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:

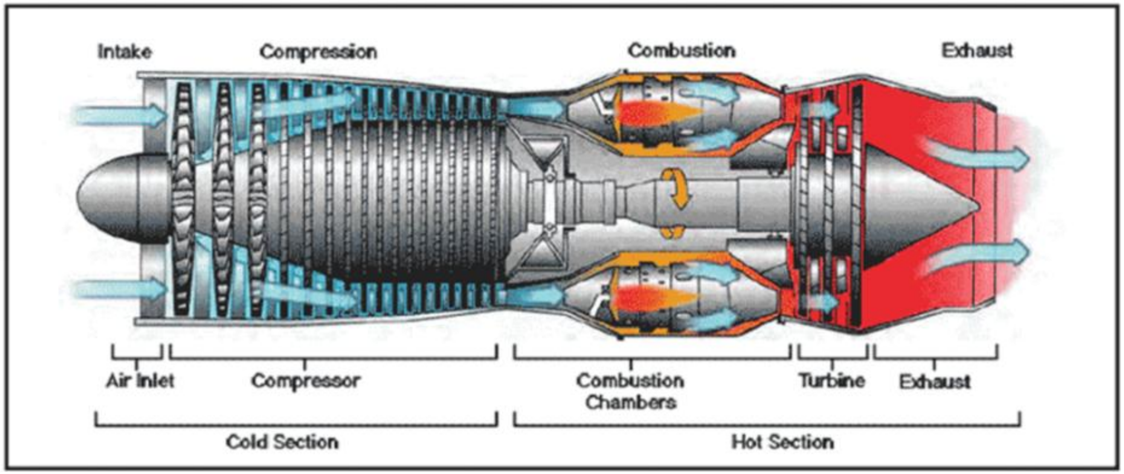
- Electronic devices: microwave, semiconductors, ferromagnetics, ferroelectrics, lasers and phosphors
- High-Temperature Materials: refractory bricks and coatings

Coating applications:

Ceramics in non-moving parts:

- Combustor liners
- Exhaust nozzles

Eventually moving parts!

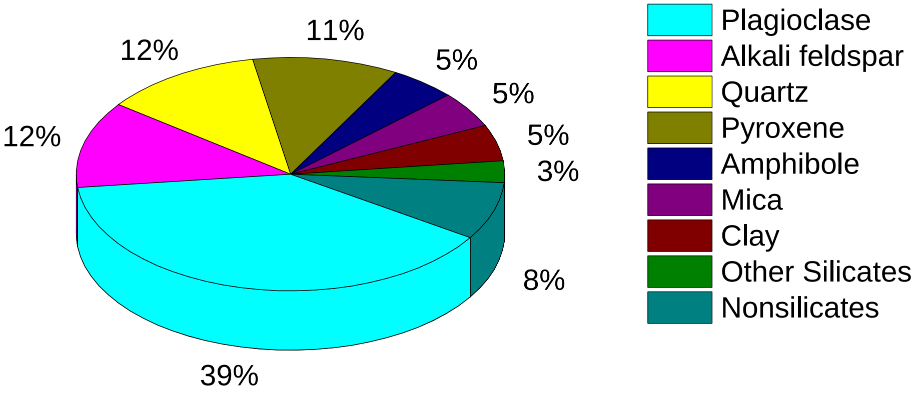


Felsche, “The Crystal Chemistry of the Rare-Earth Silicates, Springer 1973, 99-197. Melde et al, Sensors, 2008, 8, 5202-5228.

Silicates in Geology, Mineralogy and Planetary Science

Ocurrence

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



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

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

..Hot, rocky exoplanets

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

Silicate Mineral Subclasses

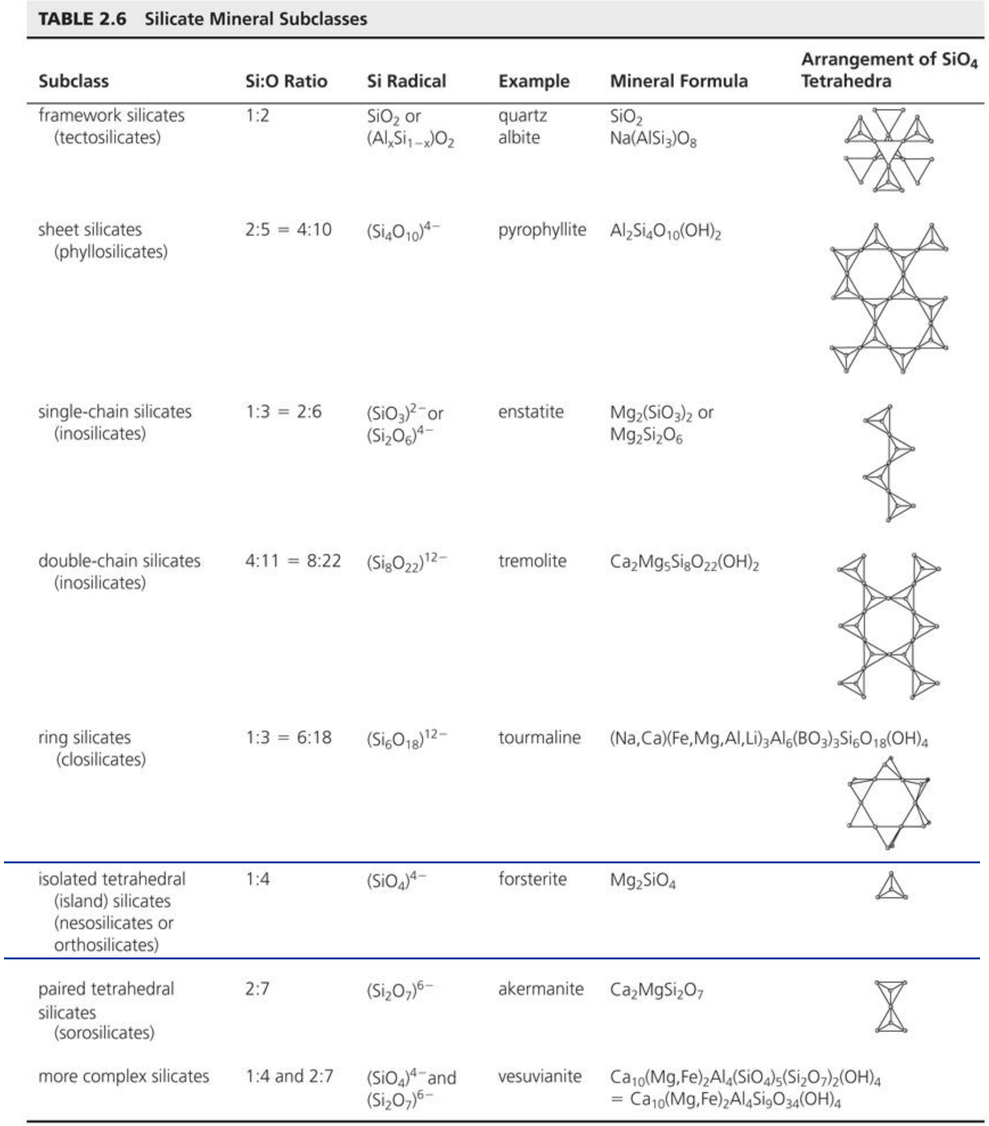
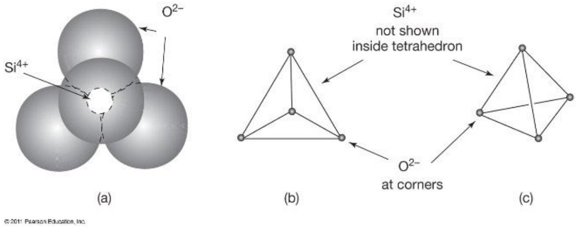
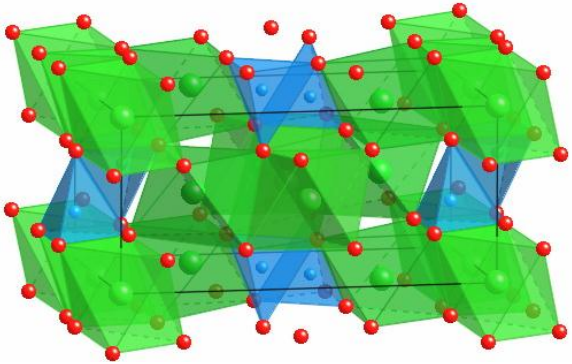


TABLE 2.6 Silicate Mineral Subclasses

Subclass	Si:O Ratio	Si Radical	Example	Mineral Formula	Arrangement of SiO_4 Tetrahedra
framework silicates (tectosilicates)	1:2	SiO_2 or $(Al_xSi_{1-x})O_2$	quartz albite	SiO_2 $Na(AlSi_3)O_8$	
sheet silicates (phyllosilicates)	2:5 = 4:10	$(Si_4O_{10})^{4-}$	pyrophyllite	$Al_2Si_4O_{10}(OH)_2$	
single-chain silicates (inosilicates)	1:3 = 2:6	$(SiO_3)^{2-}$ or $(Si_2O_6)^{4-}$	enstatite	$Mg_2(SiO_3)_2$ or $Mg_2Si_2O_6$	
double-chain silicates (inosilicates)	4:11 = 8:22	$(Si_8O_{22})^{12-}$	tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	
ring silicates (closilicates)	1:3 = 6:18	$(Si_6O_{18})^{12-}$	tourmaline	$(Na,Ca)(Fe,Mg,Al,Li)_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$	
isolated tetrahedral (island) silicates (nesosilicates or orthosilicates)	1:4	$(SiO_4)^{4-}$	forsterite	Mg_2SiO_4	
paired tetrahedral silicates (sorosilicates)	2:7	$(Si_2O_7)^{6-}$	akermanite	$Ca_2MgSi_2O_7$	
more complex silicates	1:4 and 2:7	$(SiO_4)^{4-}$ and $(Si_2O_7)^{6-}$	vesuvianite	$Ca_{10}(Mg,Fe)_2Al_4(SiO_4)_5(Si_2O_7)_2(OH)_4$ $= Ca_{10}(Mg,Fe)_2Al_4Si_9O_{34}(OH)_4$	

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





- $(Fe_xMg_{1-x})_2SiO_4$
- Ortorrombic structure (*Pbnm*).
- Red – oxygen.
- Blue – A sites, silicon.
- Green – B sites, magnesium or iron.

Thermodynamics and Acid-Base Chemistry

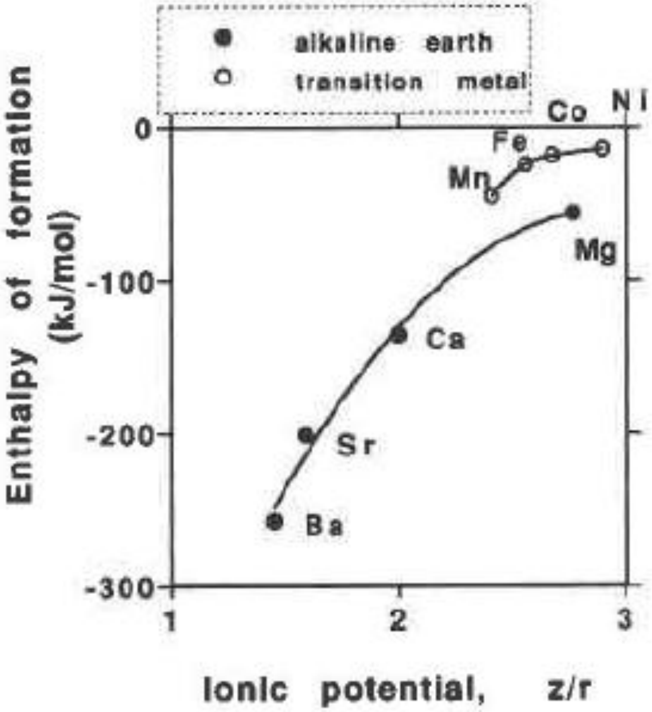
$MgO + SiO_2 = MgSiO_3$

Base Acid Enstatite

Ionic Potential (z/r)
and
Acid-Basic 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?

$$a = \gamma \cdot C$$

Concentration

Activity
coefficient

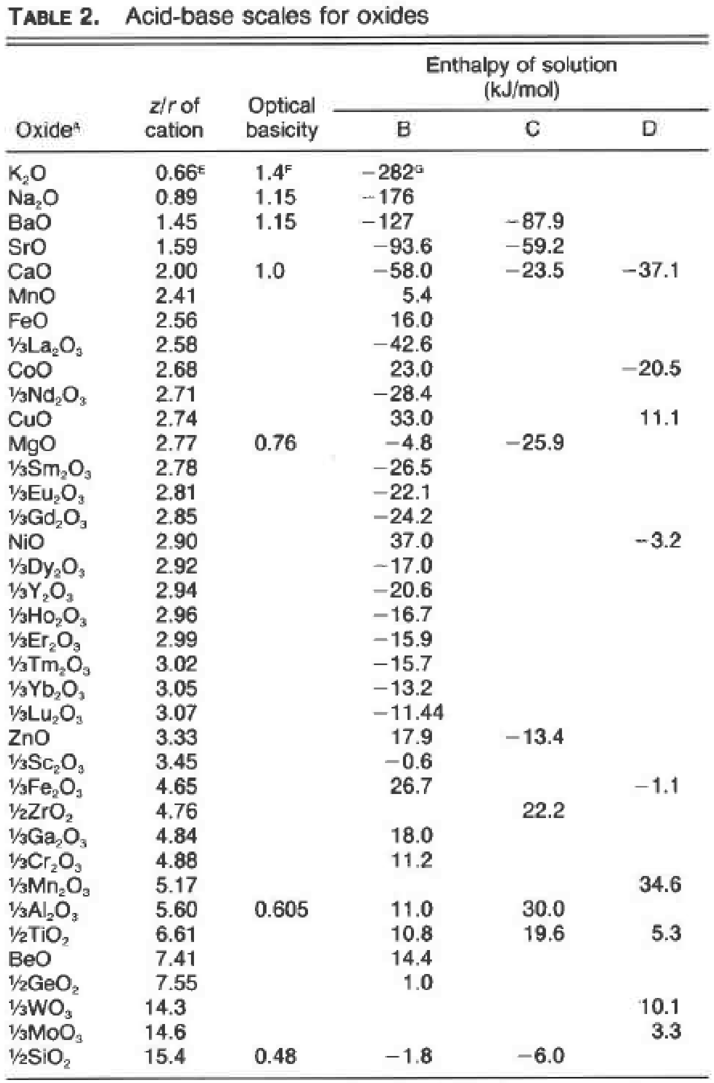


TABLE 2. Acid-base scales for oxides

Oxide[A]	z/r of cation	Optical basicity	Enthalpy of solution (kJ/mol)		
			B	C	D
K_2O	0.66[E]	1.4[F]	−282[G]		
Na_2O	0.89	1.15	−176		
BaO	1.45	1.15	−127	−87.9	
SrO	1.59		−93.6	−59.2	
CaO	2.00	1.0	−58.0	−23.5	−37.1
MnO	2.41		5.4		
FeO	2.56		16.0		
⅓La_2O_3	2.58		−42.6		
CoO	2.68		23.0		−20.5
⅓Nd_2O_3	2.71		−28.4		
CuO	2.74		33.0		11.1
MgO	2.77	0.76	−4.8	−25.9	
⅓Sm_2O_3	2.78		−26.5		
⅓Eu_2O_3	2.81		−22.1		
⅓Gd_2O_3	2.85		−24.2		
NiO	2.90		37.0		−3.2
⅓Dy_2O_3	2.92		−17.0		
⅓Y_2O_3	2.94		−20.6		
⅓Ho_2O_3	2.96		−16.7		
⅓Er_2O_3	2.99		−15.9		
⅓Tm_2O_3	3.02		−15.7		
⅓Yb_2O_3	3.05		−13.2		
⅓Lu_2O_3	3.07		−11.44		
ZnO	3.33		17.9	−13.4	
⅓Sc_2O_3	3.45		−0.6		
⅓Fe_2O_3	4.65		26.7		−1.1
½ZrO_2	4.76			22.2	
⅓Ga_2O_3	4.84		18.0		
⅓Cr_2O_3	4.88		11.2		
⅓Mn_2O_3	5.17				34.6
⅓Al_2O_3	5.60	0.605	11.0	30.0	
½TiO_2	6.61		10.8	19.6	5.3
BeO	7.41		14.4		
½GeO_2	7.55		1.0		
⅓WO_3	14.3				10.1
⅓MoO_3	14.6				3.3
½SiO_2	15.4	0.48	−1.8	−6.0	

A. Navrotsky, American Mineralogist, 79, 589-605, 1994..

Partial Thermodynamics Quantities: Activity and Vapor Pressure Measurement

Activity   Pressure

$\mathrm{M\ (s) = M\ (g)}$

$\mathrm{Au}(\ell) = \mathrm{Au(g)}$

$\Delta_v H^o$ = -R*(-41.162) = 342.20 kJ/mol

Tables = 342 kJ/mol

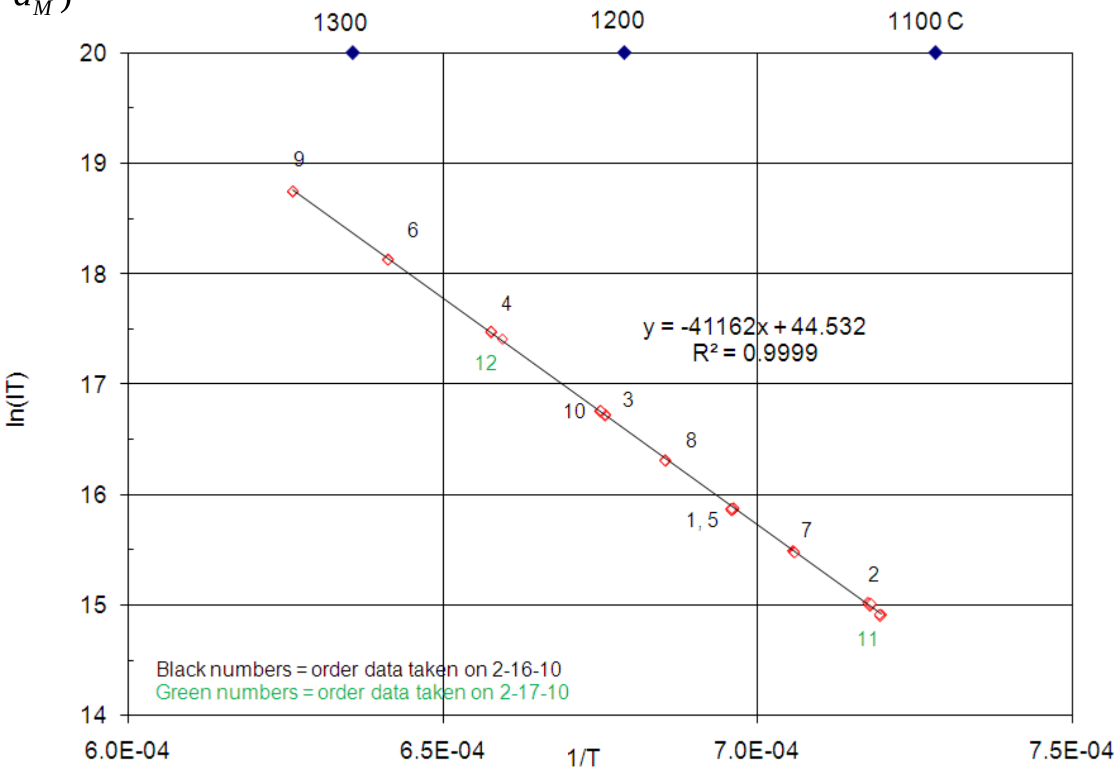
$$\Delta_v G = \Delta_v H - T\Delta_v S = -RT \ln K_p = -RT \ln(P_M / a_M)$$

$$\mathrm{a} = \gamma \cdot C$$

γ = activity coeficient; C = concentration

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

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



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

Mass Spectrometer $\quad \mathrm{P_M} = \dfrac{kIT}{\sigma}$

$\mathrm{P_M}$ = partial pressure of M;
k = instrument constant; I = ion intenisty;
T = Absolute temperature;
σ = ionization cross section

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(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

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

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

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

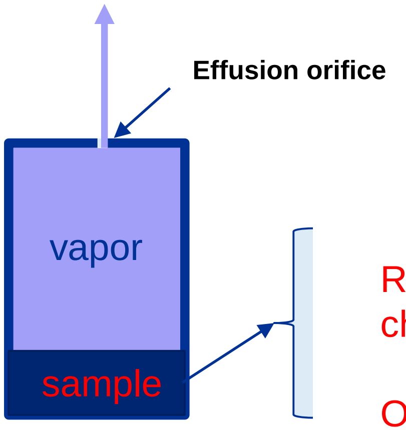
$$\mathrm{K_p} = \frac{P_{Fe}[P_{O_2}]^{1/2}}{a_{FeO}}$$

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

Methods to measure silica activity

- Oxidation-reduction equilibrium using gas mixtures or electrochemical cells
- High temperature reaction calorimetry
- **Knudsen Effusion Mass Spectrometry**

Mass spectrometer: Intensity → Pressure→ Activity



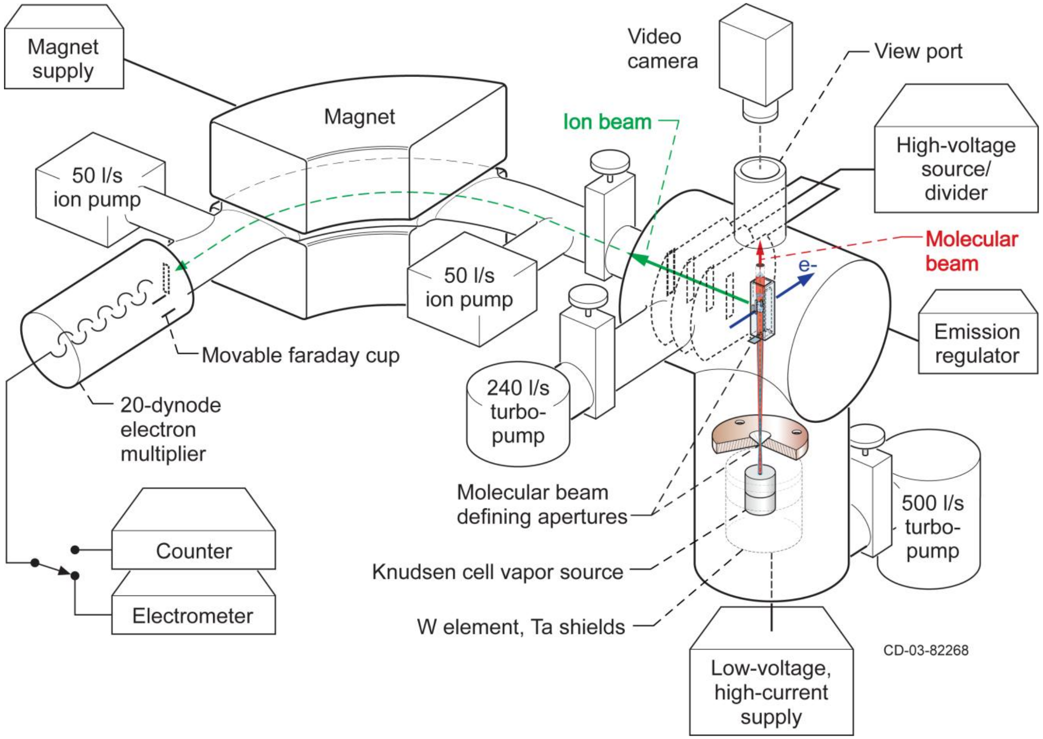
Exact approach depends on the system

RE-silicates - Reducing agent is used for to boost vaporization of SiO_2 without changing solid composition

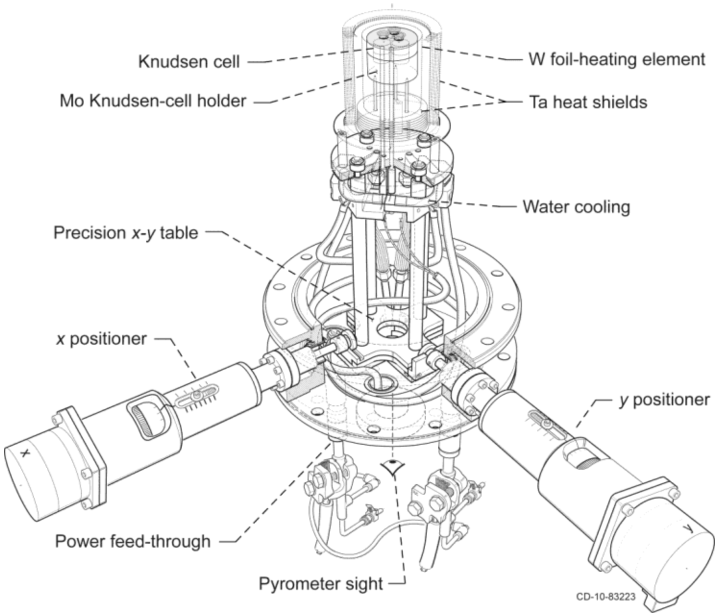
Olivine – Single cell configuration is used to attain higher temperatures

*A. I Zaitsev and B. M. Mogutnov, J Mater Chem 5, 1063 (1995)

Knudsen Effusion Mass Spectrometry (KEMS)

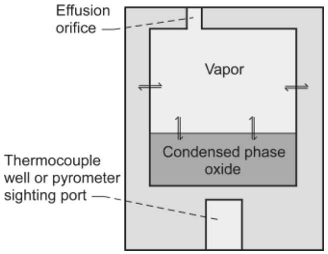


Use Multi-Cell Flange for a(SiO_2)



Design of E. Copland 2002

- 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

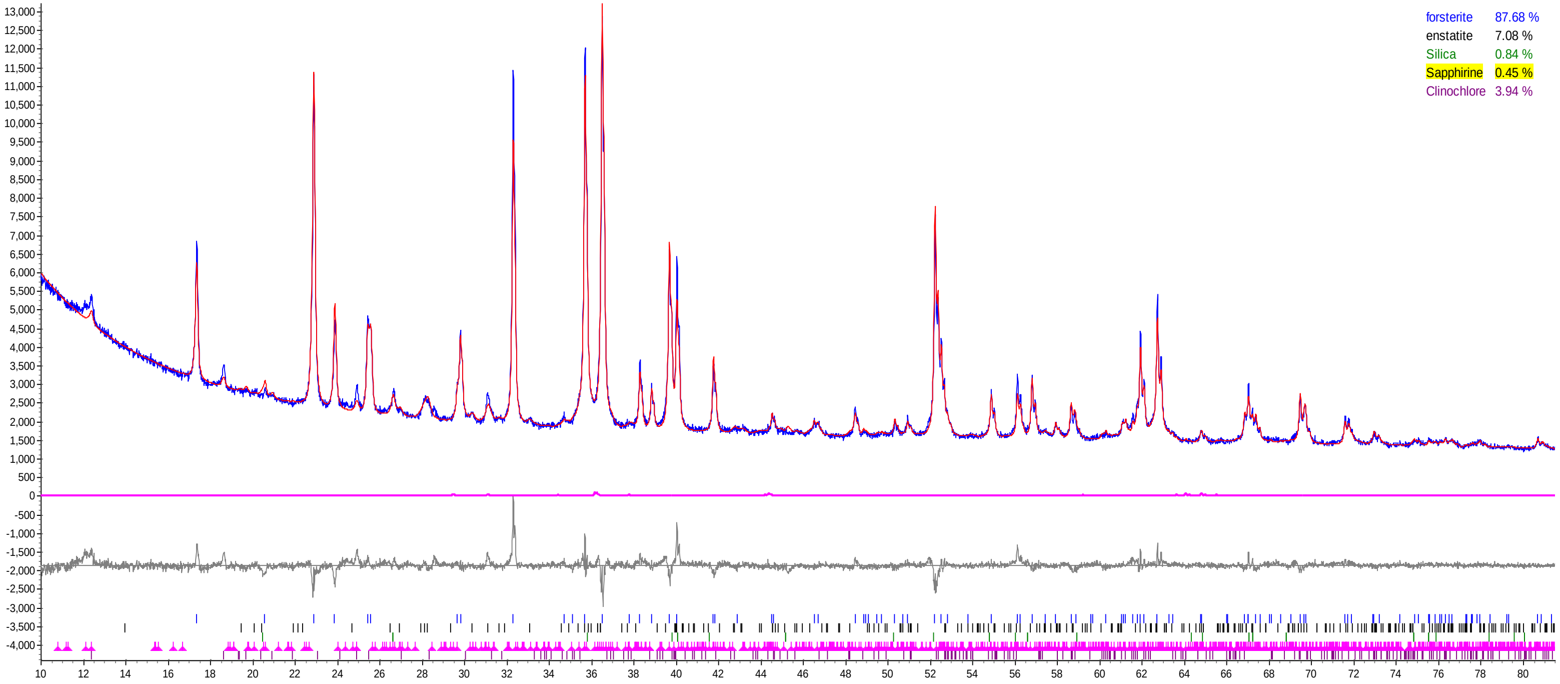
Olivine and Rare – Earth Silicates

Intensity → Pressure → Activity

Olivine - Results

Olivine – Starting Material and Characterization

93% forsterite and 7% fayalite, $Fo_{93}Fa_7$ - $(Fe_{0.7}Mg_{0.93})_2SiO_4$



XRD pattern and Rietveld refinement of the as received olivine samples.

ICP-OES analysis of the as received olivine samples.

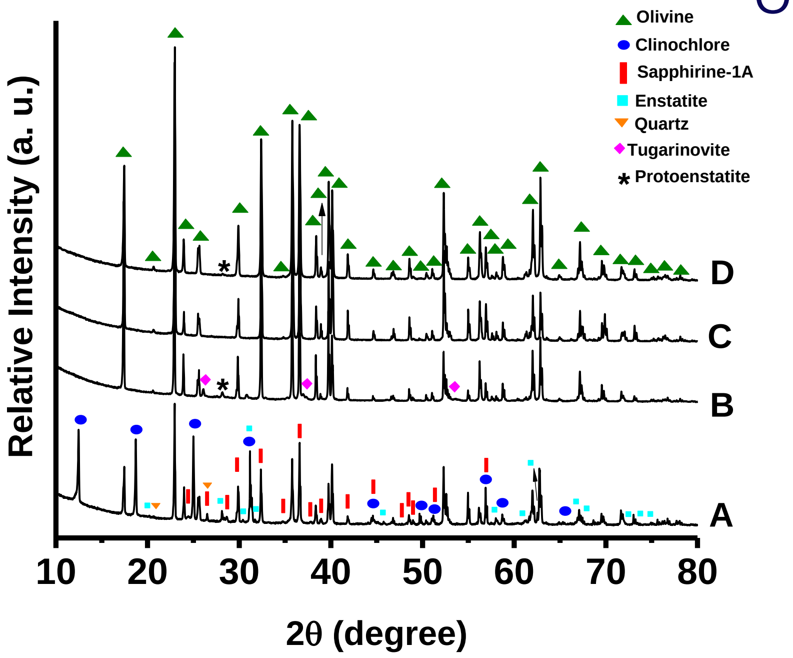
Element	*Wt (%)
Al	0.0120(6)
Ca	0.035(2)
Co	0.0120(6)
Cr	0.052(3)
Fe	5.01(3)
Mg	30(2)
Mn	0.075(4)
Na	0.0080(4)
Ni	0.27(1)
Sc	0.0040(2)
Si	20(1)

*Uncertainties of the analyses are given in parentheses.

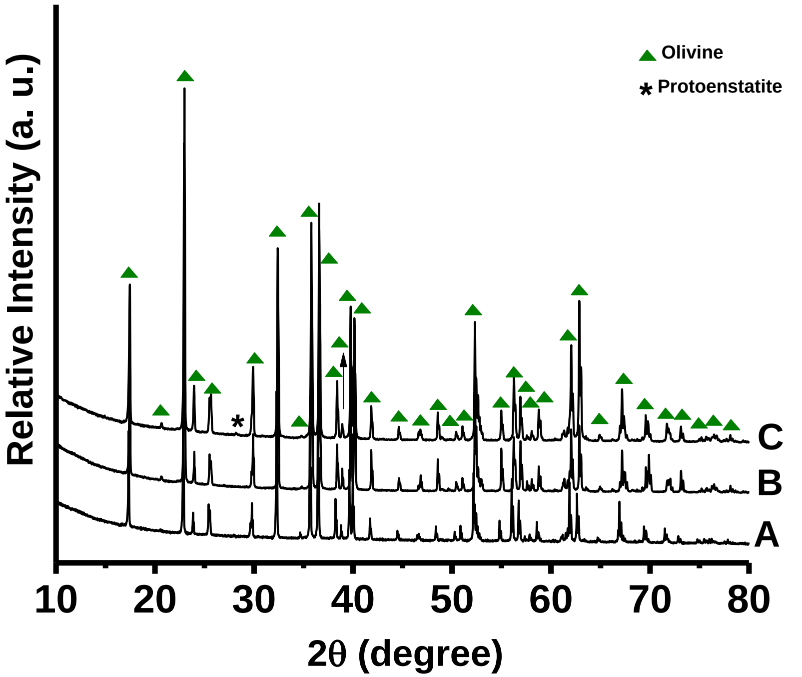
Phase content

- 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%

Olivine – Impurities and Container Issues



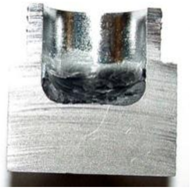
XRD patterns of the olivine samples : (**A**) as received , (**B**) after KEMS up to 2084 K in a Mo Knudsen cell (**C**) after KEMS up to 1850 K in a Mo Knudsen cell (**D**) after KEMS up 2079 K in an Ir Knudsen cell.



XRD patterns of the olivine samples : (**A**) green sand from Hawaii, (**B**) after KEMS up to 1850 K in a Mo Knudsen cell (**C**) 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.

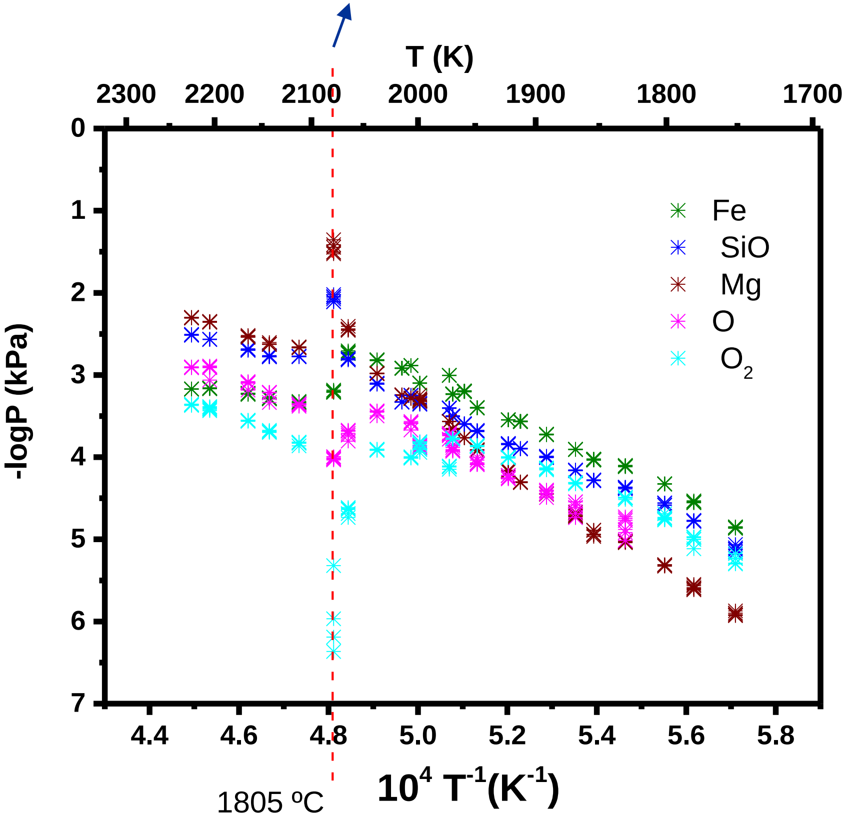
Element	**Wt (%)**		
	Sample as received[a]	After KEMS in a Mo cell	After KEMS in a Ir cell
Al	0.0120(6)	0.016(6)	0.2(1)
Ca	0.035(2)	0.009(2)	0.04(2)
Co	0.0120(6)	0.003(2)	0.004(3)
Cr	0.052(3)	0.035(4)	0.06(1)
Fe	5.01(3)	0.006(3)	0.93(3)
Mg	30(2)	35.0(1)	34(1)
Mn	0.075(4)	0.003(1)	0.031(3)
Na	0.0080(4)	-	-
Ni	0.27(1)	0.005(3)	0.006(3)
Sc	0.0040(2)	-	-
Si	20(1)	19.3(1)	21.8(8)
Mo	0	0.04(2)	0
Ir	0	0	0.06(3)



Side view (cross-section) of the Mo Knudsen cell containing the olivine sample heat treated up to 2084 K.

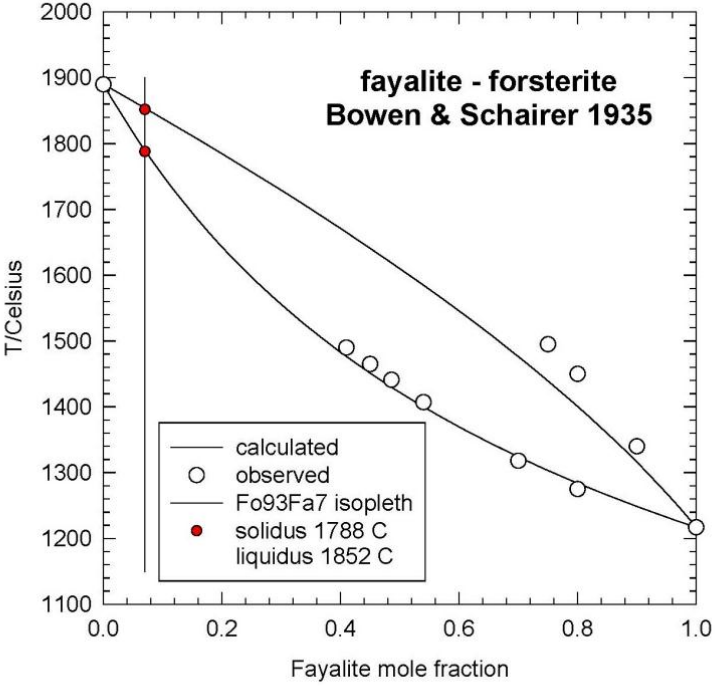
Complete van't Hoff Plot

Interesting discontinuity at melting



1805 ºC

Temperature dependence of ion intensity ratios of Mg^+, Fe^+, SiO^+, O^+ and O_2^+ in the olivine sample.

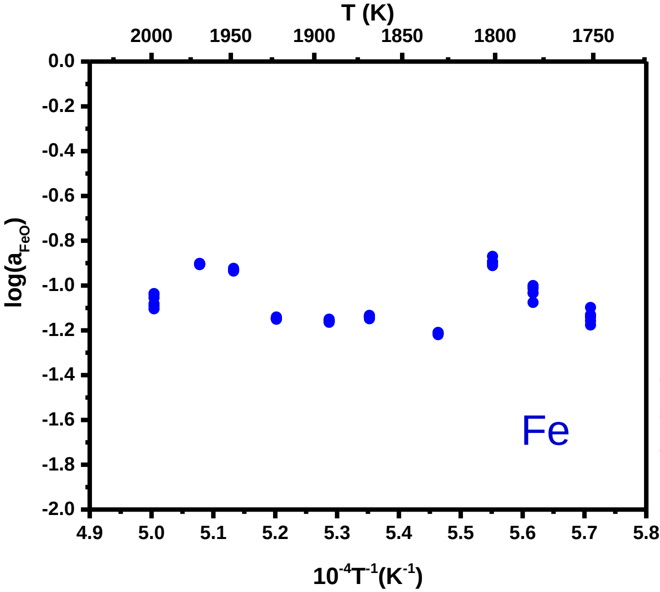


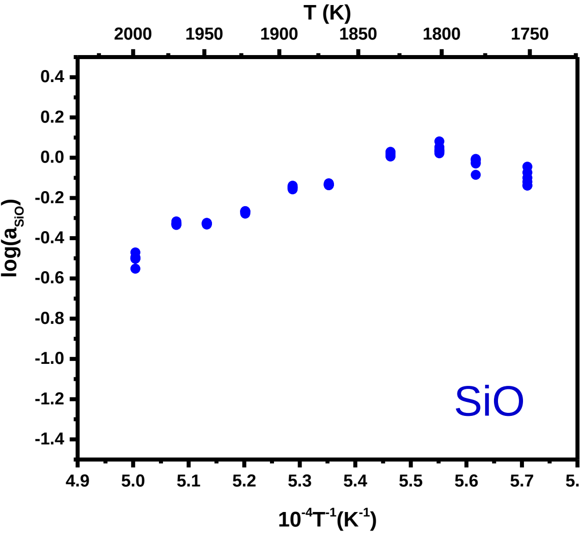
Fegley and Osborne, "Practical Chemical Thermodynamics For Geoscientists, Elsevier 2013, Fig. 12-11.

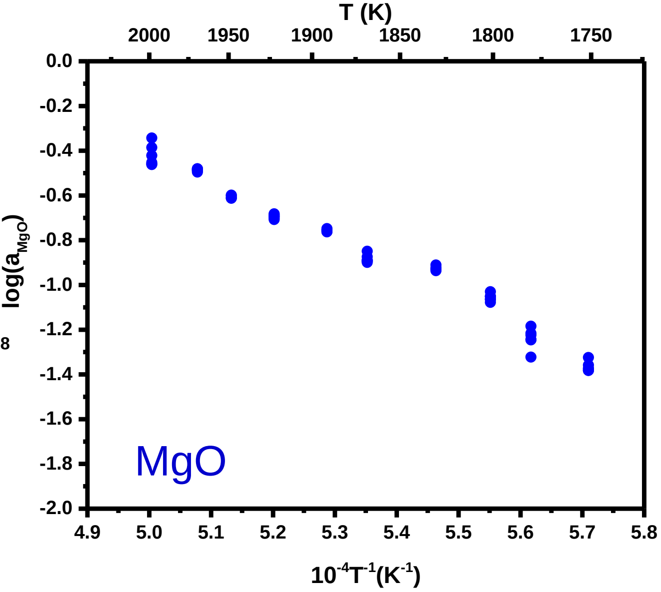
Measurements show good agreement with the phase diagram calculated by Bowen and Shairer.

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

Thermodynamic Activities in Olivine - $(Fe_xMg_{1-x})_2SiO_4$







Fe, Mg or Si

$$MO_{(solution,\ a<1)} = M_{(g)} + 1/2O_{2(g)}$$

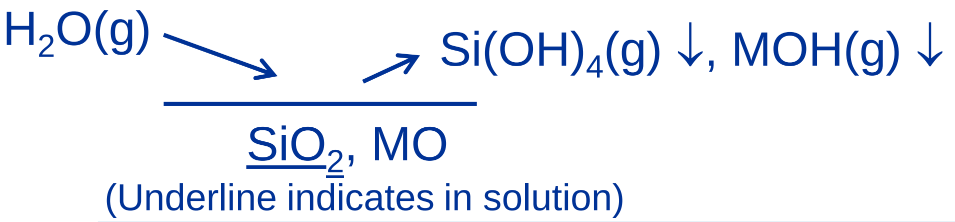
$$K_p = \frac{P_M[P_{O_2}]^{1/2}}{a_{FeO}}$$

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

→ From FactSage or measured by KEMS

Rare earth Silicates

Low Reactivity of Rare earth Silicates



$H_2O(g)$ → → $Si(OH)_4(g)$ ↓, $MOH(g)$ ↓

$\underline{SiO_2}$, MO

(Underline indicates in solution)

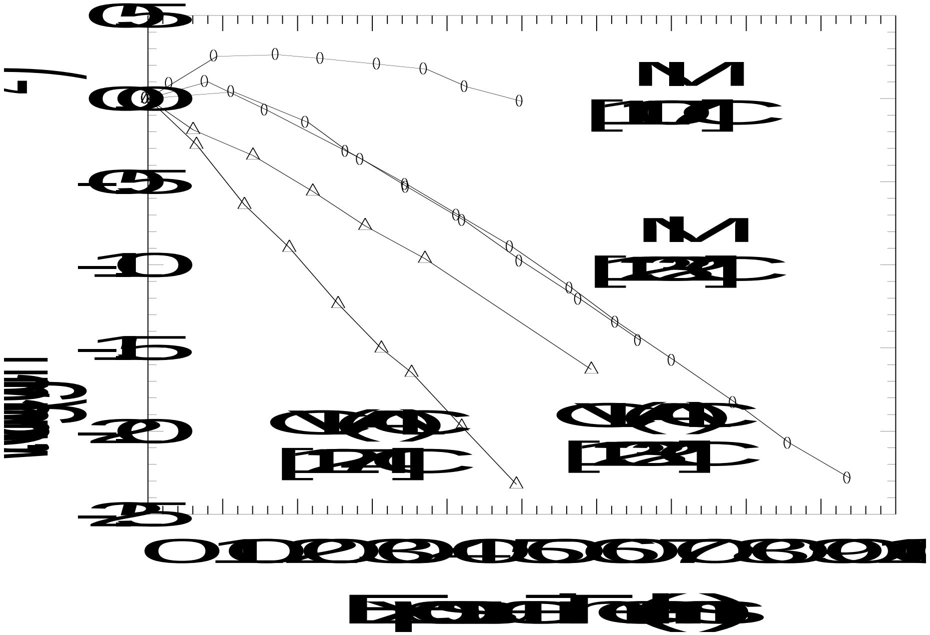
$SiC + 3/2\ O_2(g) = SiO_2 + CO(g)$

- $\underline{SiO_2} + 2\ H_2O(g) = Si(OH)_4(g)$

$P[Si(OH)_4] = K\ a\ SiO_2\ [P(H_2O)]^2$

Y and Yb silicates
Need to be measured!

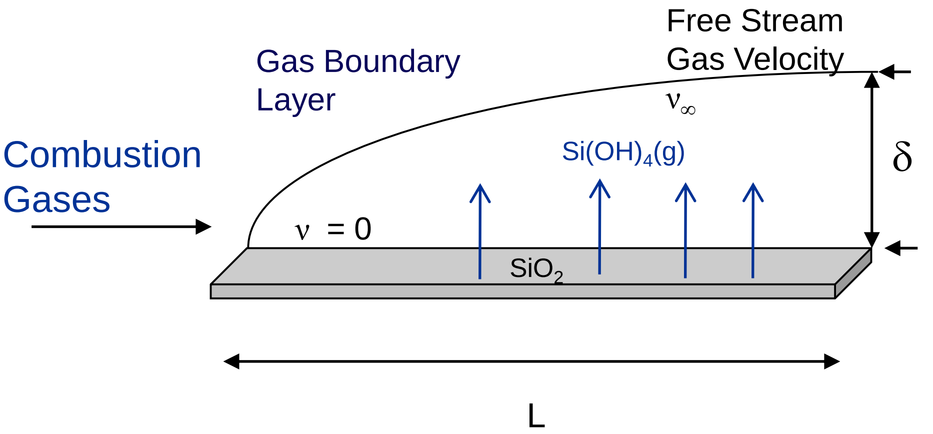
SiC/SiC CMC HPBR Paralinear Weight Change
(1100 °-1300°C, 6 atm; Robinson/Smialek 1998)
$Si(OH)_4$ volatility (Opila et al., 1998-2006)



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

Key Parameters in Boundary Layer Limited Transport Modeling

- SiO_2(pure or in silicate soln) + 2 H_2O(g) = $Si(OH)_4$(g)



$$Flux = 0.664\left(\frac{\nu_\infty \rho_\infty L}{\eta}\right)^{0.5}\left(\frac{\eta}{D_{Si(OH)_4}\rho_\infty}\right)^{0.33}\frac{D_{Si(OH)_4}P_{Si(OH)_4}}{R\,T\,L} =$$

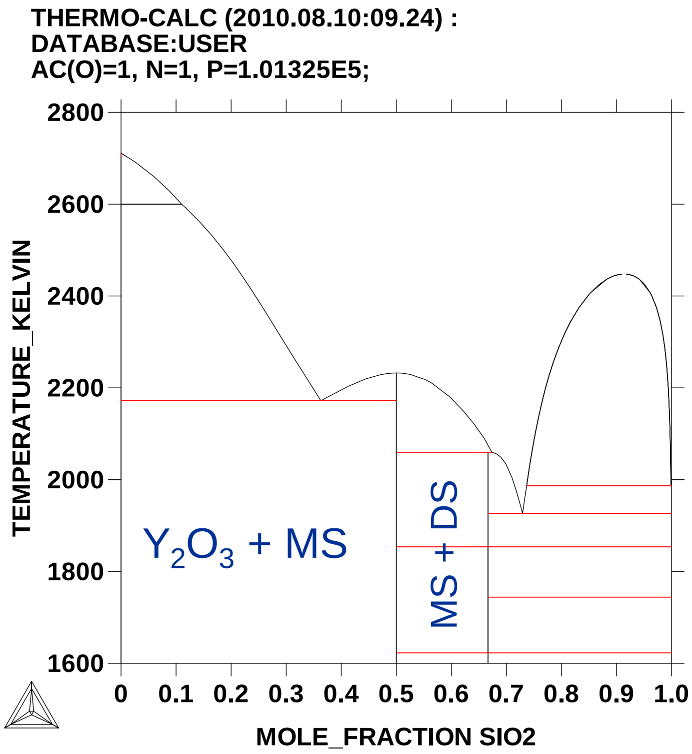
$$0.664\left(\frac{\nu_\infty \rho_\infty L}{\eta}\right)^{0.5}\left(\frac{\eta}{D_{Si(OH)_4}\rho_\infty}\right)^{0.33}\frac{D_{Si(OH)_4}}{R\,T\,L}K\,a_{SiO_2}\left(P_{H_2O}\right)^2$$

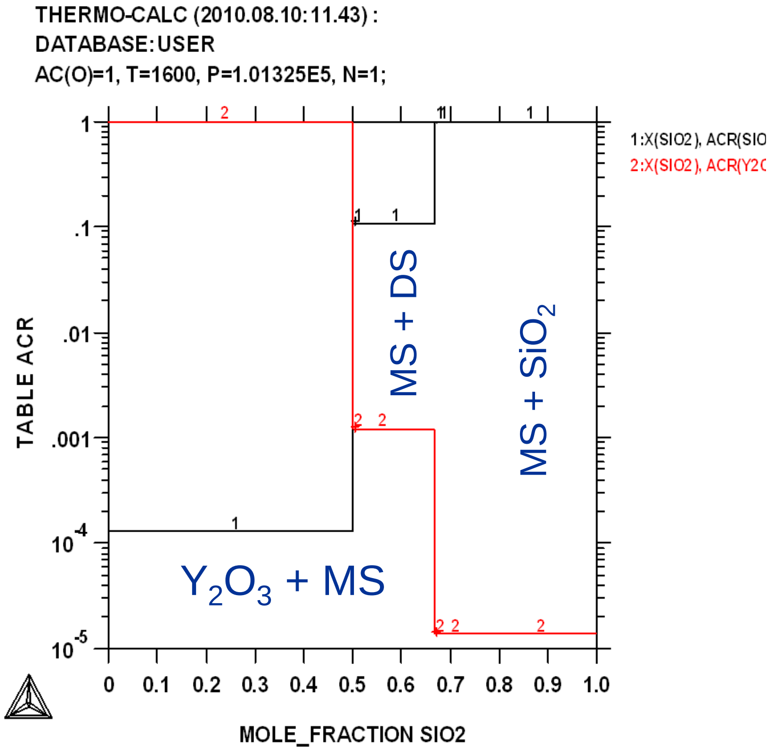
ν_∞ = free stream velocity ρ_∞ = free stream gas density L = characteristic dimension

η = viscosity $D_{Si(OH)_4}$ = gas phase diffusivity of $Si(OH)_4$

- Reduce $a(SiO_2) \Rightarrow$ reduce recession. Recession drives need for coatings

Calculated Y_2O_3-SiO_2 Phase Diagram: Fabrichnaya-Seifert Database





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!

Issues with Measuring a(SiO_2) in RE Silicates

- Vapor pressure of SiO_2 too low to measure in temperature range of interest

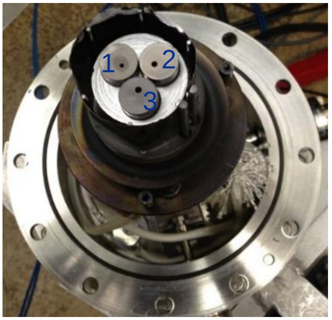
- Need measurable signal for SiO_2—use reducing agent to make excess SiO(g). Tried several, selected Mo or Ta
  - For a(SiO_2) < ~0.02
    - $2Ta(s) + 2\underline{SiO_2}(soln) = 2SiO(g) + TaO(g) + TaO_2(g)$
  - For a(SiO_2) > ~0.02
    - $Mo(s) + 3\underline{SiO_2}(soln) = 3SiO(g) + MoO_3(g)$
  - Note 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
  - Gettering pump for CO_2

Approaches use two phase regions

Cells are part of the system



1 – Monosilicate + RE_2O_3

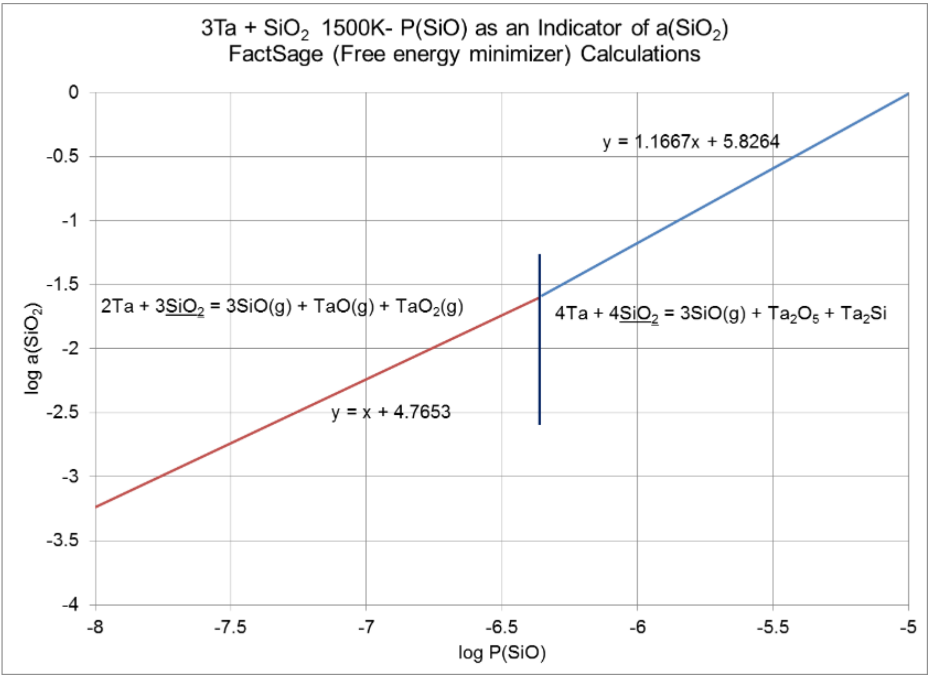
Two cells:

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

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

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

- Correction for non-equilibrium vaporization



2 – Monosilicate + Disilicate

Three cells:

- Au (reference)
- $3Mo + Y_2O_3 \cdot 2SiO_2 + Y_2O_3 \cdot SiO_2$
- $3Mo + SiO_2$

$Mo(s) + 3\underline{SiO_2}(soln) = 3SiO(g) + MoO_3(g)$

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

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

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

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

$$Mo + 3\underline{SiO_2} = 3SiO + MoO_3$$

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

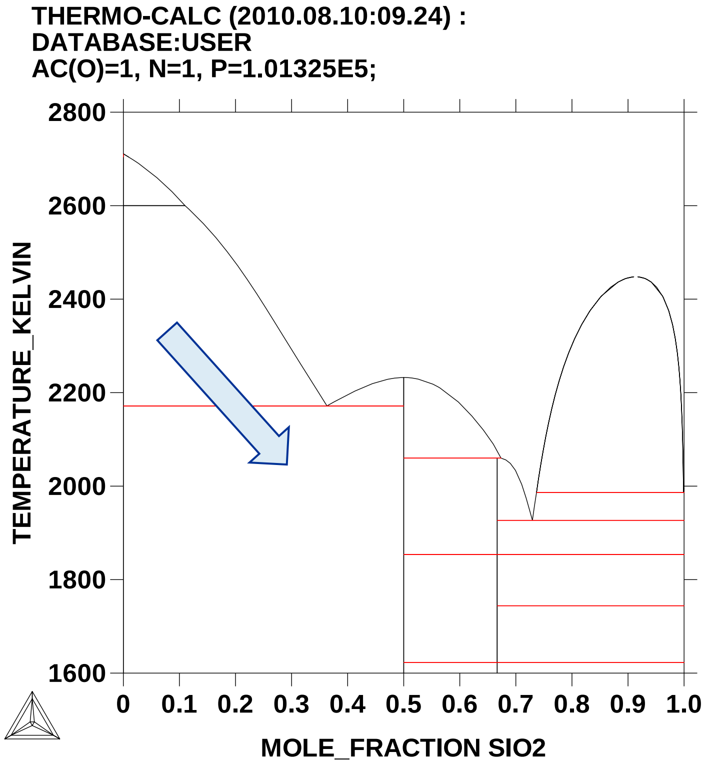
Cell 2

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

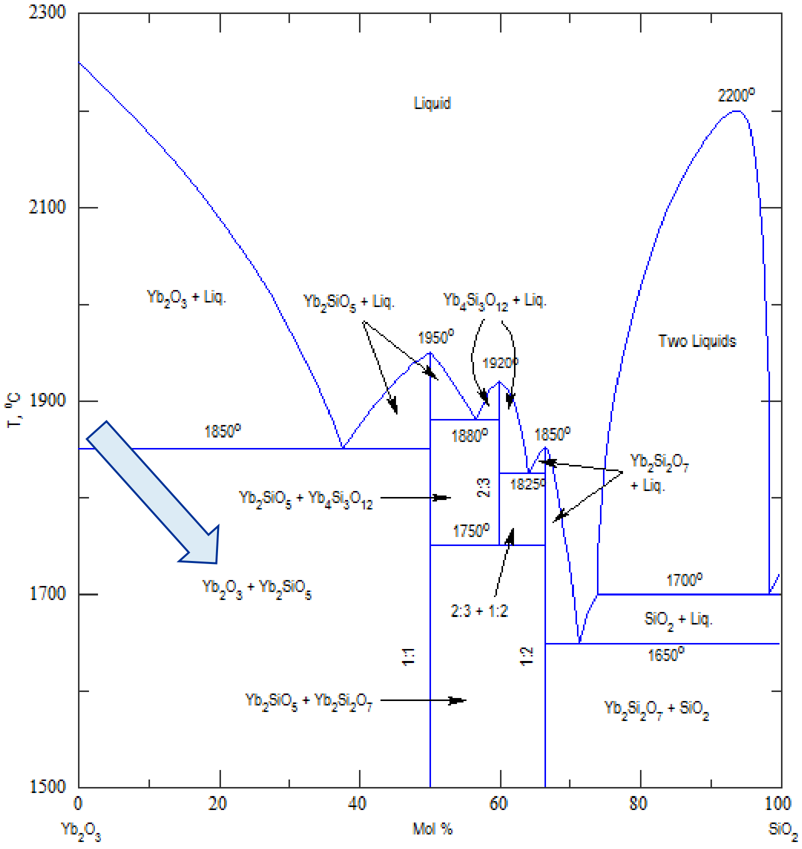
Cell 3

Monosilicate + RE_2O_3

Y_2O_3-SiO_2

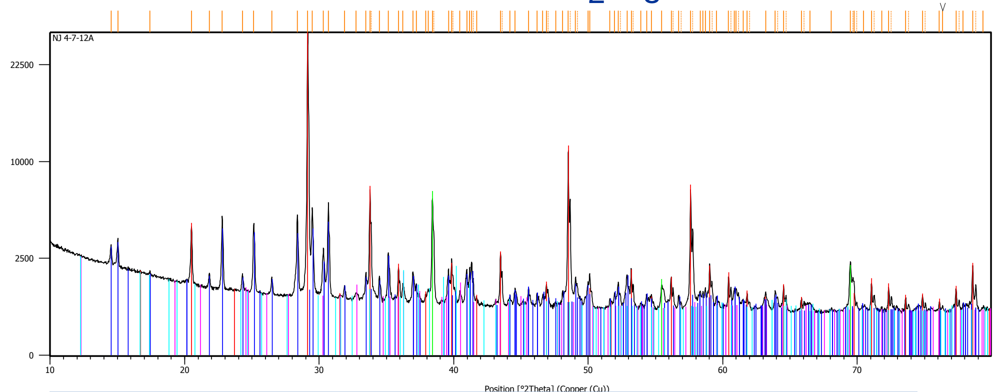


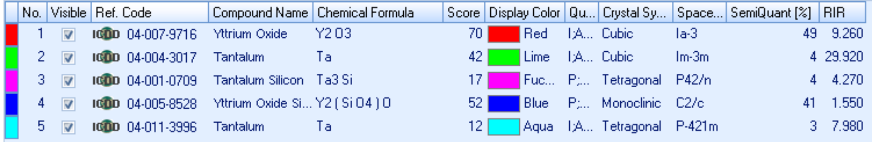
Yb_2O_3-SiO_2



XRD after KEMS Measurements of RE Monosilicates + RE_2O_3 + Ta:

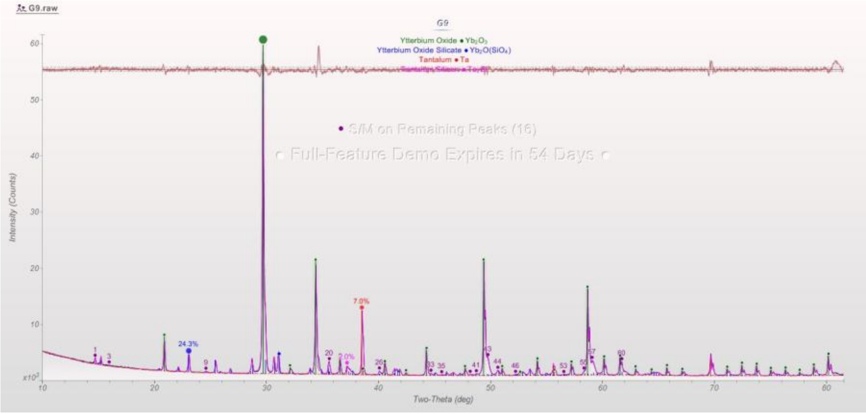
Yttrium monosilicate + Y_2O_3 + Ta





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

Ytterbium monosilicate + Yb_2O_3 + Ta

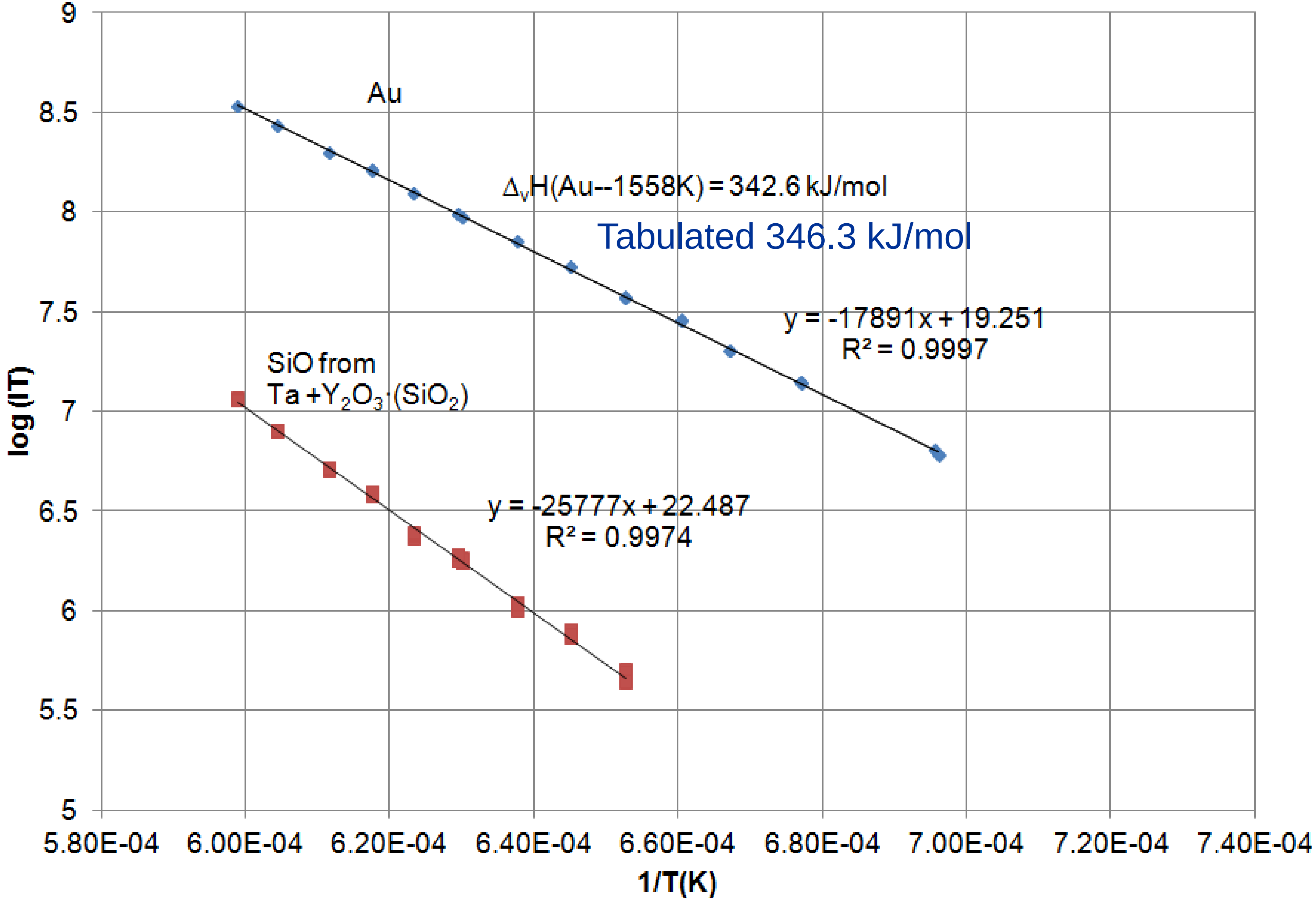


Phase	wt (%)
$Y_2O_3.(SiO_2)$	41
Y_2O_3	49
Ta	4
Ta_3Si	4

Phase	wt (%)
$Yb_2O_3.(SiO_2)$	24
Yb_2O_3	66
Ta	2
Ta_2Si	2

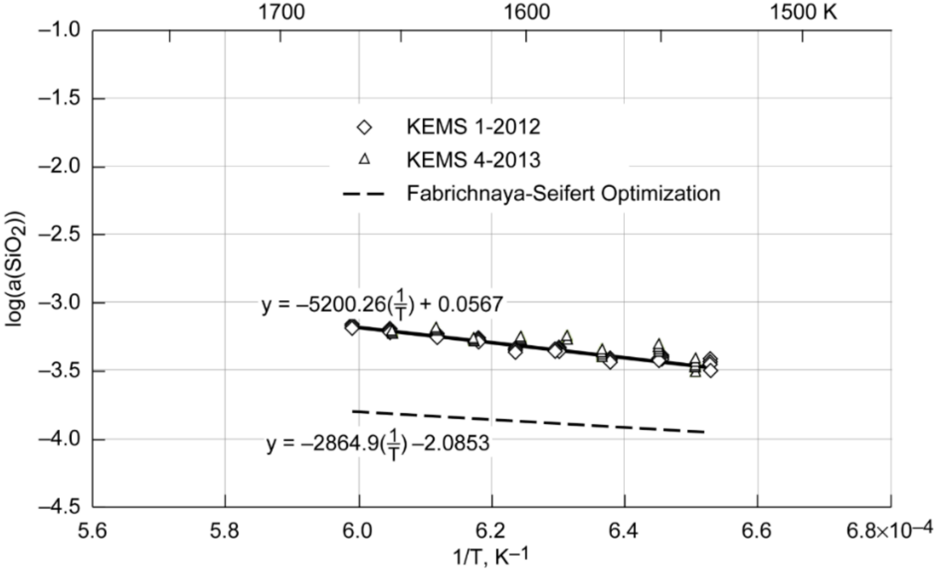
Raw Data—log (IT) vs 1/T

Cell (1): Au Reference Cell (2): Ta + Y_2O_3 + MS



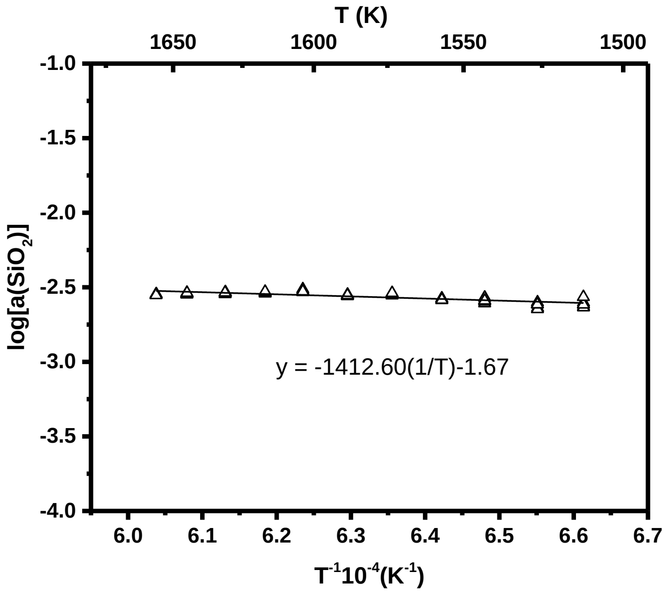
Tabulated 346.3 kJ/mol

Y_2O_3 + $Y_2O_3.(SiO_2)$



$\Delta H_{(SiO2,\ 1600\ K)}$ = (5200.26)·R·2.303 = 99.57 kJ/mol

Yb_2O_3 + $Yb_2O_3.(SiO_2)$



$\Delta H_{(SiO2,\ 1600\ K)}$ = (1412.60)·R·2.303 = 27.05 kJ/mol

$RE_2O_{3(s,\ 1600\ K)} + SiO_{2(s,\ 1600\ K)} \rightarrow RE_2SiO_{5(s,\ 1600\ K)}$	ΔH_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*	Optical basicity**	$a(SiO_2)$, 1650 K
$Y_2O_3.(SiO_2)$	-2907 ± 16	-2868.54 ± 5.34	0.786	0.000804
$Yb_2O_3.(SiO_2)$	-2744 ± 11	-2774.75 ±16.48	0.729	0.00298

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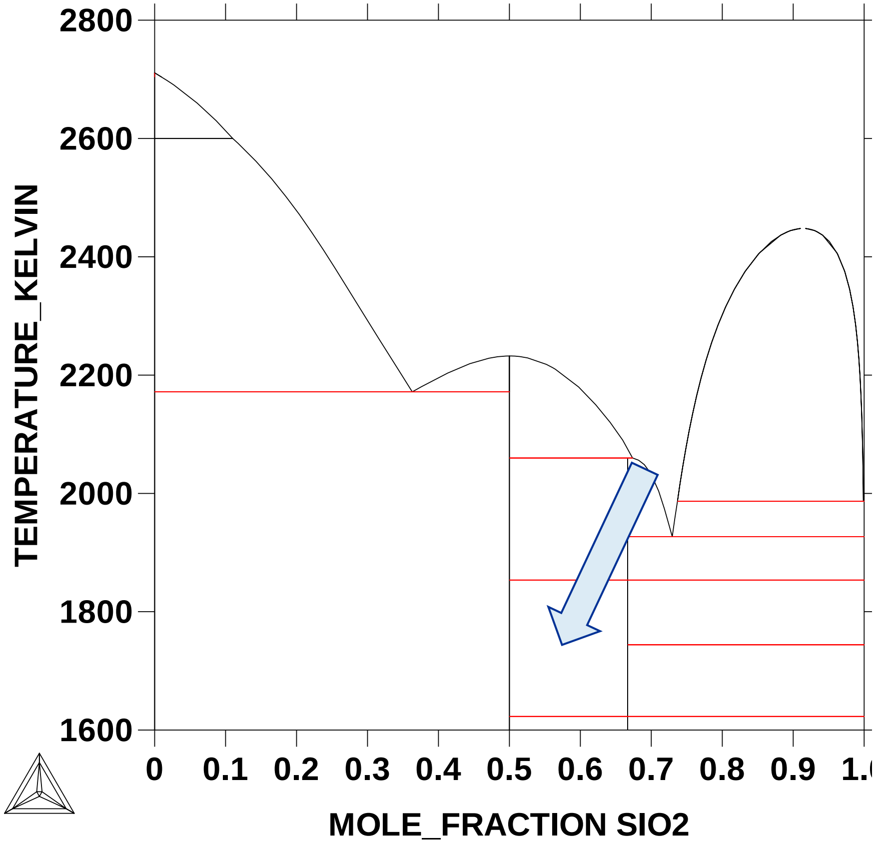
*Liang et al. “Enthalpy of formation of rare-earth silicates Y_2SiO_5 and Yb_2SiO_5 and N-containing silicate $Y_{10}(SiO_4)_6N_2$”, J. Mater. Res. 14 [4], 1181-1185. **J. A. Duff, J. Phys. Chem. A 110, 13245 (2006)

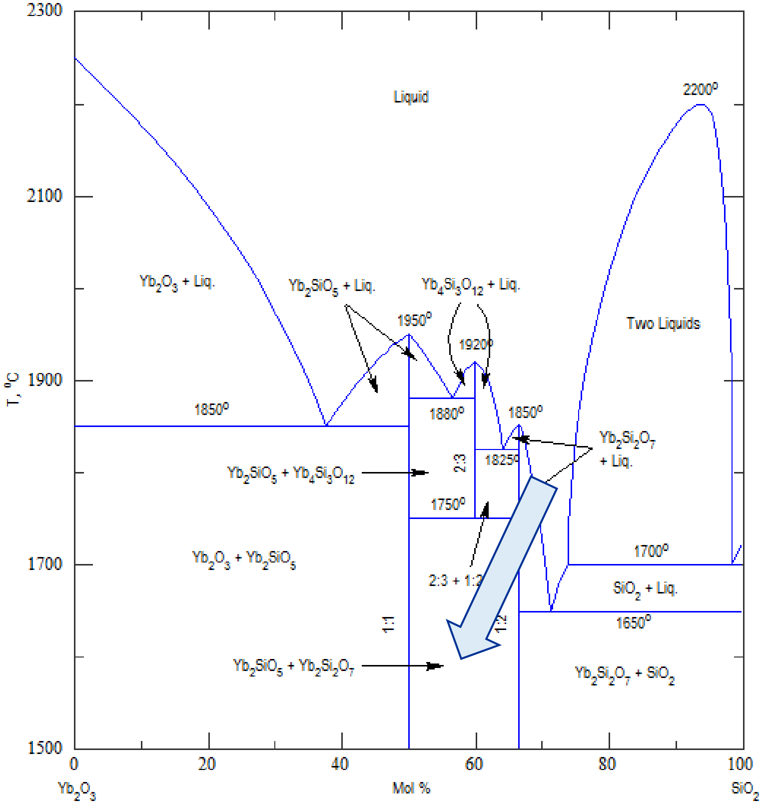
Monosilicate + Disilicate

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;

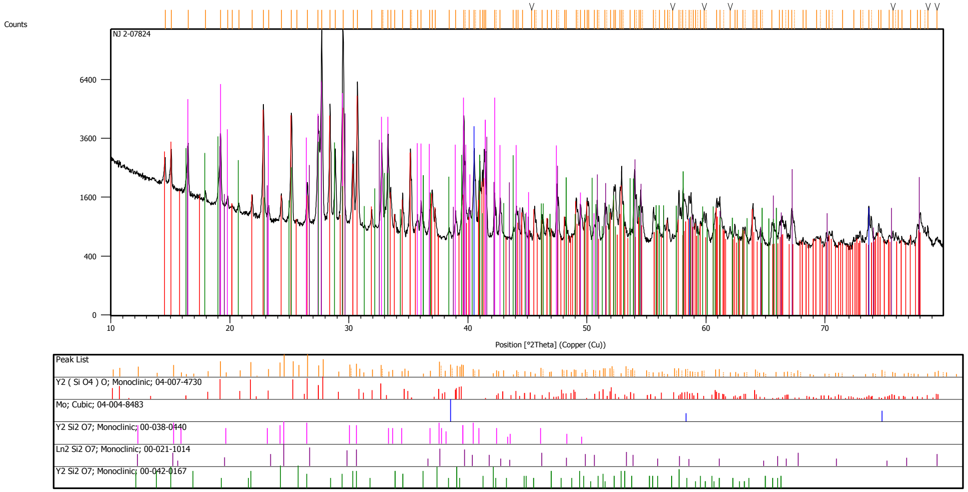


Yb_2O_3-SiO_2+ Yb_2O_3-$2SiO_2$



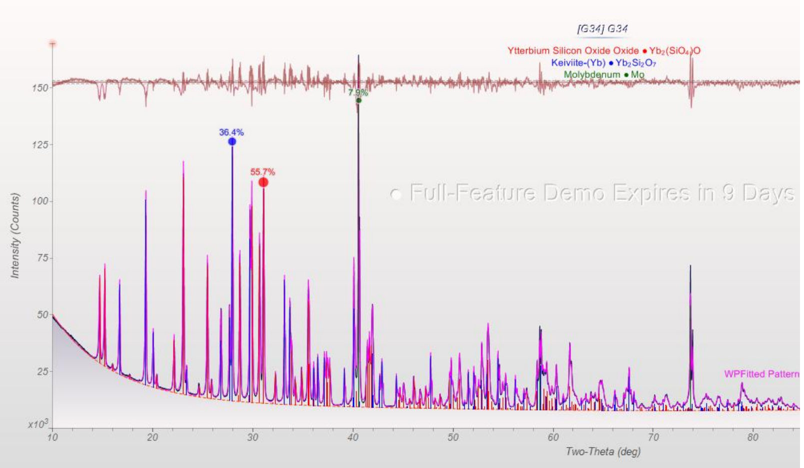
XRD after KEMS Measurements of RE Monosilicates + Disilicates + Mo:

Yttrium monosilicate + disilicate +Mo



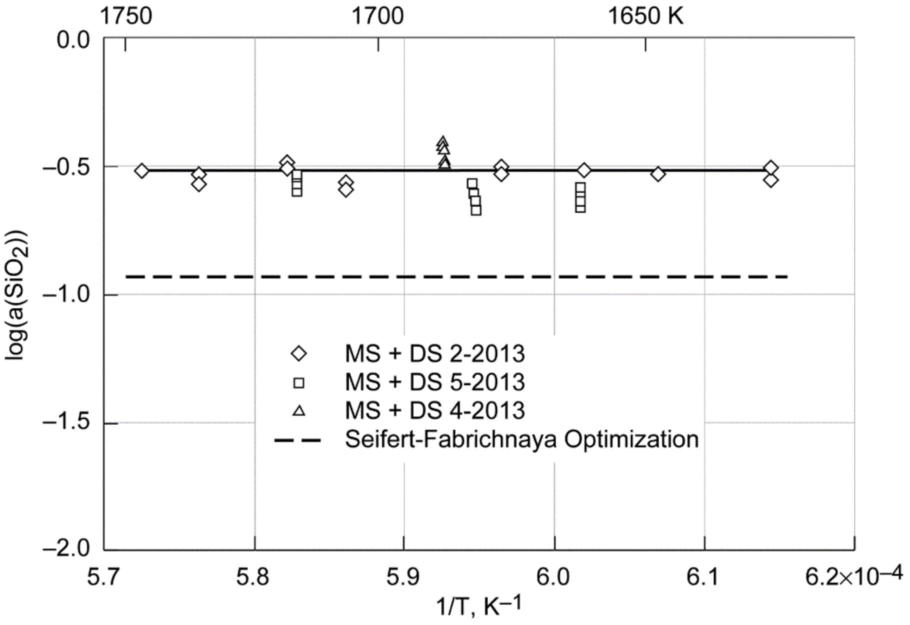
Phase
$Y_2O_3.(SiO_2)$
$Y_2O_3.2(SiO_2)$
Mo

Ytterbium monosilicate + disilicate + Mo

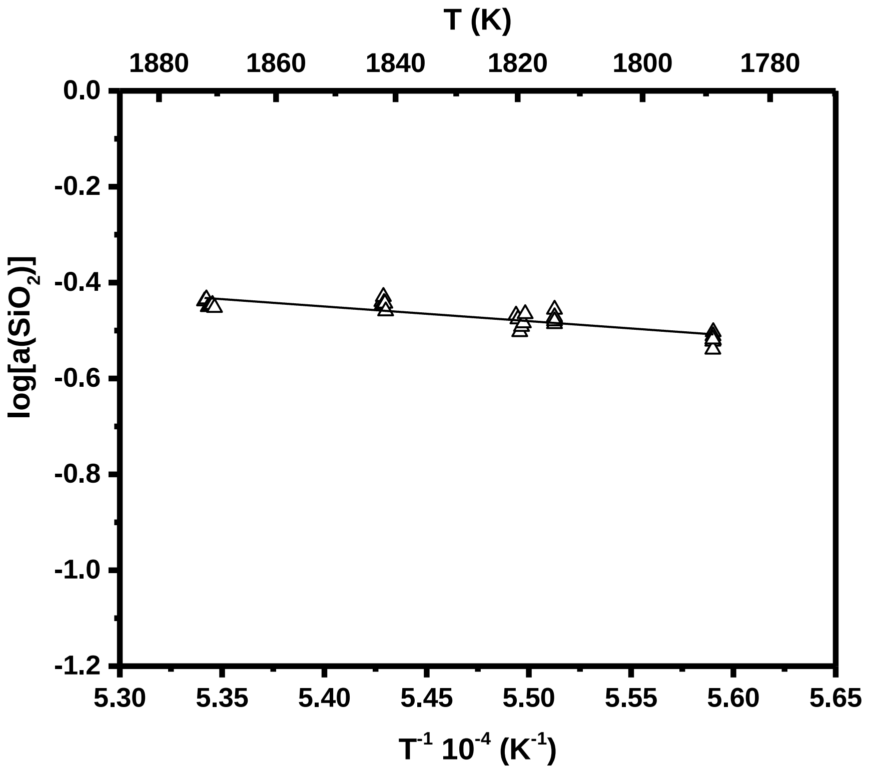


Phase	wt (%)
$Yb_2O_3.(SiO_2)$	56
$Yb_2O_3.2(SiO_2)$	36
Mo	8

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

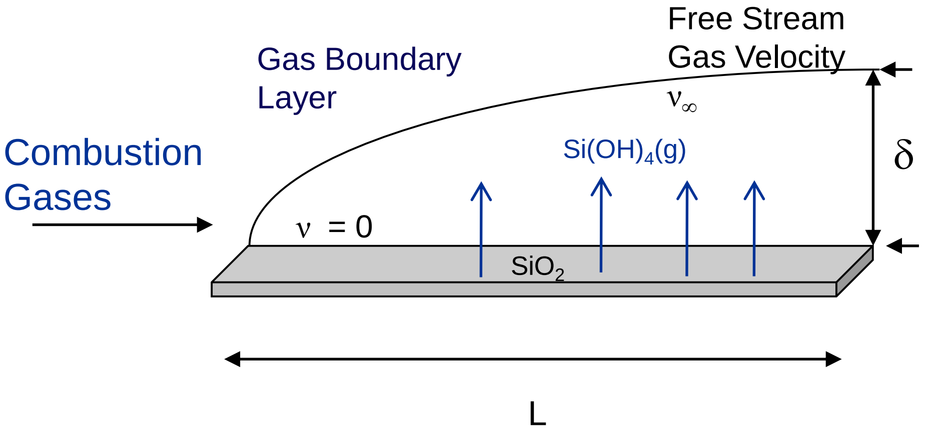


$Yb_2O_3.(SiO_2)$ + $Yb_2O_3.2(SiO_2)$

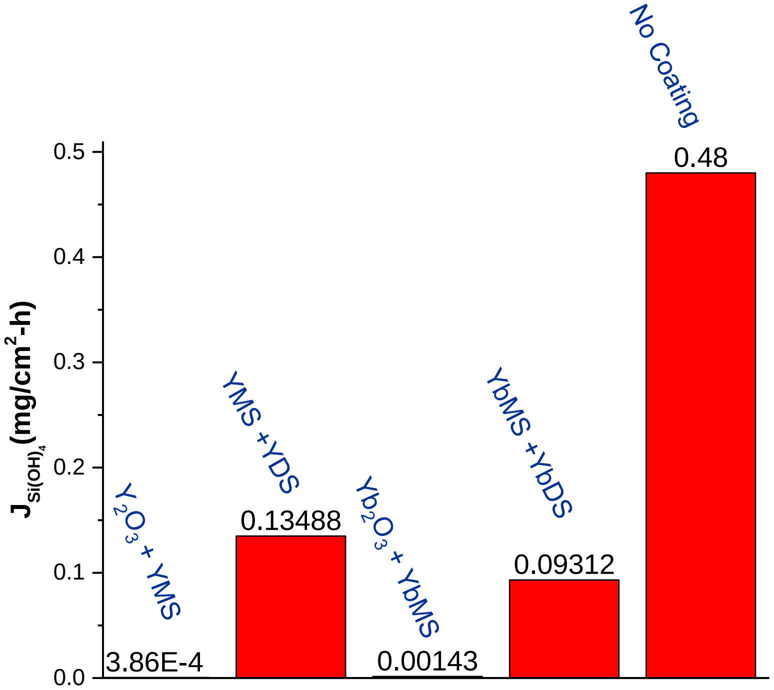


Optical basicity**		$a(SiO_2)$, 1650 K
$Y_2O_3.(SiO_2)$	$Y_2O_3.2(SiO_2)$	
0.786	0.699	0.281
$Yb_2O_3.(SiO_2)$	$Yb_2O_3.2(SiO_2)$	
0.729	0.657	0.194

Now Have the Needed Quantities for Modeling Recession



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



- T = 1300°C; P = 10 bar; $P(H_2O)$ = 1 bar
- v_∞ = 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

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 $\Rightarrow$ recession modeling input data

Acknowledgements

- Helpful discussions with B. Opila (Formerly NASA Glenn now University of Virginia)
- Multiple cell and sampling system improvements to mass spectrometer: E. Copland (formerly NASA Glenn now CSIRO, Sydney, Australia)
- XRD: R. Rogers (NASA Glenn)
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