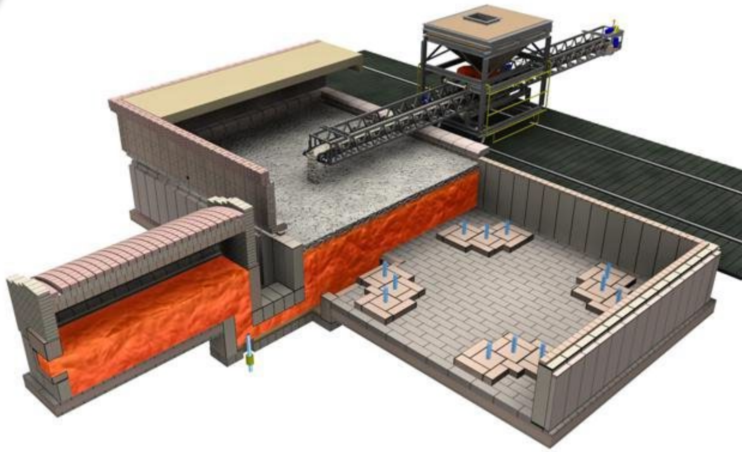
Amber Glass Foam Reduction



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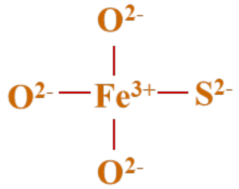
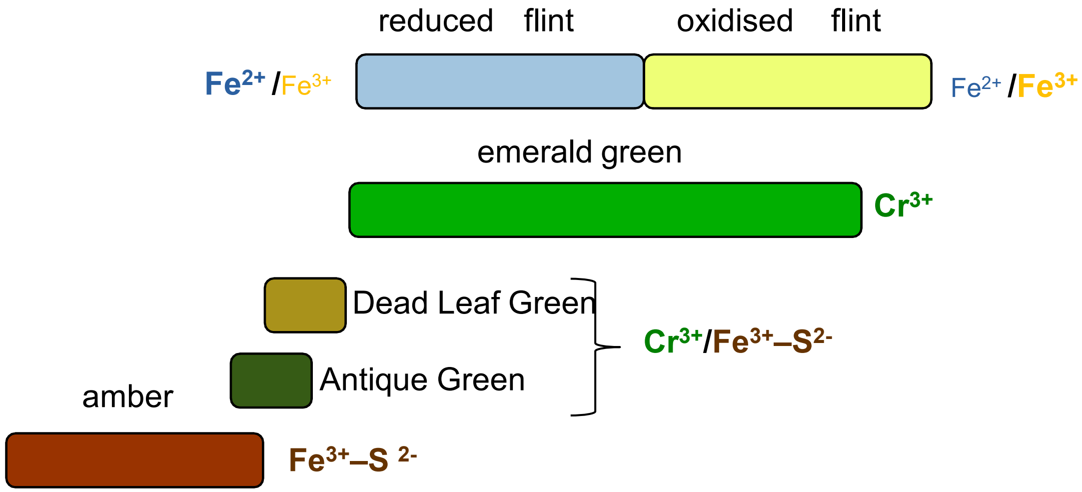
PACIFIC NORTHWEST NATIONAL LAB

Amber Glass Foam Reduction

- Approx. 25% of container glass production
- Chromophore:
  - Iron in an oxidized state (Fe^{3+})
  - Sulfur in a reduced oxidation state (S^{2-})
- Strong UV blocking
- Gases produced during melting → foaming
- Carbon is most common reducing agent
- Test methods:
  - Feed expansion tests (FETs) → compare foaming
  - UV-Vis spectroscopy → confirm chromophore



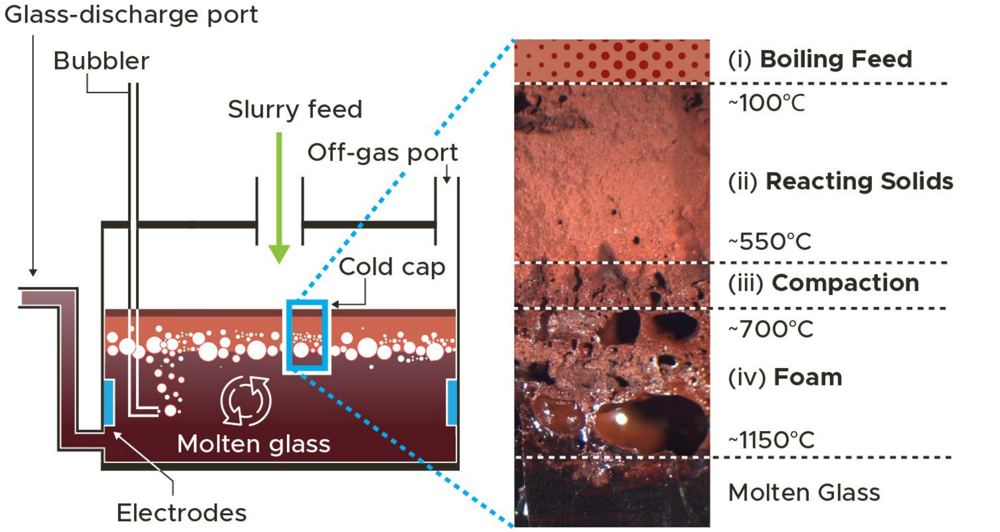
Redox Range of Commercial Glasses



Batch Redox	Color
0 to +20	White/Colorless
-15 to 0	Green
-25 to -15	Dead Leaf/ Antique Green
-30 to -20	Amber

PNNL Glass Vitrification Work

- Focus on slurry feed (waste + glass formers) → molten glass interactions
- Cold cap studies: minimizing foaming & bubbling
- 30+ years modeling & testing vitrification at Hanford

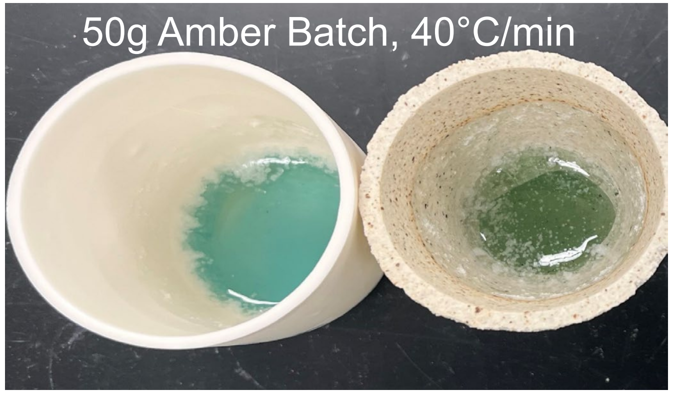


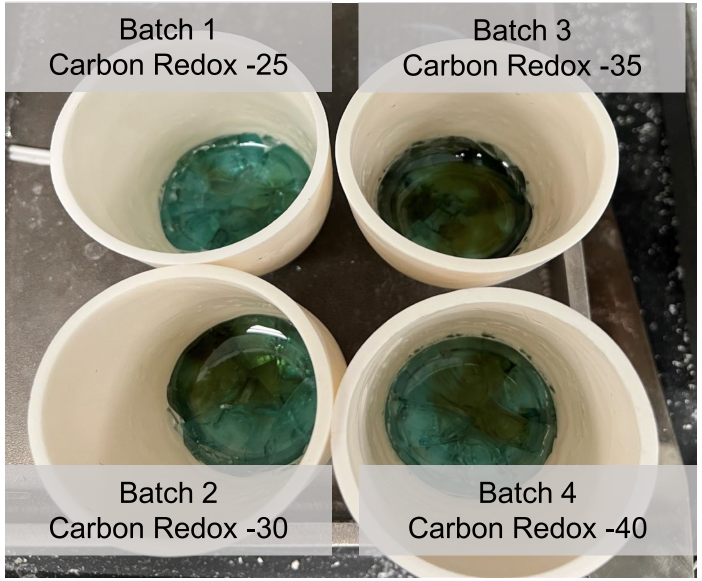
Hanford Melter and Foaming

- Hanford wastes (nitrate + organics) → vitrified as oxide glass for isotope immobilization
- Reductants reduce nitrates → control foaming & glass redox
- Carbon-based reductants studied since 1990s: organic acids, sucrose, graphite, etc.[1,2,3]
- Sucrose (Hanford baseline) → high acetonitrile in off-gas[4]
- Formic acid (DWPF baseline) → flammability risk; replaced by glycolic acid[5]
- **Ceramic reductants** for low activity waste (BN, SiC, B_4C, B_6Si, VB_2)[6,7]

References
1. Ryan, J. L. et al., PNL-10510 (1995).
2. 2. Seymour, R. G. et al., WHC-SD-WM-SP-008 (1995).
3. Seymour, R. G. et al., WHC-SD-WM-SP-009 (1995).
4. Matlack, K., and Pegg, I. et al., VSL-19S4573-1, Rev A (2019).
5. Choi, A. S. et al., SRNL-STI-2014-00355 (2014).
6. Rigby, J. C. et al., Journal of the American Ceramic Society. (2024)
7. Rigby, J. C. et al., International Journal of Applied Glass Science. (2025)

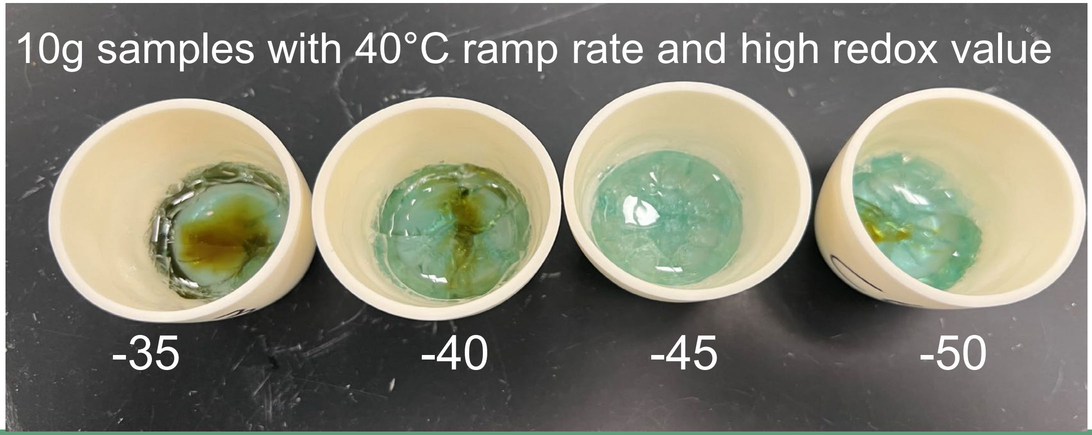
Challenges of Amber Glass at Lab Scale

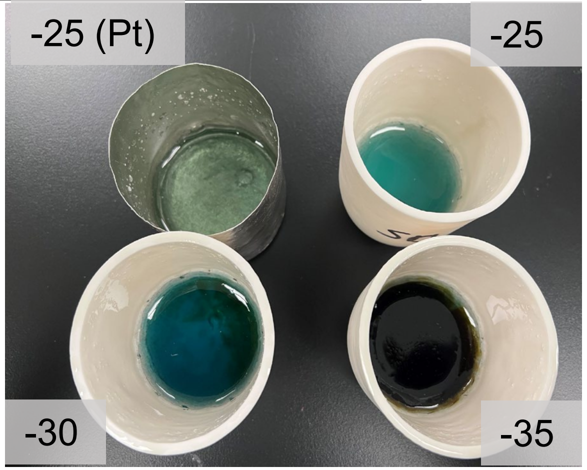


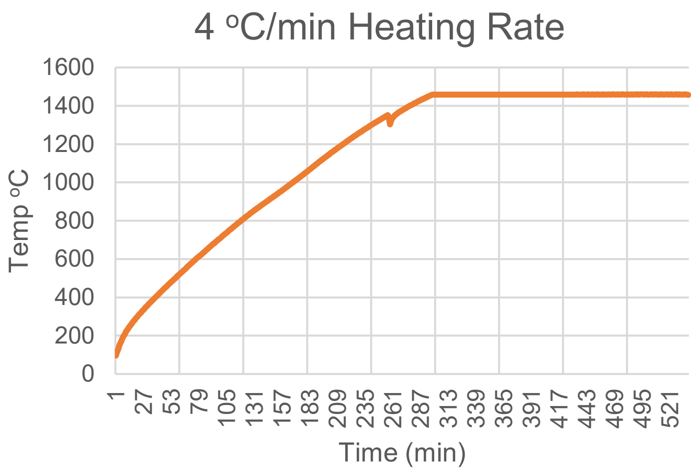


100g Amber batch, 10°C/min

- Lab scale atmospheric furnace conditions
  - Small furnaces used with room atmosphere
- Volume to surface area
  - Smaller batch → more oxidized glass
- Ramp Rate
  - Slow ramp rates → more oxidized glass

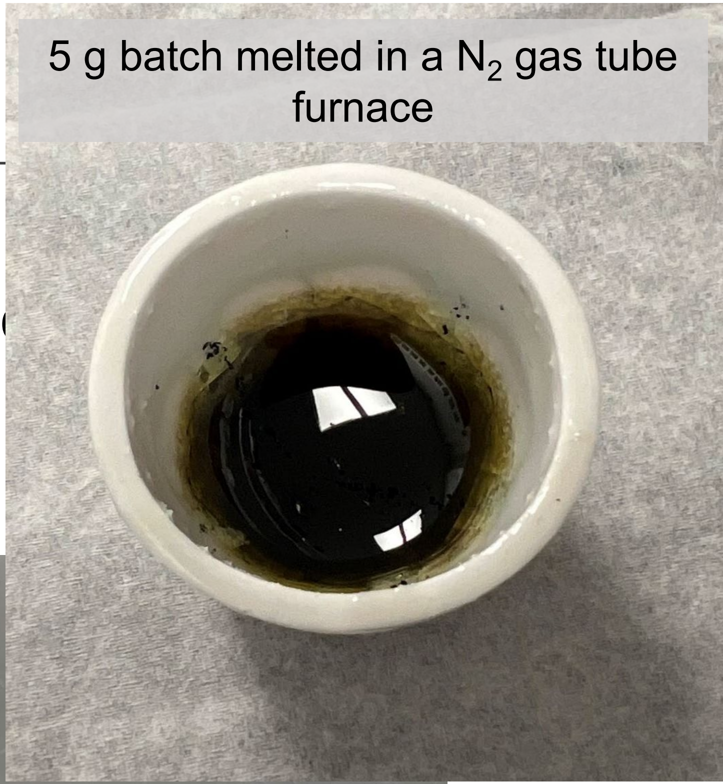


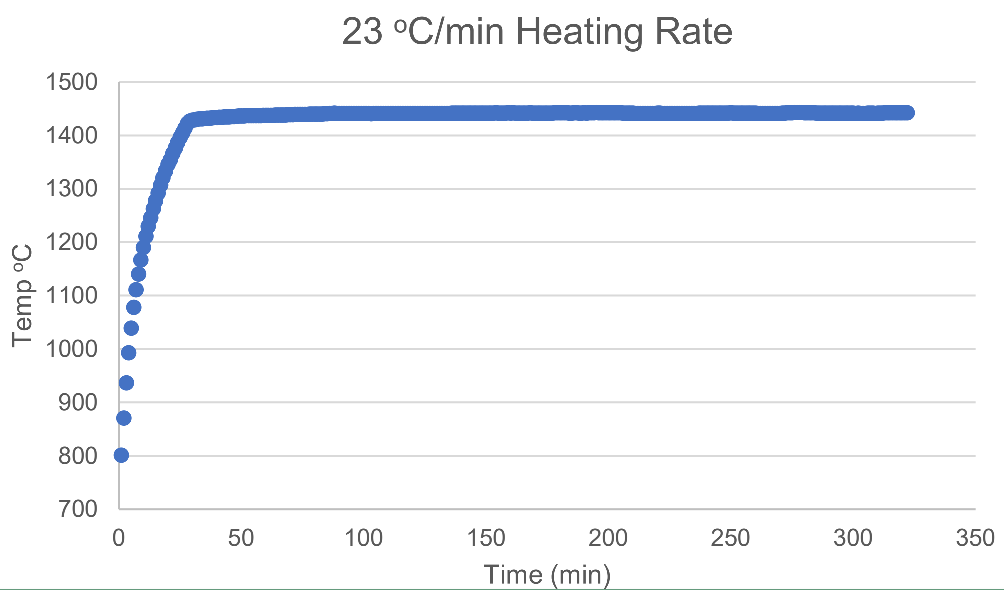


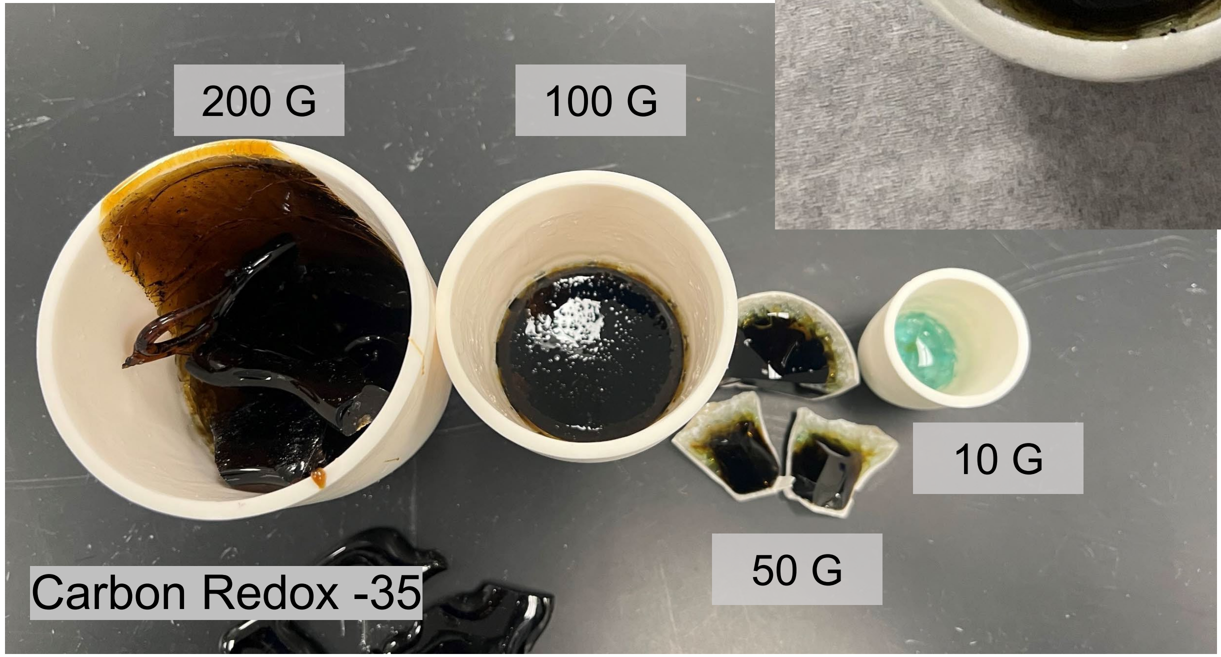


Lab Scale Oxidized State Solutions

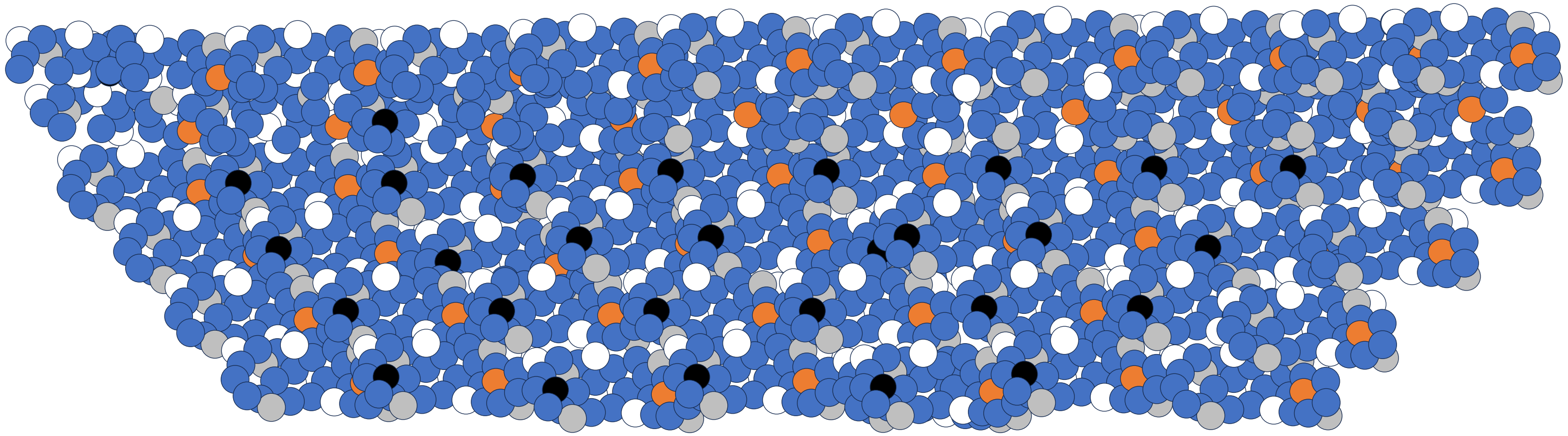
- Larger batches to reduce surface to volume ratio
- Faster heating rates to reduce time for batch to interact with the atmosphere
- Inert gas for small batches (N_2)







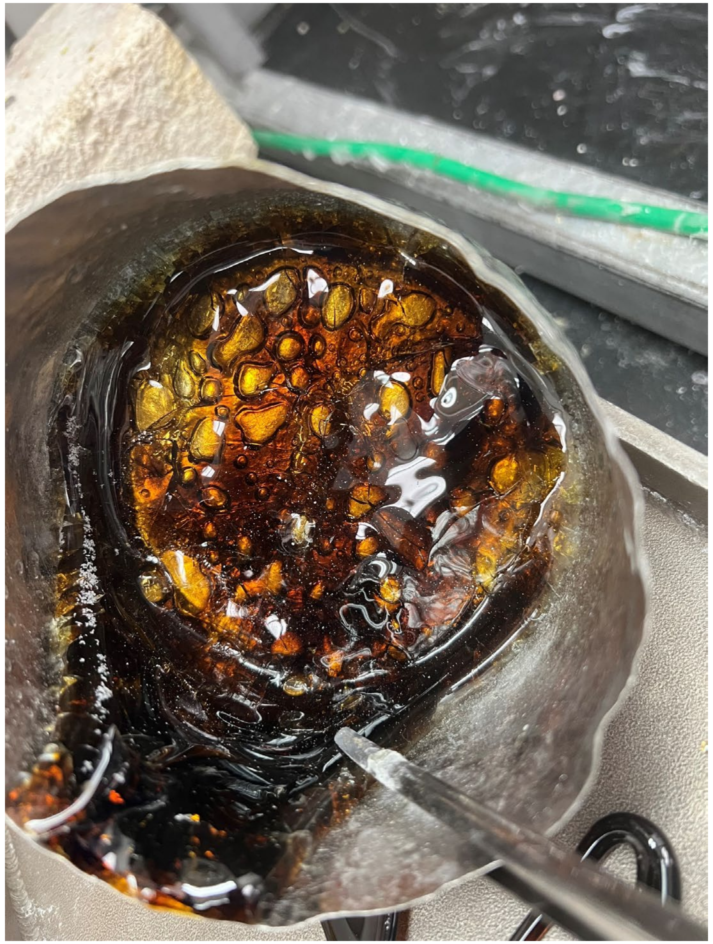
Previous: Amber Glass Reduced with Carbon



- Silica
- Soda Ash
- Limestone
- Carbon
- Saltcake

Carbon-reduced batches: sensitive to batch size, heating rate, and atmosphere

Initial Amber Glass Melt

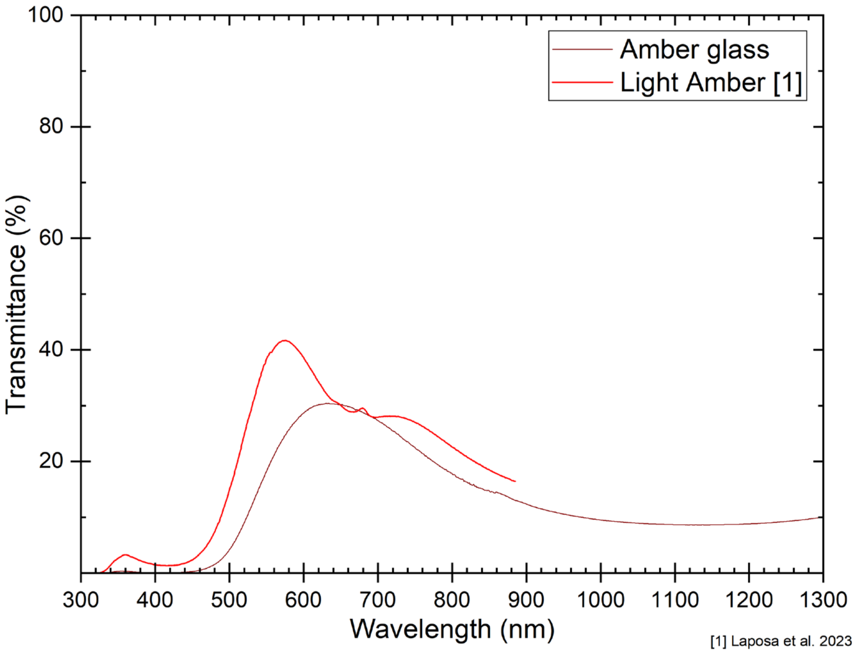


- Industrial raw materials (provided by Gallo Glass)
- 200 g batch melted in platinum crucible
- Room temperature to 1450 °C at 40 °C/min
- Dwell at 1450 °C for 4 hours

SEM EDS Analysis

SEM Results			Amber Batch Recipe	
Element	**Oxide**	**Oxide %**	**Component**	**Target (%)**
Si	SiO_2	72.17	SiO_2	72.734
Ca	CaO	10.95	CaO	11.35
Mg	MgO	0.7	MgO	0.856
Al	Al_2O_3	1.59	Al_2O_3	1.5
Fe	FeO	0.37	Fe_2O_3	0.44
Ti	TiO_2	0.02	TiO_2	0.035
S	SO_3	0.05	SO_3	0.08
Cl	Cl	0	Cl	0.004
Na	Na_2O	13.7	Na_2O	12.673
K	K_2O	0.35	K_2O	0.327

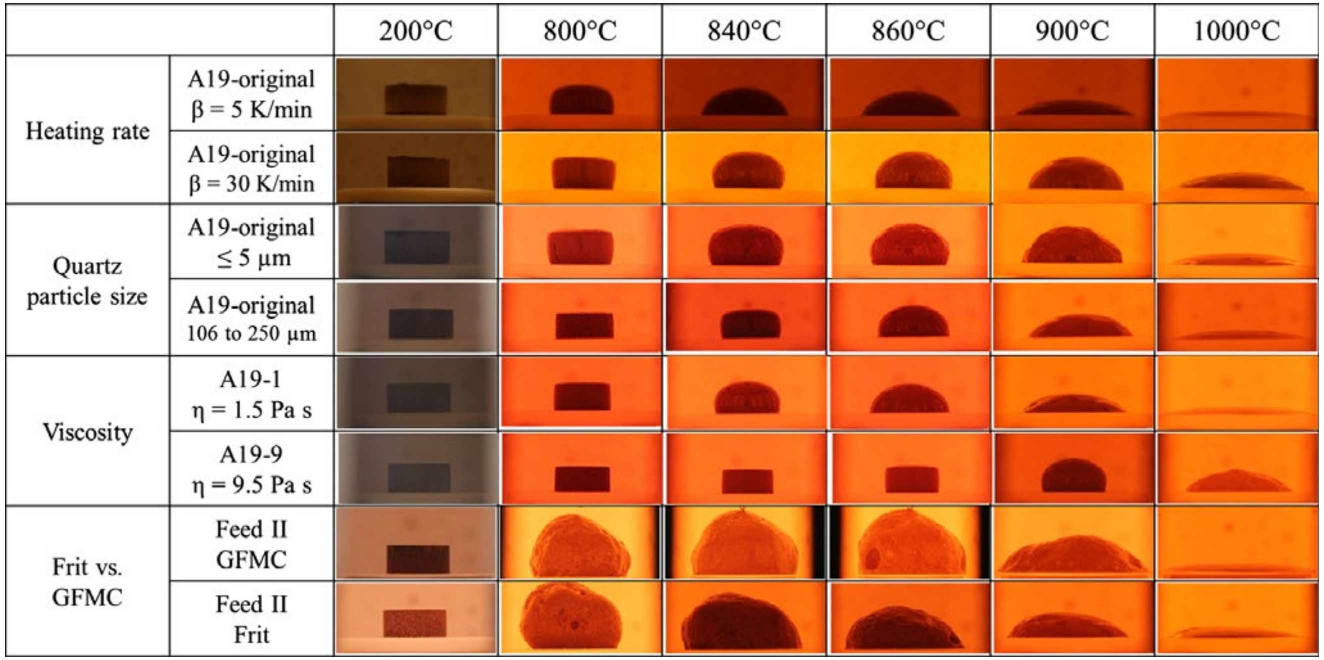
UV-Vis of amber glass in Pt Melt vs Literature



[1] Laposa et al. 2023

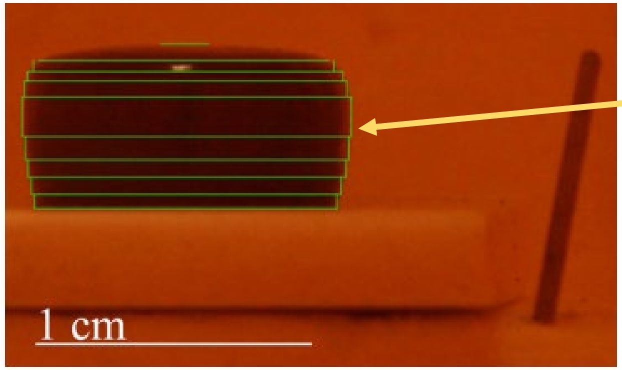
Feed Expansion Test (FET)

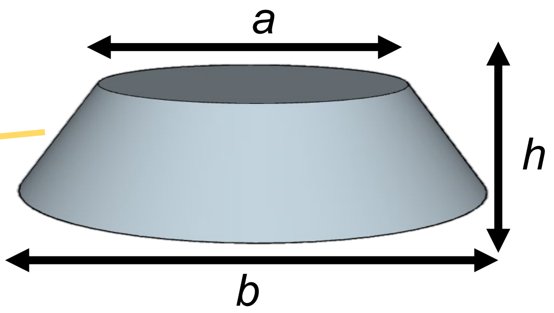
- 1 g pressed pellet heated from room temperature at 10 ^{o}C/min
- Simple test to observer and measure foaming
- Used to compare different variables effects
- Video recorded of the test



Feed expansion test (FET) volumetric expansion

- Using pellets allows for easy calculation of volume and porosity
  - Assume that feed pellets have rotational symmetry during melting
  - Approximate volume as stacked cylinders:



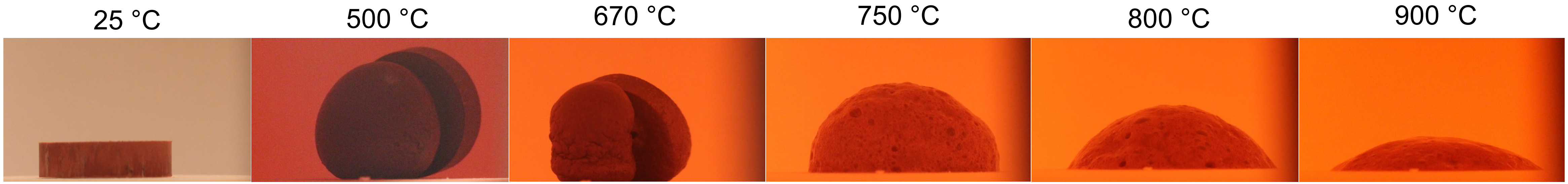


$$V_i = \frac{\pi}{12}\left(a_i^2 + a_i b_i + b_i^2\right)h_i$$

$$V = \delta^3 \sum_i V_i$$

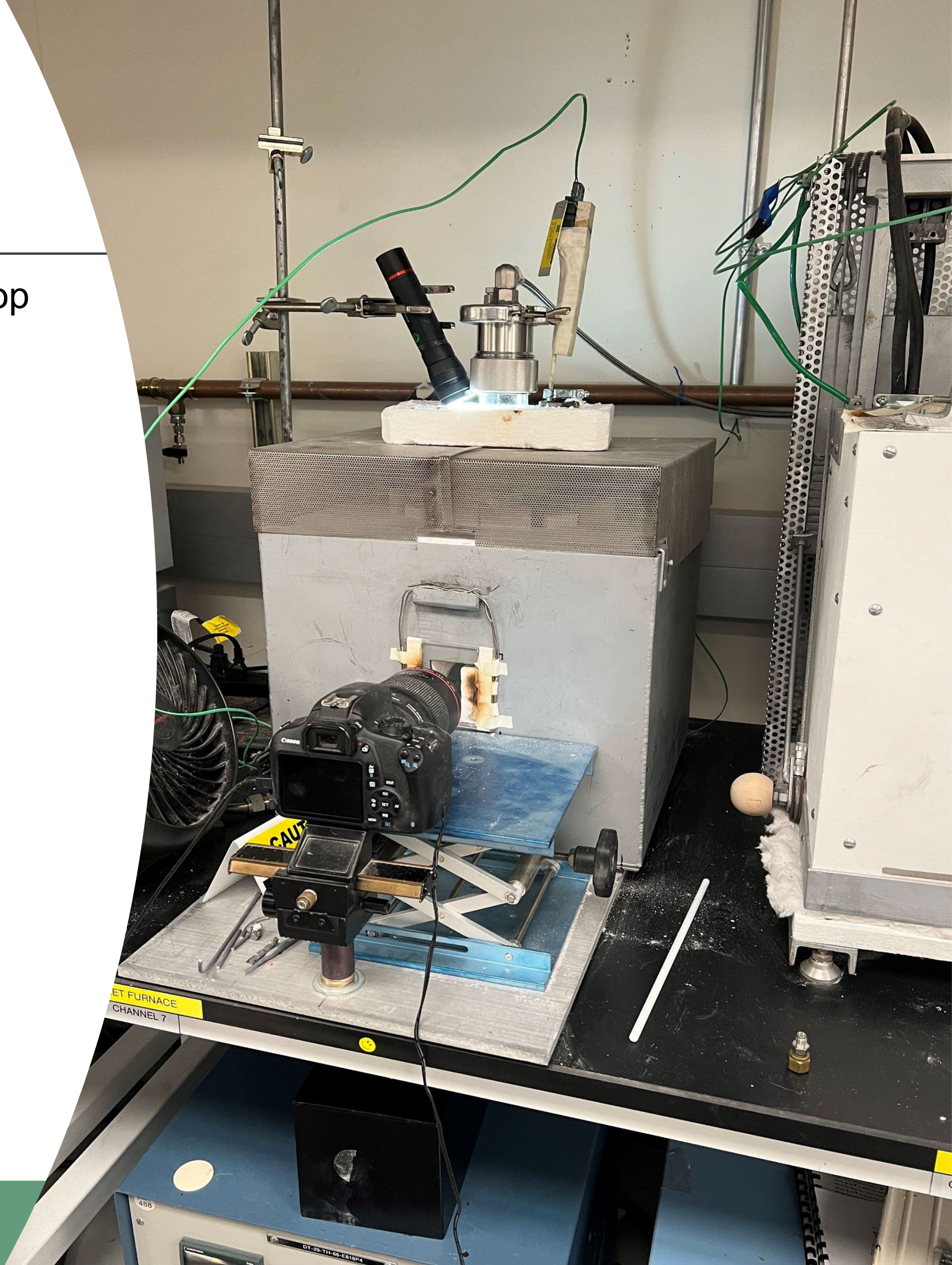
$$\delta = scale\ factor$$

Hilliard, Z. and P. Hrma. J. Am. Ceram. Soc. 1-8 (2015).

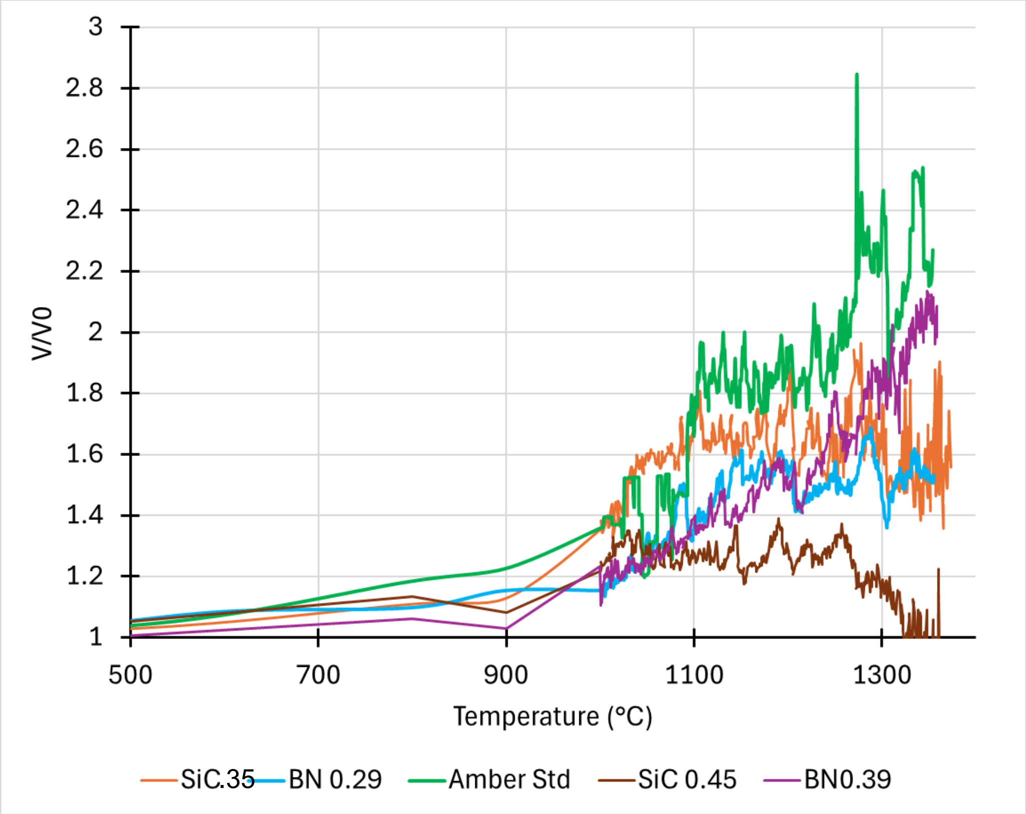


N_2 Amber FET

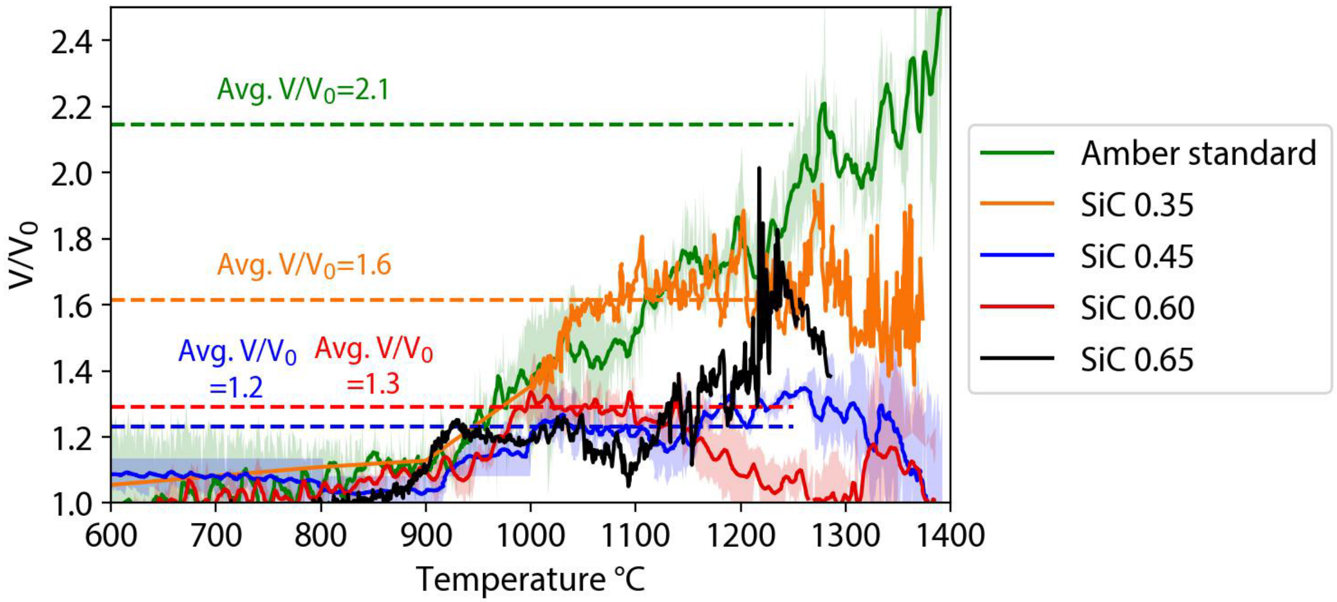
- 3-inch diameter quartz tube with N_2 hose connected from the top of the furnace.
- 1 g pellet
- On an alumina disc
- Alumina disk sits on insulation with quartz tube resting on insulation around the alumina disk
- Ramp rate: 10 ^{o}C/min, room temperature to 1400 ^{o}C
- Tested various reducing agents:
    - Standard amber (C),
    - High amber (C3),
    - Boron Nitride (BN),
    - Silica Carbide (SiC)
    - Vanadium Diboride (VB_2)



FET Results

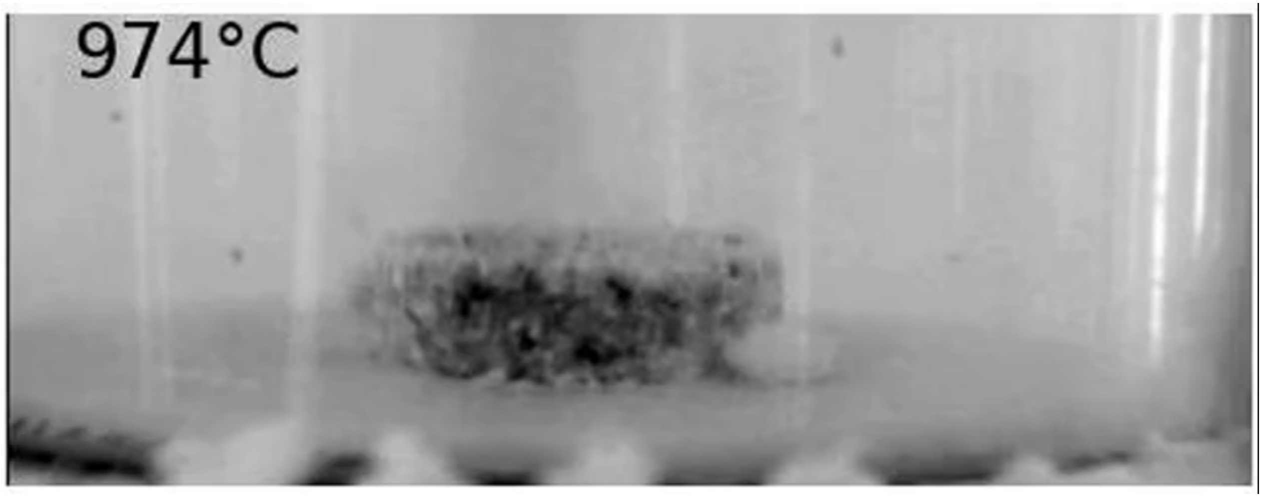


- Expansion volume (V) is divided by initial (V_o)
- Foam reduction of 43 % with Silicon Carbide (0.45) replacing carbon as a reductant



FET Test Videos

Carbon-reduced Amber Batch



SiC (0.45) Reduced Amber Batch

Silicon Carbide

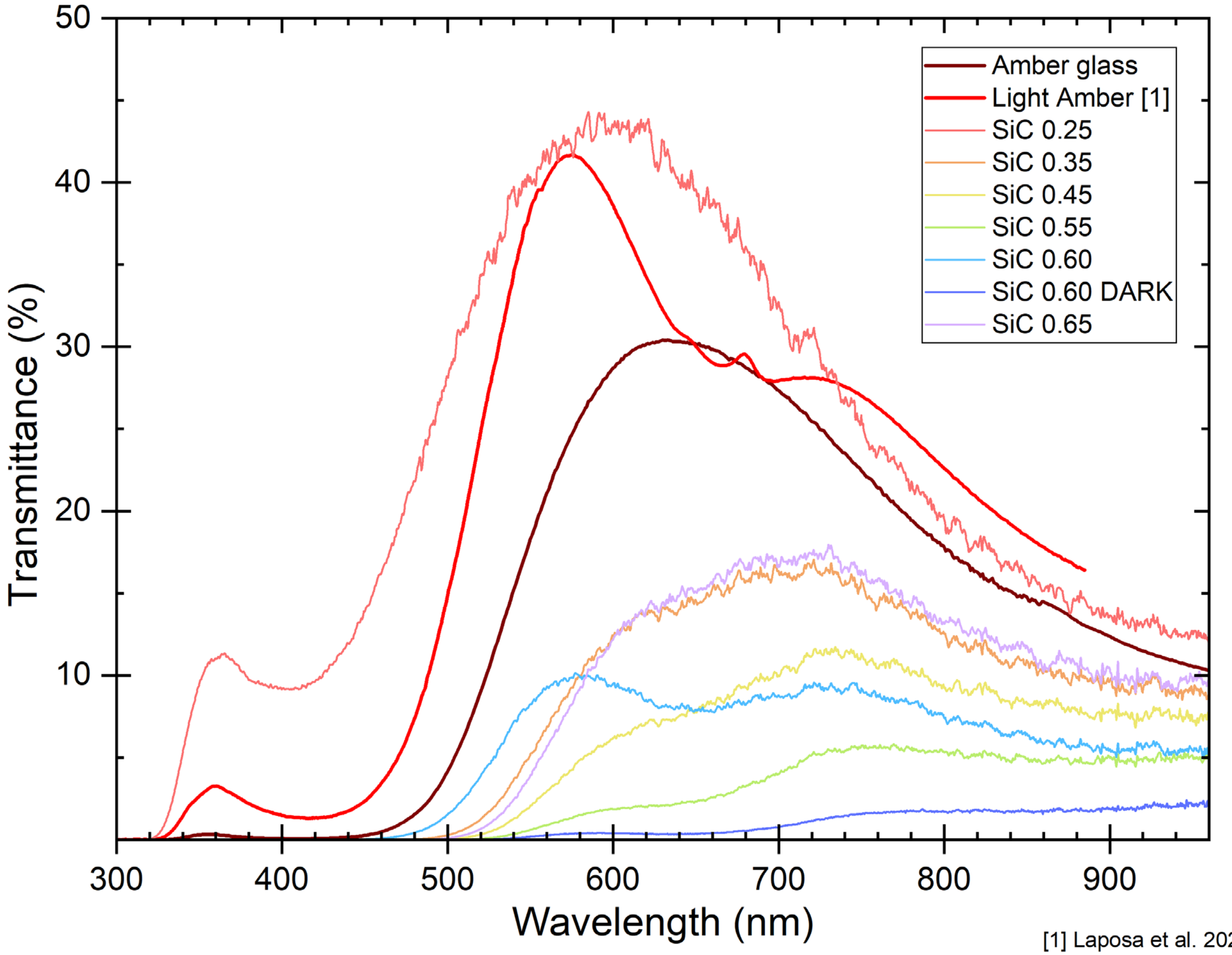
Silicon Carbide (SiC)

- "Refractory" compound (~2700 °C melting point)
- Protective oxidation starting at 600 °C[9]:
  - $2SiC + 3O_2 \rightarrow SiO_2 + 2CO$
- 2 micron powder used in tests

	SiC .25	SiC .35	SiC .45	SiC .55	SiC .60	SiC .65	Std Amber
Silica	69.71	69.56	69.41	69.41	69.41	69.41	70.09
Limestone	22.39	22.39	22.39	22.39	22.39	22.39	22.39
Soda Ash	20.57	20.57	20.57	20.57	20.57	20.57	20.57
Nepheline	4.88	4.88	4.88	4.88	4.88	4.88	4.88
Saltcake	0.41	0.41	0.41	0.41	0.41	0.41	0.41
Iron Scale	0.37	0.37	0.37	0.37	0.37	0.37	0.37
SiC	**0.25**	**0.35**	**0.45**	**0.55**	**0.60**	**0.65**	**0.00**
Carbon	0.00	0.00	0.00	0.00	0.00	0.00	0.21
Total	118.58	118.53	118.48	118.58	118.63	118.68	118.92

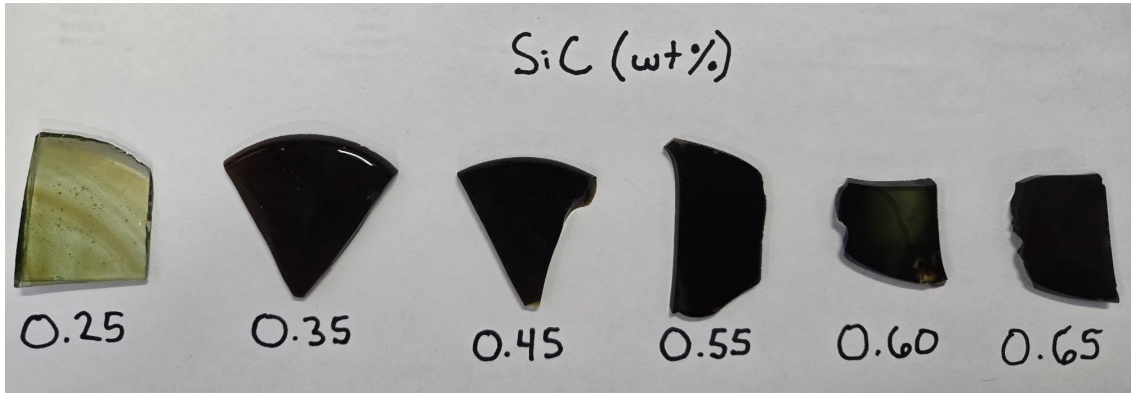
9. Roy, et al. Rev.Adv. Mater. Sci. 38 (2014) 29-39

UV-Vis of Silicon Carbide Glasses



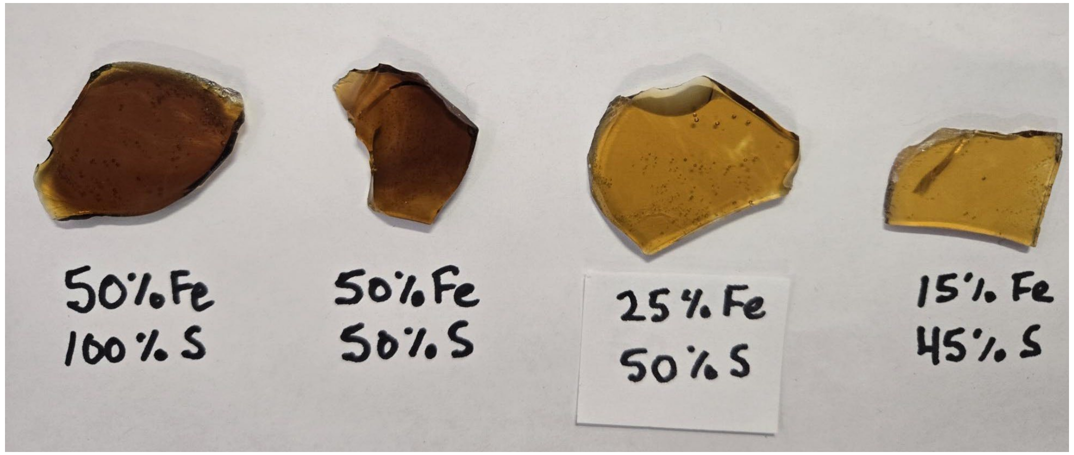
[1] Laposa et al. 2023

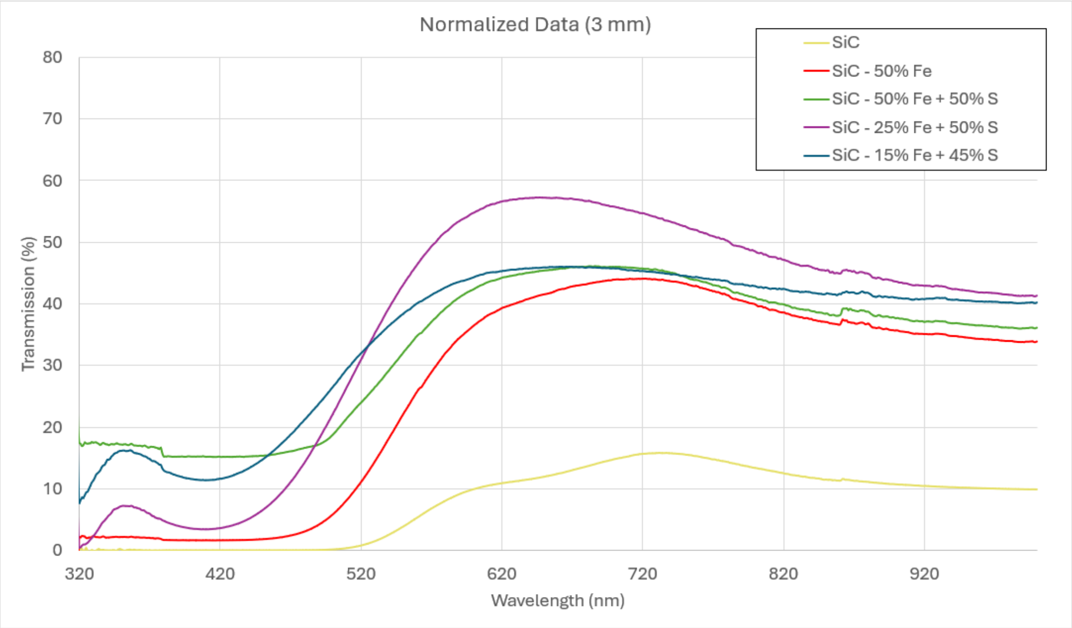
- 200 g samples, melted in air
- SiC0.25 is the only glass that was lighter than typical amber glass[1]
- Strong reduction potential of the SiC powder



Reduce Iron and Sulfur to Correcting UV Absorbance

- 200 g samples melted under air
- Reduction of Fe_2O_3 and Na_2SO_4 to dilute amber chromophore
- 50% Iron sample in range of industry spec (18-24% transmission at 550 nm)



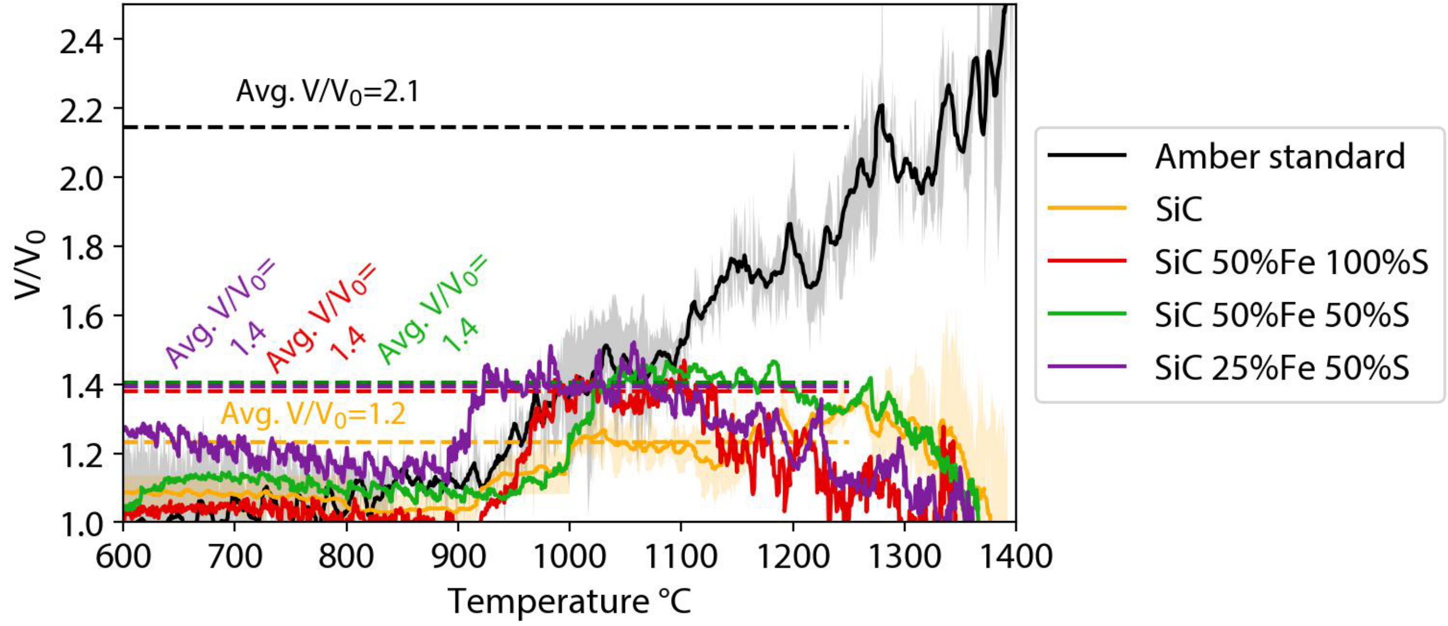


SiC0.45 with Reduced Iron and Sulfur

- Reduced iron and sulfur does not appear to further reduce foaming but still has a 33.3% reduction compared to standard amber

- Change in foaming onset temperature, which can be beneficial

FET Results



Future Tests

- Continuation "refractory reducing agents":
  - Testing in CT-HTMOS
  - Solid-state NMR spectroscopy to understand chemical reaction of SiC
  - Affects of particle size, balance of amber coloring agents
- Alternative pathways to amber without foaming:
  - Evaluate redox state starting raw materials (pyrite, slag, etc.)
  - Oxidized amber chemistries

In conclusion

- Carbon’s reducing power is subject to process conditions
- Silicon Carbide (SiC) has shown to reduce foaming in amber glass by feed expansion test (FET) by up to 43%.
- Suspect due to a different reaction temperature for SiC vs. C with early glass melt
- Reached amber color spec with SiC and less iron and sulfur.

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