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Supplement of

Boron incorporation in the foraminifer *Amphistegina lessonii* under a decoupled carbonate chemistry

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MATERIAL AND METHODS

1.1 Determination of the B isotopic composition of the culture media

A detailed description of the method used for the analysis of the $\delta^{11}B$ of the culture media is given in Misra et al. (2014). All samples and standards were analyzed in 0.3M HF matrix to facilitate rapid boron wash out. We used Savillex® self-aspirating C-flow nebulizers with sample uptake rate of 50μl/min for sample aspiration. High performance extraction cones (Jet sampler and 'X' skimmer) were used to boost boron sensitivity. The instrumental plasma conditions and mass calibration were appropriately adjusted to eliminate any artificial mass bias caused by $^{20}Ne^{2+}$ and $^{40}Ar^{4+}$ peak tailing into the $^{10}B^+$ peak. Before each analytical session the instrument was optimized for maximum boron sensitivity (1 M-cps / ppb on ^{11}B) and samples were analyzed at a signal to blank intensity ratio of > 500. An optimal analyses time of ~12 minutes per sample was adopted to obtain ≥ 2500 $^{11}B/^{10}B$ ratios to achieve the desired external precision of $\leq 0.5‰$ per quintuplicate analysis ($2\sigma/\sqrt{n}$). Based on sample aspiration rate and analysis time at total of ~3 ng B was consumed per analysis. Instrumental settings are given in table S2.

Prior to mass spectrometric analysis boron was separated from the sample matrix by a single-step micro-distillation method, modified after (Gaillardet et al., 2001) and (Wang et al., 2010) as described in Misra et al. (2014). Savillex® Teflon® fin legged 5 ml beakers with conical interior were used as the distillation reservoir. Samples were loaded on to the cap of a pre-cleaned beaker – the beaker was tightly closed to avoid boron loss – set on a hotplate at 95ºC with the conical end pointing up. The distillation process was carried out for 15 to 18 hours to achieve a quantitative distillation of boron from the load into the distillate. Sample load volume was kept below 50 μl to avoid the accumulated droplet at the conical end from dropping back onto the cap. Post distillation, beakers were taken off the hotplate, allowed to cool for ~ 15 minutes, then 0.5 ml of 0.3 M HF was added and the beakers were capped with pre-cleaned caps.

1.2 Boron analysis of the tests

Detailed information about the simultaneous determination of B/Ca and $\delta^{11}B$ of foraminifer using LA-MC-ICP-MS and OES are given in Kaczmarek et al. (accepted).

1.2.1 Laser Ablation

The in-house built laser ablation system (Solstice Newport/Spectra Physics) is based on a 100 femtosecond Ti-sapphire regenerative amplifier system operating at a fundamental wavelength of 777 nm in the infrared spectrum. Subsequent harmonic generations produce the wavelengths 389 nm in the second, 259 nm in the third and 194 nm in the fourth harmonic. The pulse energies measured with a pyroelectric sensor (Molectron, USA) are 3.2mJ/pulse at 777nm, 0.7 mJ/pulse at 259 nm, and 0.085 mJ/pulse at 194 nm. After the fourth harmonic generation stage the 194 nm beam is streered by eight dichronic mirrors into a 8x objective (NewWave-Research, USA) and focussed onto the sample. Spot size was set to 50 µm for standard and samples. Within this spot an energy density of 2 J/cm^2 is maintained.

Table S3 shows different laser efficiencies applied to foraminifers and NISTSRM 610 from different treatments. Laser ablation on NISTSRM 610 was performed in raster mode setting a ~ 150 x150µm raster with a spot size of 50 µm. For foraminifers the raster mode was applied, too. However, the size of the raster varied dependent upon the individual size of each foraminifer. Laser ablation of foraminifers was always performed on the so-called knob, a massive calcite without pores, located in the middle on the spiral side of the foraminifer. Figure S1 shows an example of a foraminifer from the pH_8.1[160] treatment after laser ablation.

1.2.2 Isotope Analysis - Acquisition parameters

All measurements were carried out in low mass resolution ($\Delta m/m = 350$ where m is the mass of the ion of interest and Δm is the mass difference between its 5 and 95% peak height). Compact discrete dynode multipliers (CDD, Thermo) were attached to faraday cups at the low site on L4 and the high site on H4. The low resolution mode is sufficient enough to resolve potential interferences from doubly charged ions due to the intrinsic high resolution in the low mass region. Possible

54 interferences are the clusters of $^{40}Ar^{4+}$ or $^{20}Ne^{2+}$ which are well resolved to the background level.

55 Working with ion counters it is necessary to determine the detector dead time especially for isotope

56 ratios with large isotope abundance differences. The dead time corrections have been performed by

57 measuring the $^{238}U/^{235}U$ ratio using SRM 981 in a multidynamic measuring sequence. Subsequently,

58 the dead time has been checked prior to every analytical session by analysing NISTSRM 610 using

59 different repetition rates of laser, resulting in a counting range between 300000 – 1000000 cps. Prior

60 to each analytical session the instrument was tuned for optimal peak shape. All measurements were

61 performed at plateau voltage of the CDDs which was checked prior to every analytical session. Before

62 the beginning of samples analysis measurements of NISTSRM 610 were continued until instrumental

63 drift due to warm-up was less than 300 ppm over a bracketing sequence duration of twelve minutes.

64 Boron signal intensities of the reference material, NISTSRM 610, and samples were matched within

65 10% in signal intensity by adapting the laser repetition rate. For analysis we adopt the standard sample

66 bracketing procedure using NISTSRM 610 as reference material containing 351 ppm B and 8.45 %

67 Ca. The acquisition parameters in static mode for analysis of NISTSRM 610 and samples were set to

68 acquire 200 cycles of 1 s integrations each. During the first 40 cycles the background signal was

69 acquired whereas the remaining cycles represent the sum of the background + reference material, or

70 background + sample signals. The B isotopic composition is reported using the delta notation:

71
$$\delta^{11}B_{sample}(‰) = \left[\frac{\left(^{11/10}B\right)_{sample}}{\left(^{11/10}B\right)_{NIST610}} - 1\right] \times 1000 \qquad (S2)$$

72 The $^{11/10}B$ ratio of NIST 610 represents a mean value calculated from the NIST 610 measurements

73 performed before and after the sample. The errors of $\delta^{11}B$ of the foraminifers were calculated by

74 propagating the $SE/^{11/10}B$ for NIST610 and samples respectively according to the standard bracketing:

$$2RSE_{\delta^{11}B}(‰) = \sqrt{\left(\frac{SE}{^{11/10}B}\right)^2_{NIST-1} + \left(\frac{SE}{^{11/10}B}\right)^2_{sample} + \left(\frac{SE}{^{11/10}B}\right)^2_{NIST+1}} \times 1000 \times 2 \qquad (S3)$$

75 Where NIST-1 and NIST+1 refer to NIST610 measurements performed before and after the sample. It

76 should be noted that the 2RSE of foraminifers represents a criterion for the homogeneity of B isotope

77 distribution rather than an analytical uncertainty. The analytical uncertainty and external

78 reproducibility is given best by repeated measurements of a homogenous material such as NIST 610.

79 Delta [11]B values of NIST 610 were calculated by:

80
$$\delta^{11}B \quad (\text{\textperthousand}) = \left[\frac{^{11/10}B_0}{\left(^{11/10}B_{-1} + {}^{11/10}B_{+1} \right)/2} - 1 \right] \times 1000 \qquad \text{(S4)}$$

81 Where the measurements of the $(^{11/10}B)_{-1}$ and $(^{11/10}B)_{+1}$ ratios of NIST 610 were performed before and

82 after the measurement of $(^{11/10}B)_0$, respectively. For the determination of the analytical uncertainty and

83 external reproducibility all measurements of NIST 610 performed between each sample measurement

84 in this study were taken into account and are on average 0.4 ± 0.5 (2sd) ‰.

85 As shown by Fietzke et al. (2010) no matrix dependent offsets between silicate and carbonate

86 matrices exist suggesting that silicate glass standards, as NIST 610, may serve as adequate reference

87 material. Therefore, we consider the analytical uncertainty of NIST 610 as an adequate external error

88 of the foraminiferal samples. Operating conditions for La-MC-ICP-MC are given in table S4.

89 *1.2.2 Determination of B/Ca of the test by Optical Emission Analysis*

90 Ocean Optics Maya2000 Pro is a high-sensitivity fiber optical spectrometer. It exhibits a

91 measuring range of 250 to 460 nm with a resolution of 0.11 nm covering the first order emission lines

92 of Mg II, Ca II, Sr II Ba II and Li II. It is equipped with a back-thinned 2D FFT-CCD detector, and a

93 grating with a groove density of 1200 lines/mm. More technical information about Maya2000 Pro can

94 be found on http://www.oceanoptics.com/products/maya.asp. The optical fiber used is two meters long

95 (attenuation of the photon flux is length dependent) connecting the spectrometer with the coupling lens

96 at the end of the plasma torch of the MC-ICP-MS. Ca II ion lines were measured at a wavelength of

97 393.48 nm and 396.86. At these wavelengths the Ca spectra shows no detectable interferences for the

98 matrices used. The acquisition parameters were set to acquire 220 cycles per analysis with an

99 integration time of 1 s for each cycle. Because of the stable BG signal detected for the first 40 cycles

100 BG correction was done by subtracting its intensity from the intensity of the reference material and

101 samples. For the determination of the relative error of the B concentration and B/Ca we considered the

102 B and Ca concentrations of SRMNIST 610 and their uncertainties known from literature (lit) and the

103   intensities of B and Ca and their uncertainties measured (m) in this study with respect to SRMNIST

104   610 and the samples where B cps were normalized to Ca cps:

105

$$RSD\ (\%) = \sqrt{\begin{array}{c}\left(\frac{SD\ B\ conc_{NIST}}{B\ conc_{NIST}}\right)^2_{lit} + \left(\frac{SD\ Ca\ conc_{NIST}}{Ca\ conc_{NIST}}\right)^2_{lit} + \left(\frac{SD\ B\ cps_{NIST}}{B\ cps_{NIST}}\right)^2_{m} + \left(\frac{SD\ Ca\ cps_{NIST}}{Ca\ cps_{NIST}}\right)^2_{m} + \\ \left(\frac{SD\ B\ cps_{sample}}{B\ cps_{sample}}\right)^2_{m} + \left(\frac{SD\ Ca\ cps_{sample}}{Ca\ cps_{sample}}\right)^2_{m}\end{array}} \times 100 \qquad (S5)$$

106   Based on all measurements of NIST 610 performed in this study the precision for the B

107   concentration (and subsequently B/Ca) was 3 %. Measuring the B concentration of NIST 612

108   (calibrated against NIST 610) yielded 35 ± 1 ppm which is in excellent agreement with the value

109   reported in literature (34 – 39 ppm, (Tiepolo et al., 2005; Jacob et al., 2006; Hu et al., 2009; Liu et al.,

110   2008; Deschamps et al., 2010; Lazarov et al., 2012)).

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REFERENCES

Catanzaro, E.J., Champion, C.E., Garner, E.L., Marinenko, G., Sappenfield, K.M., Shields, W.R., 1970. Boric Acid. Isotopic, and Assay Standard Reference Materials Nat. Bur. Stand. (U.S.) Spec. Publ. 260-17, 70.

Deschamps, F., Guillot, S., Godard, M., Chauvel, C., Andreani, M., Hattori, K., 2010. In situ characterization of serpentinites from forearc wedges: Timing of serpentinization and behavior of fluid-mobile elemnts in subduction zones. Chemical Geology 269, 262-277.

Gaillardet, J., Lemarchand, D., Gopel, C., Manhes, G., 2001. Evaporation and sublimation of boric acid: Application for boron purification from organic rich solutions. Geostandards Newsletter 25, 67-75.

Fietzke, J., Heinemann, A., Taubner, I., Bohm, F., Erez, J., Eisenhauer, A., 2010. Boron isotope ratio determination in carbonates via LA-MC-ICP-MS using soda-lime glass standards as reference material. Journal of Analytical Atomic Specztometry 25, 1953-1957.

Hu, Z., Liu, Y., Li, M., Gao, S., Zhao, L., 2009. Results for rerely determined elements in MPI-DING, USGS and NIST SRM glasses using laser ablation ICP-MS. Geostandards and Geoanalytical Research 33, 319 -335.

Jacob, D.E.,2006. High sensitivity analysis of trace element poor geological reference glasses by laser ablation-inductively coupled plasma-mass spectrometry. Geostandards and Geoanalytical Research 30, 221-235.

Kaczmarek, K., Horn, I., Nehrke, G., Bijma, J. Simultaneous determination of $\delta^{11}B$ and B/Ca in marine biogenic carbonates at nano gram level. Chemical Geology, accepted.

Lazarov, M., Brey, G.P., Weyer, S., 2012. Evolution of the South African mantle- A case study of garnet peridotites from the Finsch diamond mine (Kaapvaal craton); part1: Inter-mineral trace element and isotopic equilibrium. Lithos 154, 193-209.

Liu, Y., Hu, Z., Gao, S., Günther, D., Gao, C., Chen, H., 2008. *In situ* analysis of major and trace elements of anhydrous minerals by LA-ICP-MS without applying an internal standard. Chemical Geology 257, 34-43.

Longerich, H.P., Jackson, S.E., Gunther, D., 1996. Inter-laboratory note. Laser ablation inductively coupled plasma mass spectrometric transient signal data acquisition and analyte concentration calculation. Journal of Analytical Atomic Spectrometry 11, 899-904.

Misra, S., Owen, R., Kerr, J., Greaves, M., Elderfield, H., 2014. Determination of $\delta^{11}B$ by HR-ICP-MS from Mass Limited Samples: Application to Natural Carbonates and Water Samples. Geochimica et Cosmochimica Acta 140, 531-552.

Tiepolo, M., Zannetti, A., Vannucci, R.2005. Determination of lithium, beryllium, and boron at trace levels by laser ablation-inductively coupled plasma-sector field mass spectrometry. Geostandards and Geoanalytical Research 29, 211-224.

Wang, B.-S., You, C.-F., Huang, K.-F., Wu, S.-F., Aggarwal, S.K., Chung, C.-H., Lin, P.-Y., 2010. Direct separation of boron from Na- and Ca-rich matrices by sublimation for stable isotope measurement by MC-ICP-MS. Talanta 82, 1378-1384.

TABLES

Table S1

Composition of the culture media. Shown are the calculated carbonate systems using different pairs of input parameters. m - measured, cal - calculated. For information about errors on measured parameters see paper text section 2.3.

Input pH and DIC	pH_m total	DIC_m µmol/kg	TA_m µmol/kg	TA_{cal} µmol/kg	$CO_3^{2-}{}_{cal}$ µmol/kg	$HCO_3^-{}_{cal}$ µmol/kg	$B(OH)_4^-{}_{cal}$ [a] µmol/kg	$pCO_2{}_{cal}$ µatm	B_m µmol/kg	Ca_m µmol/kg	$δ^{11}B_m$ ‰	$δ^{11}B\ B(OH)_4^-{}_{cal}$ ‰
pH_8.1[160]	8.115	1257	2501	2456	155	1096	1062	213	4233	8503	-9.22	-29.01
pH_8.1[260]	8.111	2093	3232	3387	257	1826	1016	356	4063	9638	-9.00	-28.81
pH_8.1[540]	8.142	4128	5626	5748	538	3573	1098	652	4177	9692	-8.88	-28.37
pH_8.1[640]	8.109	5736	7392	7295	643	5064	1053	1006	4240	9360	-8.73	-28.59
pH_8.6[640]	8.560	2261	5387	4925	638	1620	1904	113	3944	9688	-9.00	-22.75
pH_7.9[260]	7.858	3890	4691	4789	280	3576	647	1254	4136	9580	-9.11	-31.34

Input pH and TA	pH_m total	TA_m µmol/kg	DIC_m µmol/kg	DIC_{cal} µmol/kg	$CO_3^{2-}{}_{cal}$ µmol/kg	$HCO_3^-{}_{cal}$ µmol/kg	$B(OH)_4^-{}_{cal}$ [a] µmol/kg	$pCO_2{}_{cal}$ µatm	B_m µmol/kg	Ca_m µmol/kg	$δ^{11}B_m$ ‰	$δ^{11}B\ B(OH)_4^-{}_{cal}$ ‰
pH_8.1[160]	8.115	2501	1257	1297	160	1131	1062	220	4233	8503	-9.22	-29.01
pH_8.1[260]	8.111	3232	2093	1955	240	1706	1016	333	4063	9638	-9.00	-28.81
pH_8.1[540]	8.142	5626	4128	4020	524	3479	1098	635	4177	9692	-8.88	-28.37
pH_8.1[640]	8.109	7392	5736	5669	691	4952	1037	975	4240	9360	-8.73	-28.69
pH_8.6[640]	8.560	5387	2261	2348	663	1682	1904	117	3944	9688	-9.00	-22.75
pH_7.9[260]	7.858	4691	3890	3798	273	3491	647	1225	4136	9580	-9.11	-31.34

Input DIC and TA	pH_m total	pH_{cal} total	DIC_m µmol/kg	TA_m µmol/kg	$CO_3^{2-}{}_{cal}$ µmol/kg	$HCO_3^-{}_{cal}$ µmol/kg	$B(OH)_4^-{}_{cal}$ [a] µmol/kg	$pCO_2{}_{cal}$ µatm	B_m µmol/kg	Ca_m µmol/kg	$δ^{11}B_m$ ‰	$δ^{11}B\ B(OH)_4^-{}_{cal}$ ‰
pH_8.1[160]	8.115	8.136	1257	2501	162	1090	1100	202	4233	8503	-9.22	-28.77
pH_8.1[260]	8.111	8.045	2093	3232	223	1858	901	424	4063	9638	-9.00	-29.54
pH_8.1[540]	8.142	8.100	4128	5626	494	3614	1022	725	4177	9692	-8.88	-28.83
pH_8.1[640]	8.109	8.086	5736	7392	667	5040	1012	1045	4240	9360	-8.73	-28.84
pH_8.6[640]	8.560	8.689	2261	5387	783	1476	2195	76	3944	9688	-9.00	-20.81
pH_7.9[260]	7.858	7.806	3890	4691	250	3601	714	1424	4136	9580	-9.11	-30.92

[a] Calculation of $B(OH)_4^-$ was performed using a pK_B of 8.59 corrected for S and T according to Dickson 1990.

Table S2

ICP-MS settings for B isotopes determination of culture media and standards.

Parameter	Isotope mode
Plasma RF Power	1250 W
Nebulizer	Savillex[TM]-50 µl (C-flow)
Spray Chamber	Teflon Scott type (single pass)
Injector	ESI[TM] Platinum (1.8 mm I.D)
Sample Cone	Ni - JET
Skimmer Cone	Ni- X
Extraction Voltage	-2000 V
Sample Matrix	0.3 M HF
Uptake time	60 s
Analysis time	210 s
Washout time	150 s
Mass Resolution	Low
Magner Mass	10.012 (fixed)
^{10}B Mass Range	10.012 - 10.013
^{11}B Mass Range	11.008 - 11.009
Samples per peak	200 (^{10}B and ^{11}B)
Runs	225
Passes	10
Detection mode	Analog

Table S3

Laser efficiencies applied to NISTSRM 610 and foraminifers.

treatment	pH_8.1[160]	pH_8.1[260]	pH_8.1[540]	pH_8.1[640]	pH_8.6[640]	pH_7.9[260]
Laser efficiency (Hz) NIST 610	15	10	8	15	10	10
Laser efficiency (Hz) foraminifers	5	10	12	20	5	14
Spot size sample (μm)	50	50	50	50	30	50

Table S4

Instrumental operating conditions for Neptune MC-ICP-MS and LA.

Extraction[V]:	-2000
Focus[V]:	-759.2
Source Quad1[V]:	229.1
Rot-Quad1[V]:	12.8
Foc-Quad1[V]:	-19.8
Rot-Quad2[V]:	6.1
Source Offset[V]:	-13
Matsuda Plate[V]:	0.1
Cool Gas[l/min]:	14.6
Aux Gas[l/min]:	1.2
Sample Gas[l/min]:	1.3
Add Gas[l/min]:	0.3
Org Gas[l/min]:	0
Operation Power[W]:	1268.9
X-Pos[mm]:	1.5
Y-Pos[mm]:	-1.3
Z-Pos[mm]:	-4
Ampl.-Temp[°C]:	46.6
Fore Vacuum[mbar]:	2.31E-04
High Vacuum[mbar]:	1.27E-07
IonGetter-Press[mbar]:	3.22E-08
Guard electrode	on

Table S5 Results from single B measurements of foraminifers. Errors are calculated according to formulas S3 (error of $\delta^{11}B$) and S5 (error of B/Ca).

Treatment pH_8.1[160] N = 50			
Foram #	**$\delta^{11}B$ (‰)**	**±(‰)**	**B/Ca (mmol/l)**	**±(mmol/mol)**
1	-33.88	0.87	5.16	0.06
1	-32.08	1.04	4.55	0.18
2	-33.43	1.00	5.37	0.05
2	-33.27	0.97	5.60	0.07
3	-31.98	1.10	5.22	0.09
3	-32.84	0.95	5.95	0.08
3	-33.69	1.18	3.47	0.06
4	-32.11	1.20	3.18	0.02
5	-35.33	1.15	3.91	0.06
5	-29.75	1.03	3.80	0.02
6	-31.11	1.14	3.43	0.03
7	-33.77	1.05	6.48	0.35
7	-33.38	1.12	5.21	0.23
8	-33.91	1.17	5.59	0.30
8	-33.47	1.48	4.90	0.26
9	-32.44	1.19	4.63	0.20
10	-32.20	0.85	5.26	0.20
11	-32.05	0.80	4.27	0.15
12	-33.32	0.91	6.27	0.09
12	-33.29	0.82	5.70	0.05
13	-32.27	0.99	5.48	0.06
13	-32.75	1.08	5.61	0.08
14	-31.83	0.90	5.57	0.05
14	-33.87	0.96	6.85	0.08
15	-32.05	0.93	6.74	0.09
16	-29.83	0.98	5.24	0.06
16	-29.51	0.87	4.81	0.07
17	-32.46	0.98	5.80	0.05
17	-32.90	0.94	5.53	0.06
18	-32.87	0.90	6.75	0.17
19	-31.88	0.96	6.90	0.06
19	-33.51	0.88	7.20	0.06
20	-32.27	0.98	6.21	0.06
20	-29.75	1.08	6.26	0.06
21	-32.75	0.88	7.17	0.08
22	-32.60	0.94	4.61	0.07
22	-32.43	0.85	4.90	0.08
23	-33.29	0.82	5.33	0.05
24	-33.55	0.86	5.47	0.06
24	-35.05	0.80	4.93	0.10
25	-34.84	0.83	4.08	0.04
26	-32.28	1.18	3.53	0.18
26	-31.46	1.06	3.47	0.20
27	-33.54	1.00	4.03	0.19
27	-32.75	1.21	4.79	0.33
28	-32.31	1.83	4.26	0.17
28	-31.48	0.85	3.83	0.18
29	-33.57	1.59	5.39	0.27
30	-34.71	1.31	6.89	0.76
31	-33.67	1.32	5.81	0.32

Treatment pH_8.1[260] N = 41				
Foram #	$\delta^{11}B$ (‰)	±(‰)	B/Ca (mmol/l)	±(mmol/mol)
32	-33.13	1.05	3.39	0.04
32	-32.11	0.97	2.79	0.02
32	-32.22	0.94	2.82	0.03
32	-32.89	1.80	4.60	0.10
33	-33.23	1.03	3.09	0.03
33	-33.10	0.95	3.28	0.04
33	-33.49	1.00	3.38	0.03
34	-30.58	1.11	2.51	0.05
34	-32.90	1.04	2.09	0.02
34	-32.36	1.05	2.52	0.04
35	-29.98	1.50	2.86	0.13
35	-32.97	1.37	3.35	0.27
36	-32.23	1.23	2.80	0.21
36	-32.37	1.29	3.06	0.20
37	-30.25	1.40	2.49	0.15
37	-31.77	0.99	2.36	0.10
38	-34.47	1.69	2.80	0.12
38	-32.88	1.38	2.73	0.13
39	-30.91	1.26	2.86	0.21
40	-31.87	0.94	3.38	0.19
41	-31.50	0.90	3.30	0.18
41	-31.09	0.91	3.11	0.11
42	-29.21	0.95	2.63	0.12
43	-32.44	1.01	3.88	0.33
44	-30.23	1.07	2.60	0.44
44	-31.50	0.91	2.52	0.06
44	-33.56	0.90	2.92	0.04
45	-33.31	0.84	3.84	0.06
45	-31.89	0.99	2.93	0.06
45	-31.56	0.88	2.84	0.03
46	-31.91	0.81	3.29	0.03
46	-30.53	0.84	2.54	0.04
46	-32.36	0.86	2.90	0.03
47	-30.21	0.91	3.41	0.16
47	-30.11	0.82	2.74	0.13
48	-33.77	0.99	3.85	0.17
49	-31.94	0.76	3.18	0.03
50	-31.13	0.62	2.84	0.09
51	-30.42	0.80	2.07	0.06
52	-30.83	1.13	1.91	0.04
53	-31.82	0.64	2.29	0.05

Treatment pH_8.1[540] N = 15				
Foram #	δ¹¹B (‰)	±(‰)	B/Ca (mmol/l)	±(mmol/mol)
54	-29.19	0.98	1.59	0.01
54	-30.84	0.96	1.69	0.01
55	-31.09	0.97	1.85	0.01
55	-31.10	0.93	1.79	0.01
56	-31.69	0.92	1.64	0.01
56	-31.88	0.92	1.96	0.02
57	-33.08	0.98	1.74	0.01
57	-31.38	0.98	1.87	0.01
58	-32.26	0.95	1.73	0.01
58	-30.44	0.96	1.79	0.01
59	-31.23	1.02	1.84	0.02
59	-32.25	0.99	1.86	0.02
60	-34.40	1.25	1.65	0.03
61	-31.31	1.01	1.57	0.01
62	-33.14	1.13	1.71	0.04

Treatment pH_8.1[640] N = 12				
Foram #	δ¹¹B (‰)	±(‰)	B/Ca (mmol/l)	±(mmol/mol)
63	-31.66	1.19	1.61	0.02
63	-29.72	1.22	1.36	0.02
64	-35.89	1.16	1.37	0.02
65	-31.76	1.70	1.42	0.16
66	-33.19	1.13	1.73	0.03
66	-32.87	1.00	1.72	0.03
67	-32.76	1.48	1.57	0.01
67	-31.66	0.91	1.60	0.02
68	-33.57	1.12	1.66	0.02
68	-32.97	1.29	1.67	0.08
69	-31.41	0.89	1.67	0.02
69	-31.97	0.92	1.58	0.03

Treatment pH_8.6[640] N = 12				
Foram #	δ11B (‰)	±(‰)	B/Ca (mmol/l)	±(mmol/mol)
70	-26.53	0.88	8.86	0.07
70	-25.57	0.97	8.11	0.08
71	-26.27	1.07	4.98	0.11
72	-24.14	1.09	7.37	0.10
73	-24.71	0.93	4.60	0.10
74	-23.56	0.89	6.67	0.05
74	-21.50	0.85	6.67	0.07
75	-23.79	0.88	7.07	0.09
75	-20.89	0.96	6.37	0.06
76	-24.12	0.95	4.77	0.04
77	-22.53	0.87	5.65	0.15
77	-20.13	0.87	5.22	0.08

Treatment pH_7.9[260] N = 11				
Foram #	δ11B (‰)	±(‰)	B/Ca (mmol/l)	±(mmol/mol)
78	-33.57	1.19	1.04	0.01
78	-34.89	1.36	1.18	0.01
79	-36.14	1.39	1.34	0.02
79	-35.08	1.29	1.26	0.03
80	-36.29	1.50	1.24	0.02
81	-38.64	1.21	1.19	0.02
81	-35.67	0.93	1.15	0.01
82	-35.28	1.05	1.10	0.01
82	-36.13	1.02	1.16	0.01
83	-34.78	1.19	1.27	0.02
83	-35.07	1.10	1.29	0.02

Figure S1

HV	Spot	WD	Tilt	Mag	Sig	3/6/2012	400.0µm
5.0 kV	3.0	10.6 mm	0.7 °	300x	SE	3:35:04 PM	sample 9
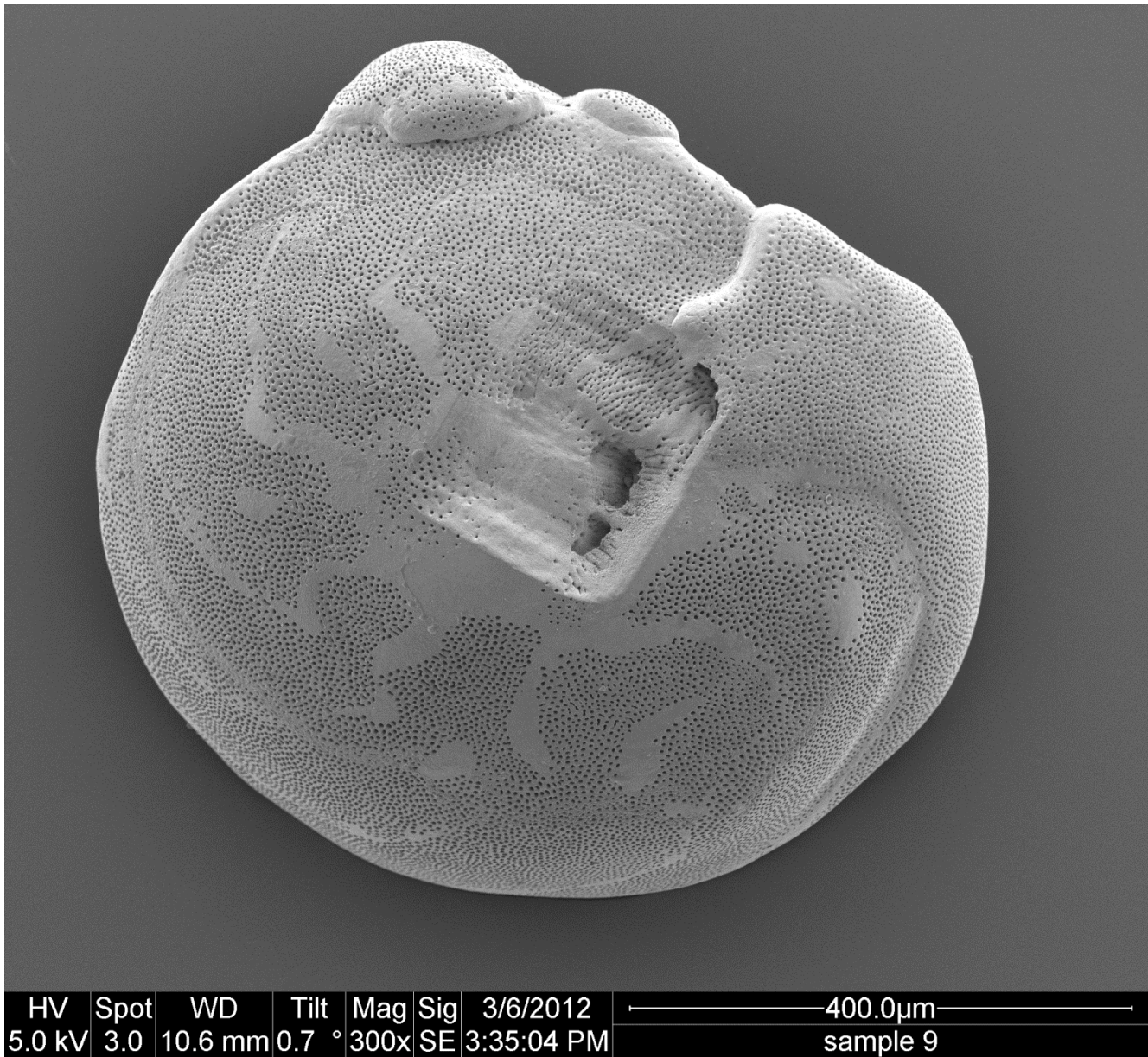
A foraminifer from the pH_8.1[160] treatment after laser ablation. The knob was measured twice.