ELECTRONIC ANNEXES CAPTIONS

Electronic annex 1. a) Mounting of suspended diatom opal on a polished and cleaned aluminum weighting dish (70 mm). b) Finished indium mount (central area of ~ 10 mm diameter and ~4 mm depth) after final repressing for ion probe analysis. c) Finished epoxy mount (10-21 mm diameter) ready for LA-ICPMS analysis.

Electronic annex 2. $^{11}B/^{30}Si$ ratios (black), ^{30}Si (blue) and ^{11}B (green) (cps) from four locations within the same epoxy-mounted sample (a, b, c and d) of *T. weissflogii* cultured at pH = 7.87, and from three locations within the same indium-mounted sample (e, f and g) of *T. pseudonana* cultured at pH = 8.28, analyzed via ion probe on February 2013 and May 2012, respectively. 10 cycle presputtering was conducted on epoxy-mounted samples and no data are therefore registered. $^{11}B/^{30}Si$ ratios from b), c), d), e) and g) were considered, since variation (% v) of the ratio stable region (> 15 cycles) was < 15%.

Electronic annex 3. Calibration curve for a) Ion Probe (May- 2012) using powdered NIST 610, NIST 612, and glass NIST 615 (equation: y = 11148x). $^{11}B/^{30}Si$ ratios for glass NIST 610 and 612 are also shown. b) LA-ICPMS (07/11/2011) using powdered NIST 612 and 614 standards (equation: y = 4024x). $^{11}B/^{29}Si$ ratios for glass NIST 612 and 614 are also shown.

Electronic annex 4. $^{11}B/^{29}Si$ ratios, ^{29}Si and ^{11}B counts from two tracks (a and b) analyzed via LA-ICPMS on 28/11/2011 of *T. weissflogii* cultured at pH = 7.87. Gray bars show time interval limits for median calculation where $^{11}B/^{29}Si$ ratios are stable, being longer in some tracks (a) than in others (b).

Electronic annex 5. Approach to reduce non-matrix matched standard effects in measured B concentrations as described by (Hill et al., 2012) showing the calculations performed to obtain homogenized B content from raw values measured via LA-ICPMS and ion probe. Data were

obtained during 9 different sessions (A-I). For each session, the mean B content from three samples common to other sessions (reference sample set -RSS-) was calculated. Subsequently, the B anomaly with respect to the mean B content within each session was calculated for each sample. A global mean for all sessions that have the same RSS was calculated by averaging over all individual session means. The homogenized B content was finally obtained for each measurement by the addition of the B anomaly to the global mean previously calculated.

Electronic annex 6. Raw (colored) and homogenized (circle-solid black) B concentrations in frustules from *T. pseudonana* (left panel) and *T. weissflogii* (right panel) obtained during the 9 different sessions of analysis (A-I) using LA-ICPMS (solid colored) and ion probe (open colored). Homogenization of data yielded to lower standard deviations in five out of seven samples for which standard deviations of raw B concentrations were higher than 0.9 ppm.

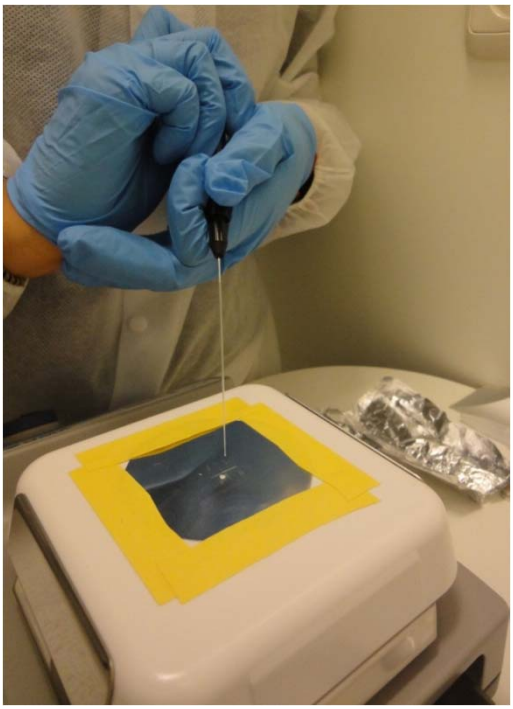
Electronic annex 7. Measured frustule B content (ppm) in *T. pseudonana* as a function of seawater pH from samples cultured at varying pH conditions via a) LA-ICPMS (pH = 7.50-8.63), and b) Ion probe (pH = 7.99-8.63). No growth rate (< 5% uncertainty) effect was observed with varying pH conditions, which is evidenced from the absence of a linear relationship between variables as shown in a) ($r = 0.384$; $p = 0.524$; $n = 5$). Similar B content of the sample *T. weissflogii* pH = 7.54, measured on the 20/03/2012, was observed during a subsequent session. Overlapping errors between measurements suggest that there is no offset in the B content of the *T. pseudonana* lowest pH sample measured as well on the 20/03/2012. Error bars represent the 2 standard analytical error of LA-ICPMS and ion probe determinations in each sample. An increasing trend of B content with pH is observed with both analytical methods (LA-ICPMS: $r = 0.756$; $p = 0.018$; $n = 9$; equation: $y = 7.020x - 48.324$ and ion probe: $r = 0.674$; $p = 0.097$; $n = 7$; equation: $y = 2.192x - 10.620$). Linear regressions are shown as dashed lines and were calculated including all measurements; continuous lines indicate 90% confidence intervals of each regression.

Electronic annex 8. Measured frustule B content (ppm) in *T. weissflogii* as a function of seawater pH from samples cultured at varying pH conditions (pH = 7.54-8.33) via a) LA-ICPMS and b) Ion probe. No growth rate (~10% uncertainty) effect was observed with varying pH conditions, which is evidenced from the absence of a linear relationship between variables as shown in a) ($r = -0.488$; $p = 0.404$; $n = 5$). Error bars represent the 2 standard analytical error of LA-ICPMS and ion probe determinations in each sample. An increasing trend of B content with pH is observed with both analytical methods (LA-ICPMS: $r = 0.806$; $p = 0.009$; $n = 9$; equation: $y = 4.168x – 26.209$ and ion probe: $r = 0.906$; $p = 0.094$; $n = 4$; equation: $y = 9.940 x - 71.443$). Linear regressions are shown as dashed lines and were calculated including all measurements; continuous lines indicate 90% confidence intervals of each regression.

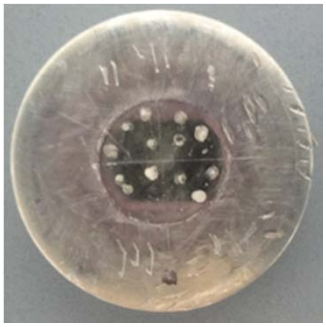
Electronic annex 9. Correlation of average B content with pH, photosynthesis HCO_3^- uptake, growth rate (μ), Si quotas (pg Si/cell), C quotas (pg C/cell) and Si/C ratios and significance levels (in parentheses), including only data from pH experiments and from fully-cleaned samples for *T. pseudonana* and *T. weissflogii* measured via LA-ICPMS (n = 5 except when indicated by *, where n = 4) and ion probe (n = 4 except when indicated by *, where n= 3). Bold characters reflect significant relationships ($p<0.1$).

Electronic annex 1

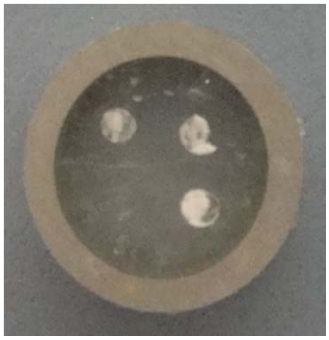
a)



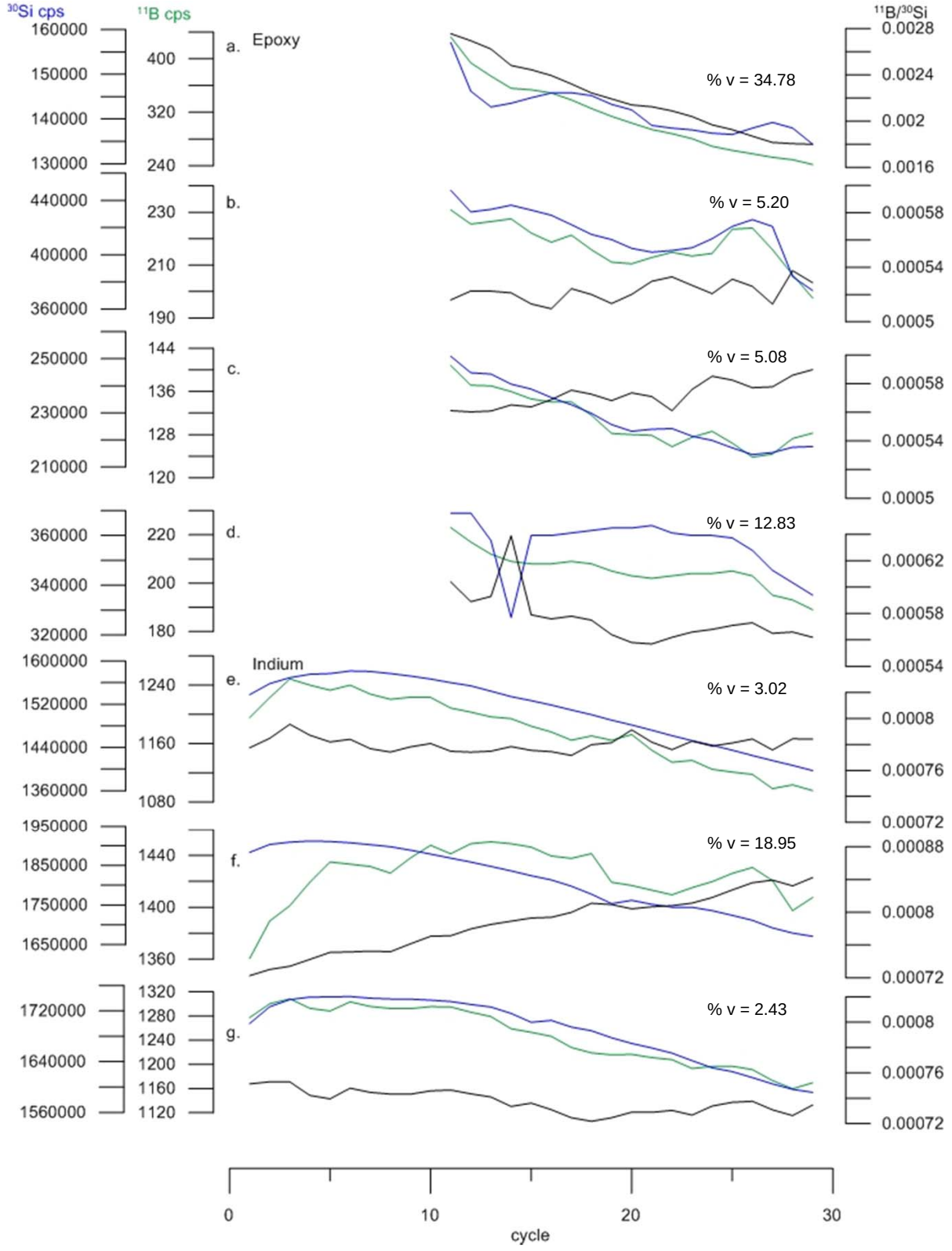
b)



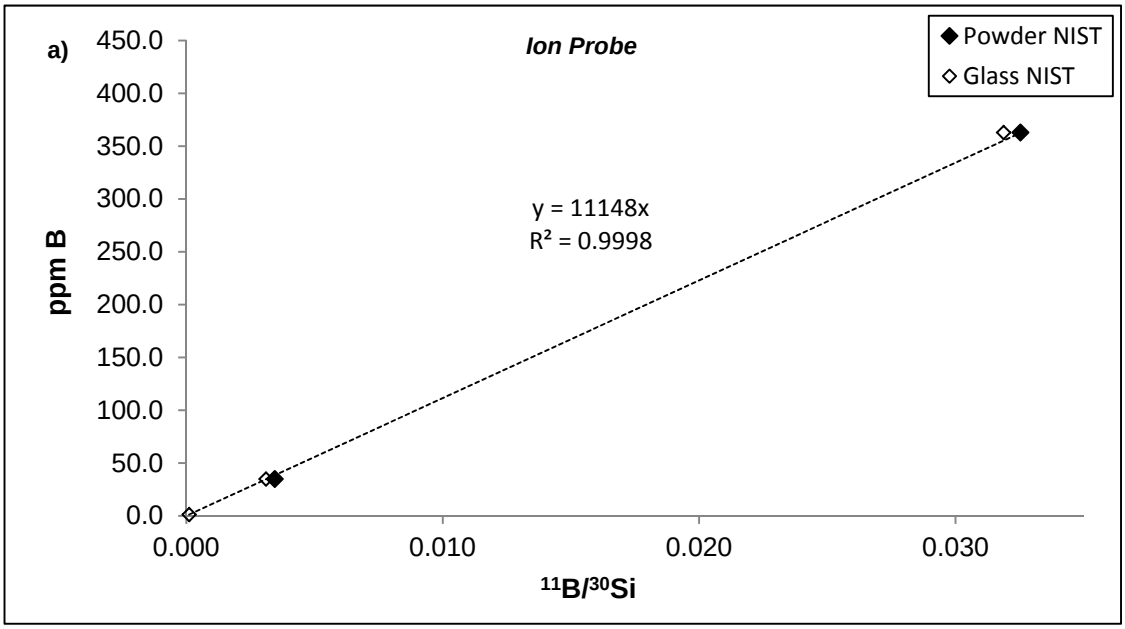
c)

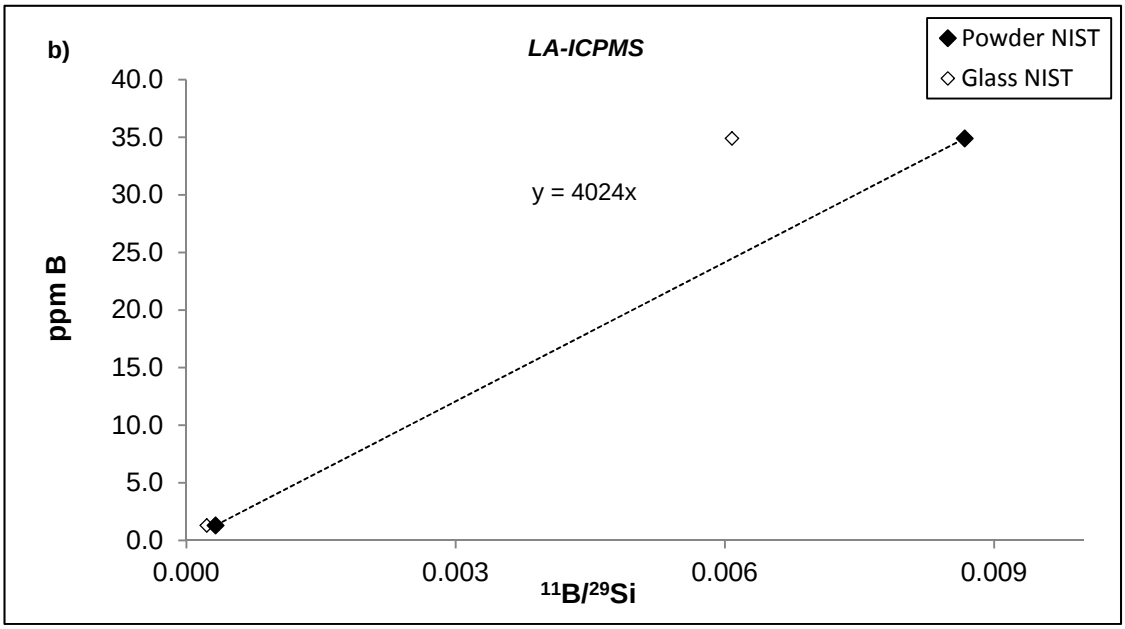


Electronic annex 2

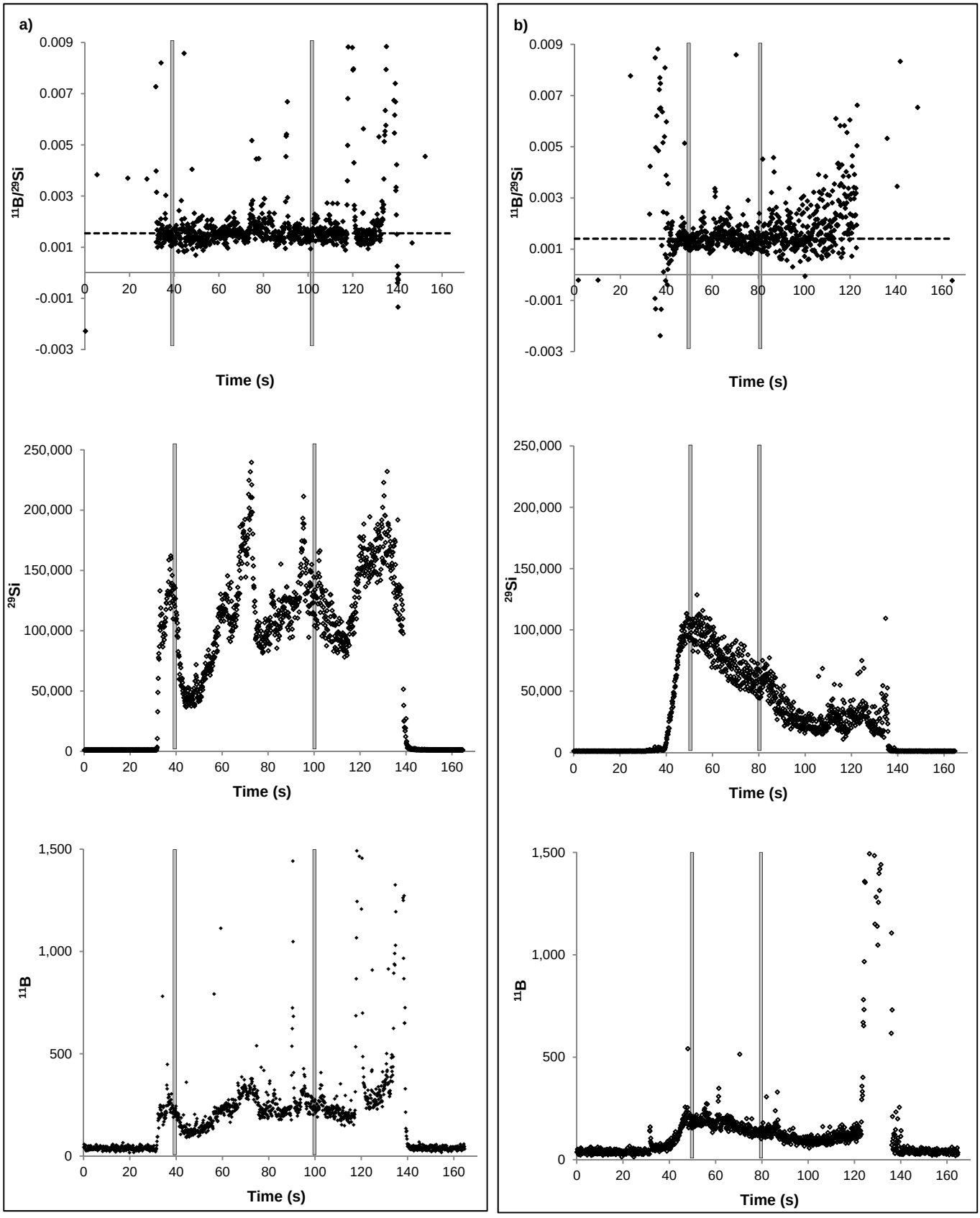


Electronic annex 3





Electronic annex 4



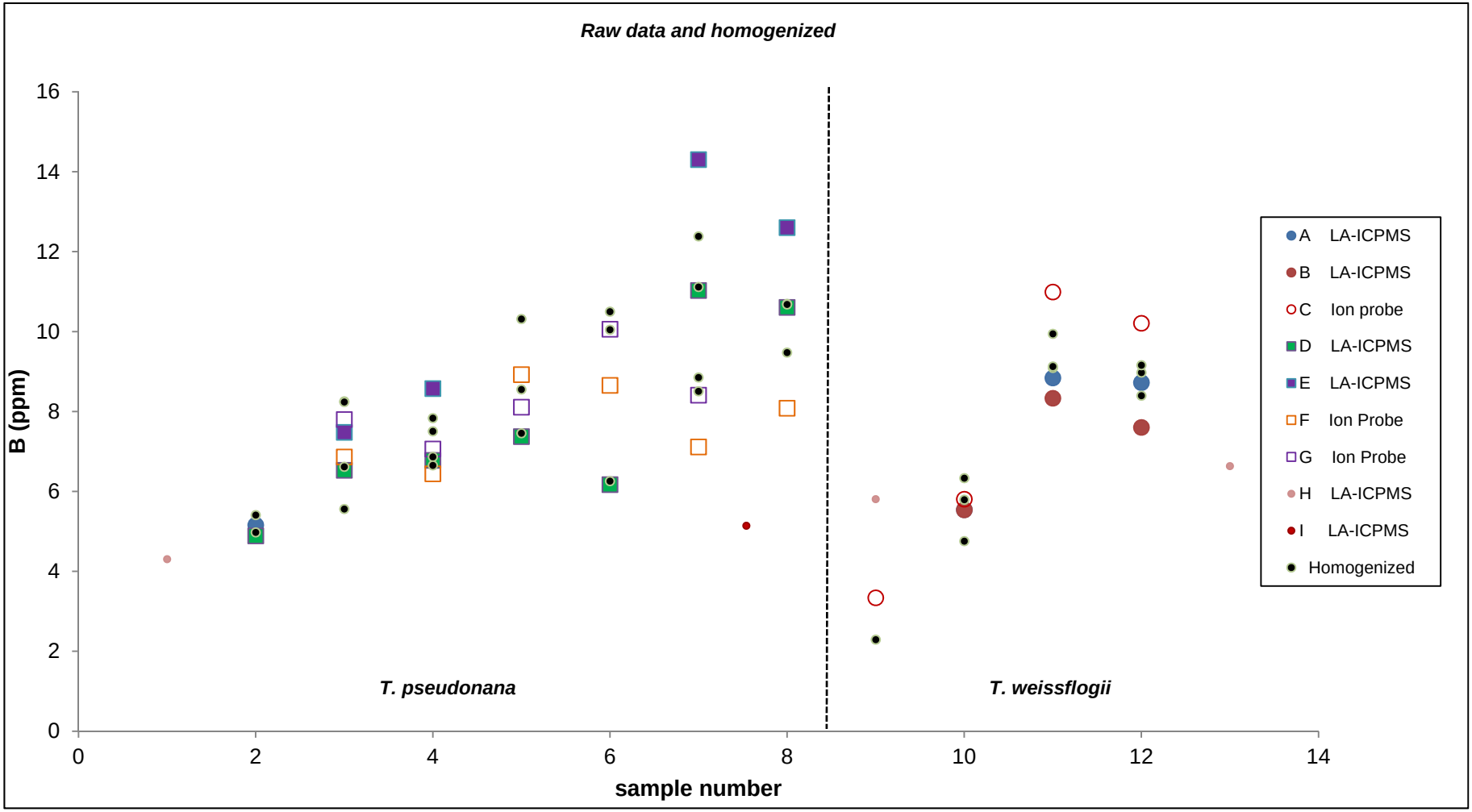
Electronic annex 5.

Sample	Session	Species	Analytical method	Date of analysis	pH	Raw B ppm	Sample for RSS	Session mean (ppm B)	B anomaly within session	Global mean sessions with same RSS (ppm B)	Homogenized B (ppm)
2	A	*T. pseudonana*	LA-ICPMS	27/10/2011	8.01	5.16	10,11,12	7.70	-2.54	7.95	5.41
10	A	*T. weissflogii*	LA-ICPMS	27/10/2011	7.87	5.54	10,11,12	7.70	-2.16	7.95	5.79
11	A	*T. weissflogii*	LA-ICPMS	27/10/2011	8.07	8.84	10,11,12	7.70	1.14	7.95	9.09
12	A	*T. weissflogii*	LA-ICPMS	27/10/2011	8.33	8.72	10,11,12	7.70	1.02	7.95	8.98
10	B	*T. weissflogii*	LA-ICPMS	28/11/2011	7.87	5.54	10,11,12	7.16	-1.62	7.95	6.34
11	B	*T. weissflogii*	LA-ICPMS	28/11/2011	8.07	8.33	10,11,12	7.16	1.17	7.95	9.13
12	B	*T. weissflogii*	LA-ICPMS	28/11/2011	8.33	7.60	10,11,12	7.16	0.45	7.95	8.40
9	C	*T. weissflogii*	Ion probe	Feb 2013	7.54	3.34	10,11,12	9.00	-5.66	7.95	2.29
10	C	*T. weissflogii*	Ion probe	Feb 2013	7.87	5.81	10,11,12	9.00	-3.20	7.95	4.76
11	C	*T. weissflogii*	Ion probe	Feb 2013	8.07	10.99	10,11,12	9.00	1.99	7.95	9.94
12	C	*T. weissflogii*	Ion probe	Feb 2013	8.33	10.21	10,11,12	9.00	1.21	7.95	9.16
2	D	*T. pseudonana*	LA-ICPMS	28/10/2011	8.01	4.89	3,4,7	8.11	-3.22	8.20	4.98
3	D	*T. pseudonana*	LA-ICPMS	28/10/2011	8.18	6.53	3,4,7	8.11	-1.58	8.20	6.62
4	D	*T. pseudonana*	LA-ICPMS	28/10/2011	7.99	6.78	3,4,7	8.11	-1.33	8.20	6.87
5	D	*T. pseudonana*	LA-ICPMS	28/10/2011	8.17	7.37	3,4,7	8.11	-0.74	8.20	7.46
6	D	*T. pseudonana*	LA-ICPMS	28/10/2011	8.03	6.17	3,4,7	8.11	-1.94	8.20	6.26
7	D	*T. pseudonana*	LA-ICPMS	28/10/2011	8.28	11.03	3,4,7	8.11	2.92	8.20	11.12
8	D	*T. pseudonana*	LA-ICPMS	28/10/2011	8.63	10.61	3,4,7	8.11	2.49	8.20	10.69
3	E	*T. pseudonana*	LA-ICPMS	07/11/2011	8.18	7.48	3,4,7	10.12	-2.64	8.20	5.56
4	E	*T. pseudonana*	LA-ICPMS	07/11/2011	7.99	8.58	3,4,7	10.12	-1.55	8.20	6.66
7	E	*T. pseudonana*	LA-ICPMS	07/11/2011	8.28	14.31	3,4,7	10.12	4.18	8.20	12.39
8	E	*T. pseudonana*	LA-ICPMS	07/11/2011	8.63	12.60	3,4,7	10.12	2.48	8.20	10.68

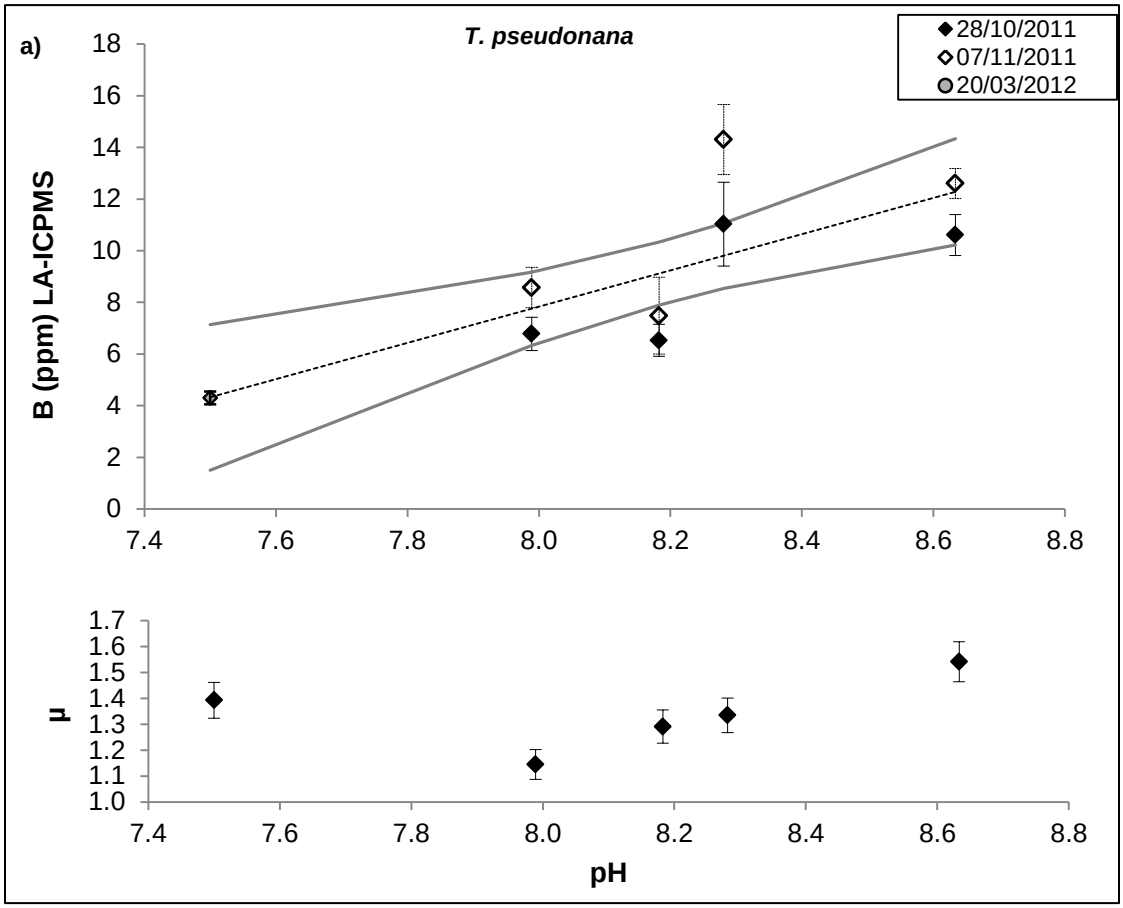
Continuation Electronic annex 5.

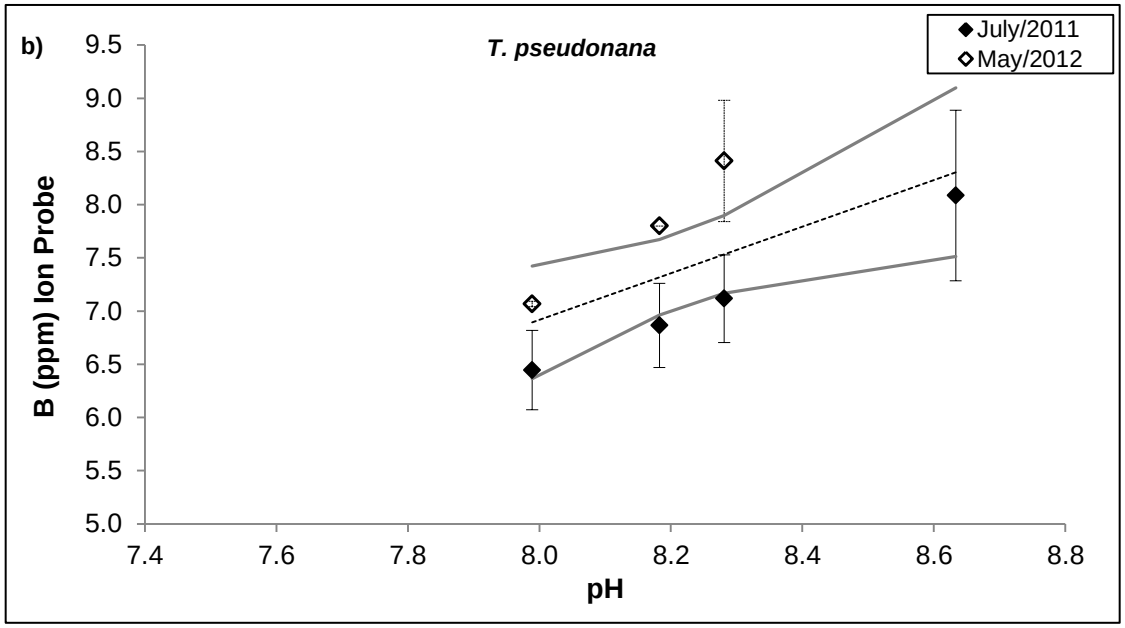
Sample	Session	Species	Analytical method	Date of analysis	pH	Raw B ppm	Sample for RSS	Session mean (ppm B)	B anomaly within session	Global mean sessions with same RSS (ppm B)	Homogenized B (ppm)
3	F	*T. pseudonana*	Ion probe	July 2011	8.18	6.87	3,4,7	6.81	0.06	8.20	8.26
4	F	*T. pseudonana*	Ion probe	July 2011	7.99	6.44	3,4,7	6.81	-0.36	8.20	7.84
5	F	*T. pseudonana*	Ion probe	July 2011	8.17	8.93	3,4,7	6.81	2.12	8.20	10.32
6	F	*T. pseudonana*	Ion probe	July 2011	8.03	8.66	3,4,7	6.81	1.85	8.20	10.05
7	F	*T. pseudonana*	Ion probe	July 2011	8.28	7.12	3,4,7	6.81	0.31	8.20	8.51
8	F	*T. pseudonana*	Ion probe	July 2011	8.63	8.09	3,4,7	6.81	1.28	8.20	9.48
3	G	*T. pseudonana*	Ion probe	May 2012	8.18	7.80	3,4,7	7.76	0.04	8.20	8.24
4	G	*T. pseudonana*	Ion probe	May 2012	7.99	7.07	3,4,7	7.76	-0.69	8.20	7.51
5	G	*T. pseudonana*	Ion probe	May 2012	8.17	8.11	3,4,7	7.76	0.35	8.20	8.55
6	G	*T. pseudonana*	Ion probe	May 2012	8.03	10.06	3,4,7	7.76	2.30	8.20	10.50
7	G	*T. pseudonana*	Ion probe	May 2012	8.28	8.41	3,4,7	7.76	0.65	8.20	8.85
1	H	*T. pseudonana*	LA-ICPMS	20/03/2012	7.50	4.31					
9	H	*T. weissflogii*	LA-ICPMS	20/03/2012	7.54	5.81					
13	H	*T. weissflogii*	LA-ICPMS	20/03/2012	7.90	6.63					
9	I	*T. weissflogii*	LA-ICPMS	29/06/2012	7.54	5.14					

Electronic annex 6

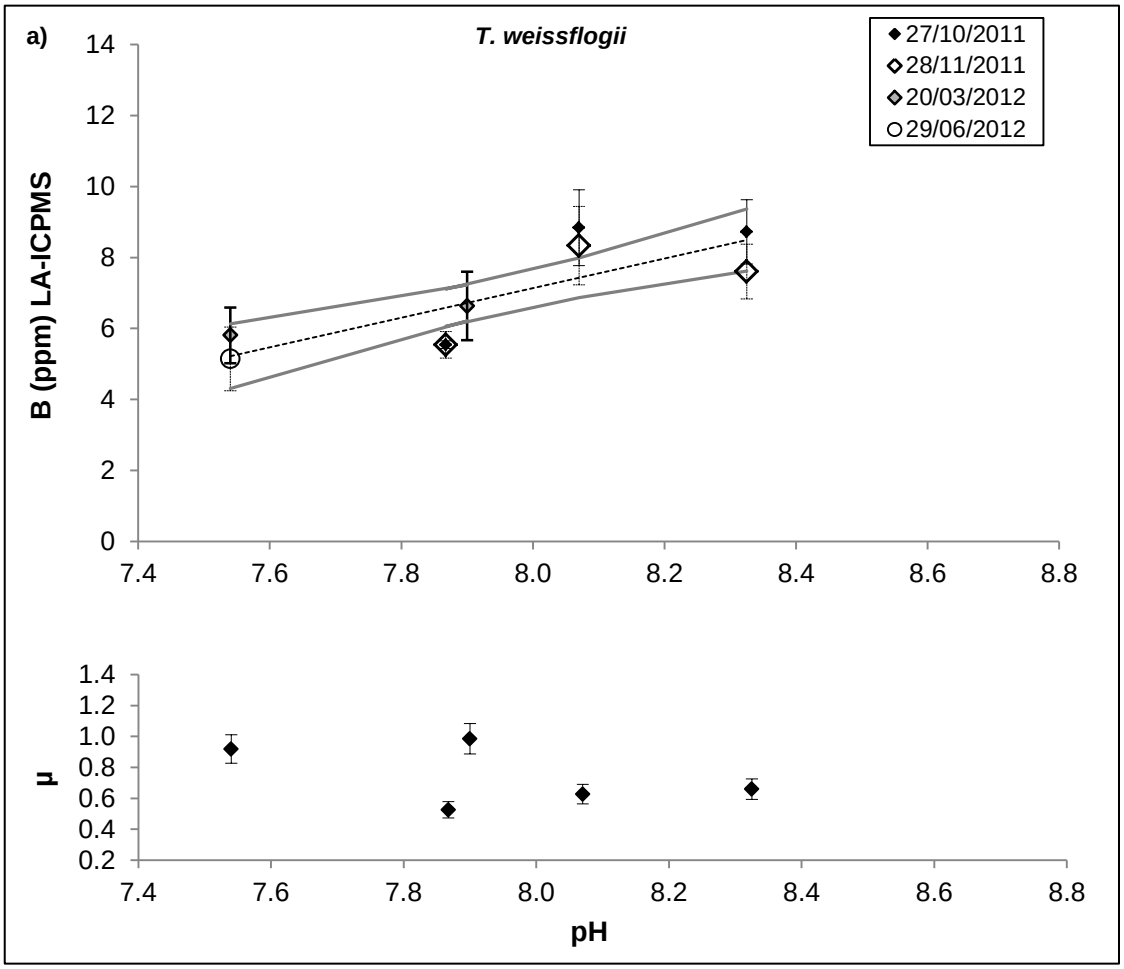


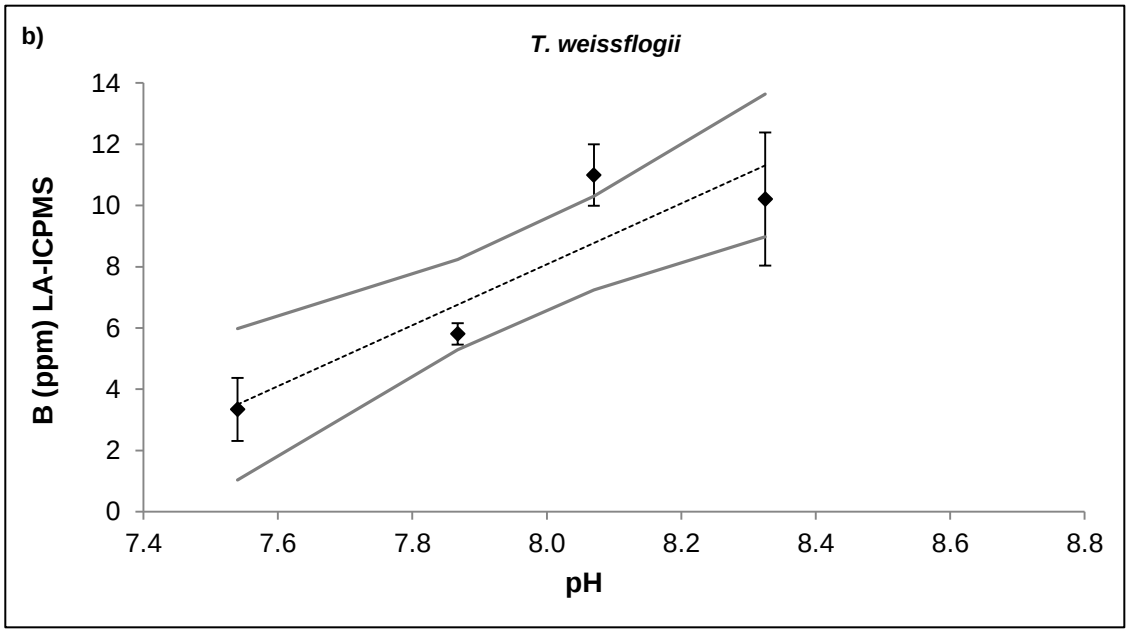
Electronic annex 7





Electronic annex 8





Electronic annex 9.

	T. pseudonana LA-ICPMS	*T. pseudonana* Ion Probe	*T. weissflogii* LA-ICPMS	*T. weissflogii* Ion Probe
	B (ppm)	**B (ppm)**	**B (ppm)**	**B (ppm)**
pH	**0.851 (0.068)**	**0.943 (0.057)**	**0.830 (0.082)**	**0.906 (0.094)**
f (HCO_3^-) (%)	-	-	0.249 (0.751)*	-0.374 (0.756)*
μ	0.309 (0.612)	**0.952 (0.048)**	-0.280 (0.648)	-0.534 (0.466)
pg Si/cell	-0.271 (0.659)	**-0.977 (0.023)**	0.403 (0.502)	0.719 (0.281)
pg C/cell	**-0.829 (0.083)**	**-0.949 (0.051)**	-0.651 (0.234)	**-0.985 (0.015)**
Si/C	0.626 (0.259)	-0.214 (0.786)	0.718 (0.172)	0.897 (0.103)