



# Thermochemistry of Rare Earth Silicates for Environmental Barrier Coatings

Gustavo Costa and Nathan Jacobson  
NASA Glenn Research Center  
Cleveland, OH  
[gustavo.costa@nasa.gov](mailto:gustavo.costa@nasa.gov)

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# Outline of Presentation

- Advantages of Rare earth silicates as Environmental Barrier Coatings (EBCs)
- Essential parameter –  $a(\text{SiO}_2)$
- Methods to measure silica activity
  - **Thermodynamics of rare earth silicates: Knudsen Effusion Mass Spectrometry**
- Results of  $\text{Y}_2\text{O}_3\text{-SiO}_2$  and  $\text{Yb}_2\text{O}_3\text{-SiO}_2$  systems
- Benefits of coating - example

## Rare Earth Silicates as Coatings for Silicon-based Ceramics

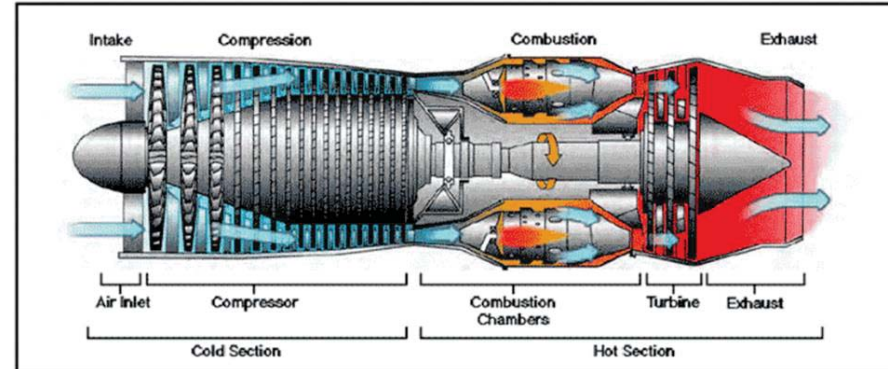
- Stable to high temperatures
- Disilicate: Appropriate thermal expansion match to SiC and SiC composites
- Lower reactivity than pure  $\text{SiO}_2$

### Applications:

#### Ceramics in non-moving parts:

- Combustor liners
- Exhaust nozzles

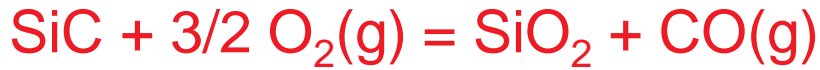
#### Eventually moving parts!



## Sensors and Electronic Circuits in Extreme Environments: Space and Deep Oil Exploration



# Low Reactivity of Rare earth Silicates



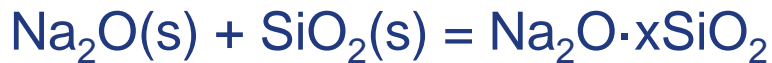
SiO<sub>2</sub>, MO  
(Underline indicates in solution)

**SiC/SiC CMC HPBR Paralinear Weight Change**  
(1100 °-1300°C, 6 atm; Robinson/Smialek 1998)  
Si(OH)<sub>4</sub> volatility (Opila et al., 1998-2006)

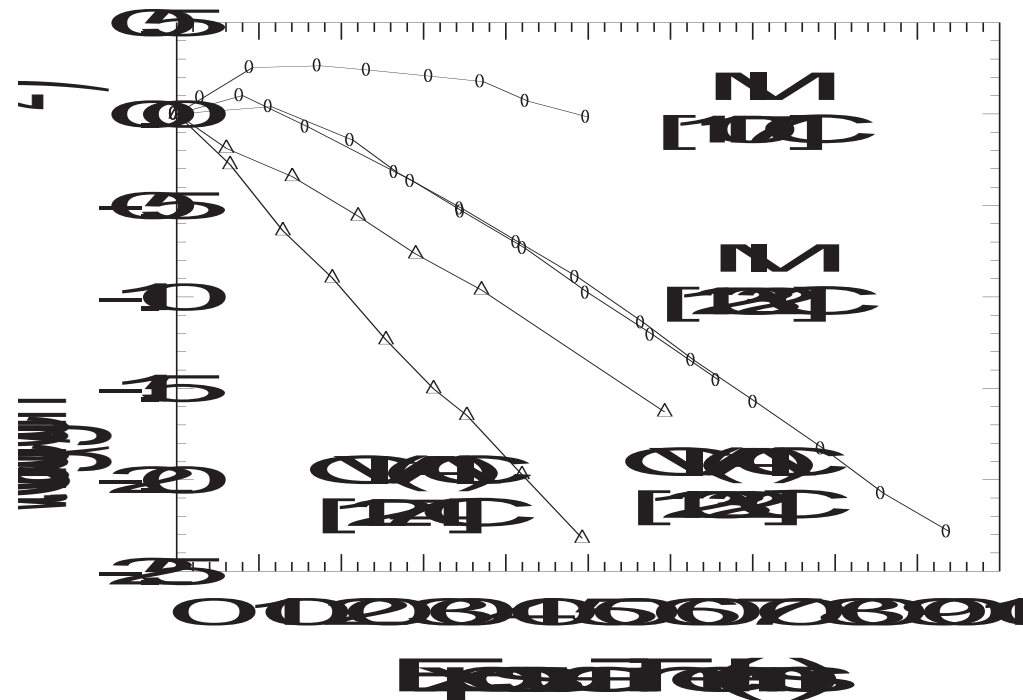
$$P[\text{Si}(\text{OH})_4] = K a_{\text{SiO}_2} [P(\text{H}_2\text{O})]^2$$

Y and Yb silicates  
Need to be measured!

- Molten Salt Reaction



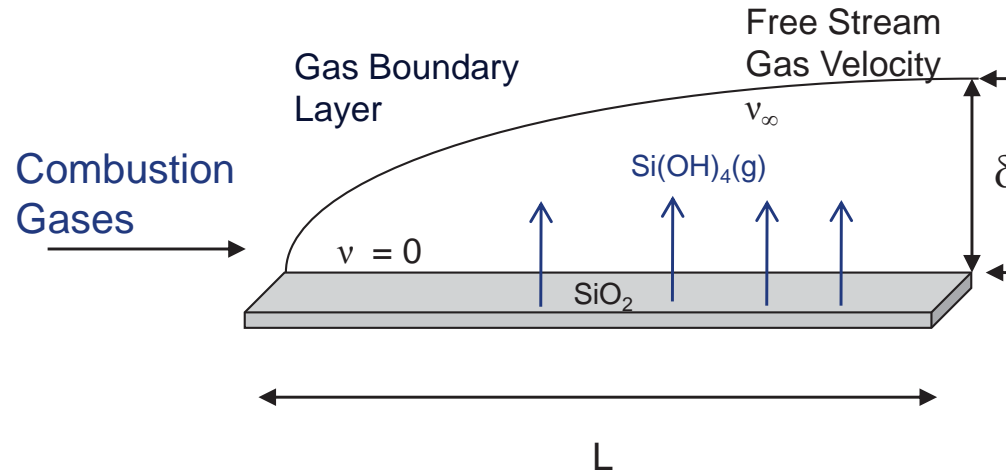
Lower  $a(\text{SiO}_2)$  –less reaction



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

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



$$\text{Flux} = 0.664 \left( \frac{v_\infty \rho_\infty L}{\eta} \right)^{0.5} \left( \frac{\eta}{D_{\text{Si}(\text{OH})_4} \rho_\infty} \right)^{0.33} \frac{D_{\text{Si}(\text{OH})_4} P_{\text{Si}(\text{OH})_4}}{RT L} =$$

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

$v_\infty$  = free stream velocity    $\rho_\infty$  = free stream gas density    $L$  = characteristic dimension

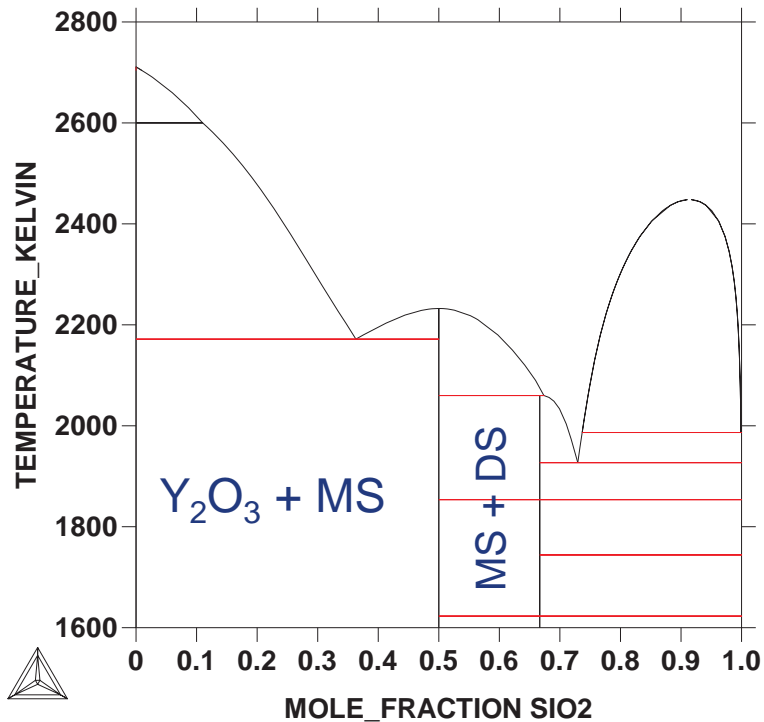
$\eta$  = viscosity    $D_{\text{Si}(\text{OH})_4}$  = gas phase diffusivity of  $\text{Si}(\text{OH})_4$

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

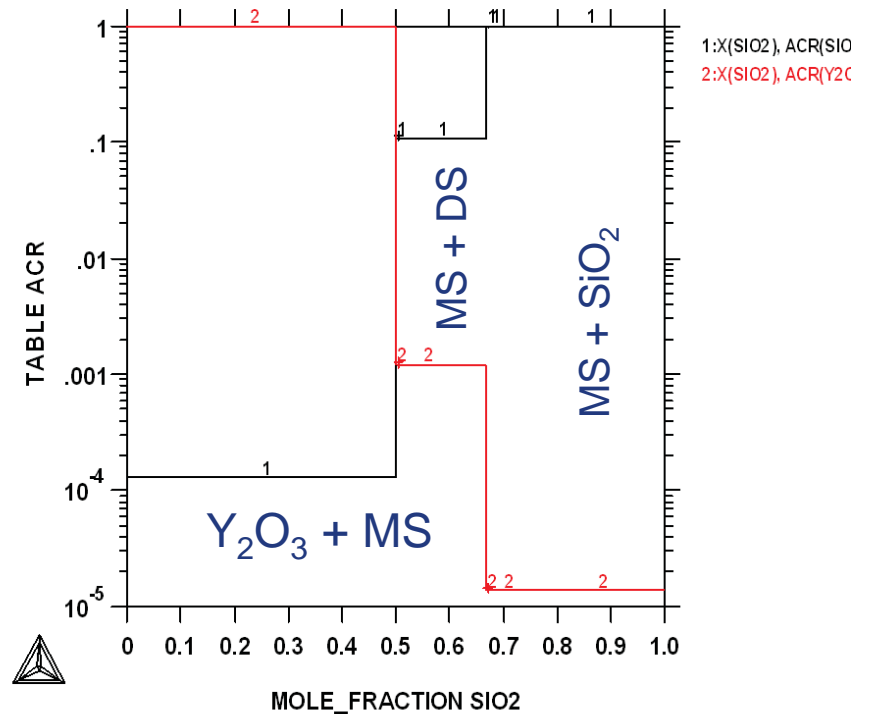


# Calculated $Y_2O_3$ - $SiO_2$ Phase Diagram: Fabrighnaya-Seifert Database

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



THERMO-CALC (2010.08.10:11.43) :  
DATABASE:USER  
AC(O)=1, T=1600, P=1.01325E5, N=1;

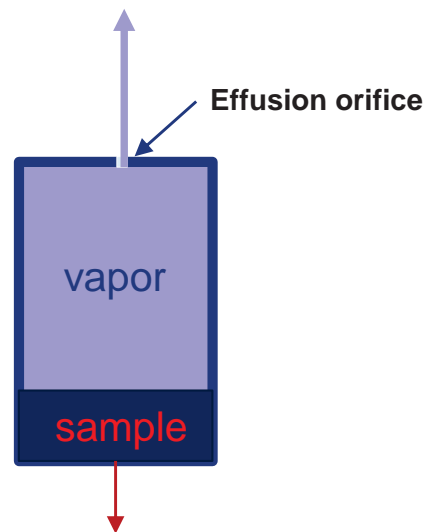


Indirect evidence suggests that the  $SiO_2$  thermodynamic activity is lower in the  $Y_2O_3$ - $Y_2SiO_5$  and  $Y_2SiO_5$ - $Y_2Si_2O_7$  regions  
But there are no direct measurements!

## Methods to measure silica activity

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

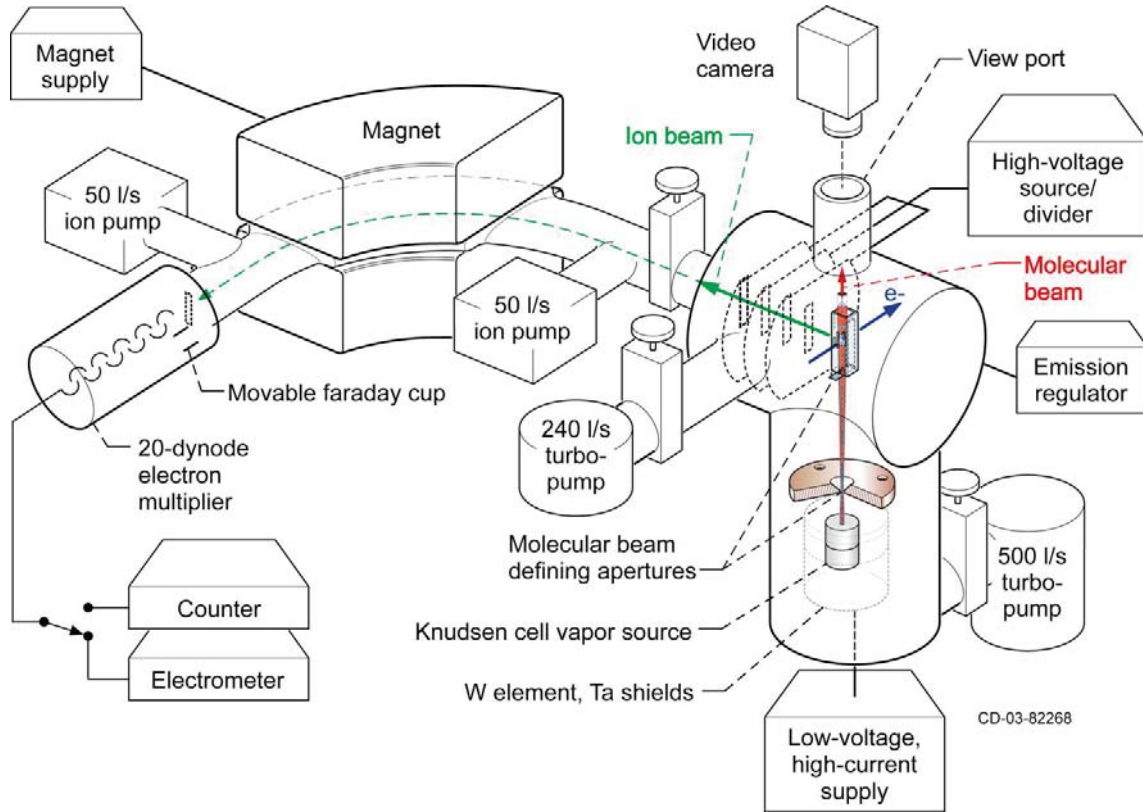
Mass spectrometer:  $I(\text{SiO}) \rightarrow P(\text{SiO}) \rightarrow a(\text{SiO}_2)$



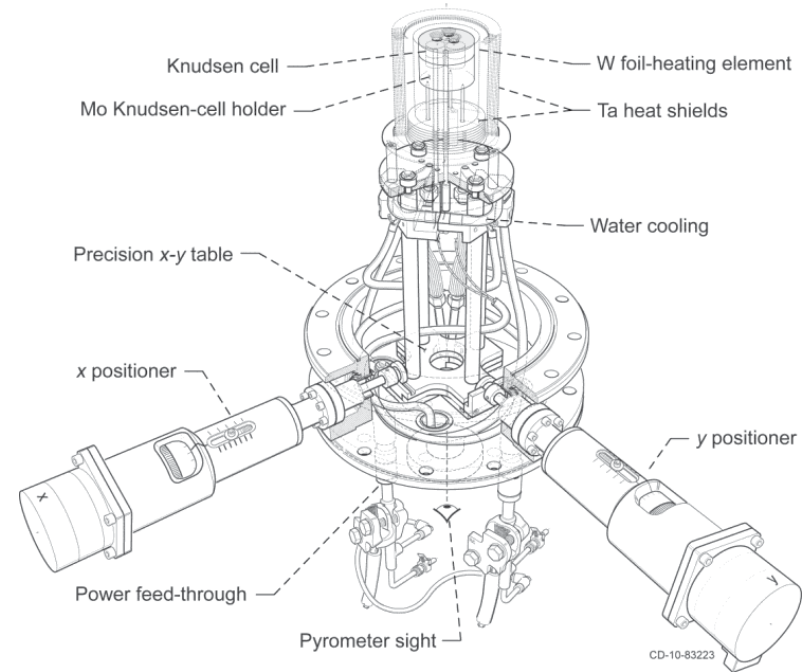
Two approaches

Y and Yb silicates + \*reducing agent to boost vaporization of  $\text{SiO}_2$  without changing solid composition!

# Knudsen Effusion Mass Spectrometry (KEMS)

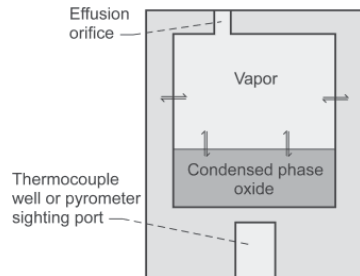


## Use Multi-Cell Flange for a(SiO<sub>2</sub>)



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<sup>-10</sup> 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





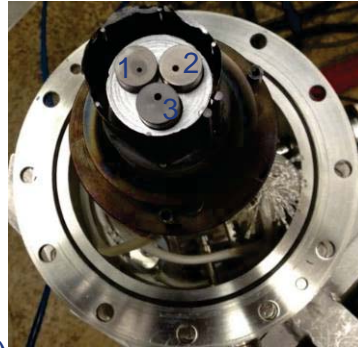


# Issues with Measuring $a(\text{SiO}_2)$ in RE Silicates

- Vapor pressure of  $\text{SiO}_2$  too low to measure in temperature range of interest
- Need measurable signal for  $\text{SiO}_2$ —use reducing agent to make excess  $\text{SiO}(\text{g})$ . Tried several, selected Mo or Ta
  - For  $a(\text{SiO}_2) < \sim 0.02$ 
    - $2\text{Ta}(\text{s}) + 2\text{SiO}_2(\text{soln}) = 2\text{SiO}(\text{g}) + \text{TaO}(\text{g}) + \text{TaO}_2(\text{g})$
  - For  $a(\text{SiO}_2) > \sim 0.02$ 
    - $\text{Mo}(\text{s}) + 3\text{SiO}_2(\text{soln}) = 3\text{SiO}(\text{g}) + \text{MoO}_3(\text{g})$
  - 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  $\text{CO}_2$  ( $m/e = 44$ )
  - Use  $\text{LN}_2$  cold finger for improved pumping
  - Shutter to distinguish vapor from cell and background
  - Gettering pump for  $\text{CO}_2$

# Approaches use two phase regions

Cells are part of the system



## 1 – Monosilicate + RE<sub>2</sub>O<sub>3</sub>

Two cells:

- Au
- 3Ta + Y<sub>2</sub>O<sub>3</sub> + Y<sub>2</sub>O<sub>3</sub> · SiO<sub>2</sub>

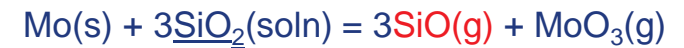


- Using P<sub>eq</sub>(SiO) and FactSage (free energy minimization)
- Correction for non-equilibrium vaporization

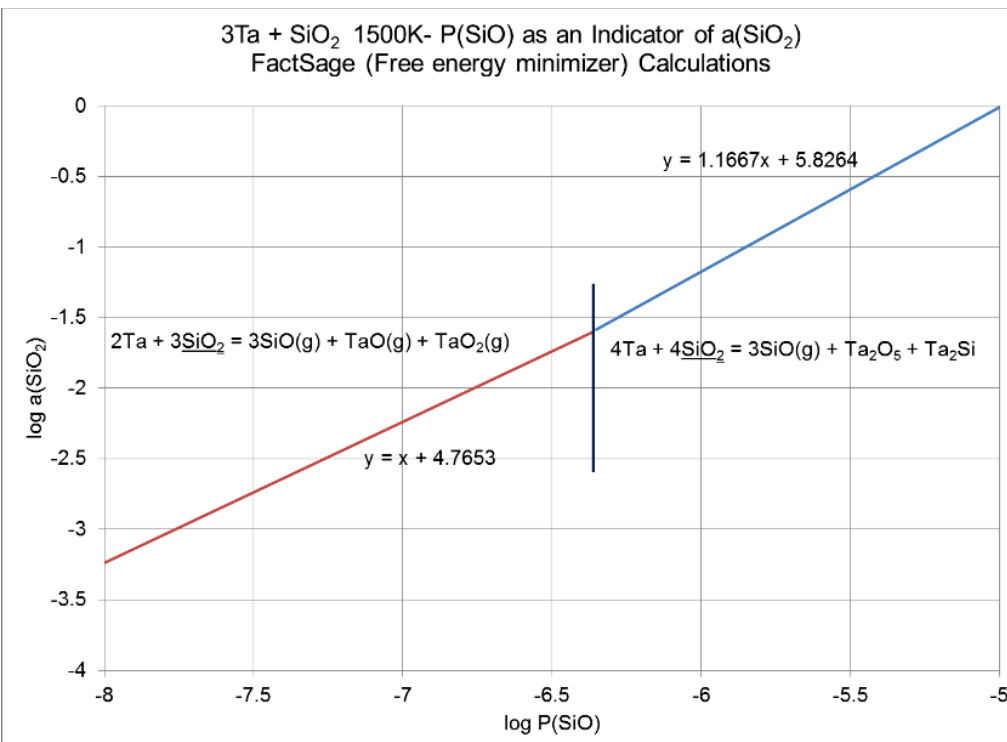
## 2 – Monosilicate + Disilicate

Three cells:

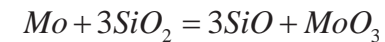
- Au (reference)
- 3Mo + Y<sub>2</sub>O<sub>3</sub> · 2SiO<sub>2</sub> + Y<sub>2</sub>O<sub>3</sub> · SiO<sub>2</sub>
- 3Mo + SiO<sub>2</sub>



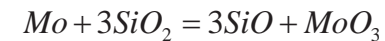
- Compare cells 1 and 2
- Less data processing than with Ta
- Correction is not needed.



$$K = \frac{[P(\text{SiO})]^3 P(\text{MoO}_3)}{[a(\text{SiO}_2)]^3}$$



$$a(\text{SiO}_2) = 1 = \left\{ \frac{[P^\circ(\text{SiO})]^3 P^\circ(\text{MoO}_3)}{K} \right\}^{0.33}$$



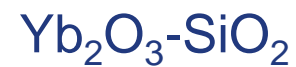
$$a(\text{SiO}_2) = \left\{ \frac{[P(\text{SiO})]^3 P(\text{MoO}_3)}{K} \right\}^{0.33}$$

$$\text{Cell 2} \leftarrow a(\text{SiO}_2) = \left\{ \frac{[I(\text{SiO})]^3 I(\text{MoO}_3)}{[I^\circ(\text{SiO})]^3 I^\circ(\text{MoO}_3)} \right\}^{0.33}$$

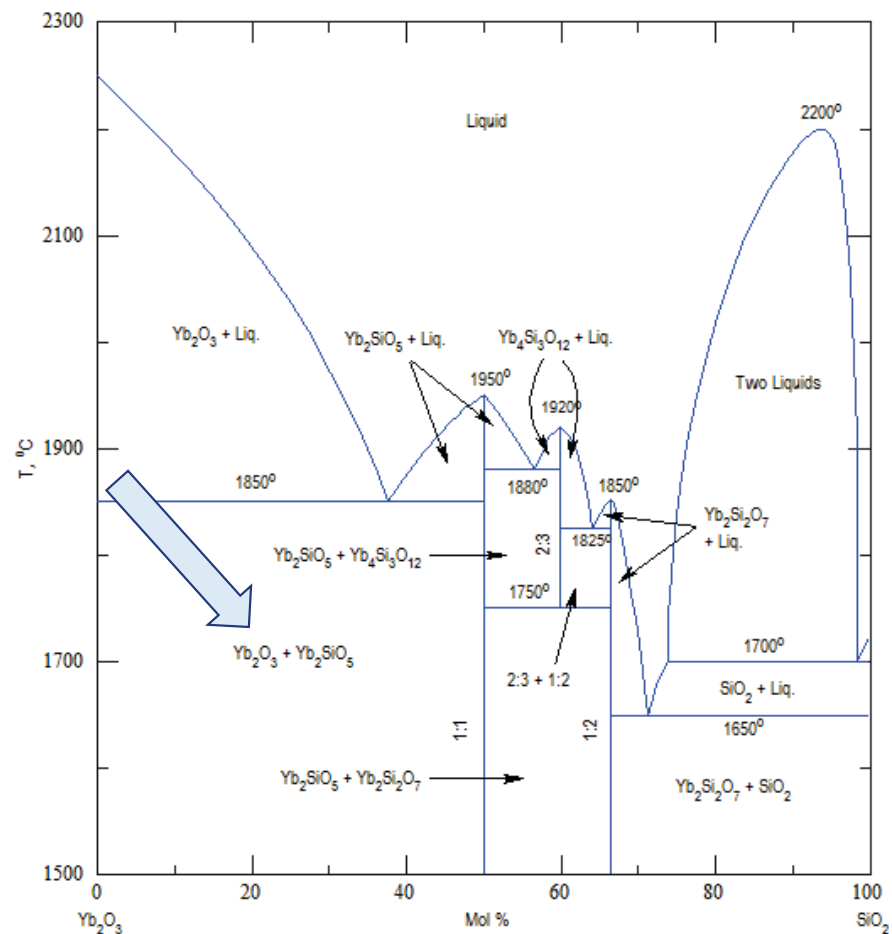
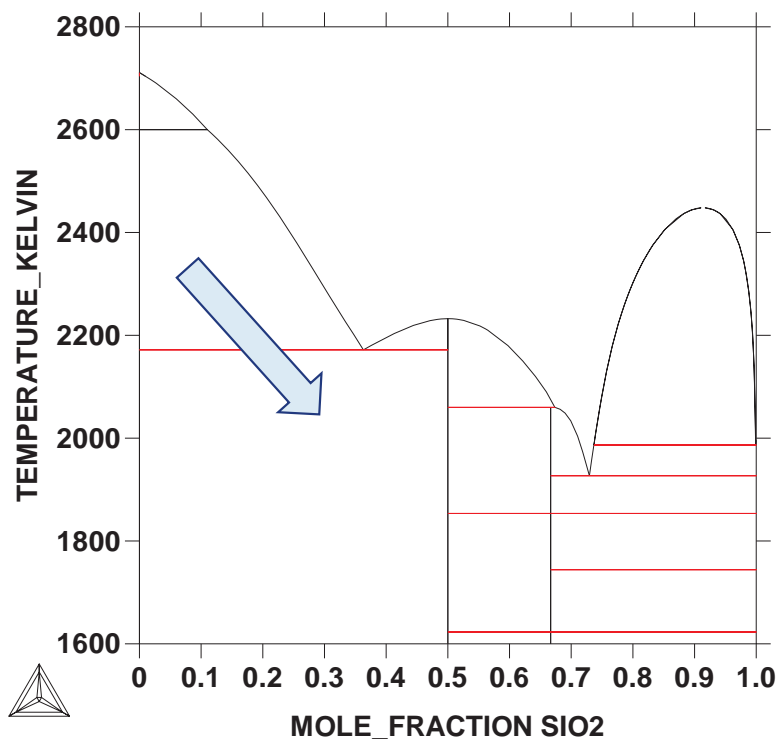
$$\text{Cell 3} \leftarrow$$



# Monosilicate + RE<sub>2</sub>O<sub>3</sub>



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



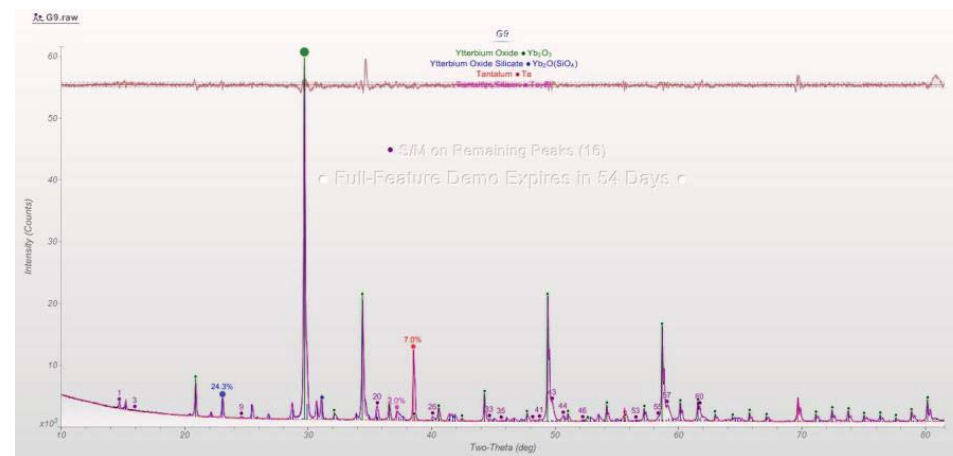


# XRD after KEMS Measurements of RE Monosilicates + $\text{RE}_2\text{O}_3$ + Ta:

## Yttrium monosilicate + $\text{Y}_2\text{O}_3$ + Ta



## Ytterbium monosilicate + $\text{Yb}_2\text{O}_3$ + Ta



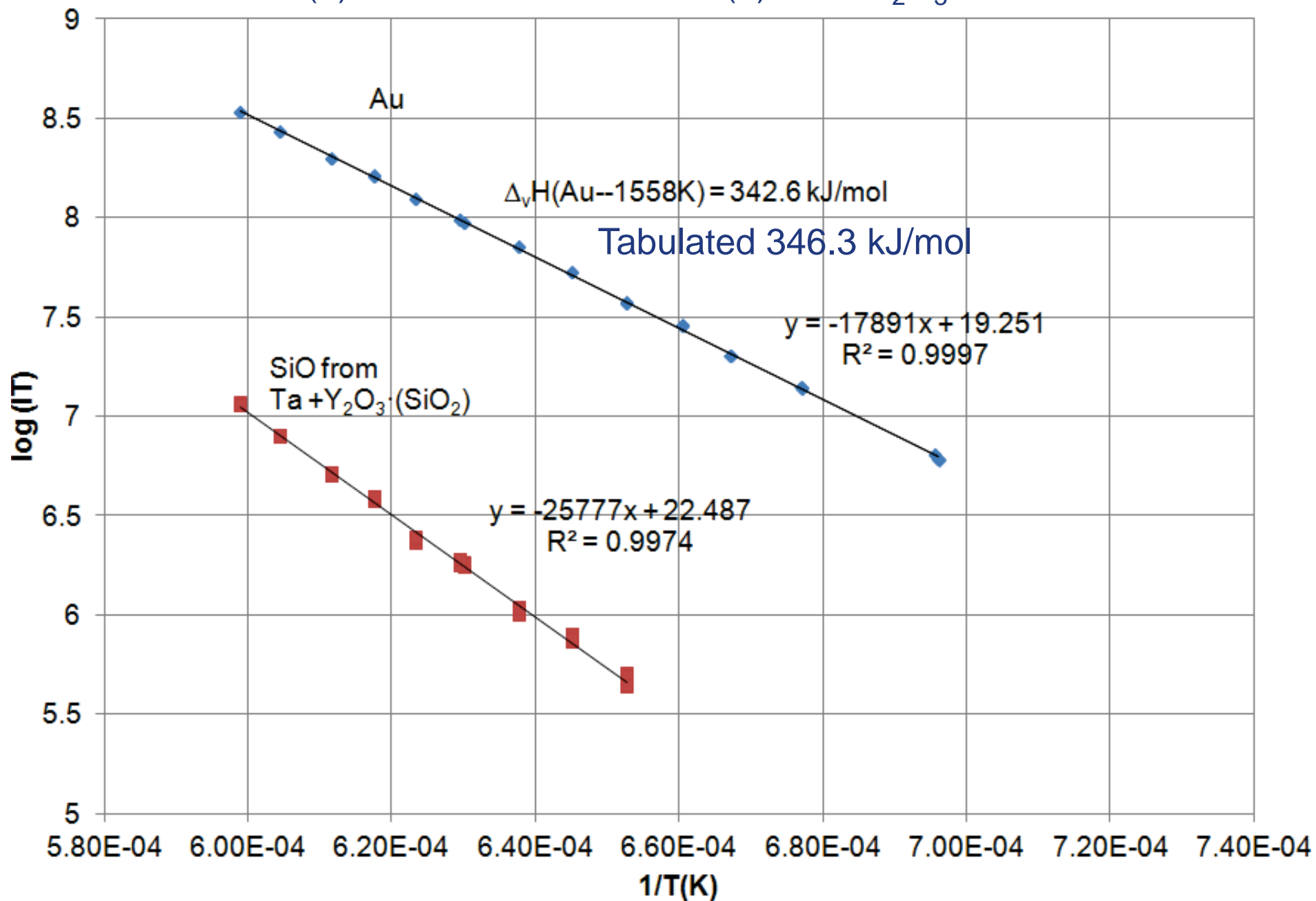
Phase	wt (%)
$\text{Y}_2\text{O}_3 \cdot (\text{SiO}_2)$	41
$\text{Y}_2\text{O}_3$	49
Ta	4
$\text{Ta}_3\text{Si}$	4

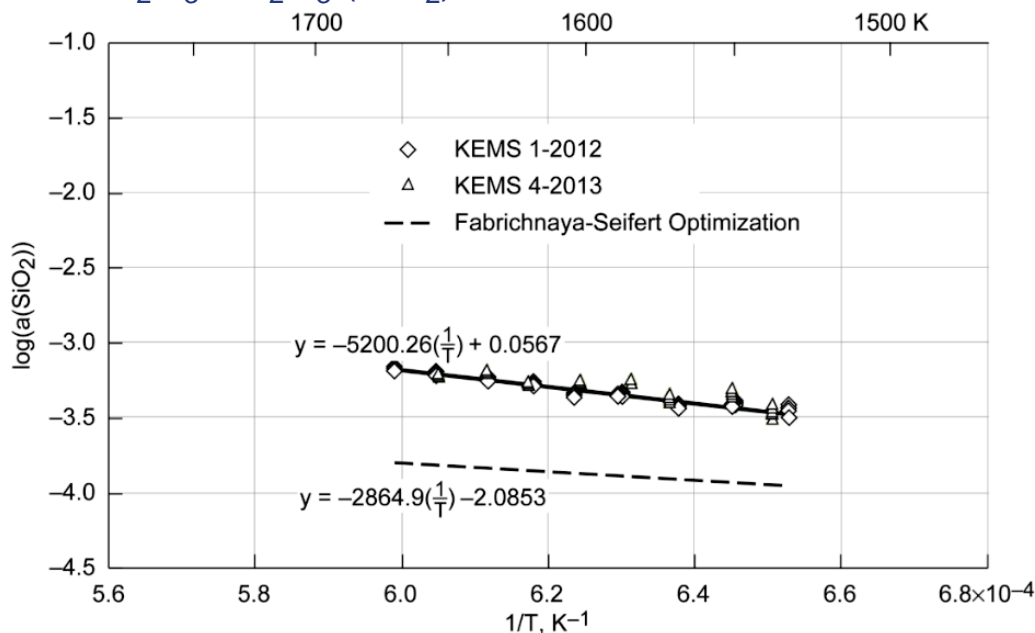
Phase	wt (%)
$\text{Yb}_2\text{O}_3 \cdot (\text{SiO}_2)$	24
$\text{Yb}_2\text{O}_3$	66
Ta	2
$\text{Ta}_2\text{Si}$	2



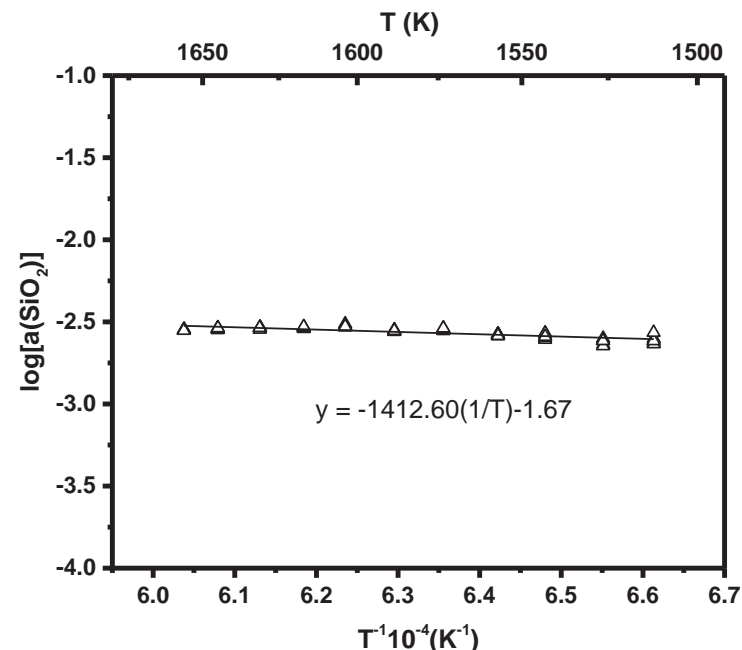
## Raw Data—log (IT) vs 1/T

Cell (1): Au Reference

Cell (2): Ta + Y<sub>2</sub>O<sub>3</sub> + MS



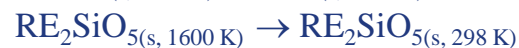
$$\Delta H_{(SiO_2, 1600 K)} = (5200.26) \cdot R \cdot 2.303 = 99.57 \text{ kJ/mol}$$



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



$$\Delta H_1 = \text{measured in this work}$$



$$\Delta H_2 = H_{1600 K} - H_{298 K}$$



$$\Delta H_3$$



$$\Delta H_4$$



$$\Delta H_5$$



$$\Delta H_6$$



$$\Delta H_7 = \Delta H_{f, RE_2SiO_5, 298 K}$$

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

	KEMS	Calorimetry*	Optical basicity**	a(SiO <sub>2</sub> ), 1650 K
Y <sub>2</sub> O <sub>3</sub> ·(SiO <sub>2</sub> )	-2907 ± 16	-2868.54 ± 5.34	0.786	0.000804
Yb <sub>2</sub> O <sub>3</sub> ·(SiO <sub>2</sub> )	-2744 ± 11	-2774.75 ± 16.48	0.729	0.00298

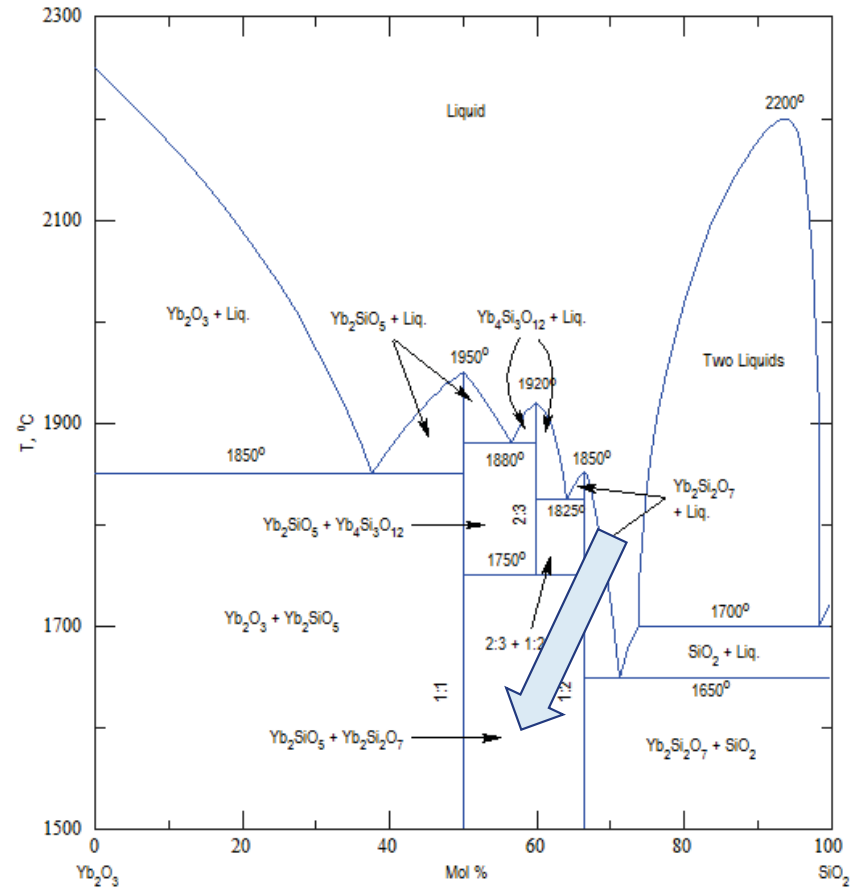
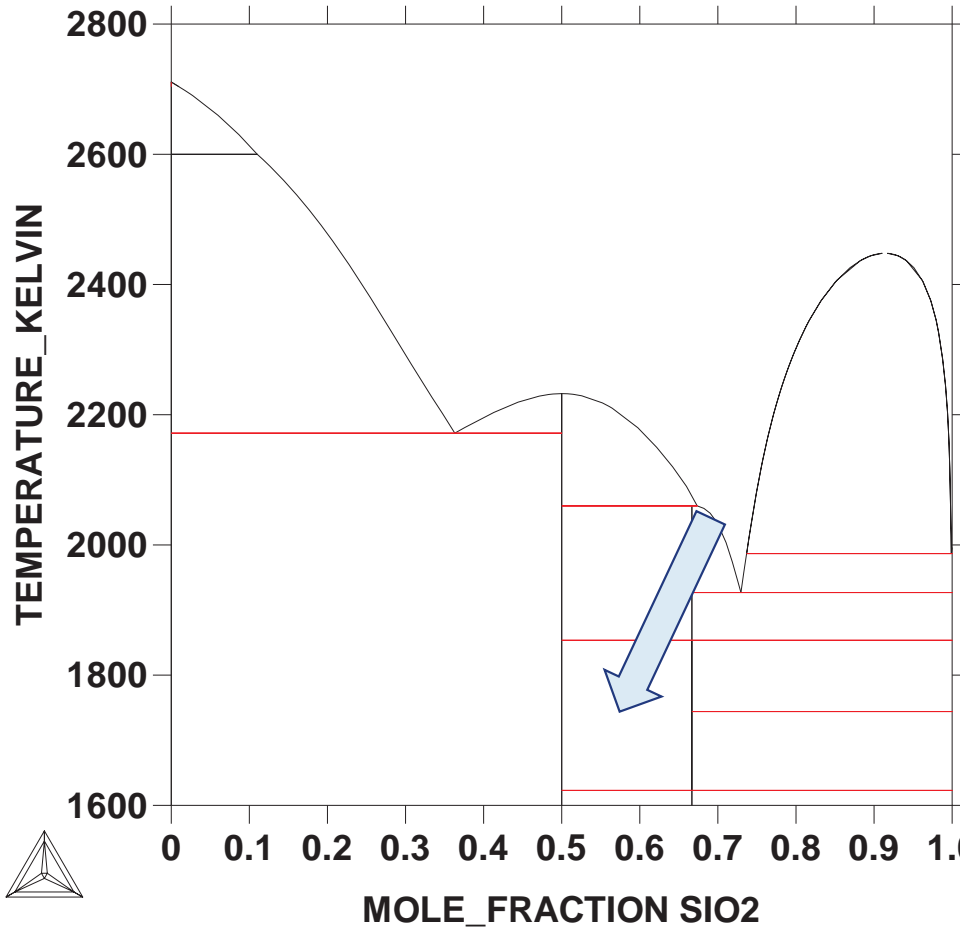
\*Liang et al. "Enthalpy of formation of rare-earth silicates Y<sub>2</sub>SiO<sub>5</sub> and Yb<sub>2</sub>SiO<sub>5</sub> and N-containing silicate Y<sub>10</sub>(SiO<sub>4</sub>)<sub>6</sub>N<sub>2</sub>", J. Mater. Res. 14 [4], 1181-1185. \*\*J. A. Duff, J. Phys. Chem. A 110, 13245 (2006)



# Monosilicate + Disilicate

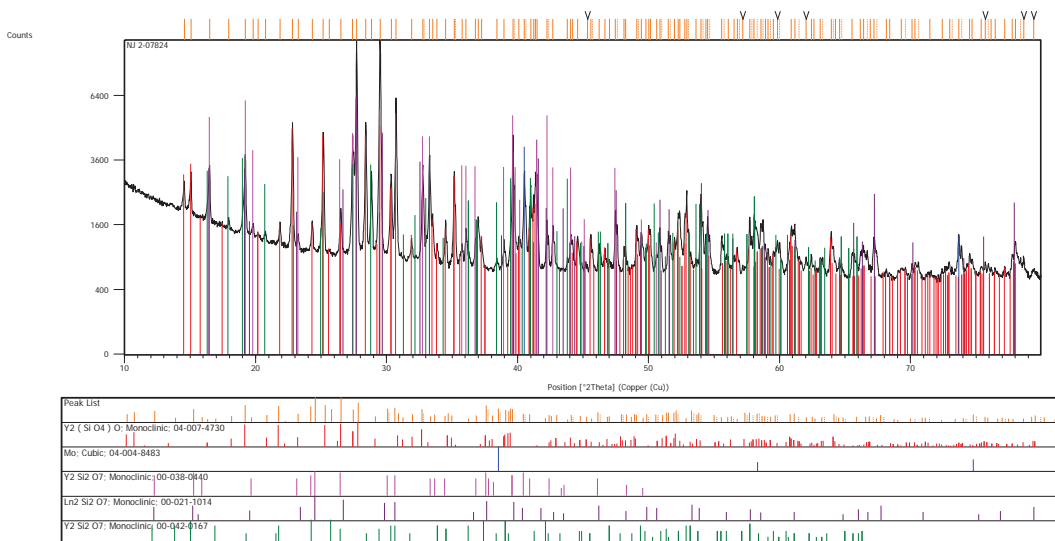


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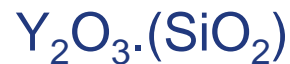


# XRD after KEMS Measurements of RE Monosilicates + Disilicates + Mo:

## Yttrium monosilicate + disilicate + Mo

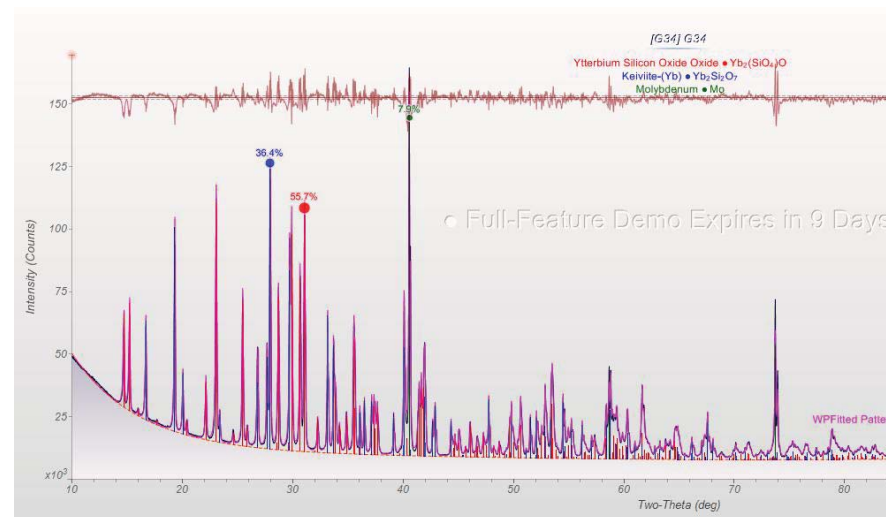


### Phase



Mo

## Ytterbium monosilicate + disilicate + Mo



### Phase



Mo

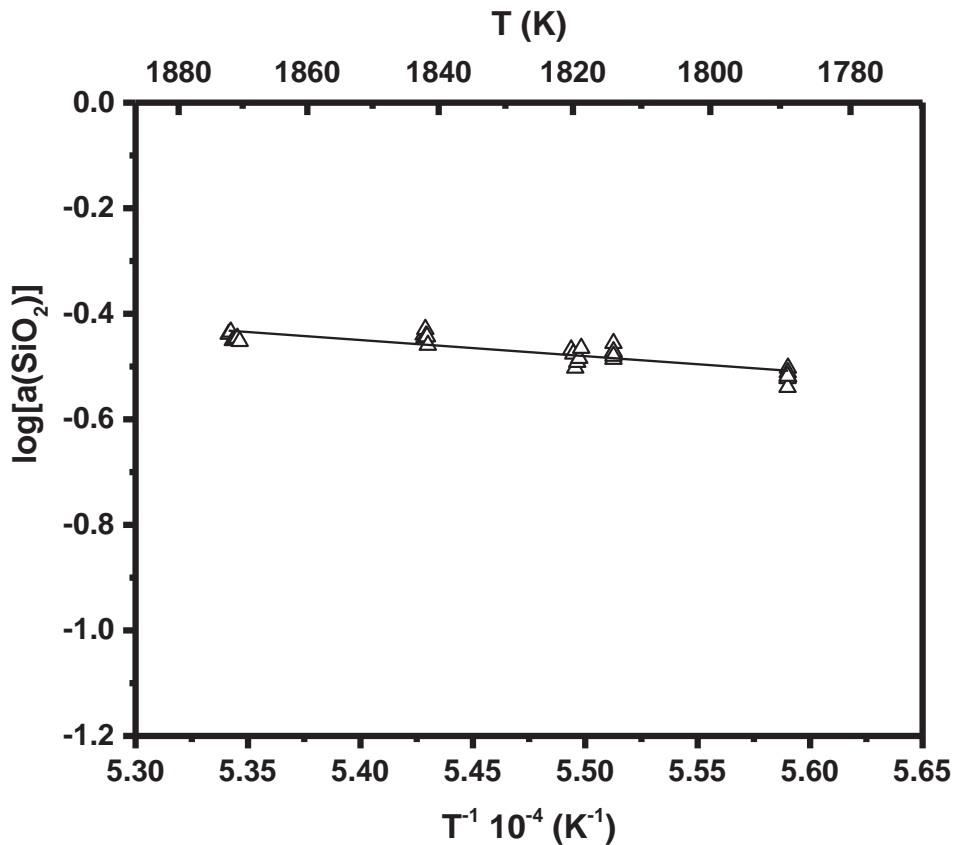
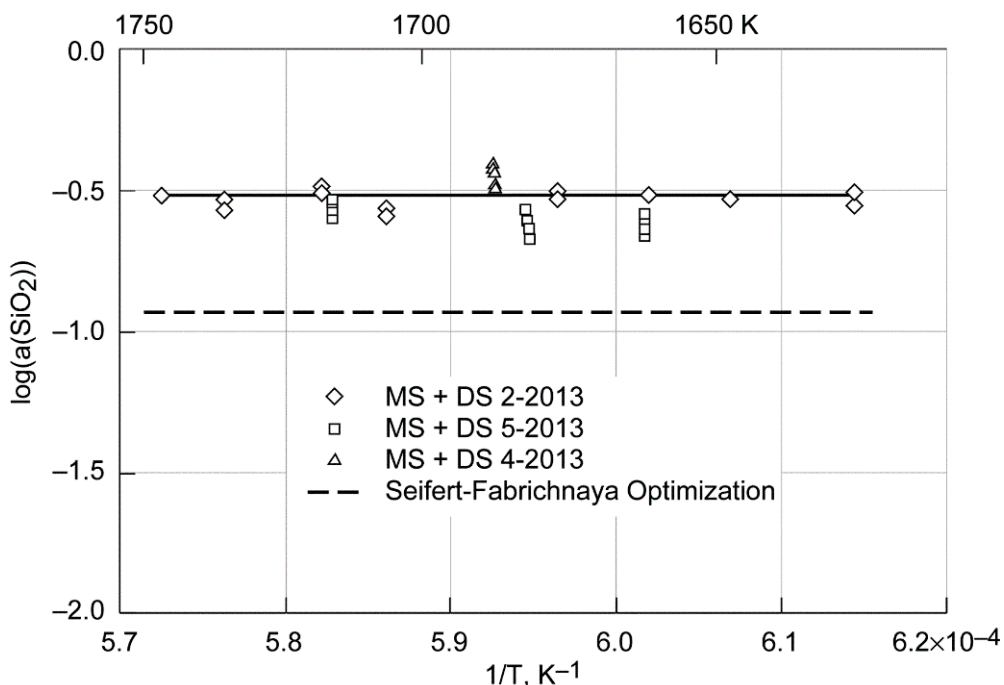
wt (%)

56

36

8





Optical basicity\*\*

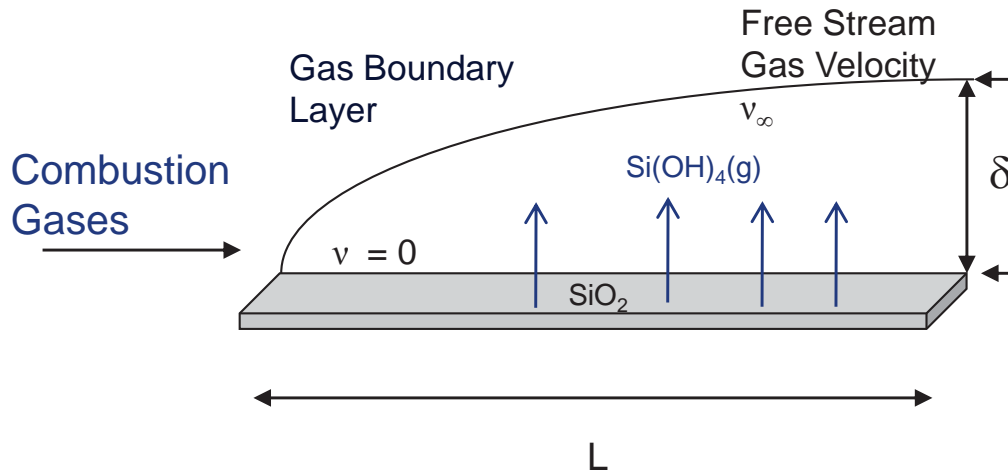
$Y_2O_3 \cdot (SiO_2)$	$Y_2O_3 \cdot 2(SiO_2)$
0.786	0.699
$Yb_2O_3 \cdot (SiO_2)$	$Yb_2O_3 \cdot 2(SiO_2)$
0.729	0.657

$a(SiO_2)$ , 1650 K

0.281
0.194

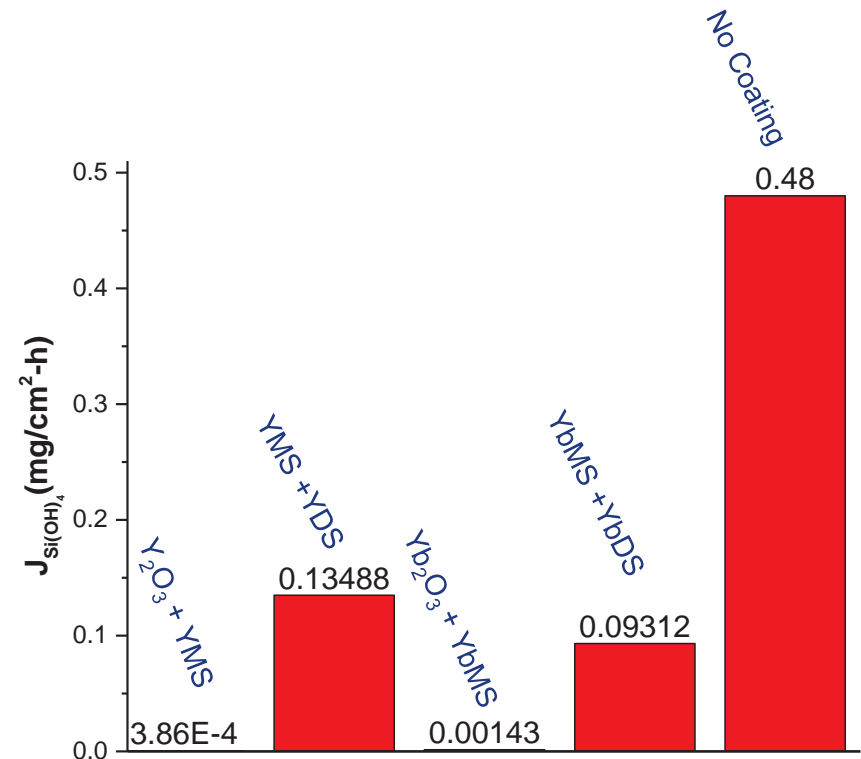


# Now Have the Needed Quantities for Modeling Recession



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

- $T = 1300^\circ\text{C}$ ;  $P = 10$  bar;  $P(\text{H}_2\text{O}) = 1$  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
- $D_{\text{Si(OH)}_4} = 0.19$  cm<sup>2</sup>/s
- $\log K = -2851.2/T - 3.5249$  ( $\text{Si(OH)}_4(\text{g})$  transpiration measurements)
- $a(\text{SiO}_2)$  from activity measurements





# Summary: Thermochemistry of EBC materials

- The reduced  $\text{SiO}_2$  activity in Rare-earth silicates should limit their reactivity with water vapor
- Solid State rare earth oxides—activity of  $\text{SiO}_2$ 
  - Vapor pressure techniques—Knudsen effusion mass spectrometry
  - Need reducing agent to obtain a measurable signal for  $\text{SiO}(\text{g})$ , which in turn relates to activity of  $\text{SiO}_2$ . 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 Univ 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)