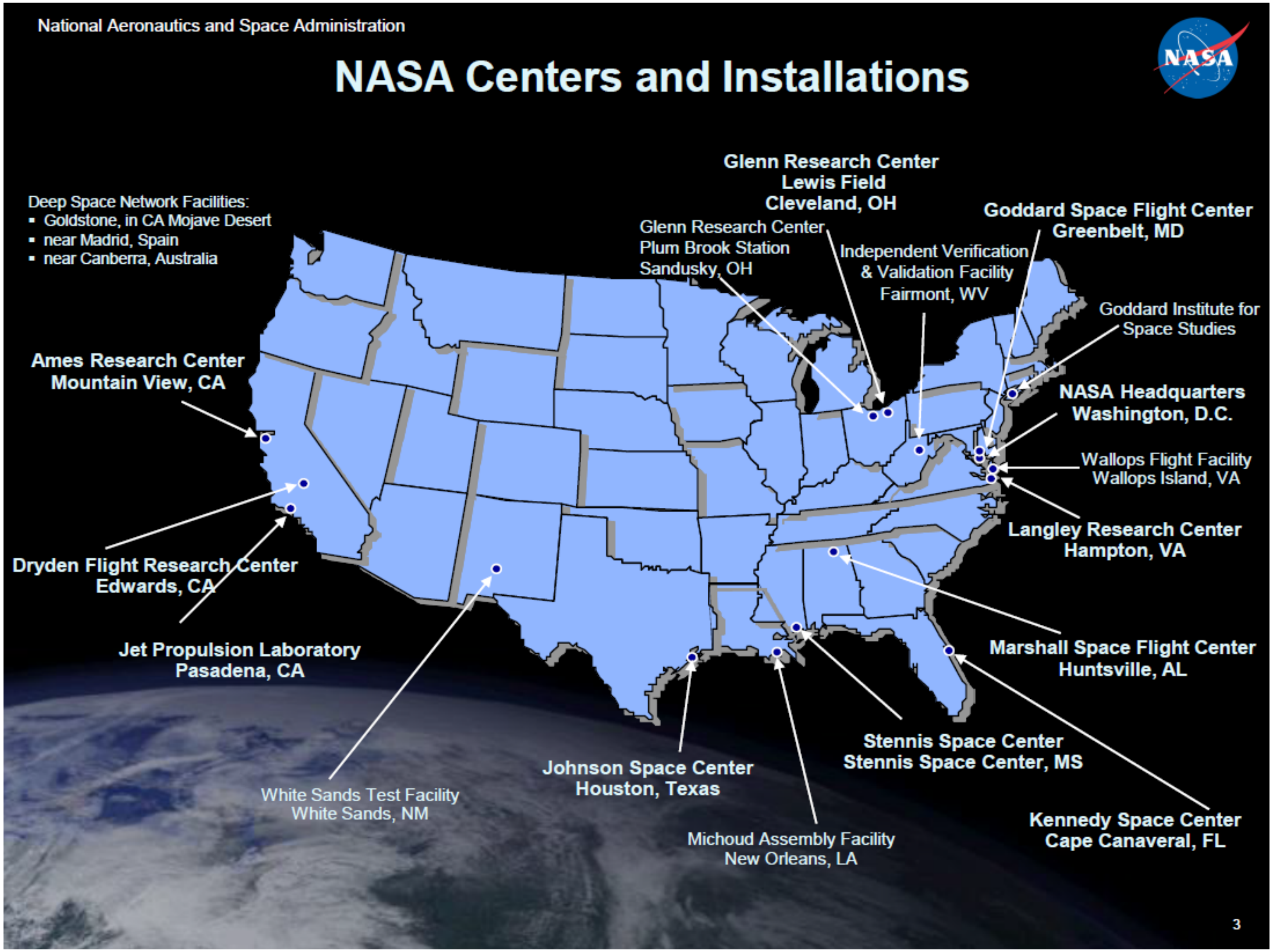
Selected Studies in High Temperature Chemistry at the NASA Glenn Research Center

Nathan Jacobson
NASA Glenn Research Center/HX5
Cleveland, OH

Arizona State University
Geo/Environmental Seminar
January 23, 2023



National Aeronautics and Space Administration

NASA Centers and Installations

Deep Space Network Facilities:
- Goldstone, in CA Mojave Desert
- near Madrid, Spain
- near Canberra, Australia

Ames Research Center
Mountain View, CA

Dryden Flight Research Center
Edwards, CA

Jet Propulsion Laboratory
Pasadena, CA

White Sands Test Facility
White Sands, NM

Johnson Space Center
Houston, Texas

Michoud Assembly Facility
New Orleans, LA

Stennis Space Center
Stennis Space Center, MS

Kennedy Space Center
Cape Canaveral, FL

Marshall Space Flight Center
Huntsville, AL

Langley Research Center
Hampton, VA

Wallops Flight Facility
Wallops Island, VA

NASA Headquarters
Washington, D.C.

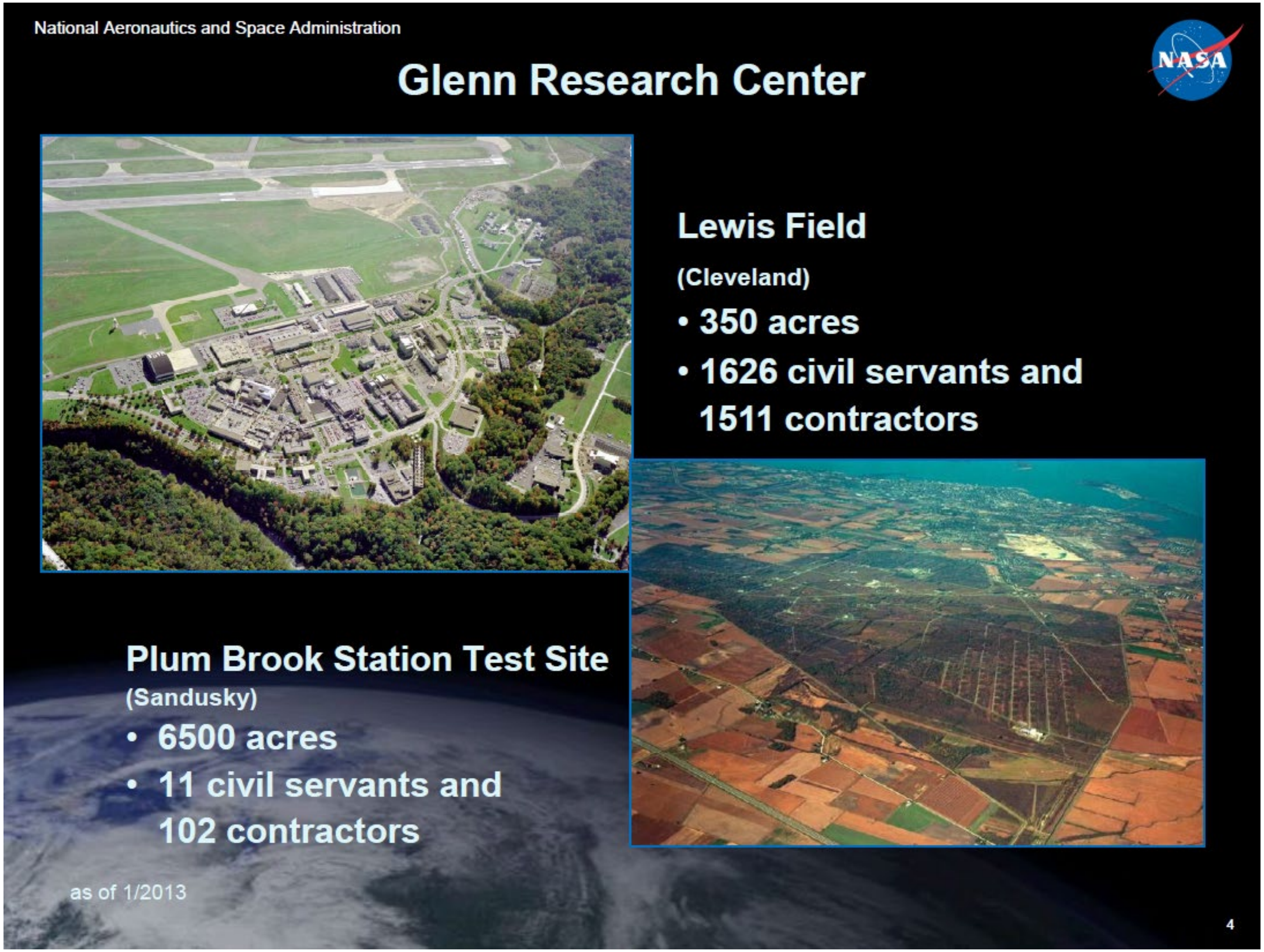
Goddard Institute for
Space Studies

Goddard Space Flight Center
Greenbelt, MD

Independent Verification
& Validation Facility
Fairmont, WV

Glenn Research Center
Lewis Field
Cleveland, OH

Glenn Research Center
Plum Brook Station
Sandusky, OH



National Aeronautics and Space Administration

Glenn Research Center

Lewis Field

(Cleveland)

- 350 acres
- 1626 civil servants and 1511 contractors

Plum Brook Station Test Site

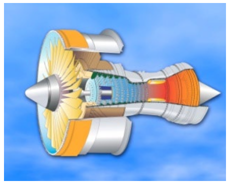
(Sandusky)

- 6500 acres
- 11 civil servants and 102 contractors

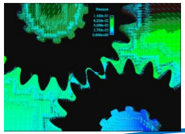
as of 1/2013

4

Structures and Materials Research Supports a Wide Range of NASA Missions

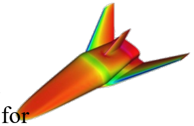


High-temperature and lightweight gas turbine engine components

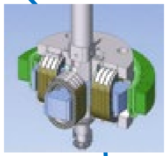


Variable speed transmission for large tilt rotor

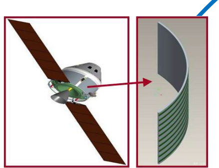
Inflatable structure for Mars entry, descent, and landing



Ultra-high temperature material and integrated TPS for reusable hypersonic vehicles



Superconducting motor for turboelectric propulsion



Lightweight radiators for Crew Exploration vehicle (CEV)

Multidisciplinary Themes

High Temperature Structure and Materials

Multi-Functional Structures

Long-Life Mechanical Systems

Active Structures

More Electric Power and Propulsion

Capabilities

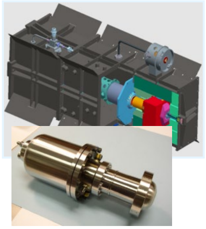
- High temperature alloys
- Smart materials
- Ceramics
- Polymers
- Composites
- High temperature reactions
- Thermochemistry
- Protective coatings
- Mechanics of materials
- Life prediction
- Nanotechnology
- Structural optimization
- Probabilistic methodology
- Structural dynamics
- Rotordynamics
- Tribology
- Surface science
- Gears and bearings
- Terramechanics
- Seals

Large composite structure for Ares V launch vehicle

Long-life lunar wheels and mechanisms

CEV heat shield seal

ISS low impact docking seal



Durable components for radioisotope power system

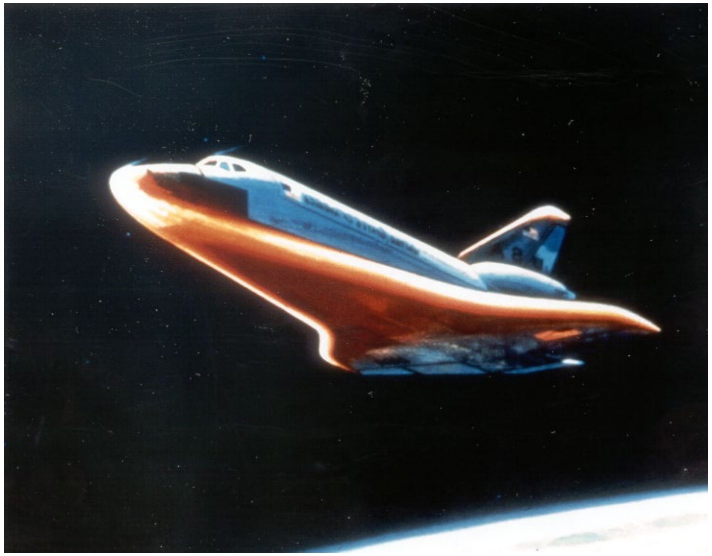
Space Nuclear Propulsion

Selected Studies of High Temperature Chemistry Related to NASA Missions

- Space Shuttle Orbiter Wing Leading Edge
- Environmental Barrier coatings for Ceramic Turbine parts
- Chemistry on other worlds: Exoplanets
- K/Ar dating of minerals
- Teams and collaborations for all studies

Knudsen Effusion Mass Spectrometry

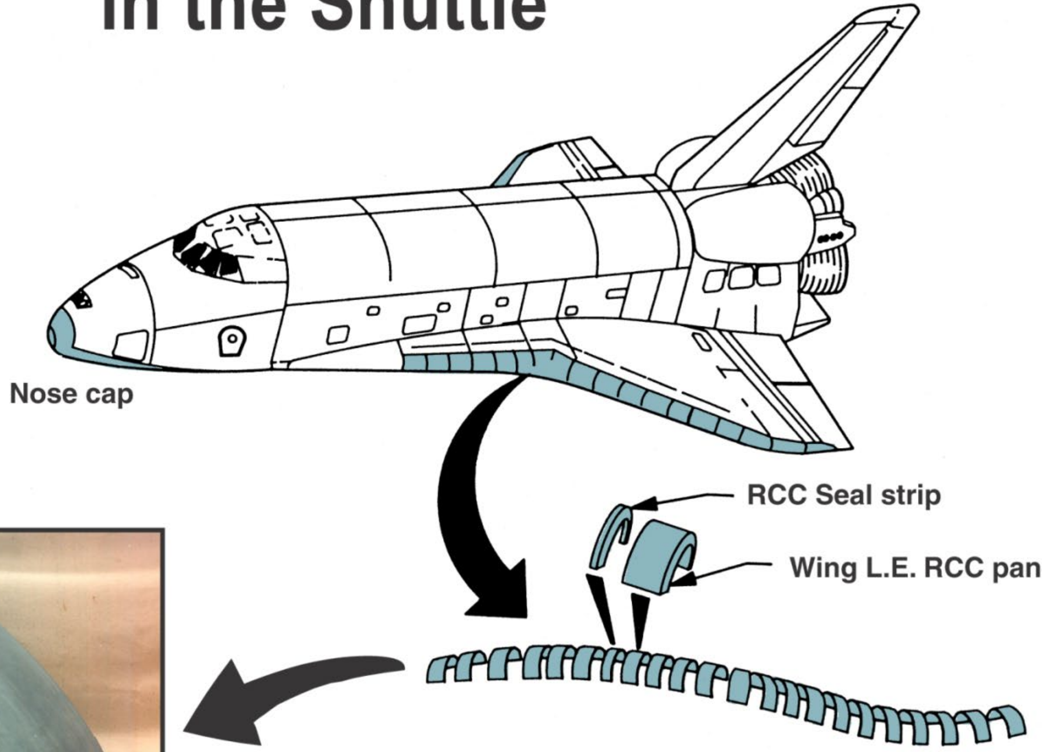
Re-entry: Orbiter’s Nose Cap and Wing Leading Edges Take the Heat



- Temperatures: To 1650°C
- Atmosphere: O_2, N_2 as atoms and molecules
- Pressures: 0.005-0.010 atm
- Material: SiC Coated Reinforced Carbon/Carbon Composite (RCC)

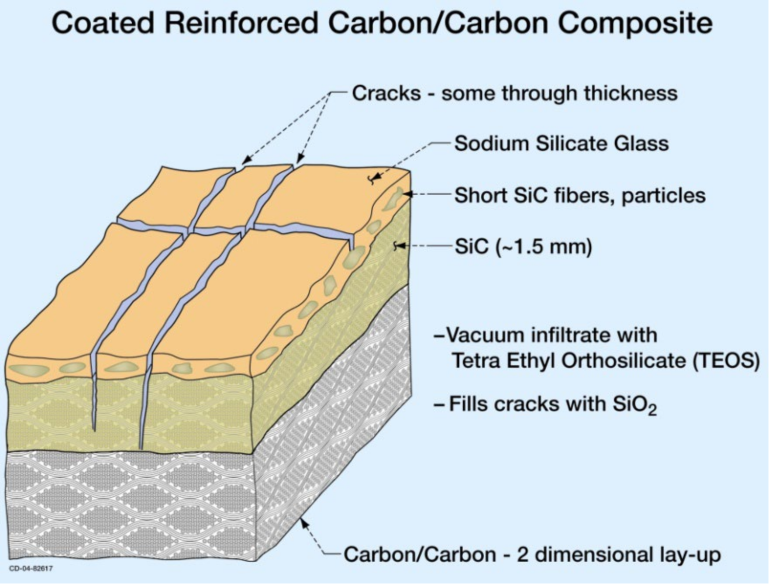
- Leading Edge Sub-System Problem Resolution Team (LESS-PRT)
  ~50 members from NASA Centers, Lockheed-Martin, Southern Research Institute, University Consultants, etc.

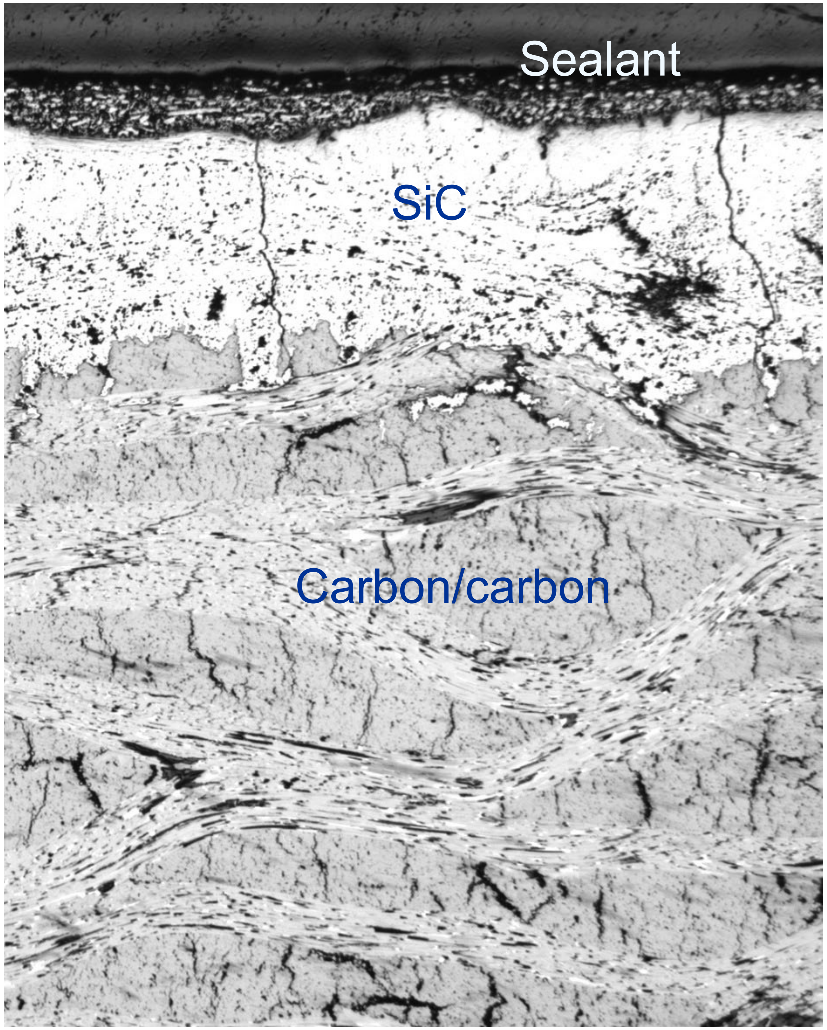
Reinforced Carbon/Carbon (RCC) in the Shuttle



CD-97-76505

- Composite of Carbon Fibers in a Carbon Matrix → “Carbon/Carbon”
- Remarkably effective > 130 flights



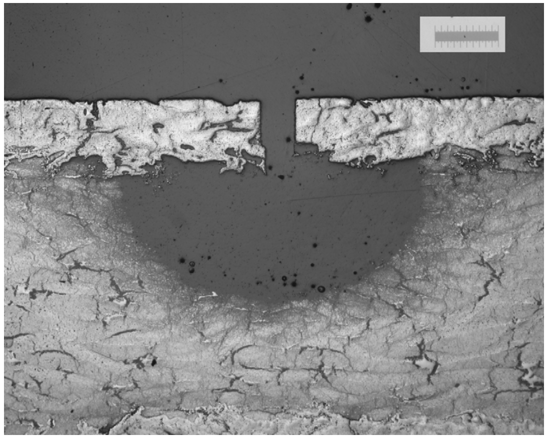


SiC/C-C Coefficient of thermal expansion mismatch leads to cracking in SiC

Is there Oxidation below cracks?

GRC asked by LESS-PRT to Model Oxidation below these Cracks
Start with machined slot (articial crack) in SiC

1200°C/2.5 hr/air

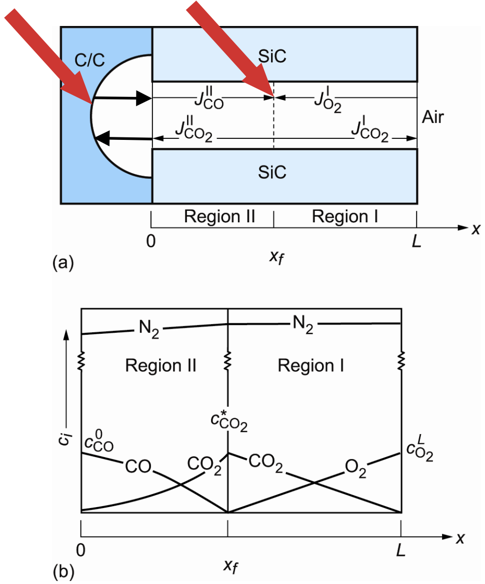


Optical Image (bar is 1 mm)
Symmetric Slot indicates
Diffusion Controlled Reaction

Image Analysis:
Approximate as semi-circle
and extract radius

Jacobson et al., "Oxidation through coating cracks of SiC-protected carbon/carbon," Surf. Coat. Tech. (2008) 203, 372-383 (2008).

Model of Diffusion Controlled Oxidation



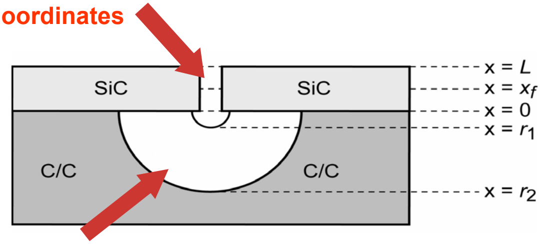
$CO_2 + C = 2\ CO$

$CO + ½\ O_2 = CO_2$

- Two step oxidation of carbon
  - **Can't have direct oxidation:**
    $C + ½\ O_2(g) = CO(g)$
  - Based on
    - Thermodynamic incompatibility of CO/O_2
    - Experimental observations of carbon burning (flame front)
  - Two steps
    - $CO_2(g) + C(s) = 2CO(g)$
      At the carbon surface
    - $CO(g) + ½\ O_2(g) = CO_2(g)$
      At a position x_f away from the surface
    - Net reaction
      - $C + ½\ O_2(g) = CO(g)$

Equations

Rectangular Coordinates



Polar Coordinates

$$J_i = D_i^{eff}\left(\frac{\partial c_i}{\partial x}\right) + v_i^{ave} c$$

- Diffusion in SiC slot/crack (rectangular coordinates)

Diffusive and Convective Flux

B.C.

$$At\ x = 0: \quad c_{CO} = c_{CO}^{0} \quad c_{CO_2} = c_{CO_2}^{0}$$

CO_2 + C = 2CO

$$At\ x = x_f: \quad c_{CO_2} = c_{CO_2}^{*} \quad c_{O_2} = c_{CO} = 0$$

CO + ½ O_2 = CO_2

$$At\ x = L: \quad c_{O_2} = c_{O_2}^{L} \quad c_{CO_2} = 0$$

- Diffusion in growing ‘trough’ (polar coordinates)

$$J_{CO_2}^{tr} A' = -D_{CO_2} A'\left(\frac{\partial c_{CO_2}}{\partial r}\right) - \frac{A' c_{CO_2} J_{CO_2}^{tr}}{c_T}$$

Solutions: Express Oxidation as Cavity Growth or Weight Loss

- Growth in terms of radii

$$t = \frac{M_{CO_2}}{M_C}\frac{\rho}{D_{CO_2}c^*_{CO_2}}\left[\frac{r_2^2}{2}\ln(r_2) - \frac{r_2^2}{4} - \frac{r_2^2}{2}\ln r_1 + \frac{r_2^2}{2}\left(\frac{\pi x_f\left(c_T + c^*_{CO_2}\right)}{r_1 c_T}\right) + \frac{r_1^2}{4} - \frac{r_1^2}{2}\left(\frac{\pi x_f\left(c_T + c^*_{CO_2}\right)}{r_1 c_T}\right)\right]$$

- Growth in terms of weight loss

$$t = \frac{M_{CO_2}}{M_C}\frac{\rho}{D_{CO_2}c^*_{CO_2}}\left[\begin{array}{l} \dfrac{\left(\sqrt{\dfrac{2W}{\pi\rho l}} + r_1\right)^2}{2}\ln\left(\sqrt{\dfrac{2W}{\pi\rho l}} + r_1\right) - \dfrac{\left(\sqrt{\dfrac{2W}{\pi\rho l}} + r_1\right)^2}{4} - \dfrac{\left(\sqrt{\dfrac{2W}{\pi\rho l}} + r_1\right)^2}{2}\ln r_1 \\ + \dfrac{\left(\sqrt{\dfrac{2W}{\pi\rho l}} + r_1\right)^2}{2}\left(\dfrac{\pi x_f\left(c_T + c^*_{CO_2}\right)}{r_1 c_T}\right) + \dfrac{r_1^2}{4} - \dfrac{r_1^2}{2}\left(\dfrac{\pi x_f\left(c_T + c^*_{CO_2}\right)}{r_1 c_T}\right) \end{array}\right]$$

Results: Using Oxidation Trough Radius as Indicator of Oxidation

1200°C/air/0.53 mm slot

1200°C/air/1.05 mm slot

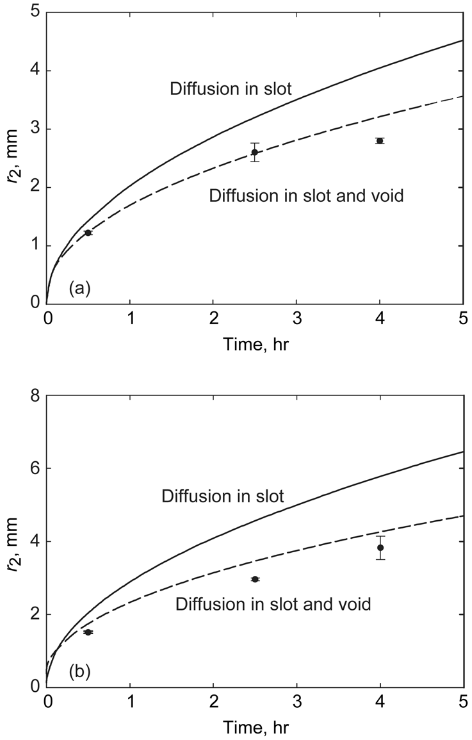
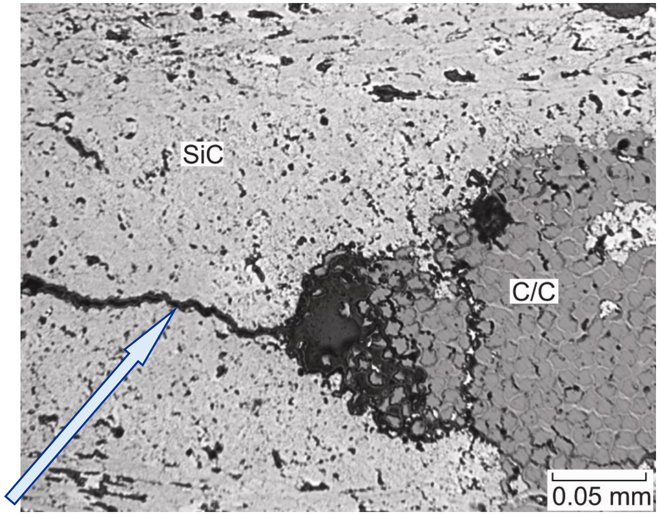


Figure 9

Oxidation through Natural Craze Cracks



“Craze Crack” from shrinkage of SiC
Pathway for oxygen in and CO outward

Actual Cracking in SiC

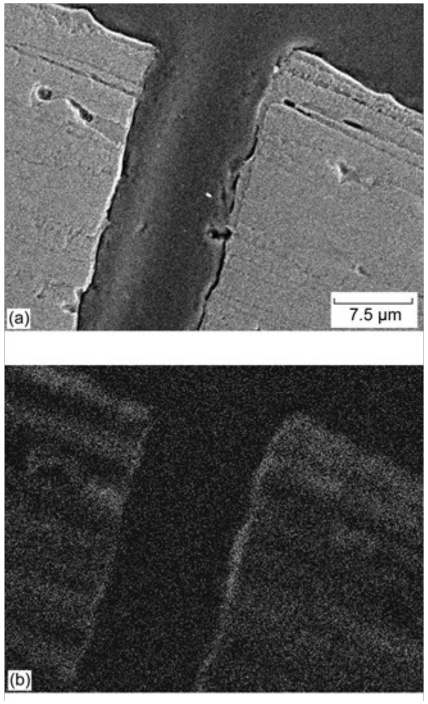
- On cooling from processing temperature, SiC (CTE = 5 ppm/K) shrinks faster than C/C (CTE = 1 ppm/K)
  - Tensile stresses develop in SiC
  - At some temperature stresses are enough to develop cracks to relieve stresses
  - Ideally would close on heating, but do not
  - Use Room temperature dimensions

- Oxidation films on walls of cracks
  - Thin enough to ignore

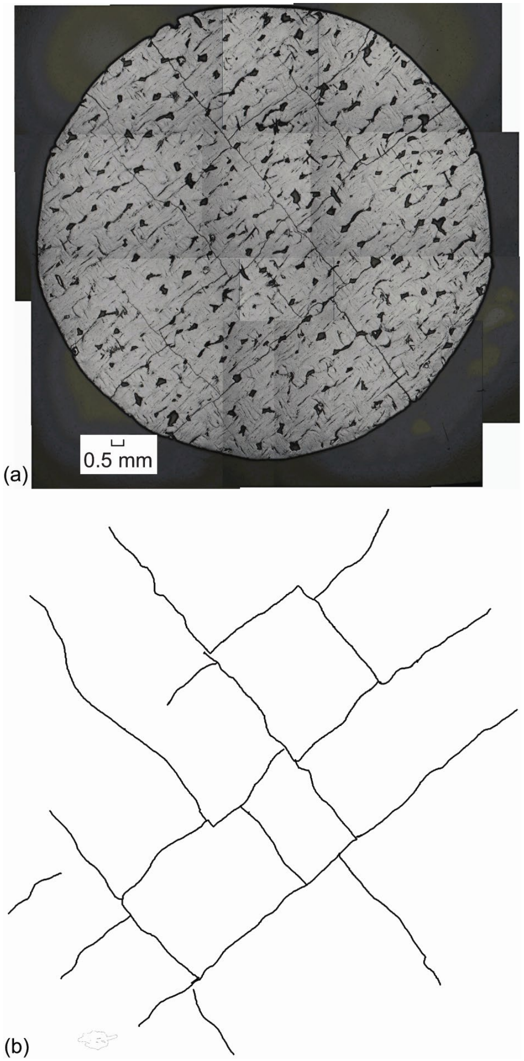
SiC SiC SiC

Carbon/Carbon

SiC crack mouth 1200°C/0.5 hr/air



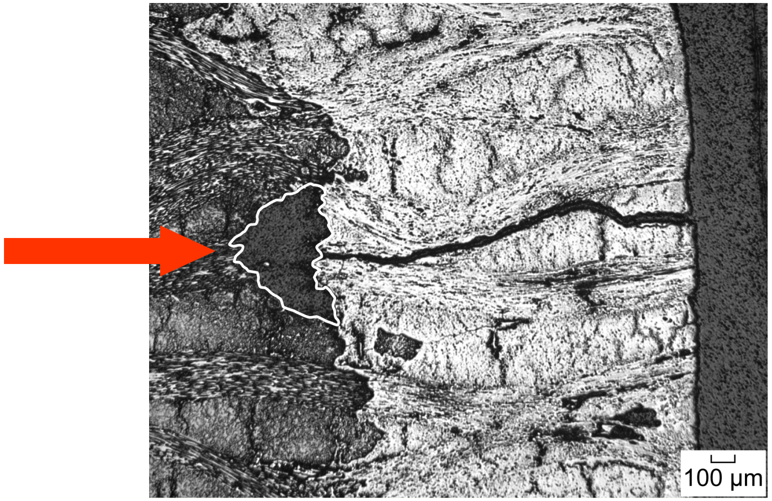
Characterize Craze Cracks



(a) Surface of disc, polished to reveal cracks
(b) ‘Skeleton’ trace of cracks

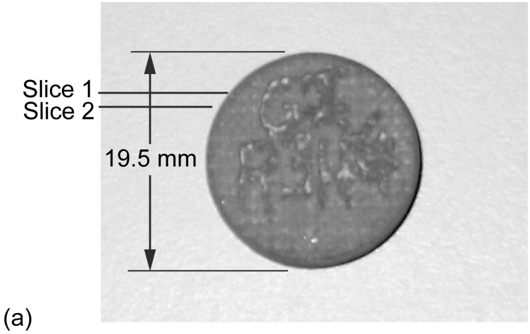
Crack Parameters for Model—From Cross Sections & Image Analysis

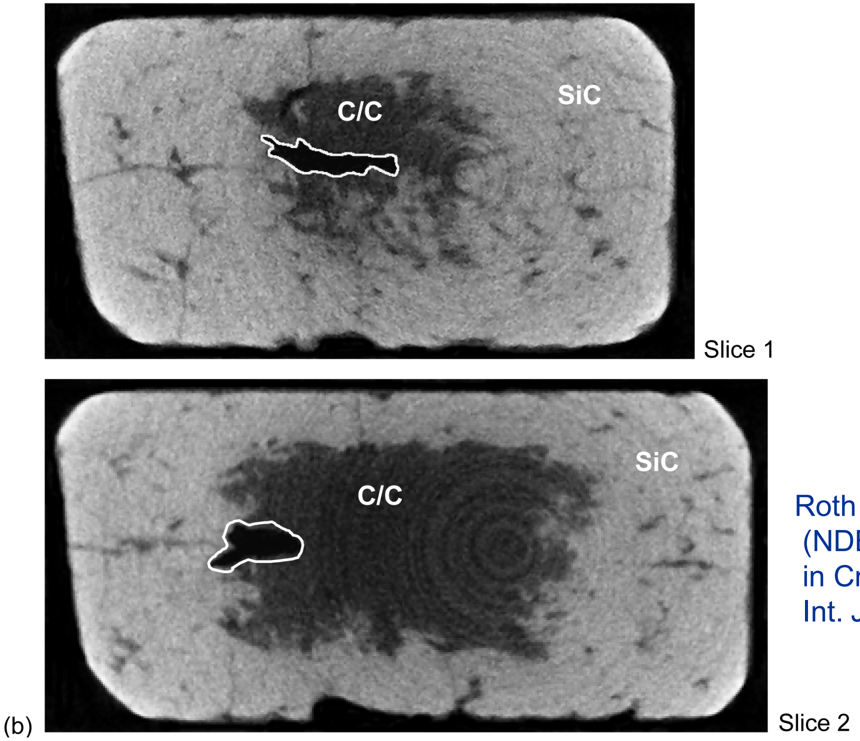
Coating thickness, mm	0.78 ± 0.14
Crack length/unit area, mm^{-1}	0.33 ± 0.04
Crack spacing, mm	3.4 ± 0.9
Crack width, µm	12.8 ± 1.41
Crack area/unit area	4.2×10^{-3}



Oxidation cavity 1300°C/2.5 h/air

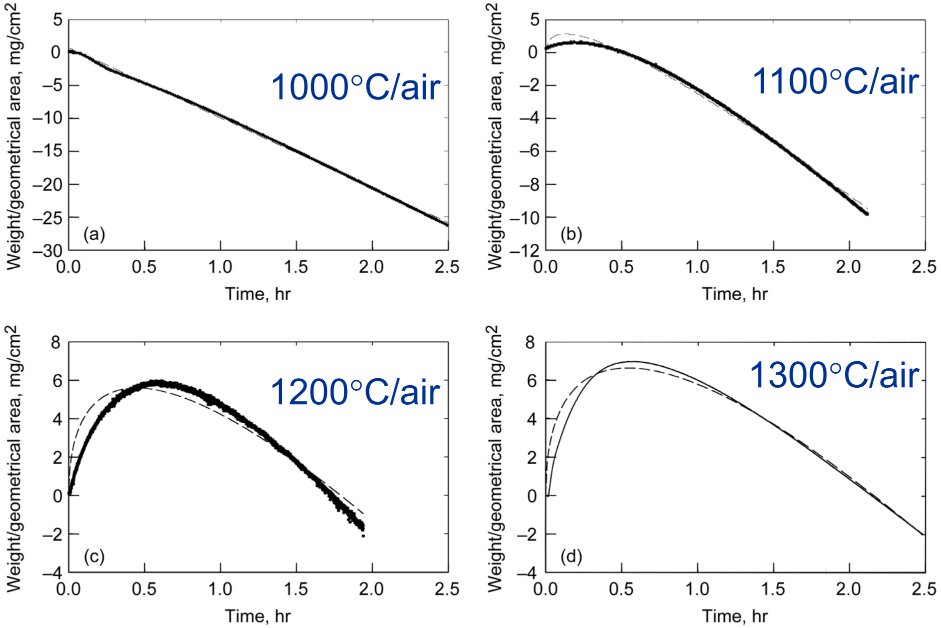
X-ray CT Shows irregular Oxidation Cavities below Cracks



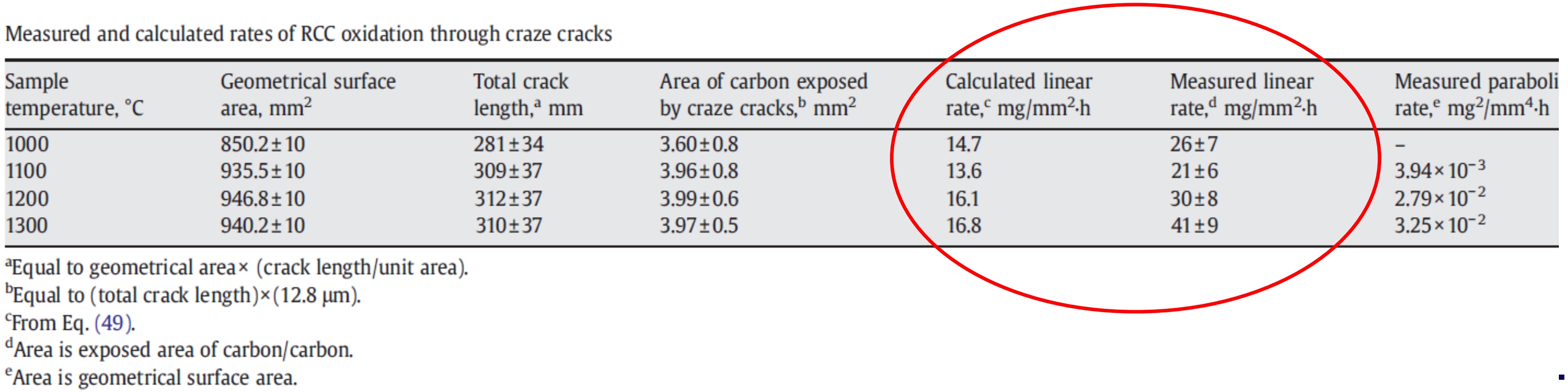


Roth et al, “Nondestructive Evaluation (NDE) for Characterizing Oxidation Damage in Cracked Reinforced Carbon-Carbon,” Int. J. Appl. Ceram. Tech. 7 [5], 652-661 (2010).

Use Continuous Recording Balance to Obtain Weight Loss Rates



Parabolic region: SiC oxidation + C/C weight loss
Linear region: C/C weight loss
Dashed lines: Fits to extract linear and parabolic rate constants



Measured and calculated rates of RCC oxidation through craze cracks

Sample temperature, °C	Geometrical surface area, mm^2	Total crack length,[a] mm	Area of carbon exposed by craze cracks,[b] mm^2	Calculated linear rate,[c] $mg/mm^2{\cdot}h$	Measured linear rate,[d] $mg/mm^2{\cdot}h$	Measured paraboli rate,[e] $mg^2/mm^4{\cdot}h$
1000	850.2±10	281±34	3.60±0.8	14.7	26±7	–
1100	935.5±10	309±37	3.96±0.8	13.6	21±6	3.94×10^{-3}
1200	946.8±10	312±37	3.99±0.6	16.1	30±8	2.79×10^{-2}
1300	940.2±10	310±37	3.97±0.5	16.8	41±9	3.25×10^{-2}

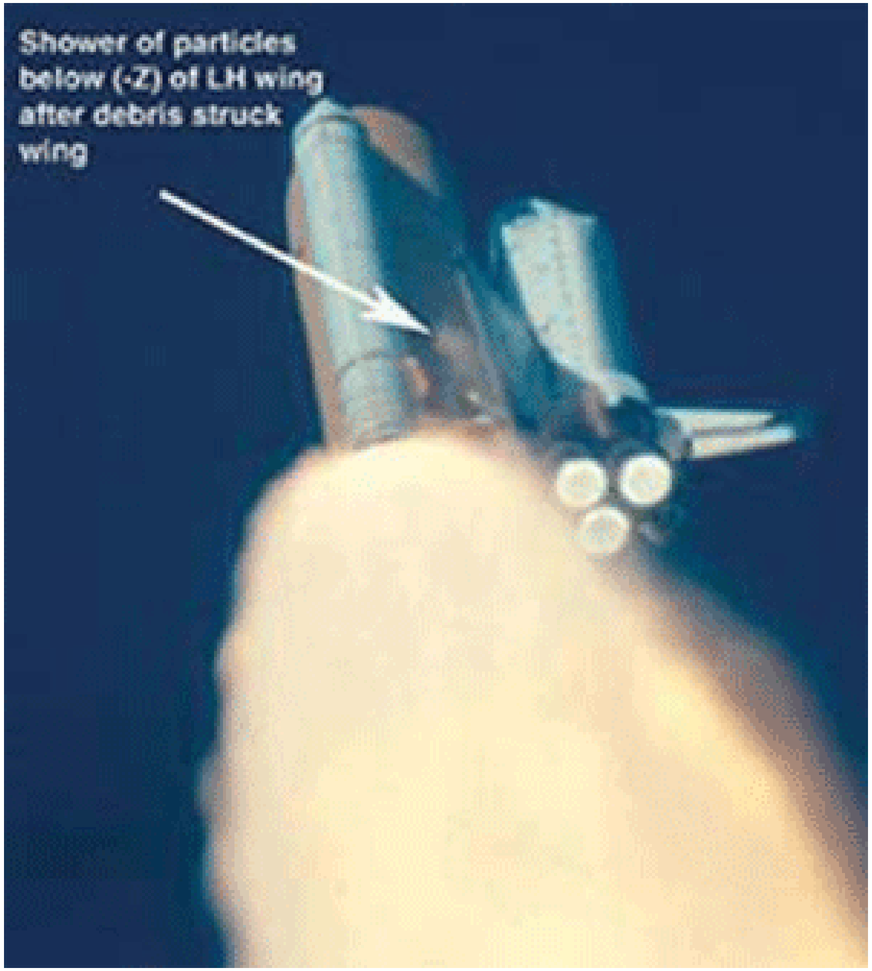
[a] Equal to geometrical area× (crack length/unit area).
[b] Equal to (total crack length)×(12.8 μm).
[c] From Eq. (49).
[d] Area is exposed area of carbon/carbon.
[e] Area is geometrical surface area.

Summary: Oxidation of RCC below Cracks in SiC Coating

- Oxidation study of SiC-protected carbon/carbon (1000-1300°C)
  - Well-characterized samples with machined slots and/or natural craze cracks
  - Compare to model developed from diffusion equation
    - Very good agreement with model for machined slots
    - Reasonable agreement with natural craze cracks. Weight loss from other sources

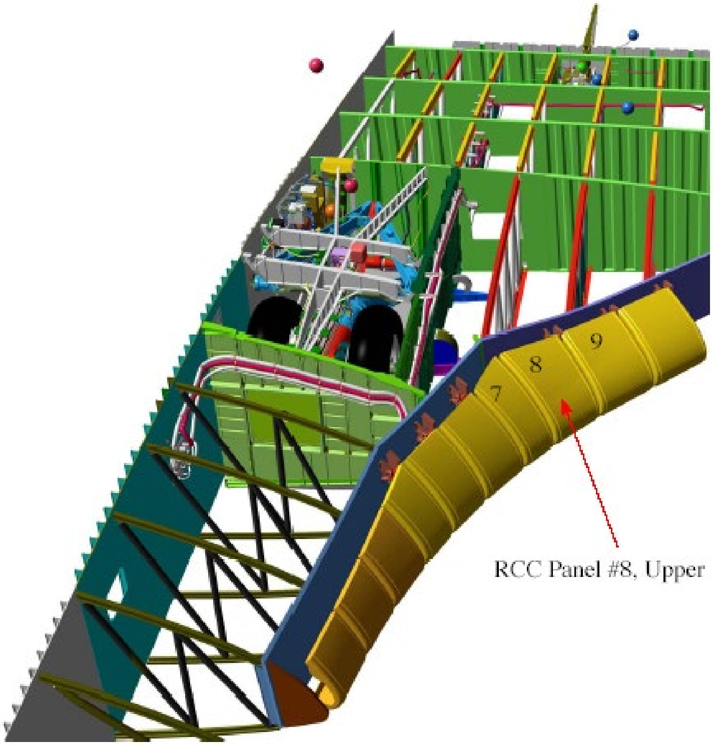
- Oxidation very limited by fume of CO(g) oxidation product
  - Limited damage seen in flown hardware

The Columbia Disaster: February 1, 2003
Shedding from External Fuel Tank Damaged Left Wing
Tragically Showed How Important RCC is to the Orbiter



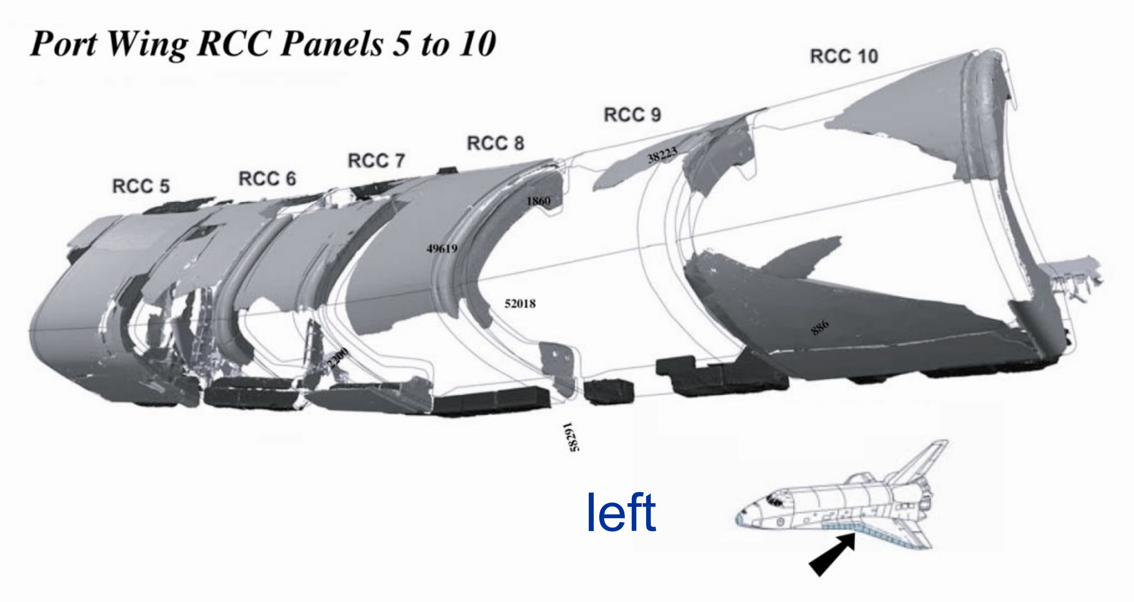
The Columbia Disaster

- Many large teams at NASA and other organizations involved in determining cause of accident
- Impact damage of RCC panel led to entry of hot re-entry gases, melted wing structure, and brought vehicle down



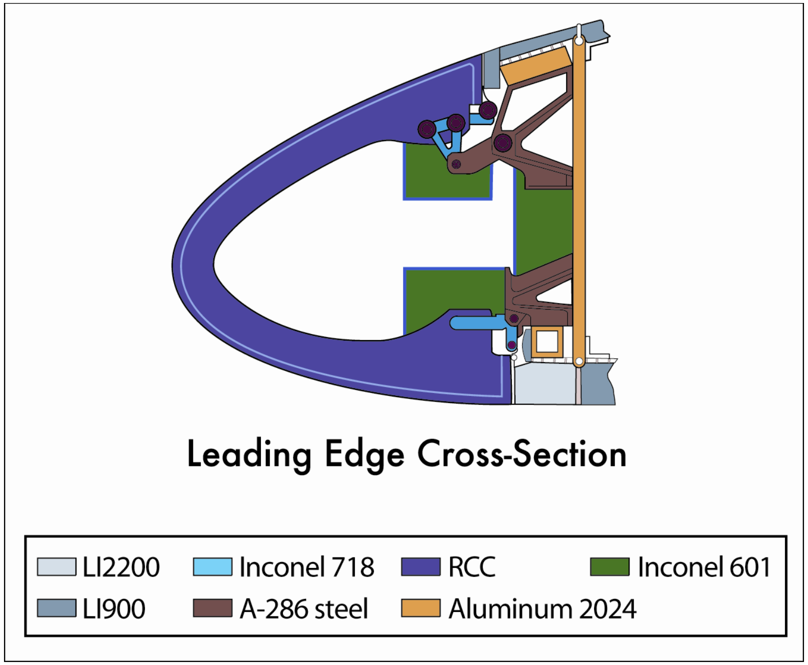
Recovered Pieces of RCC Provided Clues to Cause of Accident

Brought to hanger
at Kennedy Space Center



left

Attachment Hardware in Wing Leading Edge Structure

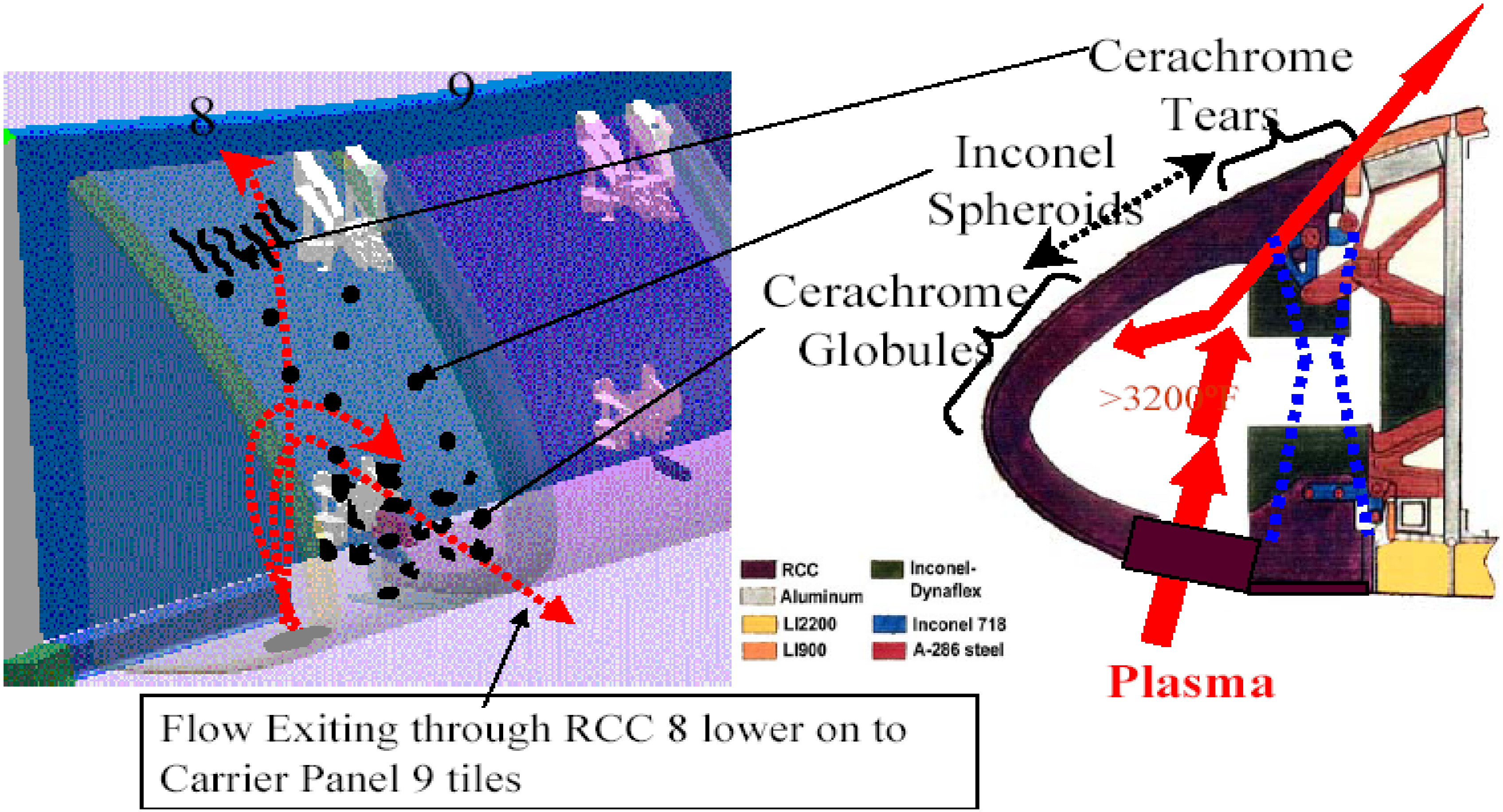


Leading Edge Cross-Section

Pattern of solidified droplets defined location of breach

Alloy	Use	Maximum Service Temperature (°C)	~MP (°C)
Al 2024	Wing spar	NA	650
A286	Spar attachment fitting	815	1370
IN718	Clevis, spanner beam	980	1370
IN601	Spar insulation foil	1090	1370

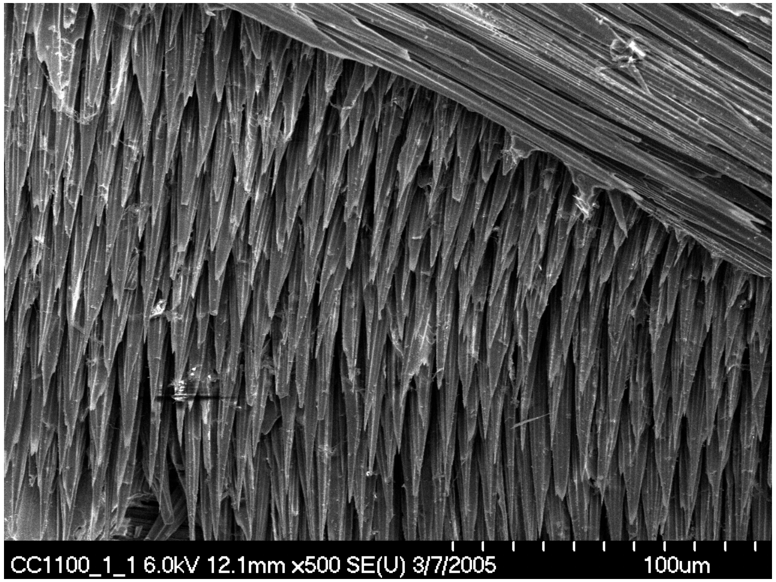
Proposed Breach Location and Plasma Flow Based on Results of Deposit Analysis



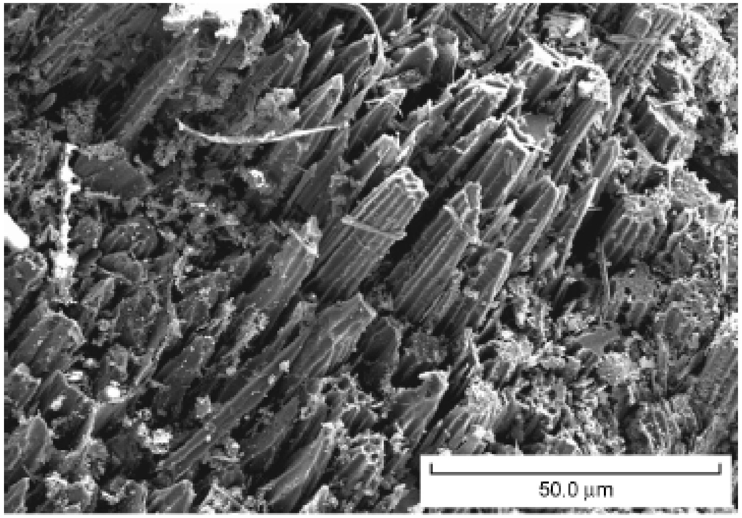
Flow Exiting through RCC 8 lower on to Carrier Panel 9 tiles

Opila, Jacobson, Jerman, “Columbia Tragedy: High-Temperature Materials Chemistry and Thermodynamic Considerations of the Breached Wing Leading Edge,” J. Fail. Anal. Prev. 6 [1], 86-94 (2006).

Oxidation Morphology helped with interpretation of fragments
Unique appearance of remaining Fibers



- Laboratory oxidation of uncoated carbon/carbon
- Oxidation Morphology: Fibers thinner and pointed



- Edge of recovered fragment from Columbia
- Pointed fibers indicated burning when vehicle broke-up
- Flat fracture surfaces indicated fracture on impact with ground

In Memoriam . . .

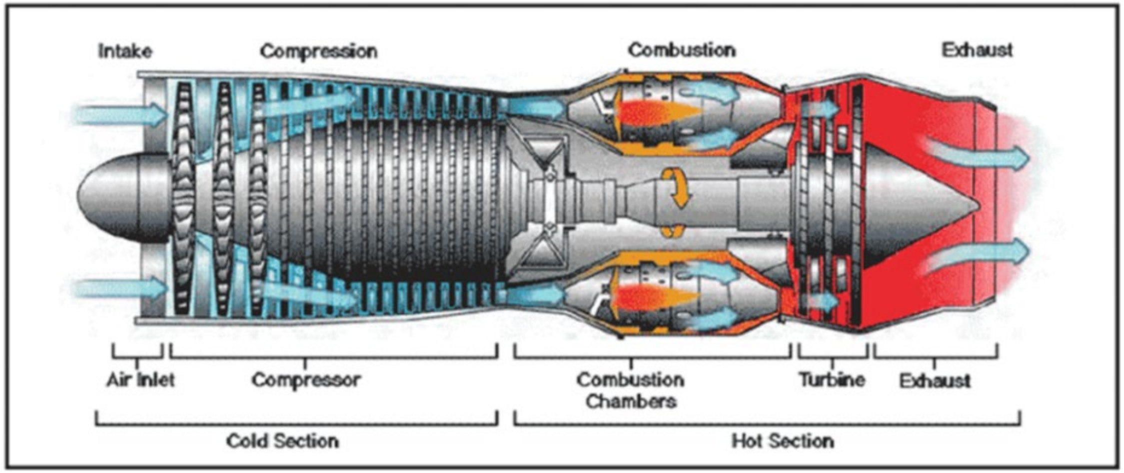
Selected Studies of High Temperature Chemistry Related to NASA Missions

- Space Shuttle Orbiter Wing Leading Edge
- Environmental Barrier coatings for Ceramic Turbine parts
- Chemistry on other Worlds: Exoplanets
- K/Ar dating of minerals

Knudsen Effusion Mass Spectrometry

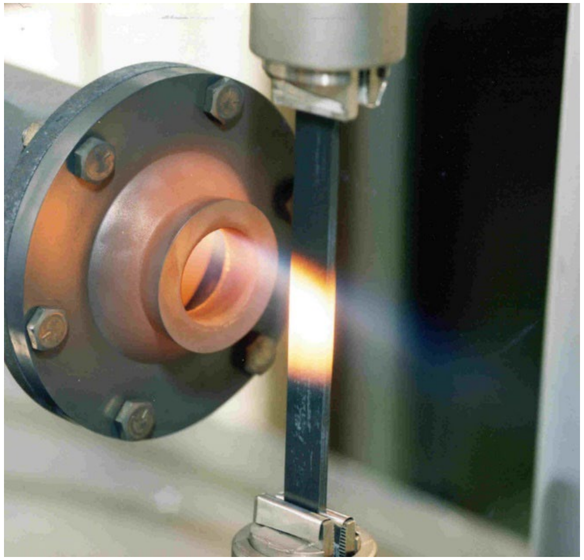
Rare Earth Silicate Coatings (with G. Costa, B. Kowalski)

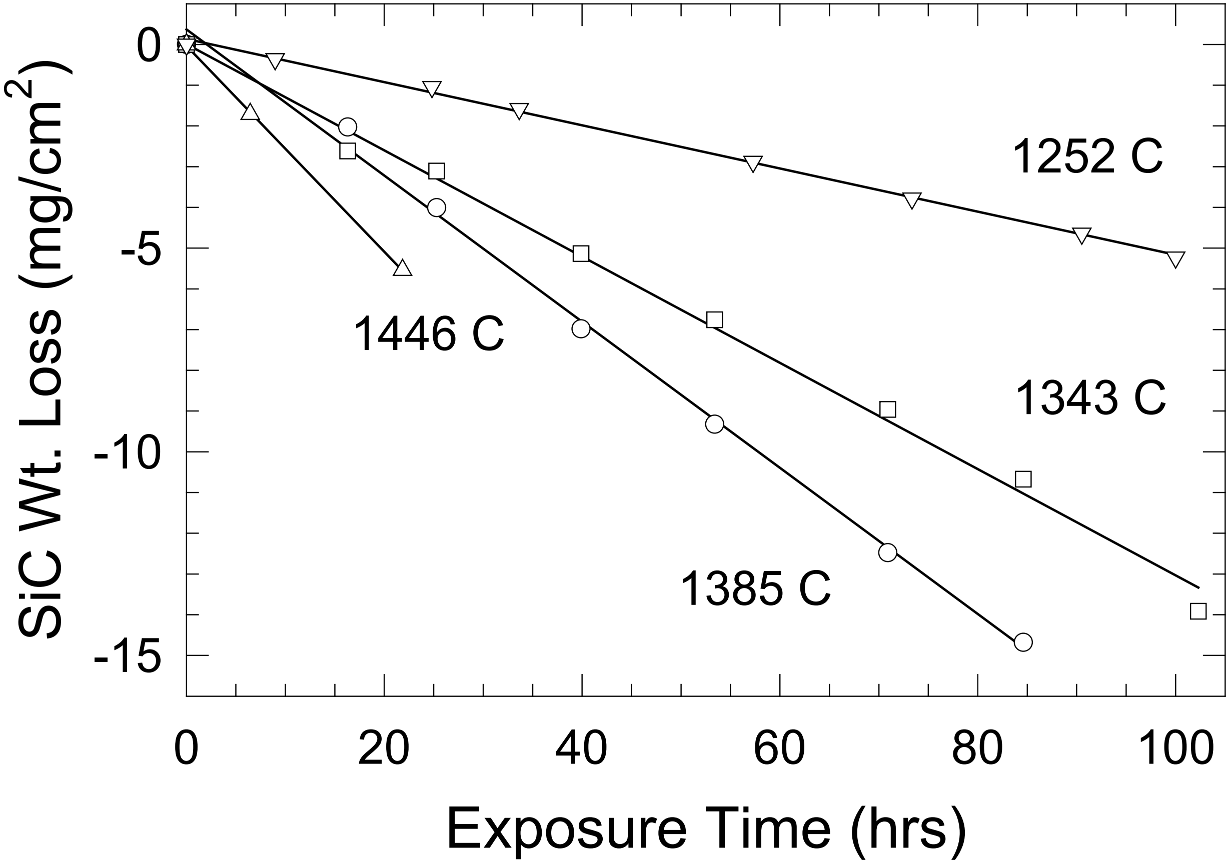
- High-Temperature Materials: Silicate Coatings



- Hot section: Currently advanced Co-Ni based superalloys.
- Always a push to higher temperature, lighter materials: better fuel efficiency
- Future silicon-based ceramics and composites: combustion chambers, static parts in turbine
- Need 1000s of hours reliable operation

Weight Loss of SiC in High Pressure Jet Fuel Burner (6 atm, 20 m/s)

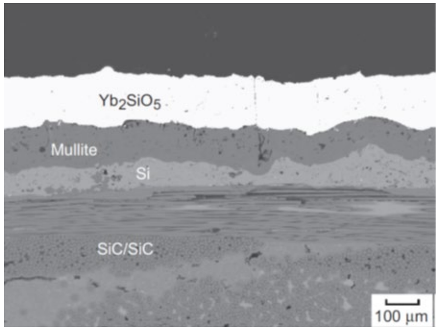




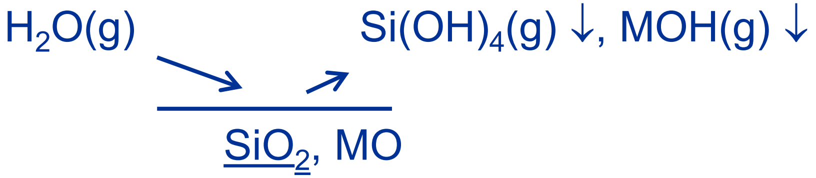
Opila: $SiC(s) + 3/2\ O_2(g) = SiO_2(s) + CO(g)$
$SiO_2(s) + 2H_2O(g) = Si(OH)_4(g)$
Structural part is vaporizing out exhaust!
Needs to last 1000s of hours…

Robinson and Smialek,
J Am Ceram Soc 82, 1817 (1999)

Use Activities as an Index of Reactivity



- Lower activity of silica ⇒ less reaction
- Corrosion: Water vapor enhanced volatilization
  - $SiC + 3/2\ O_2(g) = SiO_2 + CO(g)$
    $\underline{SiO_2} + 2\ H_2O(g) = Si(OH)_4(g)$
  - $P[Si(OH)_4] = K\ a(SiO_2)\ [P(H_2O)]^2$



$$\begin{tikzcd} H_2O(g) \arrow[dr] & & Si(OH)_4(g)\downarrow,\ MOH(g)\downarrow \\ & \underline{SiO_2},\ MO \arrow[ur] & \end{tikzcd}$$

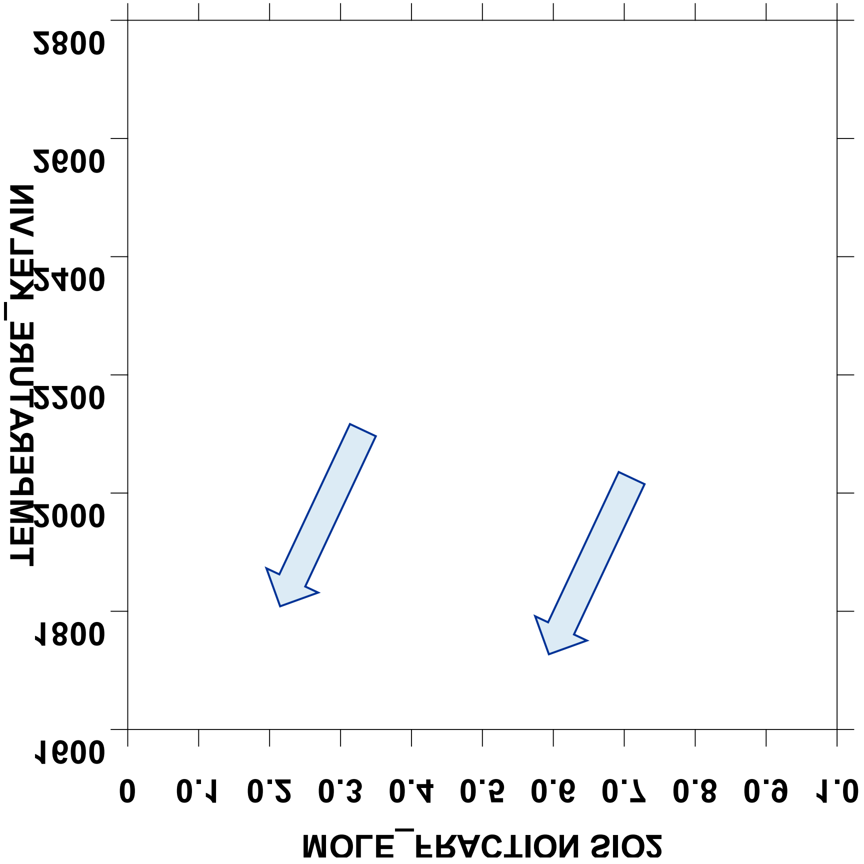
(Underline indicates in solution)

- $Si(OH)_4(g)$ vapor flux ∝ $a(SiO_2)$
- Need to measure $a(SiO_2)$ in candidate coating materials

Meschter, Opila, Jacobson, Ann Rev Mater Res 43, 559 (2013)
Jacobson, J Am Ceram Soc 97, 1959 (2014)

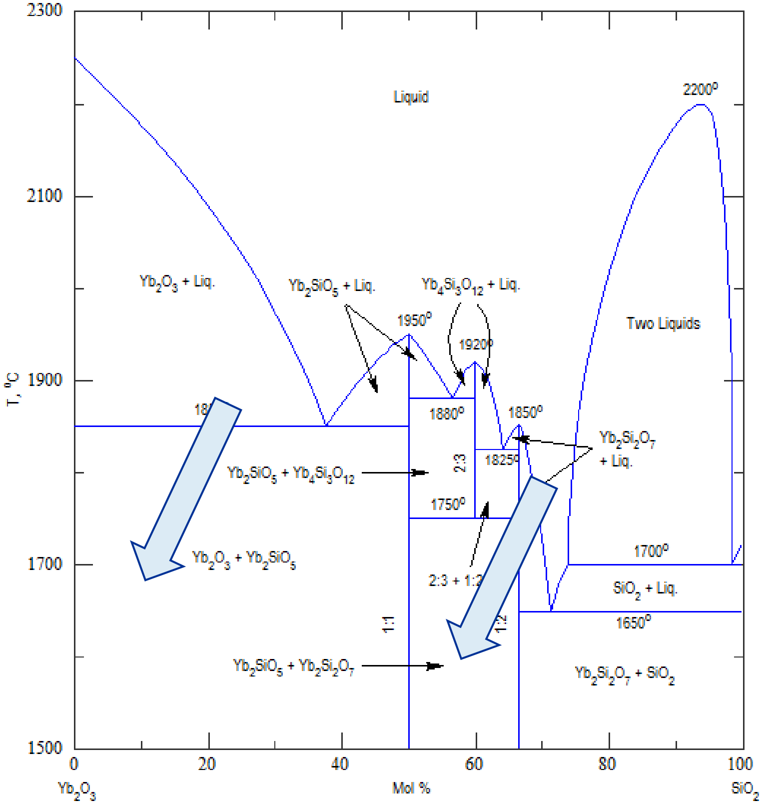
Measure Activities
Work in two Phase Regions (Constant activity)
Lose a little SiO_2 on heating—still good measurements

Y_2O_3-SiO_2



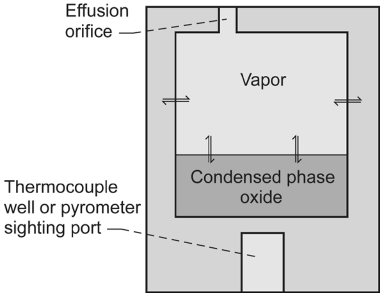
Fabrichinaya, Seifert calculated

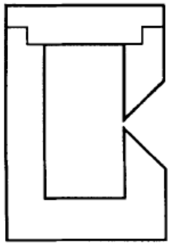
Yb_2O_3-SiO_2



Toropov et. al. (1962)

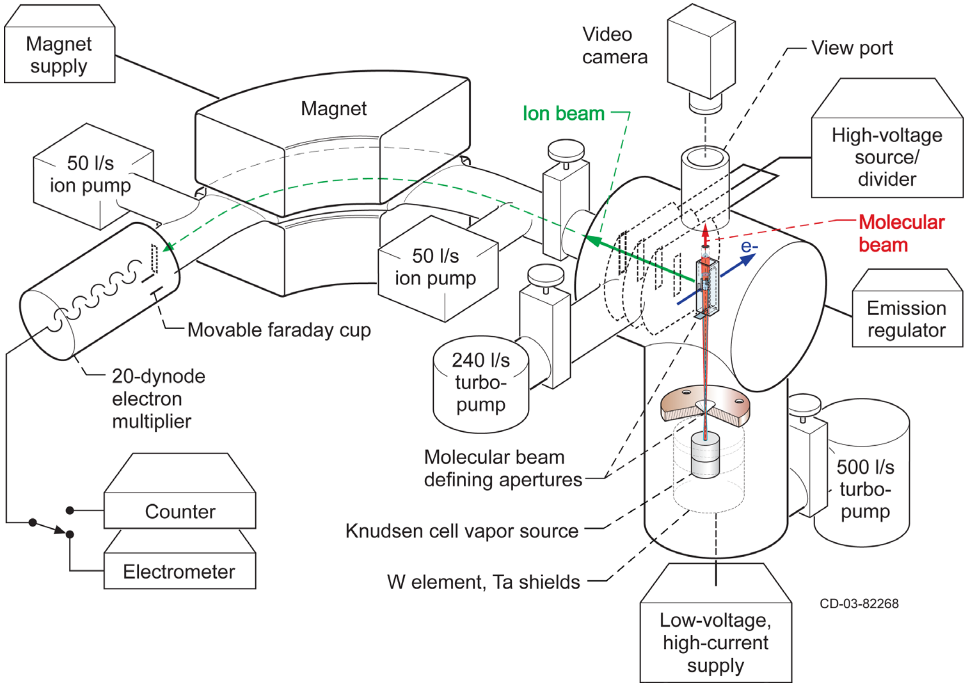
Measure Thermodynamic Activities “Escaping Tendency”
Knudsen Cell Method to Measure Partial Pressure

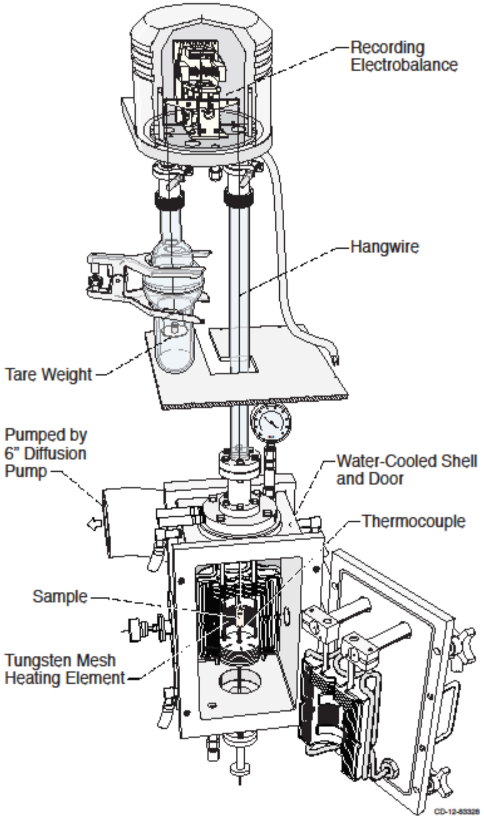




- – Obtain near equilibrium between condensed phase/vapr
- – First developed by Knudsen (Denmark), 1909: Measure Hg vapor pressures
- – Vapor effusing from orifice leads to a weight loss rate which relates to pressure; vapor can also be analyzed with spectrometer
    - First developed by Inghram (Chicago) 1950s
    - Knudsen effusion mass spectrometry (KEMS) Remarkably versatile method
- – Major issues: temperature measurement and sample/cell interactions

Methods of Measuring Vapor Pressure based on Knudsen Cell (Low Ambient Pressure)





Mass spectrometry: direct molecular beam from K-cell to spectrometer

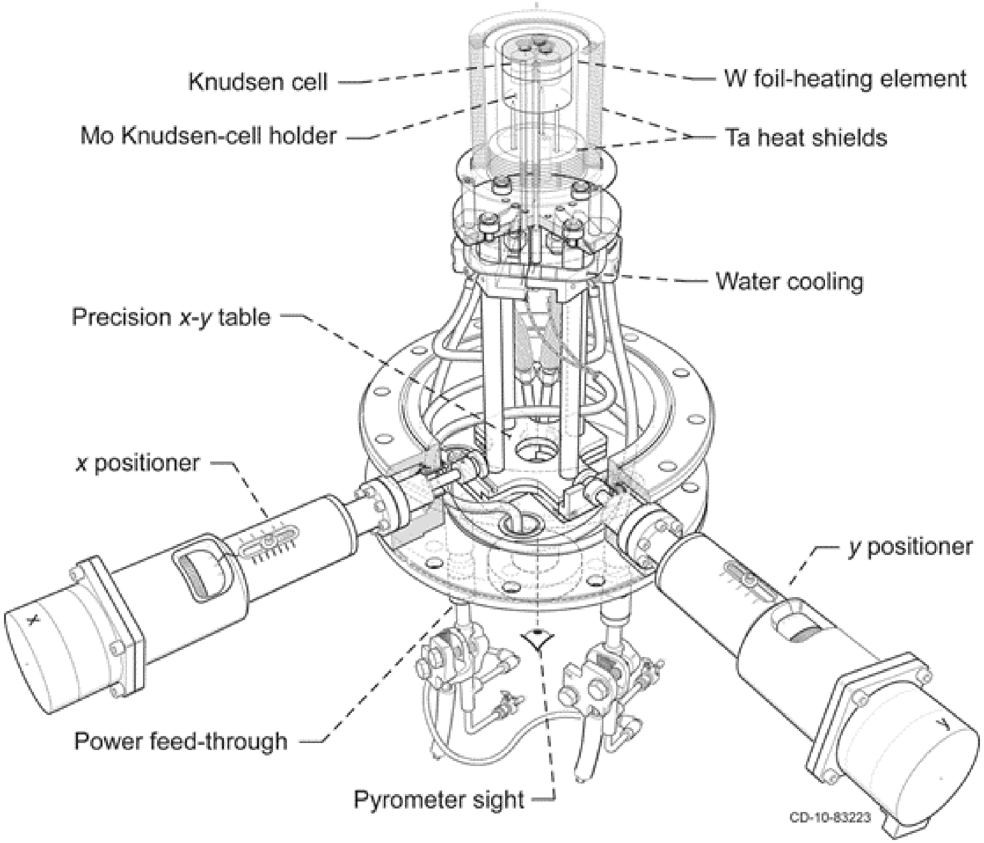
$$P_i = \frac{kI_iT}{\sigma_i}$$

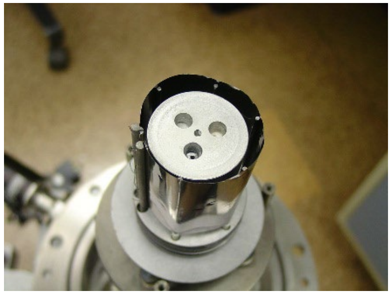
Vacuum Weight loss: Measure vapor flux

$$J = \frac{P}{\sqrt{2\pi MRT}}$$

Procedure for Measuring Thermodynamic Activities

- Ion intensity measurements of relevant species for:
  1. Pure compound
  2. Solution… $a_i = {}^{I_i}/_{I_i^o}$ (for alloys; more complex for oxides)
- Best to have *in-situ* pure compound and solution: Use multiple cell furnace





E. Copland, 2000

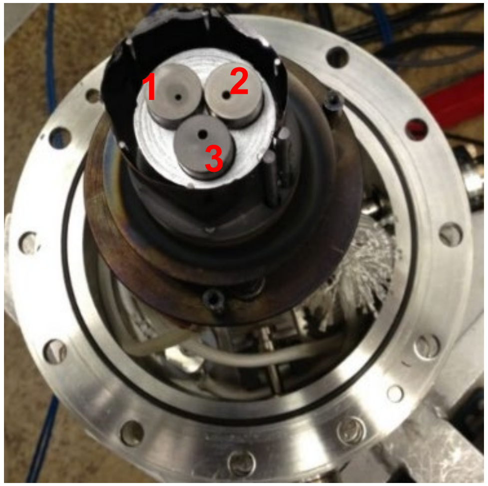
Monosilicate + Disilicate: Constant Activity
SiO(g) relates to a(SiO_2)
Mo (reducing agent) added to boost SiO(g) Signal

Three cells:

- Cell (1) Au (reference: temperature calibration)
- Cell (2) 3Mo + $Yb_2O_3 \cdot 2SiO_2 + Yb_2O_3 \cdot SiO_2$
- Cell (3) 3Mo + SiO_2
- Mo as powder and cell material

Note that cell is part of the thermodynamic system:

Best way to overcome container issue!



Cell 2: SiO_2 in silicate

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

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

Cell 3: pure SiO_2

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

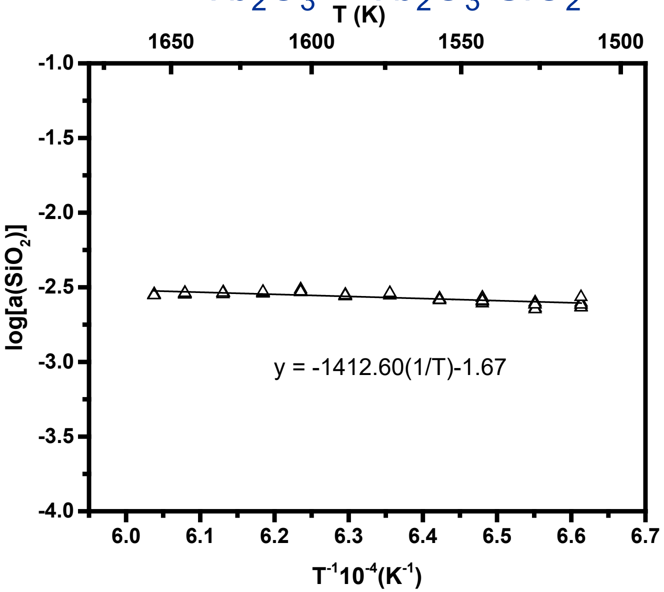
$$Mo + 3SiO_2 = 3SiO + MoO_3$$

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

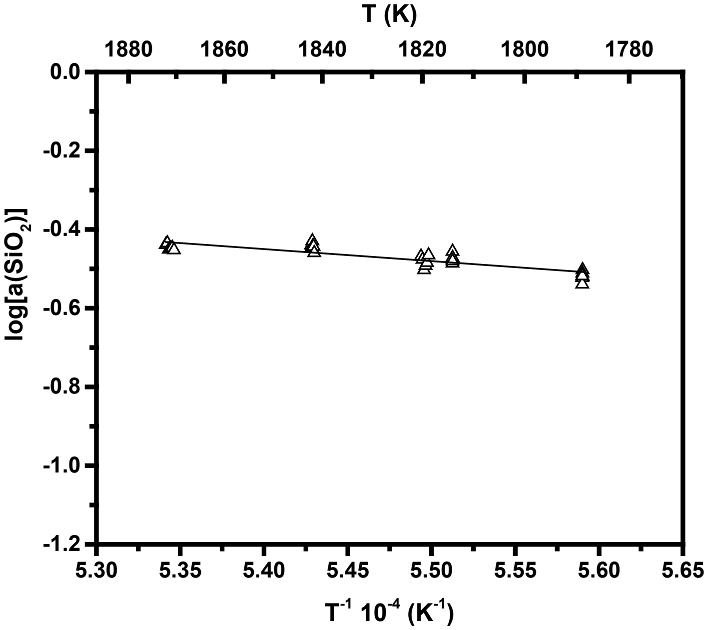
$$a(SiO_2) = \left\{ \frac{[I(SiO)]^3 I(MoO_3)}{[I^o(SiO)]^3 I^o(MoO_3)} \right\}^{0.33}$$

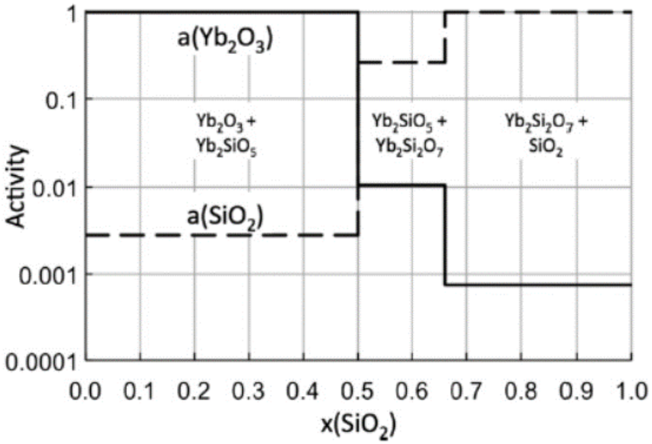
Activity across phase diagram 1600K

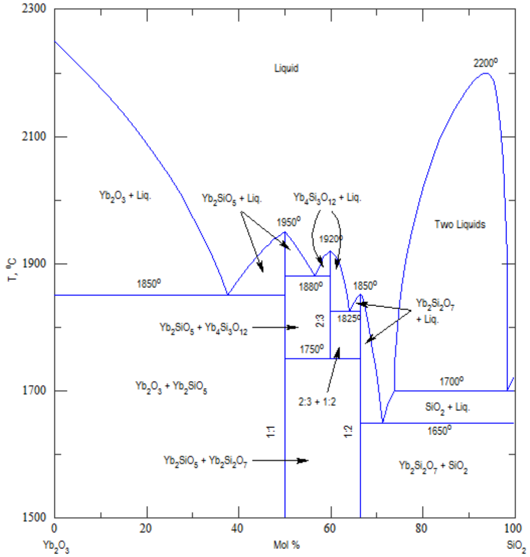
Yb_2O_3 + Yb_2O_3-SiO_2



Yb_2O_3-SiO_2+ Yb_2O_3-$2SiO_2$







Jacobson (2014). JACerS, *97*(6), 1959-1965.
Costa and Jacobson (2015) J Eur Ceram Soc 35, 4259-67.

Enthalpies of Formation from Thermodynamic Cycles

$RE_2O_{3(s,\ 1600\ K)} + SiO_{2(s,\ 1600\ K)} \rightarrow RE_2SiO_{5(s,\ 1600\ K)}$	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
$2\ RE_{(s,\ 298\ K)} + Si_{(s,\ 298\ K)} + 5/2\ O_{2(g,\ 298\ K)} \rightarrow RE_2SiO_{5(s,\ 298\ K)}$	**$\Delta H_7 = \Delta H_{f,RE_2SiO_5,298\ K}$**

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

	KEMS	Calorimetry*
$Y_2O_3.(SiO_2)$	-2907 ± 16	-2868.54 ± 5.34
$Yb_2O_3.(SiO_2)$	-2744 ± 11	-2774.75 ±16.48

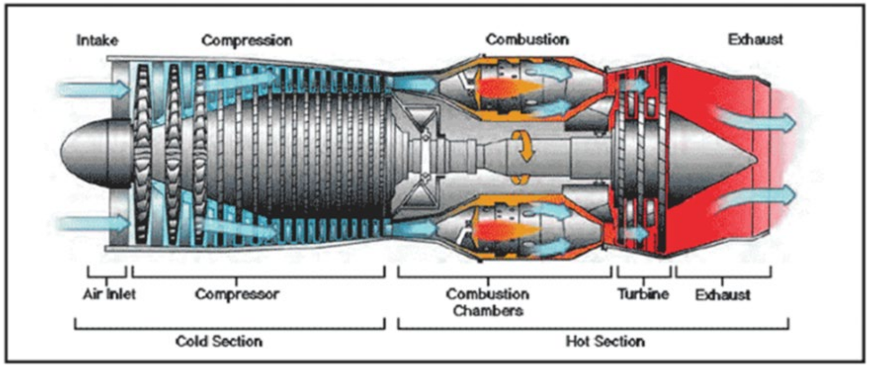
---

*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.

Silica activity in Rare Earth Silicates

- Candidate Environmental Barrier Coatings for SiC ceramics and coatings: Achieve water vapor resistance with low (< 1) silica activity
- Examined Y_2O_3-SiO_2, Yb_2O_3-SiO_2 (Costa), and Lu_2O_3-SiO_2 (Kowalski) systems
- Similar behavior with the monosilicate showing lowest silica activity
- Other problems with RE monosilicates: CTE mismatch to SiC composite

Hot Stage Static Components in Gas Turbines



HPT CMC Shrouds

- HPT (High Pressure Turbine) Shrouds on CFM International LEAP engine since 2016—Airbus A320Neo, Boeing 737 Max; GE9X Combustor Liners, HPT Shrouds, HPT stage 1 and 2 Vanes on Boeing 777X

- Optimize protective coating for maximum corrosion protection
  - Thermomechanical testing and modeling
  - Basic thermochemistry: critical tool

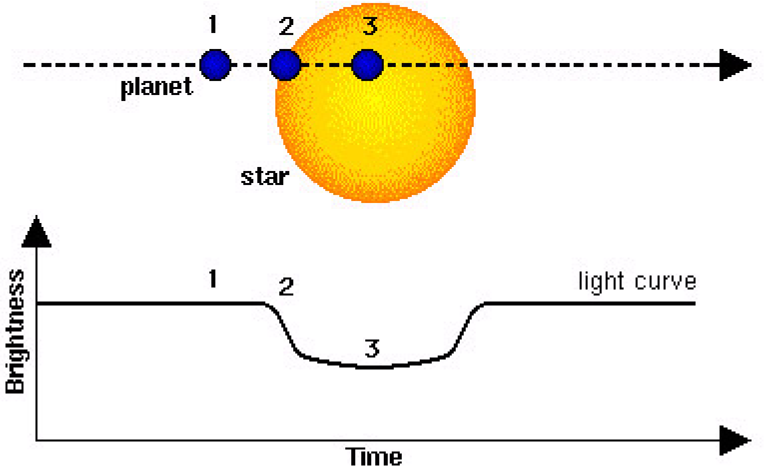
Selected Studies of High Temperature Chemistry Related to NASA Missions

- Space Shuttle Orbiter Wing Leading Edge
- Environmental Barrier coatings for Ceramic Turbine parts
- Chemistry on other Worlds: Exoplanets
- K/Ar dating of minerals

Knudsen Effusion Mass Spectrometry

Exoplanets: Planets outside our Solar System

- Confirmed discoveries:
  - 1988—First discovery, confirmed 2002
  - 2009—300
  - 2010—453
  - exoplanets.org (2023)—3262
    - Kepler Candidates—2584



- Most commonly found by transit method

- Hot, rocky Exoplanets
  - Short orbital periods
  - Tidally locked/strongly irradiated
  - CoRoT-7b, Kepler 10b, 55 Cnc e
  - 2000 C and above!

Atmospheres of Hot, Rocky Exoplanets
CoRoT-7b, Kepler 10b, 55 Cnc e

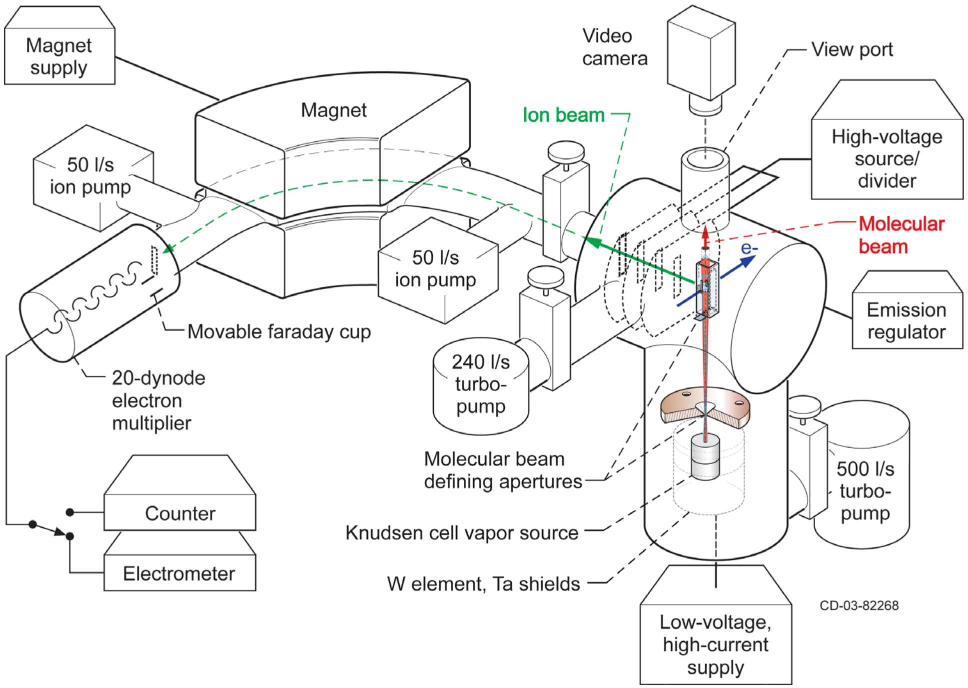
- Estimated densities suggest BSE (basic silicate earth: SiO_2-MgO-FeO-CaO) or moon-like compositions

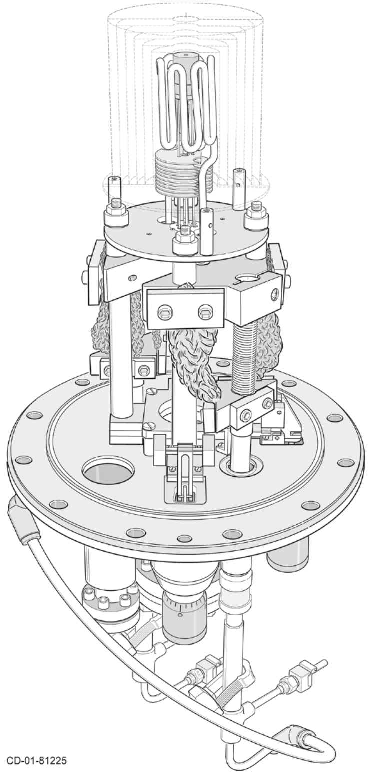
- Inorganic vapors above lava oceans—molten silicates (Fegley)

- Major species are Fe(g), SiO(g), Mg(g) above olivine
  - Can also form silicate 'clouds'

- Grant with MSU (Reed, Cornelison), Wash U (Fegley), and NASA (Jacobson, Costa).

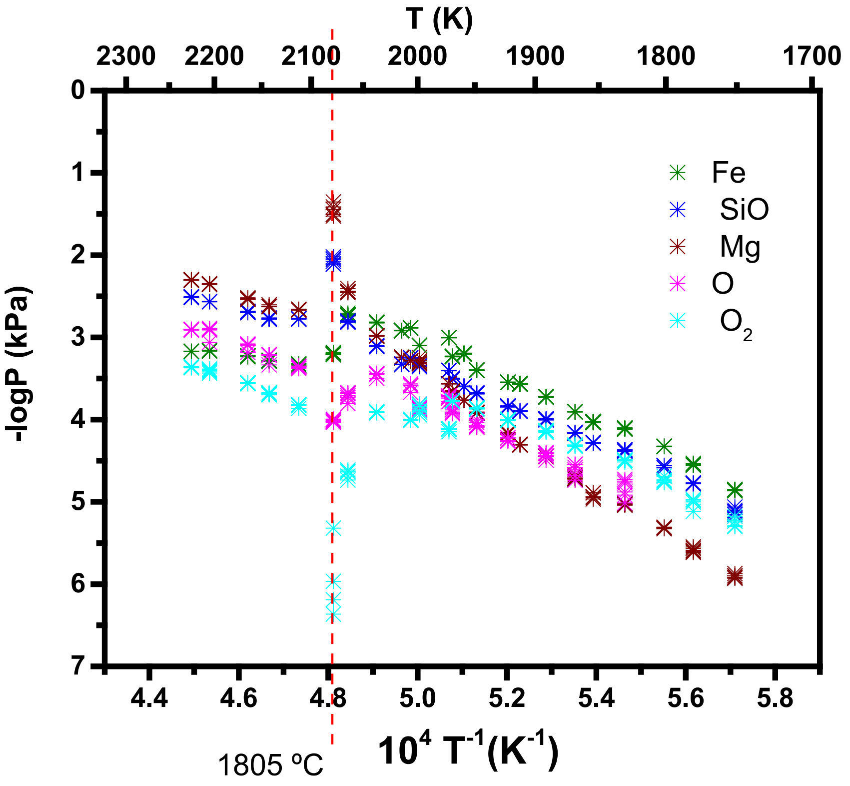
Use Knudsen Effusion Mass Spectrometry (KEMS)



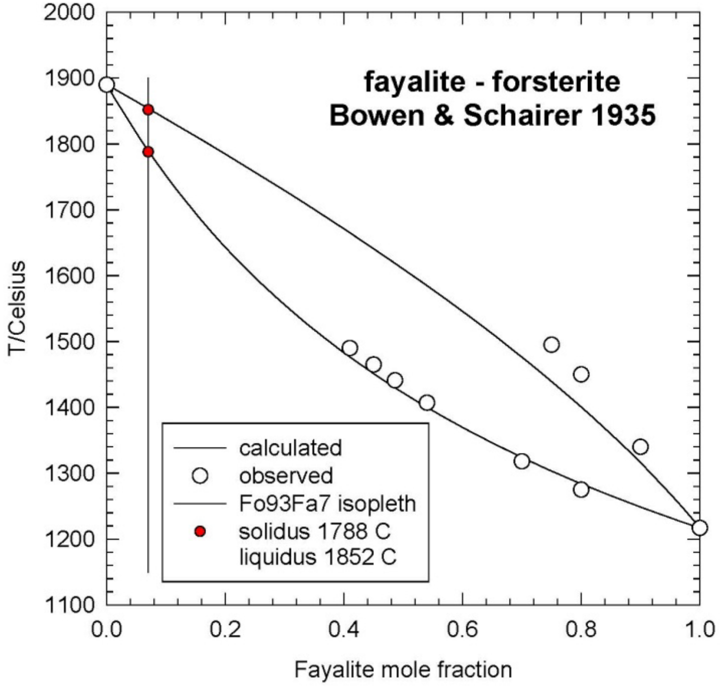


- Single Cell—can reach T >2000C
- Simulation of hot, rocky exoplanet??

Psuedo-Binary Forserite (Fo)-Fayalite (Fa) (Mg_2SiO_4-Fe_2SiO_4) System (with G. Costa)



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



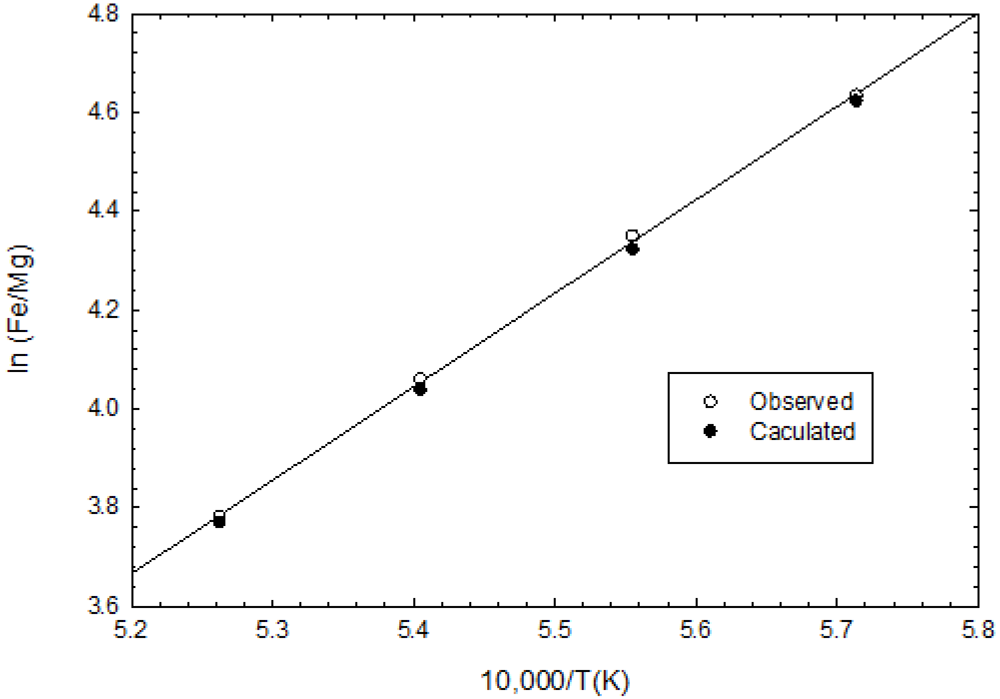
Fegley and Osborne, Practical Chemical Thermodynamics For Geoscientists, Elsevier 2013, Fig. 12-11.

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

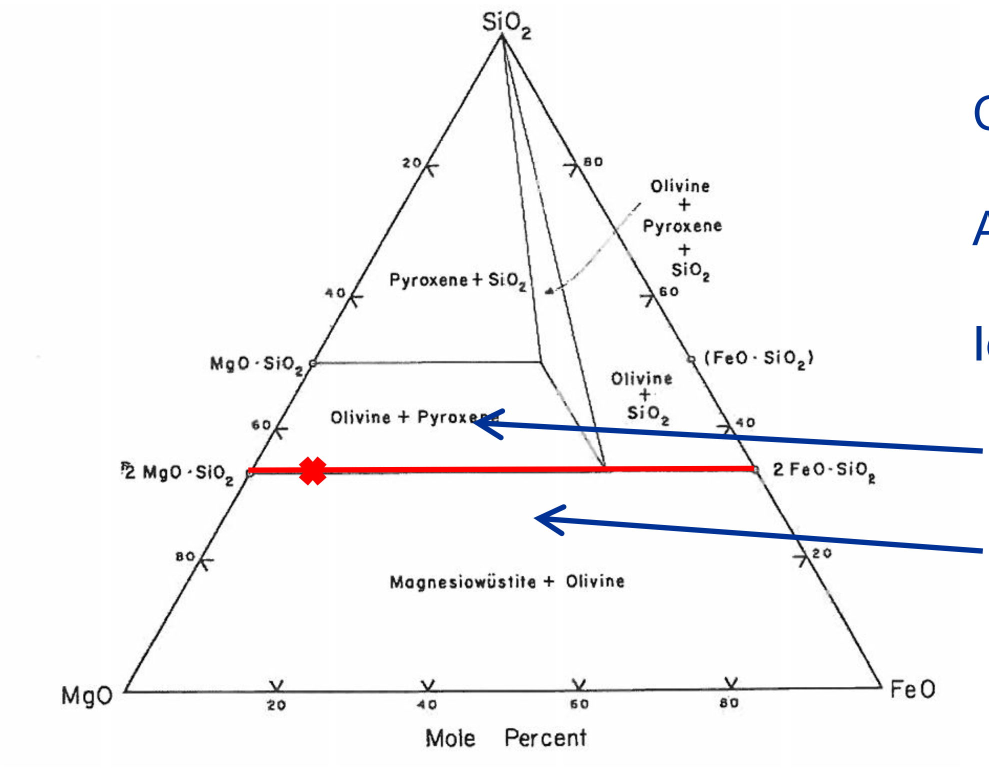
Bowen and Schairer, Am. J. Sci. 29, 151-171 (1935).

Pseudo Binary Forsterite-Fayalite (Mg_2SiO_4-Fe_2SiO_4) System

- Derive from equilibrium constants for Fo, Fa constituents of solution
  - $\ln\left(\frac{P(Fe)}{P(Mg)}\right)_{gas} = \ln\left(\frac{a_{Fa}}{a_{Fo}}\right)_{Olv} - \ln\left(\frac{-\Delta G^{o}_{vap}(Fo)/RT}{-\Delta G^{o}_{vap}(Fa)/RT}\right)$
  - Ideal Solution $\frac{a_{Fa}}{a_{Fo}} = \text{constant}$, $\ln\left(\frac{P(Fe)}{P(Mg)}\right)_{gas}$ $vs\ 1/T$ linear



Psuedo-Ternary: MgO-'FeO'-SiO_2



Composition of Interest: $Fo_{0.93}Fa_{0.07}$

Activity gradient across olivine line

Ideally work in three phase regions to fix P_i

- Excess SiO_2: Olivine + Pyroxene
- Excess MgO: Olivine + Magnesiowustite

Nafziger & Muan (1967)

Solutions: Measure Partial Thermodynamic Quantities

Olivine: $(FeO)_{2-\alpha}(MgO)_{2-\beta}(SiO_2)_{1-\gamma}$

Pure Compound:

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

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

Solution:

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

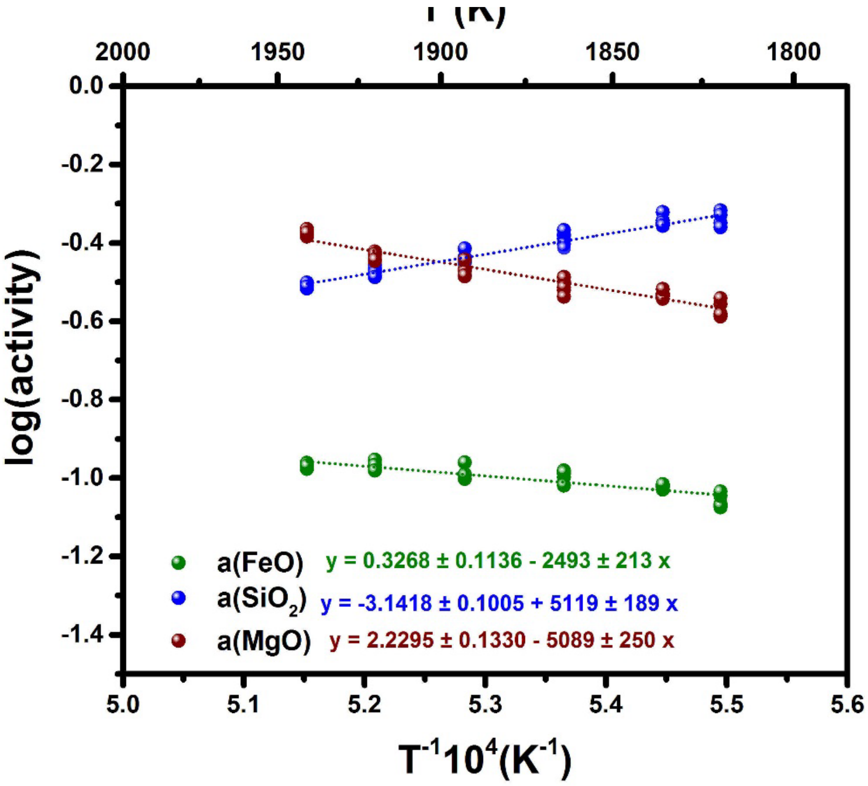
$$K_p = \frac{P_{Fe}[P_{O_2}]^{1/2}}{a_{FeO}}$$

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

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

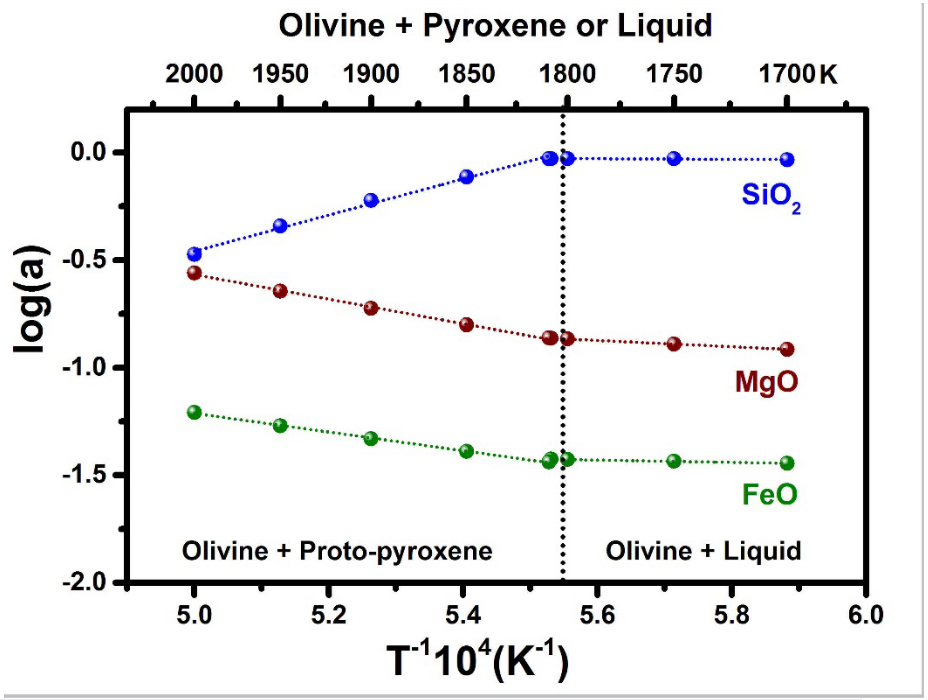
Apply to $\mathrm{SiO_2 = SiO(g) + 1/2\,O_2}$, $\mathrm{MgO = Mg(g) + 1/2\,O_2}$

Thermodynamic Activities in Olivine – $(Fe_2SiO_4)_{0.07}(Mg_2SiO_4)_{0.93}$ SiO_2 Side: Qualitative Comparison



Olivine + SiO_2
XRD: Only olivine…may be small amounts of pyroxene

Sublattice Model: Fabrichnaya (1998)
Olivine + Pyroxene
Olivine + Liquid



Hot, Rocky Exoplanets

- Lava oceans, inorganic vapors as atmosphere
  - Olivine-like: Mg, Fe, SiO, O, O_2 Vapors
  - Lunar Basalt-like: SiO, Fe, Na, K, O, O_2, Mg, SiO_2, TiO_2, TiO, Ca, Al Vapors (DeMaria et al., Apollo 12 Sample Vaporization)

- When we can view exoplanet atmospheres spectroscopically—look for these vapors

Selected Studies of High Temperature Chemistry Related to NASA Missions

- Space Shuttle Orbiter Wing Leading Edge
- Environmental Barrier coatings for Ceramic Turbine parts
- Chemistry on other Worlds: Exoplanets
- K/Ar dating of minerals

Knudsen Effusion Mass Spectrometry

K-Ar Dating of Minerals
with K. Farley/Caltech and J. Hurowitz/NASA JPL

- Decay sequence $^{40}K \rightarrow$ ^{40}Ca
  ^{40}Ar $t_{1/2}$ = 1.25 billion years
- Determine when rock was molten—all ^{40}Ar escaped and process reset

$$t = \frac{1}{\lambda} \ln\left(\boxed{\frac{^{40}Ar^{*}}{^{40}K_{u}}} \left(\frac{\lambda}{\lambda_{e}} \right) + 1 \right)$$

$\lambda =$ total decay constant $\lambda_e =$ decay constant of $^{40}K \rightarrow {}^{40}Ar$

$^{40}Ar^{*} =$ in situ radiogenic Ar from sample

$^{40}K_{u} =$ amount of K in sample

- Difficult to measure these quantities $\frac{^{40}Ar^{*}}{^{40}K_{u}}$
  - ^{40}K -- 0.012%
  - $^{40}Ar^{*}$--want radiogenic component, need to separate from ^{40}Ar in air

^{39}K—93.083
^{40}K—0.012
^{41}K—6.905

^{36}Ar—0.327
^{38}Ar—0.063
^{40}Ar—99.600

Unique Features of this Approach

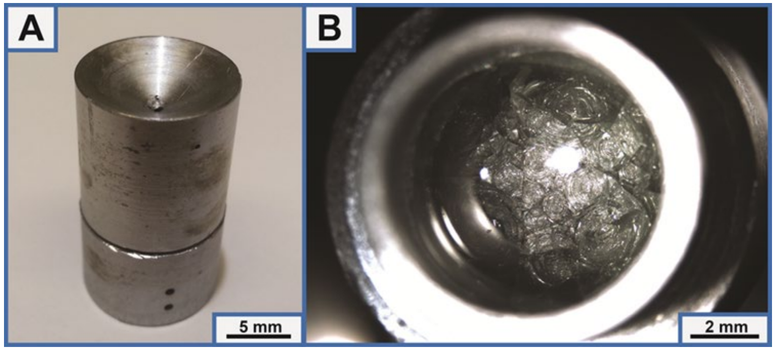
- Isotope dilution method:
  - Add a known amount of ^{41}K to an unknown amount ^{39}K
    - Measure R = ^{41}K /^{39}K
    - ^{39}K = ^{41}K/R
  - Know total moles of K in mineral [^{39}K + ^{41}K]—multiply by 0.00013 to get ^{40}K
  - Many modifications:
    - Works if some of the added isotope already in unknown
    - *Double isotope dilution* for several isotopes

^{39}K—93.083
^{40}K—0.012
^{41}K—6.905

^{36}Ar—0.327
^{38}Ar—0.063
^{40}Ar—99.600

- Low melting borate flux to make homogeneous mixture

Sample Preparation



- Mo Knudsen cell
  - 10 mg basalt
  - 150 mg $LiBO_2$-$Li_2B_4O_7$ flux
  - 179 μg Spike albite-like glass
    - Enriched in ^{41}K (>95%)
    - Enriched in ^{39}Ar (from neutron irradiation of traces ^{39}K)

- Required Ar isotope ratios measured with inert gas methods (Caltech)
  - Very clean vacuum system—high capacity getters

- Required K isotope ratios measured with KEMS (NASA GRC)
  - Flux creates homogeneous mixture with near unit activity of K $\Rightarrow$ high vapor pressure

Determine $\frac{^{40}Ar^*}{^{40}K_u}$ from Double Spiked Glass + Unknown

- $^{40}Ar_m = {}^{40}Ar^* + {}^{40}Ar_{air} + {}^{40}Ar_{spk}$
- $^{36}Ar_m = {}^{36}Ar_{air}$
- $^{39}Ar_m = {}^{39}Ar_{spk}$

- $^{39}K_m = {}^{39}K_u + {}^{39}K_{spk}$
- $^{41}K_m = {}^{41}K_u + {}^{41}K_{spk}$
- $^{40}K_u = r_{40}\ {}^{39}K_u$

* Radiogenic

$$\frac{^{40}Ar^*}{^{40}K} = \frac{\left(\boxed{R_m} - \boxed{\left(\frac{^{40}Ar}{^{36}Ar}\right)}_{air}\left(\frac{^{36}Ar}{^{39}Ar}\right)_m - R_{spk}\right)}{\boxed{r_m}\left(\dfrac{r_{spk} - \boxed{r_m}}{\dfrac{\boxed{r_m}}{r_{nat}} - 1}\right)}\left(\frac{^{39}Ar}{^{41}K}\right)_{spk}$$

m = measured
spk = spike
u = unknown in sample
r_{40} = natural $^{40}K/^{39}K$
$R_m = (^{40}Ar/^{39}Ar)_m$
$R_{spk} = (^{40}Ar/^{39}Ar)_{spk}$
$r_m = (^{39}K/^{41}K)_m$
$r_{spk} = (^{39}K/^{41}K)_{spk}$
$r_{nat} = (^{39}K/^{41}K)_{nat}$

Need only measure circled quantities

Calculation of Age

Sample	Ratio	Measurement	Method
10 mg Basalt + 179 μg Spike	$^{40}Ar/^{39}Ar$	44300 ± 740	Inert Gas Mass Spec
10 mg Basalt + 179 μg Spike	$^{36}Ar/^{39}Ar$	102 ± 1.8	Inert Gas Mass Spec
Spike Glass	$^{39}K/^{41}K$	0.0390 ± 0.0006	Preparation of Spike
10 mg Basalt + 179 μg Spike	$^{39}K/^{41}K$	4.71 ± 0.07	KEMS
Spike Glass	$^{39}Ar/^{41}K$	1.453 ± 0.037	Preparation of Spike

$$t = \frac{1}{\lambda}\ln\left(\frac{{}^{40}Ar^{*}}{{}^{40}K_{u}}\left(\frac{\lambda}{\lambda_{e}}\right)+1\right)$$

Basalt from Viluy traps (lava coated region), Eastern Siberia
t = 347 ± 19 Ma (million years) Only ± 5% !

Compare to: 351.4 ± 5 Ma (K-Ar) and 354.3 ± 5 Ma ($^{40}Ar/^{39}Ar$)
(Courtillot et al. (2010), Earth Planet Sci Let 300, 239)

K. A. Farley, et al. (2013), Geochimica et Cosmochimica Acta 110, 1-12.

K-Ar Dating of Minerals for Mars or other Planetary Probes

Advantages:

- Do not need to weigh sample; Only need a known amount of spike glass
- Li Borate flux lowers temperature to achieve homogeneous mixture and strong K signal (~1000ºC)
- Single instrument
- High accuracy ~5%
- Future probes

Summary: Selected Studies in High Temperature Chemistry

- Space Shuttle Orbiter Wing Leading Edge
  - With NASA’s LESS-PRT
  - Model damage due to SiC cracks
  - Accident investigation

- Coatings for ceramic turbine parts
  - Part of larger project with GRC colleagues and engine companies
  - Measure activities in rare earth silicates to determine resistance to water vapor attack

- Chemistry on other worlds
  - GRC colleagues and Universities (Fegley/WUSTL, Harvey/CWRU)
  - Hot, Rocky exoplanets: High temperature vapors

- K-Ar dating of minerals
  - With JPL and Caltech (Farley)
  - Unique method using double isotope dilution and borate flux

NASA Glenn Research Center
Cleveland, OH

NASA Glenn Research

@NASAglenn

An extraordinary career opportunity could be a few clicks away—we're hiring. Monitor @USAJOBS for openings @NASAGlenn in #Cleveland, Ohio. Positions are available in both engineering and administrative fields: nasai.usajobs.gov.