# Reliability of Materials and Components for Solid Oxide Fuel Cells

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Oak Ridge National Laboratory

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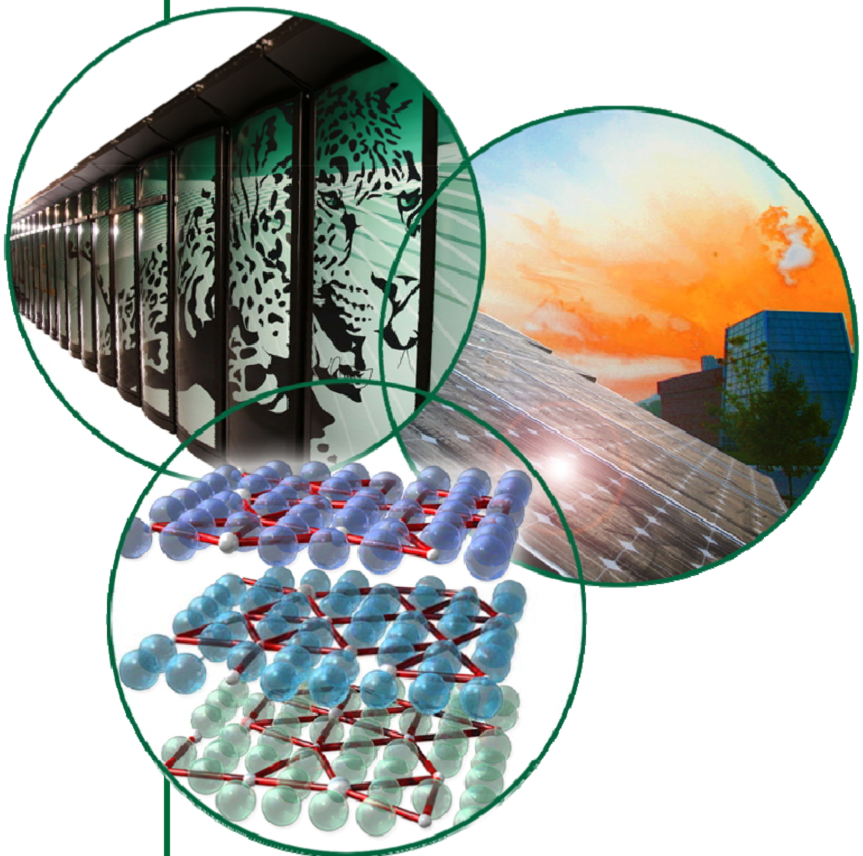
Pittsburgh, PA



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# Outline

- Background and Objective
- Approach
- Results
    - Dimensional Stability, Microstructural Evolution and Chemical Stability
    - Viscosity, Glass Transition Temperature and Thermal Expansion
    - Wetting behavior
- Summary and Future Work

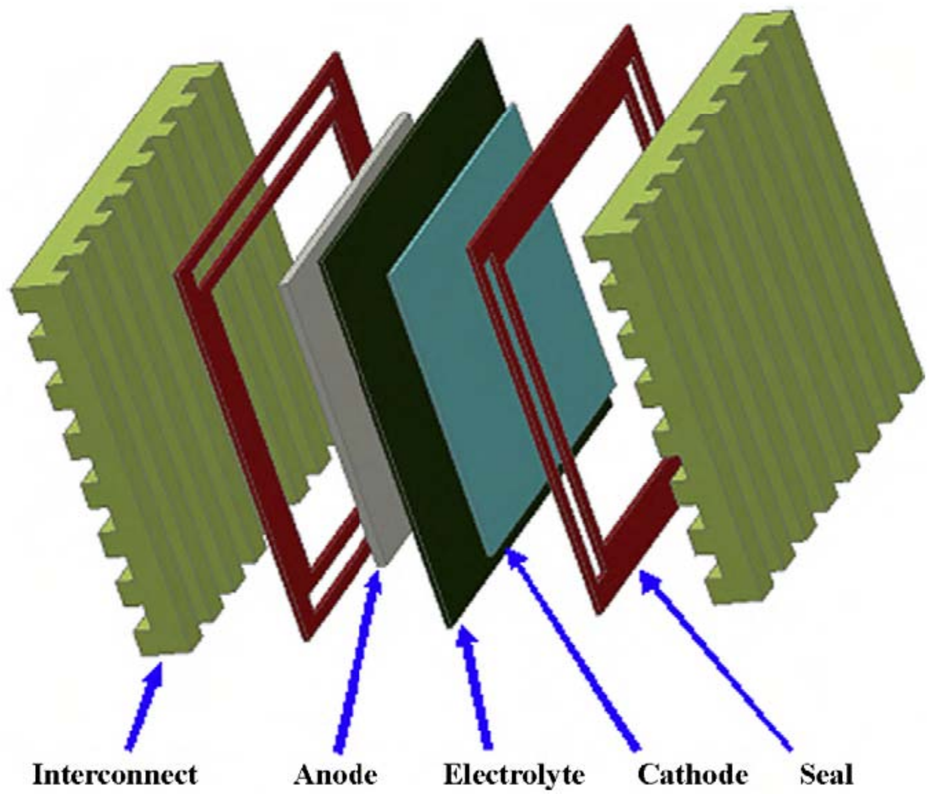
# Background and Objective

## Requirements for SOFC Seals

- Simultaneous fulfillment of thermal, physical, chemical, mechanical and electrical property requirements.
- Phase stability and chemical compatibility without substantial property degradation for 40,000 hours at elevated temperature in oxidizing and wet reducing environments.

## Objectives

- To characterize the physical and mechanical properties of candidate SOFC glass seals.
- To assess the effect of long-term exposure to SOFC relevant environments on the dimensional, microstructural and chemical stability and flow characteristics of candidate SOFC glass seals.



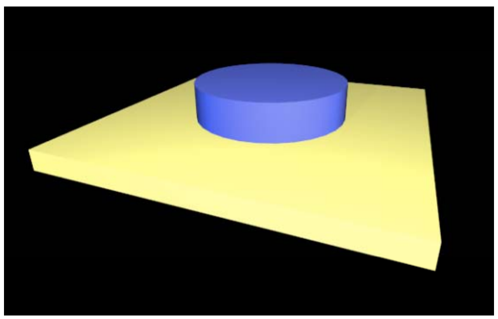

*Mahapatra and Lu, *J Power Sources*, 2010

# SCN – An Alkali Barium Silicate Glass

- Manufactured by SEM-COM, Toledo, OH.
- Glass received in powder form.  Powder cold pressed into pellet form.

| Ingredient | Concentration |
| --- | --- |
| $SiO_2$ | <75% |
| $K_2O$ | <12% |
| BaO | <10% |
| $Na_2O$ | <8% |
| $Al_2O_3$ | <5% |
| $TiO_2$ | <1% |
| $CeO_2$ | <1% |
| $As_2O_3$ | <1% |
| $Sb_2O_3$ | <1% |
| MgO | <2% |
| CaO | <5% |
| $F_2$ | <1% |

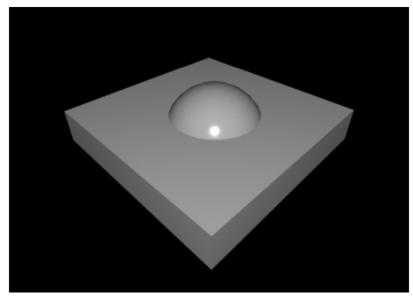
# Approach



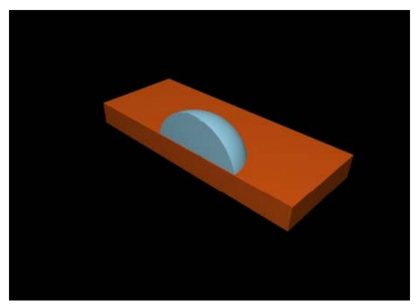
Substrates
- $Al_2O_3$
- 8YSZ

Sintering $850^oC$ for 2 hours →

Environmental Exposure at $800^oC$
- Air
- Steam + $H_2$ + $N_2$



Test specimens are removed from furnace every 1,000 hrs for non-destructive microstructural analysis
- Surface XRD
- SEM on surface
- EDS



Cross-section

Microstructural Analysis on metallographically prepared specimens
- XRD of glass powder
- SEM on cross-section
- EDS

# Characterization of SCN Glass

- Characterized the properties of the glass relevant for SOFC sealing application
  - Microstructural Stability – Devitrification and porosity evolution
  - Chemical compatibility with alumina and 8YSZ substrates
  - Thermal properties (Thermal Expansion and $T_g$)
  - Mechanical Properties and Viscosity
  - Wetting behavior and Dimensional Changes
  - Effect of long term exposure (~5,000 hrs*) on properties and microstructure

*Longer duration tests on properties are in progress

# Outline

- Background and Objective
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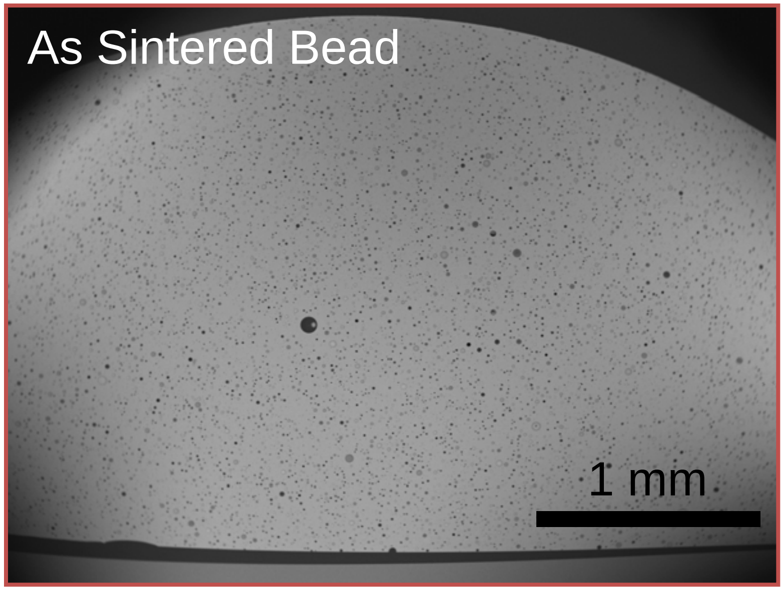
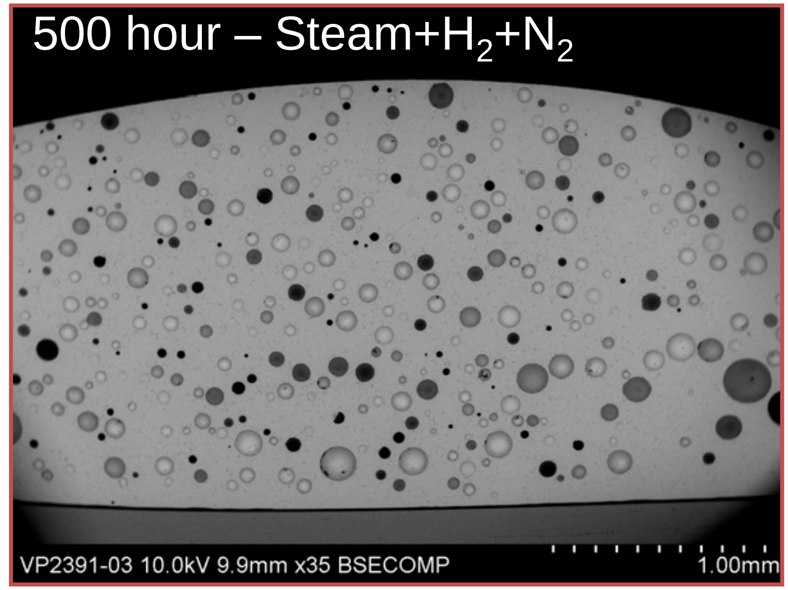
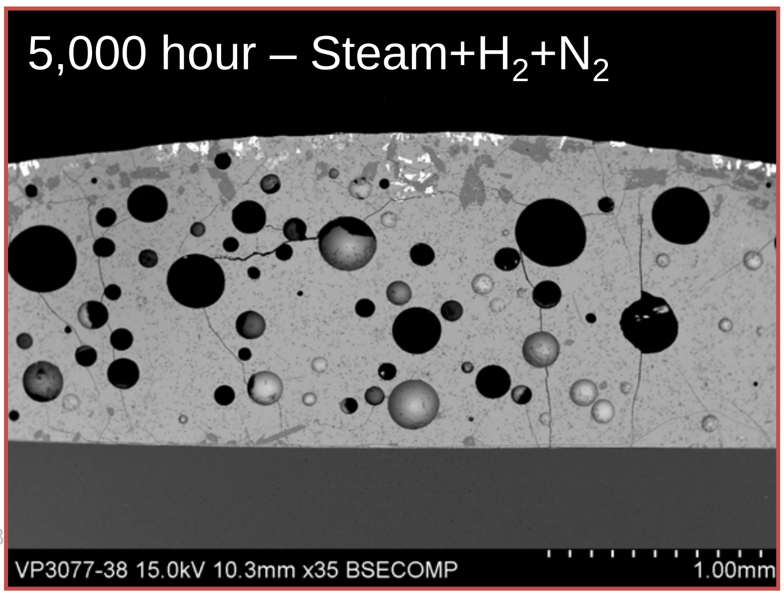
  - Microstructural Evolution and Chemical Stability for SCN glass sintered on $Al_2O_3$ substrate

# Effect of time of exposure on microstructure of SCN glass – Alumina Substrate



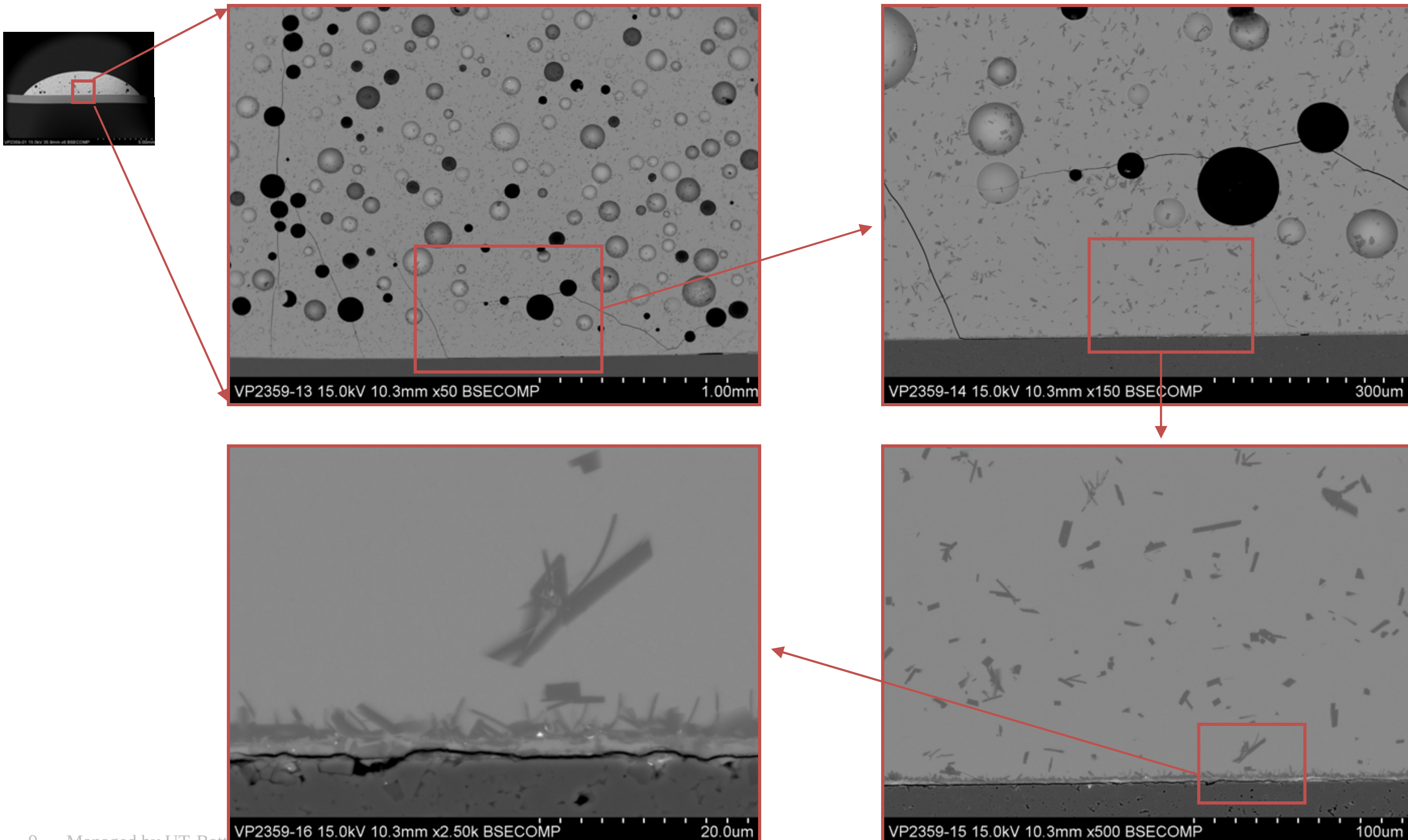




- Long term exposure results in significant microstructural changes
- Pore sizes increase with time
- New phases appear and coarsen with time
  - $KAlSi_3O_8$ (bulk)
  - BaO (surface)
  - Ca rich silicate (surface)
  - Cracks in bulk but glass remains bonded at 5,000 hrs

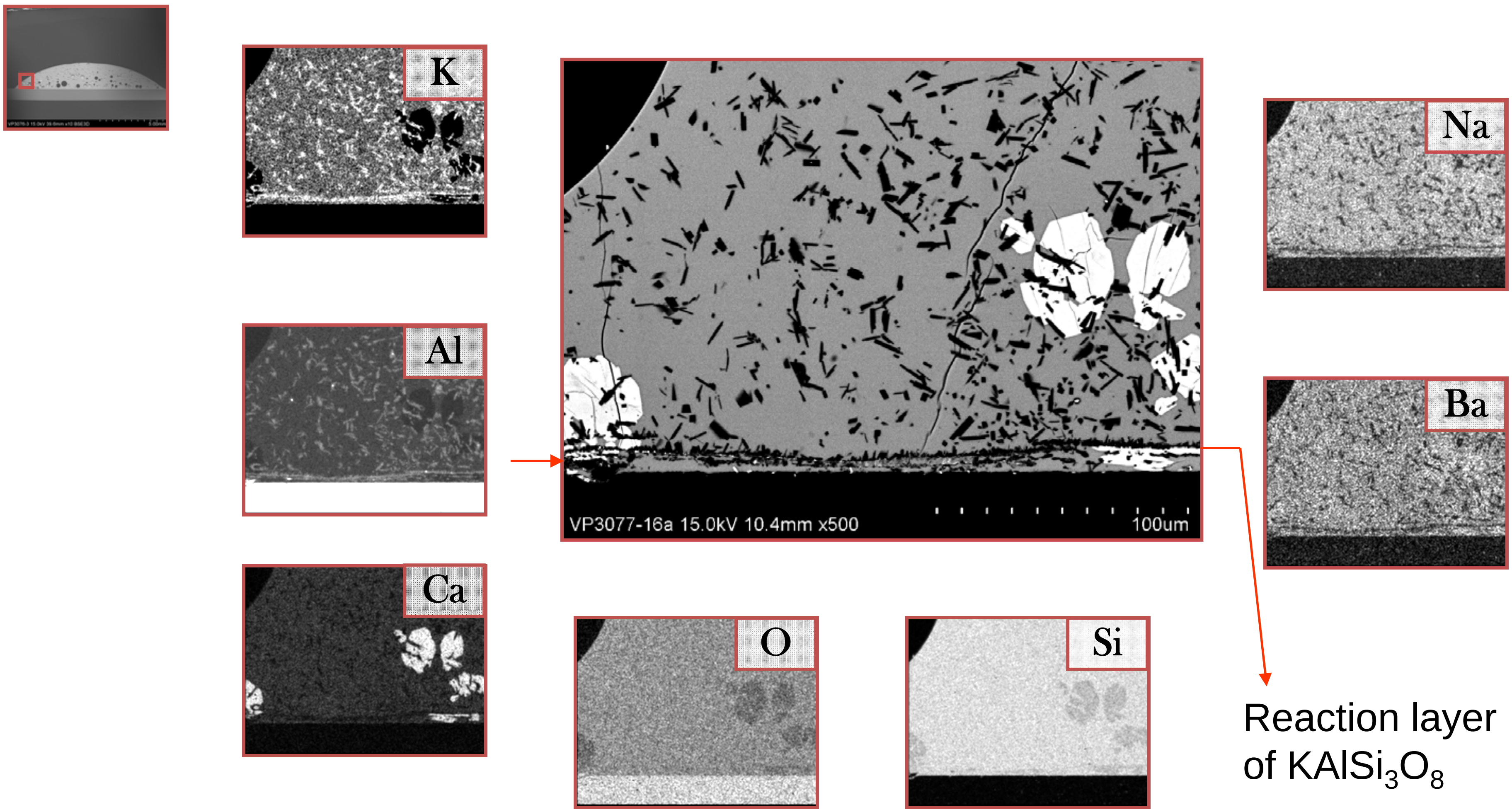
# Formation of reaction layer between glass and alumina

On Alumina Substrate After 865 Hours in Air

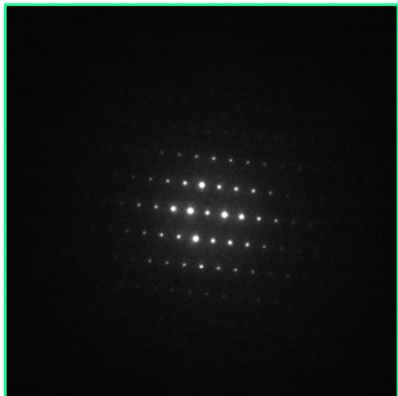


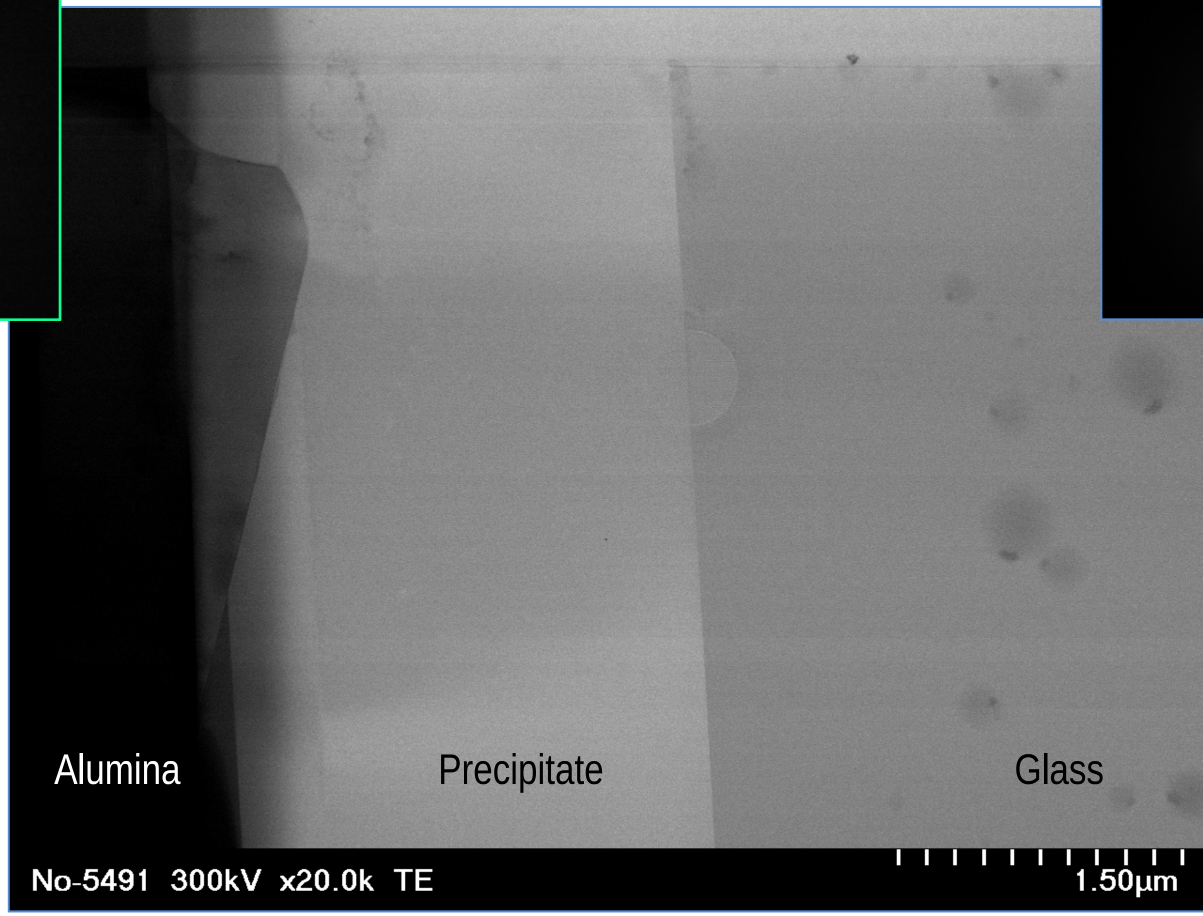
# Formation of reaction layer between glass and alumina

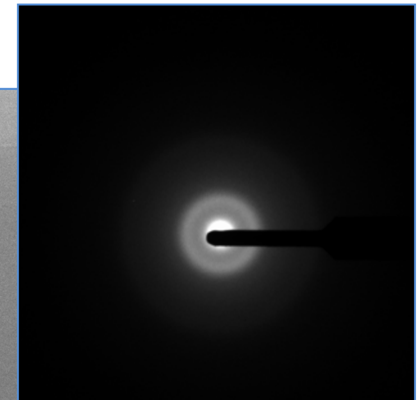
On Alumina Substrate After 5,000 Hours in Air



# Chemical Compatibility – Glass on Alumina





- 850 hours – Steam+$H_2$+$N_2$ Exposure
- 3 – 4 µm phase at alumina SCN glass interface rich in K and Al – likely $KAlSi_3O_8$

# Effect of time of exposure on phase stability of SCN - Alumina substrate

| Exposure Condition | Glass | $KAlSi_3O_8$ | BaO | Ca-rich silicate | $SiO_2$ | Bead Attached |
|---|---|---|---|---|---|---|
| SCN Glass – As sintered | ✓ | x | x | x | x | x |
| 100 hours – Air | ✓ | ✓ | x | x | x | x |
| 100 hours – Steam+$H_2$+$N_2$ | ✓ | ✓ | ✓(s) | x | x | x |
| 500 hours – Air | ✓ | ✓ | x | x | x | x |
| 500 hours – Steam+$H_2$+$N_2$ | ✓ | ✓ | ✓(s) | x | x | x |
| 865 hours – Air | ✓ | ✓ | ✓(s) | x | x | ✓(r) |
| 850 hours – Steam+$H_2$+$N_2$ | ✓ | ✓ | ✓(s) | ✓(s) | x | x |
| 5,000 hours – Air | ✓ | ✓ | ✓(s) | ✓ | x | ✓(r) |
| 5,000 hours – Steam+$H_2$+$N_2$ | ✓ | ✓ | ✓(s) | ✓(s) | x | ✓(r) |

✓(s) – Phase forms only on the surface of the bead

✓(r) – Bead remains attached due to formation of reaction layer

# Outline

- Background and Objective
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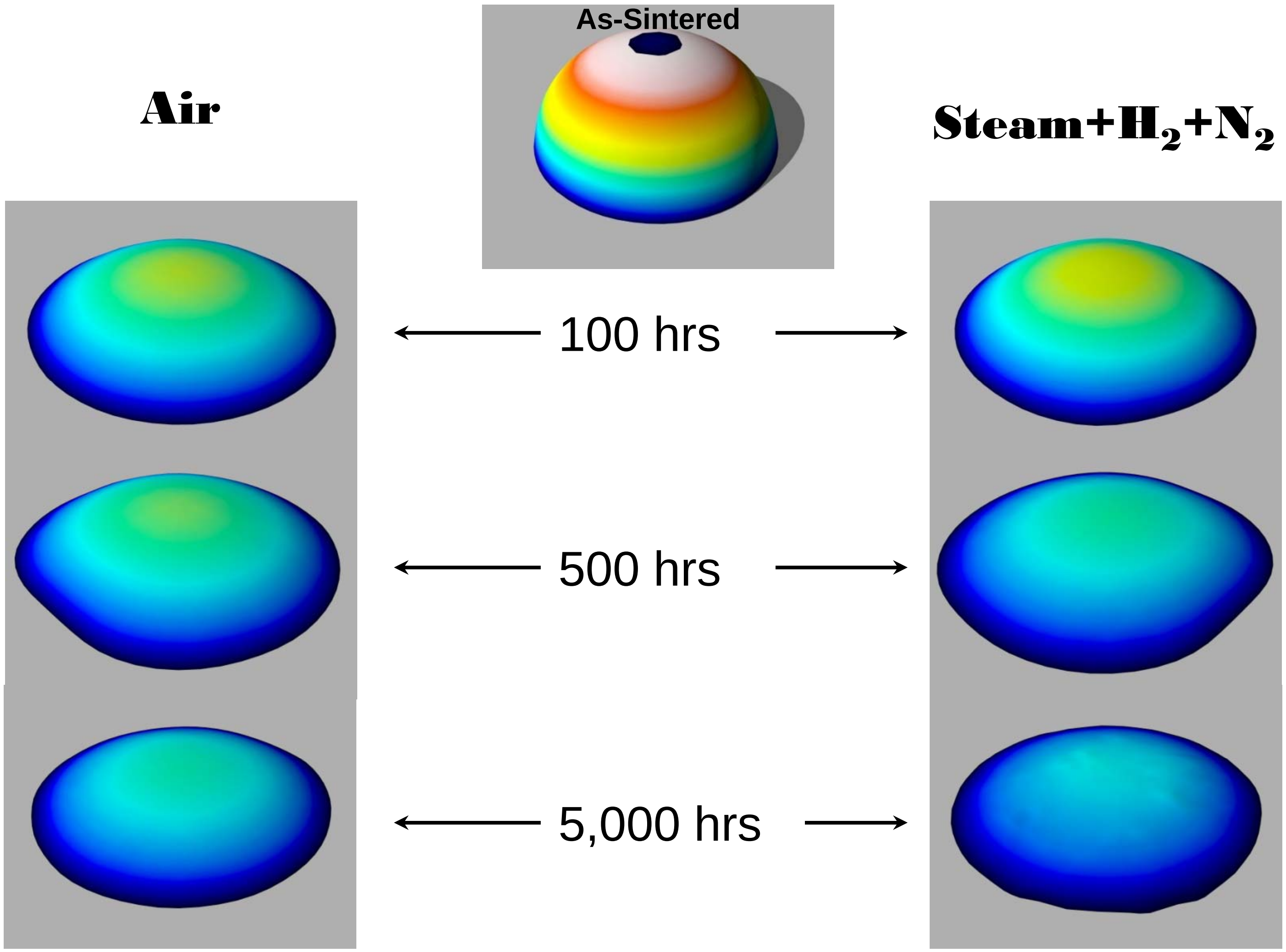
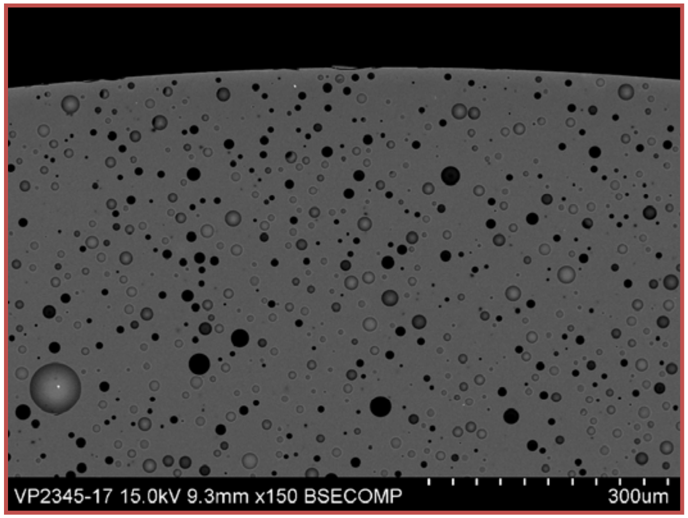
- Results
  - Microstructural Evolution and Chemical Stability for SCN glass sintered on $Al_2O_3$ substrate
  - Dimensional Stability, Microstructural Evolution and Chemical Stability for SCN glass sintered on 8YSZ substrate

# Effect of long term exposure on dimensional stability (8YSZ Substrate)

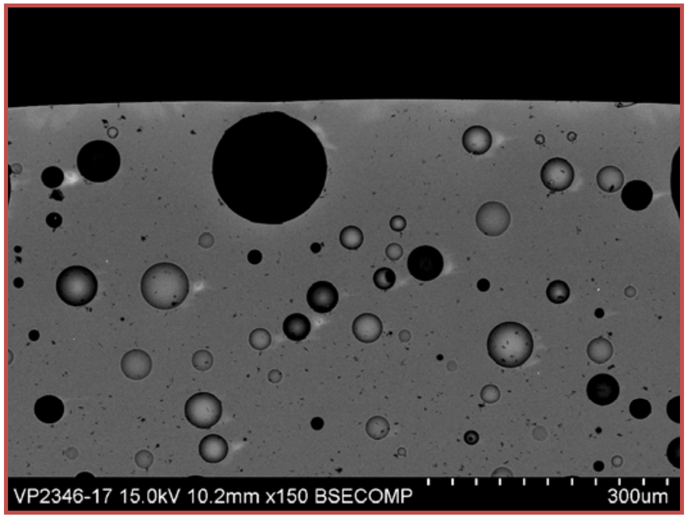



• Mass changes after 5,000 hr exposure were <<1%.

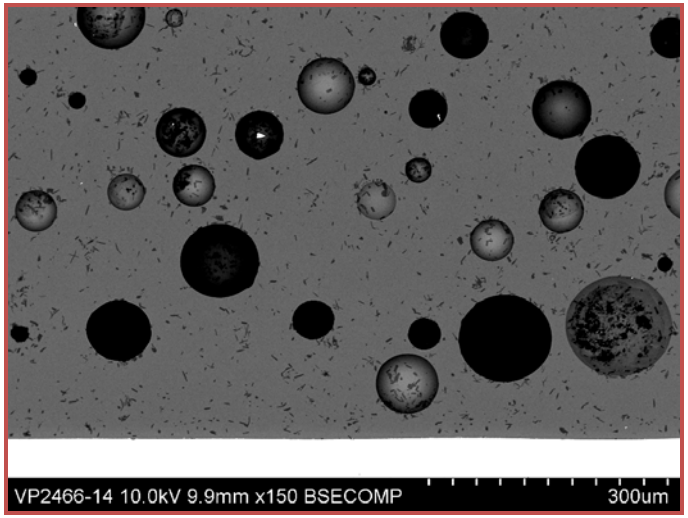
# Effect of air exposure on microstructural evolution – 8YSZ Substrate



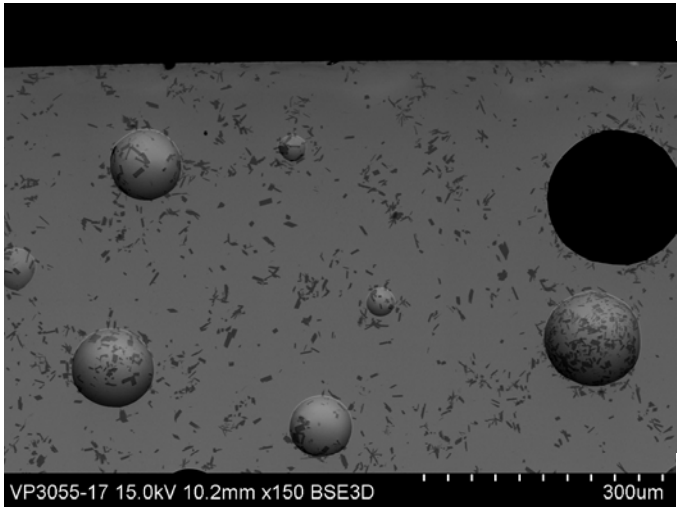

As Sintered




100 hour - Air



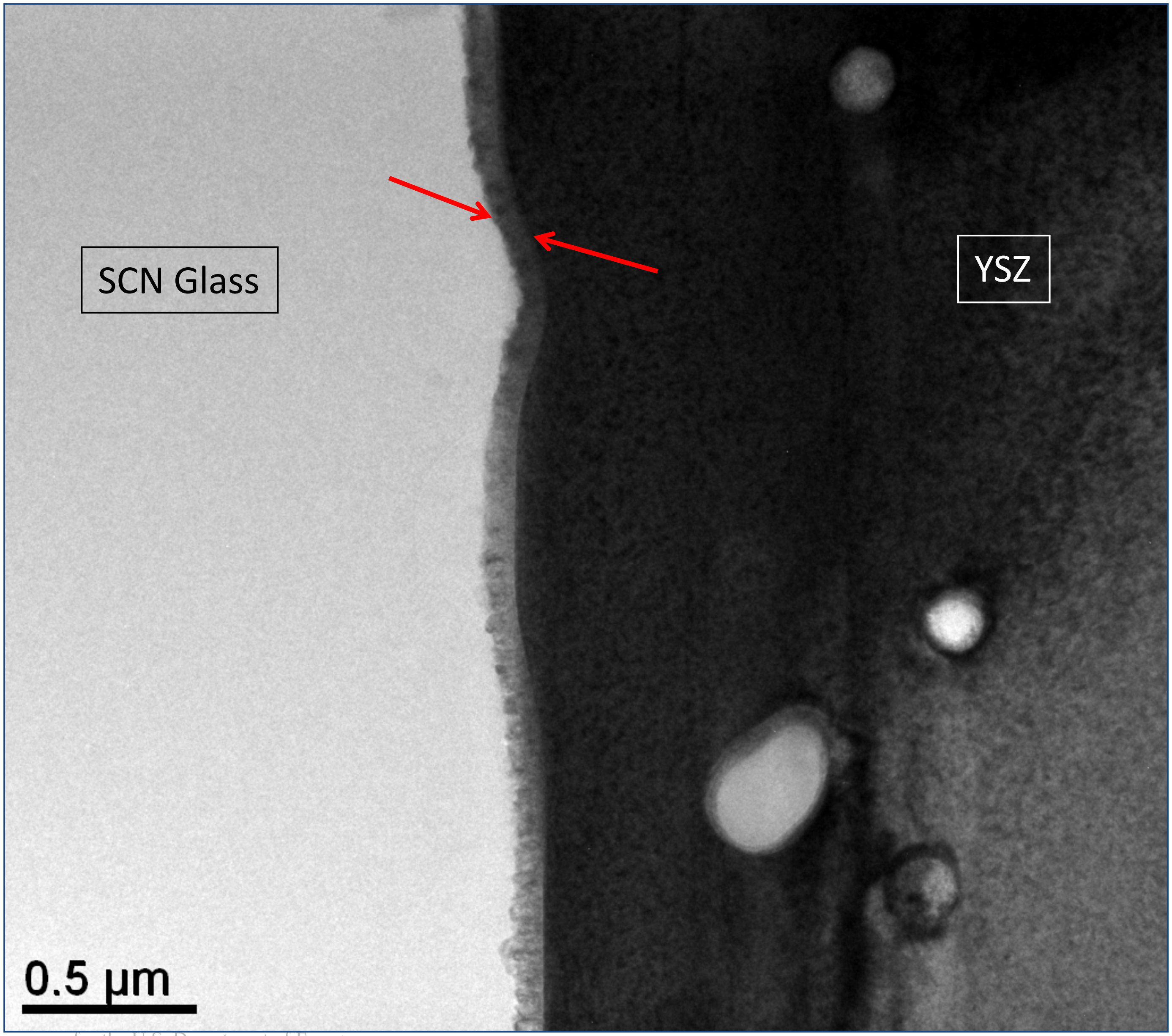

500 hour - Air




5,000 hour - Air

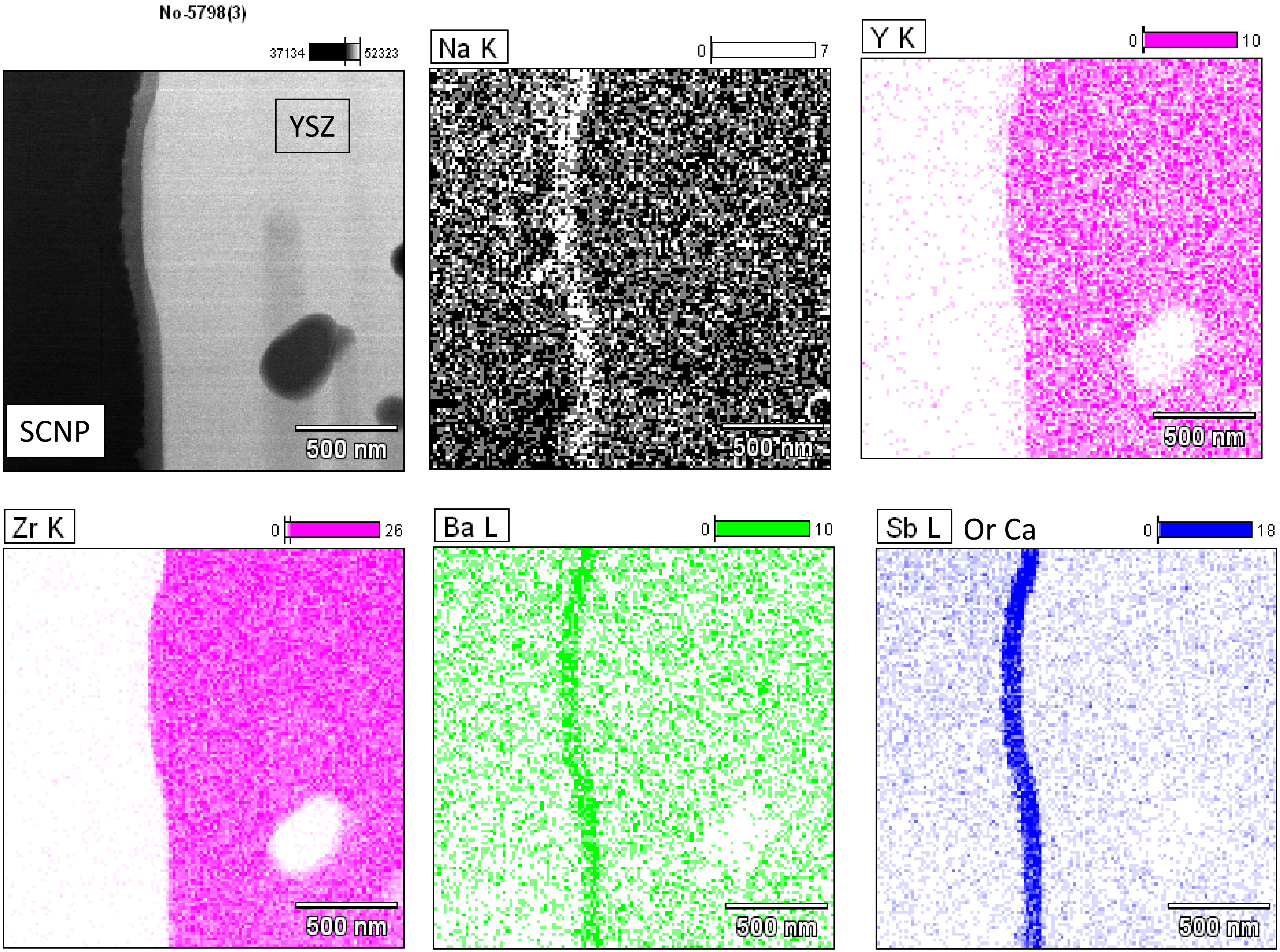
- Pores coarsen; volume fraction of $KAlSi_3O_8$ precipitates increase

# Chemical Compatibility – Glass on 8YSZ



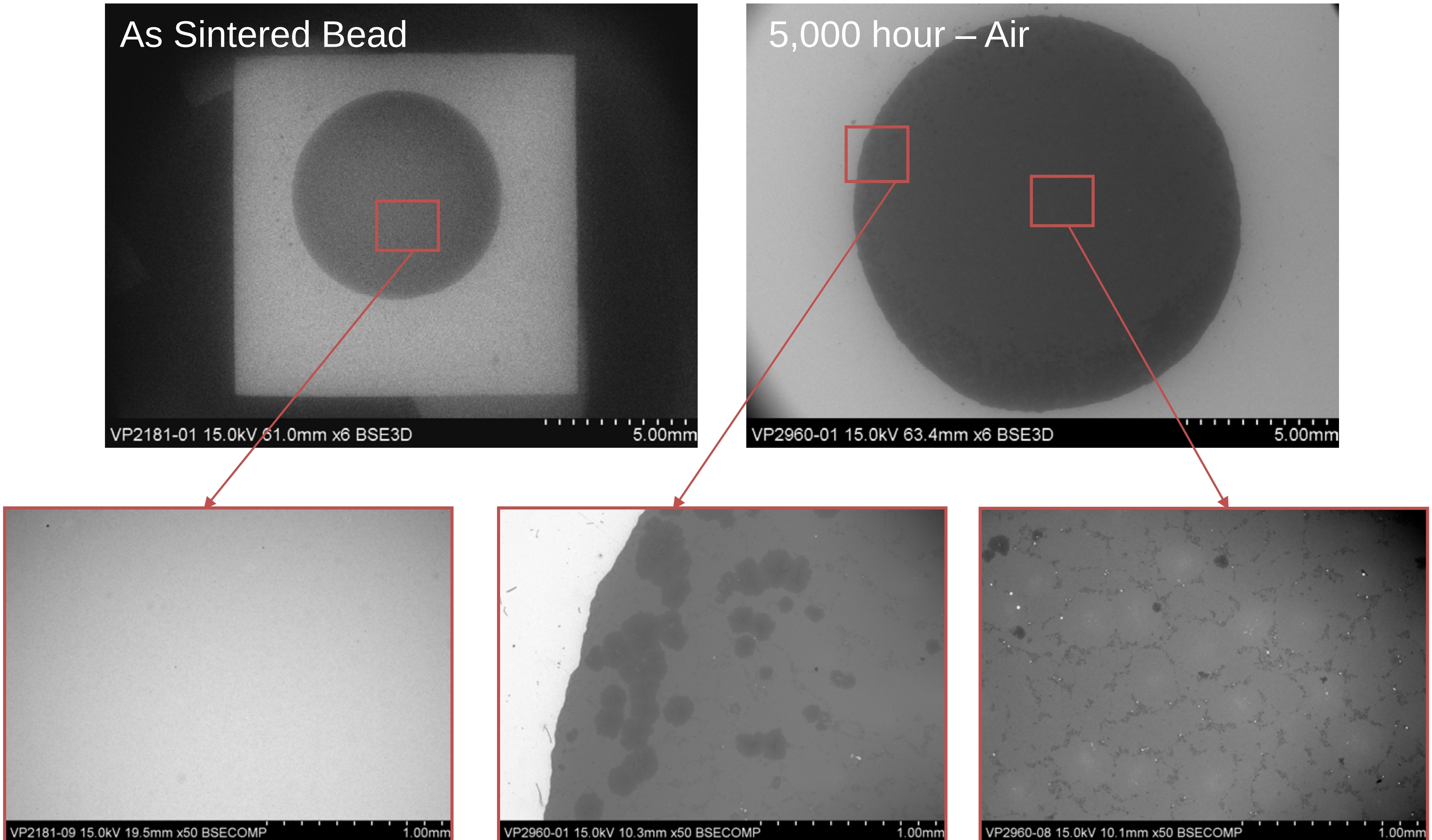


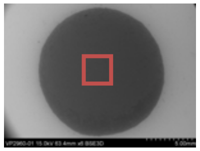

- 865 hours in Air
- Thin layer (100 nm) of phase rich in Na, Ba and Ca/Sb



No-5798(3)
37134
52323
YSZ
SCNP
500 nm
Na K
0
7
500 nm
Y K
0
10
500 nm
Zr K
0
26
500 nm
Ba L
0
10
500 nm
Sb L
Or Ca
0
18
500 nm

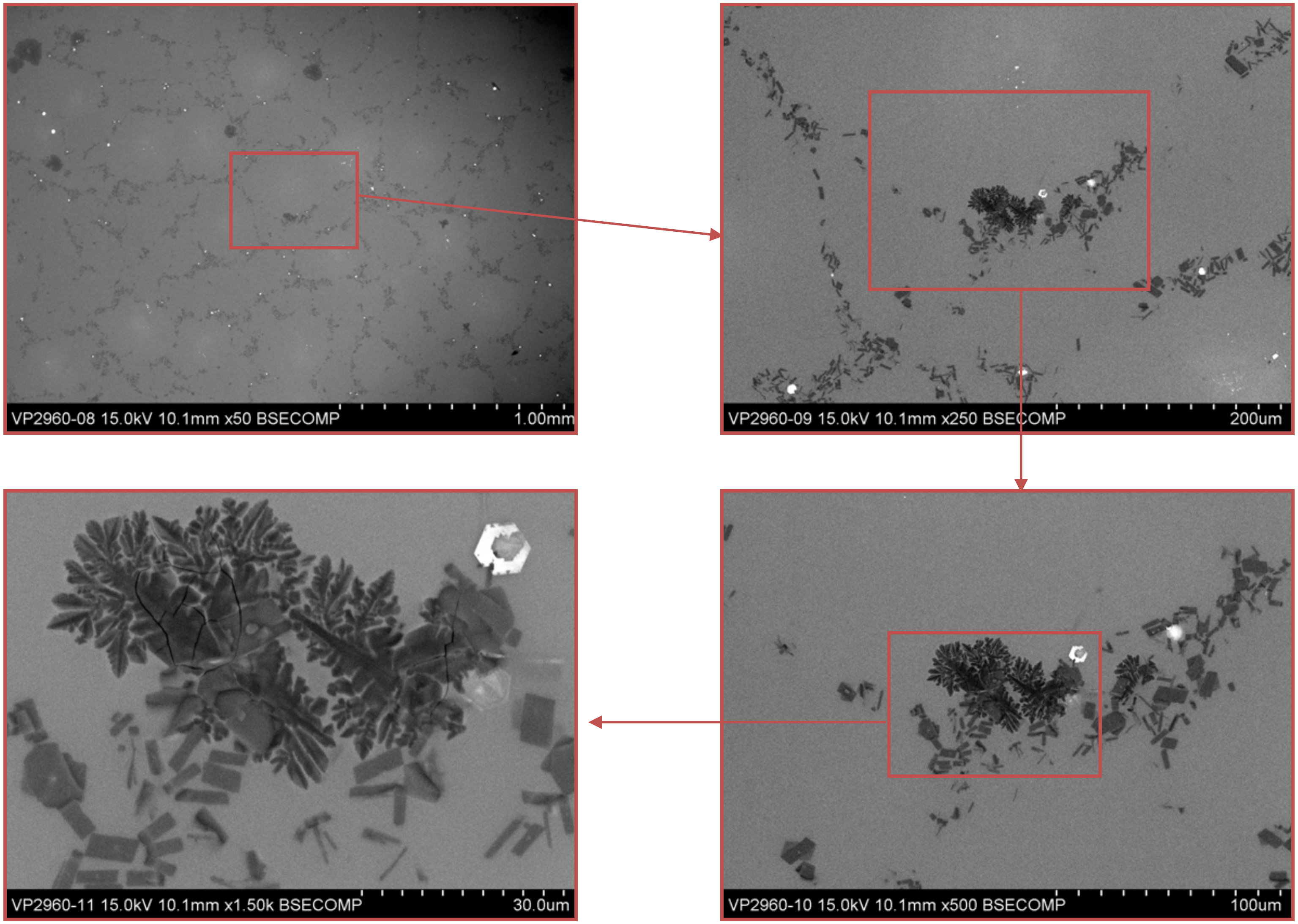
# Surface phase evolution - Aging in *Air* - *8YSZ* Substrate

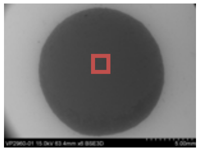




# Surface phase evolution in SCN Glass

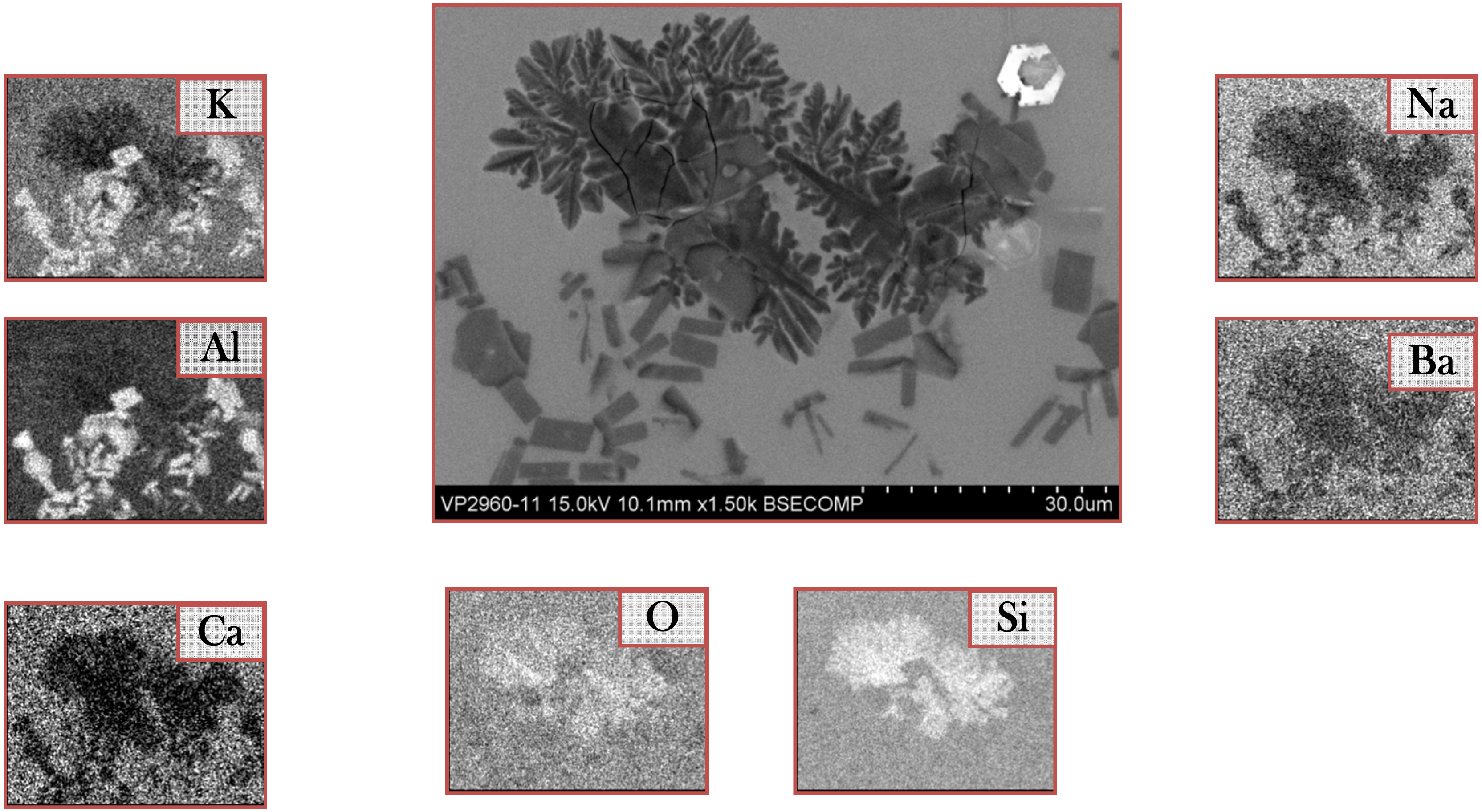
## On 8YSZ Substrate After 5,000 Hours in Air





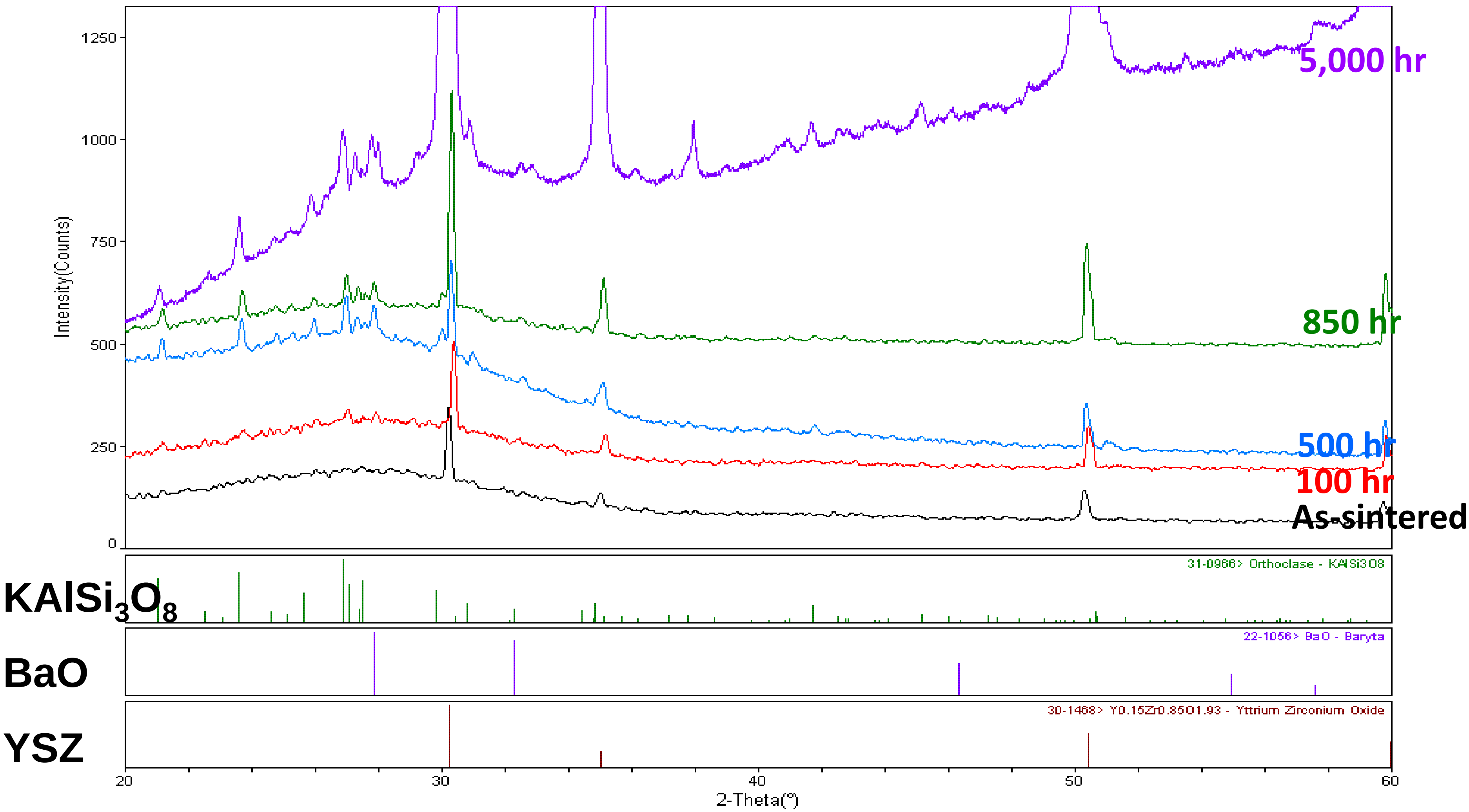
# Surface phase evolution in SCN Glass

On 8YSZ Substrate After 5,000 Hours in Air Exposure




- Presence of $SiO_2$, and $KAlSi_3O_8$ in this region under this exposure condition

# Effect of steam+$H_2$+$N_2$ exposure on phase evolution – 8YSZ Substrate




- $KAlSi_3O_8$ precipitates detected at 500 hours by XRD; intensity increases
- BaO detected after 5000 hours of exposure

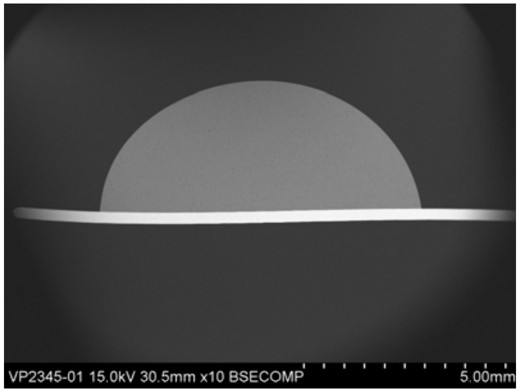
# Effect of long term exposure on phase stability of SCN – *8YSZ* substrate

| Exposure Condition | Glass | $KAlSi_3O_8$ | BaO | Ca-rich silicate | $SiO_2$ | Bead Attached |
|---|---|---|---|---|---|---|
| SCN Glass – As sintered | ✓ | x | x | x | x | ✓ |
| 100 hours – Air | ✓ | ✓ | x | x | x | ✓ |
| 100 hours – Steam+$H_2$+$N_2$ | ✓ | ✓ | ✓(s) | x | x | ✓ |
| 500 hours – Air | ✓ | ✓ | x | x | x | ✓ |
| 500 hours – Steam+$H_2$+$N_2$ | ✓ | ✓ | ✓(s) | x | x | ✓ |
| 865 hours – Air | ✓ | ✓ | ✓(s) | x | x | ✓ |
| 850 hours – Steam+$H_2$+$N_2$ | ✓ | ✓ | ✓(s) | ✓(s) | x | ✓ |
| 5,000 hours – Air | ✓ | ✓ | ✓(s) | ✓ | ✓(s) | ✓ |
| 5,000 hours – Steam+$H_2$+$N_2$ | ✓ | ✓ | ✓(s) | ✓ | x | ✓ |

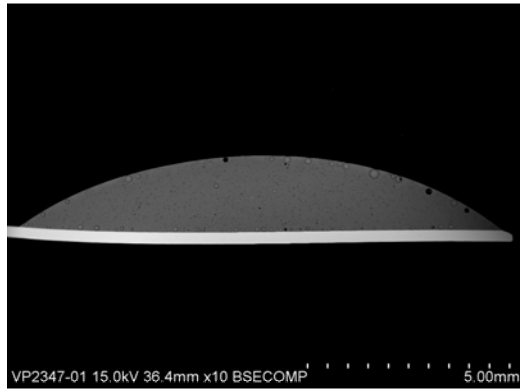
✓(s) – Phase forms only on the surface of the bead

# Quantification of microstructural features

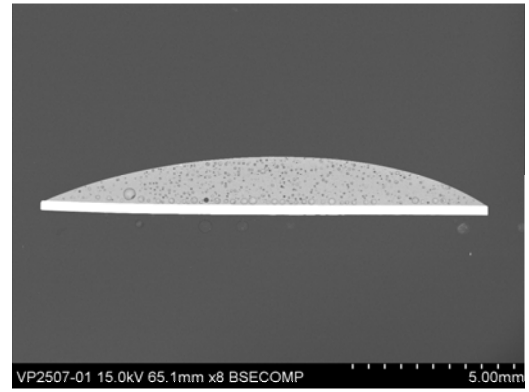
On 8YSZ Substrate in steam+$H_2$+$N_2$ environment



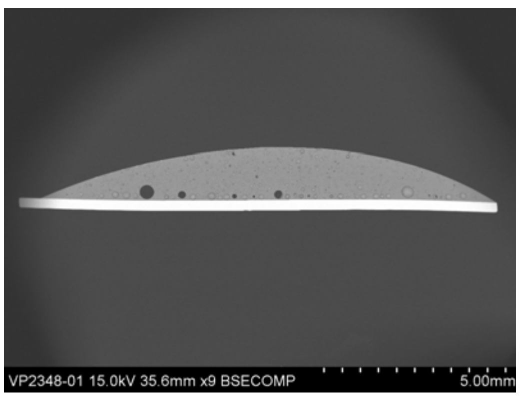

Before Exposure



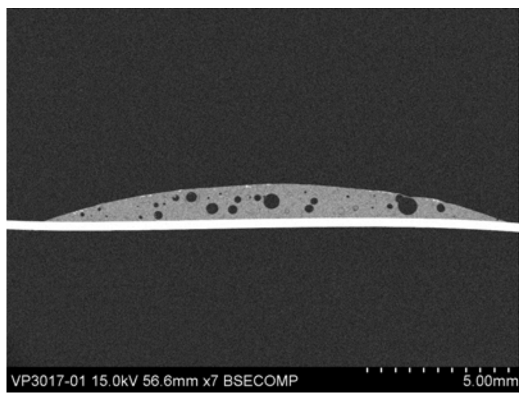

100 hr




500 hr



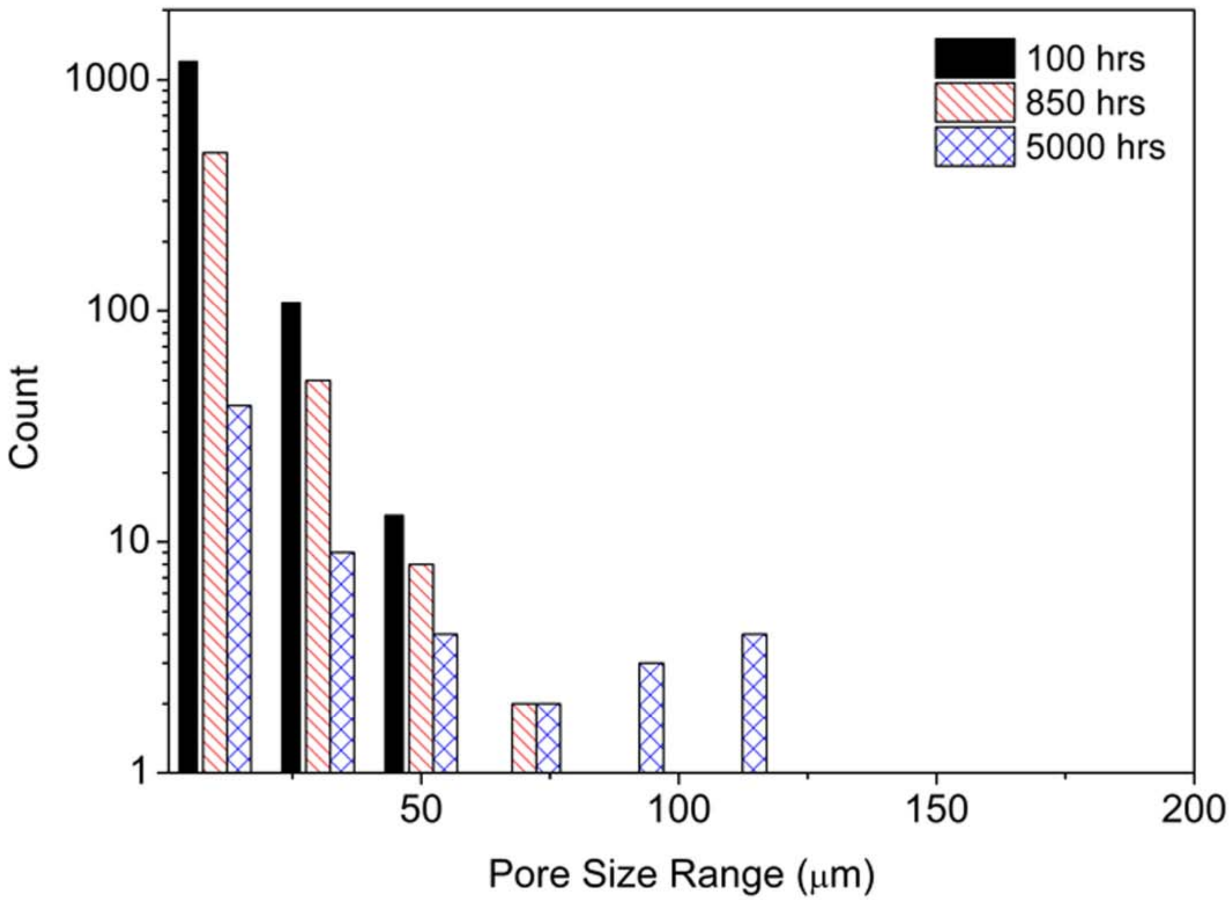

865 hr

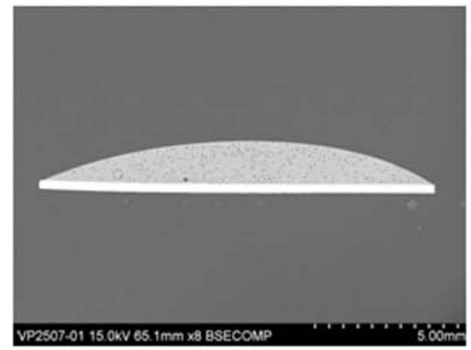



5000 hr

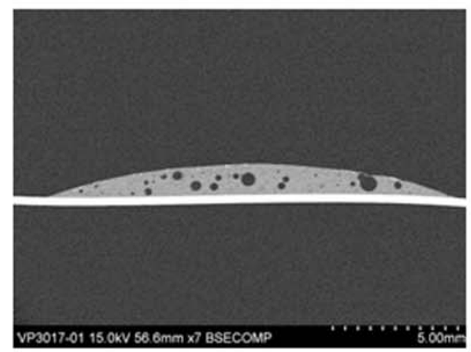
- Coarsening of pores can be observed

# Pore Coarsening in *8YSZ* Substrate – steam+$H_2$+$N_2$



500 hours

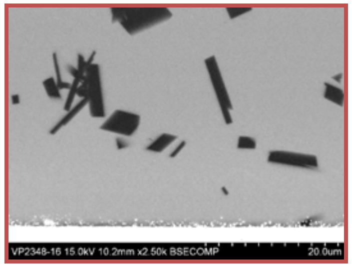


5000 hours

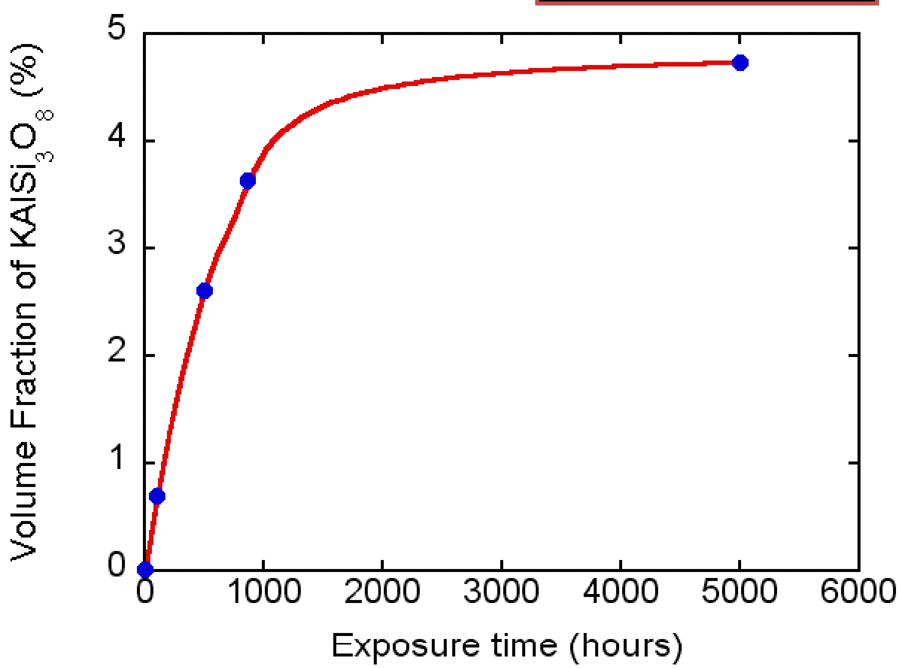
- Fewer but larger pores at longer times of exposure
- Heterogeneity in seal properties

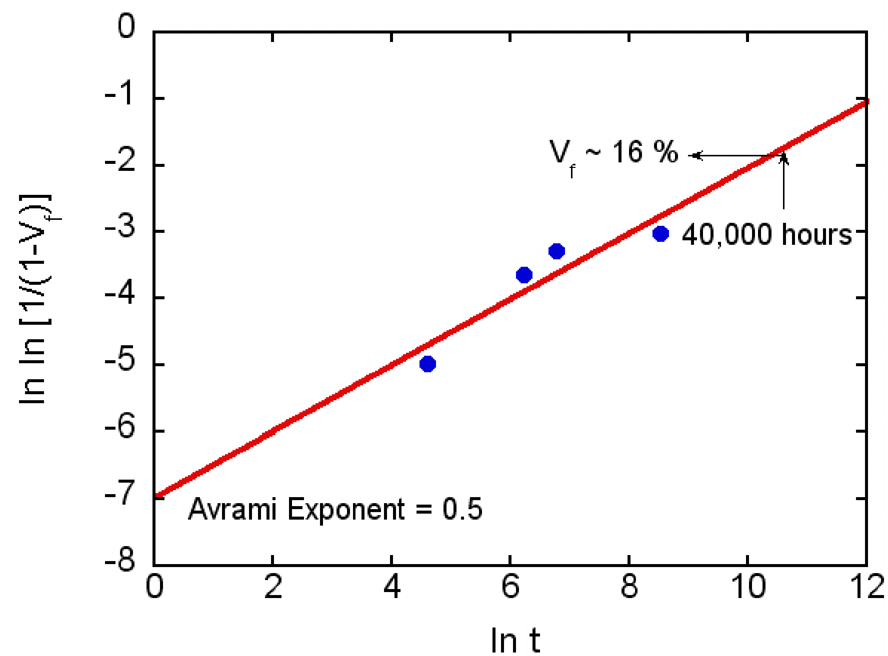
# Devitrification kinetics of $KAlSi_3O_8$ 8YSZ Substrate in Air

- Volume fraction of $KAlSi_3O_8$ precipitates calculated by image analysis of cross sections




$$V_f = 1 - \exp[-(kt)^n]$$




- At present rate ~15% of glass transform into precipitate after 40,000 hours

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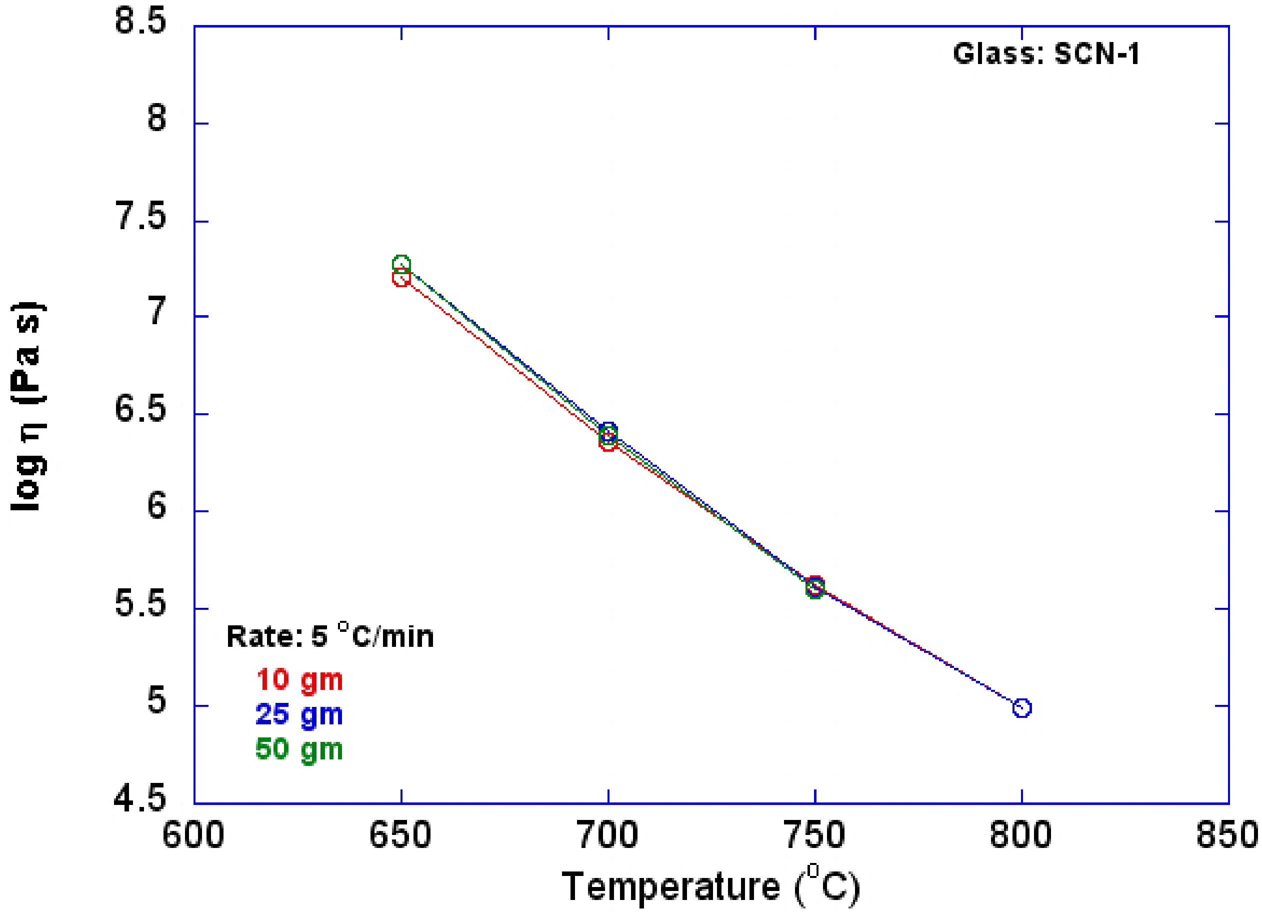
  - Viscosity, Glass Transition Temperature and Thermal Expansion of SCN glass

Measurements of viscosity, CTE and $T_g$ with thermomechanical analyzer (TMA)

Before Viscosity Measurements

After Viscosity Measurements

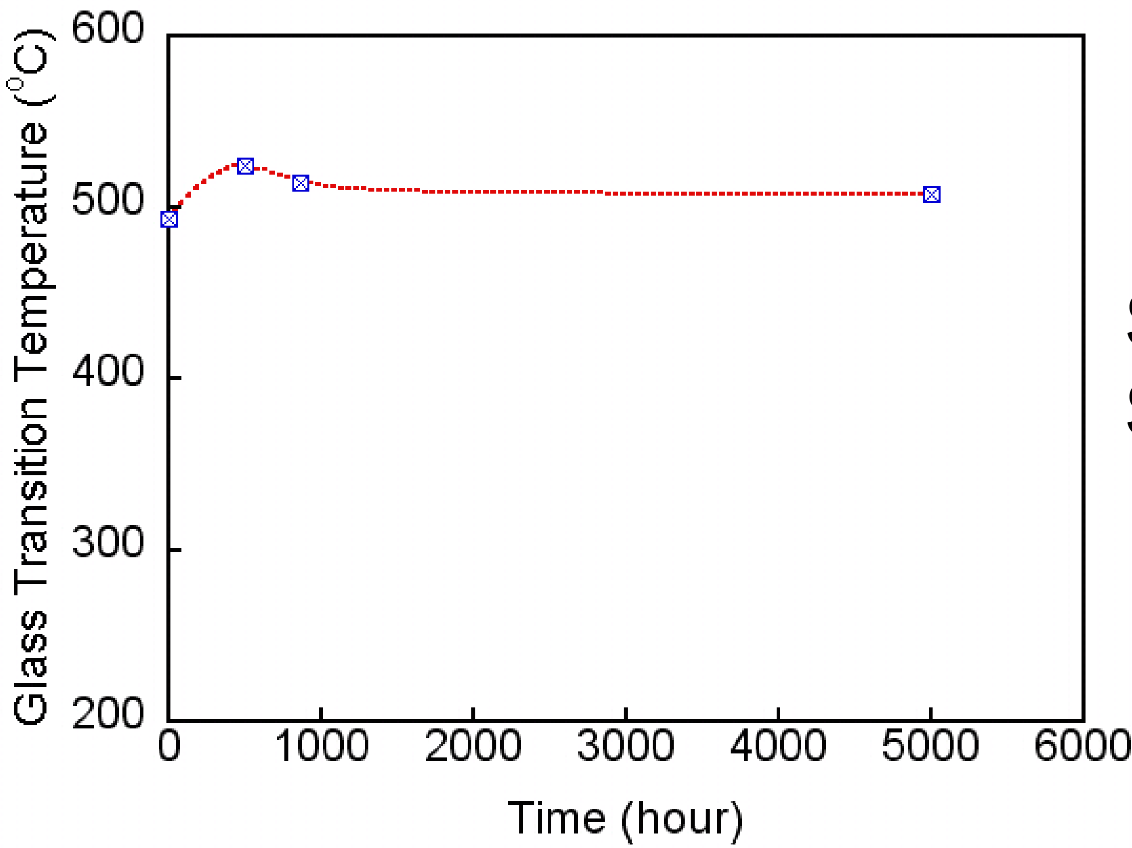
# Viscosity of SCN Glass




- Measurements performed according to ASTM Standard C1351
- Individual measurements performed at constant load and temperature
- Activation energy of viscosity in this temperature range ~ 280 kJ/mol

# CTE and Glass Transition for SCN glass

- Glass transition temperature is around 500$^{o}$C for as-sintered and exposed specimens




SCN Glass on 8YSZ Substrate in Air

- Average linear CTE for as-sintered SCN Glass is 11.7 x $10^{-6}$ per $^{o}$C between 20°C and 400°C

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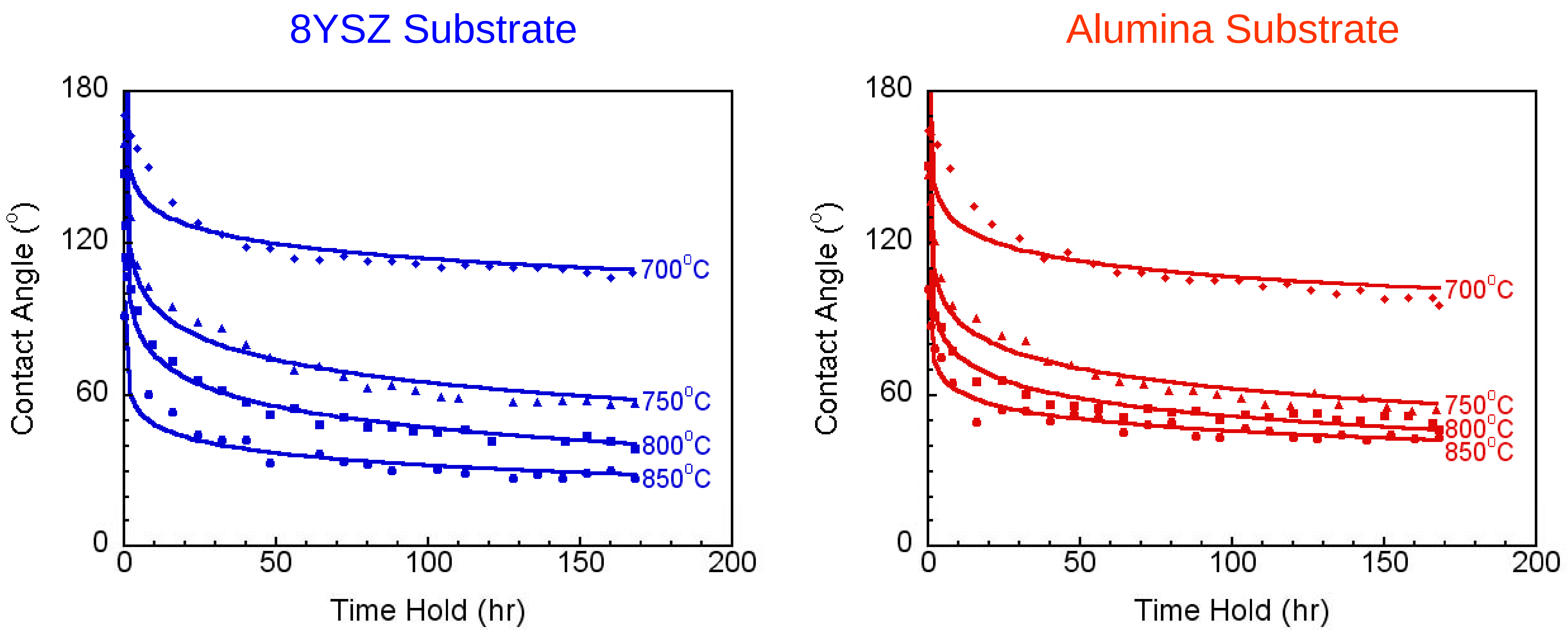
  - Viscosity, Glass Transition Temperature and Thermal Expansion
  - Wetting behavior

# *In-situ* contact angle meaurements

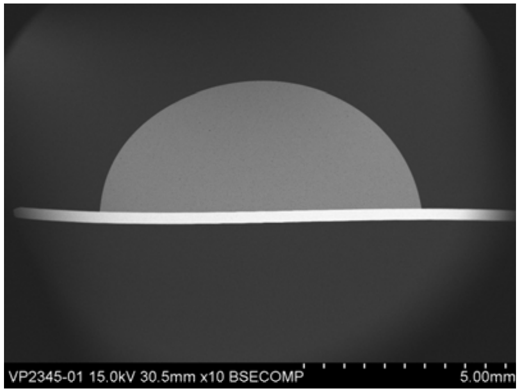
SCN Glass – 800°C on 8YSZ – 168 hour exposure

# *In-situ* contact angle measurements

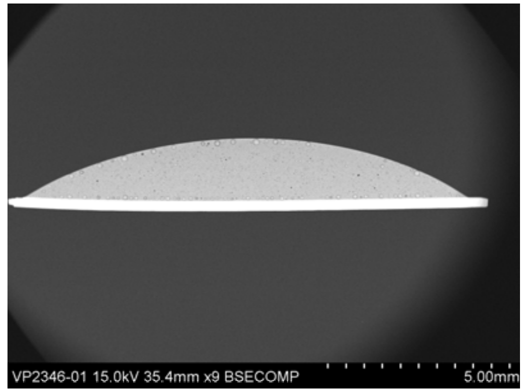



- Wetting behavior well characterized up to 1 week as a function of temperature and substrate
- The glass wets the substrates at temperatures > 750°C.

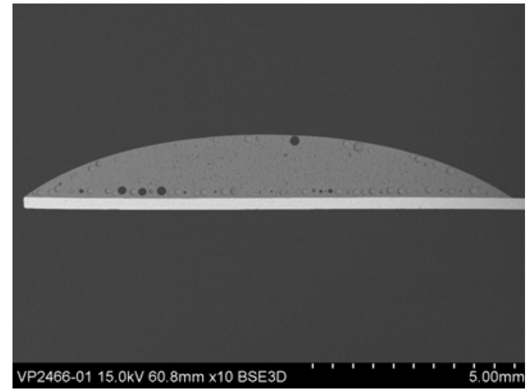
# Effect of Environmental Exposure SCN Glass on 8YSZ substrate - air



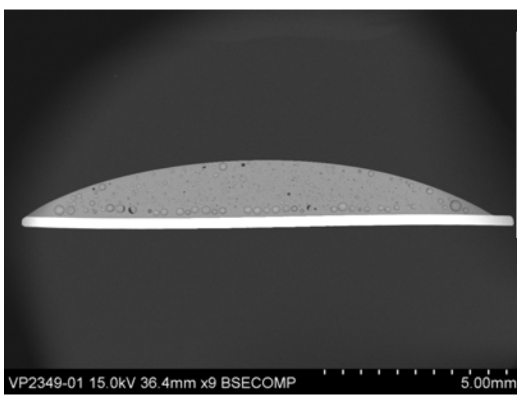
Before Exposure



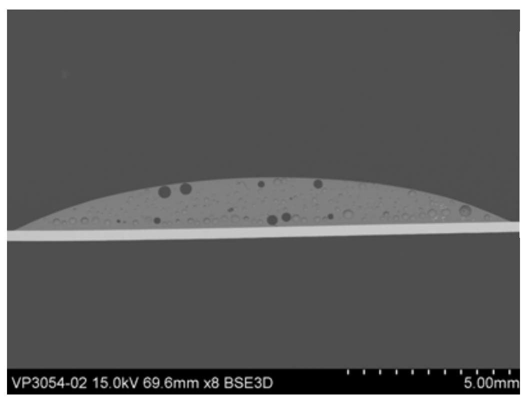
100 hr



500 hr



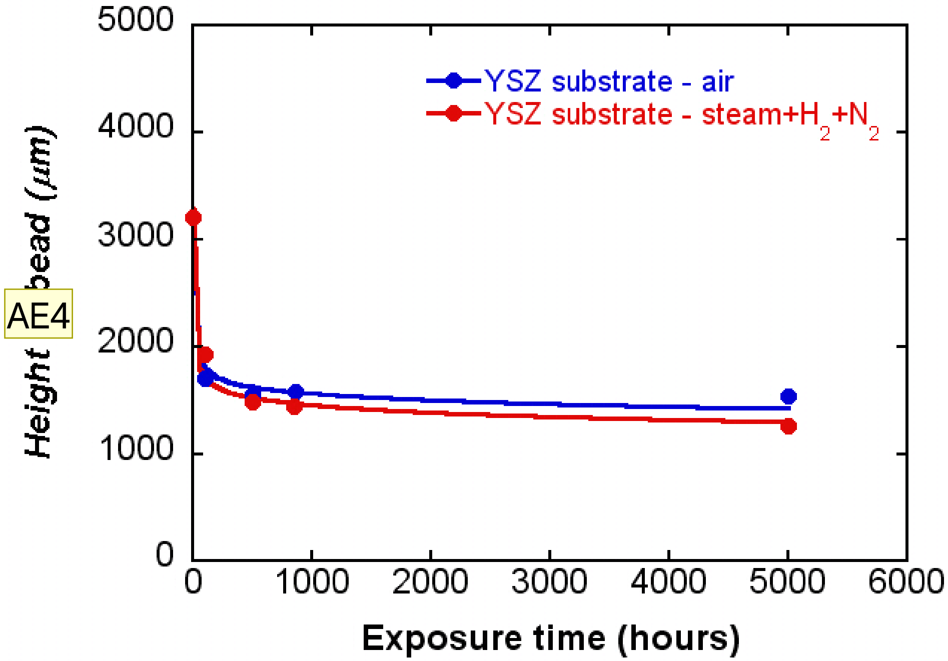
865 hr

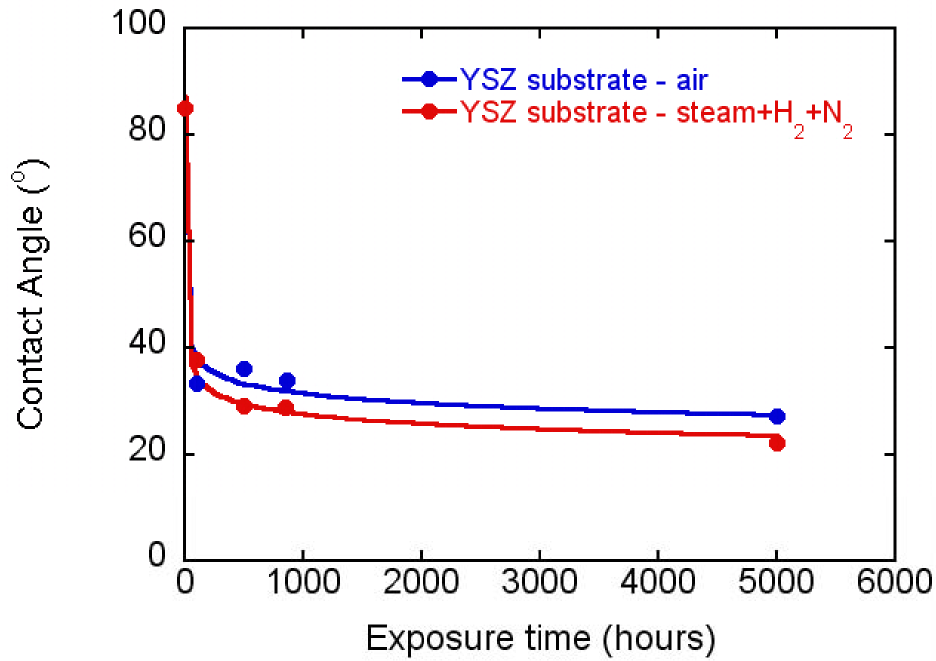


5000 hr

- Exposure temp is 800°C
- Dome height and contact angles decrease with time

# Effect of Environment on Glass Flow
# (*ex-situ* - Air versus steam+$H_2$+$N_2$)




- For longer times glass flows more in the steam rich environment
- Surface tension may change in gas mixture containing steam.**

**Simhan et al., *J. Mater. Sci*, **20** (1985) pp. 1748-1752.

**Slide 33**

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**AE4** font type
Associate Editor, 7/24/2010

# Summary

- The effect of long-term exposure at 800ºC to air and steam $+H_2+N_2$ on the microstructural, dimensional and chemical stability of SCN in contact with 8YSZ and alumina was investigated
- The glass is resistant to severe microstructural changes under SOFC (oxidizing and wet-reducing) conditions
- The glass is chemically compatible with both alumina and zirconia substrates but a thin reaction layer forms
- Coarsening of pores observed in glass after long term exposure
- Longer term exposure (20,000+ hours) is in progress

# Acknowledgements


- Matt Chou and Jeff Stevenson (PNNL)

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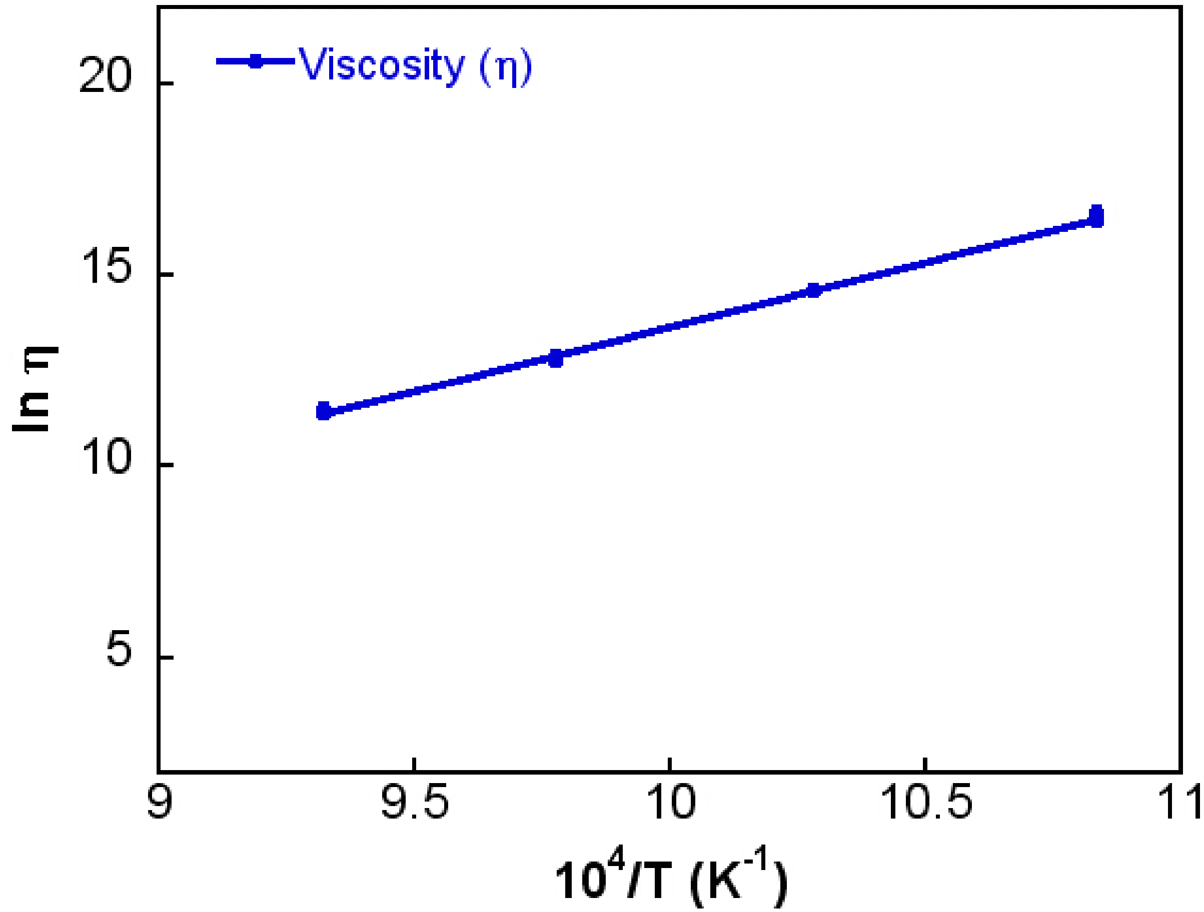
# Extra Slides

# Activation energy calculations – Viscosity

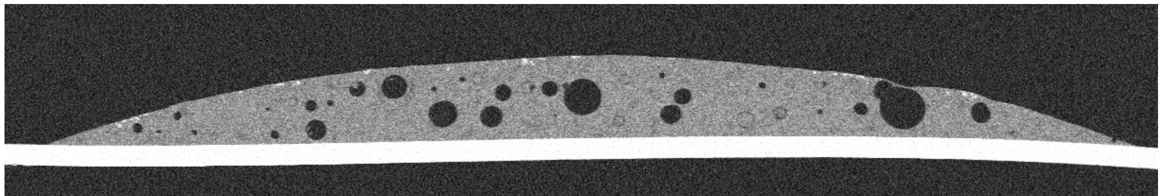
Assume the form:

$$\eta = \eta_o \exp\left(\frac{Q_V}{RT}\right)$$

$Q_V$ = 283.32 kJ/mol

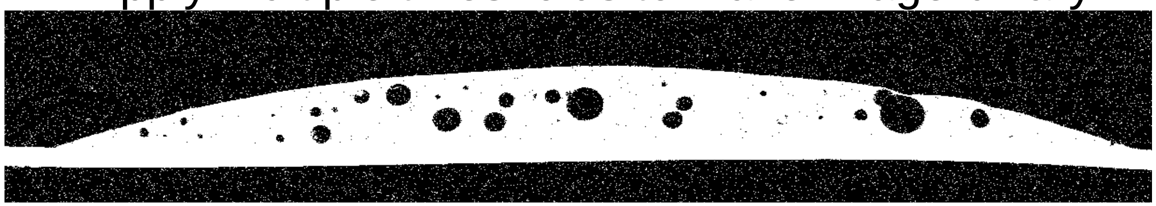


# Pore-size distribution changes with exposure – methodology with ImageJ®

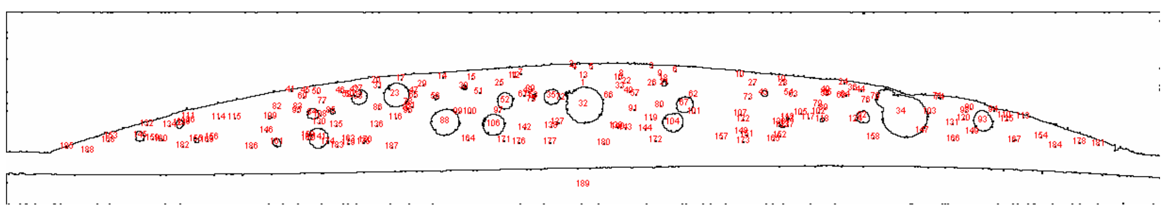


Set Scale

Apply multiple thresholds to make image binary

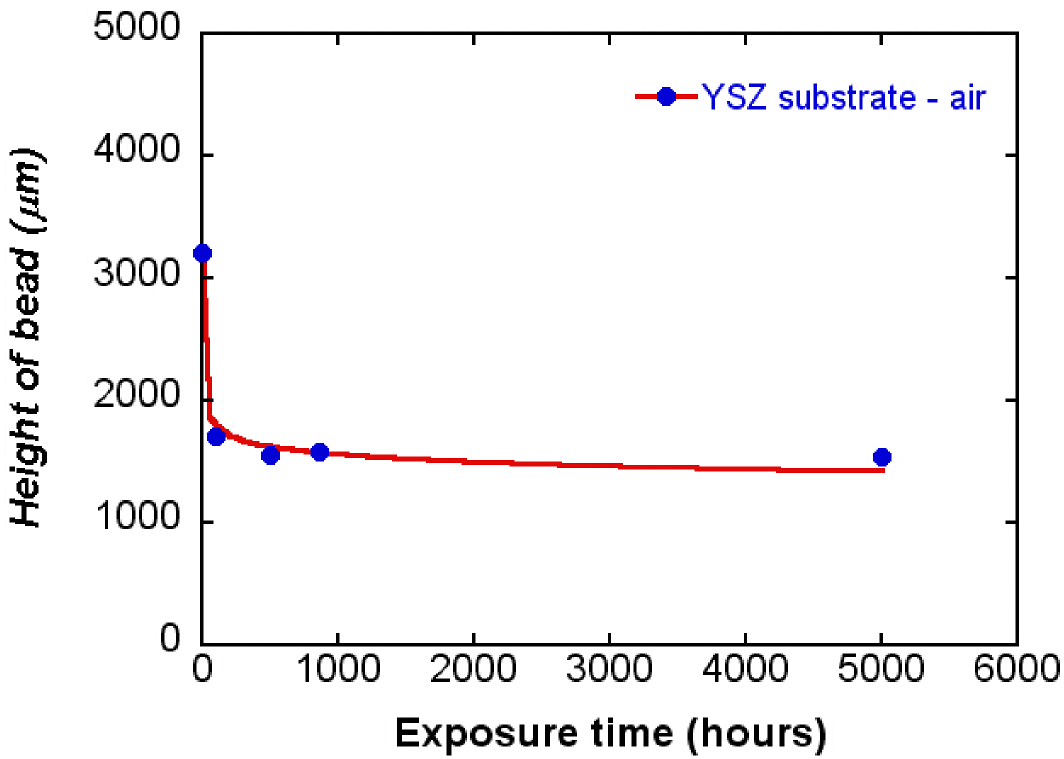


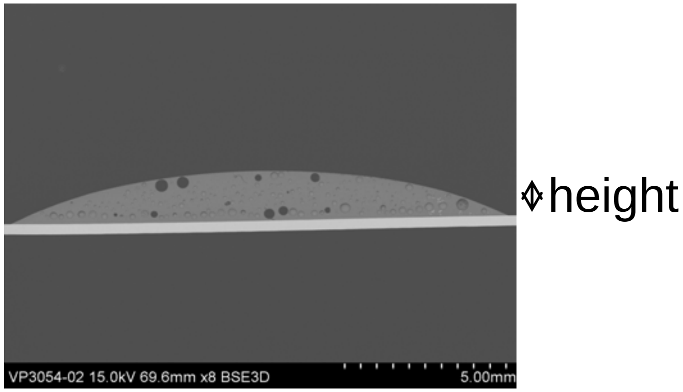
Analyze particles (pores) by setting size-range (>100 $\mu m^2$) and circularity



Pore-size distribution

# Effect of Environmental Exposure
# SCN Glass on YSZ substrate in air




- Height of bead decreases with time

# Viscosity, Thermal Expansion and Glass Transition Temp of SCN-1 Glass

Before Viscosity Measurements

After Viscosity Measurements

Measurements of viscosity, CTE and $T_g$ with thermomechanical analyzer (TMA)

Isothermal conditions (different temperatures between 600°C and 850°C) at 3 different loads (according to ASTM standard C1351)