### 1.1. Diffusion models

Model 1 (Equation [S1]) is a solution to Fick's second law for diffusion from a semi-infinite planar source, with the glass surface implicitly assumed to be non-reactive with a pristine glass-solution interface which recedes further into the pristine glass as dissolution progresses[1,2]. Where $^{11}B/^{10}B$ is the isotope ratio of the solution at a given time $t$, $erfc$ is the complementary error function, $x$ is the distance from the pristine glass into the altered glass, $D$ is the apparent diffusivity of a given B isotope in the altered glass, and $C_0$ and $C_0^{10B}$ represent the concentrations of $^{11}$B and $^{10}$B in the pristine glass, respectively. $D^{11B}$ is related to $D^{10B}$ through the masses of $^{11}$B and $^{10}$B, $m^{10B}$ and $m^{11B}$ respectively, and the empirical parameter $\beta_m$ using Equation (S2), where $\beta_m = 0.5$ represents an ideal gas at low pressure[3–5].

$$\frac{^{11}B}{^{10}B} = \frac{\int_0^{e_B} C_0^{11B} erfc\left(\frac{x}{2\sqrt{\left(\frac{m^{10B}}{m^{11B}}\right)^{\beta_m} D^{10B} t}}\right) dx}{\int_0^{e_B} C_0^{10B} erfc\left(\frac{x}{2\sqrt{D^{10B} t}}\right) dx} \qquad \text{(S1)}$$

$$\frac{D^{11B}}{D^{10B}} = \left(\frac{m^{10B}}{m^{11B}}\right)^{\beta_m} \qquad \text{(S2)}$$

Model 2 assumes $D^{10B}$ varies linearly with $NR_B$ (Equation [S3]), where $D^{10B}_{Max}$ represents the maximum apparent diffusivity of $^{10}$B in the altered glass, $D^{10B}_{Min}$ represents the apparent diffusivity of $^{10}$B in a nanoporous altered layer component, and $r_0$ and $r_r$ represent the most rapid (initial) and long-term (residual) rates of dissolution, respectively. For $^{10}$B-ISG, literature values reported for ISG were used: $6.0 \times 10^{-19}$ m$^2$ s$^{-1}$ for $D^{10B}_{Max}$ [1], $1.4 \times 10^{-21}$ m$^2$ s$^{-1}$ for $D^{10B}_{Min}$ [6], 1.7 g m$^{-2}$ d$^{-1}$ for $r_0$ [6] and $1.1 \times 10^{-4}$ g m$^{-2}$ d$^{-1}$ for $r_r$ [6]. For $^6$Li-Mg-EM, values of 2.22 g m$^{-2}$ d$^{-1}$ for $r_0$ and $9.6 \times 10^{-4}$ g m$^{-2}$ d$^{-1}$ for $r_r$ were taken from studies on Mg-EM (Li-free Li-Mg-EM)[7] and on the complex (multi-component) simulant waste glass which $^6$Li-Mg-EM aimed to represent[8], respectively. In the absence of reported apparent B diffusivities for $^6$Li-Mg-EM, a $D^{10B}_{Max}$ of

$7.4 \times 10^{-19}$ m$^2$ s$^{-1}$ was calculated for $^6$Li-Mg-EM using the $^{10}$B-ISG $D^{10B}_{Max}$ and $r_0$ with the $^6$Li-Mg-EM $r_0$ through assuming proportionality between $D^{10B}_{Max}$ and $r_0$ for both compositions. $D^{10B}_{Min}$ was then assumed to be two orders of magnitude lower than $D^{10B}_{Max}$ ($7.4 \times 10^{-21}$ m$^2$ s$^{-1}$).

$$\boldsymbol{D^{10B} = NR_B \left[\frac{D^{10B}_{Max} - D^{10B}_{Min}}{r_0 - r_r}\right] + \left(D_{Max} - r_0 \left[\frac{D^{10B}_{Max} - D^{10B}_{Min}}{r_0 - r_r}\right]\right)} \qquad \text{(S3)}$$

Model 3 assumes $D^{10B}$ and $D^{11B}$ are functions of local water species concentrations in the altered layer (approximated as the inverse of the local concentration of B at a given distance in the altered layer) as given in Equations (S4) and (S5), respectively[1]. The diffusivities at point $x$, $D_x^{10B}$ and $D_x^{11B}$ respectively, are inversely dependent upon the calculated total concentration of B at the previous point $x-1$ in the altered layer, $C^B_{x-1}$, where the altered layer was divided into 100 segments. $\alpha$ and $\beta_c$ in Equations (S4) and (S5) are fitting parameters [1]. Solution B isotope ratios were then calculated using Equation (S6).

$$\boldsymbol{D_x^{10B} = D^{10B}_{Max} \left[10^{-\beta_c \left(\frac{C^B_{x-1}}{C^B_0}\right)^{\frac{1}{\alpha}}}\right]} \qquad \text{(S4)}$$

$$\boldsymbol{D_x^{11B} = D^{11B}_{Max} \left[10^{-\beta_c \left(\frac{C^B_{x-1}}{C^B_0}\right)^{\frac{1}{\alpha}}}\right] = D^{10B}_{Max} \left(\frac{m^{10B}}{m^{11B}}\right)^{\beta_m} \left[10^{-\beta_c \left(\frac{C^B_{x-1}}{C^B_0}\right)^{\frac{1}{\alpha}}}\right]} \qquad \text{(S5)}$$

$$\boldsymbol{\frac{^{11}B}{^{10}B} = \frac{\int_0^{e_B} C_0^{11B}\, erfc\left(\frac{x}{2\sqrt{D_x^{11B} t}}\right) dx}{\int_0^{e_B} C_0^{10B}\, erfc\left(\frac{x}{2\sqrt{D_x^{10B} t}}\right) dx}} \qquad \text{(S6)}$$

In fitting each of the three models, a pristine glass $^{11}$B/$^{10}$B ratio of 1.045 mol mol$^{-1}$ (−741.54 ‰) was used based upon the average of the 6-hour (non-renewal) and 14-, 21-, and 28-day (renewal) solution $\delta^{11}$B values. Other parameters during fitting were sequentially held or unconstrained, with the parameter combinations used in fitting and the resulting fitted values summarised in Supplementary. Table S2. In addition to fitting assuming an altered layer of thickness $e_B$ (*i.e.*, calculated using the leached fractions of B), fits were repeated assuming an altered layer of thickness $e_B - e_{Si}$ (latter calculated using the leached fractions of Si) where $e_{Si}$ effectively represented the thickness of the altered layer that had undergone hydrolysis[9]. Further, for Model 2, fits were repeated excluding the 112-day value (*i.e.* only times ≤28 days were considered).

### 1.2. Mass balance calculations: 98-day $^6$Li-Mg-EM solutions

To assess whether the decrease in $^6$Li-Mg-EM experiment solution $\delta^{11}$B values from 2.34 ± 0.74 ‰ (2 S.D., n = 5) at 28 days to 0.12 ± 0.09 ‰ (2 S.D., n = 2) at 98 days could be explained solely by congruent dissolution of the pristine glass, mass balance calculations were used as a first order approximation (Equation S7).

$$\boldsymbol{\delta_{Sol}^{98\,Days}[B]_{Sol}^{98\,Days} = \delta_{Sol}^{28\,Days}[B]_{Sol}^{28\,Days} + \delta_{Glass}\left([B]_{Sol}^{98\,Days} - [B]_{Sol}^{28\,Days}\right)} \qquad \text{(S7)}$$

Where $\delta$ are $\delta^{11}$B values, *[B]* represent molar amounts, and subscripts *Sol* and *Glass* represent the solution at the time given by the superscript and the unreacted glass, respectively. Such calculations assumed (1) no B (de)sorption or B uptake/release processes contributed to the change in $\delta^{11}$B values, (2) dissolution of the glass at ≤ 28 days occurred congruently such that the reacted glass at 28 days had a $\delta^{11}$B value equal to the unreacted (pristine) glass, and (3) the change in solution B concentrations between 28 and 98 days, whilst insignificant (1 S.D.), was equal to the sum of the uncertainties (1 S.D.) associated with the 28 and 98-day values (Equation S8). That is, whilst $[B]_{Sol}$ at 28 and 98 days were within 1 S.D. uncertainty, a difference of 1 S.D., $\sigma$, at each time was assumed as the concentration change with time:

$$\boldsymbol{[B]_{Sol}^{98\,Days} = [B]_{Sol}^{28\,Days} + \sigma_{[B]}^{28\,Days} + \sigma_{[B]}^{98\,Days}} \qquad \text{(S8)}$$

Substituting this into Equation S7 yielded the mass balance equation to be solved for the solution $\delta^{11}$B value at 98 days (Equation S9), where the uncertainties (2 S.D.) associated with the pristine glass and 28-day solution $\delta^{11}$B values were propagated accordingly.

$$\delta_{Sol}^{98\,Days}\left([B]_{Sol}^{28\,Days}+\sigma_{[B]}^{28\,Days}+\sigma_{[B]}^{98\,Days}\right)$$

$$=\delta_{Sol}^{28\,Days}[B]_{Sol}^{28\,Days}+\delta_{Glass}\left(\sigma_{[B]}^{28\,Days}+\sigma_{[B]}^{98\,Days}\right) \qquad \text{(S9)}$$

### 1.3. Mass balance calculations: $^{10}$B-ISG solutions

Using a similar approach to Supplementary Text 1.2, mass balance calculations were applied as a first order approximation to assess whether congruent dissolution of the pristine $^{10}$B-ISG glass at its measured $\delta^{11}$B value alongside sorption processes could account for the observed solution $\delta^{11}$B trends. Using the B concentration and $\delta^{11}$B value of the 6-hour $^{10}$B-ISG solution as initial solution reservoir, mass balance solely with respect to congruent primary phase dissolution and sorption was expressed using Equation S10:

$$\delta_{Sol}^{t}[B]_{Sol}^{t}=\delta_{Sol}^{6\,h}[B]_{Sol}^{6\,h}+\delta_{Glass}\left([B]_{Sol}^{t}-[B]_{Sol}^{6\,h}+[B]_{Sorp}^{t}\right)-\delta_{Sorp}^{t}[B]_{Sorp}^{t} \qquad \text{(S10)}$$

Where the $\delta_{Sorb}$ and $[B]_{Sorb}$ are the $\delta^{11}$B value associated with the sorption or structural incorporation of B and B molar amounts associated with these processes, respectively, and the superscript $t$ represents time for timescales >6 hours (initial solution conditions at 6 hours are given with the superscript *6 h*). As in the previous section, dissolution was assumed to be congruent throughout, such that the $\delta^{11}$B value of the glass at a given time was equal to that of the pristine glass, $\delta_{Glass}$. Given that the $\delta^{11}$B values and B concentrations of the solutions as a function of time and of the pristine glass were known and the $\delta^{11}$B value of sorption can be varied, the molar ratio of sorbed B to that released into solution from 6 hours onwards may be calculated using Equation S10. Alternatively, for an assumed fraction of sorbed or structurally incorporated B, the $\delta^{11}$B value of sorption at a given time, $\delta^{t}_{Sorb}$, required to replicate the measured solution $\delta^{11}$B values could be calculated.

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