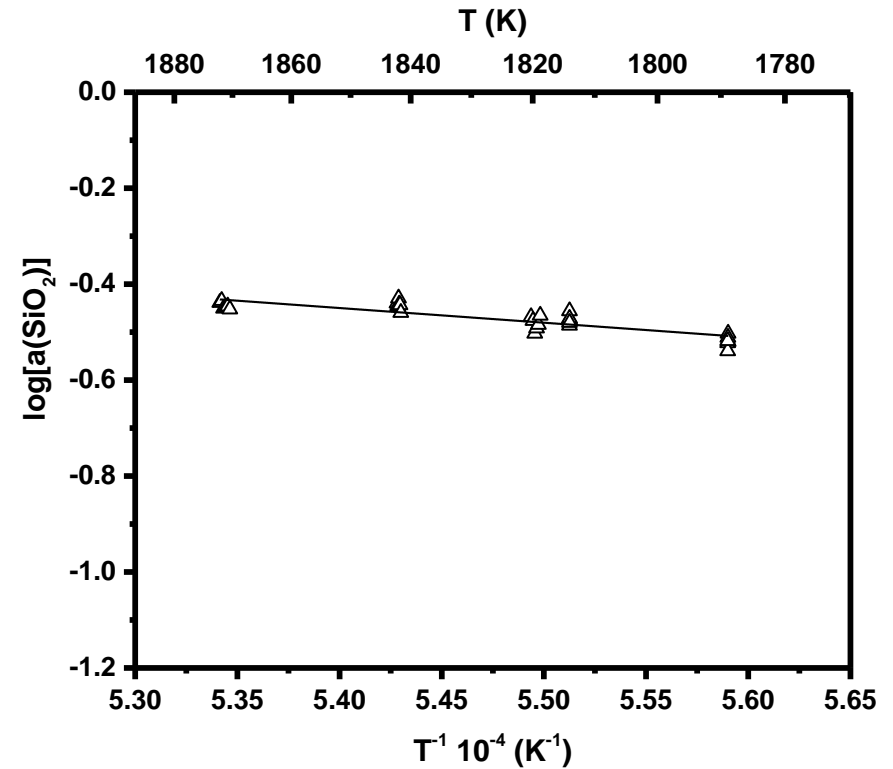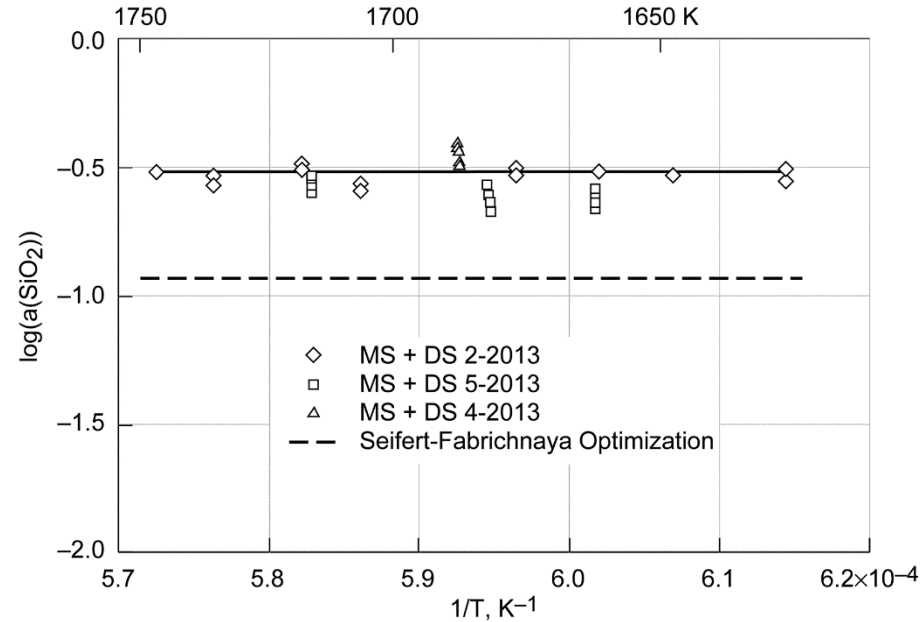
Two Phase Mixture	a(SiO_2), 1650K
$Y_2O_3.(SiO_2) + Y_2O_3.2(SiO_2)$	0.281
$Y_2O_3.(SiO_2) + Y_2O_3.2(SiO_2)$	0.194

XRD after KEMS Measurements of RE Monosilicates + Disilicates + Mo:

Yttrium monosilicate + disilicate +Mo
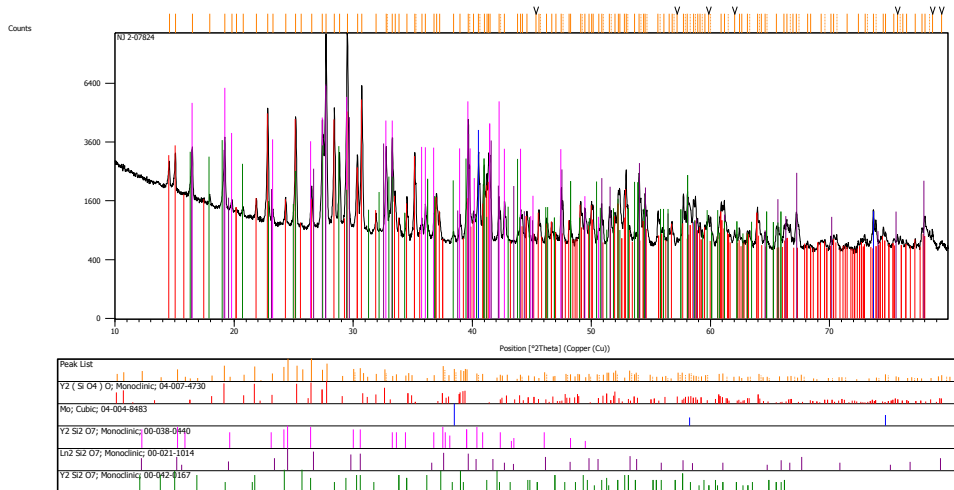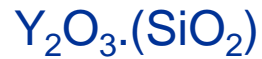
Phase
$Y_2O_3.(SiO_2)$
$Y_2O_3.2(SiO_2)$
Mo

Ytterbium monosilicate + disilicate + Mo
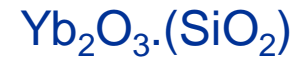
Phase	wt (%)
$Yb_2O_3.(SiO_2)$	56
$Yb_2O_3.2(SiO_2)$	36
Mo	8

Monosilicate + RE$_2$O$_3$

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

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

Monosilicate + RE_2O_3

Two cells:

- Au

- $3Ta + Y_2O_3 + Y_2O_3 \cdot SiO_2$

  - Ta as powder and cell material—cell is part of system

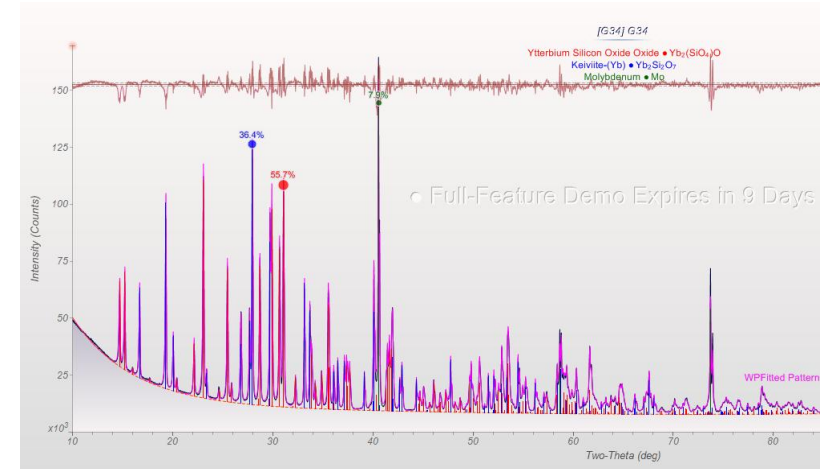$2Ta(s) + 3\underline{SiO_2}(soln) = 3SiO(g) + TaO(g) + TaO_2(g)$

- Using $P_{eq}(SiO)$ and FactSage (free energy minimization)

- Correction for non-equilibrium vaporization

3Ta + SiO₂ 1500K- P(SiO) as an Indicator of a(SiO₂)
FactSage (Free energy minimizer) Calculations

$y = 1.1667x + 5.8264$

$2Ta + 3\underline{SiO_2} = 3SiO(g) + TaO(g) + TaO_2(g)$

$4Ta + 4\underline{SiO_2} = 3SiO(g) + Ta_2O_5 + Ta_2Si$

$y = x + 4.7653$

y-axis: $\log a(SiO_2)$
x-axis: $\log P(SiO)$
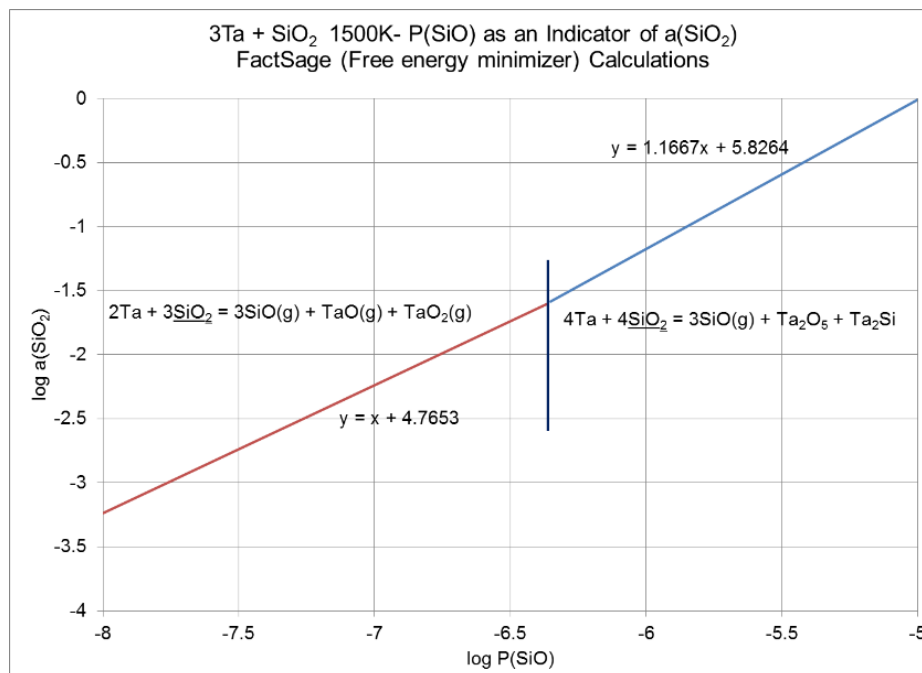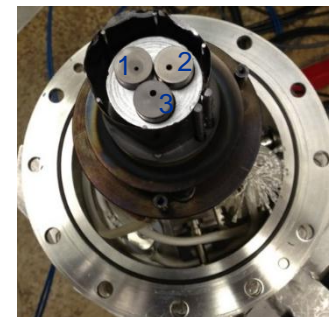
XRD after KEMS Measurements of RE Monosilicates + RE_2O_3 + Ta:

Yttrium monosilicate + Y_2O_3 + Ta

No.	Visible	Ref. Code	Compound Name	Chemical Formula	Score	Display Color	Qu...	Crystal Sy...	Space...	SemiQuant [%]	RIR
1	✓	04-007-9716	Yttrium Oxide	Y2 O3	70	Red	I;A...	Cubic	Ia-3	49	9.260
2	✓	04-004-3017	Tantalum	Ta	42	Lime	I;A...	Cubic	Im-3m	4	29.920
3	✓	04-001-0709	Tantalum Silicon	Ta3 Si	17	Fuc...	P;...	Tetragonal	P42/n	4	4.270
4	✓	04-005-8528	Yttrium Oxide Si...	Y2 (Si O4) O	52	Blue	P;...	Monoclinic	C2/c	41	1.550
5	✓	04-011-3996	Tantalum	Ta	12	Aqua	I;A...	Tetragonal	P-421m	3	7.980

Ytterbium monosilicate + Yb_2O_3 + Ta

Phase	wt (%)
$Y_2O_3.(SiO_2)$	41
Y_2O_3	49
Ta	4
Ta_3Si	4
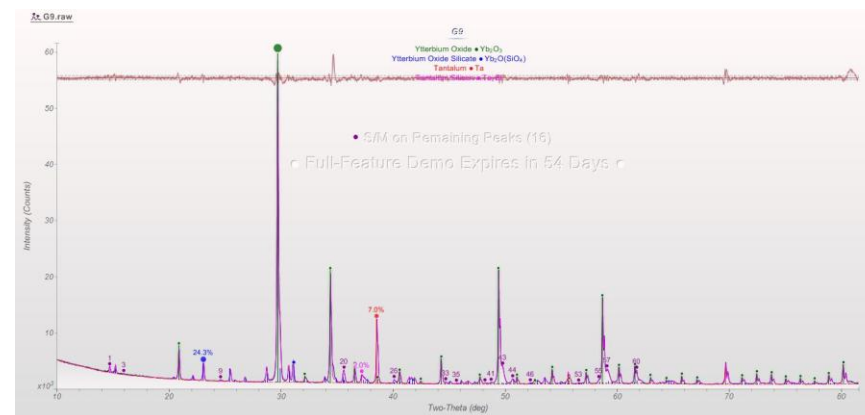
Phase	wt (%)
$Yb_2O_3.(SiO_2)$	24
Yb_2O_3	66
Ta	2
Ta_2Si	2

$Y_2O_3 + Y_2O_3\cdot(SiO_2)$

$$y = -5200.26\left(\tfrac{1}{T}\right) + 0.0567$$

$$y = -2864.9\left(\tfrac{1}{T}\right) - 2.0853$$

Legend:
- ◇ KEMS 1-2012
- △ KEMS 4-2013
- – – Fabrichnaya-Seifert Optimization
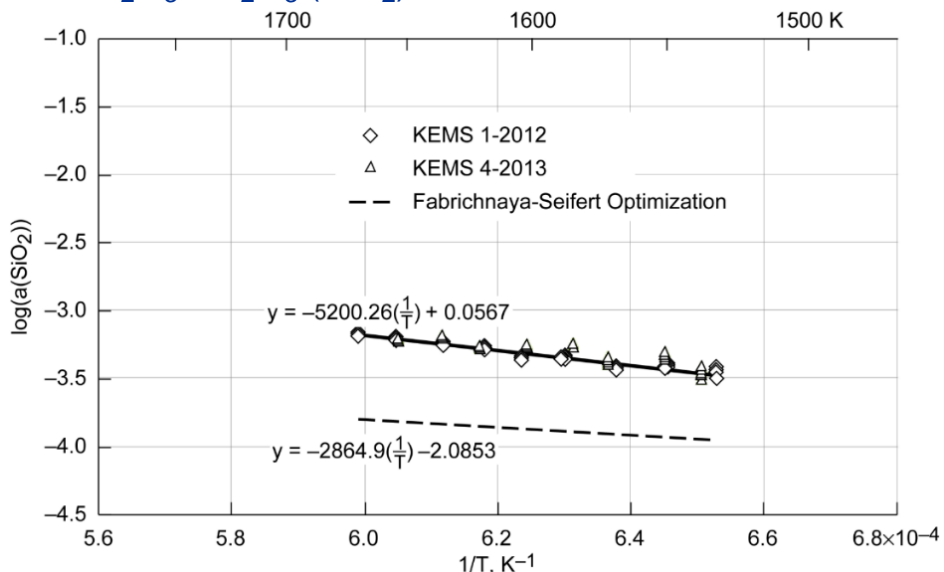
$\Delta H_{(SiO2,\ 1600\ K)} = (5200.26)\cdot R\cdot 2.303 = $ **99.57 kJ/mol**

$Yb_2O_3 + Yb_2O_3\cdot(SiO_2)$

$$y = -1412.60(1/T) - 1.67$$
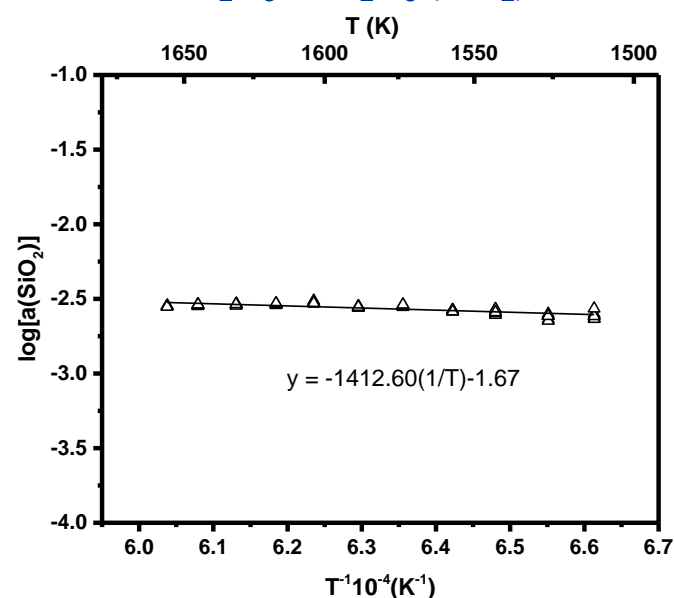
$\Delta H_{(SiO2,\ 1600\ K)} = (1412.60)\cdot R\cdot 2.303 = $ **27.05 kJ/mol**
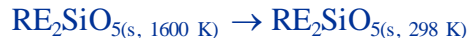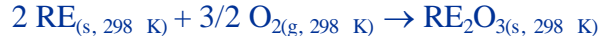
Reaction	
$RE_2O_{3(s,\ 1600\ K)} + SiO_{2(s,\ 1600\ K)} \rightarrow RE_2SiO_{5(s,\ 1600\ K)}$	$\Delta H_1 = $ measured in this work
$RE_2SiO_{5(s,\ 1600\ K)} \rightarrow RE_2SiO_{5(s,\ 298\ K)}$	$\Delta H_2 = H_{1600\ K} - H_{298\ K}$
$RE_2O_{3(s,\ 298\ K)} \rightarrow RE_2O_{3(s,\ 1600\ K)}$	ΔH_3
$SiO_{2(s,\ 298\ K)} \rightarrow SiO_{2(s,\ 1600\ K)}$	ΔH_4
$2\,RE_{(s,\ 298\ K)} + 3/2\,O_{2(g,\ 298\ K)} \rightarrow RE_2O_{3(s,\ 298\ K)}$	ΔH_5
$Si_{(s,\ 298\ K)} + O_{2(g,\ 298\ K)} \rightarrow SiO_{2(s,\ 298\ K)}$	ΔH_6
$2\,RE_{(s,\ 298\ K)} + Si_{(s,\ 298\ K)} + 5/2\,O_{2(g,\ 298\ K)} \rightarrow RE_2SiO_{5(s,\ 298\ K)}$	$\Delta H_7 = \Delta H_{f,RE_2SiO_5,298\ K}$

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

|	KEMS	Calorimetry*	a(SiO_2), 1650 K
$Y_2O_3\cdot(SiO_2)$	-2907 ± 16	-2868.54 ± 5.34	0.000804
$Yb_2O_3\cdot(SiO_2)$	-2744 ± 11	-2774.75 ±16.48	0.00298

*Liang et al. "Enthalpy of formation of rare-earth silicates Y_2SiO_5 and Yb_2SiO_5 and N-containing silicate $Y_{10}(SiO_4)_6N_2$", J. Mater. Res. 14 [4], 1181-1185. **J. A. Duff, J. Phys. Chem. A 110, 13245 (2006)
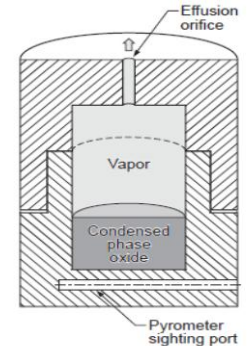
Vaporization Coefficients

- Vapor Flux (mole/unit area-unit time) leaving a free surface into a vacuum: Described by Hertz-Knudsen-Langmuir (HKL) equation

$$J(\text{max}) = \frac{P_{eq}}{\sqrt{2\pi MRT}}$$
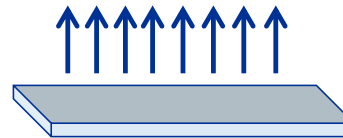
- Measured flux--Modified by a factor α: Vaporization Coefficient

$$J(measured) = \frac{\alpha P_{eq}}{\sqrt{2\pi MRT}}$$

  - Metals: Generally unity; Oxides 10^{-1} to 10^{-5}!

- Free surface vaporization = Langmuir vaporization

- Important parameter—relatively little expt'l or theoretical work since 1970s
  - True vapor flux in a deposition processes
  - High temperature material vaporization limit
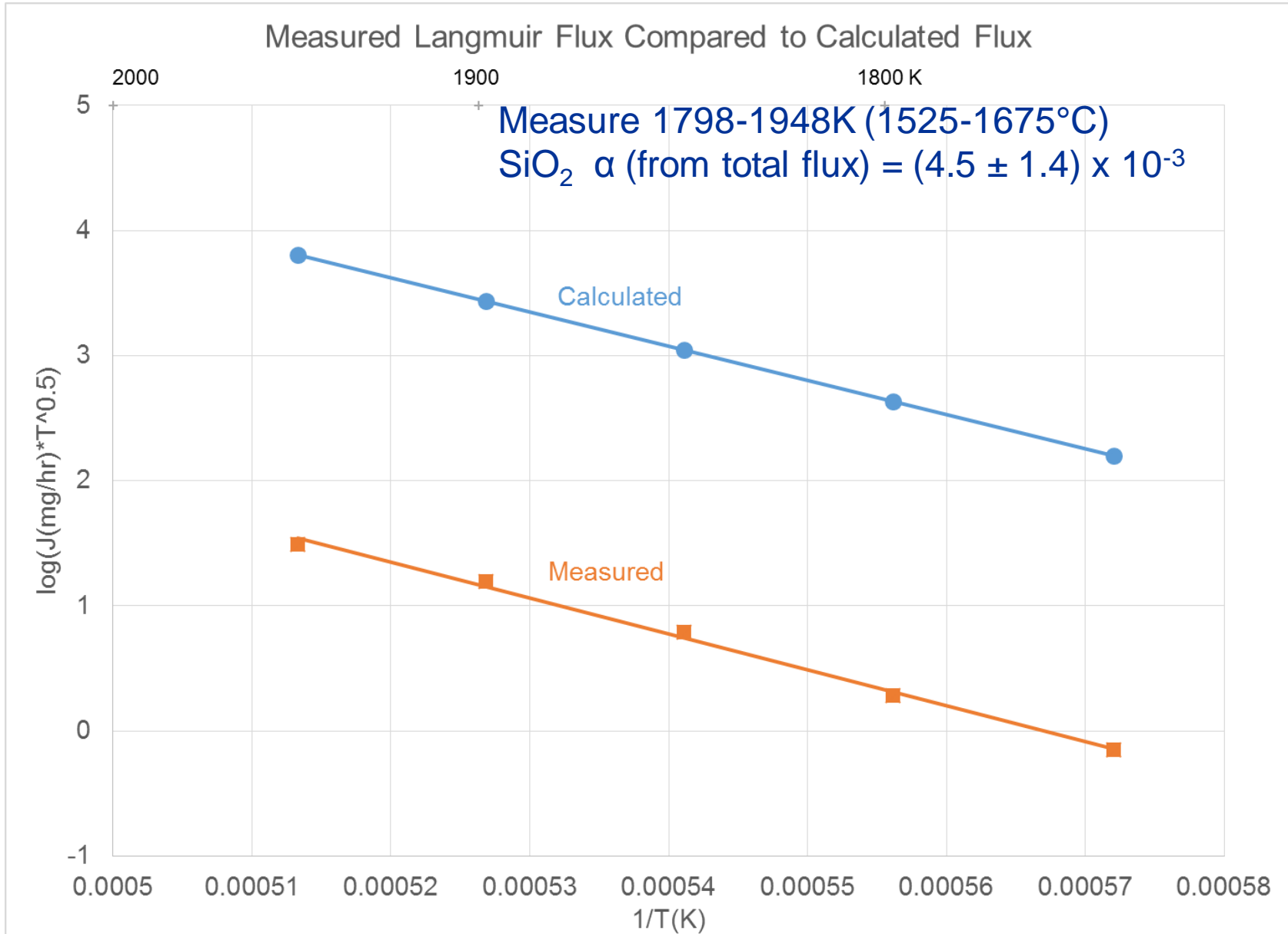 - True vapor flux in a geochemical/cosmochemical processes

What Leads to non-unity Vaporization Coefficients?
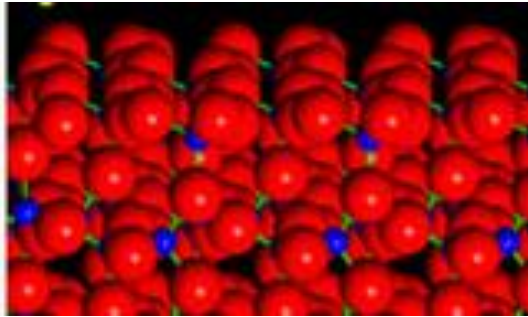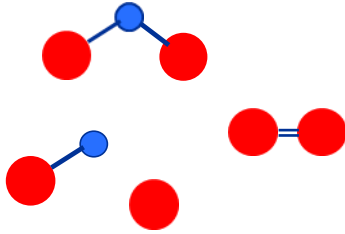
- Vaporization of silica
  - $SiO_2(s) = SiO_2(g)$
  - $SiO_2(s) = SiO(g) + \frac{1}{2} O_2(g)$
  - $SiO_2(s) = SiO(g) + O(g)$

- Complex process
  - Break apart SiO_4^{-2}
  - Adsorbed $SiO_2(a)$, $SiO(a)$, $O_2(a)$, $O(a)$
  - Desorption to $SiO_2(g)$, $SiO(g)$, $O_2(g)$, $O(g)$
  - Break O-O, Si-O bonds; make O=O double bond

- Expect a kinetic barrier $\Rightarrow$ flux reduced from equilibrium

Measured Langmuir Flux Compared to Calculated Flux

Measure 1798-1948K (1525-1675°C)
SiO_2 α (from total flux) = $(4.5 \pm 1.4) \times 10^{-3}$

Importance of Vaporization Coefficient

- Calculate vapor pressures above a condensed phase oxide:
    - Modify by vaporization coefficient

- Thermodynamic measurements
    - Implicitly assume that $\alpha(A(g), \text{solution}) = \alpha(A(g), \text{pure component})$
    - A(g)—particular species

- Measurements of these until 1970s, then relatively little work

- Important parameter has major effect on vapor pressures

Summary

- Knudsen Effusion Mass Spectrometry
    - Powerful tool for thermodynamic measurements
    - In use for many years; but still very useful particularly for solutions
    - Procedures are system specific

- Example: Olivine
    - Challenge to find 'inert' cell material. Iridium probably the best
    - Treat as solid solution of 'FeO', MgO, SiO_2
    - The melting point of the olivine sample was determined by the ion intensity discontinuity to be 1805 °C
    - Compare to standards and derive thermodynamic activities in solid phase. Appears to be significant partial molar heats, deviations from ideality

- Example: 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

- Vaporization Kinetics: Described by vaporization coefficient

Acknowledgements

- Helpful discussions with E. Opila (Formerly NASA Glenn now Univ of Virginia); B. Fegley (WUSTL)

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

- XRD: R. Rogers (NASA Glenn)