Understanding The Accelerated Oxidation Behavior Observed In ORNL's Keiser Rig

P.F. Tortorelli, K.L. More

Oak Ridge National Laboratory

Task 2 Review

March 20, 2000

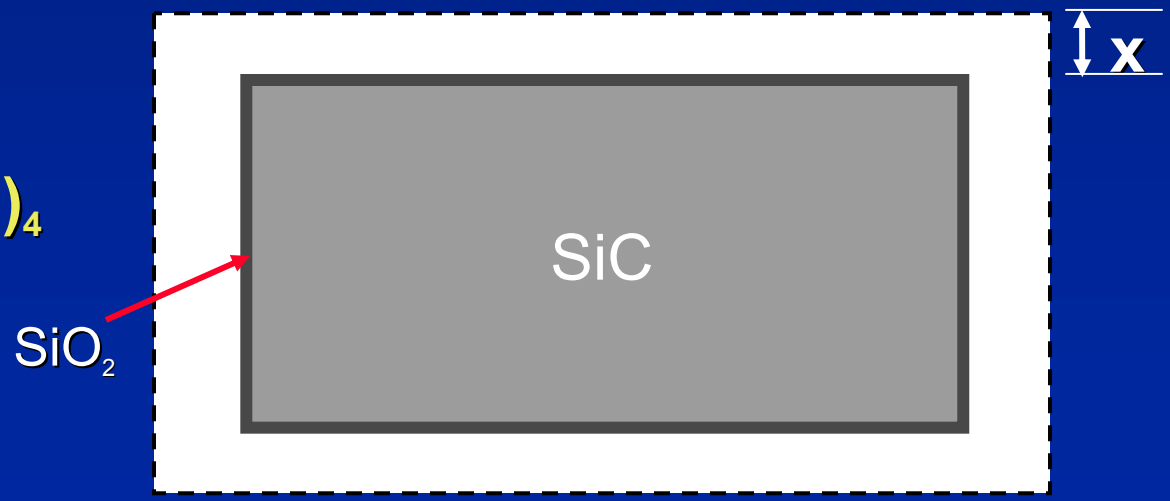
Little Good Comes From The Reactions Of Si-Based Ceramics With H_2O

- **Increases k_p**

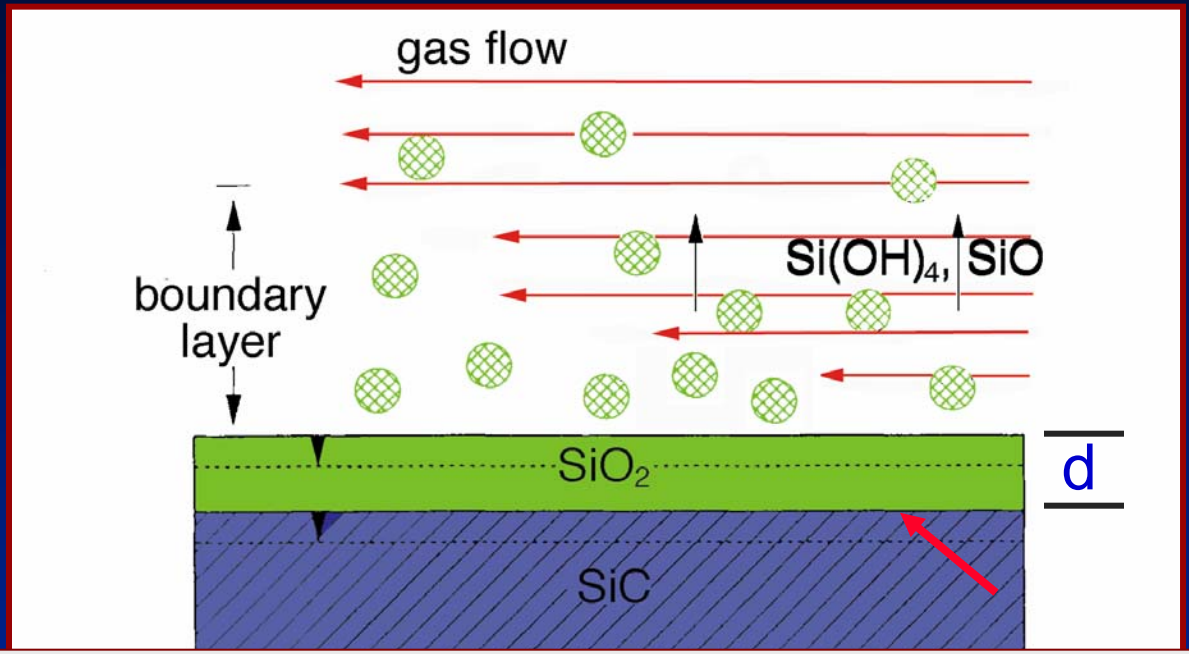
$$x = \sqrt{(k_p \cdot t)}$$

- **Facilitates volatilization of SiO_2**

$$SiO_2 + H_2O = Si(OH)_4$$



Volatility Of SiO_2 Can Lead To Substantial Recession Of Si-Based Materials



SiC Recession Rate = k_l = const.• $\underline{v}^{1/2}\{\exp(-\Delta G_o/RT)\}\underline{P}^{3/2}$

Robinson & Smialek, 1999; Opila et al., 1999

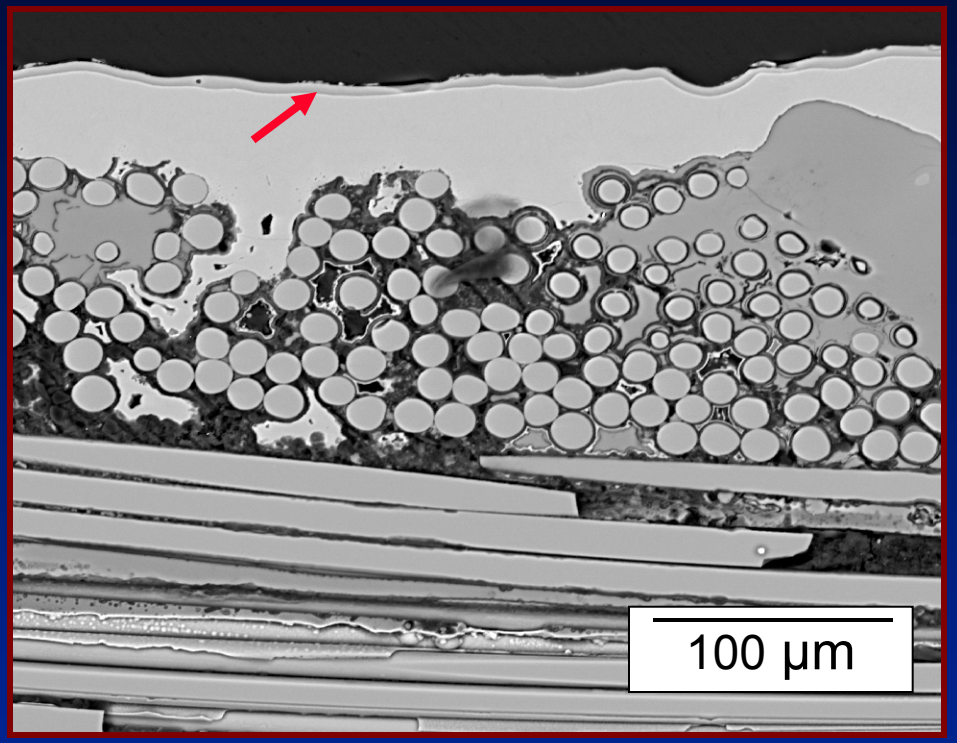
<u>Paralinear kinetics (moving boundary):</u>

SiO_2 volatilization controls SiC recession: $k_l t$

d = constant with time = $k_p/2k_l$

Opila & Hann, 1997

Under High-Velocity Conditions, Only A Thin Silica Layer Is Present



Second Texaco Liner

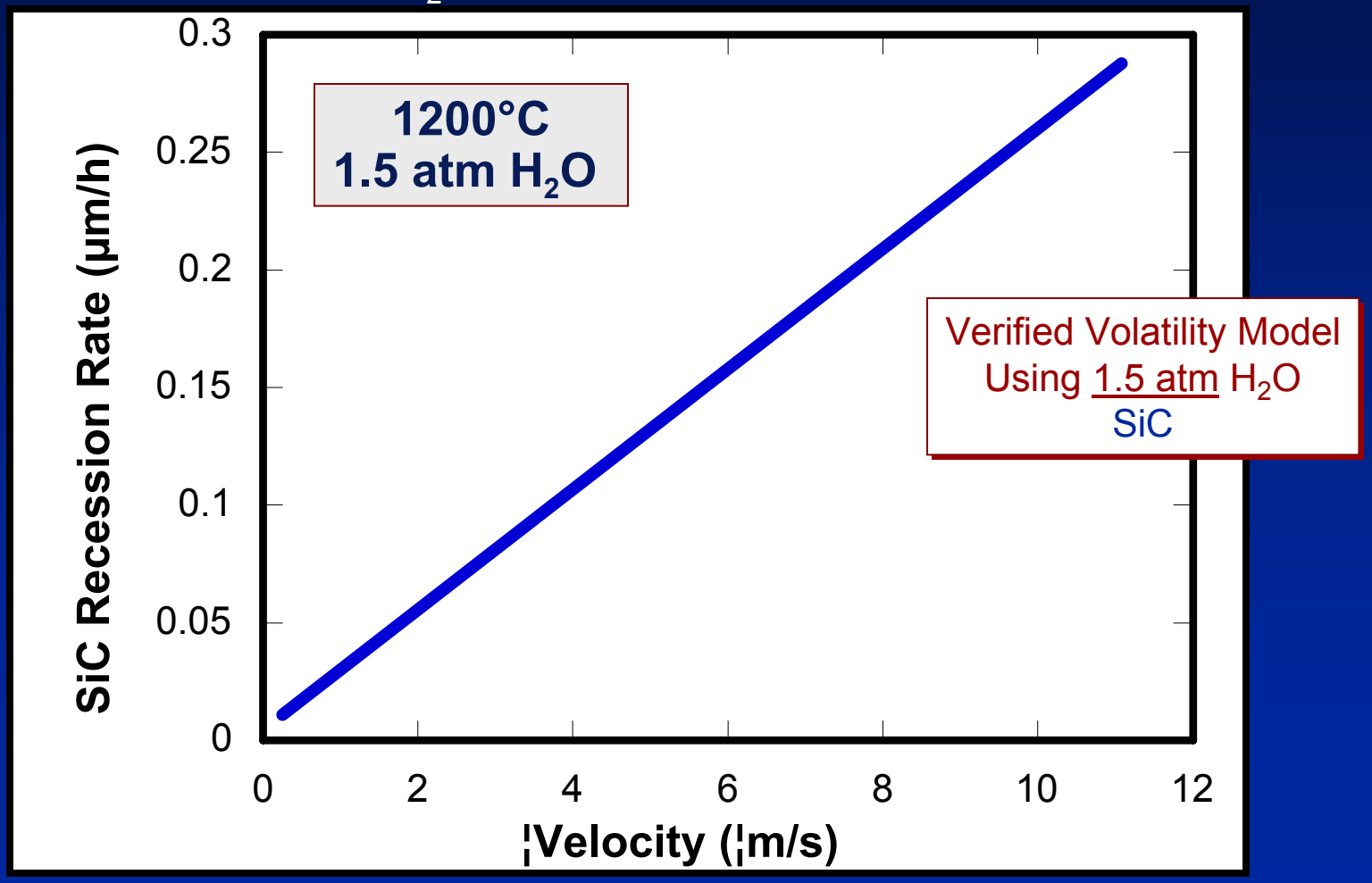
BUT, this doesn't mean the rate of SiC oxidation/recession is low!!

$$d \neq \sqrt{(k_p \cdot t)}$$

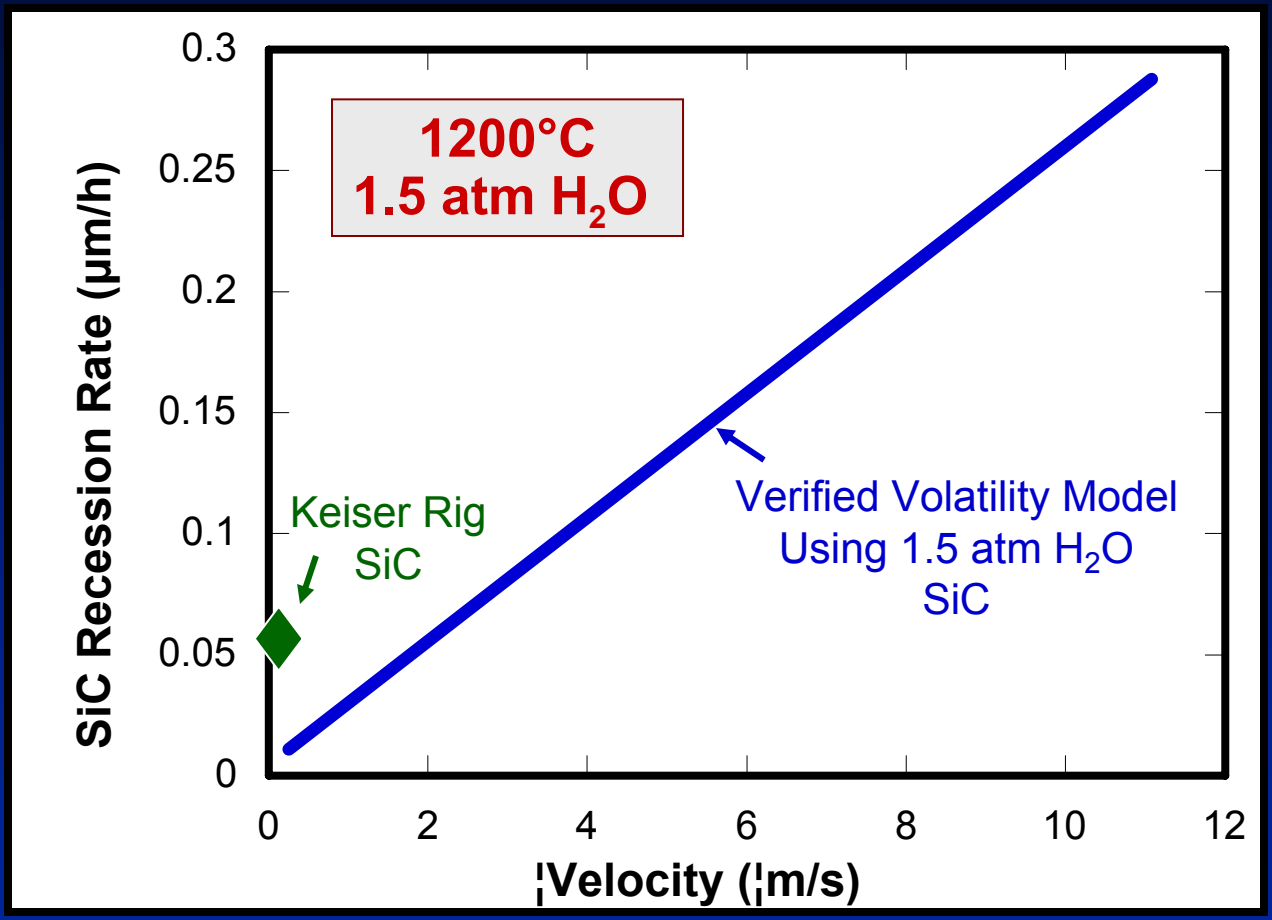
NASA Volatility Model Effectively Describes Recession Of SiC Over Appreciable Range Of v, P, And T

$$\text{SiC Recession Rate} = k_l = \text{const.} \cdot \underline{v}^{1/2}\{\exp(-\Delta G_o/RT)\}\underline{P}^{3/2}$$

0.3-0.9 atm H_2O, 0.05-150 m/s, 1150 - 1500°C

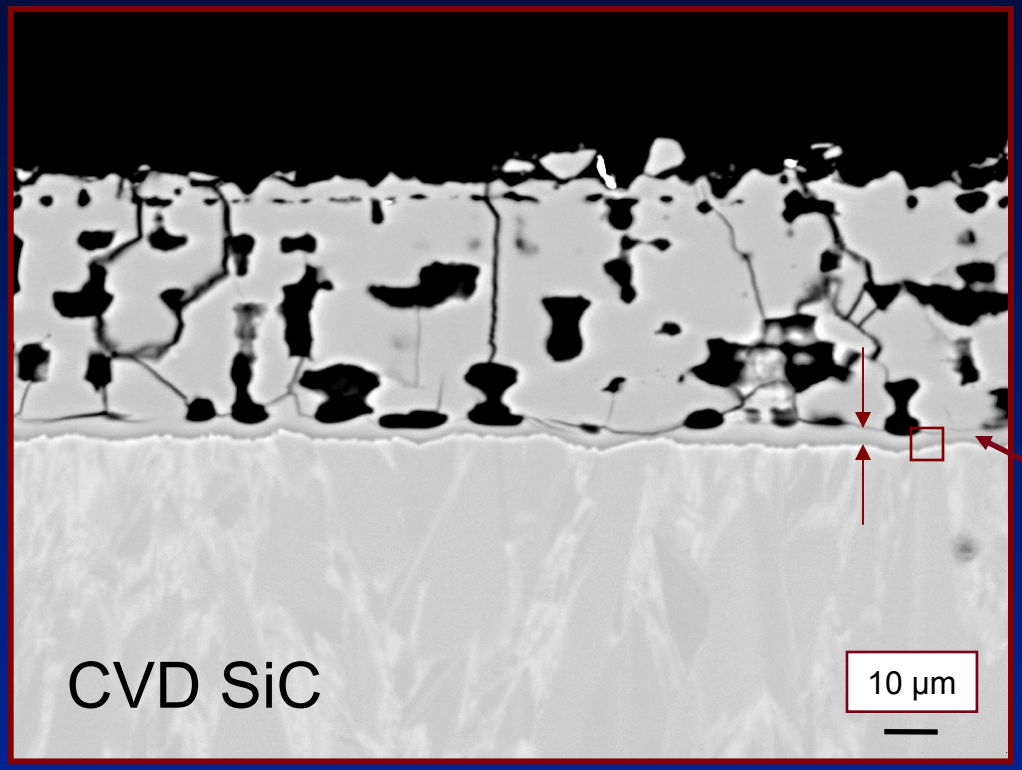


Despite Slow Flow In Keiser Rig, Substantial Oxidation-Induced SiC Recession Is Observed



At This High H_2O Pressure, Rapid Oxidation Can Also Occur At Very Low Gas Flow Rates

Typical Surface Features Observed After Exposure To High Water-Vapor Pressure And Low Gas Velocities

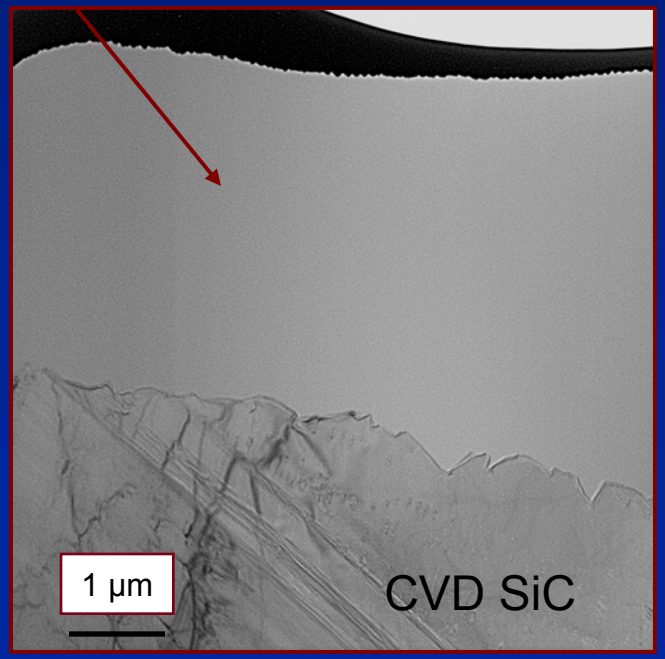


Cristobalite

SiO_2 (total)

d

Vitreous SiO_2



500 h, 1200°C, 1.5 atm H_2O

Vitreous (~ amorphous) layer is dense and thickness (d) is constant with time!

Constancy Of Thickness Of Dense (Vitreous) SiO_2 Layer Suggests A Moving Boundary Phenomenon

For SiC:

Form Silica By Solid-State Oxidation

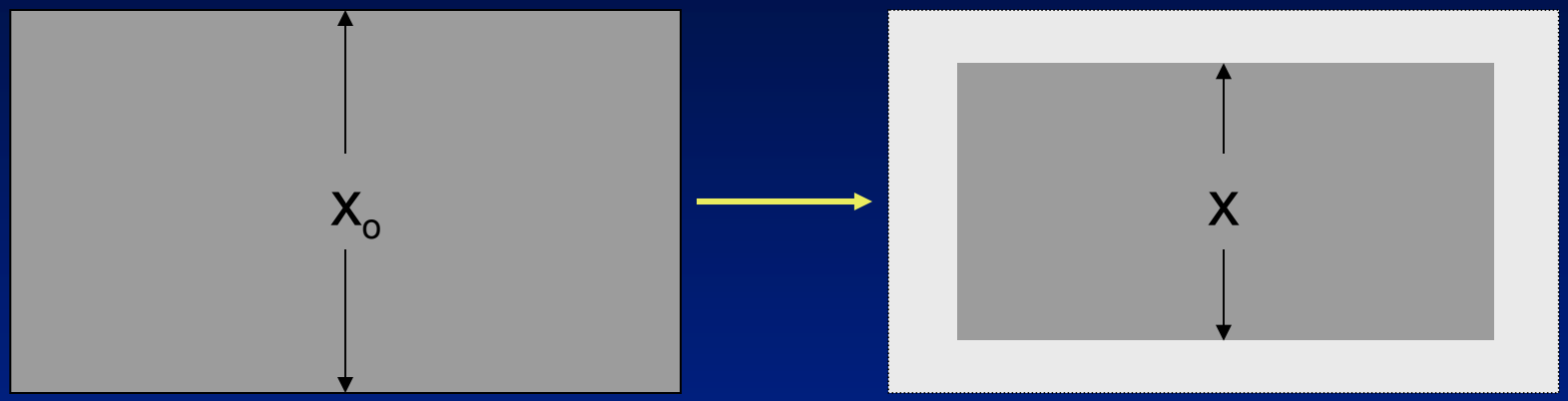
Convert Dense Vitreous Silica To Porous, Nonprotective Cristobalite

From paralinear kinetics:

$$d = k_p/2k_l$$

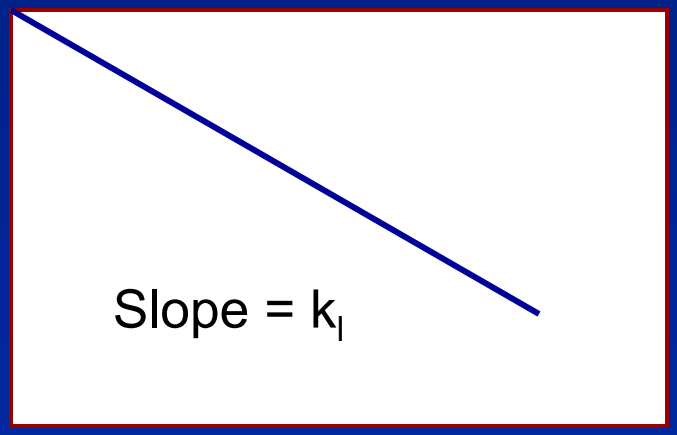
Extent Of Oxidation Is Determined By Microstructural Analysis

SiC Recession By Oxidation Is Measured From Cross Sections



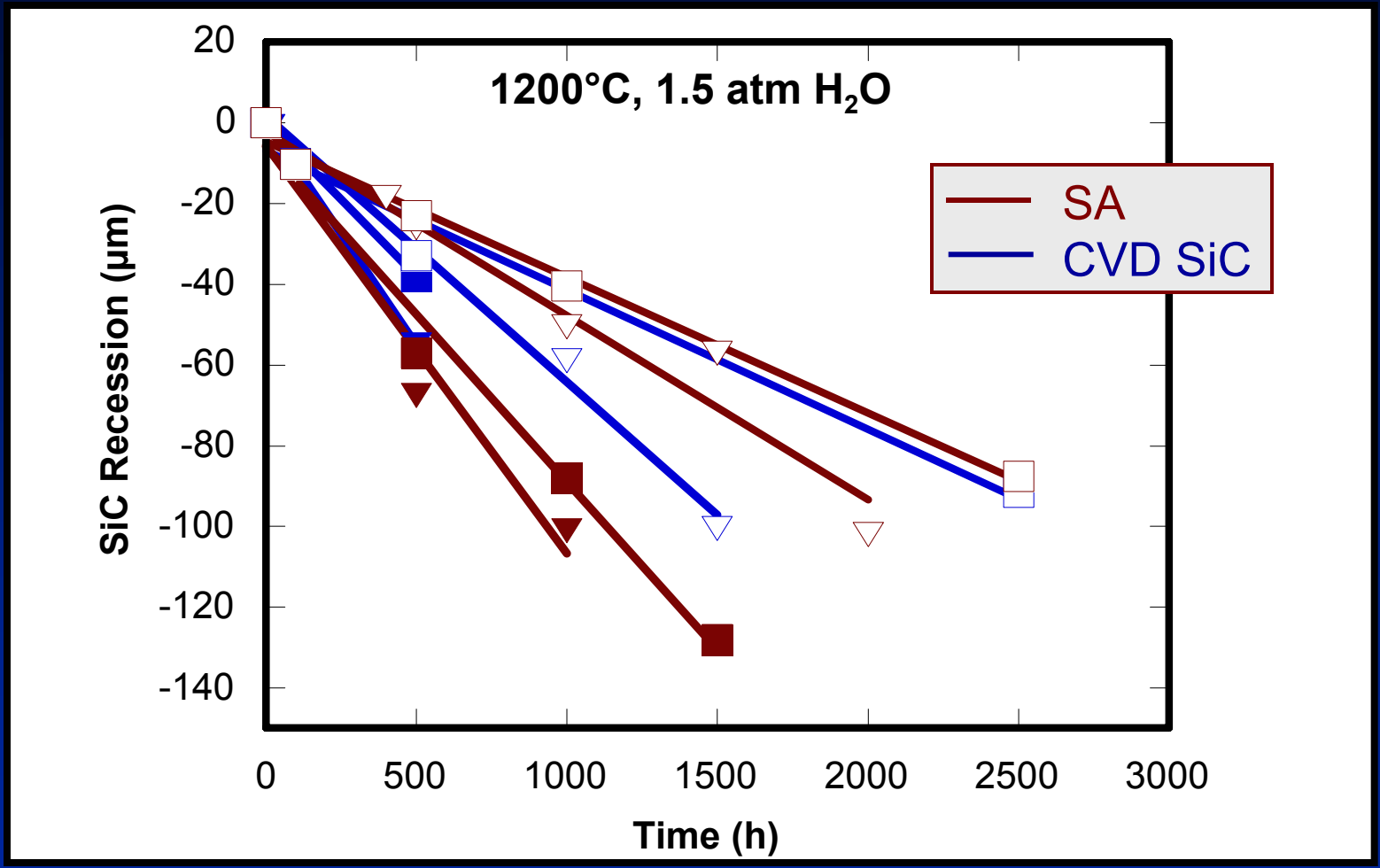
Before Exposure **After Exposure**

$$\text{Recession} = \frac{X - X_o}{2}$$



Oxidation Time

Rates (k_l's) Were Measured For Different Types Of SiC



CVD SiC: 0.04 - 0.07 µm/h

Sintered α-SiC: 0.04 - 0.10 µm/h

Measurements Of d and k_l (Recession Rate) For CVD SiC Yield Correct k_p

$$d = k_p/2k_l$$

For CVD SiC, 1200°C, 1.5 atm H_2O

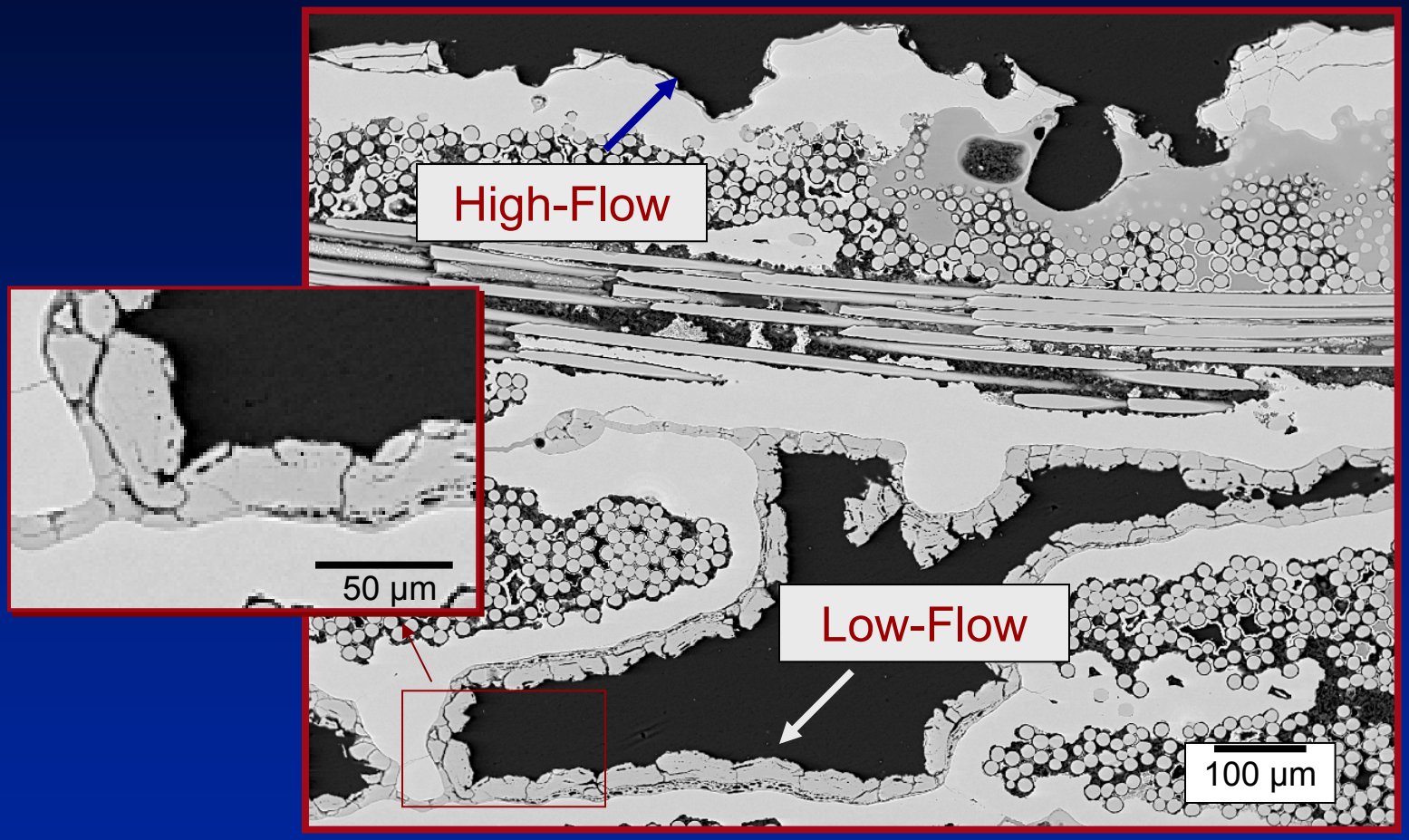
$d = 4\ \mu m$

k_l (from slope of SiC recession curves) = 0.06 µm/h

$$k_p = d \bullet 2\ k_l = 0.48\ \mu m^2/h$$

k_p (Opila, 1999) = 0.49 $\mu m^2/h$!!!

At Very High H_2O Pressures (> ~1 atm), Accelerated Oxidation Occurs At Both High- and Low-Flow Rates



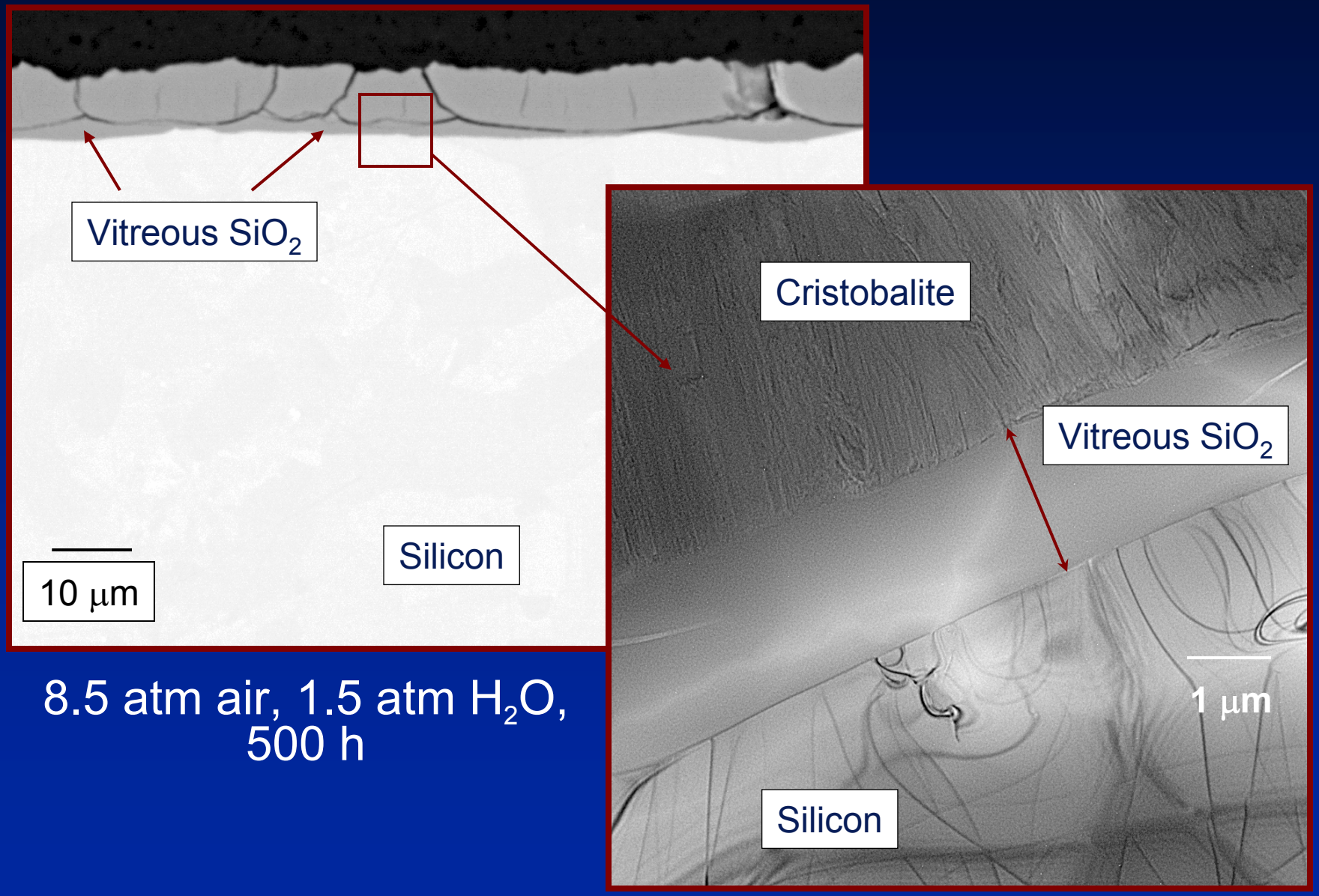
Inner Liner, 1960 h of engine testing in Texaco facility
SiC-seal-coated SiC-based CFCC
1200°C, 35 m/s, 1.5 atm H_2O (appx.)

At Very High H_2O Pressures (> ~1 atm), Accelerated Oxidation Occurs At Both High- and Low-Flow Rates

- Gives us a means (Keiser Rig) to effectively conduct first-stage evaluation of materials for use in combustion environments

- In both high- and low-velocity cases, results can be described by a paralinear kinetics (moving boundary) model
  - mechanism of SiO_2 growth is same
  - process controlling SiC recession is different

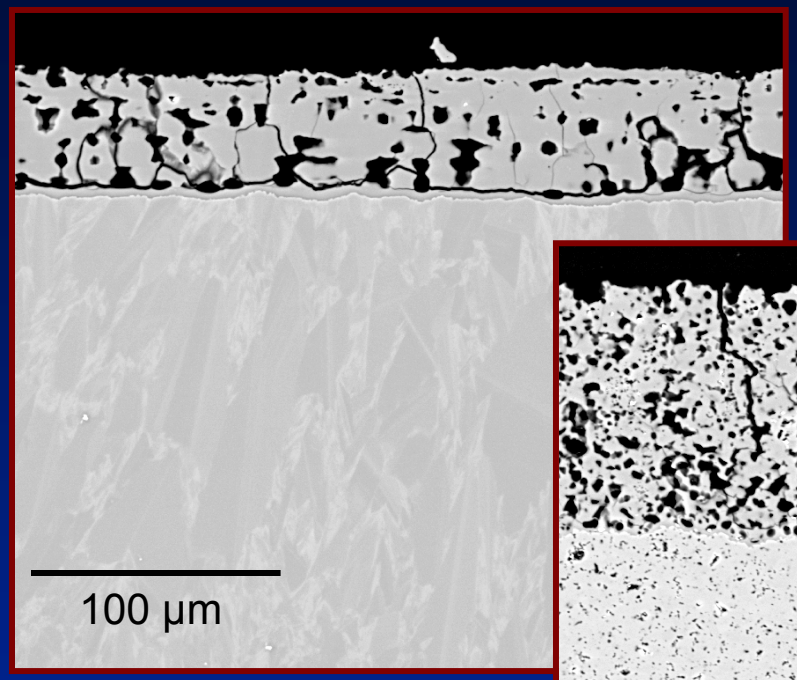
Exposure Of Si Resulted In Similar Two-Layer Scale But Cristobalite Was Dense In This Case



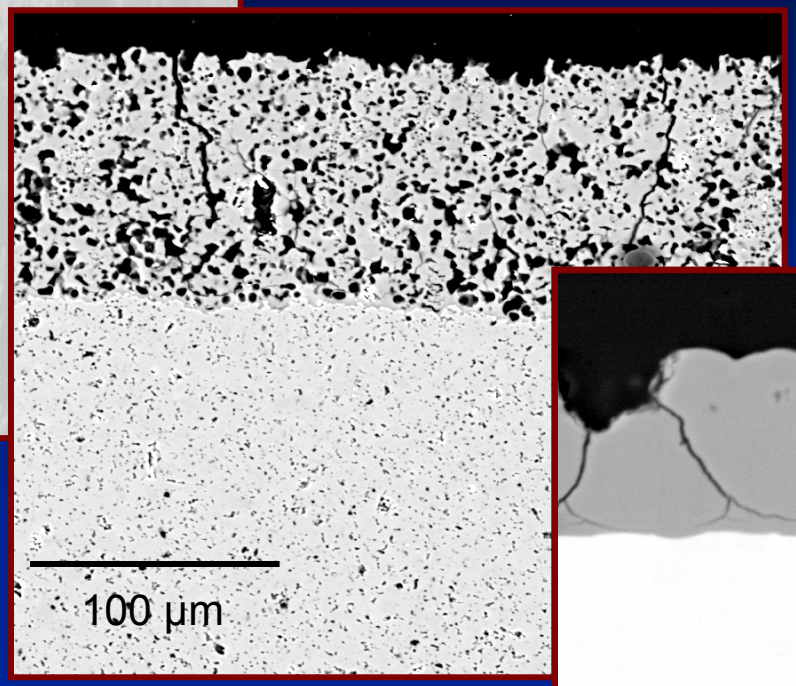
8.5 atm air, 1.5 atm H_2O, 500 h

Few Pores When Pure Si Oxidized; For SiC, Porosity Development In Cristobalite Was Substrate Sensitive

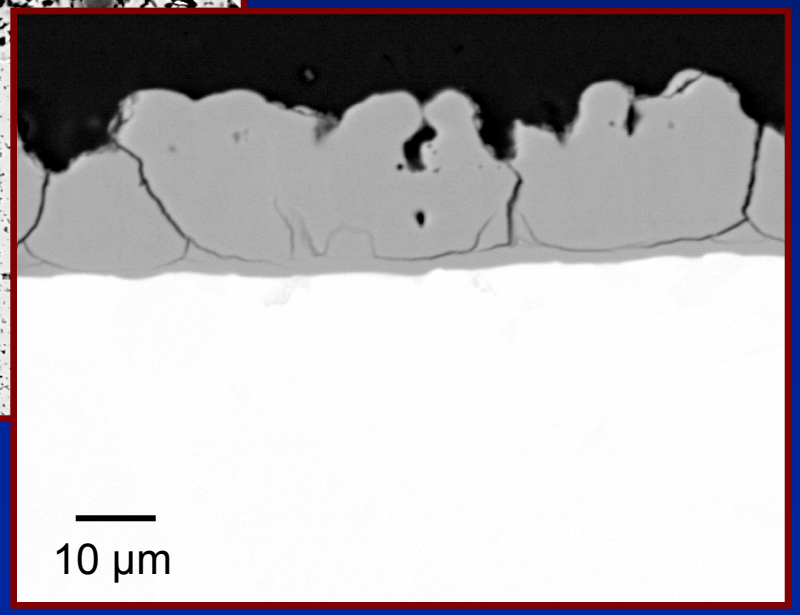
8.5 atm air, 1.5 atm H_2O, 500 h



CVD SiC

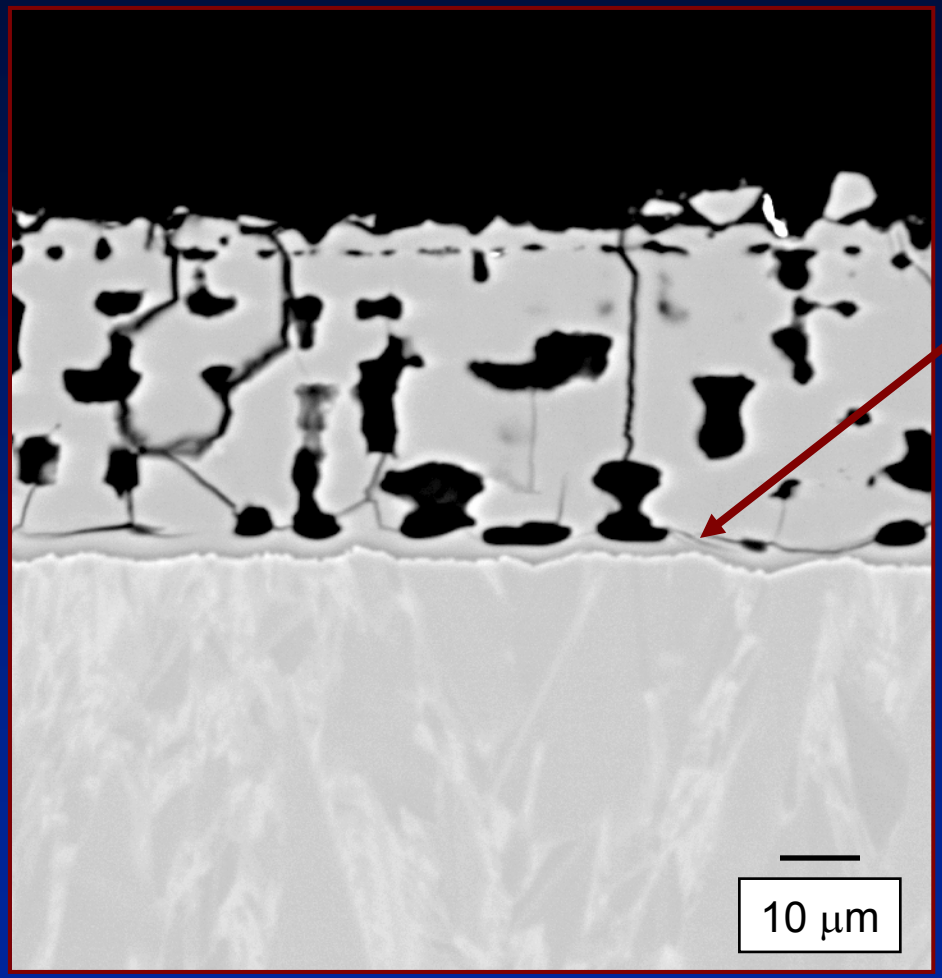


SA

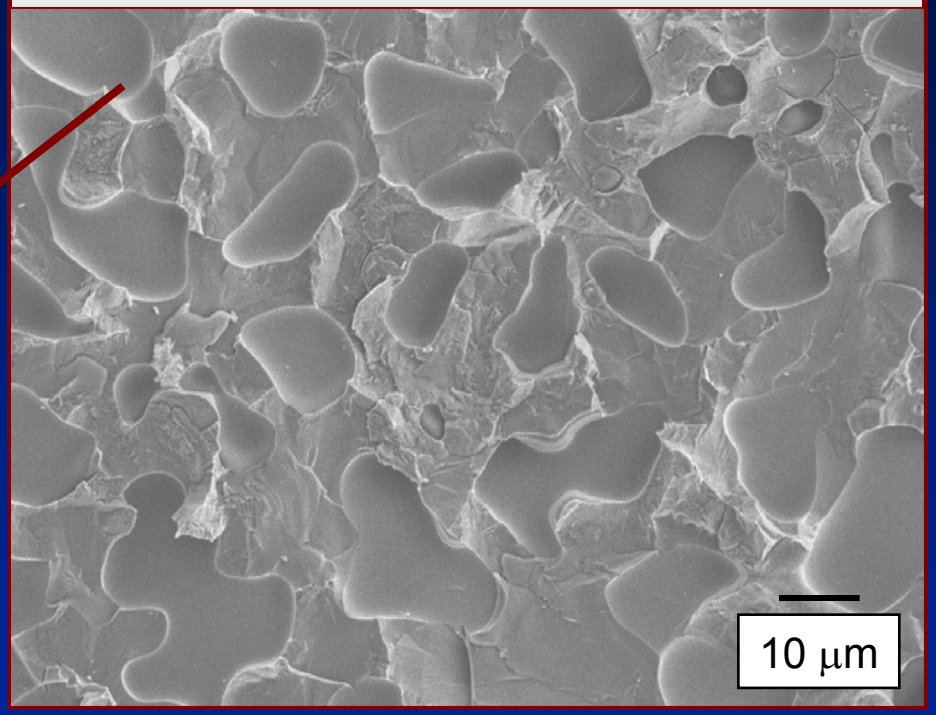


Pure Si

Porosity In Cristobalite And At Its Interface With Vitreous SiO_2 For Oxidized CVD SiC



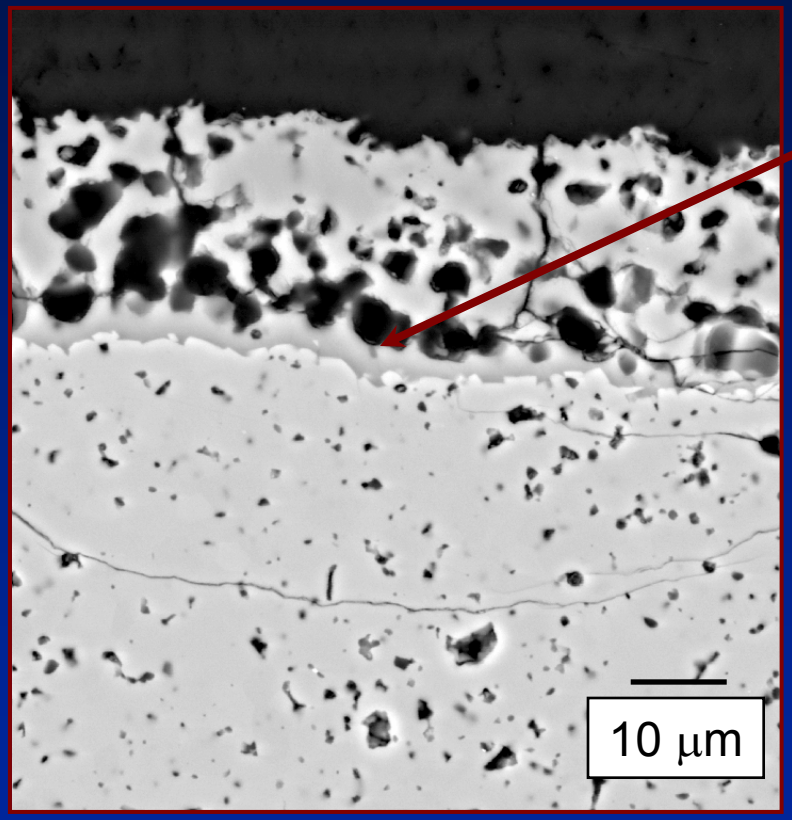
Pores Formed At The Vitreous SiO_2/Cristobalite Interface

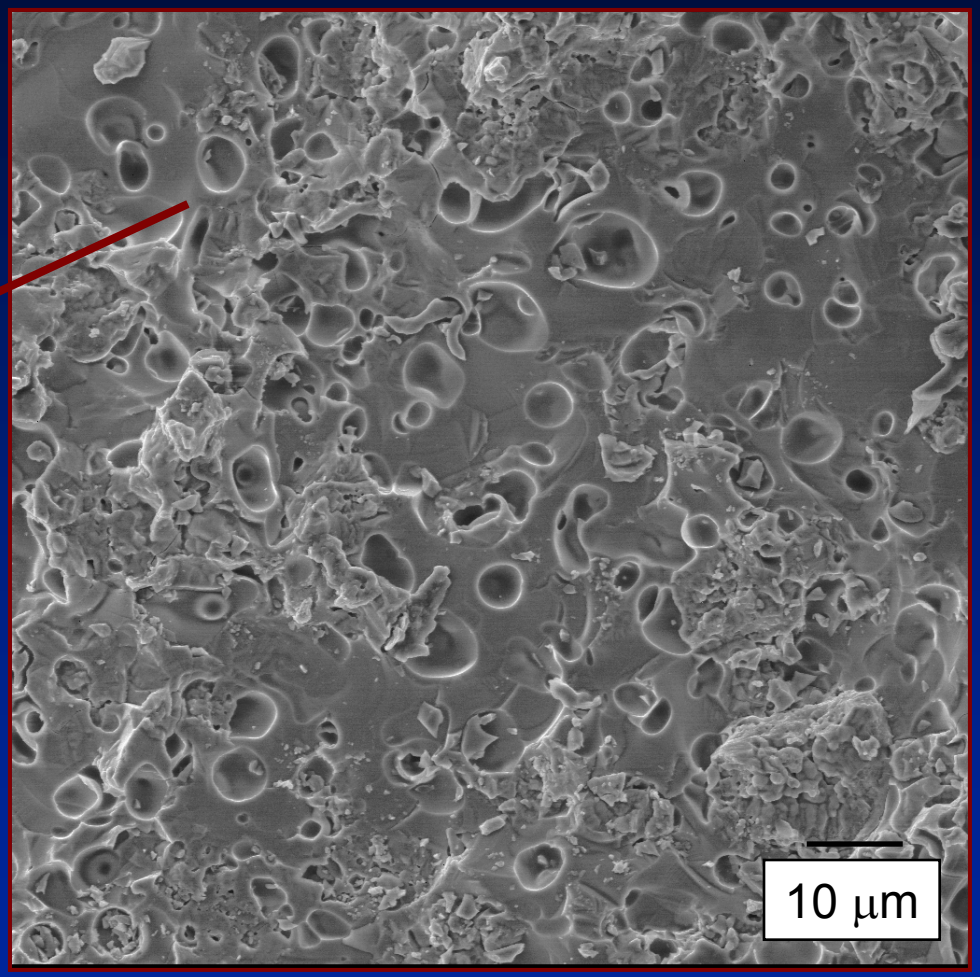


CVD SiC
Exposed 500 h @ 1200°C, 1.5 atm H_2O

…Was Different Than That Formed On SA SiC

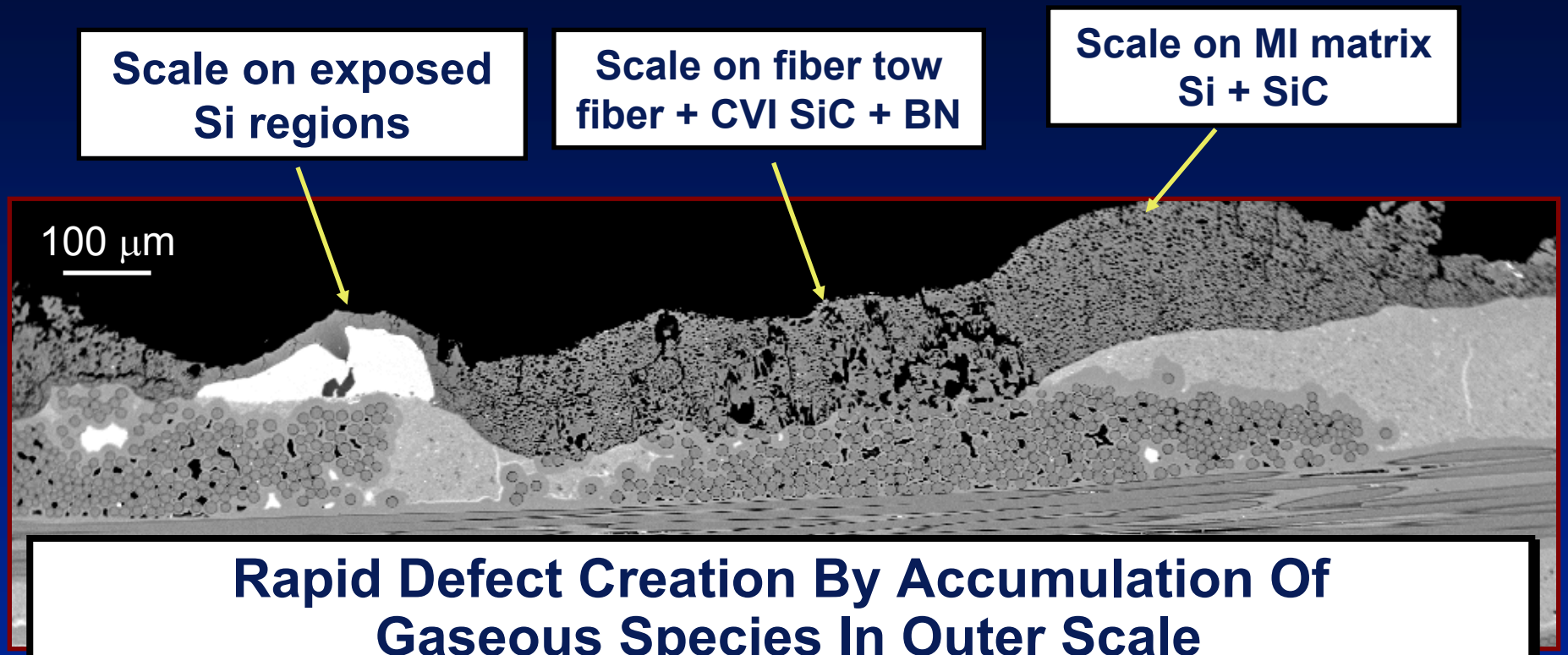
Sintered α-SiC
Exposed 100 h @ 1200°C, 1.5 atm H_2O





Pore Morphology Related To Impurity Distribution And Amount In Substrate, Including Influence Of Grain Boundaries

This Substrate Dependence Has Also Been Observed On Composite Specimens Exposed In Keiser Rig

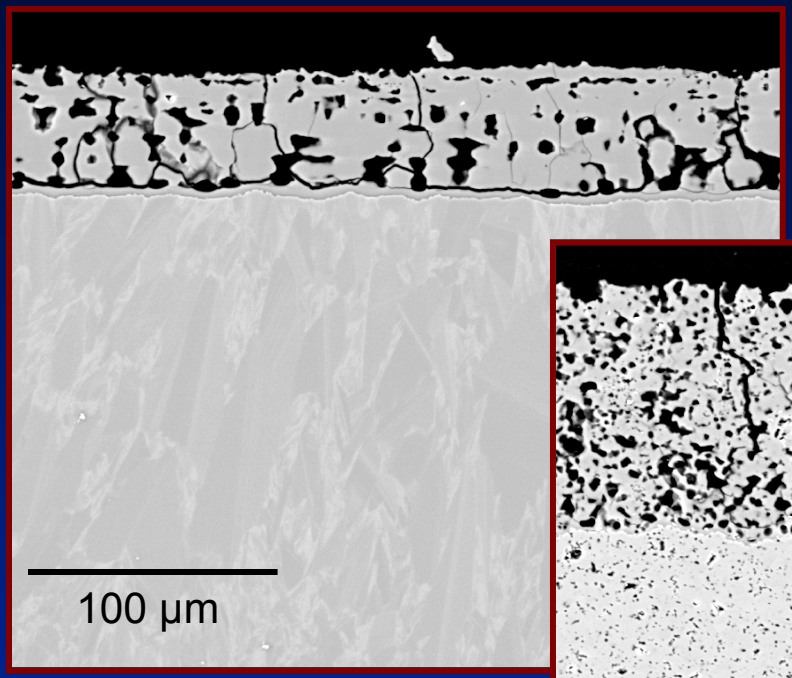


Rapid Defect Creation By Accumulation Of Gaseous Species In Outer Scale

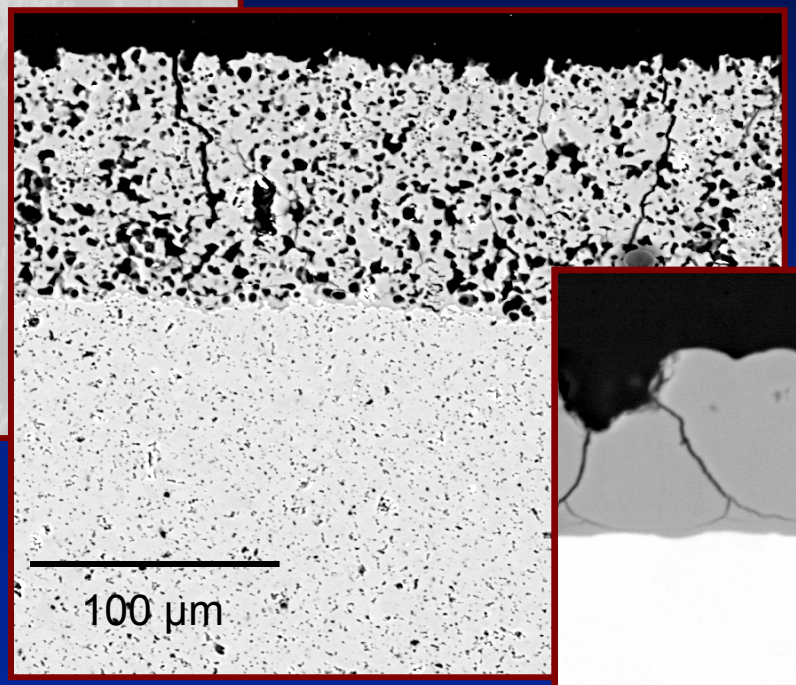
$$Si + 2H_2O\ (g) = SiO_2 + 3H_2\ (g)$$
$$SiC + 3/2O_2\ (g) = SiO_2 + CO\ (g)$$
$$SiC + 3H_2O\ (g) = SiO_2 + CO\ (g) + 3H_2\ (g)$$
$$2BN + 3/2O_2\ (g) = B_2O_3\ (l) + N_2\ (g)$$
$$B_2O_3\ (l) + H_2O\ (g) = 2HBO_2\ (g)$$

Recession Of Si Should Be Less Than That Of SiC If Gas Bubble Formation Is Controlling

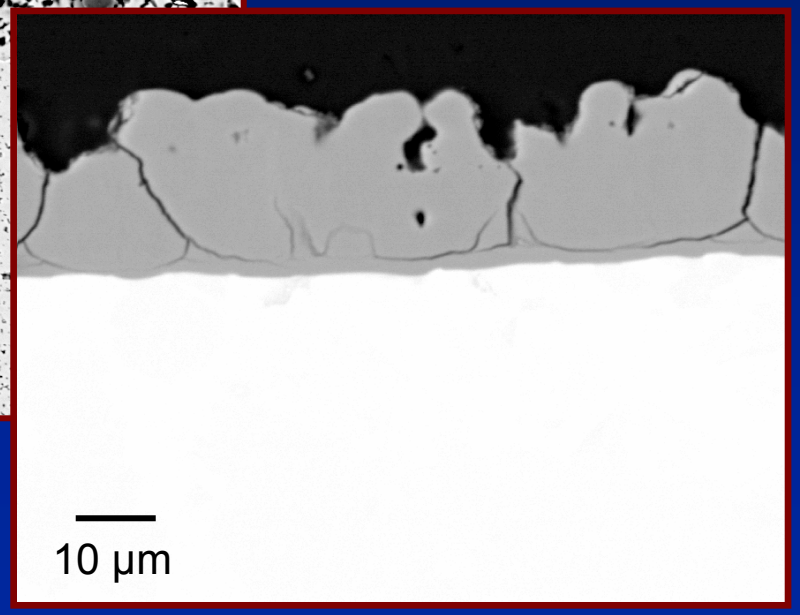
8.5 atm air, 1.5 atm H_2O, 500 h



CVD SiC

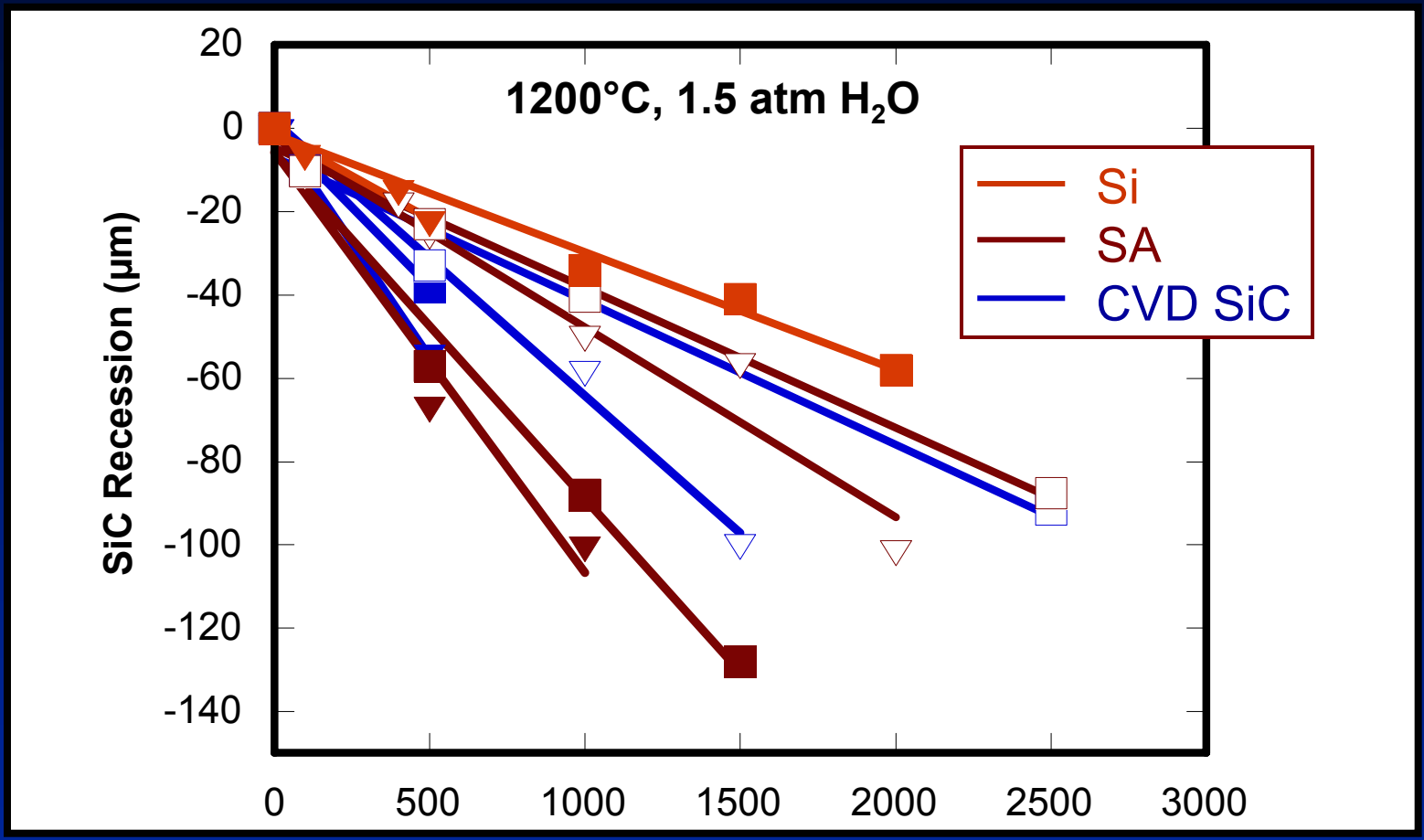


SA



Pure Si

Recession Rate For Silicon Was Lower Than That Of SiC (But Still Fairly High)

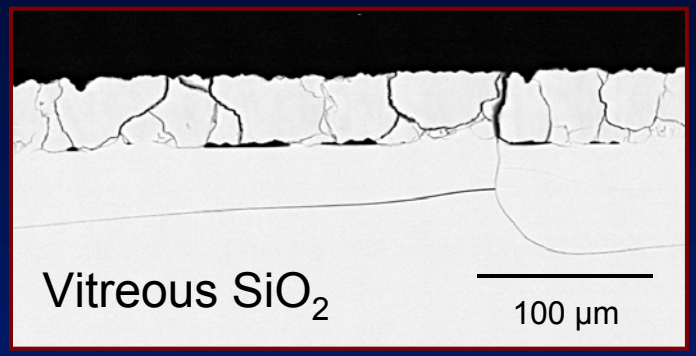


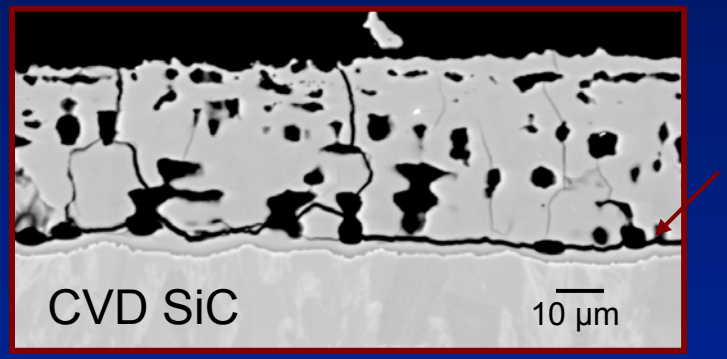
Si: 0.03 - 0.04 μm/h

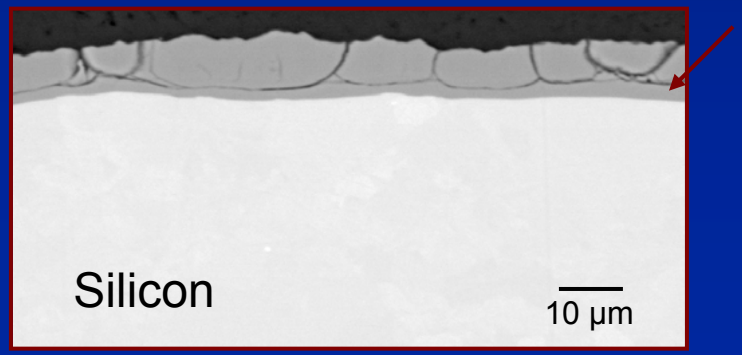
CVD SiC: 0.04 - 0.07 μm/h

SA: 0.04 - 0.10 μm/h

Conversion Of Dense To Nonprotective SiO_2 Controlled By Rapid Defect Creation Involving Gaseous Products





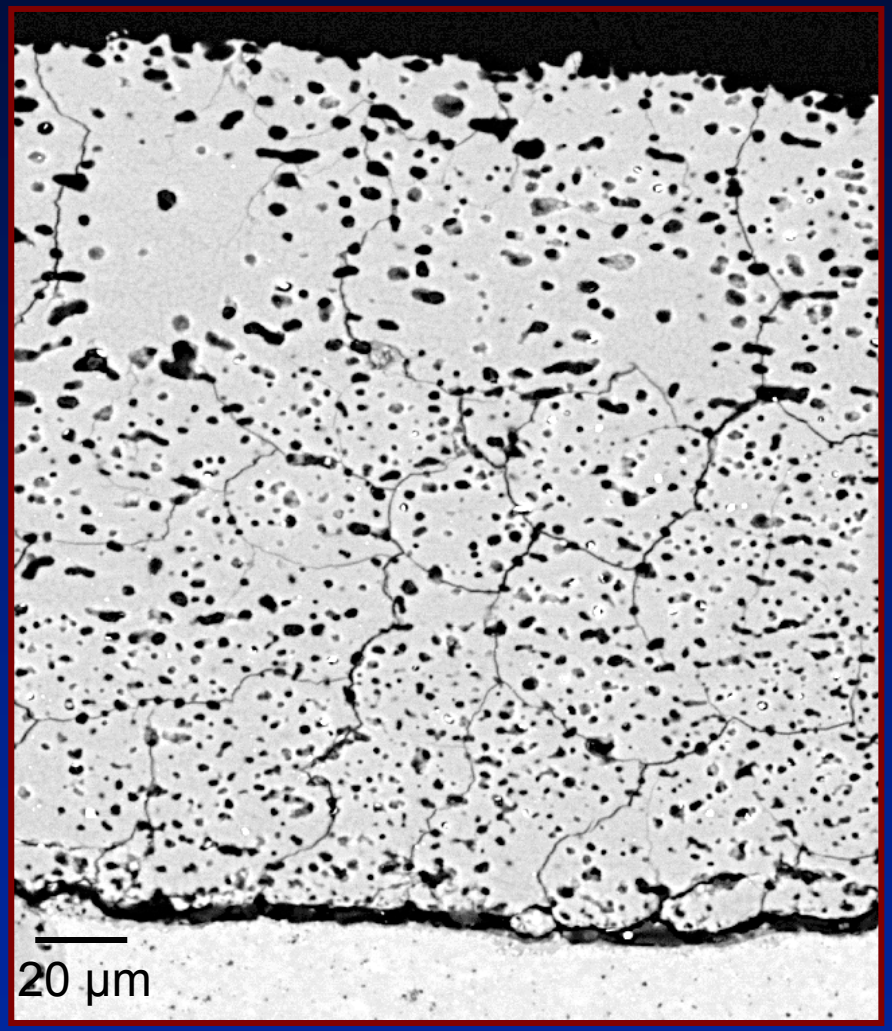


Experiments With Si And Fused Quartz Helped Eliminate Other Possibilities

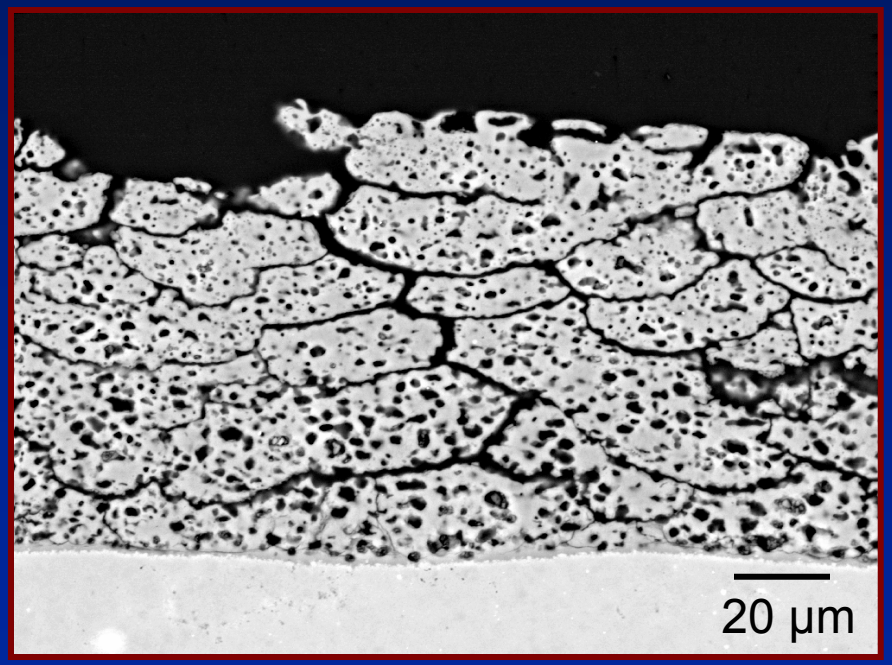
* Gas Bubble/Defect Formation
? Crystallization (0.09 µm/h)
? Local Gas Phase Transport
? Stress

8.5 atm Air, 1.5 atm H_2O, 500 h, 1200°C

Material Composition And Water Vapor Pressure Are Key To Scale Morphology And Recession Rate



500 h, 1200°C, 1.5 atm H_2O

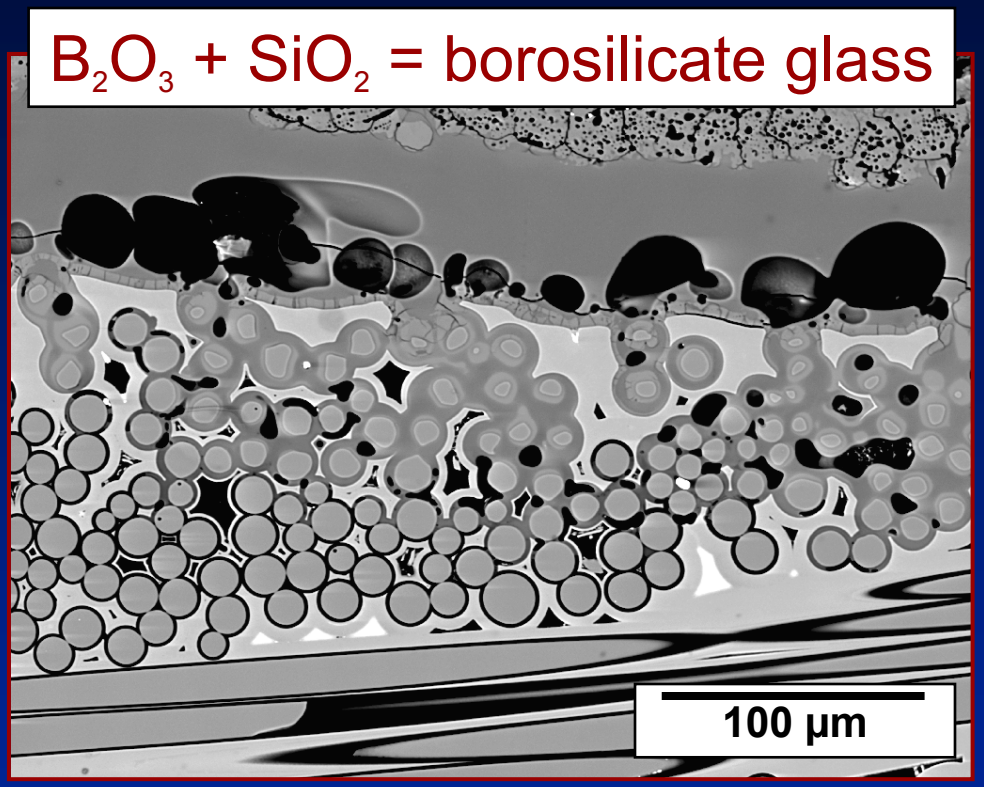


500 h, 1200°C, 0.9 atm H_2O

MI SiC

SiC Composites Are Even More Susceptible At High H_2O Pressures

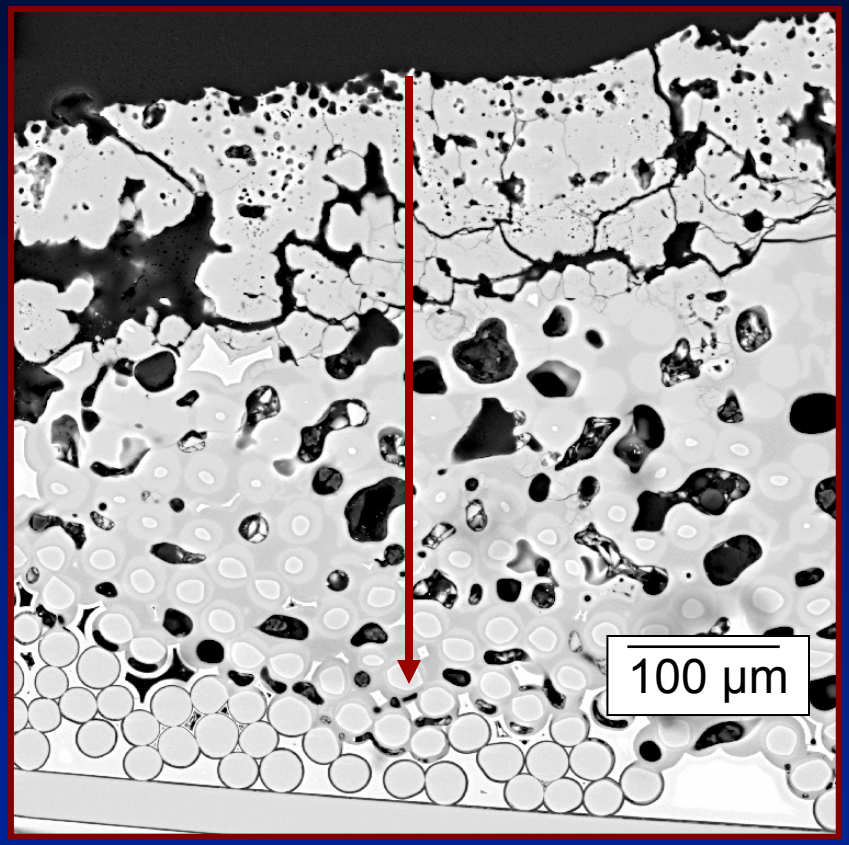
- SiC of various purities (matrix, fiber)
- Si of various purities (matrix)
- B-containing constituents (fiber coatings, matrix)
- Other additives



1200°C, 500 h, Air-1.5 atm H_2O (10 atm)

Reactions Affecting Composite Degradation Not As Sensitive To Gas Velocity

Recession Rates For SiC-Based Composites Are Much Higher Than Those Of SiC



MI Composite
500 h, 1200°C, Keiser Rig

~1200°C, 1.5 atm H_2O

	µm/h
CVD SiC (Solar Liner):	0.11
CVD SiC (Keiser Rig):	0.06
Enhanced SiC/SiC (Solar Liner):	0.5
Enhanced SiC/SiC (Keiser Rig):	0.4

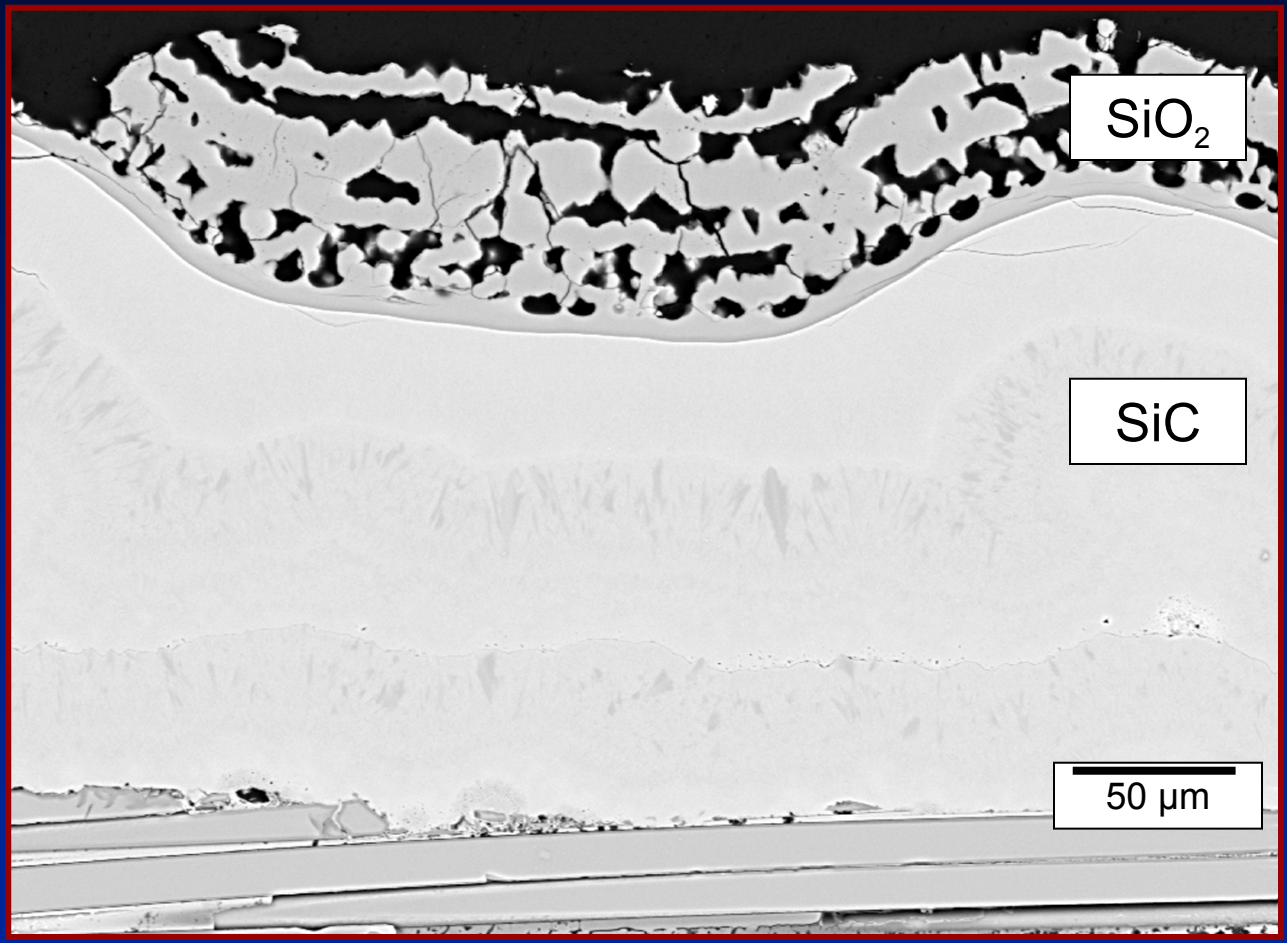
Consistent With Multiple Oxidation Reactions And Borosilicate Glass Formation

Accelerated Environmental Degradation Under Low Velocity, High H_2O-Pressure Conditions (Keiser Rig)

- Reasonable accelerated oxidation (recession) rates of SiC arising from high rate of defect production by various oxidation reactions involving H_2O
- Good match of rates measured for composite consumption because degradation reactions are not strongly influenced by gas velocity effects

BACKUP

Similar Features And Rates Have Been Observed In Slow-Flow Areas Of Combustor Liners



Inner Liner, 1960 h of engine testing in Texaco facility
SiC-seal-coated SiC-based CFCC
1200°C, 1.5 atm H_2O (appx.)

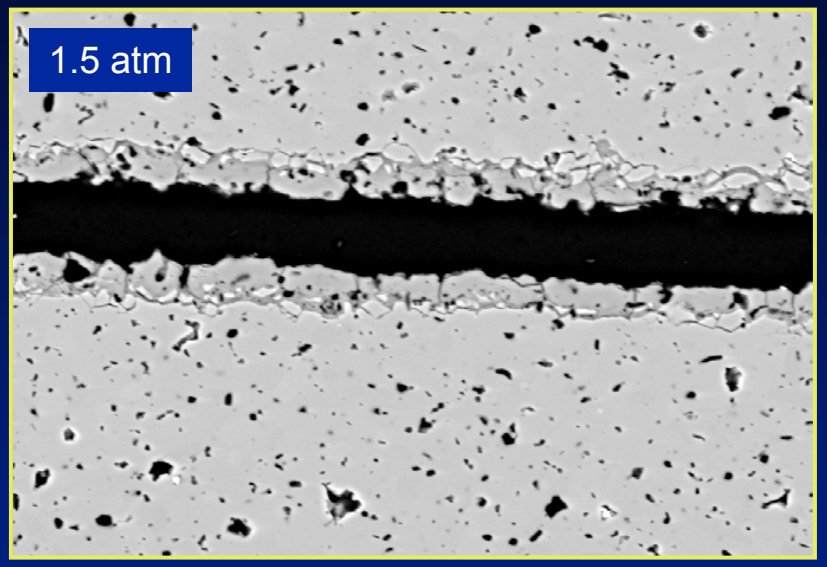
ORNL Keiser Rig Exposures Fall Outside Range Of Most Combustion-Related Studies Of Ceramics

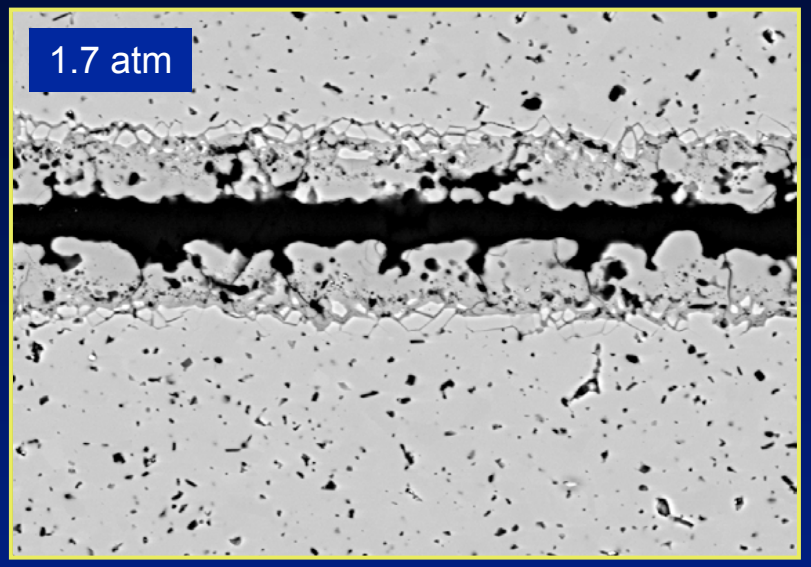
- 1200°C

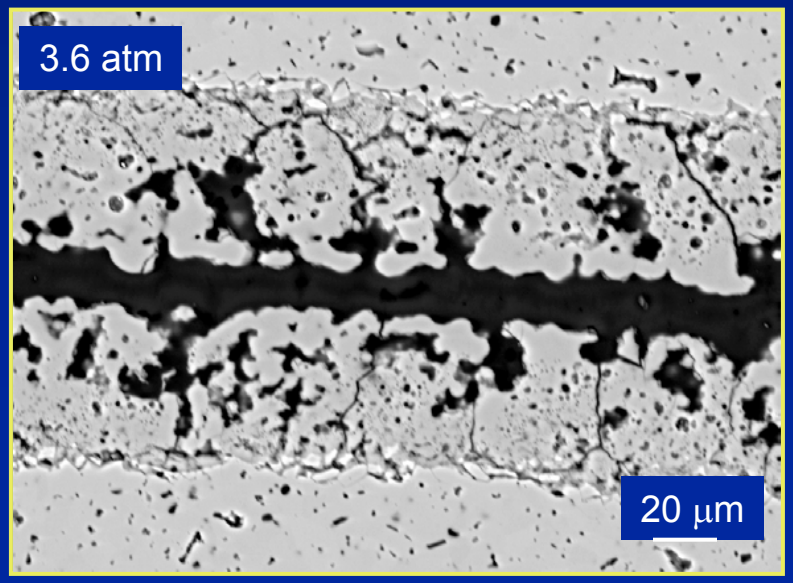
- H_2O pressure of 1.5 atm

- <u>Very low</u> gas velocities (0.05 - 0.3 cm/s)

Cristobalite Scale Thickness Increased With Increasing H_2O Pressure

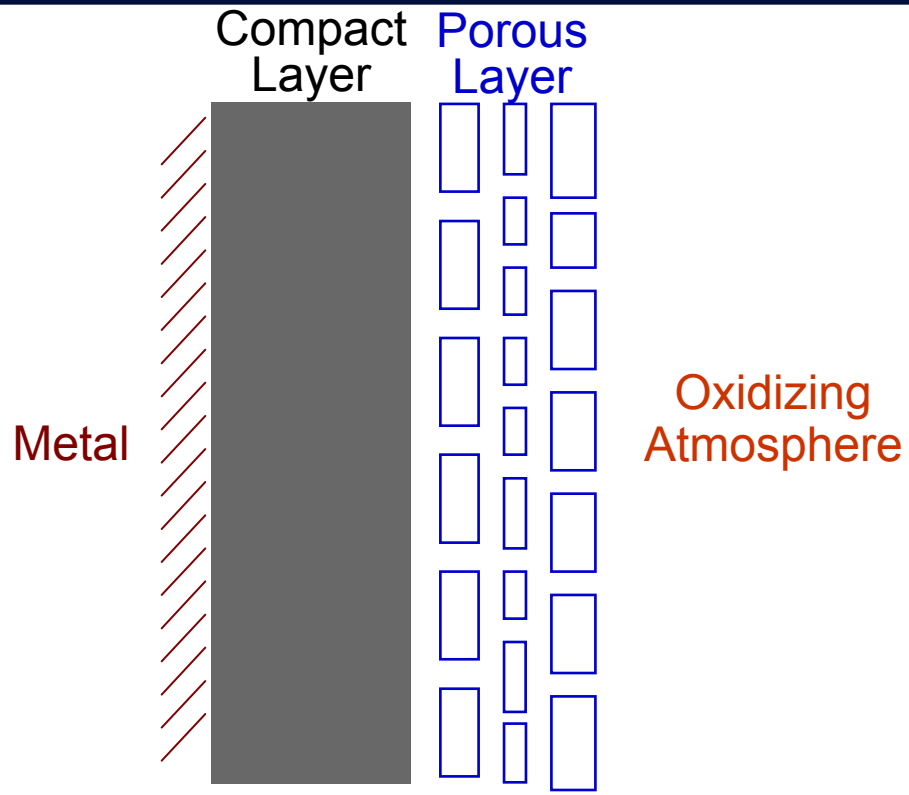






Sintered α-SiC
Exposed at 1260°C
For 100 h

Haycock's Classic Paralinear Treatment Was For Compact Oxide Transforming To Porous Layer



Haycock, 1959