Alumina Volatility in Water Vapor at Elevated Temperatures

Elizabeth Opila, NASA Glenn Research Center
Dwight Myers, East Central University, Ada, OK

Environmental Barrier Coatings for Microturbine and
Industrial Gas Turbine Ceramics Workshop
November 18–19, 2003
Nashville, TN

Motivation

- Drive to increase operating temperatures of turbine engines for power generation and propulsion
- Need for material systems that can be used at temperatures of 1200 to 1650°C in combustion environments
- Al_2O_3 is possible component of high temperature material systems
  - oxide/oxide composites
  - high temperature alumina-containing coatings
- Understand chemical durability of Al_2O_3 in water vapor-containing combustion environments

Background

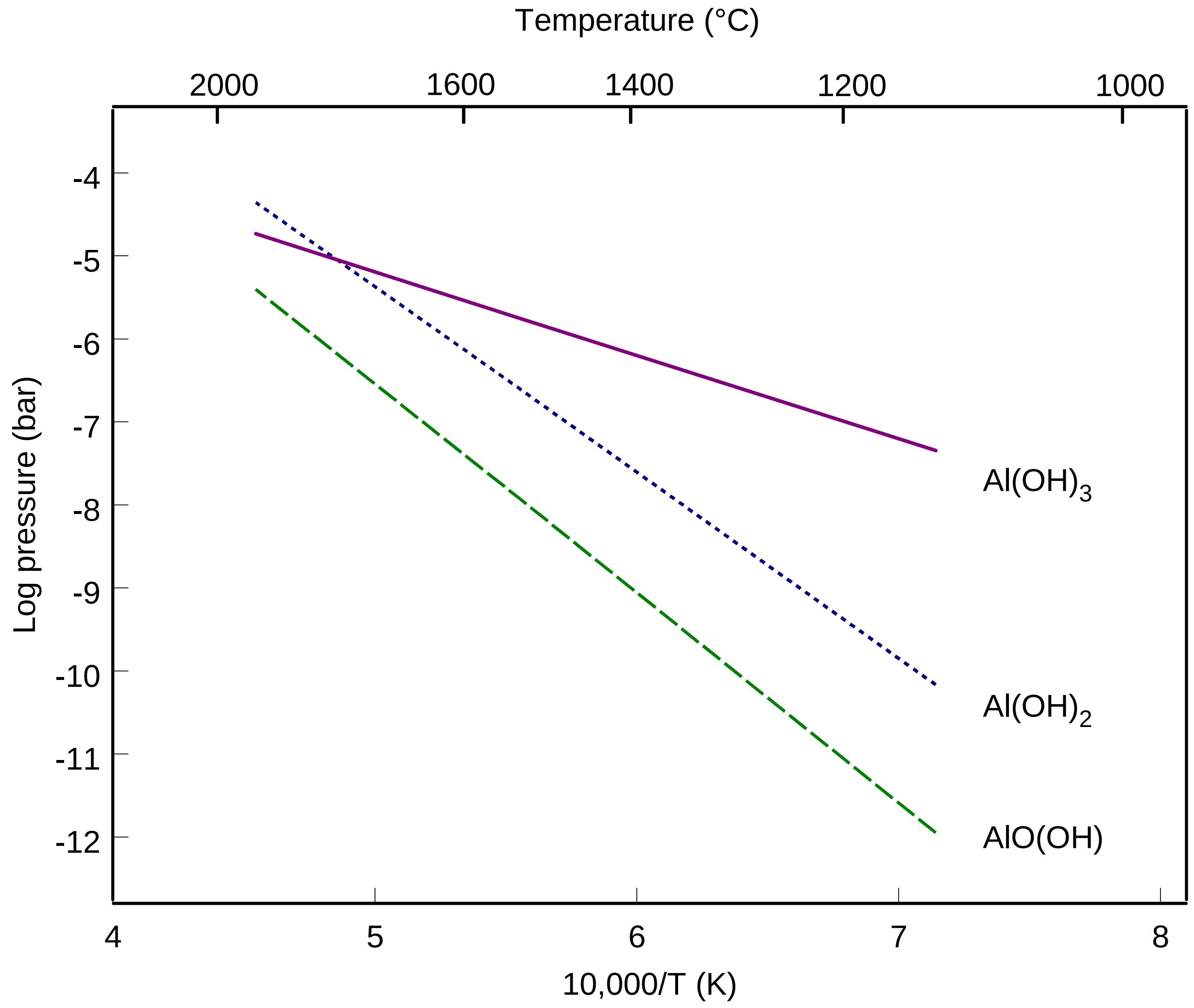
Primary volatilization reaction for alumina in water vapor:

$$1/2\ Al_2O_3(s) + 3/2\ H_2O(g) = Al(OH)_3(g)$$

- Thermochemical data estimated for $Al(OH)_3(g)$ using partition functions and structures of similar molecules, e.g., $AlF_3(g)$, $B(OH)_3(g)$
  - L.V. Gurvich, I.V. Veyts, C.B. Alcock, Thermodynamic Properties of Individual Substances, Begell House, Inc., New York, 1996.
- $Al(OH)_3(g)$ identified as volatile species from a transpiration study of a mixture of $CaAl_2O_4(s)$ and $CaAl_4O_7(s)$
  - A. Hashimoto, Geochim. Cosmochim. Acta 56, 511-32 (1992).
- $Al_2O_3(s)$ recession measured and quantified in combustion test rig. Pressure and temperature dependence consistent with $Al(OH)_3(g)$ formation.
  - I. Yuri, T. Hisamatsu, ASME Turbo Expo, paper GT2003-38886.

Volatile Species in Al-O-H System

Calculated using Gurvich data: Al_2O_3 + 1 bar H_2O(g) + 1 bar O_2(g)



Objectives

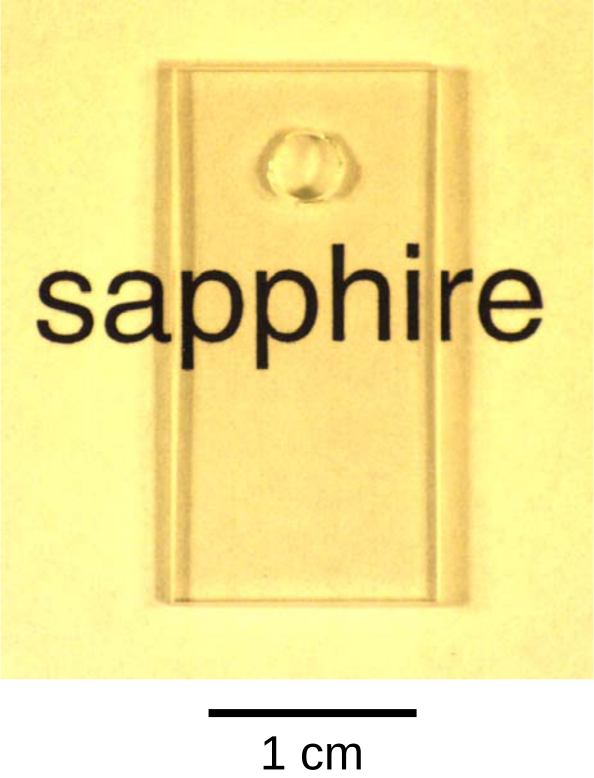
- Experimentally determine temperature and water vapor partial pressure dependence of alumina volatility directly from alumina

- Confirm identity of volatile aluminum hydroxide species

- Identify combustion conditions where alumina volatility limits useful component life

Material Description

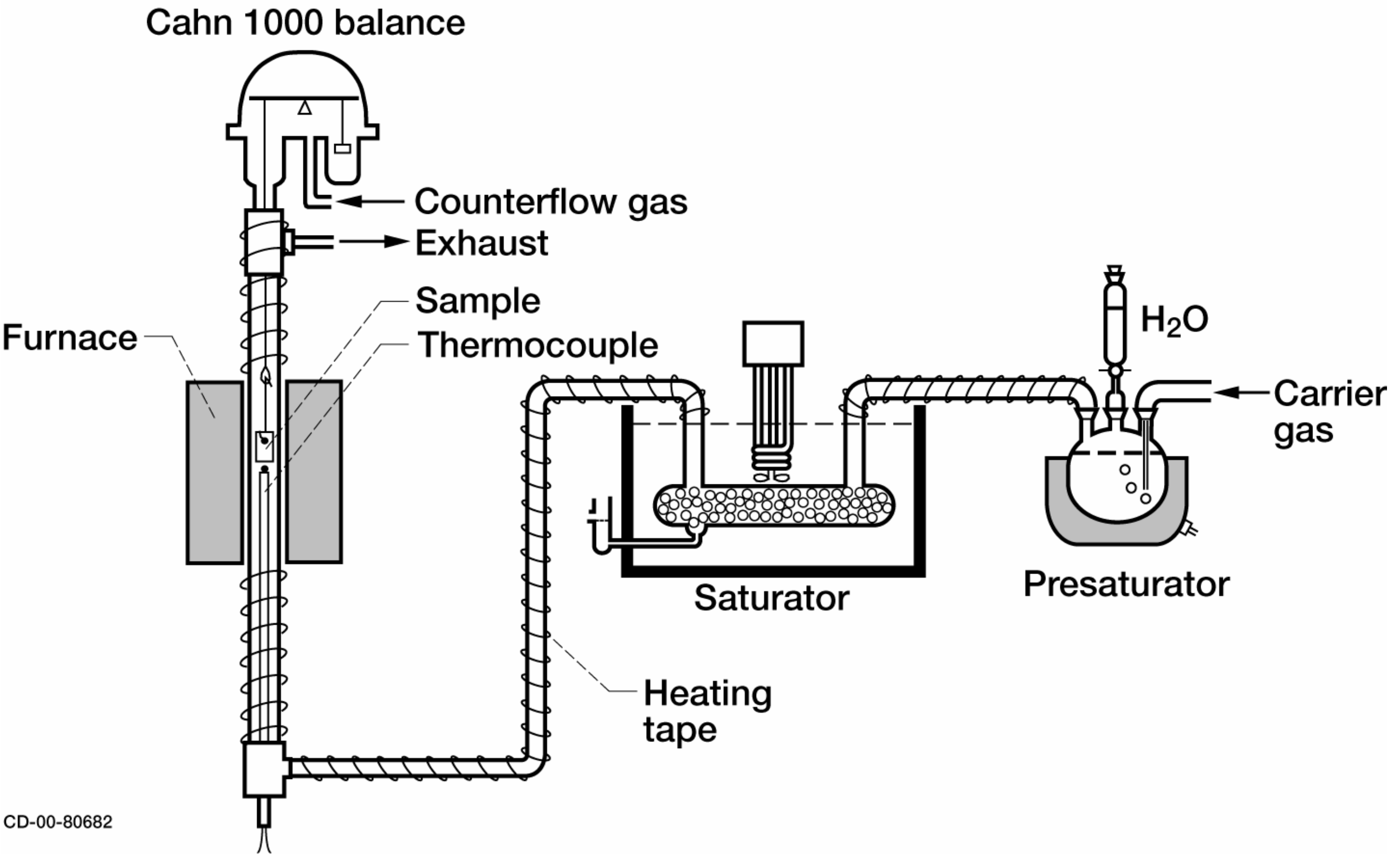
- sapphire coupons
- 2.5 x 1.25 x 0.2 cm
- flame fusion grown
- <100 ppm impurities
- (0001) basal plane orientation
- General Ruby and Sapphire Corp., New Port Richey, FL



Experimental Procedure

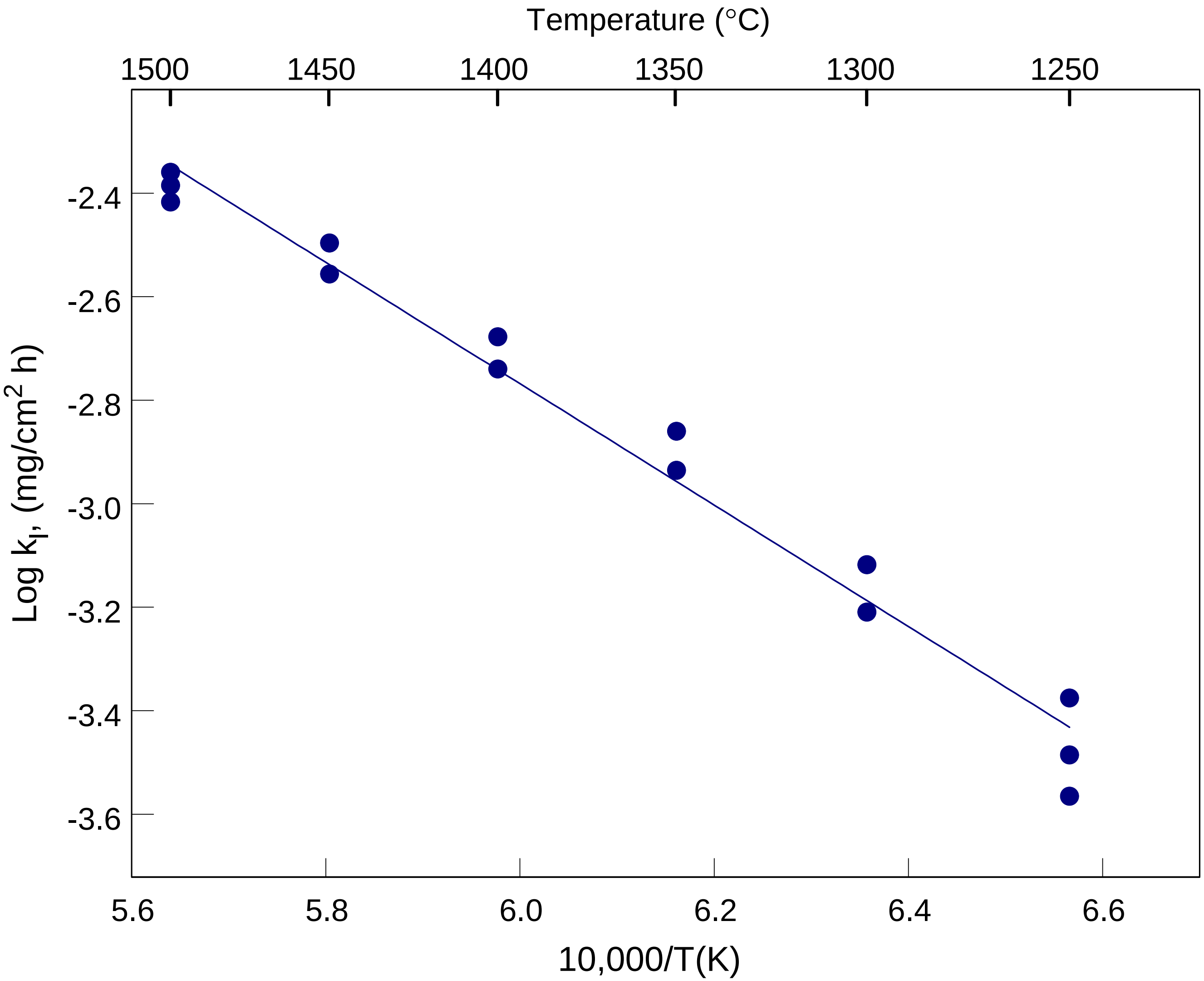
- Thermogravimetric Analysis Apparatus
  - coupon weight measured before and after exposure
  - TGA only used to monitor weight anomalies during experiment
  - volatiles condense on cool portion of sample hanger
  - TGA apparatus allows laminar flow over coupon
- T=1250 to 1500°C
- $P(H_2O) = 0.15$ to 0.68 atm, balance O_2
- $P_{total} = 1$ atm

Schematic Drawing of TGA Apparatus



Alumina Volatility: Weight Loss Rates

Al_2O_3, 0.5 atm H_2O/0.5 atm O_2



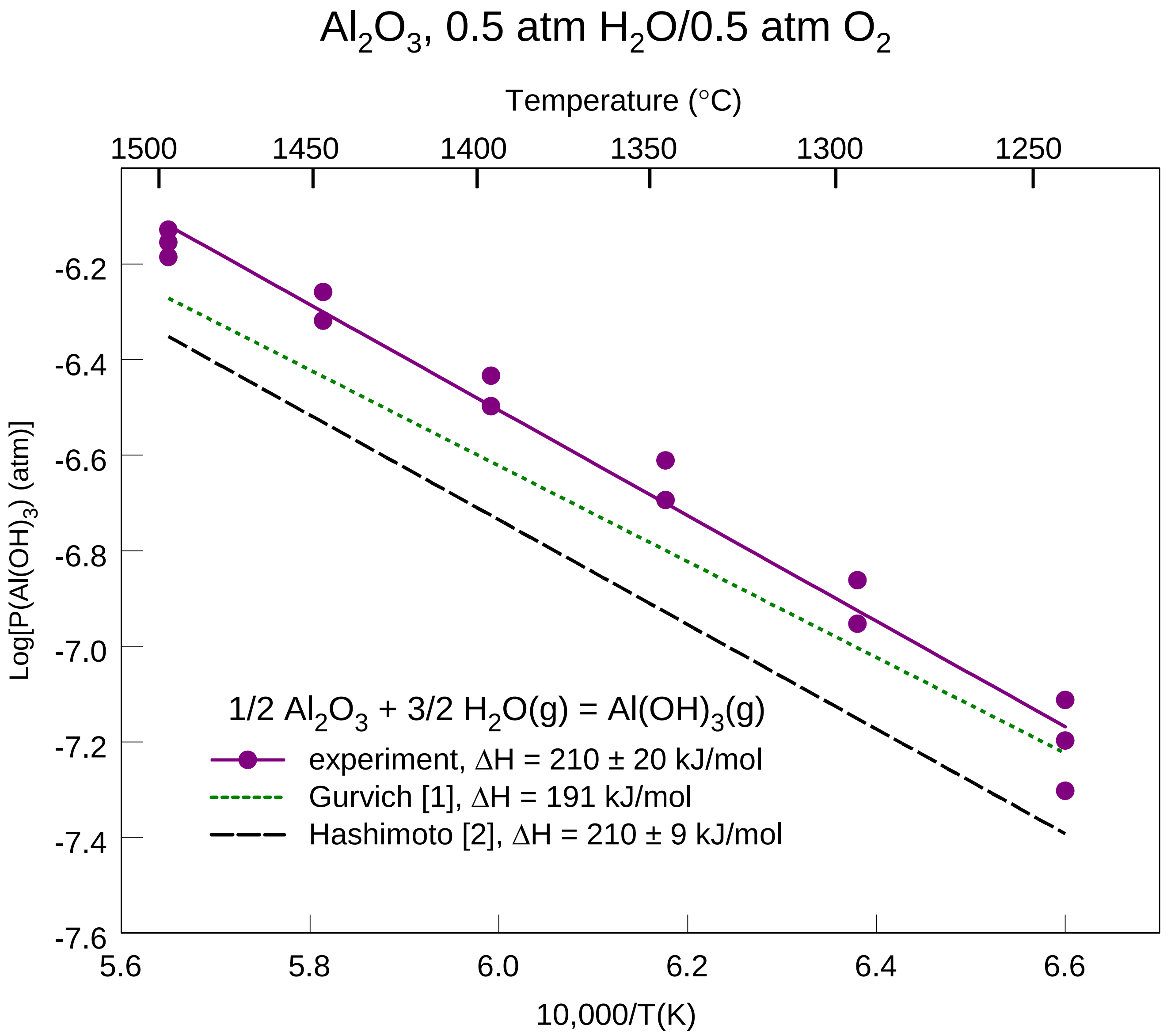
Determination of $Al(OH)_3$(g) Partial Pressure from Weight Change

- Measure Δw, calculate P

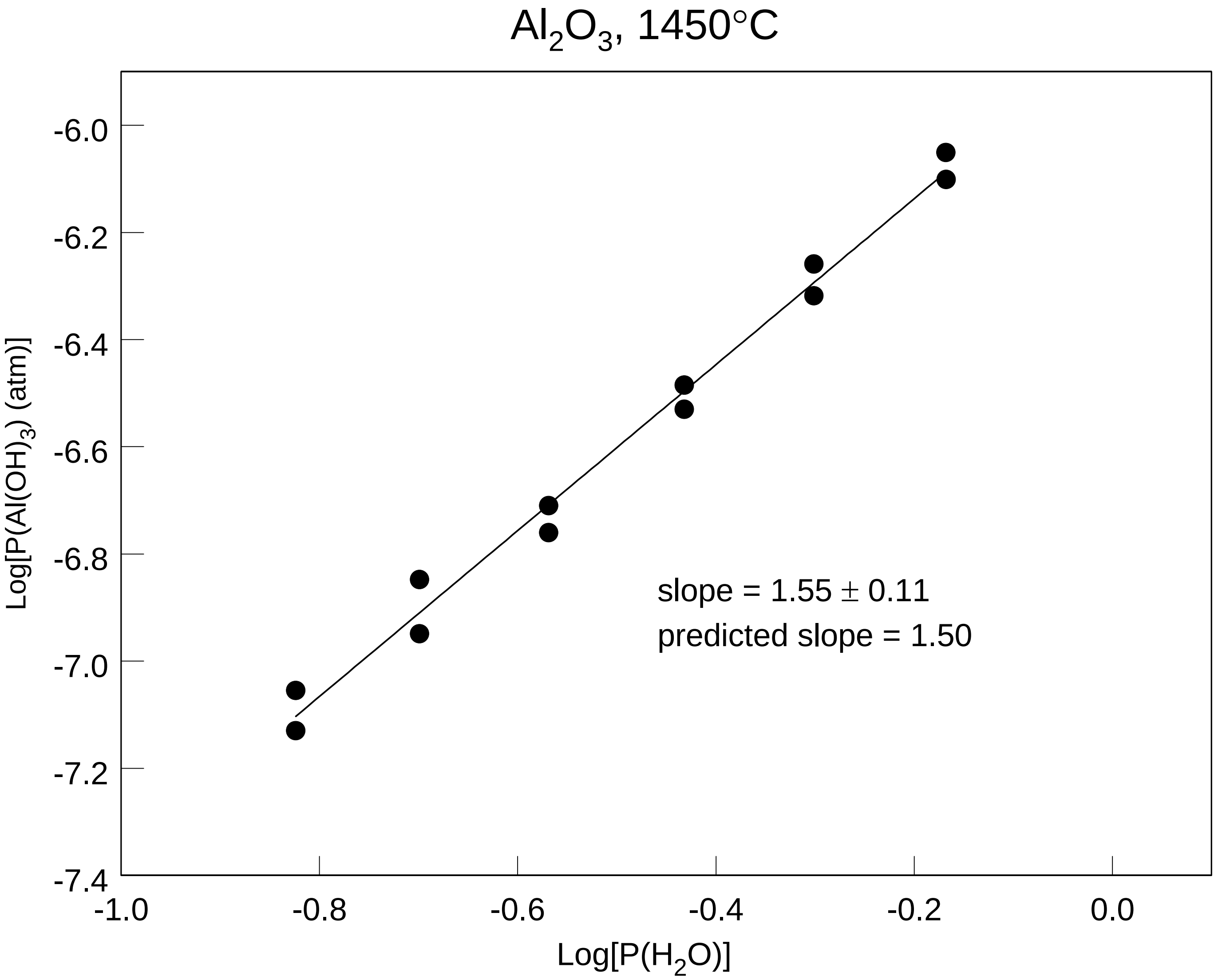
$$\frac{\Delta w}{At} = 0.664\left(\frac{\rho' v L}{\eta}\right)^{1/2}\left(\frac{\eta}{\rho' D}\right)^{1/3}\frac{DPM}{LRT}$$

- Assumptions:
  - volatility is controlled by transport of volatile species through gas boundary layer
  - laminar flow over flat plate
  - D is interdiffusion of $Al(OH)_3$(g) in H_2O(g)
  - use collision diameter and integral of AlF_3(g) as approximation for $Al(OH)_3$(g)

Temperature Dependence of $Al(OH)_3(g)$ formation

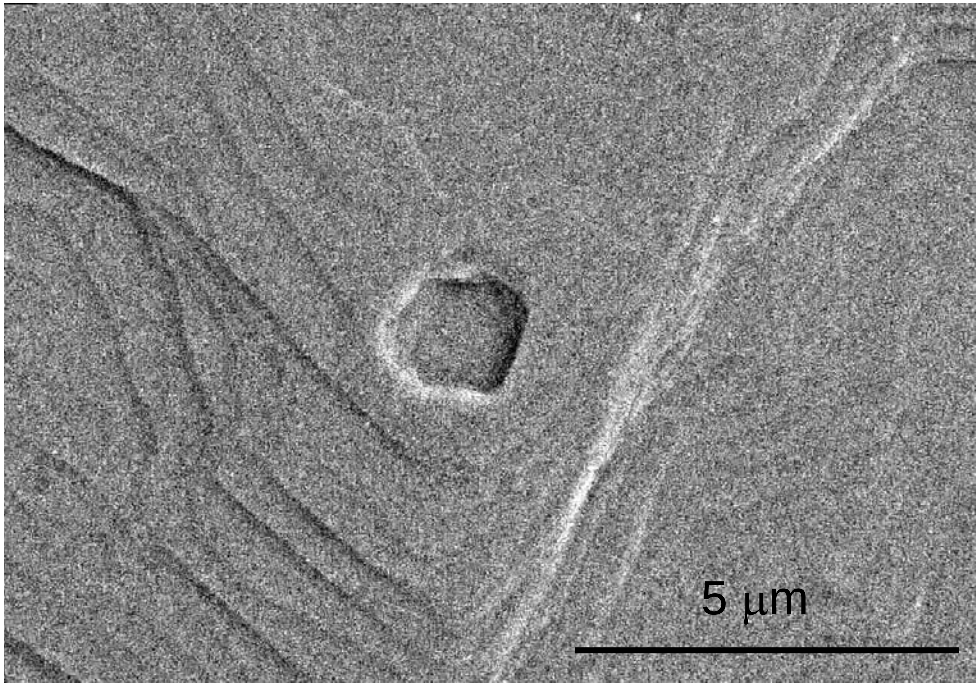


Pressure Dependence of $Al(OH)_3$(g) formation



Surface Etching of Sapphire after Exposure in High Temperature Water Vapor

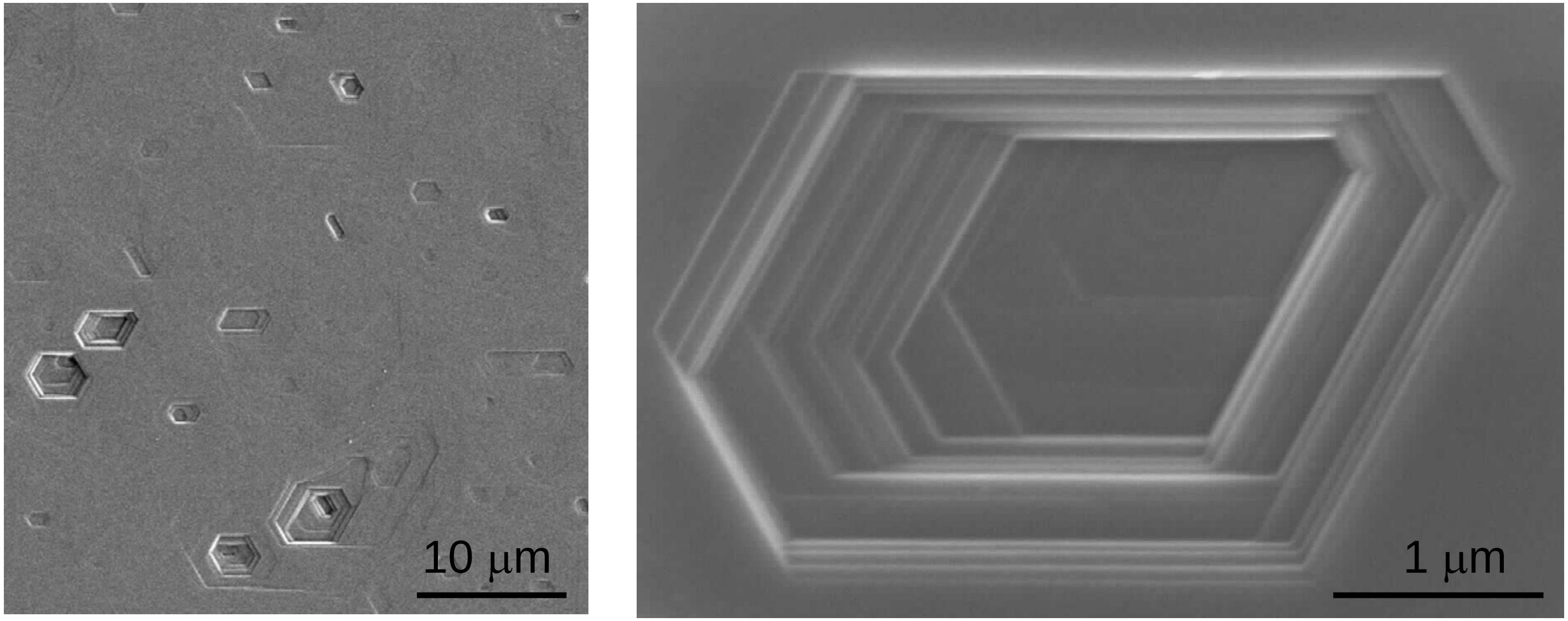
typical surface, (0001) basal plane



1250°C, 0.5 atm H_2O, 240h

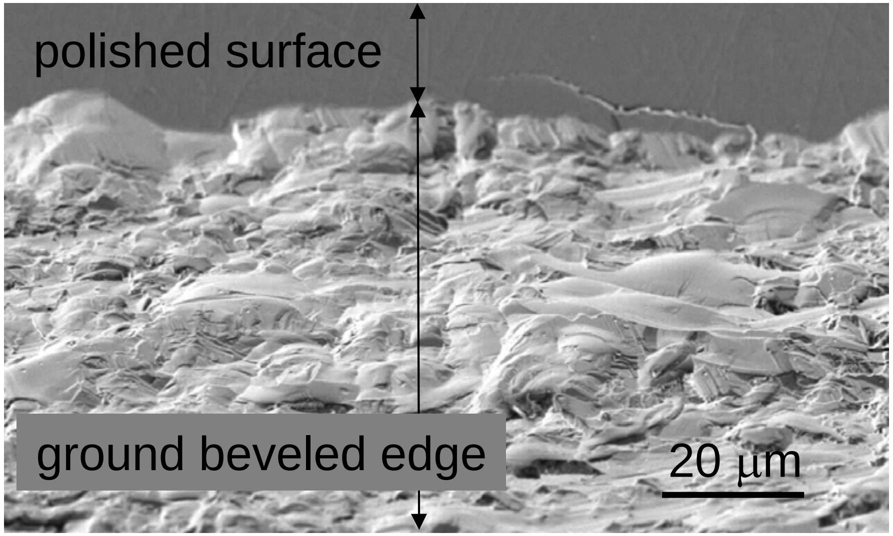
Surface Pitting of Sapphire after Exposure in High Temperature Water Vapor

Hole put in coupon by grit blasting, (0001) basal plane surface

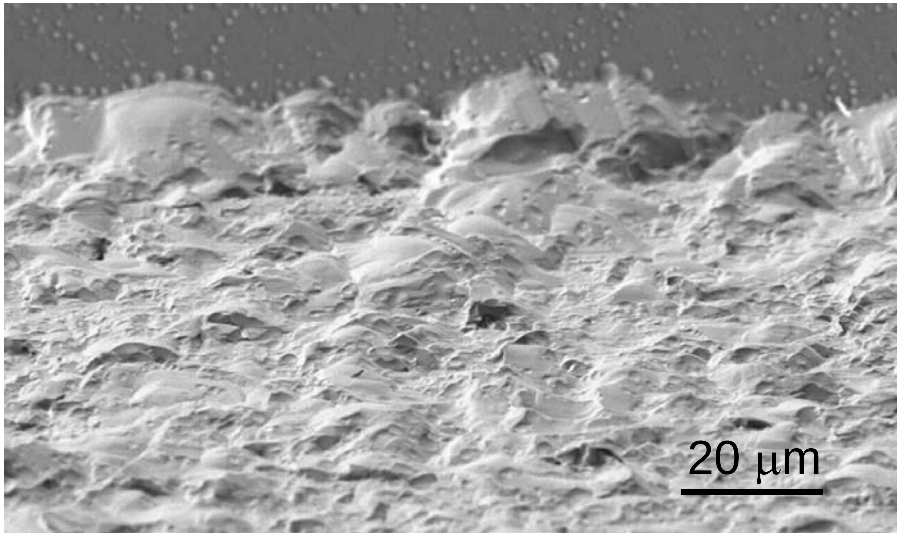


1350°C, 0.5 atm H_2O, 94h

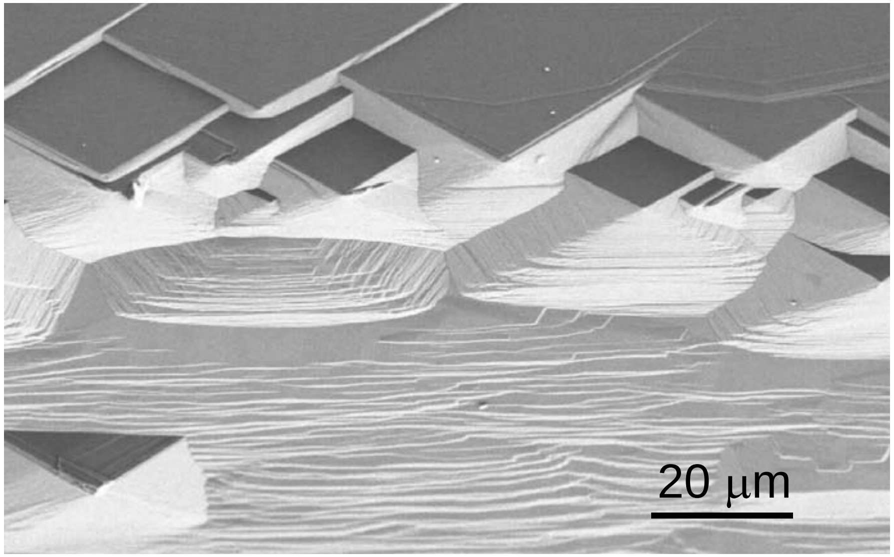
Etching of Sapphire Coupon Edge after Exposure in High Temperature Water Vapor



as-received

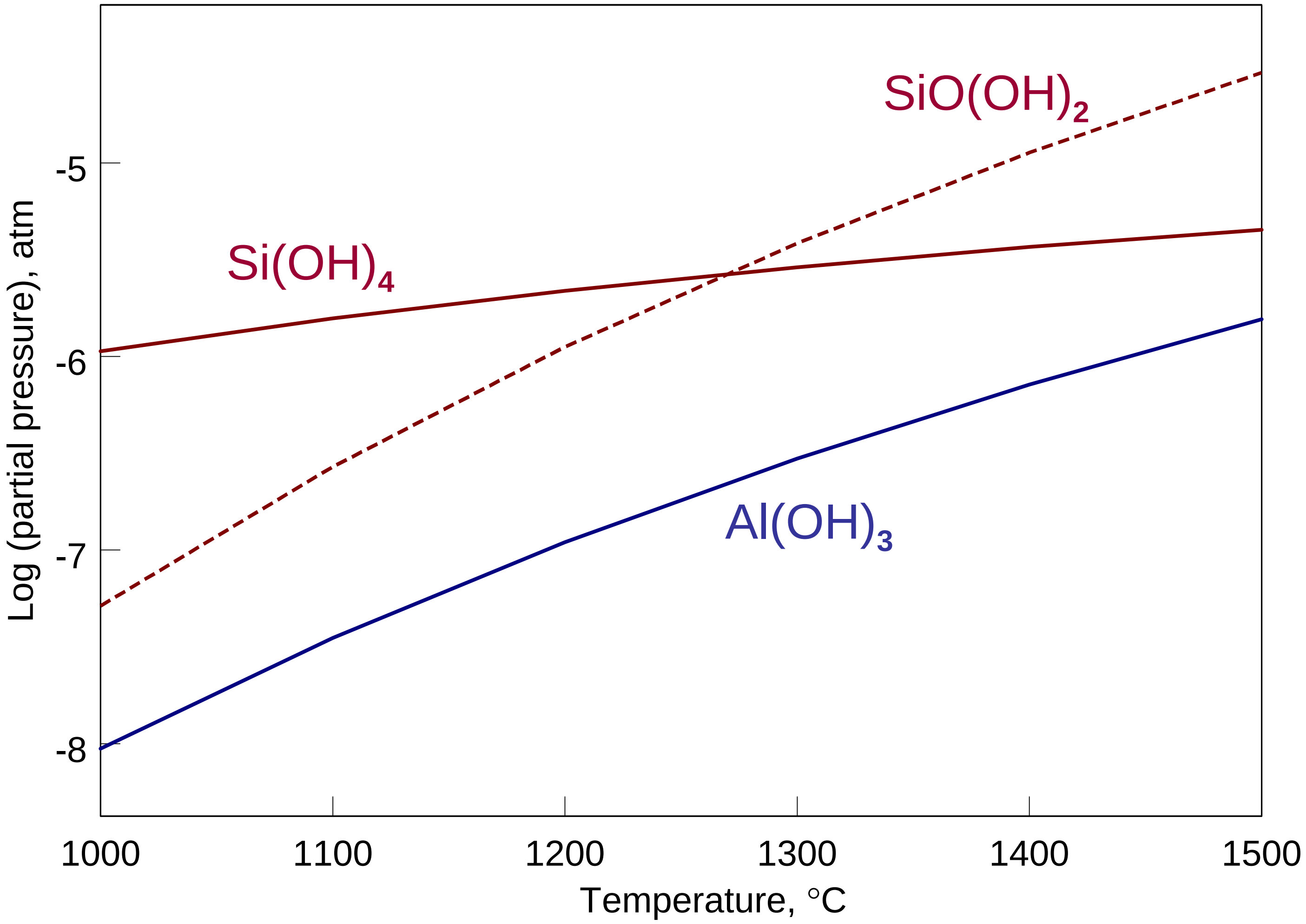


1500°C, 235h, O_2



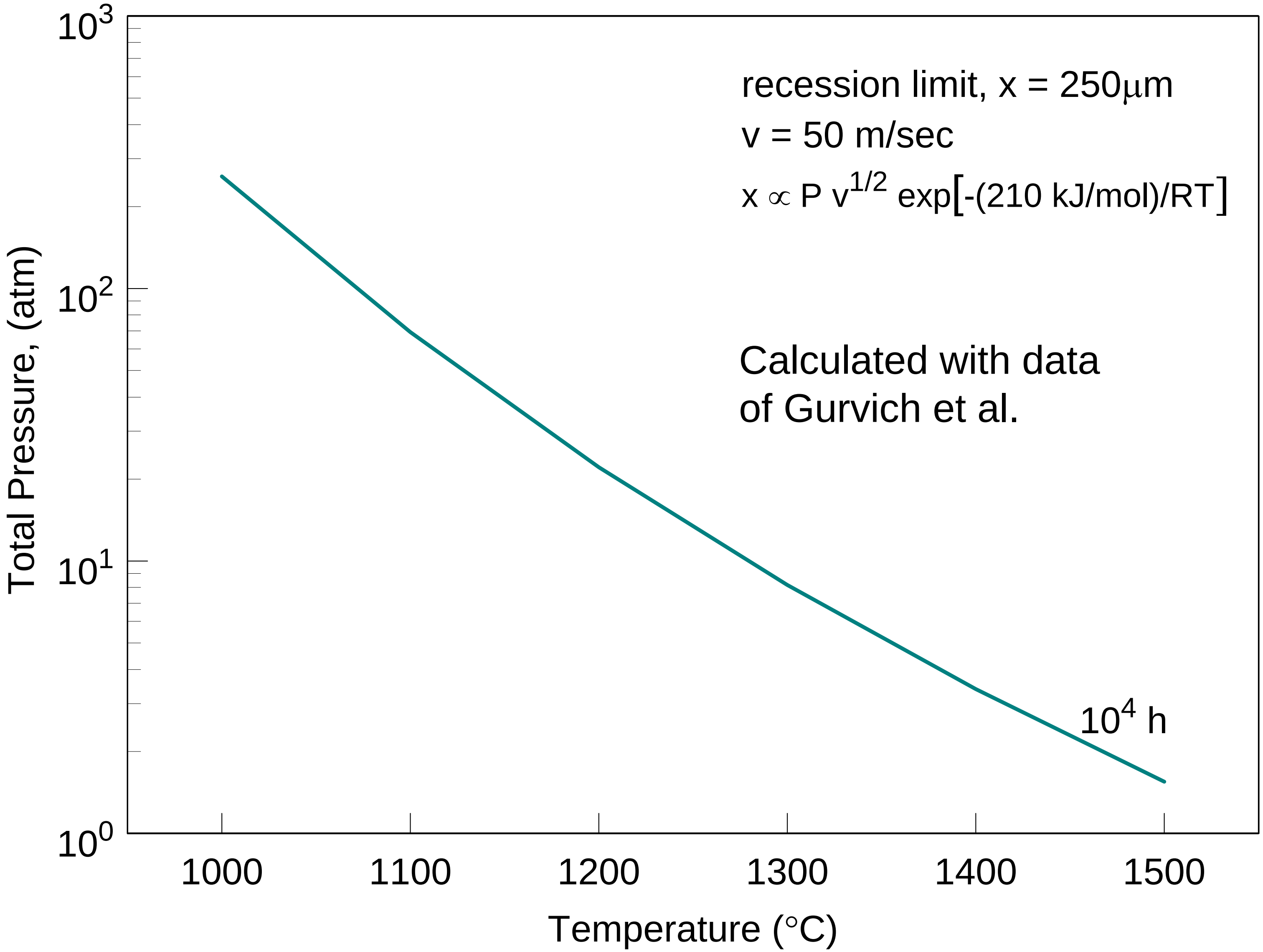
1450°C, 72h,
0.68 atm H_2O

Comparison of Alumina and Silica Volatility in High Temperature Water Vapor



Volatile species in 1 atm water vapor

Recession Map for Al_2O_3 Use in Combustion Environments



Summary and Conclusions

- Alumina volatility in water vapor measured directly by weight loss and found to agree with literature values.
- Pressure dependence of volatility consistent with $Al(OH)_3(g)$ formation.
- Surface etching of sapphire coupons observed in high temperature water vapor.
- Recession $\propto P\ v^{1/2} \exp[-(210\ kJ/mol)/RT]$.
- Alumina volatility will limit lifetimes of components and coatings for long term applications in combustion environments, e.g.,

  250 μm recession in 10,000 h

  T=1300°C, P=10 atm, v=50 m/sec

Possible Future Work

- Transpiration studies on Al_2O_3 + H_2O
  - more precise thermochemical data possible
  - complement Hashimoto's study on mixed calcium aluminates
  - requires fusion technique to dissolve condensed volatile species

- Free jet sampling mass spectrometry of Al_2O_3 + H_2O
  - first mass spectrometric identification of $Al(OH)_3(g)$
  - complement study of Vasiliy Smirnov conducted at much higher temperatures for other Al-O-H species

Acknowledgments

Ralph Garlick, Nathan Jacobson, Serene Farmer, all from NASA Glenn Research Center

This work was funded by the Aeropropulsion and Power Program at NASA Glenn Research Center