**APPENDIX**

**Hydrogen diffusion mechanisms in quartz: insights from H-Li, 2H-H and 2H-H-Li exchange experiments**

Jollands, M.C. *et al*.

**Note -** All FTIR spectra and LA-ICP-MS data are available at doi.org/10.17632/v3p5fw65bv.1

**Experimental sample introduction and quench**

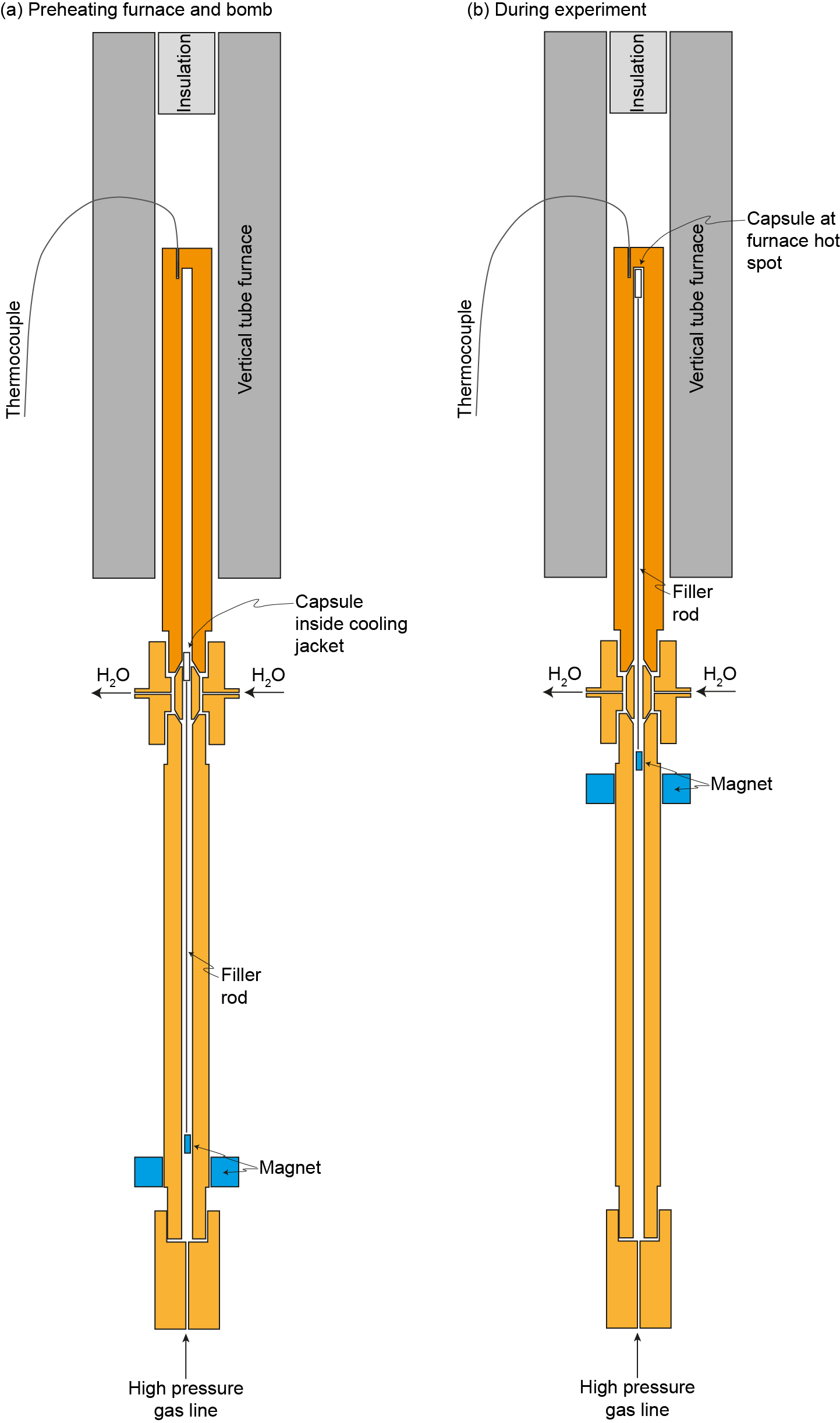
The high thermal mass of the hydrothermal bombs used in these experiments, as well as limitations of our furnaces, means that the ramp-up rates are slow. In early tests, the capsule was welded, loaded into a bomb on top of a filler rod, which was then placed into a vertical tube furnace, pressurised and heated. It was found that the ramp-up rate was too slow to be practical for these diffusion experiments – around 45 minutes of ramp-up was required to bring the measured temperature to 800 °C, where the hot-junction of the thermocouple was located in a hole in the top of the bomb. This is impractical for a diffusion experiment at 800 °C, where the total duration is one hour – ideally P-T-t paths in diffusion experiments should be controlled in such a way that ramp-up (and down) times are negligible relative to the total experimental duration. On the other hand, the cooling time is not problematic with this simple set up. In the early tests, the bombs were cooled by turning off the power to the furnaces, extracting the bombs, and blowing cold pressurised air onto them, upon which the temperature dropped by several hundred degrees within a minute.

To solve the issue associated with slow ramp-up times, we applied an experimental design developed for rapid quench, in reverse. In this method, the sample sits inside the bomb on top of a filler rod, which sits on top of a magnet. This magnet is located inside an extension of the main bomb, with the two parts both joined to a sleeve through which cooling water runs. To enable the magnet inside the extension to be moved, a hollow cylindrical magnet sits outside the bomb extension. This magnet can be moved up and down. In a fast quench experiment, the sample sits in the bomb, in the hot zone of the furnace, on top of the filler rod, on top of the internal magnet, which is held in place by the external magnet. At the end of the experiment, the external magnet is dropped downwards, which moves the internal magnet, filler rod and sample downwards, with the aim being that the sample ends up inside the section of the assembly around which the cooling water runs.

For our experiments, the sample initially sat, under pressure, atop the filler rod at the very base of the bomb within the cooling jacket, while the furnace was heated up. Once the furnace had reached 800 °C, it was left for a few hours to stabilise. Then, the sample was introduced upwards into the hot spot of the furnace by moving the external magnet upwards, which generally took a few seconds. The temperature on the control thermocouple would not change by more than a few degrees during sample introduction.

At the end of the experiment, the sample was either quenched by dropping the magnet, or the standard method of turning off the furnace power and blowing high-pressure air onto the bomb was also used. In either case, the total cooling procedure took <3 minutes.

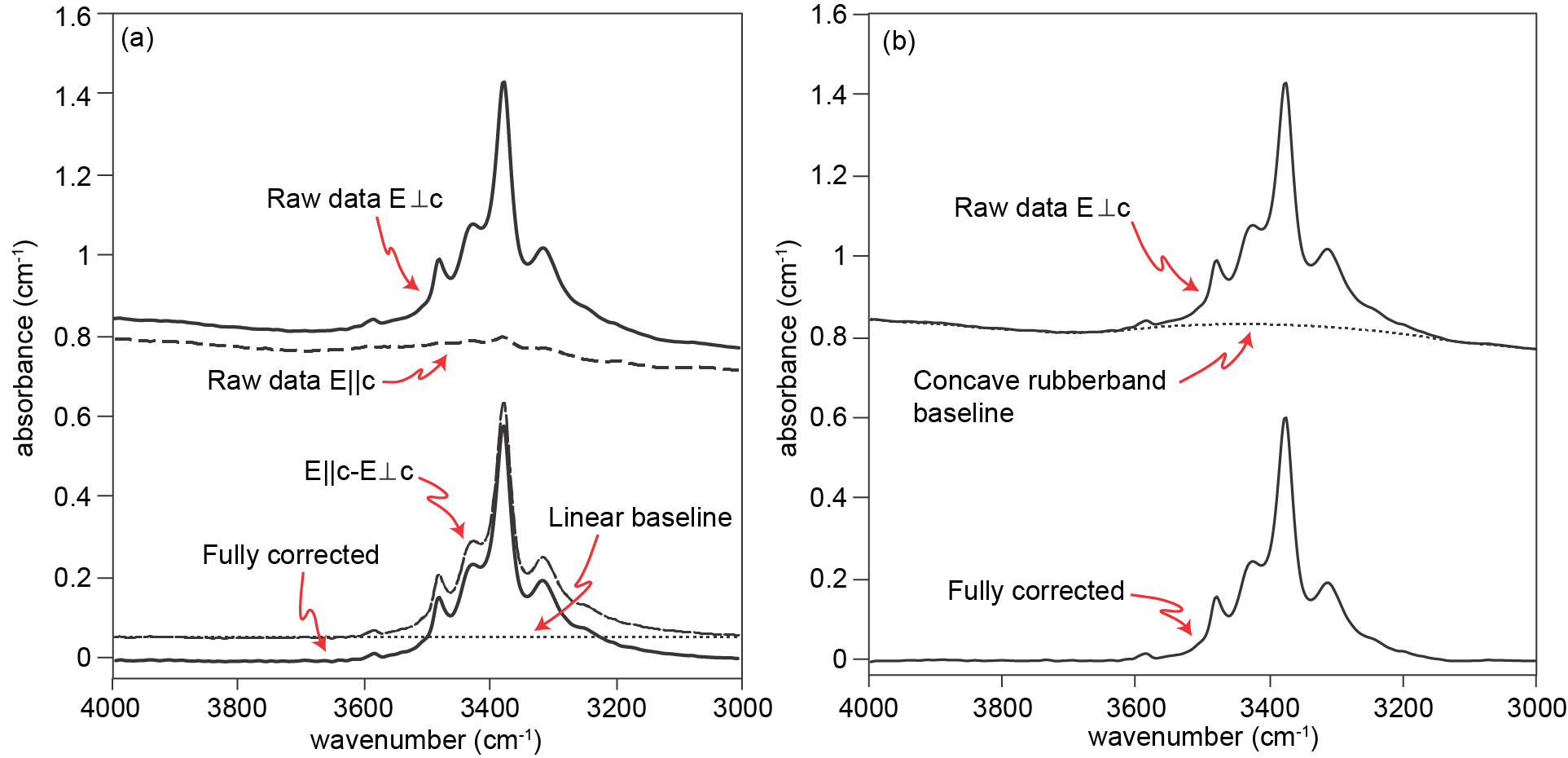
A schematic of the apparatus is shown in the following figure.



Supplementary Figure 1: The experimental design with rapid sample introduction, described above.

**Concave rubberband correction**

An example of a raw E⟂c spectrum (not thickness-corrected) from crystal TIB2 is shown in the following figure, corrected in two ways, for comparison. In (a), the E||c spectrum has been subtracted from the E⟂c spectrum – this method is used to subtract the broad, isotropic band generally assigned to H2O (e.g. Potrafke *et al.*, 2019). Then, a simple linear baseline is applied. In (b), the concave rubberband is applied, as described in the text. The final result is that the integrated absorbance derived using the two methods is similar – integrating the whole region between 3000 and 3600 cm-1 gives 57.1 cm-2 in (a) and 54.2 cm-2 in (b), i.e. the integrated absorbance in (b) is 95% of that in (a). A 5% difference is negligible for the purpose of our study.



Supplementary Figure 2: Baseline corrections, as described in the text above.

**Resolving FTIR spectra into pseudo-Voigt peaks**

Sepctra were resolved into a series of individual pseudo-Voigt peaks, as follows. We use the approximations of the probability density function of the Voigt line provided by Thompson *et al.* (1987) and Ida *et al.* (2000).

Pseudo-voigt (pV) peak shapes (absorbance (Abs) as a function of wavenumber (ω)) are modelled as a linear combination of Gaussian (G) and Lorentzian (L) forms. The inputs are the full widths at half maximum (Γ) of the Gaussian and Lorentzian components:

|  |  |
| --- | --- |
|  | ( 1 ) |

In order to determine η, firstly Γ for the pseudo-Voight component is calculated as:

|  |
| --- |
| ( 2 ) |

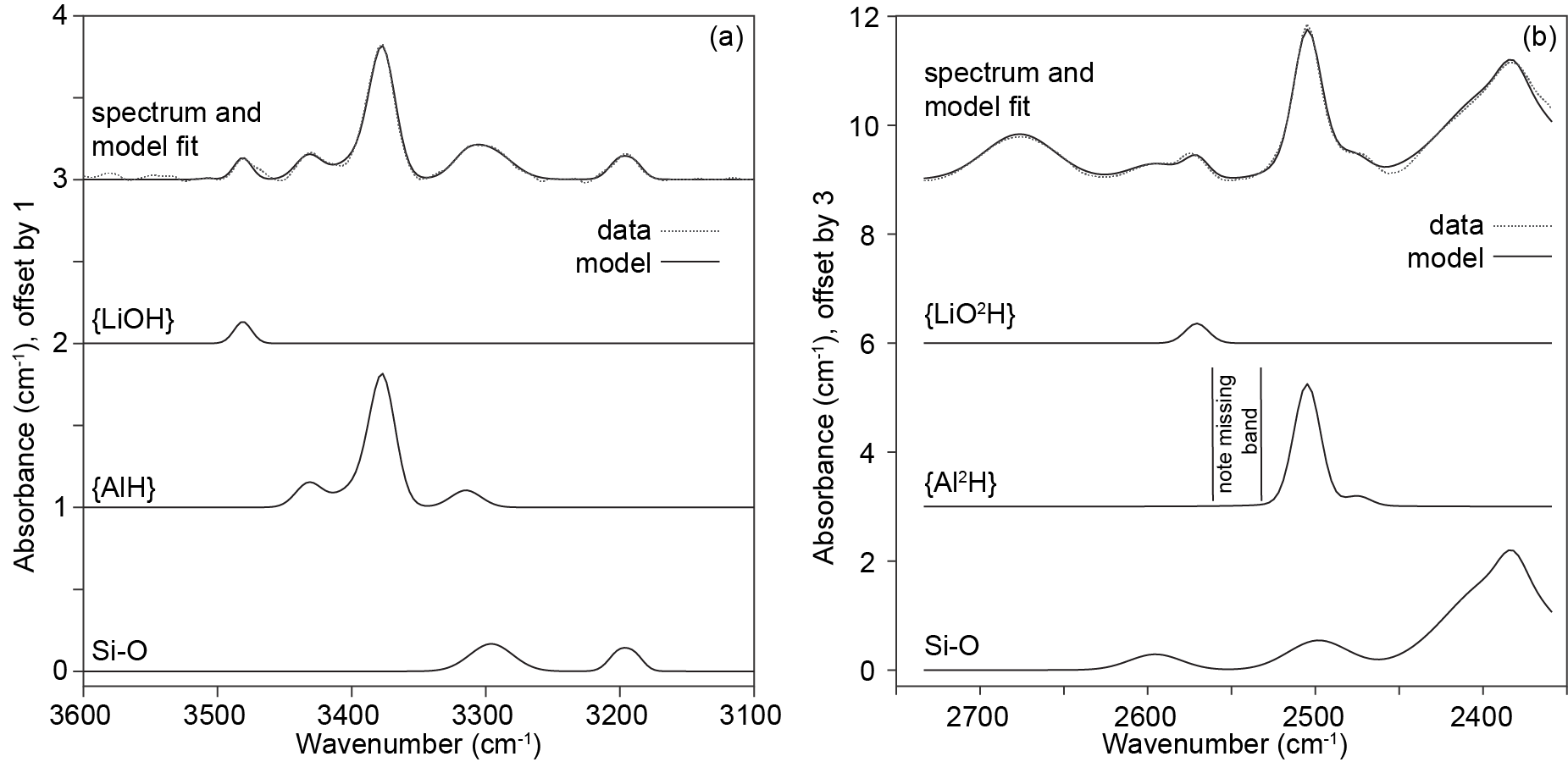
then η is:

|  |  |
| --- | --- |
|  | ( 3 ) |

from which can be determined. Early tests showed that the use of pseudo-Voigt peak shapes appeared to be superior to either Gaussian or Lorentzian peaks for quartz.

For fitting, firstly, a mean ("reference") spectrum was calculated for each profile from >10 individual spectra. This was done for each combination of quartz type and experiment type, e.g. one reference spectrum was created for all HQHP-pH experiments, and another for the HQHP-TIB2 experiment. The best fit to the reference spectrum was then found using least squares regression with at least 100 initial guesses for peak positions, widths and heights. The number of peaks was set manually. The fitting extracts 1) the peak positions 2) ΓG (the full-width at half maximum for the Gaussian components) and 3) ΓL (the full-width at half maximum for the Lorentzian components). These parameters were then used to fit all other spectra from the same experiment, with only the individual peak heights being permitted to vary between spectra. It is important to note that such fitting, where all parameters except height are fitted, gives internally consistent results, but this may be to the detriment of the goodness of fit. The latter will naturally improve as more parameters are allowed to vary during fitting. However, internal consistency is considered more important for the purposes of this study.

An example of a spectrum resolved into a series of peaks which are then grouped into defect associations is shown in the following figure. The importance of resolving spectra is especially clear when considering the bands in the O-2H region, which are superimposed onto, and sometimes minor in comparison to, bands associated with Si-O bonds.

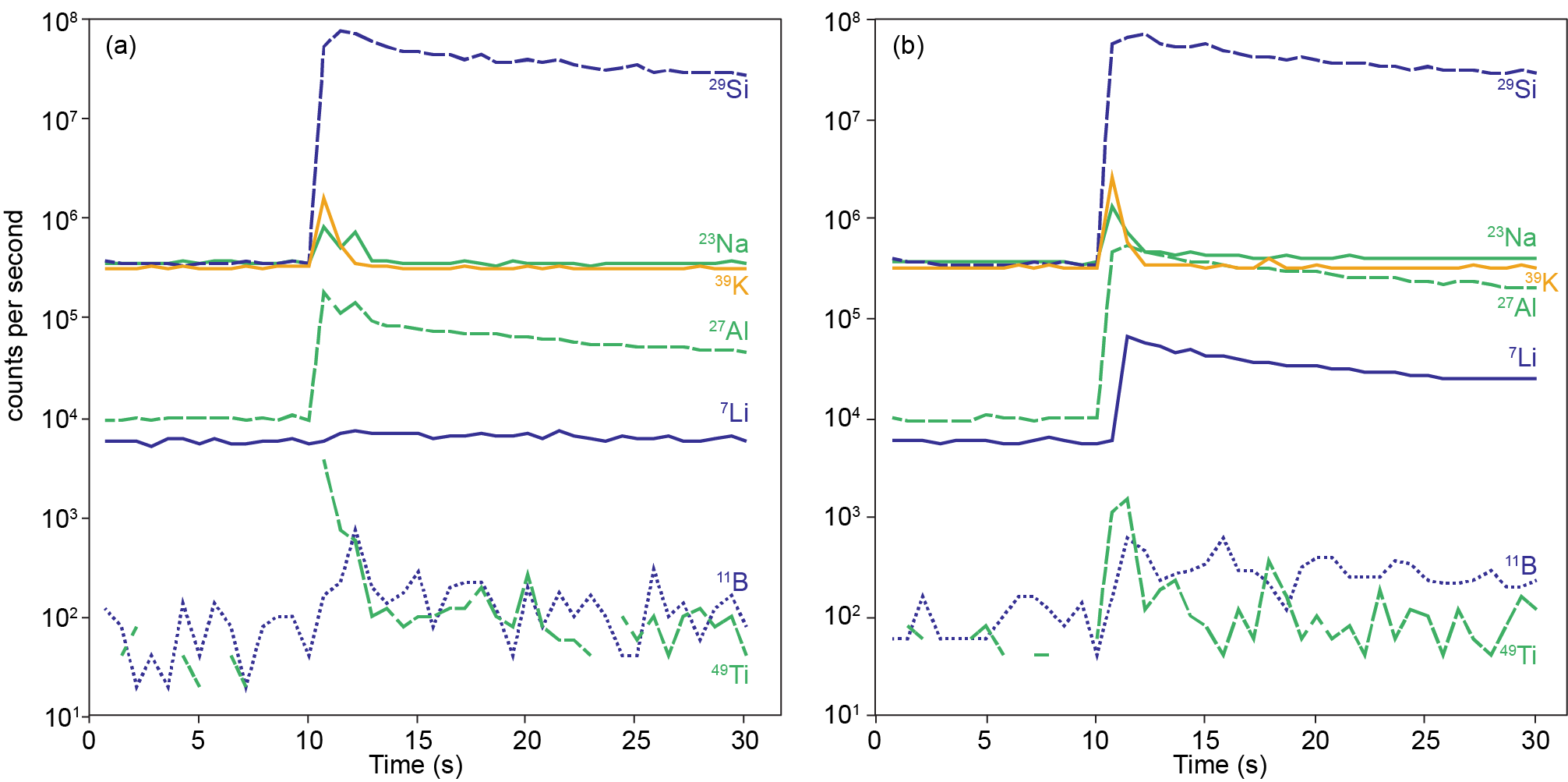


Supplementary Figure 3: An example spectrum (total absorbance) from experiment DQHP-TIB2, close to the crystal edge, resolved into a series of peaks, then grouped into defect associations. (a) shows the O-H stretching region and (b) shows the O-2H region from the same experiment. In both cases, it is necessary to remove the contribution of bands associated with Si-O bonds, although this has a considerably greater effect in the O-2H region. Note that the y-axis scale is not the same in the two figures. Also note that the {AlH} defect is represented by three clear bands, whereas {Al2H} has two.

**LA-ICP-MS**

The validity of the LA-ICP-MS technique was checked once by analysing several pieces of standard quartz (Audétat *et al.*, 2015) in the same LA-ICP-MS routine. The results are described by Jollands *et al.* (2020b), who showed that there might be a slight deficit in Li (~5-10%) relative to the standard values. This is not consequential for this study, given that it is in any case necessary to adjust the H content by means of changing the absorption coefficient to match the Li content, so absolute values presented need to be taken with caution.

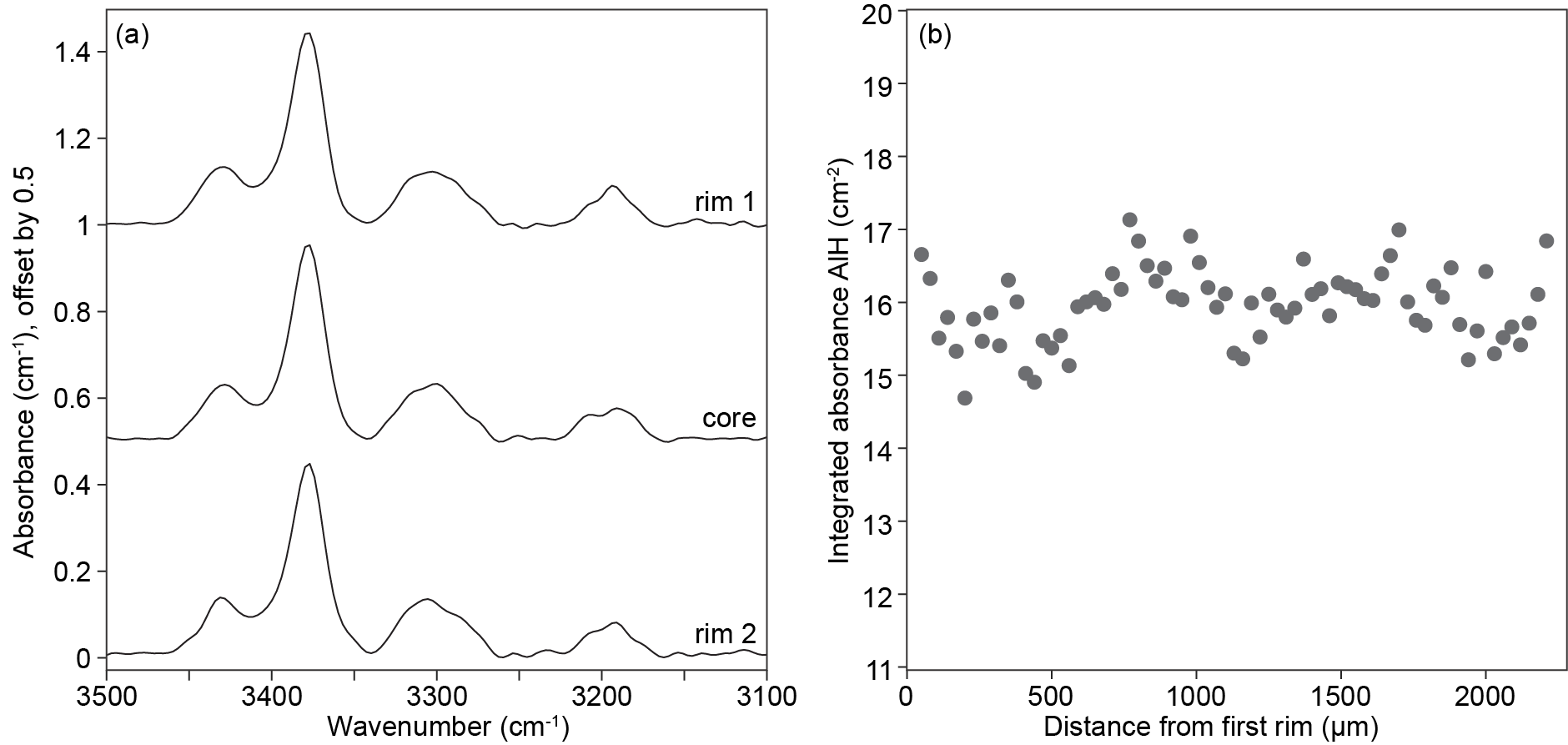
The below figure shows two examples of raw LA-ICP-MS data, (a) being from a sample with low Al, low Li, and (b) from one with relatively high Al and Li. Data from the first few seconds of ablation show enrichment in K and Na, presumably from surface contamination (e.g. residue of fingerprints), thus quantification did not include these data – the first four seconds of each analysis after the onset of ablation was removed. This was done automatically using Iolite software (Paton *et al.*, 2011).



Supplementary Figure 4: Example of raw LA-ICP-MS data. (a) analysis close to a crystal rim, with very low Li. (b) analysis from a crystal core, with relatively high Li contents. Note the spikes in Na and K, both likely associated with surface contamination.

**Crystal following H equilibration (before 2H-in/H-out experiment)**

The below figure shows FTIR spectra recorded from both rims and the core of the crystal post-equilibration with H, prior to the 2H-in/H-out diffusion experiment, along with a transect of the numerically integrated area between 3342 and 3460 cm-1 (i.e. not resolved into pseudo-Voigt peaks). The Li content measured by LA-ICP-MS is below the limit of detection, as are the Na and K contents. This suggests that we can consider this crystal as fully equilibrated and devoid of any other monovalent cations, thus the 2H-in/H-out experiment can reasonably be considered as representing pure H-2H exchange.

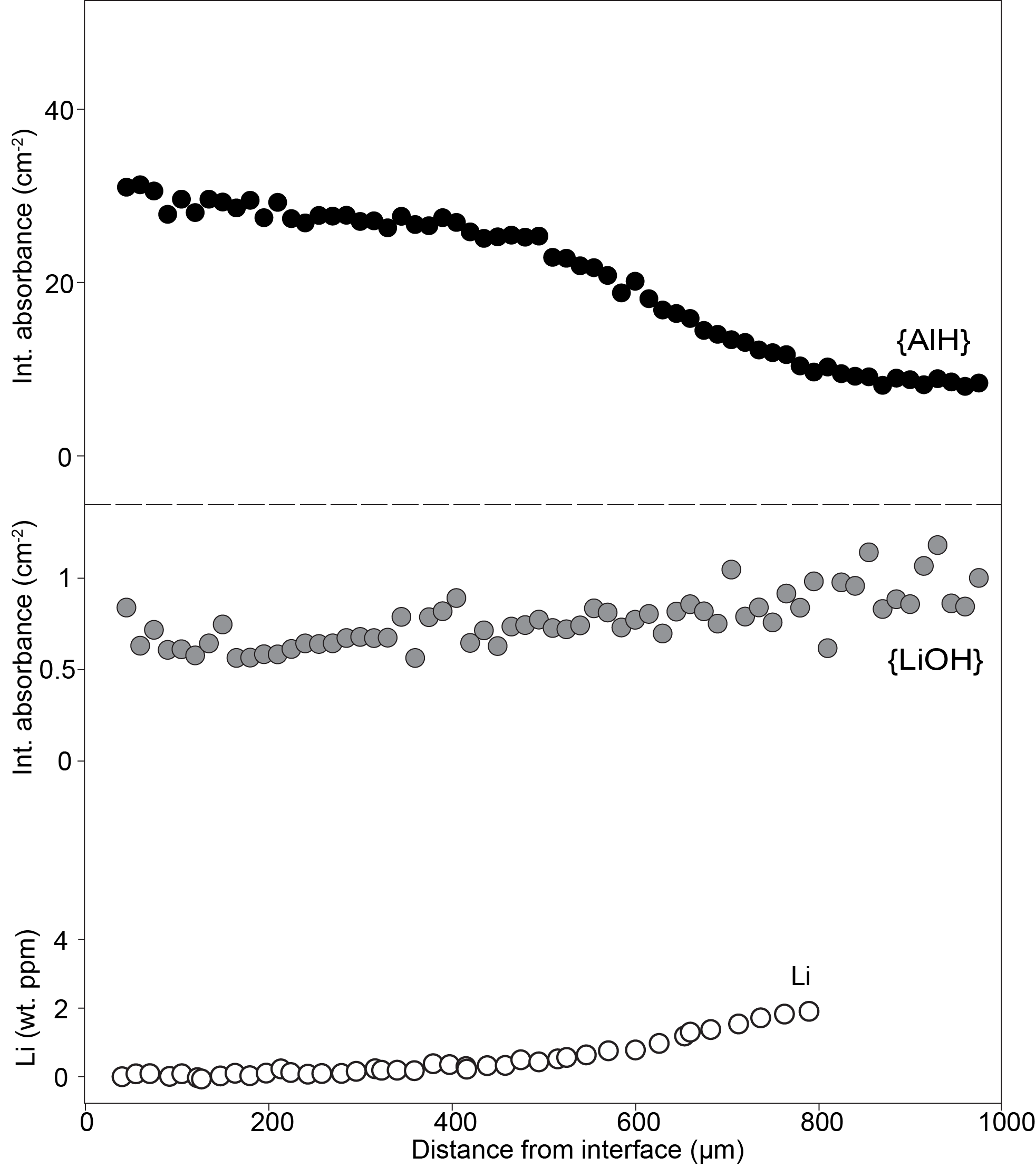


Supplementary Figure 5: Spectra from both rims and the core of the quartz crystal following equilibration with H, prior to the 2H-in/H-out diffusion experiment. (b) shows a transect of integrated absorbance across the crystal.

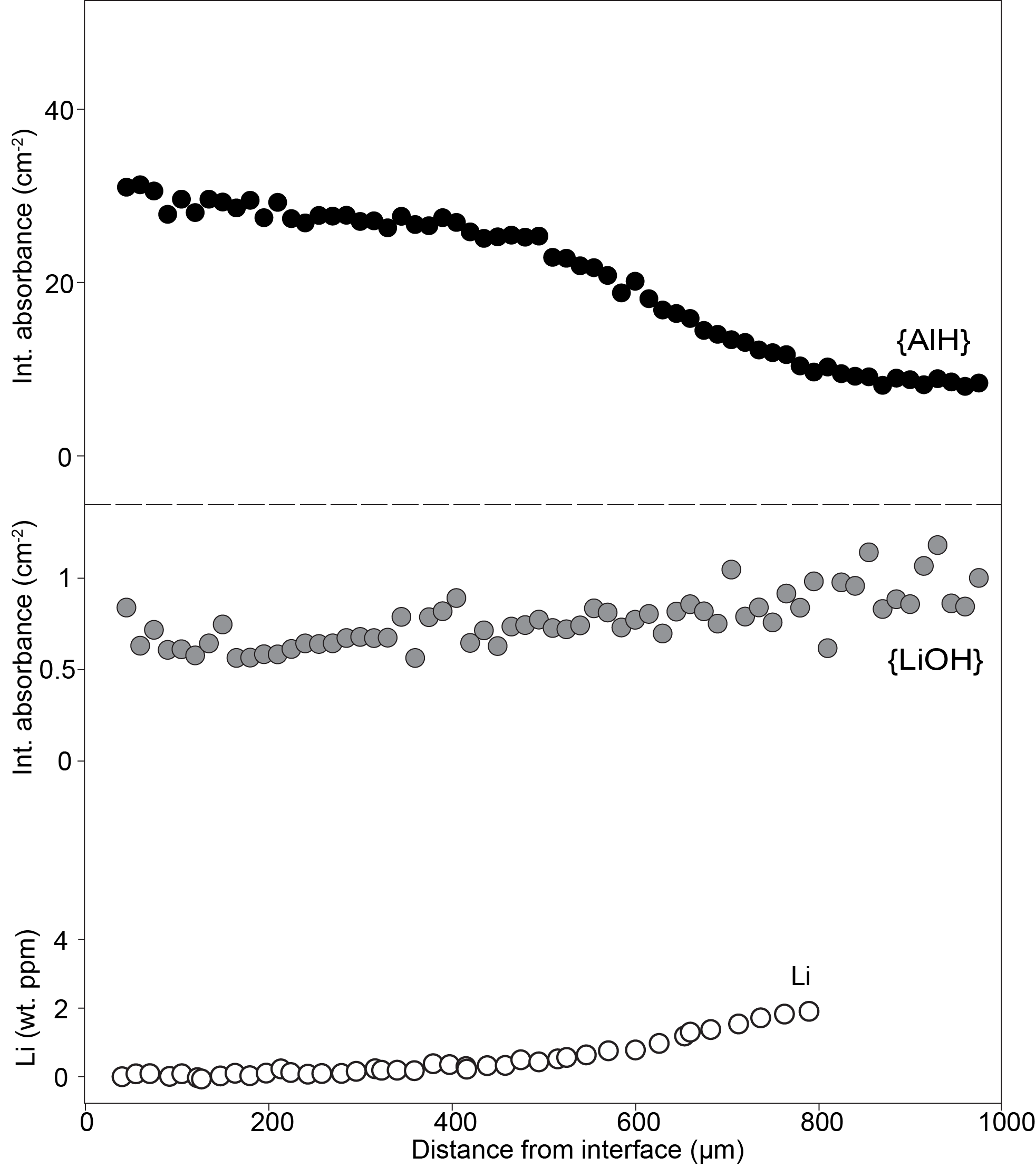
**Enlarged versions of profiles from Fig. 3 in the main text.**

Some of the features in Fig. 3 in the main text are challenging to make out given space constraints – mainly the {LiOH} bands, which have relatively low absorbance compared to the {AlH} bands. Therefore, the following figures show some of the sub-figures from Fig. 3, enlarged for clarity, with split scales where needed.

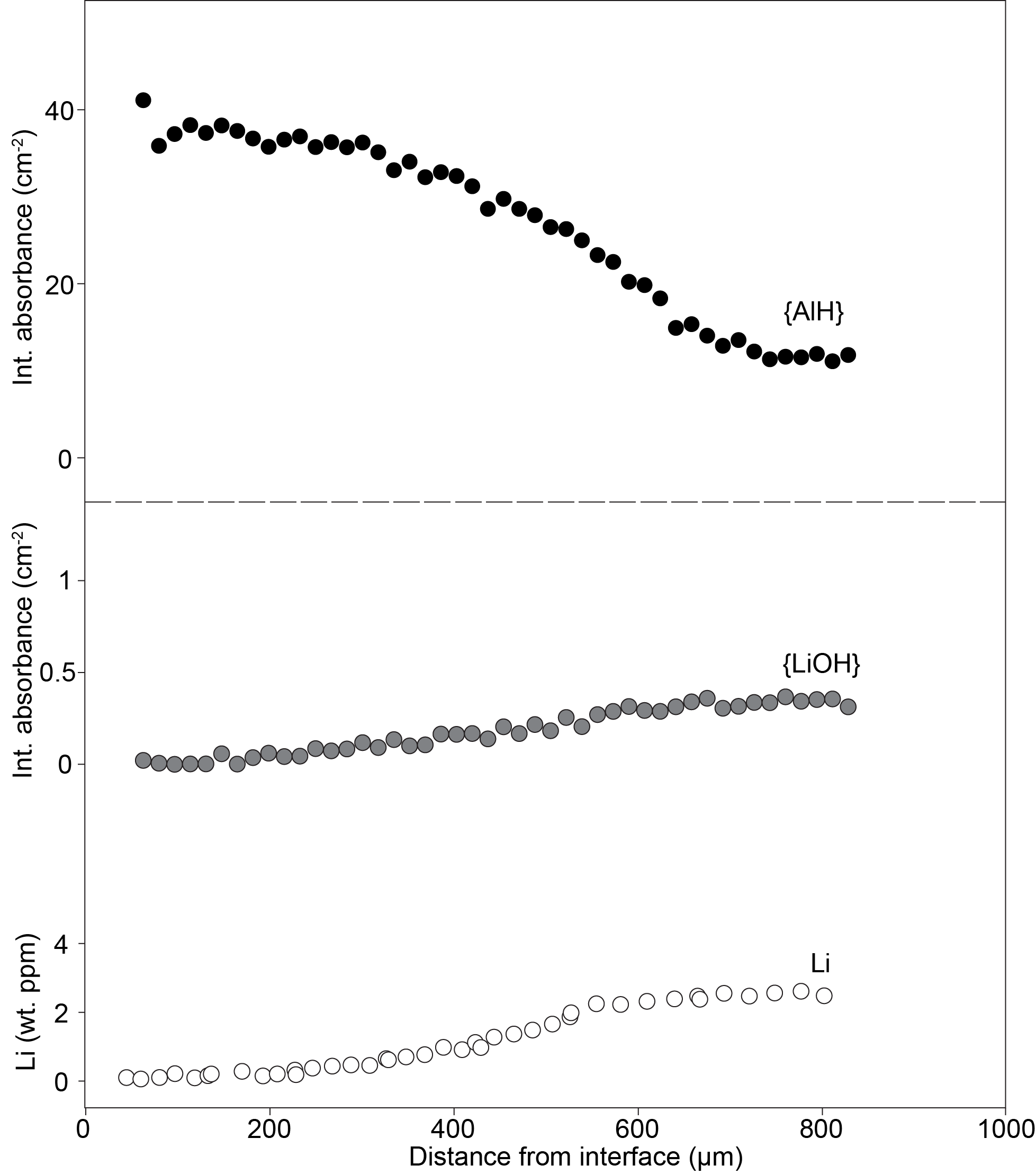
**HQHP-pH1**

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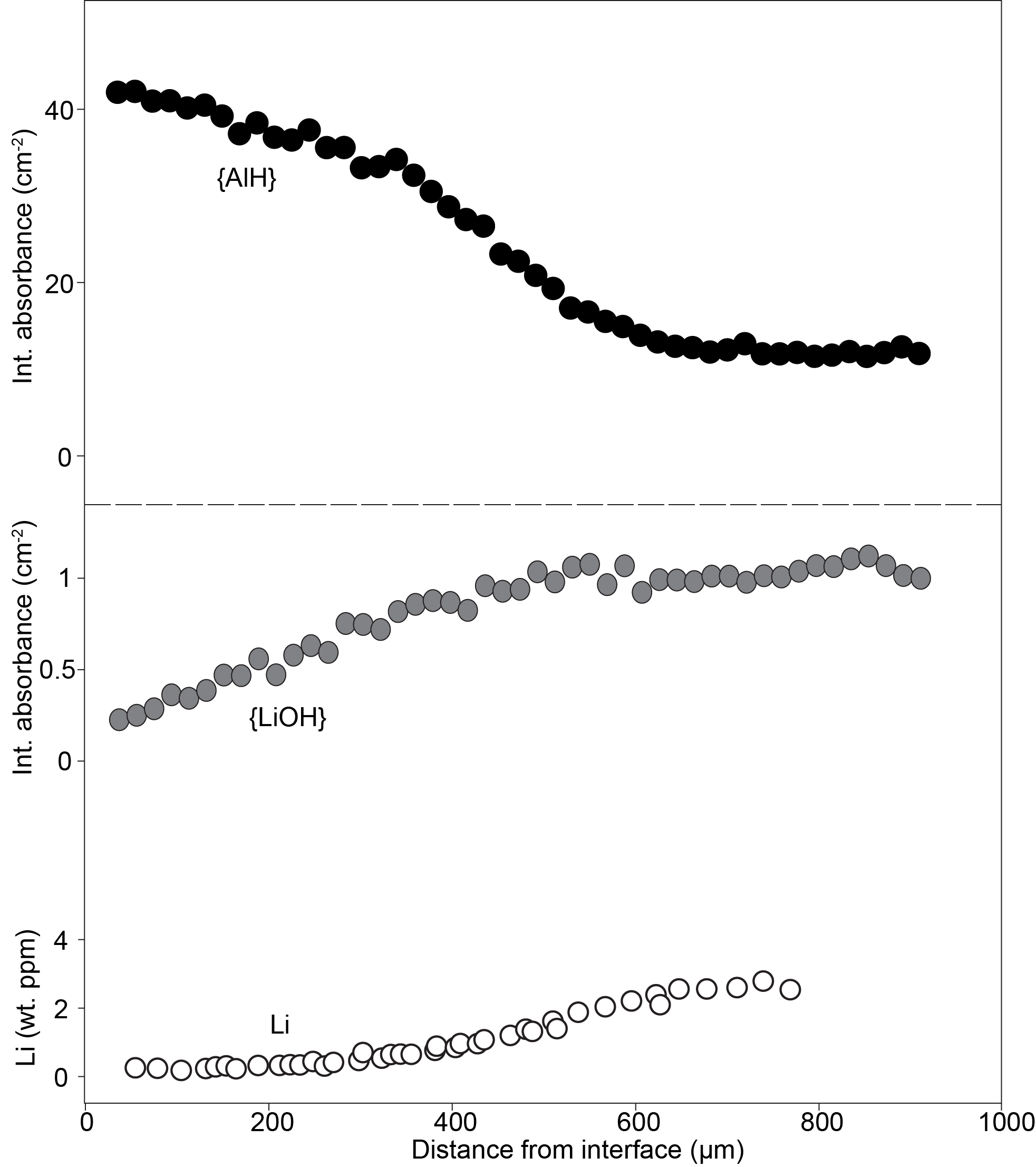
**HQHP-pH3**

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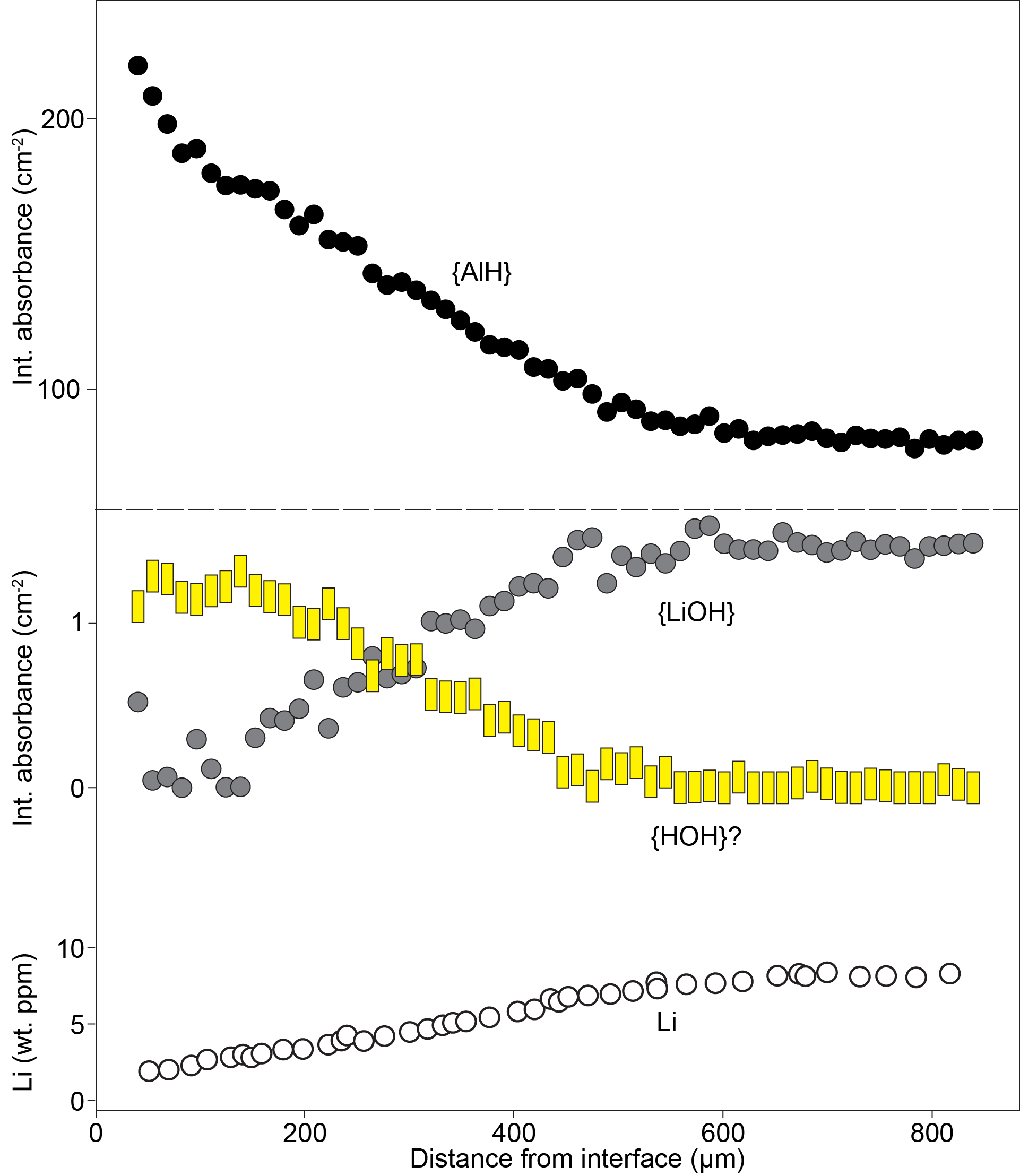
**HQHP-pH5**

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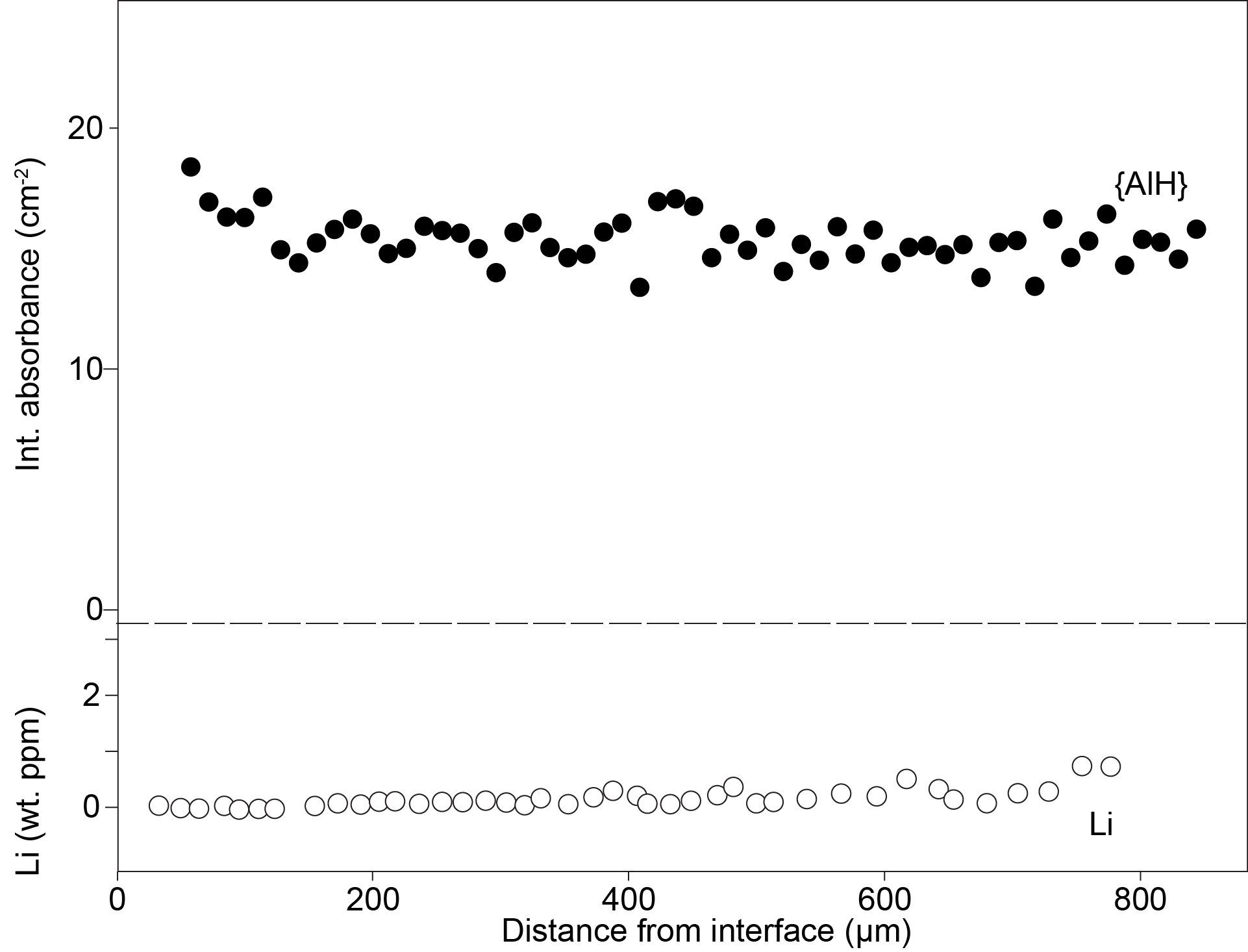
**HQHP-pH7**



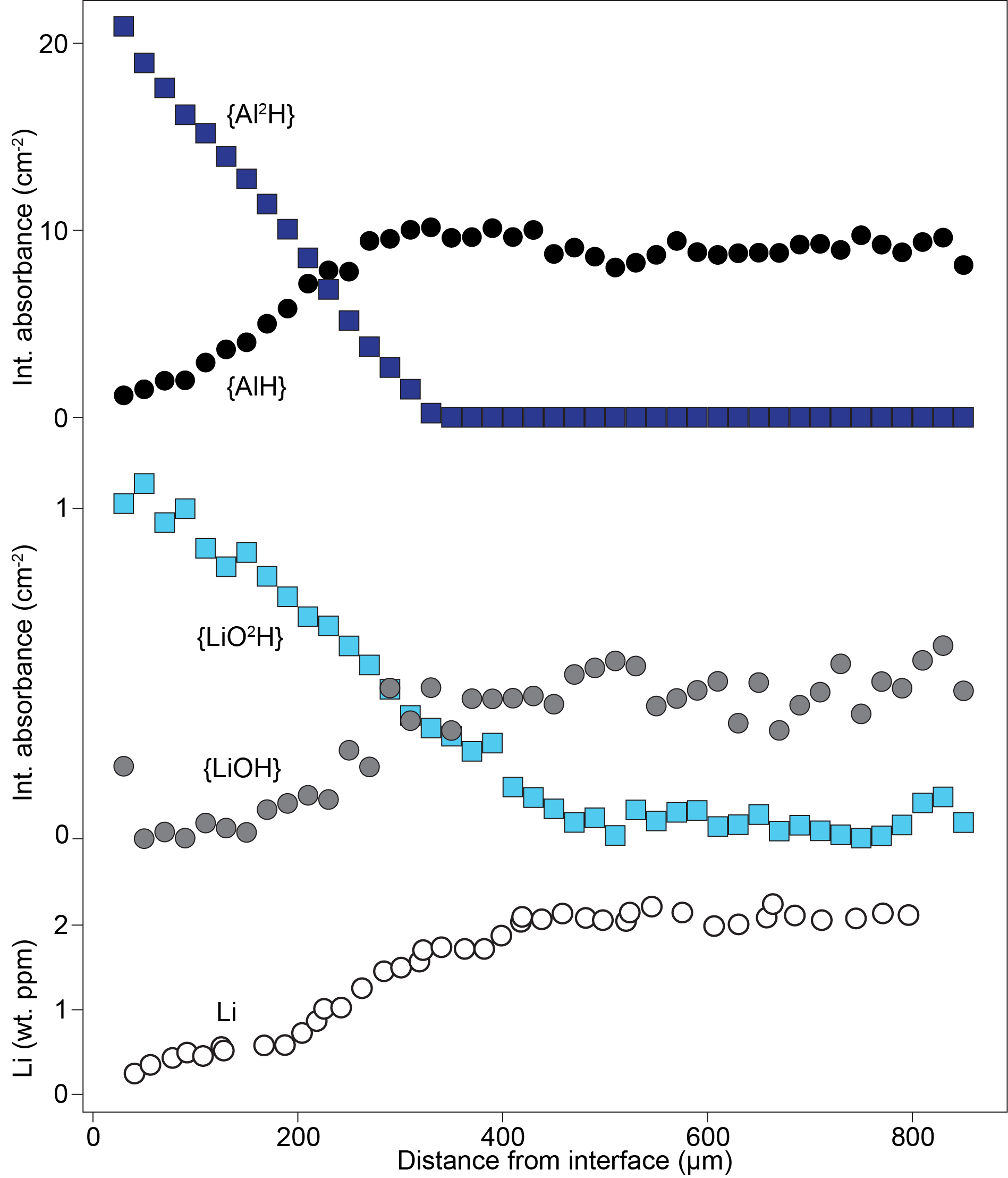
**HQHP-TIB2**



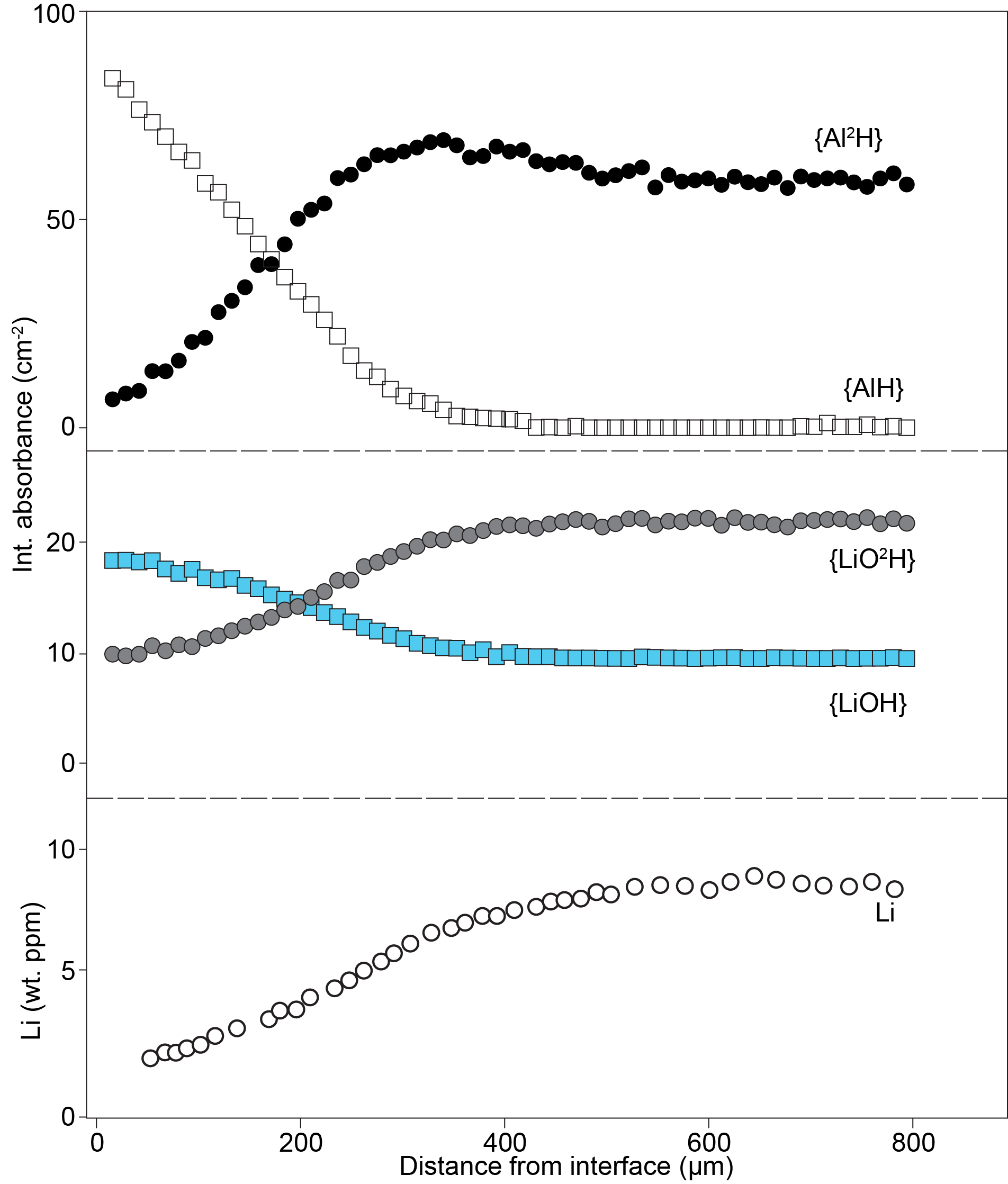
**HQHP-TIB6**



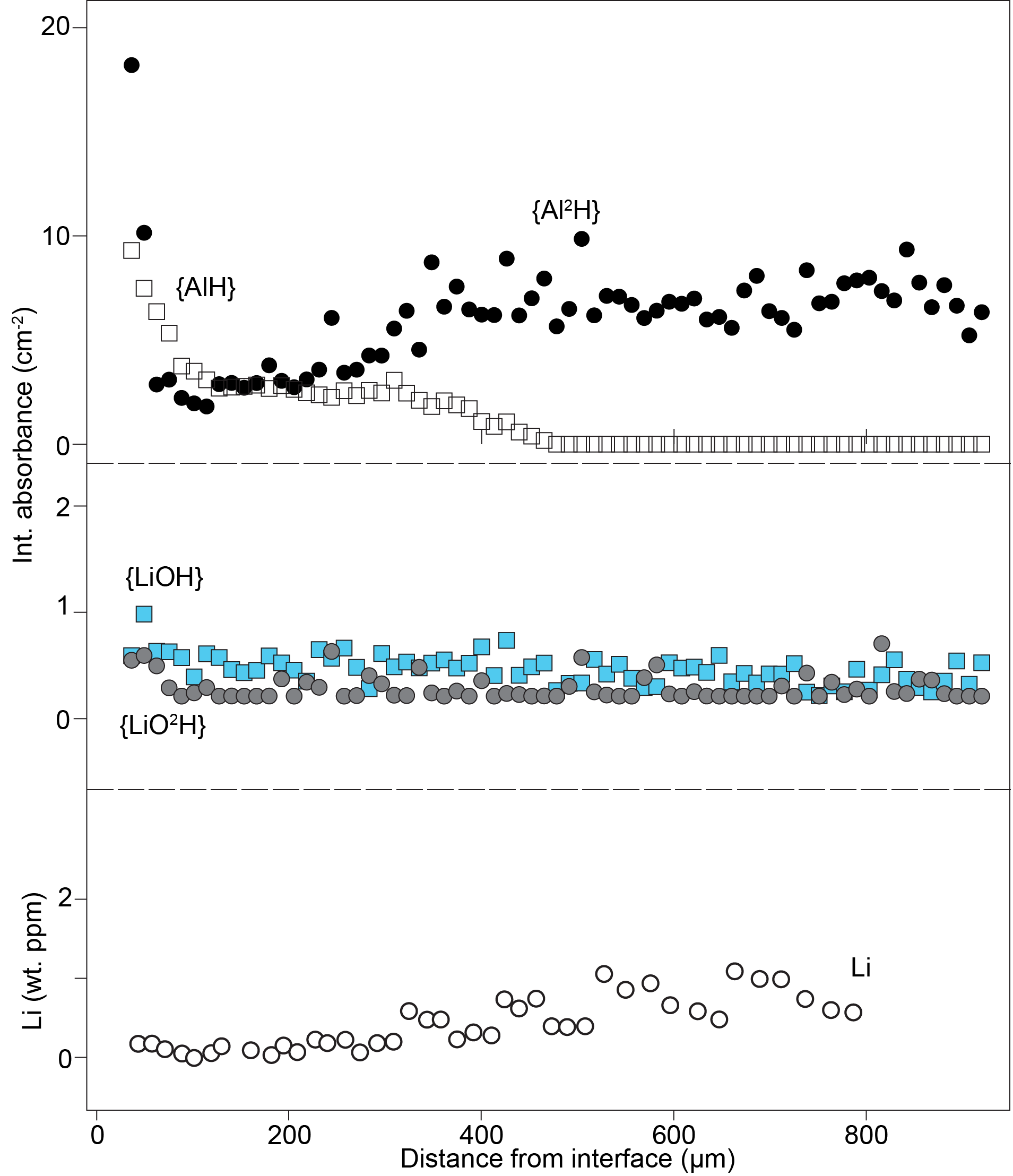
**DQHP-BRA3**



**DQHP-TIB2**

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**DQHP-TIB6**

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**Wavenumber difference between O-H and O-2H bonds**

As a first order approximation, the fact that O-2H bonds have wavenumbers (ω, in cm-1) around 1000 cm-1 lower than the equivalent O-H bonds is described using:

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| --- | --- |
|  | ( 4 ) |

where *c* is the speed of light (cm s-1), k is the force constant (kg s-2, equivalent to N m-1), and *µ* is the reduced mass (kg):

|  |  |
| --- | --- |
|  | ( 5 ) |

where m1 and m2 are molar masses, and N is Avogadro's number (mol-1). µ for O-1H and O-2H bonds is 1.56x1027 and 2.95x1027 kg, respectively. If we assume that *k* is approximately equal for O-1H and O-2H bonds, then we arrive at . This is a simplification, mainly because the force constants are unlikely to be equal, but gives a first order explanation of the ~1000 cm-1 wavenumber difference.

**Relative absorption coefficients between O-2H and O-H**

Following 2H-in/H-out experiments, bands representing {Al2H} appear in the O-2H stretching region at the expense of {AlH} bands in the O-H region.

A useful additional outcome of H-2H exchange experiments, aside from any diffusion considerations, is the ability to determine relative absorption coefficients (ε) associated with the O-H and O-2H stretching regions. This is only possible in these experiments because the only monovalent cations present are H+ and 2H+, thus we can reasonably assume that all H loss is balanced by 2H gain.

Total integrated absorbance (∑Abs) and concentration (C), here of H2O, are related via the Beer-Lambert law:

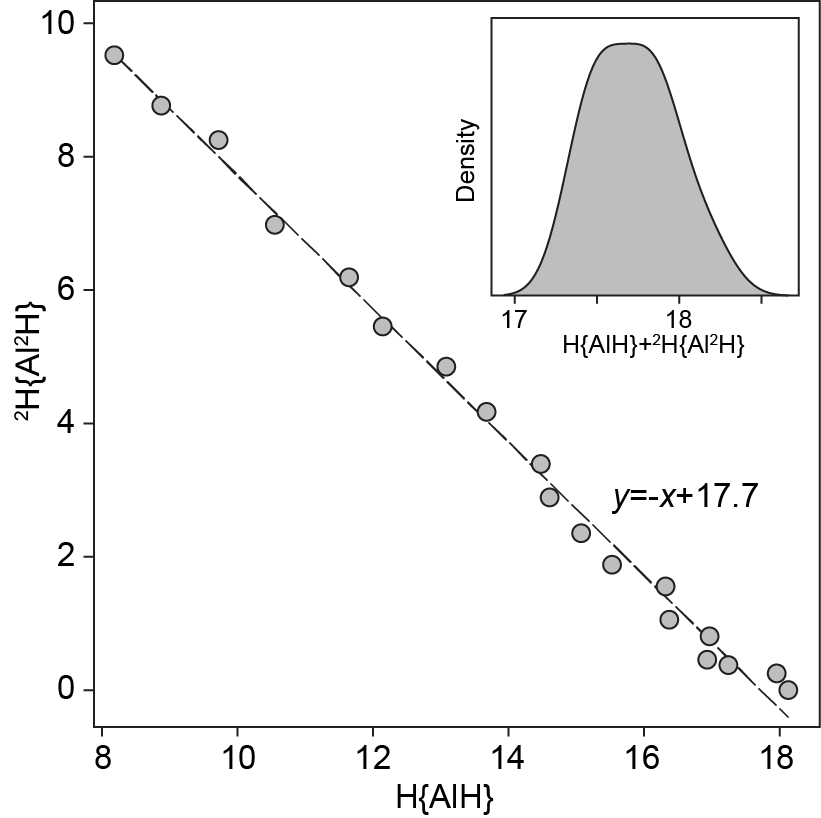
|  |  |
| --- | --- |
|  | ( 6 ) |

where ε is the absorption coefficient and d is the thickness. The density of quartz is estimated as 2.65 g cm-3. To constrain the relative absorption coefficients, we assume that every point along the profile has the same atomic ∑xH=H+2H. This is a particular advantage of diffusion experiments – a single profile gives a wide range of H/∑xH values in a a sample which has constant orientation, constant thickness, constant major element chemistry, etc.

Firstly, the integrated absorbance of the resolved {AlH} bands from every measured point along the profile was converted to wt. ppm H2O using the absorption coefficients of Thomas *et al.* (2009). In fact, because we are considering relative ε, the choice of value is unimportant. Then, the wt. ppm H2O was converted to atomic H.

Next, the same was done for the {Al2H} bands, but with ε for the O-H region multiplied by a constant representing (ε(O-2H)/ε(O-H)), to give ε for the O-2H region. The wt. ppm 2H2O values were then converted to atomic 2H.

Then, the atomic H values were added to atomic 2H, and the skewness of the resulting distribution was determined. The ε(O-2H)/ε(O-H) term giving the lowest skewness was then found. The best-fit ε(O-2H)/ε(O-H) was 0.896, i.e. if we take ε=89,000 Lmol-1cm-2 for the O-H stretching region from Thomas *et al.* (2009) as correct, then ε(O-2H) is 79,700 Lmol-1cm-2. A potential caveat of our determination is that the baseline correction routine will affect the O-H and O-2H regions differently, given that the O-2H bands are superimposed onto Si-O overtone bands, whereas the O-H bands are not. Our determination is internally consistent, but caution should be applied if: applying the values to other quartz crystals / using different routines for resolving spectra into their components / applying the values where the H or 2H concentration is considerably different to the concentrations in this study.



Supplementary Figure 6: Atomic concentrations of H and 2H associated with {AlH} and {Al2H} defects, respectively, where the absorption coefficient for 2H2O has been modified such that the distribution of H+2H has the lowest skewness. The distribution is shown in the inset. The dashed line has a slope of -1, i.e. negative correlation. This plot only includes data from the ~350 µm closest to the crystal edge, i.e. does not include data from the part of the profile where the absorbance associated with {AlH} and {Al2H} are effectively constant as a function of distance.

**Diffusion-reaction models**

**Determining absorption coefficients**

Therefore, prior to each model fit, the best-fit absorption coefficient is determined assuming that plus must be constant along each profile – this is done by minimising skewness, as in the method for determining relative absorption coefficients.

Because the LA-ICP-MS and FTIR data were acquired at different grid spacings, the two channels were interpolated onto a single distance vector (generally that associated with the FTIR spectra). Then, an absorption coefficient was guessed, and the defect specific atomic H content was determined from the FTIR data (for both {AlH} and {LiOH} in the H-in/Li-out experiments), and the atomic Li content from the LA-ICP-MS data. In the {LiOH} defect, the atomic Li equals atomic H, thus this Li was subtracted from total Li, which should leave the concentration of Li associated with {AlLi}. It is then the skewness of the sum of the {AlLi} plus {AlH} vectors that is minimised.

We also assumed that a single ε was appropriate for the whole O-H stretching region. The determined ε values were generally on the order of 50,000 to 70,000 Lmol-1cm-2, but as low as 32,000 and as high as 113,000 Lmol-1cm-2 (see Table 3 in the main text). The main range is lower than ε from Libowitzky and Rossman (1997) (~70,000-110,000 Lmol-1cm-2), Thomas *et al.* (2009) (72,000-108,000 Lmol-1cm-2, suggested value of 89,000 Lmol-1cm-2). A possible explanation for the difference would be different baseline subtraction routines – the Bruker OPUS concave rubber band method, used in this study, can be quite aggressive with baseline removal on relatively broad peaks (i.e. as in quartz). This would artificially decrease the absorbance in our spectra thus requiring a lower ε to balance the Li. For this reason, we do not recommend that our determined ε values be applied outside of this study, but note that they are internally consistent.

**H-in/Li-out experiments (Al defects only)**

A framework for such modelling is provided by Dohmen *et al.* (2010). Whilst Crank (1975) presents several analytical solutions describing systems where diffusion is coupled to some form of reaction, the Dohmen *et al.* (2010) method is advantageous in that it is flexible in terms of initial and boundary conditions, and relatively straightforward and computationally inexpensive to model.

The modelling proceeds as follows. The total duration of the model is divided into a large number of small time steps. In each time step, diffusion occurs, using the standard one-dimensional, concentration-independent, explicit finite difference method. In a 'normal' diffusion model, all of the diffusant would be allowed to move at each time step, but in this model, only some of the diffusant is allowed to move (that which is in a 'mobile' configuration, and ). Then, following the diffusion part, a reaction is modelled. This effectively returns the relative concentrations of H, Li, etc., in each defect to local equilibrium, with 'local' referring to the length of the pixel represented by a single distance step. Modelling the reaction step basically involves solving a series of simultaneous equations. The aim is to find the concentrations of all mobile and immobile defects whilst maintaining mass balance, site balance, etc., with the relative proportions of each defect defined by an equilibrium constant, K.

Consider the reaction relevant for the H-in/Li-out experiments:

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| --- | --- |
|  | ( 7 ) |

In this reaction, we have four unknowns, being the concentrations of each term in the equation. This means that we need at least four equations to solve the system. Again, i1 represents the interstitial site where H or Li are allowed to diffuse, and i2 represents that where the H or Li are fixed.

The first equation defines an equilibrium expression for the reaction (here K1):

|  |  |
| --- | --- |
|  | ( 8 ) |

where square brackets indicate molar or atomic concentrations. We use atomic concentrations per 106 Si – effectively identical results would be obtained using end-member proportions or molar concentrations, but using atoms per 106 Si is preferable simply as the numbers are similar to the respective wt. ppm values.

One peculiar observation in this study, and previous work (Jollands *et al.*, 2020b; Potrafke *et al.*, 2020) is that there appears to be some excess Al in the system. Because it is not clear why this is the case, we simplify the model and convert simply to , and to . Thus K1 is redefined as:

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| --- | --- |
|  | ( 9 ) |

reminding that i2 refers to ions immobilised by association with Al, and i1 ions are free to move.

We can then define equations setting the sum of i1 and i2 sites:

|  |  |
| --- | --- |
|  | ( 10 ) |
|  | ( 11 ) |

We can also define the sum of Li and H:

|  |  |
| --- | --- |
|  | ( 12 ) |
|  | ( 13 ) |

With five equations and four unknowns (, , and ) the system is over-determined. We therefore choose to fix K1, ∑i1, ∑i2 and ∑Li, and then calculate ∑H from:

During the diffusion part of each time step, the concentrations of and change. Therefore, ∑H and ∑Li are calculated at each position along the profile after the diffusion step, prior to the reaction. With these updated values, and keeping K1, ∑i1 and ∑i2 constant at all time and distance steps, the system is solved.

In this particular case, there is an analytical solution to the system of equations. can be determined using:

then the other unknowns are determined from:

The previous discussion describes a single time and distance step. These calculations need to be done for every distance step, then another diffusion step occurs, then reaction, and so on, until the total model time is reached. In this case, all models simulated 1 hour (3600 s) of diffusion, given that this was the duration of all experiments.

The outputs of the model after the final time step are , , , , and therefore ∑H and ∑Li, as a function of distance. Herein lies one major issue with the model. The FTIR spectra show the presence of {AlH} defects, i.e. , but show no H that could be considered as free, i.e. . Therefore, is effectively a fictitious component that is required by the model, but one for which our experiments provide no independent evidence (except the success of the model fits). For Li, we only have ∑Li as measured by LA-ICP-MS.

The way we reconcile this issue is by assuming that the and defects exist only during the high temperature portion of the experiment, then collapse into the and associations upon cooling, which is intuitive if one assumes that the dissociation reactions are endothermic.

Using this assumption, following the final time step of the model, [] is added to [] and [] to []. These summed values are those which are presented in all plots.

The next issue also relates to the necessity to invoke a fictitious mobile component. We have no *a priori* constraint on ∑i1, i.e. the total concentration of mobile ions. We also assume that it is constant as a function of time and distance, an assumption for which we have no evidence. As would be expected from simple considerations of flux, as ∑i1 decreases, the diffusion coefficient must increase to compensate, i.e. to move as much H into the crystal over a given time. The ∑i1 parameter is discussed further below with regards to uncertainty estimates.

**Least-squares regression and uncertainty estimates for H-in/Li-out experiments**

Where analytical solutions existed, the models were placed into MATLAB functions, then fitted to the data using non-linear least squares regression (MATLAB function *lsqnonlin*). This was only done for the models with analytical solutions.

Prior to fitting, various data adjustments were necessary. Firstly, the Li concentrations determined by LA-ICP-MS needed to be adjusted such that they only represented {AlLi} and not {LiOH}, which was not included in the modelling at this point (but is added later). Because the LA-ICP-MS and FTIR data were not acquired at the same spacing, the Li concentrations from LA-ICP-MS were linearly interpolated onto the same grid spacing as the FTIR data (after converting both to atomic concentrations), then the Li ({LiOH}) concentration was subtracted from the total Li concentration for each point in the interpolated vector, which we assume then gives the concentration of {AlLi}.

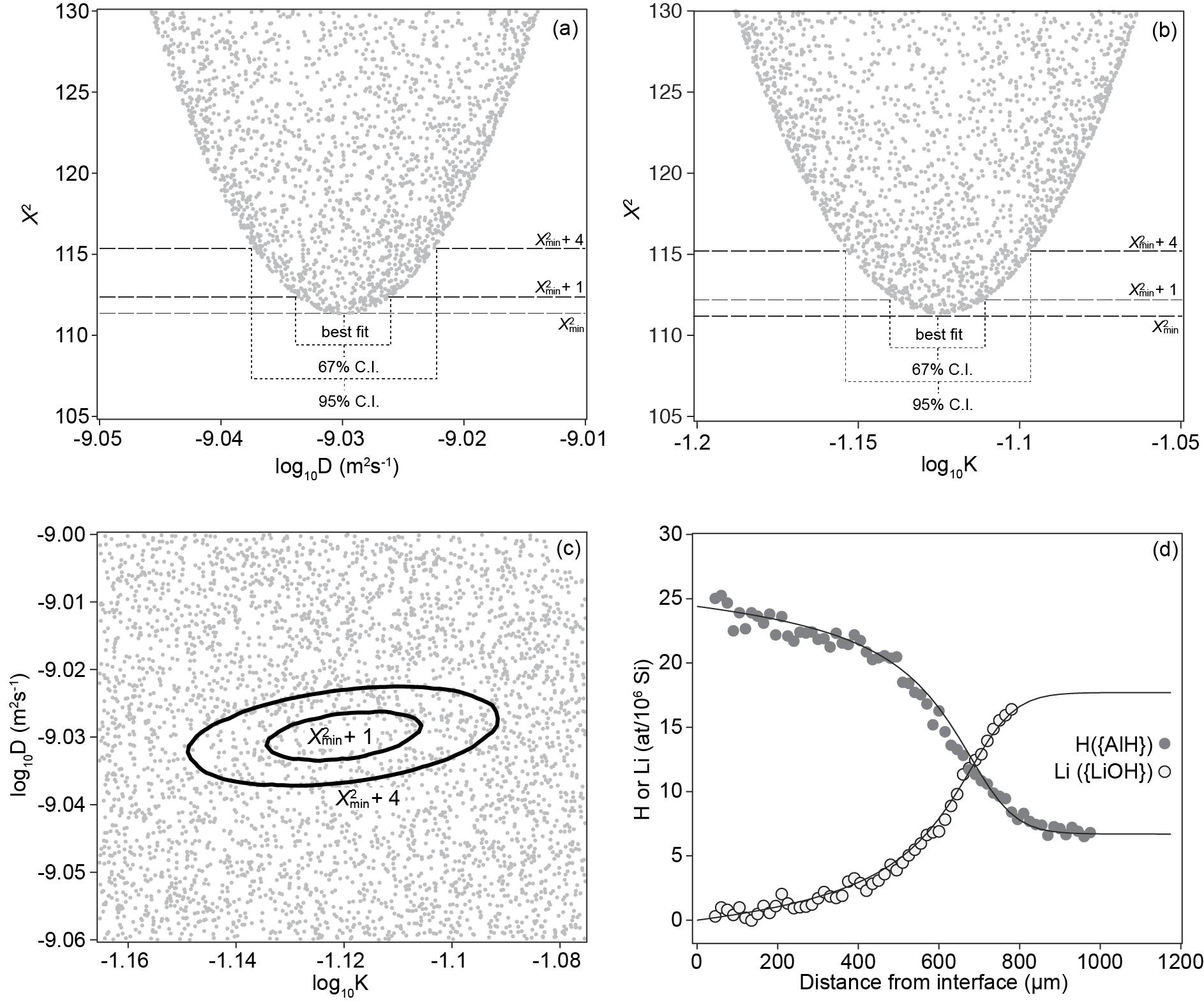
Next, the uncertainties for each point in both the {AlH} and {AlLi} vectors were estimated. For {AlH}, a five-point moving standard deviation was calculated along the vector. The rationale behind this is that such an uncertainty will be considerably greater than that associated with resolving the spectra into pseudo-Voigt peaks, and that taking the uncertainty of data over a ~75 µm length (5 points, 15 µm spacing) is not unreasonable given the interaction volume of the infrared beam and sample. The uncertainties for the Li concentrations were those associated with the LA-ICP-MS analyses, as outputted from Iolite (Paton *et al.* 2011).

The non-linear least squares regression was set up such that it minimised the sum of the squared difference between the model and the data divided by the variance (i.e. the chi-squared value) by changing only the values of K1 and log10*D*. All other values were fixed. To account for the unknown ∑i1 parameter, the model was run with a range of different values of ∑i1.

The chi-squared statistic divided by the number of degrees of freedom gives the reduced chi-squared, which is used to assess the goodness of fit – these values are presented in Table 2 in the main text – most reduced chi squared values fall between 0.5 and 1.5.

Uncertainties on fits were determined using the constant chi-squared boundary method (Press *et al.*, 2007). This involves simulating a large number of models, varying the input parameters, then calculating the chi-squared statistic for each model fit. The best fit model is associated with the minimum chi-squared value, and ideally, the boundaries associated with the minimum chi-squared + 4 represent the 95% confidence limits. Even in cases where it might not be appropriate to formally determine uncertainties, this method is useful for assessing the sensitivity of the goodness of fit to the different input parameters.

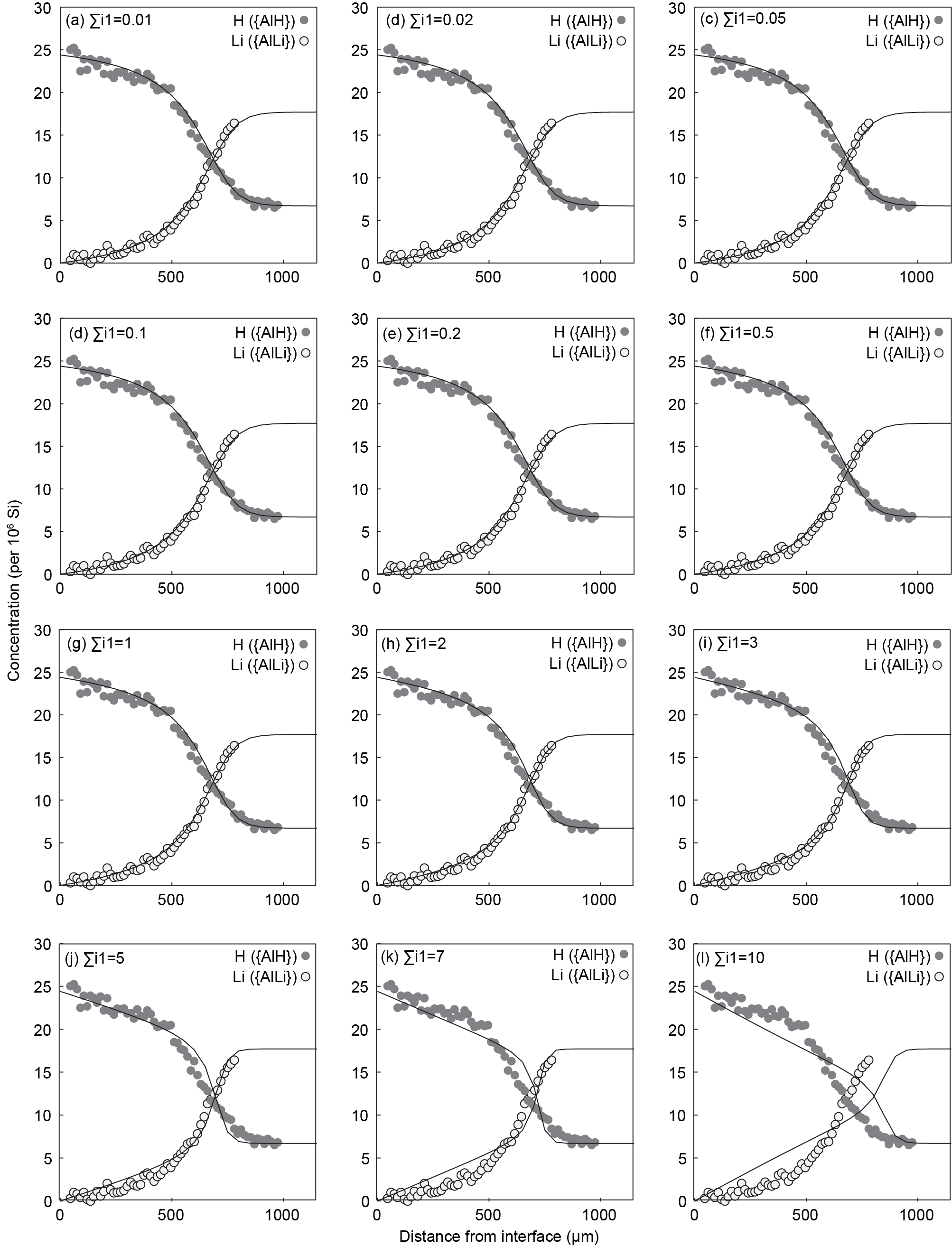
As an example, the following shows the distribution of chi-squared values as a function of log10K and log10*D* for experiment HQHP-pH1, where the ∑i1 parameter (mobile sites) is set to an arbitrary value of 1. The ∑i2 and interface and boundary ∑Li values are set manually. The figure shows the result of 25,000 simulations with log10K and log10*D* varying randomly around the best-fit values that were previously determined by non-linear least squares regression. Supplementary Figure 7 (a) shows chi-squared as a function of log10*D*, (b) shows chi-squared as a function of log10K, and (c) shows log10K versus log10*D*, with contours of constant Δ𝜒2, which is the difference between the chi-squared statistic for the input values of K and D, and the minimum chi-squared value. (d) shows the fit to the data associated with the best fit values.



Supplementary Figure 7: See description in the text, above.

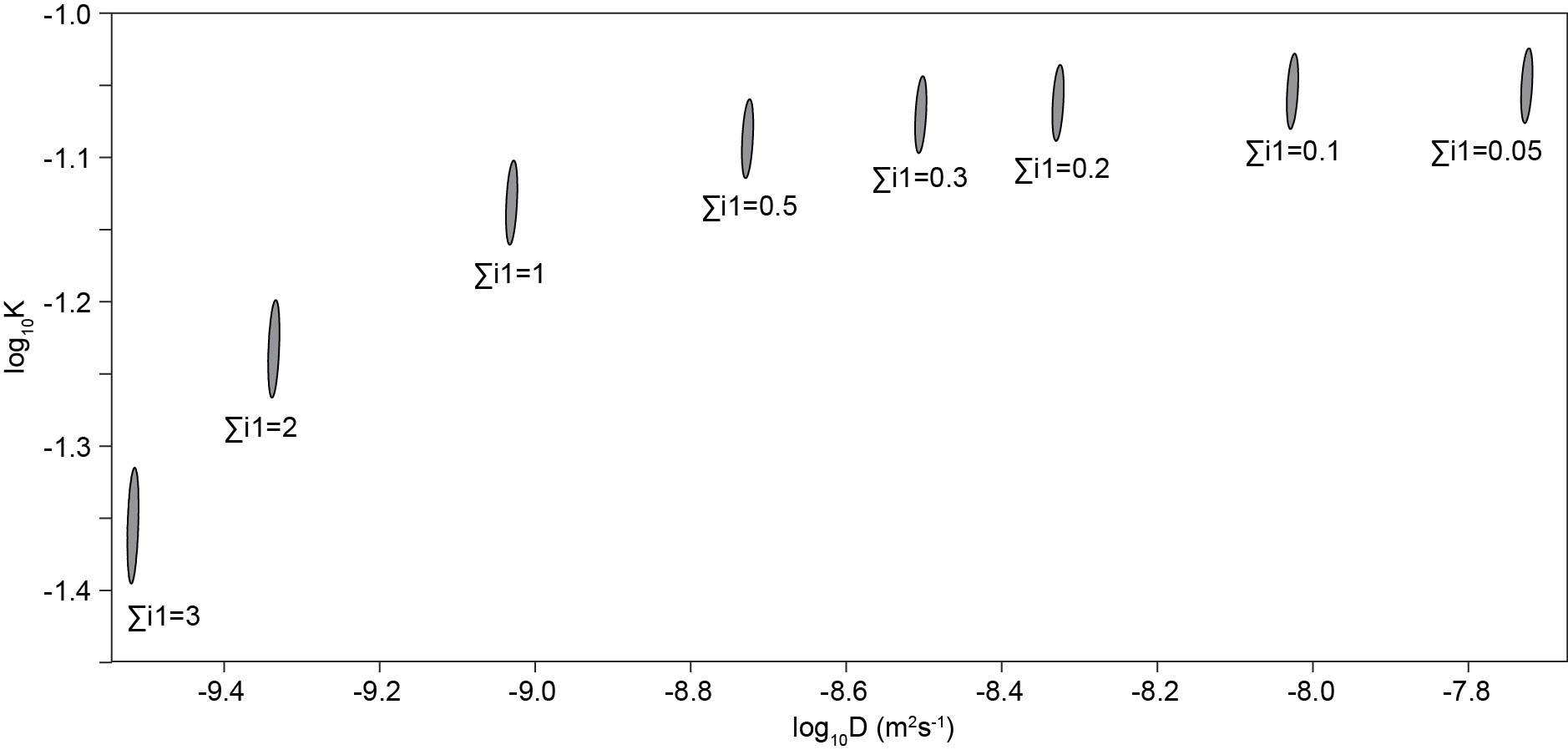
In this case, with ∑i1 fixed, it is possible to confidently determine the confidence intervals around the best fit value, specific for this particular value of ∑i1.

However, if ∑i1 is also allowed to vary, then the results become more complex. Generally, similarly good fits can be obtained over a wide range of ∑i1 up to some maximum value. Supplementary Figure 8 shows fits to the data from experiment HQHP-pH1 with different values of ∑i1 from 0.01 to 10 (per 106 Si). It is clear, simply from looking at the fits, that the curve shapes and hence fit quality are more or less constant when ∑i1<1, then the model forms begin to change (the transition of the step becomes steeper). When ∑i1>5, adequate fits (as assessed visually) can no longer be obtained.



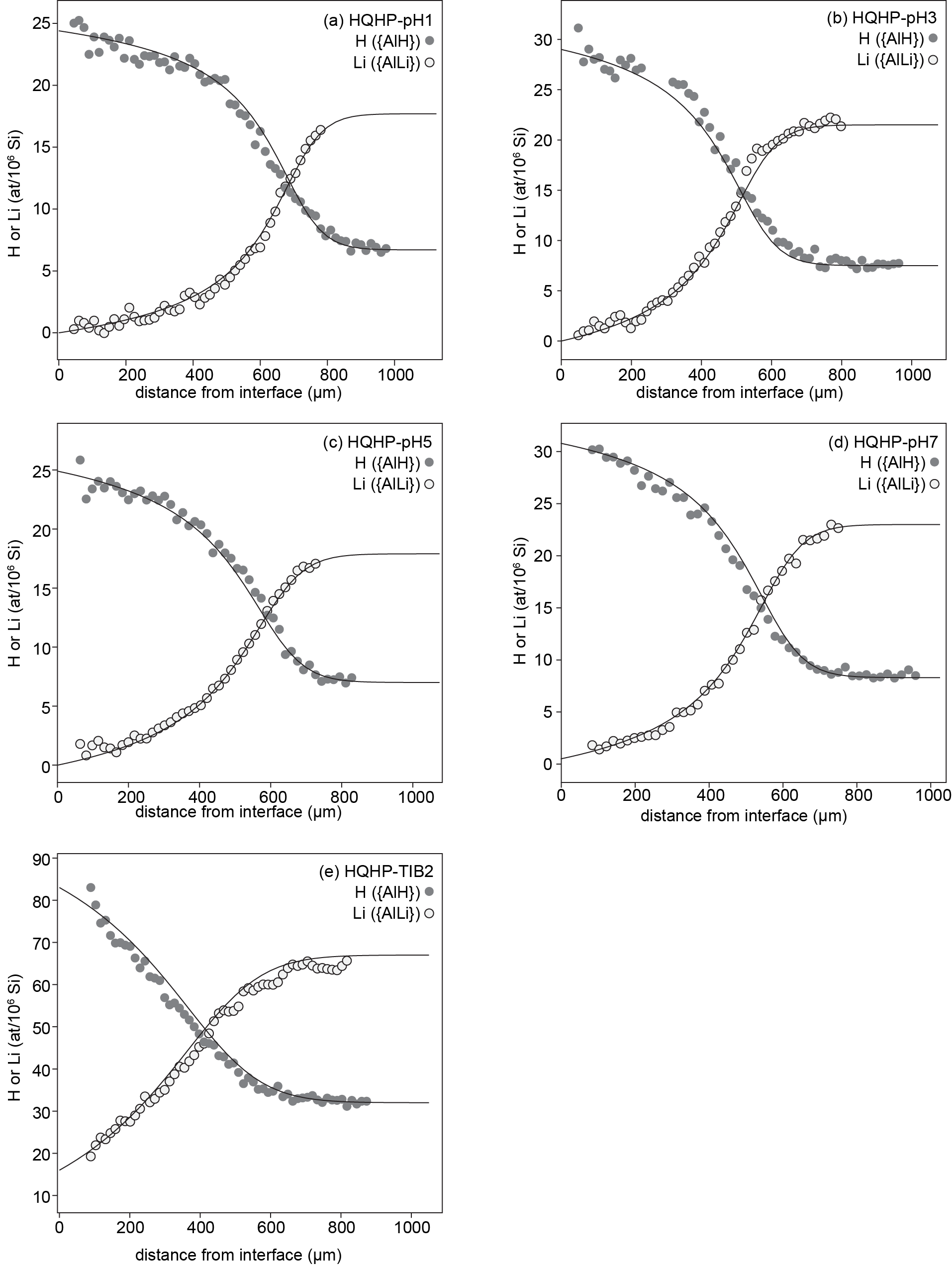
Supplementary Figure 8: Model fits to the data from experiment HQHP-pH1 with different values of ∑i1. The fit quality starts to decrease when ∑i1 exceeds 1, then is clearly unacceptable when ∑i1 > 5.

As ∑i1 decreases, log10*D* increases, seemingly without limit. It is challenging to model profiles with very low ∑i1 and high log10*D* given the necessity to maintain numerical stability in the diffusion model, but it appears to be possible to generate good fits for all experiments in the pH series using any value of ∑i1 below around 5. Interestingly, whilst *D* increases as ∑i1 decreases, K hardly changes, as shown below:



Supplementary Figure 9: K and D determined from fitting experiment HQHP-pH1, with associated 95% confidence ellipses, for different values of ∑i1. As ∑i1 decreases, D increases, but K stays more or less constant at low values of ∑i1.

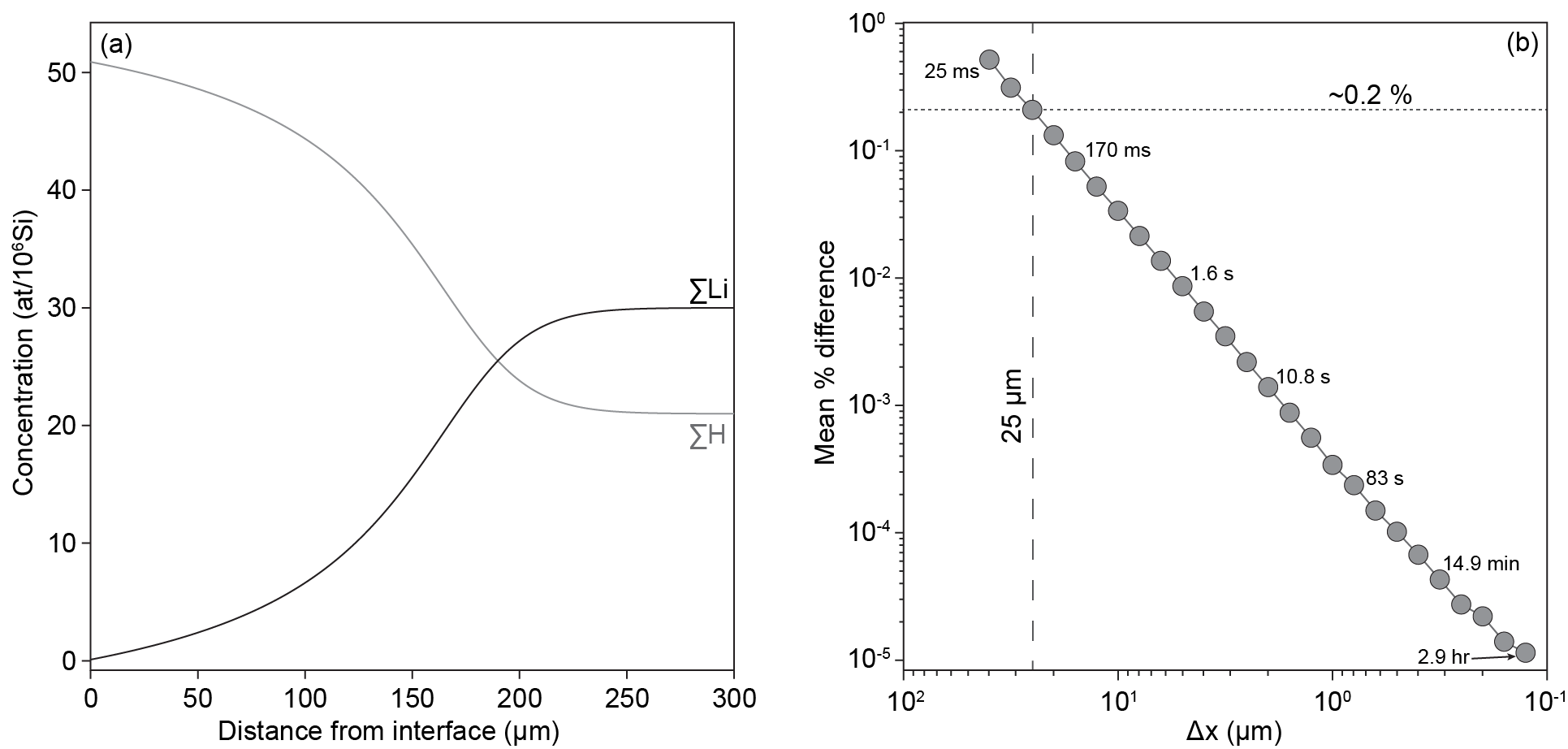
Therefore, in order to present *internally consistent* results, we determine the best fit values of D and K, along with their uncertainties, with ∑i1 fixed at 0.1 and 1 atoms per 106 Si.



Supplementary Figure 10: All fits from the HQHP-pH… series and HQHP-TIB2

**Model convergence**

In this study, a relatively coarse Δx was used (25 µm), which is a trade-off between computational speed and accuracy. To determine the extent to which this could affect the modelled profiles, one model was run repeatedly with a wide range of Δx values, from 10-1 to 101.6 µm (0.1 to ~40 µm). Taking the model with the lowest Δx to be a reference, the mean difference was calculated for all values along the diffusion profiles between the reference model and the model run with a higher Δx. The results are shown in the following figure. In this case, the mean % difference between the values determined using Δx=0.1 µm and Δx=25 µm is around 0.2 % i.e. negligible relative to other sources of uncertainty. Also shown are the times taken to run the models (MacBook Pro 2015, 2.2 GHz Intel i7 processor, 16 GB RAM, running MATLAB 2019a on macOSX High Sierra 10.13.6), measured using the MATLAB *tic* and *toc* functions.



Supplementary Figure 11: The effect of changing Δx on model outputs. (a) ∑H and ∑Li as a function of distance from the interface for a 'reference' model with the following parameters (concentrations in at/106Si): ∑Li (initial) = 30; ∑Li(interface)=0.1; ∑i1=1; ∑i2=50; K1=0.1; log10D=-10 m2s-1; total time = 3600 s; Δx=0.1 µm. (b) the mean % difference between the model in (a) with Δx=0.1 µm and models run with higher Δx. With Δx=25 µm, the difference in this case is around 0.2% (dashed lines). Also shown are the computational times for each model, using the hardware described in the text above.

**H-in/Li-out experiments (including both Al and O defects)**

In this case, we model not only the Al-associated defects ({AlH} and {AlLi}) but also the O-associated defects ({H2O} and {LiOH}, omitting Li2O). Models in this system were constructed in the same way as above, but with the difference being that there is no analytical solution to the solution of equations.

The equations are:

|  |  |
| --- | --- |
|  | ( 14 ) |

(i.e. as above),

|  |  |
| --- | --- |
|  | ( 15 ) |

where 'i3' is one of the sites associated with the {LiOH} and {H2O} defects. This is a simplification, there is clearly more than one i site associated with both of these defects.

We then have the equations keeping Li and H constant:

|  |  |
| --- | --- |
|  | ( 16 ) |
|  | ( 17 ) |

and keeping the total number of the different i sites constant:

|  |  |
| --- | --- |
|  | ( 18 ) |
|  | ( 19 ) |
|  | ( 20 ) |

Again, this is an over determined system, so ∑i1, ∑i2, ∑i3 and ∑Li are fixed, and ∑H is determined from:

|  |  |
| --- | --- |
|  | ( 21 ) |

This system of equations does not have an analytical solution. Instead, the concentration of (H associated with {LiOH}) is determined from the root of the following, where [z]=.

|  |
| --- |
|  |
| ( 22 ) |

Then the other unknowns are found:

|  |  |
| --- | --- |
|  | ( 23 ) |
|  | ( 24 ) |
|  | ( 25 ) |
|  | ( 26 ) |
|  | ( 27 ) |

At the end of the model, the H and Li left in the mobile i1 site are moved into the {AlH} and {AlLi} defects, rather than being placed into {LiOH} and {H2O} defects. This is purely for simplicity, there is no theoretical reason to do this.

**2H-in/H-out experiments**

In these experiments, the relevant exchange reaction is:

|  |  |
| --- | --- |
|  | ( 28 ) |

which is the same as eq. ( 7 ) but with 2H replacing Li.

As before, the Al is omitted, thus the equilibrium constant for this reaction (K3) is defined as:

|  |  |
| --- | --- |
|  | ( 29 ) |

We define the sums of the i sites, 2H and H:

|  |  |
| --- | --- |
|  | ( 30 ) |
|  | ( 31 ) |
|  | ( 32 ) |
|  | ( 33 ) |

As before, because the system is over-determined:

|  |  |
| --- | --- |
|  | ( 34 ) |

The solution here has the same form as the H-in/Li-out experiments, but with Li replaced by 2H, and K1 replaced by K3:

|  |
| --- |
|  |
| 35 ) |

then:

|  |  |
| --- | --- |
|  | ( 36 ) |
|  | ( 37 ) |
|  | ( 38 ) |

It was stated in the text that the equilibrium constant for the reaction, K3, should be approximately equal to 1. However, the analytical solution ends with /(K3-1), thus where K=1, =∞. Therefore, the model was actually run using log10K3=10-10.

**2H-in/H+Li out experiments**

This model proceeds in much the same way as the model of the H-in/Li-out experiments where both O and Al-associated defects were considered, i.e. numerically solving the equations at every time and distance step. The solutions are found as follows.

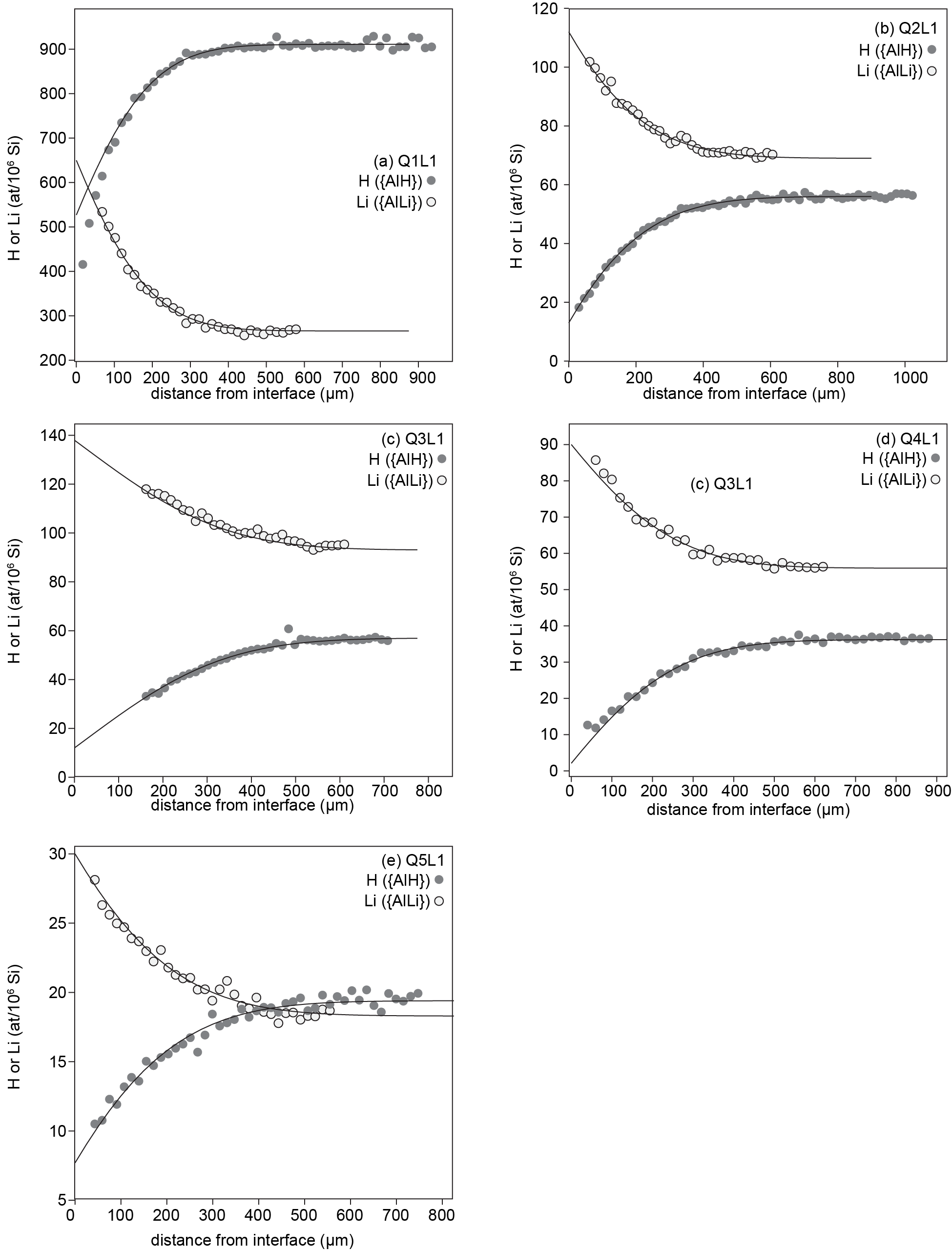
Firstly is found as the root of the following equation, where [z] = .

|  |
| --- |
|  |
| ( 39 ) |

Then the other five unknowns are calculated:

|  |  |
| --- | --- |
|  | ( 40 ) |
|  | ( 41 ) |
|  | ( 42 ) |
|  | ( 43 ) |
|  | ( 44 ) |

Five profiles were fitted from experiment QxL1 from Jollands *et al.* (2020b). All fits are shown in the following figure.

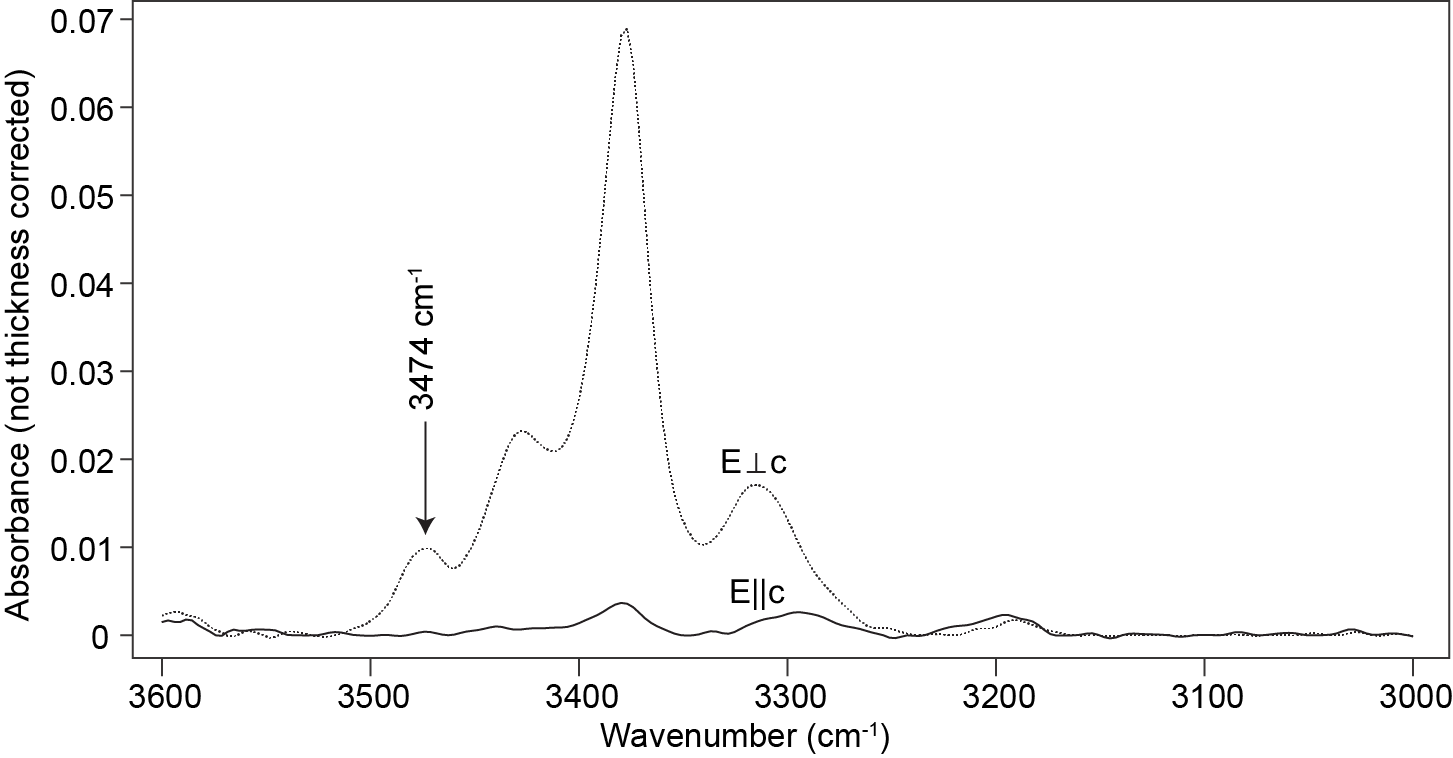


Supplementary Figure 12: fits to the data from experiments QxL1, from Jollands *et al.* (2020b).

**Li-in/H-out experiments**

These experiments were modelled using the same model as the H-in/Li-out experiments, but with different initial and boundary conditions to induce Li loss and H gain.

**FTIR spectra of the 3475 cm-1 band**



Supplementary Figure 13: Polarised FTIR spectra from the rim of experiment HQHP-TIB2, showing the 3475 cm-1 band, with all absorbance shown when E⟂c.

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