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

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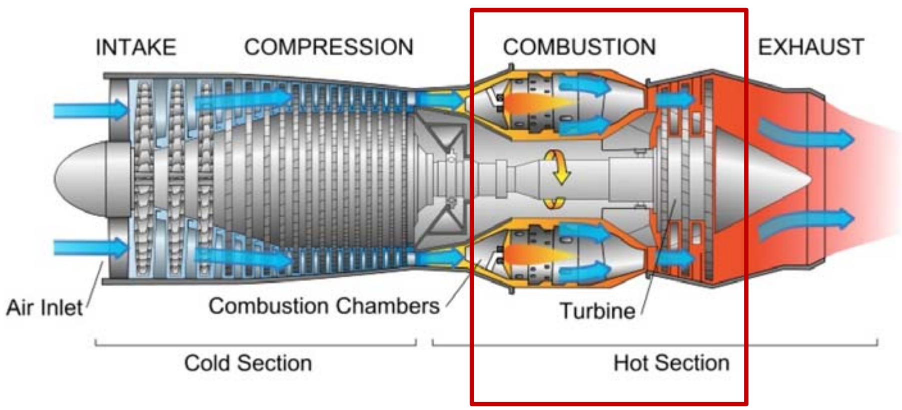
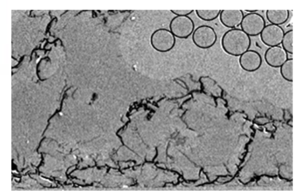
Enabling Game-Changing Materials for Commercial Aviation

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

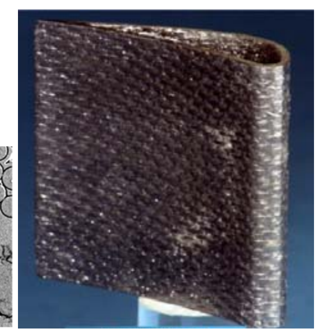
- **6% increase in fuel efficiency → savings of ~$400,000/plane/year**



Target: 1482ºC



Micrograph of CMC cross-section

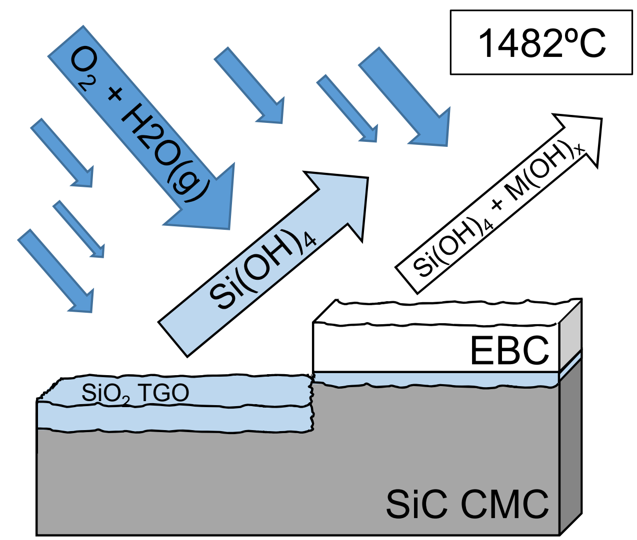


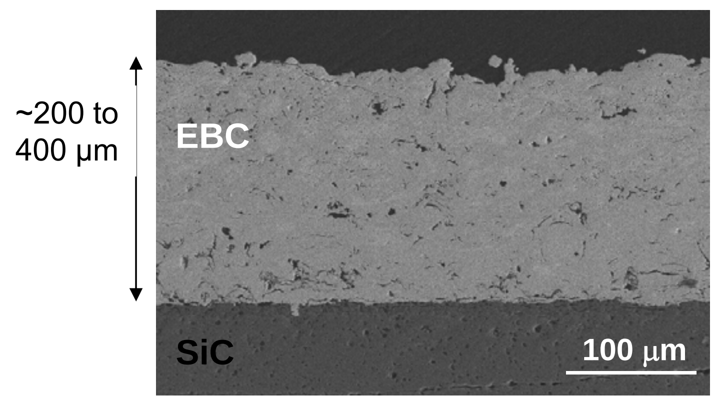
SiC/SiC CMC inlet turbine vane

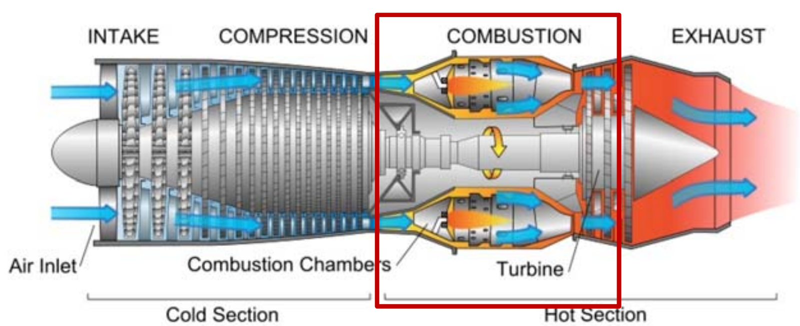
D. Zhu et al., "EBCs for Turbine Engines," *NTRS* (2009).
Image credit: NASA Glenn Research Center

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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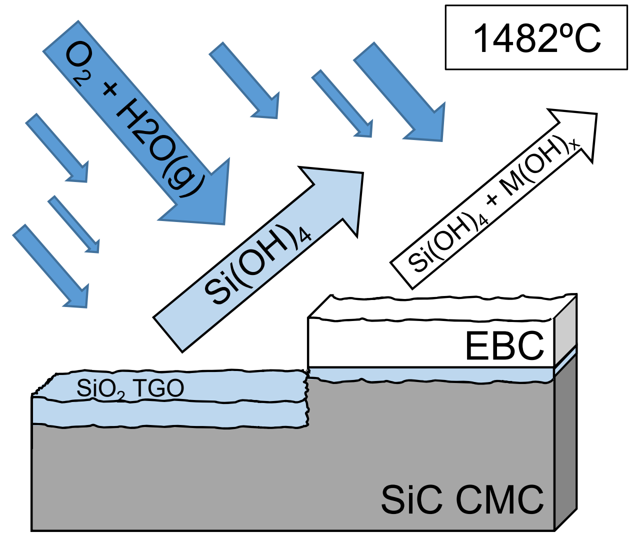
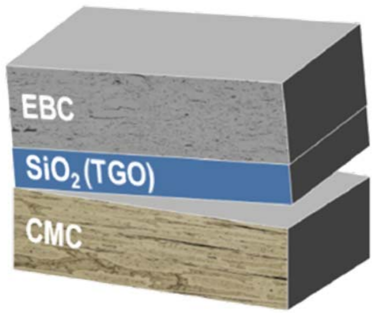


Intrinsic Material Selection Criteria

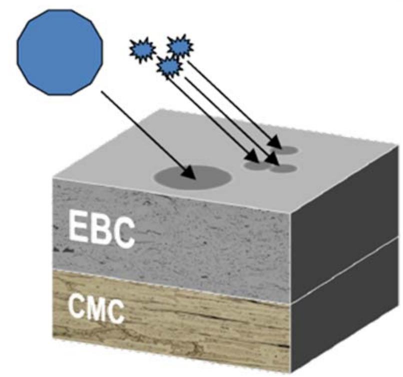
- **Coefficient of thermal expansion (CTE)**
- **Sintering resistance**
- **Low H_2O and O_2 diffusivity/solubility**
- **Phase Stability**
- **Low Modulus**
- **Limited coating interaction**

Environmental Barrier Coating Failure Modes

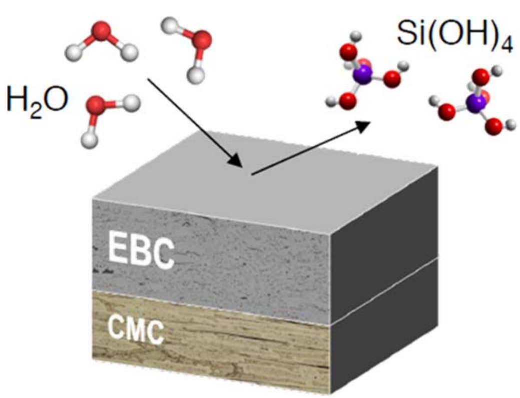


Steam Oxidation

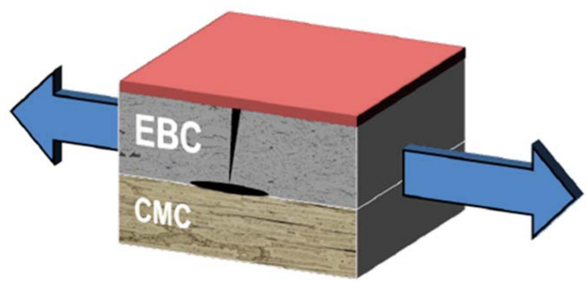
EBC lifetime and design requirements determined by combination of extrinsic failure modes



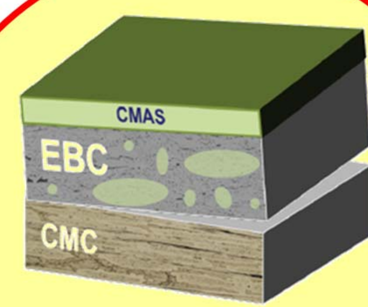
Erosion and FOD



Hydroxide Formation/Recession



Thermomechanical Durability



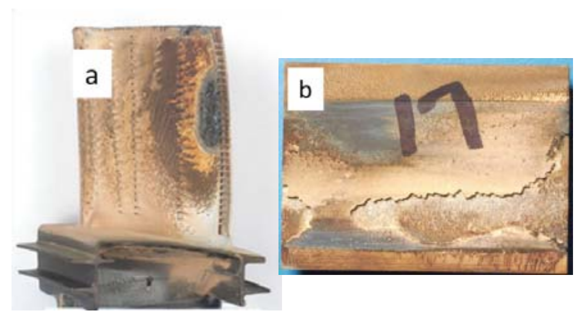
CMAS Attack & Infiltration

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)



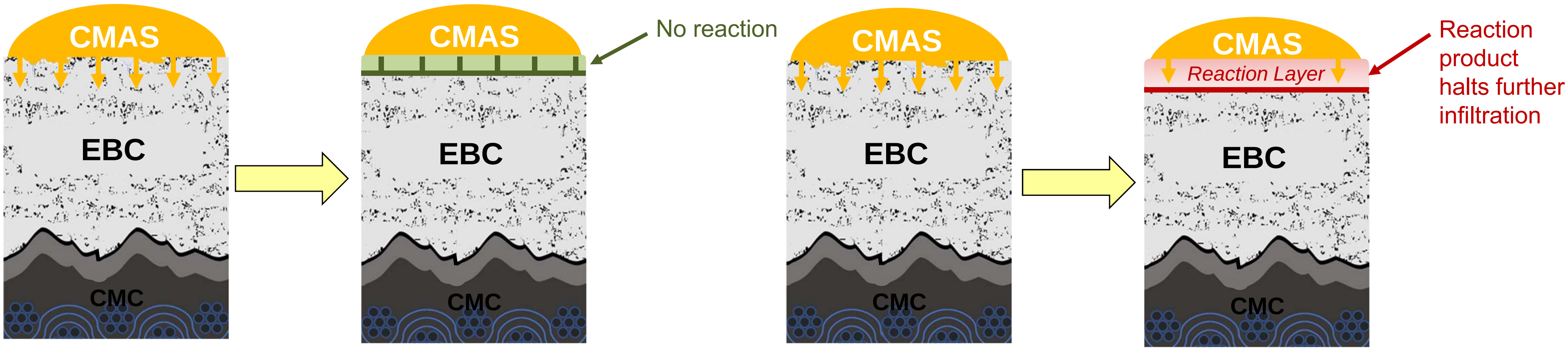
Coating loss on (a) high-pressure turbine blade and (b) turbine shroud caused by CMAS >1200ºC

➢ **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
- *Maximize* reactivity of coating material with CMAS deposits to induce crystallization
  - Crystallized reaction product barrier



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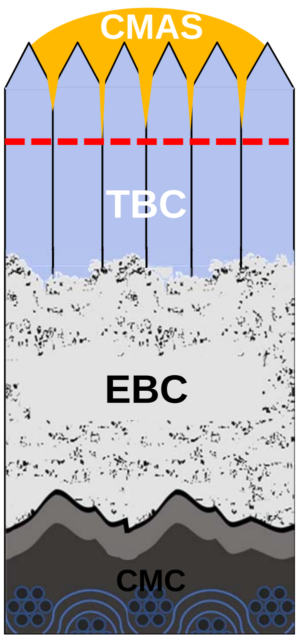
  - Thermodynamic stability over reaction products
- *Maximize* reactivity of coating material with CMAS deposits to induce crystallization
  - Crystallized reaction product barrier
- Multi-layered T/EBC architecture
  - Sacrificial topcoat
  - Larger thermal gradient

➢ **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?

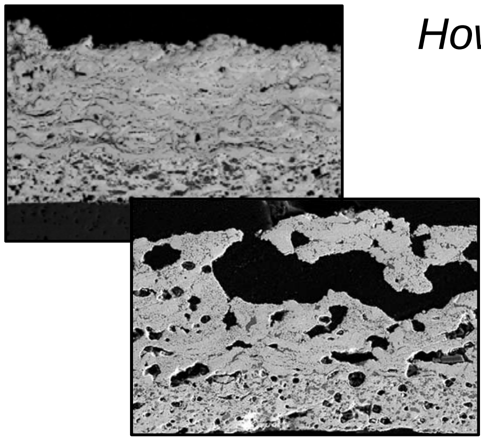
What materials are stable with CMAS?

↓

Can we design CMAS resistant EBCs?

Can we develop accurate tests for CMAS?

Critical Questions



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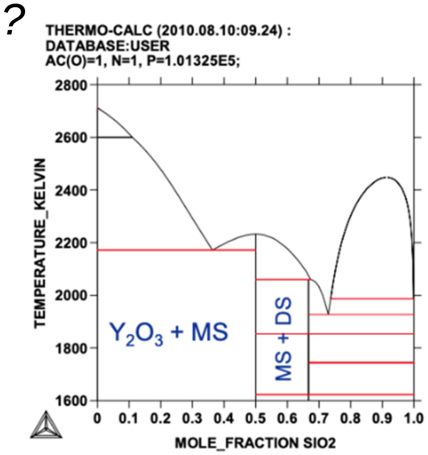


Experimental Measurements	Experimental Thermodynamics	Computational Thermodynamics
• Expose CMAS to various EBC materials • Single-point analysis	• Determination of quantities with experimentation • Single-point measurement for periodic trend modeling • Calorimetry, mass spectrometry	• First principles approach • Periodic trends • 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!

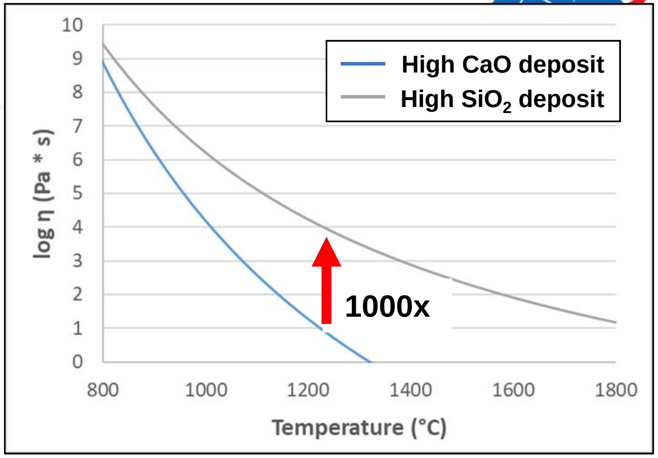
"Minority" minerals such as NaO K_2O, etc may provide complexity

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

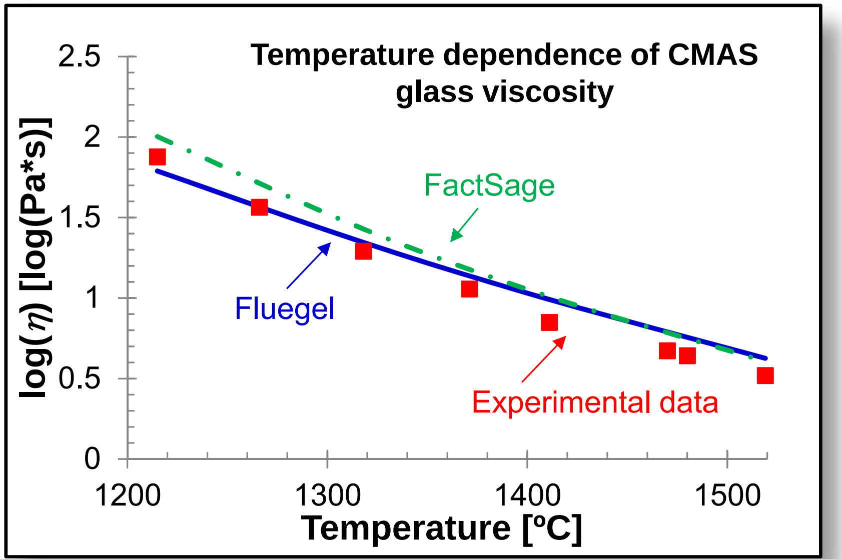
- Viscosity of melt
- Precipitation of apatite ($Ca_2RE_8(SiO_4)_6O_2$)

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

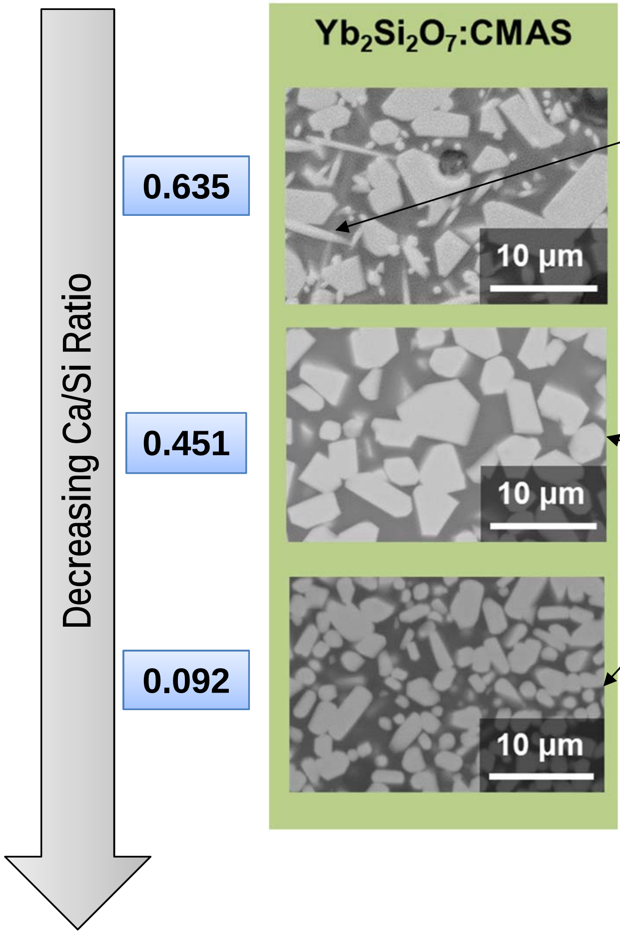


POC: Valerie Wiesner, Narottam Bansal

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.

1400°C/1hr
50:50 mol% ratio

How Do Different CMAS Compositions React with EBCs?



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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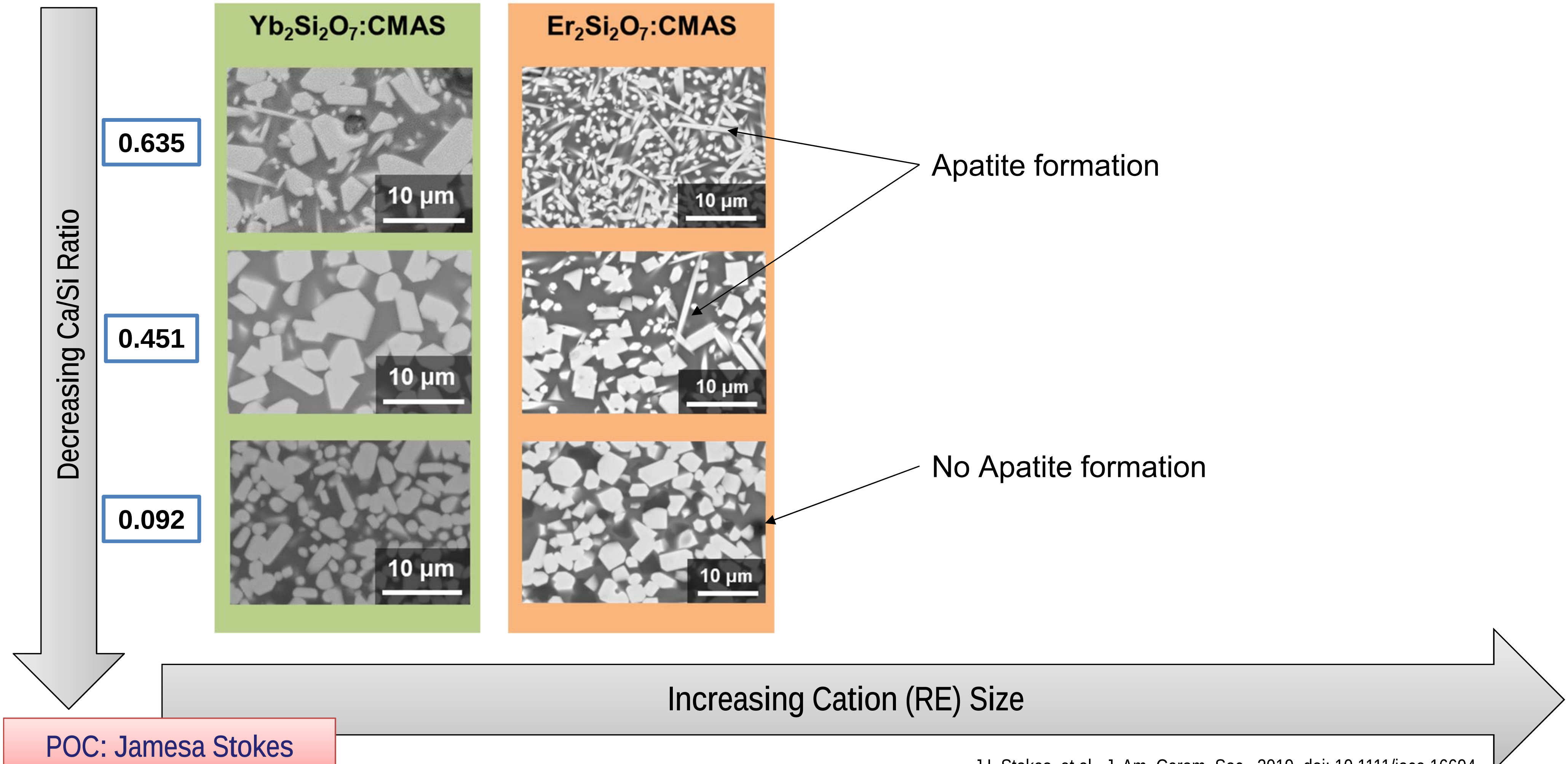

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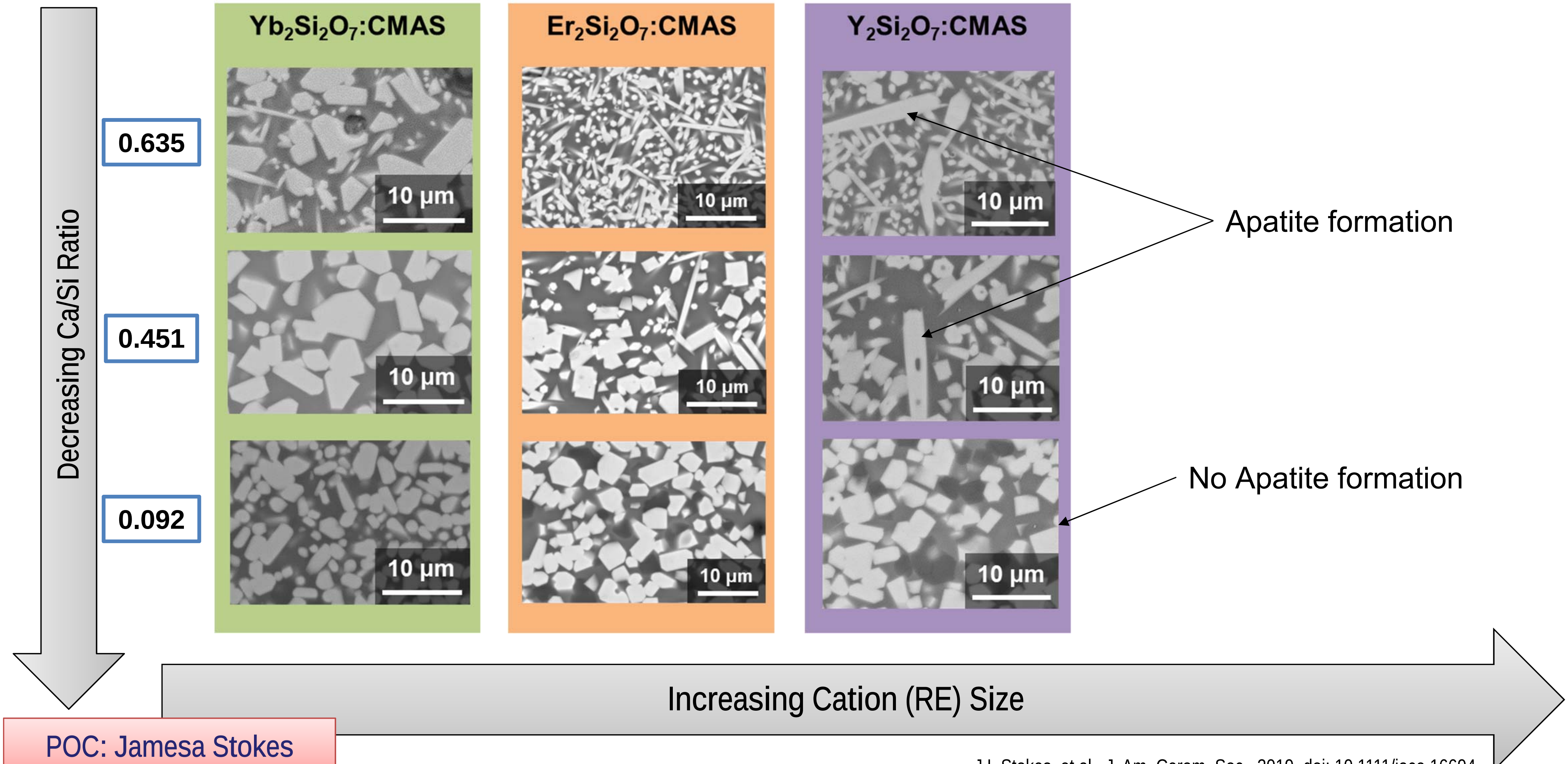

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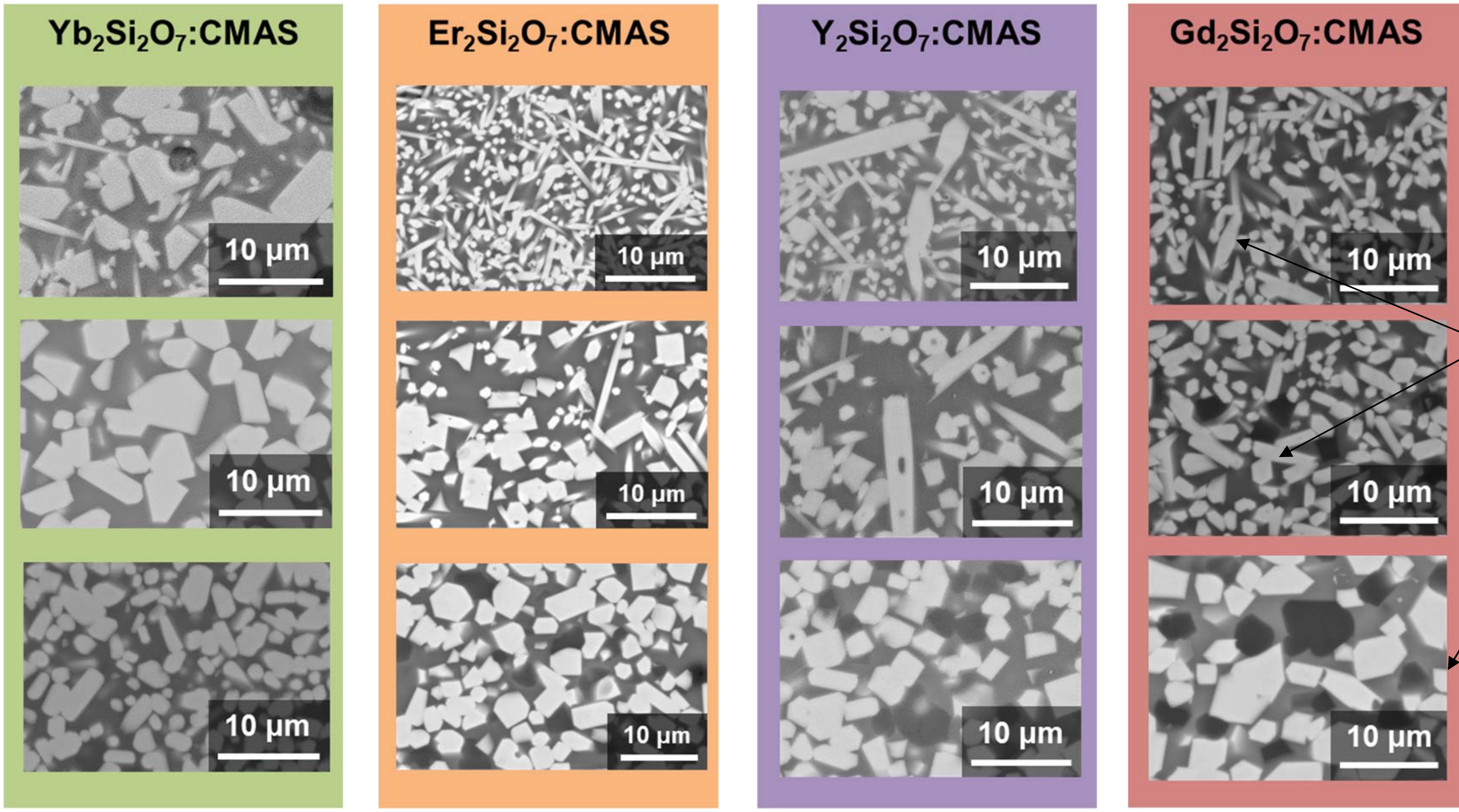
1400°C/1hr
50:50 mol% ratio

Decreasing Ca/Si Ratio

0.635

0.451

0.092



Apatite formation

Some Apatite formation

Increasing Cation (RE) Size

POC: Jamesa Stokes

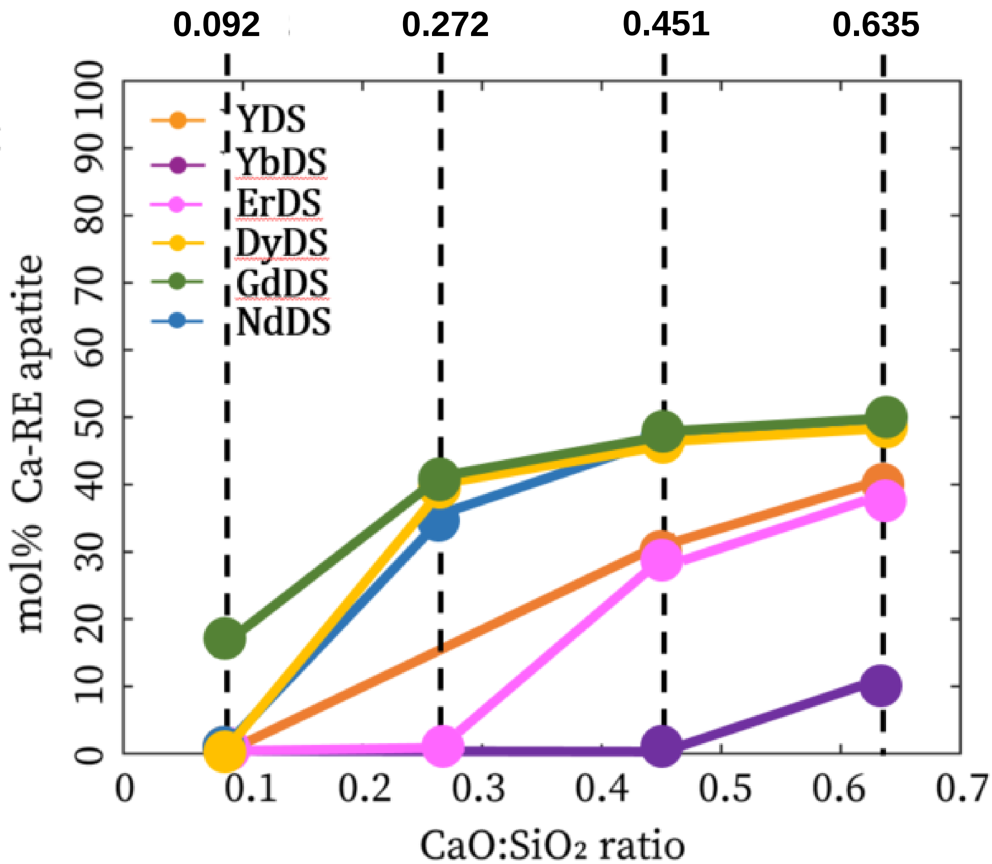
J.L.Stokes, et al., J. Am. Ceram. Soc., 2019, doi; 10.1111/jace.16694

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

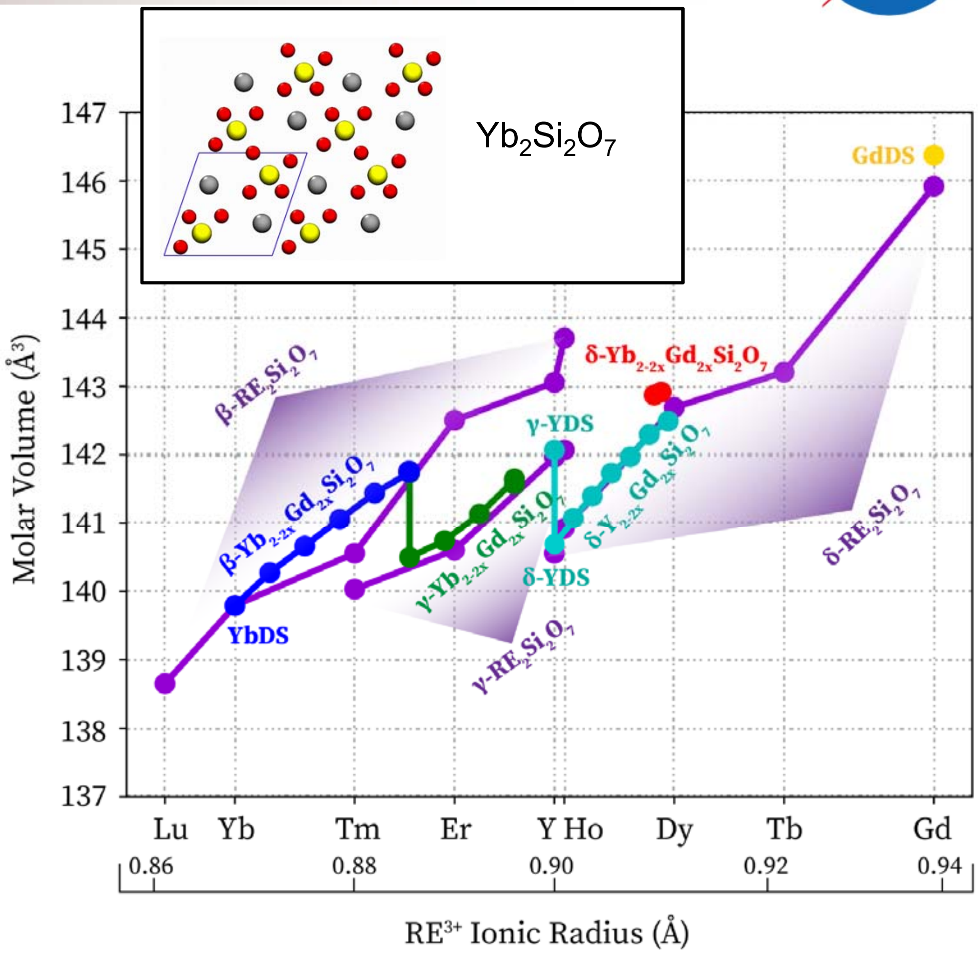


POC: Jamesa Stokes, Brian Good

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

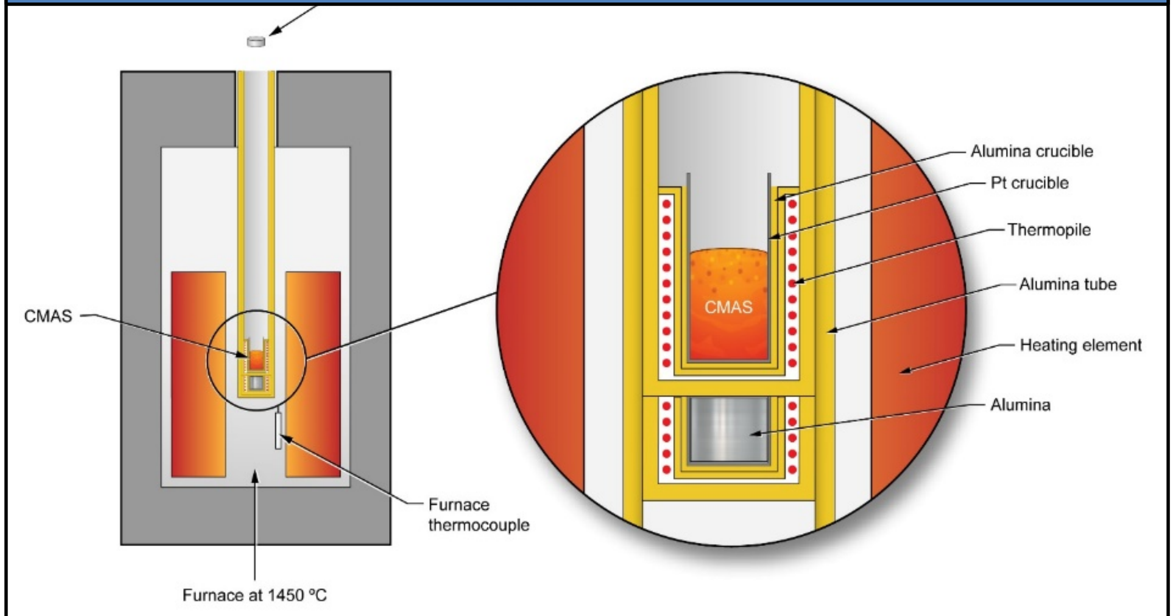


POC: Brian Good, Jamesa Stokes

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 (ΔH_s), mixing (ΔH_{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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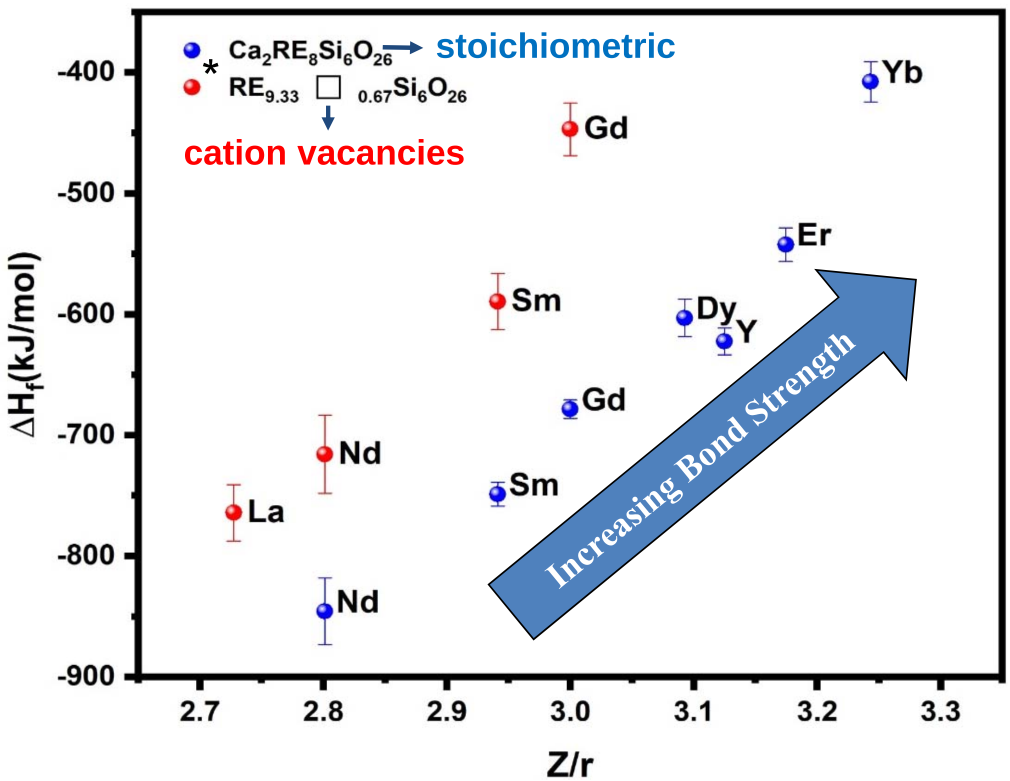
Enthalpy of formation of the RE-apatites

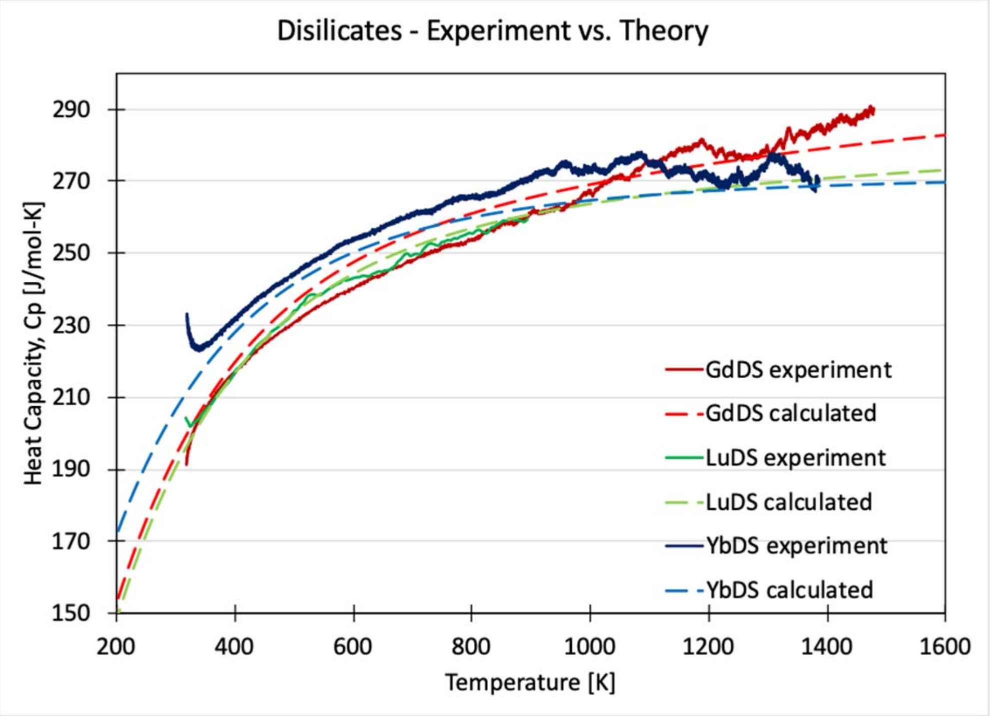


POC: Gustavo Costa

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

Can we calculate CMAS reactions or stability?

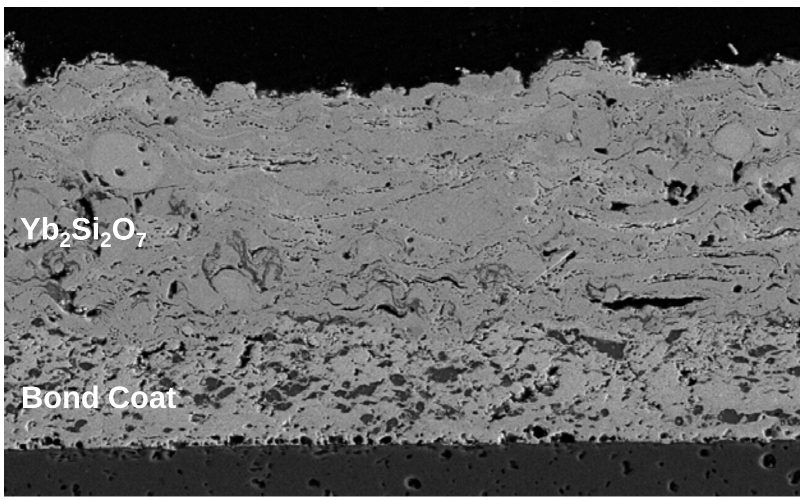
- First principles methods using density functional theory (DFT) can provide thermodynamic quantities
- Phonon calculations for RE-silicate materials can generate:
  - Heat capacity (c_p)
  - Entropy
  - Coefficient of Thermal Expansion (CTE)
  - Enthalpy of formation
- RE-silicates challenging due to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



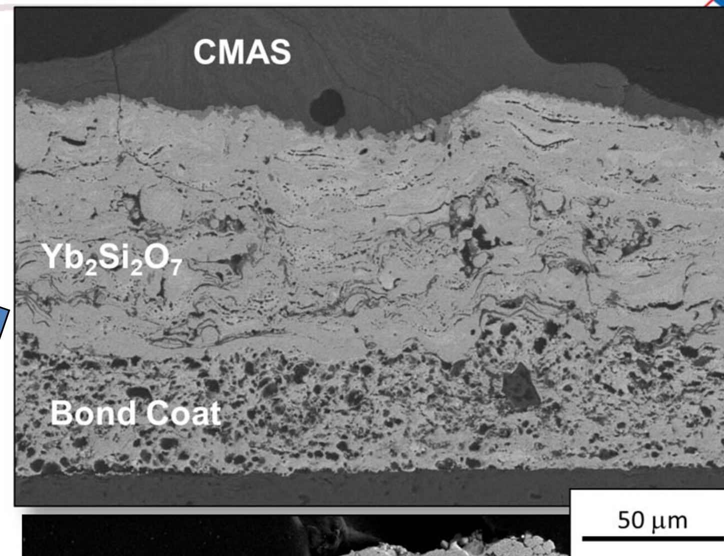
POC: Cameron Bodenschatz, Brian Good, Michael Kulis

How will CMAS React with Coatings?

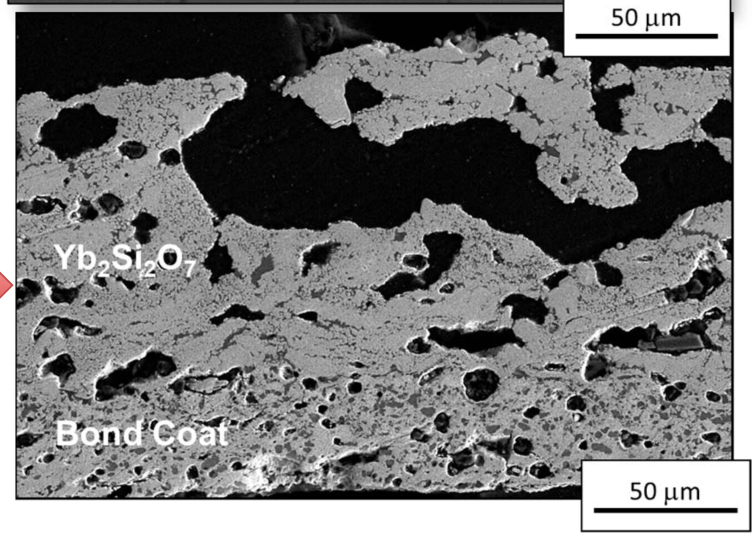
- Yb-silicate does not react strongly with CMAS but affords no protection in the coating system
- Tested with a CMAS loading of 35 mg/cm^2
- Molten CMAS infiltrates by a combination of dissolution-precipitation and grain boundary penetration mechanisms



1200°C/10hr (air)



1400°C/1 hr (air)



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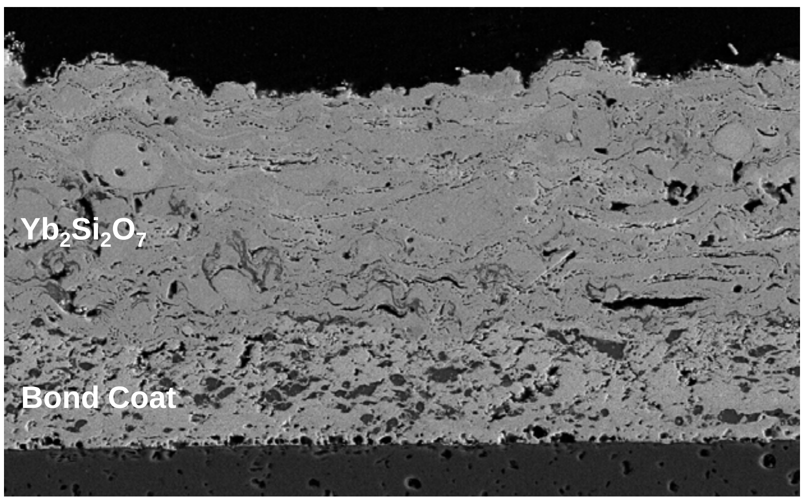

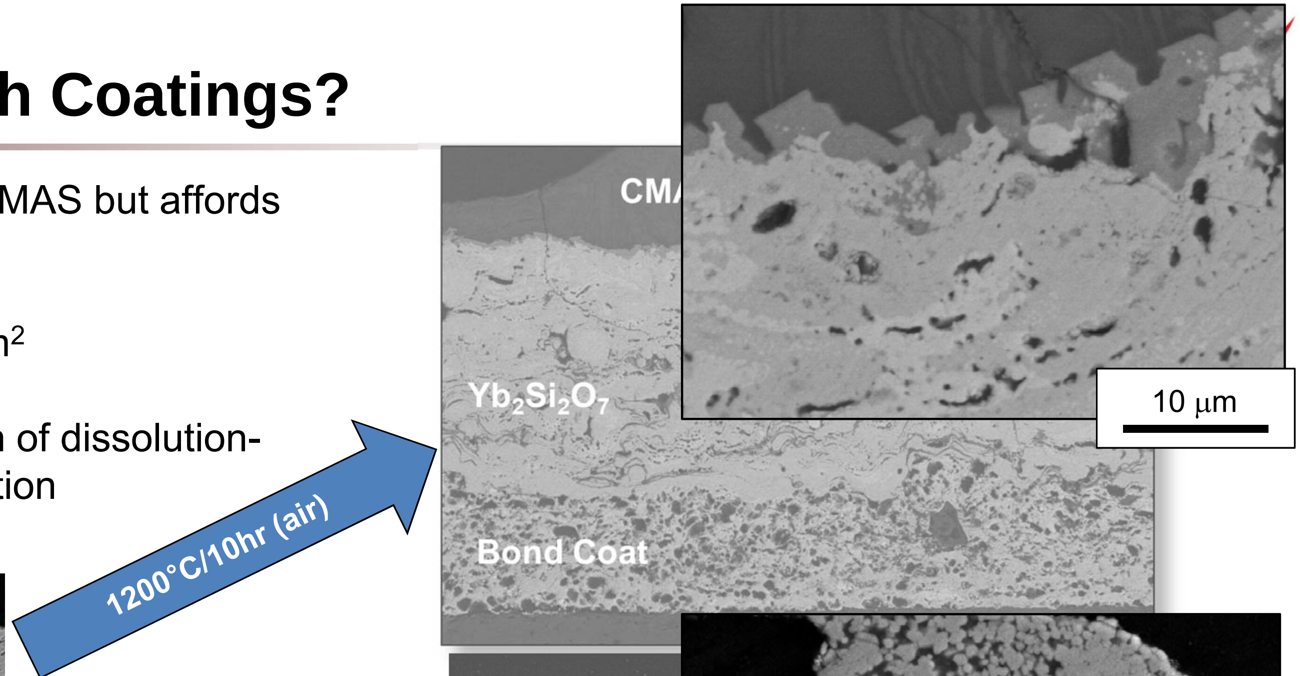

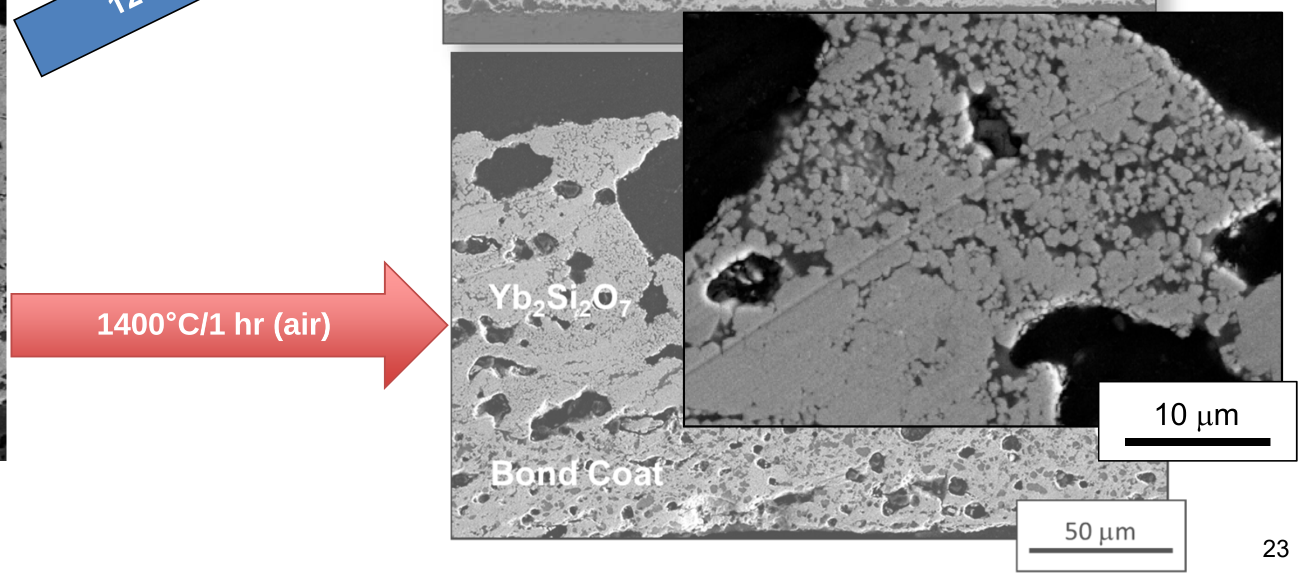

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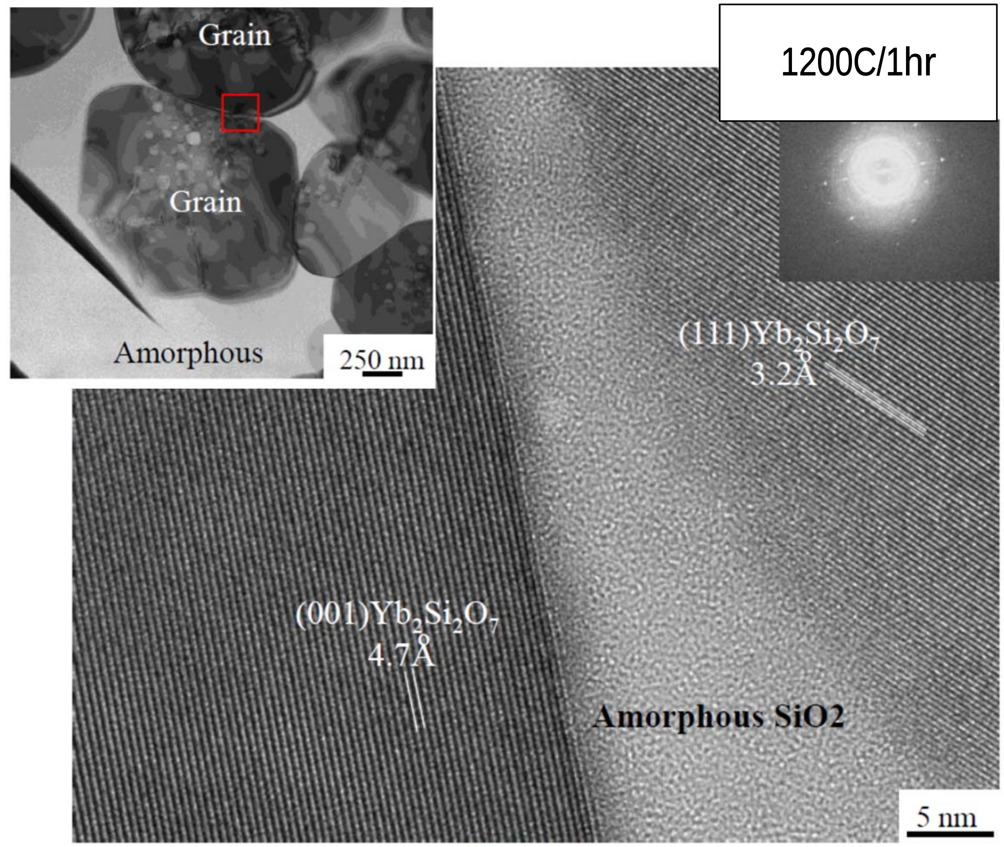
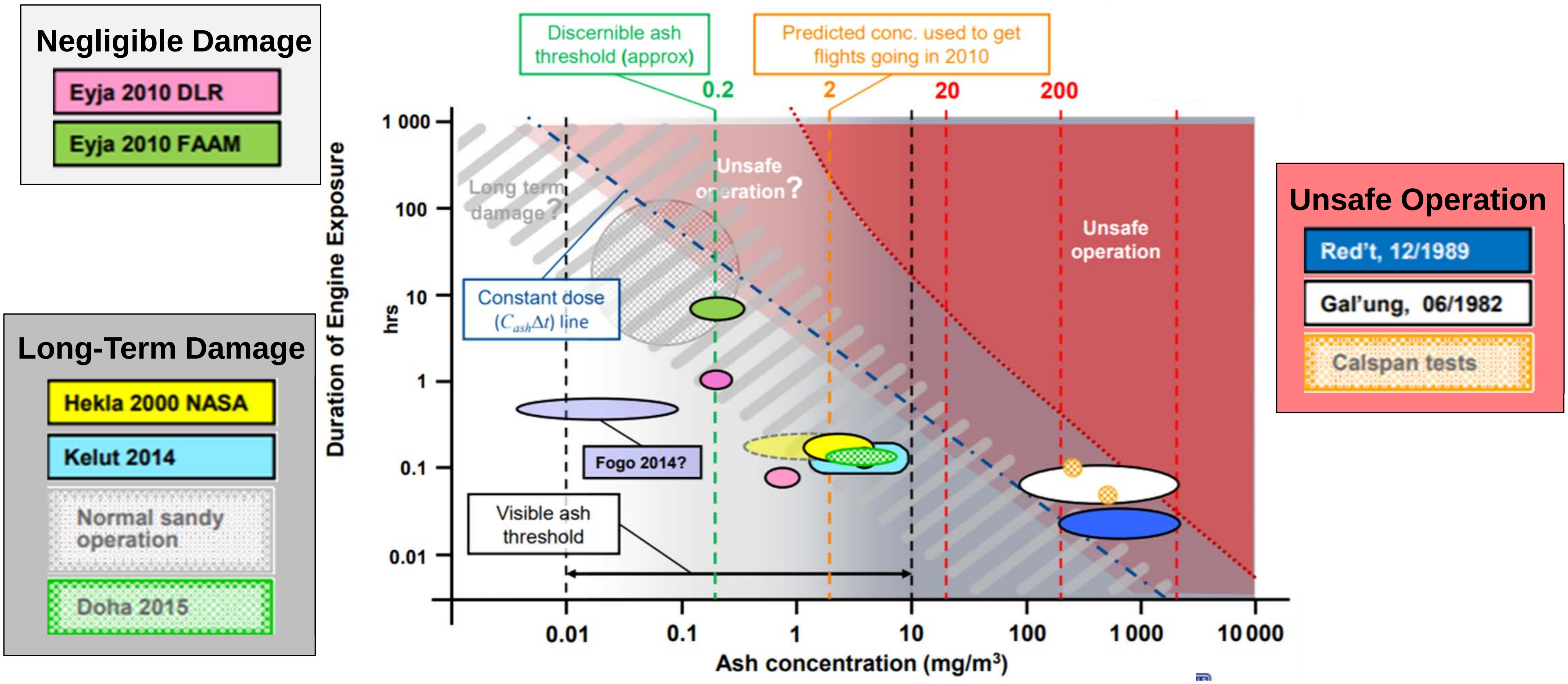
- Tested with a CMAS loading of 35 mg/cm^2
- Molten CMAS infiltrates by a combination of dissolution-precipitation and grain boundary penetration mechanisms
- TEM results have indicated significant SiO_2 present between the grains of $Yb_2Si_2O_7$
  - Infiltration may occur quickly at very low concentrations



POC: Valerie Wiesner, Bryan Harder

How can we accurately test EBCs with CMAS?

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



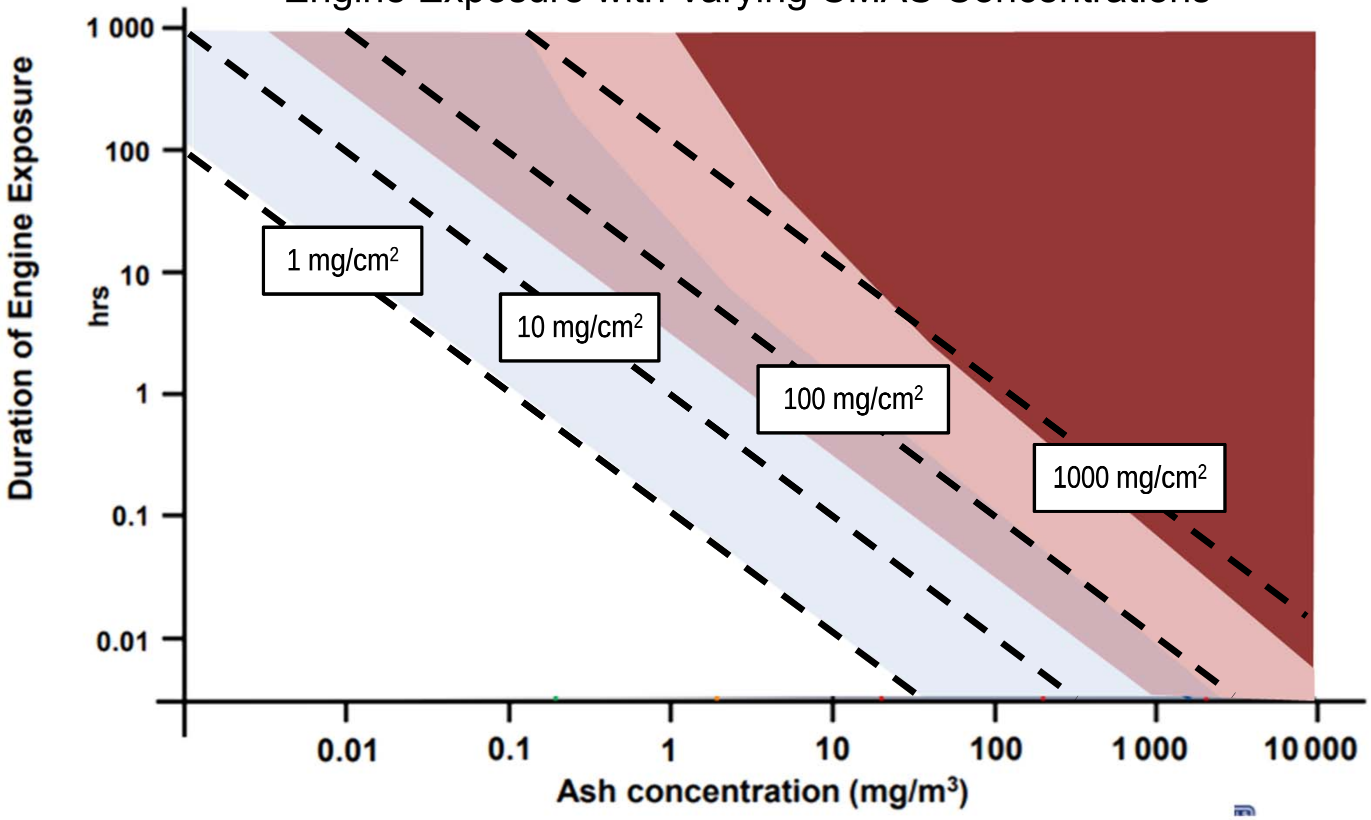
R. Clarkson and H. Simpson, "Maximising Airspace Use During Volcanic Eruptions: Matching Engine Durability against Ash Cloud Occurrence," (2019)

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

Engine Exposure with Varying CMAS Concentrations



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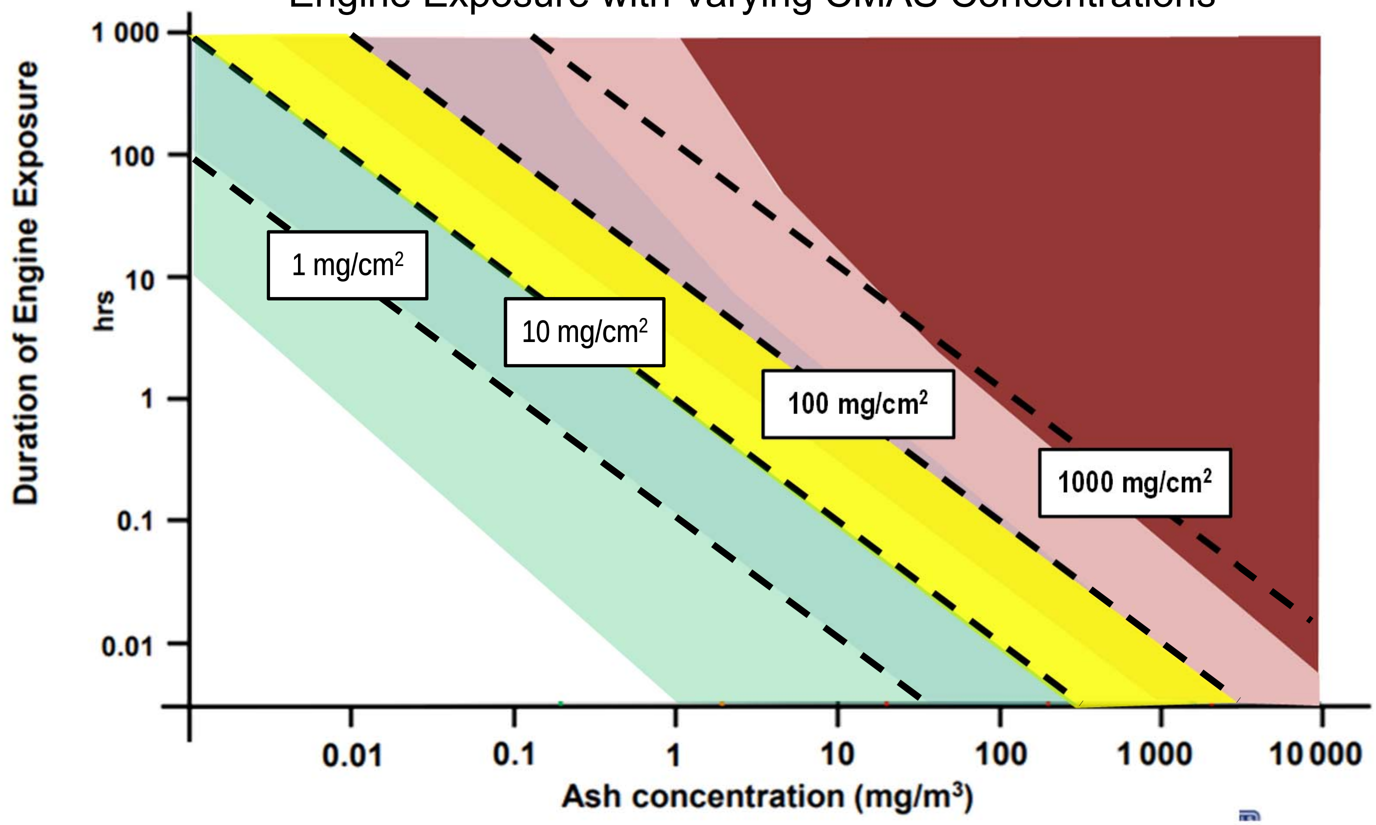
How can we accurately test coatings with CMAS?

- 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

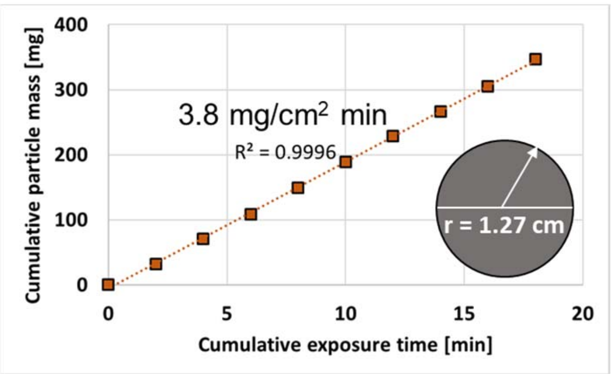


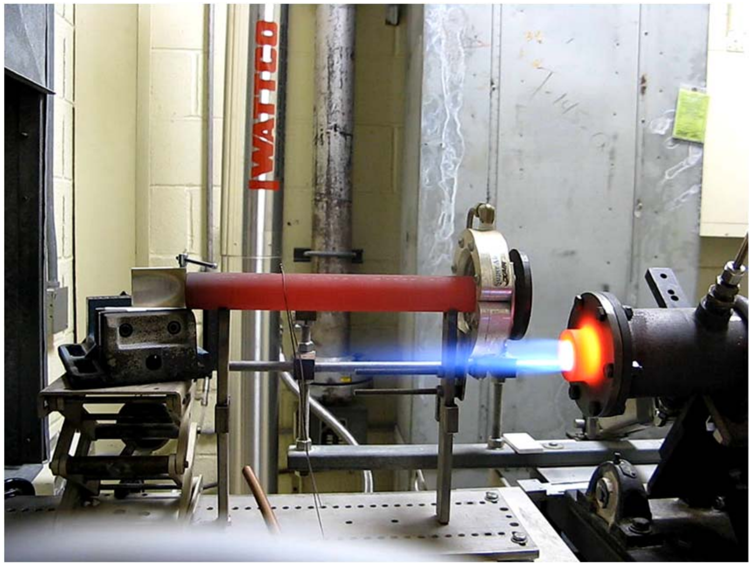
R. Clarkson and H. Simpson, "Maximising Airspace Use During Volcanic Eruptions: Matching Engine Durability against Ash Cloud Occurrence," (2019)

How can we accurately test EBCs with CMAS?

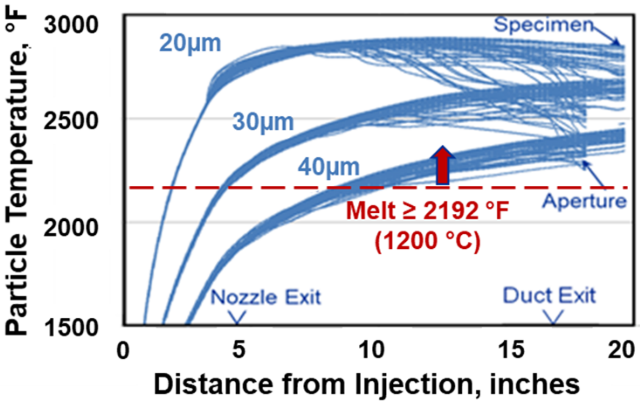
- CMAS deposition can be performed with modified Mach 0.3 – 1.0 burner test rig at NASA GRC
- Computational fluid dynamics (CFD) modeling predicts CMAS glass particles injected into the burner should be molten by the time they reach/impinge on the target
- ‘Low’ CMAS feeding rates can be achieved with 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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