Reliability and Durability Testing of Glass Ceramic Seals for Praxair's Oxygen Transport Membranes

David Reed[1], Nathan Canfield[1], Sadashiv Swami[2], Joey Corpus[2]

[1]Pacific Northwest National Laboratory
Richland, WA

[2]Praxair, Inc.
Tonawanda, NY & Indianapolis, IN

-

2019 Annual Project Review

Gasification Systems

Pittsburgh, PA

April 10, 2019

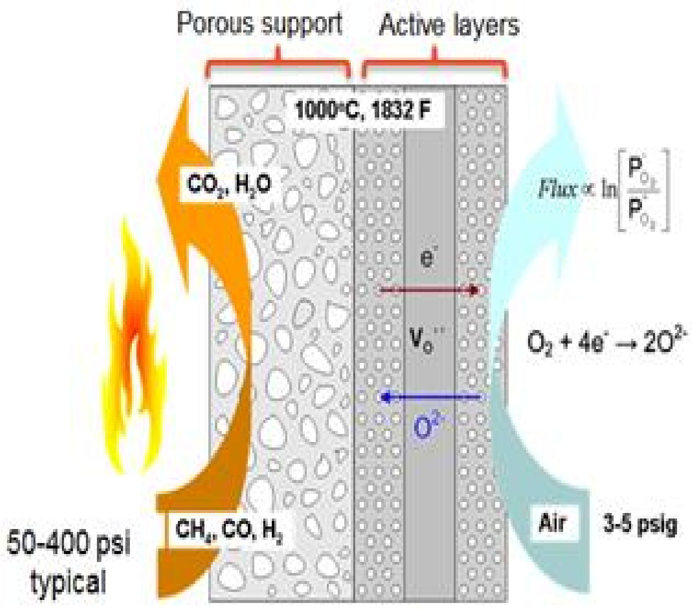
Outline

- **Project Objectives**
- **Background**
- **Experimental Procedure and Analysis Methods**
- **Project Update**
  - **Glass 1 (ceramic-ceramic seal)**
  - **Glass 2 (ceramic-ceramic, and ceramic-metal seal)**
- **Next Steps and Concluding Remarks**

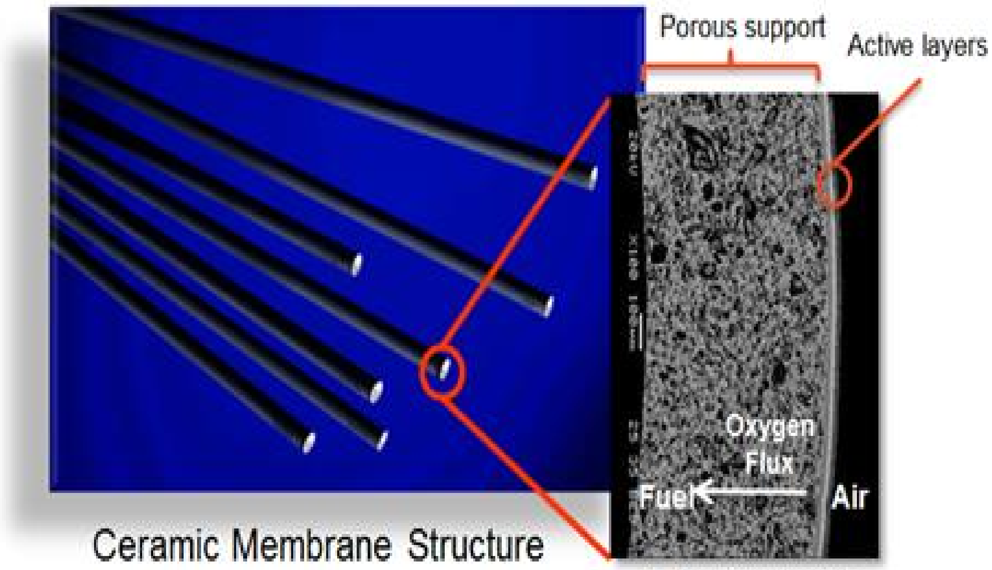
Project Description and Objectives

- Understand crystallization behavior of the barium alumino-silicate glass ceramic as a function of temperature and time.
- Implement accelerated life testing and characterize long-term failure mechanisms
- Correlate accelerated life testing to testing in working systems at Praxair facilities.

Background – OTM Technology



Ceramic Membrane Function



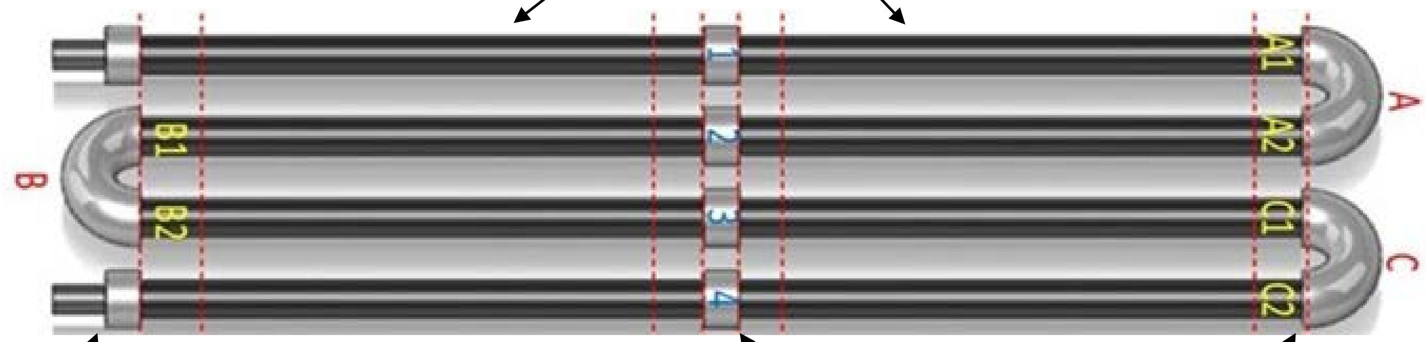
Ceramic Membrane Structure

Tube cross-section

- Utilize ceramic tubes to separate oxygen from air to upgrade methane to more valuable chemical products such as syngas
- Technology integrates air separation and reforming of methane into a single operation

Background – OTM Design

OTM Tube



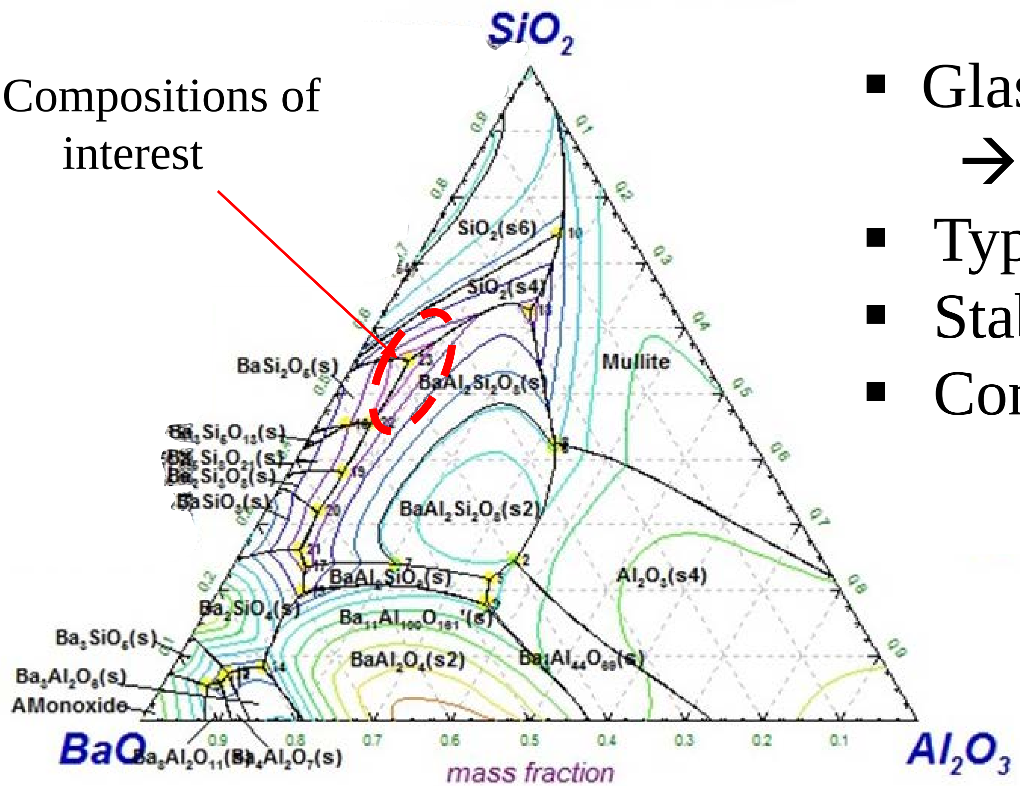
Ceramic-Metal Seal

Ceramic-Ceramic Seal

- Assemblies contain ceramic-ceramic seals and ceramic-metal seals

Background – barium alumino-silicate seals

Compositions of interest



- Glass ceramic seal
  → melt then crystallize
- Typically stronger than glass
- Stable
- Composition dictates phases

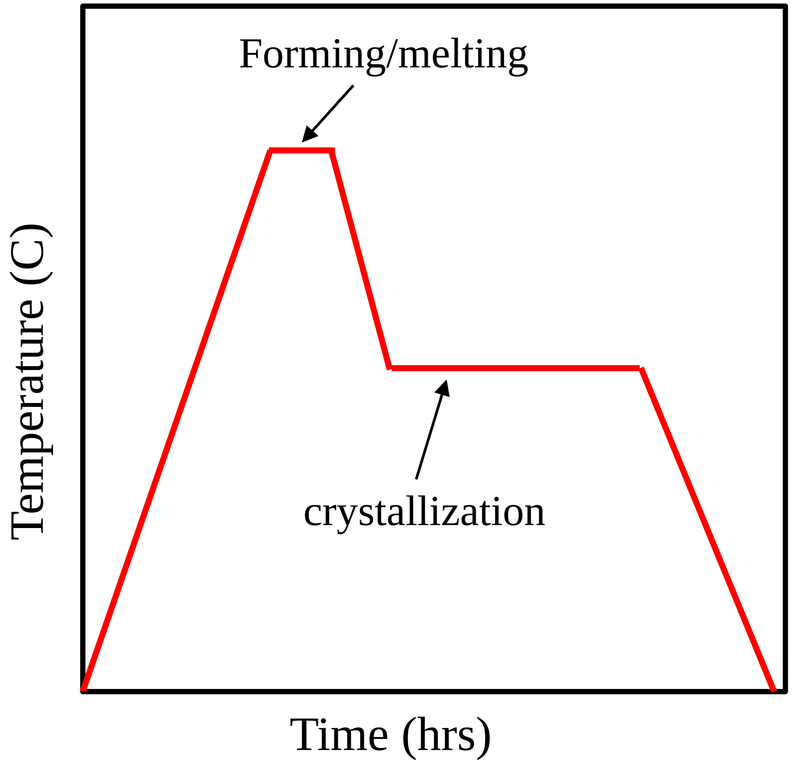
Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle Since 1965

PRAXAIR

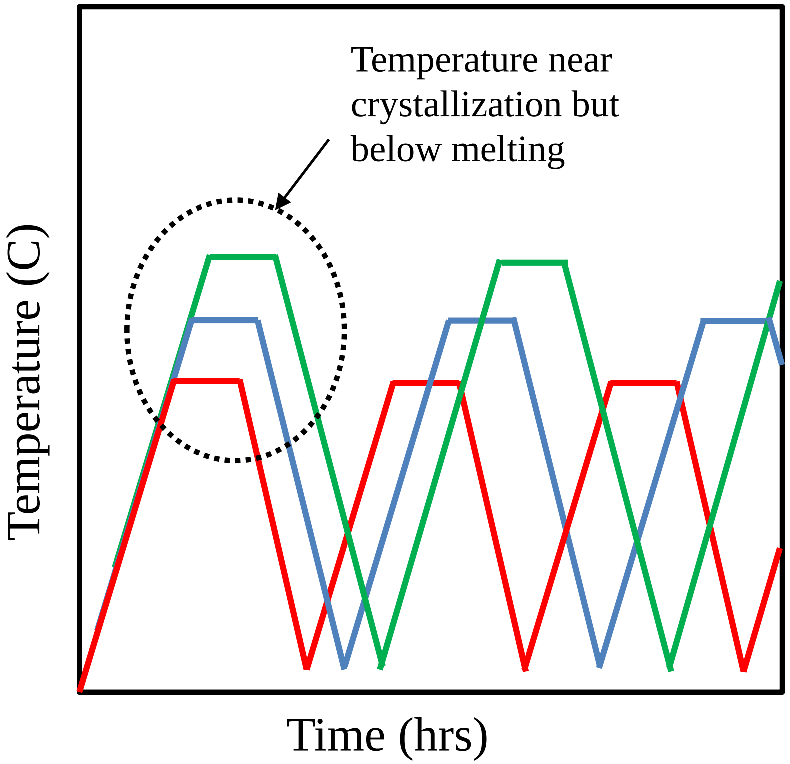
Background – Thermal cycling (accelerated aging)

Initial "***setting***" of glass-ceramic

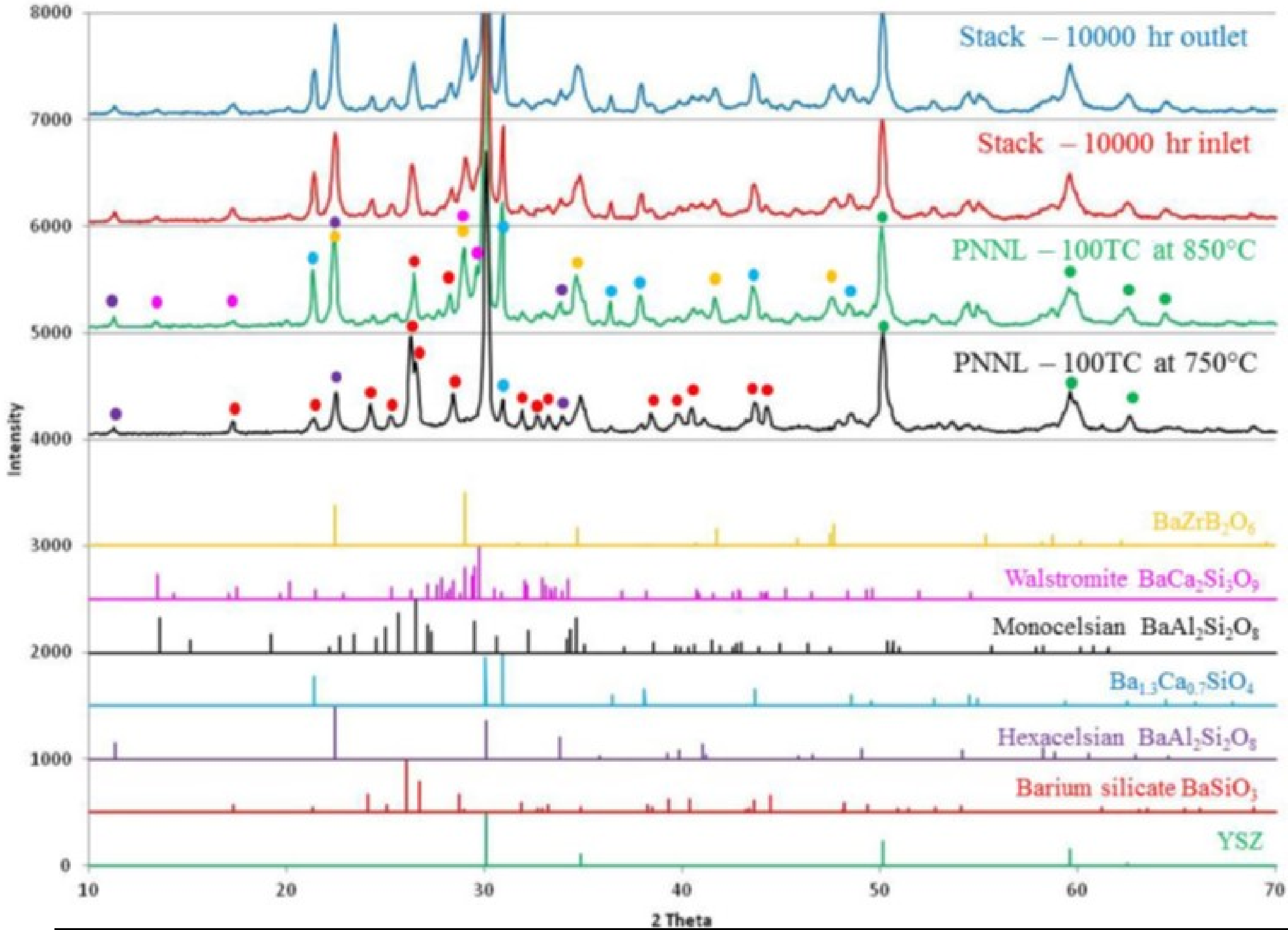


Thermal cycling of glass-ceramic

"Accelerated Condition"



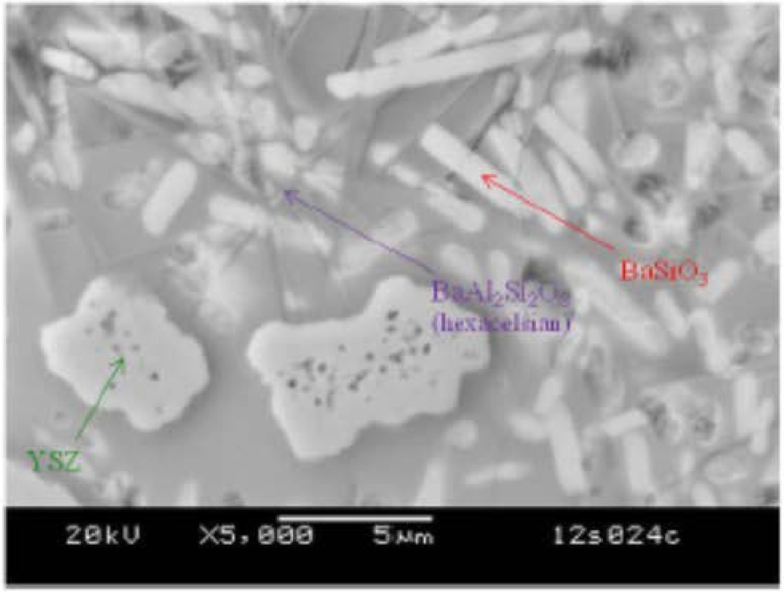
Background - accelerated test development (XRD)



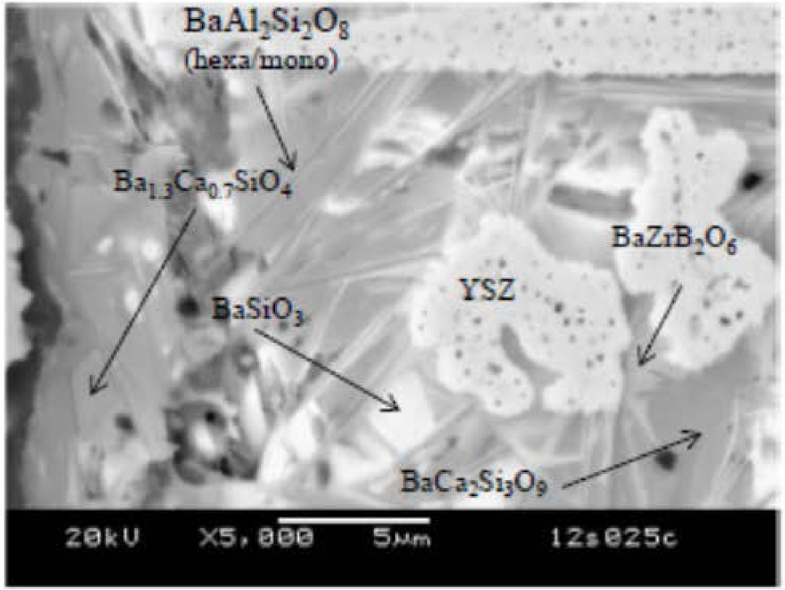
Accelerated conditions (100TC at 850C) gives similar phase formation as stack durability test.

Background - accelerated test development (SEM)

As set



100TC – 850°C



SEM with EDS used to identify phases formed in glass ceramic

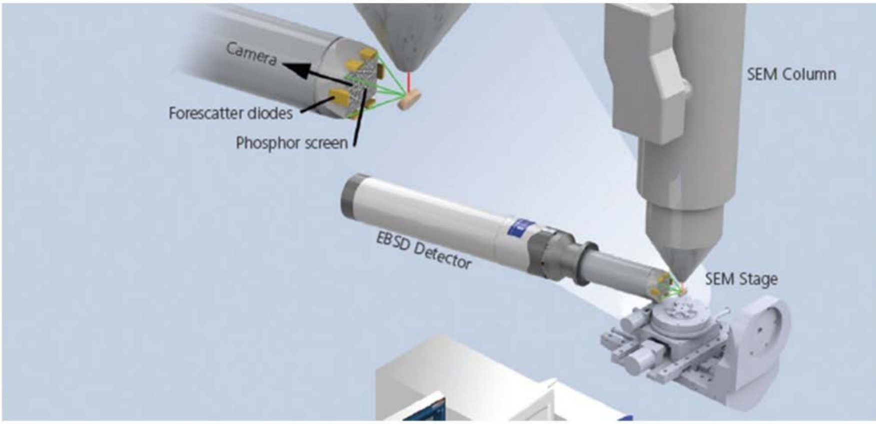
PRAXAIR

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle *Since 1965*

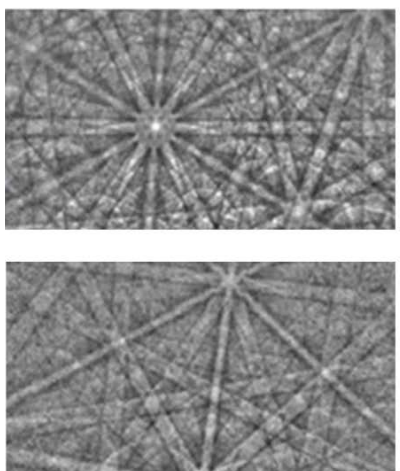
Background - electron backscattered diffraction (EBSD)

EBSD Principles of Operation

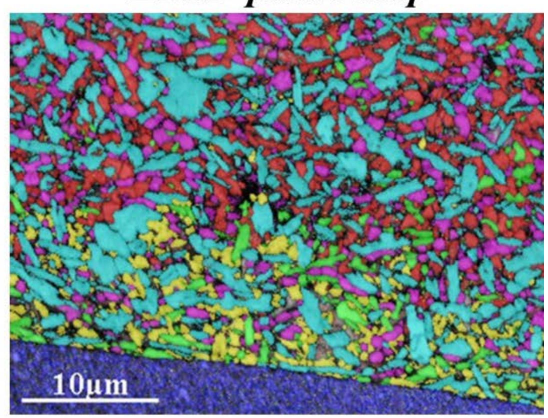


- Accelerated e^- diffracted by atomic layers in crystalline materials.
- Diffracted e- are detected when they impinged on a phosphor screen and generate "Kikuchi bands".
- Patterns are projections of the lattice planes in the crystal and can give structural information about phase of interest

Kikuchi bands



EBSD phase map



Phase Color	Phase
	Hexacelsian
	YSZ
	Celsian
	$Ba_5Si_8O_{21}$
	Sanbornite
	Hashemite
	Zero Solutions

Experimental Procedure

1. Analyze seals tested at various times at Praxair facilities using EBSD
2. Develop a thermal cycle matrix *"accelerated condition"* for the two barium alumino-silicate glasses
3. Analyze resultant microstructures using EBSD
4. Correlate accelerated life testing to testing in working systems at Praxair facilities.
5. Understand crystallization behavior of glass ceramic seals as a function of Temp and time.

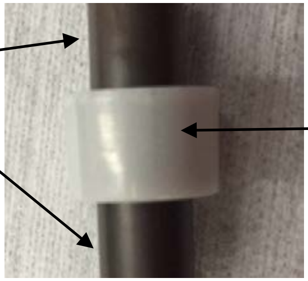
Experimental Procedure

Thermal cycle Matrix

		Conditions					
Seal Type	Unaged	900°C	950°C	1000°C	1050°C	1100°C	1150°C
Glass 1 (ceramic-ceramic seal)	✓	50 TC	50 TC	50 TC	50 TC	50 TC	50 TC
		100 TC	100 TC	100 TC	100 TC	100 TC	100 TC
Glass 2 (ceramic - ceramic seal)	✓	50 TC	50 TC	50 TC	50 TC	50 TC	50 TC
		100 TC	100 TC	100 TC	100 TC	100 TC	100 TC
Glass 2 (ceramic - metal seal)	✓	50 TC	50 TC	50 TC	50 TC	50 TC	
		100 TC	100 TC	100 TC	100 TC	100 TC	

Ceramic - ceramic seal

OTM tube



Ceramic adapter

Ceramic - metal seal

OTM tube

Ceramic adapter

Metal tube

Pacific Northwest NATIONAL LABORATORY

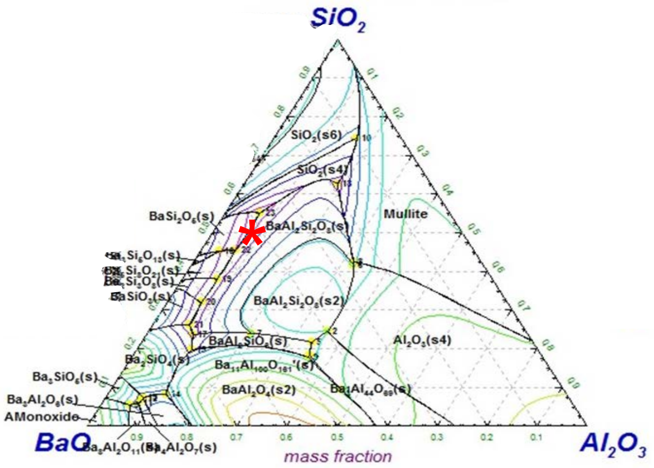
PRAXAIR

Proudly Operated by Battelle Since 1965

Results and Discussion – Glass 1 (C-C seal)

<u>Glass 1</u>

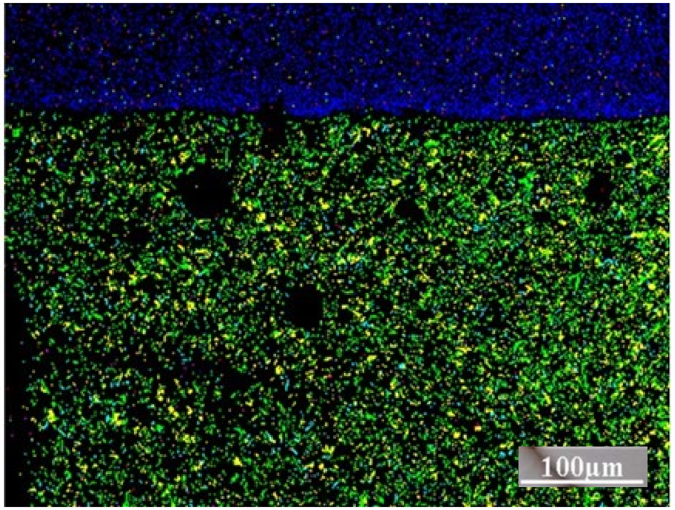
- Barium alumino-silicate glass ceramic seal
- Ceramic- ceramic seal
- Thermal cycled f(T, TC)
- Praxair samples (4200 hr and 27,000 hr)
- Crystallization behavior



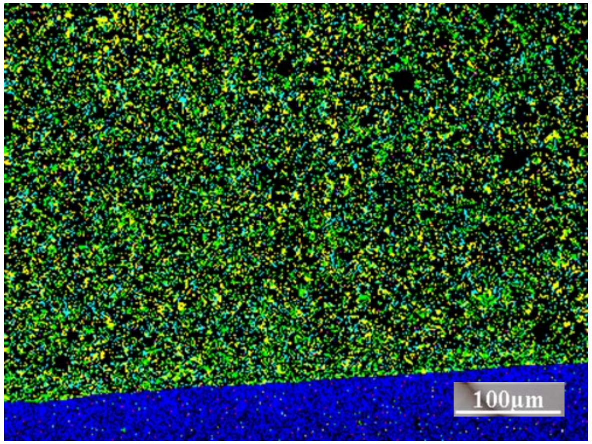
Proudly Operated by Battelle Since 1965

Results and Discussion – Glass 1 (C-C seal)

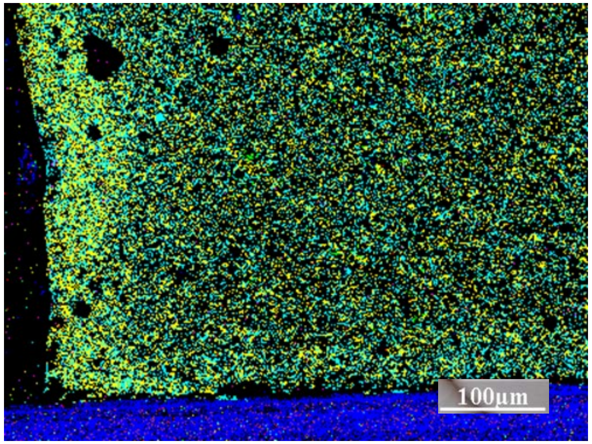
As set



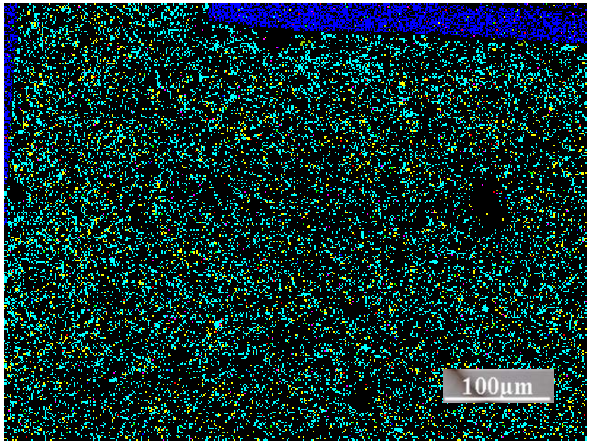
100 TC – 1050°C



100 TC – 1100°C



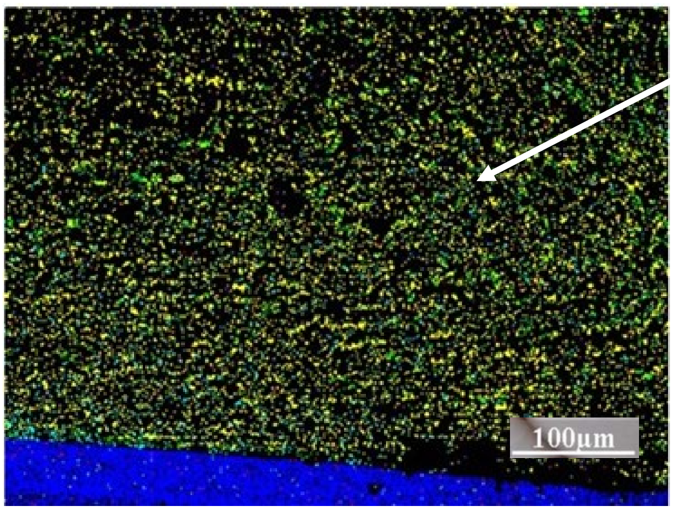
100 TC – 1150°C



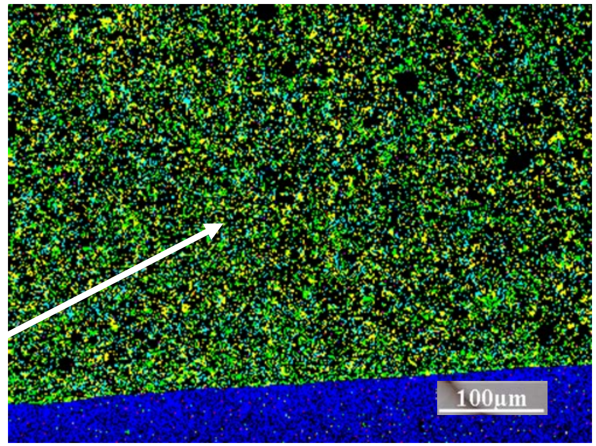
Phase Color	Phase
(blue)	YSZ
(green)	Hexacelsian $BaAl_2Si_2O_8$
(light blue)	Monocelsian $BaAl_2Si_2O_8$
(yellow)	$Ba_5Si_8O_{21}$
(red)	$BaSi_2O_5$
(magenta)	BaCrO4
(black)	Zero solutions

Results and Discussion – Glass 1 (C-C seal)

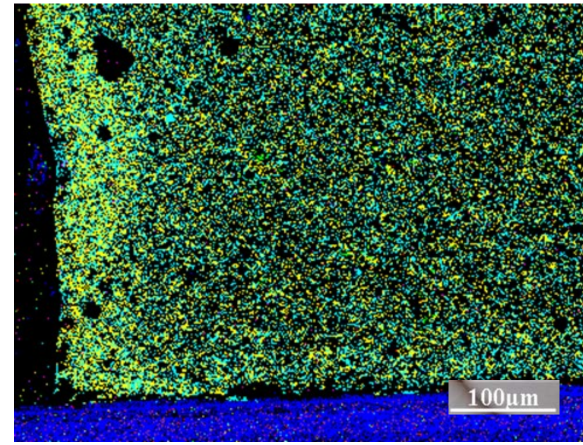
Tested at Praxair
4200 hrs



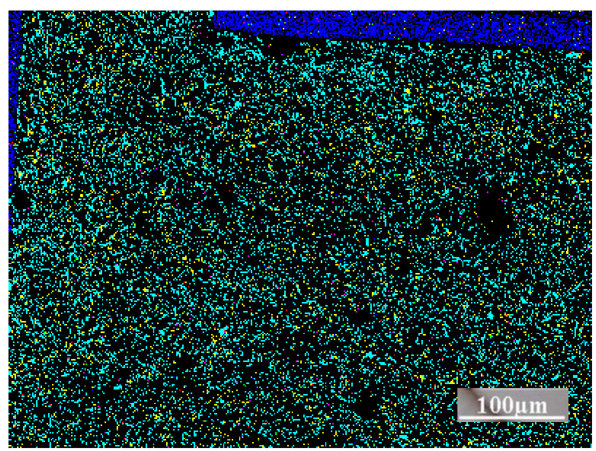
100 TC – 1050°C



100 TC – 1100°C



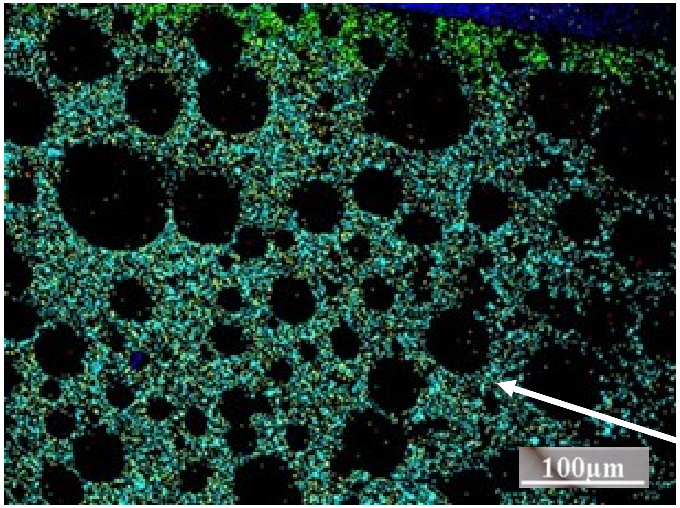
100 TC – 1150°C



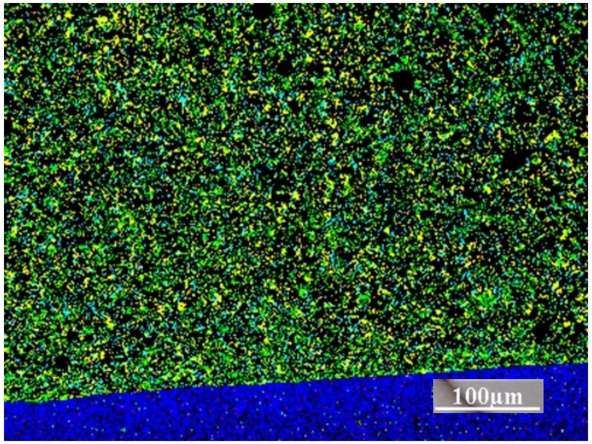
Phase Color	Phase
(blue)	YSZ
(green)	Hexacelsian $BaAl_2Si_2O_8$
(light blue)	Monocelsian $BaAl_2Si_2O_8$
(yellow)	$Ba_5Si_8O_{21}$
(red)	$BaSi_2O_5$
(magenta)	BaCrO4
(black)	Zero solutions

Results and Discussion – Glass 1 (C-C seal)

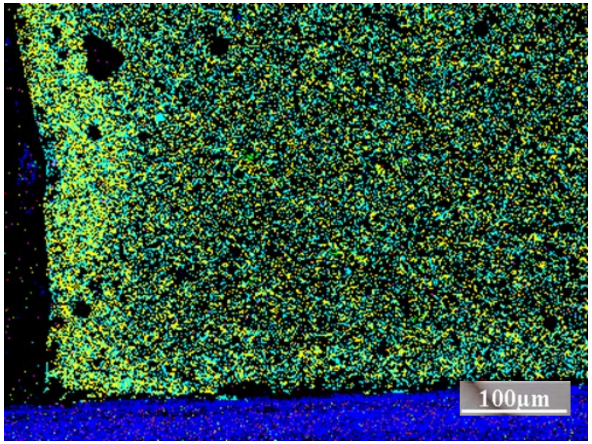
Tested at Praxair
27000 hrs



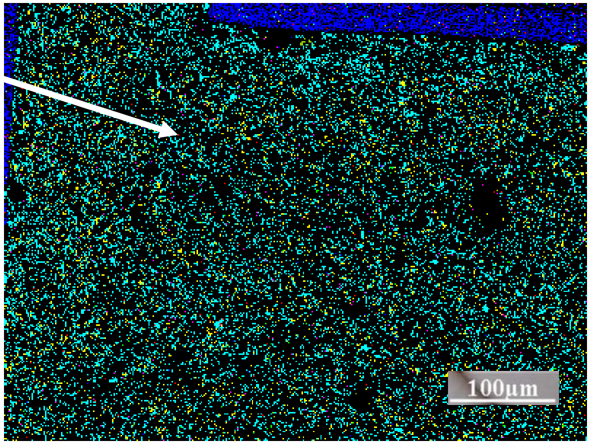
100 TC – 1050°C



100 TC – 1100°C



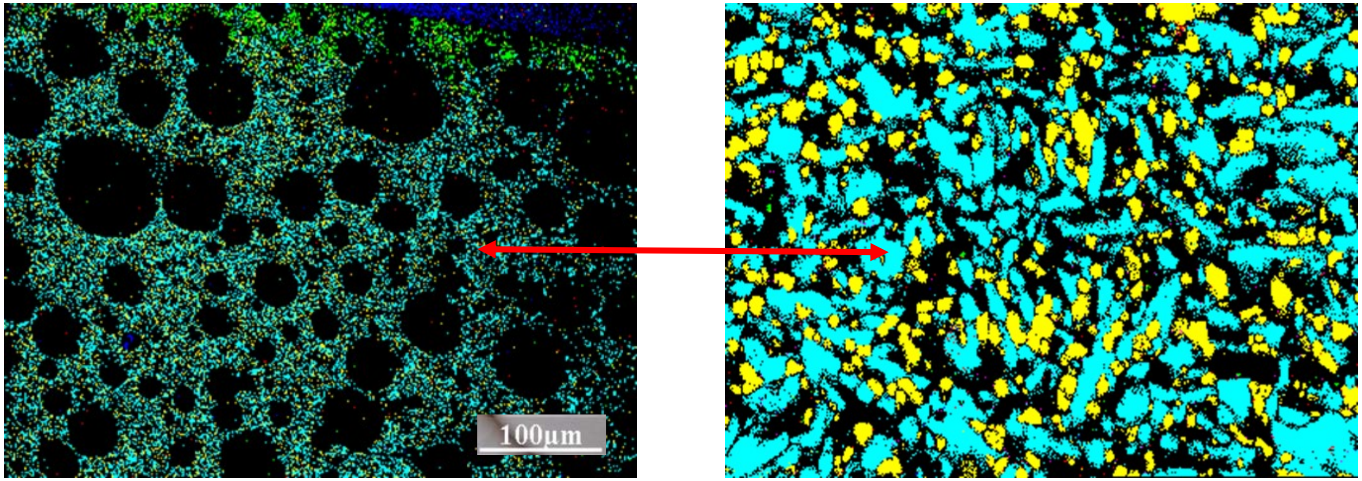
100 TC – 1150°C



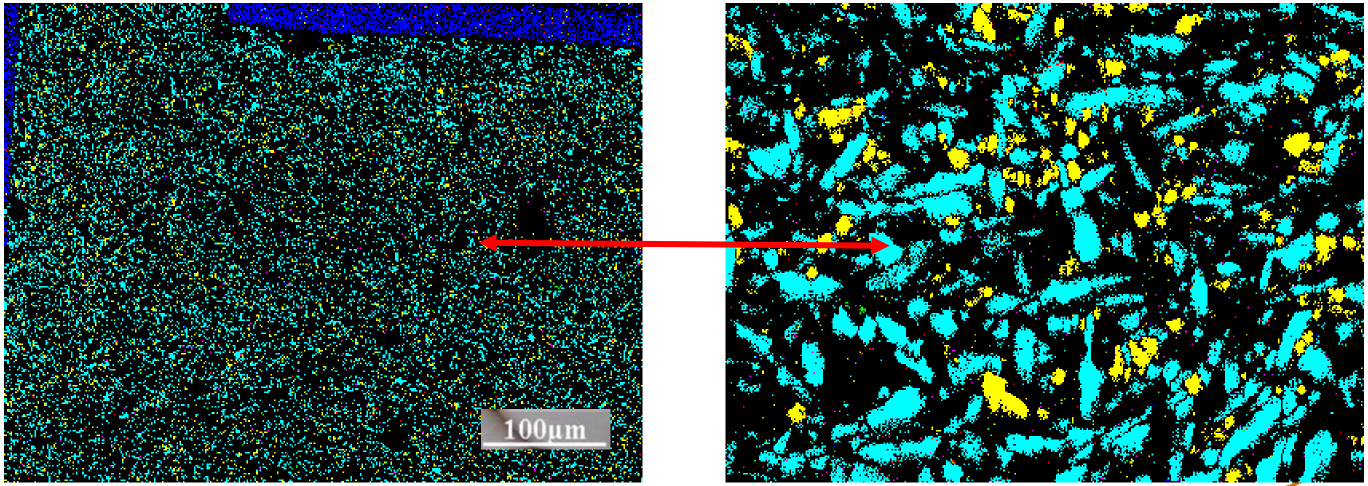
Phase Color	Phase
(blue)	YSZ
(green)	Hexacelsian $BaAl_2Si_2O_8$
(light blue)	Monocelsian $BaAl_2Si_2O_8$
(yellow)	$Ba_5Si_8O_{21}$
(red)	$BaSi_2O_5$
(magenta)	BaCrO4
(black)	Zero solutions

Results and Discussion – Glass 1 (C-C seal)

Tested at Praxair
27000 hrs



Accelerated
100 TC – 1150°C

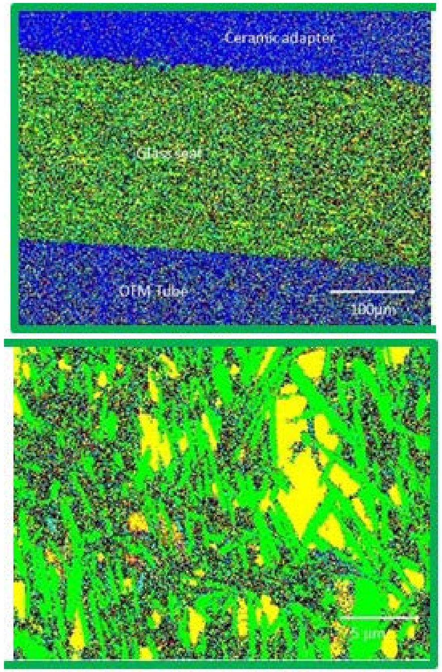


Pacific Northwest
NATIONAL LABORATORY

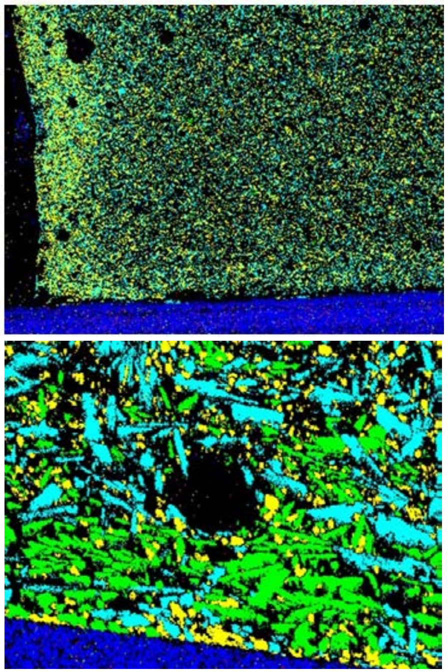
Proudly Operated by Battelle Since 1965

Results and Discussion – Glass 1 (C-C seal)

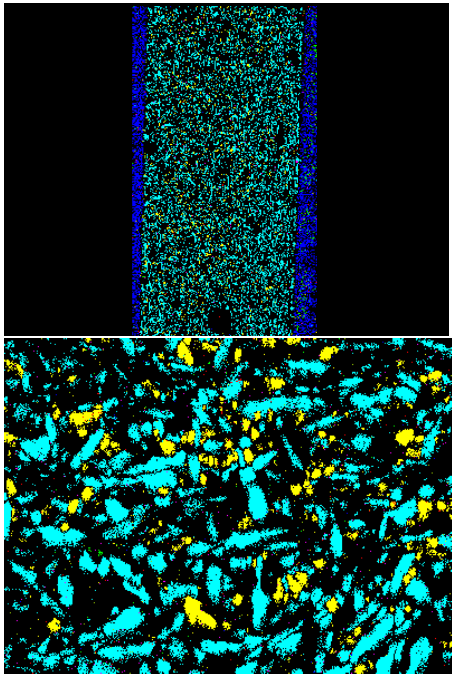
Crystallization behavior as a function of temperature and time



Initial $Ba_5Si_8O_{21}$ and hexacelsian $BaAl_2Si_2O_8$ formation



Some hexacelsian $BaAl_2Si_2O_8$ transforming into monocelsian $BaAl_2Si_2O_8$



Predominant monocelsian $BaAl_2Si_2O_8$ and $Ba_5Si_8O_{21}$

Results and Discussion – Glass 1 (C-C seal)

Thermal Expansion Coefficients of Important Phases

Phase	*Crystal Structure*	*Thermal Expansion (ppm/° C)*
YSZ	*cubic* *tetragonal*	*10.5 - 11* *10.5 - 11*
$BaAl_2Si_2O_8$	*hexagonal*	*8.2*
$BaAl_2Si_2O_8$	*monoclinic*	*2.7*
$BaSi_2O_5$	*orthorhombic*	*15*
$Ba_5Si_8O_{21}$	*orthorhombic*	*13.7*
$BaCrO_4$	*orthorhombic*	*23.5*

Predominant monocelsian as the crystalline phase could be detrimental to the glass/ceramic seal.

Pacific Northwest NATIONAL LABORATORY

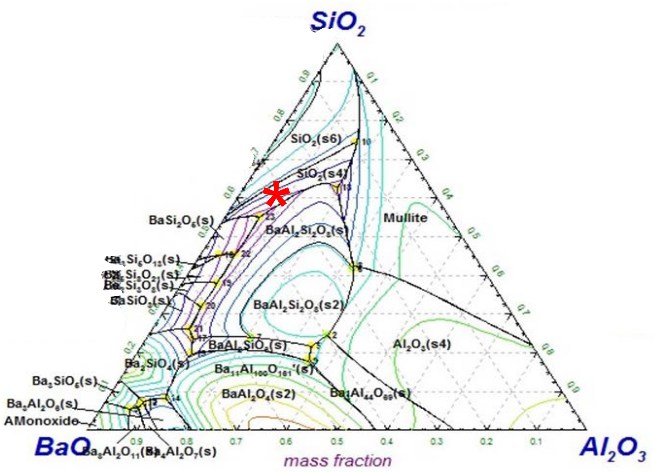
PRAXAIR

Proudly Operated by Battelle Since 1965

Results and Discussion – Glass 2 (C-C, C-M seal)

<u>Glass 2</u>

- Barium alumino-silicate glass ceramic seal
- Ceramic - ceramic, and ceramic - metal seal
- Thermal cycled f(T, TC)
- Praxair samples (2000 and 12,500 hr)
- Crystallization behavior

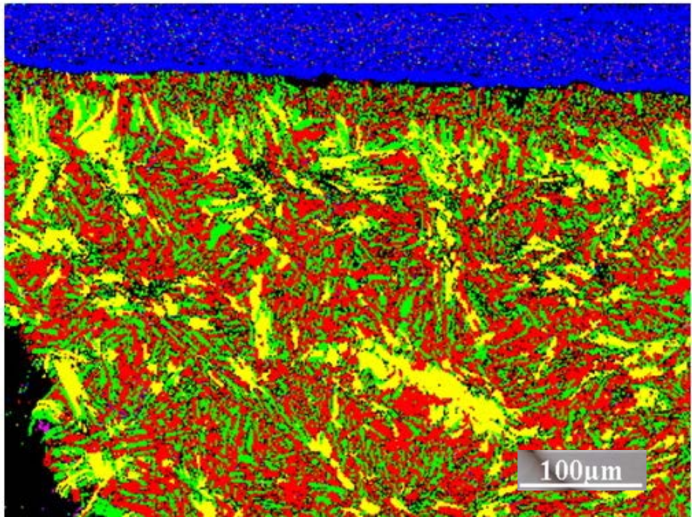


Pacific Northwest NATIONAL LABORATORY

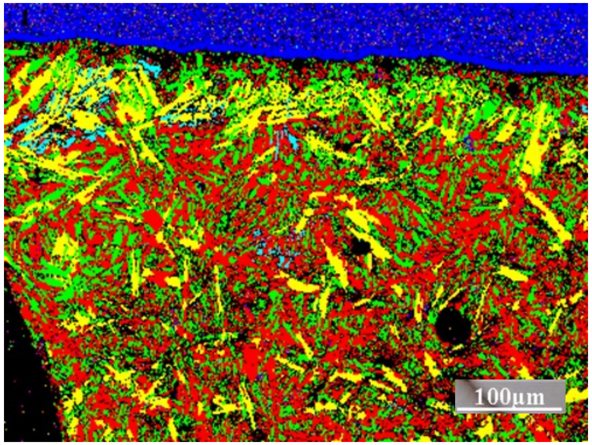
Proudly Operated by Battelle Since 1965

Results and Discussion – Glass 2 (C-C seal)

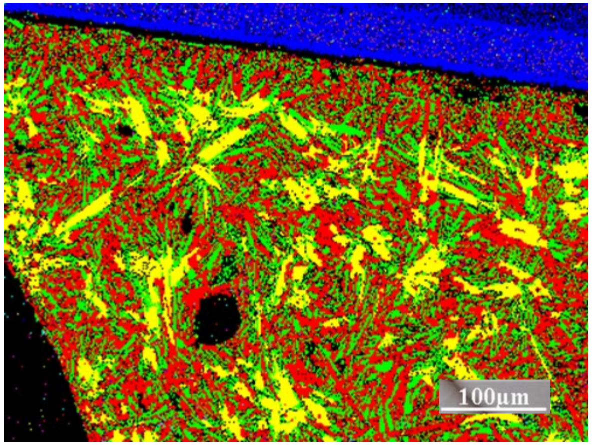
As set



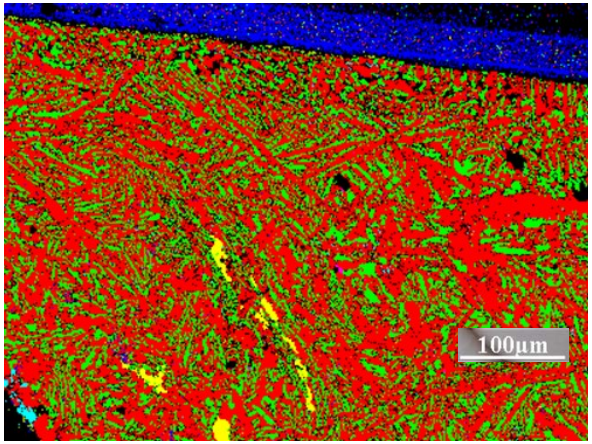
100 TC – 1050°C



100 TC – 1100°C



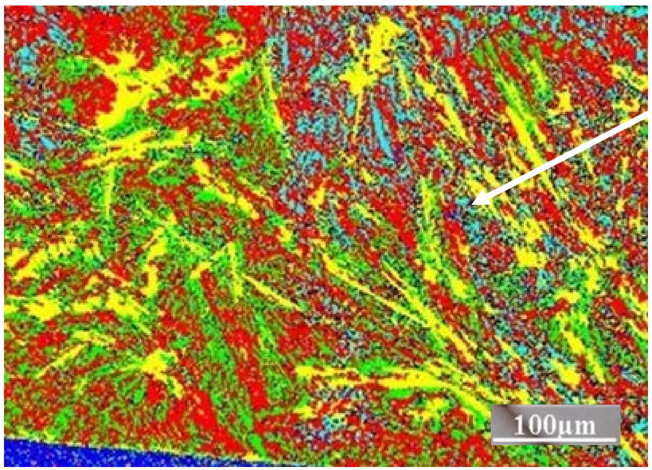
100 TC – 1150°C



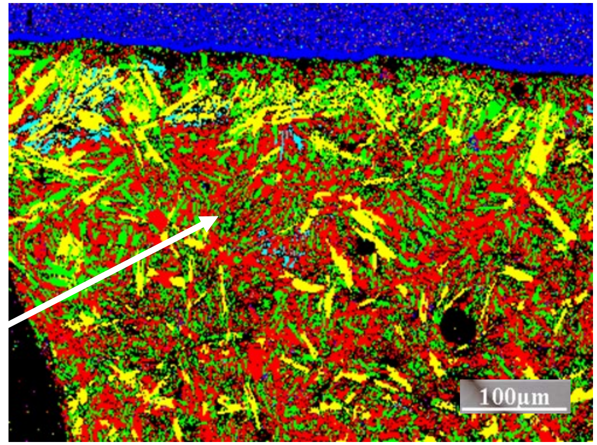
Phase Color	Phase
	YSZ
	Hexacelsian $BaAl_2Si_2O_8$
	Monocelsian $BaAl_2Si_2O_8$
	$Ba_5Si_8O_{21}$
	$BaSi_2O_5$
	BaCrO4
	Zero solutions

Results and Discussion – Glass 2 (C-C seal)

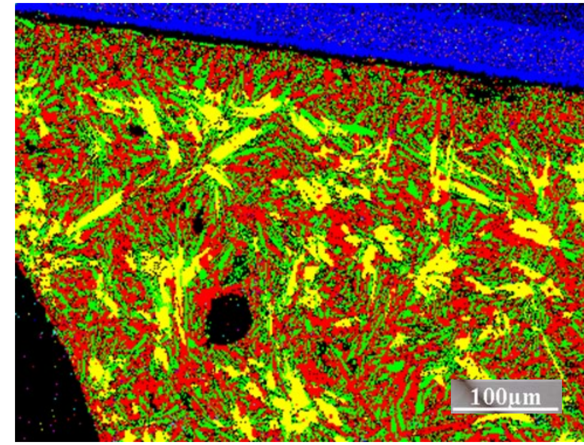
Tested at Praxair
2000 hrs



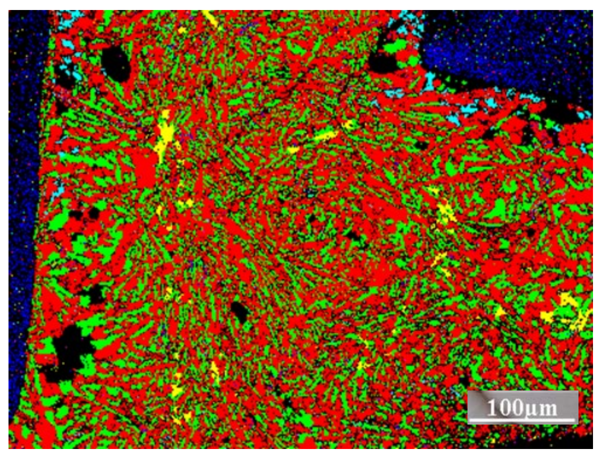
100 TC – 1050°C



100 TC – 1100°C



100 TC – 1150°C



Phase Color	Phase
	YSZ
	Hexacelsian $BaAl_2Si_2O_8$
	Monocelsian $BaAl_2Si_2O_8$
	$Ba_5Si_8O_{21}$
	$BaSi_2O_5$
	BaCrO4
	Zero solutions

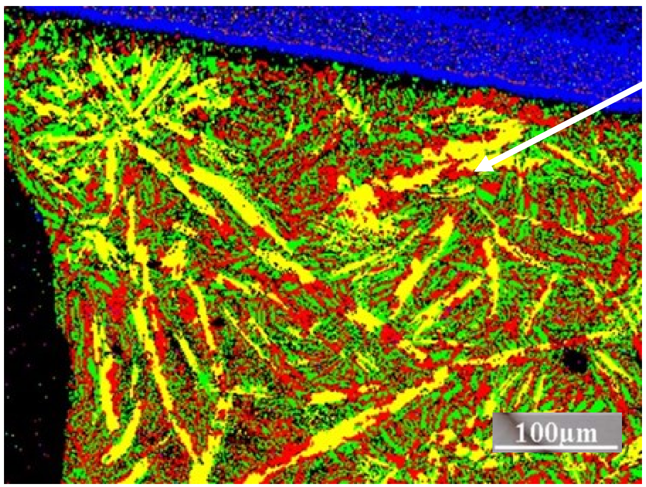
PRAXAIR

Pacific Northwest
NATIONAL LABORATORY

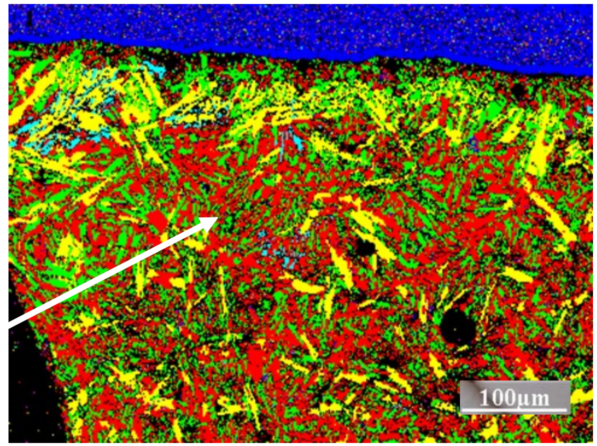
Proudly Operated by Battelle *Since 1965*

Results and Discussion – Glass 2 (C-C seal)

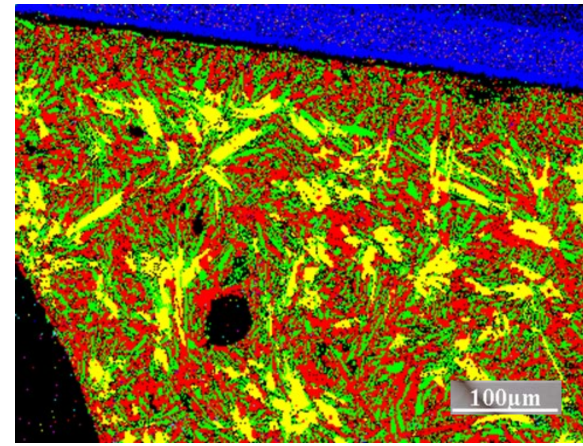
Tested at Praxair
12,500 hrs



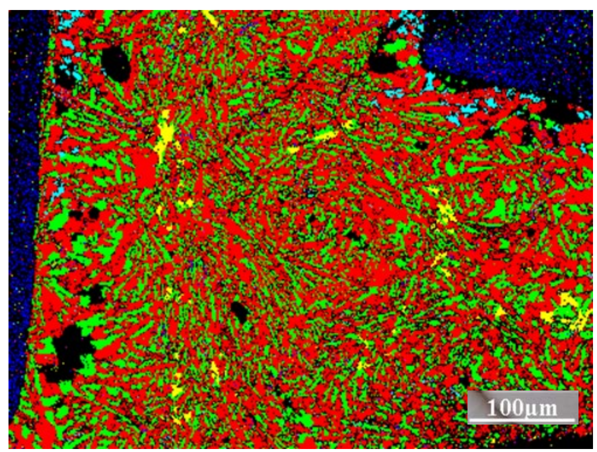
100 TC – 1050°C



100 TC – 1100°C



100 TC – 1150°C



Phase Color	Phase
	YSZ
	Hexacelsian $BaAl_2Si_2O_8$
	Monocelsian $BaAl_2Si_2O_8$
	$Ba_5Si_8O_{21}$
	$BaSi_2O_5$
	BaCrO4
	Zero solutions

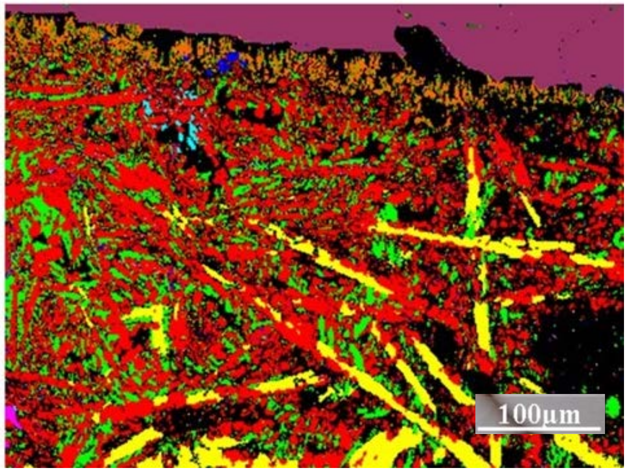
PRAXAIR

Pacific Northwest
NATIONAL LABORATORY

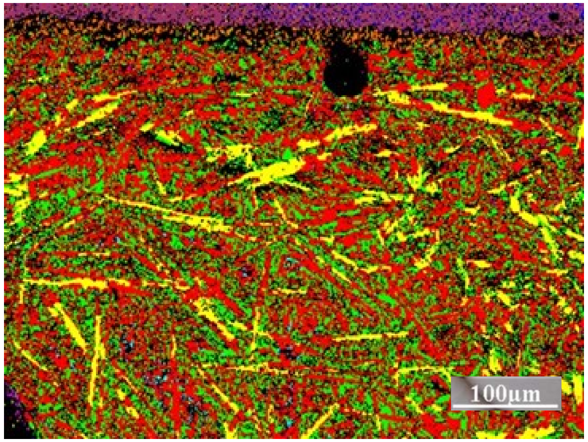
Proudly Operated by Battelle Since 1965

Results and Discussion – Glass 2 (C-M seal)

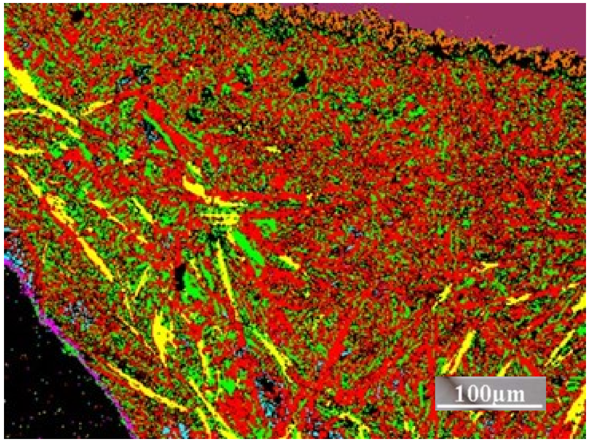
As set



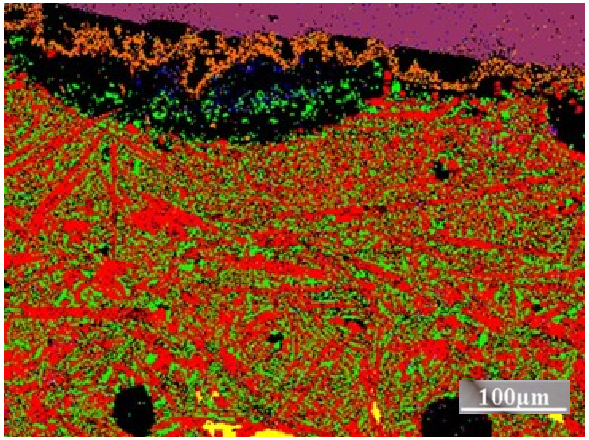
100 TC – 1000°C



100 TC – 1050°C



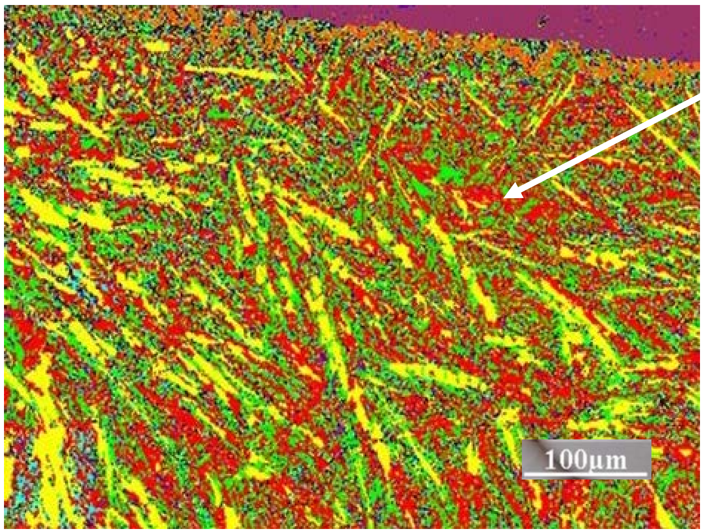
100 TC – 1100°C



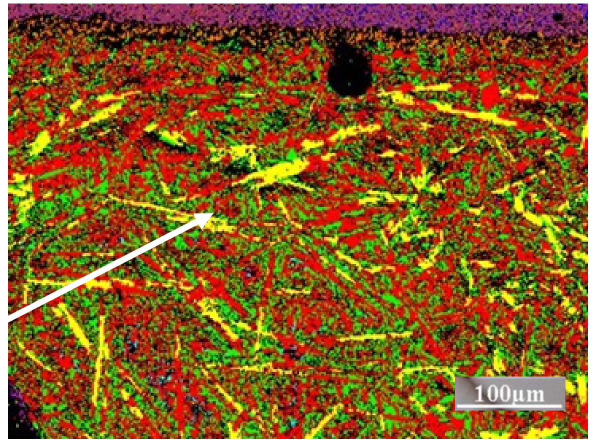
Phase Color	Phase
(green)	Hexacelsian $BaAl_2Si_2O_8$
(blue)	YSZ
(cyan)	Celsian $BaAl_2Si_2O_8$
(yellow)	$Ba_5Si_8O_{21}$
(red)	Sanbornite $BaSi_2O_5$
(orange)	Eskolaite Cr_2O_3
(dark magenta)	Ferchromide (FeCr)
(magenta)	Hashemite $BaCrO_4$
(black)	Zero Solution

Results and Discussion – Glass 2 (C-M seal)

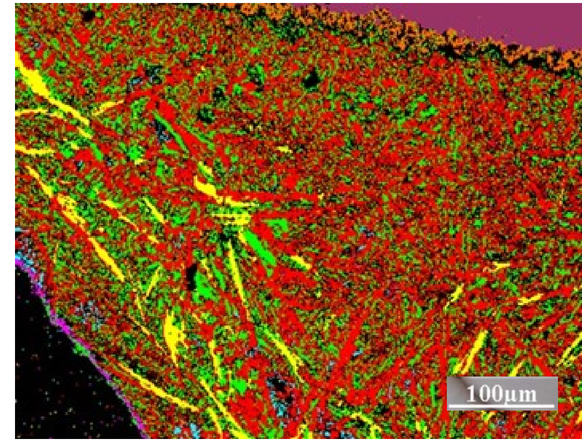
Tested at Praxair
2000 hrs



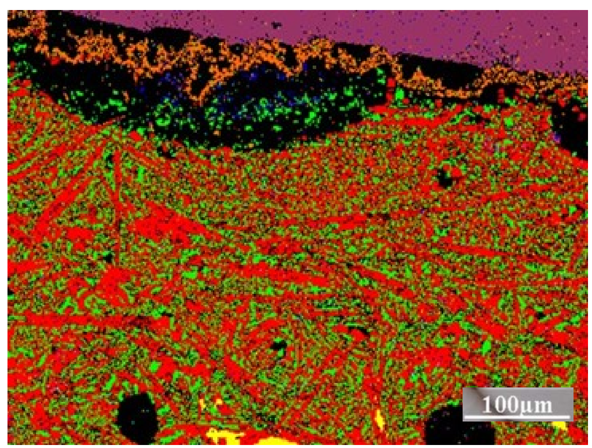
100 TC – 1000°C



100 TC – 1050°C



100 TC – 1100°C



Phase Color	Phase
	Hexacelsian $BaAl_2Si_2O_8$
	YSZ
	Celsian $BaAl_2Si_2O_8$
	$Ba_5Si_8O_{21}$
	Sanbornite $BaSi_2O_5$
	Eskolaite Cr_2O_3
	Ferchromide (FeCr)
	Hashemite $BaCrO_4$
	Zero Solution

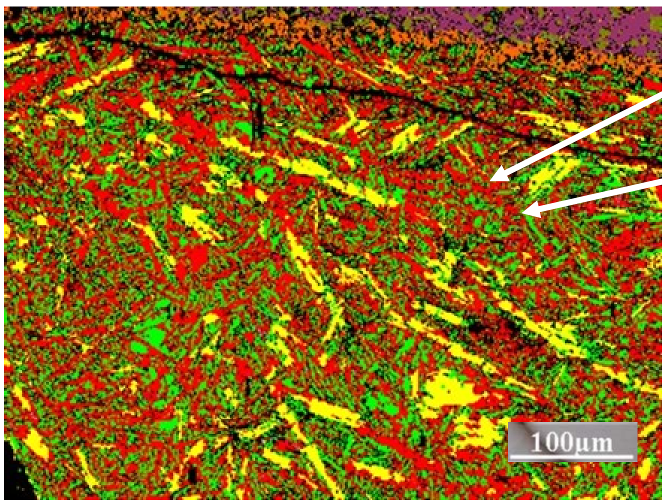
PRAXAIR

Pacific Northwest
NATIONAL LABORATORY

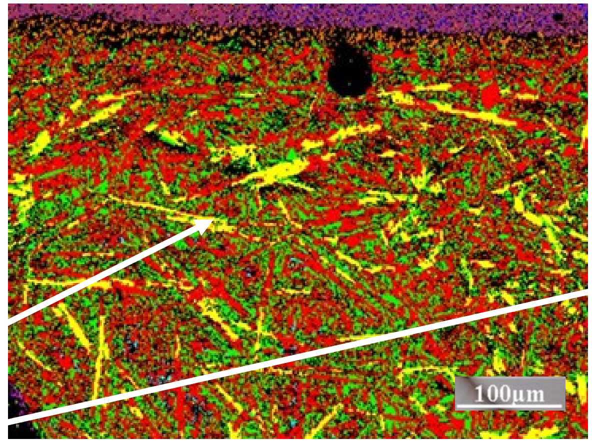
Proudly Operated by Battelle Since 1965

Results and Discussion – Glass 2 (C-M seal)

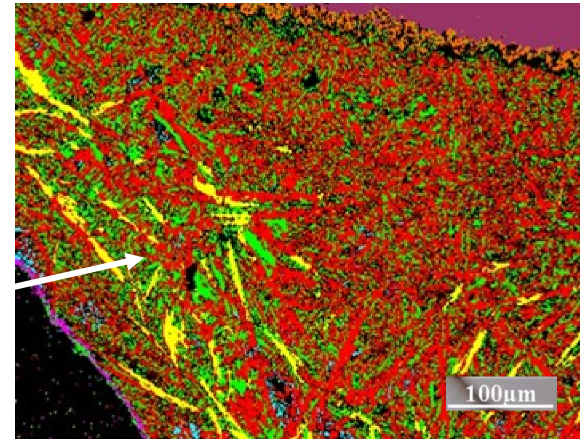
Tested at Praxair
12,500 hrs



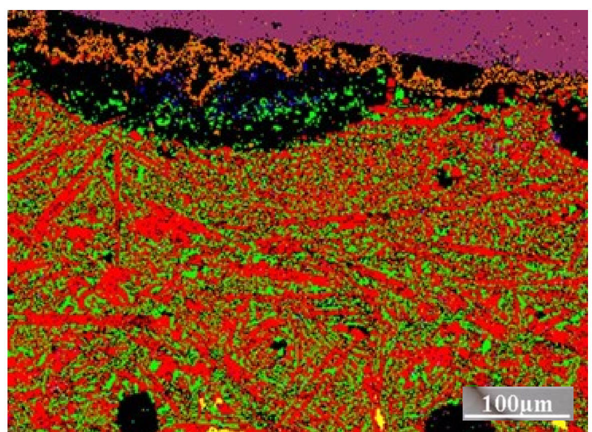
100 TC – 1000°C



100 TC – 1050°C



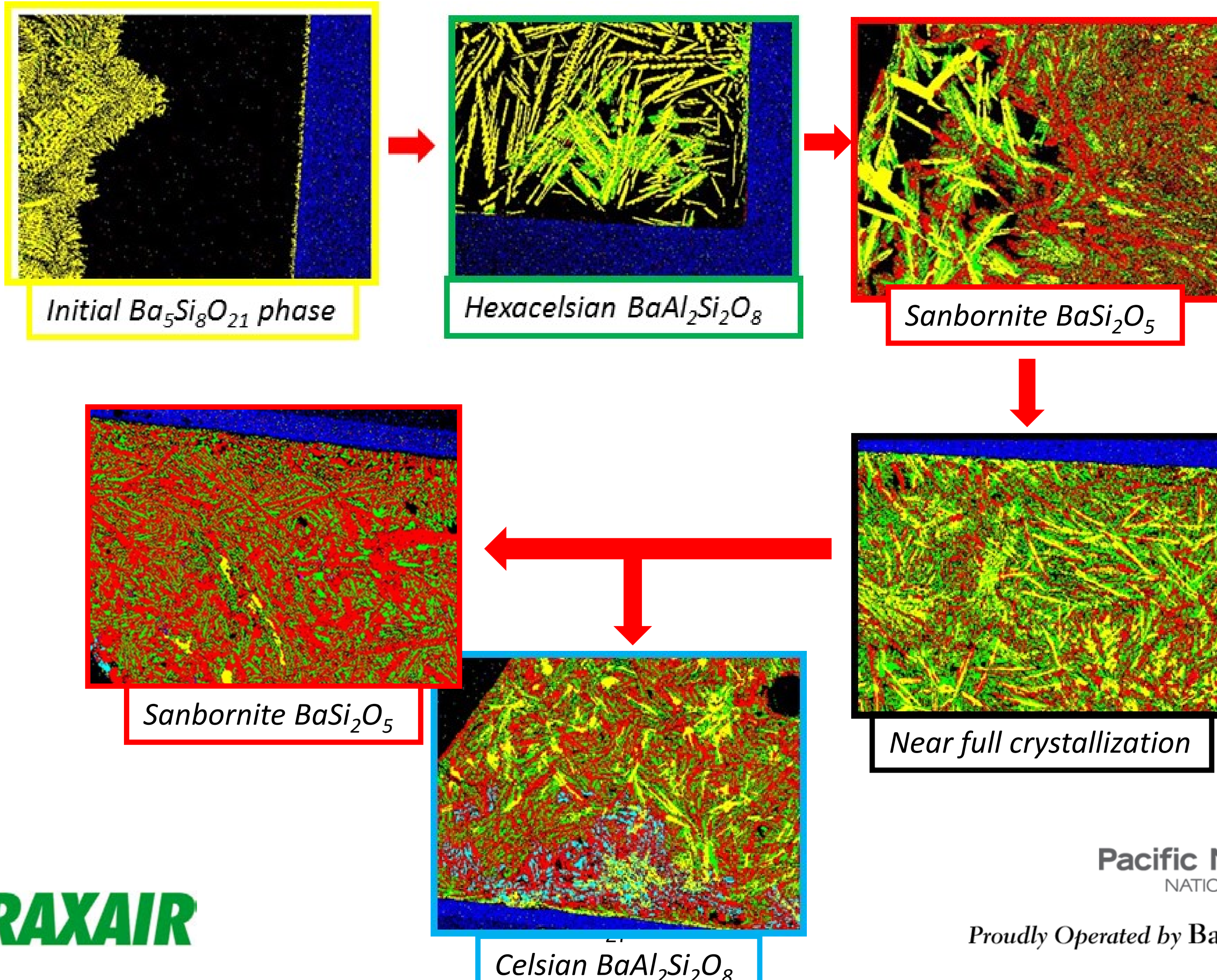
100 TC – 1100°C



Phase Color	Phase
(green)	Hexacelsian $BaAl_2Si_2O_8$
(blue)	YSZ
(cyan)	Celsian $BaAl_2Si_2O_8$
(yellow)	$Ba_5Si_8O_{21}$
(red)	Sanbornite $BaSi_2O_5$
(orange)	Eskolaite Cr_2O_3
(purple)	Ferchromide (FeCr)
(magenta)	Hashemite $BaCrO_4$
(black)	Zero Solution

Results and Discussion – Glass 2 (C-M seal)

Crystallization behavior as a function of temperature and time



Next Steps and Concluding Remarks

Next Steps

- Complete accelerated testing to real working system for Glass 2
- Analyze additional long term tested samples at Praxair.

Concluding Remarks

- Accelerated life testing enables the prediction of the crystallization behavior at long times in real test atmospheres
- Glass 1 will likely form predominately monocelsian at long times which will induce stress in the seal potentially leading to failure
- Glass 2 has preferred crystallization behavior and is predicted to be stable over long times

Acknowledgements

The authors wish to thank the Office of Technology Transitions and Jai-Woh Kim and Steve Markovich from DOE Office of Fossil Energy for their support of this project as part of the Technology Commercialization Funding

PRAXAIR

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle Since 1965