Structure and Reactivity of Calcium Alumino-Silicate Glass Surfaces

Liaoyuan Wang[1]

Prof. Alastair N Cormack[1]

Dr. Robert Manley[2]

Dr. Nicholas Smith[2]

Dr. Gabriel Agnello[2]

1. The New York State College of Ceramics at the Alfred University

2. Corning Incorporated

06/11/2019

This work is supported by Corning, Incorporated, and the Center for Advanced Ceramic Technology at Alfred University

Outline

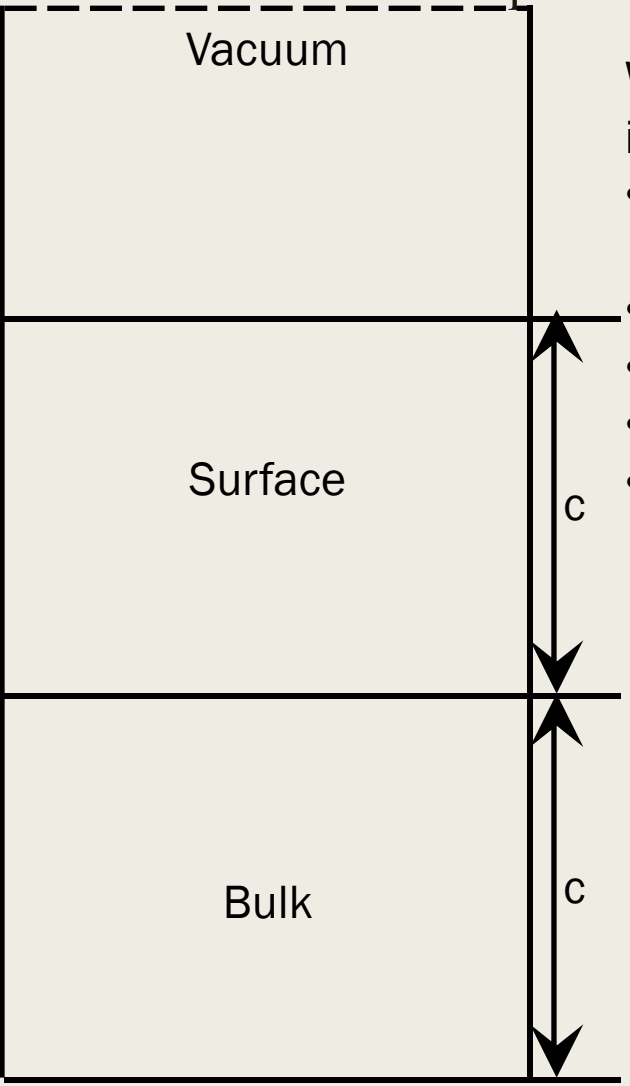
- Introduction
- Modeling and methodology
  - Four models (presented in molar ratio of SiO_2: Al_2O_3: CaO): (80:10:10), (70:15:15), (60:20:20) and (50:25:25)
- Surface structures of water-free models
  - CN/Q_n distribution of bulk vs. surface
- Observation of structure moieties formed on the surface up to 5ns
  - CN/Q_n distribution as a function of time
  - Target species distribution as a function of time
  - Species distribution as a function of component ratio
- Dynamic surface reactivity of water models (movie)
- Summary

Introduction

- Properties of materials are highly determined by their structures, particularly for glass materials
  - correlation between the properties and structures
  - mechanism behind such correlations
- Goal
  - **Explore such correlation using data and figures**
  - Understand the mechanism behind it
- Challenges
  - lack of periodicity and long-range order
  - complex composition
  - Reactivity
  - No existing tool to track the transition of species
  - …
- Methods
  - MD methods
  - Self-written programs

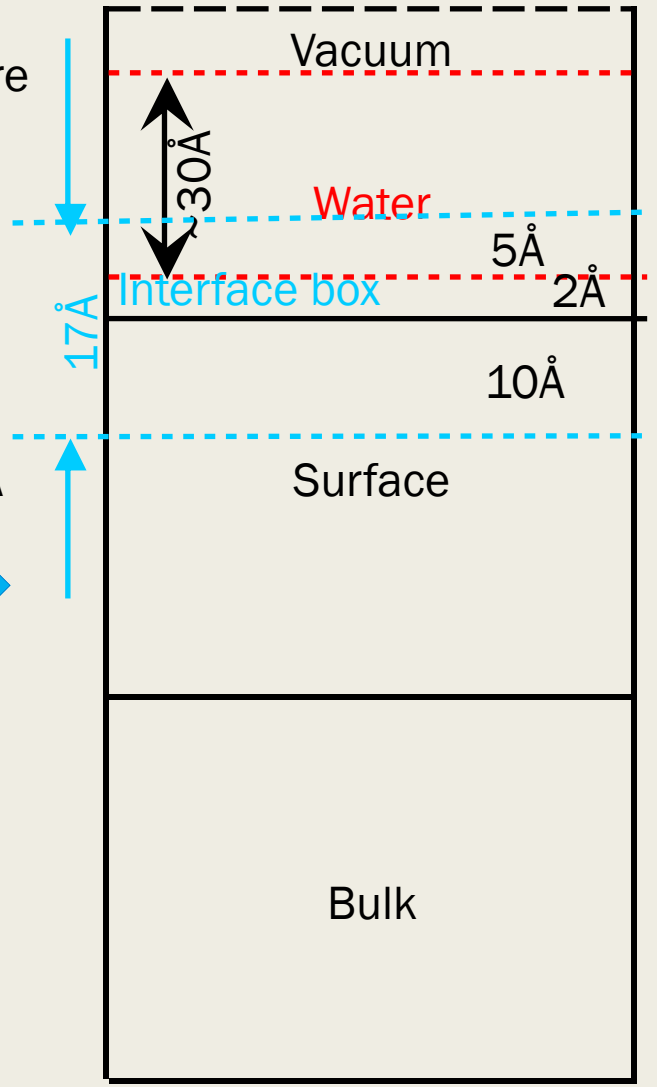
Modeling & Methodology

- Gromacs was employed to build CAS models with different molar ratios of components



Water molecules (5427 H_2O) are introduced into the vacuum

- Two boxes are put together along z direction
- Upper box: surface
- Bottom box: bulk
- Vacuum: 30 Å
- Water box above surface 2 Å



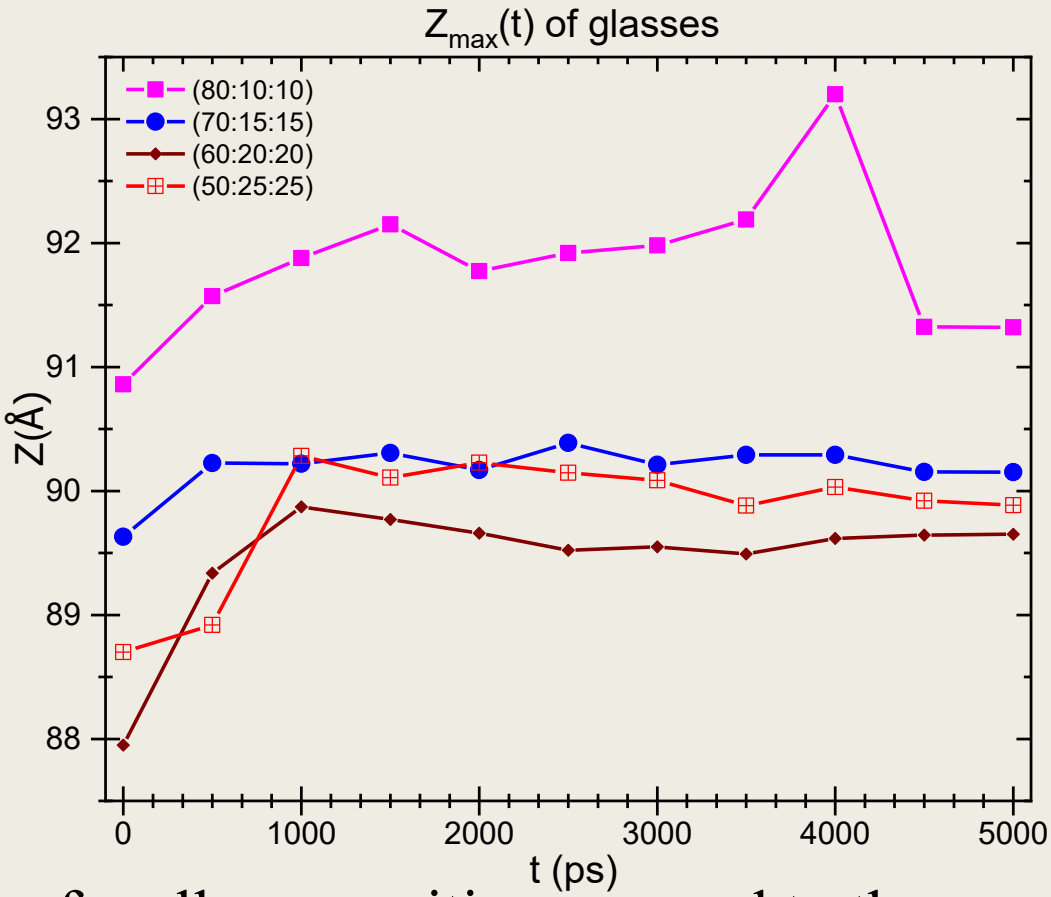
Simulations Overview

- LAMMPS simulations
  - Reax/c potential
  - NVT (300K) ensemble
  - Simulated time: **5ns**
  - Time steps: 0.25fs
  - Dump time steps:
    - 100 timesteps/frame ➔ dump one trajectory/frame every 25fs (0.25x100=25fs)
  - Total # of trajectories: 200,000

Comparison of Components between Bulk & Interface

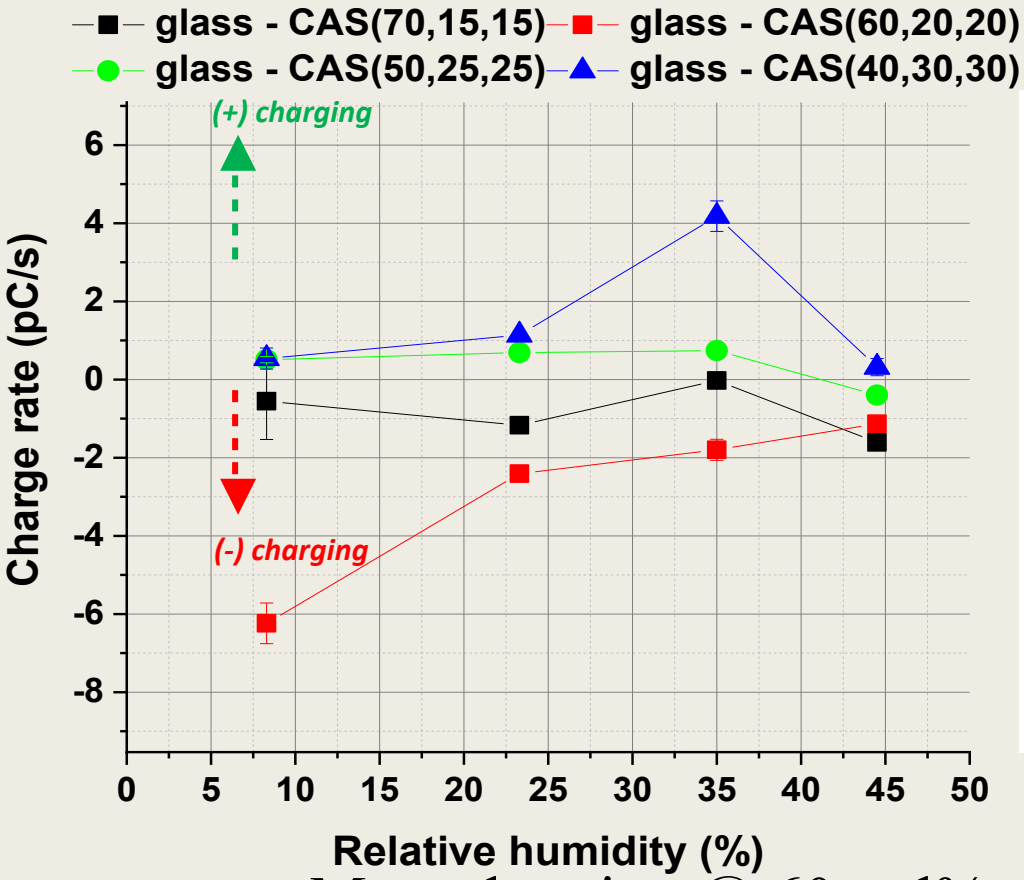
composition	Si mol% in interface #_of_Si/∑#_of_species	Al mol% in interface #_of_Al/∑#_of_species
(80:10:10)	~81%	10%
(70:15:15)	~65%	~17%
(60:20:20)	~57%	~22%
(50:25:25)	~51%	~24%

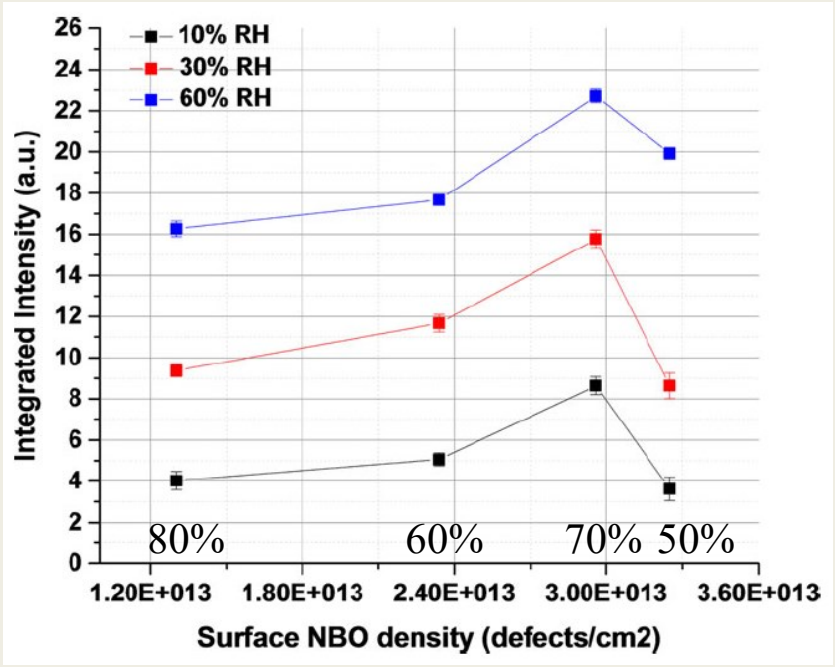
Surfaces “expand”



- Surfaces for all compositions expand to the vacuum layers
- The expansion mainly occurred within 1ns
- Each composition expands 1-2 Å
  - Composition (60:20:20) has the maximum expansion

Initial focus on 60 mol% silica composition





[NBO] not a linear function of composition

- Most charging @ 60mol%
- DRIFTS trend: as [NBO] increases, [H_2O] increases
- But: < 60 mol% silica trend reverses
- Associated above slides, we would focus on (60:20:20) first

Gabriel Agnello *et al* *Int J Appl Glass Sci. 2018;9:3–15*

Comparison of CN Distribution for Formers in Bulk and Surface

	Si				Al			
CN	80:10:10	70:15:15	60:20:20	50:25:25	80:10:10	70:15:15	60:20:20	50:25:25
CB1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CB2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CB3	0.00	0.00	0.00	0.00	**1.15**	**0.46**	**0.14**	**0.09**
CB4	100.00	100.00	100.00	100.00	**97.54**	**98.19**	**99.16**	**98.62**
CB5	0.00	0.00	0.00	0.00	**1.31**	**1.25**	**0.70**	**1.29**
CB6	0.00	0.00	0.00	0.00	0.00	0.10	0.00	0.00
CS1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CS2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CS3	1.09	0.00	0.00	0.00	**23.77**	**11.99**	**9.10**	**8.90**
CS4	98.91	100.00	100.00	100.00	**75.68**	**87.92**	**89.76**	**90.56**
CS5	0.00	0.00	0.00	0.00	**0.55**	**0.09**	**1.14**	**0.55**
CS6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

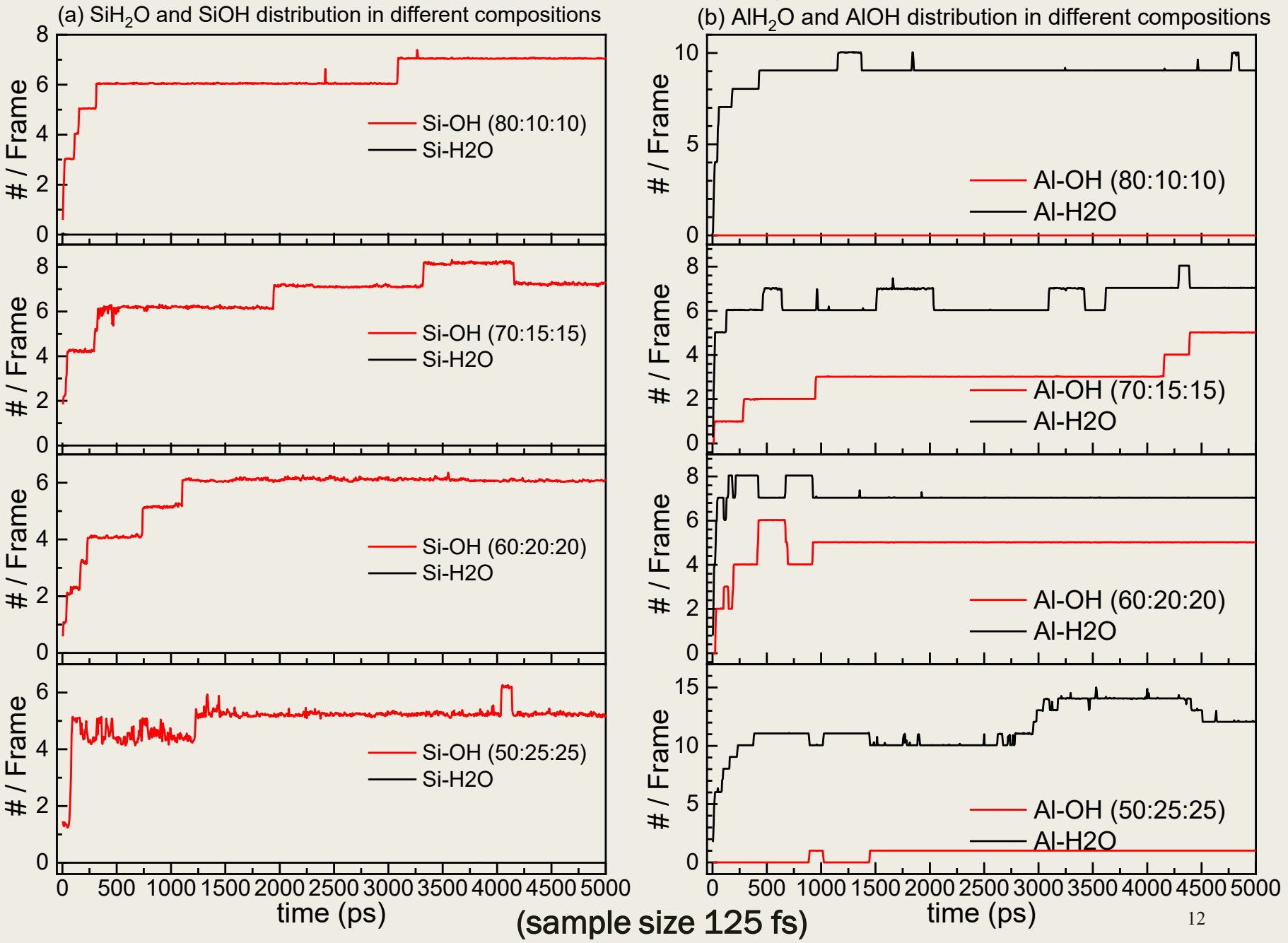
Comparison of Q_n Distribution for Formers in Bulk and Surface

	Si				Al			
Qn	80:10:10	70:15:15	60:20:20	50:25:25	80:10:10	70:15:15	60:20:20	50:25:25
QB1	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00
QB2	**0.21**	**0.21**	**0.51**	**1.09**	**0.00**	**0.00**	**0.00**	**0.00**
QB3	**7.54**	**9.24**	**15.09**	**17.78**	**2.70**	**2.11**	**2.28**	**3.64**
QB4	**92.25**	**90.51**	**84.40**	**81.13**	**95.99**	**96.54**	**97.02**	**95.07**
QB5	0.00	0.00	0.00	0.00	1.31	1.25	0.70	1.29
QB6	0.00	0.00	0.00	0.00	0.00	0.10	0.00	0.00
QS1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
QS2	**0.01**	**1.74**	**0.00**	**0.56**	**0.00**	**0.90**	**0.00**	**0.00**
QS3	**8.84**	**14.16**	**13.26**	**21.37**	**23.77**	**16.50**	**14.26**	**13.61**
QS4	**91.16**	**84.11**	**86.74**	**78.06**	**75.68**	**82.51**	**84.61**	**85.85**
QS5	0.00	0.00	0.00	0.00	0.55	0.09	1.14	0.55
QS6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Surface CN/Q_n distribution of Formers

	Si				Al			
CN/Q_n	80:10:10	70:15:15	60:20:20	50:25:25	80:10:10	70:15:15	60:20:20	50:25:25
CS1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CS2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CS3	1.09	0.00	0.00	0.00	23.77	11.99	9.10	8.90
CS4	98.91	100.00	100.00	100.00	75.68	87.92	89.76	90.56
CS5	0.00	0.00	0.00	0.00	0.55	0.09	1.14	0.55
CS6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
QS1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
QS2	0.01	1.74	0.00	0.56	0.00	0.90	0.00	0.00
QS3	**8.84**	**14.16**	**13.26**	**21.37**	**23.77**	**16.50**	**14.26**	**13.61**
QS4	**91.16**	**84.11**	**86.74**	**78.06**	**75.68**	**82.51**	**84.61**	**85.85**
QS5	0.00	0.00	0.00	0.00	0.55	0.09	1.14	0.55
QS6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Time Evolution of Target Species



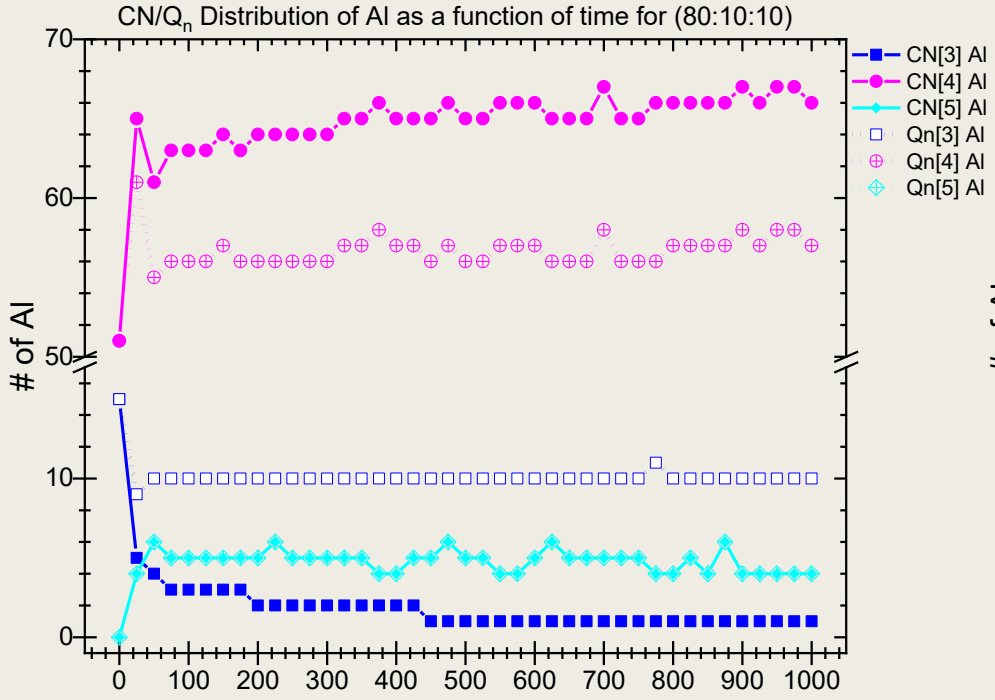
(sample size 125 fs)

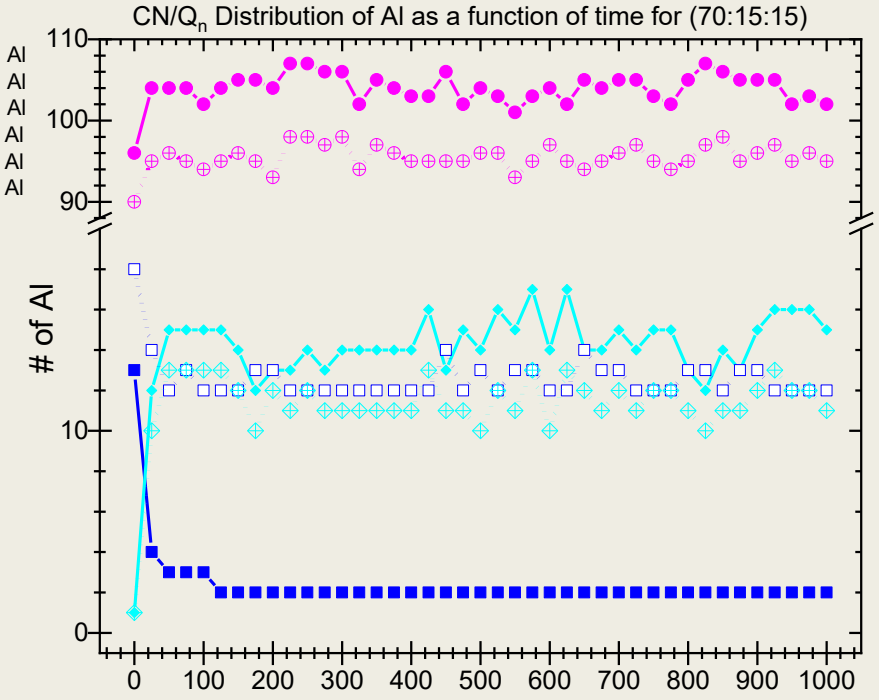
Reactivity of Surface Defects

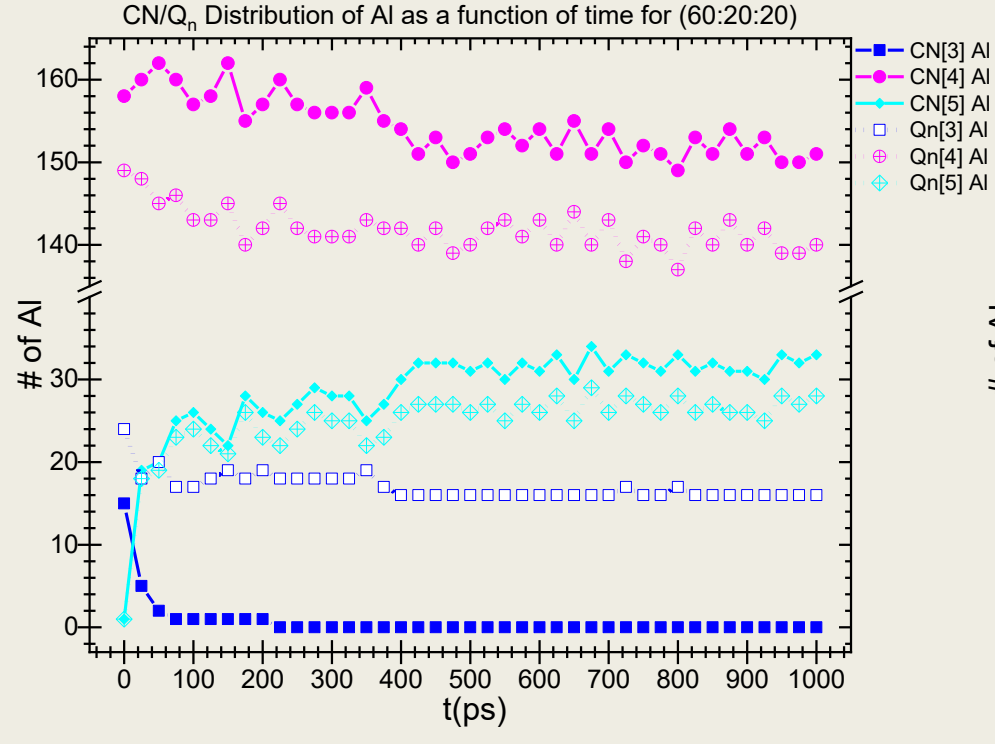
	[3]Si				[5]Si			
	80:10:10	70:15:15	60:20:20	50:25:25	80:10:10	70:15:15	60:20:20	50:25:25
Total	4	0	0	0	0	0	0	0
Si-OH	6	6	5	3	0	0	0	0
$Si-OH_2$	0	0	0	0	0	0	0	0
	[3]Al				[5]Al			
	80:10:10	70:15:15	60:20:20	50:25:25	80:10:10	70:15:15	60:20:20	50:25:25
Total	16	15.5	13	14	2.5	5.5	6.5	4
Al-OH	0	0	0	0	0	3	5	1
$Al-OH_2$	9	6	7	10	0	0	0	0

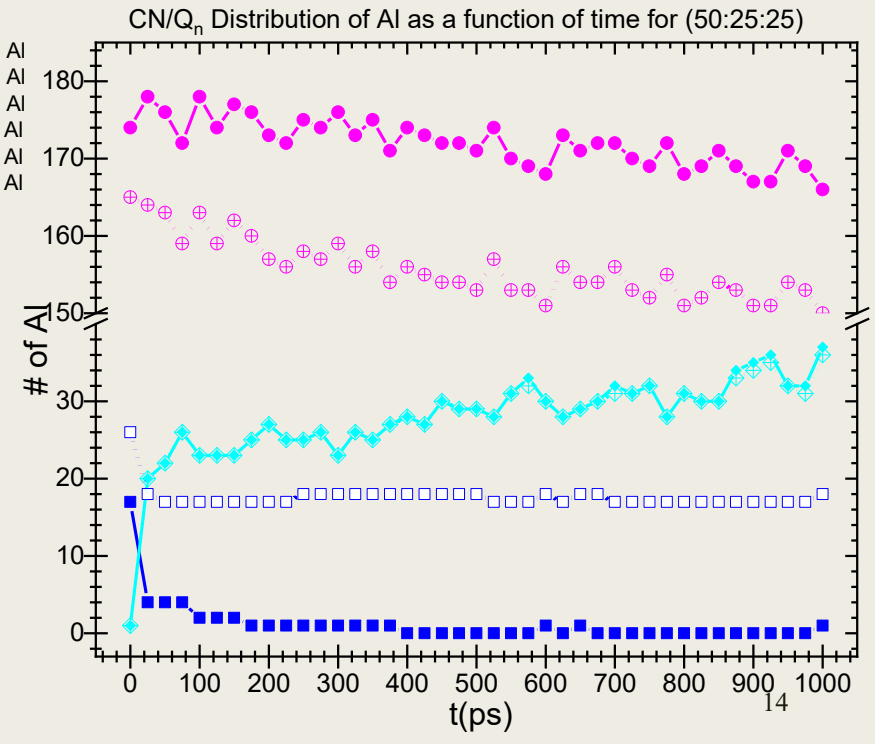
	NBO			
	80:10:10	70:15:15	60:20:20	50:25:25
# @ t = 0	25	44	37	53
# @ t = 1ns	18	39	31	37
Δ	7	5	6	16

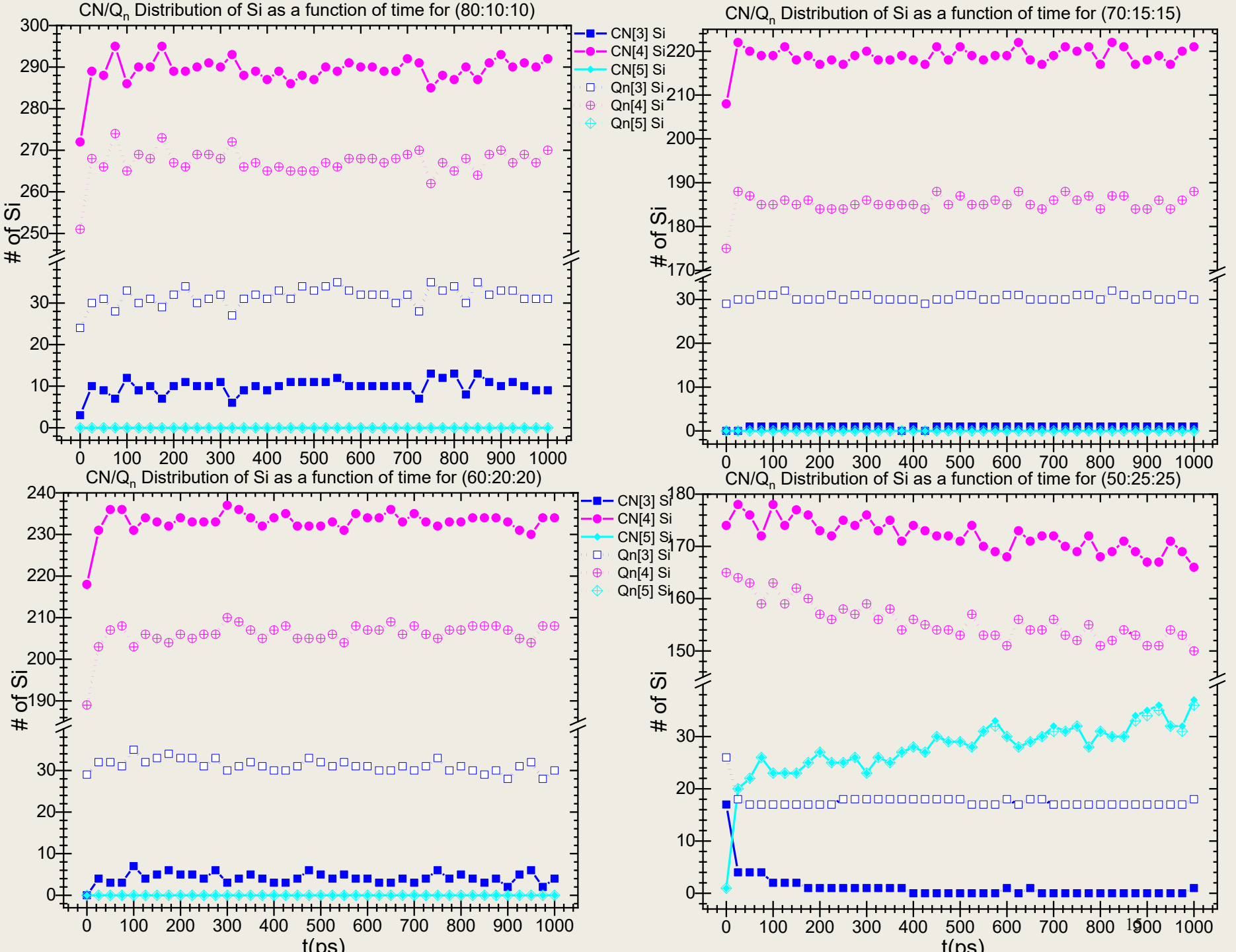
- ✓ Si-OH formed from NBO
- ✓ Al-OH associated with [5]Al
- ✓ $Al-OH_2$ associated with [3]Al
- ✓ No $Si-OH_2$ observed

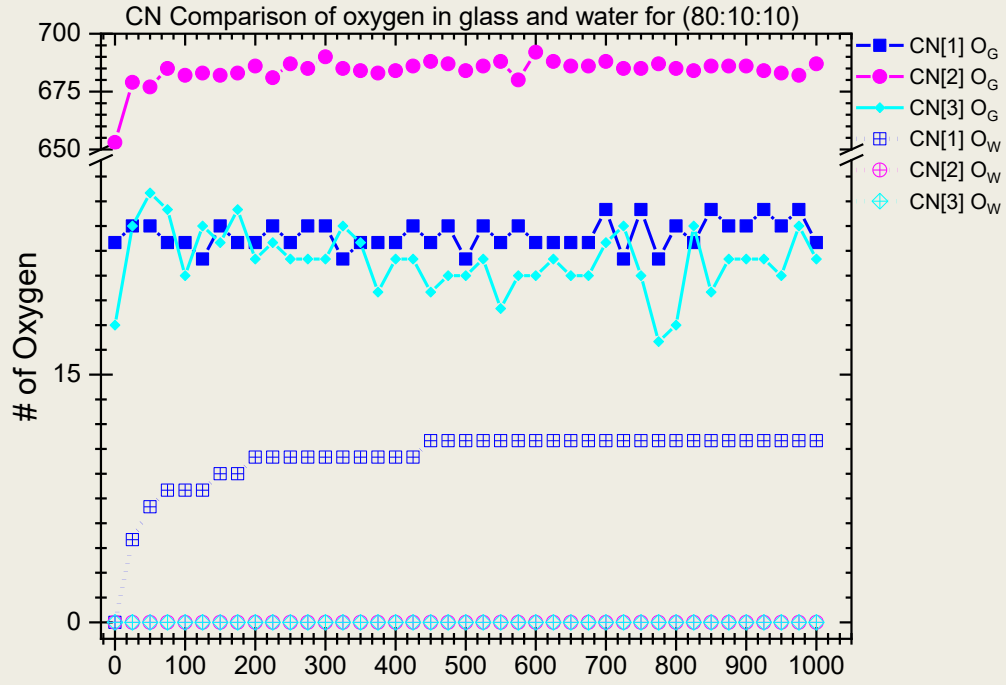

CN/Qn Distribution of Al as a function of time for (80:10:10)
CN[3] Al
CN[4] Al
CN[5] Al
Qn[3] Al
Qn[4] Al
Qn[5] Al
# of Al

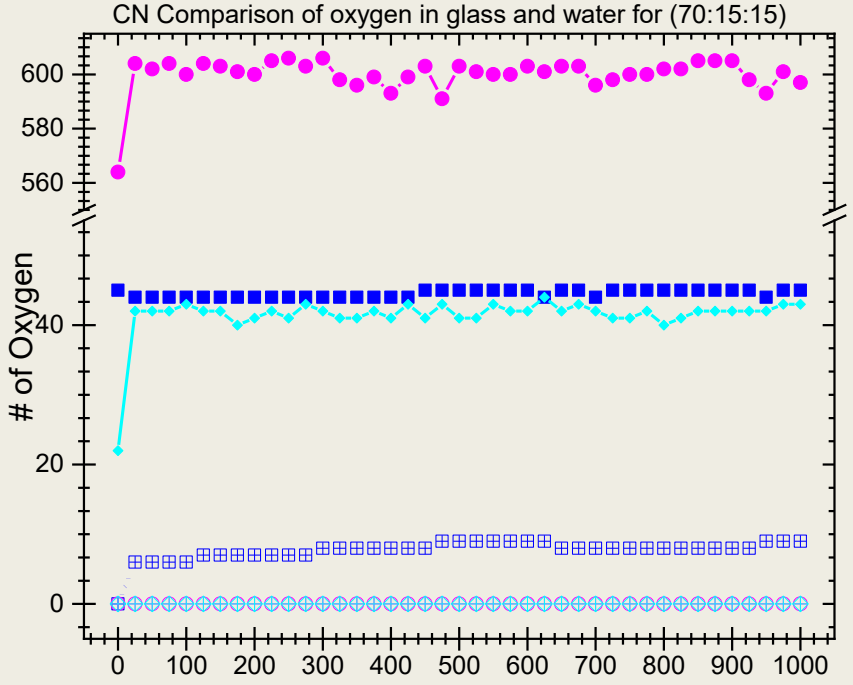

CN/Qn Distribution of Al as a function of time for (70:15:15)
# of Al

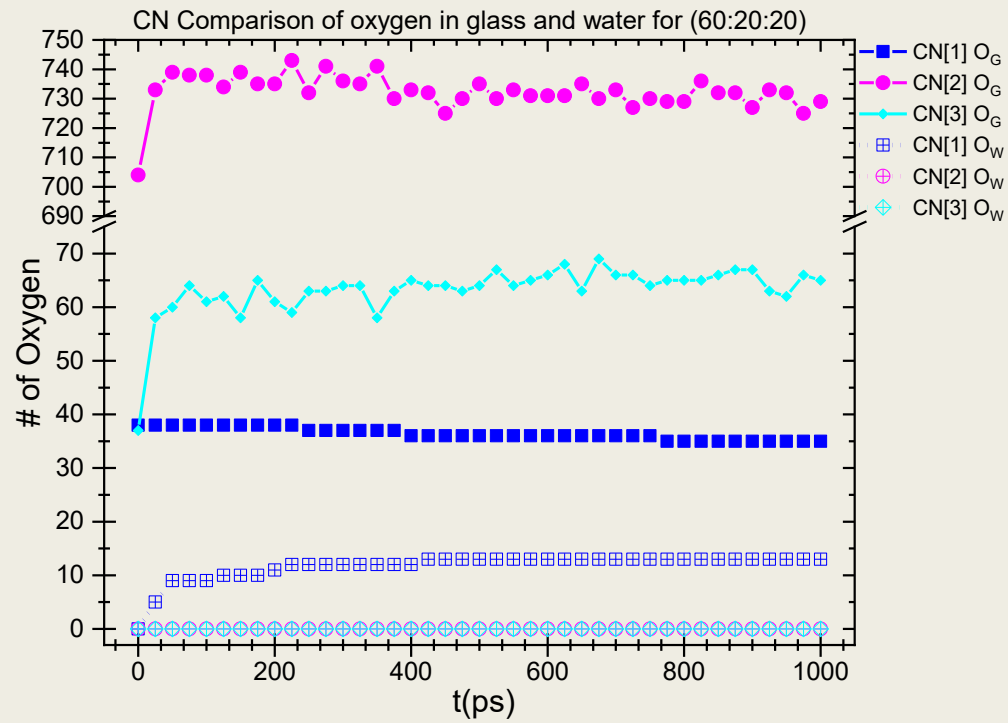

CN/Qn Distribution of Al as a function of time for (60:20:20)
CN[3] Al
CN[4] Al
CN[5] Al
Qn[3] Al
Qn[4] Al
Qn[5] Al
# of Al
t(ps)

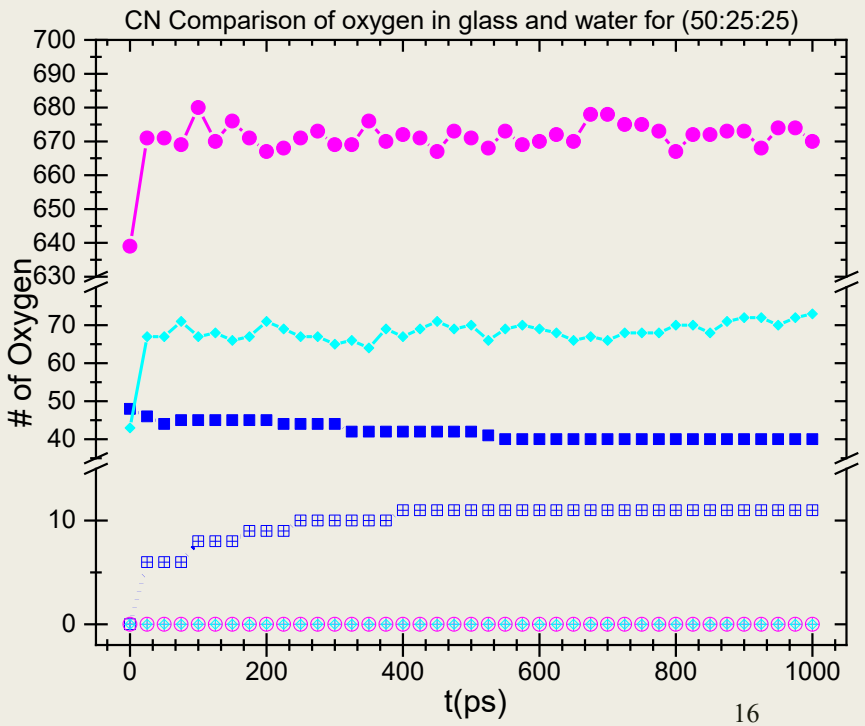

CN/Qn Distribution of Al as a function of time for (50:25:25)
# of Al
t(ps)

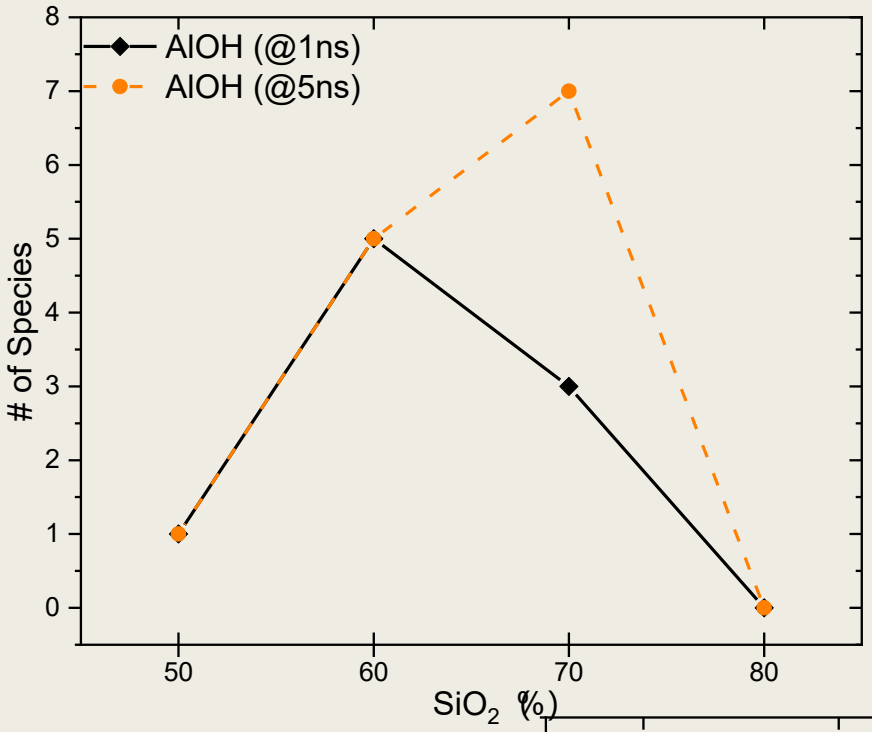

CN/Q$_n$ Distribution of Si as a function of time for (80:10:10)
CN/Q$_n$ Distribution of Si as a function of time for (70:15:15)
CN/Q$_n$ Distribution of Si as a function of time for (60:20:20)
CN/Q$_n$ Distribution of Si as a function of time for (50:25:25)
CN[3] Si
CN[4] Si
CN[5] Si
Qn[3] Si
Qn[4] Si
Qn[5] Si
# of Si
t(ps)

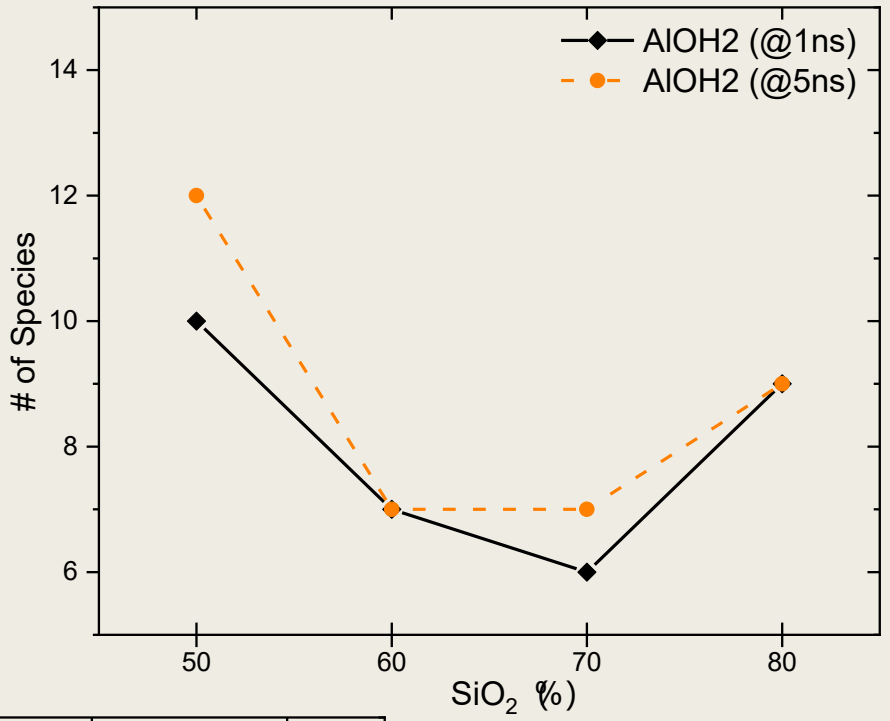

CN Comparison of oxygen in glass and water for (80:10:10)
# of Oxygen
CN[1] O_G
CN[2] O_G
CN[3] O_G
CN[1] O_W
CN[2] O_W
CN[3] O_W

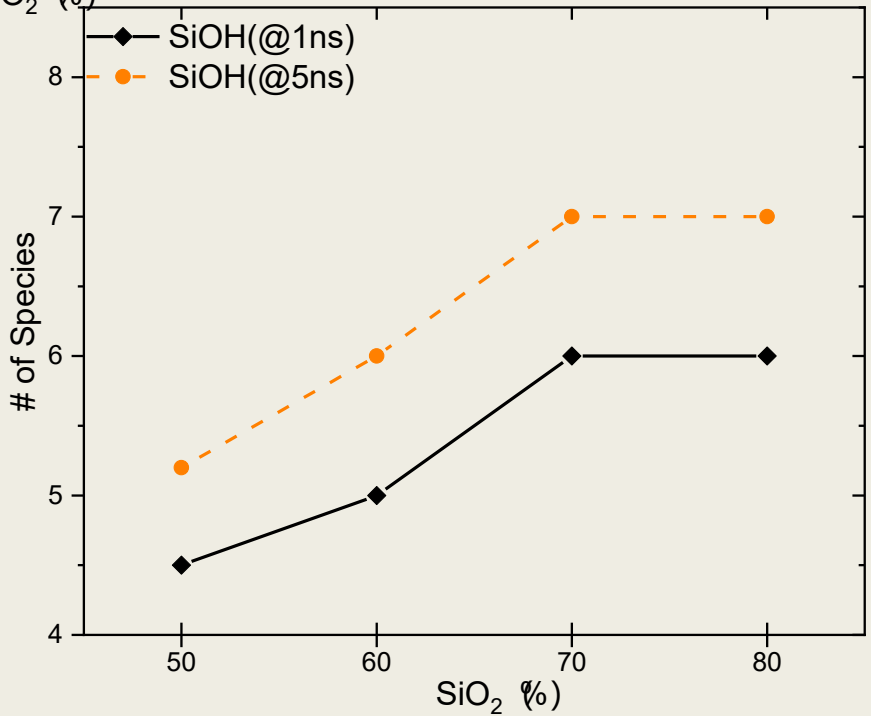

CN Comparison of oxygen in glass and water for (70:15:15)
# of Oxygen

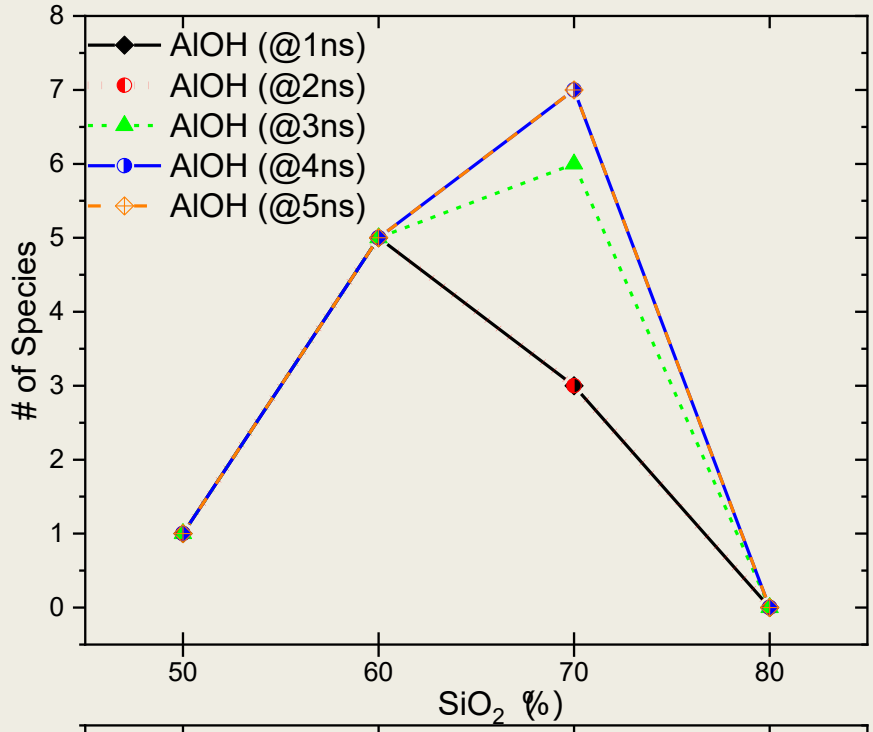

CN Comparison of oxygen in glass and water for (60:20:20)
# of Oxygen
t(ps)
CN[1] O_G
CN[2] O_G
CN[3] O_G
CN[1] O_W
CN[2] O_W
CN[3] O_W

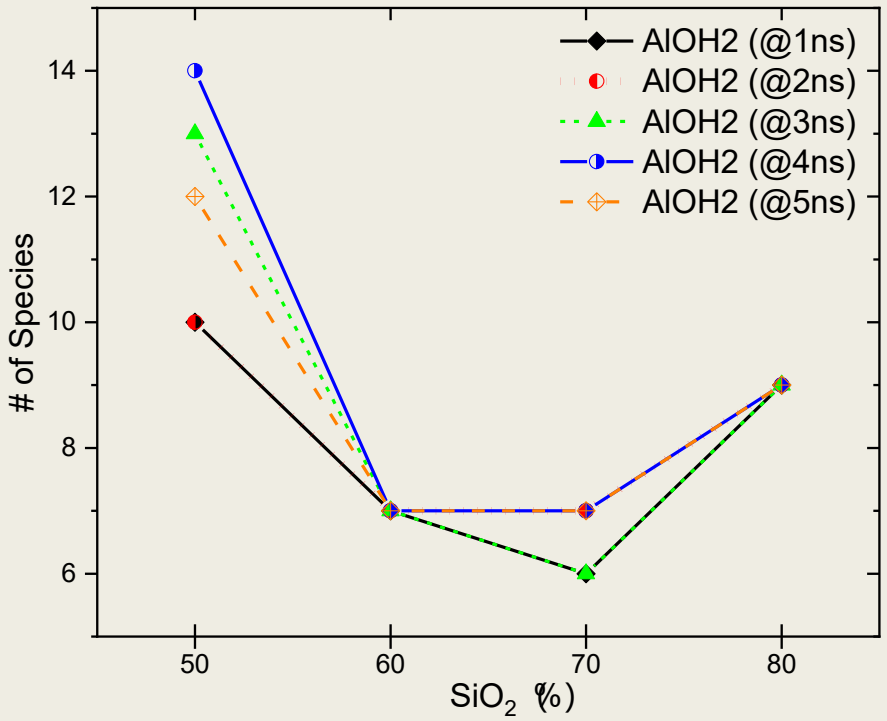

CN Comparison of oxygen in glass and water for (50:25:25)
# of Oxygen
t(ps)

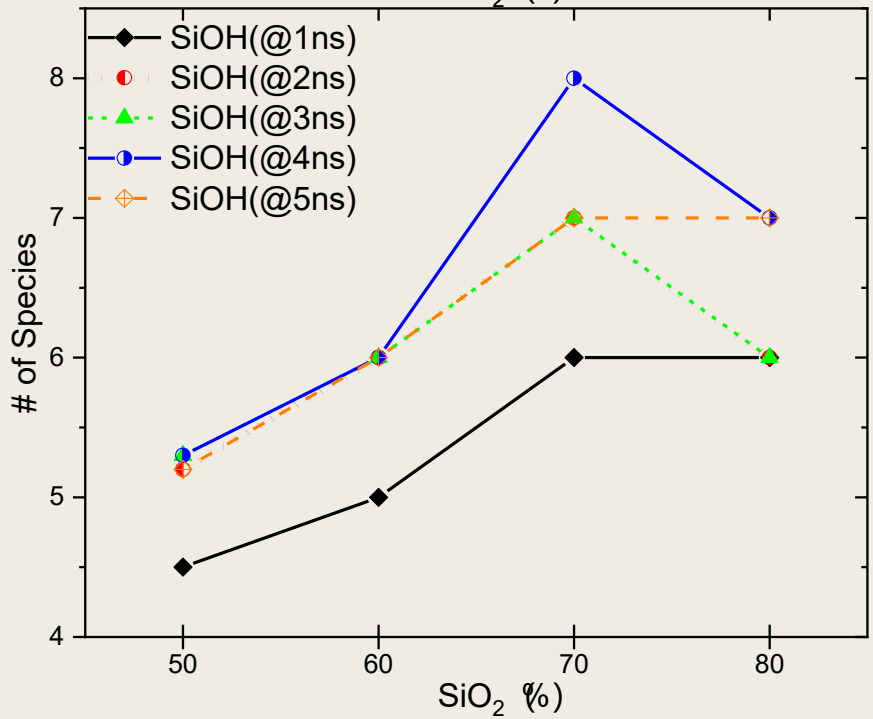

AlOH (@1ns)
AlOH (@5ns)
# of Species
SiO2 (%)


AlOH2 (@1ns)
AlOH2 (@5ns)
# of Species
SiO2 (%)


SiOH(@1ns)
SiOH(@5ns)
# of Species
SiO2 (%)

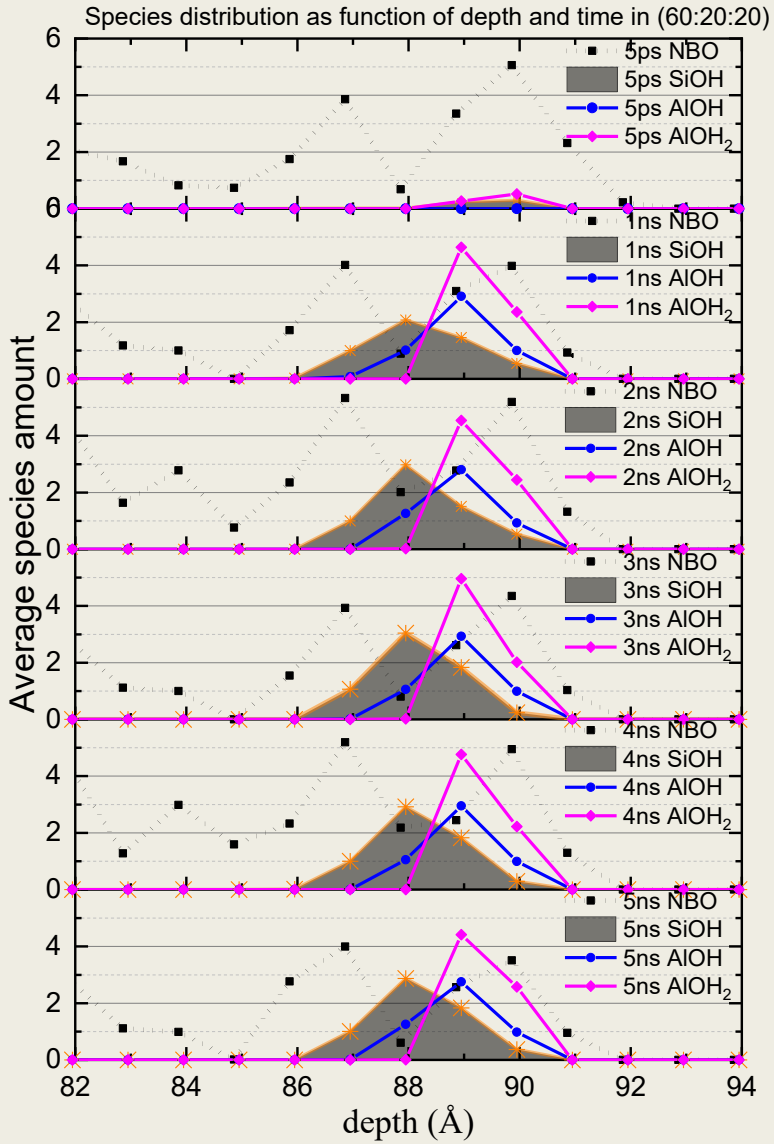






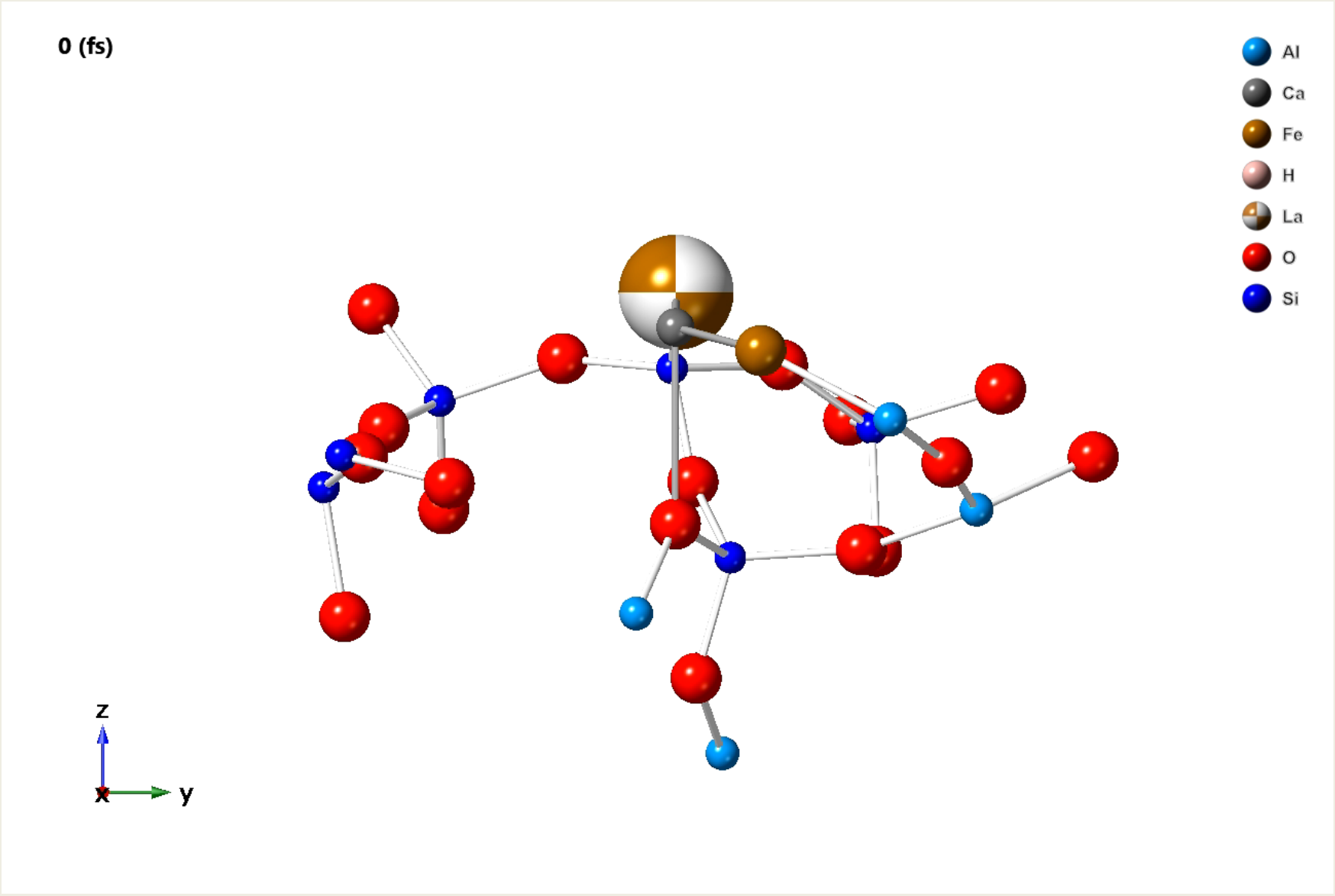
- AlOH species are suppressed at lower or higher SiO_2 percentage
- $AlOH_2$ species are suppressed at 60 and 70% of SiO_2
- SiOH species are positively correlated to SiO_2 content

Target species distribution in (60:20:20) surface



- NBO is intrinsic species in glasses and can be observed downwards to the bulk glass
- All primary target species are ONLY observed within 5-6 Å from the top surfaces in 5 ns. The "unchanging" configurations indicate all these species only form in the surface range. These species can be called "surface species"

Hydrogen hop through NBO



Summary

- CN/Q_n distribution for water-free models shows
  - Apparent difference
  - More defects exist in the surface structure
  - Defects vary with the change of component ratio
- CN/Q_n distribution as time of function displays
  - Species change greatly at the first ~25ps
  - the active [3]Al capture oxygen atoms in water so the concentration of [3]Al decreases while [4]Al increase
  - the first 30ps is the most active phase
  - CN/Q_n of Si shows the tendency is similar except for (50:25:25)
  - # of TBO increases with the decrease of SiO_2; TBO shows higher activity in the first 1ns but the total amount keeps a stable level after first ~25ps
- AlOH species are suppressed at lower or higher SiO_2 percentage
- $AlOH_2$ species are suppressed at 60 and 70% of SiO_2
- SiOH species are positively correlated to SiO_2 content
- All primary target species ONLY form within 5-6 Å from the top surface.

Thank you!