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Supplementary Information for

Simulations Reveal the Role of Composition into the Atomic-level Flexibility of Bioactive Glass Ionomers

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SI guide

Supplementary methods:

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Supplementary references:

1. W. Lowenstein, *Am. Mineral.*, 1954, **39**, 92-94.
2. M. P. Allen and D. J. Tildesley, *Computer simulation of liquids*, Oxford Science Publications, 1987.

Supplementary methods

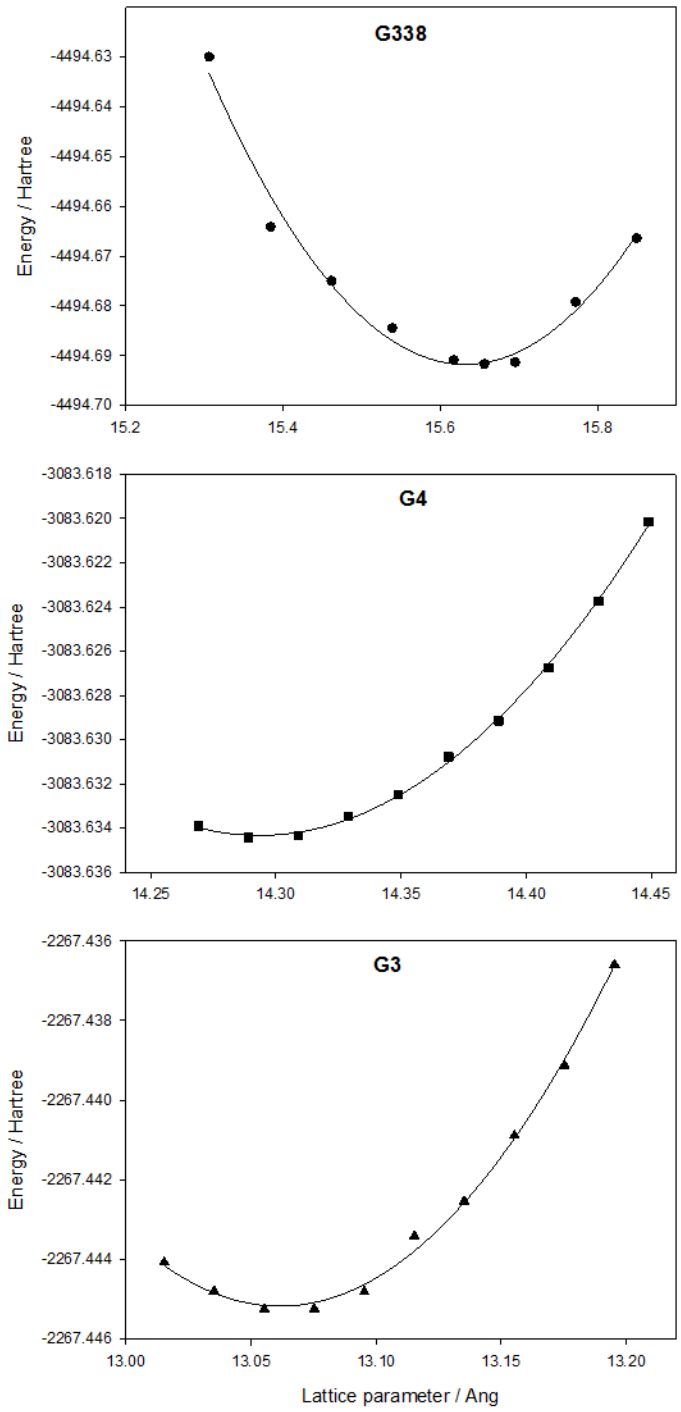
S.1. Atomic composition of the ionomer glasses investigated in this study

	G3	G4	G338
Si	17.0%	9.0%	8.1%
Al	11.8%	13.1%	13.2%
Ca	6.5%	7.5%	3.5%
F	13.1%	15.1%	21.7%
O	51.6%	50.3%	42.7%
P	–	5.0%	4.3%
Na	–	–	6.5%
Al_2O_3 : SiO_2 [a]	0.59	0.76	0.65
Al : (Si+P) ratio	0.69	0.94	1.06

[a] m/m % > 0.5 to ensure a practical glass.[1]

S.2. Isotropic relaxation of the cubic cell volume.

Figure S.2. Change in the total energy as a function of the lattice parameter for the G3, G4 and G338 ionomer glasses.



Supplementary results

S.3. Q^n distribution and Network Connectivity

Table S.3. Q^n terminology: *n* represents the number of bridging oxygens (BOs) per the network former (Si, Al and P). The network connectivity is defined as

$$NC = \sum_i p(Q^i) \times i$$

Where $(Q^i) = {Q^i}/{\sum_j Q^j}$. Tables below reports the coordination statistics around the Si, Al and P atoms. For example, to determine Q^n(Si), we have computed the existence of **Si**-O-Si, **Si**-O-Al and **Si**-O-P bridges using a cut-off radius of 2.0 Å.

Coordination statistics of the Si-O, Al-O and P-O networks:

Si	**Q^n distribution**							
	Q^0	**Q^1**	**Q^2**	**Q^3**	**Q^4**	**Q^5**	**NC**	**CN_{av}**
GIC 3c	-	-	3.8	30.8	65.4	-	3.52	3.61
GIC 4c	-	-	-	15.3	71.4	11.9	3.99	3.04
G338	-	0.6	18.4	29.3	43.5	8.2	3.40	3.38

Al	**Q^n distribution**									
	Q^0	**Q^1**	**Q^2**	**Q^3**	**Q^4**	**Q^5**	**Q^6**	**Q^7**	**NC**	**CN_{av}**
GIC 3c	-	0.0	5.7	30.7	44.9	13.7	3.9	1.0	3.83	3.47
GIC 4c	-	16.7	27.4	41.5	41.5	9.5	4.6	7.8	3.57	3.04
G338	-	0.3	21.5	42.8	17.9	13.1	3.0	1.3	3.37	2.95

P	**Q^n distribution**						
	Q^0	**Q^1**	**Q^2**	**Q^3**	**Q^4**	**NC**	**CN_{av}**
GIC 3c	-	-	-	-	-	-	-
GIC 4c	10.0	20.0	28.0	39.8	2.3	2.04	3.80
G338	0.0	18.3	21.6	36.8	23.3	2.65	3.73

Total Y-O network connectivity (Y = Si, Al and P) ($NC_{tot} = NC_{Si\text{-}O} + NC_{Al\text{-}O} + NC_{P\text{-}O}$):

NC_{tot} (G3) = 3.52 + 3.83 = 7.35

NC_{tot} (G4) = 3.99 + 3.57 + 2.04 = 9.60

NC_{tot} (G338) = 3.40 + 3.37 + 2.65 = 9.42

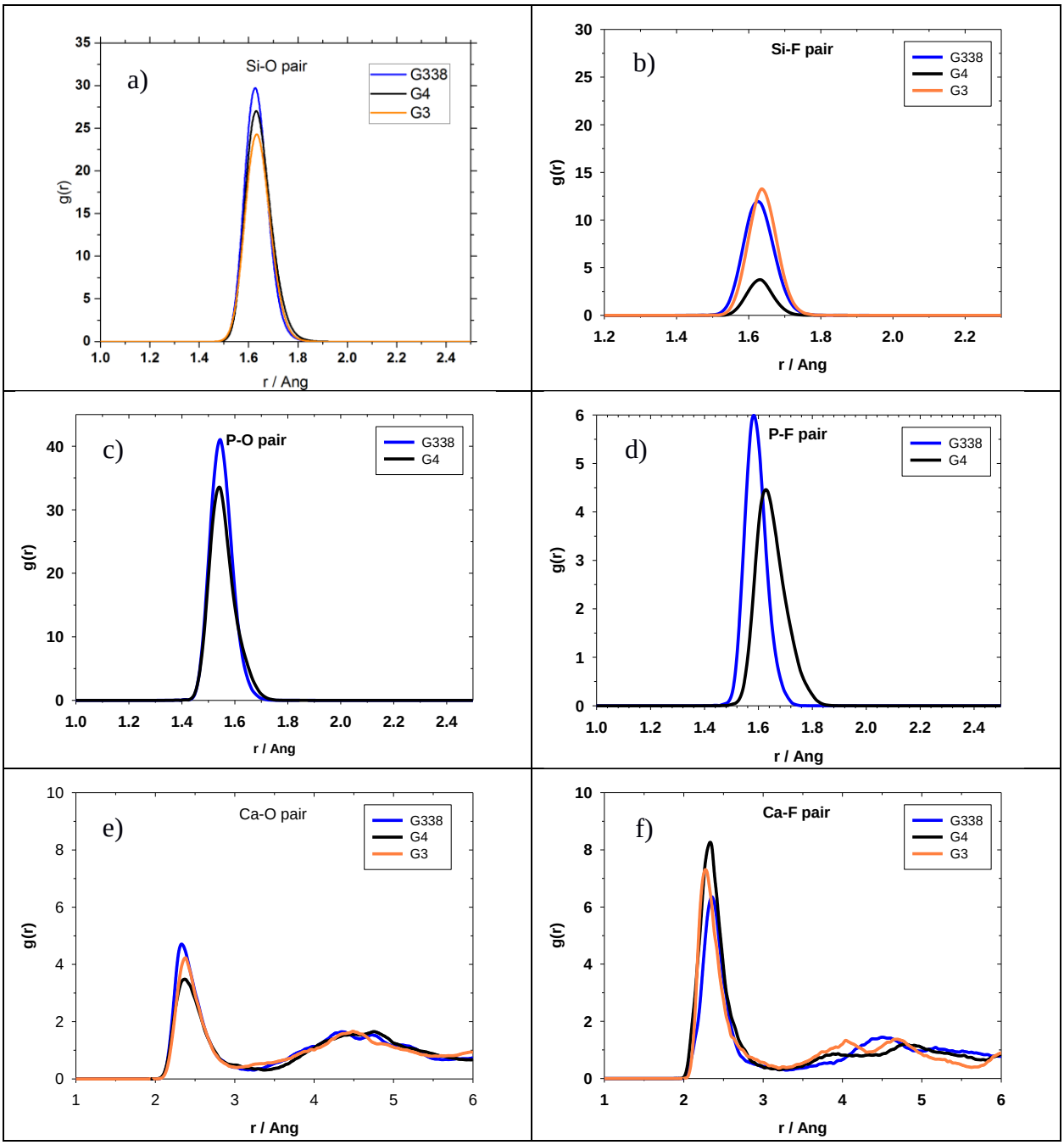
S.4. Al speciation

Table S.4. The local Aluminium environment, and their abundances, in the G3, G4 and G338 ionomer glasses.

Species	**G3**	**G4**	**G338**
AlO_2F_2	0.6	13.8	20.4
AlO_2F_3	5.0	1.8	5.9
AlO_3F	33.8	45.8	39.3
AlO_3F_2	0.0	7.2	5.9
AlO_4	49.2	23.1	20.6
AlO_4F	10.7	8.3	6.4
AlO_5F	0.8	0.0	1.6
AlO_xF_y species ($1 < x, y < 3$)	50.9	76.9	79.5

S.5. Radial distribution functions (RDFs)

Figure S.5. The radial distribution functions for the G3, G4 and G338 ionomer glasses.



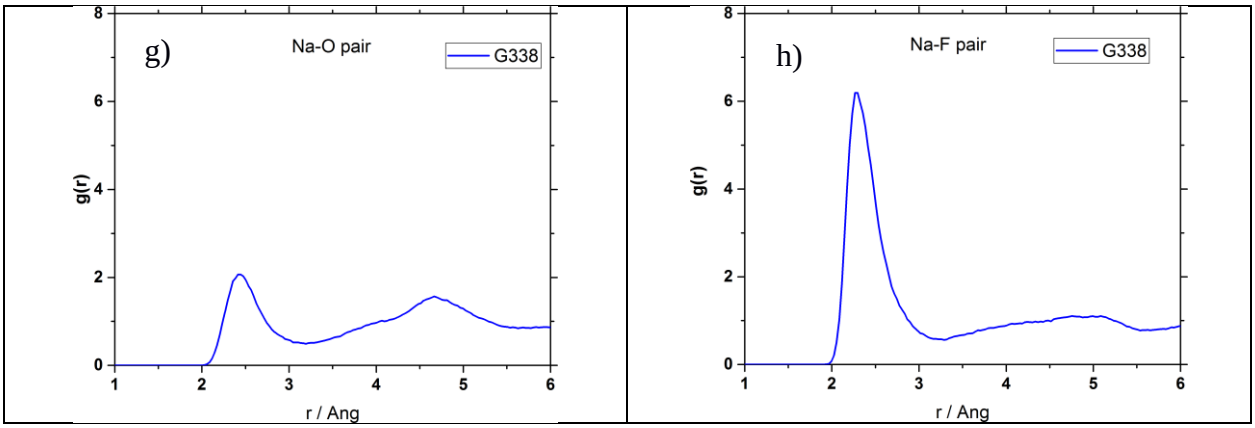
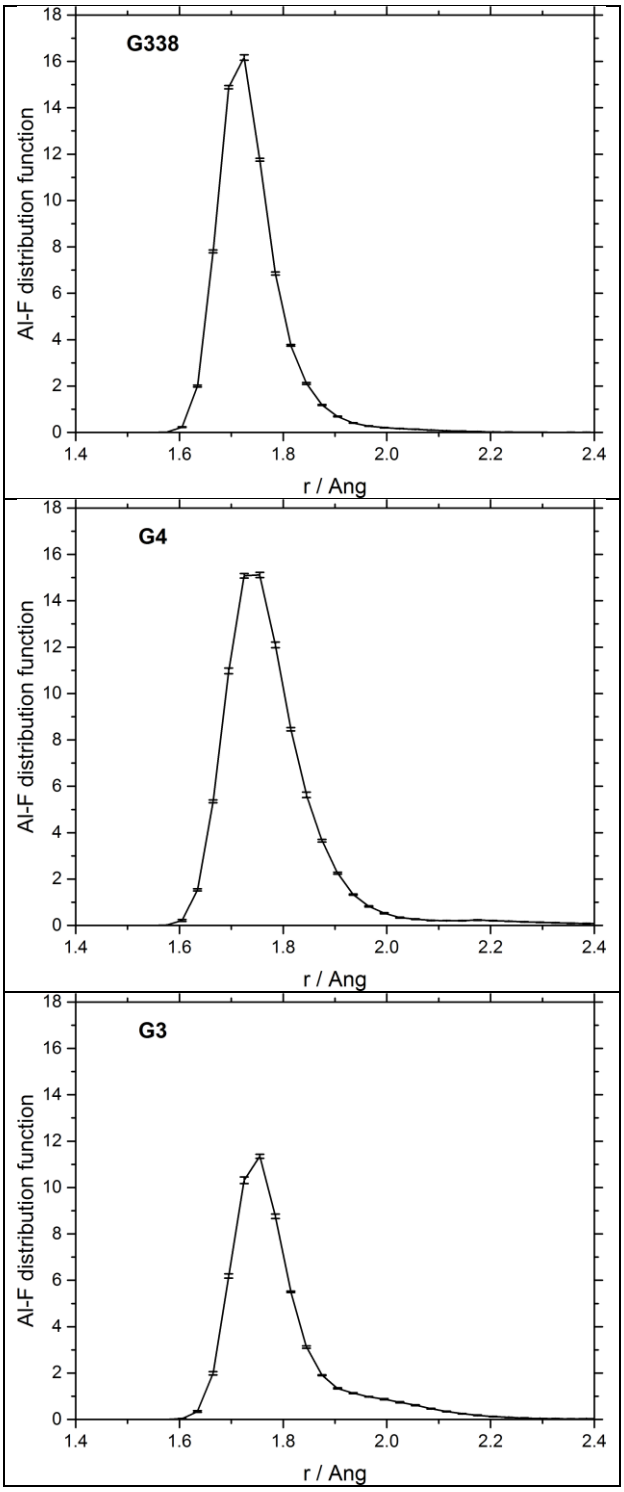


Table S.5. Positions of the maximum of the radial distribution functions of the cation-oxygen and cation-fluorine pairs (r_{max}), and partial coordination number of the cations obtained from the integration of the radial distribution functions up to the first minimum of the peak. The radial distribution functions were computed with a bin size of 0.005 Å.

		Si-O	Si-F	Al-O	Al-F	P-O	P-F	Ca-O	Ca-F	Na-O	Na-F
G338	**r_{max} (Å)**	1.627	1.627	1.762	1.717	1.542	1.587	2.337	2.332	2.432	2.297
	CN	3.4	0.6	3.0	1.2	3.7	0.3	4.3	2.7	3.1	3.4
G4	**r_{max} (Å)**	1.627	1.627	1.767	1.737	1.537	1.632	2.362	2.327	-	-
	CN	3.9	0.1	3.3	0.9	3.8	0.2	4.4	2.3	-	-
G3	**r_{max} (Å)**	1.627	1.627	1.757	1.747	-	-	2.382	2.247	-	-
	CN	3.6	0.4	3.6	0.6	-	-	4.8	1.7	-	-

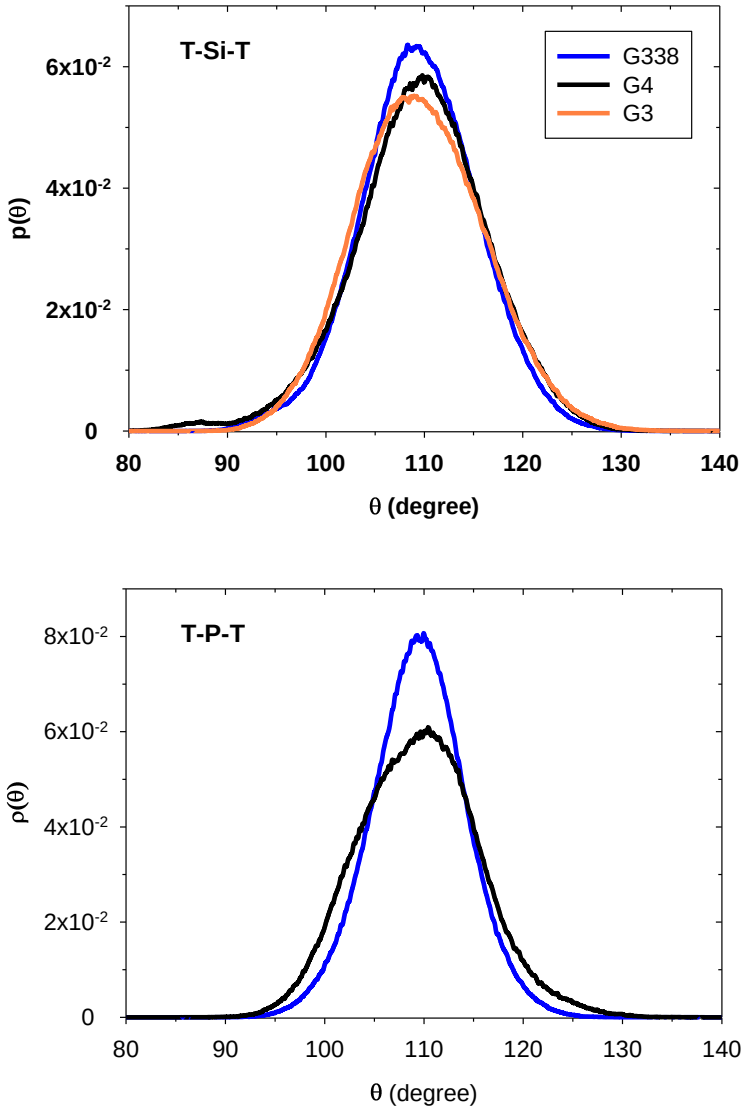
S.6. Standard error of the mean of the Al-F radial distribution functions.

Figure S.6. Radial distribution functions for the Al-F atomic-pairs in the G338, G4 and G3 glasses. Standard errors computed from the variations of block averages, each lasting 5 ps.



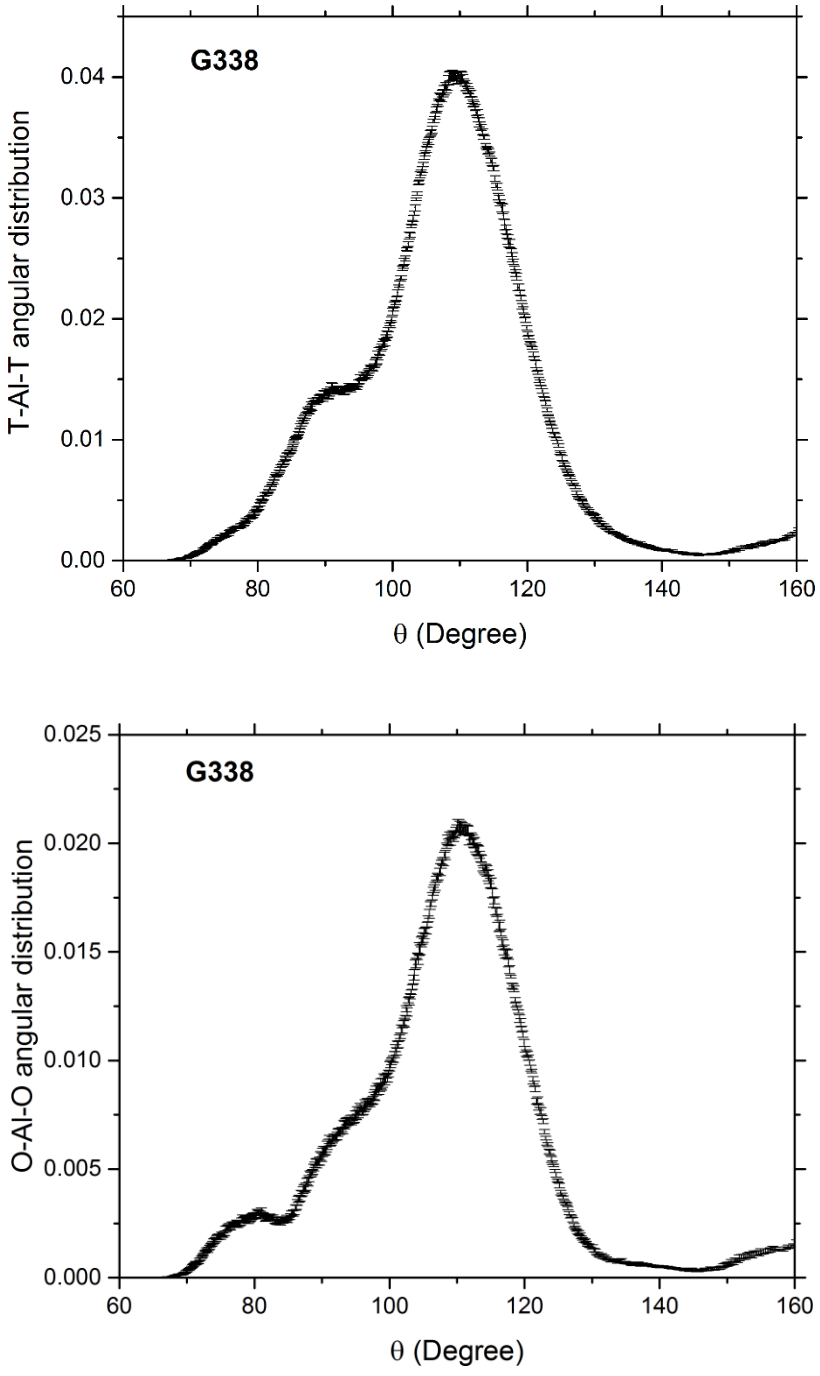
S.7. Angular distribution functions (ADFs)

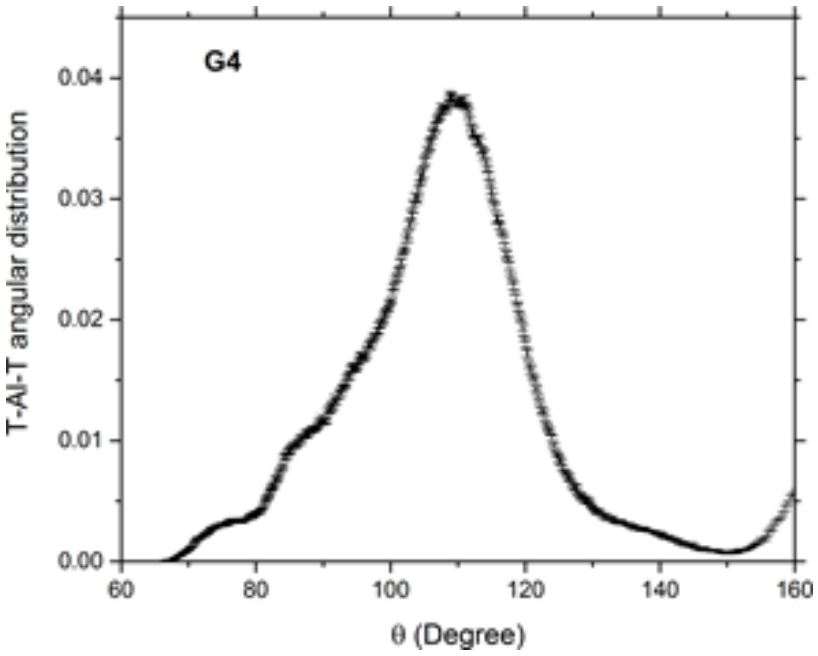
Figure S.7. The T-Si-T and T-P-T bond-angle distributions, where T = O or F, for the G3, G4 and G338 ionomer glasses.

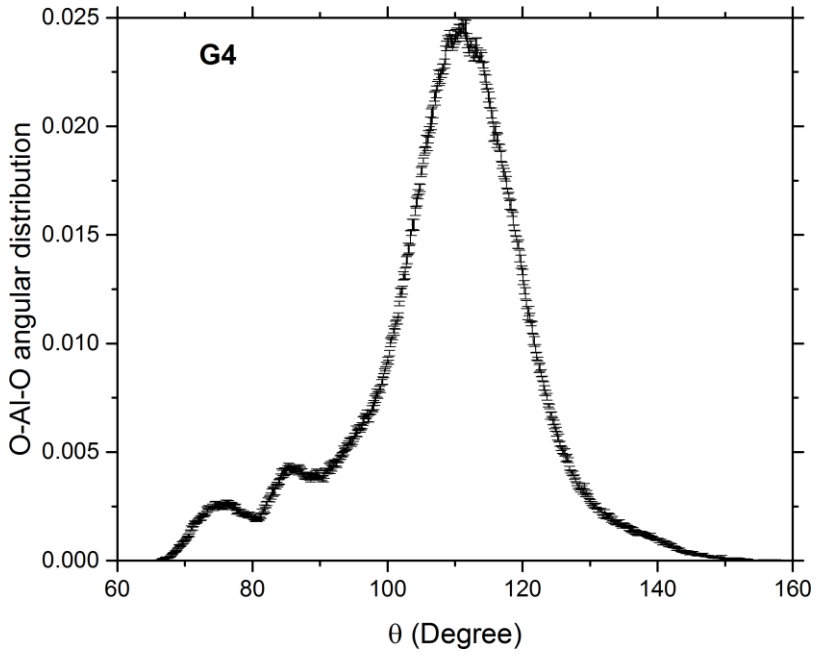


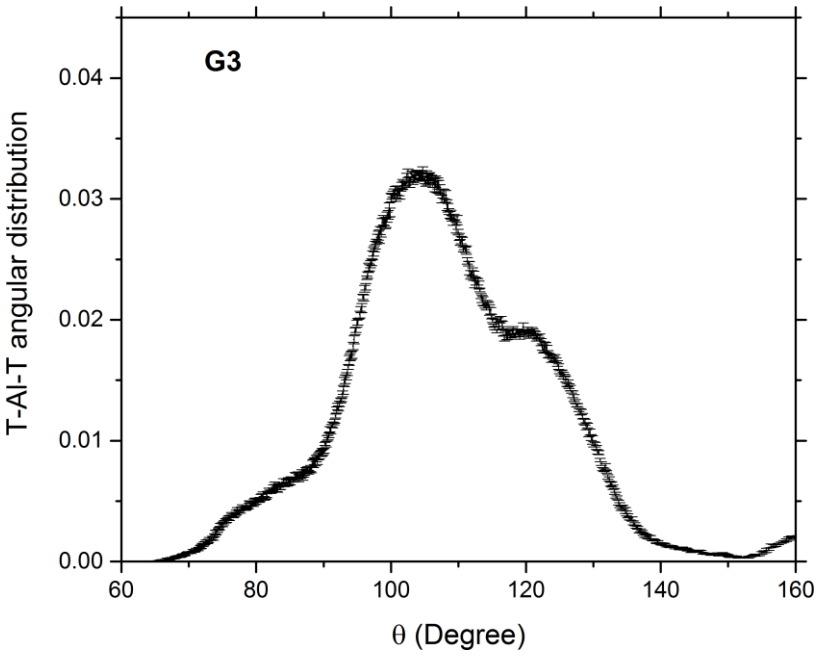
S.8. Standard error of the mean of the T-Al-T (T = O or F) and O-Al-O angular distribution functions.

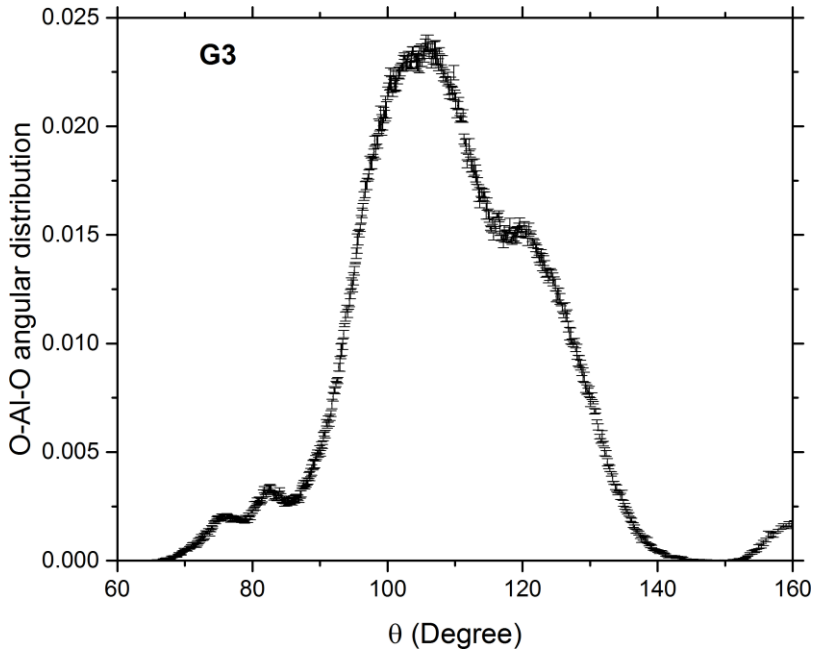
Figure S.8. The T-Al-T (T = O or F) angular distribution functions in the G338, G4 and G3 glass. Standard errors computed from the variations of block averages, each lasting 5 ps.




G4
T-Al-T angular distribution
0.04
0.03
0.02
0.01
0.00
60
80
100
120
140
160
θ (Degree)

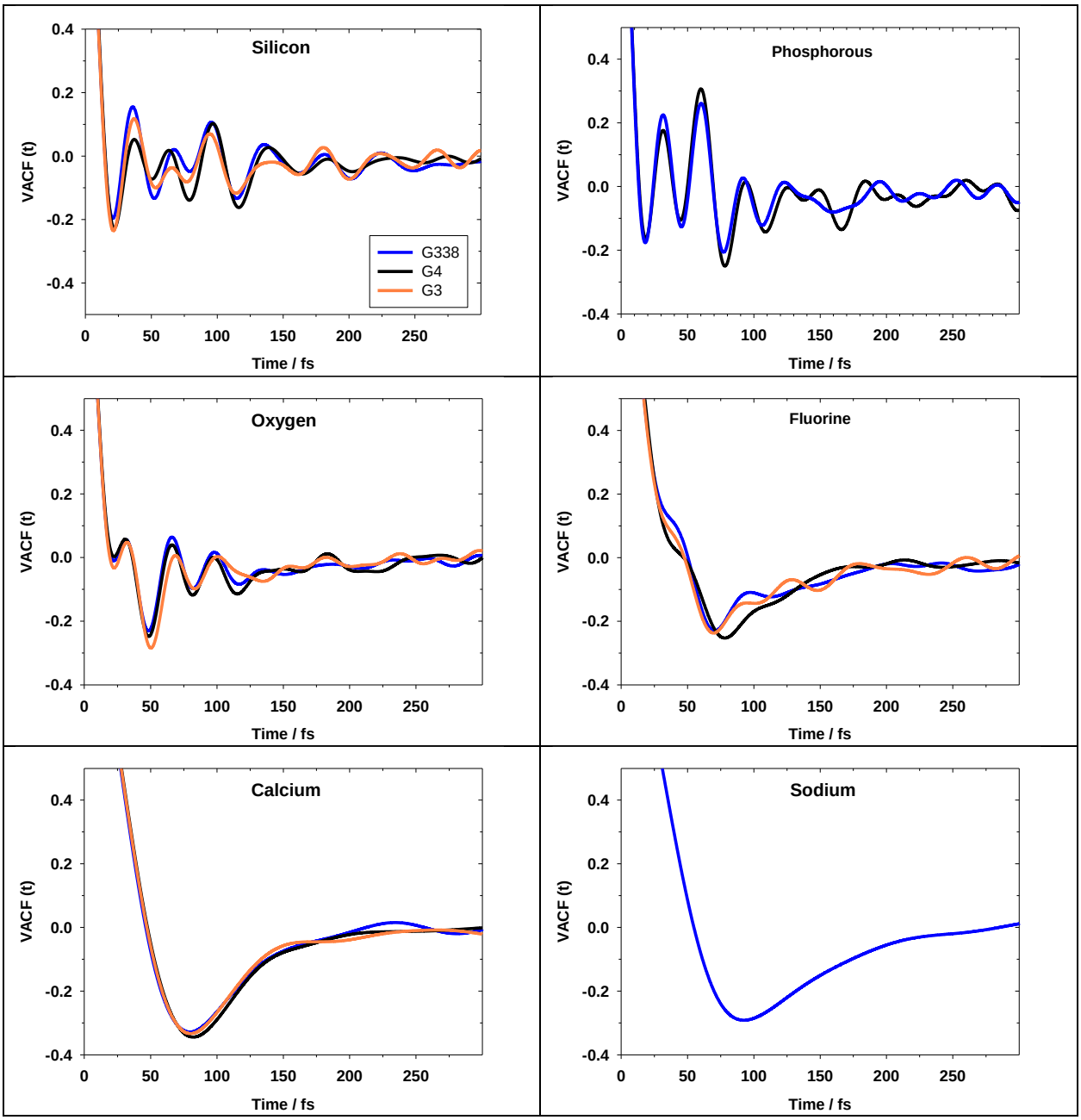

G4
O-Al-O angular distribution
0.025
0.020
0.015
0.010
0.005
0.000
60
80
100
120
140
160
θ (Degree)


G3
T-Al-T angular distribution
0.04
0.03
0.02
0.01
0.00
60
80
100
120
140
160
θ (Degree)


G3
O-Al-O angular distribution
0.025
0.020
0.015
0.010
0.005
0.000
60
80
100
120
140
160
θ (Degree)

S.9. Velocity autocorrelation functions (VACFs)

Figure S.9. VACFs of the Si, P, O, F, Ca and Na species evaluated for the for the G3, G4 and G338 ionomer glasses.



S.10. O speciation

Table S.10. Coordination statistics of $O(P)_x(Al)_y$ species in the G4 and G338 ionomer glasses.

Species	G4	G338
OAl_0P_0	9.0	9.1
OAl_0P_1	23.1	15.5
OAl_0P_2	**0.0**	**0.0**
OAl_1P_0	40.6	38.6
OAl_1P_1	**14.9**	**21.8**
OAl_2P_0	9.4	10.7
OAl_2P_1	0.0	0.0
OAl_3P_0	3.0	4.3

S.11. P coordination environment

Table S.11. The P-O and P-F average coordination numbers (CN). Cut-off distance set at 2.5 Ang. X = O or F.

	P-O			P-F		
	GIC 3c	GIC 4c	G338	GIC 3c	GIC 4c	G338
CN						
0	-	-	-	-	80	72.73
1	-	-	-	-	20	27.27
2	-	-	-	-	-	-
3	-	20.0	27.27	-	-	-
4	-	80.0	72.73	-	-	-
5	-	-	-	-	-	-
P-X	-	3.80	3.73	-	0.20	0.27

S.12. F speciation

Table S.12. The most common local Fluorine environment in the G3, G4 and G338 ionomer glasses (with abundances above 2% for at least one ionomer glass).

Species	**G3**	**G4**	**G338**
FAl	1.3	4.8	0.3
FAl_2	10.0	12.4	1.8
FAlCa	30.8	41.8	9.2
$FAlCa_2$	2.9	13.5	3.2
FAlCaNa	-	-	12.3
FAlNa	-	-	20.2
$FAlNa_2$	-	-	21.2
FAlSi	0.1	3.2	-
FCa	-	6.6	-
FCa_2	-	3.8	-
FCa_3	5.0	9.6	-
FCaSi	34.2	3.3	7.5
FCaNaSi	-	-	2.0
FNa	-	-	4.0
FNaSi	-	-	7.1
FNa_2Si	-	-	3.8
FSi	15.6	0.1	2.4

S.13. Fluorine diffusion coefficients

Table S.13. Fluorine diffusion coefficients obtained from the AIMD simulations of the G3, G4 and G338 ionomer glasses computed in the linear regime between 83 and 95 ps of the mean-squared displacement (MSD). Values obtained using the standard relationship between the diffusion coefficients and the slope of the MSD of the F species over all of the snapshots, $MSD(t) = 6Dt$.[2]

	Δ(MSD)/Δt (× 10^{-4})	**Pearson's r**	**Adj. R-Square**	**D (× 10^{-5} cm^2 s^{-1})**
G3	1.2544	0.9989	0.9977	0.2613
G4	1.4576	1.0000	1.0000	0.3037
G338	1.7520	0.9996	0.9992	0.3650