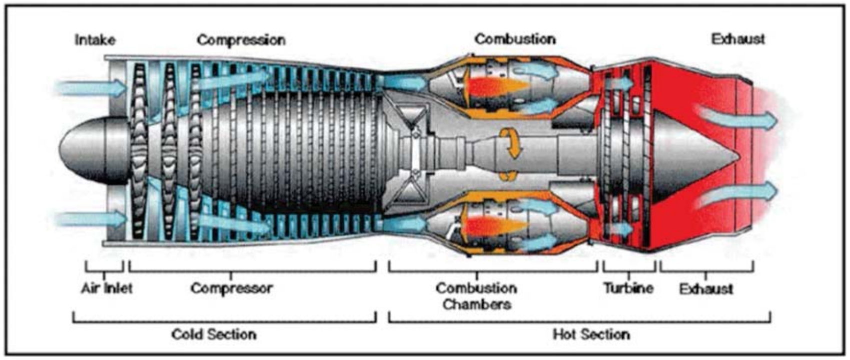
# High Temperature Chemistry at NASA: Hot Topics



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October 23, 2014

# Outline of Presentation

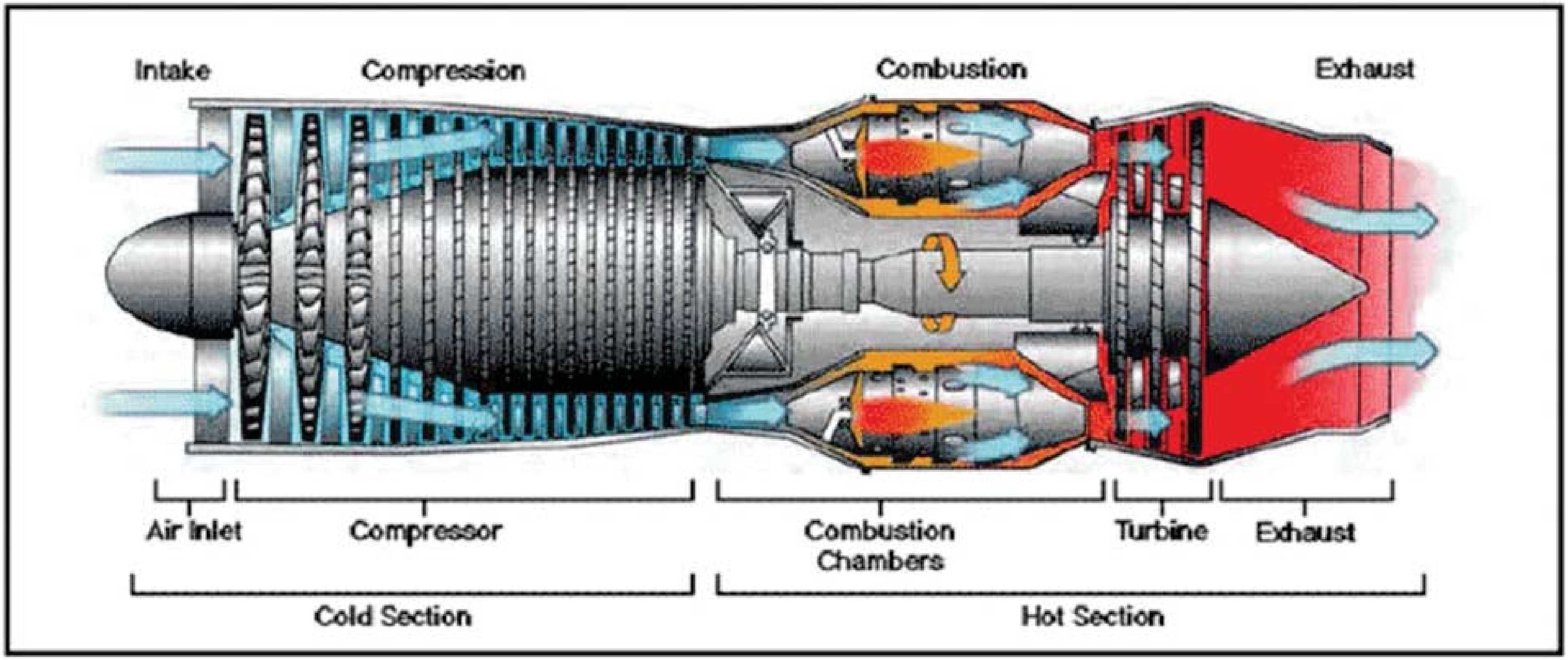
I. High Temperature issues in aircraft engines
   A. Hot section: Ni and Co based Superalloys
   B. Oxidation and Corrosion (Durability) at high temperatures

II. Thermal protection system (TPS) and RCC (Reinforced Carbon-Carbon) on the Space Shuttle Orbiter

III. High temperatures in other worlds: Planets close to their stars

IV. Summary and Questions

# Gas turbine engine



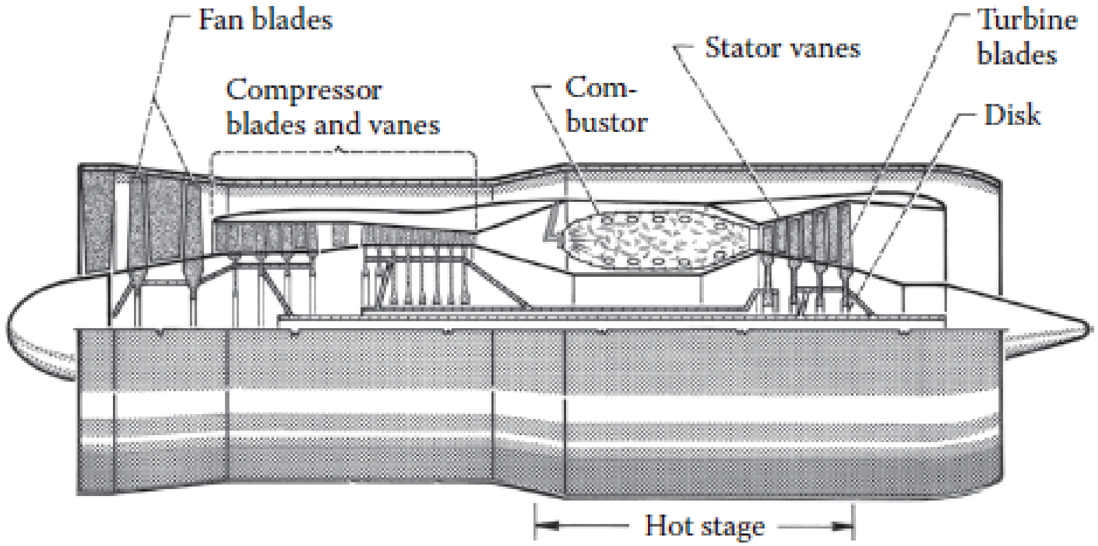
Turbine inlet temperatures in the gas path of modern high-performance jet engines can exceed 1650°C

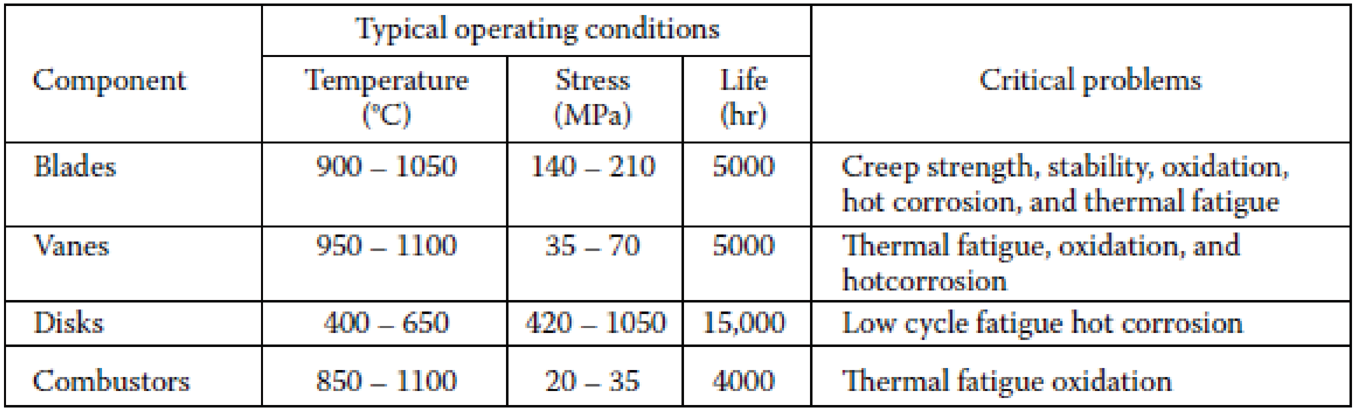
# Gas Turbine Materials

- Higher temperature, light weight, strong
- Need to understand every aspect of material
  - Mechanical behavior
  - Chemical behavior
- Materials
  - Colder sections: Ti alloys, Fe alloys
  - Hot sections: Ni- and Co- based superalloys, ceramics (some day!)

# Issues in Each Stage of a Modern Turbine

Schematic diagram of turbofan engine





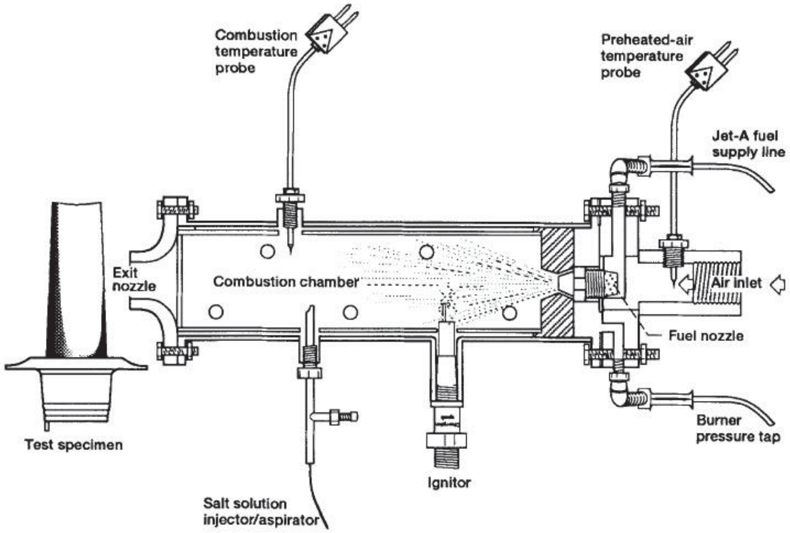
| Component | Typical operating conditions | | | Critical problems |
|---|---|---|---|---|
| | Temperature (°C) | Stress (MPa) | Life (hr) | |
| Blades | 900 – 1050 | 140 – 210 | 5000 | Creep strength, stability, oxidation, hot corrosion, and thermal fatigue |
| Vanes | 950 – 1100 | 35 – 70 | 5000 | Thermal fatigue, oxidation, and hotcorrosion |
| Disks | 400 – 650 | 420 – 1050 | 15,000 | Low cycle fatigue hot corrosion |
| Combustors | 850 – 1100 | 20 – 35 | 4000 | Thermal fatigue oxidation |

# Environmental Effects and Coatings Branch

- Chemical interactions of engine materials with the combustion environment
  - Oxygen: Oxidation
  - Water vapor, $CO_2$
  - Sulfur oxides ($SO_2$, $SO_3$)
  - Deposits: Salts, volcanic ash, desert sands

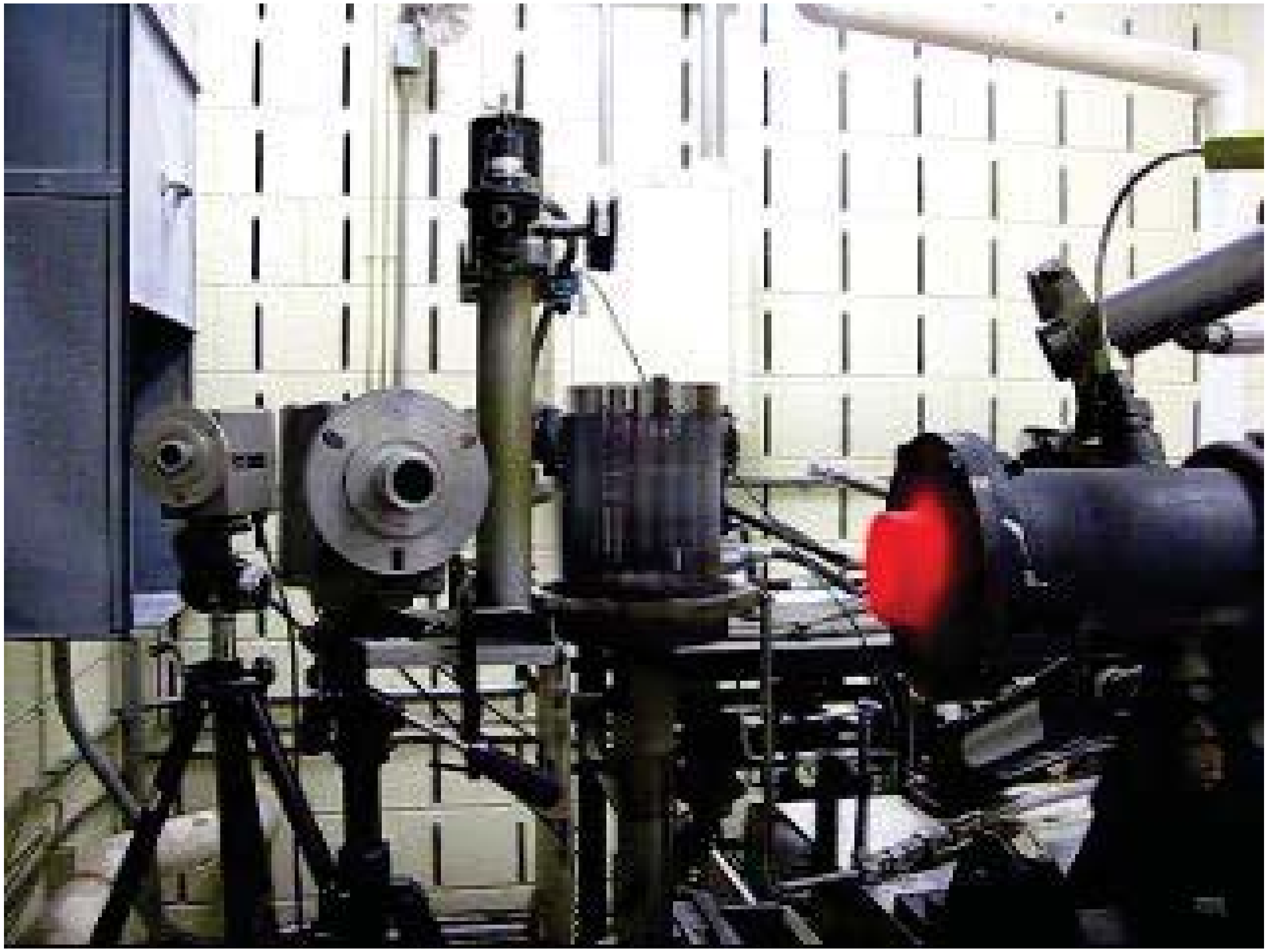
- Chemical reactions at high temperatures
  - Thermodynamics
  - Kinetics

# Tools: 1. Burner Rig--Realistically Simulates Turbine Engine and uses Less Fuel



Fuels: Aircraft fuel (high purity kerosene), Diesel Fuel
Inject: Sea salt, particulates

# Burner Rig



# Tools: 2) Thermogravimetric Apparatus (TGA)

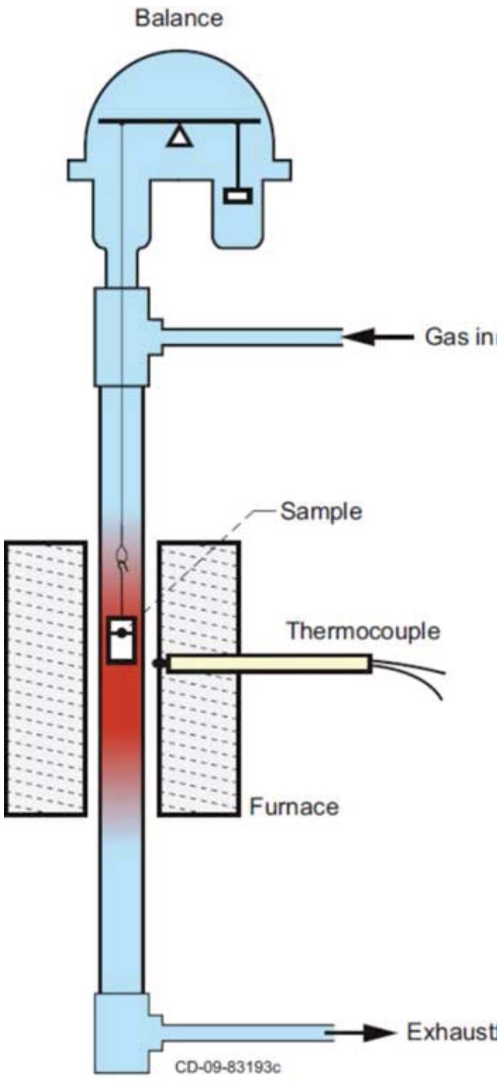


Fig. 9

Continuous weight change measurements without removing sample and controlled environment

- Flow velocity
- Temperature
- Gas composition

Sensitivity to 100 μg

# Oxidation of Metals and Ceramics

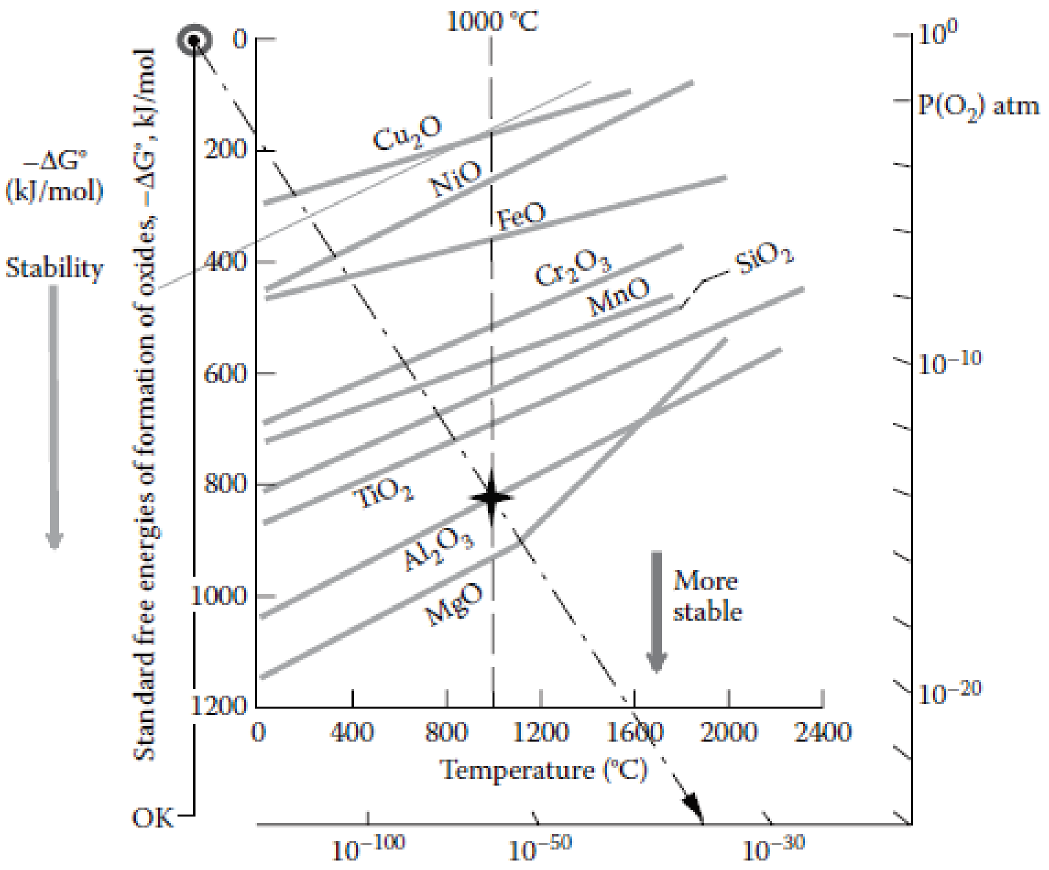
- Thermodynamics tells us oxides are the most stable

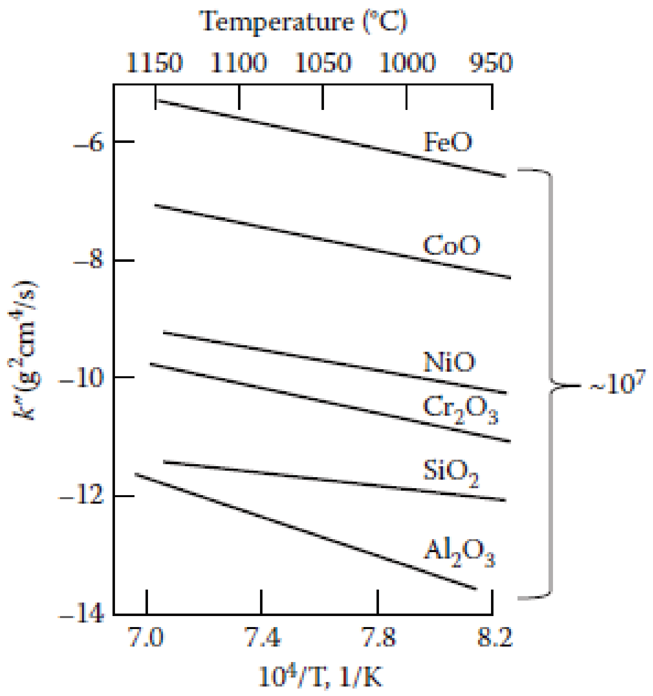
- $Al_2O_3$ forms as a thin film around metal

- Formation or “growth” rate (kinetics) $\propto t^{1/2}$
  - As film grows, the rate slows
  - Proportionality constant is the parabolic rate constant

- Want thermodynamically stable oxide, low growth rate, not sensitive to other impurities

# Thermodynamics and Kinetics

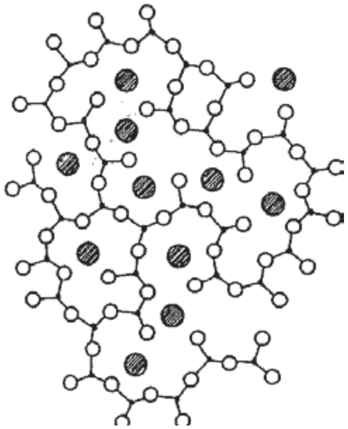




Primary protective oxides at high temperatures: $Cr_2O_3$, $SiO_2$, $Al_2O_3$

# What about other Effects?

- Water Vapor
  - $Cr_2O_3 + 2H_2O(g) + 3/2\ O_2(g) = 2CrO_2(OH)_2(g)$
    - Removes $Cr_2O_3$, more forms and is removed
    - Part is gradually vaporized!
    - Limits $Cr_2O_3$ to ~900ºC
- Na impurities (marine environment)
  - Opens $SiO_2$—more oxygen transport
- Fluxing by molten salts, volcanic ash
  - $Na_2O + SiO_2(s) = Na_2SiO_3(l)$
  - Important area of research!

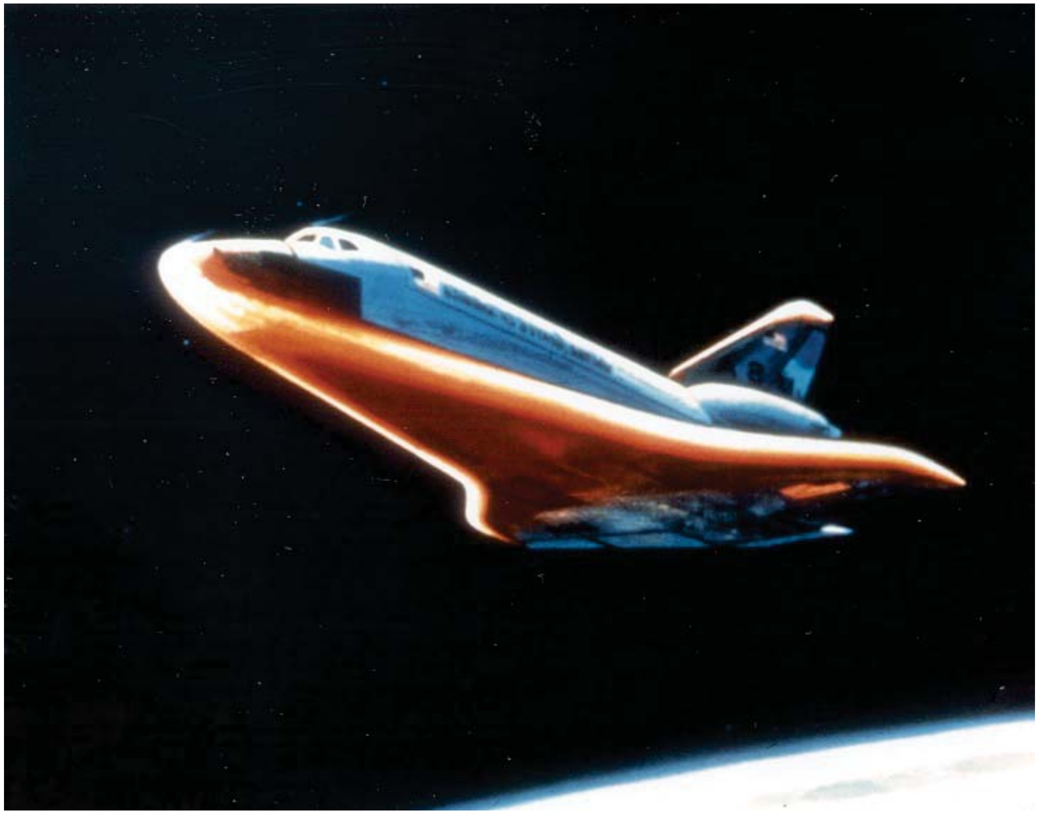


# Re-entry Heat Shields:

## Heating for Short Times
## Atmosphere of Dissociated Gases—N, O

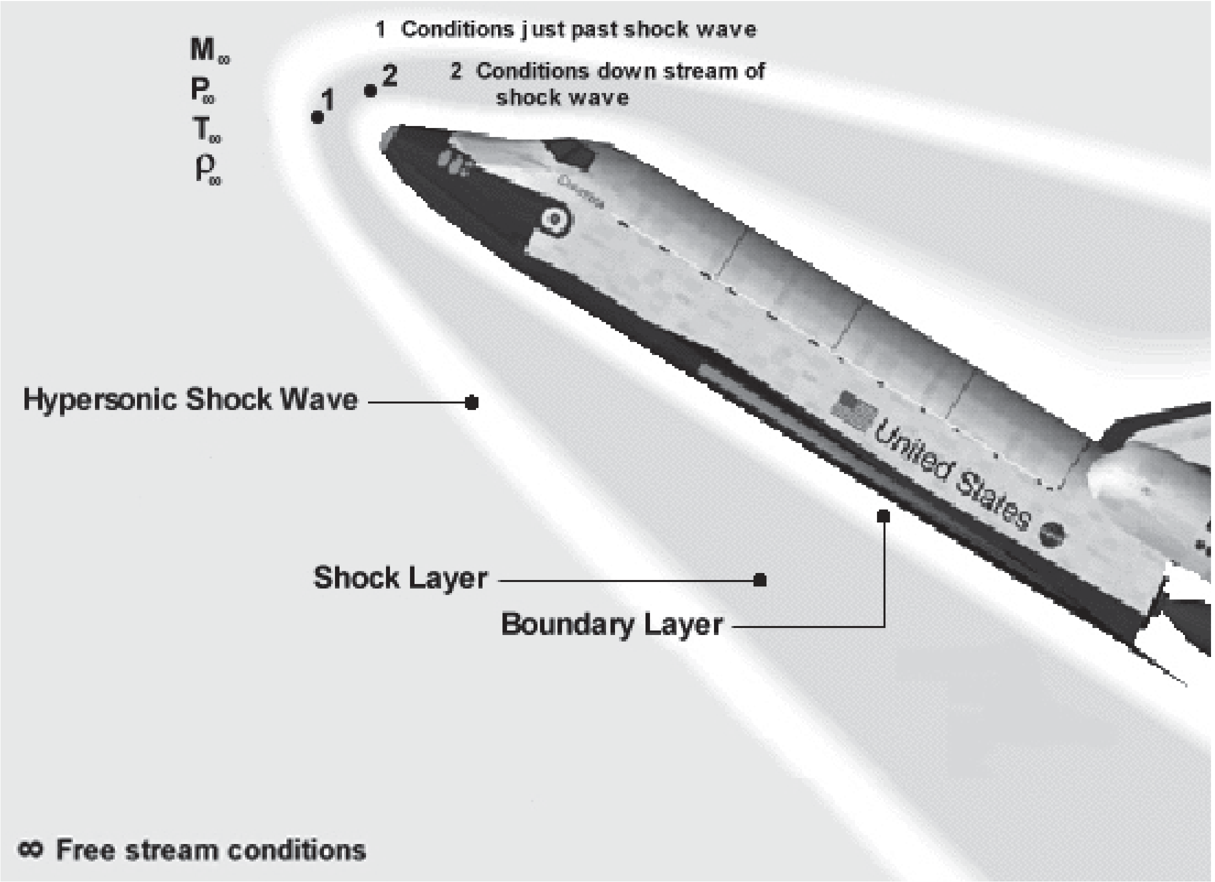
ISS011E11227

# Re-entry Heating: Why the Orbiter gets so Hot



- Orbiter begins re-entry at Mach 25 (18,000 mph) in upper atmosphere
- Must slow down on re-entry, tremendous energy must be dissipated
- “Shock waves”: Pile-up of gas molecules as vehicle slows

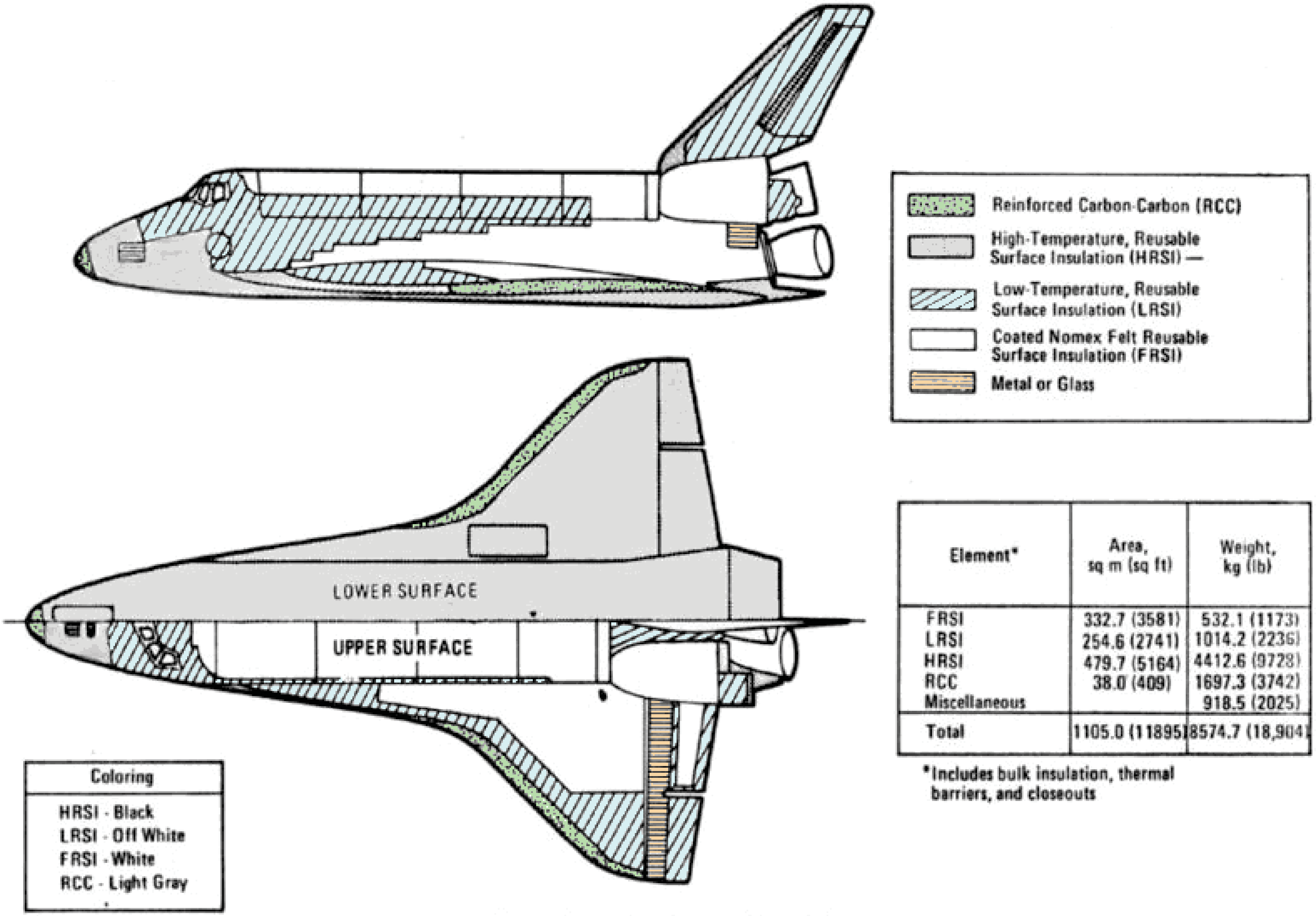
# Re-entry Heating: Why the Orbiter gets so Hot



- Blunt body: Shock spreads out and dissipates a lot of heat

- Nose cap and wing leading edges take most the heat: up to 1600°C for short periods (~5 min)

# Thermal Protection on the Orbiter: Highest Temperature Materials on Nose Cap and Wing Leading Edges

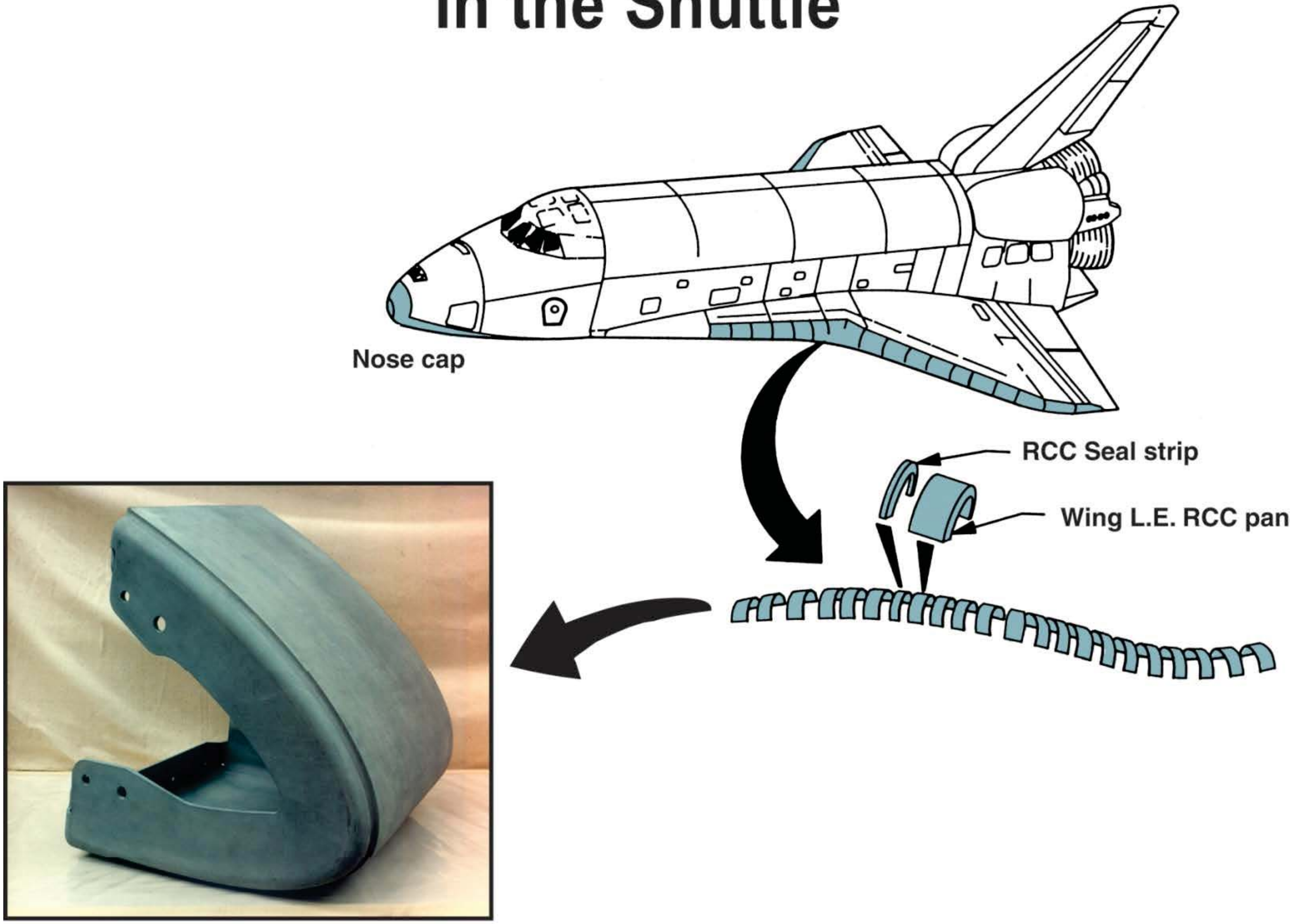


| Element* | Area, sq m (sq ft) | Weight, kg (lb) |
|---|---|---|
| FRSI | 332.7 (3581) | 532.1 (1173) |
| LRSI | 254.6 (2741) | 1014.2 (2236) |
| HRSI | 479.7 (5164) | 4412.6 (9728) |
| RCC | 38.0 (409) | 1697.3 (3742) |
| Miscellaneous | | 918.5 (2025) |
| Total | 1105.0 (11895 | 8574.7 (18,904 |

*Includes bulk insulation, thermal barriers, and closeouts

*Thermal Protection System, Orbiter 102*

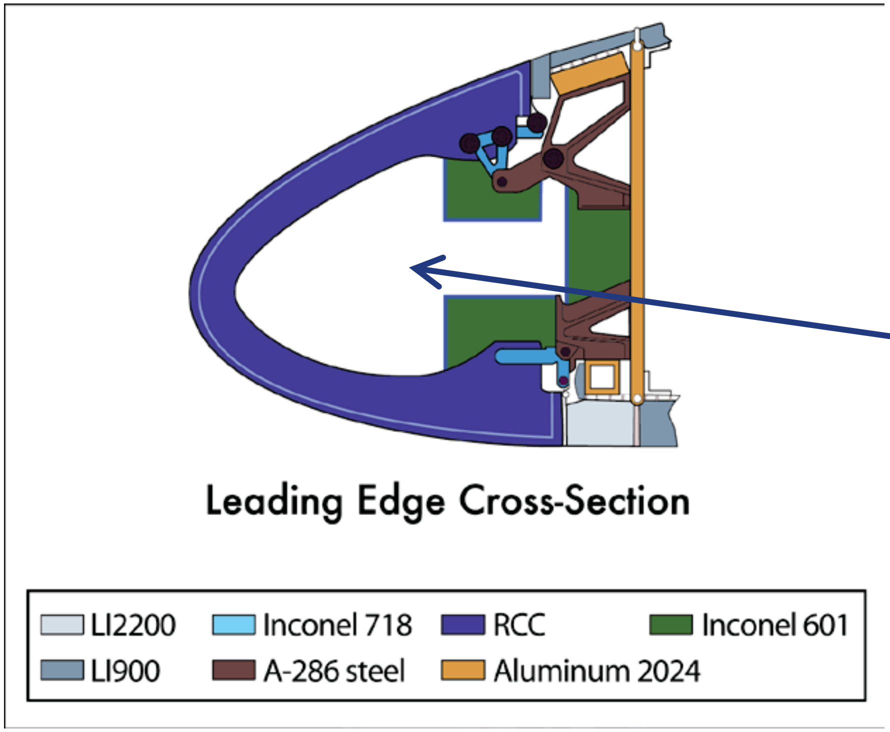
# Reinforced Carbon/Carbon (RCC) in the Shuttle



CD-97-76505

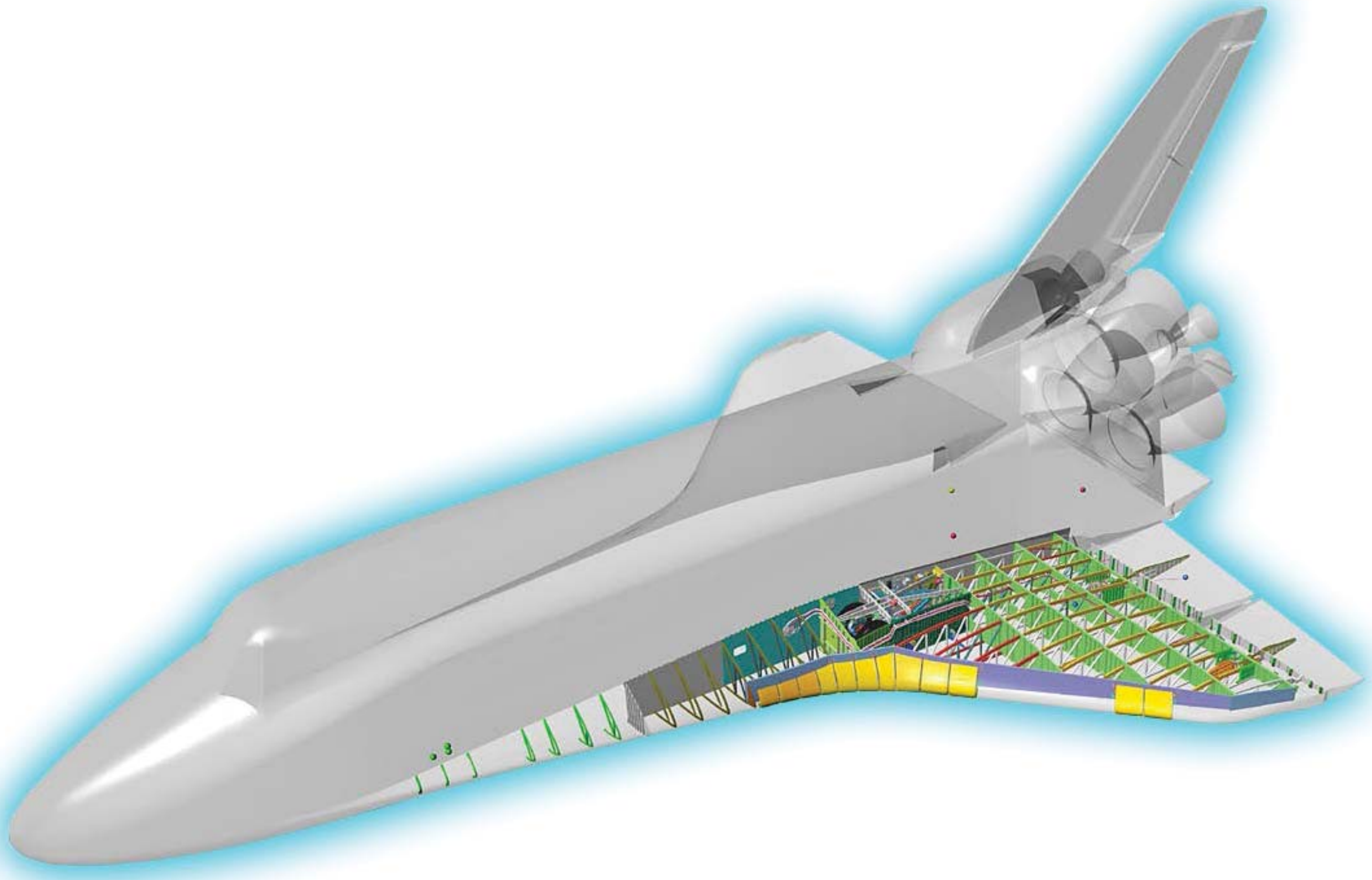
- Composite of Carbon Fibers in a Carbon Matrix → “Carbon/Carbon”
- Remarkably effective > 130 flights

# Wing Panels Attached with Complex Metal Attachment Hardware Allows for Thermal Expansion and Contraction



Amorphous aluminosilicate fibers
Thermal Insulation

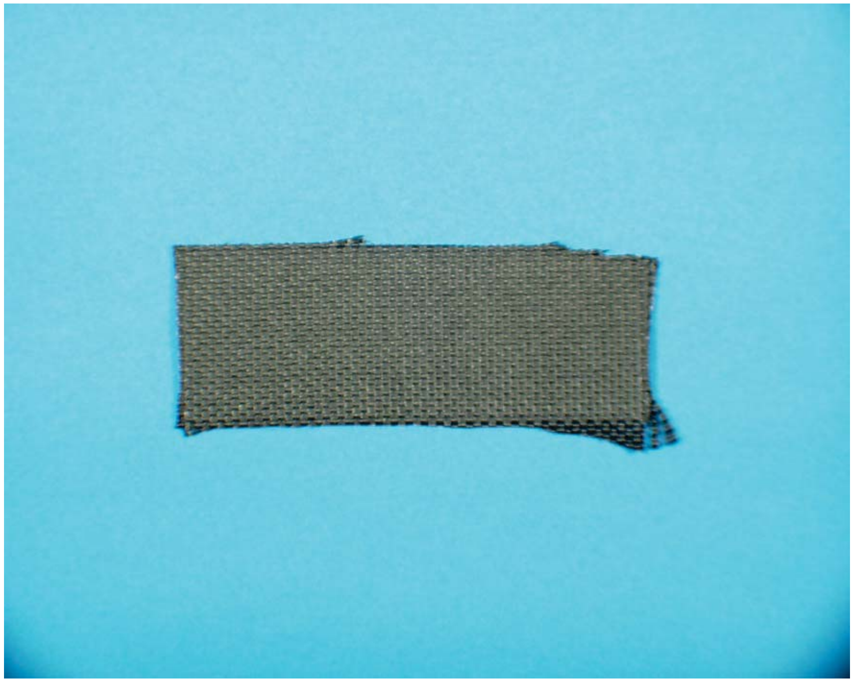
# Wing Panels Protect Aluminum Wing Structure



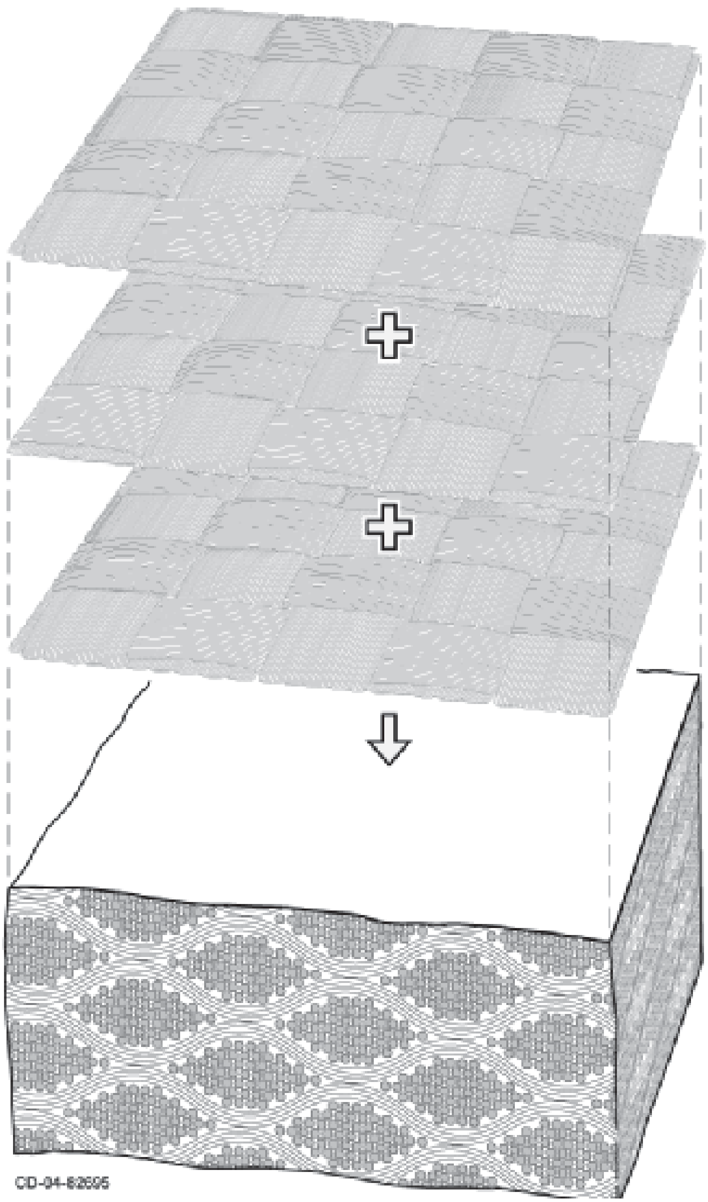
# Fabrication of Carbon/Carbon Composites
# Lockheed-Martin

- High Strength Carbon Fibers
  - ~10 μm (0.01 mm) diameter
  - 4000 MPa strength
  - Graphite (crystalline carbon)

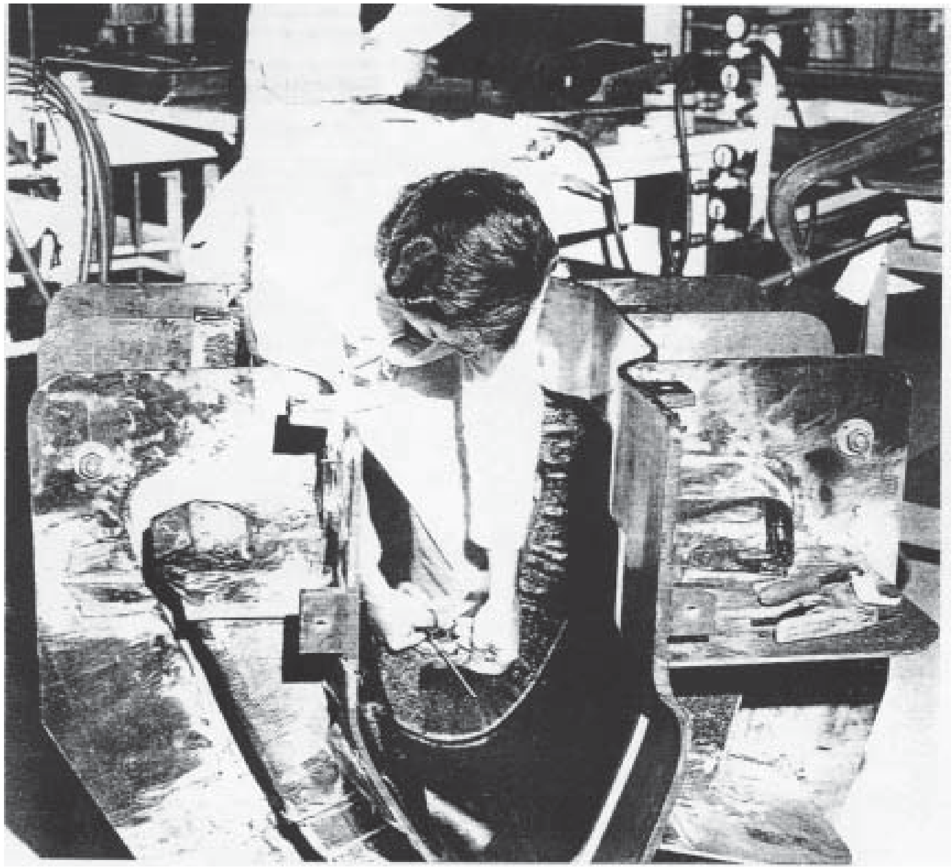
- Woven into cloth



Two Dimensional Lay-up of Graphite Cloth

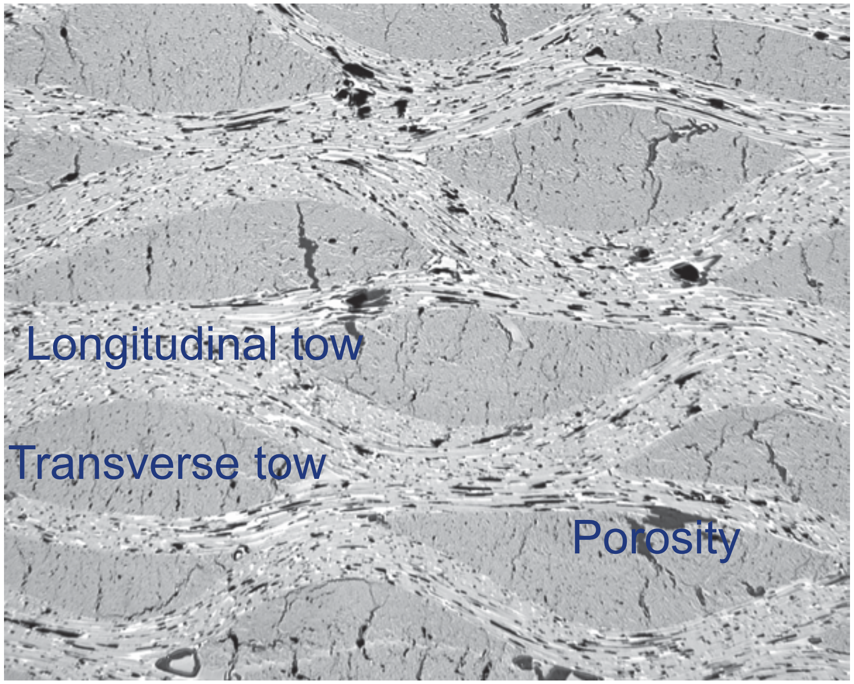


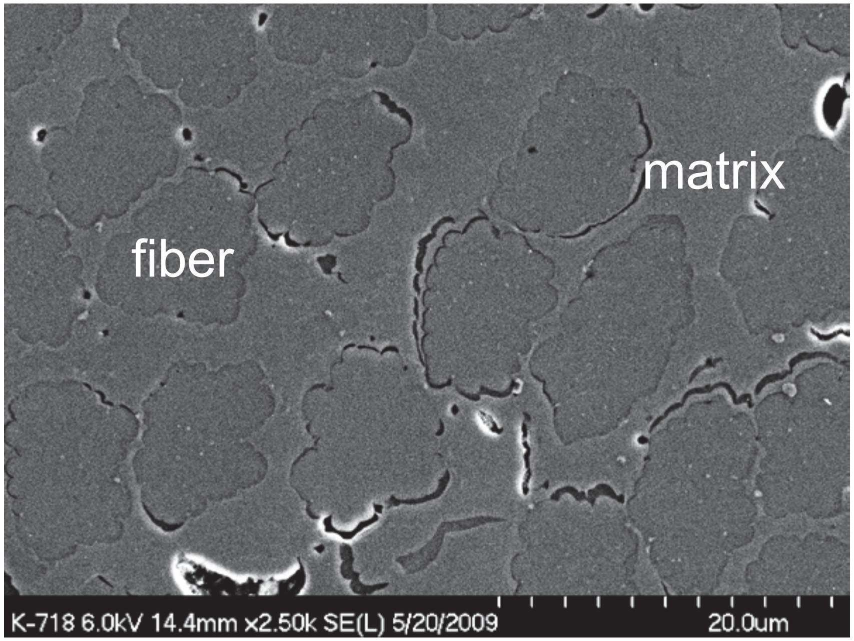
Coated with a ‘pre-preg’ and pressed into molds



Then a liquid carbon precursor is added to fill porosity: makes carbon matrix

# Cross Sectional Views of Carbon/Carbon





- 25X Showing bundles ('tows') of fibers in longitudinal and transverse directions
- Porosity due to incomplete compaction
- Important to distinguish this porosity from oxidation

- SEM Photo shows fibers and matrix
- Rayon Fibers—first generation carbon fibers Perform well in this application
- 'Crenulations' or grooves in fibers: important in oxidation

# Carbon/Carbon: The Ideal Aerospace Material

- Lightweight
- Strong: Carbon Fibers even become stronger as temperature is increased
- Drawback?
  - Oxidizes!

# Oxidation Protection of Carbon/Carbon

- Oxidation is the major barrier to widespread application of carbon/carbon

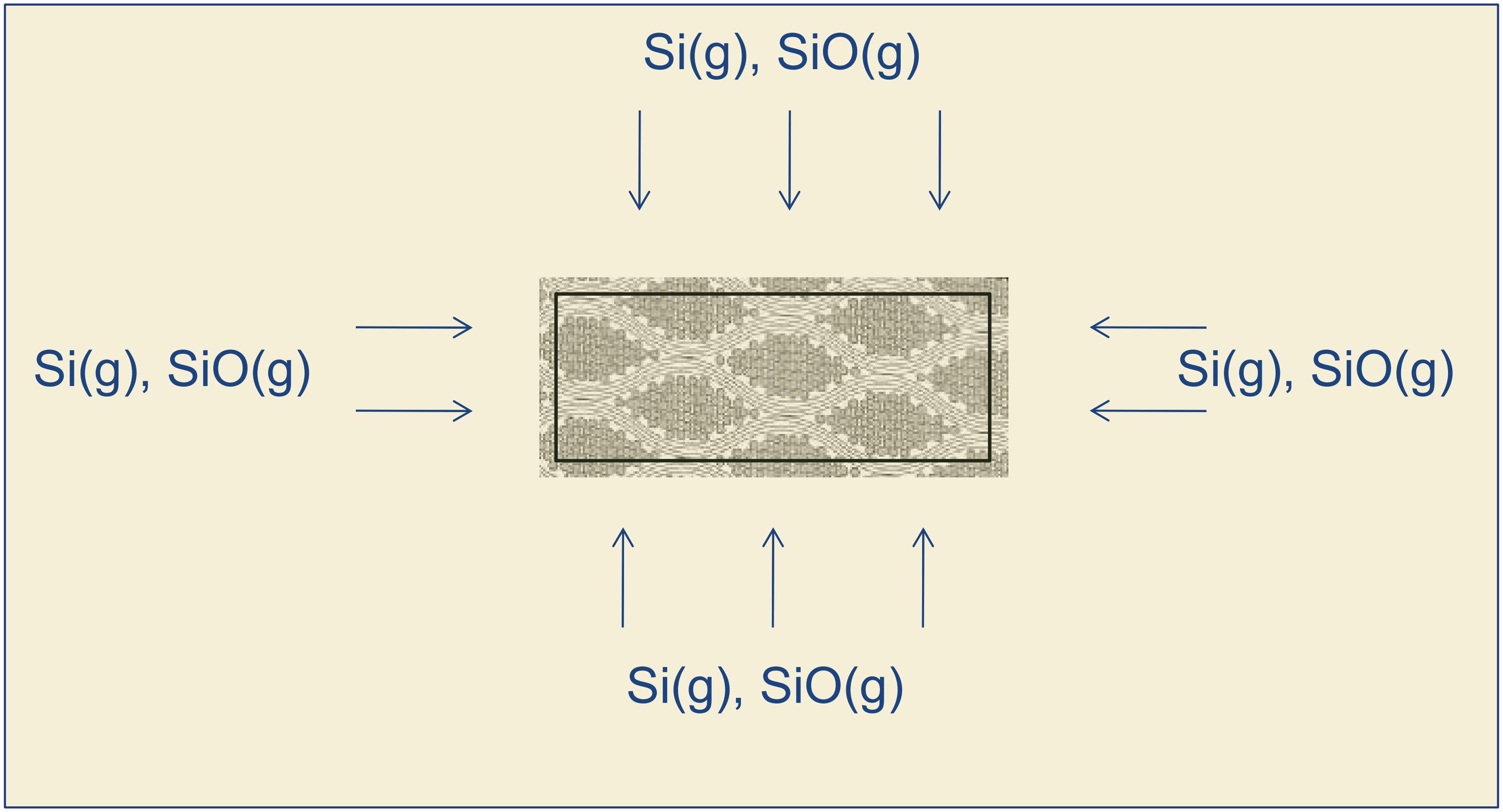
- Need to select adherent, oxidation resistant coating material that does not react with carbon

- Many years of research and development
  - Oxides
  - Metals/alloys
  - SiC

- SiC: the best choice

# Oxidation Protection of Carbon/Carbon

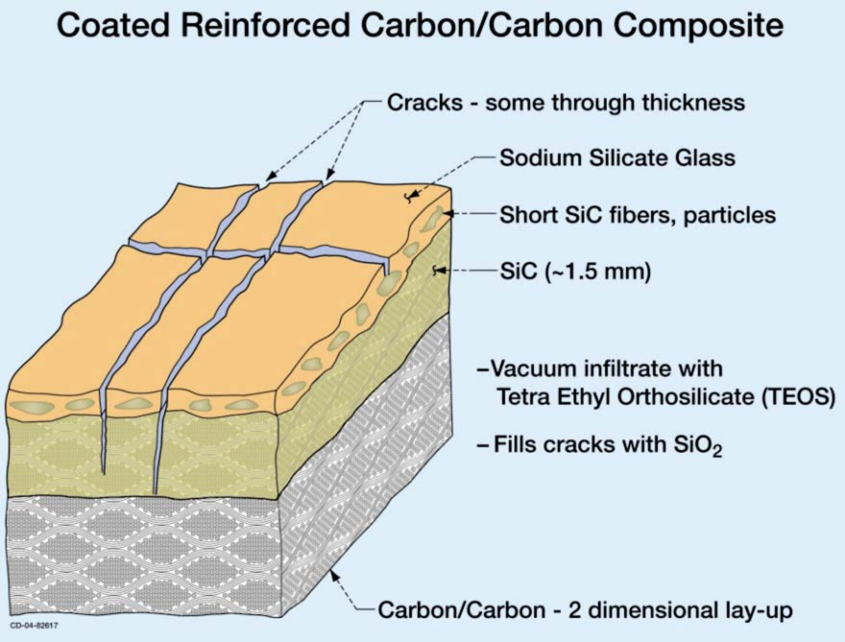
- Chemical reaction: “Conversion Coating”
- Si(vapor) + C = SiC Controlled exposure in powder pack leads to 1 mm thick coating. In pack of $Al_2O_3$, SiC, Si

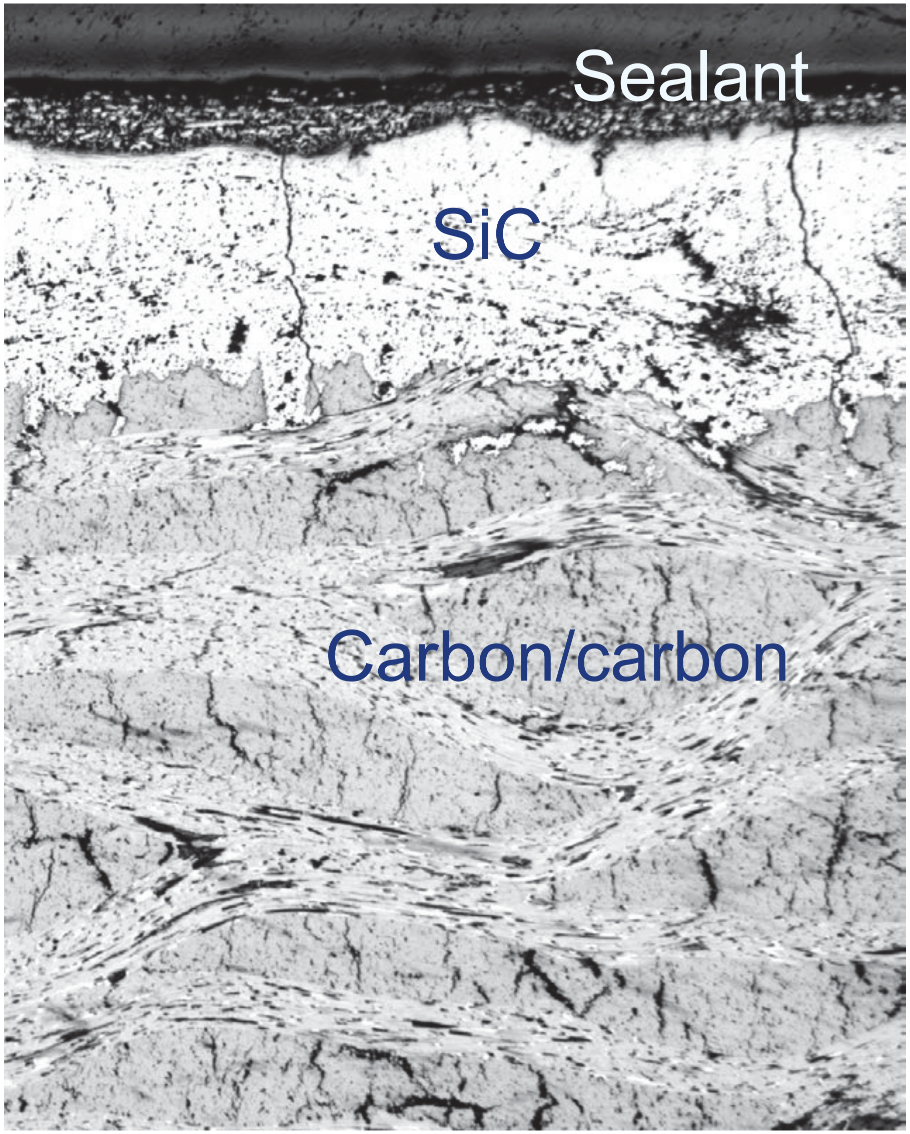


# Drawback of SiC coating on Carbon/Carbon Thermal expansion mismatch ⇒ Cracking

- On cooling from processing temperature, SiC (CTE = 5 x $10^{-6}$ /K) shrinks faster than C/C (CTE = 1 x $10^{-6}$/K)
  - Tensile stresses develop in SiC ⇒ SiC factures/cracks
  - Cracks may serve as pathways for oxidation

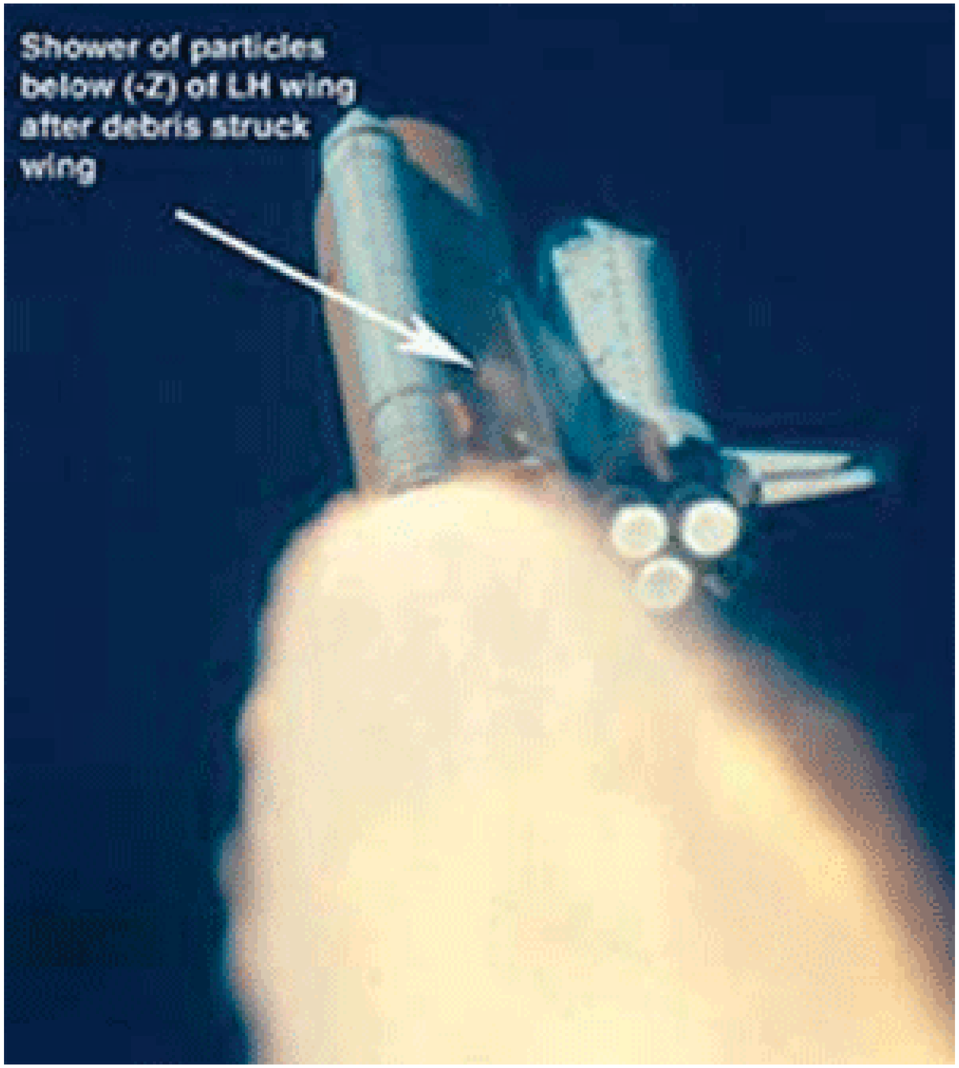
- High temperature glasses are applied, which flow at higher temperatures and seal cracks
  - Silica and sodium silicate with SiC particles
  - Surprisingly effective for the short duration of re-entry


Coated Reinforced Carbon/Carbon Composite
Cracks - some through thickness
Sodium Silicate Glass
Short SiC fibers, particles
SiC (~1.5 mm)
–Vacuum infiltrate with Tetra Ethyl Orthosilicate (TEOS)
–Fills cracks with $SiO_2$
Carbon/Carbon - 2 dimensional lay-up
CD-04-82617


Sealant
SiC
Carbon/carbon

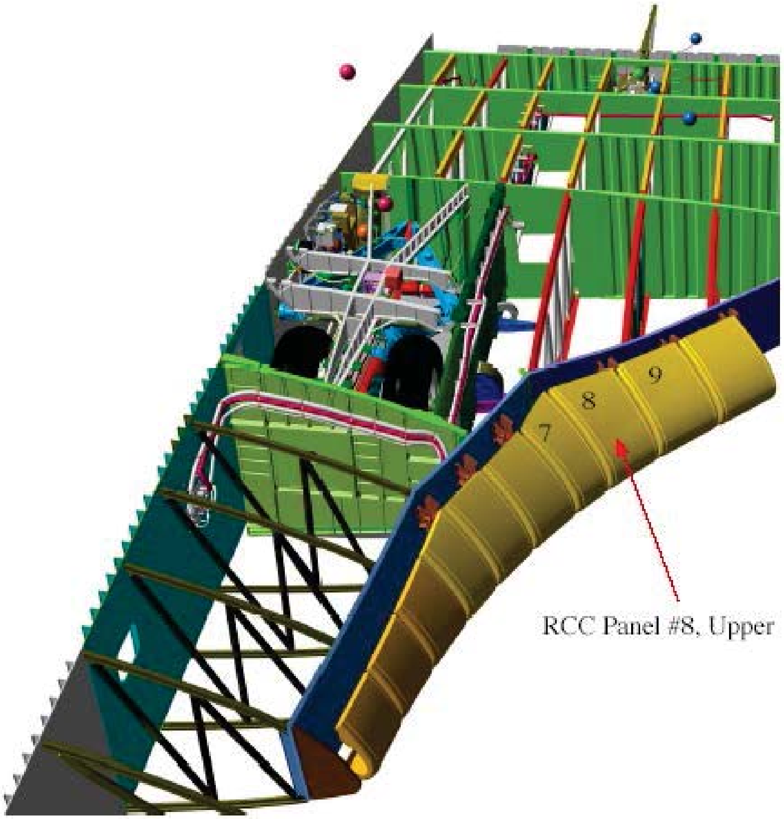
# The Columbia Tragedy:
# Damaged RCC

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



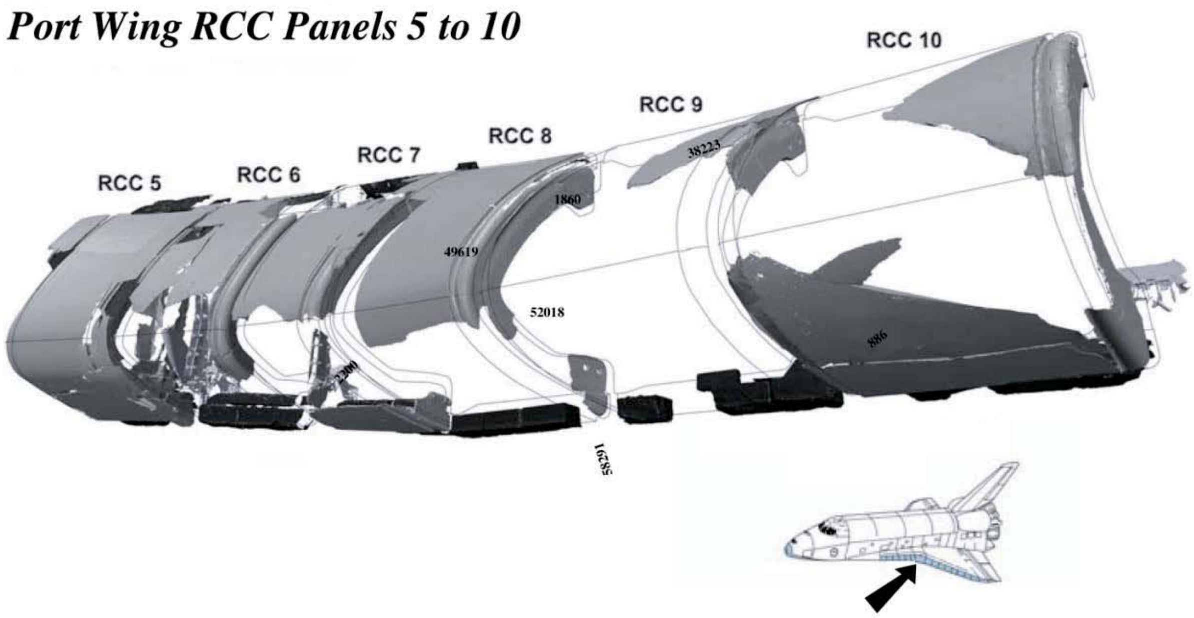
# The Columbia Disaster

- 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



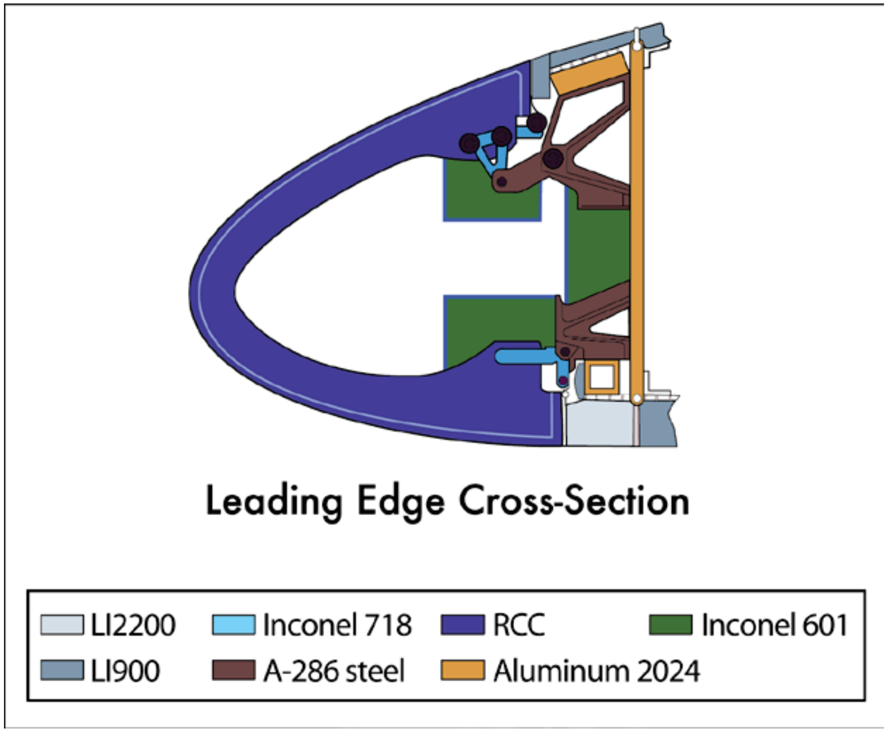
# Recovered Pieces of RCC Provided Clues to Cause of Accident

Brought to hanger
at Kennedy Space Center



*Port Wing RCC Panels 5 to 10*

# Attachment Hardware in Wing Leading Edge Structure

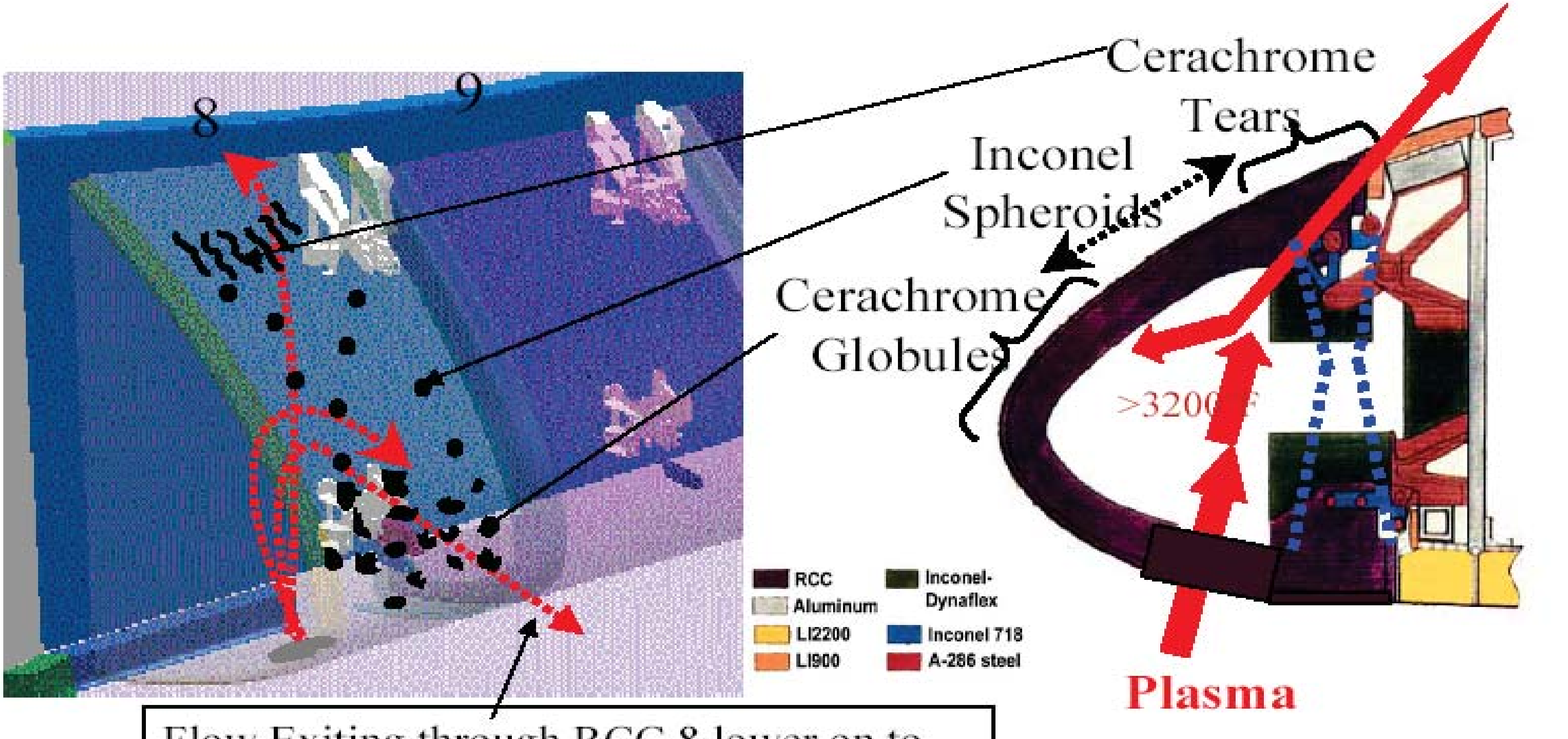


Leading Edge Cross-Section

Pattern of solidified droplets defined location of breach

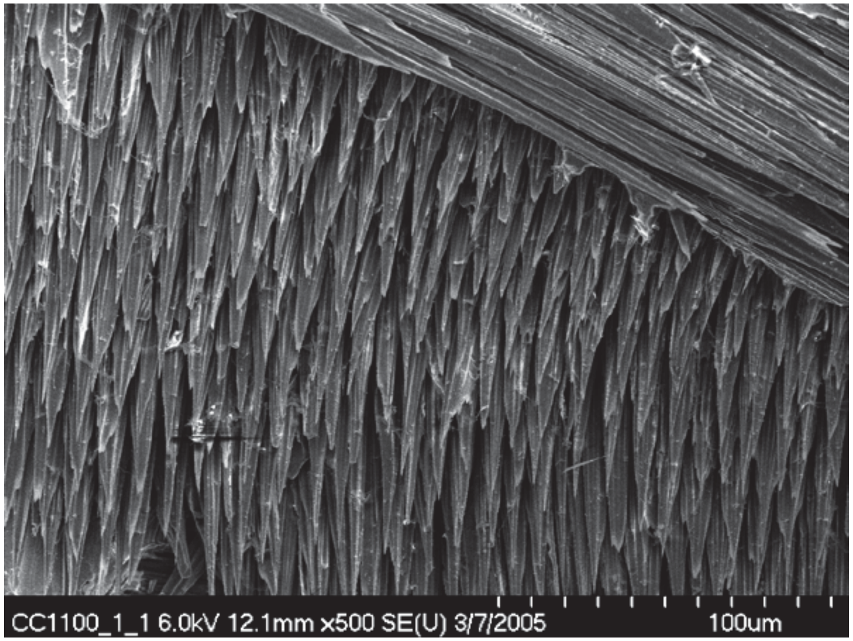
| Alloy | Use | Maximum Service Temperature (°C) | ~MP (°C) |
|---|---|---|---|
| Al 2024 | Wing spar | NA | 650 |
| A286 | Spar attachment fitting | 815 | 1370 |
| IN718 | Clevis, spanner beam | 980 | 1370 |
| IN601 | Spar insulation foil | 1090 | 1370 |

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



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

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



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

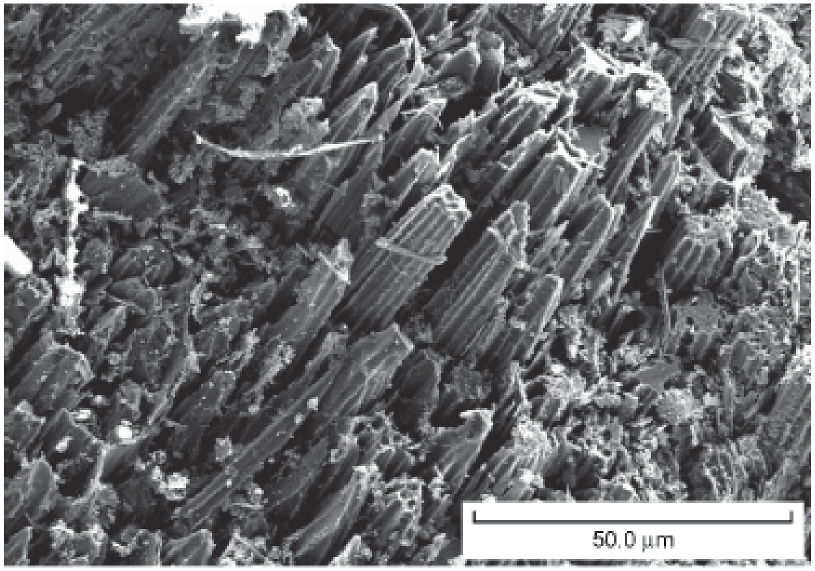
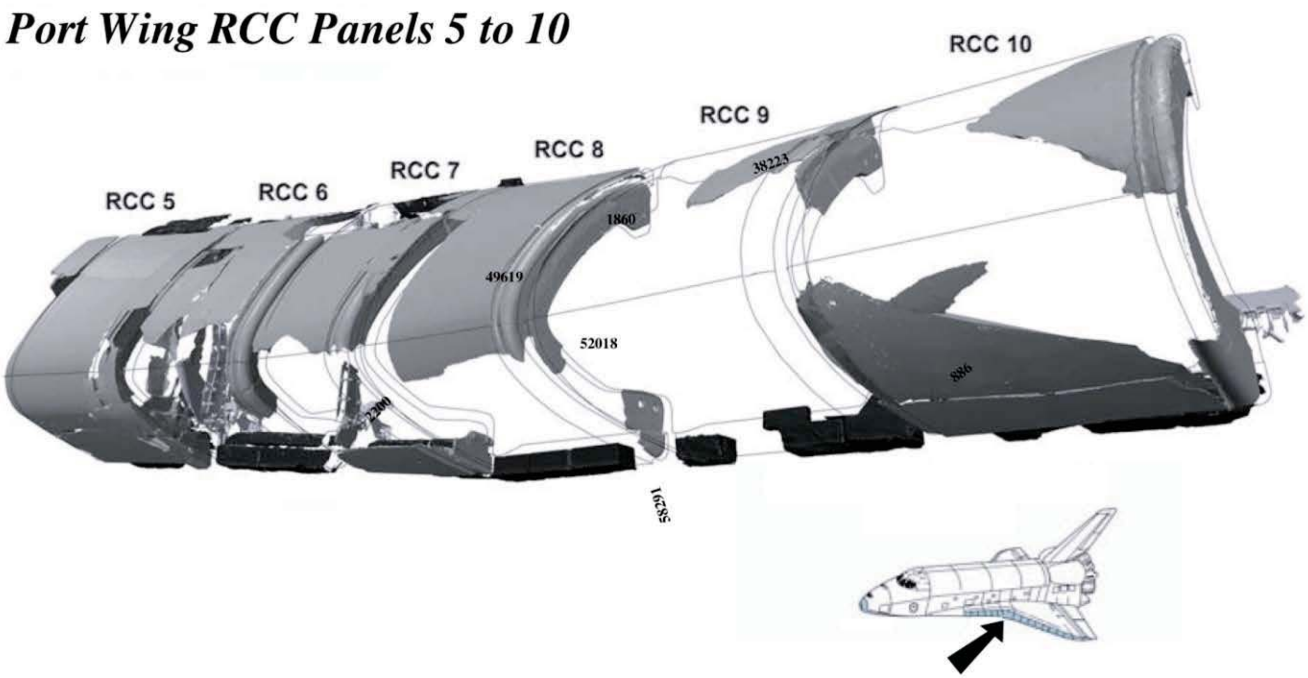


Figure 13.—Electron micrograph of exposed fibers from sample 1860B.

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

# Oxidation Pattern: Tells which fragments formed on Impact with Ground and which Burned During Break-up



# In Memoriam . . .

# Dramatic Changes in Implemented for Shuttle Operation after the Accident

- Careful examination of RCC immediately after lift-off. Camera extends on boom to photograph regions of each panel
- Careful examination of RCC before re-entry
- Extensive NDE (Non-Destructive Evaluation) examination of RCC panels on ground—before installation and on-vehicle
  - Development of novel thermography techniques(relates changes in thermal conductivity to structure) for on-vehicle examination of RCC
- Development of repair methods
- Successful missions through the last flight of the fleet

# Chemistry on Other Worlds

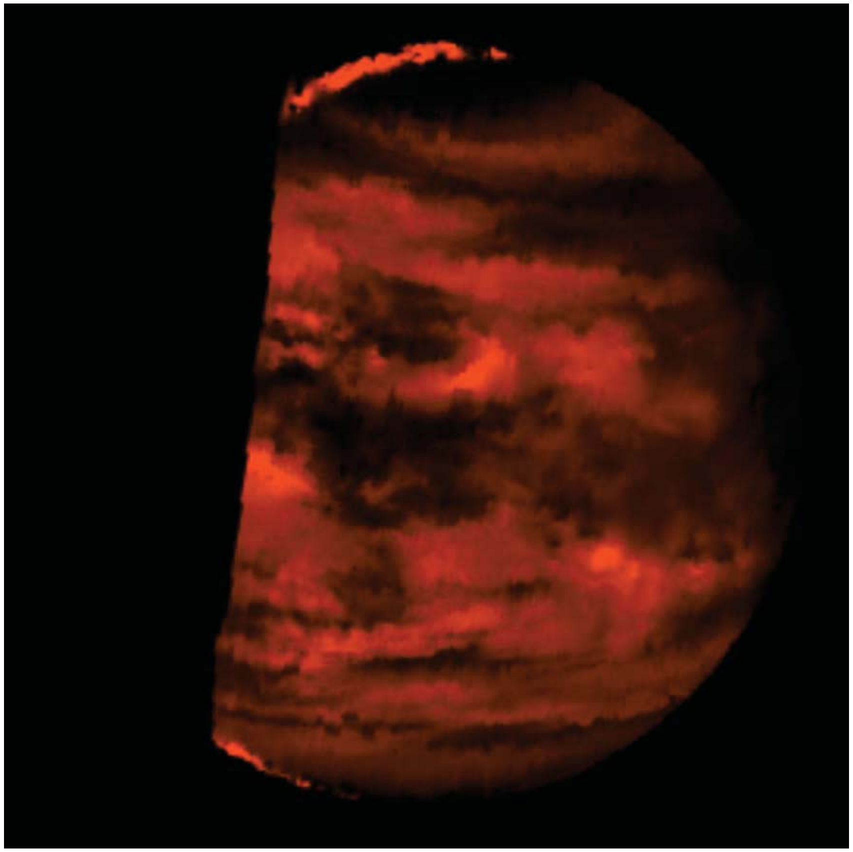
## Venus

## Exoplanets

# What is the atmosphere of Venus like?

What we once thought…

2.3 μm image from *Galileo* flyby



What we now know…

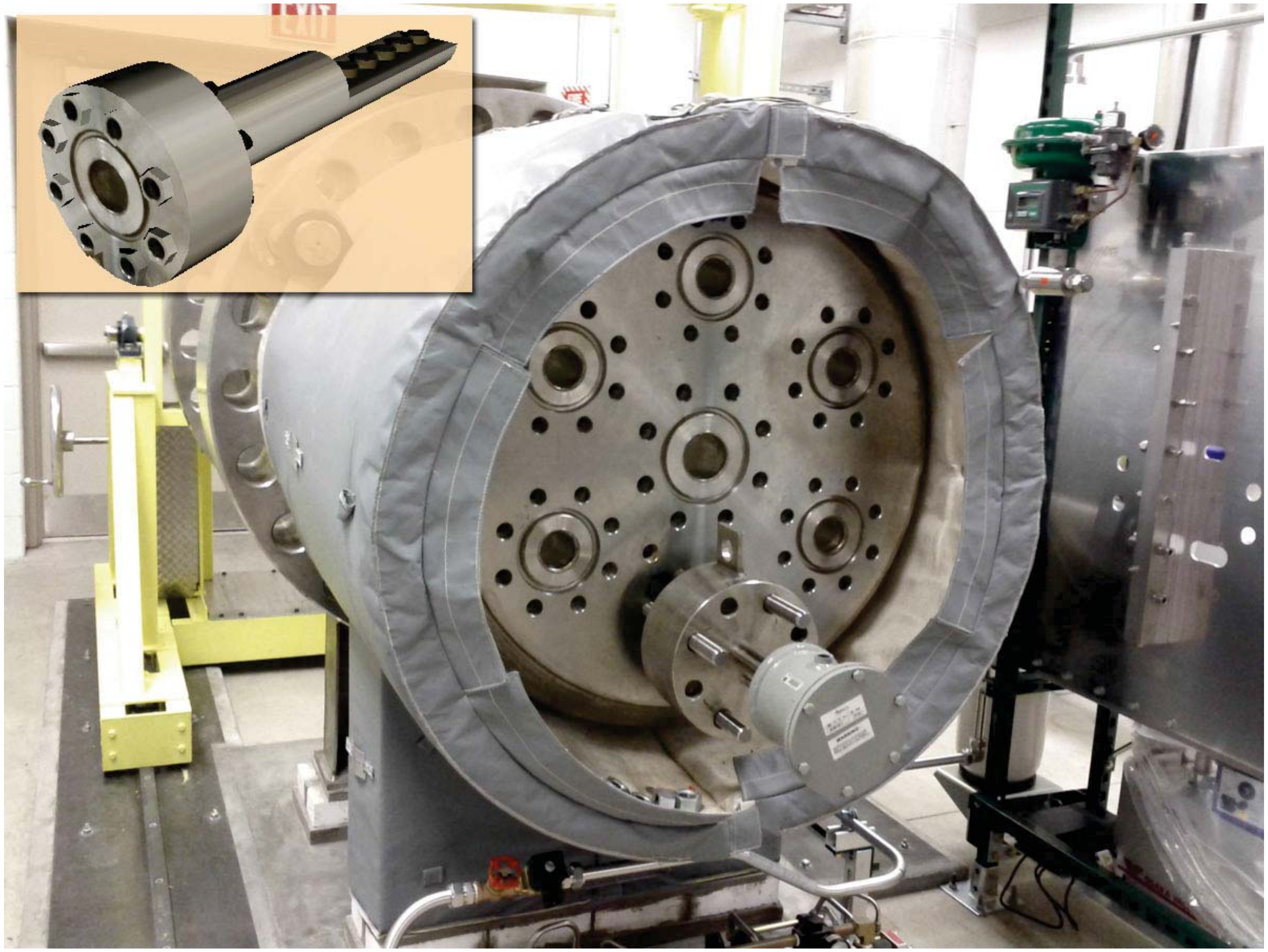
92 bar
Primary $CO_2$, small amount of $SO_2$, $N_2$
Sulfuric acid clouds
Lots of volcanic activity

# Interactions of Venusian Atmosphere with Fresh volcanic Rock

- $CaCO_3 + SiO_2 = CaSiO_3 + CO_2(g)$
  - Can create large $CO_2(g)$ pressure
  - Thought to ‘buffer’ $CO_2(g)$ pressure at surface of Venus
  - Now unlikely as not a true ‘buffer’

- $3FeS_2 + 16CO_2(g) = Fe_3O_4 + 6SO_2(g) + 16CO(g)$
  - Pyrite likely present on Venus surface
  - Reaction may ‘buffer’ $SO_2(g)$

# NASA Glenn Extreme Environments Chamber



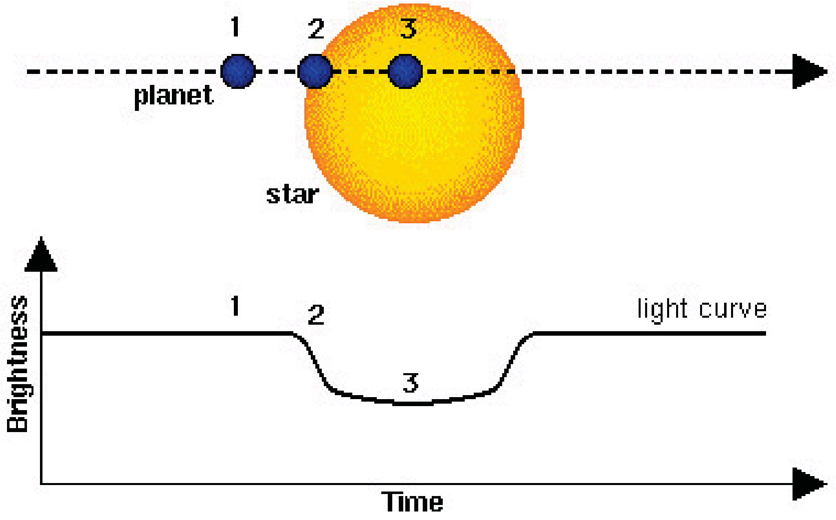
Close duplication
of Venus atmosphere
92 bar 450ºC

$CO_2$
$SO_2$
$N_2$
Ar
Traces of CO, $CO_2$,
HCl, HF

Current studies: Examine a variety of mineral interactions with this environment

# Exoplanets: Planets outside our Solar System

- Confirmed discoveries:
  - 1988—First discovery, confirmed 2002
  - 2009—300
  - 2010—453
  - exoplanets.org (2014)--1516



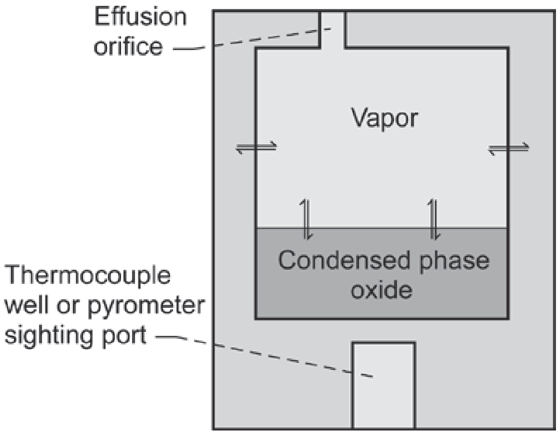
- Most commonly found by transitd method

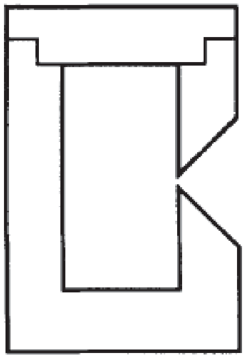
- Hot, rocky Exoplanets
  - Short orbital periods
  - Tidally locked/strongly irradiated
  - CoRot-7b, Kepler 10b, 55 Cnc e
  - Very hot!

# Atmospheres of Hot, Rocky Exoplanets
# CoRoT-7b, Kepler 10b, 55 Cnc e (55 Cancri)

- 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 Na(g), SiO(g), Mg(g)
  - Fractionating as they move to the cold side
  - Can also form silicate 'clouds'
- Grant with MSU (Reed, Cornelison), Wash U (Fegley), and NASA (Jacobson, Costa).

# Simulate these atmospheres in a Knudsen Cell

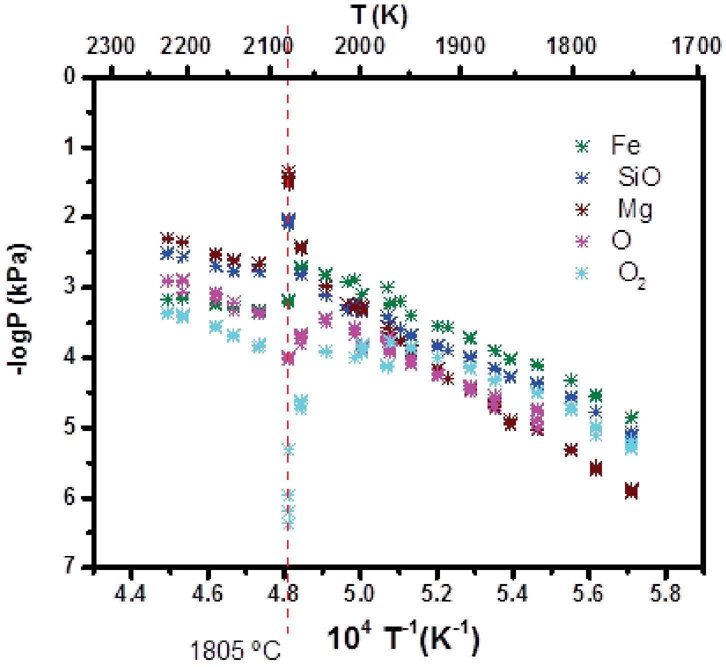




- Typically 1 cm diameter x 1 cm high with a 1 mm orifice
- Near equilibrium established in cell
- Vapor effusing from orifice forms a molecular beam which can be analyzed with a mass spectrometer (standard method from high temperture chemistry)

# Vapors above Olivine: (Mg, Fe) silicate

- Primary constituent of the earth's mantle—may be a major part of exoplanets as well
- Vapor species are Fe(g), SiO(g), Mg(g), O(g), $O_2$(g)
- Vapor pressure vs T



- Atmosphere of Fe(g), SiO(g), MgO(g)! Need specialized spectroscopic methods to confirm or refute this…

# Conclusions: Hot Topics at NASA

- Hot section of Aircraft turbines
- Re-entry shields of the Space Shuttle Orbiter
- High temperature chemistry and physics on Venus and planets beyond our solar system