

Electronic Supplementary Information

Rapid Conversion of Highly Porous Borate Glass Microspheres into Hydroxyapatite

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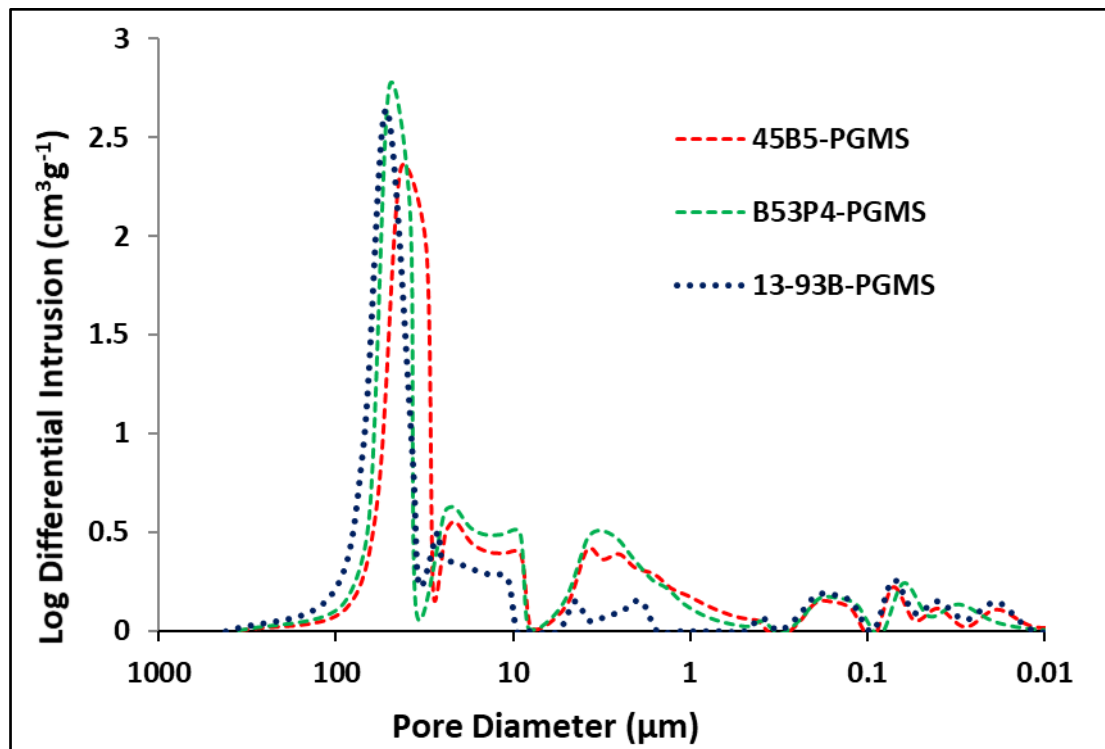
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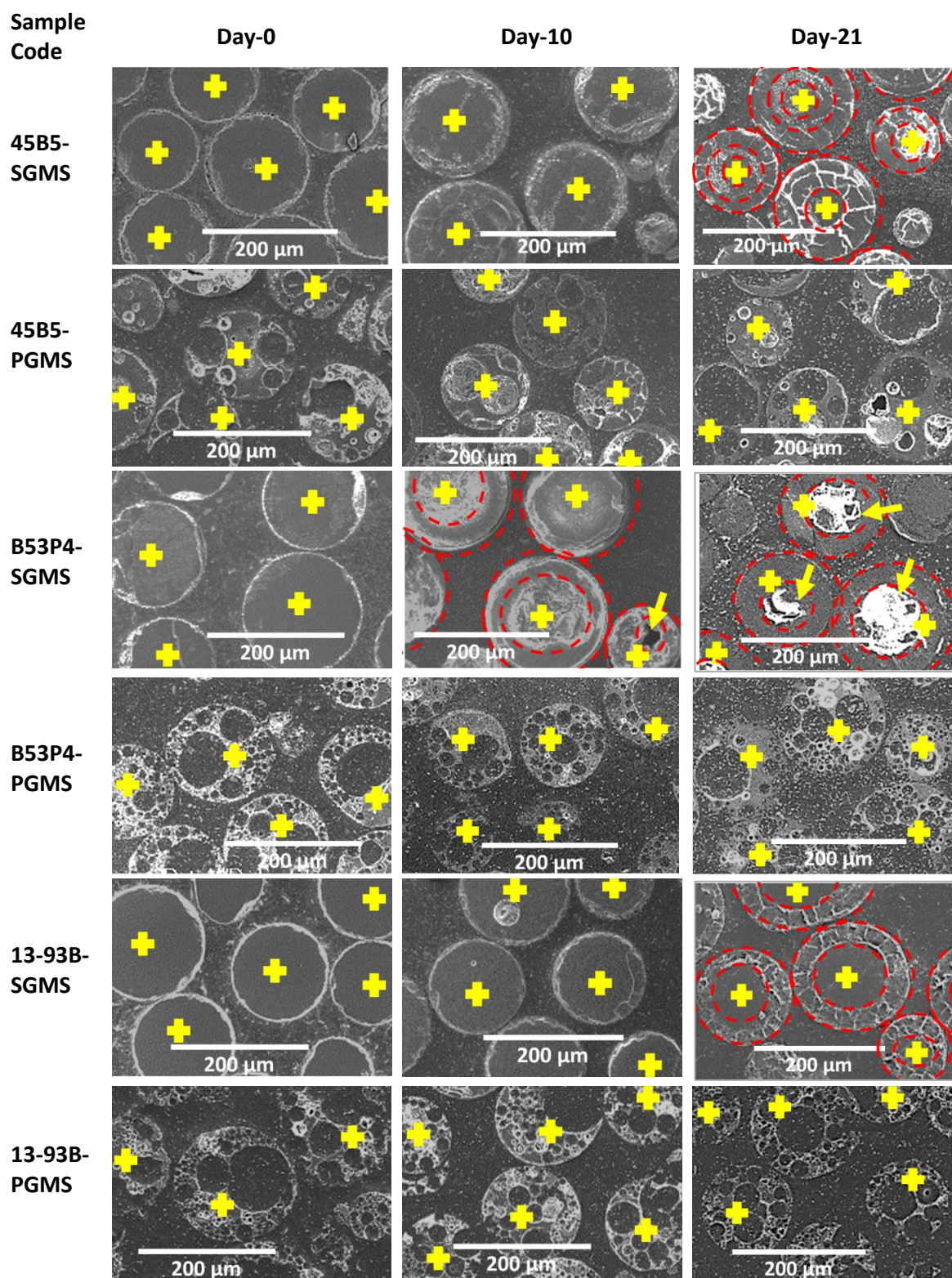
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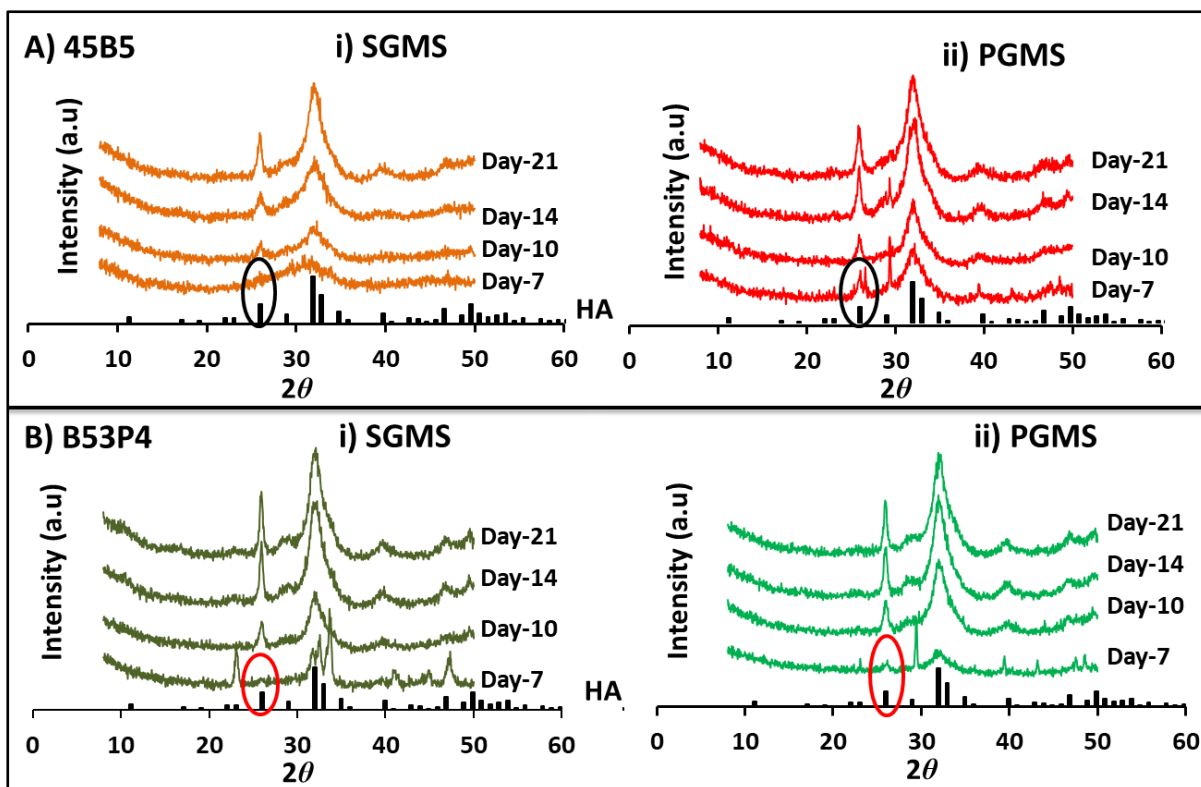
ESI Figures



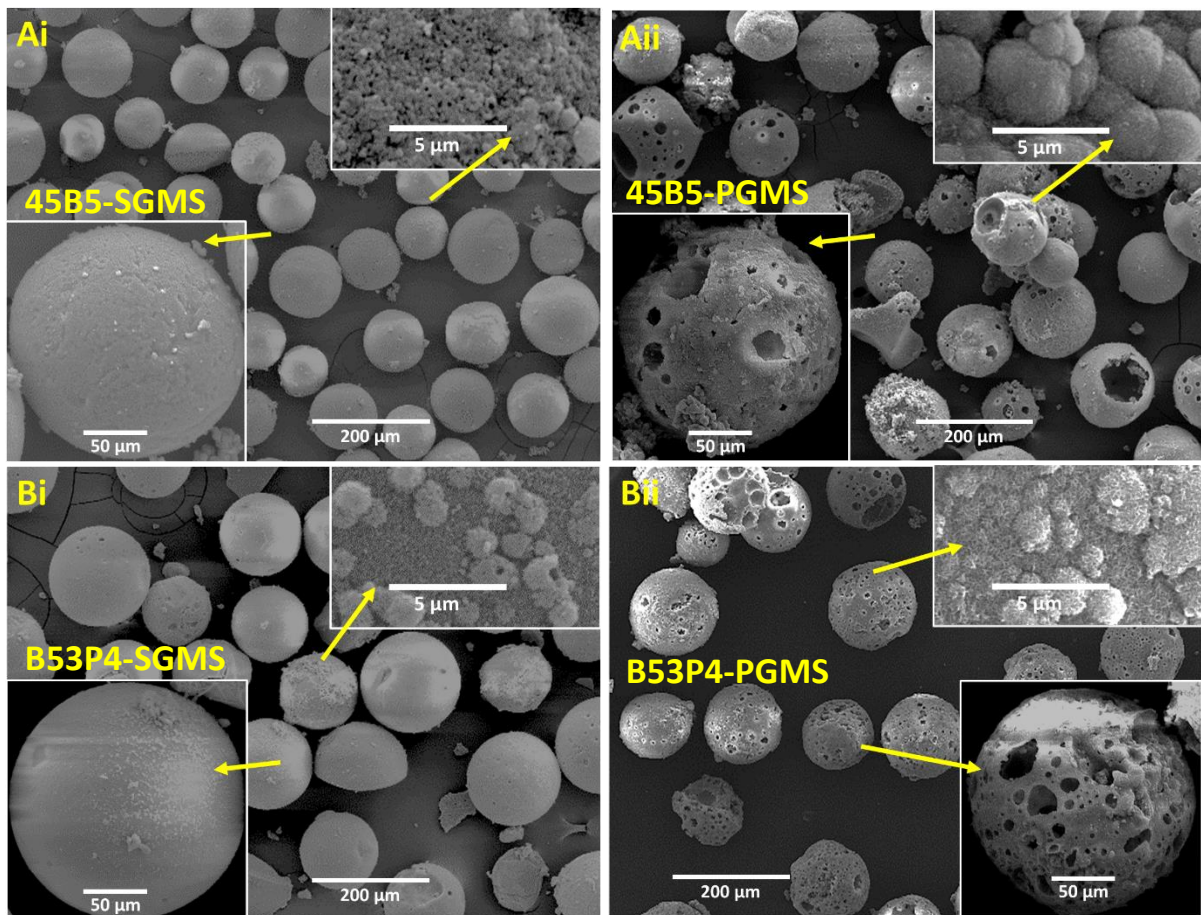
ESI Figure 1: Pore diameters measured using mercury porosimetry showing Log differential pore volume for porous 45B5, B53P4 and 13-93B borate glass microspheres.



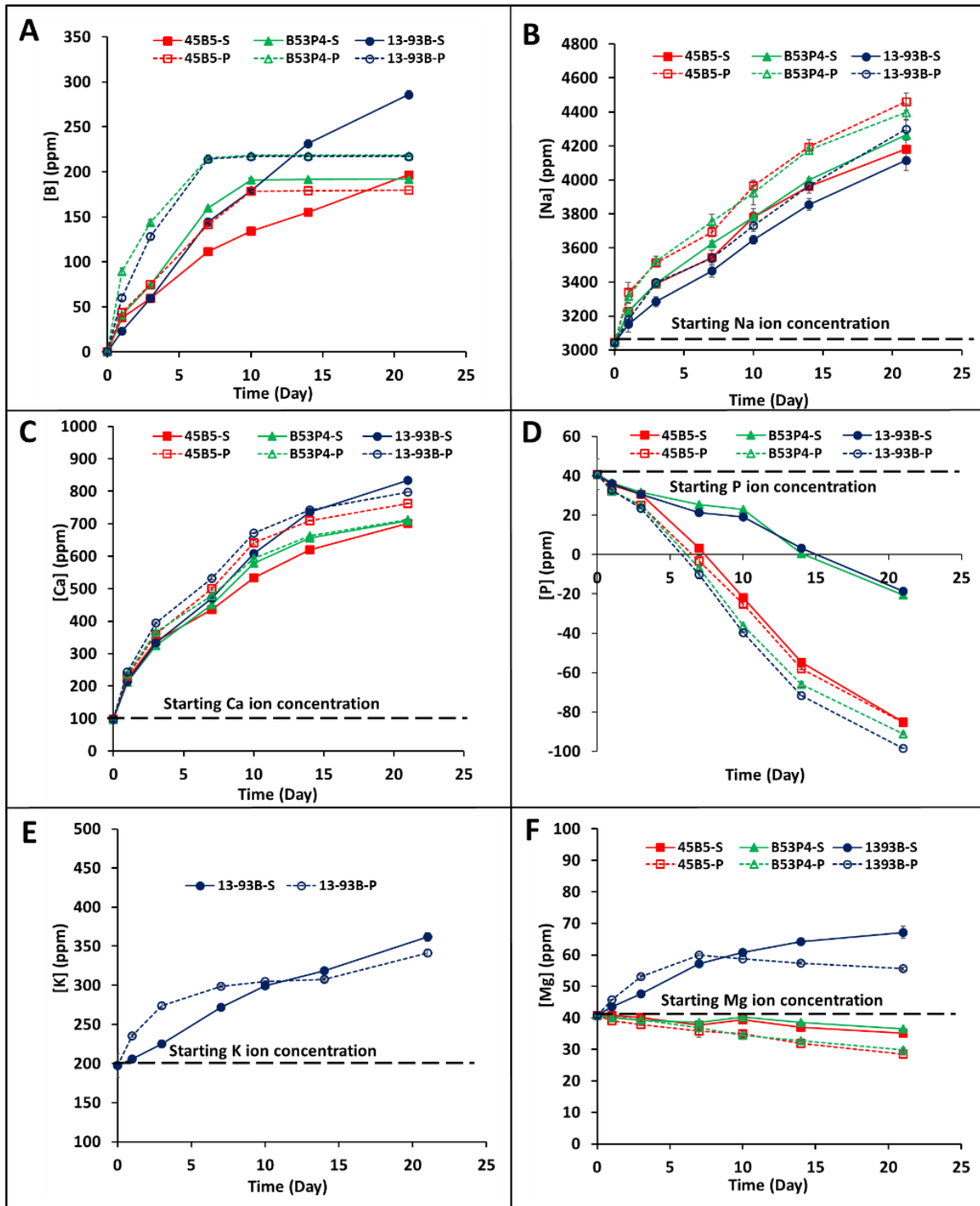
ESI Figure 2: Cross-sectional analysis for SGMS and PGMS from borate glasses prepared at day 0 (starting microspheres), day-10 and day-21 during the immersion of microspheres in 0.02 M K_2HPO_4 solution at 37 °C. EDX analysis conducted at the core of microspheres presented as '+' symbol.



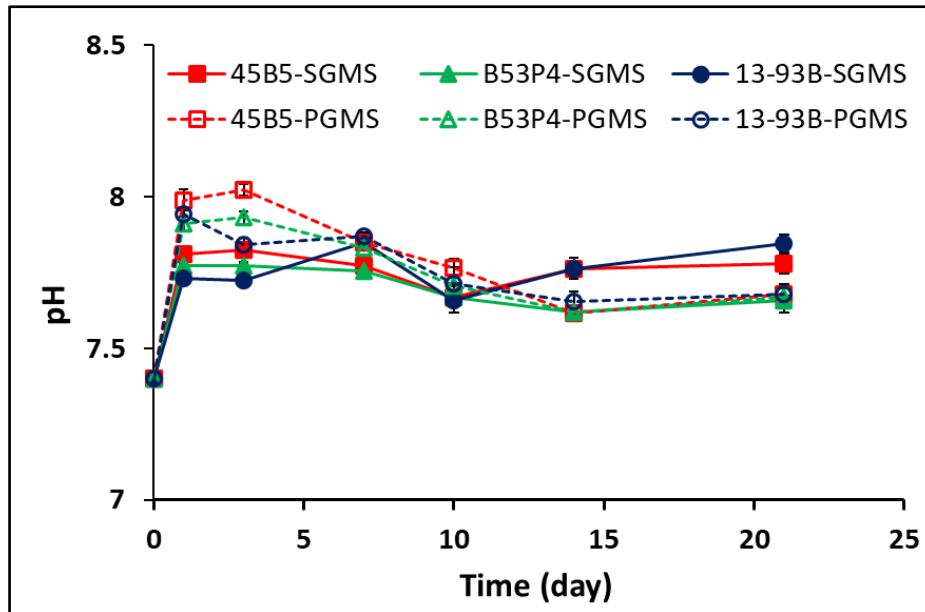
ESI Figure 3: X-ray diffraction patterns for SGMS and PGMS of **A) 45B5** and **B) B53P4** post immersion in SBF at 37 °C up to day 21. XRD spectra for HA is also shown at the bottom of each Figure for comparison.



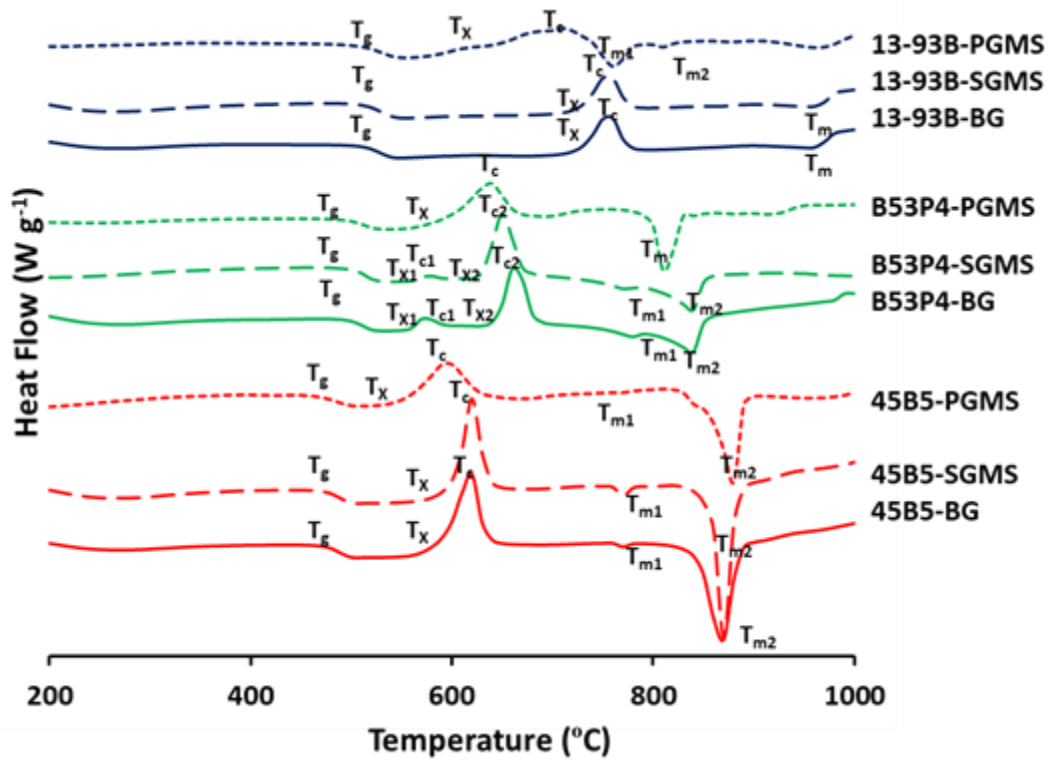
ESI Figure 4: SEM images Ai and Bi for SGMS and Aii and Bii for PGMS of 45B5 and B53P4 glasses post immersion in SBF at 37 °C at day 21. Inset images shown at higher magnification.



ESI Figure 5: Cumulative ion release profiles over 21 days immersion in SBF for A) Borate, B) Sodium, C) Calcium, D) Phosphate, E) Potassium and F) Magnesium ions as measured via ICP-MS for both SGMS and PGMS from the glasses investigated. (Error bars are also included in the data above). Black dashed lines represent the starting ion concentrations in the solution.



ESI Figure 6: pH change as a function of immersion time (days) for the SGMS (represented as solid symbols) and PGMS (represented as open symbols) of the borate glasses investigated in SBF at 37 °C, over 21 days duration.



ESI Figure 7: DSC curves for the starting glass particles (BG), SGMS and PGMS of 45B5, B53P4 and 13-93B. Bulk glass (BG) is depicted as solid line, solid glass microspheres (SGMS) shown as dashed line and the porous glass microspheres (PGMS) are shown as the dotted line.

ESI Tables

ESI Table 1: Compositional analysis for SGMS and PGMS of borate glasses investigated post immersion in SBF at day 21.

Components	45B5		B53P4		13-93B	
	SGMS (mol%)	PGMS (mol%)	SGMS (mol%)	PGMS (mol%)	SGMS (mol%)	PGMS (mol%)
B₂O₃	1.05 ± 0.91	0.15 ± 0.03	0.23 ± 0.04	0.10 ± 0.01	4.27 ± 2.73	0.08 ± 0.01
P₂O₅	23.45 ± 0.45	24.37 ± 0.15	24.77 ± 0.26	24.26 ± 0.19	22.93 ± 2.37	24.45 ± 0.35
CaO	72.85 ± 1.01	71.56 ± 0.14	70.92 ± 0.46	71.72 ± 0.32	68.51 ± 3.45	71.69 ± 0.53
Na₂O	0.48 ± 0.23	0.73 ± 0.10	0.82 ± 0.02	0.76 ± 0.02	0.62 ± 0.25	0.70 ± 0.04
MgO	2.15 ± 1.1	3.17 ± 0.12	3.23 ± 0.22	3.13 ± 0.15	3.34 ± 0.02	3.05 ± 0.22
K₂O	-	-	-	-	0.33 ± 0.22	0.02 ± 0.01

ESI Table 2: Glass transition (T_g), onset of crystallisation (T_x), glass stability (ΔT), crystallisation peak (T_c) and melting temperature (T_m) for BG, SGMS and PGMS of different borate glass formulations, using a $20\text{ }^\circ\text{C min}^{-1}$ heating rate.

Glass Formulations	Glass transition T_g ($^\circ\text{C}$)	Onset crystallisation T_{x1} ($^\circ\text{C}$)/ T_{x2} ($^\circ\text{C}$)	Glass stability $\Delta T = (T_x - T_g)$ $^\circ\text{C}$	Crystallisation Temperature T_{c1} ($^\circ\text{C}$)/ T_{c2} ($^\circ\text{C}$)	Melting Temperature T_{m1} ($^\circ\text{C}$)/ T_{m2} ($^\circ\text{C}$)
45B5-BG	484 ± 2	588 ± 3	104	$620 \pm 2/-$	$769 \pm 2/873 \pm 5$
45B5-SGMS	485 ± 2	590 ± 3	105	$623 \pm 2/-$	$769 \pm 3/869 \pm 4$
45B5-PGMS	484 ± 3	549 ± 2	65	$596 \pm 2/-$	$767 \pm 3/877 \pm 3$
B53P4-BG	508 ± 3	$559 \pm 3/641 \pm 2$	52	$573 \pm 3/664 \pm 2$	$779 \pm 3/840 \pm 4$
B53P4-SGMS	510 ± 2	$562 \pm 2/628 \pm 3$	52	$575 \pm 2/652 \pm 2$	$774 \pm 2/840 \pm 3$
B53P4-PGMS	512 ± 2	560 ± 2	48	$-/638 \pm 3$	$813 \pm 4/-$
13-93B-BG	526 ± 3	724 ± 3	198	$756 \pm 2/-$	$964 \pm 5/-$
13-93B-SGMS	527 ± 3	726 ± 2	199	$755 \pm 2/-$	$966 \pm 4/-$
13-93B-PGMS	526 ± 2	584 ± 2	58	$711 \pm 2/-$	$762 \pm 3/809 \pm 4$