Supplementary material

A unique temperate rocky coastal hydrothermal vent system (Whakaari–White Island, Bay of Plenty, New Zealand): constraints for ocean acidification studies

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Fig. S1. Diel variation in seawater pH (on the total scale, pH_T) (ignores tide) of seawater in the sampled vents (V1 and V2) and the nearby 'vent control' (C4) obtained with the SeaFET at Champagne Bay, White Island (New Zealand) in November 2015.



Fig. S2. Comparison in seawater pH (on the total scale, pH_T) between C3 and C4 ('vent control') at Champagne Bay, White Island (New Zealand) in November 2015. The SeaFET data from 9 to 12 November is from an earlier deployment by N Shears. Note that during the 1–2 December deployment there was a very large swell and a lot of mixing.

Table S1.Trace metal data of a certified reference material (SLEW-3, National Research
Council, Canada, n = 2) for accuracy assurance of the implemented high-resolution sector field
inductively coupled plasma mass spectrometer technique at the University of Otago (New
Zealand)

The quantitative metal recovery on the resin (Nobias-chelate PA1) within the SeaFAST system was evaluated for each metal by comparing the slope of the calibration line obtained from standard additions to seawater to standard additions done directly to untreated eluent acid (i.e. these samples were not passed through the SeaFAST system). Trace metal values shown in the table (n = 2) are not recovery corrected. Fit (%) denotes the percentage error between the measured metal concentration of the certified reference material and the certified value for this metal

	Mn (nM)	Fe (nM)	Co (nM)	Ni (nM)	Cu (nM)	Zn (nM)	Cd (nM)	Pb (nM)
Certified value	29.31 ± 4.00	10.17 ± 1.06	0.71 ± 0.17	20.96 ± 1.19	24.39 ± 1.89	3.07 ± 0.57	0.43 ± 0.04	0.043 ± 0.01
Measured value $(n = 2)$	30.51 ± 0.04	9.96 ^A	0.75 ± 0.00	22.44 ± 0.37	25.20 ± 0.49	3.31 ± 1.48	0.43 ± 0.00	0.042 ± 0.01
Recovery (%)	118	106	118	114	117	136	116	114
Fit (%)	3.9	2.0	5.4	6.6	3.2	7.1	0.8	3.3

 $^{A}n = 1.$

Table S2.Trace metal data of a seawater reference material (NASS-7, National Research
Council, Canada, n = 2) and an in house-standard for accuracy assurance of the implemented
ICP-MS analyses at the Jacobs University (Bremen, Germany)

Li, Rb, SR, Cs and Ba data are an in-house standard. Fit (%) denotes the percentage error between the

measured metal concentration of the certified reference material and the certified value for this metal

	Li	Rb	Sr	Мо	Cs	Ba	U
	(µM)	(µM)	(µM)	(nM)	(nM)	(nM)	(nM)
Certified value	21.99	1.16	90.16	96.83 ± 4.17	1.87	29.13	12.06 ± 0.67
Measured value $(n = 2)$	21.18 ± 0.13	1.08 ± 0.05	85.07 ± 3.23	101.18 ± 1.04	1.73 ± 0.02	31.35 ± 0.62	11.26 ± 0.12
Fit (%)	3.7	6.9	5.6	4.5	7.9	7.6	2.1

Table S3. Summary of δ^{11} B composition and calculated pH in the calcifying fluid (pH_{cf}) for sampled coralline alga at 3 different stations around Whakaari–White Island in the Bay of Plenty, New Zealand

-, not sampled; V1, large vent site; V2, small vent site; C2, White Island control

Site	Treatment	Species	$\delta^{11}B$	pH _{cf}
V1	Vent	Corallina	24.80	8.63
V2	Vent	Corallina	25.09	8.65
V2	Vent	Corallina	25.91	8.70
C2	Control	Amphiroa	26.09	8.71
C2	Control	Amphiroa	24.71	8.63
C2	Control	Corallina	25.81	8.70
C2	Control	Corallina	27.39	8.80
Average	Vent	Corallina	25.27 ± 0.58	8.66 ± 0.04
	Control	Corallina	26.60 ± 1.11	8.75 ± 0.07
	Vent	Amphiroa	_	_
	Control	Amphiroa	25.40 ± 0.97	8.67 ± 0.06