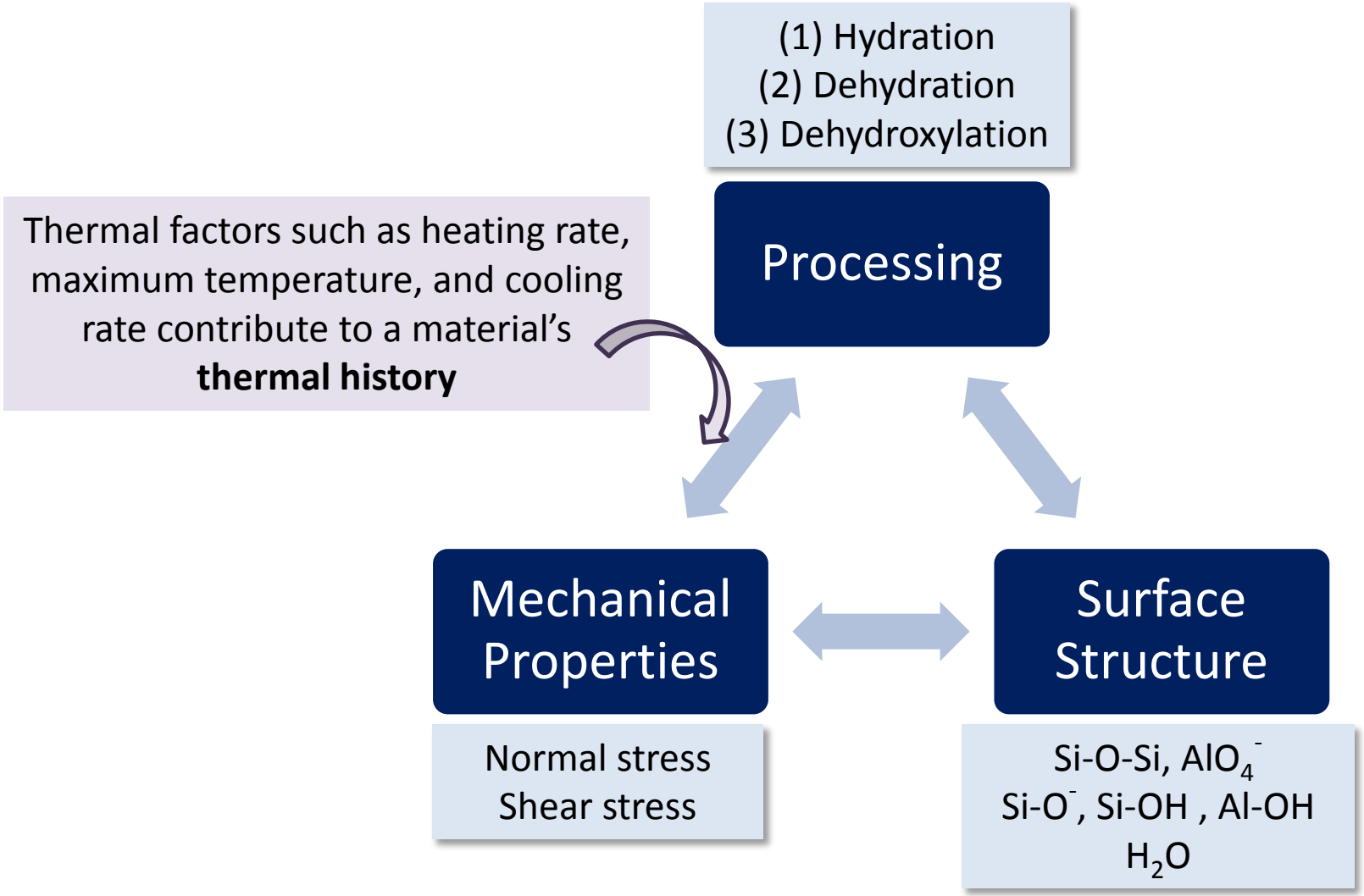
Effects of Thermal History on Surface Structures, Hydration, and Mechanical Response of PPG Float Glass

Alexandra Howzen, Nisha Sheth, Seong Kim

Sept 18, 2017

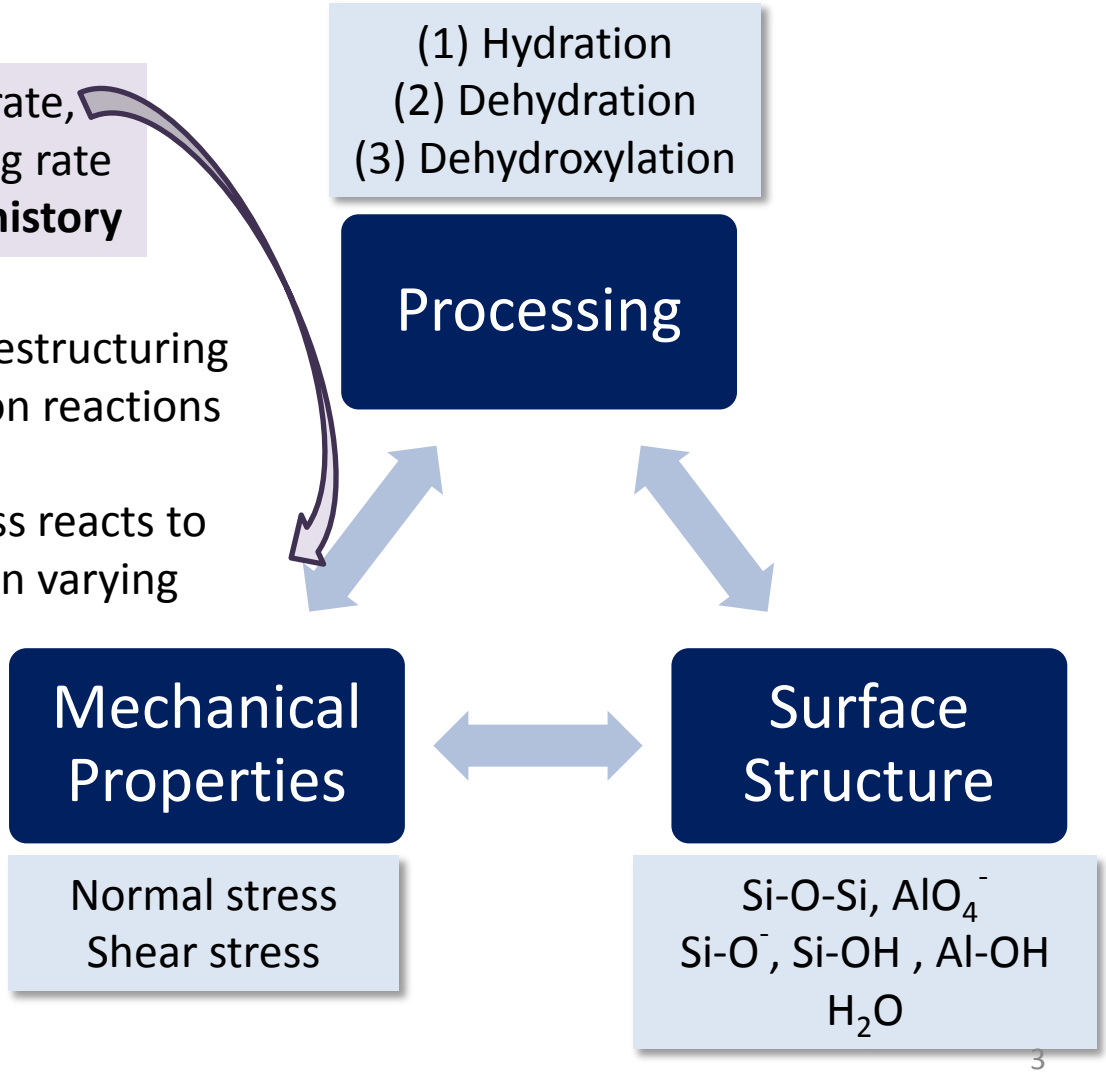
How Do Heat Treatments Alter Mechanical, Chemical, and Compositional Properties?



How Do Heat Treatments Alter Mechanical, Chemical, and Compositional Properties?

Thermal factors such as heating rate, maximum temperature, and cooling rate contribute to a material's **thermal history**

- Heat treatments allow for atomic restructuring via dehydration and dehydroxylation reactions
- These changes impact how the glass reacts to mechanical stresses especially when varying relative humidity (RH)



Sample Preparation

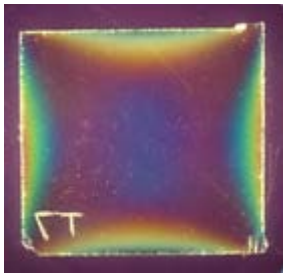
As Received
No residual stress

Cleaned by rinsing with DI Water, Ethanol, and DI water. Blow dry using nitrogen. UV-Ozone.

Annealed
No residual stress

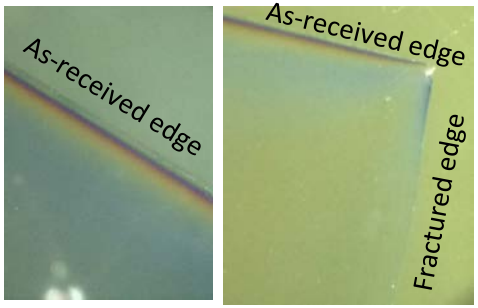
Ramp to 550°C in one hour; Soak at 550°C for 2 hours; Cool to room temperature over 10 hours.

Quenched
Complex compressive residual stress



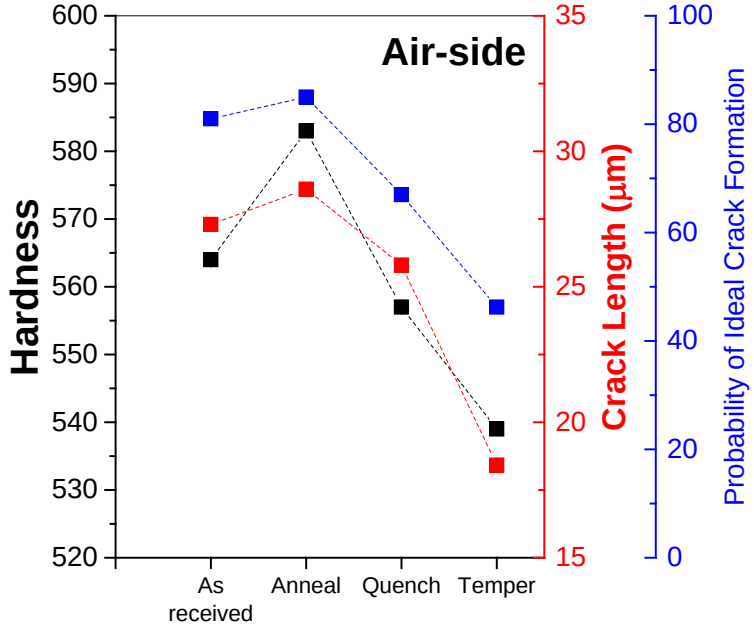
Ramp to 600°C; Heat sample for 15 minutes; remove and air-quench to room temperature.

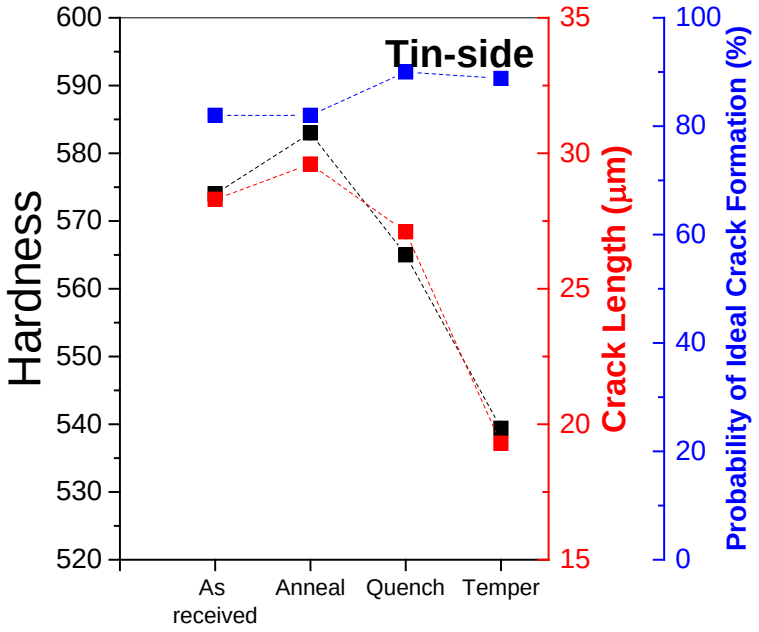
Tempered
Compressive residual stress. Complex residual stresses at edge.

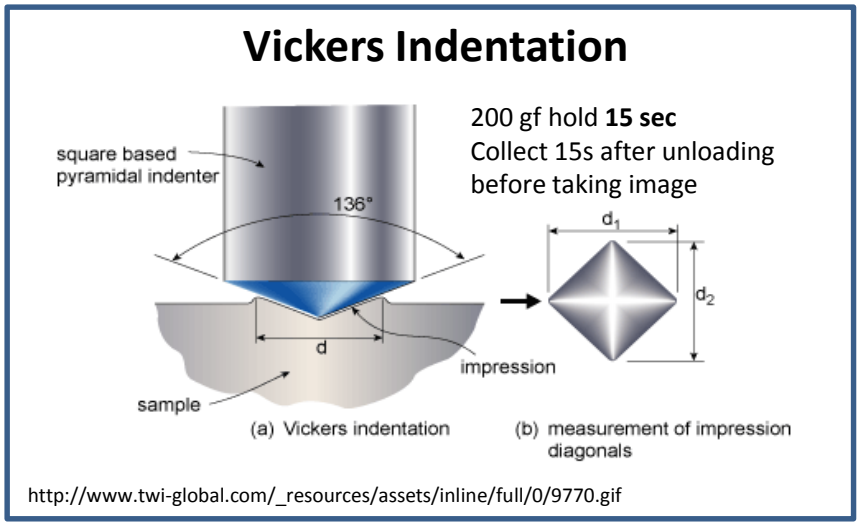


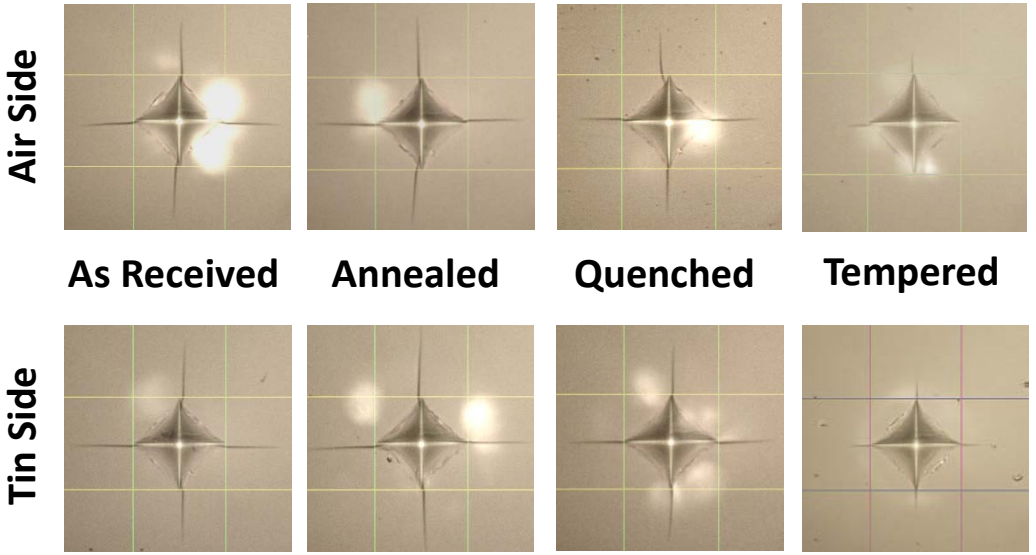
Cleaned by rinsing with DI Water, Ethanol, and DI water. Blow dry using nitrogen. UV-Ozone.

Indentation of Float Glass with Different Thermal Histories

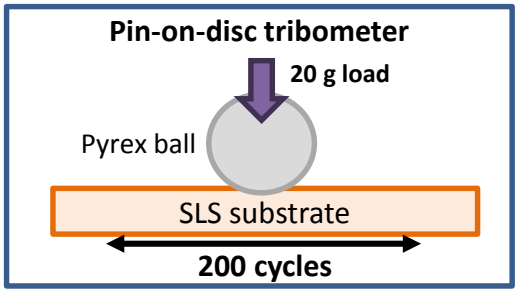








Tribology of Silicate—Glass Overview



Unlike other silicate glasses, **soda lime** wear resistance **increases** at higher humidity.

As humidity increases, the physisorbed water layer:

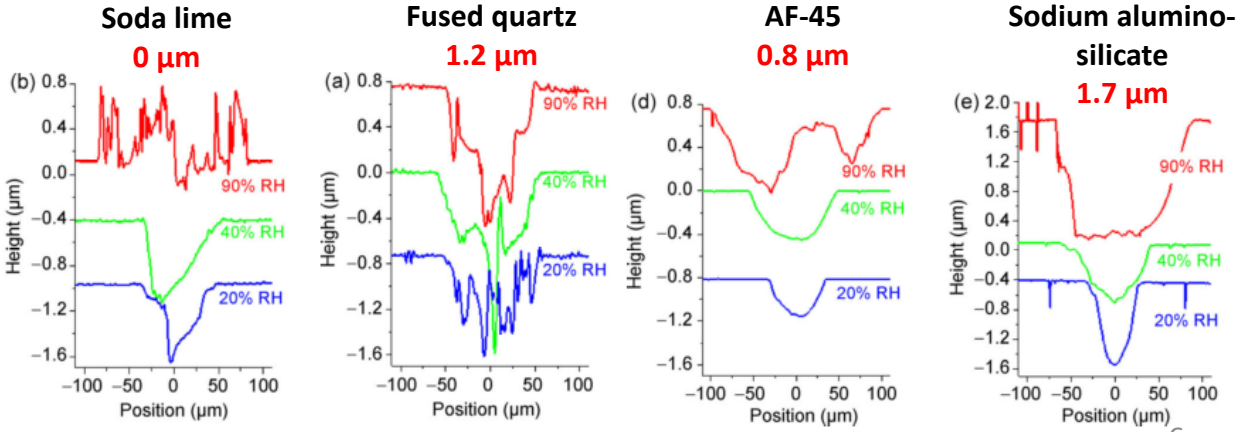
- thickness increases (IR spectroscopy)
- structure changes (SFG)
- Environmental hydrocarbons adsorb onto the water layer (SFG, GC-MS)
- Na^+ modifiers leach out

"**Mechanochemistry** is a term that describes **non-thermal chemical reactions** occurring on solid surfaces solely **due to mechanical processes** like shear, repetitive impact, and tensile and compressive stresses."

Mechanochemical reaction: shear-induced hydrolysis

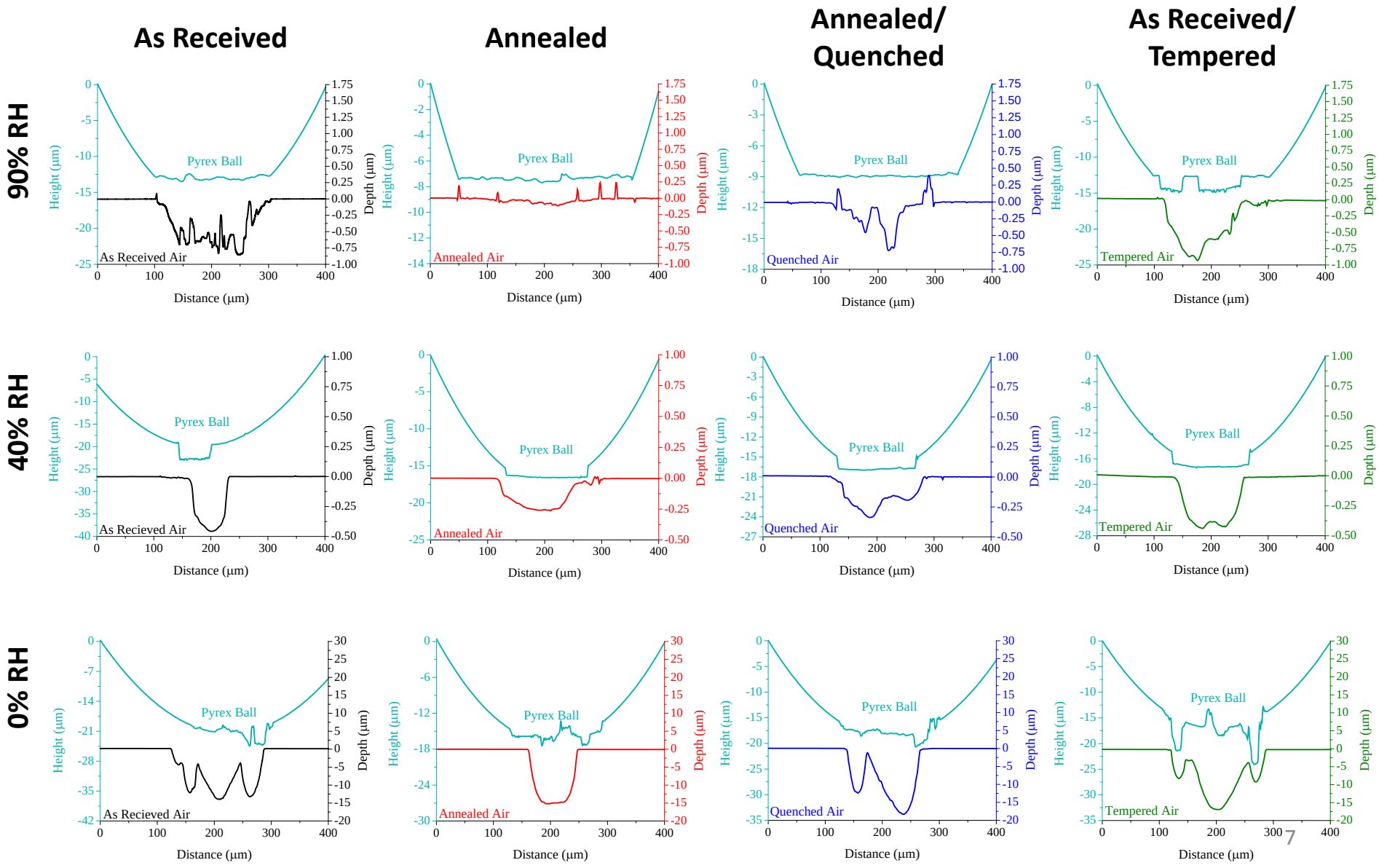
⬆

Archard relationship: In dry conditions, softer material will be damaged by the harder material

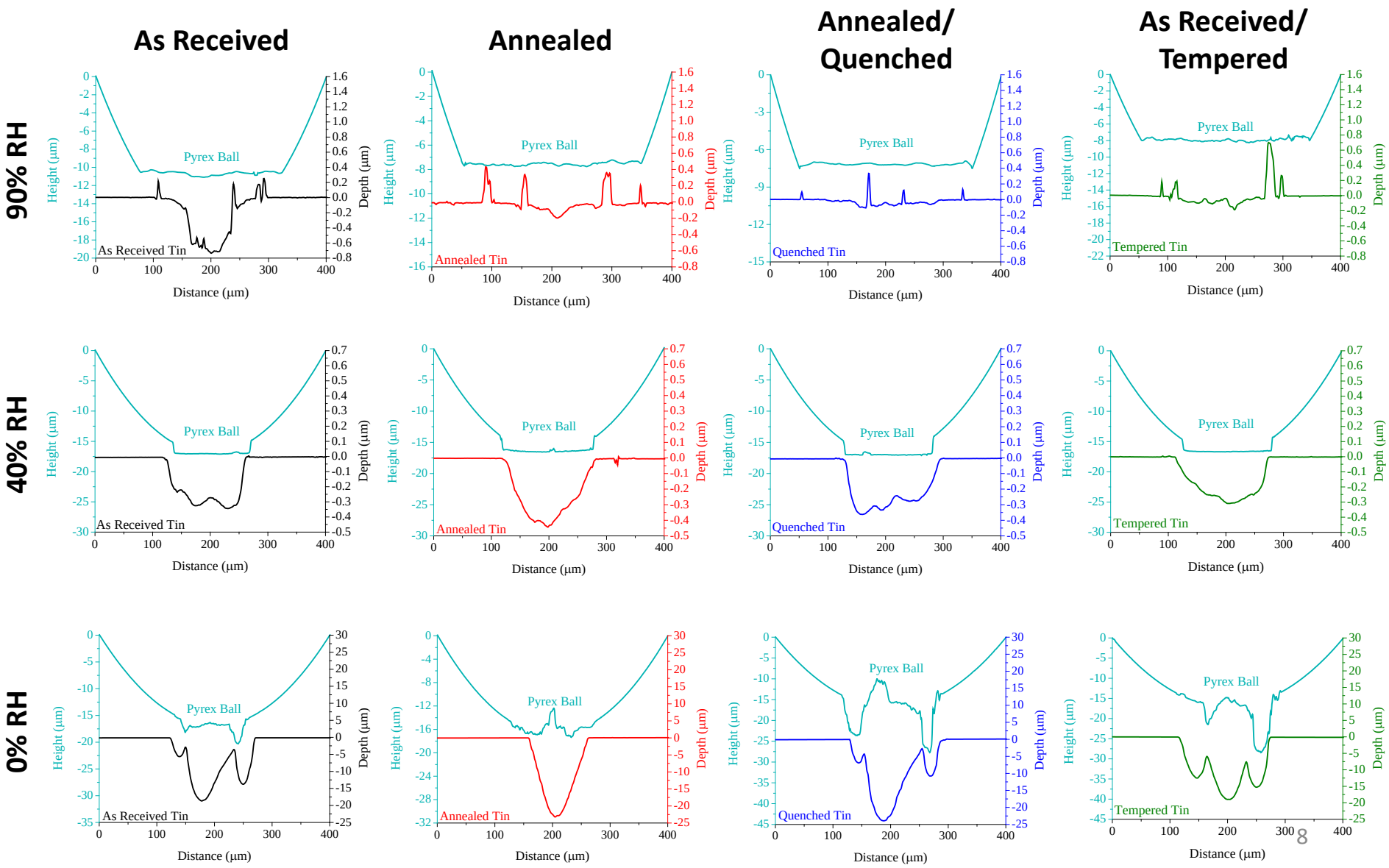


A. Alazizi, et al. Vapors in the ambient - A complication in tribological studies or an engineering solution of tribological problems?, Friction. 3 (2015) 85–114.

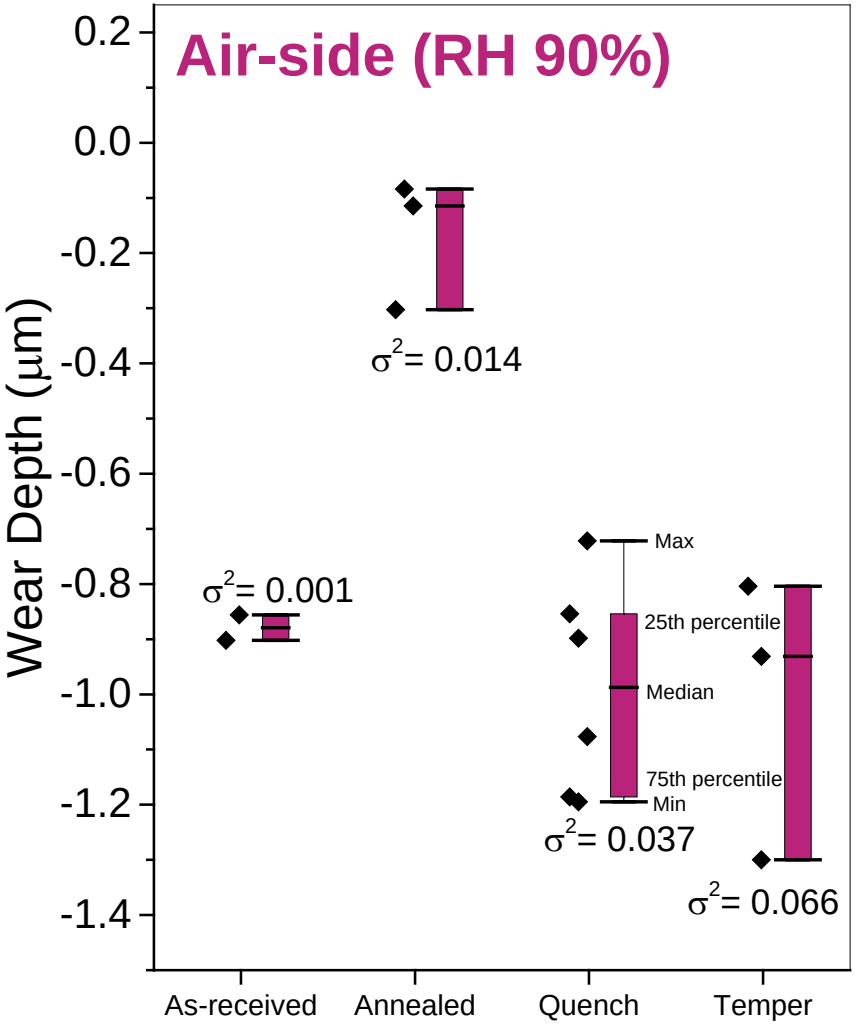
Air Side Wear Track Profiles

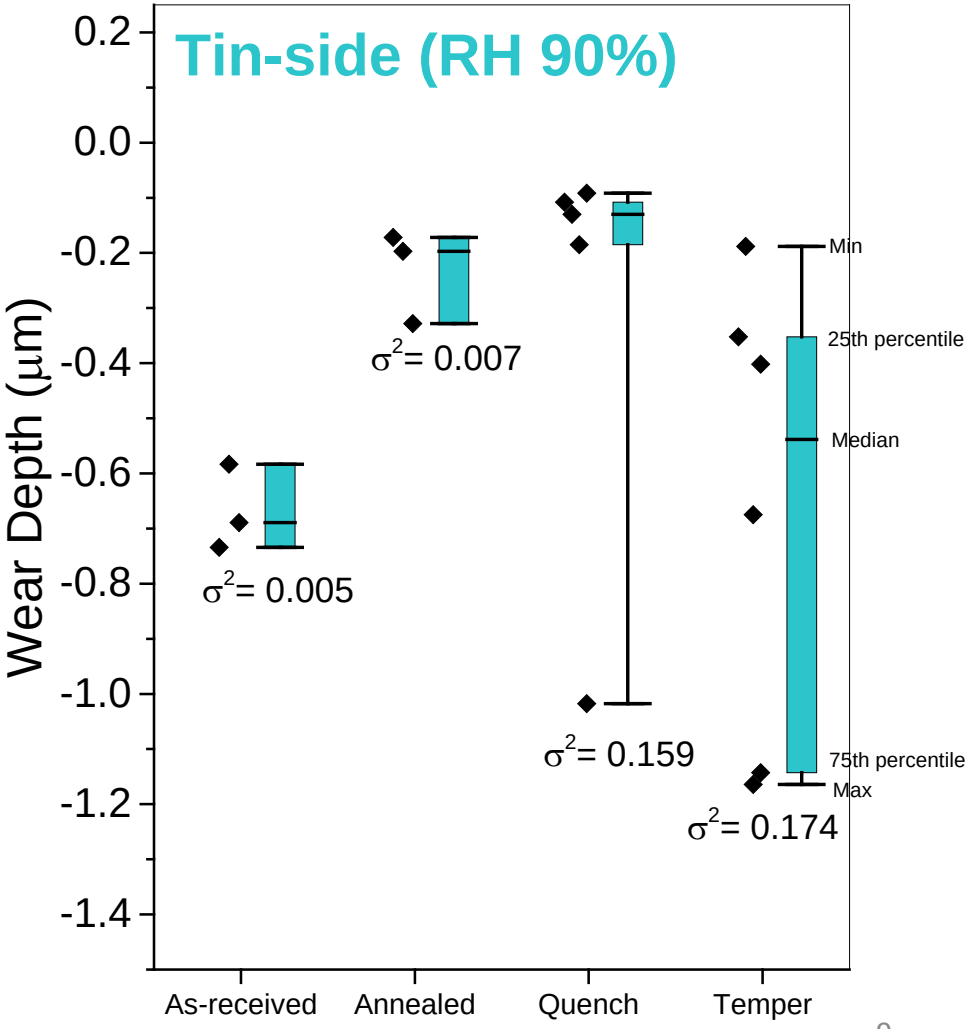


Tin Side Wear Track Profiles

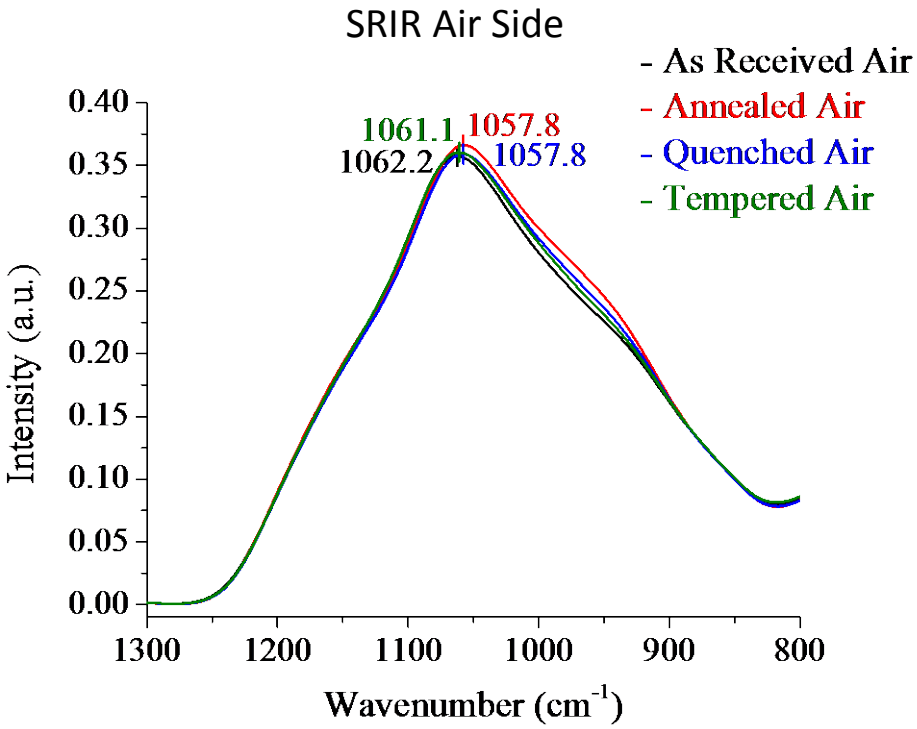


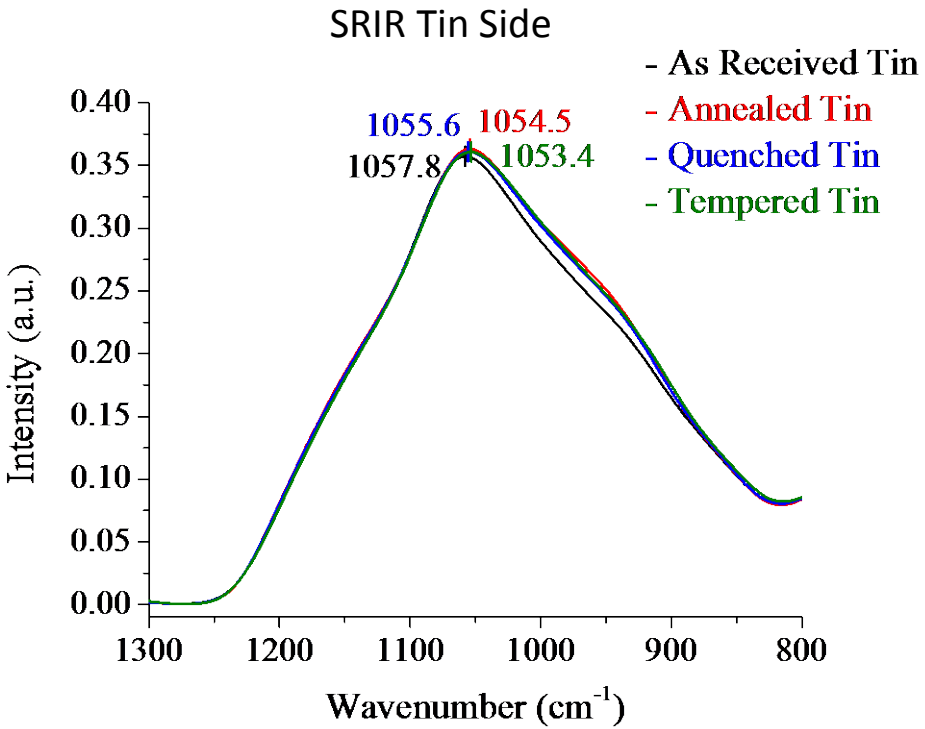
Reproducibility and variance of RH 90% wear results





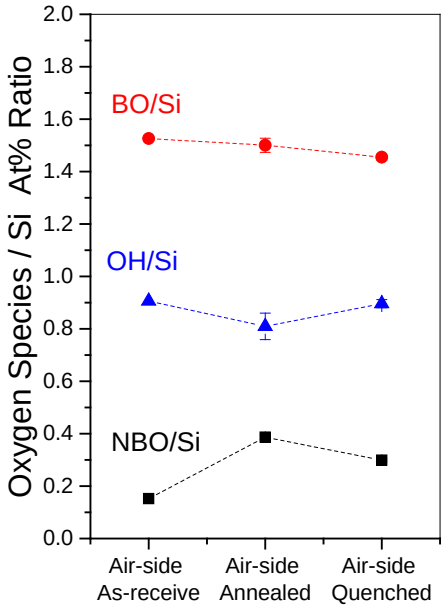
Thermal History Influences Surface Structure

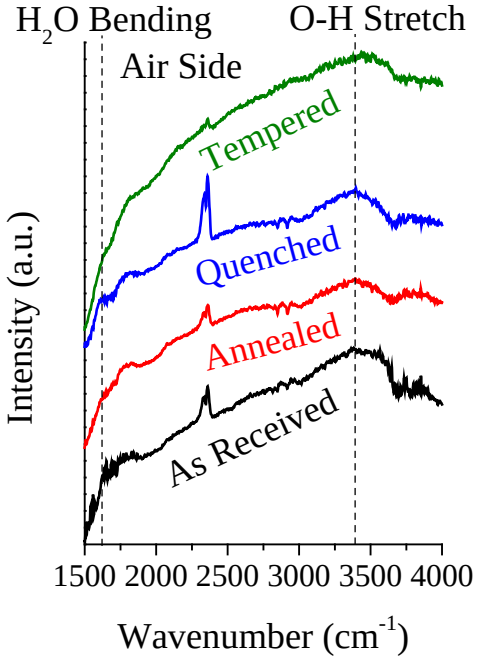


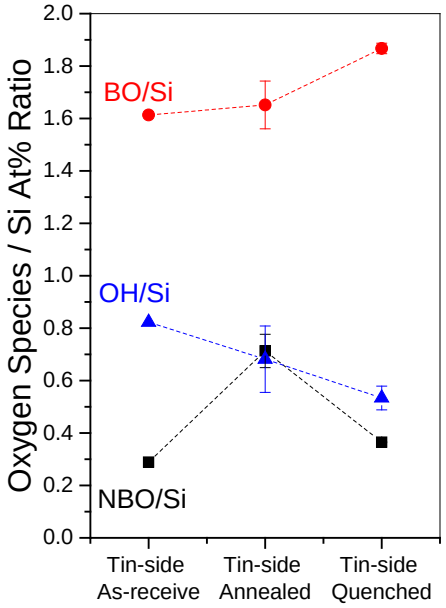


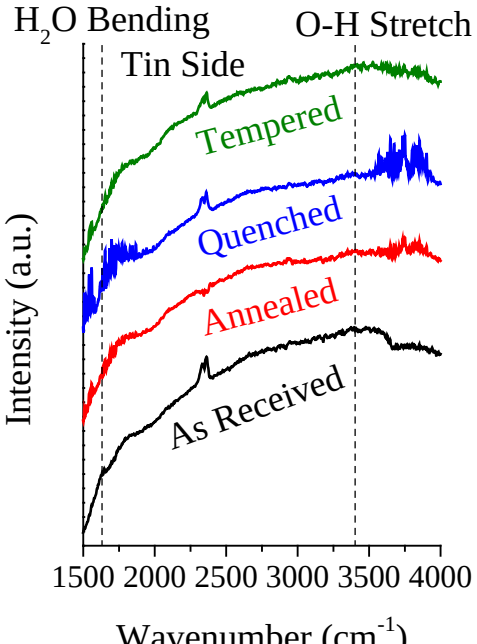
	Air Side				Tin Side			
	As-received	**Annealed**	**Annealed/ Quenched**	**As-received/ Tempered**	**As-received**	**Annealed**	**Annealed/ Quenched**	**As-received/ Tempered**
Average	1062.2	1057.7	1057.8	1061.2	1058.0	1054.6	1055.1	1053.4
Std Err	0.00	0.04	0.00	0.08	0.03	0.04	0.04	0.00

Note: These results were calculated from a pool of thirteen as received spectra, nine annealed spectra, and sixteen quenched spectra. The amounts of spectra taken were the same for both tin and air side samples.









Surface hydration

- As-received surfaces are hydrated
  - 1620 cm^{-1}: H_2O bending
  - 3000-4000 cm^{-1}: OH stretching
- Annealing allows for:
  - ion modifier diffusion from the bulk to the surface (XPS)
  - Dehydration/dehydroxylation (XPS, ATR)
- Quenching appears to deplete the surface of ion modifiers.
  - NBO, OH appear to be condensing, forming BOs.

- *BO include those that are bonded with Si or Sn.
- *Areal densities can no be calculated for surfaces with high tin content (<4 at%) due to unavailable density factors

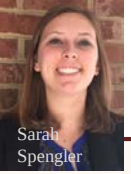
Air-side Pane 7	XPS	SR-IR	ATR-IR (sub-surface)	Wear Profile	Indention
As-received	Hydrated surface depleted in modifiers	~1062 cm^{-1} peak position	Presence of molecular H_2O and SiOH	Pyrex Ball: polished Substrate: ~ 1 µm depth	HV: 564 Crack length: 28.3
Annealed	Modifier replenishment	~4 cm^{-1} decrease from as-received Increase in 950 cm^{-1} (SiOH, NBO)	**Reduced H_2O, SiOH content**	Pyrex Ball: polished Substrate: ~ 0.2 µm depth **Wear resistance**	Increase in hardness & crack length
Annealed / Quenched	Slight increase in OH content	~4 cm^{-1} decrease from as-received Slight decrease in 950 cm^{-1} (SiOH, NBO)	Slight increase in molecular H_2O, SiOH content	Pyrex Ball: polished Substrate: ~ 1 µm depth	Decrease in hardness & crack length Delay in crack formation
As-received / Tempered		~1 cm^{-1} decrease from as-received	Presence of molecular H_2O and SiOH	Pyrex Ball: polished & debris Substrate: ~ 1 µm depth	Decrease in hardness & crack length

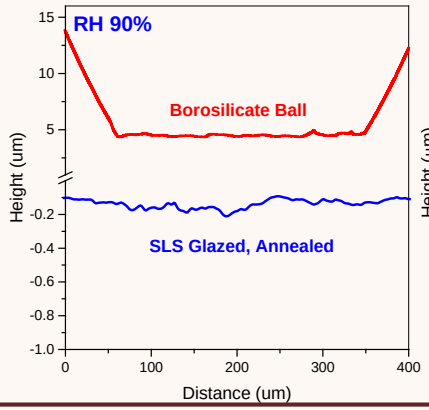
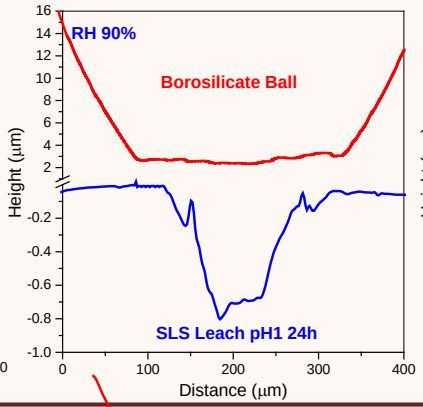
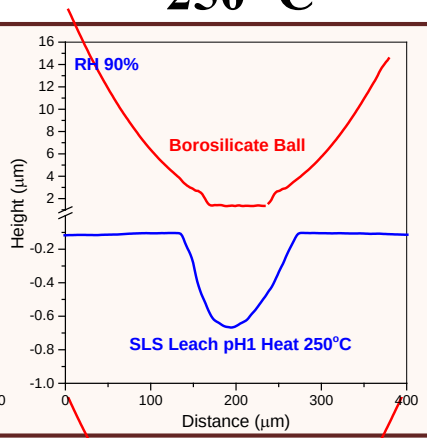
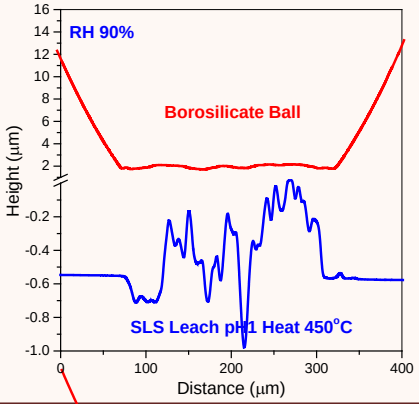
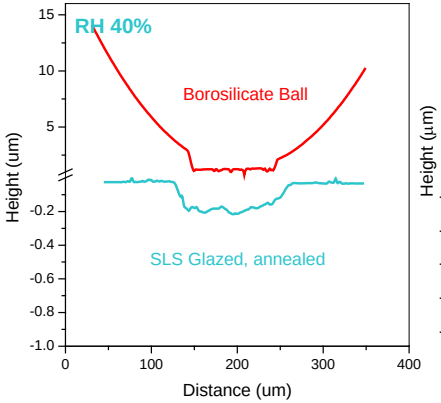
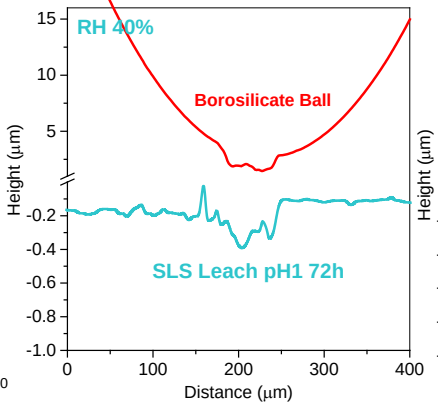
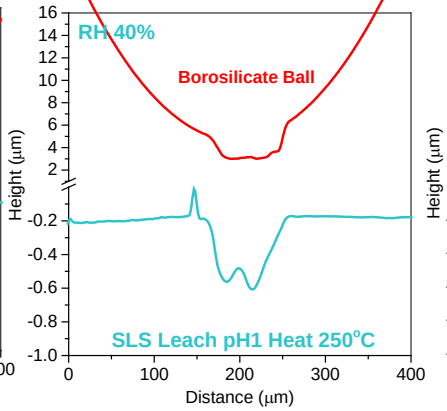
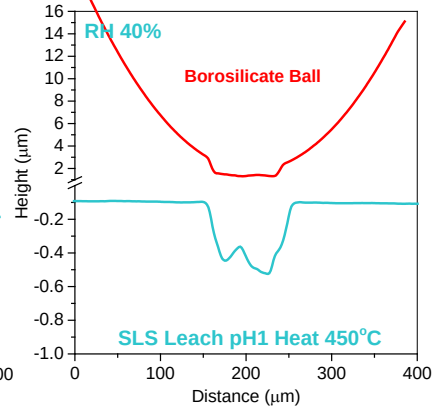
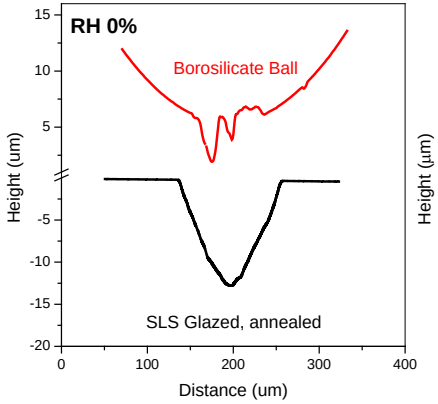
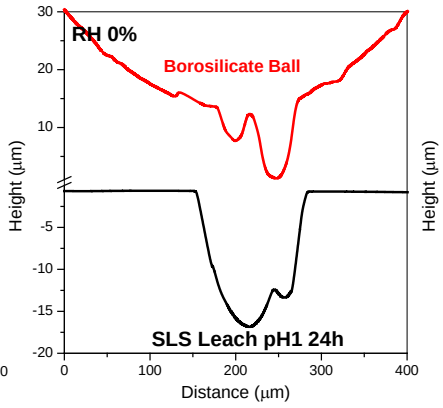
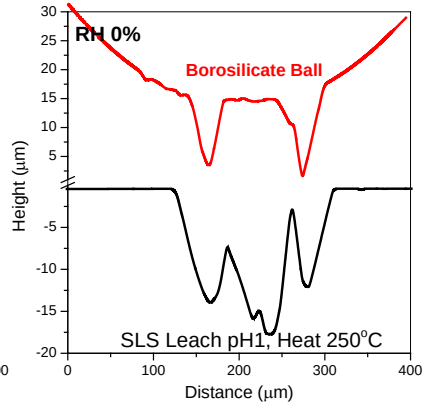
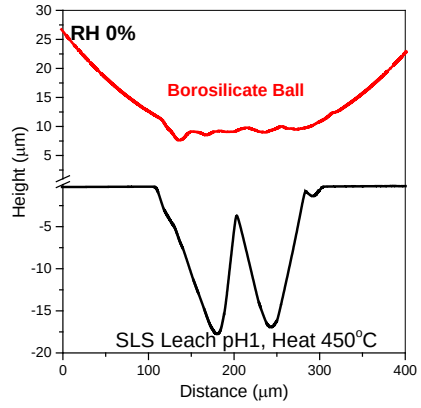
Tin-side Pane 7	XPS	SR-IR	ATR-IR (sub-surface)	Wear Profile	Indentation
As-received	Hydrated surface depleted in modifiers	~1058 cm^{-1} peak position	Presence of molecular water and SiOH	Pyrex Ball: polished Substrate: ~ 1 µm depth	HV: 574 Crack length: 28.3
Annealed	Modifier and Sn replenishment	~3.5 cm^{-1} decrease from as-received Increase in 950 cm^{-1} (SiOH, NBO)	**Reduced H_2O, SiOH content**	Pyrex Ball: polished Substrate: ~ 0.2 µm depth **Wear resistance**	Increase in hardness & crack length
Annealed / Quenched	Decrease in OH,NBO content	~3 cm^{-1} decrease from as-received Slight decrease in 950 cm^{-1} (SiOH, NBO)	**Reduced H_2O, SiOH content**	Pyrex Ball: polished Substrate: ~ 0.2 µm depth **Wear resistance**	Decrease in hardness & crack length
As-received / Tempered		~4 cm^{-1} decrease from as-received	**Reduced H_2O, SiOH content**	Pyrex Ball: polished Substrate: ~ 0.1 µm depth **Wear resistance**	Decrease in hardness & crack length

Summary

- **Annealing dehydrates and dehydroxylates the surface allowing for modifier diffusion**
  - ↑ hardness, ↑ crack length, delays crack formation (only on air side)
  - ↑ wear resistance
- **Compressive stress generated by air-quenching**
  - ↓ hardness, ↓ crack length, delays crack formation (only on air side)
  - Hydration on air-side (ATR) vs. dehydroxylation (XPS) on tin-side
  - ↓ wear resistance on air-side vs. ↑ wear resistance on tin-side
- **Compressive stress generated by tempering**
  - ↓↓ hardness, ↓ ↓ crack length, delays crack formation (only on air side)
  - Hydration on air-side (ATR) vs. dehydroxylation on tin-side
  - ↓ wear resistance on air-side vs. ↑ wear resistance on tin-side

Correlation between surface and sub-surface hydration and wear resistance for soda lime glasses.



	Glazed Annealed	Acid Leach pH 1, 90 ˚C	Heat Treatment 250 ˚C	Heat Treatment 450 ˚C
RH 90%				
RH 40%				
RH 0%				

P-Values for Vickers Analysis on PPG Glass Pane 7

Air Side

	Vickers Hardness			Crack Length (µm)			Fracture Toughness (Mpa*√m)		
	As Received	Annealed	Quenched	As Received	Annealed	Quenched	As Received	Annealed	Quenched
As Received									
Annealed	0.00			0.00			0.00		
Quenched	0.00	0.00		0.00	0.00		0.00	0.00	

Tin Side

	Vickers Hardness			Crack Length (µm)			Fracture Toughness (Mpa*√m)		
	As Received	Annealed	Quenched	As Received	Annealed	Quenched	As Received	Annealed	Quenched
As Received									
Annealed	0.00			0.00			0.00		
Quenched	0.00	0.00		0.00	0.00		0.00	0.00	

Exact Values for Vickers Indentation on Float Glass

Air Side

	As Received			Annealed			Quenched		
	Vickers Hardness	Crack Length (µm)	Fracture Toughness (Mpa*√m)	Vickers Hardness	Crack Length (µm)	Fracture Toughness (Mpa*√m)	Vickers Hardness	Crack Length (µm)	Fracture Toughness (Mpa*√m)
Average	564	27.3	0.79	583	28.6	0.73	557	25.8	0.87
Standard Error	0.5014	0.1127	0.0047	0.0000	0.0869	0.0033	0.4169	0.1140	0.0056

Tin Side

	As Received			Annealed			Quenched		
	Vickers Hardness	Crack Length (µm)	Fracture Toughness (Mpa*√m)	Vickers Hardness	Crack Length (µm)	Fracture Toughness (Mpa*√m)	Vickers Hardness	Crack Length (µm)	Fracture Toughness (Mpa*√m)
Average	574	28.3	0.74	583	29.6	0.69	565	27.1	0.80
Standard Error	0.3000	0.0805	0.0031	0.3333	0.1170	0.0040	0.0000	0.1220	0.0054

P-Test for Tin Side vs. Air Side

	As Received			Annealed			Quenched		
	Vickers Hardness	Crack Length (µm)	Fracture Toughness (Mpa*√m)	Vickers Hardness	Crack Length (µm)	Fracture Toughness (Mpa*√m)	Vickers Hardness	Crack Length (µm)	Fracture Toughness (Mpa*√m)
	Tin			Tin			Tin		
Air	0.00	0.00	0.00	0.32	0.00	0.00	0.00	0.00	0.00

Experimental Methods

- What is RH (relative humidity, amount of vapor pressure in the atmosphere?)
- How to calculate RH (Antoine eq, maybe solve for each RH)

- How is the ball on flat tribometer set up? (Picture would probably work best, but ask. Ball 90 degrees to substrate, pin moved linearly back and forth to simulate wear)

- Why is it ball on flat as opposed other set ups like pin on disk or flat on flat?
  - Contact geometry and respective contact mechanics
- What is the load you are putting on your glass? 20gf → N? → initial pressure → if you ball was polished then what is your new contact pressure (area dependent)
- What does friction coefficient mean here (contact area between BSB and flat substrate. Changes as a function of time)?
- Describe wear processing including abrasion, adhesion, and mechanochemical processes.
  - Abrasion → hardness (under nitrogen so no chemical interactions involved)
  - Adhesion → surface chemistry and chemical bonding (O-Si-O bonds between pyrex ball and SLS substrate)
  - Mechanochemical → activation energies (percent hydration/humidity to cause adhesion reactions? Not sure about this)