Engineered Glass Seals for SOFCs

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Acknowledgments

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Matt Chou, Jeff Stevenson, Moe Khaleel at al. (PNNL)

SECA Industry Teams

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Outline

- Background
- Multicomponent Silicate Glasses
- Engineered Glass Seals
- Summary and Future Work

Background

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 in oxidizing and wet reducing environments.

Objective

- To characterize the evolution of microstructure and properties of candidate crystallization-resistant glasses for SOFC sealing applications as a function of time of exposure to SOFC relevant environments.
- To develop engineered glass seals for SOFCs.

Multicomponent silicate glasses

Two multicomponent silicate glasses are being characterized

- SCN (SEM-COM Co. Inc., Toledo, OH 43623)
- G6 (Whatman, Piscataway, NJ 08855)

Mechanical and Thermophysical Properties

- Elastic constants
- Thermal expansion
- Glass transition temperature
- Viscosity
- Chemical Composition
- Phase Analysis
- Wetting Behavior (alumina, zirconia)
- Microstructure
- Porosity and its evolution
- Rates of crystallization

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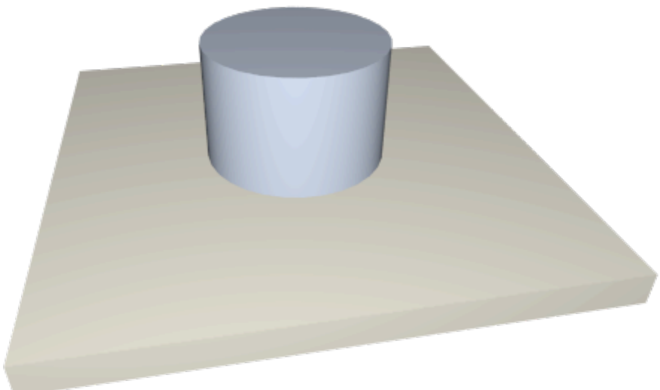
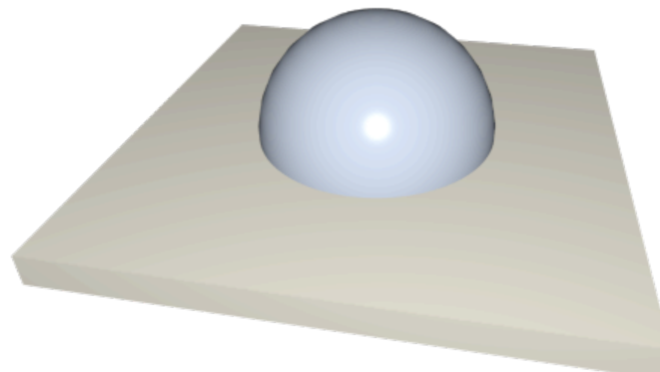
Experimental

cold compressed glass powders

after sintering in air for 2 hours at 850°C





Al_2O_3 or 8YSZ substrates

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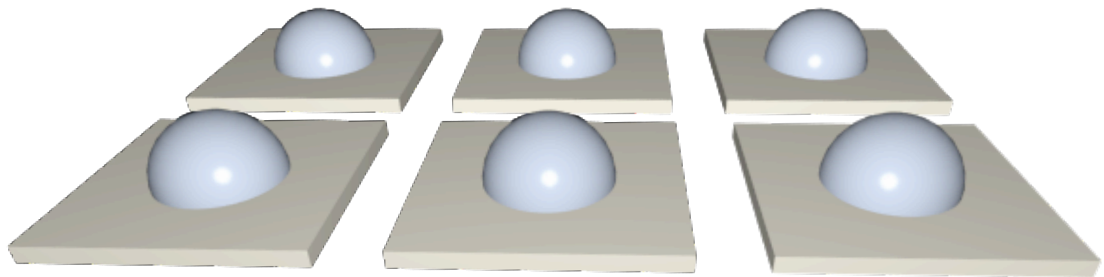
Experimental (cont.)



- Test specimens are exposed at 850°C to
  - **air**
  - gas mixture of $\mathbf{H_2+N_2+H_20}$
- Test specimens are retrieved from the furnace every 1,000 hrs for non-destructive examination.

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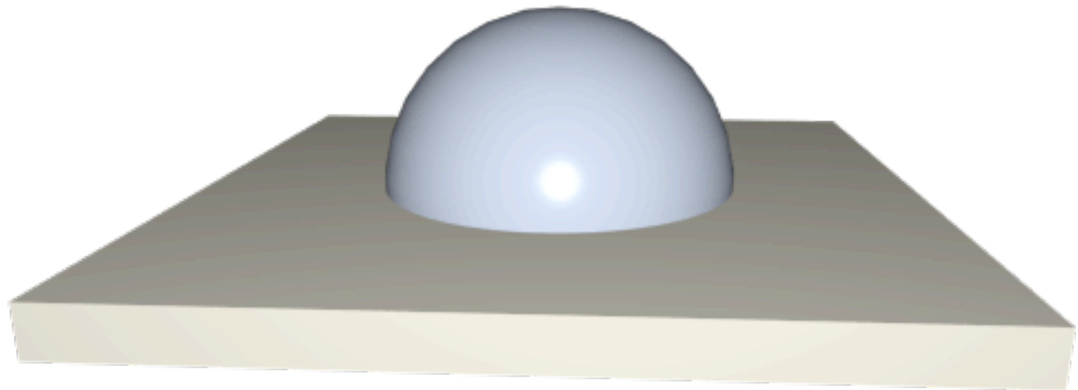
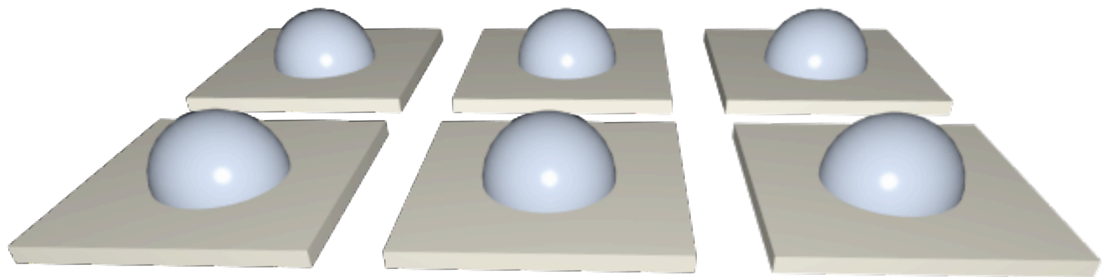
Experimental (cont.)



- Scanning electron microscopy
- EDS
- X-ray diffraction
- Dimensions

Experimental (cont.)



- Test specimens are exposed to **air** or a gas mixture of **H_2+N_2+H_20 at 850°C.**
- Test specimens are retrieved from the furnace every 1,000 hrs for non-destructive examination (SEM, XRD). Then they are returned to furnace to continue exposure.
- After predetermined periods of time, test specimens are removed for destructive examination (SEM, XRD, Tg, viscosity)

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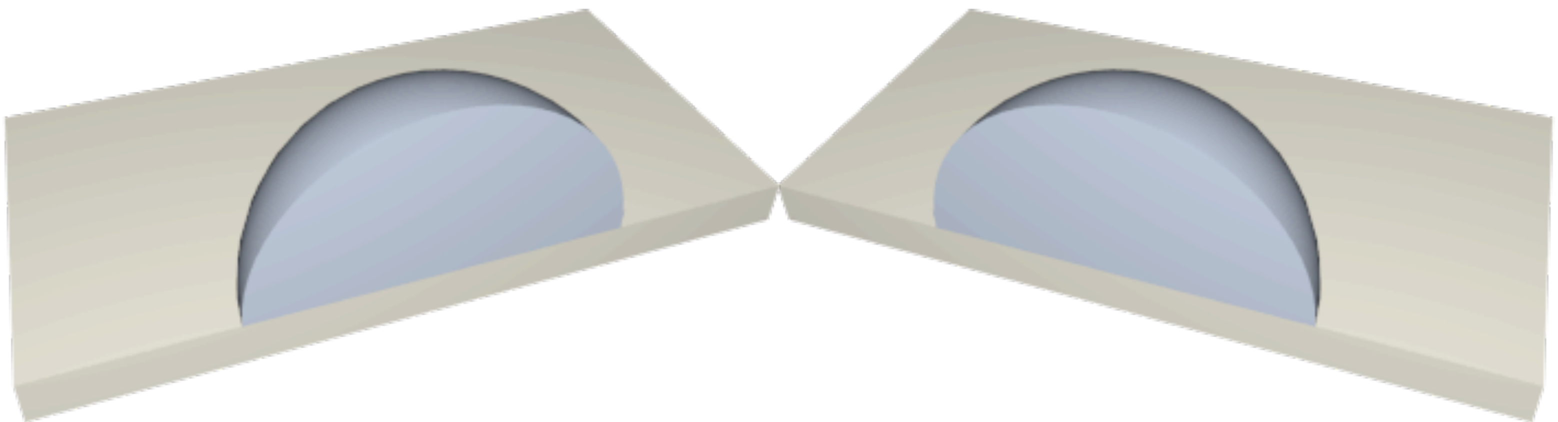
Experimental (cont.)



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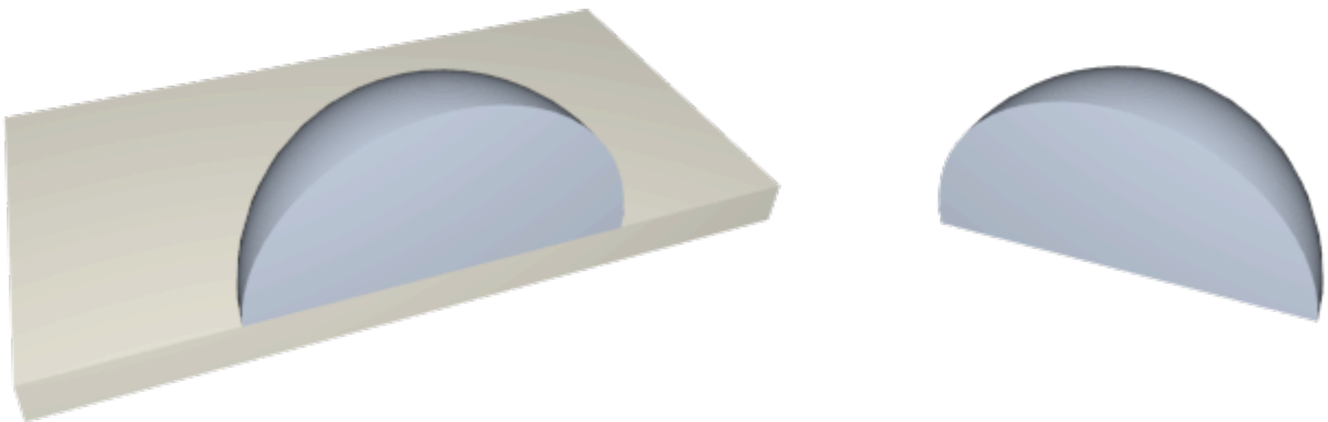
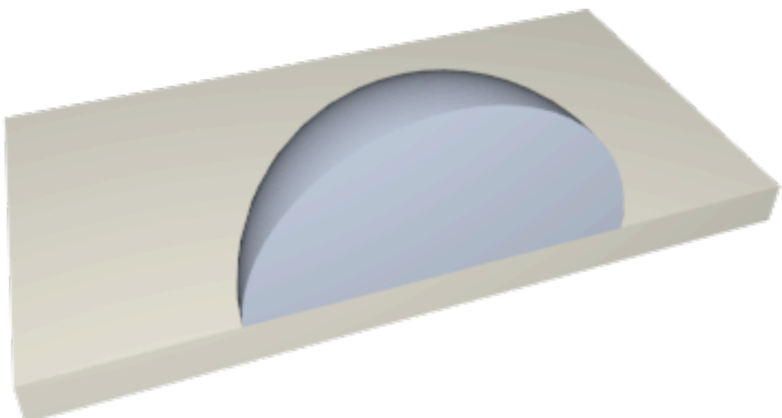
Experimental (cont.)



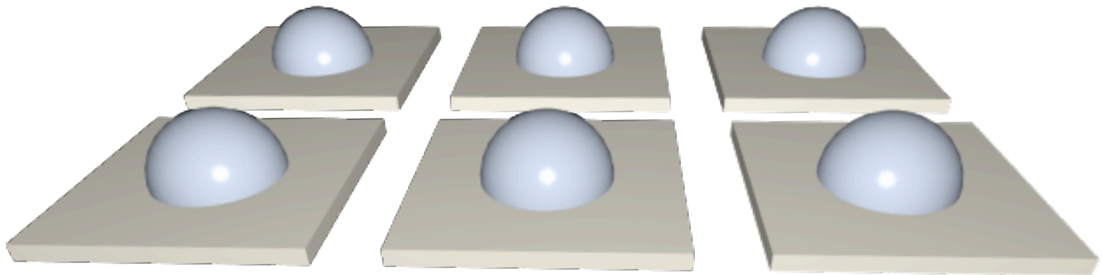
Experimental (cont.)



X-ray diffraction

- Scanning electron microscopy
- EDS

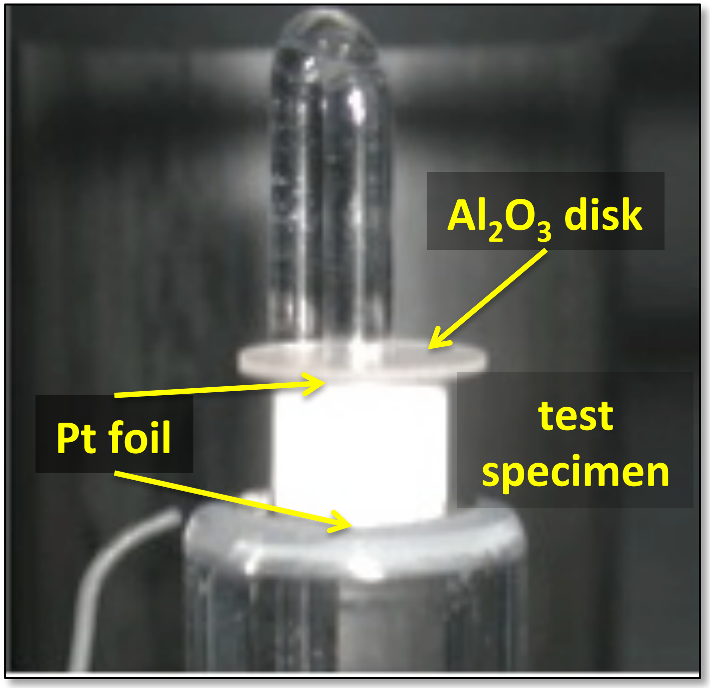
Experimental (cont.)



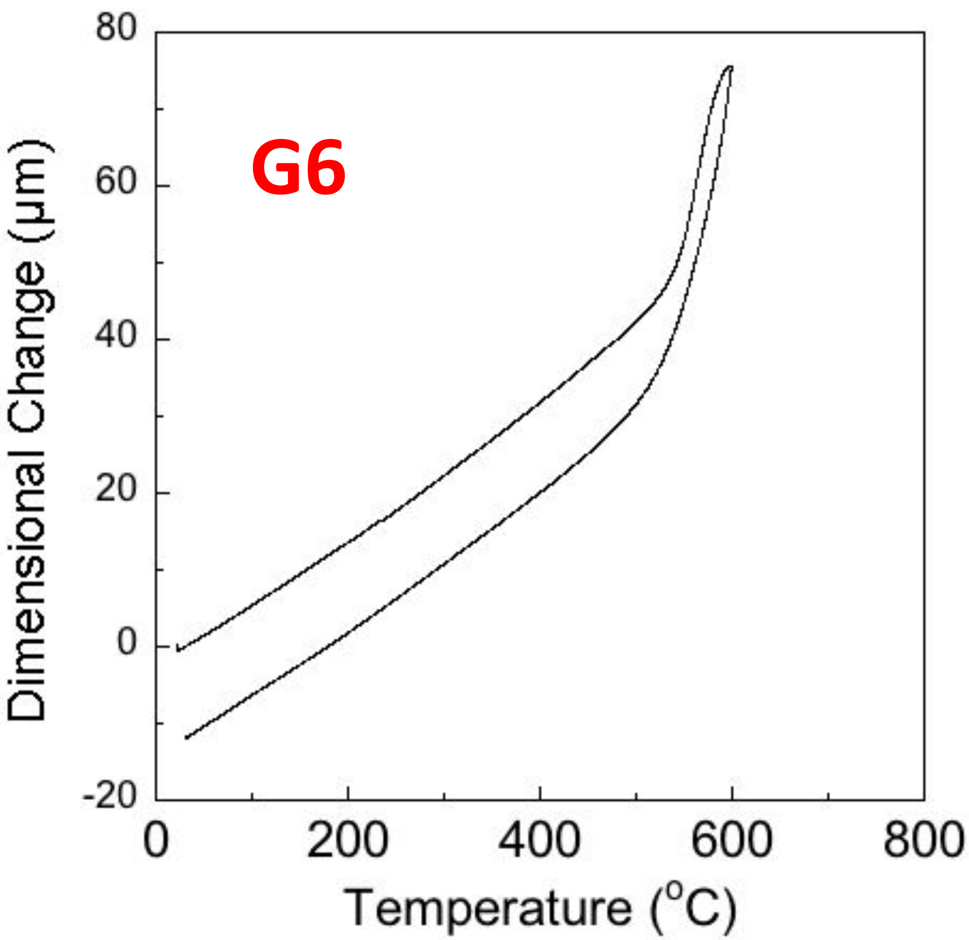
- To date we have completed the analysis of test specimens of SCN and G6 exposed for 10,000 hrs in air and (H_2+N_2+H_2O)
- Two sets of test specimens continue exposure tests (15,000+ hrs)

Results

Thermal Expansion and Glass Transition Temperature



Thermomechanical Analyzer



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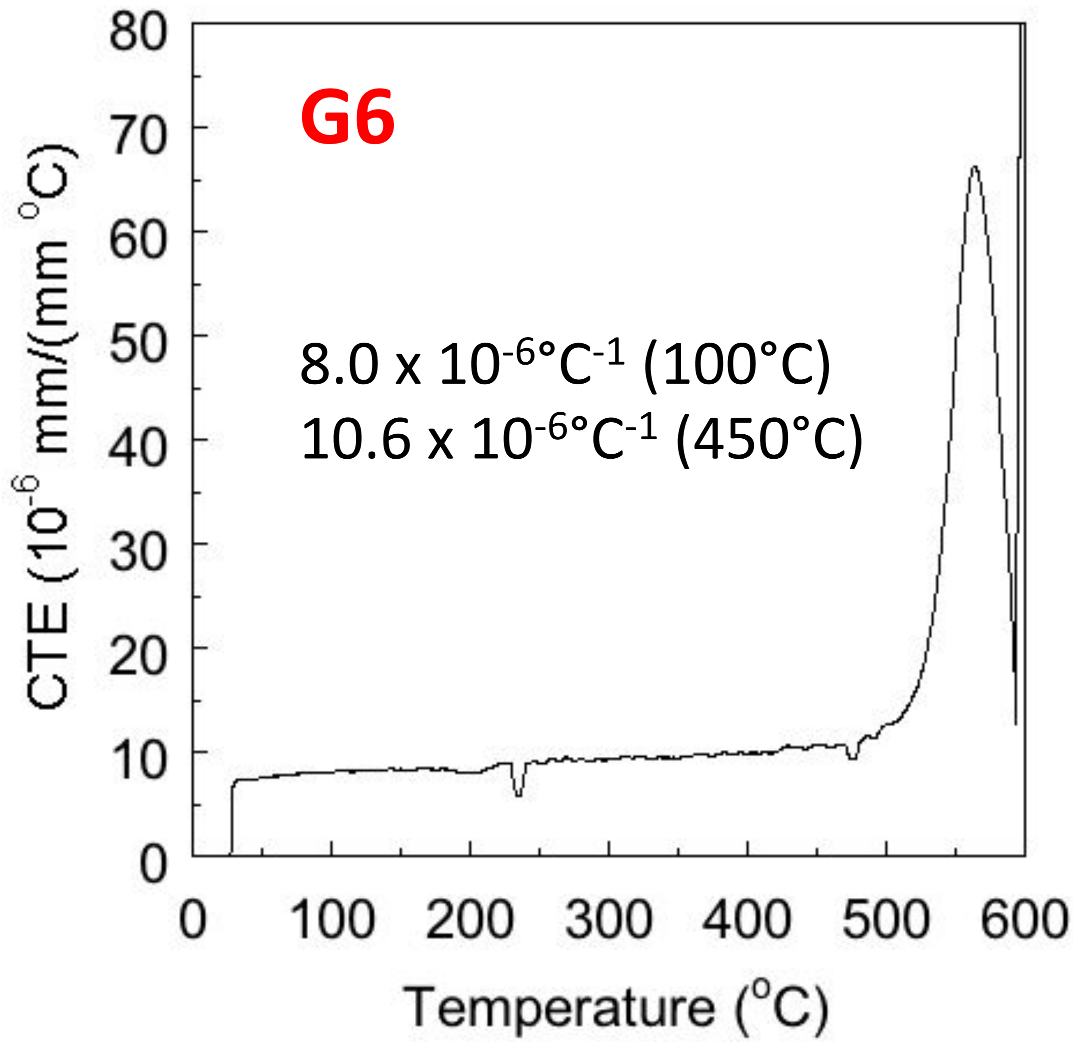
Thermal Expansion

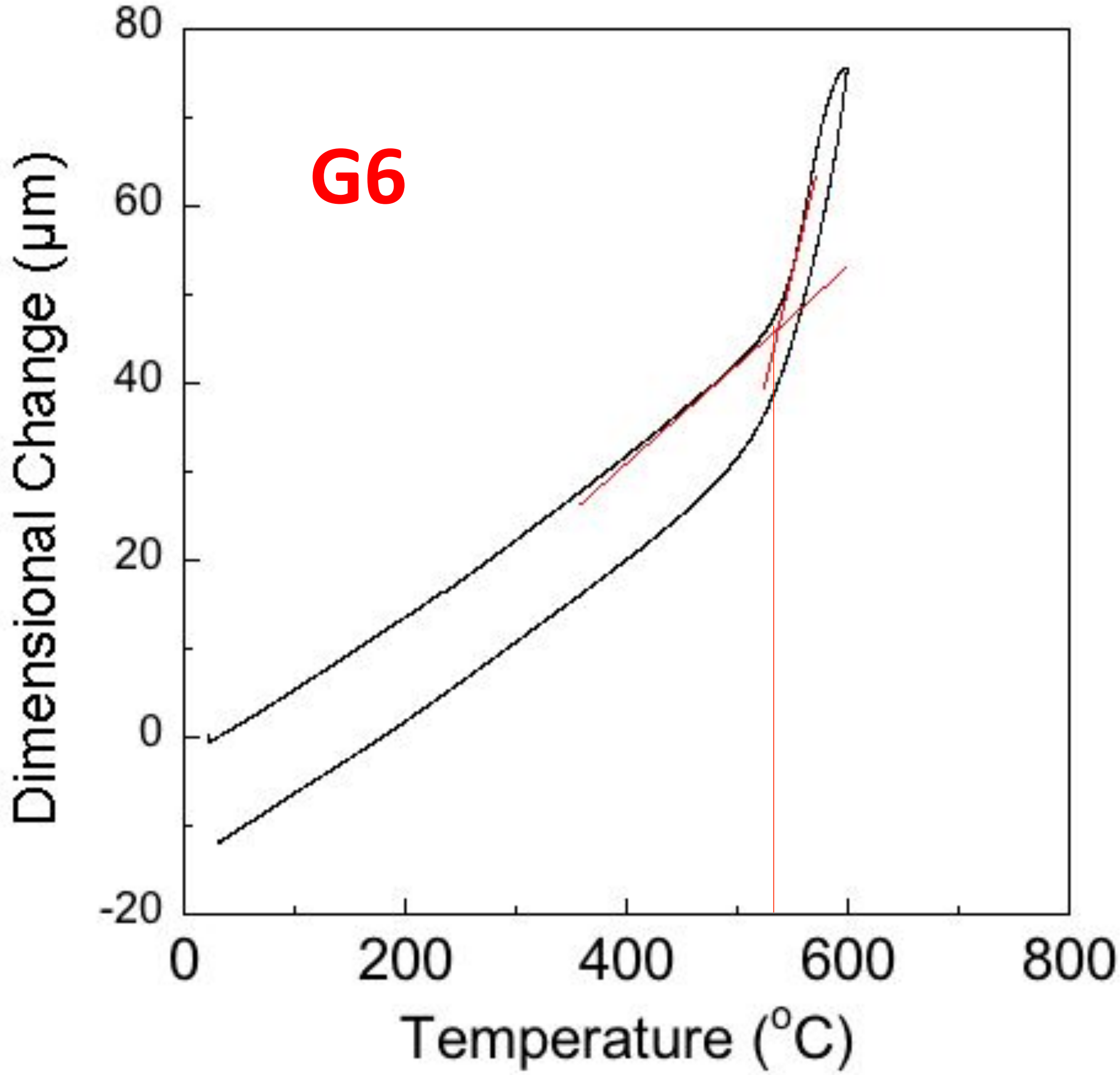


SCN

10.3×10^{-6}°C^{-1} (100°C)

12.4×10^{-6}°C^{-1} (400°C)

Glass Transition Temperature



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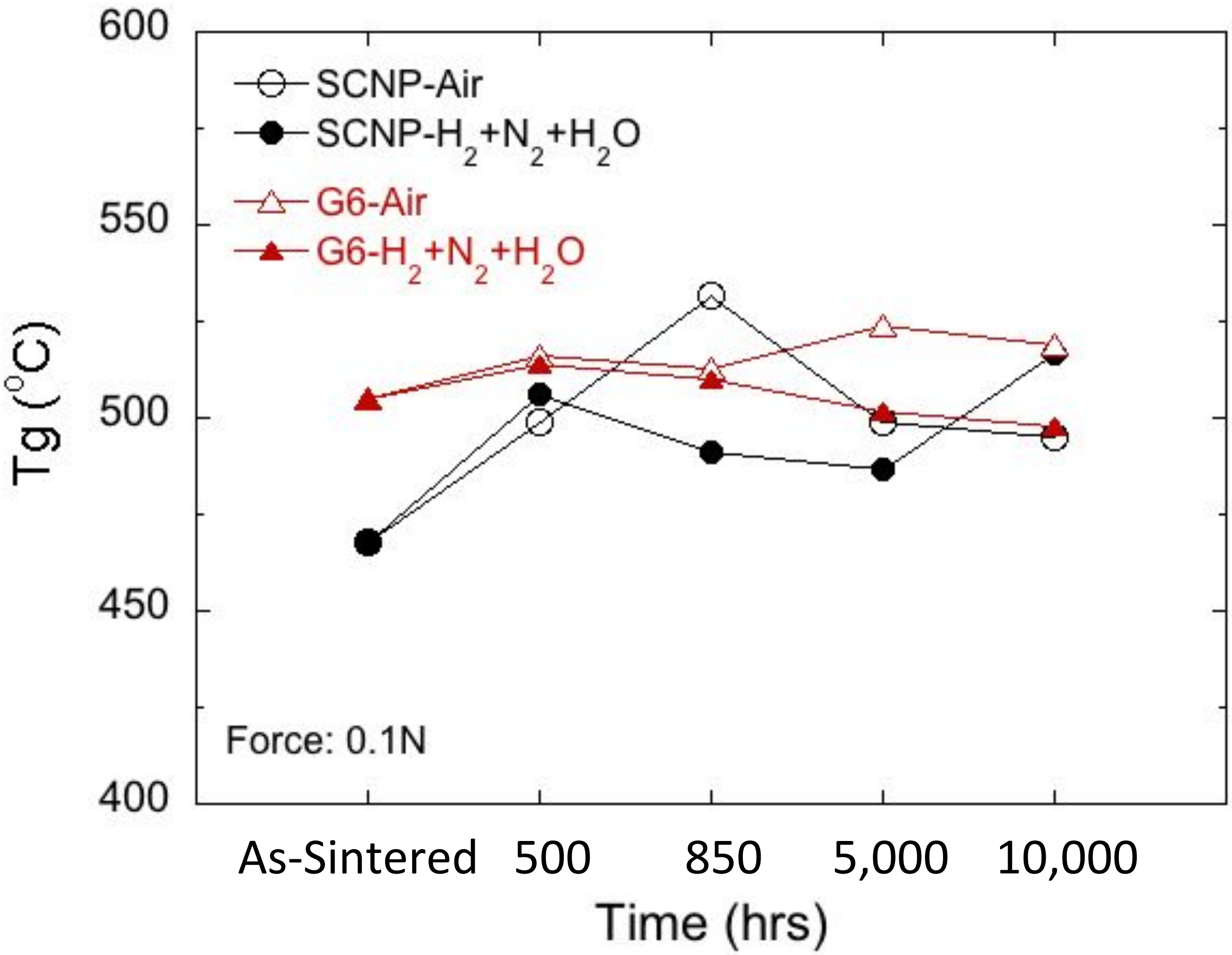
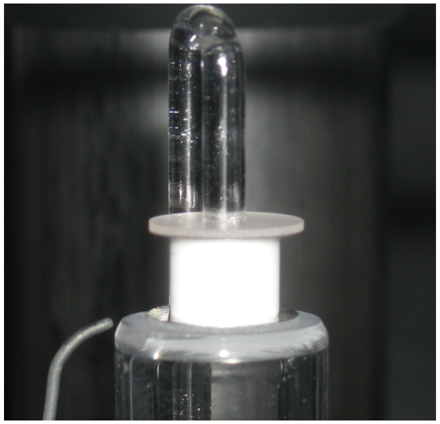
Glass Transition Temperature



Viscosity of G6 Glass



Before Viscosity Measurements

After Viscosity Measurements

Viscosity Measurements with TMA

- Isothermal conditions (different temperatures between 600°C and 850°C) at 3 different loads (according to ASTM standard C1351)
- Constant heating rate (1°C/min) under a constant load (0.25N)

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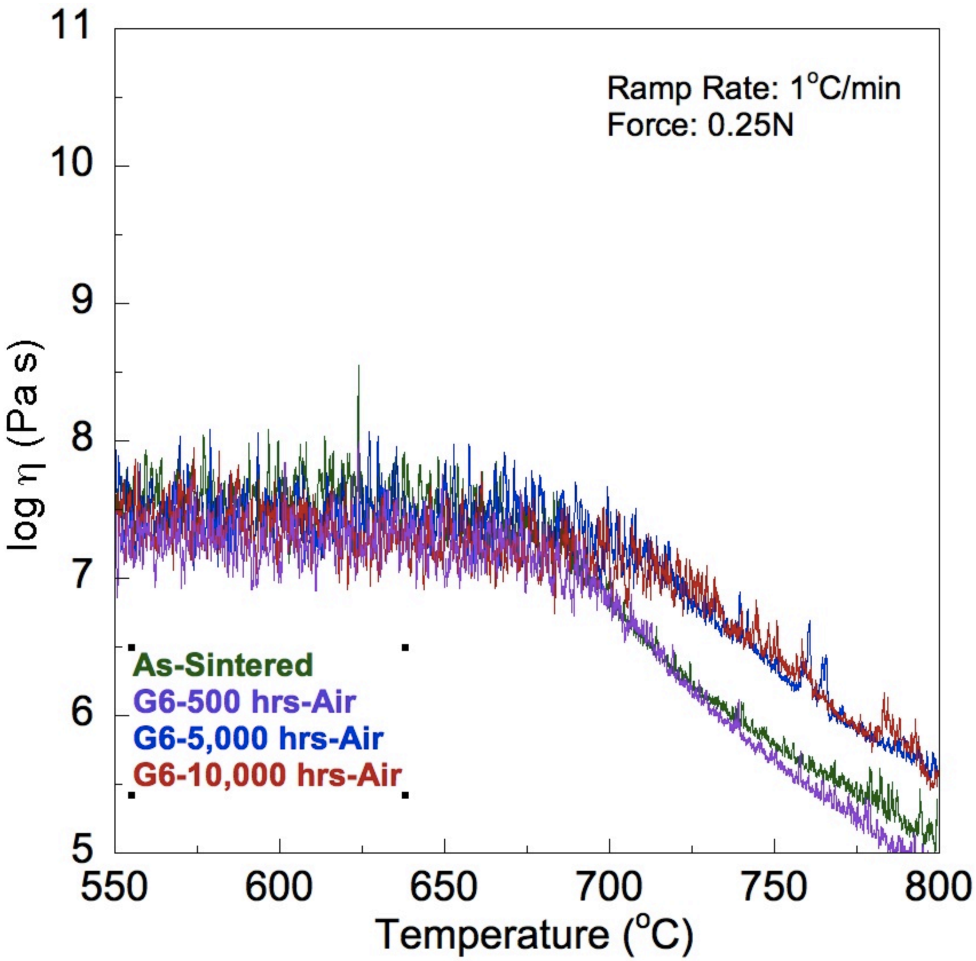
Viscosity of G6 Glass



- Viscosity decreases with temperature and increases with time of exposure.
- Increase in viscosity could be explained by precipitation of crystalline phases.

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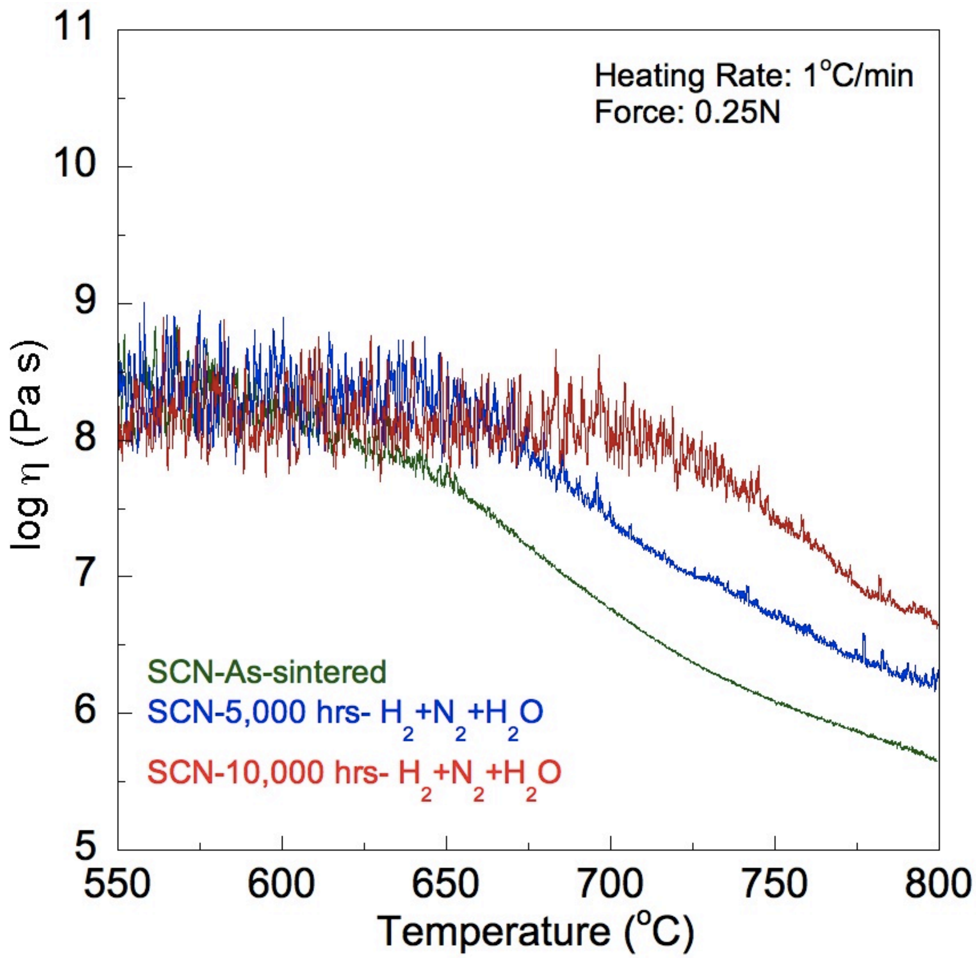
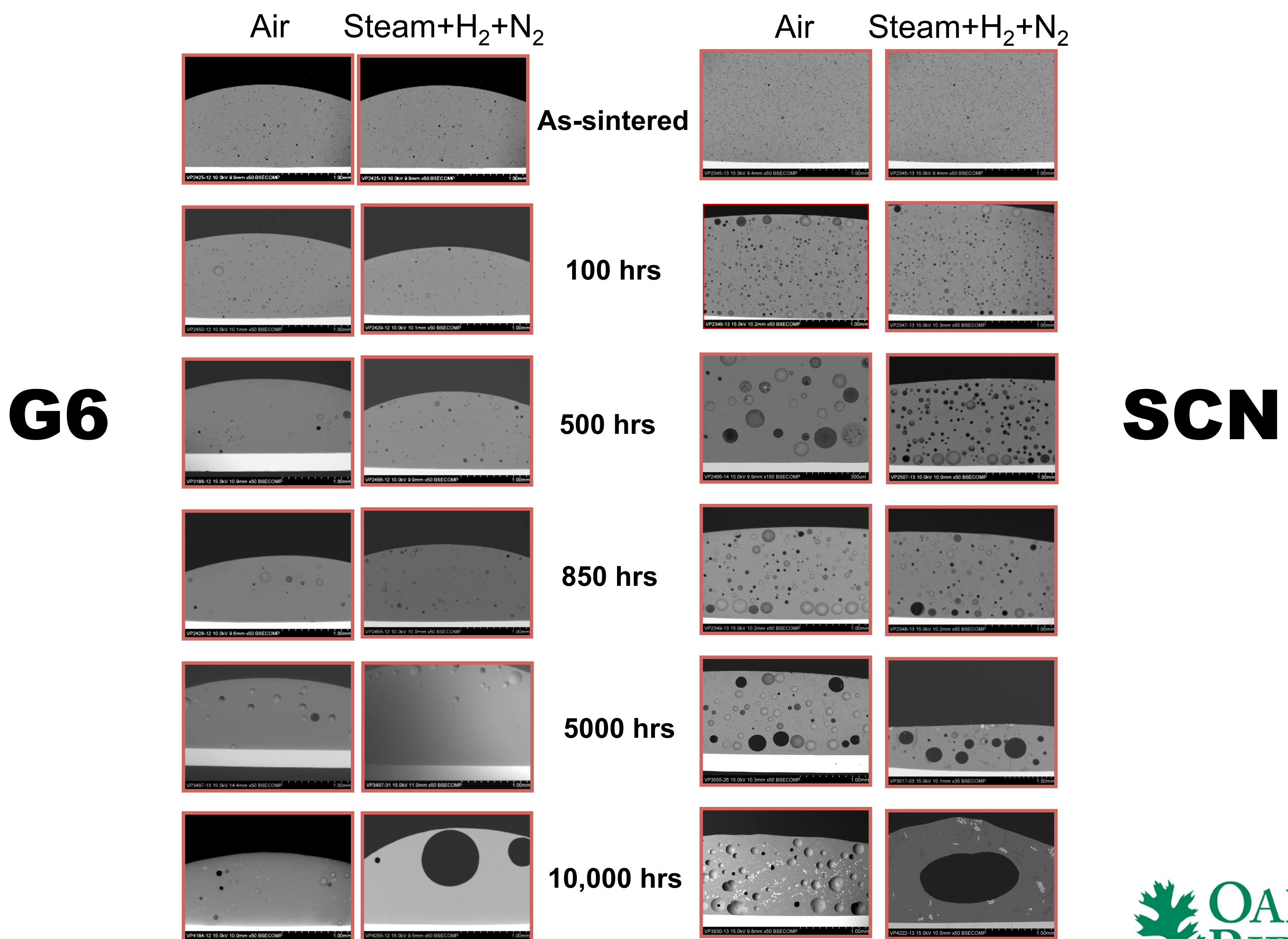
Viscosity of SCN Glass



- Viscosity decreases with temperature and increases with time of exposure.
- Increase in viscosity could be explained by precipitation of crystalline phases.

Microstructural Evolution of multicomponent silicate glasses



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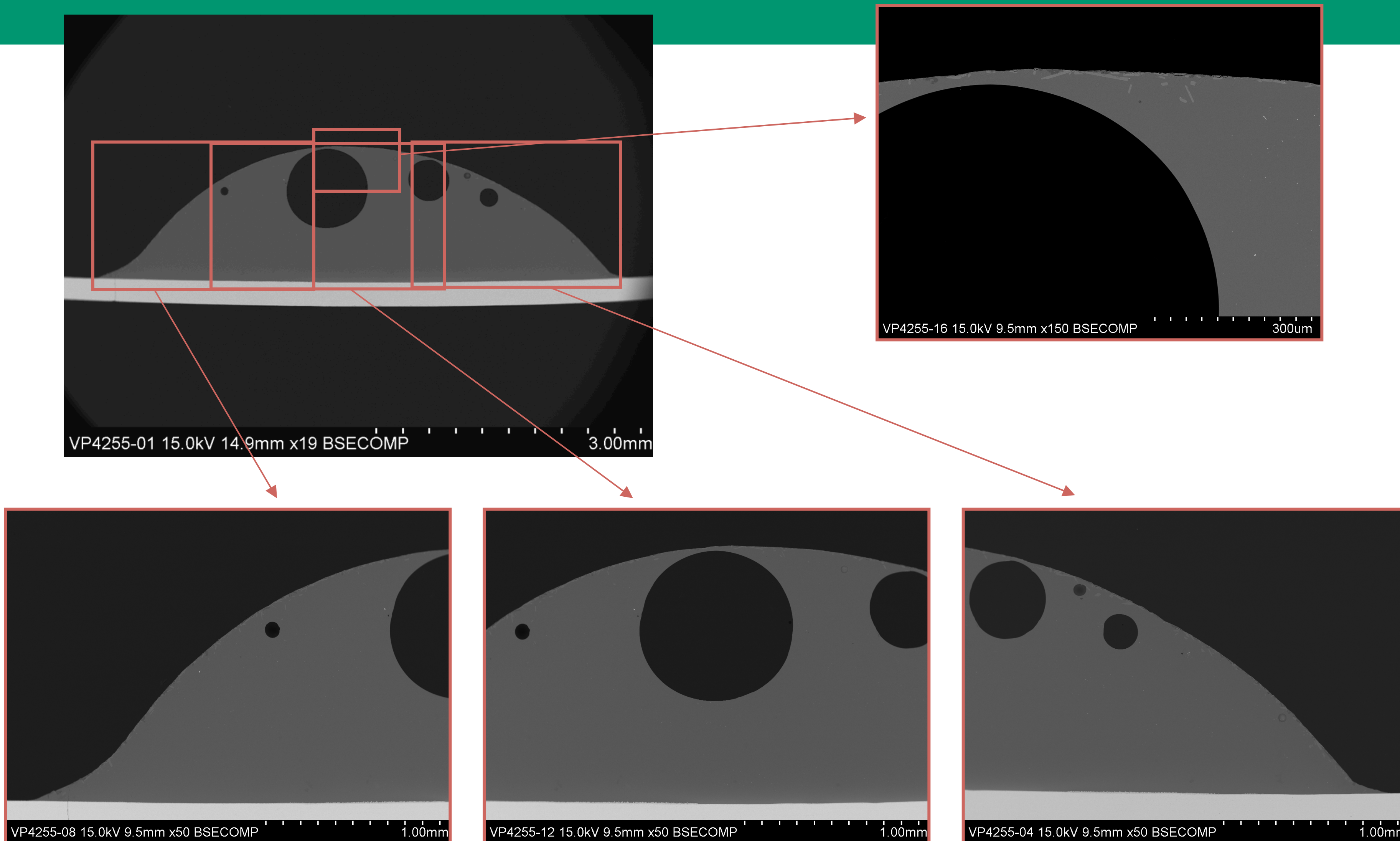
G6-YSZ-54

After 10,000 Hours in Steam+H_2+N_2



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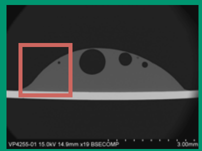
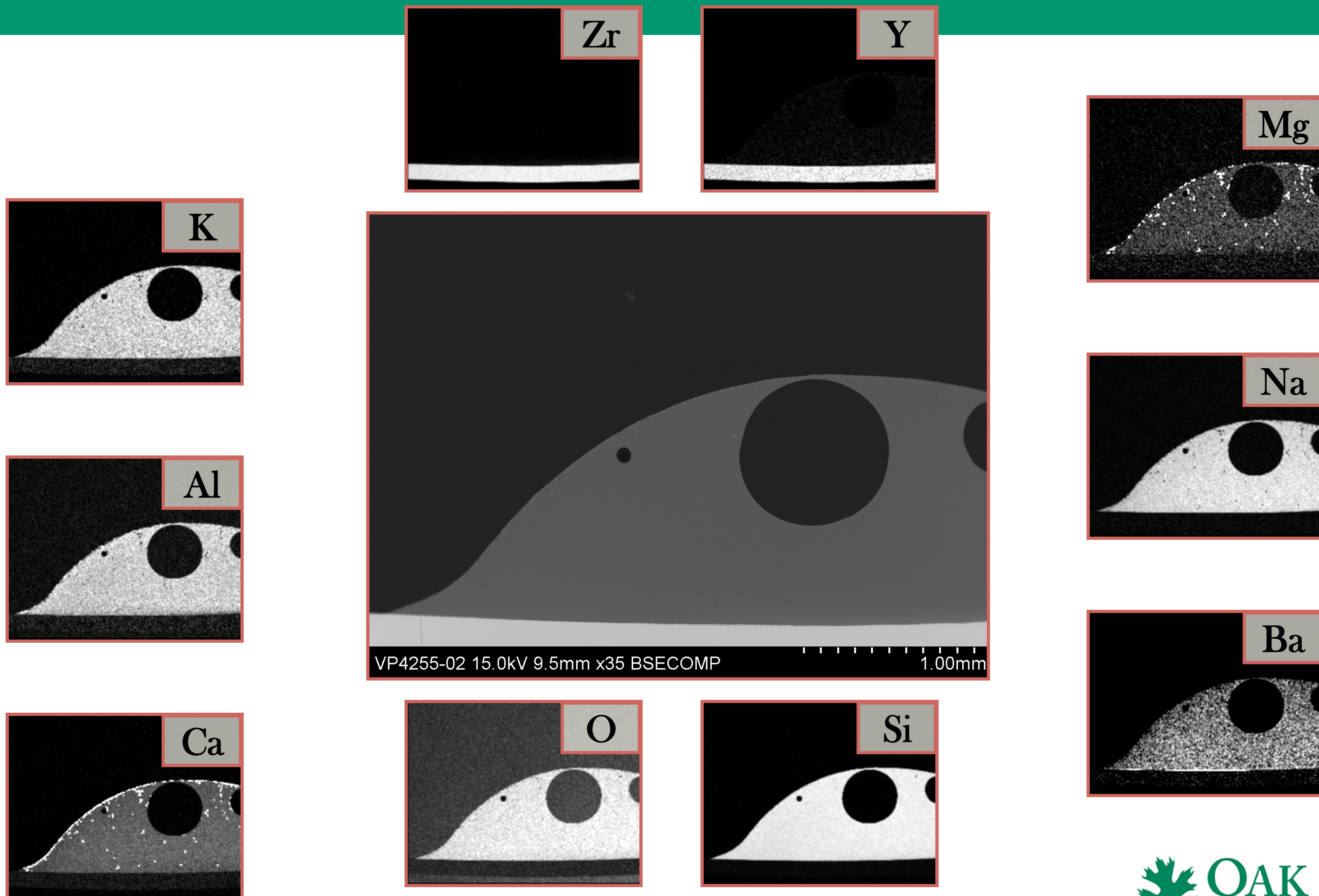


G6-YSZ-54

After 10,000 Hours in Steam+H_2+N_2



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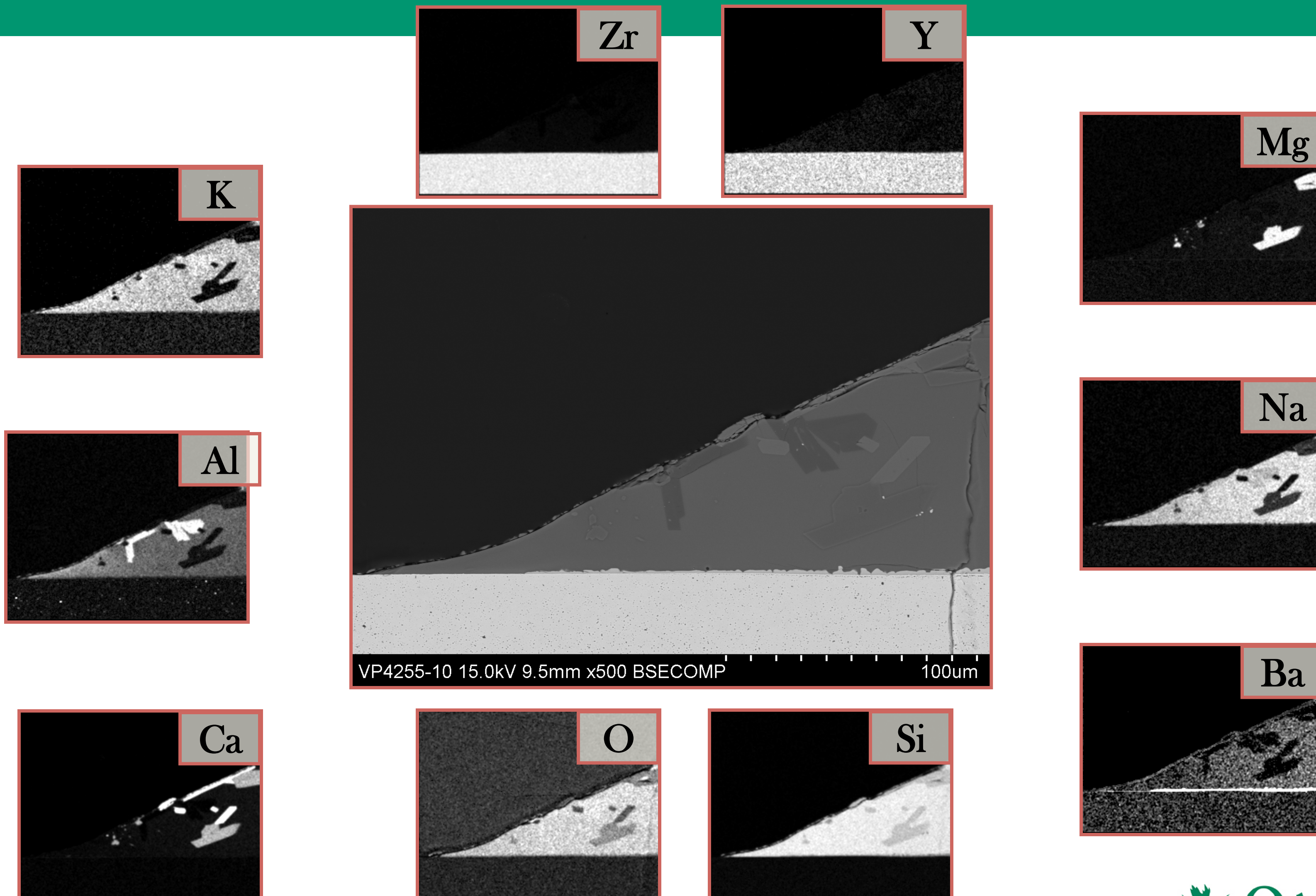
G6-YSZ-54

After 10,000 Hours in Steam+H_2+N_2



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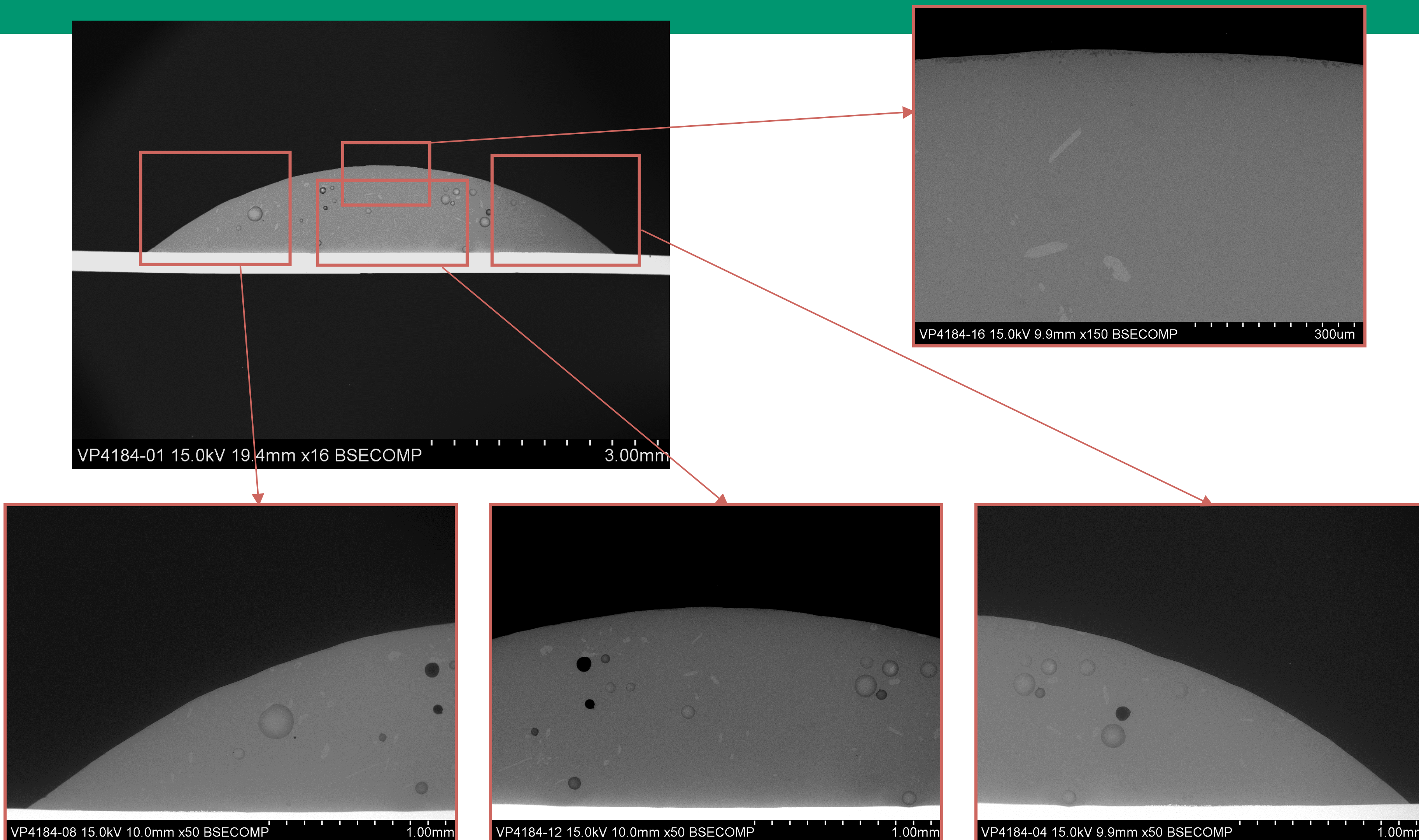
G6-YSZ-51

After 10,000 Hours in Air

G6-YSZ-51

After 10,000 Hours in Air



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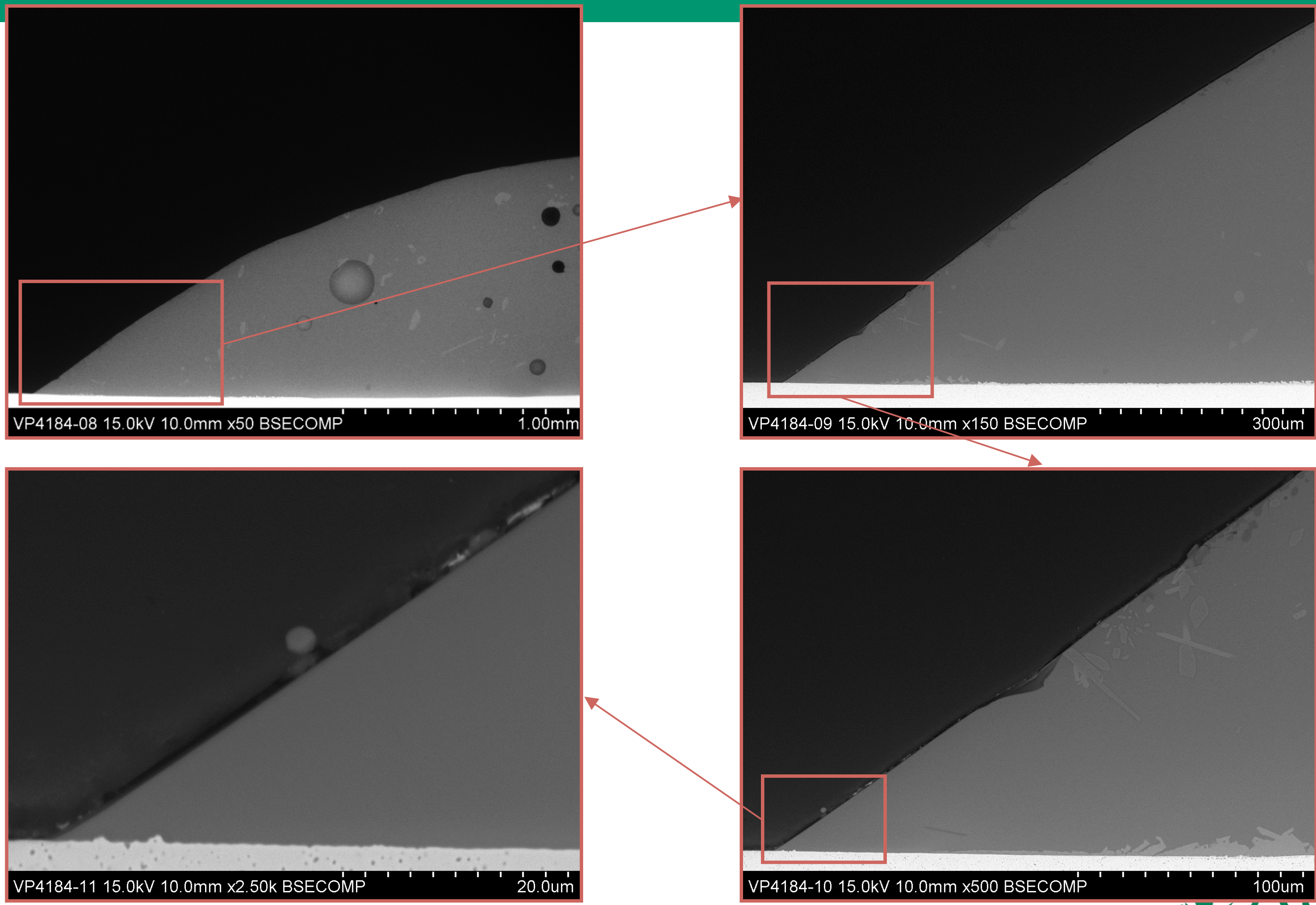
G6-YSZ-51

After 10,000 Hours in Air



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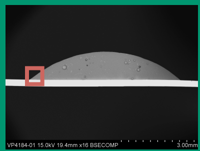

G6-YSZ-51

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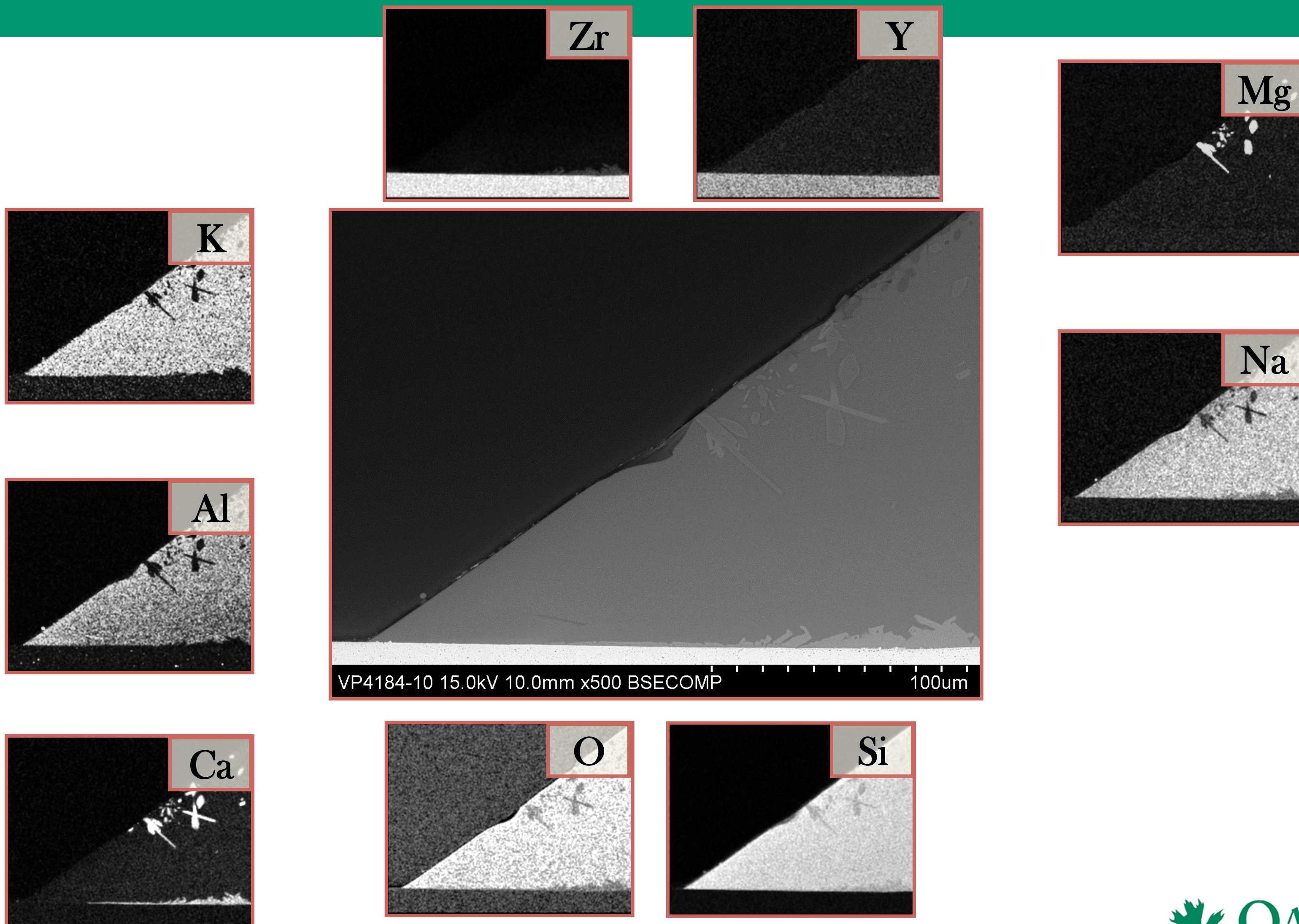

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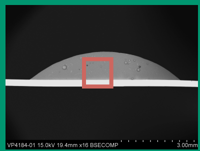

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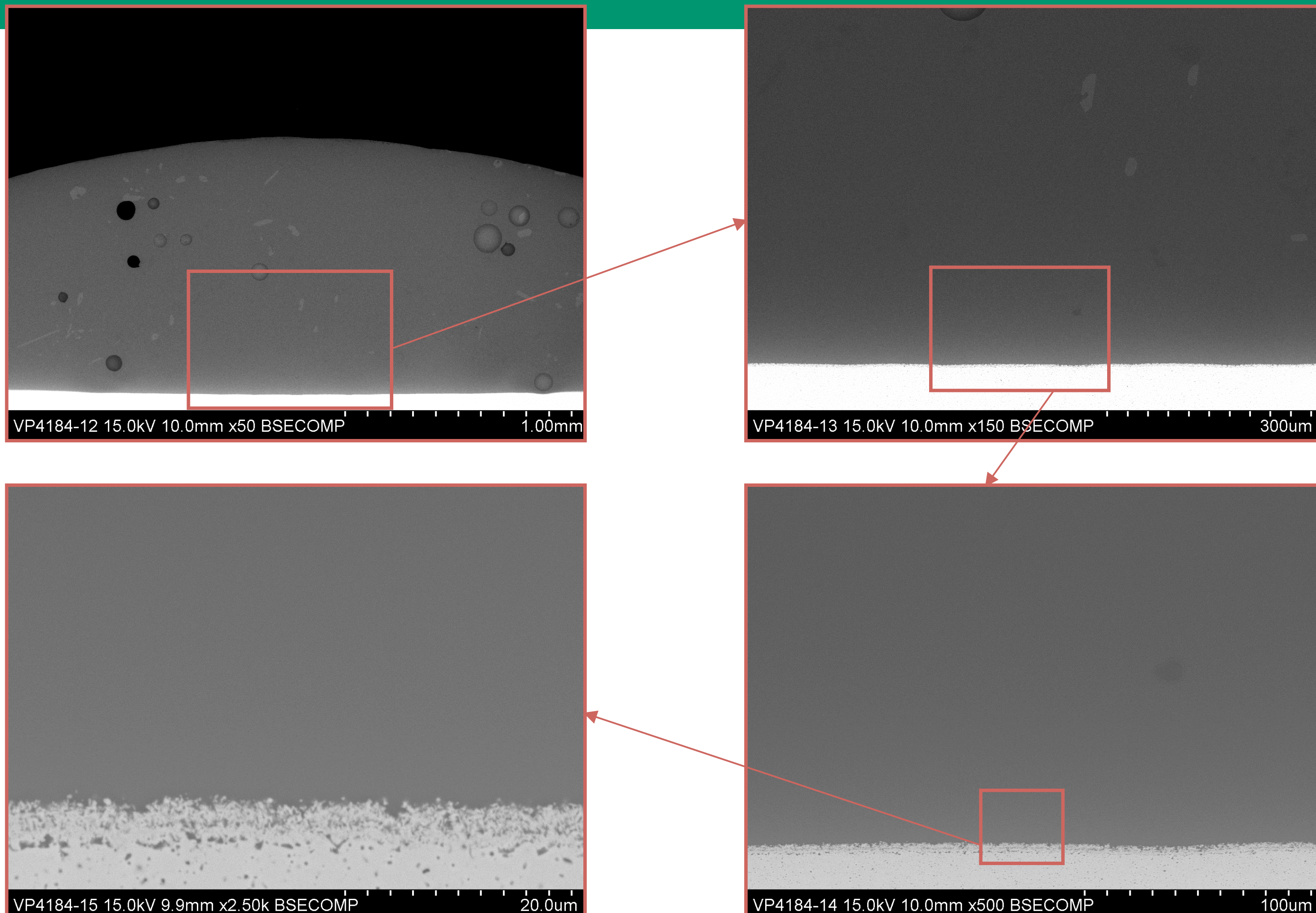

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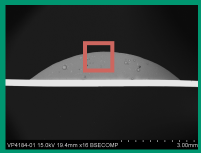

G6-YSZ-51

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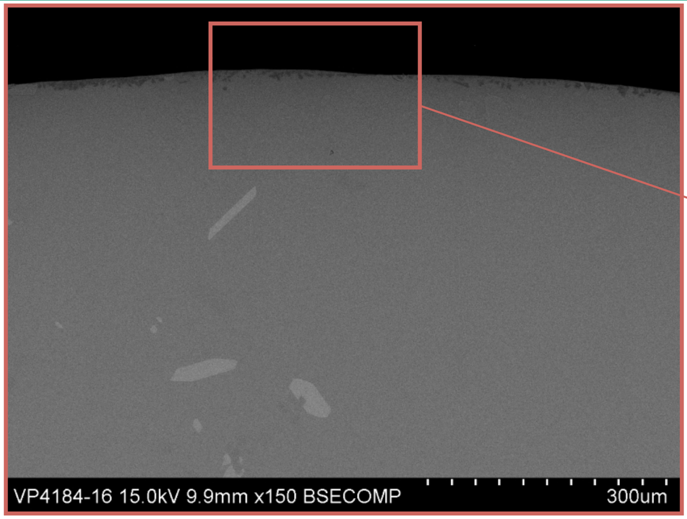

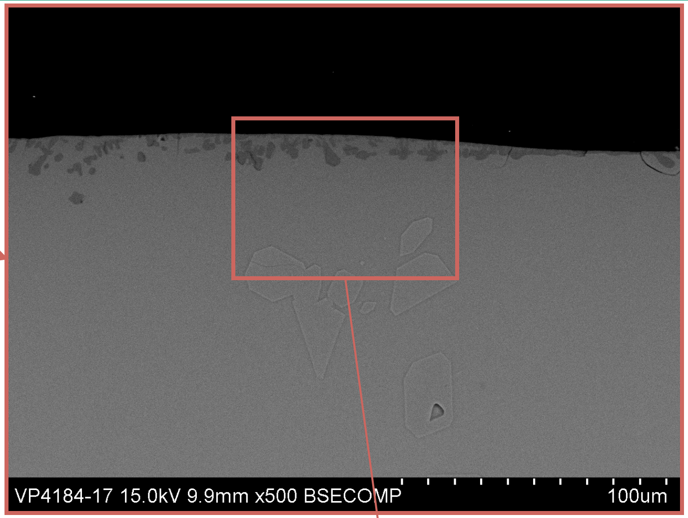

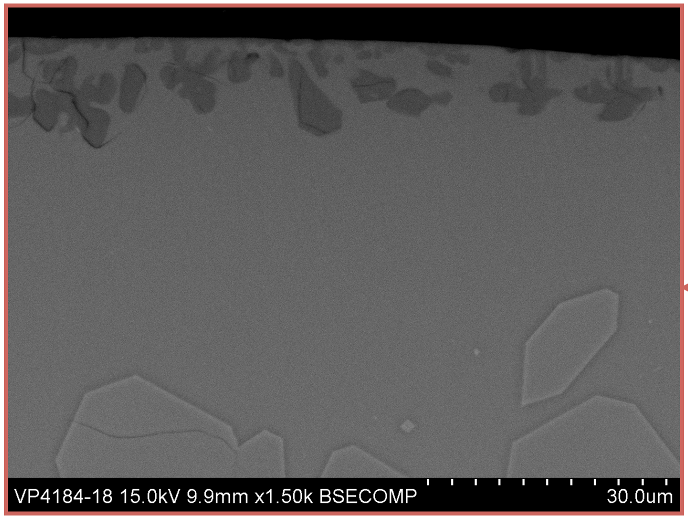

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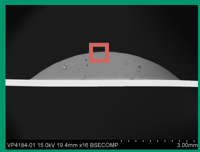
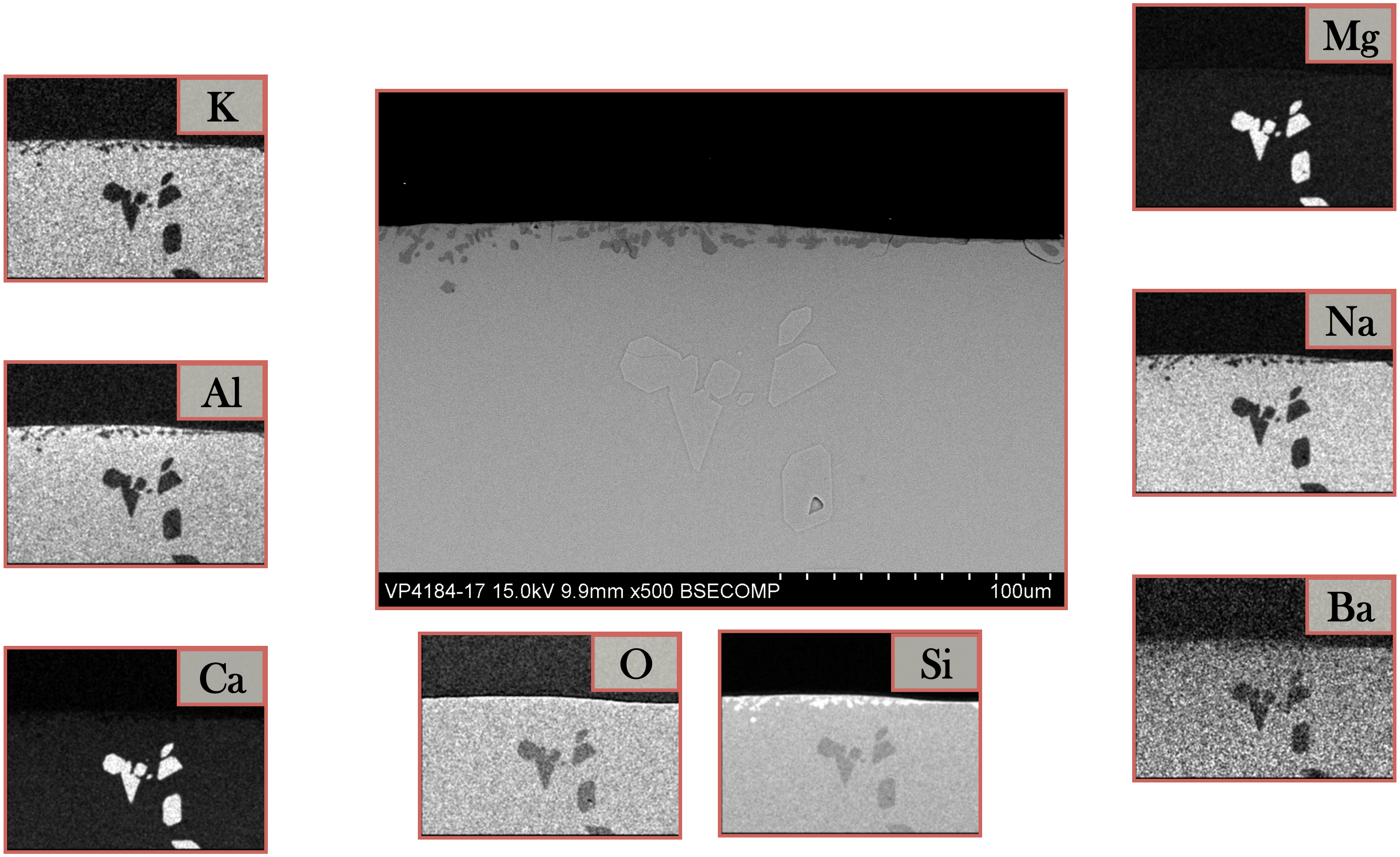


G6-YSZ-51

After 10,000 Hours in Air



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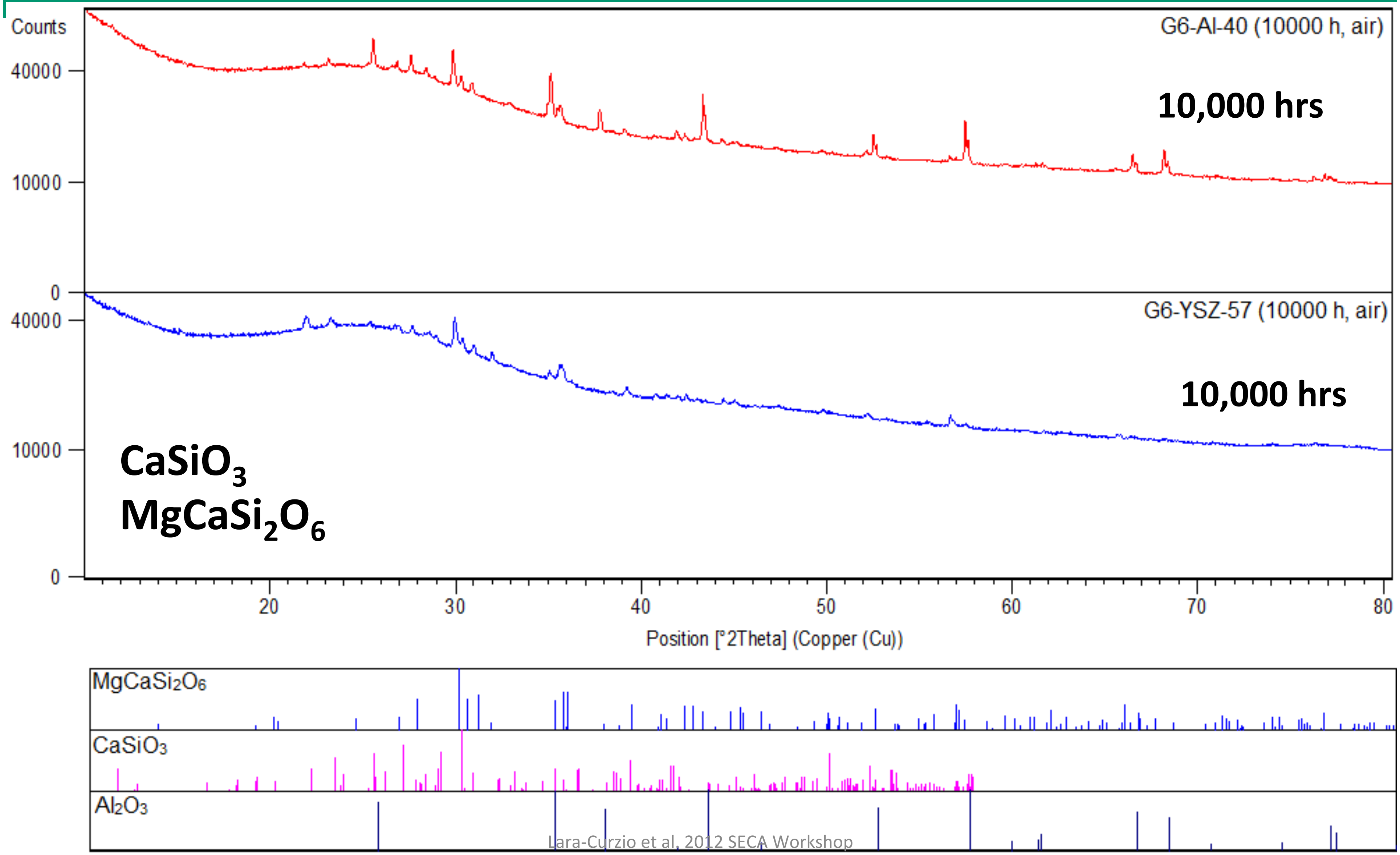
G6-Al_2O_3 and G6-YSZ (air): powder XRD



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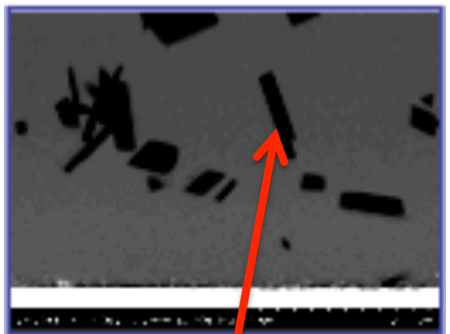
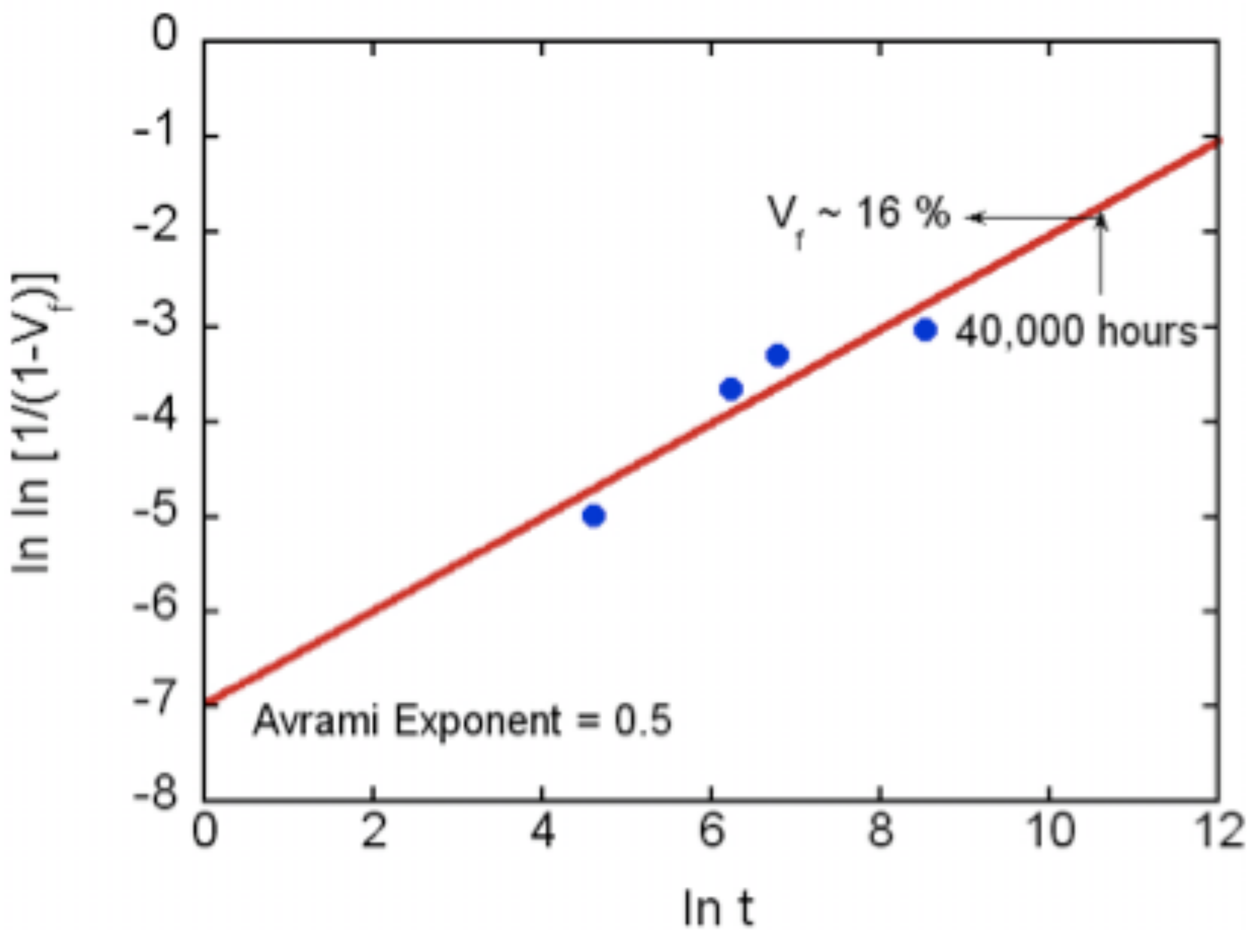
Rates of Crystallization (SCN Glass)



$KAlSi_3O_8$



Chemical Analysis

- Performed a study to assess the precision of different chemical analysis methods **(Al, B, Ba, Ca, Fe, K, Li, Mg, Na, Si, Ti, Zn, Zr)**
    - Neutron Activation Analysis
    - Inductively Couples Plasma Atomic Emission (ICPAES)
    - Inductively Couples Plasma Mass Spectroscopy (ICPMS)
    - Atom Probe Tomography

- Sample Preparation Requirements

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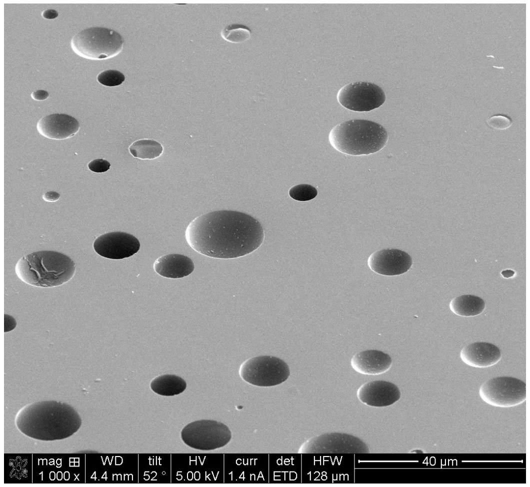
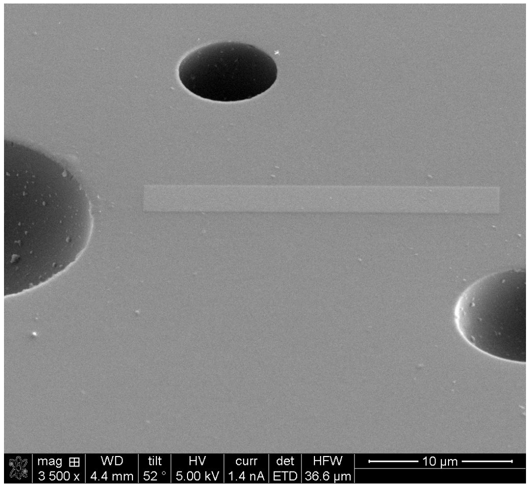
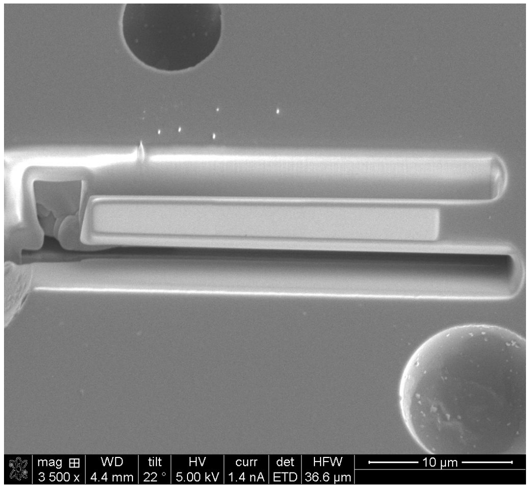
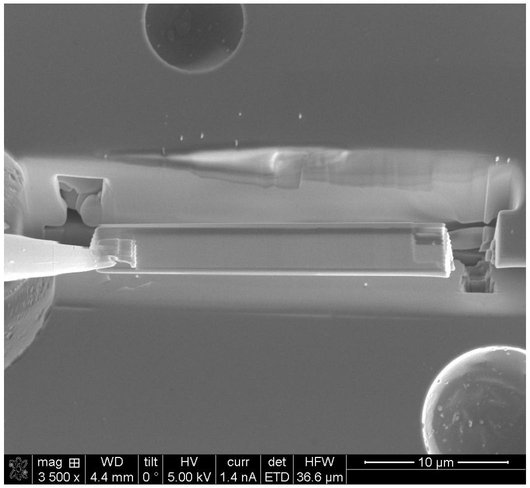
Chemical Analysis using Atom Probe Tomography









SCN glass

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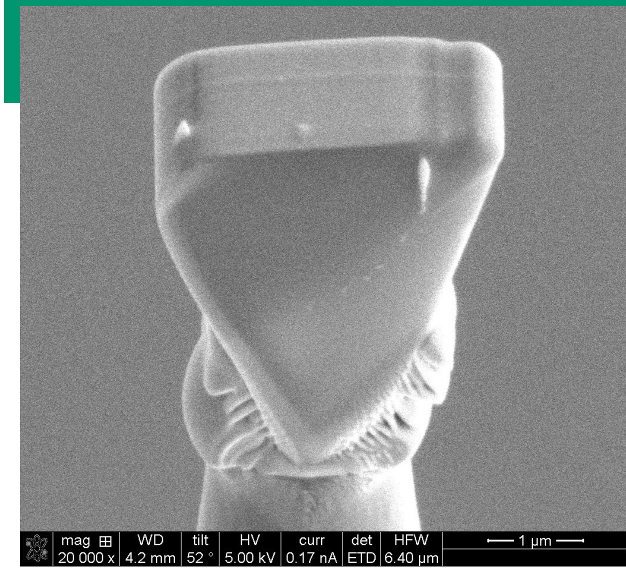
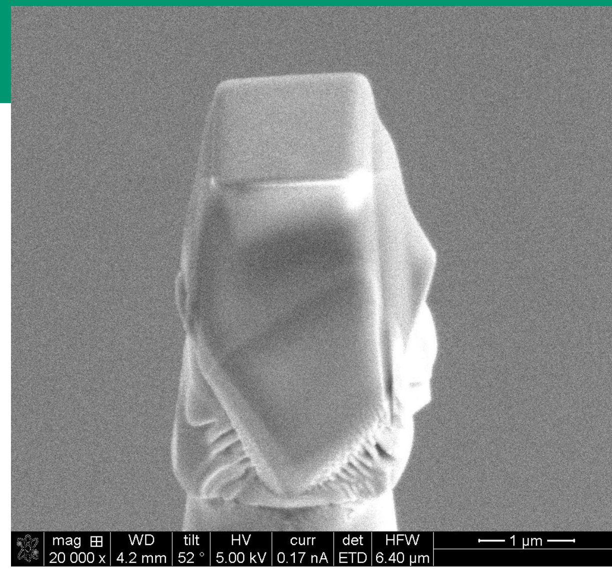
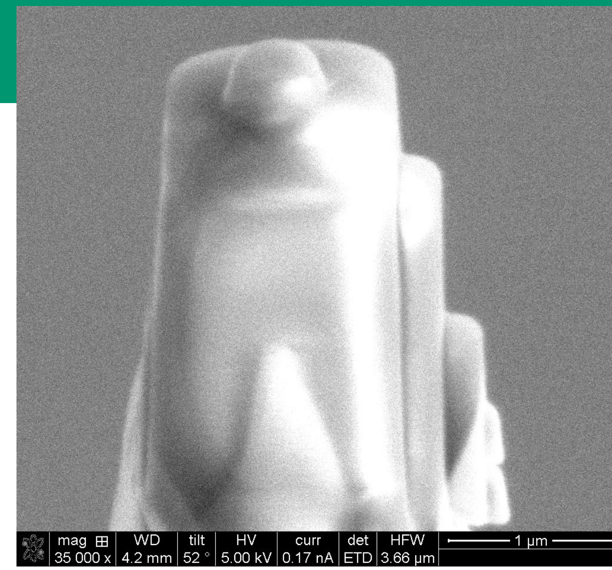
Chemical Analysis using Atom Probe Tomography



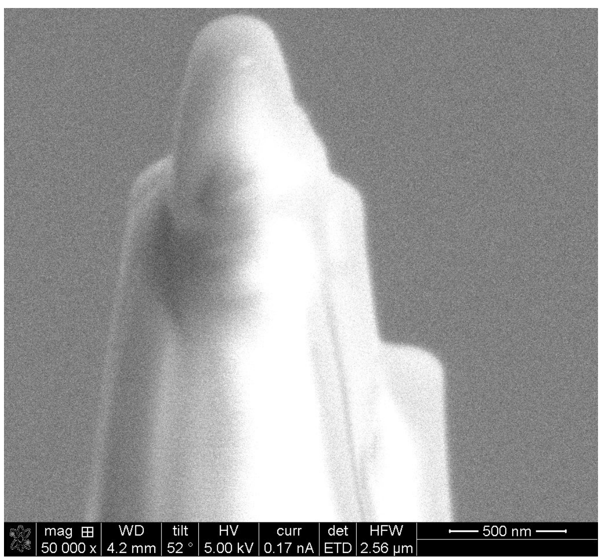
Attach to micropost



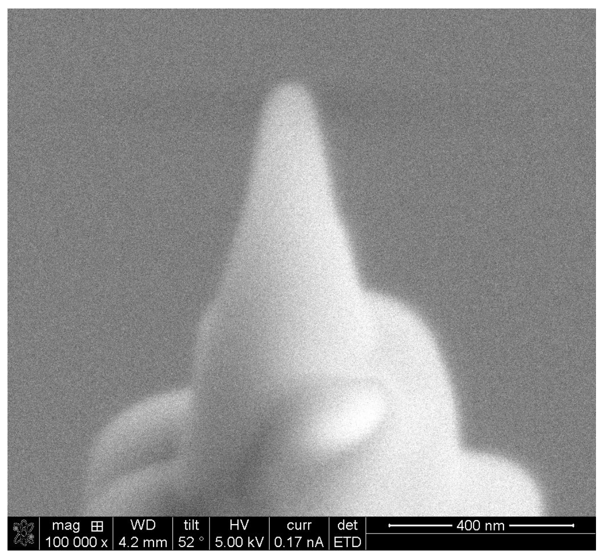
Trim square



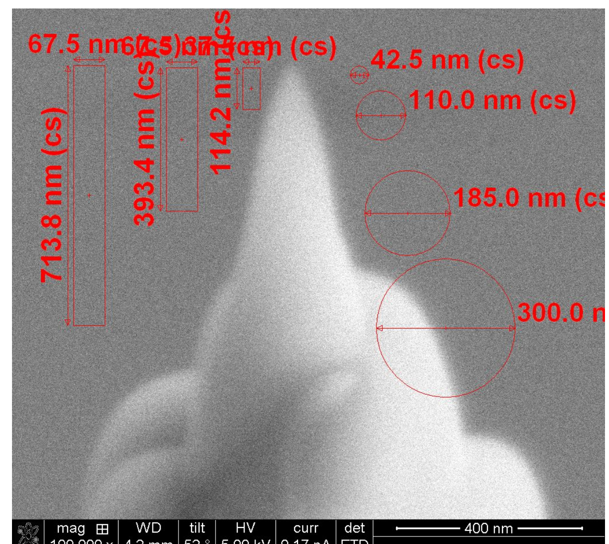
Sharpen w. annular milling pattern



30kV 280 pA ion beam annular pattern

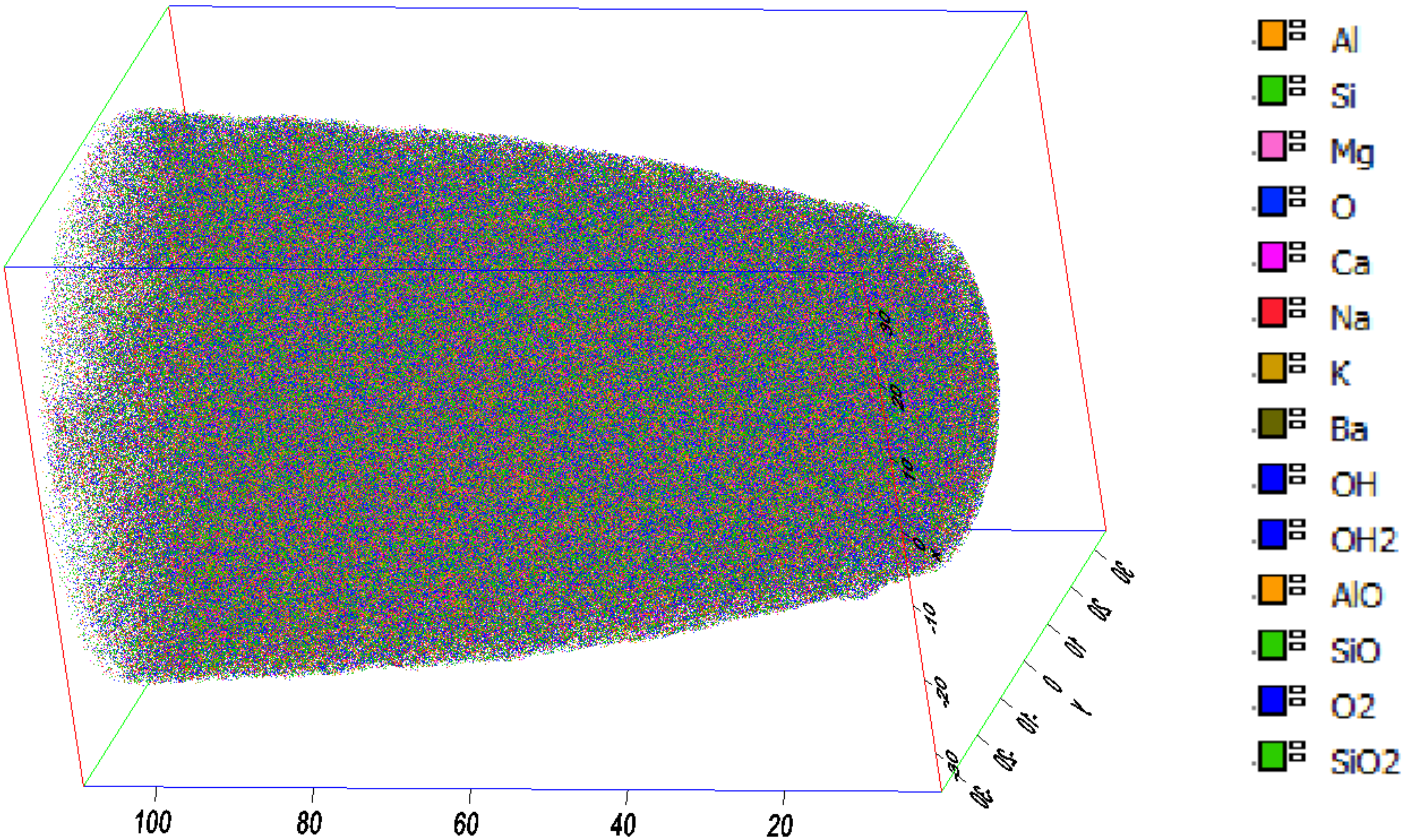


30kV 28pA ion beam annular pattern



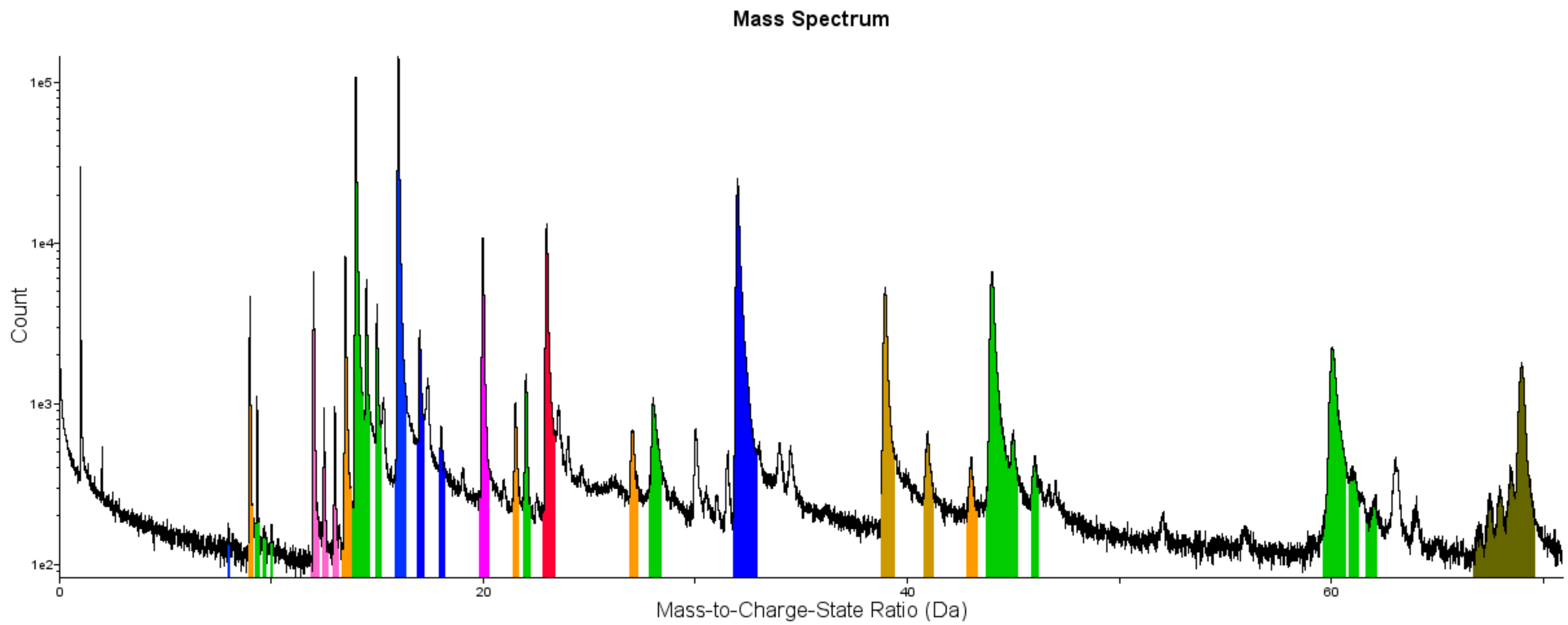
Touch up with 5kV 16pA ion beam

3D Atom Probe Tomography Reconstruction



3,997,448 ranged atoms in 70 x 70 x 109 nm^3
Reconstructed Volume

LEAP mass spectrum



3,997,448 ranged atoms in 70 x 70 x 109 nm^3 box

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Composition SCN Glass

As sintered

Element	at %
O	57.13
Si	25.64
K	2.85
Ba*	2.00
Na	3.84
Ca	2.32
Al	2.64
Mg	1.21
Ti	0.06
B	0.04
Zn	0.01

After 10,000 in air

Element	at %
O	59.26
Si	28.54
K	1.60
Ba*	1.76
Na	1.66
Ca	1.66
Al	2.34
Mg	1.36
Ti	0.06
B	0.04
Zn	0.01

Atom Probe Tomography

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Challenges for sealing SOFCs using crystallization-resistant glasses

Control of viscosity and seal compliance

- Scaling up to cells with large active surface area
  - Flatness
  - Parallelism
- Temperature gradients

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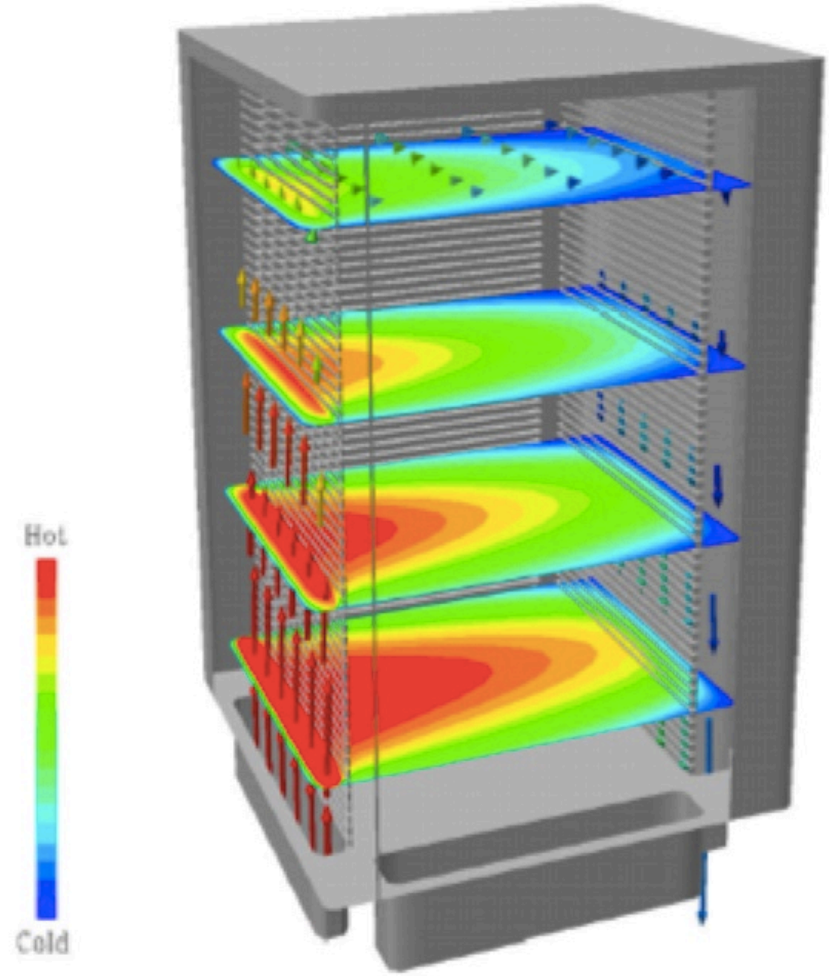
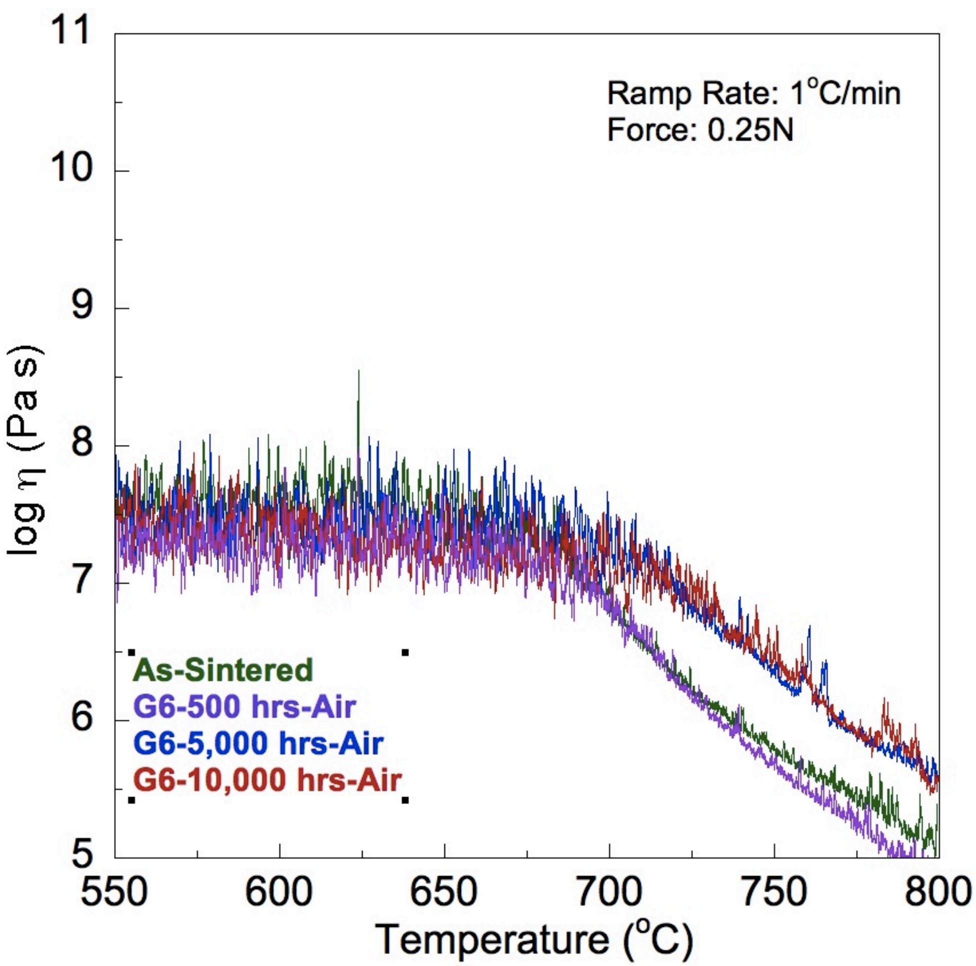
Temperature Gradients in SOFCs



PNNL (2004)

Viscosity of G6 Glass



- Viscosity decreases with temperature and increases with time of exposure.
- Increase in viscosity could be explained by precipitation of crystalline phases.

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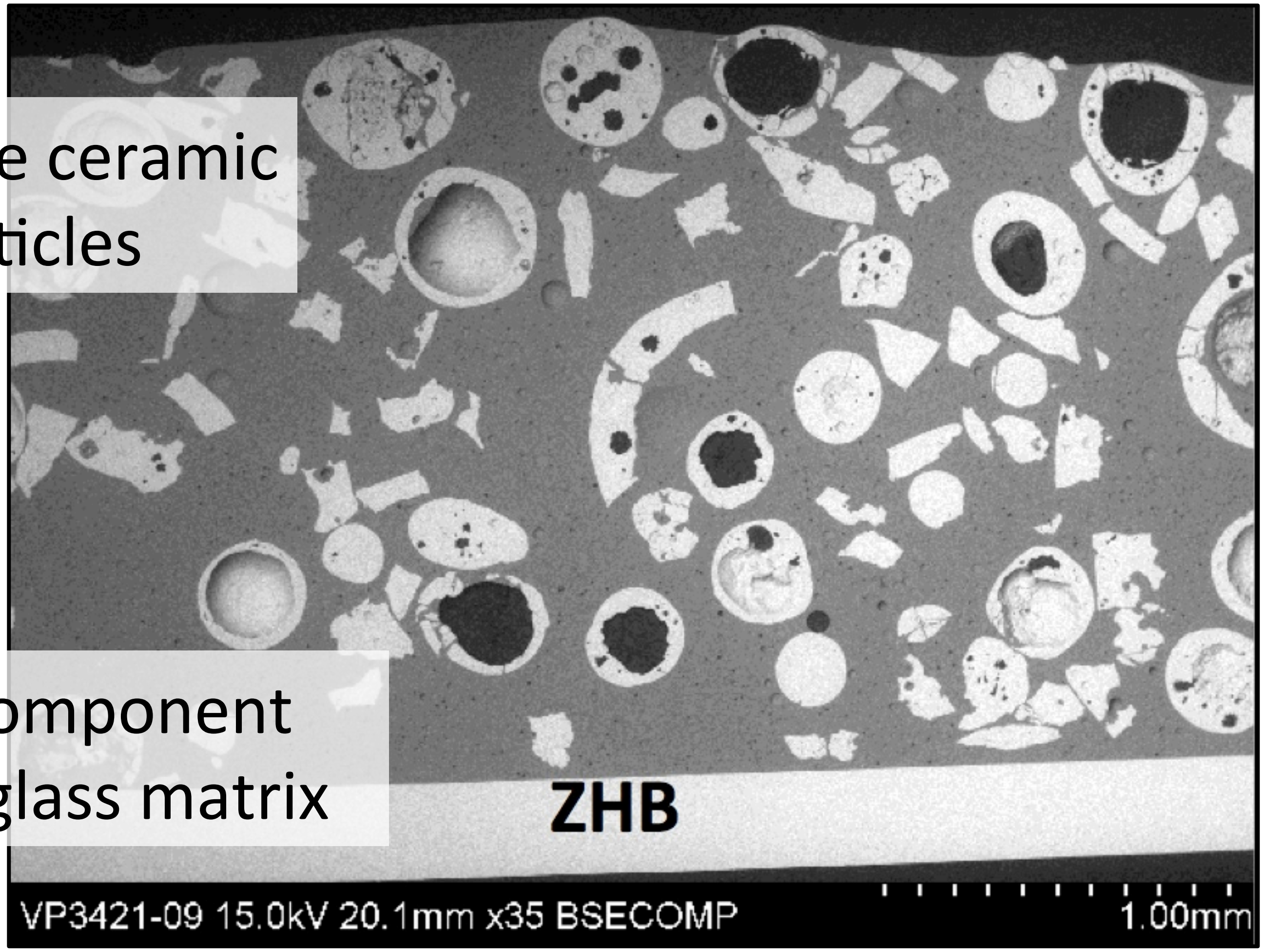
Composite Glass Seals

Frangible ceramic particles



Multicomponent silicate glass matrix

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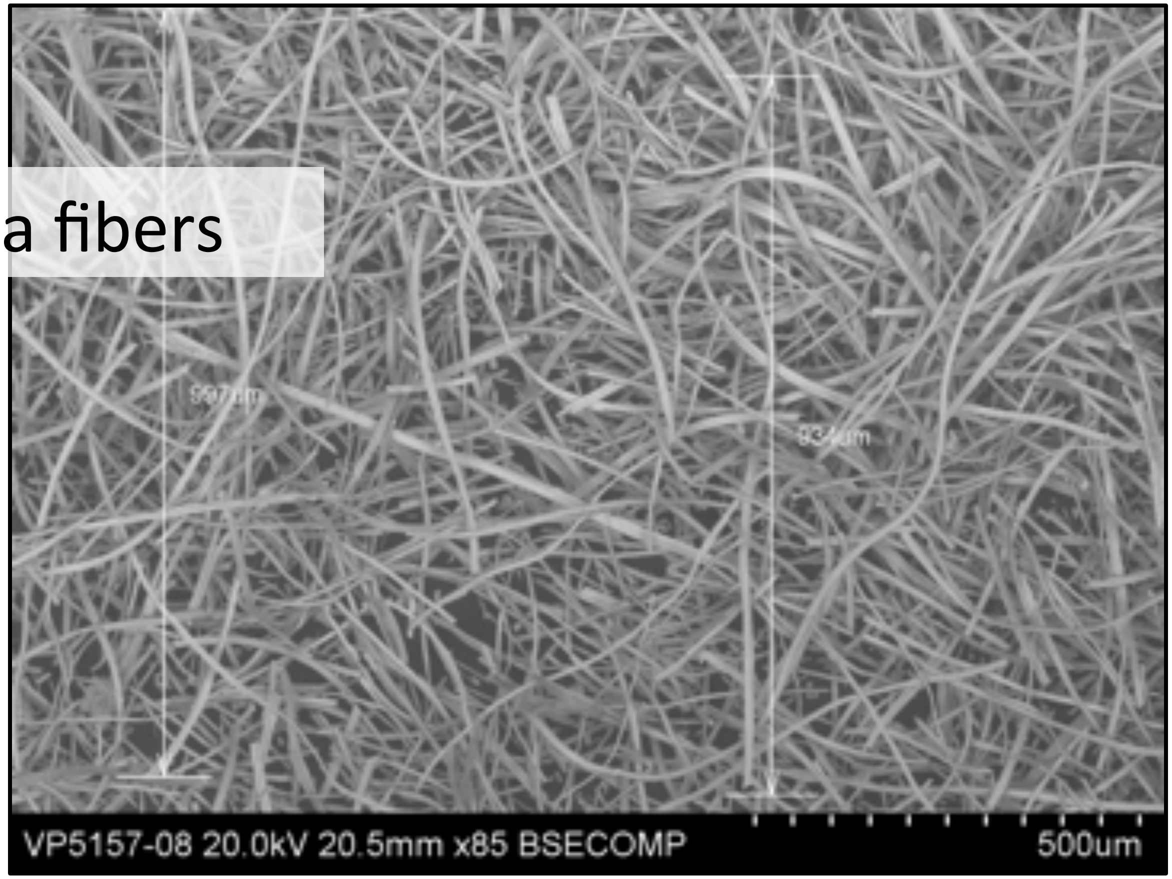
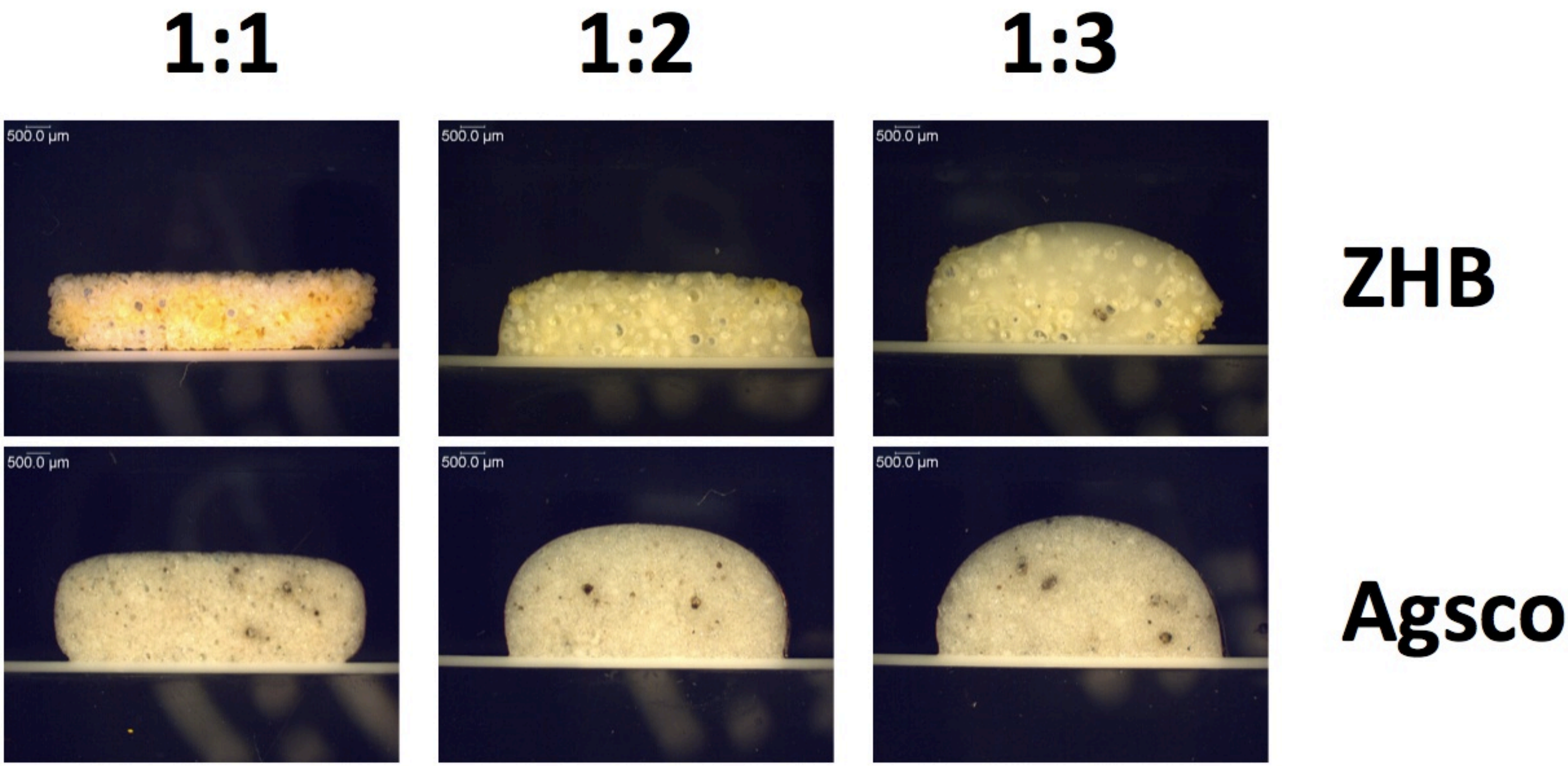
Composite Glass Seals



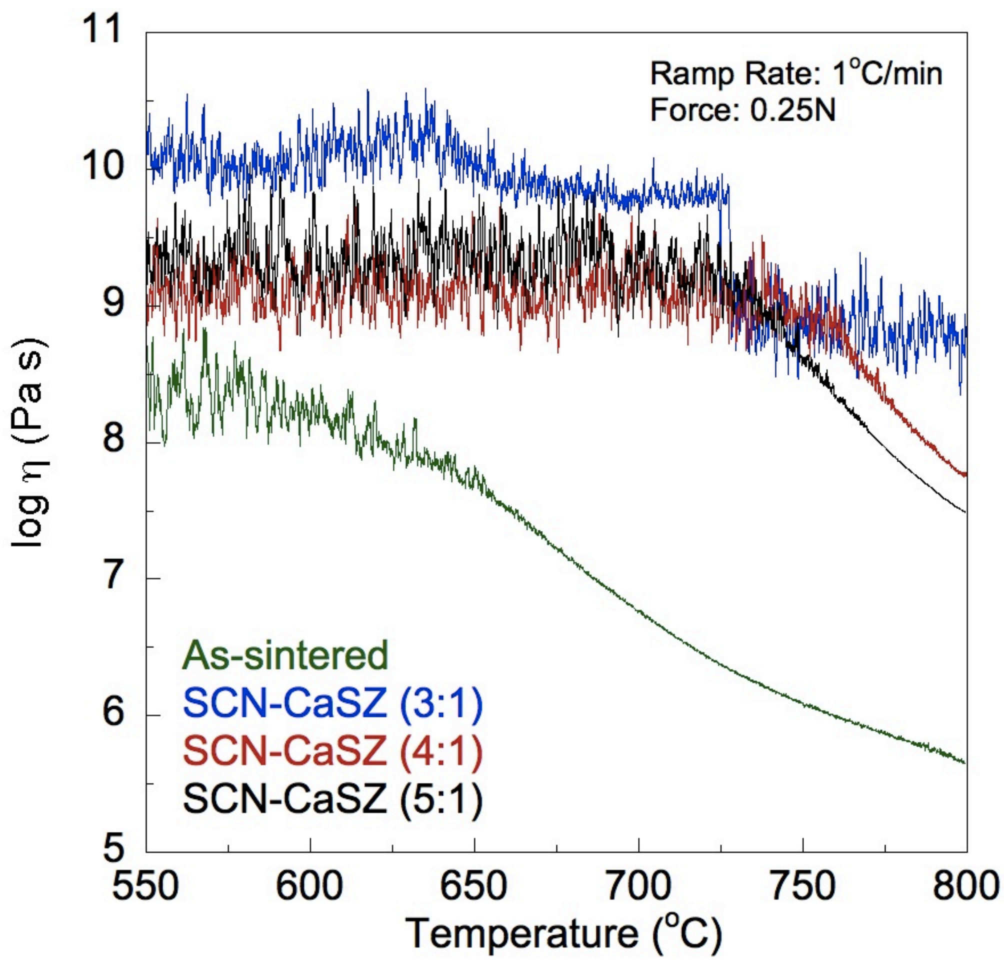
zirconia fibers

Wetting Behavior of Composite Glass Seals



SCN glass

Viscosity of Composite Glass Seals



- Viscosity can be tailored by changing the concentration of ceramic particles
- Incorporate data into models to predict time-dependent sealing behavior (PNNL).

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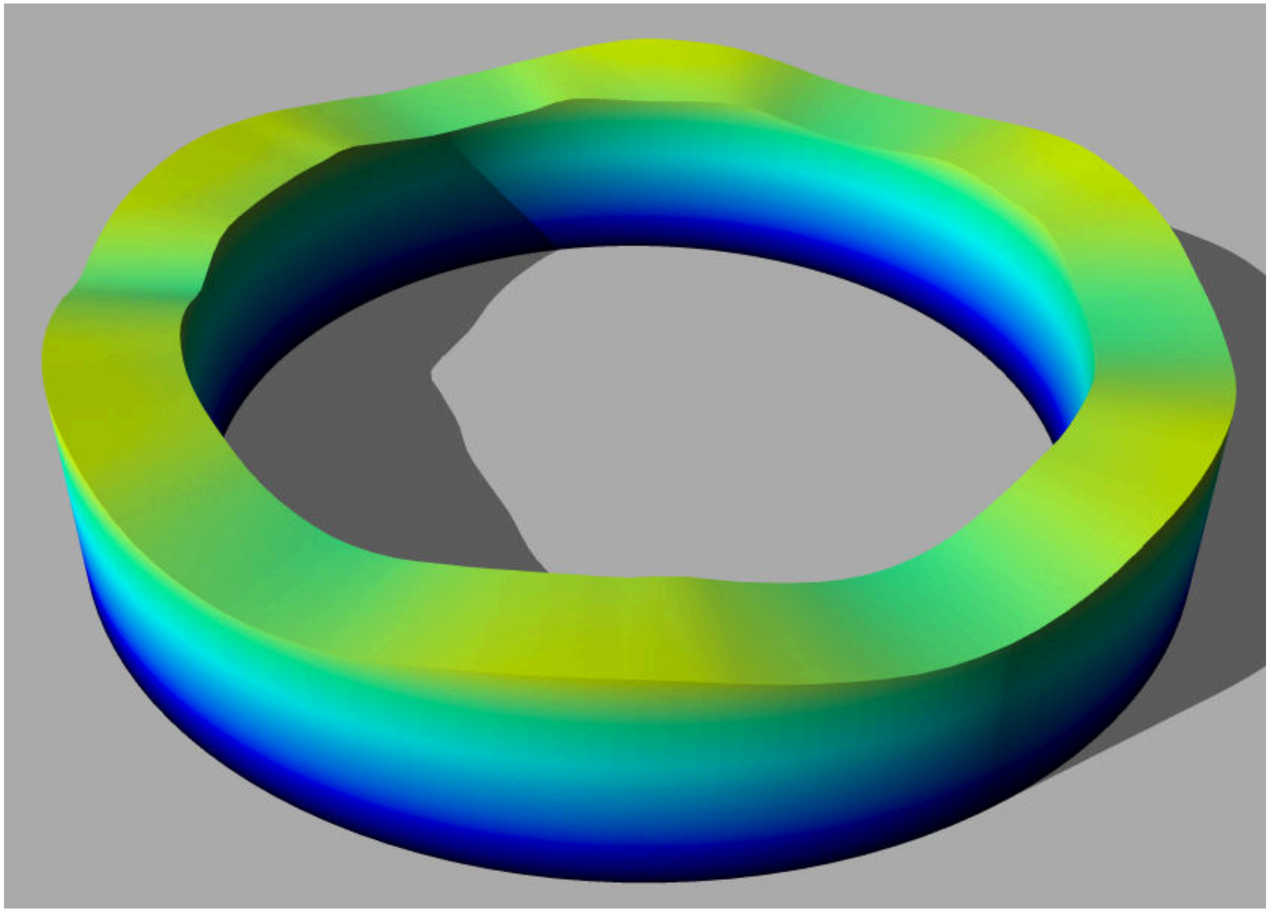
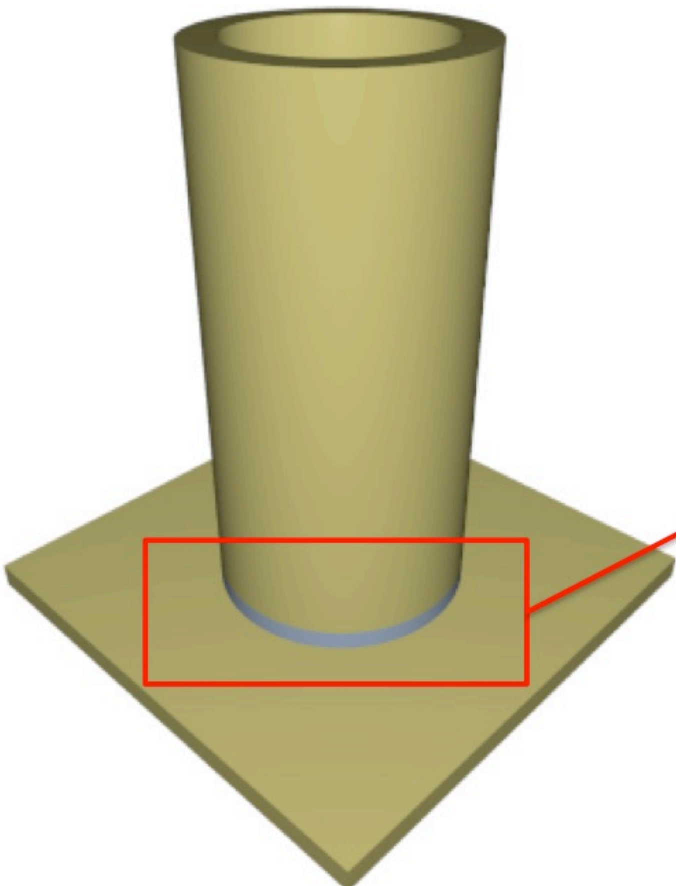
Compliance of Composite Glass Seals



Oak Ridge National Laboratory

Compliance of Composite Glass Seals

Zirconia tubes have been bonded to zirconia plates using engineered glass seal. This is the specimen configuration for testing in dual environments



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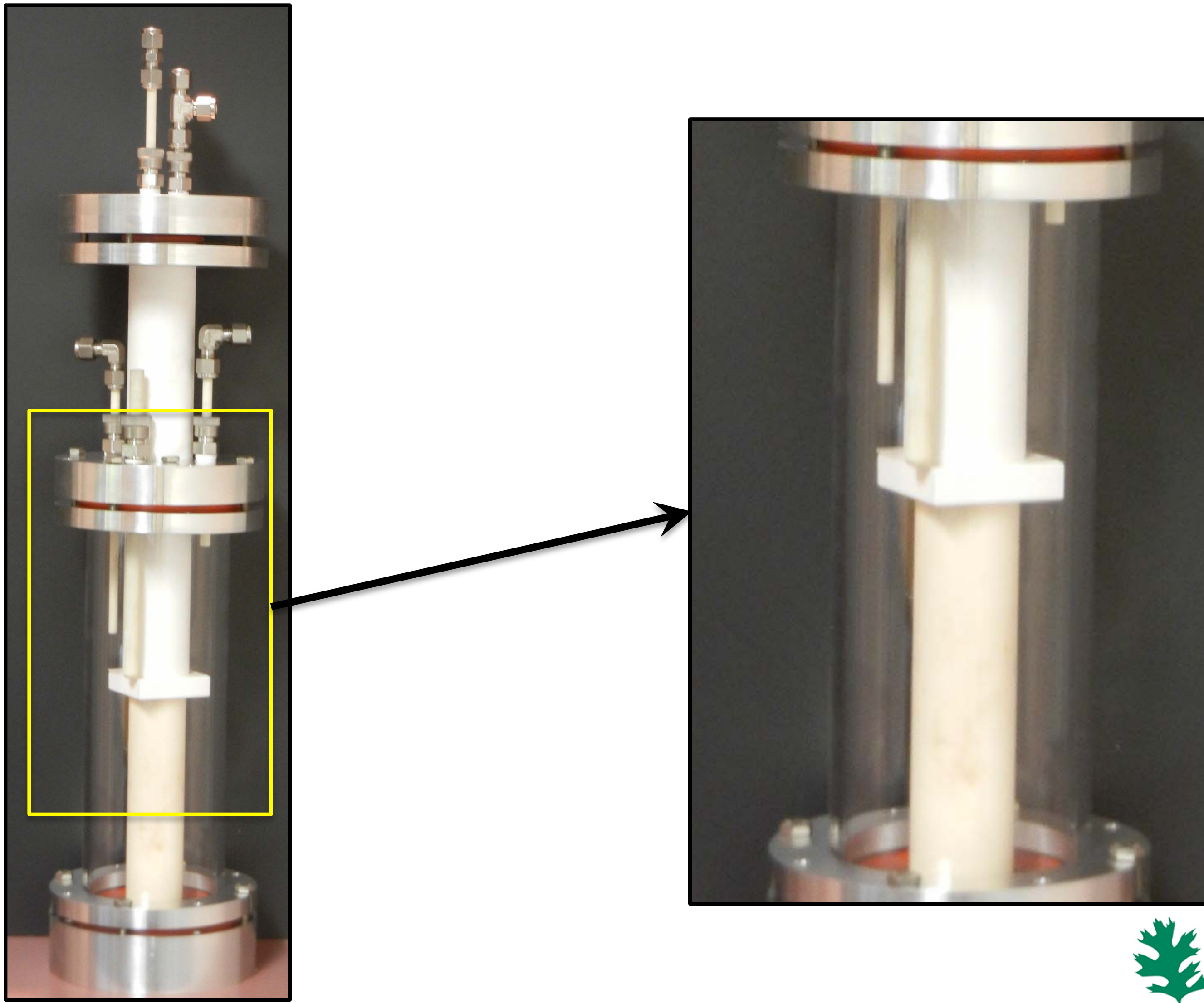
Evaluation of Seals in Dual Environment



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Compliance of Composite Glass Seals

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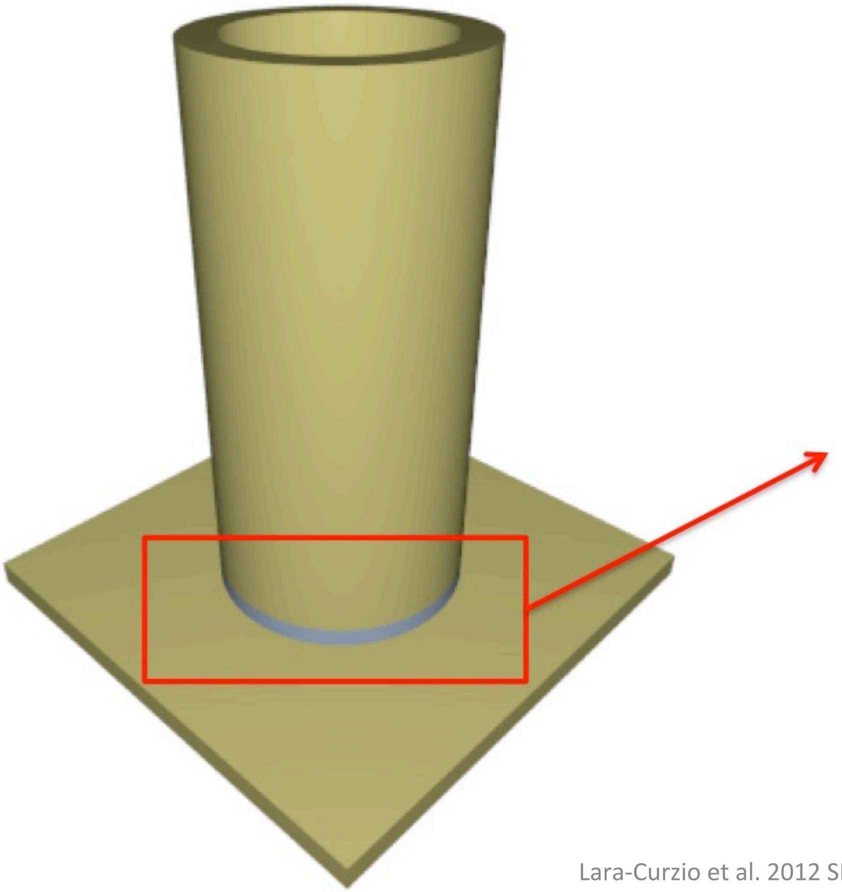
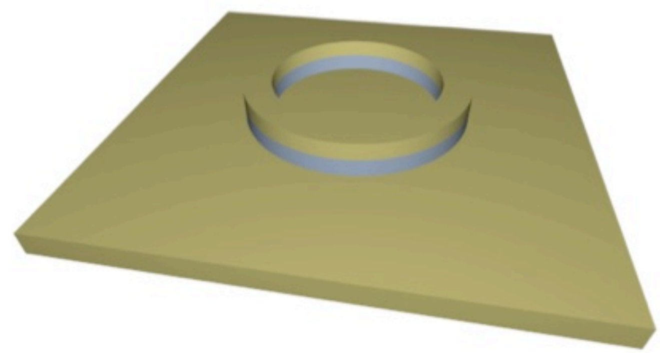


Zirconia tube is cut and ground to enable imaging of bonded area using IR imaging.



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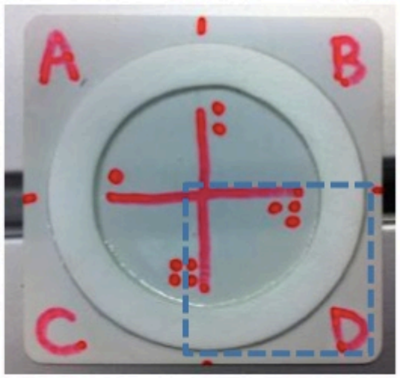
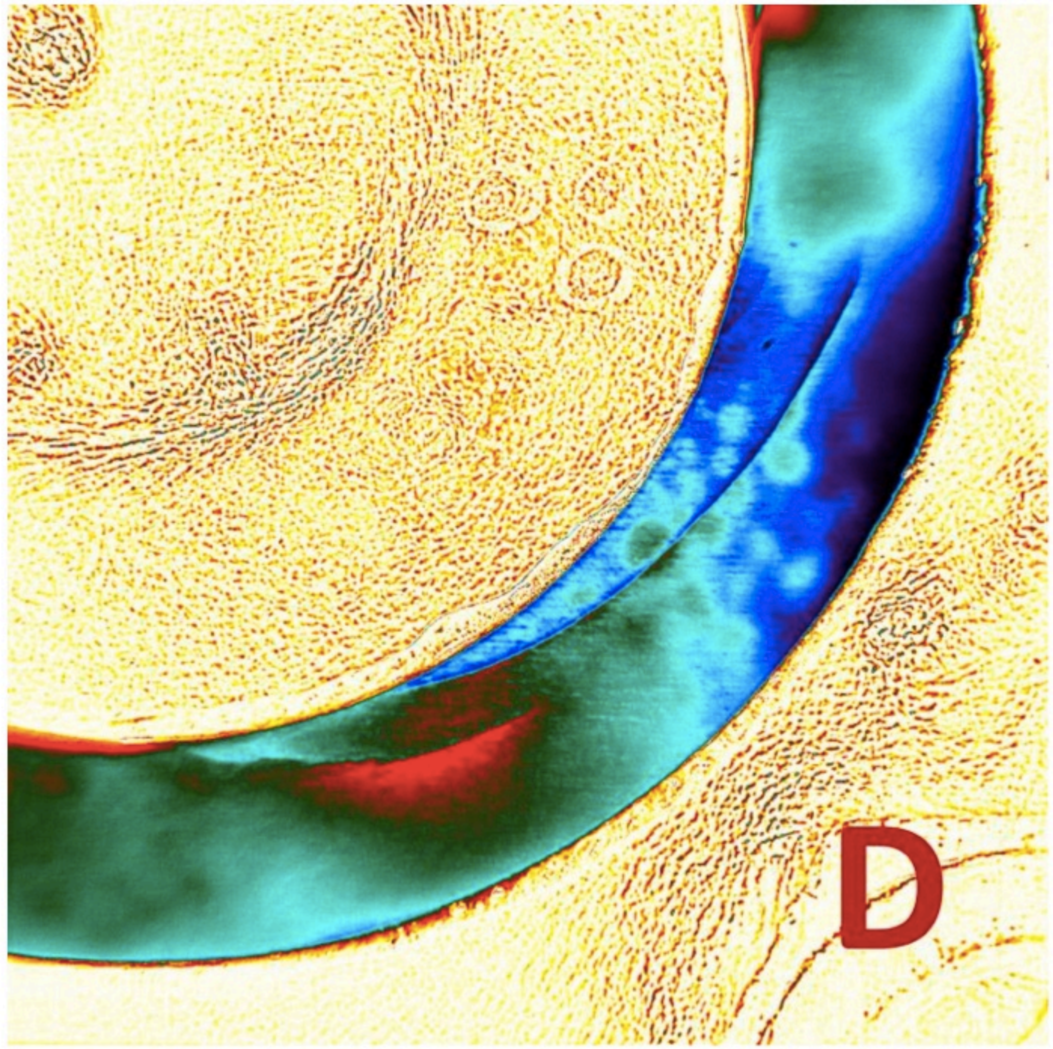
NDE of composite glass seals





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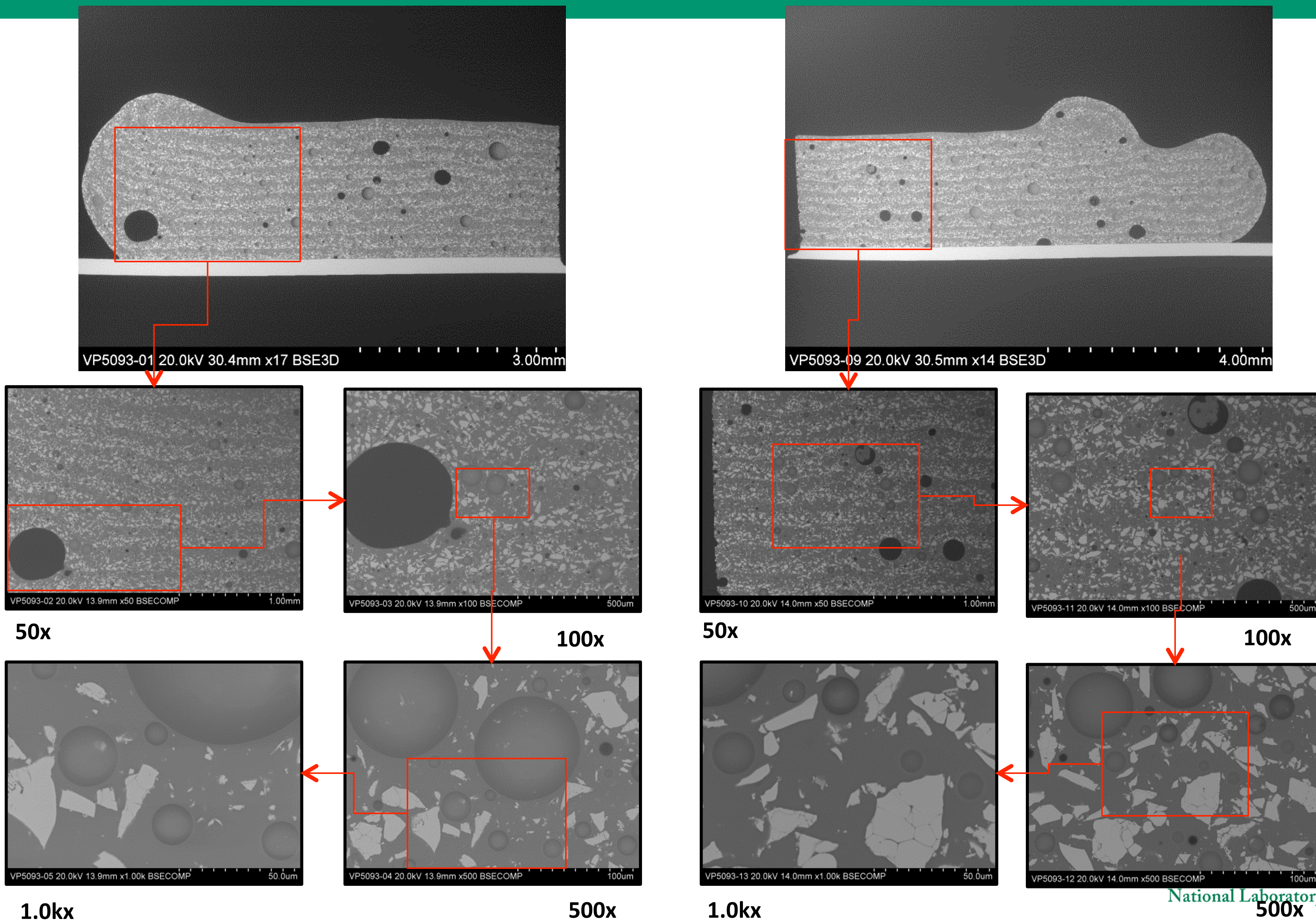
Fabrication of Composite Glass Seals

Glass-to-particle ratio 3:1



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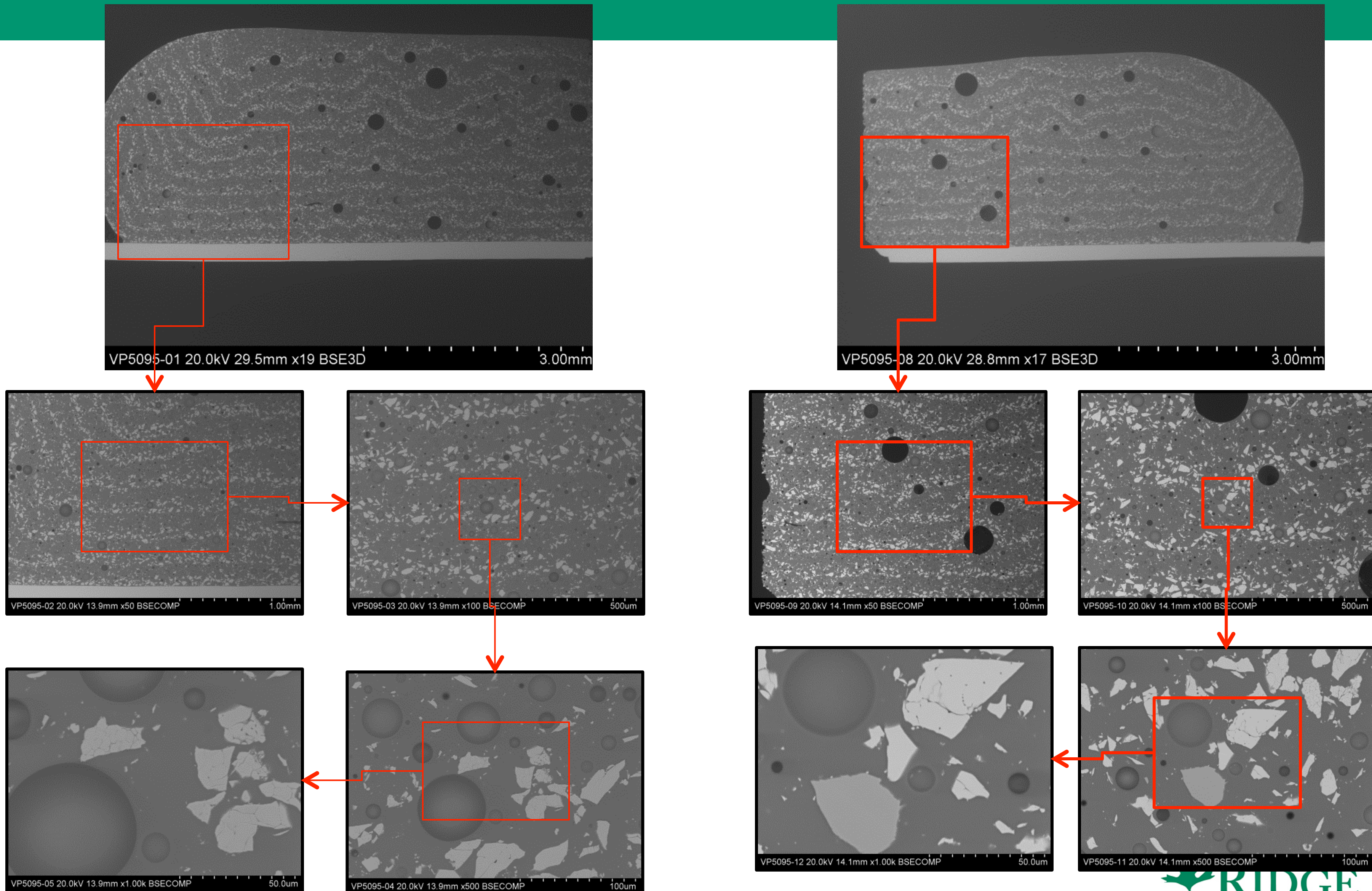
Fabrication of Composite Glass Seals

Glass-to-bead ratio 5:1



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Summary

- The effect of time of exposure in air and H_2+N_2+H_2O on the microstructure and physical and mechanical properties of two multicomponent silicate glasses (SCN, G6) have been characterized for up to 10,000 hours.
  - Test specimens continue being exposed (15,000+ hrs).
- Models are being developed to described the rates of crystallization and the evolution of microstructure and physical properties.

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Summary (cont.)

- Engineering-based models are being developed to predict the behavior of SOFC seals comprising these glasses
- Will continue working with PNNL and SECA industry teams to evaluate composite glass seals in realistic conditions
- Technology transfer