Physical and Microstructural Characterization of Barium Alkali Silicate Glasses

Edgar Lara-Curzio
Materials Science & Technology Division
Oak Ridge National Laboratory

12th Annual SECA Workshop
July 28, 2011

Acknowledgments

Amit Shyam, Rosa M. Trejo, Melani Kirkham, Valerie Garcia-Negron, Joseph Muth, Dana McClurg, Alex Ladouceur, Dieter Isheim.

This research was sponsored by the US Department of Energy, Office of Fossil Energy, SECA Core Technology Program at ORNL under Contract DEAC05-00OR22725 with UT-Battelle, LLC.

Special thanks Rin Burke, Travis Shultz and Shailesh Vora for guidance and support.

Outline

- Background
- Experimental Procedure
- Results
- Ongoing and Future Work

OAK RIDGE National Laboratory

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 microstructural evolution of candidate glasses for SOFC sealing applications when exposed to SOFC relevant environments.
- To develop models to predict microstructural changes for periods of time relevant to SOFC sealing applications.

Barium alkali silicate glasses

Two commercially available barium alkali silicate glasses are being investigated

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

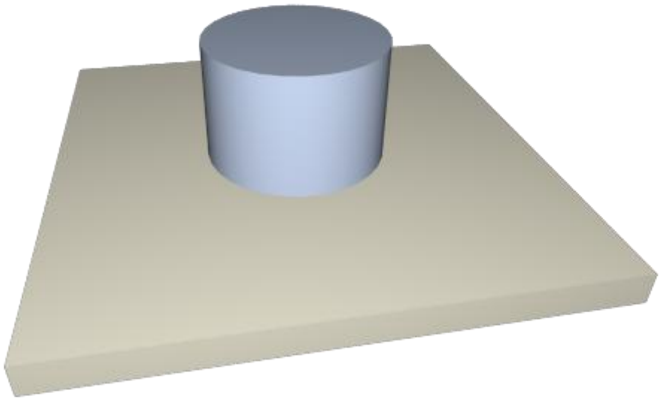
Mechanical and Thermophysical Properties

- Elastic constants
- Thermal expansion
- Glass transition temperature
- Viscosity
- Chemical Composition

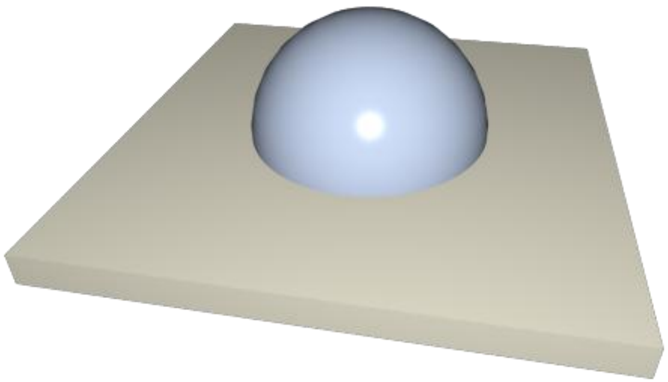
- Phase Analysis
- Wetting Behavior (alumina, zirconia)
- Microstructure
- Porosity and its evolution
- Rates of crystallization

Experimental

cold compressed
glass powders

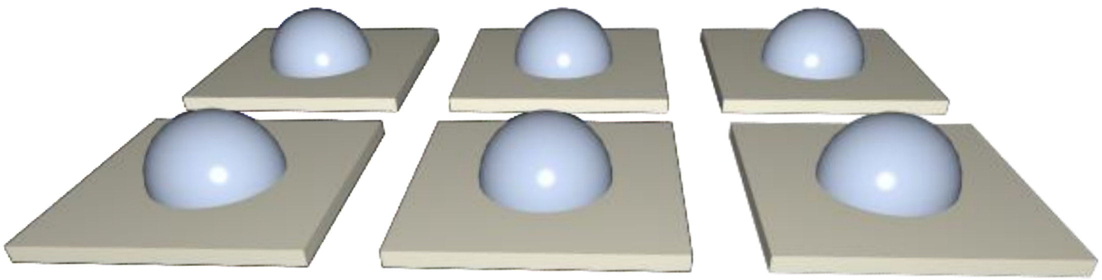


after sintering in air
for 2 hours at 850°C



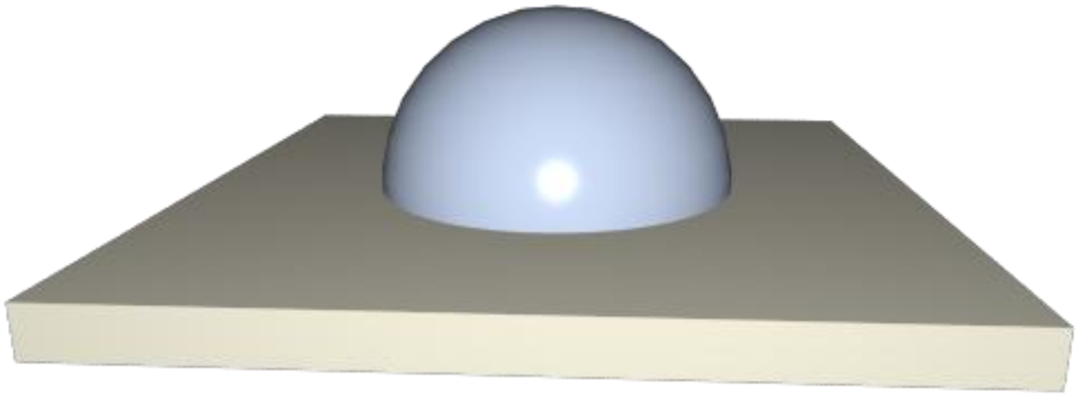
Al_2O_3 or 8YSZ
substrates

Experimental (cont.)



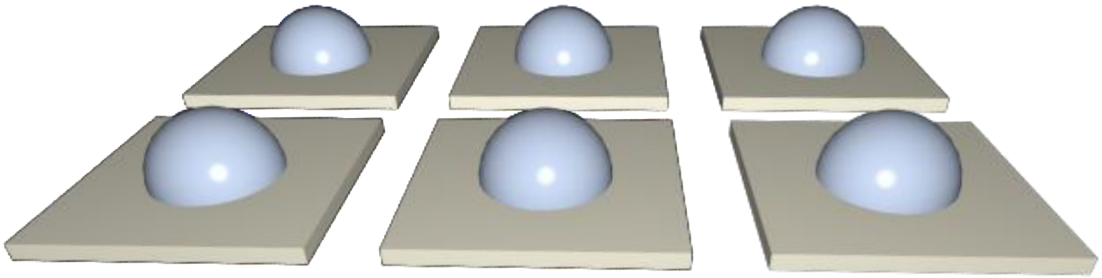
- Test specimens are exposed to **air** or a gas mixture of **H_2+N_2+H_20 at 850°C.**
- Test specimens are retrieved from the furnace every 1,000 hrs for non-destructive examination (SEM, XRD).

Experimental (cont.)



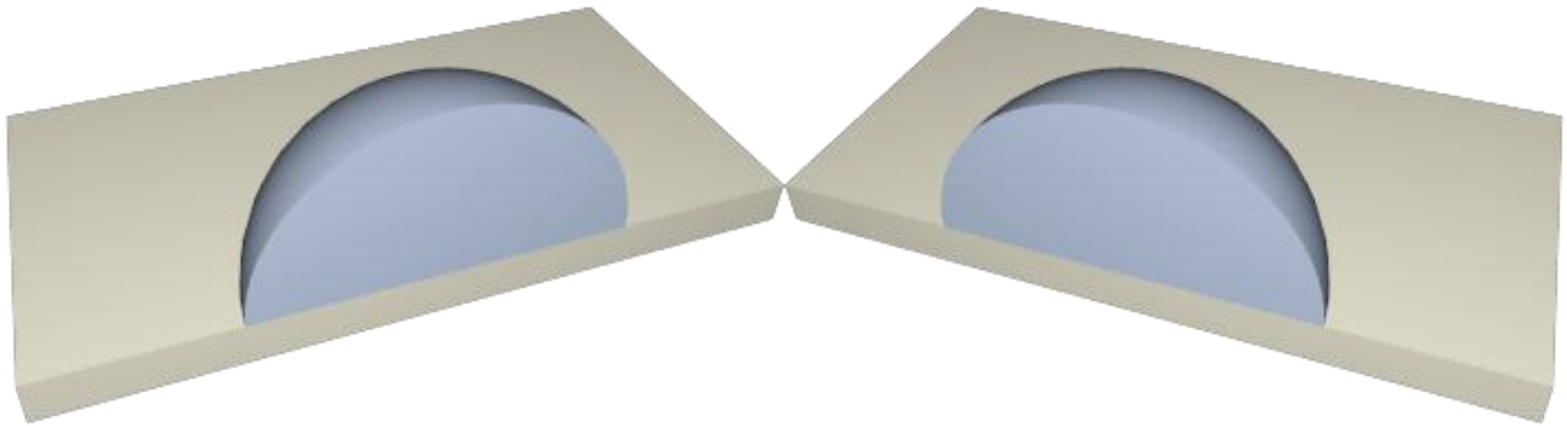
- Scanning electron microscopy
- EDS
- X-ray diffraction

Experimental (cont.)

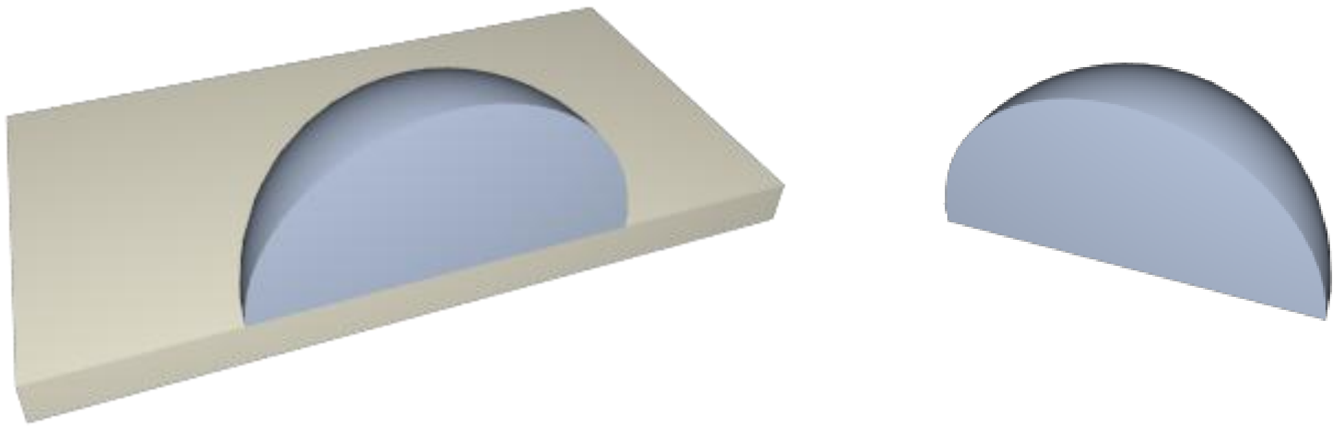


- Test specimens are exposed to **air** or a gas mixture of **H_2+N_2+$H_2$0 at 850°C.**
- Test specimens are retrieved from the furnace every 1,000 hrs for non-destructive examination (SEM, XRD). Then they are returned to continue exposure.
- After predetermined periods of time, test specimens are removed for destructive examination (SEM, XRD, Tg, viscosity)

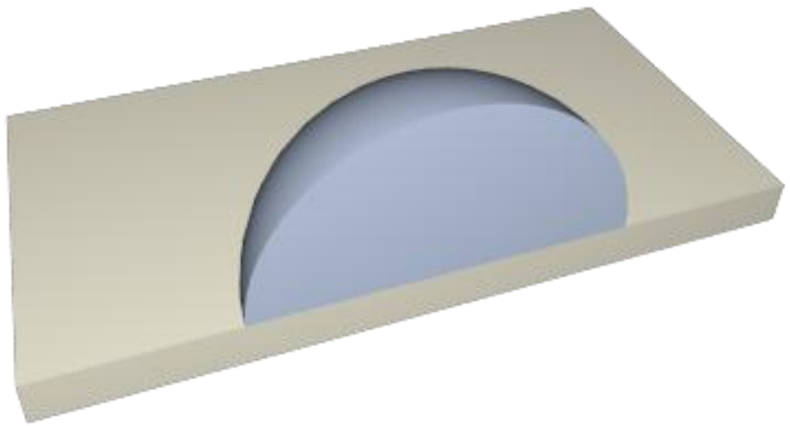
Experimental (cont.)

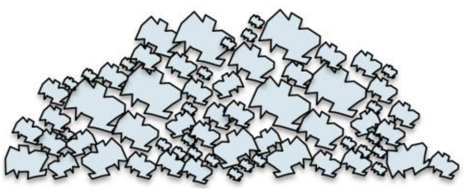


Experimental (cont.)



Experimental (cont.)

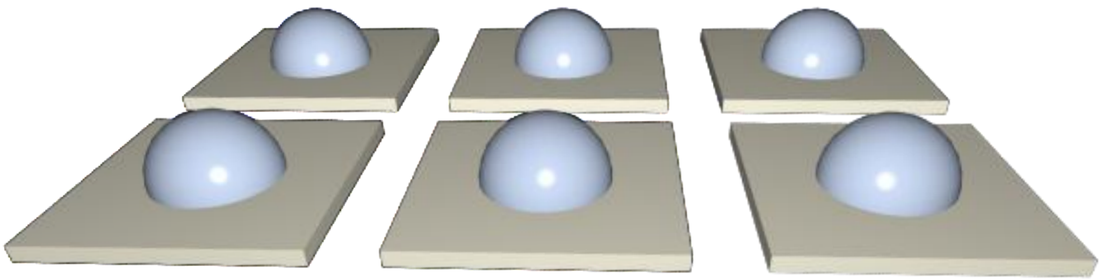




X-ray diffraction

- Scanning electron microscopy
- EDS

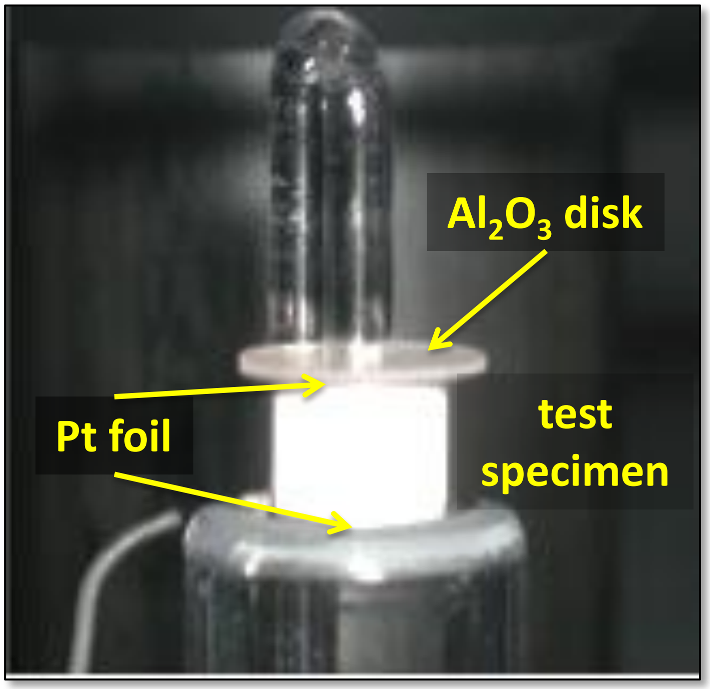
Experimental (cont.)



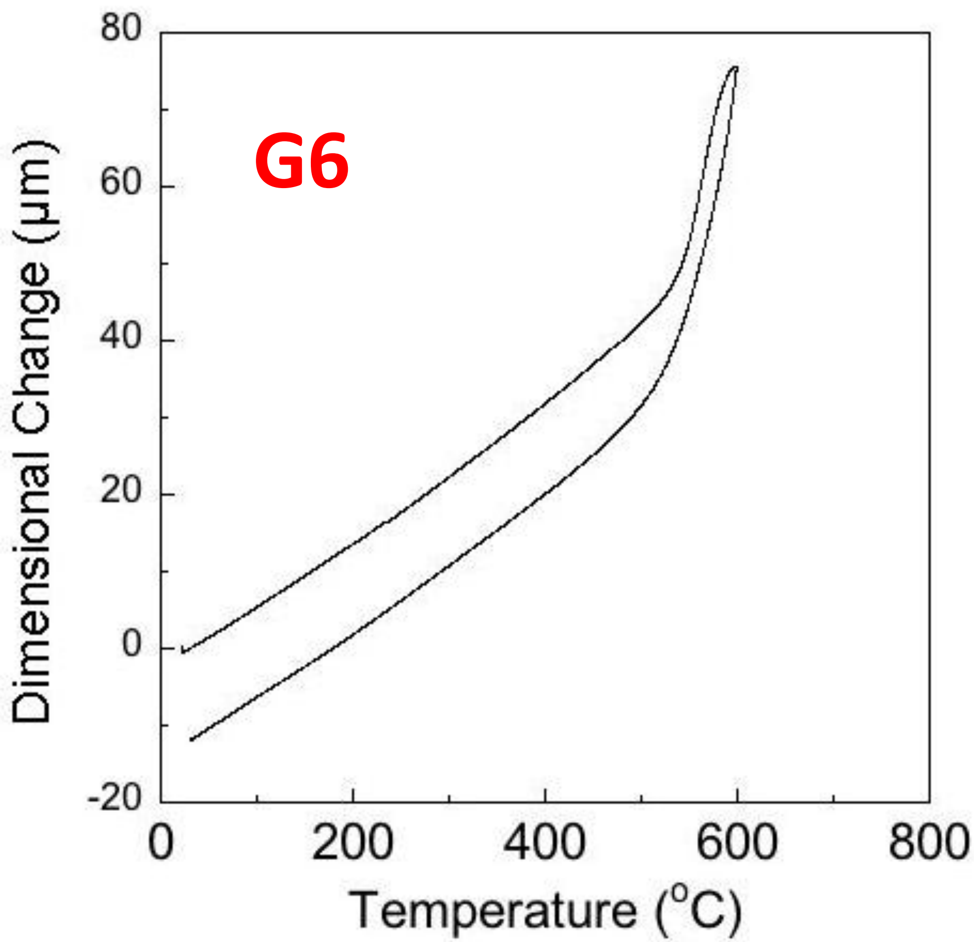
- To date we have completed the analysis of test specimens of SCN and G6 exposed for 10,000 hrs in air and H_2+N_2+H_2O
- Two sets of test specimens continue exposure tests (12,000+ hrs)

Results

Thermal Expansion and Glass Transition Temperature

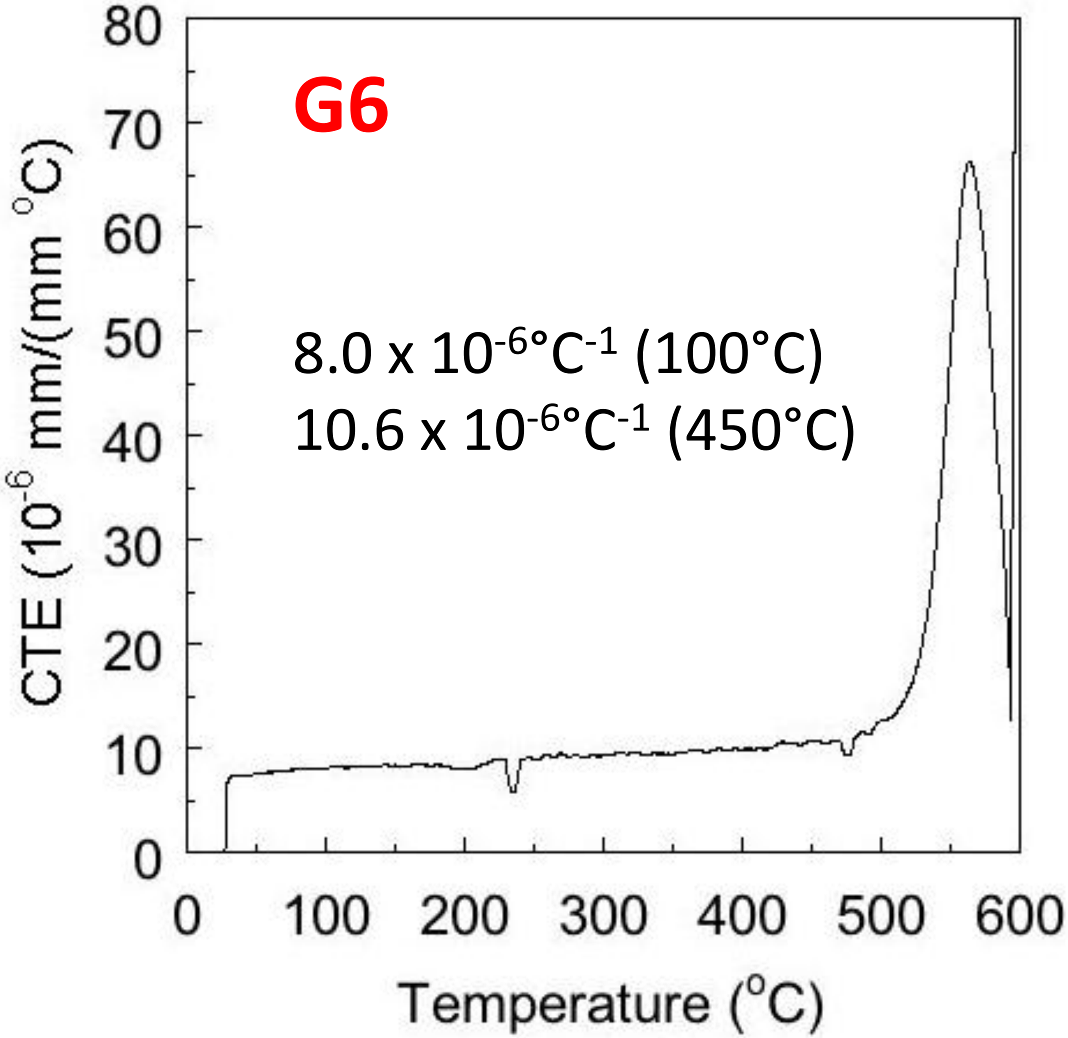


Thermomechanical Analyzer



Oak Ridge National Laboratory

Thermal Expansion

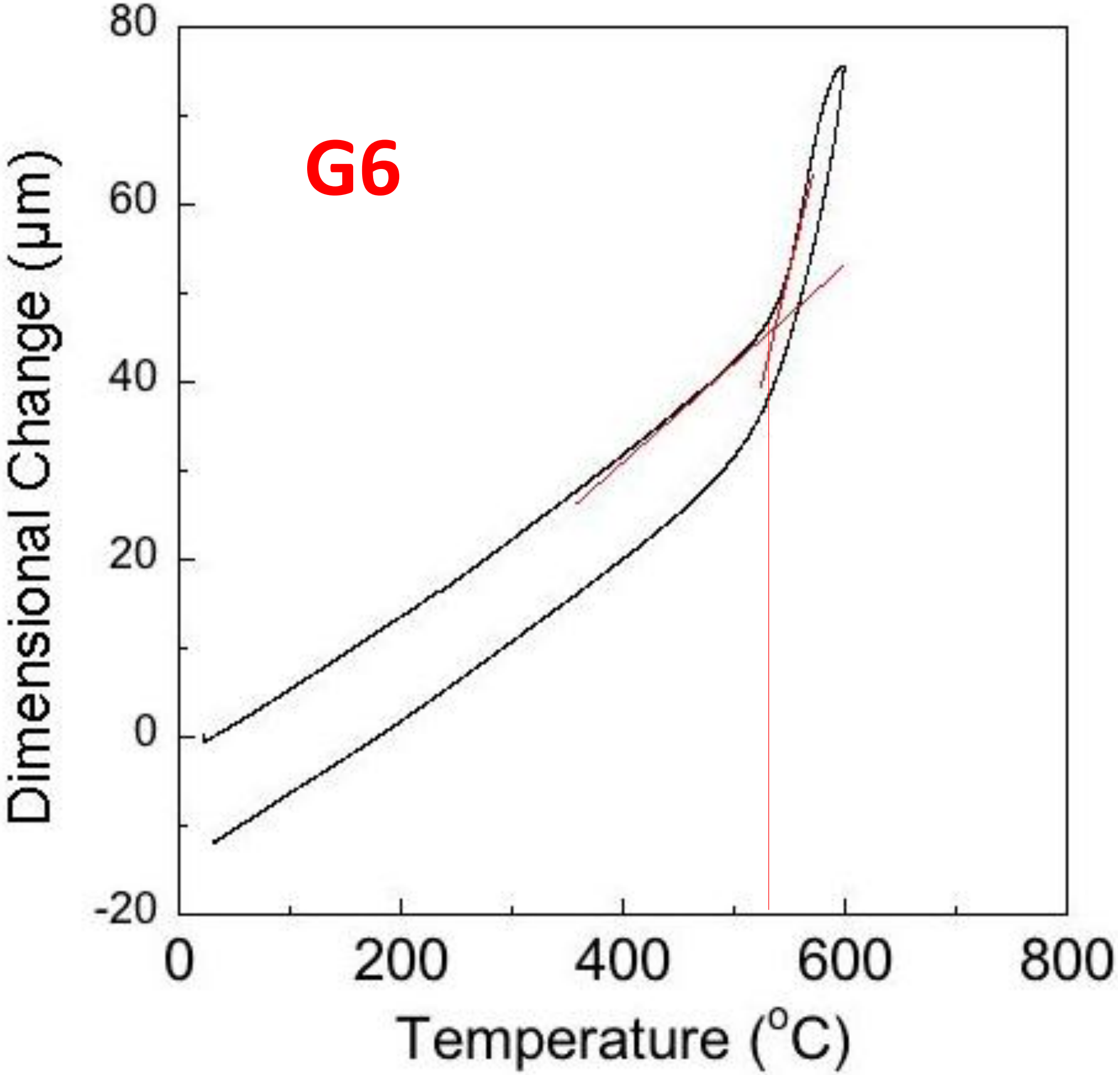


SCN

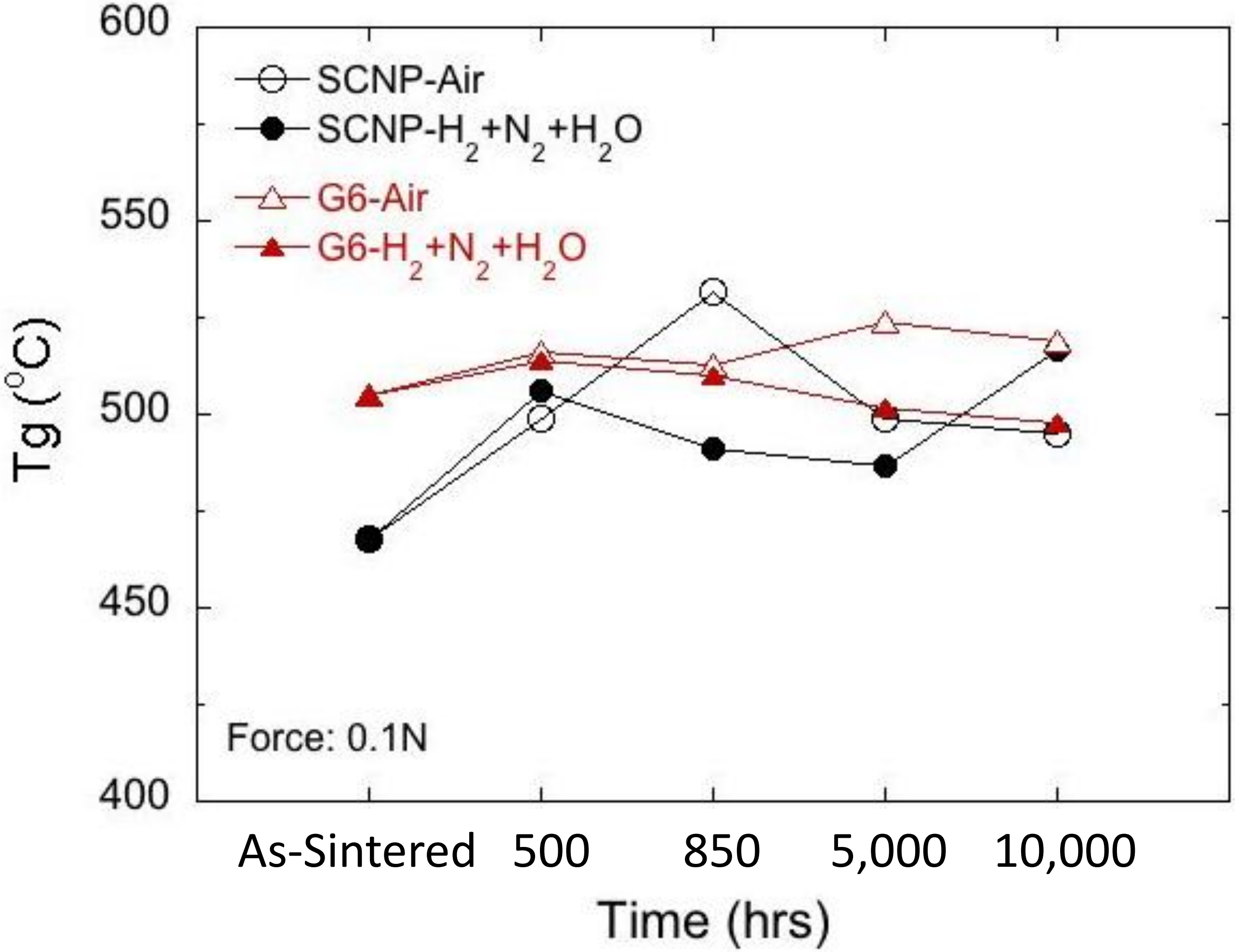
10.3×10^{-6}°C^{-1} (100°C)

12.4×10^{-6}°C^{-1} (400°C)

Glass Transition Temperature



Glass Transition Temperature



Oak Ridge National Laboratory

Viscosity of G6 Glass

Before Viscosity Measurements

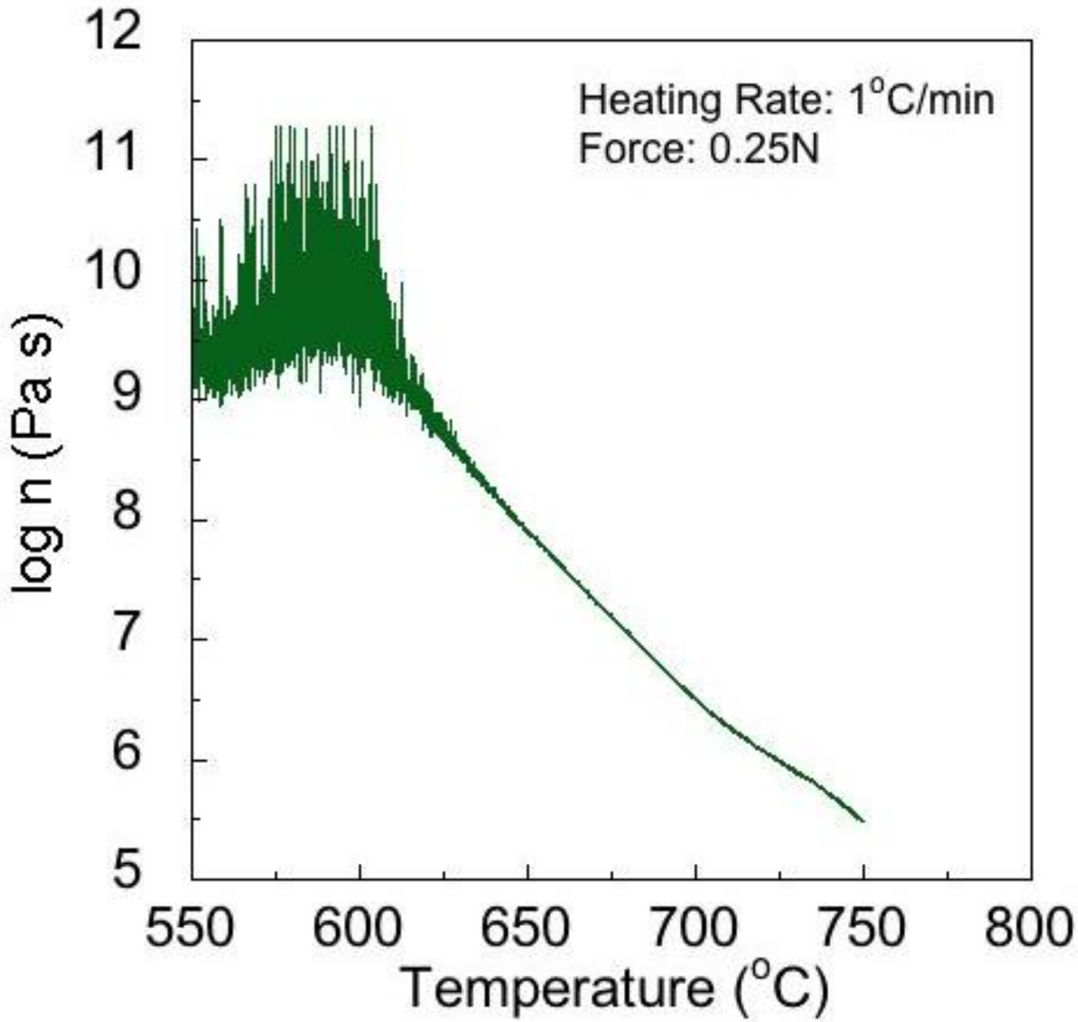
After Viscosity Measurements

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)

Oak Ridge National Laboratory

Viscosity of G6 Glass



Chemical Analysis

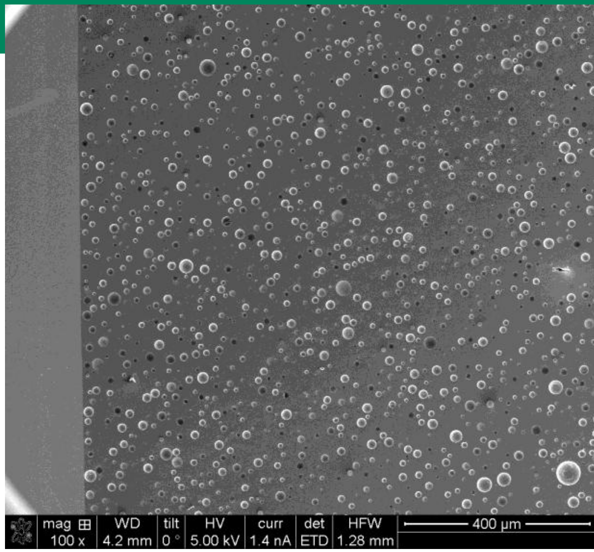
- Performed a study to assess the precision of different chemical analysis methods **(Al, B, Ba, Ca, Fe, K, Li, Mg, Na, Si, Ti, Zn, Zr)**
  - Neutron Activation Analysis
  - Inductively Couples Plasma Atomic Emission (ICPAES)
  - Inductively Couples Plasma Mass Spectroscopy (ICPMS)

- Sample Preparation Requirements
- ICPAES is the most precise of the three methods (except for Fe and Zr)

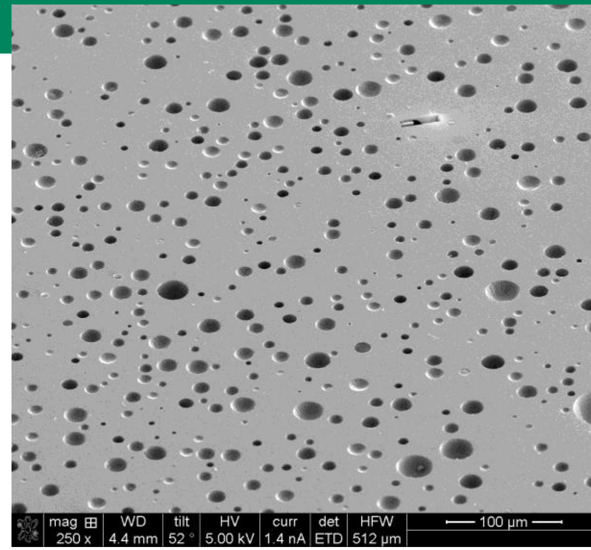
Chemical Analysis using Atom Probe

Oak Ridge National Laboratory

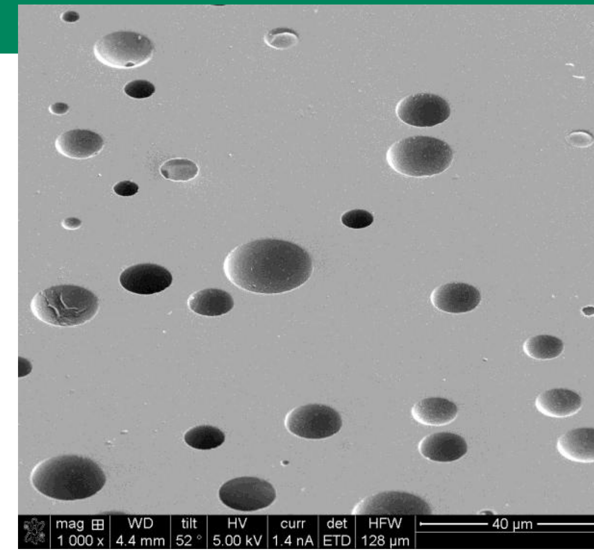
Select ROI and use FIB to lift out 3 x 25 um^2 wedge



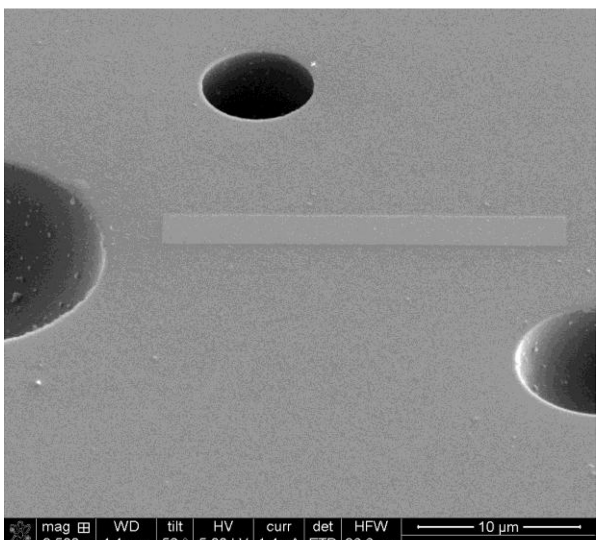
Low-magnification view



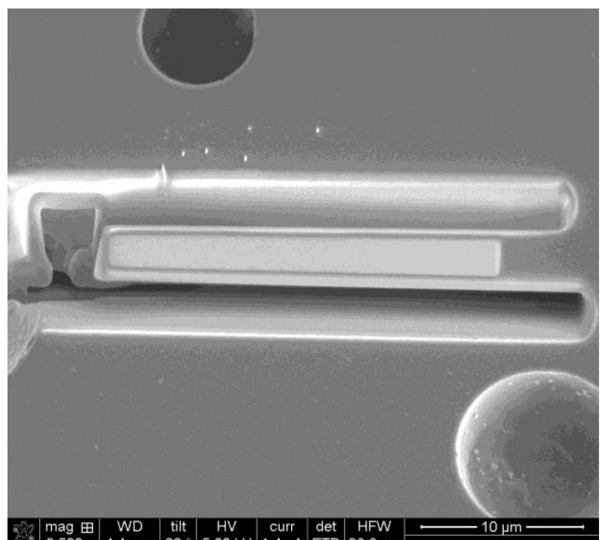
Zoom in for ROI selection



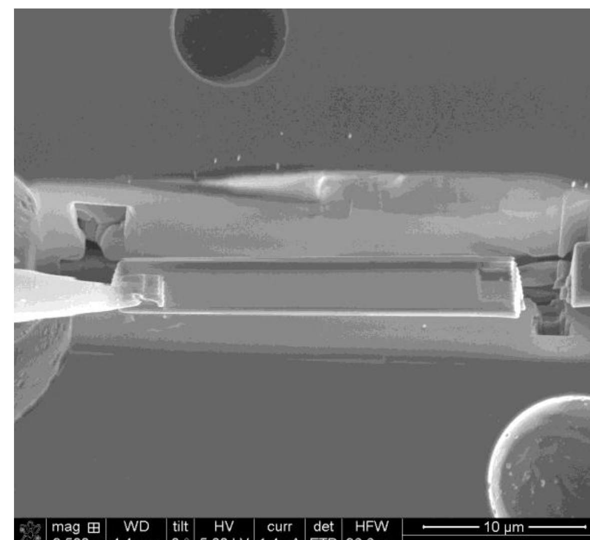
Select ROI



Cover ROI with protective Pt deposition (IB deposition at 30kV)

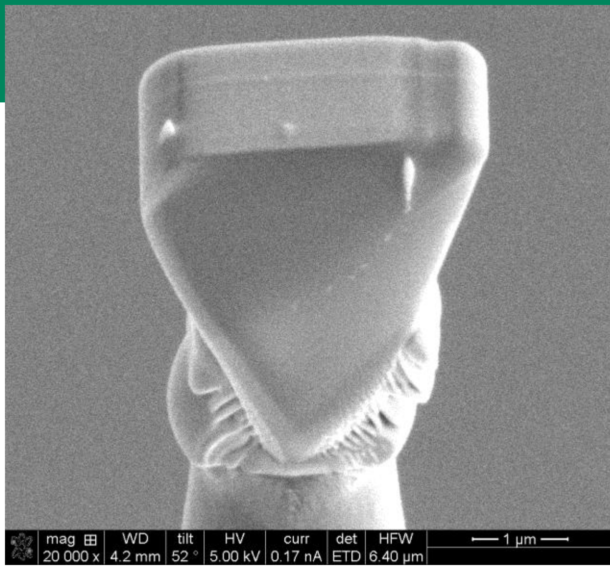


Mill trenches around ROI

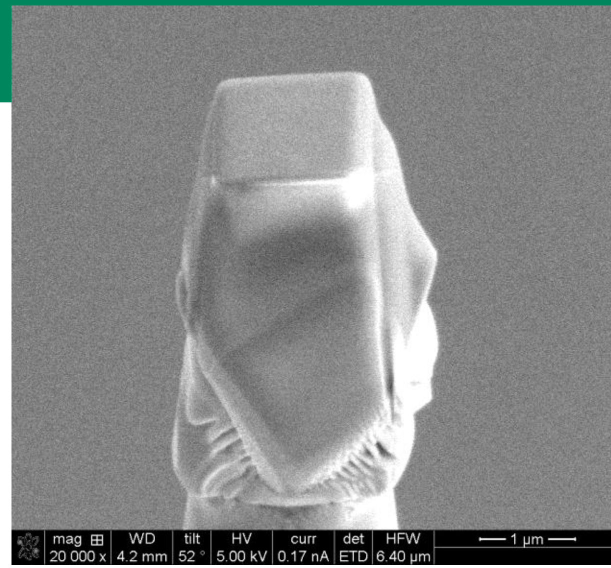


ROI lift-out with probe needle

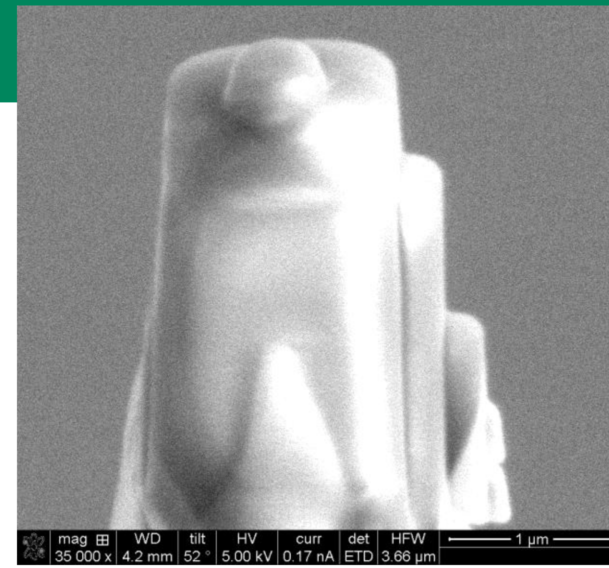
Mount slices on microtip and sharpen for APT



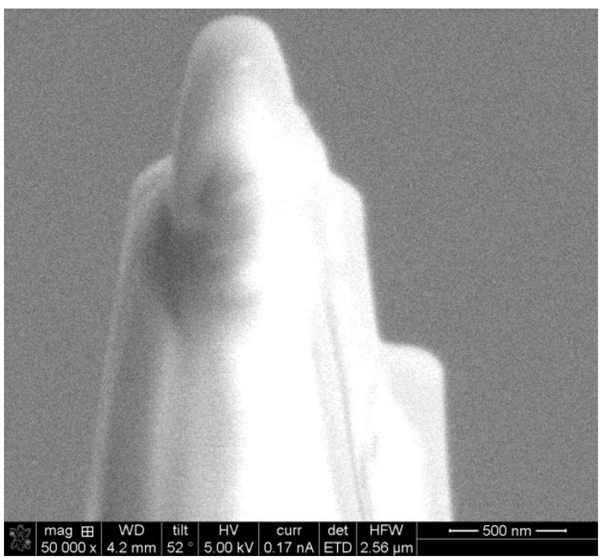
Attach to micropost



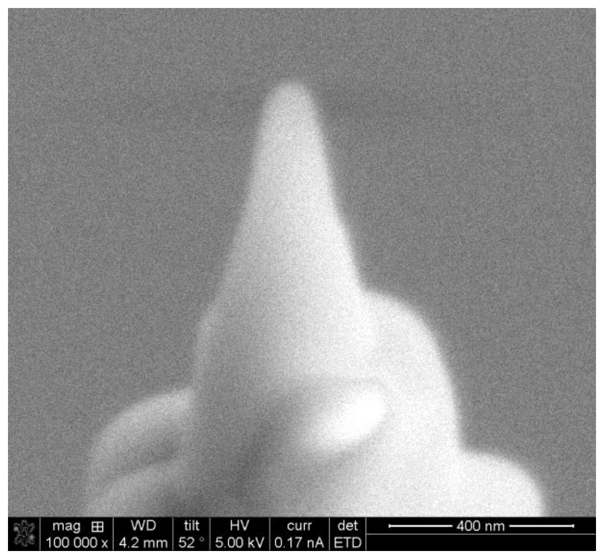
Trim square



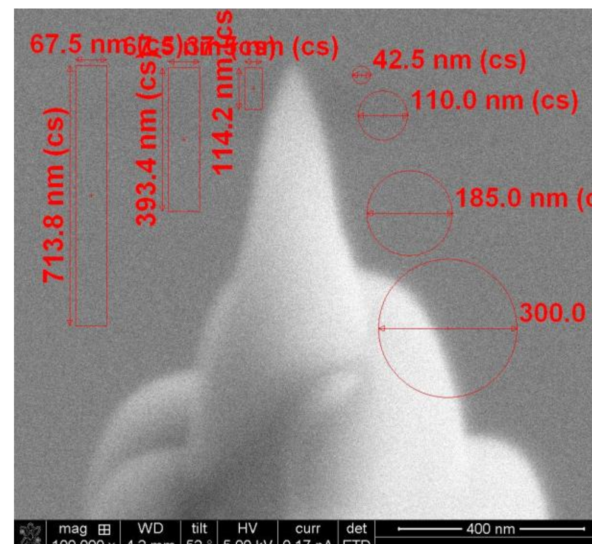
Sharpen w. annular milling pattern



30kV 280 pA ion beam annular pattern

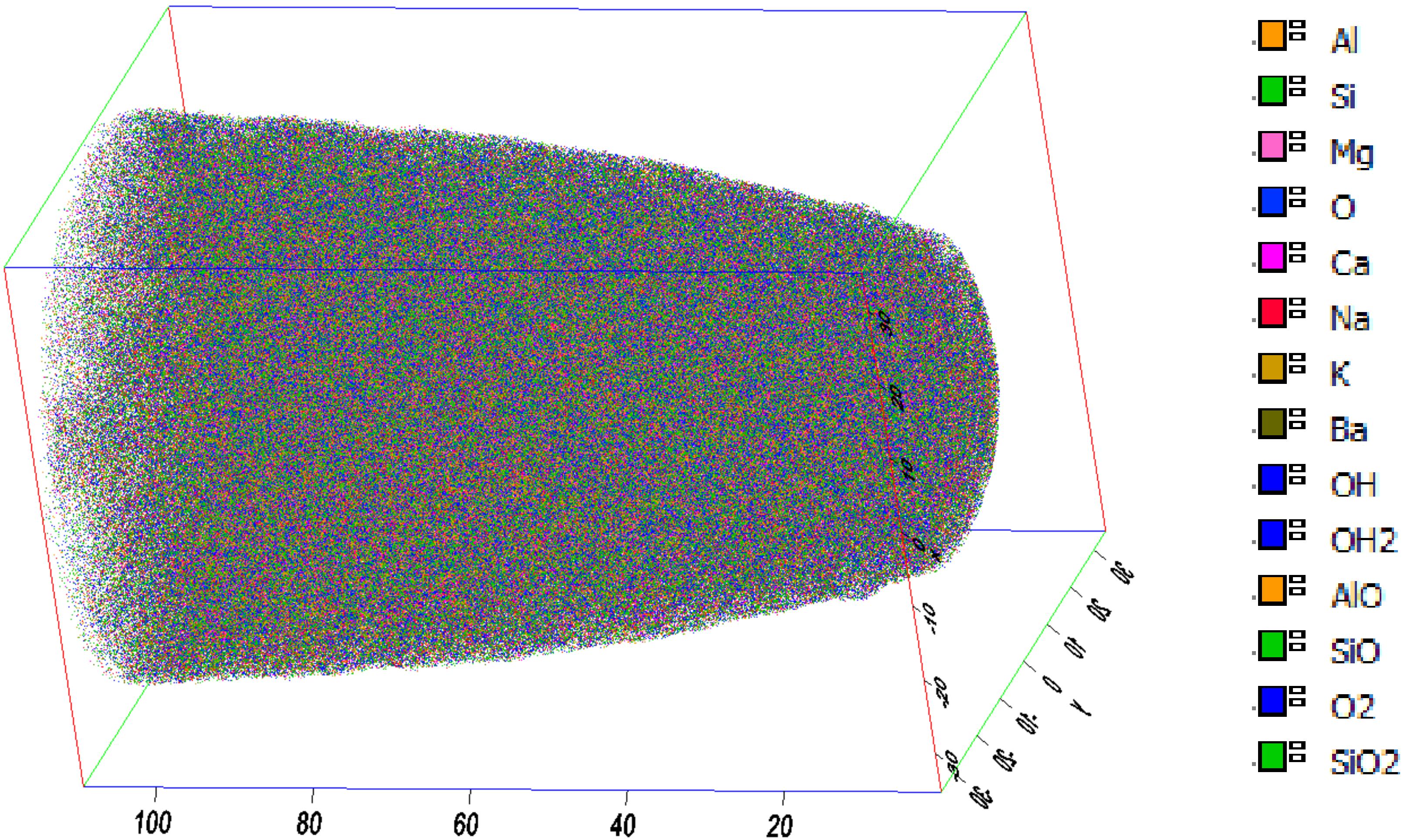


30kV 28pA ion beam annular pattern



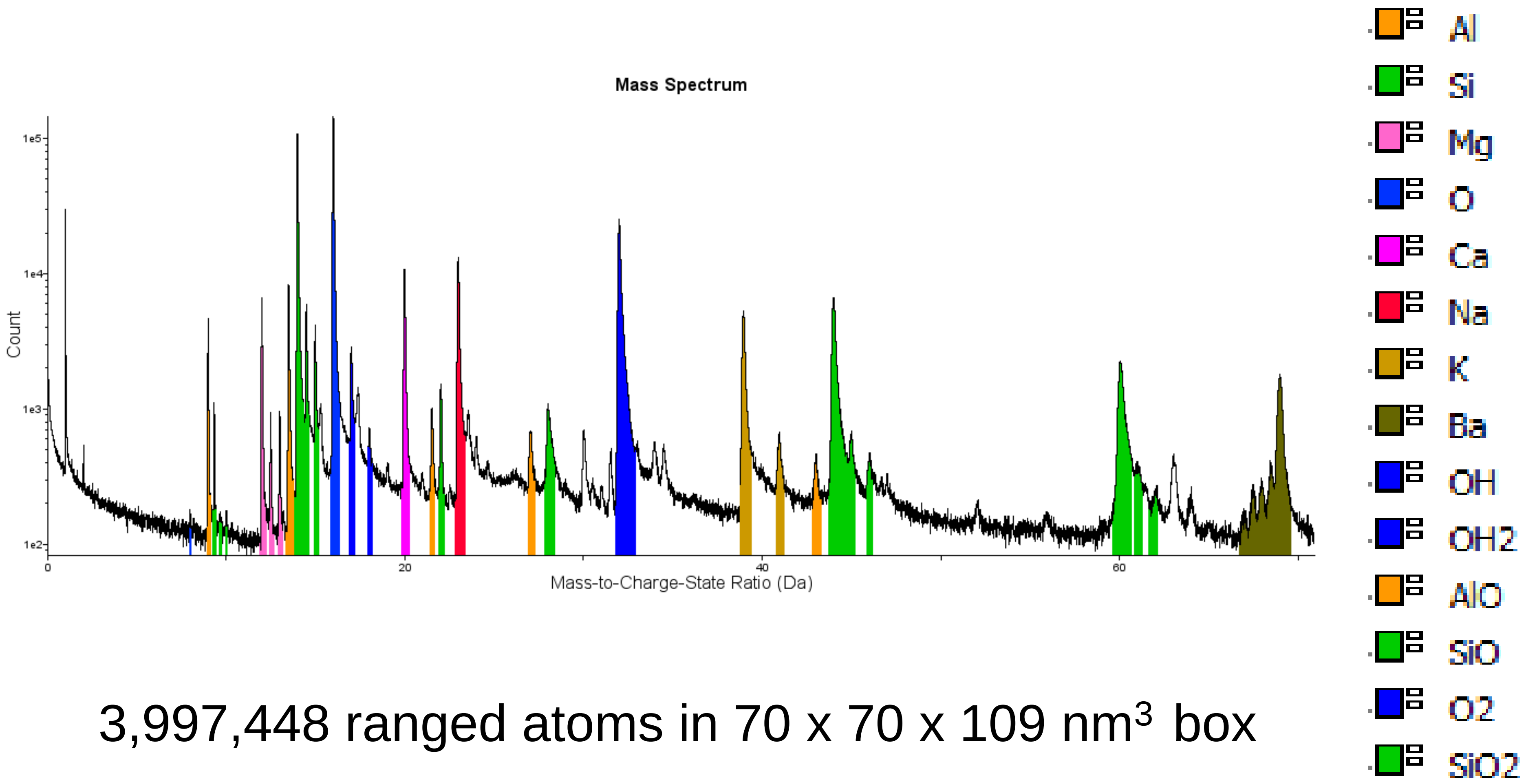
Touch up with 5kV 16pA ion beam

3D LEAP 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

Composition SCN Glass

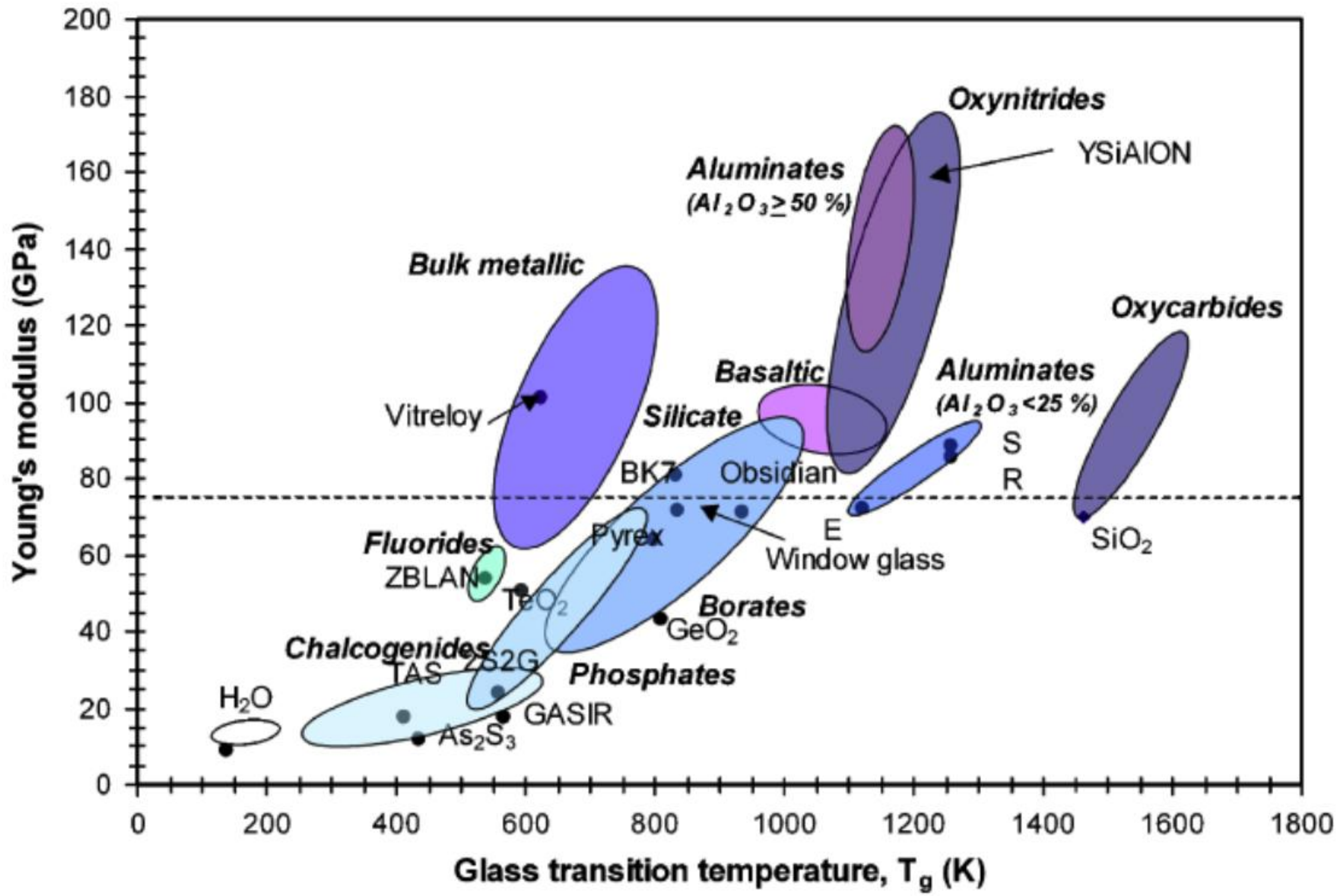
	ICPMS (ORNL)	ICPAES (ORNL)	APT Tip 1 R06_15869		APT Tip 2 R06_15853	
	at.%	at.%	at.%	statistical error (at.%)	at.%	statistical error (at.%)
O*	66.67	66.67	57.13	0.07	57.25	0.04
Si	27.38	27.96	25.64	0.04	26.65	0.03
K	1.90	1.64	2.85	0.01	2.73	0.01
Ba	0.50	0.45	2.00	0.01	2.16	0.01
Na	2.11	1.72	3.48	0.01	3.54	0.01
Ca	0.48	0.60	2.32	0.01	2.35	0.01
Al	0.62	0.60	2.64	0.01	2.78	0.01
Mg	0.24	0.26	1.21	0.01	1.23	0.00
Ti	0.05	0.06	ND		ND	
B	0.05	0.04	ND		ND	
Zn	0.01	0.01	ND		ND	
Zn	0.00	0.00	ND		ND	
Fe	0.00	0.00	ND		ND	
Zr	0.00	0.00	ND		ND	
Li	0.00	0.00	ND		ND	
H**	ND	ND	2.71	0.01	1.32	0.01
Total	100	100	100		100	

ND = not detected

* Oxygen normalized to SiO_2 stoichiometry for ICPMS and ICPAES

** Hydrogen from OH and OH_2 molecular ion peaks

Elastic Constants



T. Rouxel, *J. Am. Ceram. Soc.*, **90** [10] 3019 – 3039 (2007)

Elastic Constants

Journal of Non-Crystalline Solids, 12 (1973) 35–45. © North-Holland Publishing Company

DIRECT CALCULATION OF YOUNG'S MODULUS OF GLASS

A. MAKISHIMA and J.D. MACKENZIE
Materials Department, School of Engineering and Applied Science, University of California, Los Angeles, USA

Received 16 November 1972

An equation has been derived for the direct calculation of the Young's modulus of oxide glasses from their chemical compositions. The method is based on a consideration of dissociation energy of the oxide constituents per unit volume and the packing density. For borate glasses, the ratio of four-coordinated to three-coordinated borons must be taken into consideration. Excellent agreement is obtained between calculated and measured values of Young's modulus for over thirty different glasses.

$$E = 2V_t \sum_i G_i X_i .$$

The packing density V_t is defined by,

$$V_t = \frac{\rho}{M} \sum_i V_i X_i ,$$

- Using results from chemical analyses, an elastic modulus of 70 GPa is predicted at room temperature for SCN glass.
- Accounting for 18% porosity, the resulting elastic modulus is 57.4 GPa, which is consistent with values determined by resonant ultrasound spectroscopy

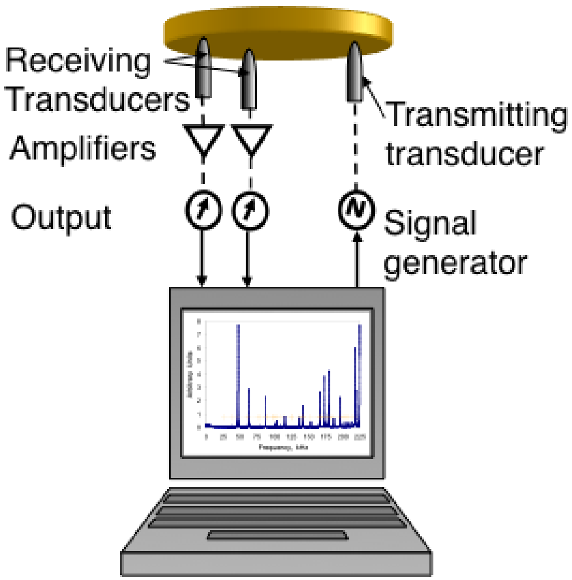
G_i: Dissociation Energy

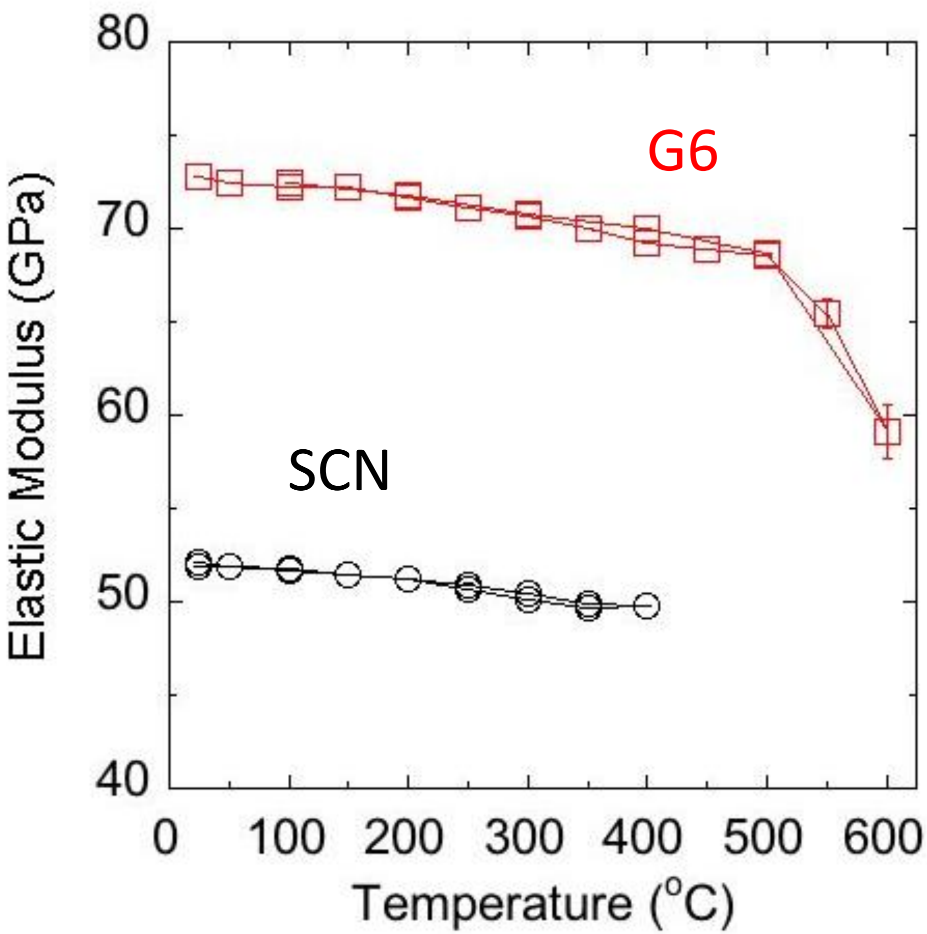
V_i: Packing factor

Oak Ridge National Laboratory

Elastic Constants

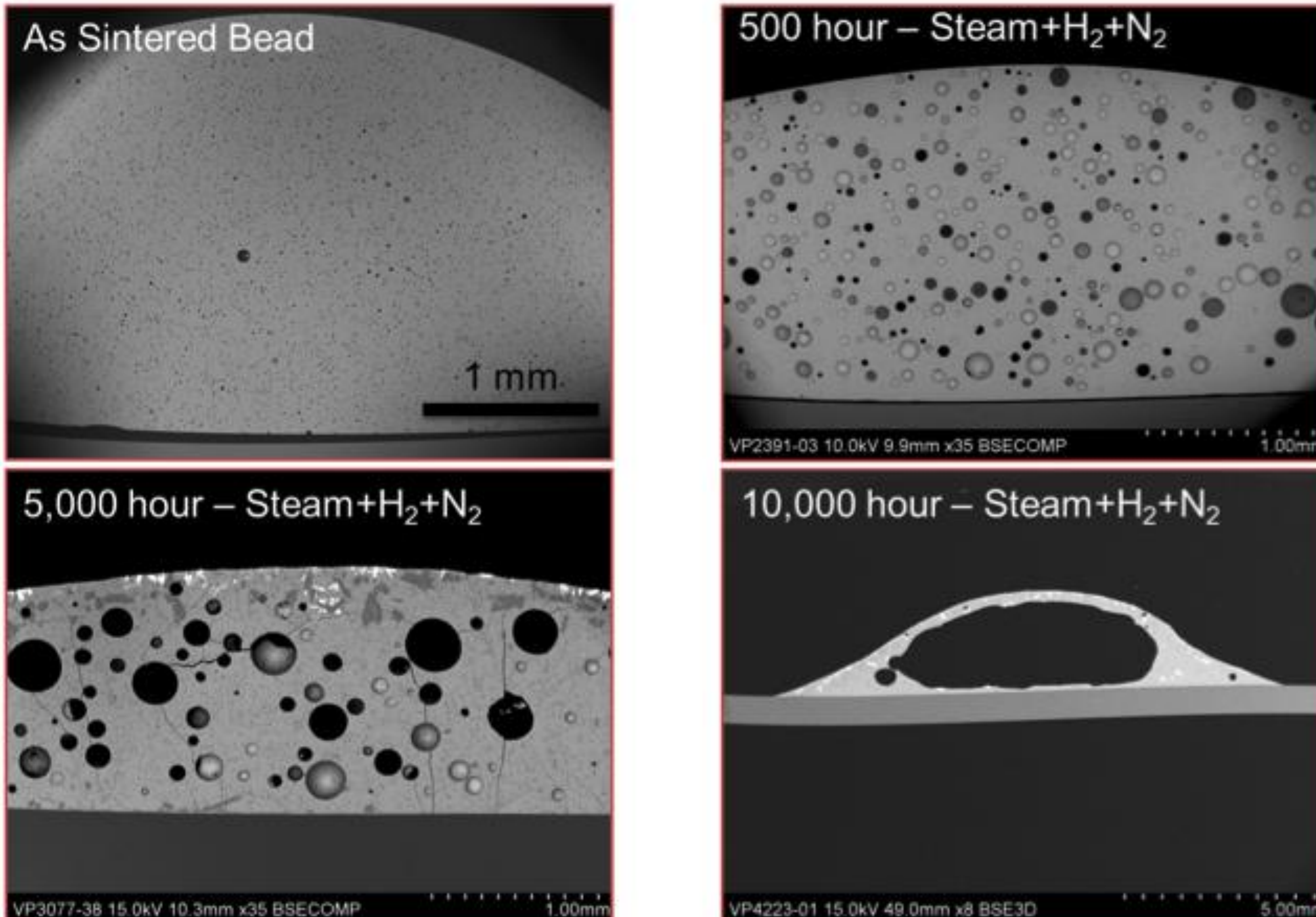
Resonant Ultrasound Spectroscopy





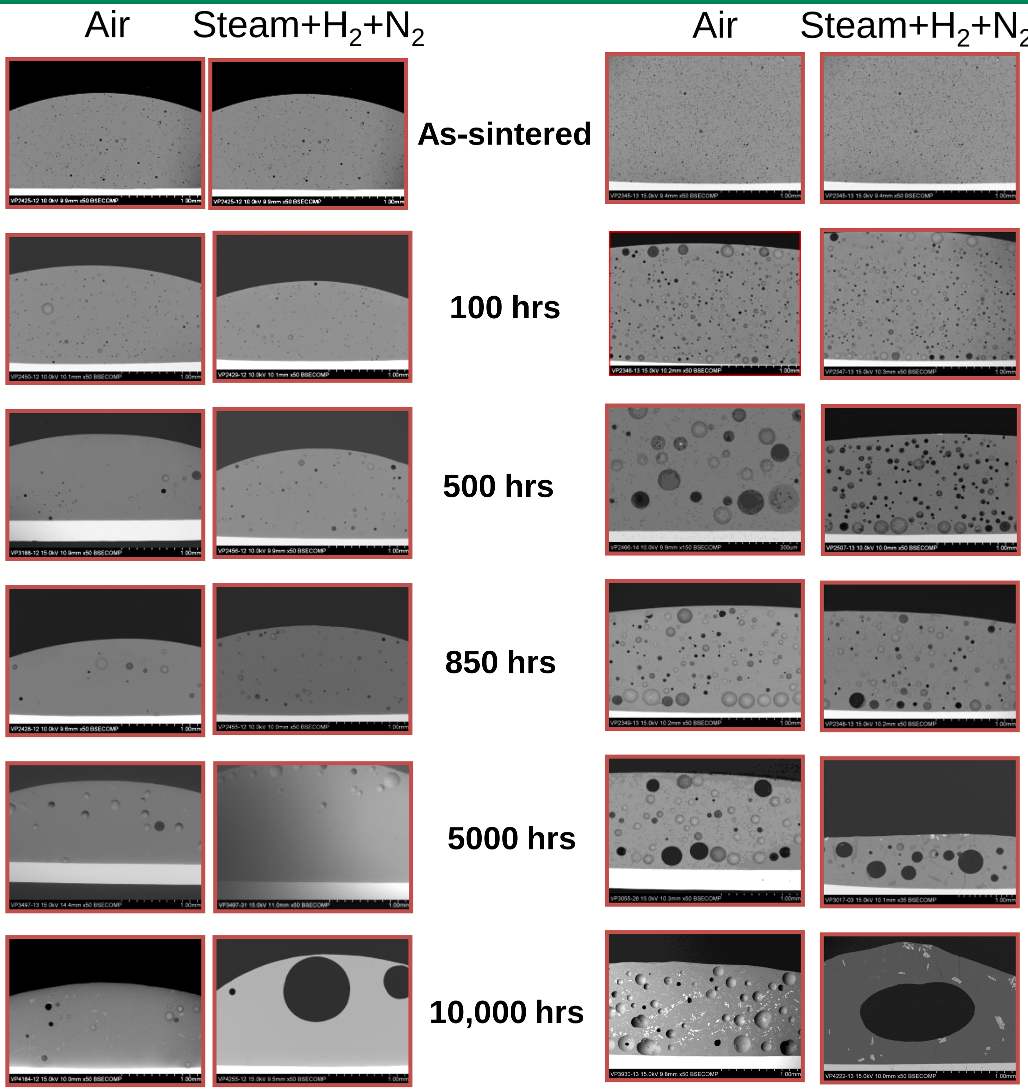
Microstructural Analysis

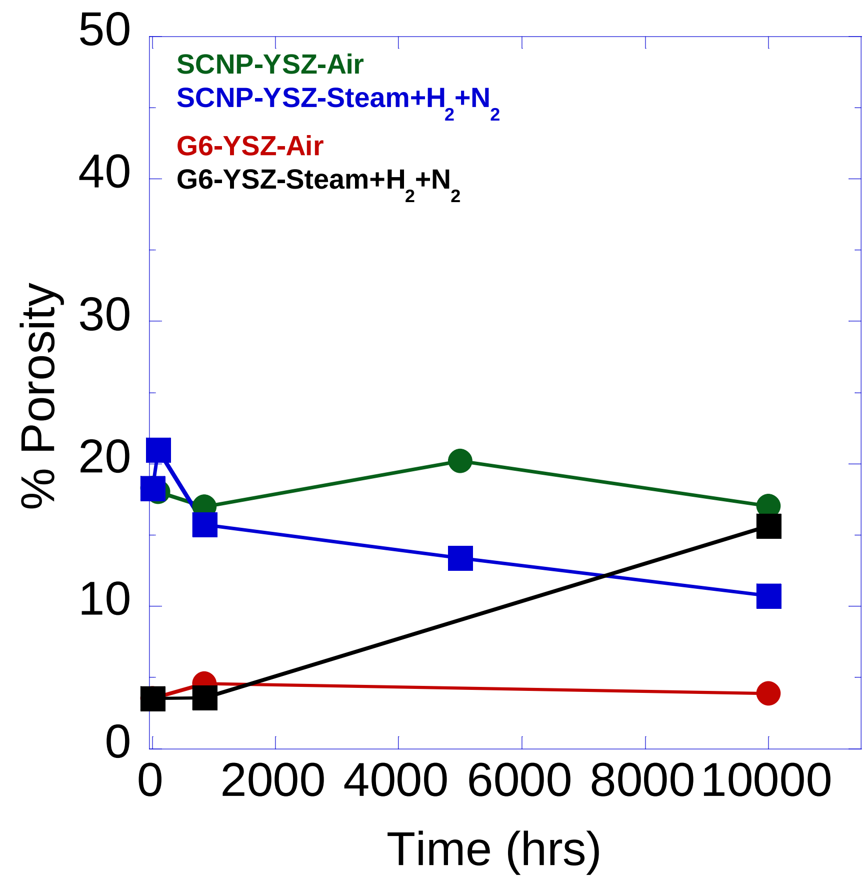
SCN



Porosity Evolution

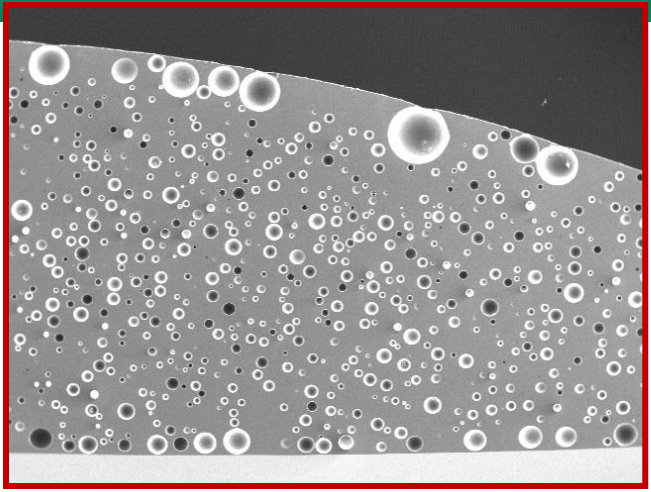
G6 SCN

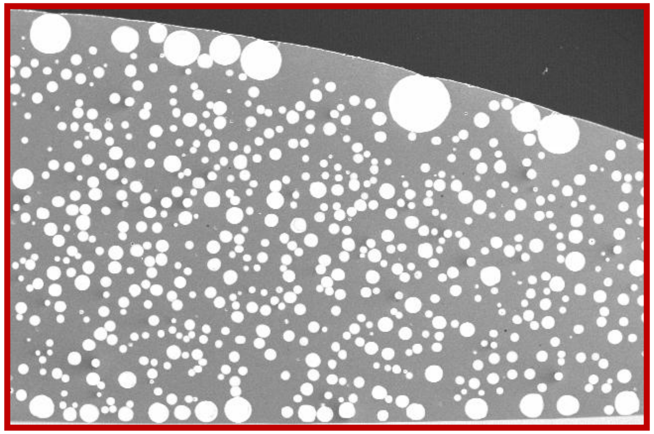


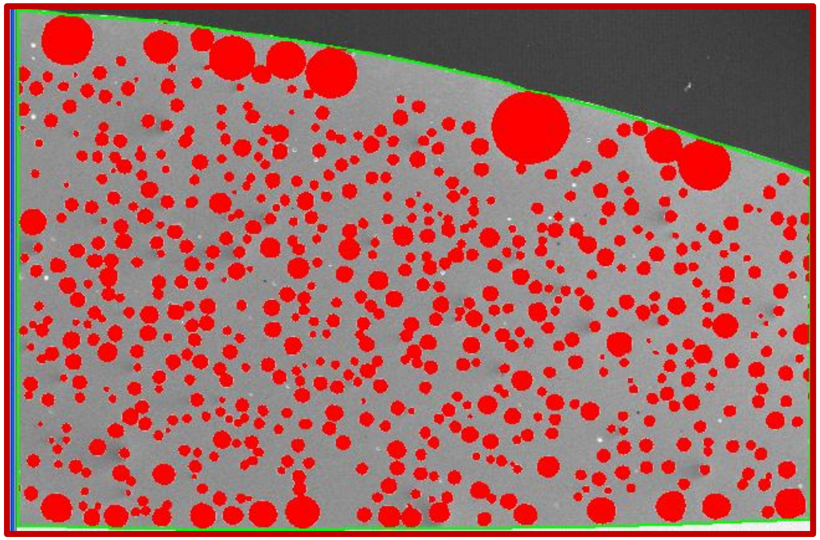


OAK RIDGE National Laboratory

Porosity Evolution







Summary of Pores

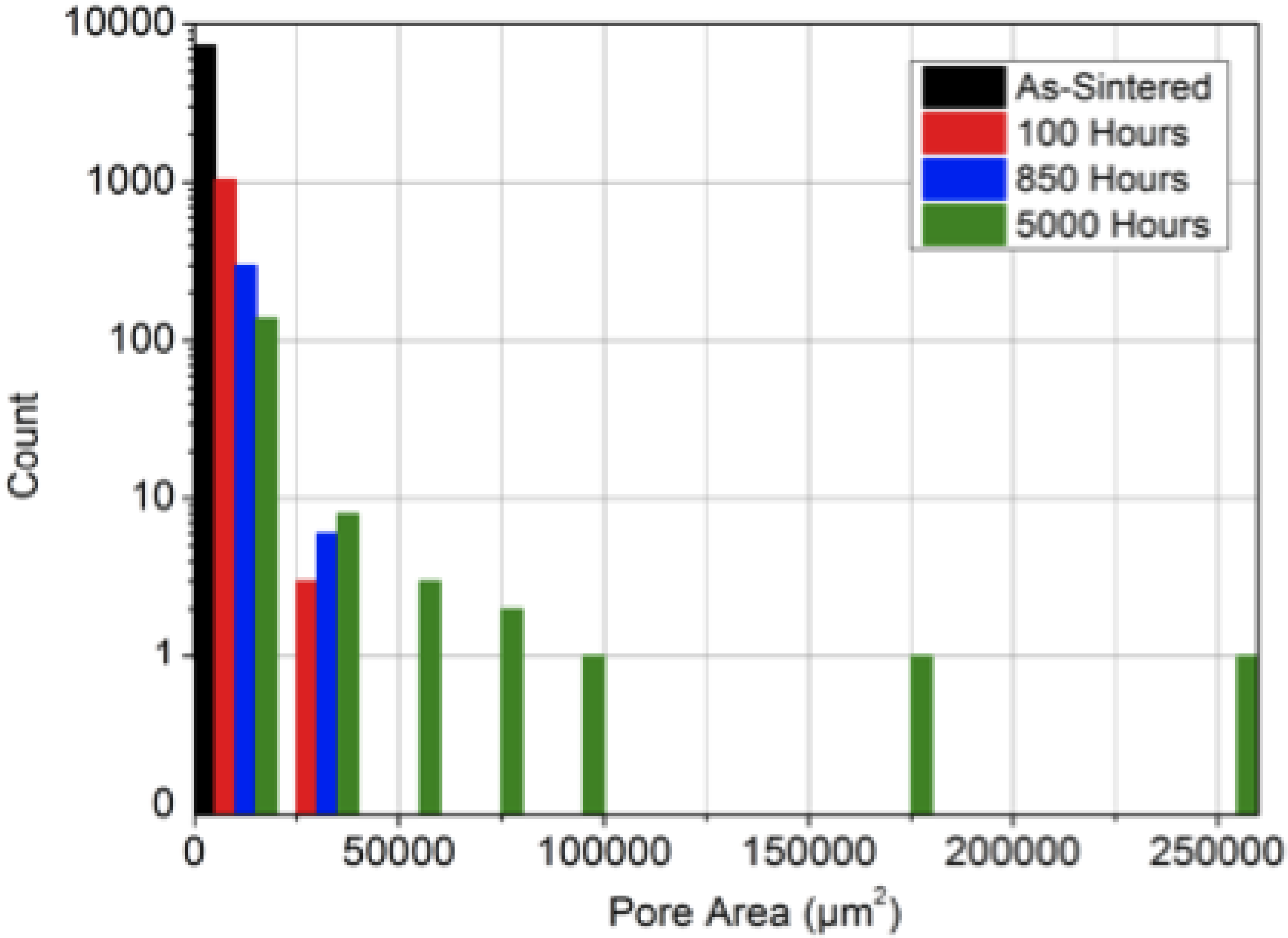
Stats	Area (um^2)	Diameter (um)	Perimeter (um)
Min	156.22803	14.033985	29.161793
(Obj.#)	167	167	84
Max	58585.512	324.83276	1624.218
(Obj.#)	6	6	6
Range	58429.285	310.79877	1595.0563
Mean	1809.3016	40.832958	134.50632
Std.Dev	3697.0122	23.671747	104.16805
Sum	998734.56	22539.793	74247.484
Samples	552	552	552

Total Area

Obj.#	Area (um^2)	Diameter (um)	Perimeter (um)
1	3649080.5	2278.2881	7714.5317

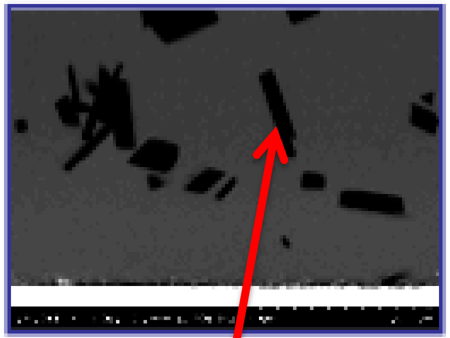
OAK RIDGE
National Laboratory

Pore Evolution: SCN-YSZ (H_2+N_2+H_2O)

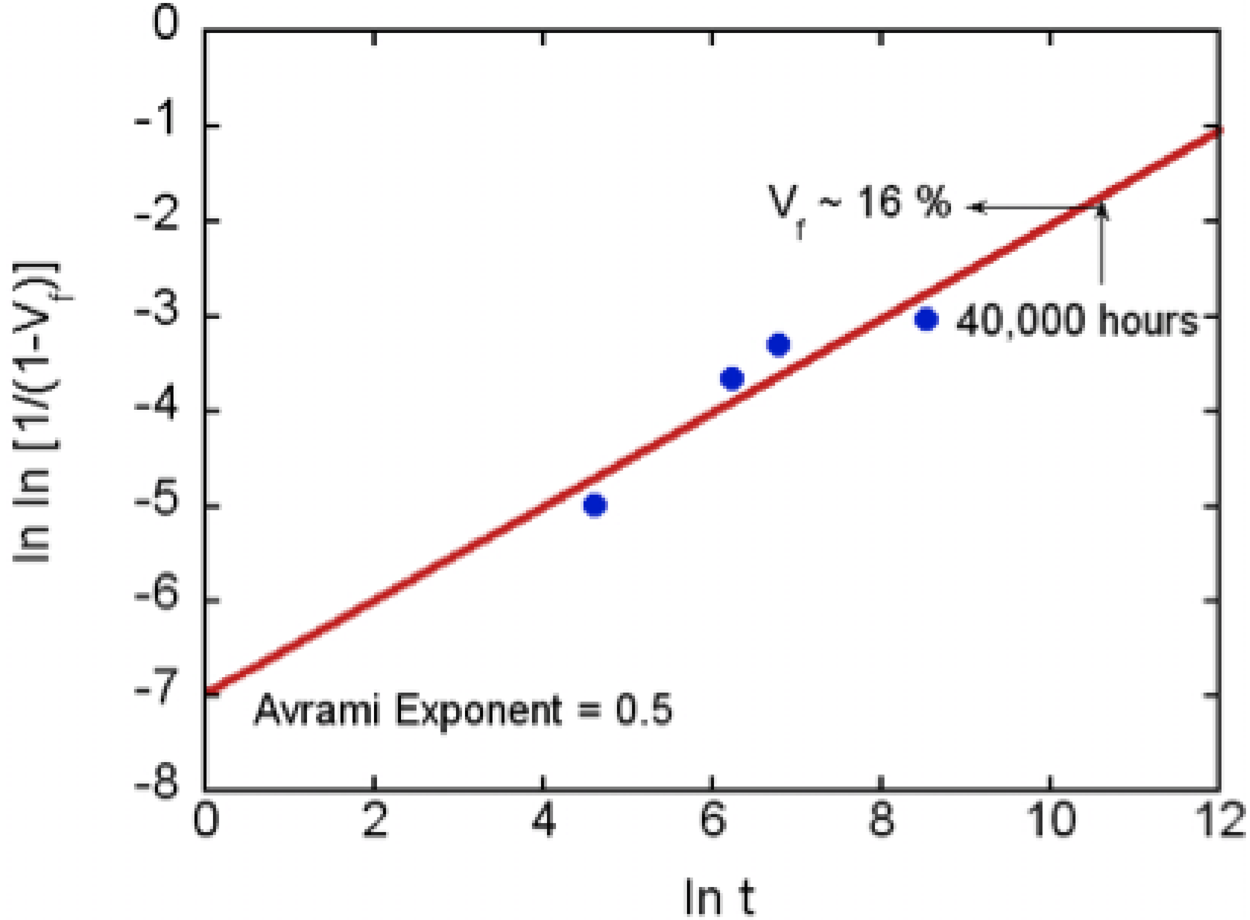


Oak Ridge National Laboratory

Rates of Crystallization



$KAlSi_3O_8$



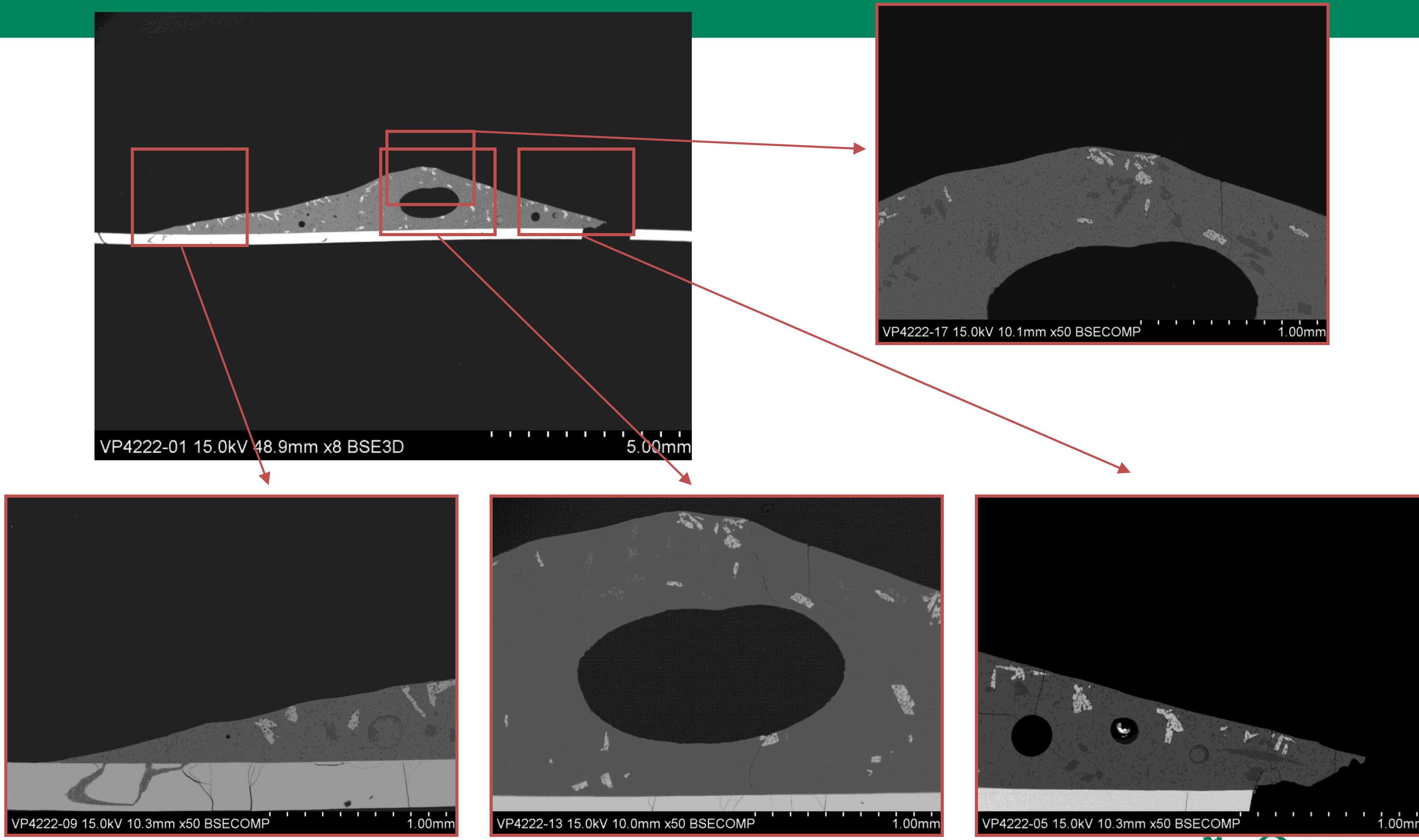
Oak Ridge National Laboratory

SCN-YSZ-49

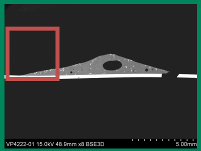
After 10,000 Hours in Steam+H_2+N_2

SCN-YSZ-49

After 10,000 Hours in Steam+H_2+N_2

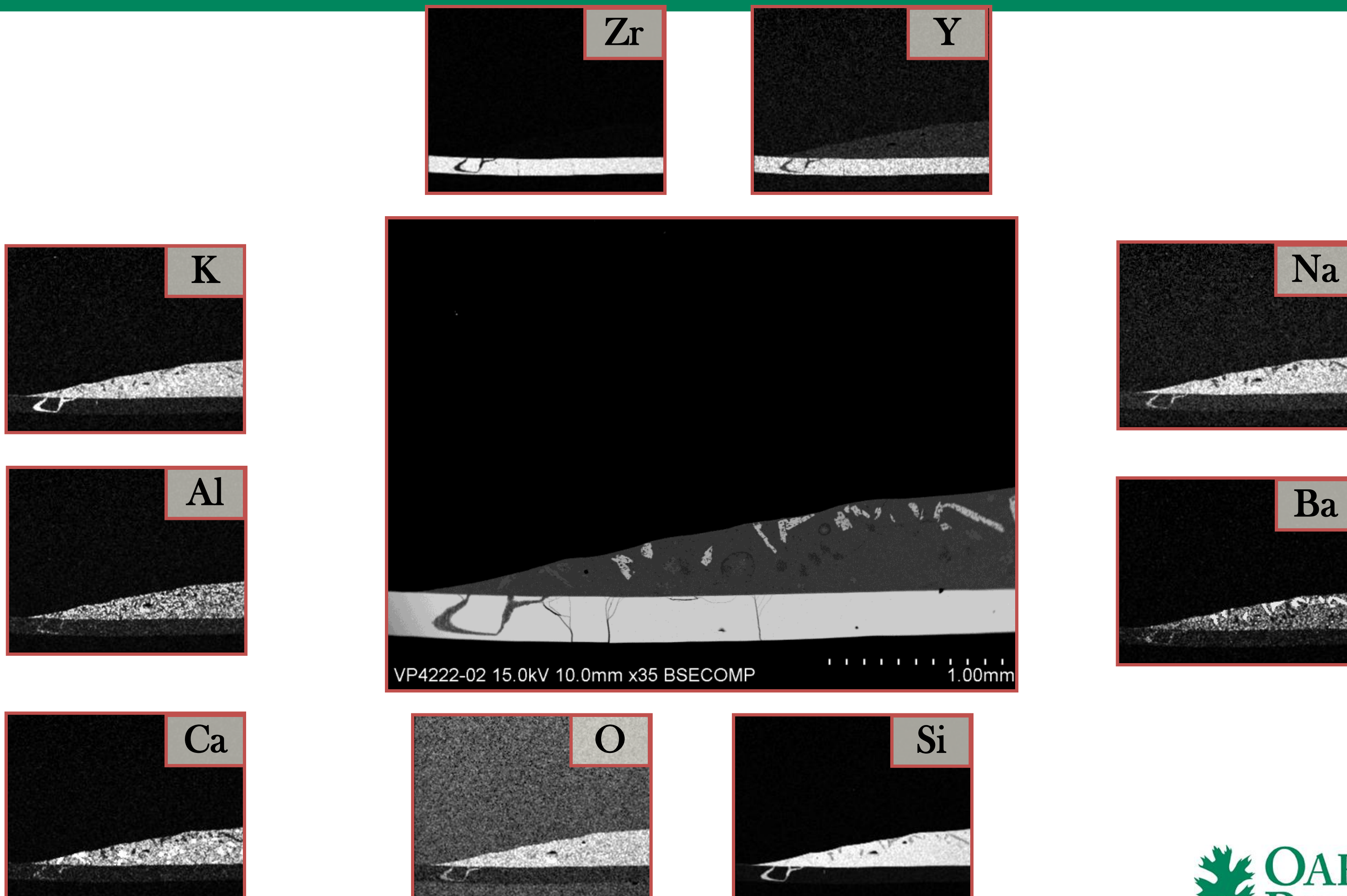


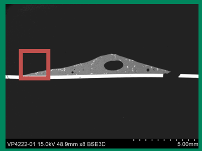
Oak Ridge National Laboratory



SCN-YSZ-49

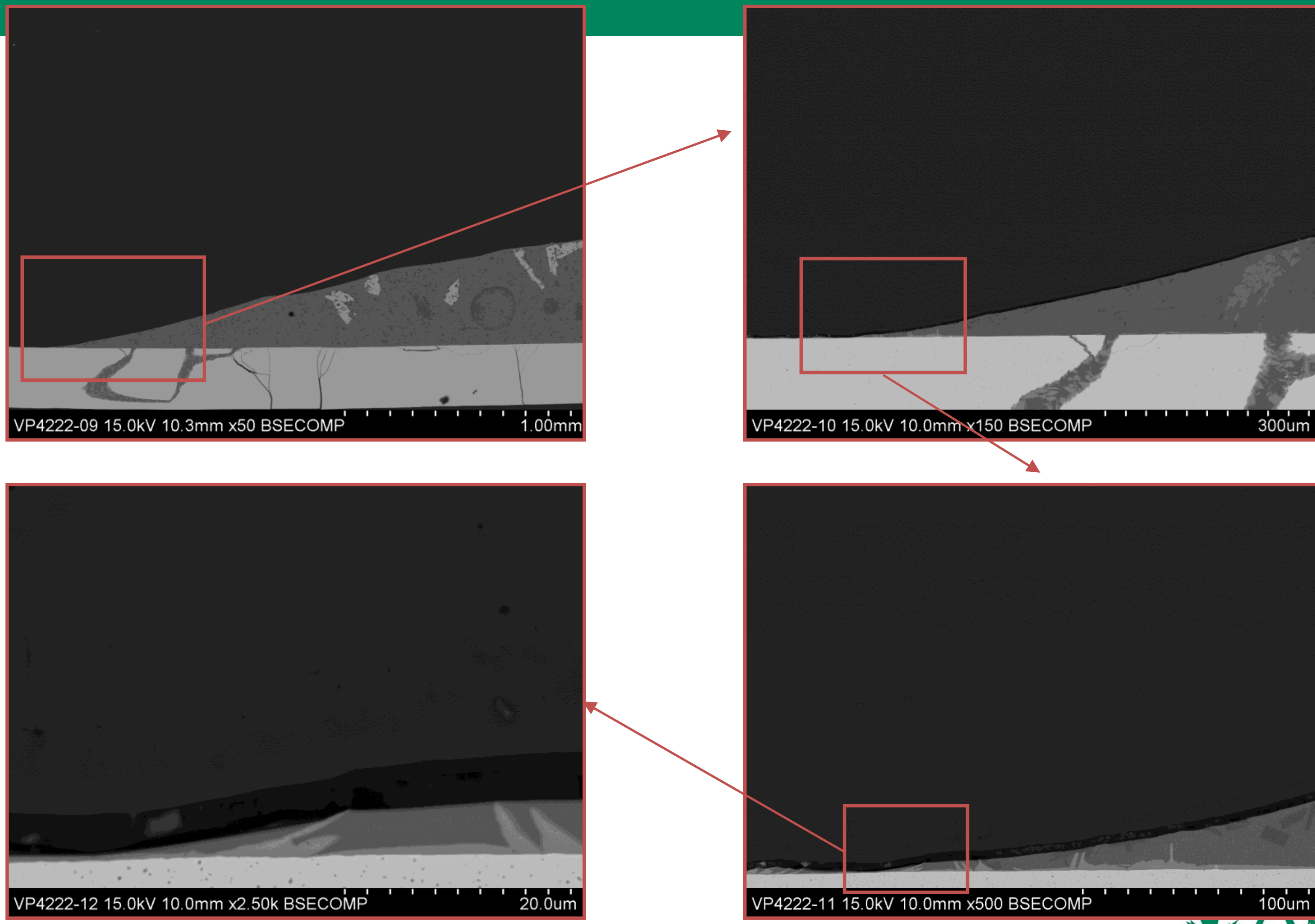
After 10,000 Hours in Steam+H_2+N_2



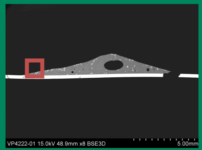


SCN-YSZ-49

After 10,000 Hours in Steam+H_2+N_2

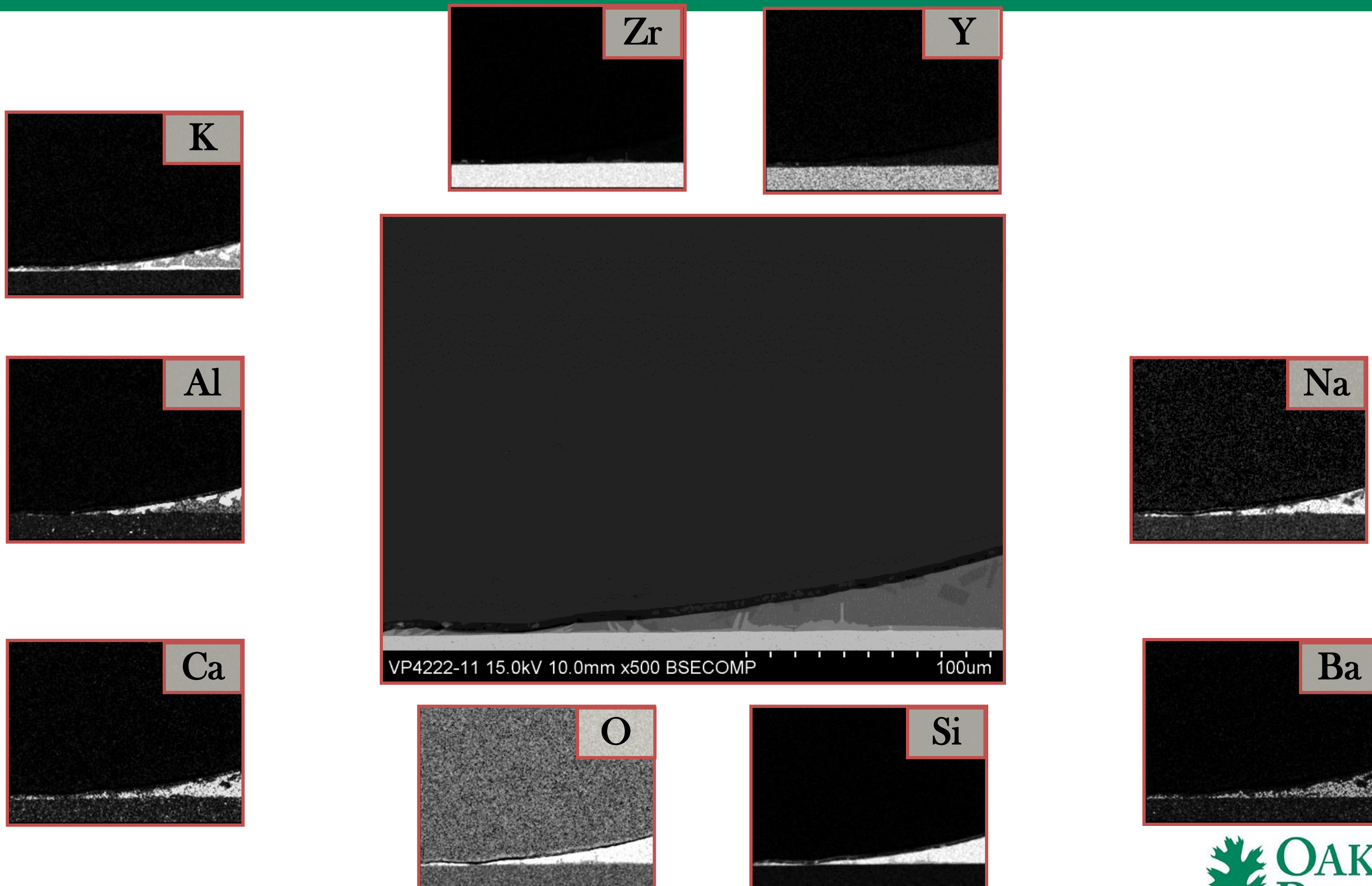


OAK RIDGE National Laboratory

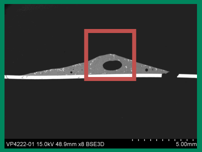


SCN-YSZ-49

After 10,000 Hours in Steam+H_2+N_2

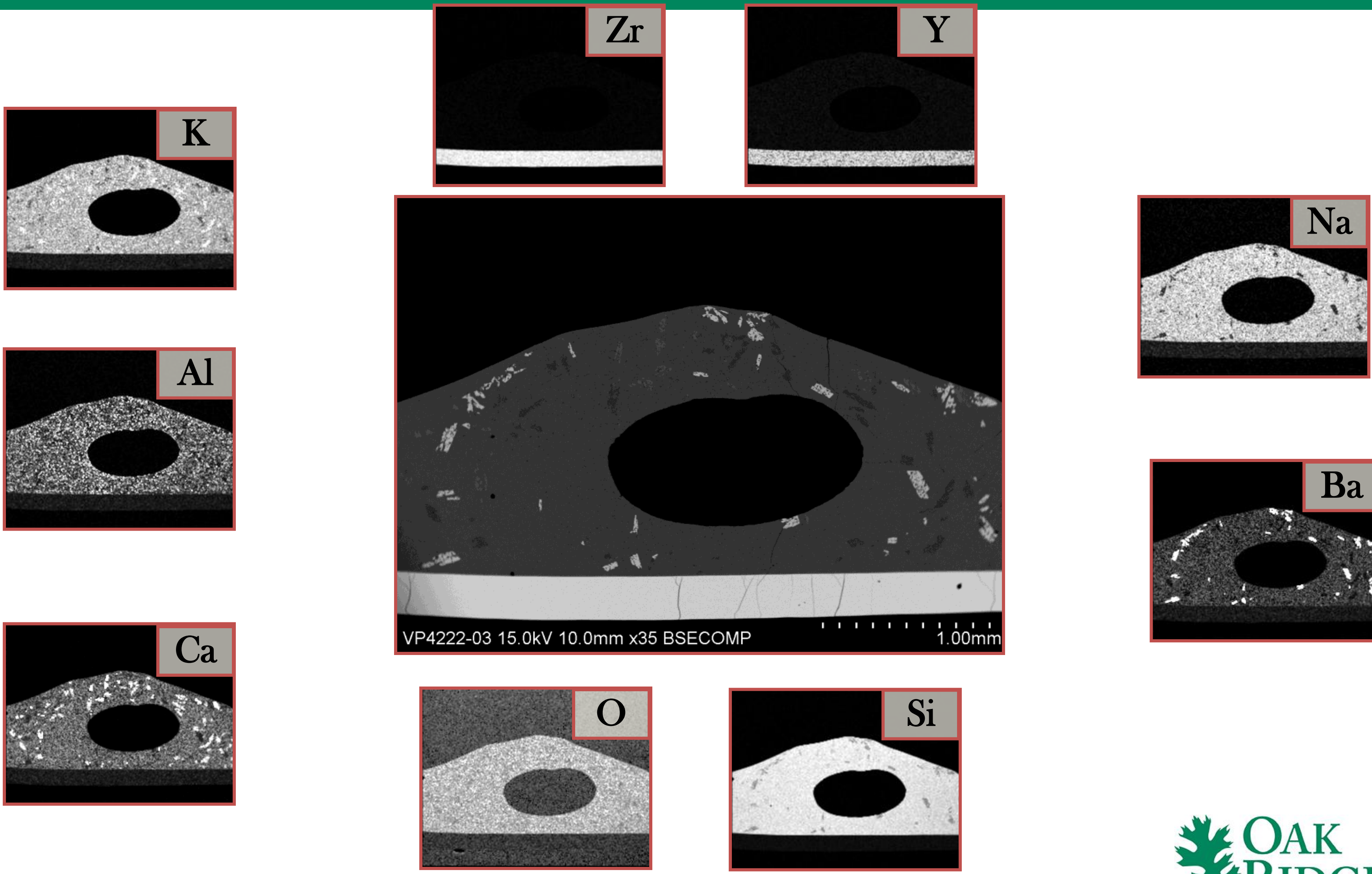


Oak Ridge National Laboratory

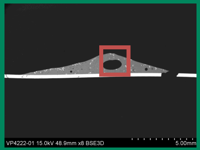


SCN-YSZ-49

After 10,000 Hours in Steam+H_2+N_2

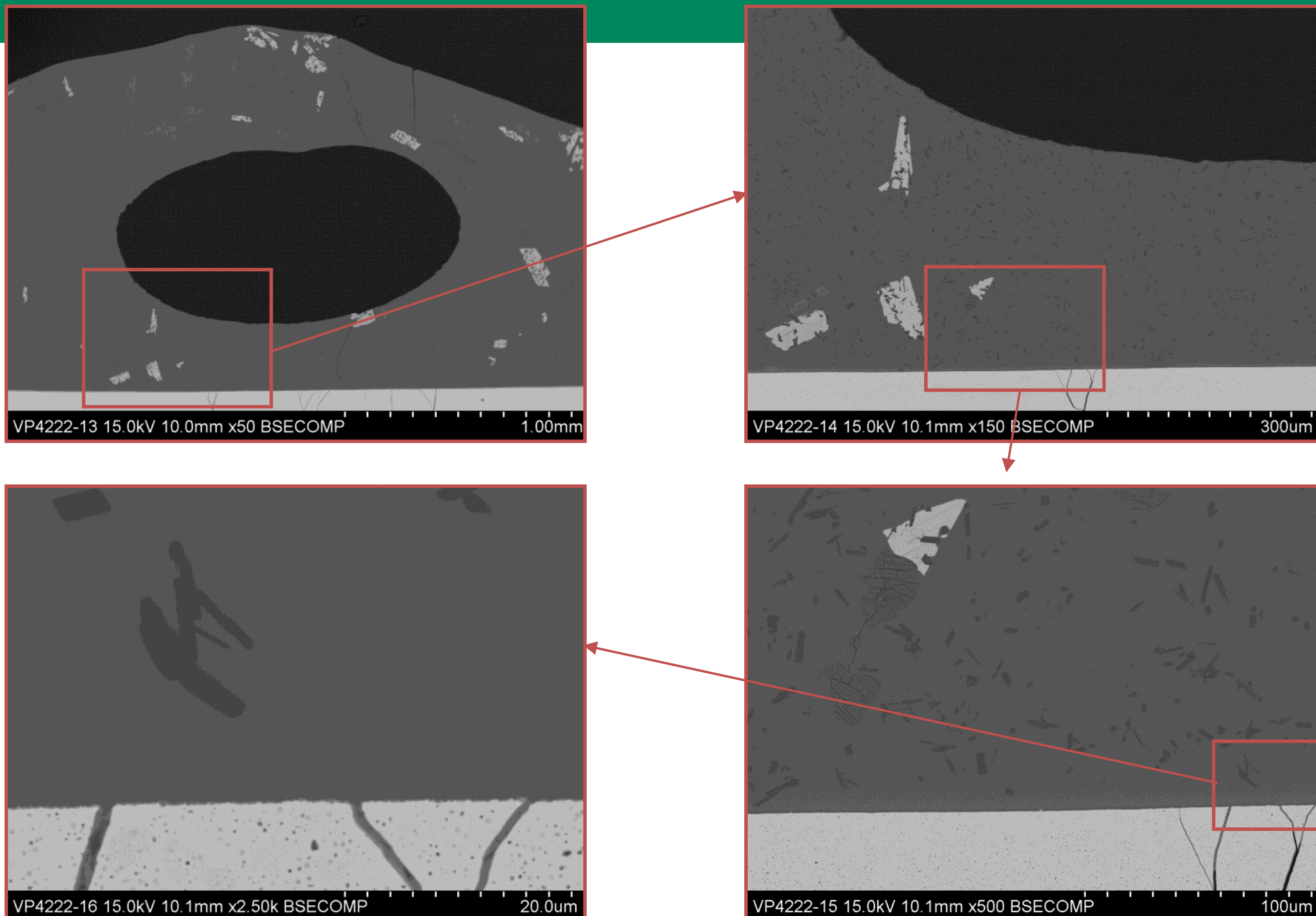


Oak Ridge National Laboratory

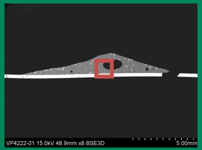


SCN-YSZ-49

After 10,000 Hours in Steam+H_2+N_2

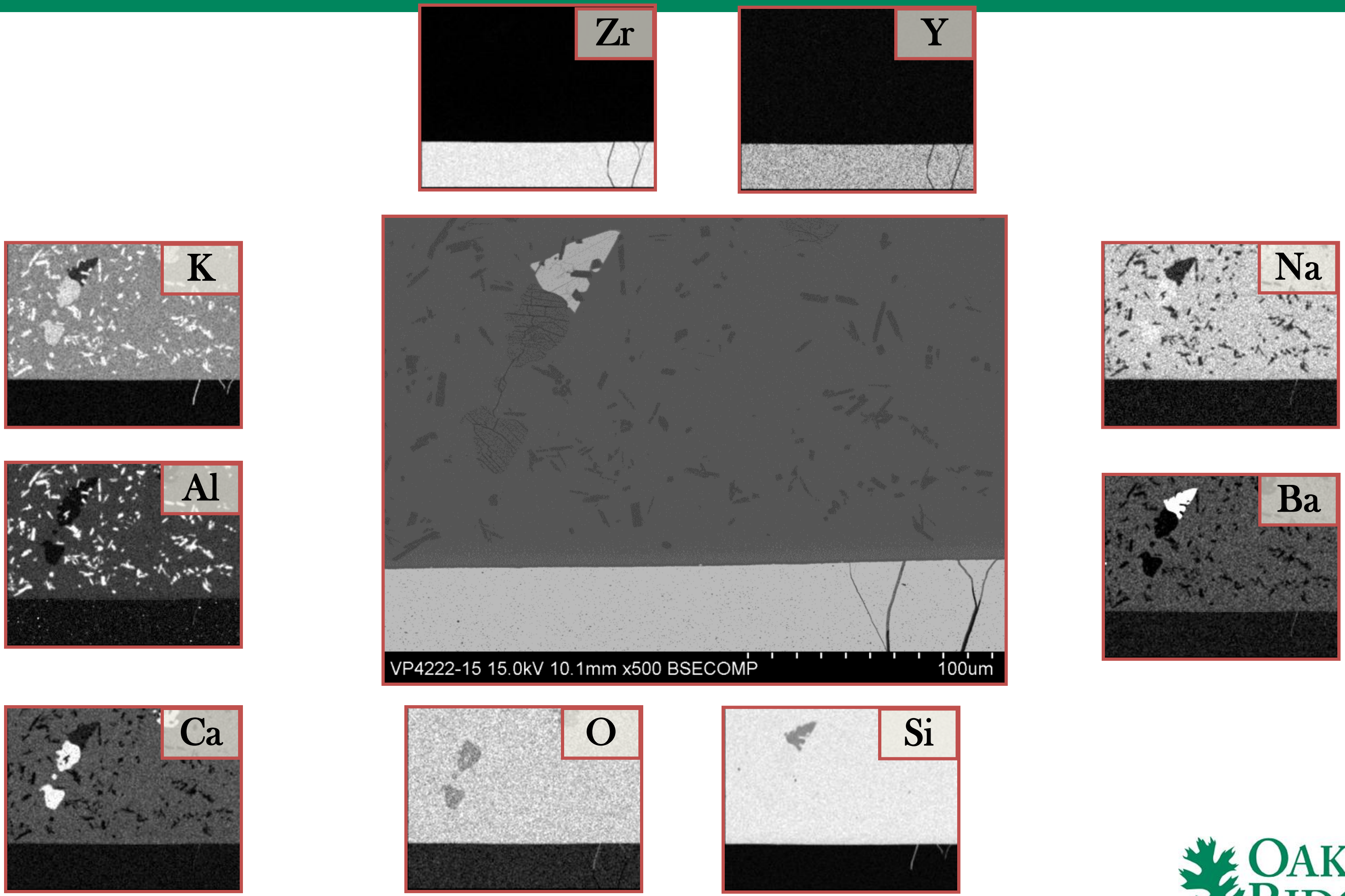


Oak Ridge National Laboratory

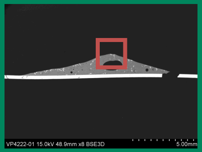


SCN-YSZ-49

After 10,000 Hours in Steam+H_2+N_2

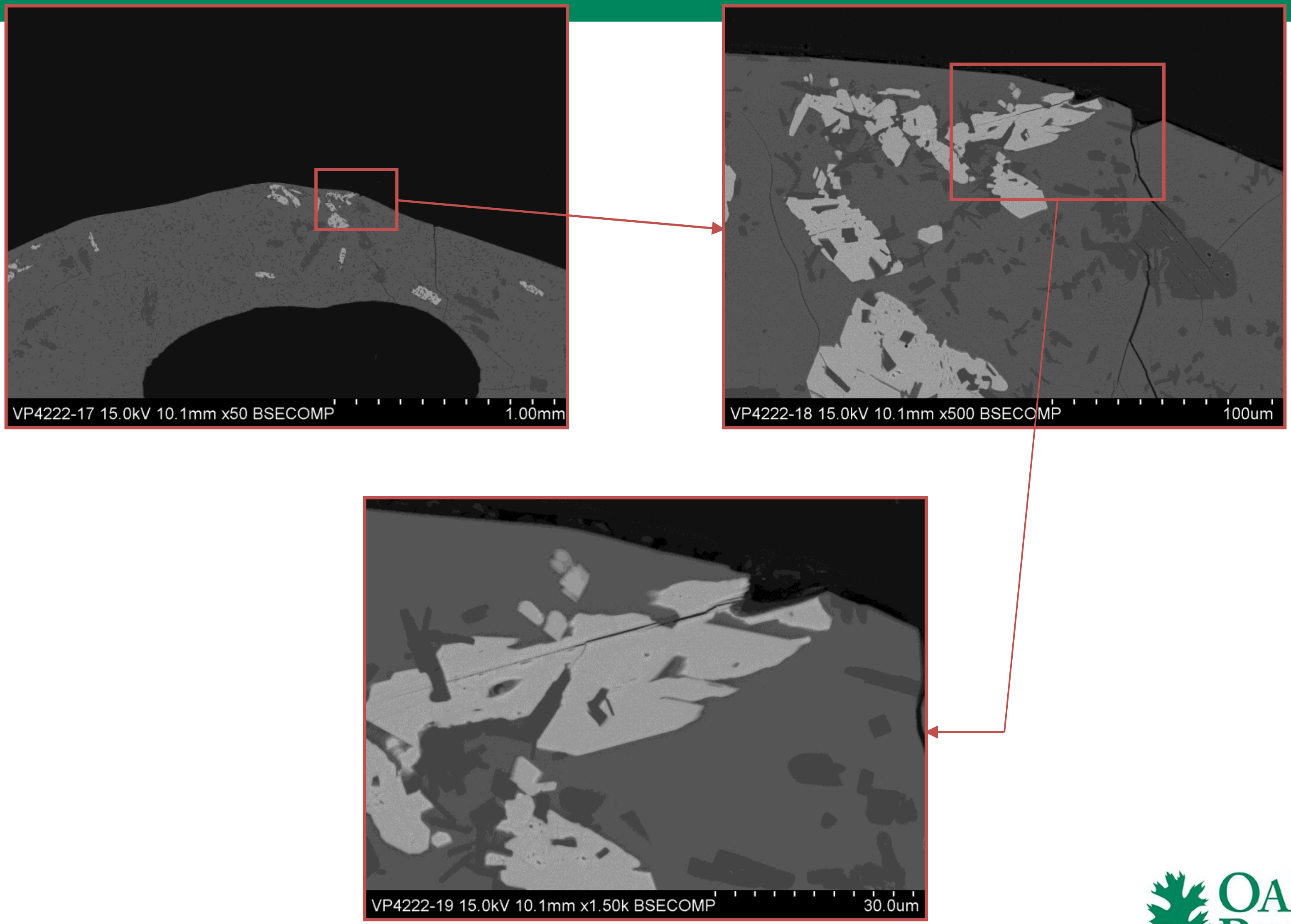


Oak Ridge National Laboratory

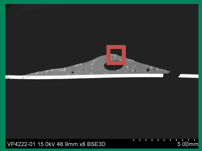


SCN-YSZ-49

After 10,000 Hours in Steam+H_2+N_2

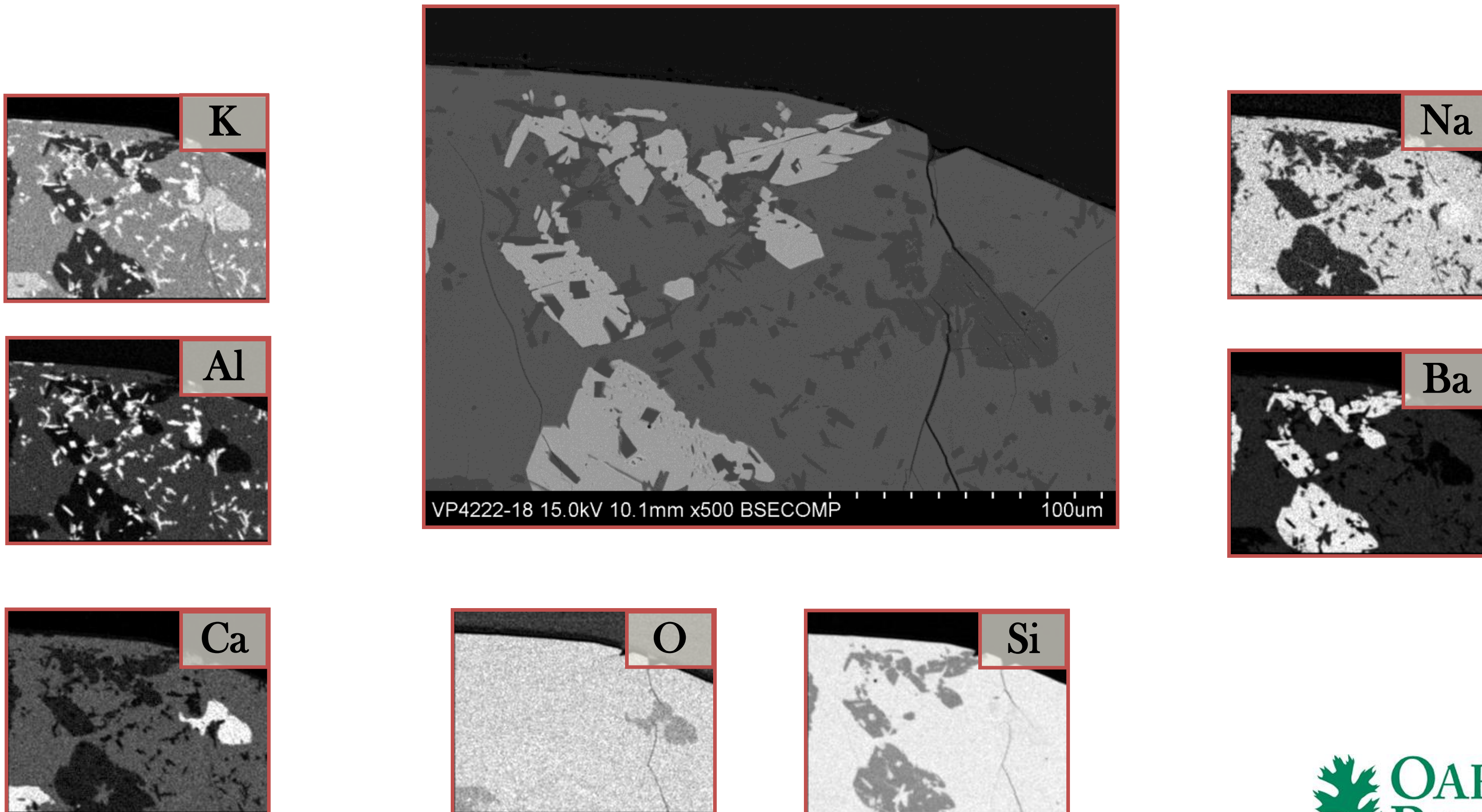


Oak Ridge National Laboratory



SCN-YSZ-49

After 10,000 Hours in Steam+H_2+N_2

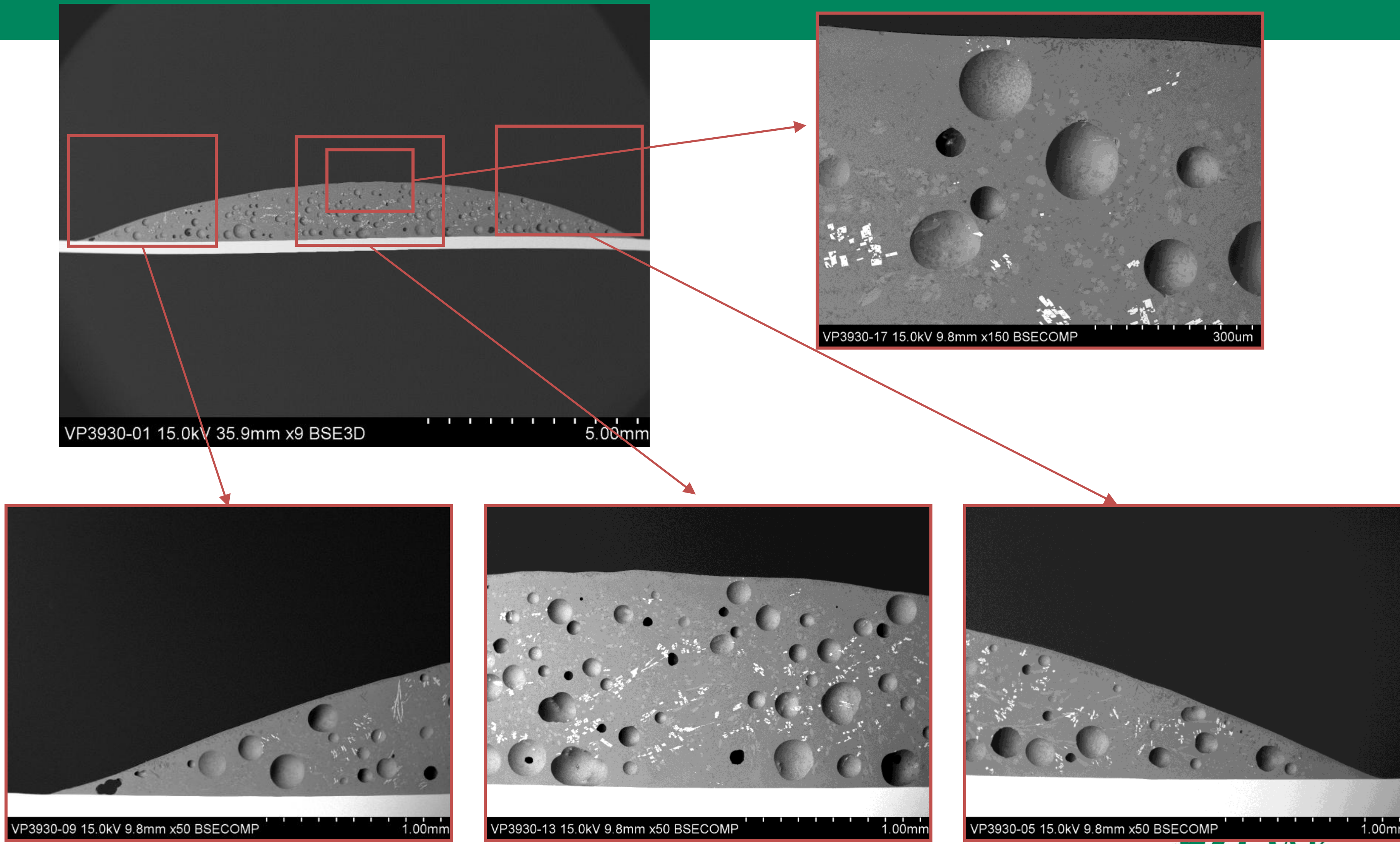


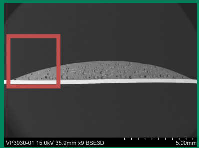
SCN-YSZ-55

After 10,000 Hours in Air

SCN-YSZ-55

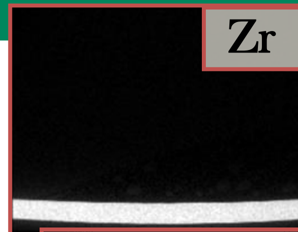
After 10,000 Hours in Air

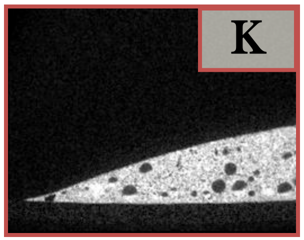


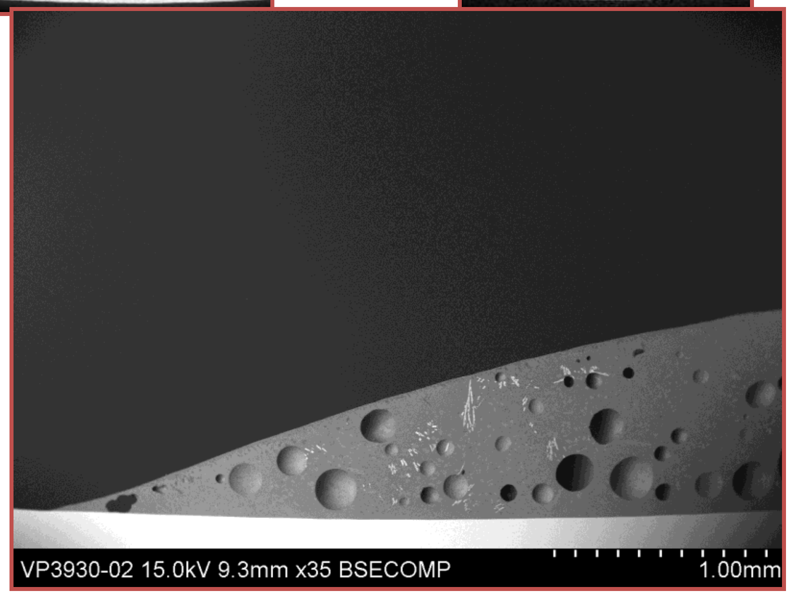


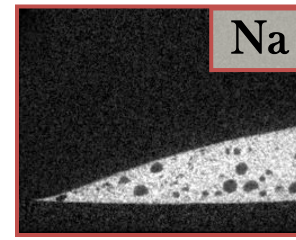
SCN-YSZ-55

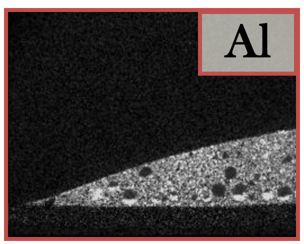
After 10,000 Hours in Air

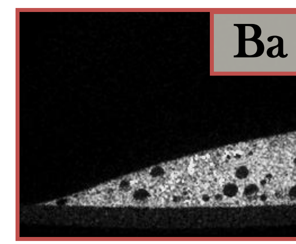


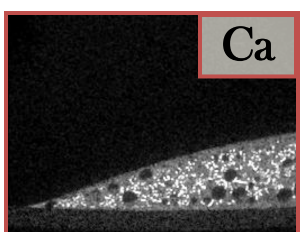


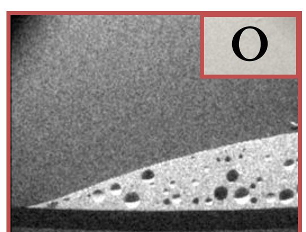


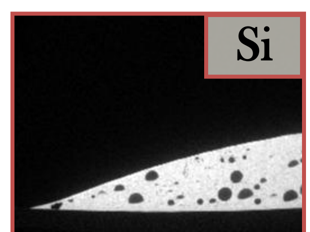




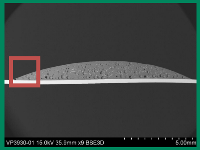






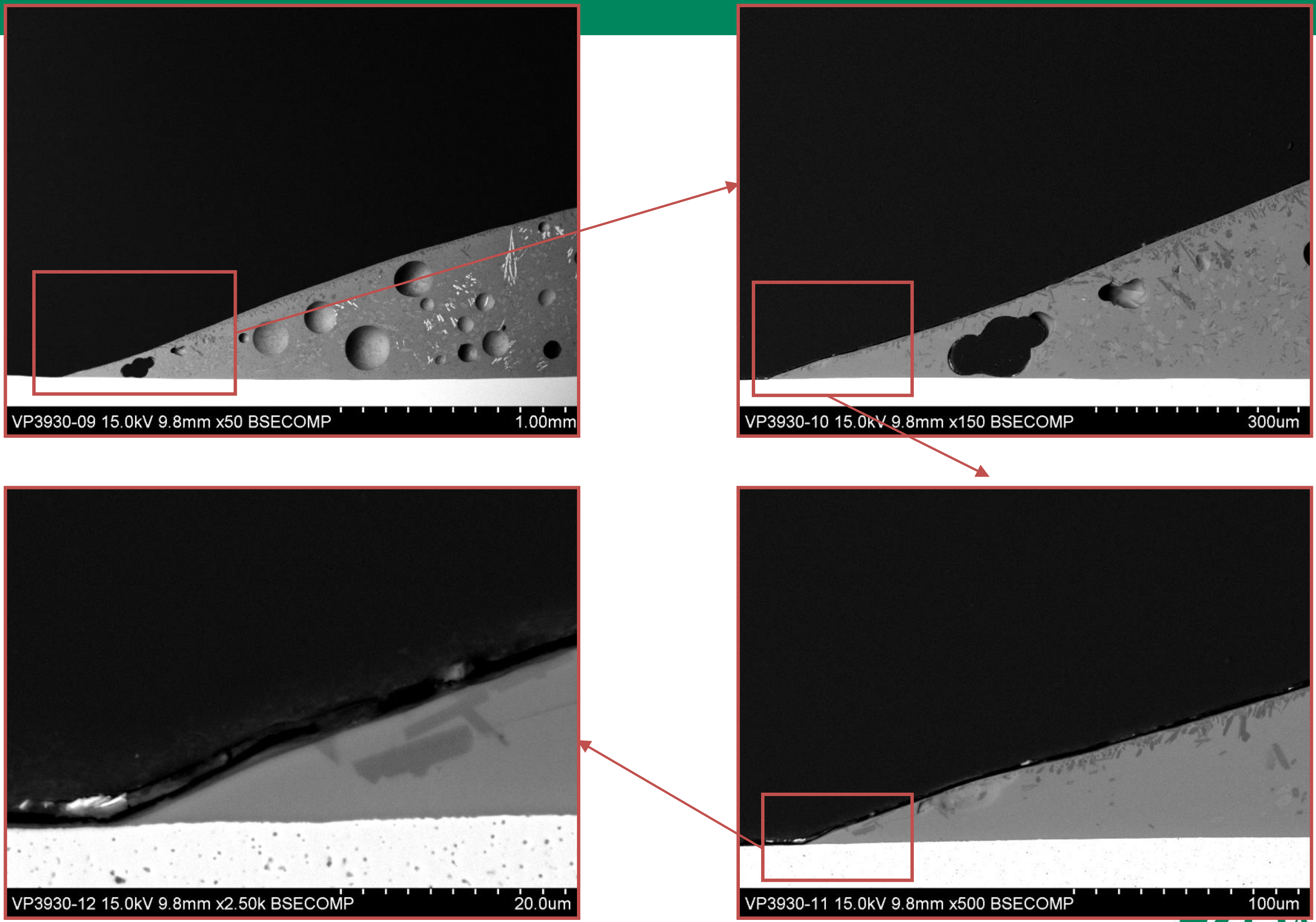


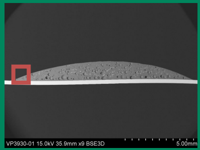
OAK RIDGE
National Laboratory



SCN-YSZ-55

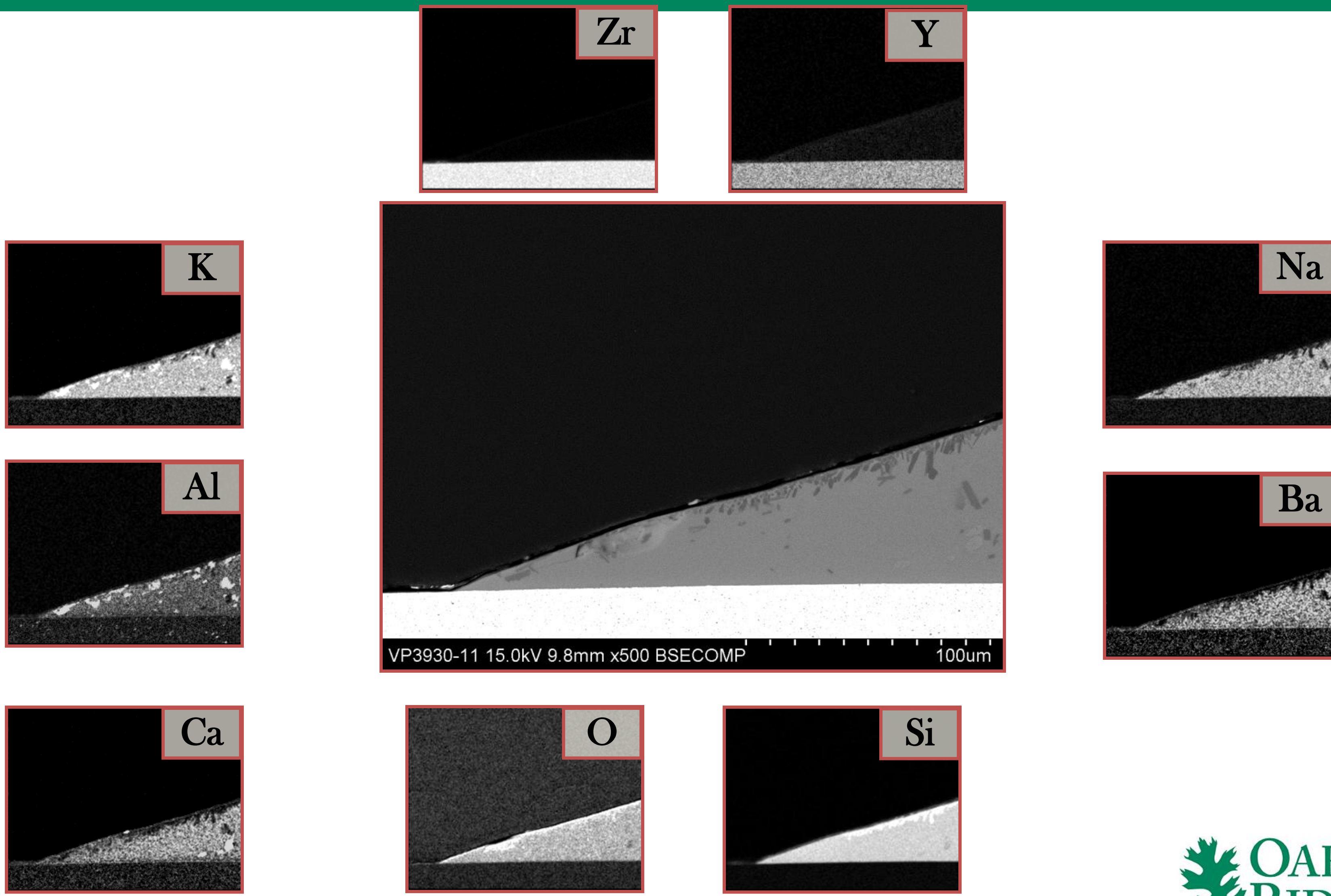
After 10,000 Hours in Air

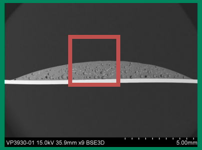




SCN-YSZ-55

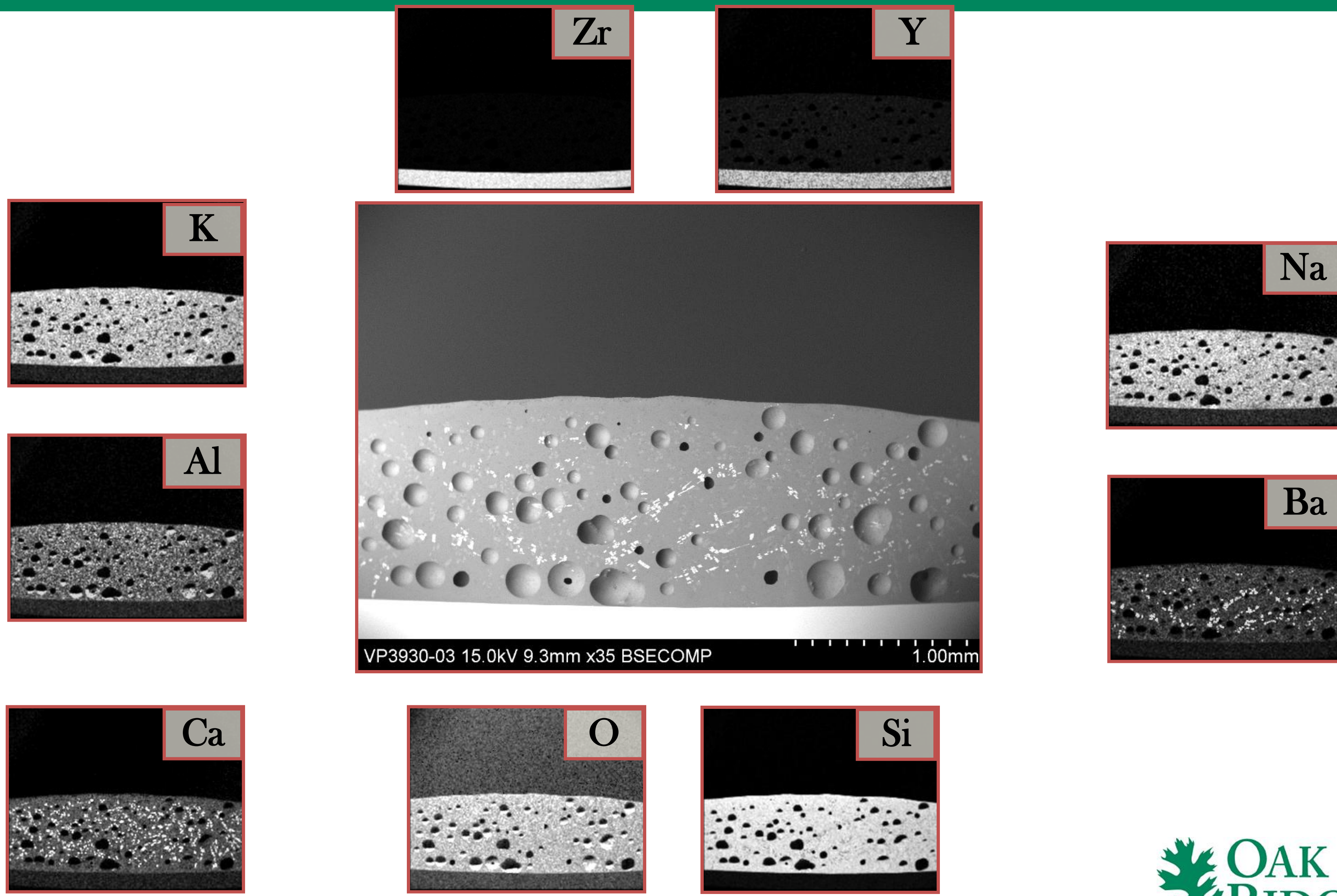
After 10,000 Hours in Air



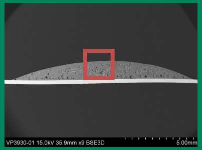


SCN-YSZ-55

After 10,000 Hours in Air

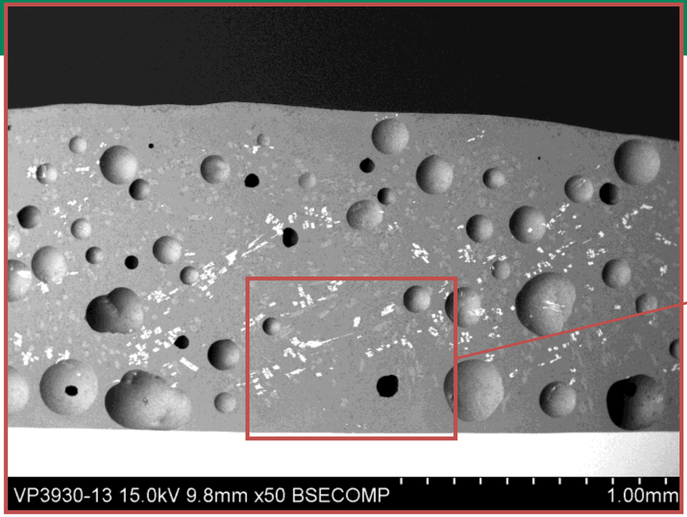


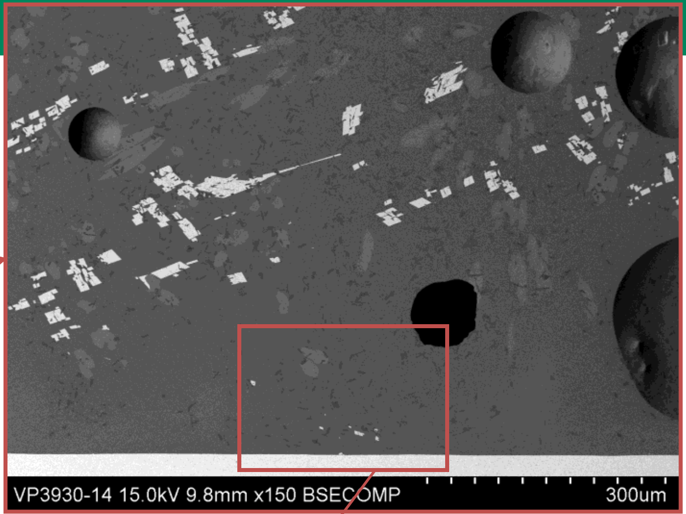
Oak Ridge National Laboratory

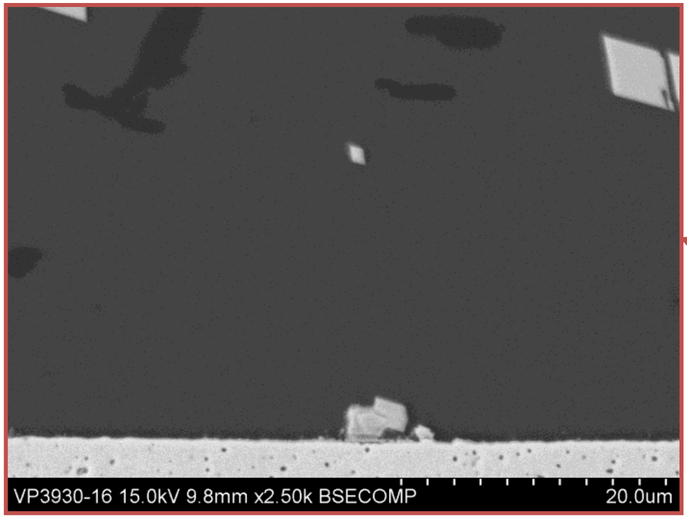


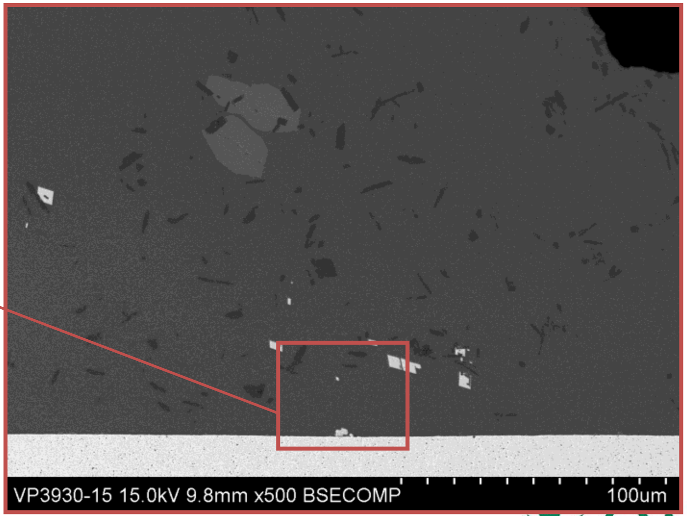
SCN-YSZ-55

After 10,000 Hours in Air

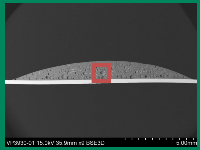






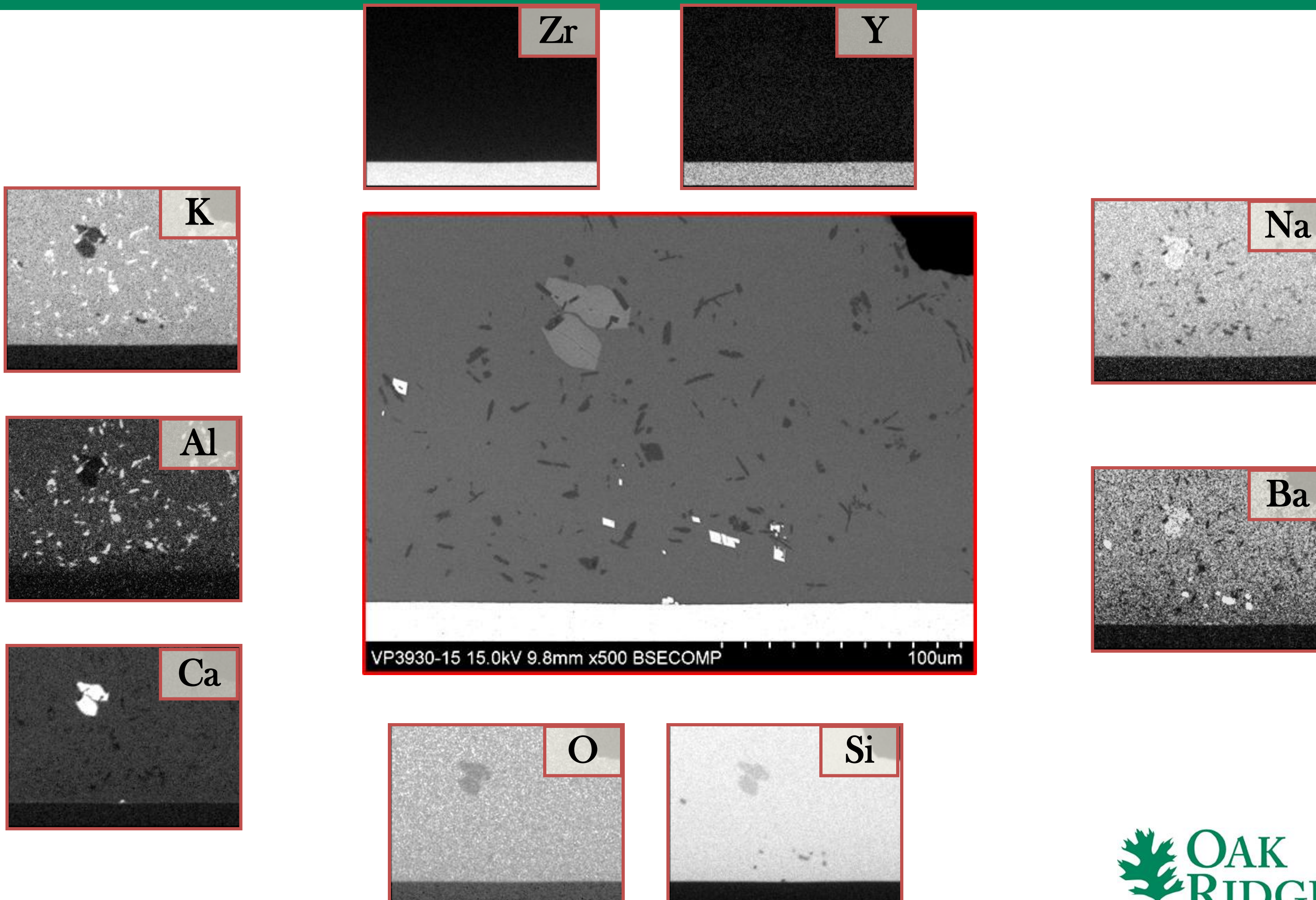


OAK RIDGE National Laboratory



SCN-YSZ-55

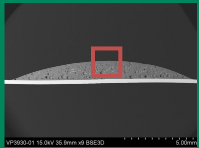
After 10,000 Hours in Air

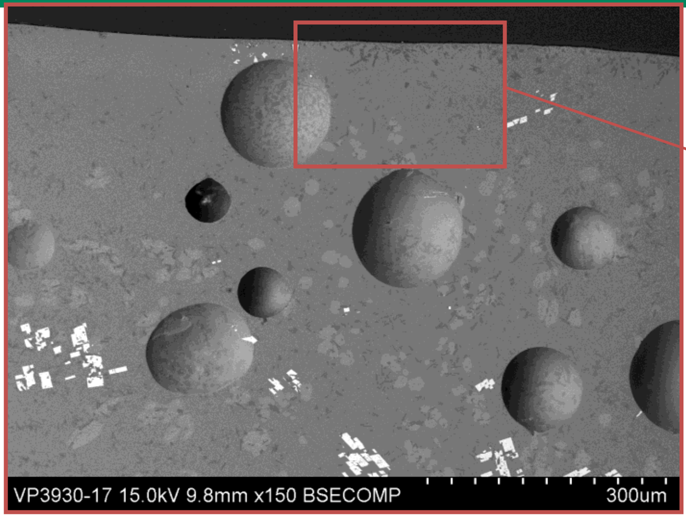


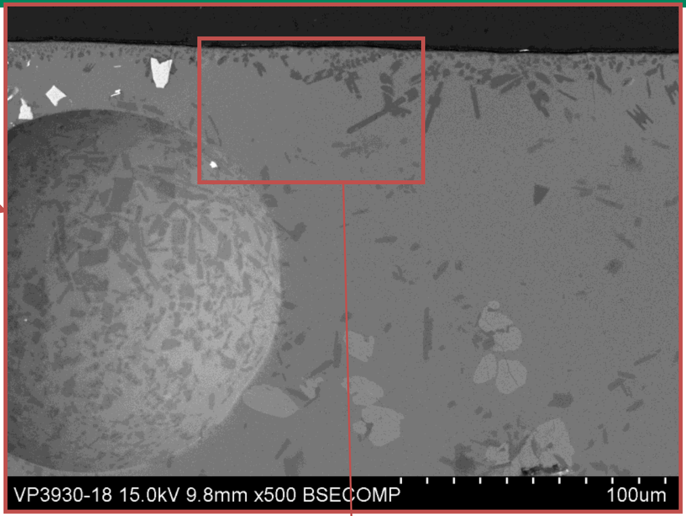
Oak Ridge National Laboratory

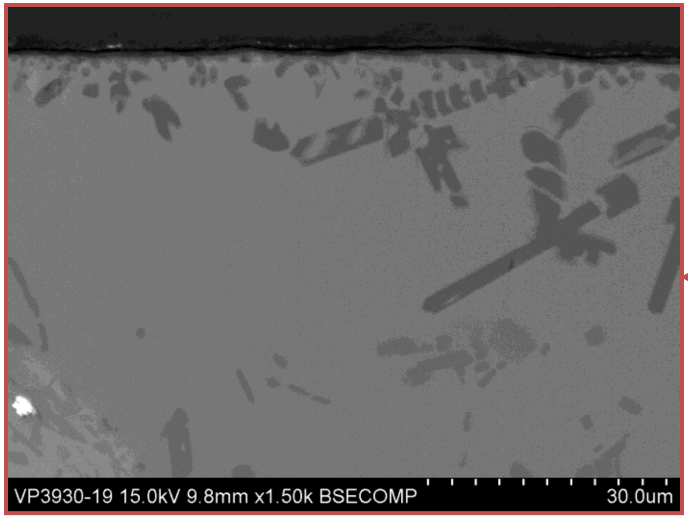
SCN-YSZ-55

After 10,000 Hours in Air

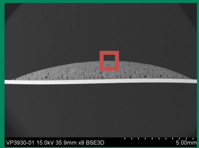






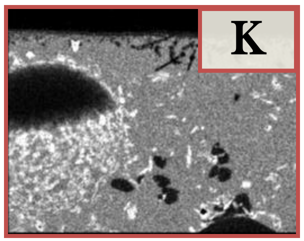


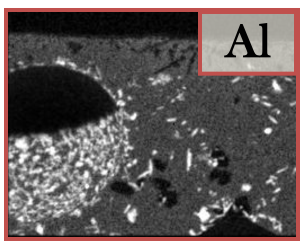
Oak Ridge National Laboratory

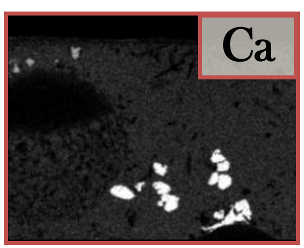


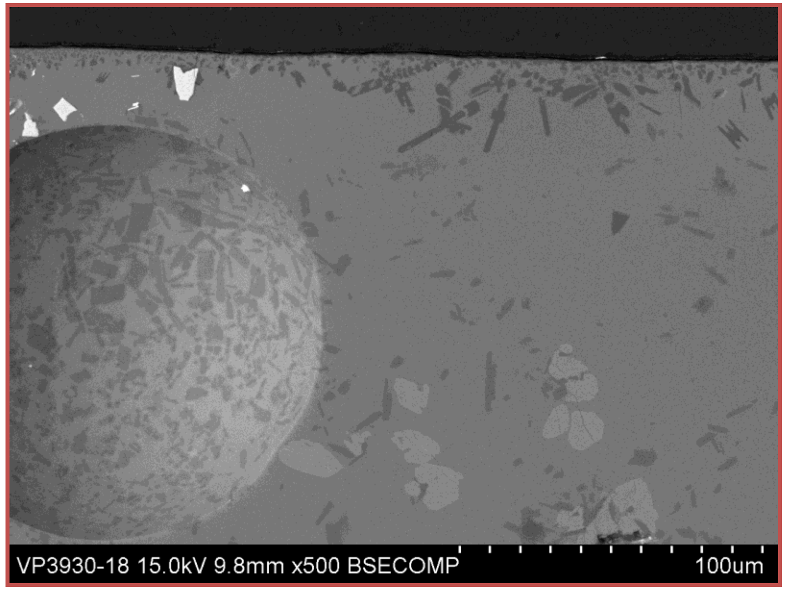
SCN-YSZ-55

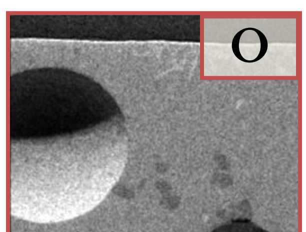
After 10,000 Hours in Air

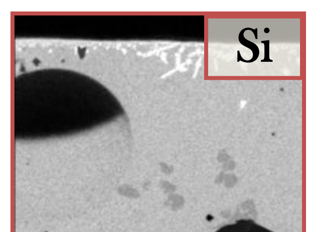


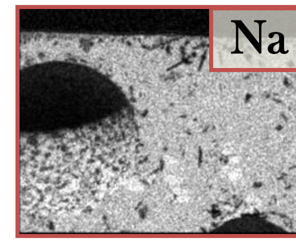


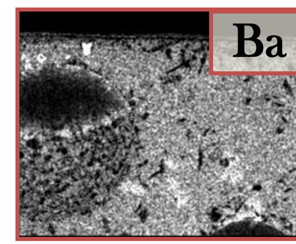












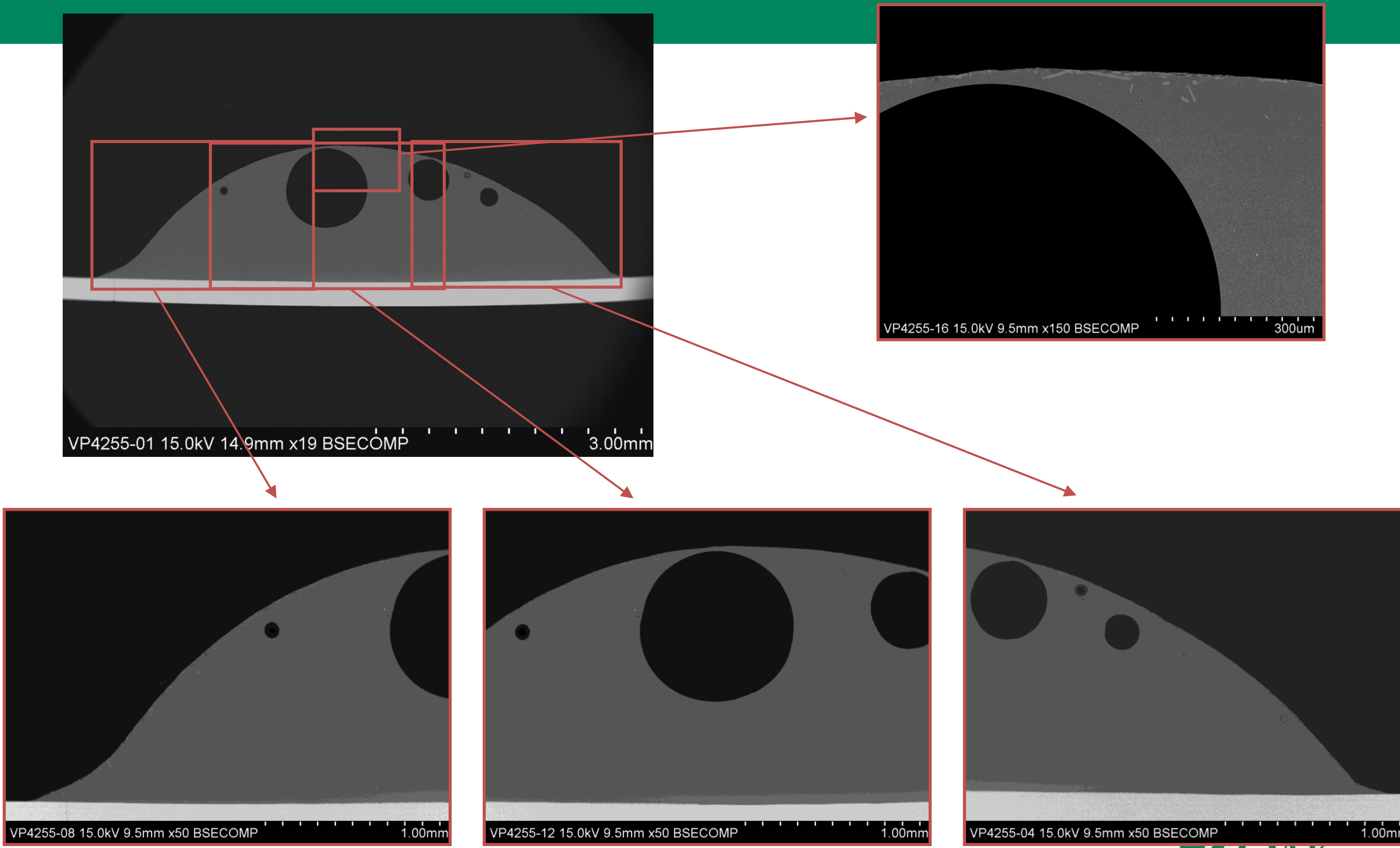
Oak Ridge National Laboratory

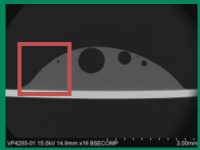
G6-YSZ-54

After 10,000 Hours in Steam+H_2+N_2

G6-YSZ-54

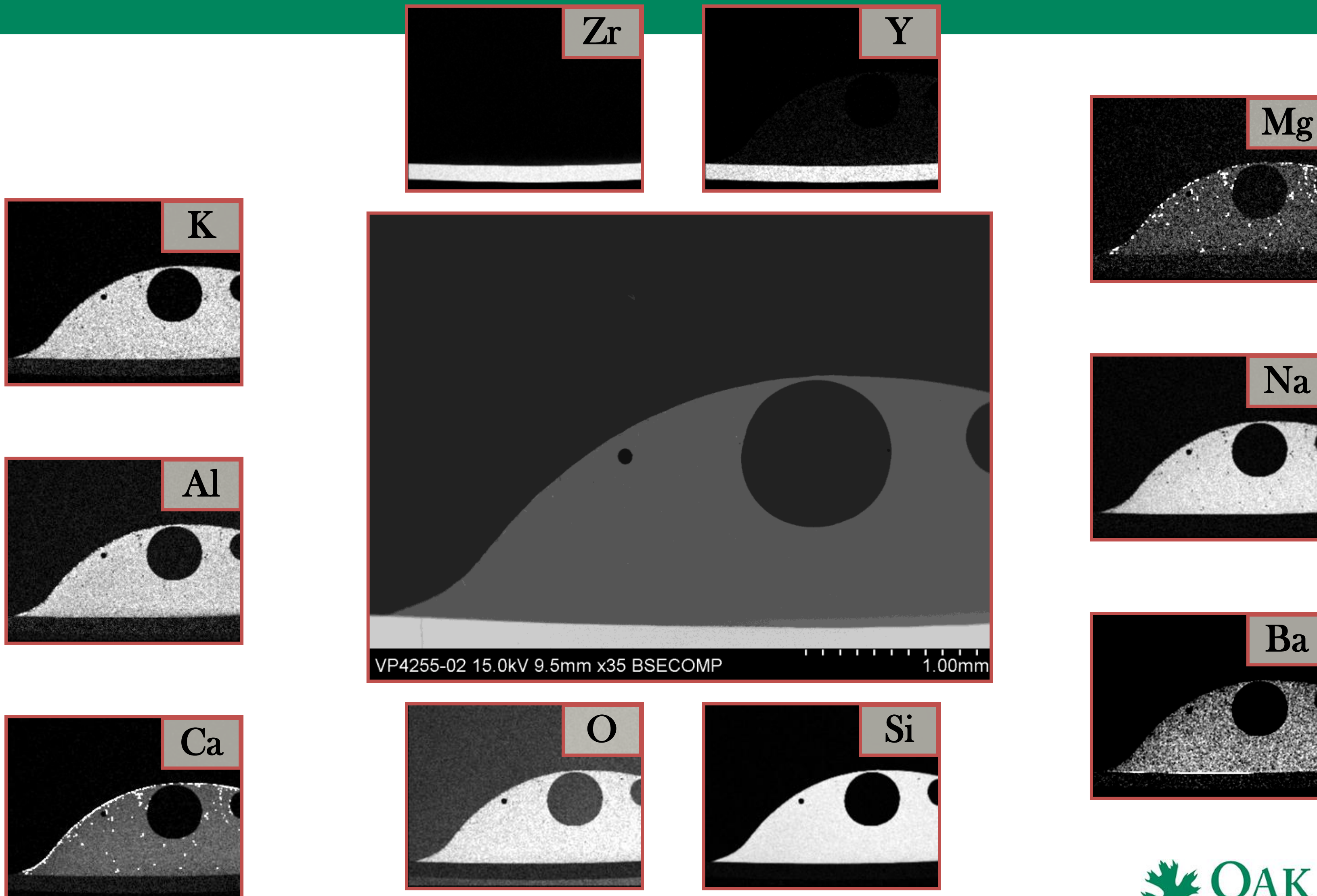
After 10,000 Hours in Steam+H_2+N_2

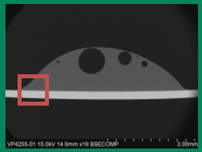




G6-YSZ-54

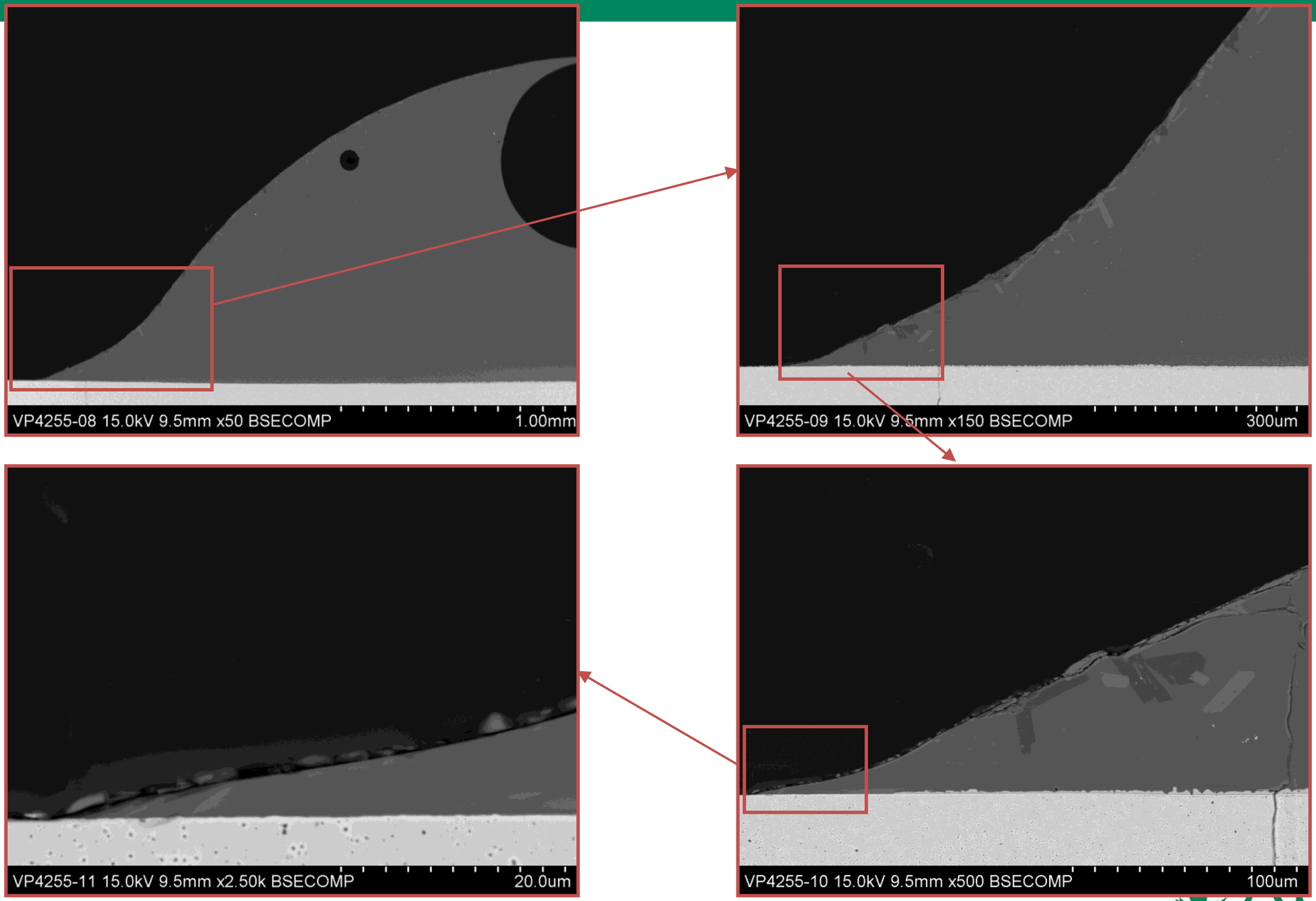
After 10,000 Hours in Steam+H_2+N_2



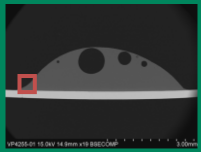


G6-YSZ-54

After 10,000 Hours in Steam+H_2+N_2

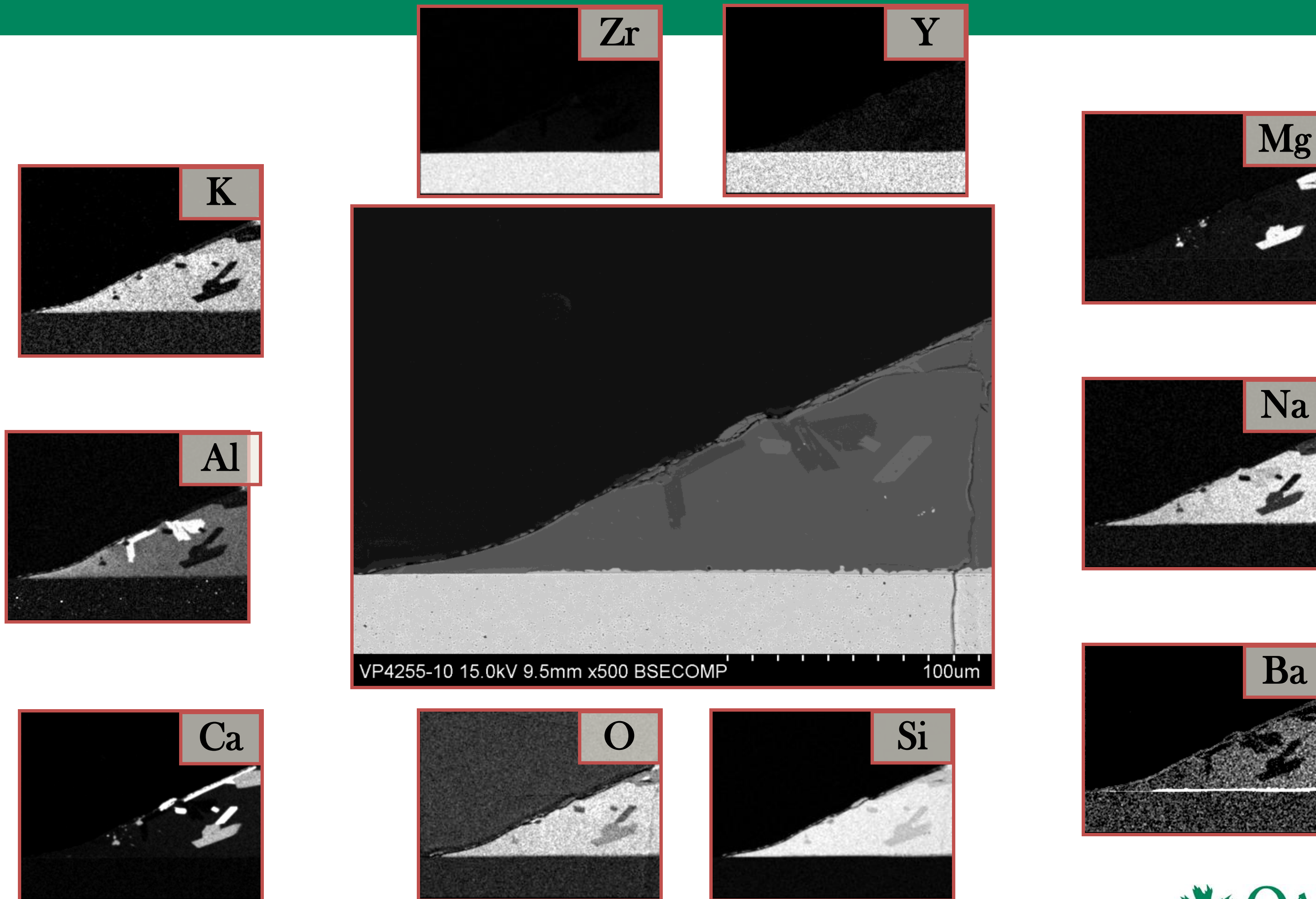


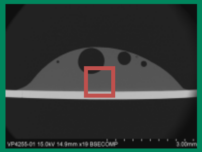
Oak Ridge National Laboratory



G6-YSZ-54

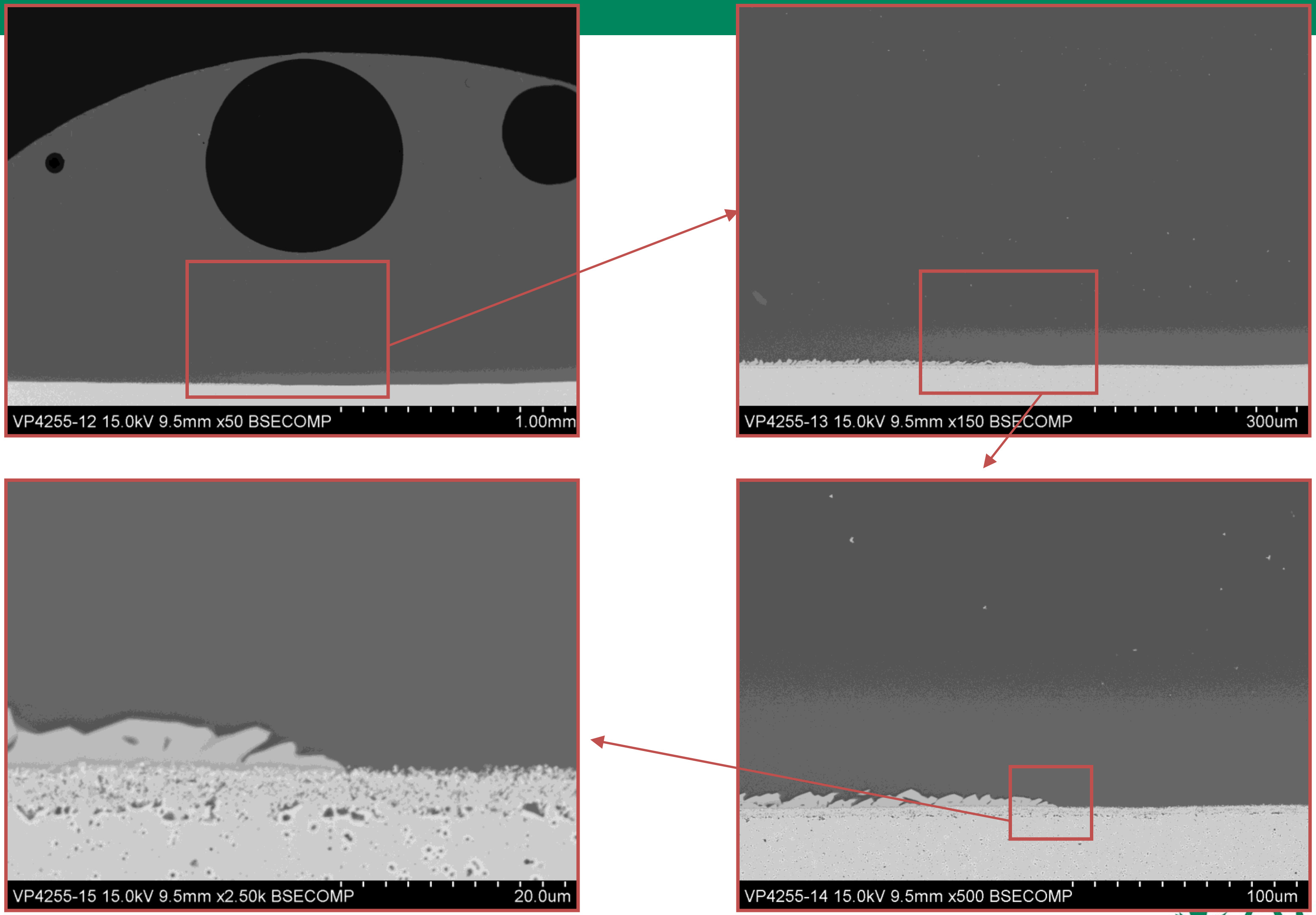
After 10,000 Hours in Steam+H_2+N_2



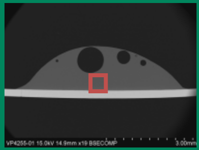


G6-YSZ-54

After 10,000 Hours in Steam+H_2+N_2

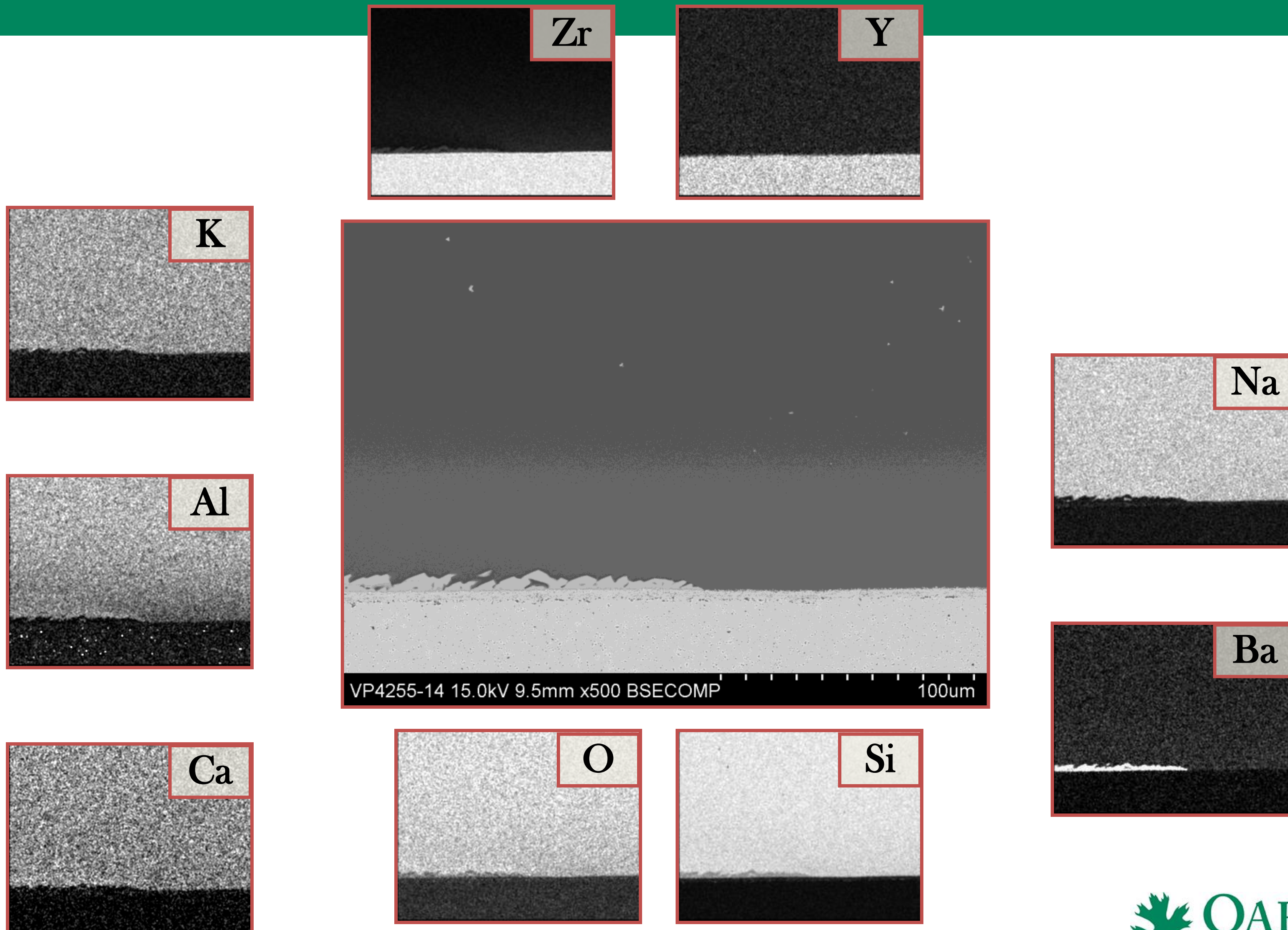


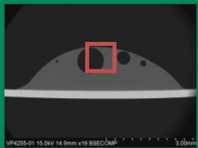
OAK RIDGE National Laboratory



G6-YSZ-54

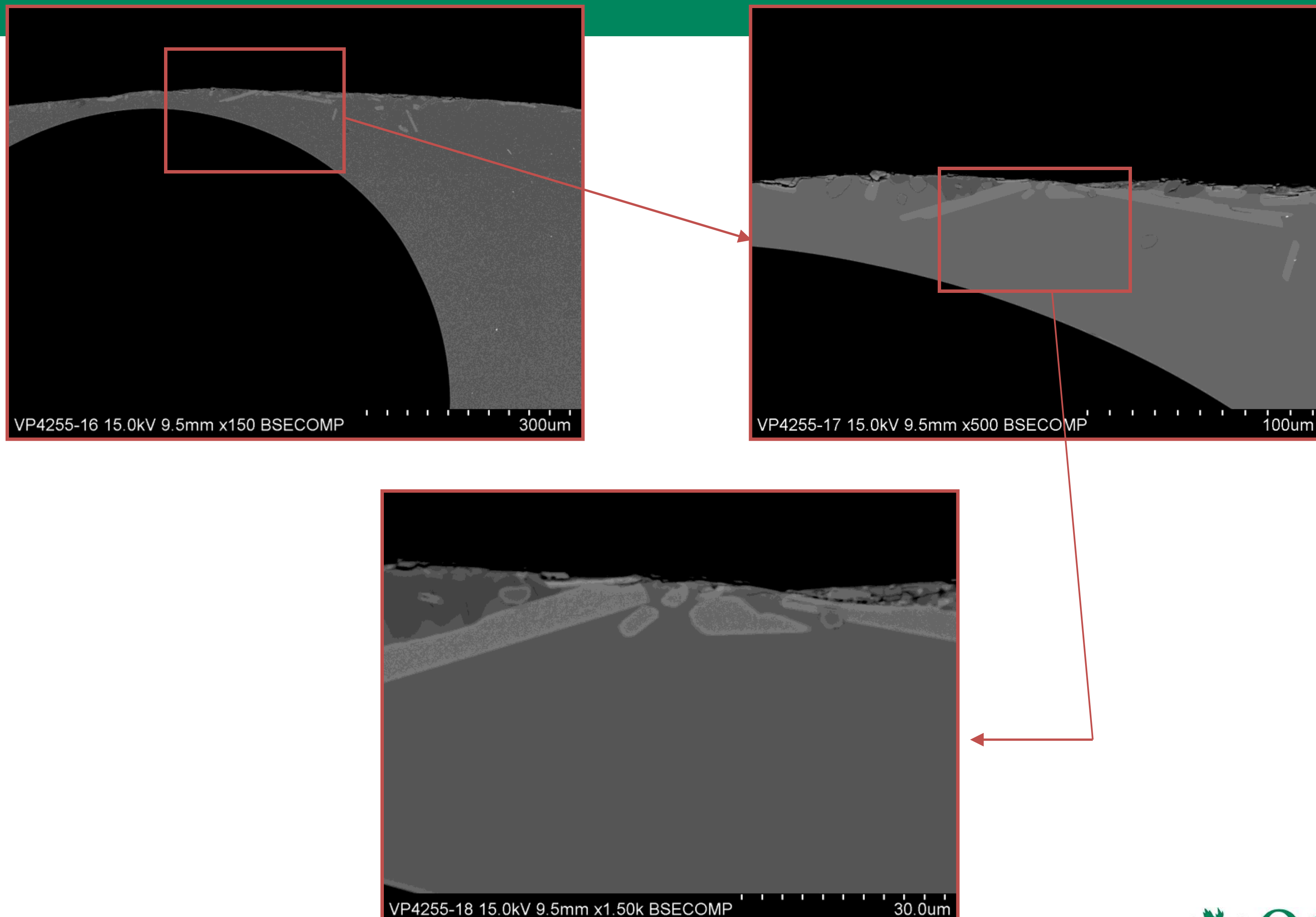
After 10,000 Hours in Steam+H_2+N_2

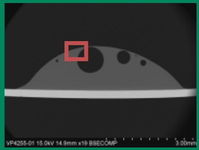




G6-YSZ-54

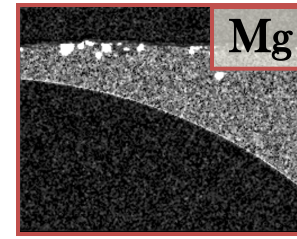
After 10,000 Hours in Steam+H_2+N_2

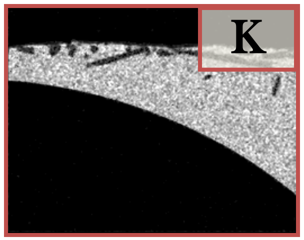


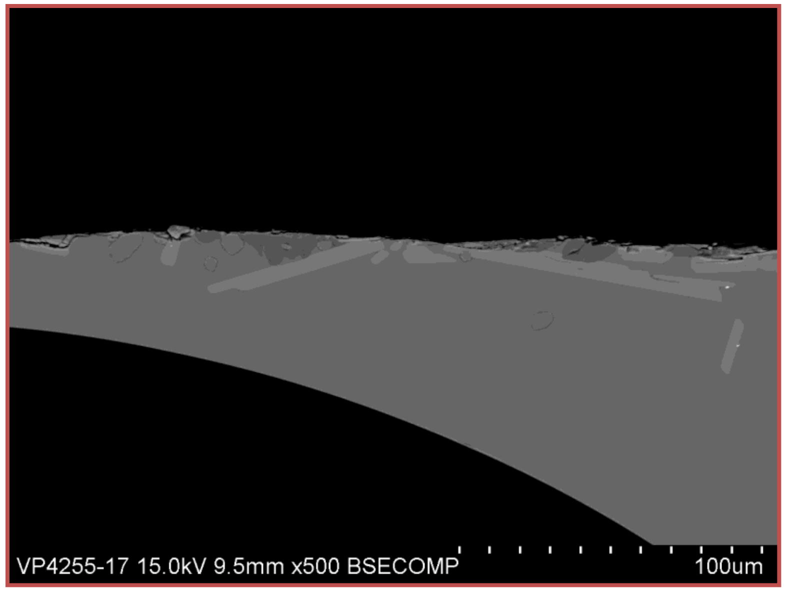


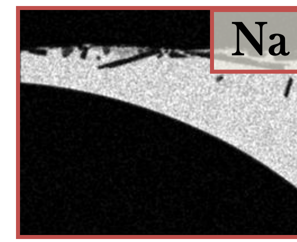
G6-YSZ-54

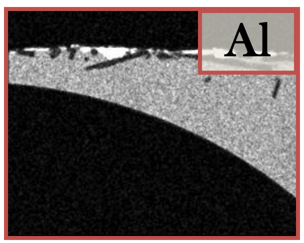
After 10,000 Hours in Steam+H_2+N_2

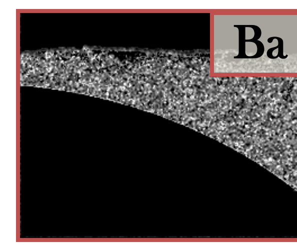


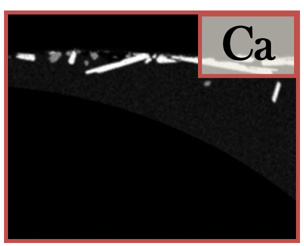


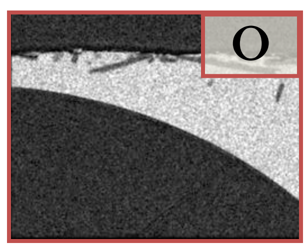


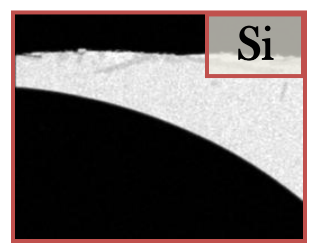












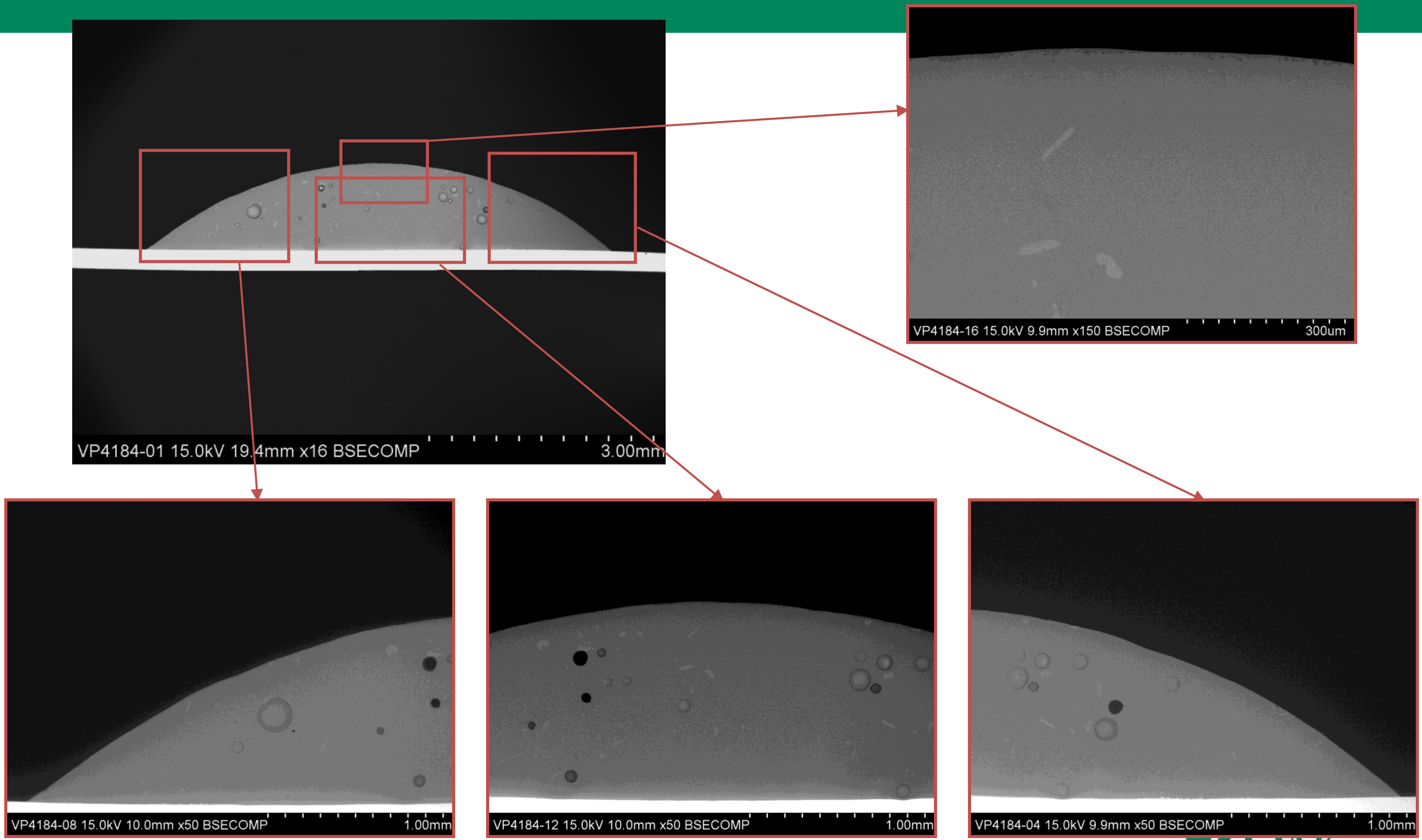
OAK RIDGE National Laboratory

G6-YSZ-51

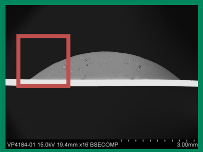
After 10,000 Hours in Air

G6-YSZ-51

After 10,000 Hours in Air

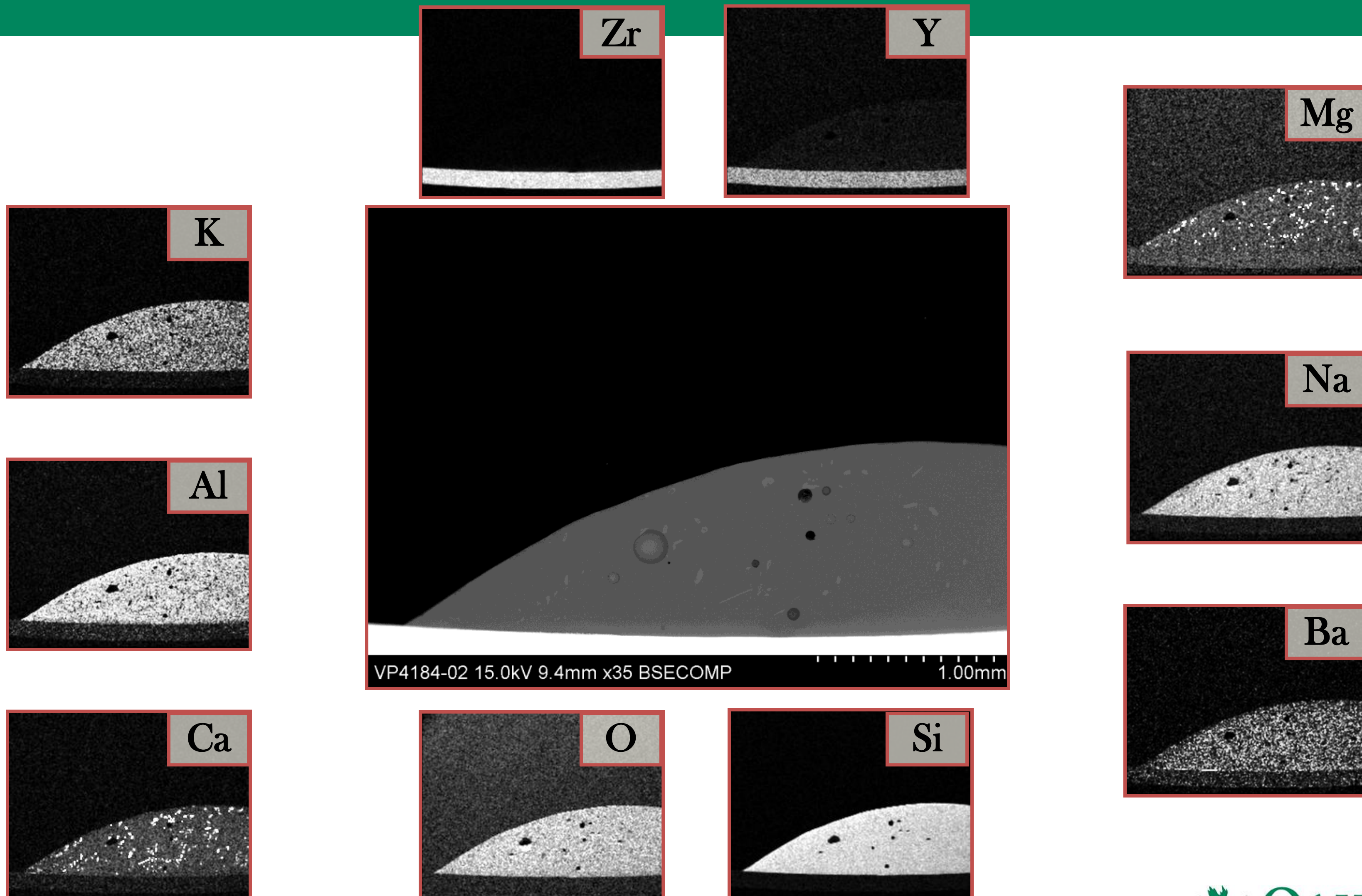


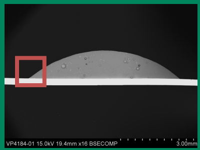
Oak Ridge National Laboratory



G6-YSZ-51

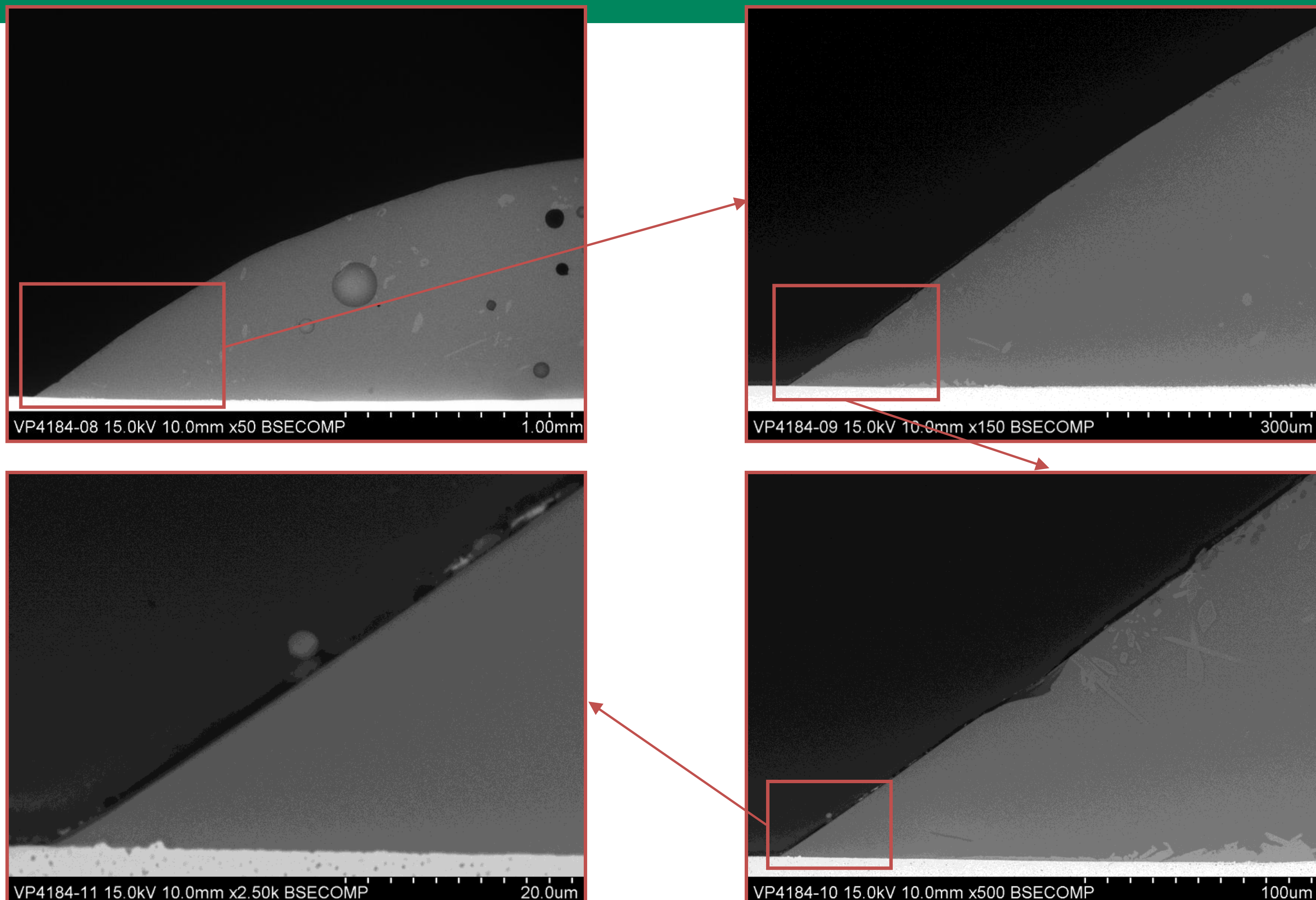
After 10,000 Hours in Air



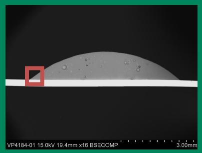


G6-YSZ-51

After 10,000 Hours in Air

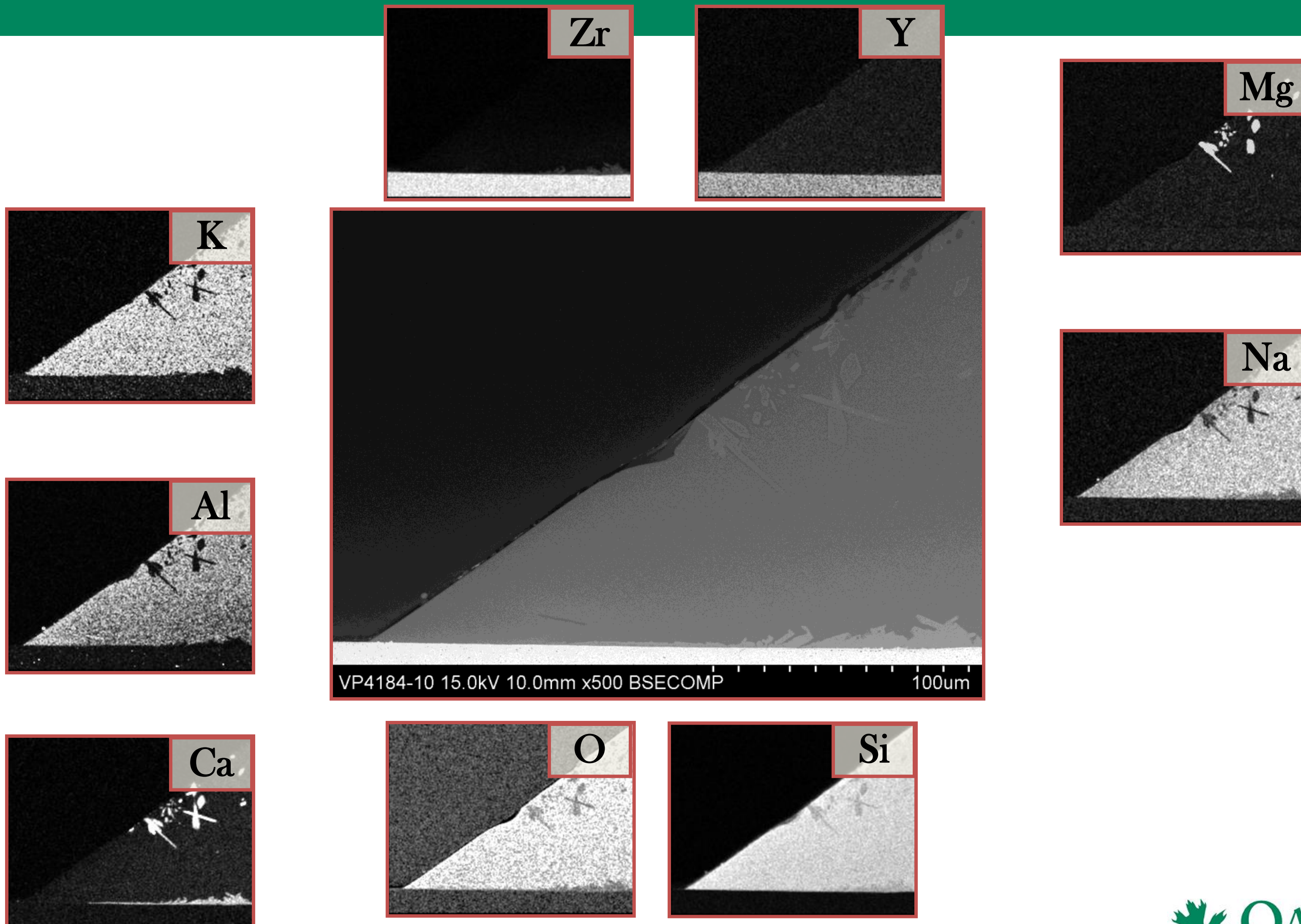


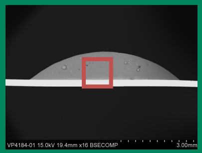
OAK RIDGE National Laboratory



G6-YSZ-51

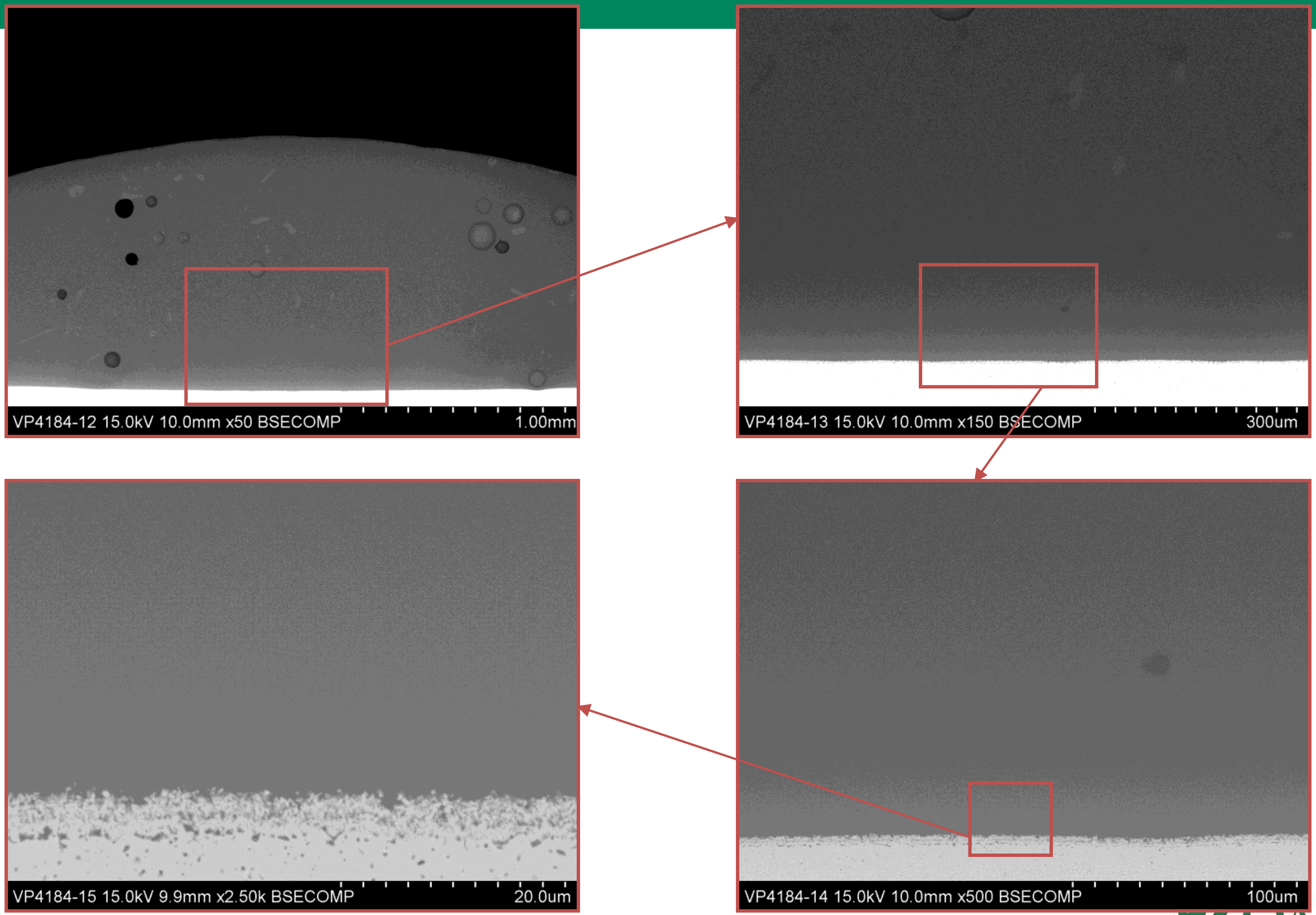
After 10,000 Hours in Air



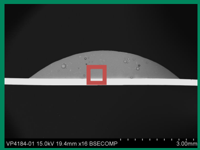


G6-YSZ-51

After 10,000 Hours in Air

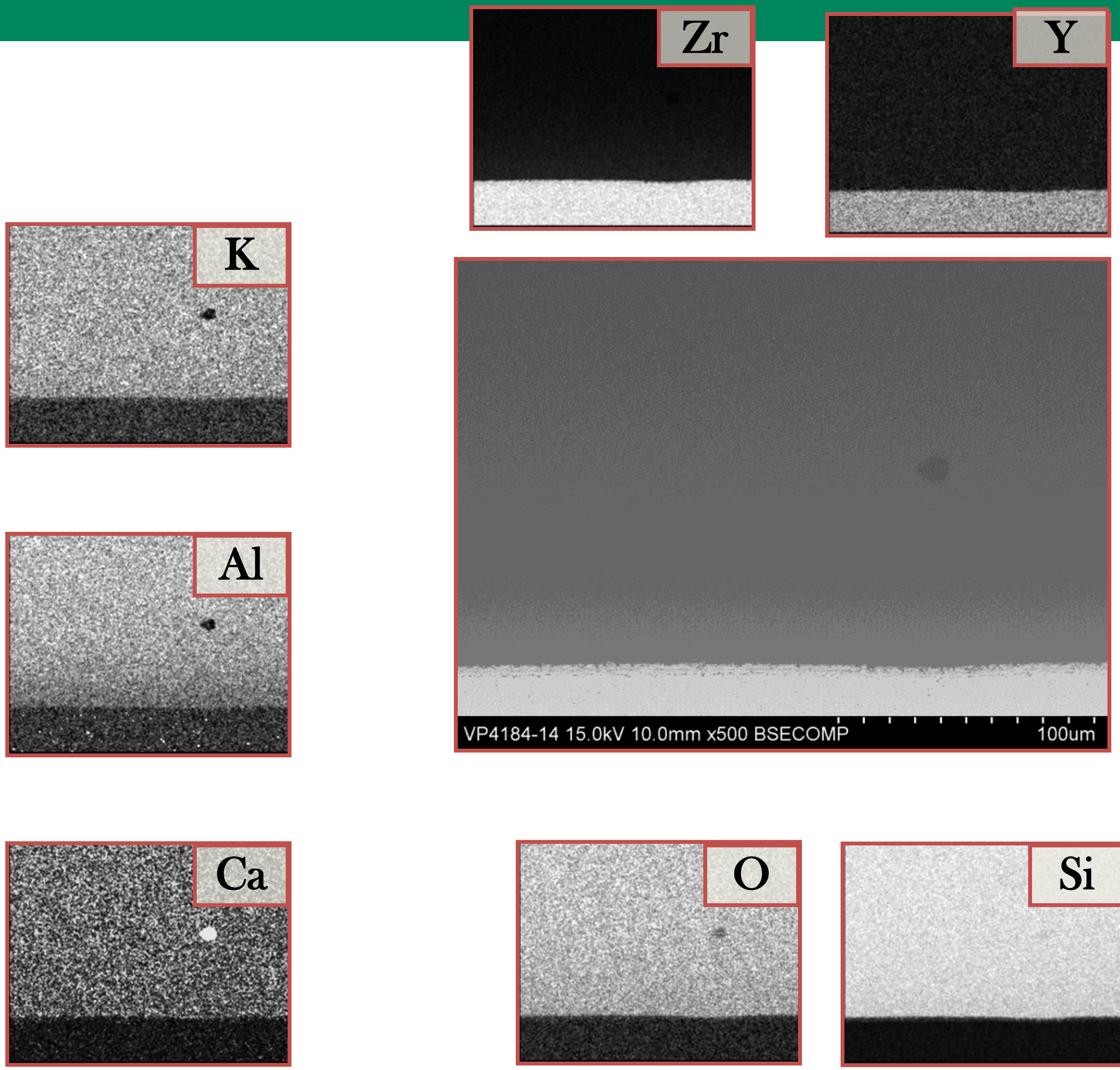


OAK RIDGE National Laboratory

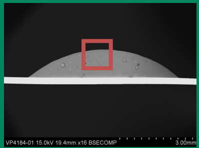


G6-YSZ-51

After 10,000 Hours in Air

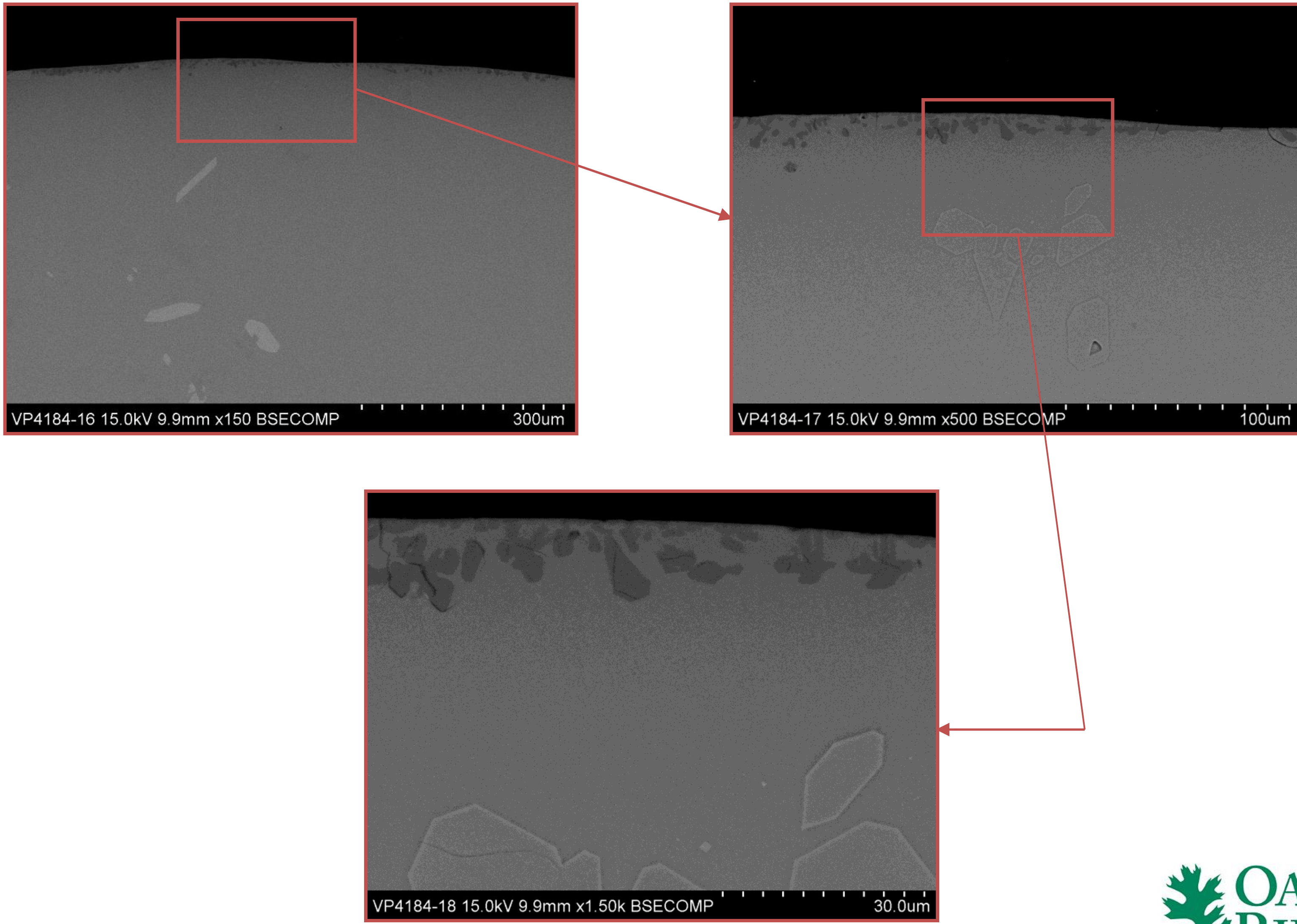


Oak Ridge National Laboratory

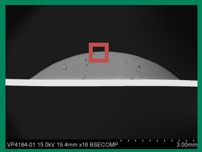


G6-YSZ-51

After 10,000 Hours in Air

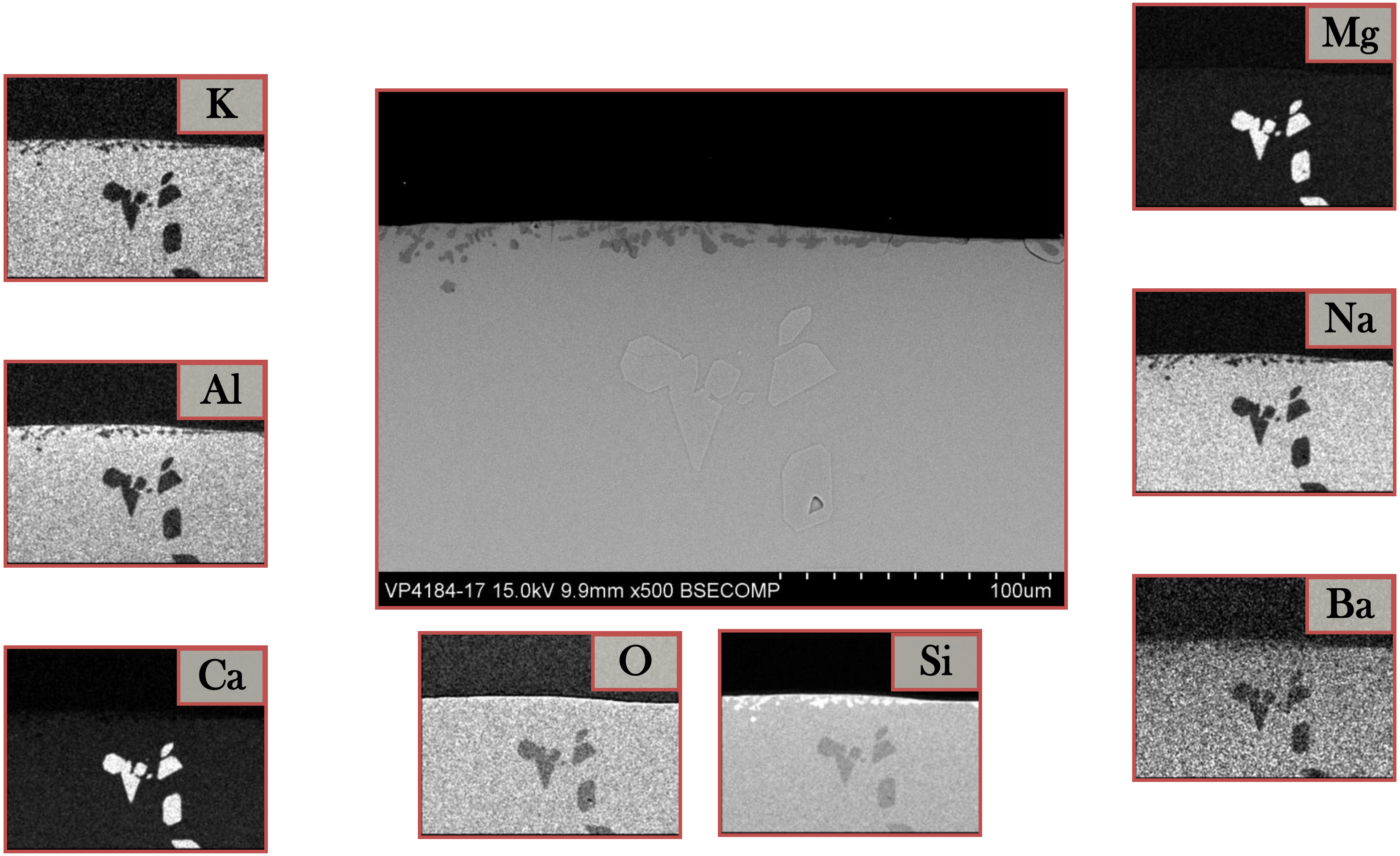


Oak Ridge National Laboratory



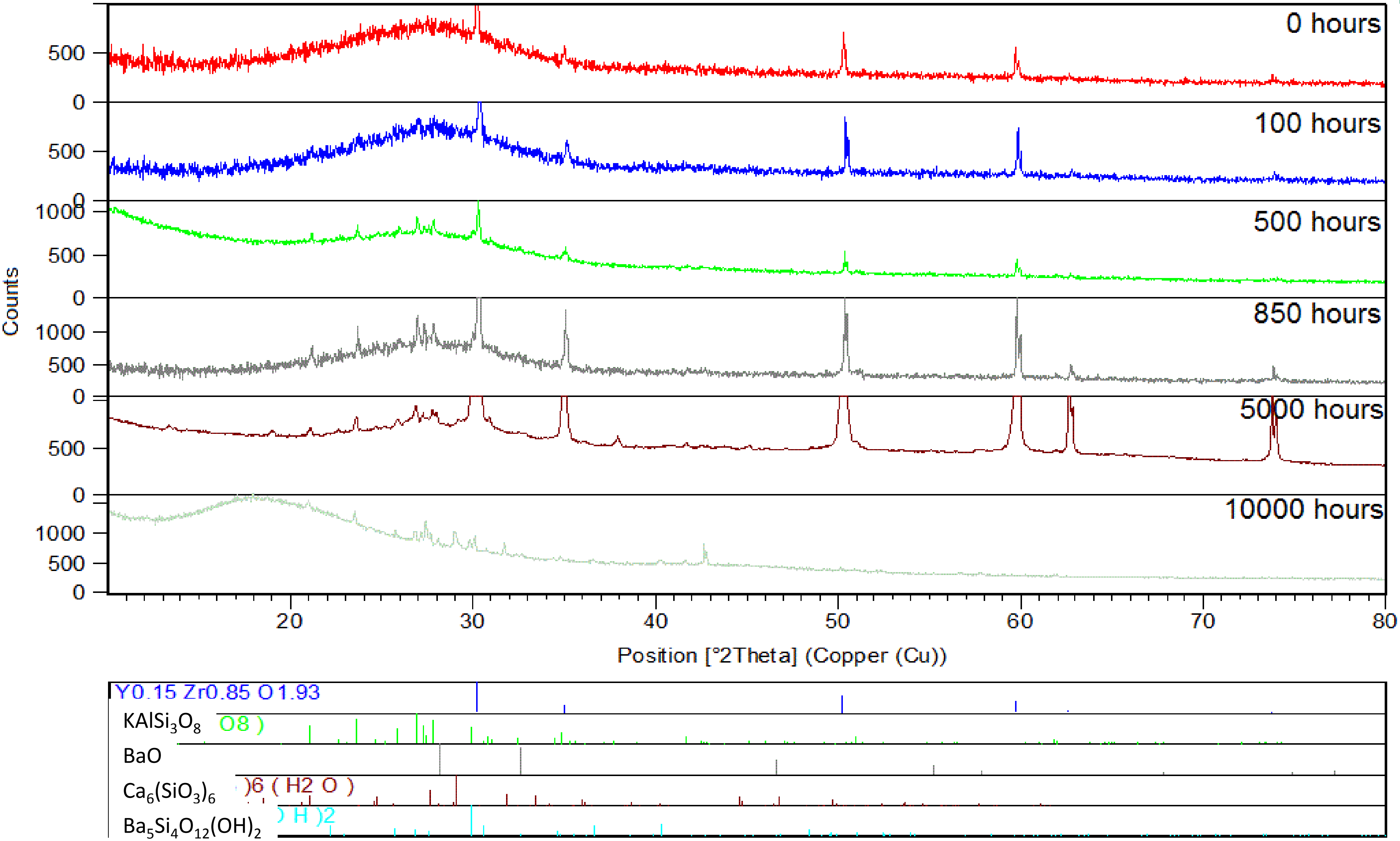
G6-YSZ-51

After 10,000 Hours in Air



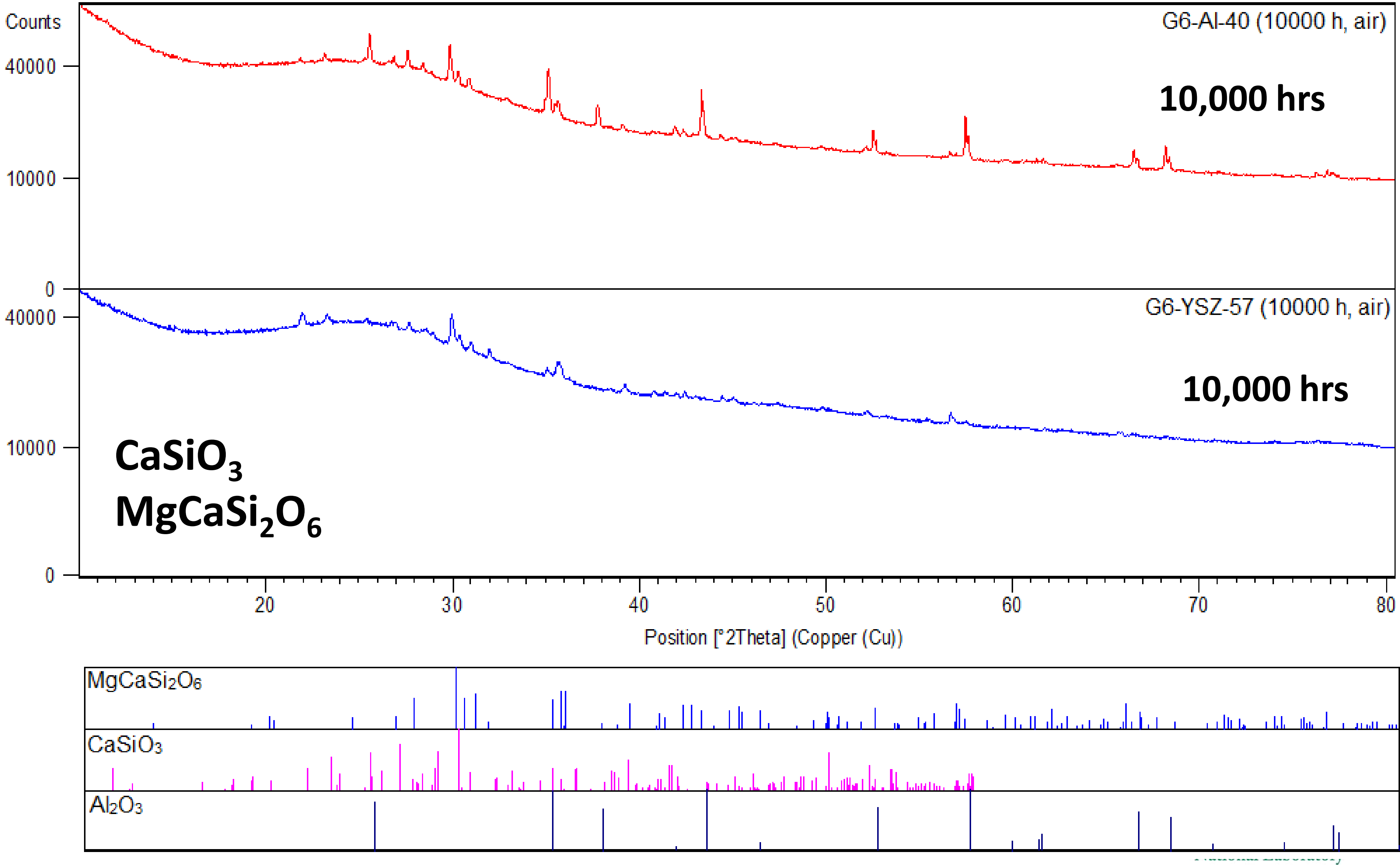
Oak Ridge National Laboratory

SCN-YSZ (steam): powder XRD

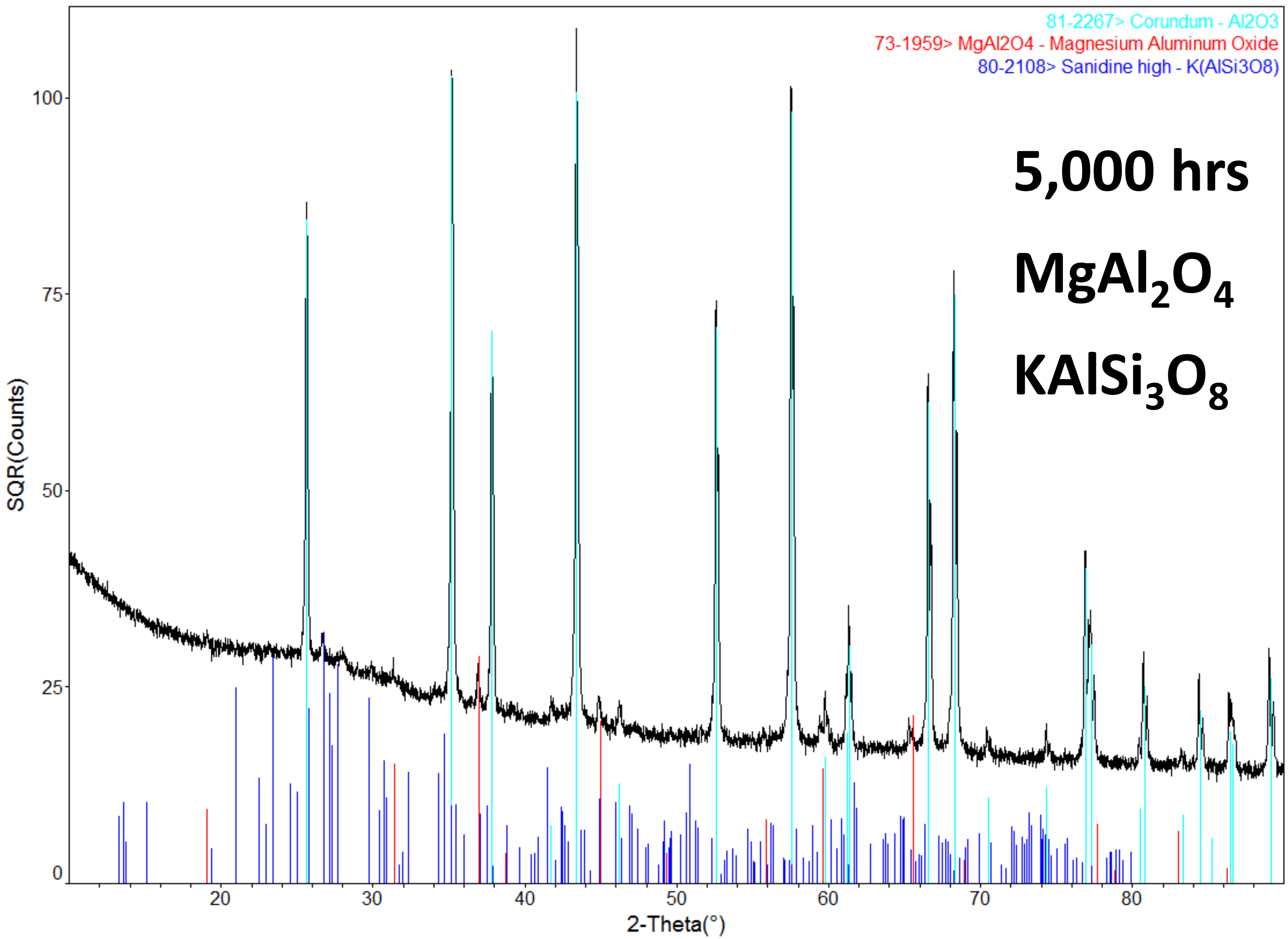


National Laboratory

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



G6-Al_2O_3 (Steam): Surface Analysis

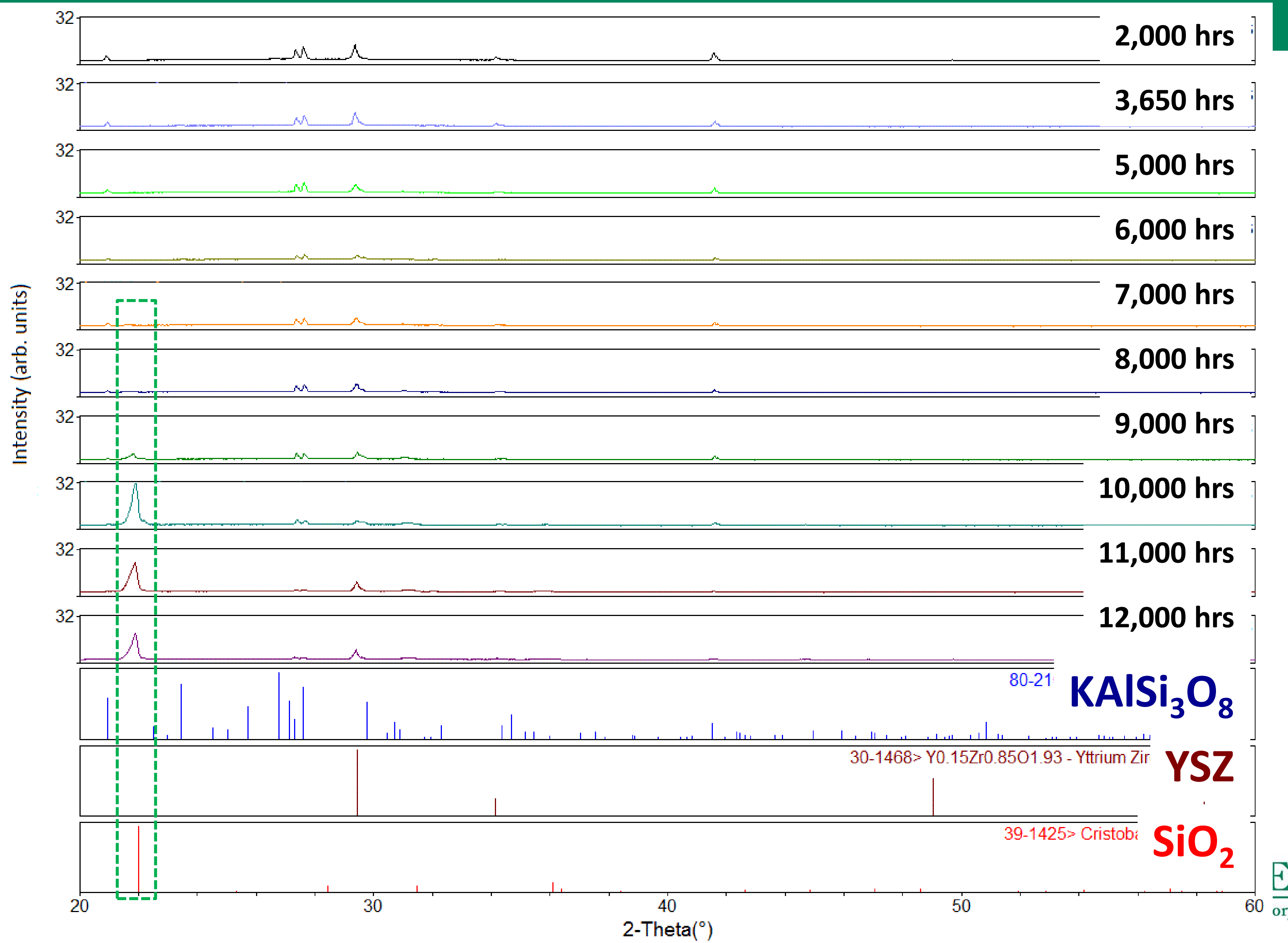


5,000 hrs

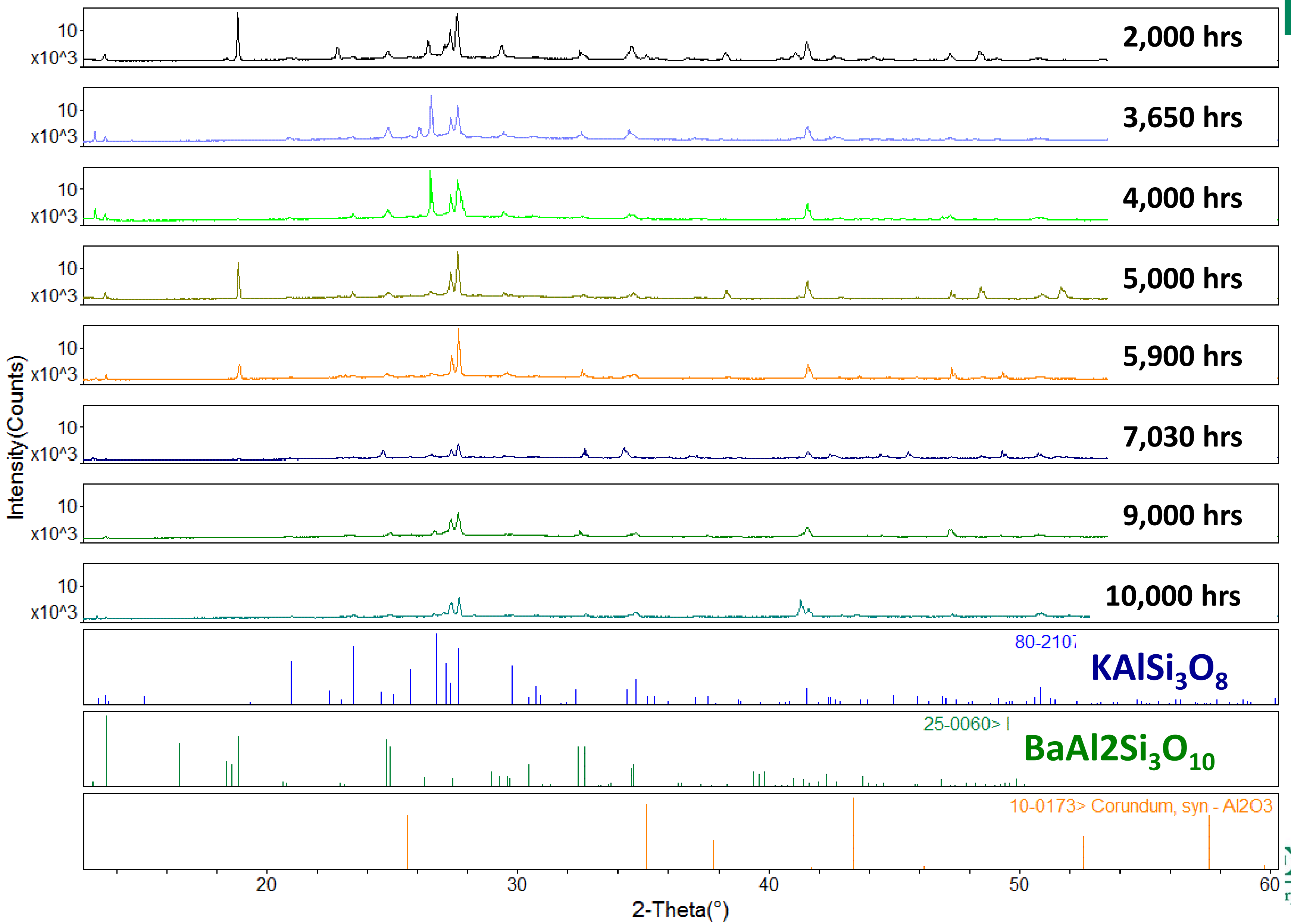
$MgAl_2O_4$

$KAlSi_3O_8$

SCN-YSZ-73 (air): Surface Analysis



SCN-Al_2O_3-64 (steam): Surface Analysis



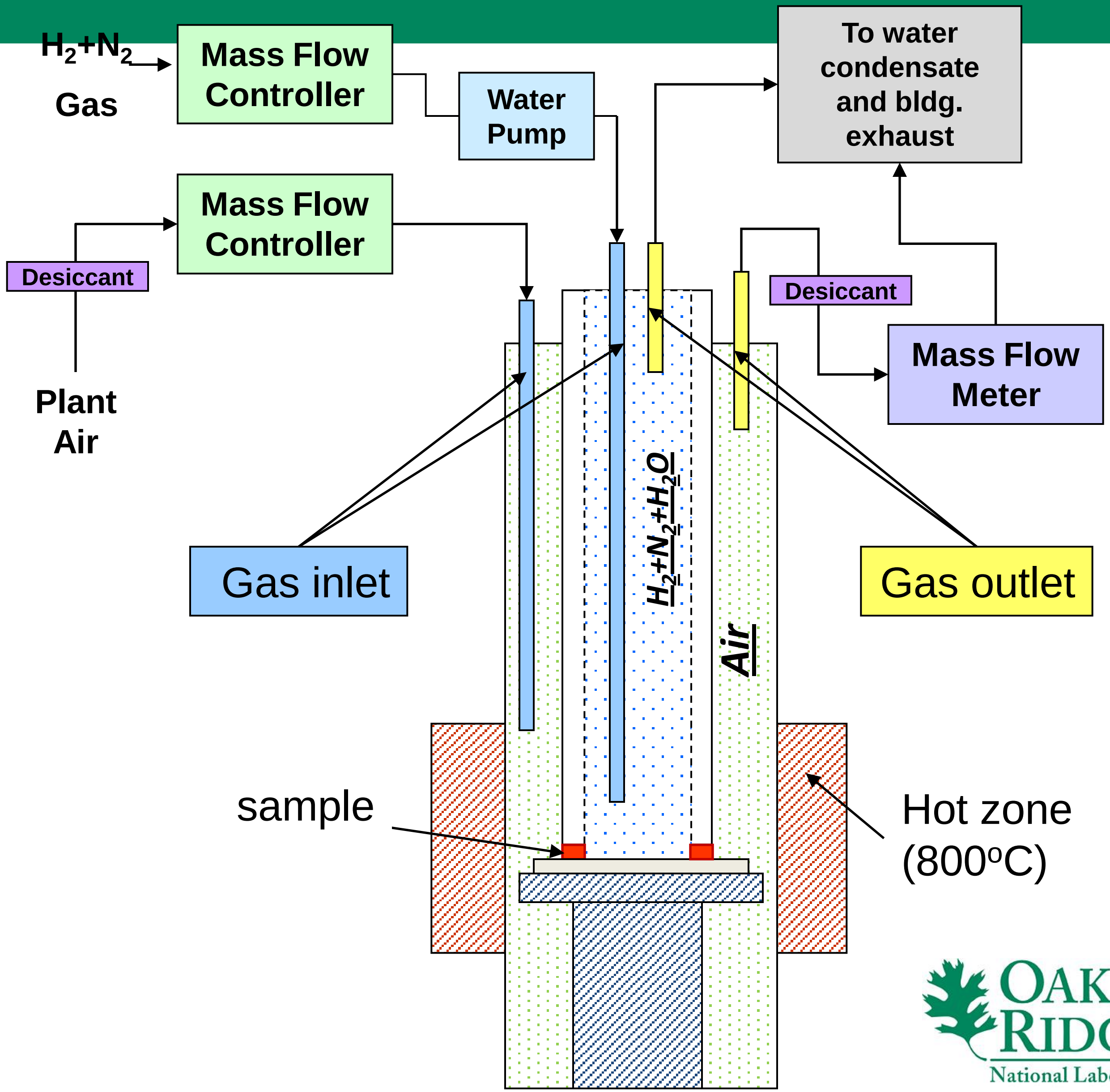
Summary

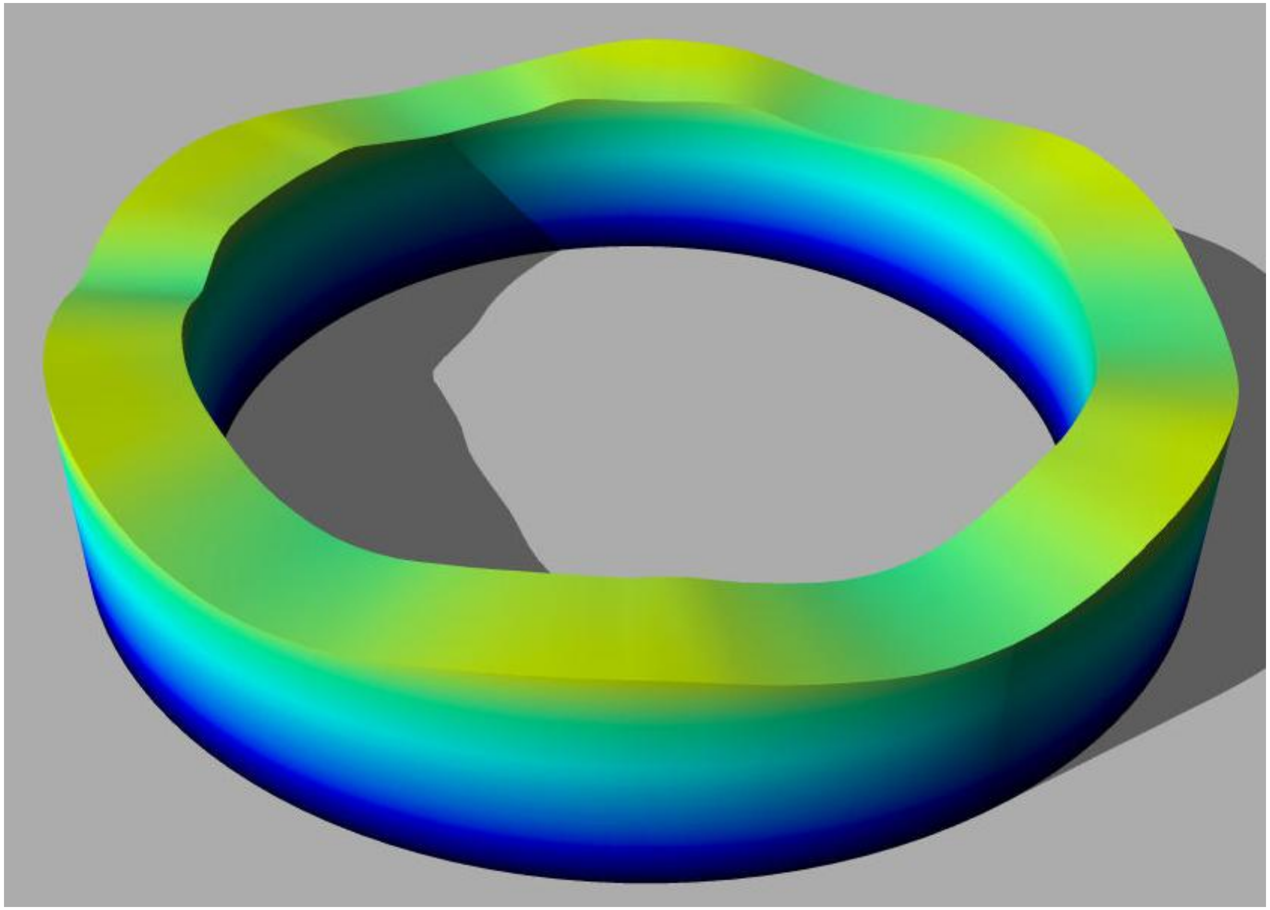
- The physical and mechanical properties of two barium alkali silicate glasses (SCN, G6) were determined as a function of temperature.
- The microstructure of these glasses has been characterized for up to 10,000 hours in air and H_2+N_2+H_2O. Test specimens continue being exposed (12,000+ hrs).
- Models are being developed to predict the rates of crystallization and the evolution of microstructure and physical properties.
- Engineering-based models are being developed to predict the behavior of SOFC seals comprising these glasses

OAK RIDGE National Laboratory

Dual Environment

- Expose samples at high temperature to both environments: Air and H_2+N_2+Steam simultaneously
- Control flow and pressure of both Environments
- Monitor Output Air Flow to detect sample leaks



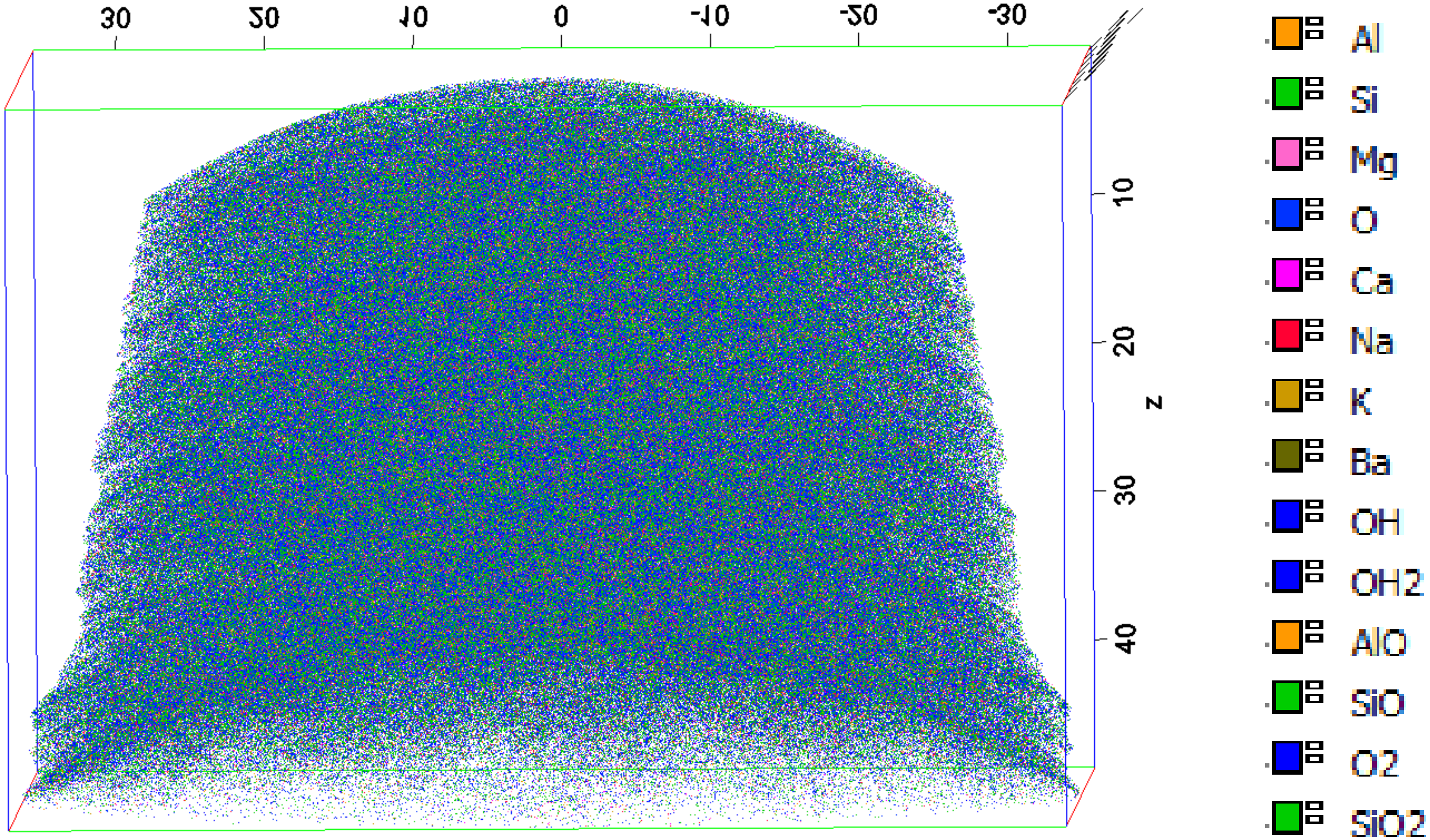


Conditions for LEAP analysis

- Tip base temperature 60 K
- Laser wavelength: 355 nm (ultraviolet)
- Laser pulse repetition frequency 250 kHz
- Laser pulse energy 200 pJ (tip 1) or 300 pJ (tip 2)
- Evaporation rate: 0.3-1.0 % Ions-per-pulse
- Fraction of "golden" events 68 %

- Two successful runs, one with 2M atoms, the second with 4M atoms in reconstruction
- Both runs terminated by tip fracture
- Reconstruction with k * E = 3.3 * 33 V/nm
- Reconstruction boxes 71 x 71 x 49 nm^3 and 70 x 70 x 109 nm^3 for the two runs

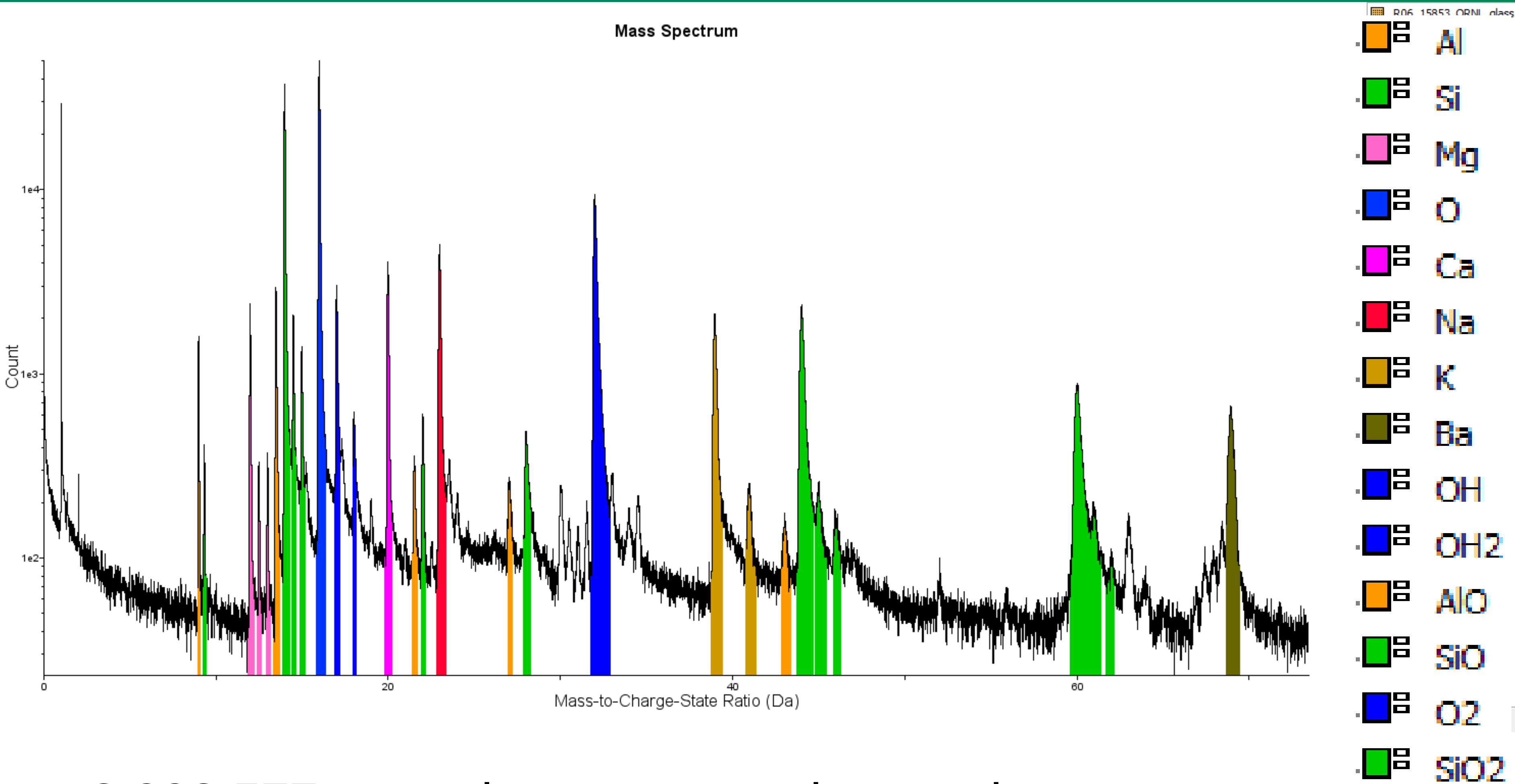
3D LEAP reconstruction tip 1



2,093,577 ranged atoms in 71 x 71 x 49 nm^3
reconstructed Volume

OAK RIDGE National Laboratory

LEAP mass spectrum tip 1



2,093,577 ranged atoms ranged atoms in $71 \times 71 \times 49\ nm^3$ reconstructed Volume