# Advancing Development of Environmental Barrier Coatings Resistant to Attack by Molten Calcium-Magnesium-Aluminosilicate (CMAS)

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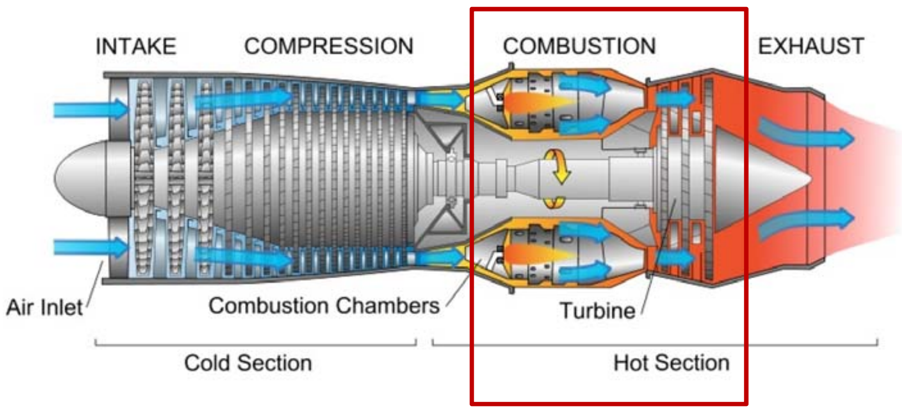
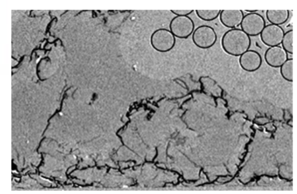
# Enabling Game-Changing Materials for Commercial Aviation

- Replace current metal-based components with **<u>ceramic matrix composites</u> (CMCs)** to *increase* turbine engine *efficiency*
  - *Higher* operating temperatures (>1200ºC)
  - *Lower* (1/3) density than conventional metal-based components

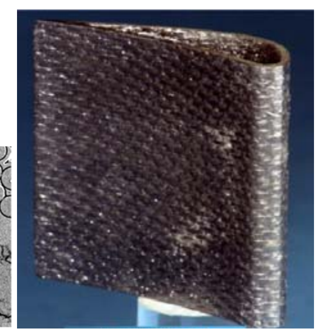
- **6% increase in fuel efficiency → savings of ~$400,000/plane/year**




**Target: 1482ºC**



Micrograph of CMC cross-section

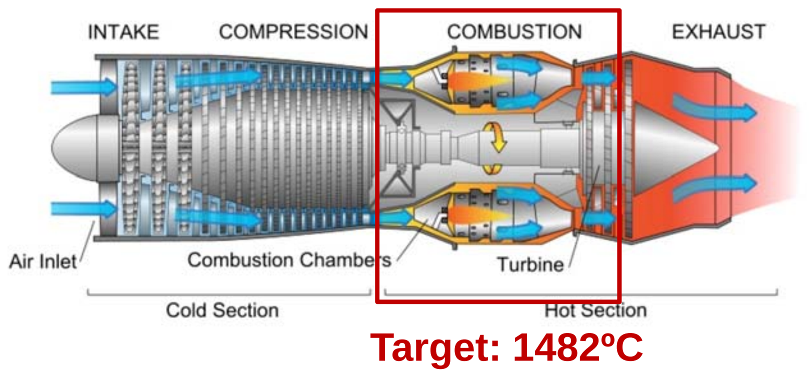


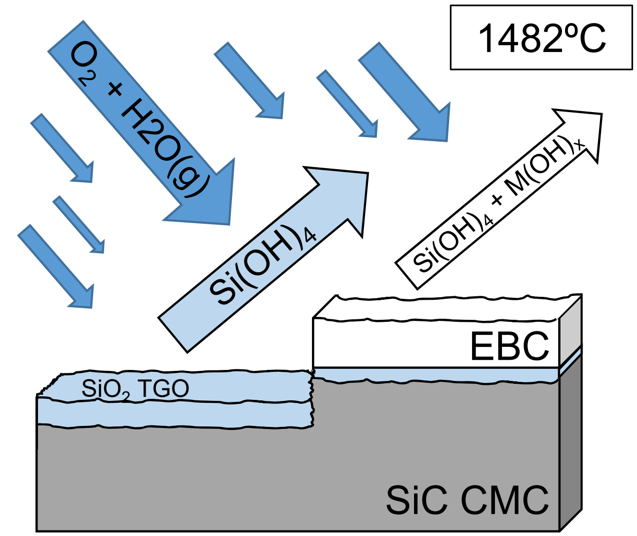
SiC/SiC CMC inlet turbine vane

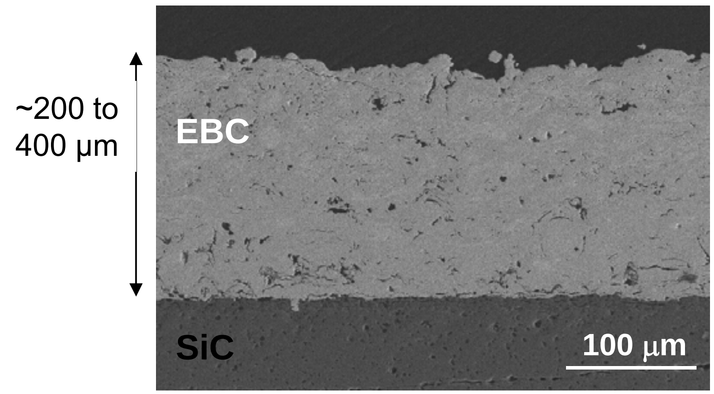
D. Zhu et al., "EBCs for Turbine Engines," *NTRS* (2009).
Image credit: NASA Glenn Research Center

# CMC Degradation in Turbine Engine Environment

- Silicon carbide (SiC) CMCs susceptible to environmental attack at temperatures >800ºC in oxygen and water vapor
  - Silica ($SiO_2$) scale formation that volatilizes in $H_2O$ environment
  - Surface recession
- Require **environmental barrier coatings (EBCs)** to protect CMC component from harsh environment



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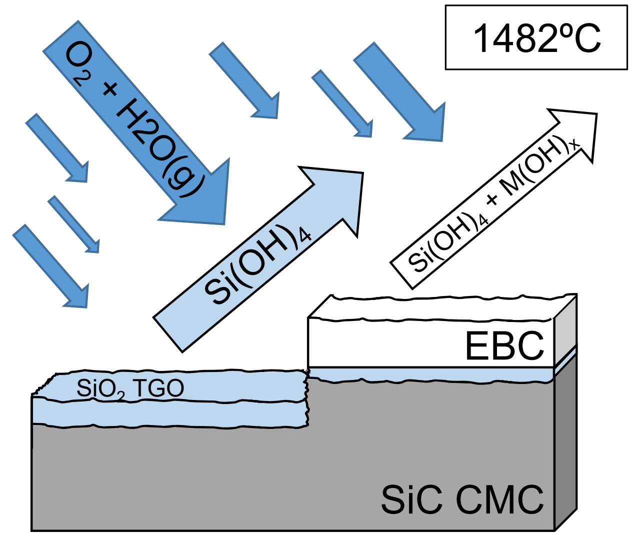
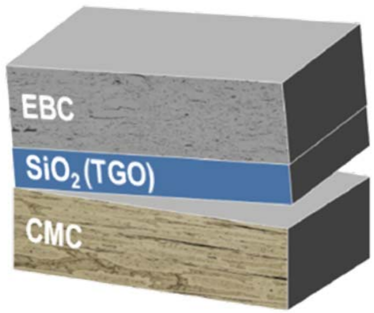



## Intrinsic Material Selection Criteria

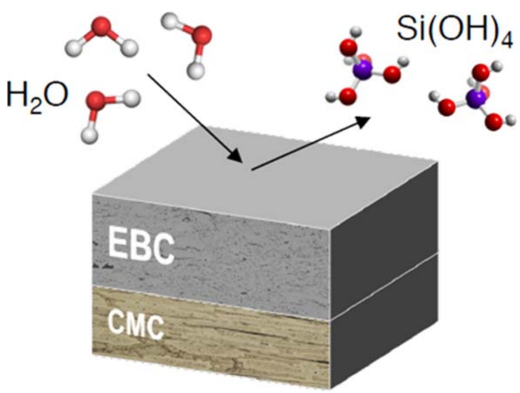
- **Coefficient of thermal expansion (CTE)**
- **Sintering resistance**
- **Low $H_2O$ and $O_2$ diffusivity/solubility**
- **Phase Stability**
- **Low Modulus**
- **Limited coating interaction**

# Environmental Barrier Coating Failure Modes

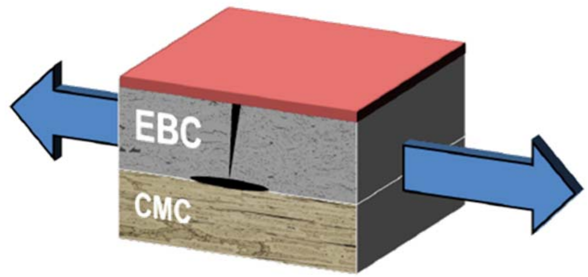
**EBC lifetime and design requirements determined by combination of extrinsic failure modes**



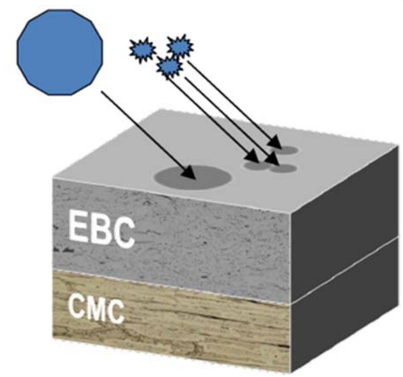

Steam Oxidation



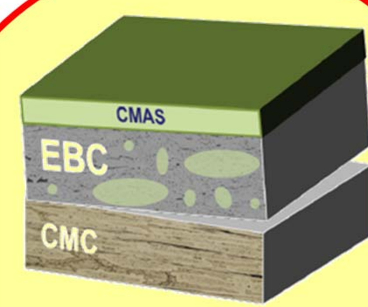

Hydroxide Formation/Recession




Thermomechanical Durability




Erosion and FOD



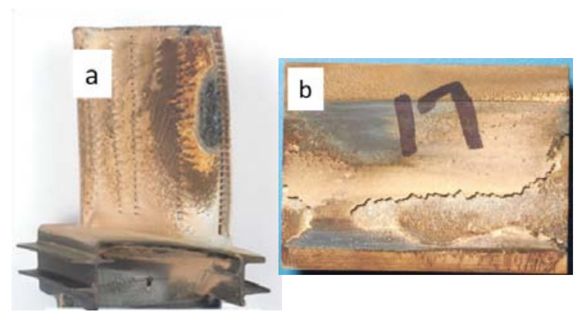

CMAS Attack & Infiltration

# Molten CMAS Damage to Protective Coatings

- Particulates (i.e. sand, volcanic ash) ingested by engine melt into **Calcium-Magnesium-Alumino-Silicate (CMAS)** deposits above 1200ºC
- Molten CMAS degrades EBCs (chemical + mechanical)
  - CMAS infiltration of EBC due to lowered CMAS viscosity at elevated temperatures → CTE mismatch
  - Thermochemical interactions of CMAS with EBC → spallation

Eyjafjallajökull volcano eruption in Iceland (2010)

Dust storm in Phoenix, Arizona (2017)




Coating loss on (a) high-pressure turbine blade and (b) turbine shroud caused by CMAS >1200ºC

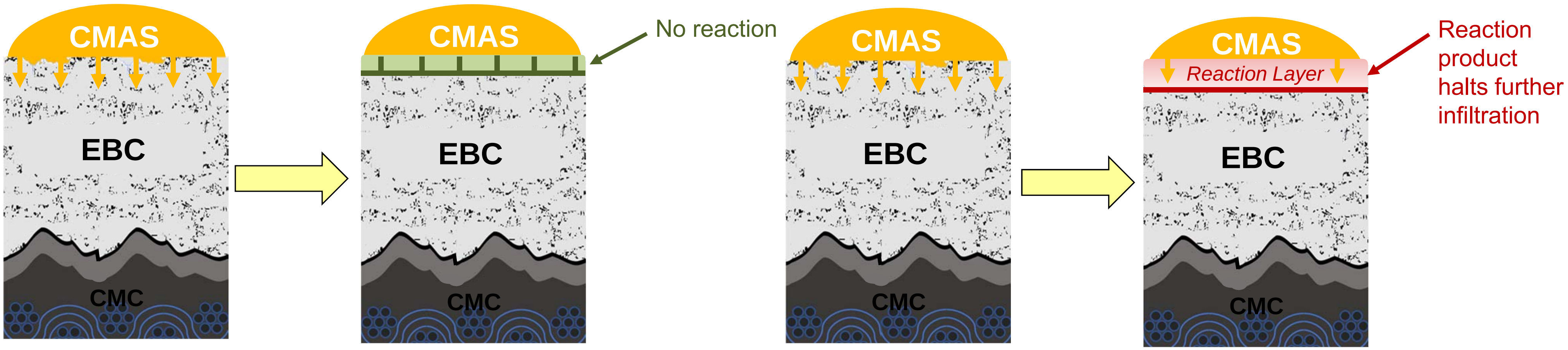
➢ **Need EBC materials resistant to molten CMAS attack above >1200ºC**

R Darolia, "Thermal Barrier Coatings Technology: Critical Review," (2015).

# CMAS Mitigation Strategies for EBCs

- *Minimize* reactivity of coating material with CMAS deposits
  - Thermodynamic stability over reaction products

- <u>*Maximize*</u> reactivity of coating material with CMAS deposits to induce crystallization
  - Crystallized reaction product barrier



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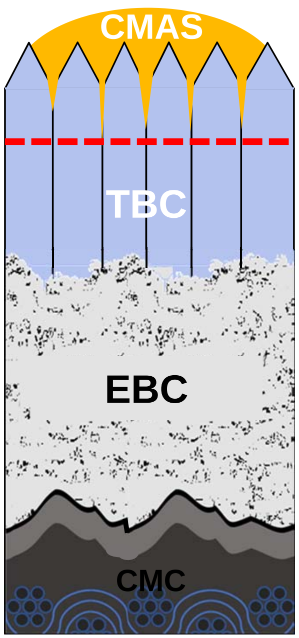
- *Minimize* reactivity of coating material with CMAS deposits
  - Thermodynamic stability over reaction products
- *Maximize* reactivity of coating material with CMAS deposits to induce crystallization
  - Crystallized reaction product barrier
- Multi-layered T/EBC architecture
  - Sacrificial topcoat
  - Larger thermal gradient




➢ **Inform evaluation and selection of candidate EBC materials and coatings**

# Critical Questions

*How do the properties of CMAS change with composition?*

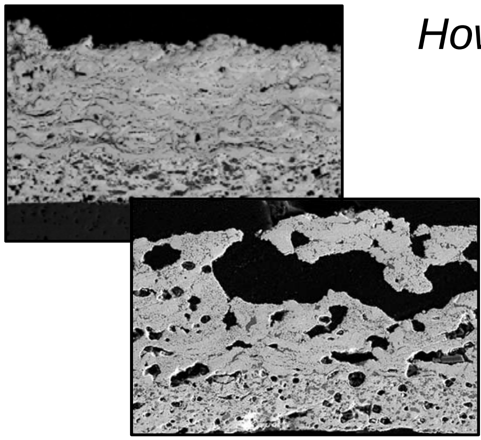
*Can we quantify CMAS/EBC reactions?*

*What materials are stable with CMAS?*

*Can we design CMAS resistant EBCs?*

*Can we develop accurate tests for CMAS?*

# Critical Questions



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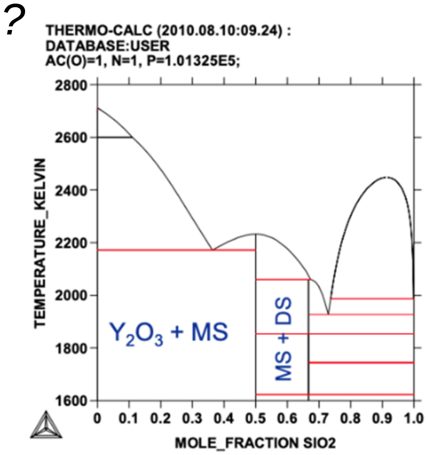



| Experimental Measurements | Experimental Thermodynamics | Computational Thermodynamics |
|---|---|---|
| • Expose CMAS to various EBC materials<br>• Single-point analysis | • Determination of quantities with experimentation<br>• Single-point measurement for periodic trend modeling<br>• Calorimetry, mass spectrometry | • First principles approach<br>• Periodic trends<br>• VASP, Thermo-Calc, FactSage |

# What Are the Various Types and Properties of CMAS?

**Relative Composition (mol%) of Sources and Deposits***

| | $SiO_2$ | CaO | MgO | $AlO_{1.5}$ | FeO | $CaO/SiO_2$ |
|---|---|---|---|---|---|---|
| Earth's Crust | 65 | 6 | 6 | 10 | 4 | 0.093 |
| Saudi Sand | 93 | 1 | < 1 | 4 | < 1 | 0.011 |
| Airport Runway Dust | 75 | 5 | 2 | 15 | 4 | 0.067 |
| Volcano Ash | 65 | 5 | 4 | 18 | 5 | 0.077 |
| Fly Ash | 40 | 5-20 | 5 | 20 | 5-20 | 0.125-0.5 |
| **Engine Deposits** | **25-40** | **20-35** | **7-15** | **10-15** | **7-15** | **0.5-1.43** |

**Engine Deposits have a wide composition range!**

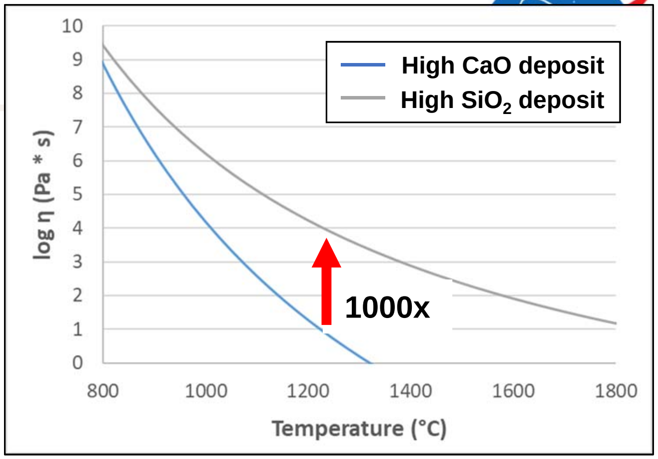
"Minority" minerals such as NaO $K_2O$, etc may provide complexity

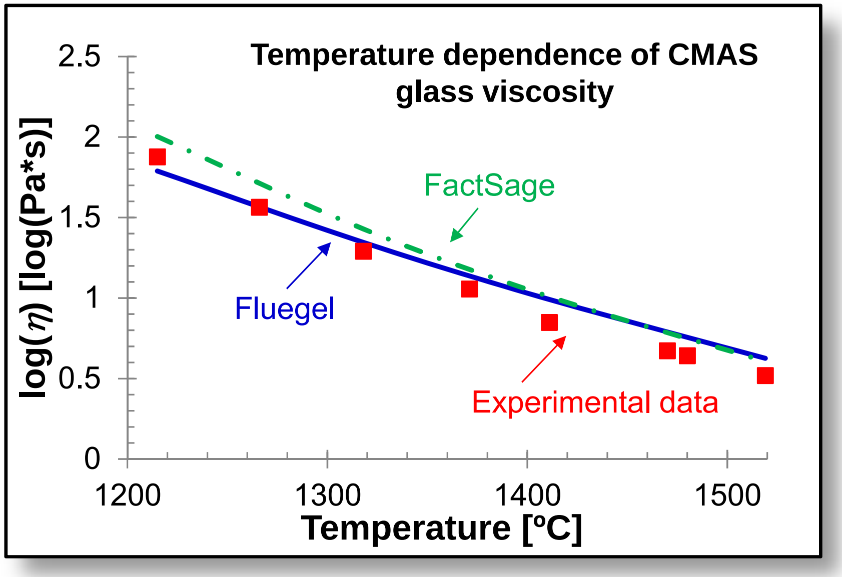
$CaO/SiO_2$ ratio is a critical factor in determining how CMAS will affect coatings

- Viscosity of melt
- Precipitation of apatite ($Ca_2RE_8(SiO_4)_6O_2$)

# Sand Composition Viscosity

- Viscosity of glass related to how fast/far the glass will infiltrate
- Low $CaO/SiO_2$ CMAS ratios have higher viscosity
  - Engine deposits can vary in viscosity by 3 orders of magnitude
- Viscosity of synthetic sand (CMAS) glass measured using high-temperature viscometer with platinum spindle
- Estimate infiltration time needed to penetrate 200 µm TBC
  - 4.3 minutes at 1200°C
  - 11 seconds at 1500°C




POC: Valerie Wiesner, Narottam Bansal


V.L. Wiesner, N.P. Bansal, Journal of the European Ceramic Society, 35 (2015) 2907-2914.
V.L. Wiesner, U. Vempati, N.P. Bansal, *Scripta Materialia*, 124 (2016) 189-192.

# How Do Different CMAS Compositions React with EBCs?

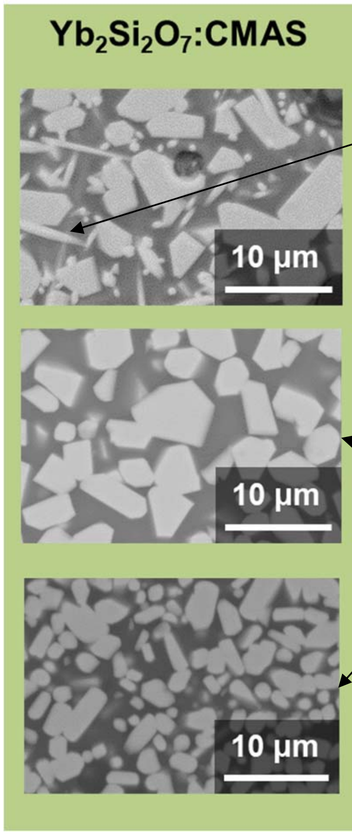
1400°C/1hr
50:50 mol% ratio

Decreasing Ca/Si Ratio

0.635

0.451

0.092




Apatite formation

$$RE_2Si_2O_{7(xl)} + 0.5CaO_{(CMAS)} = 0.5CaRE_4Si_3O_{13(xl)} + 0.5SiO_{2(CMAS)}$$

No Apatite formation

$$RE_2Si_2O_{7(xl)} + 0.5CaO_{(CMAS)} = RE_2Si_2O_{7(xl)} + 0.5CaO_{(CMAS)}$$

POC: Jamesa Stokes

J.L.Stokes, et al., J. Am. Ceram. Soc., 2019, doi; 10.1111/jace.16694

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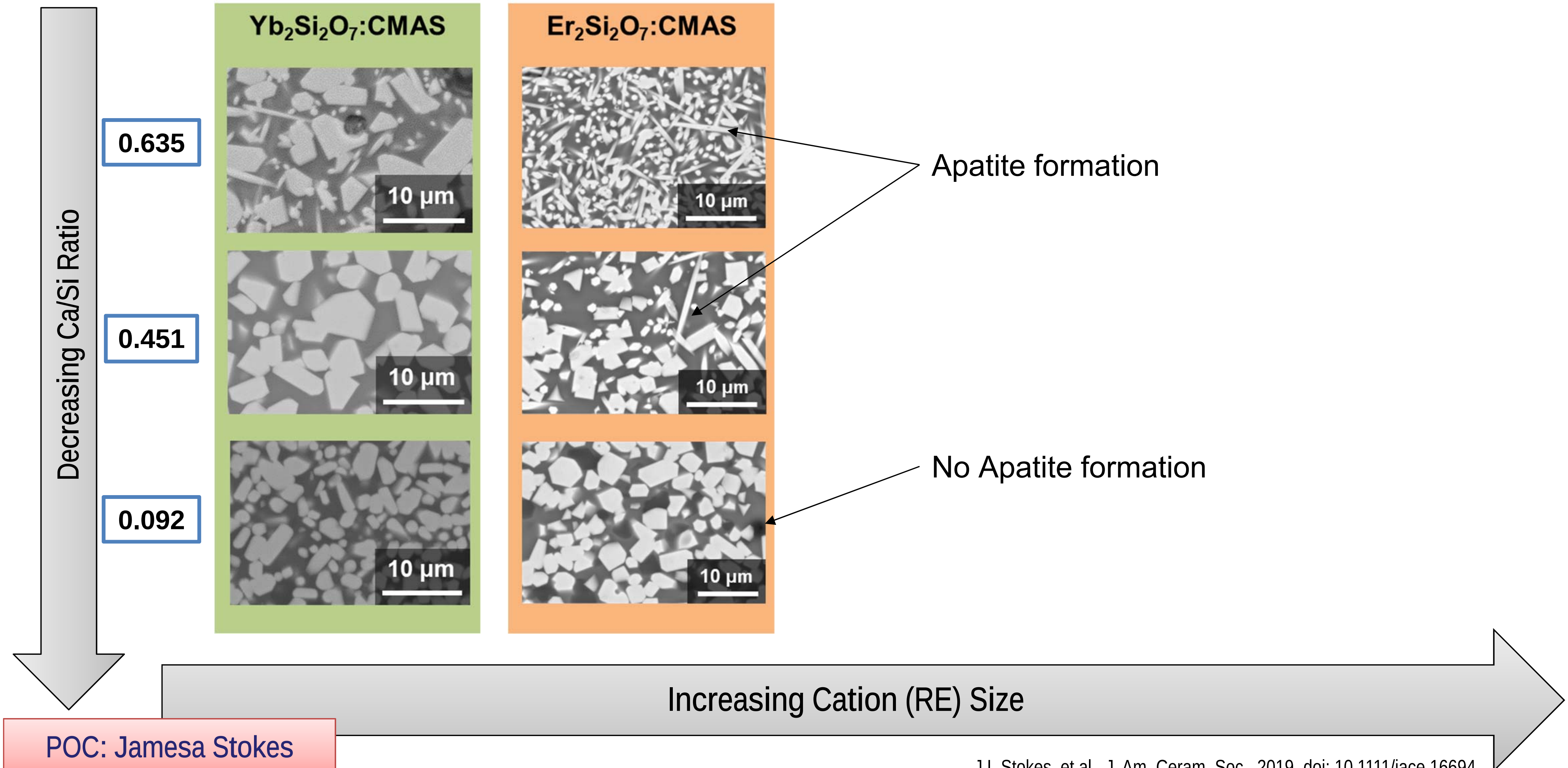


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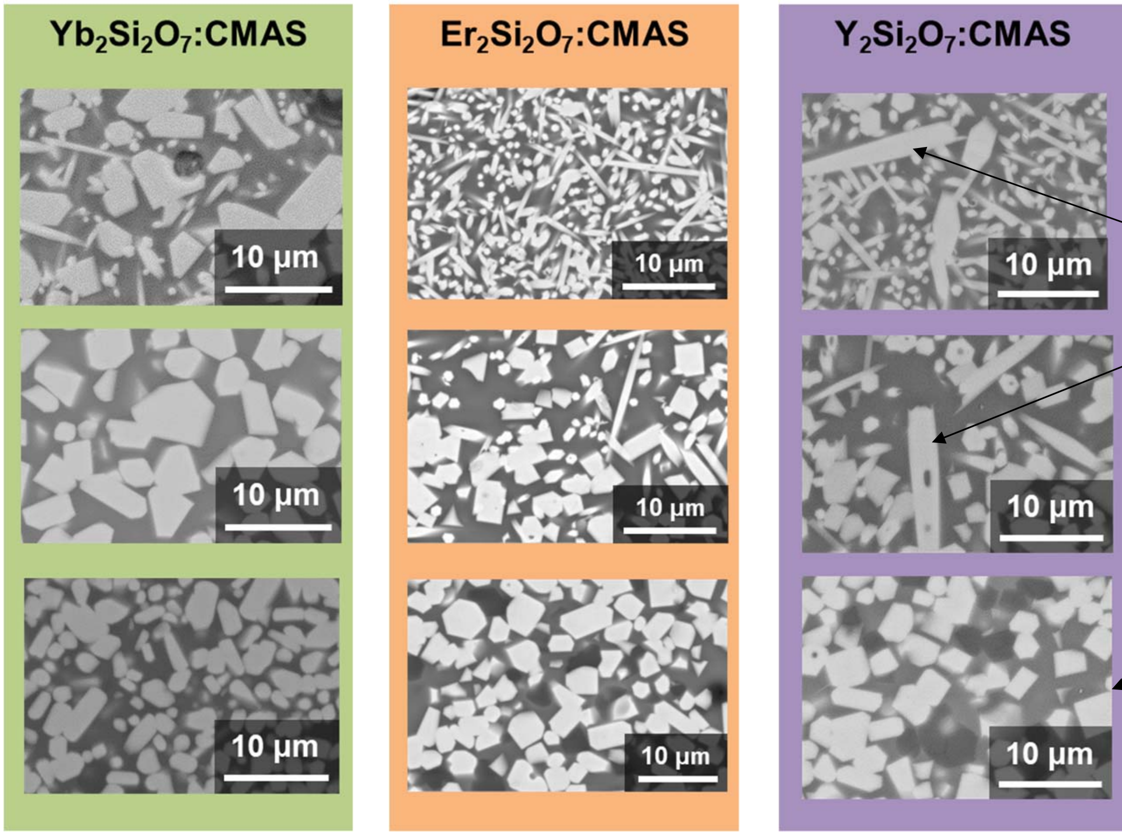


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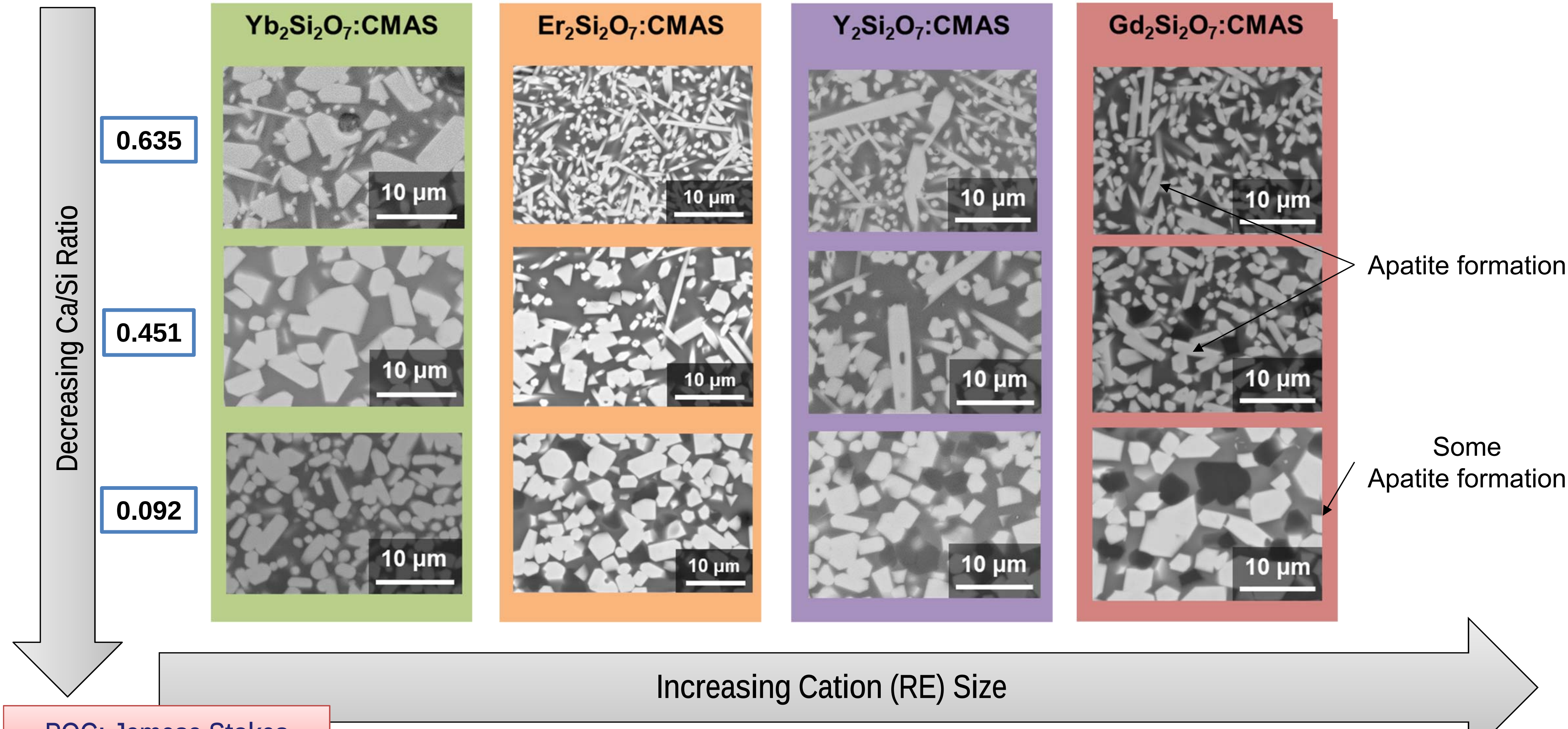


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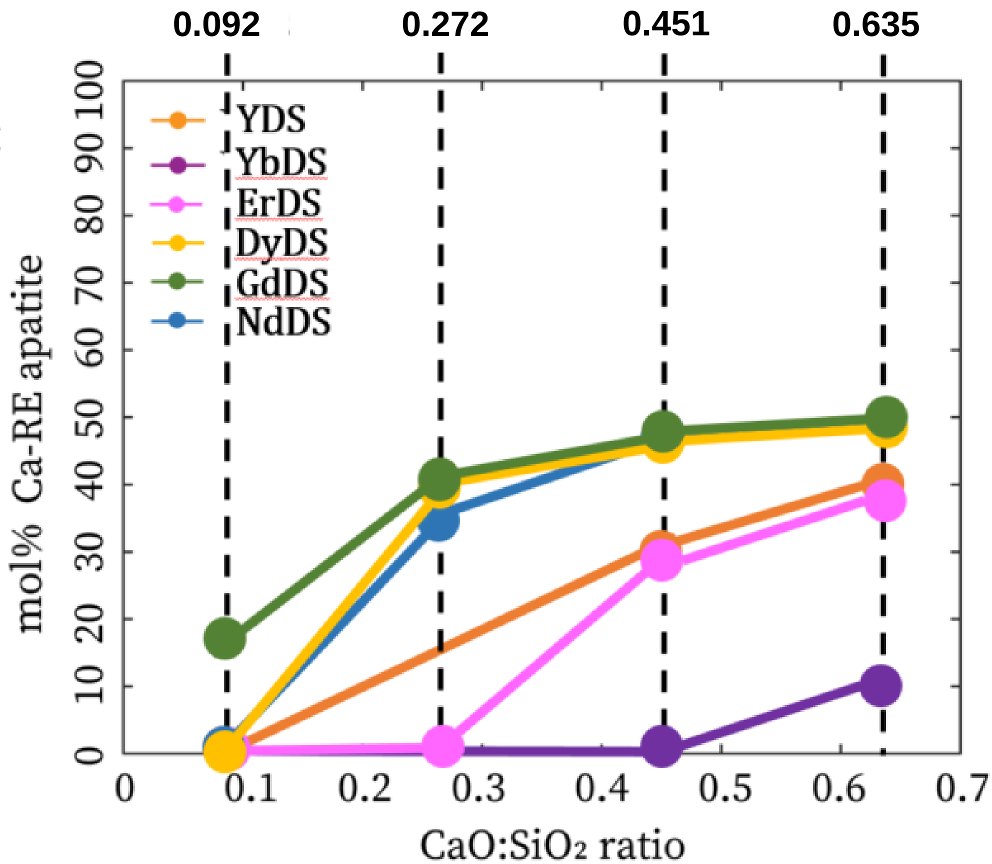
# How Do Different CMAS Compositions React with EBCs?

- Amount of apatite phase changed as a function of glass composition and RE cation species
  - Smaller RE cannot stabilize with CaO-lean compositions
  - As RE size increases, stabilization is possible but preferential liquid formation may hinder apatite formation

- Not all RE-disilicate systems have ideal CTE matches for SiC/SiC systems (~4x10$^{-6}$ /°C)

- Mixing of these silicate systems may aid in promoting crystallization of molten deposits across a range of CaO:$SiO_2$ ratios

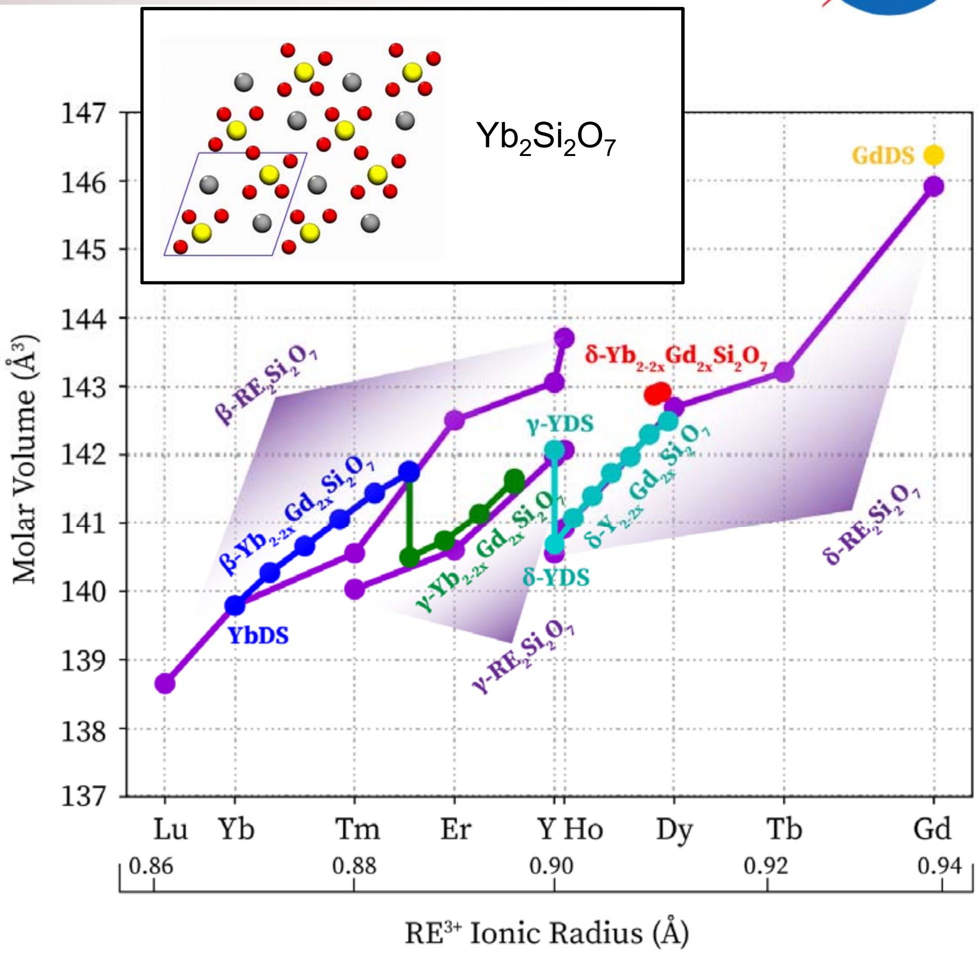



POC: Jamesa Stokes, Brian Good

J.L.Stokes, et al., J. Am. Ceram. Soc., 2019, doi; 10.1111/jace.16694

# Can We Design New EBC Compositions for CMAS Resistance?

- Density Functional Theory (DFT) can be used to predict disilicate crystal structures
- Yb-disilicate β-phase chosen as ideal phase
- When dopant atomic radii are significantly larger than the radius of Yb, the structure is more likely to be disrupted
- Results are supported by initial testing of doped Yb-silicate compositions
- CMAS resistance testing of doped coatings is ongoing

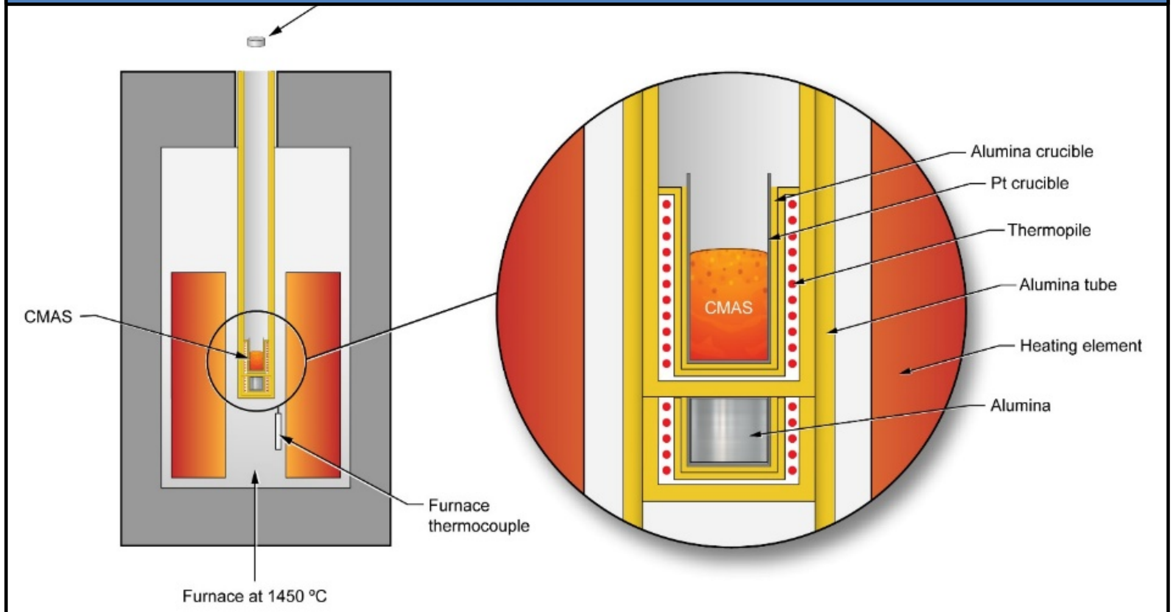



POC: Brian Good, Jamesa Stokes

# Can we measure CMAS reactions or stability?

- Drop coating material in molten CMAS or lead borate
- Measured change in temperature is related to reactivity with solvent
- Determine enthalpy of solution ($\Delta H_s$), mixing ($\Delta H_{mix}$) and reaction ($\Delta H_{reaction}$)
- Compare the stability of both the coating material and reaction products
- Results incorporated into a thermodynamic database

**Drop Solution Calorimetry**




POC: Gustavo Costa

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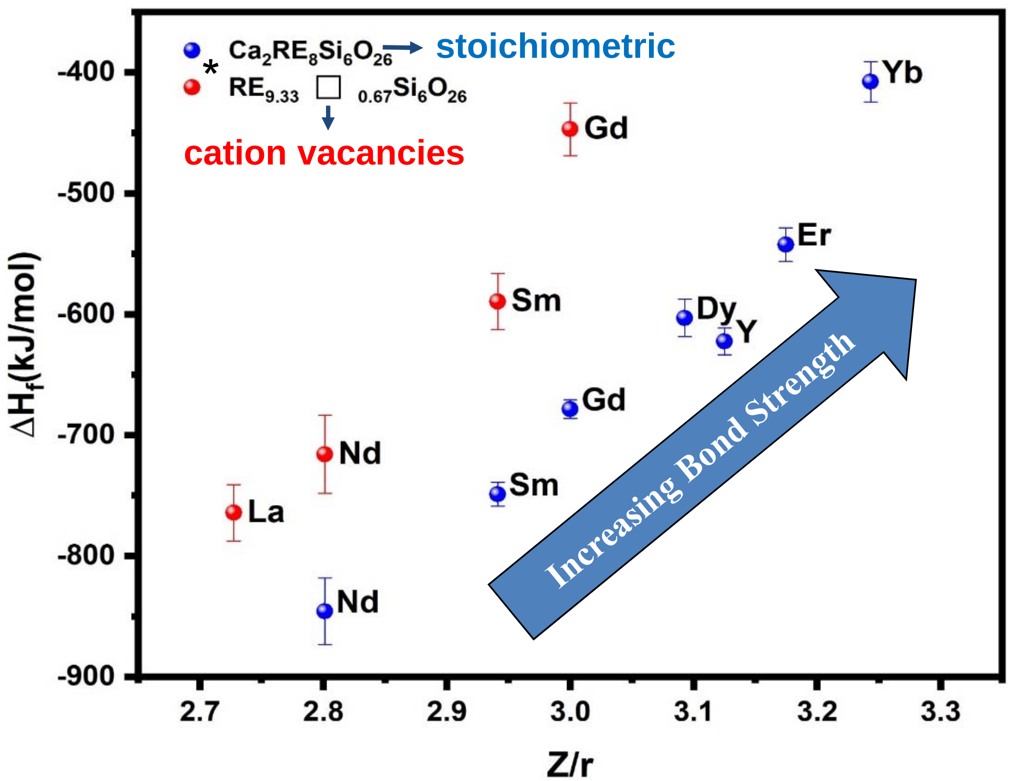
Enthalpy of formation of the RE-apatites

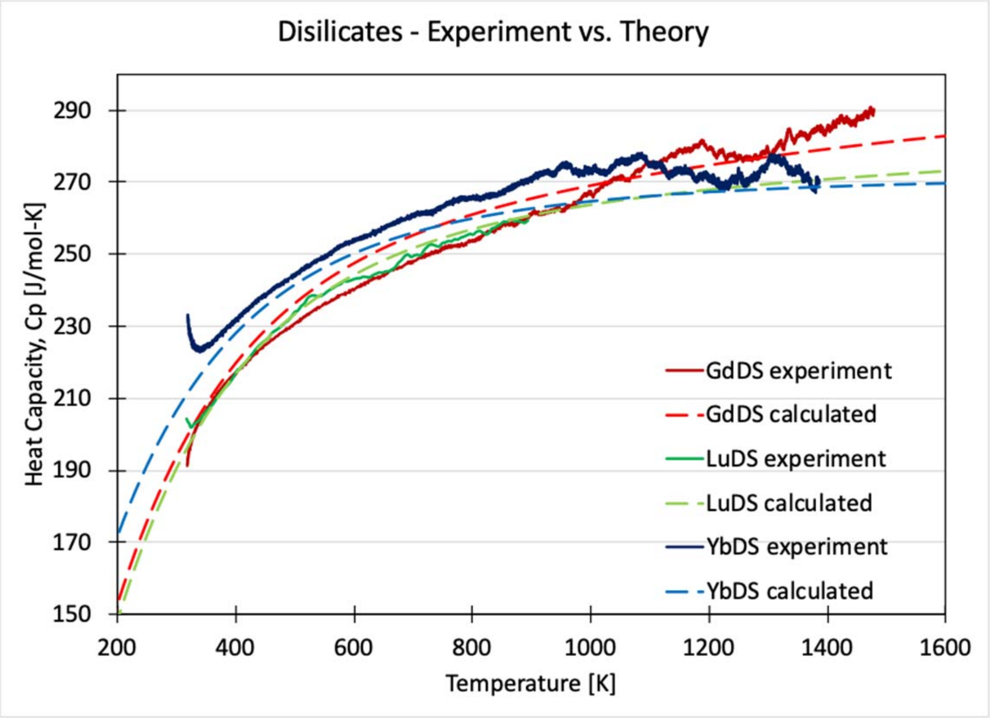



POC: Gustavo Costa

*Risbud et al J. Mater. Res. 2001. Costa et al, J. Am. Ceram Soc. 2019.

# Can we calculate CMAS reactions or stability?

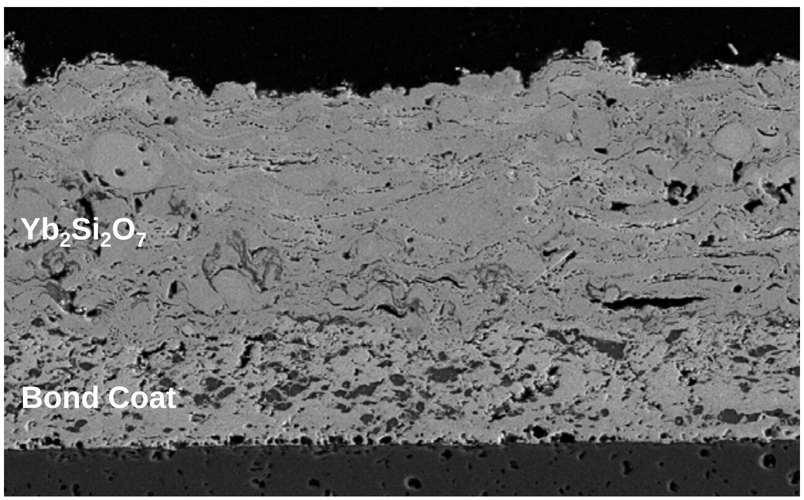
- First principles methods using density functional theory (DFT) can provide thermodynamic quantities
- Phonon calculations for RE-silicate materials can generate:
  - Heat capacity ($c_p$)
  - Entropy
  - Coefficient of Thermal Expansion (CTE)
  - Enthalpy of formation
- RE-silicates challenging due to complex electronic structure
- Initial results with heat capacity ($c_p$) and entropy are encouraging



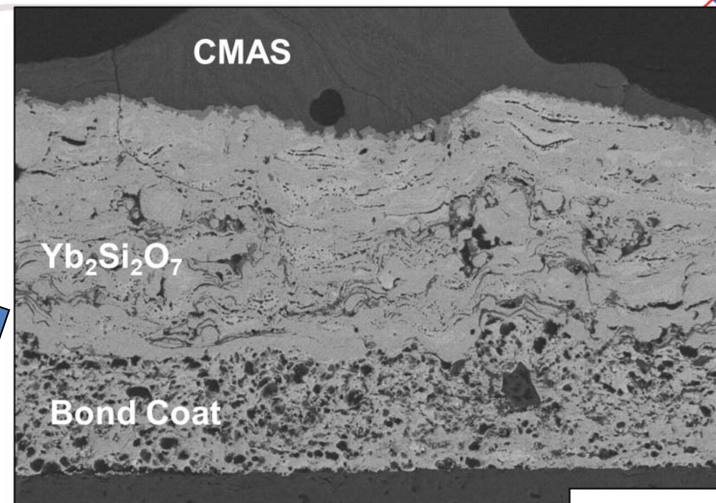

POC: Cameron Bodenschatz, Brian Good, Michael Kulis

# How will CMAS React with Coatings?

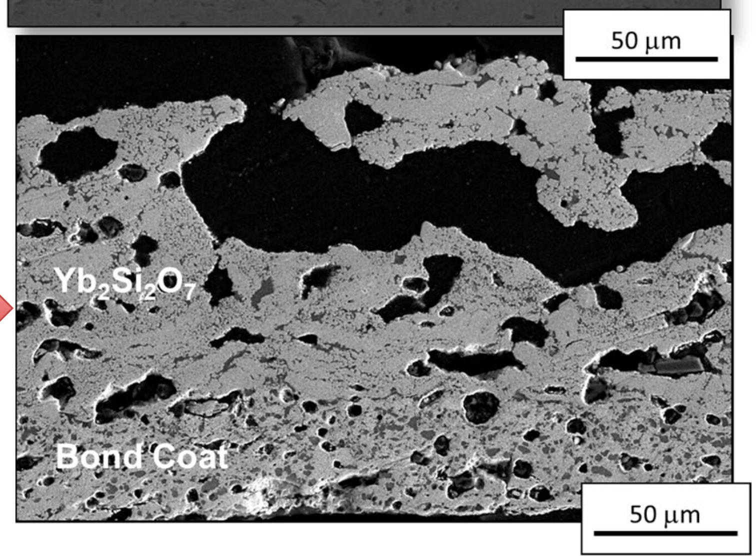
- Yb-silicate does not react strongly with CMAS but affords no protection in the coating system
- Tested with a CMAS loading of 35 $mg/cm^2$
- Molten CMAS infiltrates by a combination of dissolution-precipitation and grain boundary penetration mechanisms




1200°C/10hr (air)




1400°C/1 hr (air)

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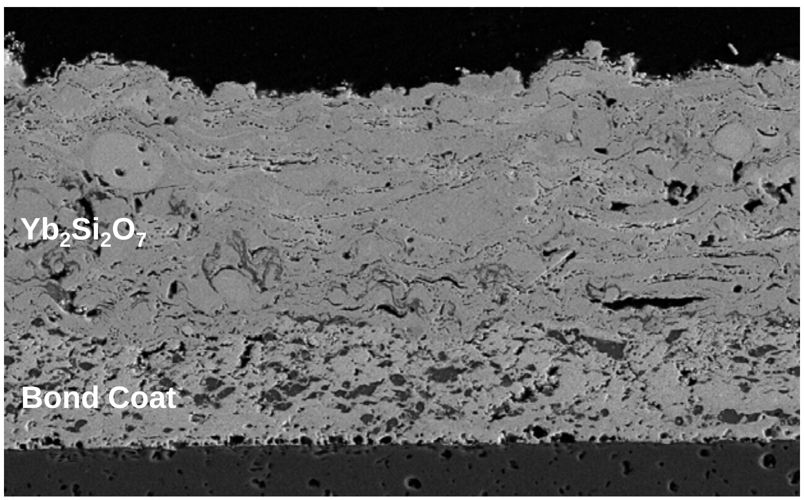


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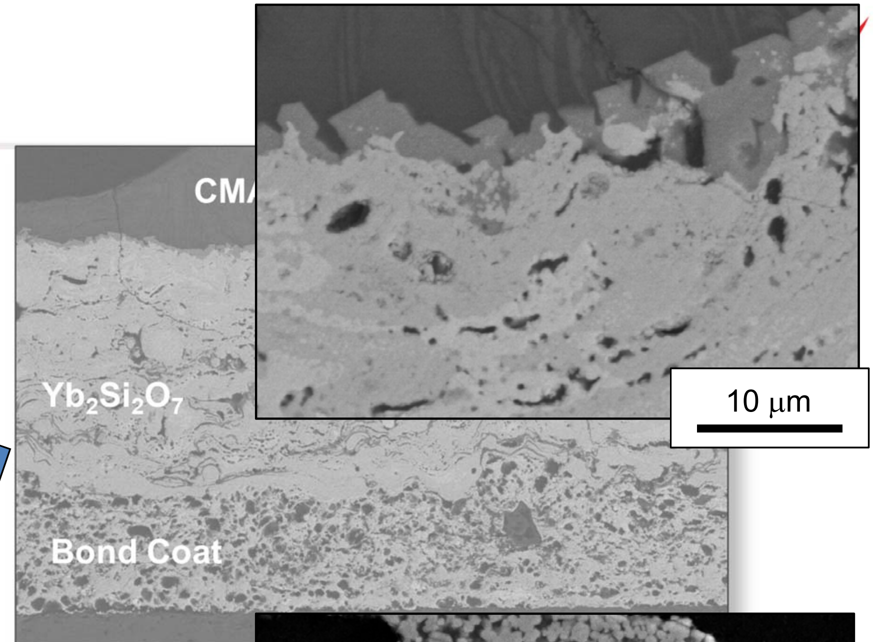


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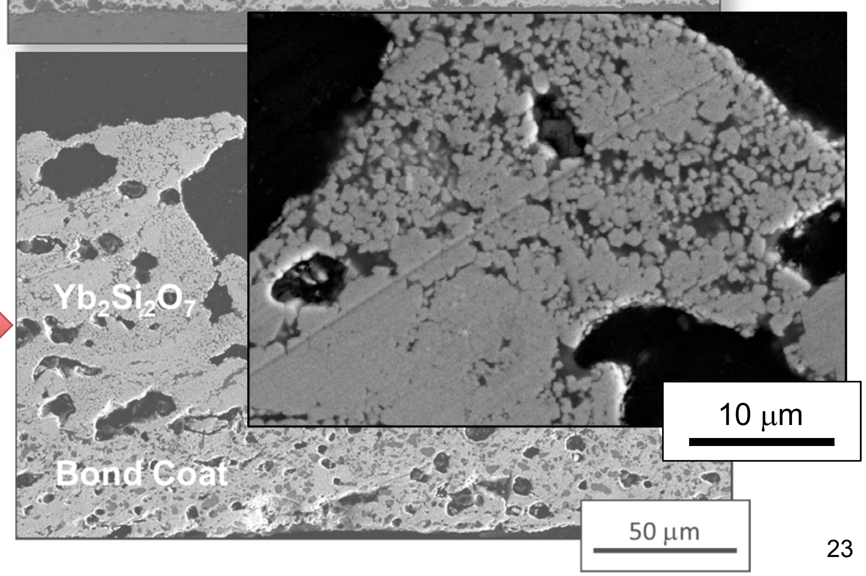


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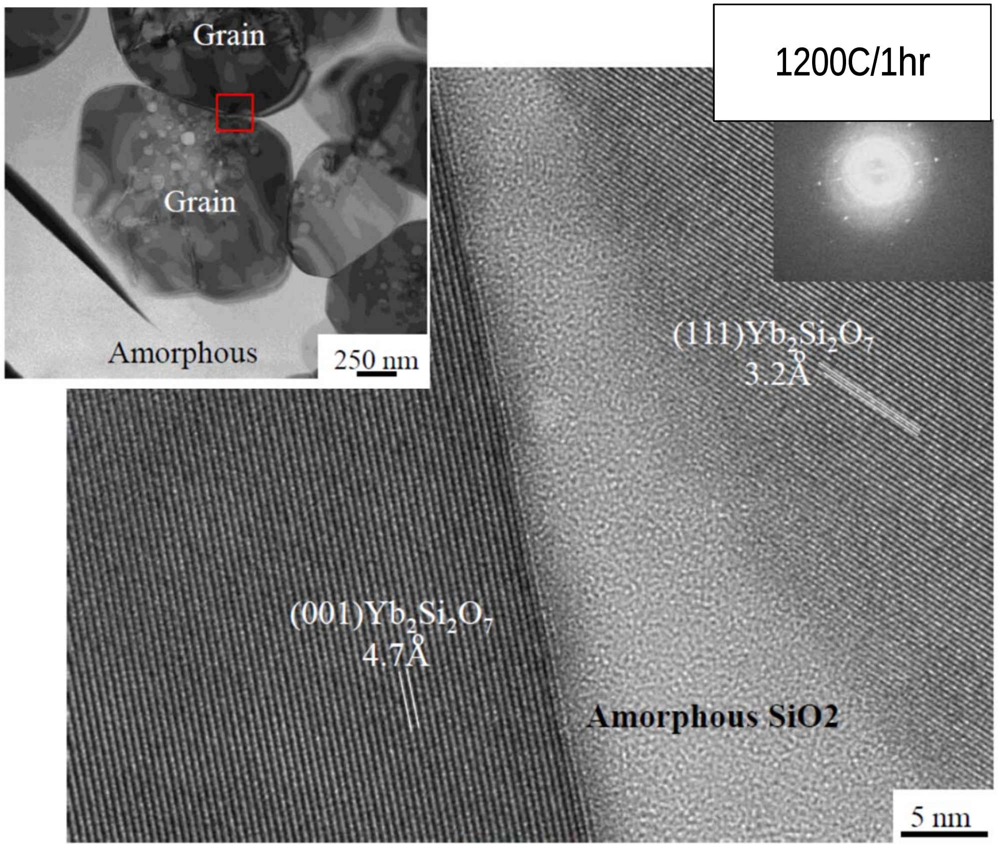
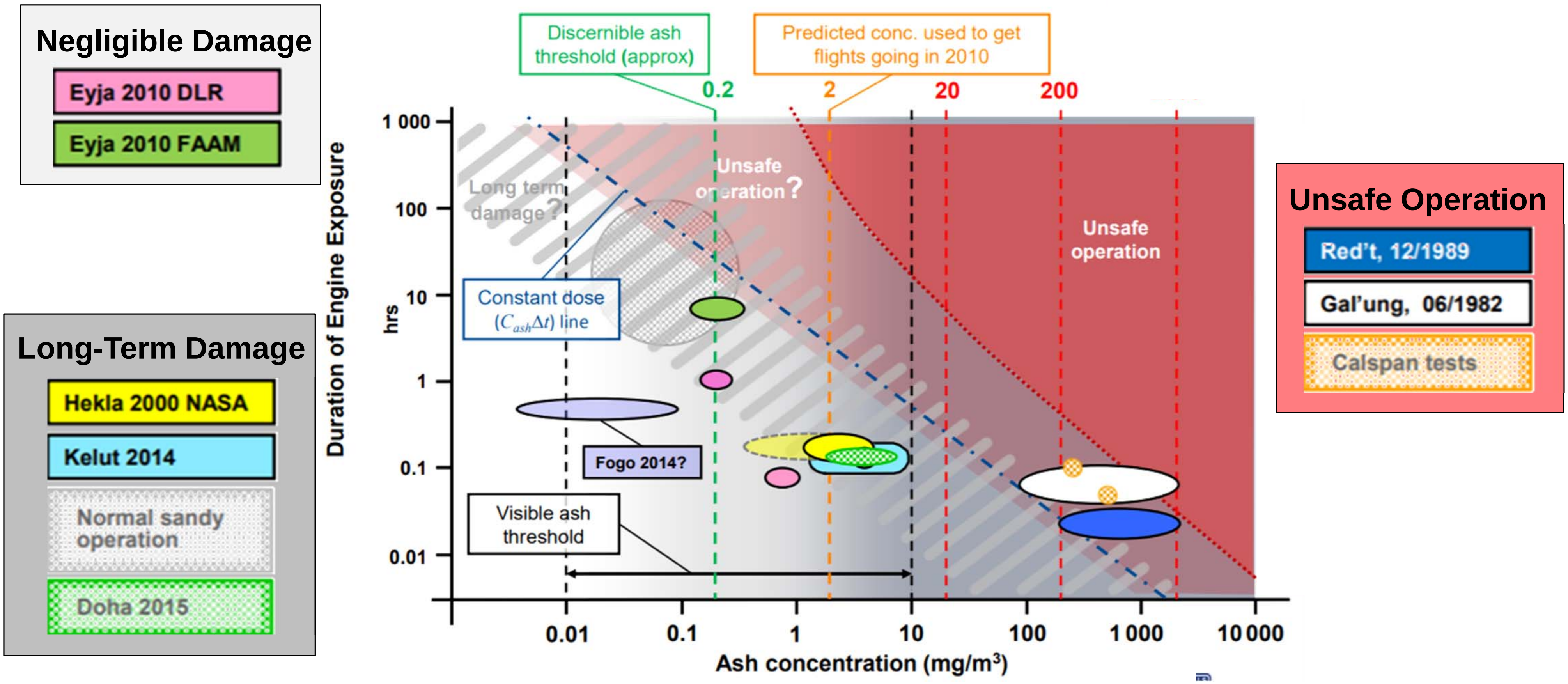
- Molten CMAS infiltrates by a combination of dissolution-precipitation and grain boundary penetration mechanisms
- TEM results have indicated significant $SiO_2$ present between the grains of $Yb_2Si_2O_7$
  - Infiltration may occur quickly at very low concentrations




POC: Valerie Wiesner, Bryan Harder

# How can we accurately test EBCs with CMAS?

- Duration of engine exposure vs. ash concentration (DEvAC)

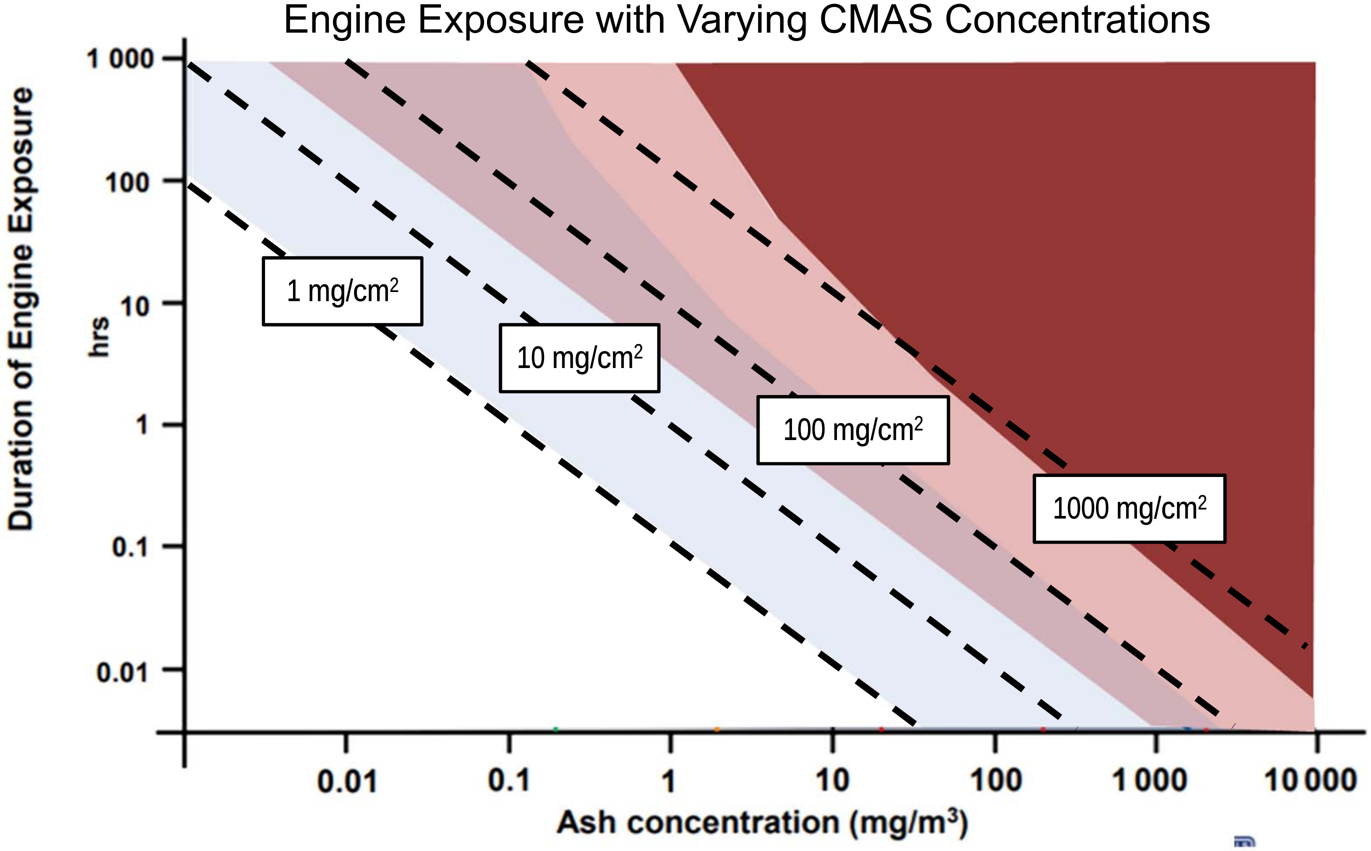



R. Clarkson and H. Simpson, "Maximising Airspace Use During Volcanic Eruptions: Matching Engine Durability against Ash Cloud Occurrence," (2019)

# How can we accurately test coatings with CMAS?

*Assumptions*

- 575 kg/s air intake during cruise
- 1 x $10^5$ $cm^2$ engine surface area
- 1% CMAS ingested sticks
- 30,000 ft altitude

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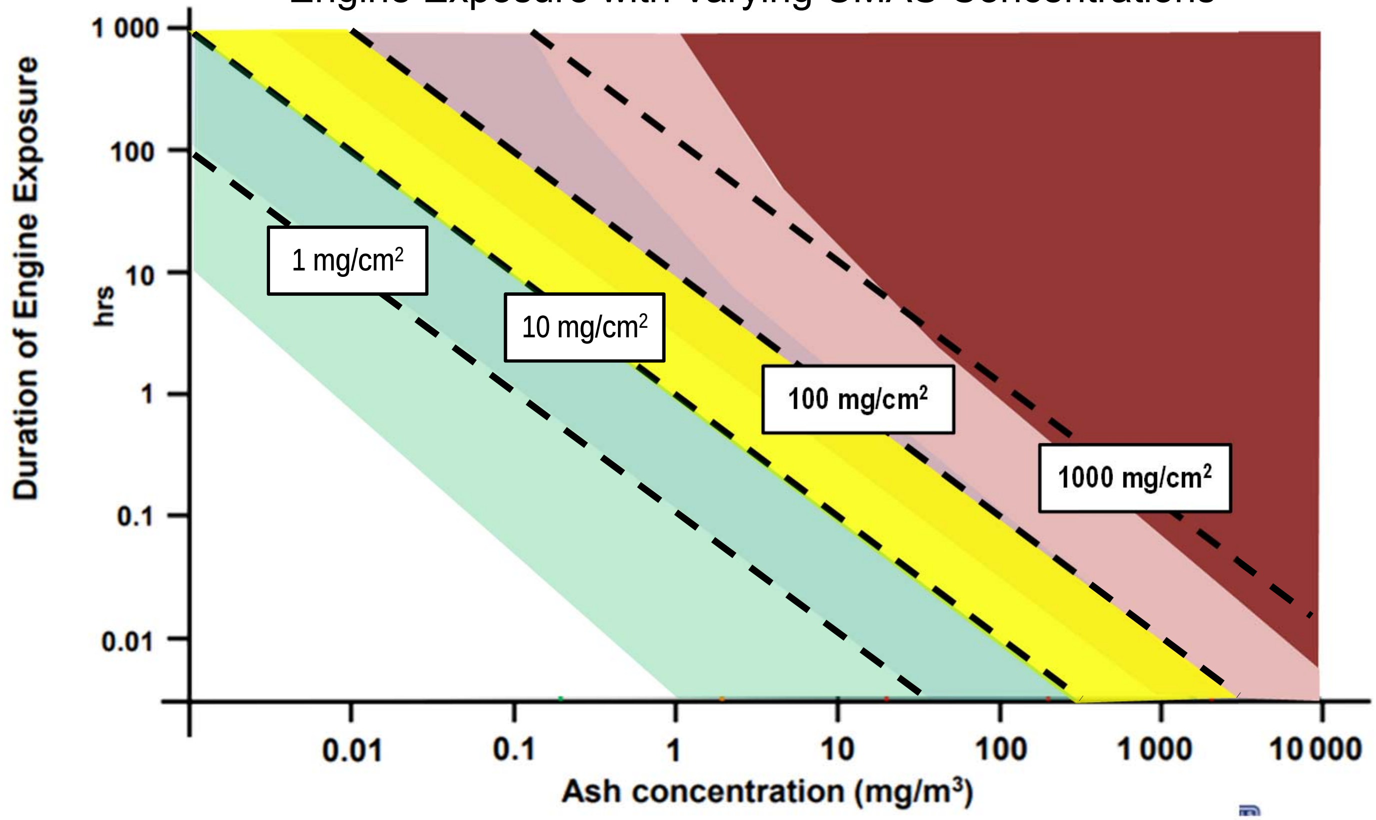
# How can we accurately test coatings with CMAS?

- Majority of testing 10-100 mg/cm$^2$
- Little known at lower concentrations
  - May affect long term operation
  - Unknown degradation modes
- Require continuous exposure for 'realistic' test

Engine Exposure with Varying CMAS Concentrations

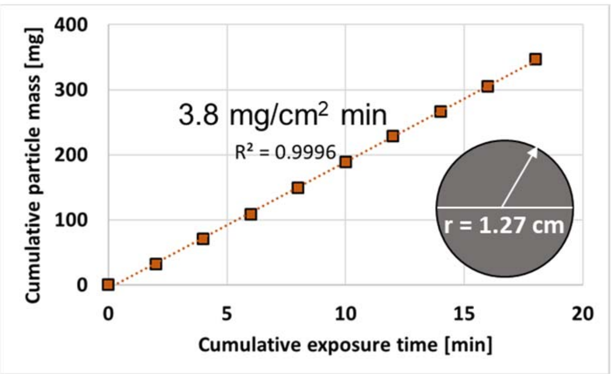


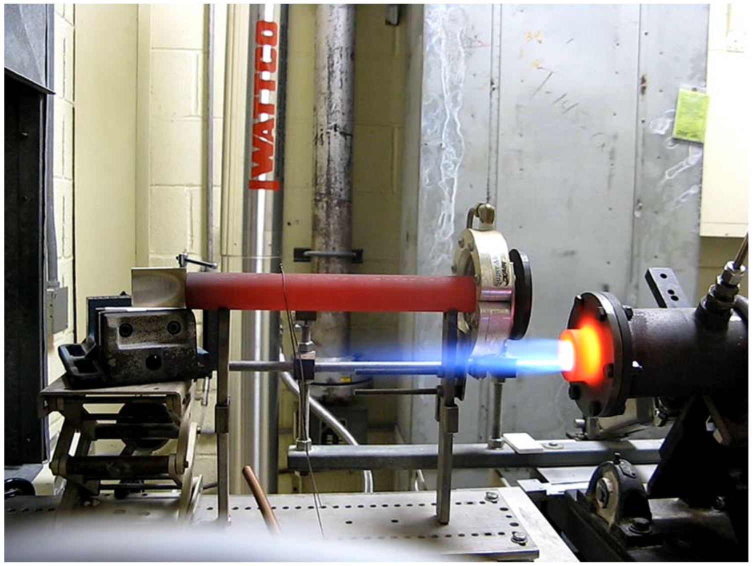

R. Clarkson and H. Simpson, "Maximising Airspace Use During Volcanic Eruptions: Matching Engine Durability against Ash Cloud Occurrence," (2019)

# How can we accurately test EBCs with CMAS?

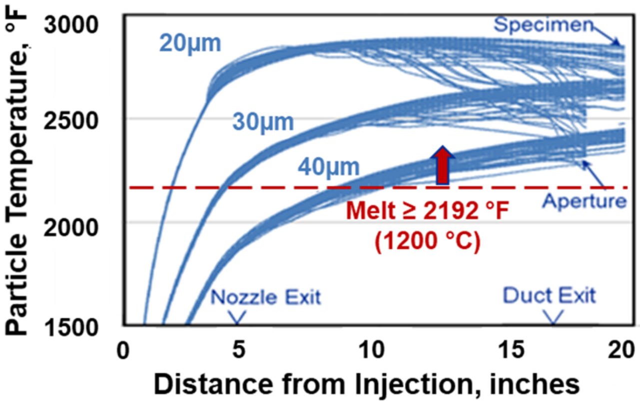
- CMAS deposition can be performed with modified Mach 0.3 – 1.0 burner test rig at NASA GRC
- Computational fluid dynamics (CFD) modeling predicts CMAS glass particles injected into the burner should be molten by the time they reach/impinge on the target
- ‘Low’ CMAS feeding rates can be achieved with consistency/repeatability
  - Continuous exposures at temperature/thermal cycling to better simulate cumulative engine exposure

**Low CMAS Feed Rate Consistency**



**Temperature History of CMAS Glass Particles**




POC: Michael Presby

# Critical Questions

- How do the properties of CMAS change with composition?

  Ca/Si ratio and viscosity are critical properties, and trace oxides may affect reactivity.

- Can we quantify CMAS/EBC reactions?

  Calorimetry and experimentation can provide quantities for determining periodic trends.

- What materials are stable with CMAS?

  Calorimetry and computational methods are beginning to measure material stabilities.

- Can we design CMAS resistant EBCs?

  Computational methods are in the early stages, but are showing promise for materials design.

- Can we develop accurate tests for CMAS?

  More ‘realistic’ methods are being developed, but nothing will be perfect (besides an engine).

## Summary

| Experimental Measurements | Experimental Thermodynamics | Computational Thermodynamics |
|---|---|---|

- Development of CMAS resistant architectures will require a combined approach of experiment and theory.
- While experimental measurements can provide valuable point information about reactions, thermodynamics should be used to generate a map for periodic trends.
- Computational methods will assist in the development of near-term trends, and will become more predictive/prescriptive in the future.
- Testing in ‘realistic’ environments is critical for model validation.

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