Durability and Reliability of Materials and Components for SOFC

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2021 SOFC Program Review

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Outline

- Background Engineered Seals for SOFCs
- Microstructural characterization of multi-component silicate glasses
- Summary

Background— Engineered Seals for SOFCs

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Surdoval et al.

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(45) **Date of Patent: Feb. 7, 2017**

(54) **ENGINEERED GLASS SEALS FOR SOLID-OXIDE FUEL CELLS**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 666 days.

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(51) **Int. Cl.**

H01M 2/08	(2006.01)
H01M 8/02	(2016.01)
C03C 8/24	(2006.01)
C03C 14/00	(2006.01)
H01M 8/12	(2016.01)

(52) **U.S. Cl.**
CPC ***H01M 8/0282*** (2013.01); ***C03C 8/24*** (2013.01); ***C03C 14/002*** (2013.01); ***C03C 14/004*** (2013.01); ***H01M 8/0286*** (2013.01); *C03C 2214/30* (2013.01); *H01M 2008/1293* (2013.01); *Y02E 60/50* (2013.01); *Y02E 60/525* (2013.01); *Y02P 70/56* (2015.11)

(58) **Field of Classification Search**
CPC H01M 8/0282; H01M 8/0286; H01M 2008/1293; C03C 8/24; C03C 14/002; C03C 14/004; C03C 2214/30; Y02E 60/525; Y02E 60/50; Y02P 70/56
USPC 429/509
See application file for complete search history.

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Chou et al., "Compliant alkali silicate sealing glass for solid oxide fuel cell applications: Thermal cycle stability and chemical compatibility", Journal of Power Sources (2011)196: 2709-2716.

(Continued)

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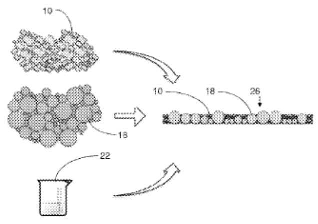
(57) **ABSTRACT**

A seal for a solid oxide fuel cell includes a glass matrix having glass percolation therethrough and having a glass transition temperature below 650° C. A deformable second phase material is dispersed in the glass matrix. The second phase material can be a compliant material. The second phase material can be a crushable material. A solid oxide fuel cell, a precursor for forming a seal for a solid oxide fuel cell, and a method of making a seal for a solid oxide fuel cell are also disclosed.

19 Claims, 7 Drawing Sheets



- A seal for a solid oxide fuel cell includes a glass matrix having glass percolation therethrough and having a glass transition temperature below 650° C.
- A deformable second phase material is dispersed in the glass matrix. The second phase material can be a compliant material. The second phase material can be a crushable material.
- A method of making a seal for a solid oxide fuel cell are also disclosed.

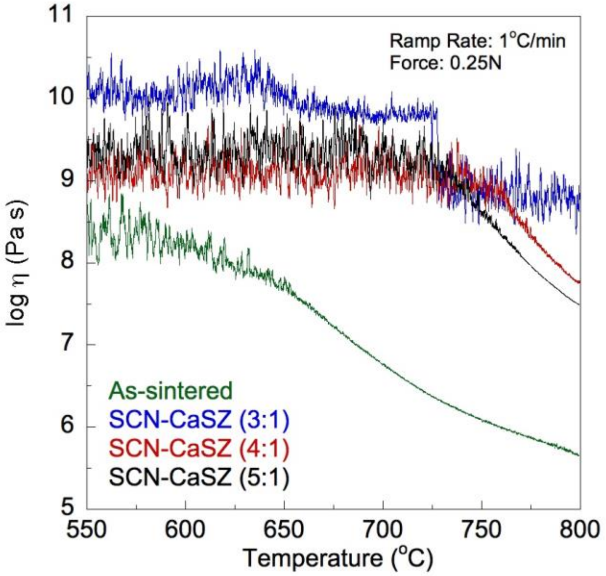
Lara-Curzio et al. (2021)

Lara-Curzio et al. (Oak Ridge National Laboratory. 2014)

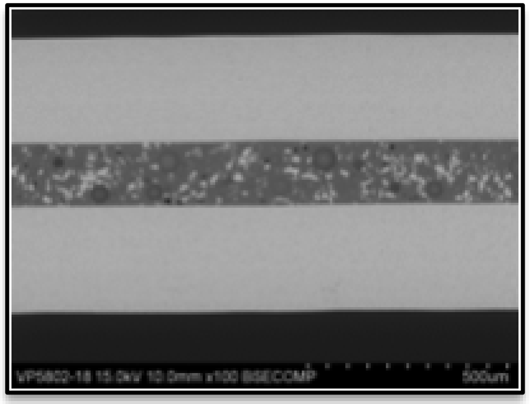
Engineered Composite Glass Seals

Engineered composite seals, consisting of a multicomponent silicate glass matrix and a zirconia-based second phase (frangible particles or fibers), have been developed for Solid Oxide Fuel Cells (SOFCs) and other high-temperature sealing applications. The physical properties (e.g., compliance, viscosity, thermal expansion) of the seals can be tailored to address, for example, the wide distribution of temperatures experienced by SOFCs and to seal cells with large active surface area, which might not be parallel or flat.

Low-cost manufacturing procedures have been developed, including fused deposition, which provides a means for printing seals of complex shape with an arbitrary spatial distribution of viscosity values and high material utilization.

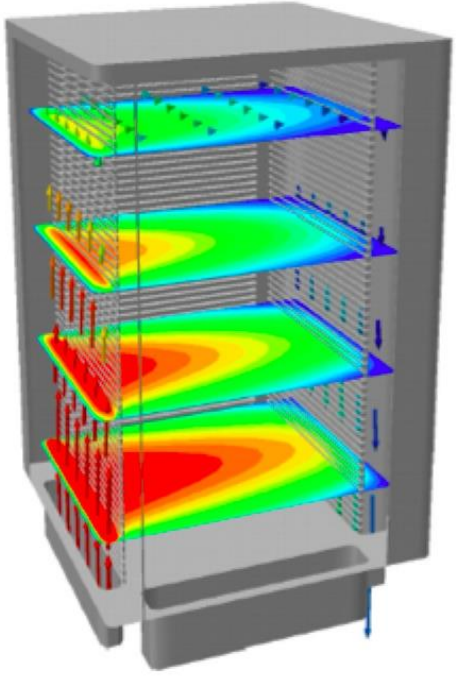


Viscosity of engineered glass seals as a function of temperature and volume concentration of second phase (zirconium oxide particles).



Scanning electron micrograph illustrating the cross section of an engineered glass seal between two aluminum oxide plates. The zirconia particles embedded in the glass are evident in the micrograph.

Picture of engineered glass seal fabricated by fused deposition using a mixture of glass and ceramic particles embedded in an organic binder.



The viscosity of engineered composite seals can be tailored to seal structures, such as SOFCs, that experience large in-plane and axial temperature gradients during operation.

Oak Ridge National Laboratory

Lara-Curzio et al. (2021)

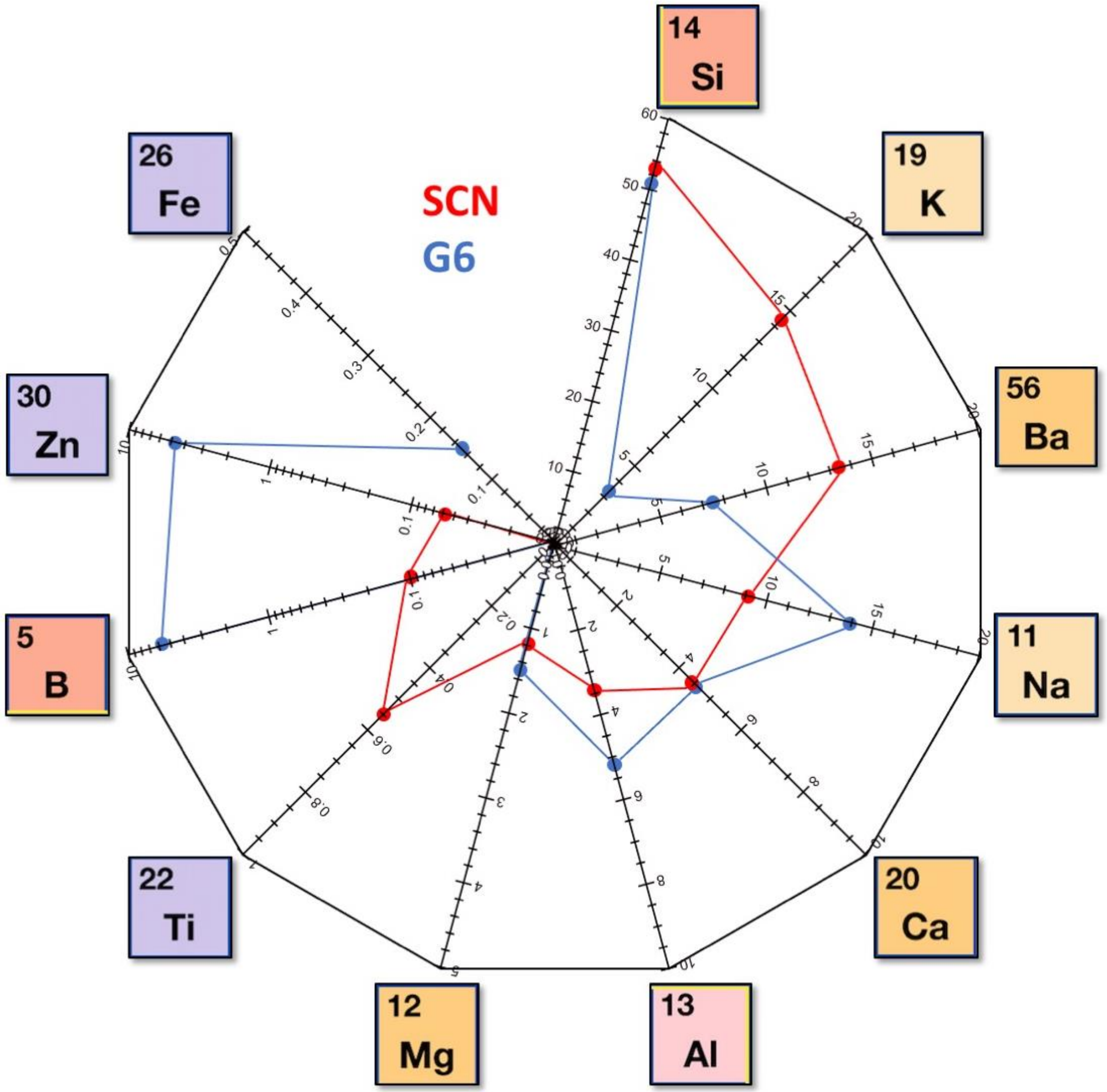
Microstructural characterization of multi-component silicate glasses

- ORNL is characterizing the evolution of the microstructure of multi-component silicate glasses for SOFC sealing applications.
- Two commercially-available glasses are being investigated: SCN and G6
- Glass samples were mounted on either YSZ or Al_2O_3 substrates and exposed at 800°C to air or gas mixtures of H_2+H_2O+N_2 for up to 40,000 hours.
- A combination of techniques, that include Raman spectroscopy, X-ray diffraction, electron microprobe and scanning electron microscopy have been used.

Lara-Curzio et al. (2021)

Chemical Composition of SCN and G6 Glasses

Boron (15.4 vs. 0.3 at.%) is added to control the thermal properties of glasses and the adhesion/wetting behavior of the glass on the substrate.



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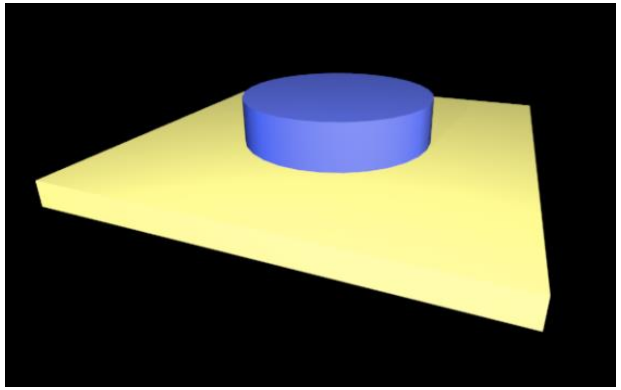
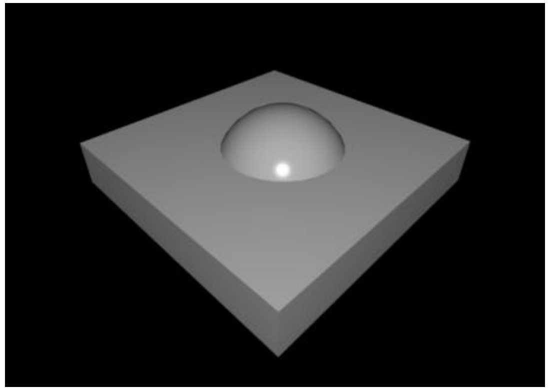
Experimental Approach

SCN and G6 glass powders cold pressed into pellets

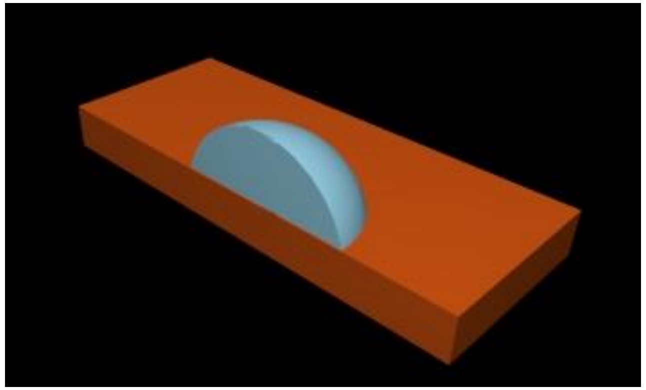


Sintering 850°C for 2 hours



Substrates
- Al_2O_3
- 8YSZ

Microstructural analysis on metallographically prepared specimens
- XRD of glass powder
- SEM on cross-section
- EDS
- Electron microprobe



Cross-section

Environmental Exposure at 800°C
- 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

Lara-Curzio et al. (2021)

Analysis and characterization after 10,000-hr exp

- SCN and G6 glasses
- 8YSZ and Al_2O_3 substrates

Exposures at 800°C in

- air
- gas mixtures of $H_2O+N_2+H_2$

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Microstructural evolution in two alkali multicomponent silicate glasses as a result of long-term exposure to solid oxide fuel cell environments

Amit Shyam · Rosa Trejo · Dana McClurg · Alexander Ladouceur · Melanie Kirkham · Xueyan Song · Jane Howe · Edgar Lara-Curzio

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Abstract The microstructural evolution in two potential solid oxide fuel cell (SOFC) sealing glass materials exposed to air and a gas mixture of steam + H_2 + N_2 at 800 °C up to 10000 h was determined. The glass exposures were performed on common SOFC substrates like alumina and zirconia. Characterization of the crystalline phases and pore size distribution was performed for the specimens with various exposure conditions. Comparison of the microstructural and chemical stability of the two glasses was performed based on known trends related to glass chemistry. It was observed that multicomponent glasses followed few rules for chemical and microstructural stability reported in the literature for glasses with fewer components. The two glasses examined in this study displayed adequate resistance to devitrification but marginal resistance to porosity changes in the SOFC environment exposure. The implications of the results for the design and long-term performance of SOFC seals are discussed.

Introduction

Solid oxide fuel cells (SOFCs) are clean technological devices that convert the chemical energy stored in fuels into electric power [1]. SOFCs are fuel flexible and can generate power from gasified coal. SOFC technology is cost-effective with high energy conversion efficiency and can be applied for carbon capture and sequestration. Planar stack SOFCs are being pursued due to the higher power density associated with this design [2]. The planar stack designs, however, require seals to prevent the intermixing of gases. Seals must operate under demanding conditions (temperature ~800 °C, oxidizing and reducing environments) by meeting thermal, physical, chemical, mechanical and electrical property requirements for up to 40000 h while maintaining their functional, that is, sealing properties [3–5]. The development of low-cost reliable seals that can meet the aforementioned requirements of SOFCs is one of the main technological hurdles for the widespread commercialization of planar solid oxide fuel cells.

Typical seal designs include glass-ceramic materials that provide a rigid bond between components being sealed [6, 7]. More recently, compliant glass seal designs have been developed where the sealing temperature is typically above the glass softening temperature [8, 9]. The advantages of incorporating compliant seal materials are that the thermal stresses in the seal and adjacent components are relieved at temperatures above the glass transition temperature and that cracks that might form during cooling can be healed during subsequent heating.

The desired initial property requirements for sealing, for example, the coefficient of thermal expansion, glass transition temperature and wetting characteristics, have been achieved for several sealing architectures. As a recent review paper [4] concluded, the long-term stability of glass seal materials has been a persistent problem. Here, we report the effect of long-term exposure on phase stability and chemical compatibility of two commercially available multicomponent silicate glasses with potential use for SOFC sealing. The microstructural evolution including the

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Analysis and characterization after 40,000-hr exp

- SCN and G6 glasses
- 8YSZ and Al_2O_3 substrates

Exposures at 800°C in

- air
- gas mixtures of $H_2O+N_2+H_2$

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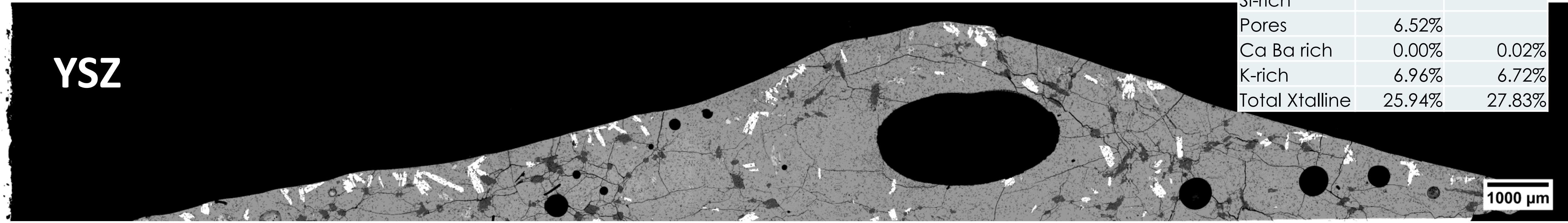
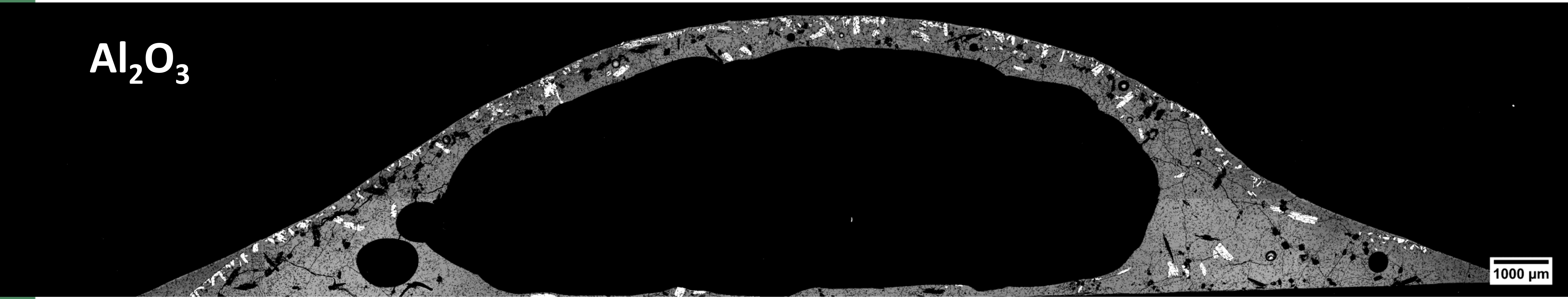
SCN Glass after 10,000 hrs in H_2+N_2+H_2O

Phase	YSZ Steam	Al_2O_3 Steam
Glass	67.54%	72.17%
Ca-rich	1.29%	3.59%
Al-rich	14.39%	13.78%
Ba-rich	3.29%	3.73%
Sb-rich	0.00%	
Si-rich		
Pores	6.52%	
Ca Ba rich	0.00%	0.02%
K-rich	6.96%	6.72%
Total Xtalline	25.94%	27.83%





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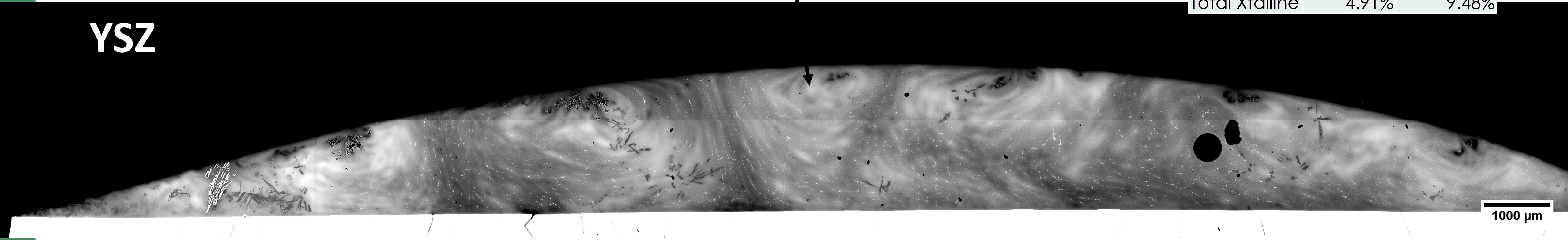
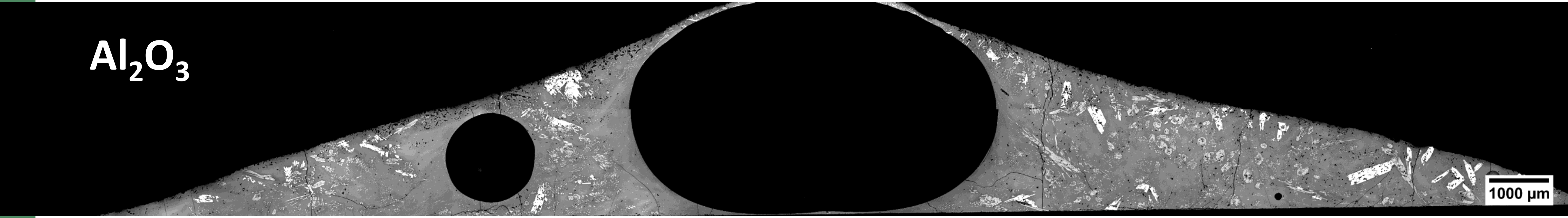
SCN Glass after 40,000 hrs in H_2+N_2+H_2O

Phase	YSZ Steam	Al_2O_3 Steam
Glass	95.09%	49.63%
Ca-rich	1.00%	4.67%
Al-rich	3.32%	2.76%
Ba-rich	0.20%	2.04%
Sb-rich	0.39%	0.00%
Si-rich		
Pores		40.89%
Ca Ba rich		
K-rich		
Total Xtalline	4.91%	9.48%

Ca and Ba rich swirls





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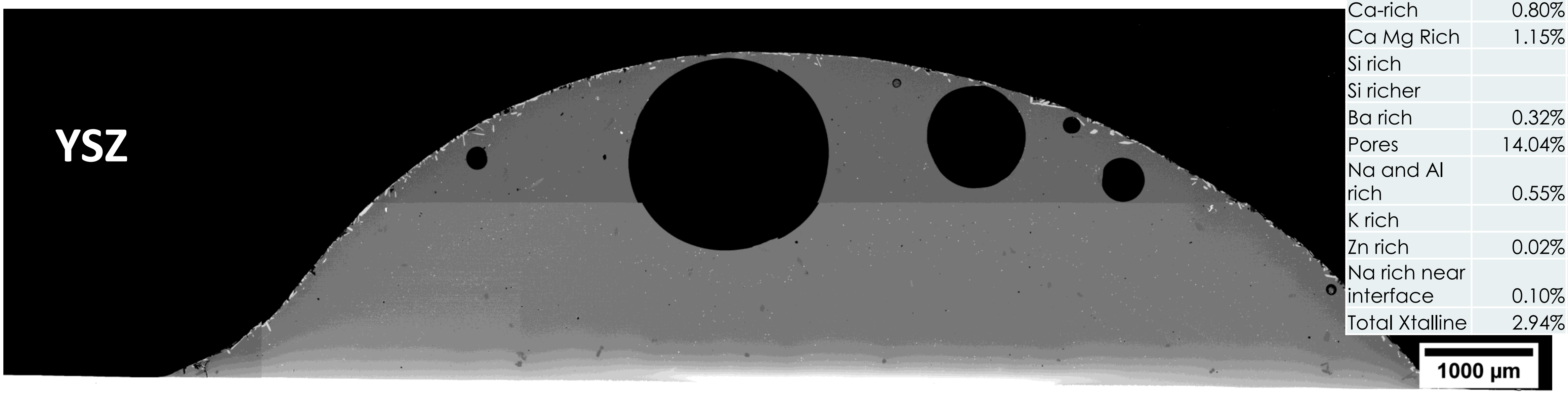
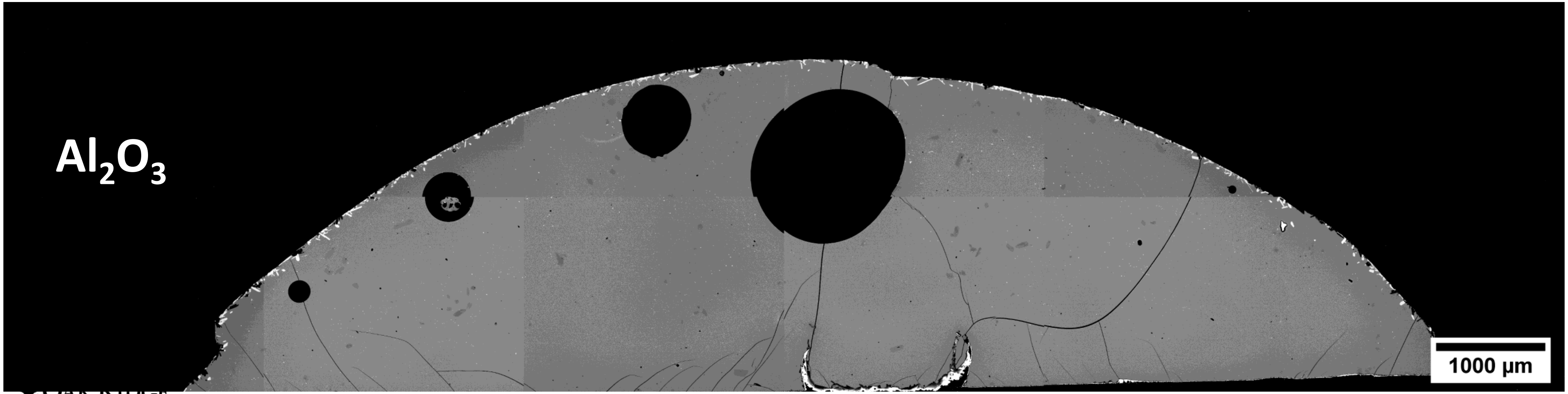
G6 Glass after 10,000 hrs in H_2+N_2+H_2O





	G6 10 kh	
hase	YSZ Steam	Al_2O_3 Steam
Glass	83.02%	95.69%
Ca-rich	0.80%	0.95%
Ca Mg Rich	1.15%	1.20%
Si rich		
Si richer		
Ba rich	0.32%	
Pores	14.04%	1.70%
Na and Al rich	0.55%	0.41%
K rich		0.02%
Zn rich	0.02%	0.04%
Na rich near interface	0.10%	
Total Xtalline	2.94%	2.61%

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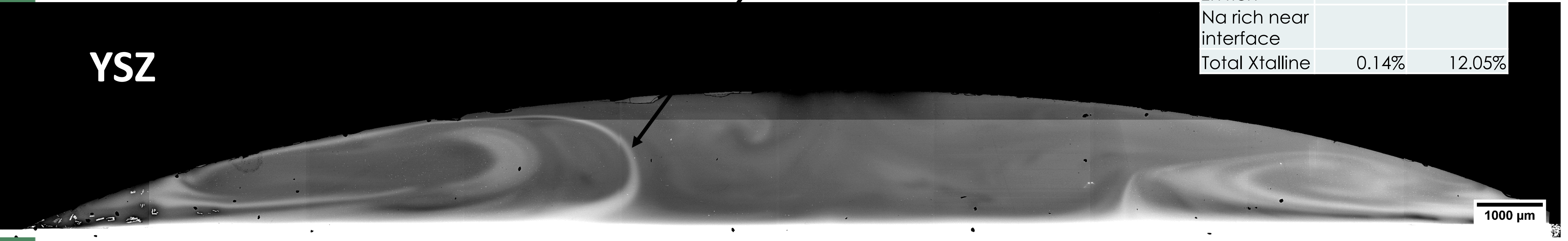
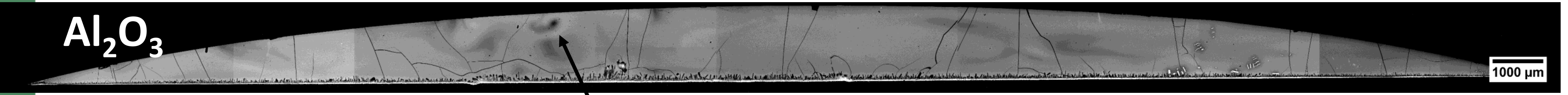
G6 Glass after 40,000 hrs in H_2+N_2+H_2O

Phase	G6 40 kh YSZ Steam	Al_2O_3 Steam
Glass	99.81%	87.95%
Ca-rich	0.14%	0.19%
Ca Mg Rich		
Si rich		
Si richer		
Ba rich		0.89%
Pores	0.05%	
Na and Al rich		10.98%
K rich		
Zn rich		
Na rich near interface		
Total Xtalline	0.14%	12.05%

Zr rich swirls





Ca rich swirls

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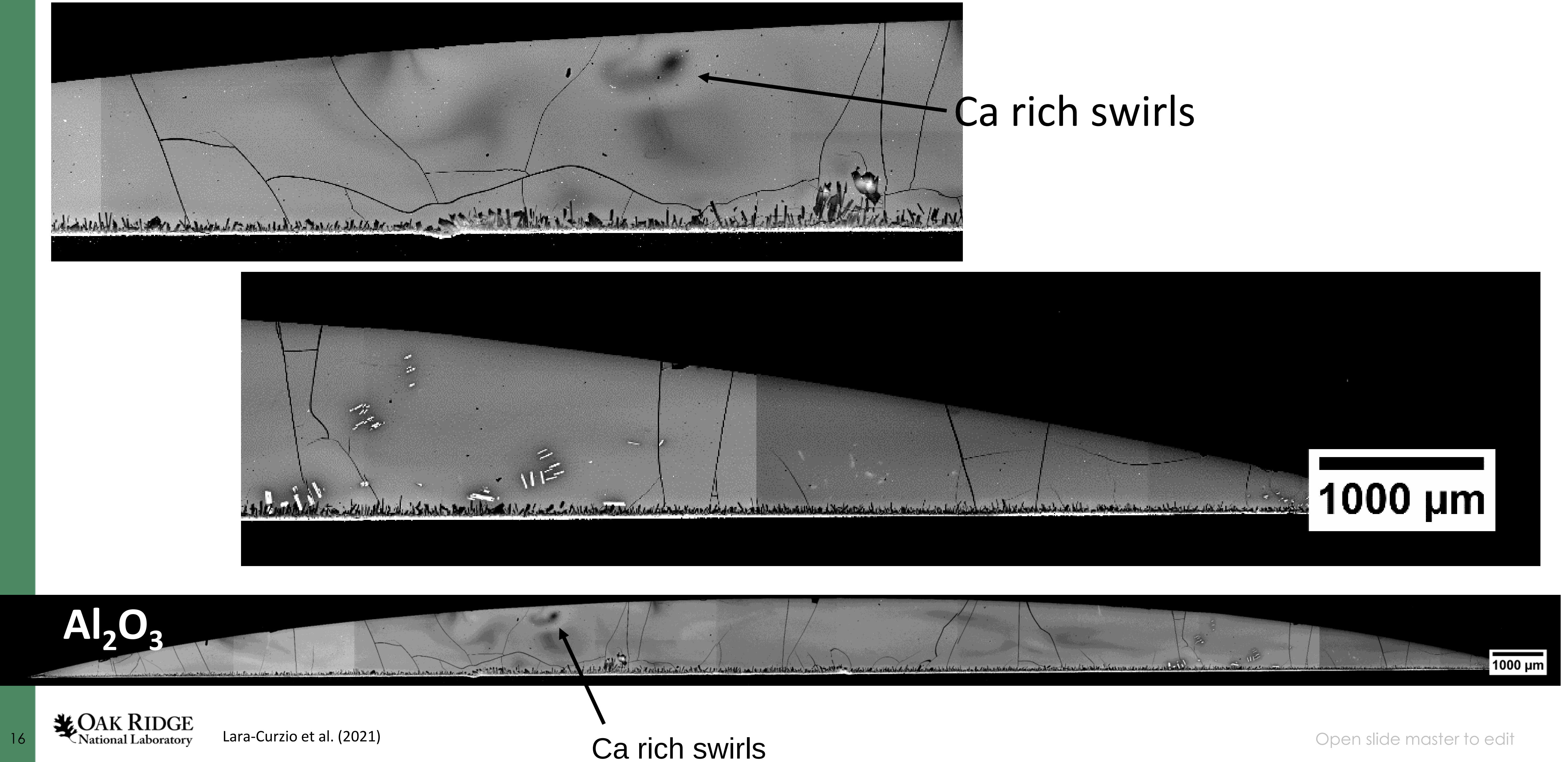
G6 Glass after 40,000 hrs in H_2+N_2+H_2O



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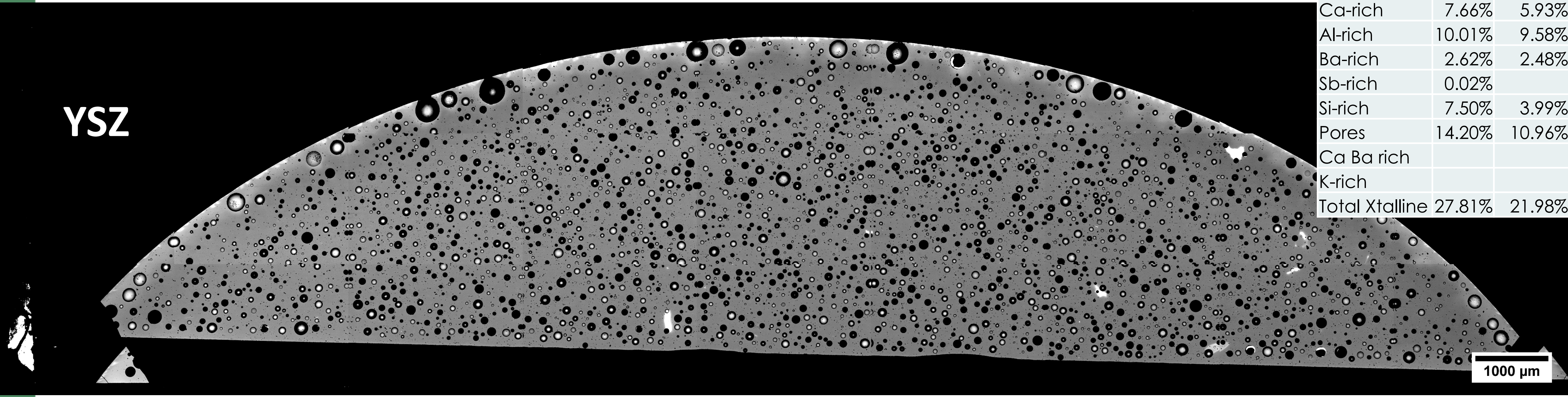
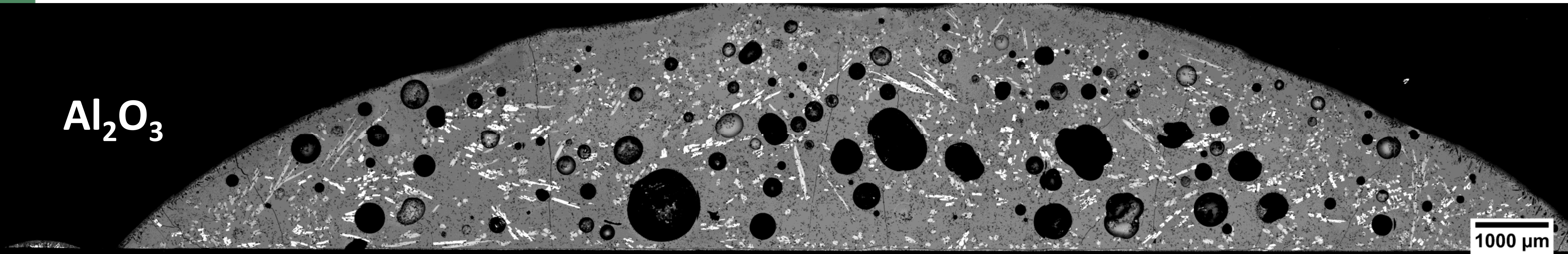
SCN Glass after 10,000 hrs in Air

	SCNP 10 kh	
Phase	YSZ Air	Al_2O_3 Air
Glass	57.99%	67.06%
Ca-rich	7.66%	5.93%
Al-rich	10.01%	9.58%
Ba-rich	2.62%	2.48%
Sb-rich	0.02%	
Si-rich	7.50%	3.99%
Pores	14.20%	10.96%
Ca Ba rich		
K-rich		
Total Xtalline	27.81%	21.98%

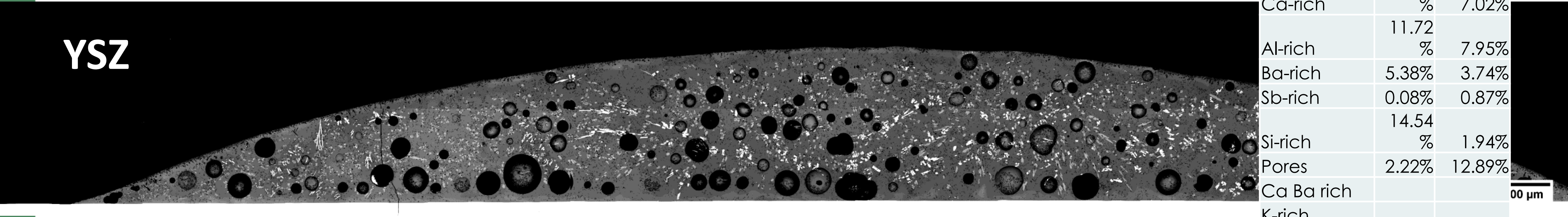




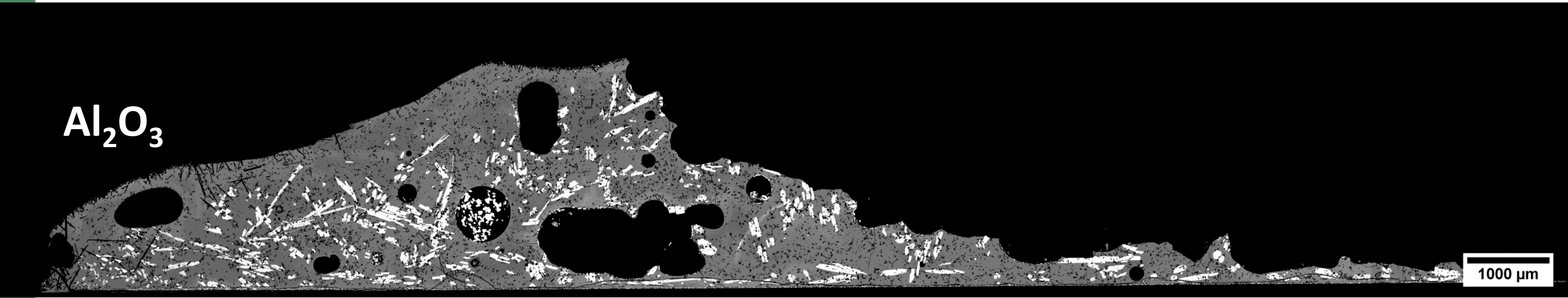
SCN Glass after 40,000 hrs in Air

	SCNP 40 kh	
Phase	YSZ Air	Al_2O_3 Air
Glass	55.49%	65.58%
Ca-rich	10.57%	7.02%
Al-rich	11.72%	7.95%
Ba-rich	5.38%	3.74%
Sb-rich	0.08%	0.87%
Si-rich	14.54%	1.94%
Pores	2.22%	12.89%
Ca Ba rich		
K-rich		
Total Xtalline	42.29%	21.53%

YSZ



Al_2O_3



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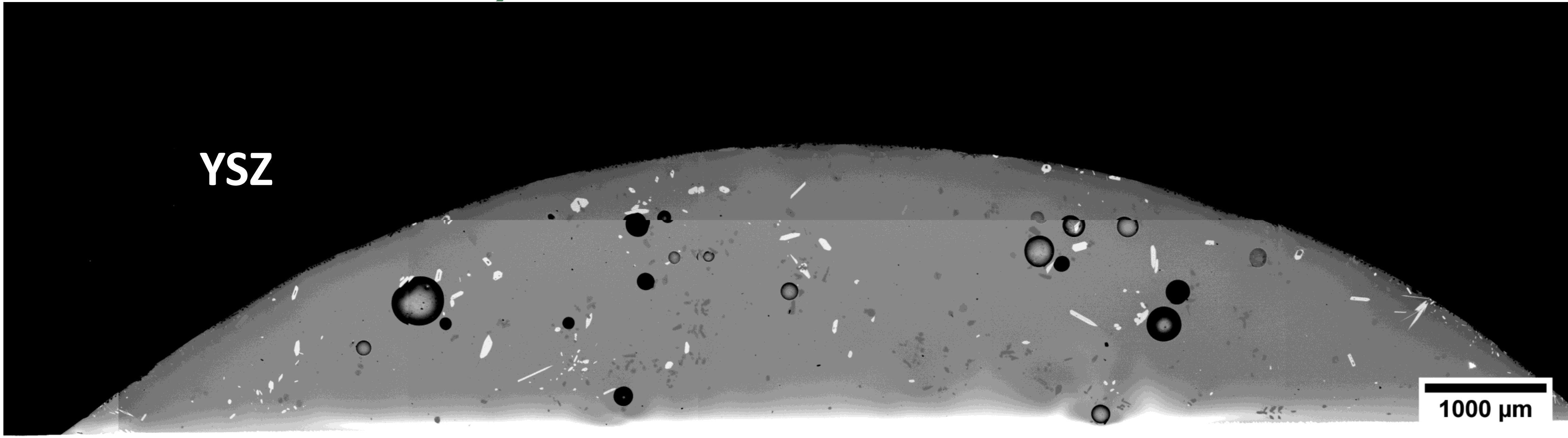
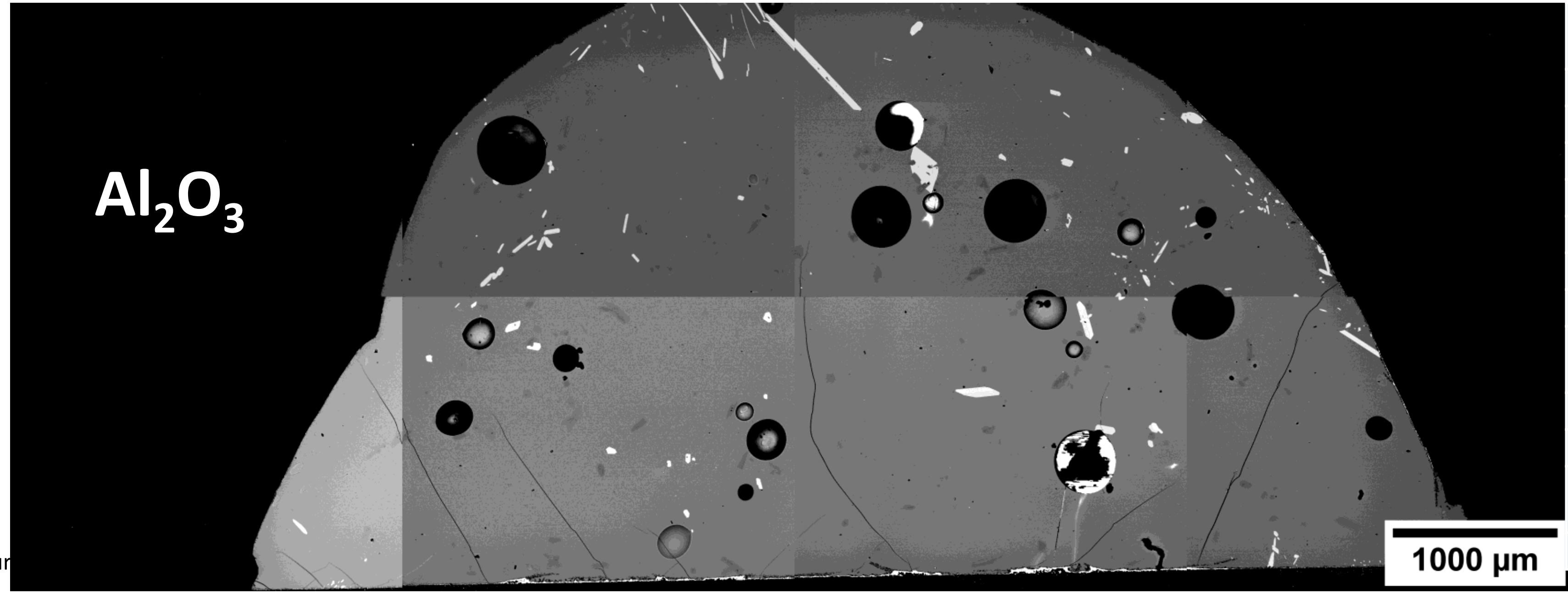
G6 Glass after 10,000 hrs in Air



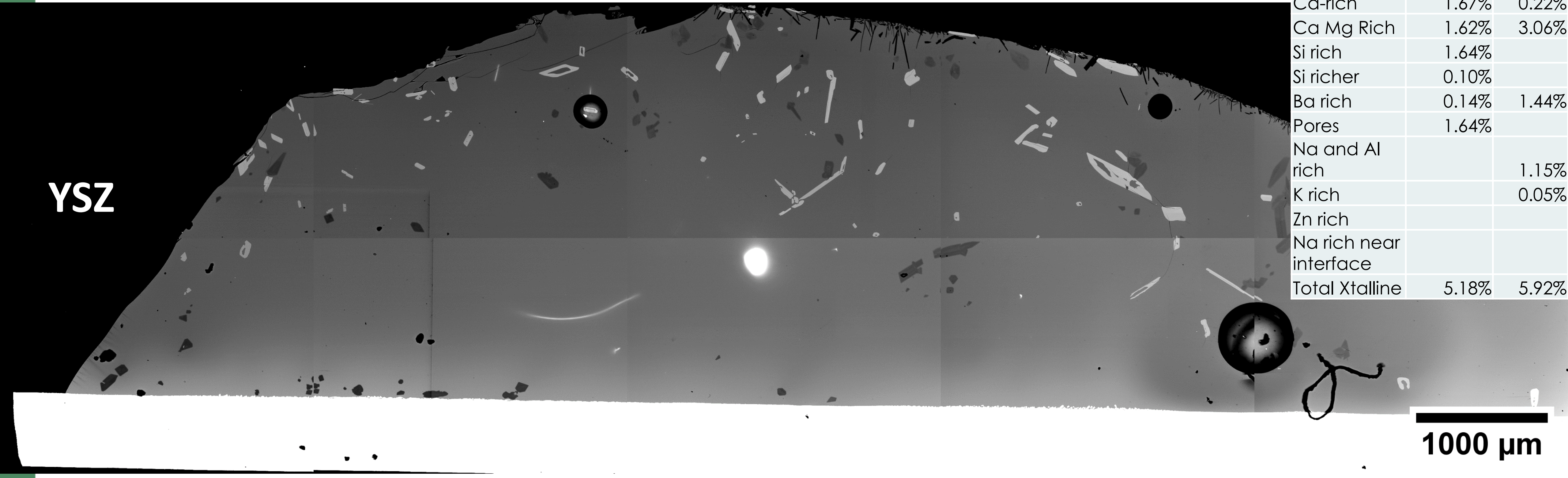


Phase	YSZ Air	Al_2O_3 Air
Glass	89.67%	91.41%
Ca-rich	1.34%	1.21%
Ca Mg Rich	2.40%	2.41%
Si rich	3.52%	
Si richer		
Ba rich	0.34%	
Pores	2.65%	4.97%
Na and Al rich	0.09%	
K rich	0.00%	
Zn rich		
Na rich near interface		
Total Xtalline	7.68%	3.62%

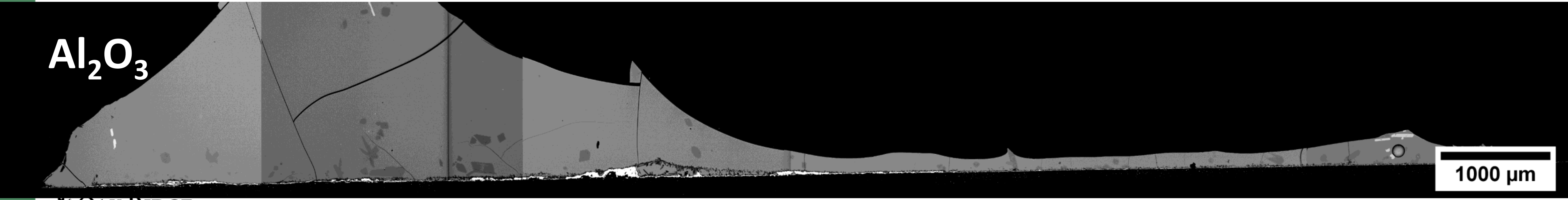
G6 Glass after 40,000 hrs in Air

	G6 40 kh	
Phase	YSZ Air	Al_2O_3 Air
Glass	93.19%	94.08%
Ca-rich	1.67%	0.22%
Ca Mg Rich	1.62%	3.06%
Si rich	1.64%	
Si richer	0.10%	
Ba rich	0.14%	1.44%
Pores	1.64%	
Na and Al rich		1.15%
K rich		0.05%
Zn rich		
Na rich near interface		
Total Xtalline	5.18%	5.92%

YSZ

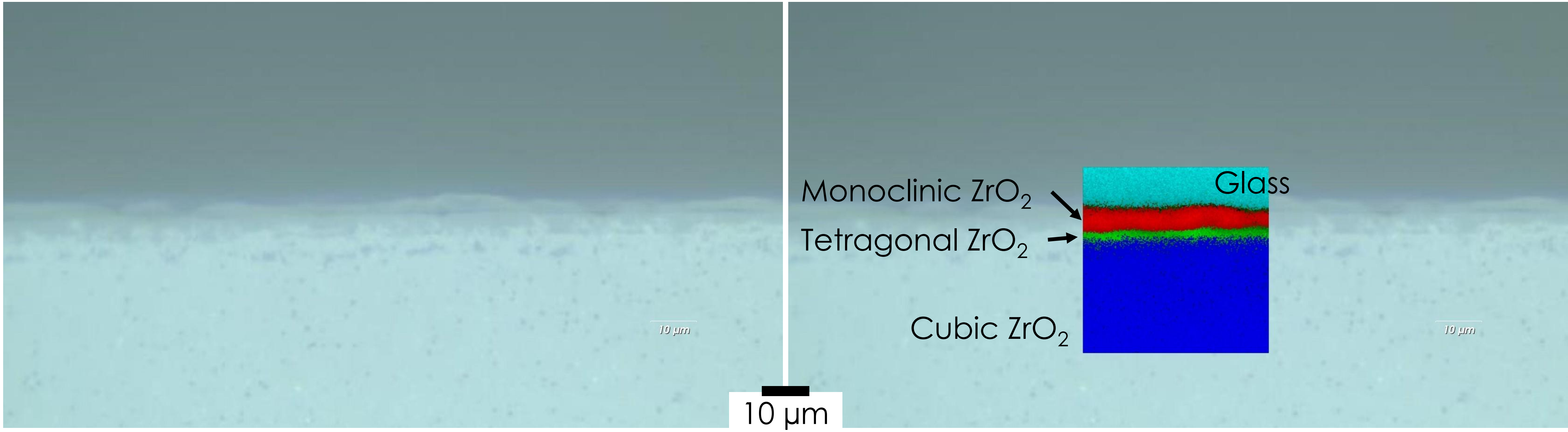


Al_2O_3



Lara-Curzio et al. (2021)

Raman spectroscopy was used to detect phase transformation of the G6 glass on an 8YSZ substrate after 40,000 hours in air



The diffusion of yttria into the glass, results in a transformation of the substrate from cubic to tetragonal to monoclinic ZrO_2.

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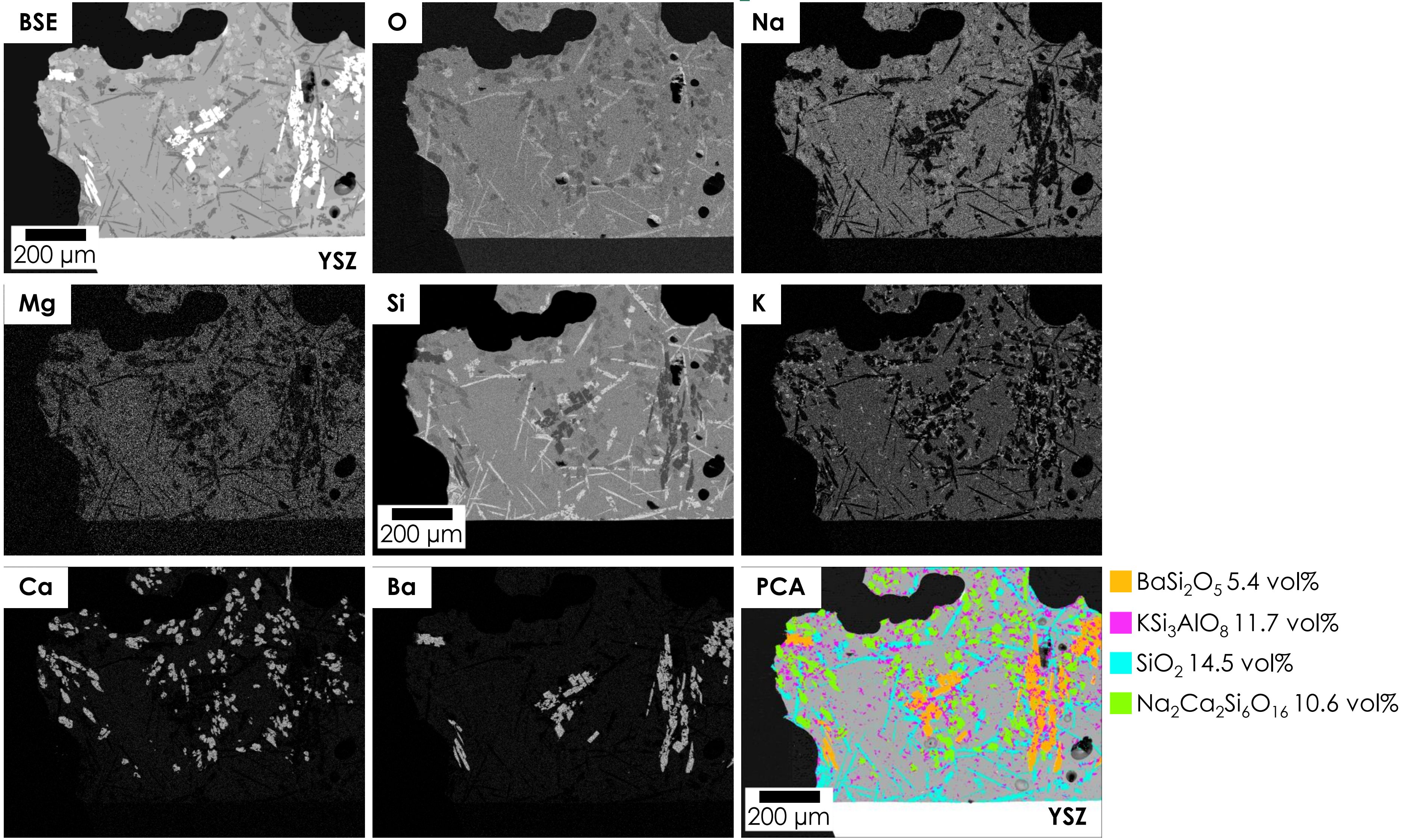
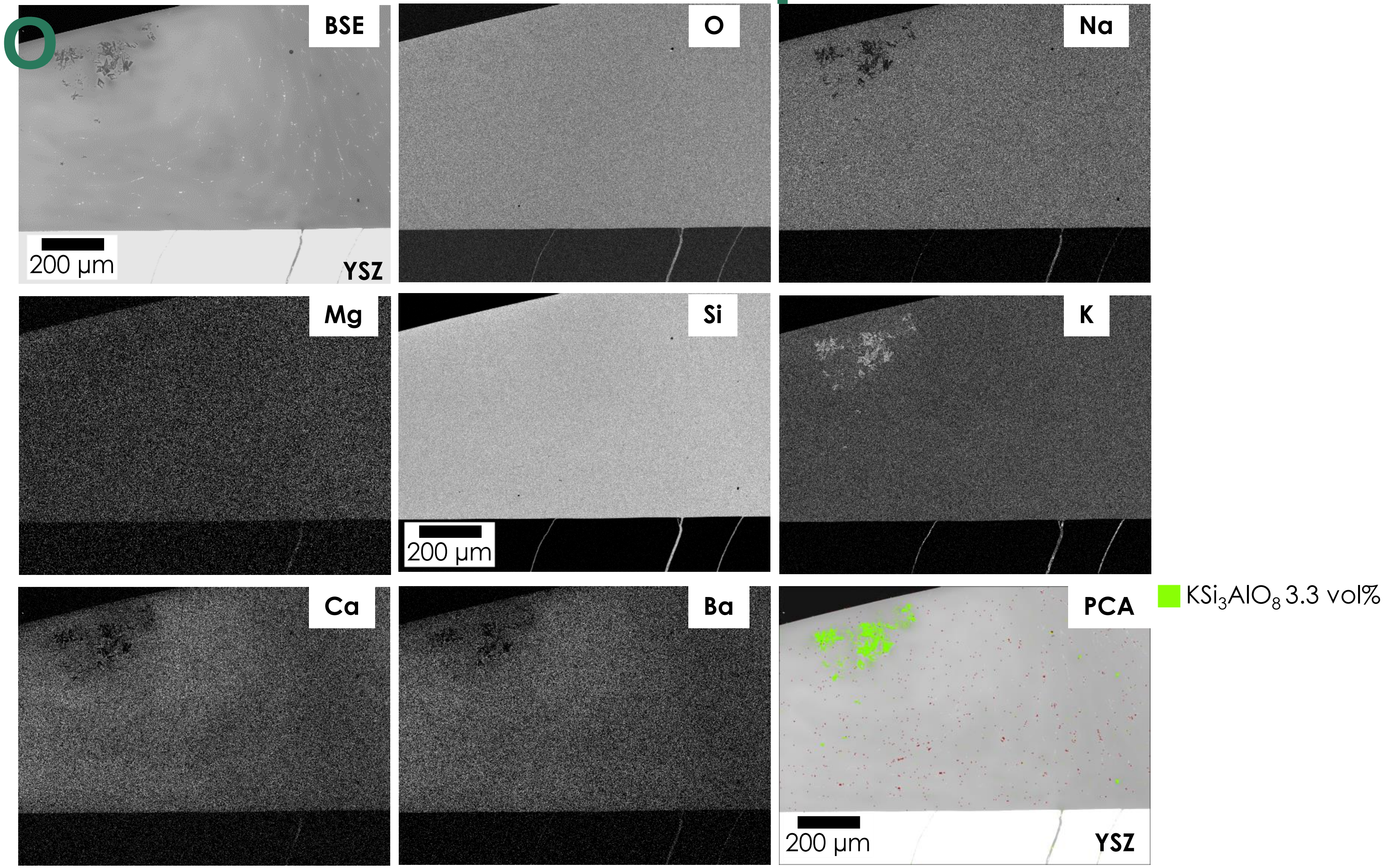
SCN on YSZ after 40,000 hrs exposure to Air



- Principal component analysis (PCA) (lower right) utilizes the EDS maps to find phases where multiple elements correlate with each other. The phase composition and vol% can then be directly measured.

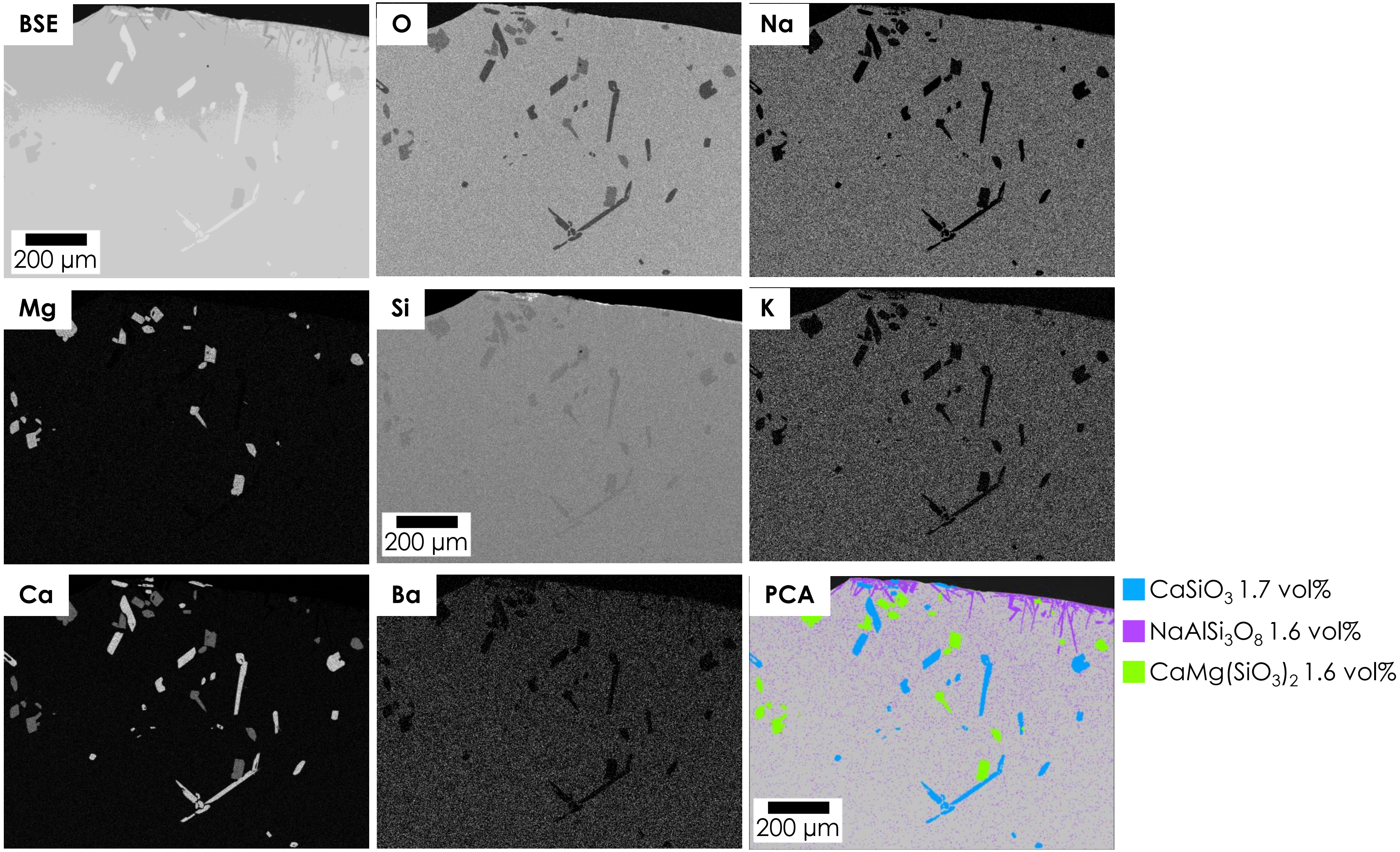
SCN on YSZ after 40,000 hrs exposure to $H_2+N_2+H_2O$



Ca and Ba formed ‘swirls’ around the KSi_3AlO_8 crystals.

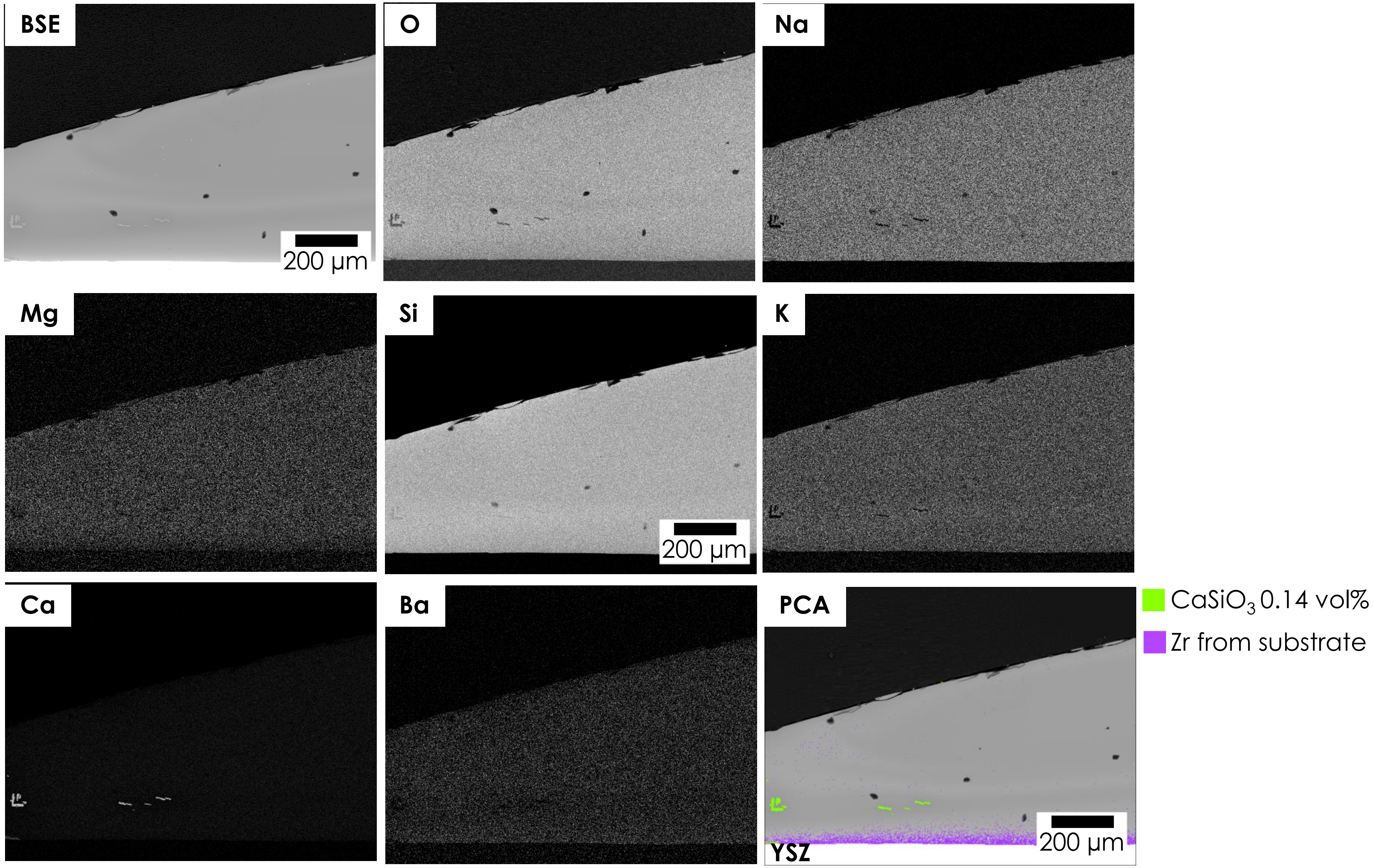
Lara-Curzio et al. (2021)

G6 on YSZ after 40,000 hrs exposure to Air



G6 glass exhibited less crystallization than the SCN glass. Exposure to air, compared to a gas mixture of H_2+N_2+H_2O increased crystallization.

G6 on YSZ after 40,000 hrs exposure to H_2+N_2+H_2O



- Limited crystallization occurred following exposure to H_2+N_2+H_2O.
- Zr diffuses from the substrate into the glass.

Microstructural characterization of multi-component silicate glasses

- ORNL is compiling the results of this extensive study into a report and journal publications.
- Analysis of the results are providing information on the kinetics of crystallization of G6 and SCN glasses as a function of substrate (YSZ or Al_3O_3) and environment (air or H_2+H_2O+N_2)

Lara-Curzio et al. (2021)

Summary

- A report documenting detailed characterization of multi-component silicate glasses as a function of time of exposure in SOFC-relevant environments is being completed

Lara-Curzio et al. (2021)