Electronic Supplementary Information

Dynamical descriptors of bioactivity: correlation between chemical durability and ion migration in biodegradable glasses

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1. Computational details

A partial-charges potential combining long-range Coulombic interactions with short-range Buckingham terms[1, 2] (Table 1) was employed. Several previous studies confirmed the suitability of this potential to model structure and ion migration in conventional and bioactive silicate glasses,[3-6] including fluorinated bioglasses (F-BGs).[7] In order to circumvent the known issue affecting the reproduction of phosphate-related features by this potential,[7, 8] phosphorus-free compositions were simulated, by converting the very small (<3%) P_2O_5 content in the original glasses to SiO_2. The small P_2O_5 content is unlikely to introduce significant differences in the dynamical properties examined. This was confirmed by simulating a corresponding P-free model of the 45S5 Bioglass ($48.8SiO_2 \cdot 24.3Na_2O \cdot 26.9CaO$, mol%) and extracting the activation energy for Na and Ca diffusion through the same procedure used for the fluorinated glasses: the calculated E_a values are 53.1 and 74.9 kJ/mol for Na and Ca, respectively, in very good agreement with the values previously obtained for the P-containing 45S5 Bioglass,[6] 50.2 and 77.2 kJ/mol (discussed in the main text), confirming that the 2.6% P_2O_5 fraction does not affect the diffusion parameters. Added to the equally good agreement between structural properties of P-free and P-containing F-BGs discussed in the main text, these data support the validity of the P-free approximation for these systems. MD simulations were performed in the NVT ensemble with a 2 fs timestep. In each case, an initial random mixture of ~3500 atoms of the appropriate composition, inserted in a periodic

cubic cell of ~36 Å, was heated to 6000 K and then cooled down to room temperature at 10 K/ps. This was followed by a further NVT equilibration of 0.5 ns at 300 K, and a final NVE run of 0.5 ns from which structural properties were calculated. The final configuration of the RT run was then equilibrated to 1000, 1200, and 1400 K for 0.5 ns, followed by NVT production runs of 2 ns at each temperature, from which the diffusive parameters for each species were calculated. Due to the infrequent nature of ion migration events at room temperature on the standard MD time scales, simulations of diffusive processes are often performed at higher temperatures in order to enhance their statistical sampling.[1, 6, 9-12] As long as the selected temperatures are such that no melting of the glass occurs during the simulation, the modifier ions migrate in an essentially static silicate network, representative –on average– of the same structural landscape along which the same ions move at room temperature; hence, the key features of the diffusive process of Na/Ca/F ions are well reproduced, particularly when the goal is comparing diffusion in two different matrixes, as in this case.

Table 1. Buckingham potential parameters: $V(r) = A\,e^{-r/\rho} - C/r^6$

	A (eV)	ρ (Å)	C (eV Å^6)
Si$^{+2.4}$-O$^{-1.2}$	$1.3702905\cdot10^4$	0.193817	54.681
Na$^{+0.6}$-O$^{-1.2}$	$4.3837555\cdot10^3$	0.243838	30.700
Ca$^{+1.2}$-O$^{-1.2}$	$7.7471834\cdot10^3$	0.252623	93.109
O$^{-1.2}$-O$^{-1.2}$	$2.0292204\cdot10^3$	0.343645	192.28
F$^{-0.6}$-F$^{-0.6}$	$1.1510594\cdot10^4$	0.225005	29.527
F$^{-0.6}$-O$^{-1.2}$	$1.8636049\cdot10^3$	0.328812	141.27
Si$^{+2.4}$-F$^{-0.6}$	$5.3193487\cdot10^4$	0.146851	5.0196
Na$^{+0.6}$-F$^{-0.6}$	$5.8286140\cdot10^4$	0.169113	4.1555
Ca$^{+1.2}$-F$^{-0.6}$	$9.7642109\cdot10^5$	0.147304	12.163

Structural properties

Table 2. Q_n distributions (%)

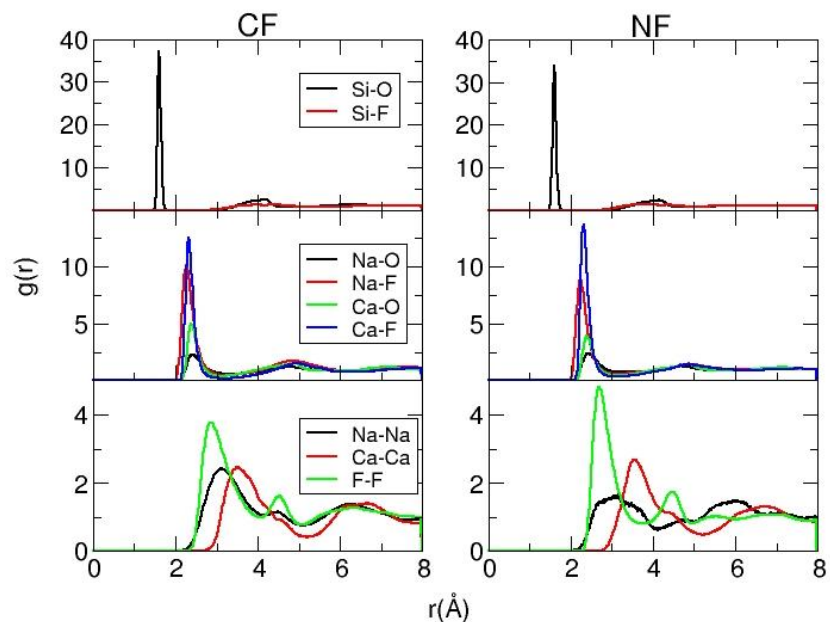| glass	Q_0	Q_1	Q_2	Q_3	Q_4
CF	1.2	7.74	27.54	43.55	19.97
NF	0.64	7.56	29.58	41.96	20.26

Figure 1. Radial distribution functions for CF and NF glasses.

Table 3. Coordination number ratios. $R_{(AB)}$ is the ratio between the number of species B found in the coordination sphere of A (calculated by integrating the radial distribution functions in Figure 1 up to the first minimum) and the number that would occupy the same region if B was homogeneously distributed in the available volume:[13] i.e., $R_{(AB)}>1$ denotes a higher population of B in the coordination shell of A, whereas $R_{(AB)}<1$ denotes a shell depleted of B species, compared to what would result from a uniform distribution of B ($R_{(AB)} = 1$)

glass	$R_{(Na-F)}$	$R_{(Ca-F)}$	$R_{(Na-Na)}$	$R_{(Ca-Ca)}$	$R_{(F-F)}$	$R_{(Ca-Si)}$	$R_{(Na-Si)}$
CF	1.95	1.59	1.59	1.68	1.95	1.1	0.83
NF	1.71	1.79	2.45	1.42	1.73	1.01	0.94

Noncovalent links

Noncovalent T-O…Ca…O-T interactions between silicate tetrahedra (T) belonging to different branches of the silicate matrix, bridged by a central Ca cation, are an important structural descriptor of the durability of glasses.[14, 15] In principle, they could be relevant to explain the different behavior of NF and

CF glasses: the replacement of CaF$_2$ for CaO in CF could lead to a partial loss of these interactions, possibly resulting in a weaker structure, more prone to dissolution compared to NF, for which the CaF$_2$ for Na$_2$O replacement could lead to a potentially higher contribution of Ca-bridged intertetrahedral links.[7] However, the OCaO angle distributions do not support this possibility: no changes had been previously observed in these distributions for different fluorinated BG compositions;[7] moreover, Fig. 2 shows that the fraction of OCaO angles around 90° (representing intertetrahedral links[16]) in CF is actually slightly higher than in NF, whereas the opposite would have been expected if the structural interpretation above was valid in this case.
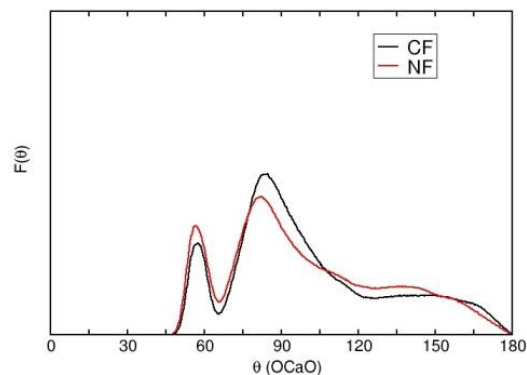

Figure 2. O-Ca-O angle distributions for CF and NF glasses.

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