Li and B diffusivity in hydrated silicate melts: an experimental study

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(1) Introduction & Study Aim

- Lithium and Boron are fluid-mobile elements, naturally dissolved in minor concentration in magmas and commonly used for tracing subduction-related processes.

- Because of their properties these elements are potential proxies for ascent-related degassing processes in volcanic systems.

- Currently available data on Lithium transport properties are mostly obtained from dry silicate melts (Fig. 3), while literature on Boron diffusion and isotopic fractionation is almost inexistent.

AIM:

- Extending Li and B diffusion coefficient data to hydrated silicate melts, while also investigating isotope fractionation.

- Correlate diffusion and isotope fractionation with our future experiments, studying Li and B behaviour during decompression-induced magma degassing.

(3) Results: Elemental Diffusion

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- Diffusion coefficients have been calculated by the Fick's law, following Zhang (2010a):

$$C(Li, t) = C_{LPR50} + \frac{(C_{LPR200} - C_{LPR50})}{2} erfc\left(\frac{x}{2\sqrt{Dt}}\right)$$

- The time used in the calculations is the sum of t@T_{run} with $\Delta t_{heating}$ (Tab. 2), because our low-temperature zero-hour experiment (DIFF 1, see Tab. 2) indicates Li migration starting already during the heating ramp at around 600° C.

- Elemental Lithium profiles (Fig. 2) confirm fast diffusion in the range of 7.5×10^{-11} to 1.32×10^{-10} m²/s (Tab. 2) showing similar values to Holycross et al. (2018).

- The difference of calculated D_{Li} values with Holycross et al. (2018) may be related to the presence of Fe-Ti oxides (0.64 and 0.13 wt. %) and higher water content (~6 wt. %) in their starting material.

- The slope of the trending lines in the Arrhenius plot (Fig. 3) graphically define the activation energy for diffusive transport. Here it significantly decreases with the presence of water. This agrees with the Li property of being a fluid-mobile element.
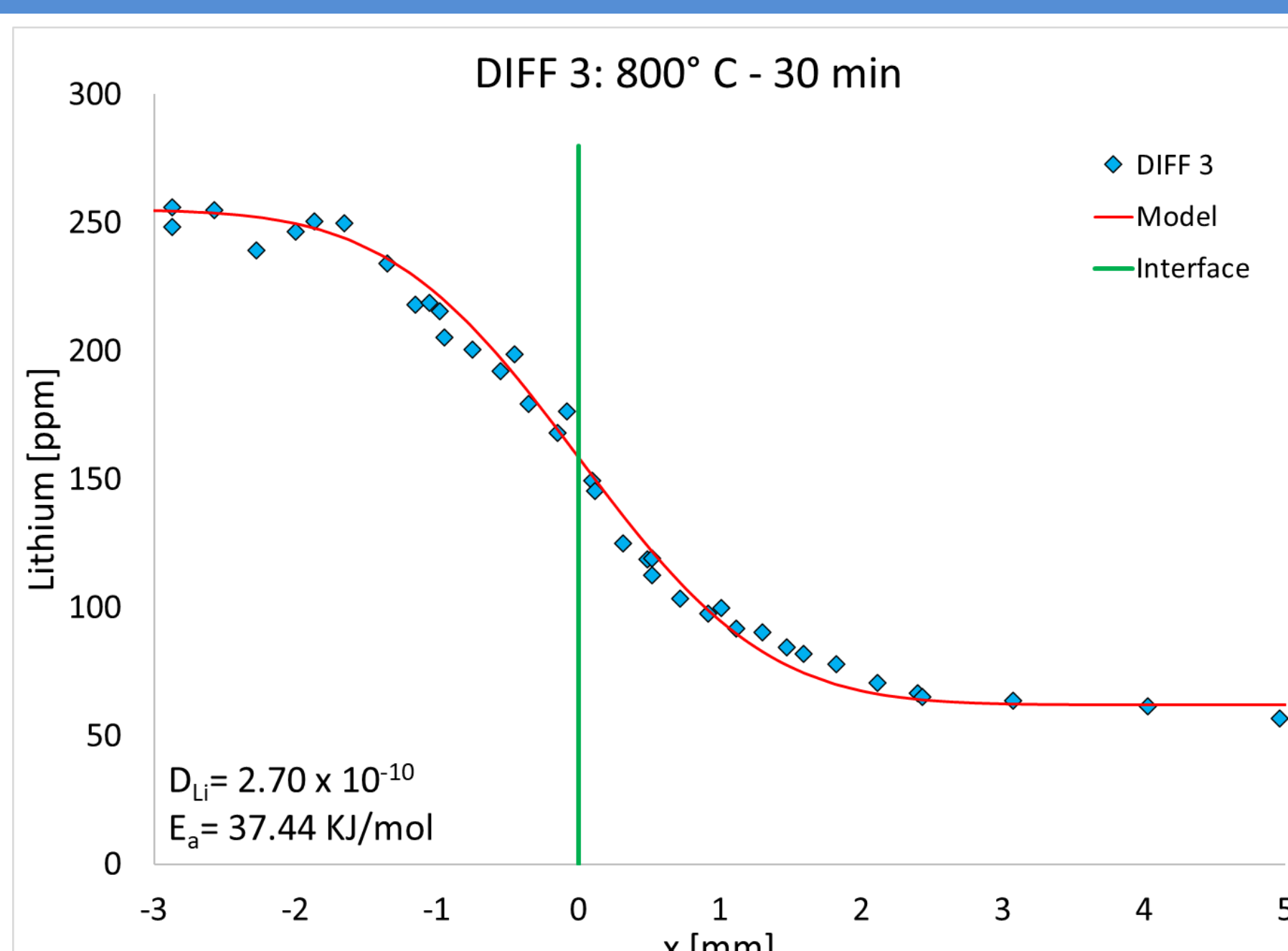

Figure 2: Diffusion profile of sample DIFF 3 (800° C, 30 min). The red line shows the best fitting model curve for these measured Lithium concentrations (blue diamonds), and the green line shows the interface between the two samples. Error bars are within the symbols.
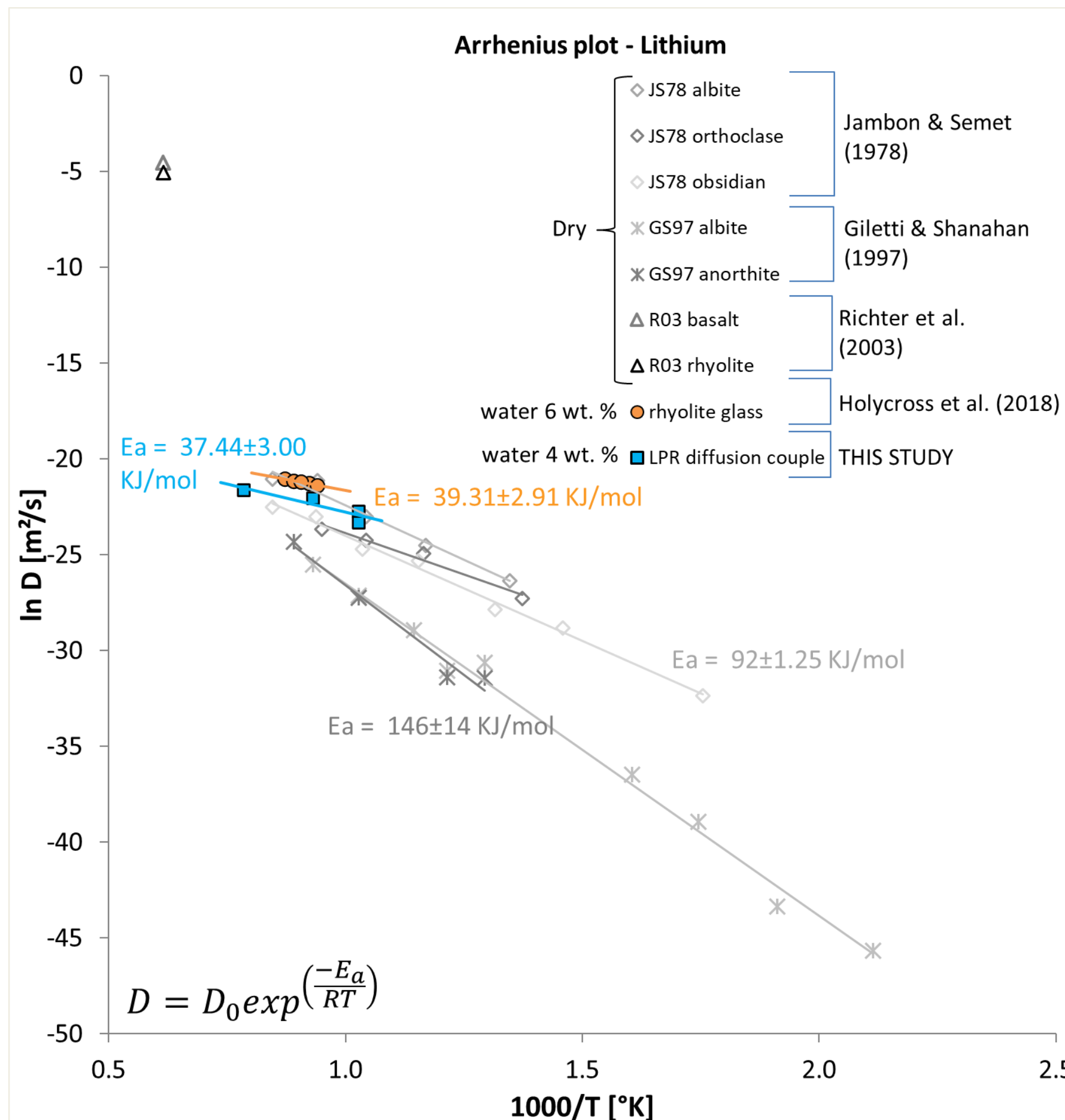
D_{Li}= 2.70 x 10⁻¹⁰
E_a= 37.44 KJ/mol

Figure 3: Compilation of literature data on experimental Li diffusion in silicate melts. It has to be pointed out that all setups were run under dry conditions apart from our study (blue squares) and Holycross et al. (2018) represented in the diagram by the orange circles.
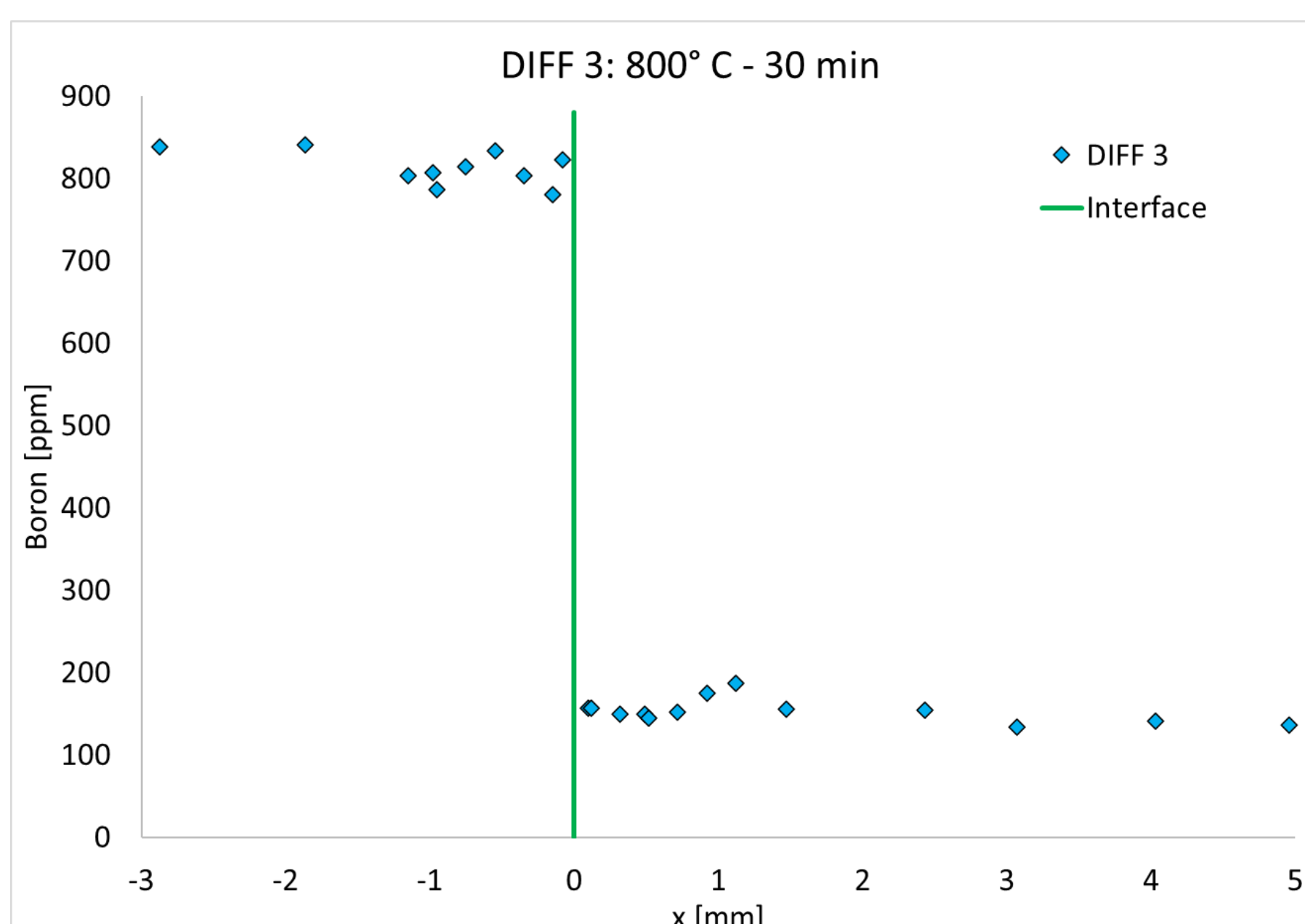
$$D = D_0 exp\left(\frac{-E_a}{RT}\right)$$

Table 2: Run durations (t@T_{run}) and temperatures (T_{run}) of our experiments performed at a constant pressure of 300 MPa, along with the calculated Li diffusion coefficients (D_{Li}). $\Delta t_{heating}$ is the heating time from 600° C until final T_{run}.

Sample	T_{run} (°C)	t @T_{run} (min)	$\Delta t_{heating}$ (min)	D_{Li} (m²/s)
DIFF 1	700	0	2	1.32 x 10⁻¹⁰
DIFF 2	700	30	2	7.50 x 10⁻¹¹
DIFF 3	800	30	4	2.70 x 10⁻¹⁰
DIFF 5	1000	0	8	4.00 x 10⁻¹⁰

BORON

- Boron diffusion is confirmed to be significantly slower than Lithium.

- No diffusion profile was visible for any of the conducted experiments, thus modelling was here not feasible.

- Two solutions are currently being under consideration:

  ➤ Very high precision analysis in the interface area (spot size of 5μm by SIMS or nanoSIMS)

  ➤ Longer experimental run durations at high temperatures

Figure 4: Boron concentrations (blue diamonds) throughout sample DIFF 3 (800°C, 34 min). The green line represents the interface between the two diffusion couples. Error bars are within the symbols.

(2) Experimental Setup

STARTING GLASS SYNTHESIS

- synthetic silica-rich, Fe-Ti-free glasses with 4 wt.% water (Table 1) doped with two distinct amounts of $Li_2B_4O_7$ and homogenized in Pt capsules at 300 MPa and 1200°C in an internally heated pressure vessel for 48 hours.

- After rapid-quench, c. 0.5 mm thick glass cylinders were cut and polished on one side.

- New Pt capsules were loaded with a set of the two different glass cylinders with a polished interface, while the high Li and B glass being set on top.

Table 1: Major elements of the synthetic glasses used for the diffusion-couple experiments. The composition was chosen to be similar to well-known Los Posos rhyolite (Stanton, 1989).

Oxides [wt.%]	LPR50	LPR200
SiO_2	73.82 (±0.88)	73.71 (±0.88)
Al_2O_3	13.69 (±0.66)	13.50 (±0.81)
Na_2O	4.27 (±0.37)	4.22 (±0.36)
K_2O	4.01 (±0.18)	4.05 (±0.09)
CaO	0.39 (±0.09)	0.40 (±0.08)
MgO	0.05 (±0.01)	0.04 (±0.01)
Li [ppm]	60	250
B [ppm]	150	800
H_2O	~4	~4

EXPERIMENTS AND ANALYSIS

- Classical diffusion-couple experiments were performed in an IHPV at a constant pressure of 300 MPa and a heating rate of 50 °C/min (individual run conditions are shown in Table 2).

- Major elements were analysed by electron microprobe, while Li and B concentrations were measured using LA-ICP-MS and their isotopes by SIMS.
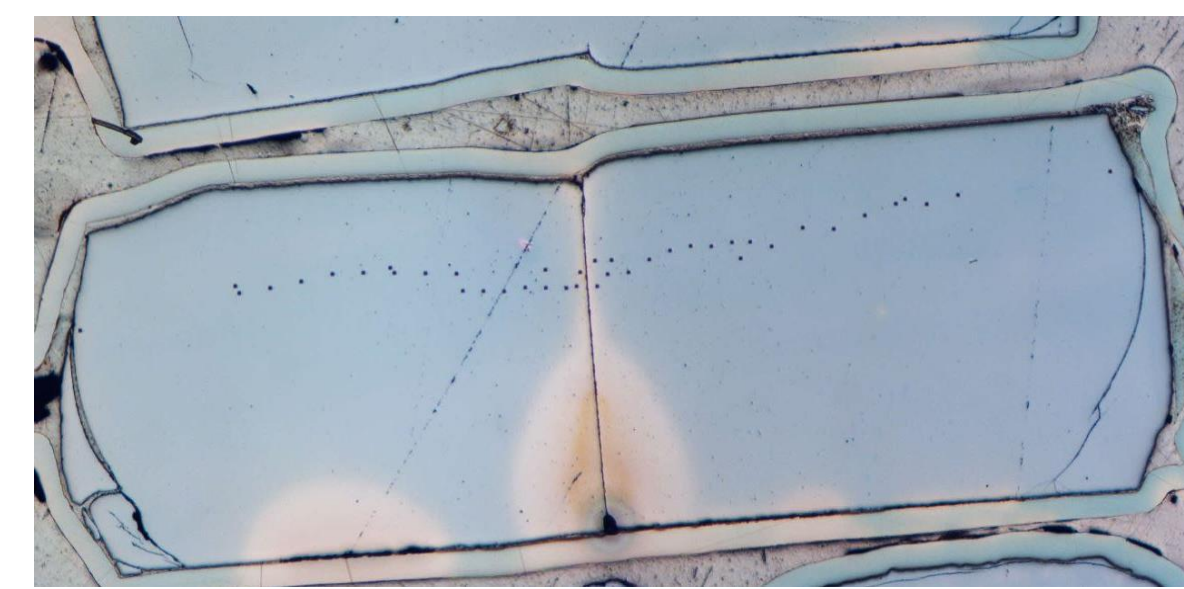

Figure 1: Microscope image of a representative diffusion-couple capsule. The black dots show the location of individual SIMS spot analyses.

(3) Results: Isotopic Fractionation

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- First glance at our experimental isotopic ratio measurements (Fig. 5) confirm former findings by Richter et al. (2003) that ^6Li diffuses faster than ^7Li.

- Variations in the isotopic ratios have been modelled following Richter et al. (1999), where the coefficient β defines the relation between the diffusion coefficient of the two isotopes:

$$\frac{D_{7Li}}{D_{6Li}} = \left(\frac{6}{7}\right)^\beta$$

- The four sample calculation give an average β value of 0.234 ± 0.006, that confirms the findings from Holycross et al. (2018).
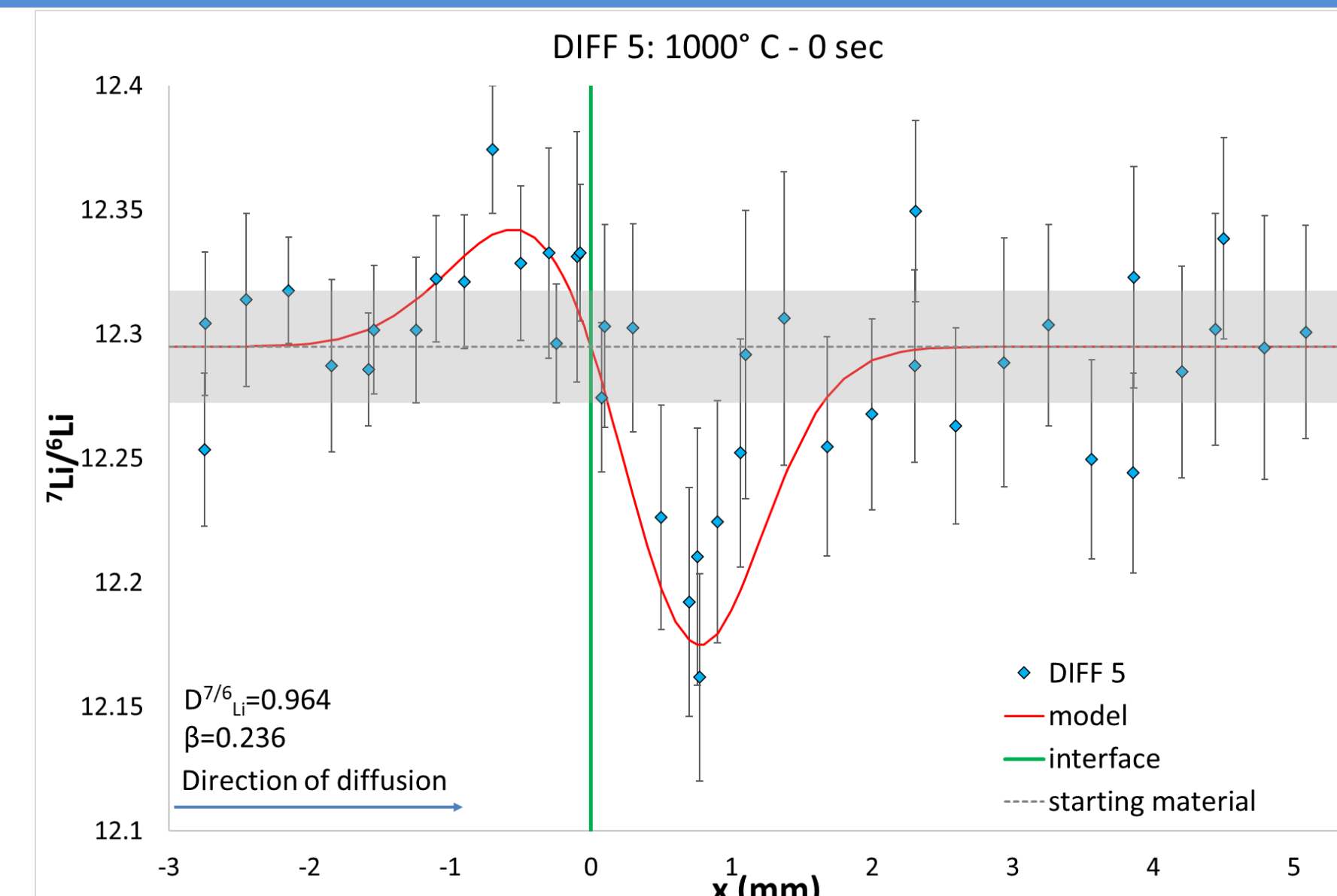

Figure 5: Lithium isotopic ratio of the sample DIFF 5 (1000 °C, 8 min). The diffusion direction goes from left to right. The grey area represents the average analytical error of the starting material, used in this study as reference for the isotopic ratio value before diffusion (dashed line), during SIMS analysis.

$D^{7/6}_{Li}$=0.964
β=0.236

BORON

- The variability of the Boron isotopic ratio results by SIMS analyses remains within the analytical error of the measurement made on the starting material (Fig. 6).

- Even at 1000 °C, the 0 seconds experiment does not show significant isotope fractionation for Boron, highlighting its reduced mobility in comparison to Lithium.
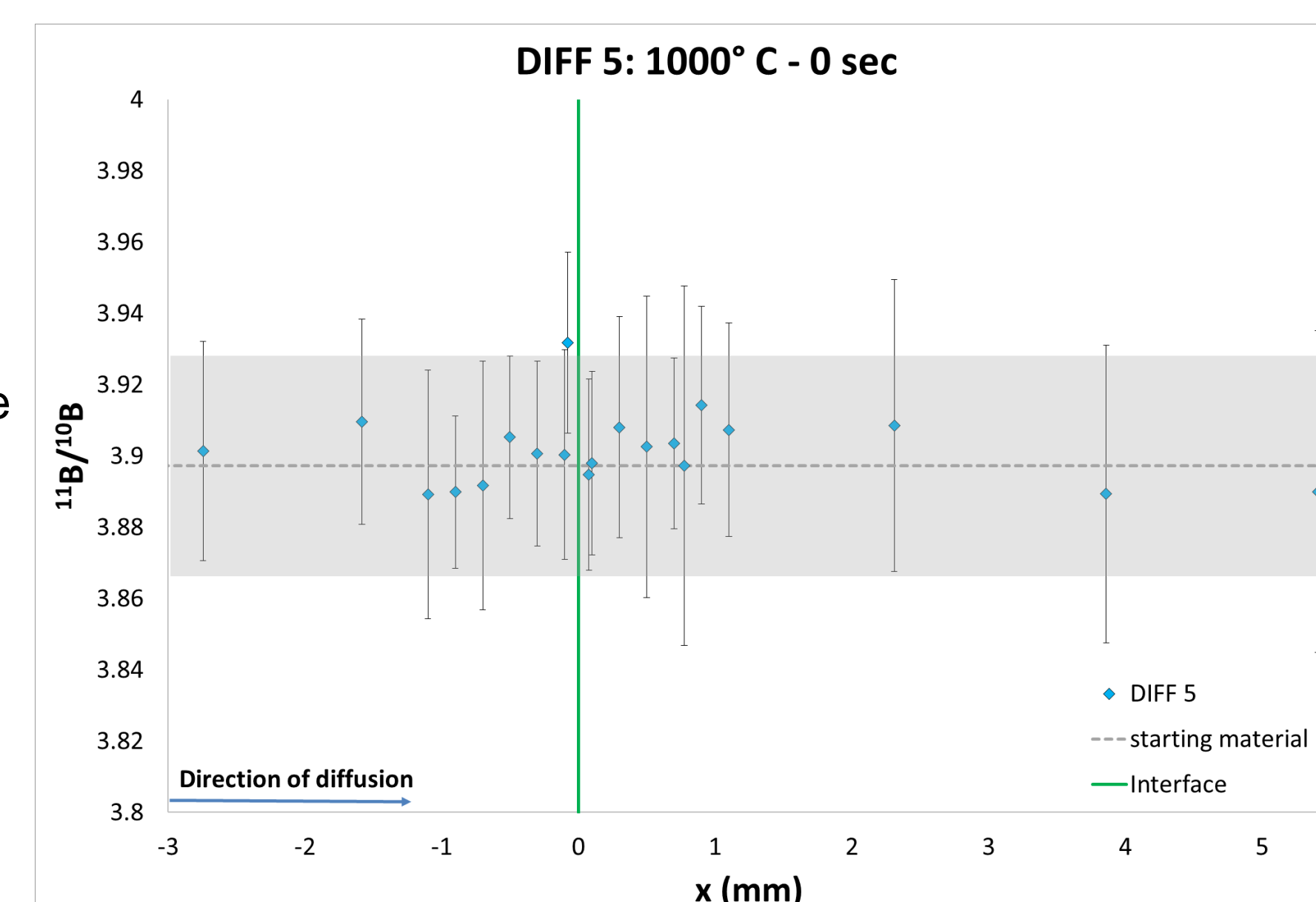

Figure 6: Boron isotopic ratio of the sample DIFF 5 (1000 °C, 0 sec). The diffusion direction goes from left to right. The grey area represents the average analytical error of the starting material, used in this study as reference for the isotopic ratio value before diffusion (dashed line), during SIMS analysis.

(4) Conclusion & Outlook

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- Our elemental Li diffusion-couple experiments produced similar values to those of other studies for dry and water-bearing systems (Fig. 3).

- Our experimental isotope fractionation patterns confirm that ^6Li diffusing faster than ^7Li (Richter et al., 2003; Holycross et al. 2018).

- The values of the coefficient β calculated in this study agrees with the study of Holycross et al. (2018), confirming the reproducibility of these data.

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- Boron mobility is too slow or inexistent for both elemental diffusion and isotopic fractionation at our experimental run conditions to show measurable changes.

- Experimental runs with longer duration and higher temperature are required and are planned in order to induce significant Boron migration and produce a clear diffusion profile as well as isotope ratio variation.

EXPERIMENTAL OUTLOOK

- Sets of continuous (and multi-step) decompression experiments have been performed and are currently being expanded, investigating Li and B behaviour during ascent-induced magma degassing in dependence on the decompression rate.

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