

**Derivation of pH-trend from both literature bulk dissolution rates and our batch dissolution rates and explanation about procedure for the calculations of the edge and basal dissolution kinetics for the pH range between 1 and 6.**

As mentioned in the methods, we have measured the elemental release *vs* time in batch and flow through dissolution experiments with the same biotite as used in the fungal experiments and measured the sizes of the biotite edge and basal plane contributions. Thus we could calculate the edge and basal plane rates at those conditions.

**Table S1:**  $r_{edge}$  and  $r_{basal}$  values at 25°C for pH between 2, 3.3 and 4 derived from the abiotic batch (bch) and flow through (ft) dissolution experiments performed with the same biotite material as used in the mycorrhizal microcosm.

	pH 2 (bch)	pH 3.3 (ft)	pH 4 (bch)
$r_{edge}$ (mol Bt m <sup>-2</sup> h <sup>-1</sup> )	1.2 – 1.9 × 10 <sup>-5</sup>	2.5 - 3.9 × 10 <sup>-6</sup>	1.2 – 1.9 × 10 <sup>-6</sup>
$r_{basal}$ (mol Bt m <sup>-2</sup> h <sup>-1</sup> )	0.8 – 3.4 × 10 <sup>-7</sup>	1.6 - 6.8 × 10 <sup>-8</sup>	0.8 – 3.4 × 10 <sup>-8</sup>

To extrapolate these edge and basal dissolution rates through the whole pH range considered (pH 1 to 6) and to compare them with the fungal dissolution rate derived from our microcosm experiment and STEM-EDX line profiles, we derived an equation describing the pH-dependency of biotite dissolution. Using a linear regression of the bulk biotite dissolution rates reported in the literature (Fig. 7), a pH-dependency can be expressed as:

$$\log r_{bulk} = -0.48 \text{ pH} - 5.85 \quad (\text{S1})$$

which is equivalent to the formalism of Kalinowski and Schweda (1996):

$$r_{bulk} = k a_{H^+}^n \quad (S2)$$

Where,  $k$  is an apparent rate constant varying between  $8 \times 10^{-8} - 1.2 \times 10^{-6}$  ( $1.4 \times 10^{-6}$  in this study) and  $n$ , an exponent ranging from 0.35 to 0.61 (0.48 in the current study). Overall, the pH-trend derived here in Eq.(S2) based on fitting all the data from the literature and the abiotic data from the current study is in line with the pH-dependency described in Kalinowski and Schweda (1996). Therefore, Eq (S1) in combination with the data from Table S1 were used to extrapolate and obtain a range for the edge and basal plane dissolution rates as a function of pH for between 1 and 6 (gray zones in Fig. 7).

#### References:

- Crank, J., 1987. *Free and Moving Boundary Problems*. Oxford University Press, Oxford.
- Kalinowski, B. E. and Schweda, P., 1996. Kinetics of muscovite, phlogopite, and biotite dissolution and alteration at pH 1-4, room temperature. *Geochim. Cosmochim. Acta* **60**, 367-385.

## Figure captions for Supplementary Information

**Figure S1:** Ratio of fluorescence emitted at 580 nm and 640 nm by the pH-sensitive molecular probe (SNARF4F) for a pH range between 4.6 to 7.8. The dotted line is the best fit of the dataset with a Boltzmann sigmoid function, used later on as a pH-calibration curve (performed with OriginLab®).

**Figure S2:** Detail of the STEM-EDX Si profile at the interface showing the sharp increase in counts between 324 and 348 nm indicating the precise position of the interface between the hypha and the biotite (336 nm, which is thus defined as the origin of the biotite depth-profile (i.e., 0 nm) as plotted in Fig. 2B).

**Figure S3:** Average of K/Si, Fe/Si, Al/Si and Mg/Si intensity count ratios measured in the bulk non-altered biotite in the four FIB sections. Standard deviations (in percent) for K/Si, Fe/Si, Al/Si and Mg/Si were 15%, 13%, 15% and 19%.

**Figure S4:** Normalized K, Fe, Al and Mg ratios to Si across the 80 nm of the biotite below the interface with the hypha plotted for FIB-sections 1 to 3; ratios of section 4 are shown in Figure 2B in the main text.

**Figure S5:** Results from the biotite abiotic dissolution experiments in batch (at pH 2 – solid squares and pH 4 – open squares) and flow-through reactors (at pH 3.3 – different symbols are replicate experiments). Note that, in the flow-through experiments, the data plotted are the dissolution rate (in mol biotite.m<sup>-2</sup>.h<sup>-1</sup>) while, for the batch experiments, concentrations of Fe, Mg and Al over time are reported. The biotite dissolution rates in batch were derived from the linear regression of the concentration values between 1.5h and 12h. All abiotic dissolution rate values are listed in Table 1.

**Figure S6:** Schematic representation of the relationship between J (elemental flux) and time in a diffusive system (Crank, 1987). See the model description in section 4 (in particular, Eq. 8 to 11) for a discussion on the derivation on  $t_f$ .

**Figure S7:** K/Si, Fe/Si, Al/Si and Mg/Si intensity count ratios (STEM-EDX) in the bulk non altered biotite (average of datasets collected in the four FIB sections) and in the “altered biotite” layer for FIB sections 3 and 4 (average on 15 and 6 data points respectively).

## **List of acronyms used**

FIB: Focused Ion Beam

STEM-EDX: Scanning Transmission Electron Microscopy-Energy Dispersive X-ray spectroscopy

SAED: Selected Area Electron Diffraction

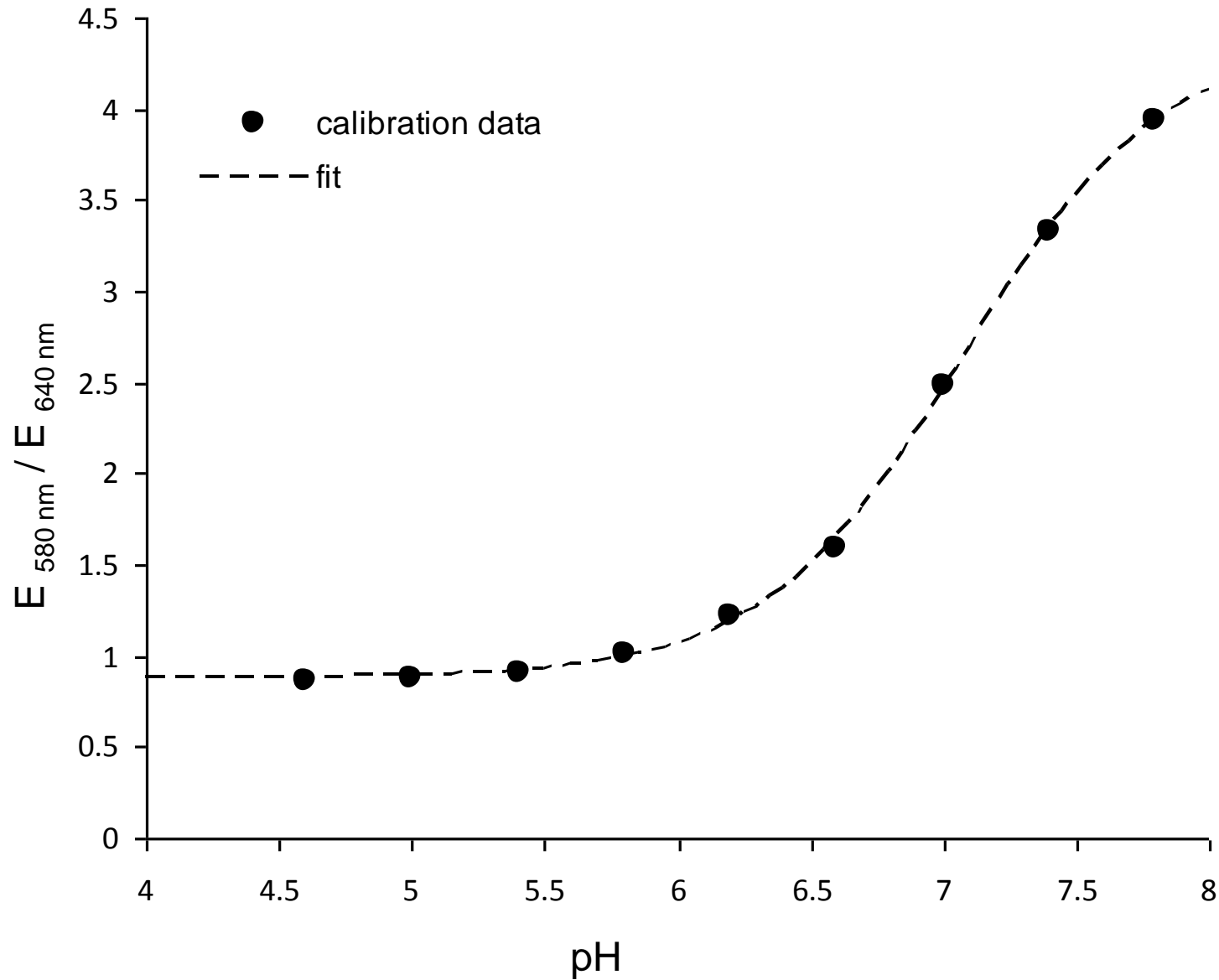
FEG-SEM: Field Emission Gun – Scanning Electron Microscopy

EMPA: Electron MicroProbe Analysis

HPLC: High-Performance Liquid Chromatography

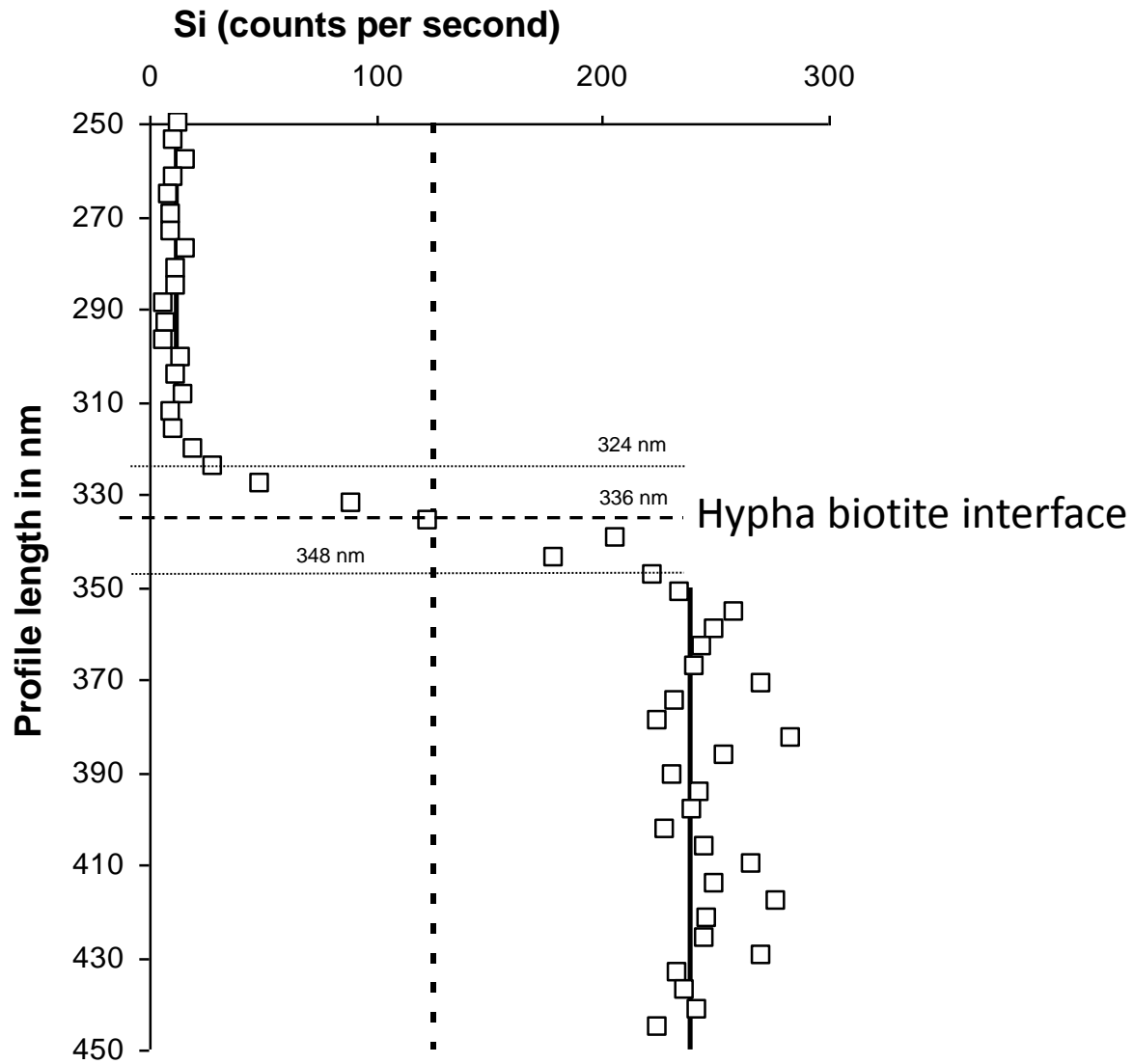
# Supplementary Information

## Figure S1



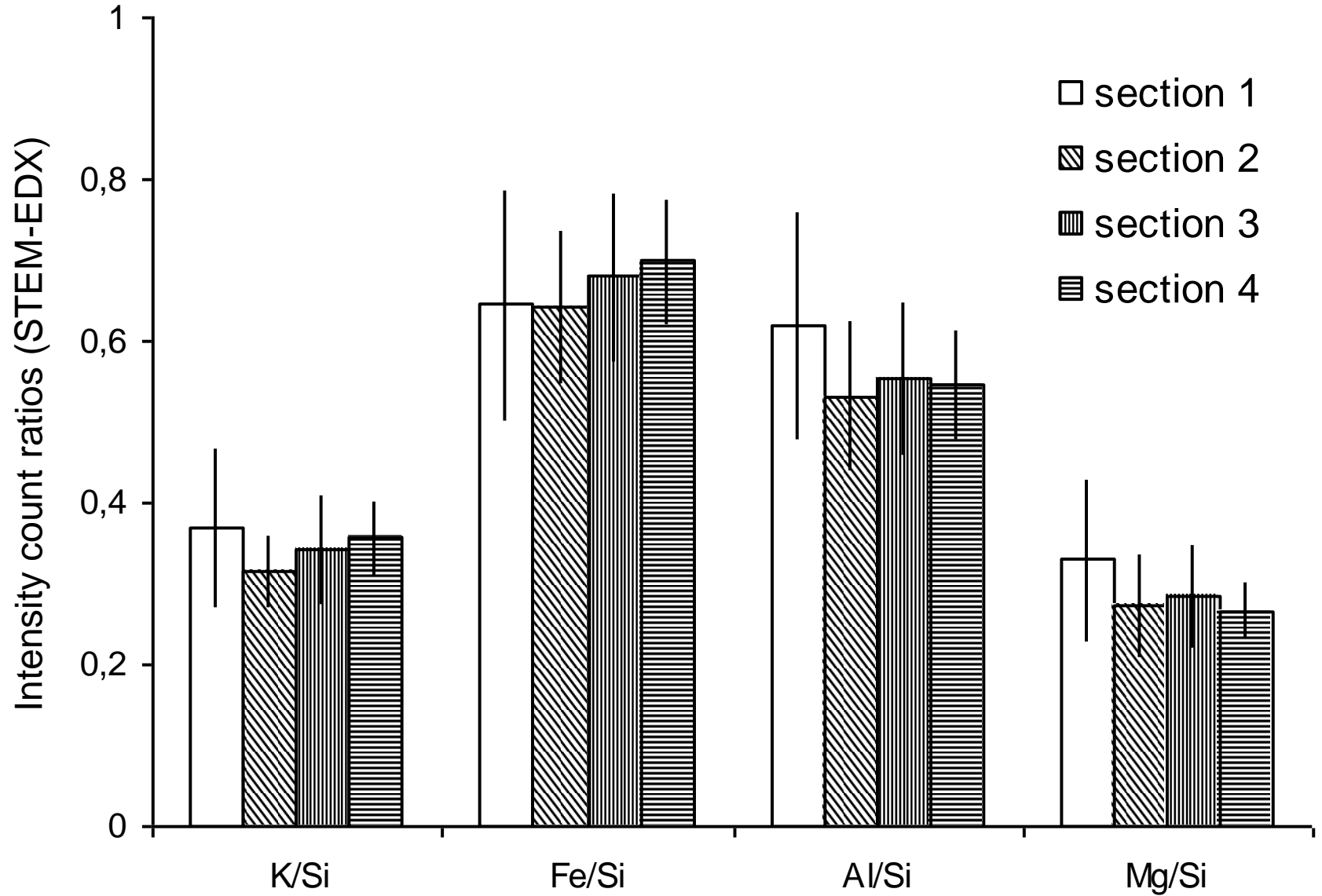
# Supplementary Information

## Figure S2



# Supplementary Information

## Figure S3



Normalized X/Si ratio

