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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Abstract. *In situ* effects of ocean acidification are increasingly studied at submarine CO_2 vents. Here we present a preliminary investigation into the water chemistry and biology of cool temperate CO_2 vents near Whakaari–White Island, New Zealand. Water samples were collected inside three vent shafts, within vents at a distance of 2 m from the shaft and at control sites. Vent samples contained both seawater pH on the total scale (pH_T) and carbonate saturation states that were severely reduced, creating conditions as predicted for beyond the year 2100. Vent samples showed lower salinities, higher temperatures and greater nutrient concentrations. Sulfide levels were elevated and mercury levels were at concentrations considered toxic at all vent and control sites, but stable organic and inorganic ligands were present, as deduced from Cu speciation data, potentially mediating harmful effects on local organisms. The biological investigations focused on phytoplankton, zooplankton and macroalgae. Interestingly, we found lower abundances but higher diversity of phytoplankton and zooplankton at sites in the direct vicinity of Whakaari. Follow-up studies will need a combination of methods and approaches to attribute observations to specific drivers. The Whakaari vents represent a unique ecosystem with considerable biogeochemical complexity, which, like many other vent systems globally, require care in their use as a model of 'future oceans'.

Additional keywords: carbon dioxide, trace metal speciation, volcanic submarine vent.

Introduction

Three methods have generally been used to estimate the effects of changing seawater chemistry: mathematical modelling anchored to observational data, controlled experimentation in the laboratory or field-based mesocosm studies, and the study of natural systems representing analogues of past, present or future climate change scenarios (e.g. Boyd *et al.* 2018). Each of these approaches has its strengths and weaknesses, but together they have proved useful in developing preliminary projections, elucidating connections and understanding synergies (Le Treut *et al.* 2007) regarding ocean warming and ocean acidification (OA; Wisshak *et al.* 2013; Riebesell and Gattuso 2015; Gattuso *et al.* 2015).

Most of our current understanding of how marine biota will respond to climate change originates from controlled, laboratory-based, short-term experiments conducted in tanks and mesocosms as well as modelling approaches based on these experimental data (Wernberg *et al.* 2012). Controlled, laboratory-based manipulations (e.g. mesocosms) are useful in establishing a mechanistic understanding of how physical climate change is likely to drive ecological changes, but they tend to exaggerate their measured effects and obscure key processes (Goldenberg *et al.* 2018) because they are based on simplified artificial model systems ruled by first-order abiotic and biotic effects and thus suffer from a lack of realism (Wernberg *et al.* 2012; González-Delgado and Hernández 2018). To increase realism and collective inference, as well as to strengthen the generality and accuracy of our understanding of climate change as a driver of chemical and biological change in marine ecosystems, researchers have started using existing natural gradients in climate variables to examine how increased pCO_2 (i.e. a change in ocean chemistry) will translate into ecological changes (e.g. Hall-Spencer *et al.* 2008; Wernberg *et al.* 2012; Teixidó *et al.* 2018). One example of an environment with natural abiotic gradients is the shallow submarine CO_2 vent, and these vents are found around the globe (Tarasov *et al.* 2005; González-Delgado and Hernández 2018). Over the past 10 years, shallow CO_2 vents have emerged as analogues to investigate the effects of OA on natural ecosystems (e.g. Hall-Spencer *et al.* 2008; Fabricius *et al.* 2011; Lombardi *et al.* 2011; Calosi *et al.* 2013; Lamare *et al.* 2016; Dahms *et al.* 2018). They have enabled research into the effects of long-term *in situ* exposure of multiple biota to elevated pCO_2 under natural environmental variability, food, light and hydrodynamic conditions, as well as natural levels of interactions between species and their environment (e.g. Hall-Spencer *et al.* 2008; Fabricius *et al.* 2011, 2014; Brinkman and Smith 2015; Nagelkerken *et al.* 2016). Thus, submarine CO_2 vents have gained increasing popularity in the past decade as natural laboratories to obtain a better understanding of CO_2 effects on community, population, ecosystem structure and functionality changes, as well as species-specific adaptation mechanisms in a natural environment (e.g. Lombardi *et al.* 2011; Calosi *et al.* 2013; Lamare *et al.* 2016; Dahms *et al.* 2018; González-Delgado and Hernández 2018).

The main limitations in using shallow marine hydrothermal systems as natural analogues of future conditions are:

- the large temporal variabilities in pH with periods of time where pH values reach ambient levels or undersaturated conditions (e.g. Boatta *et al.* 2013; Fabricius *et al.* 2014; Dahms *et al.* 2018; González-Delgado and Hernández 2018; Pichler *et al.* 2019)
- the limited area affected by vent emissions and resulting area with low pH and potentially higher temperatures (Boatta *et al.* 2013; Pichler *et al.* 2019)
- the continuous supply of larvae and propagules from outside the vent system (e.g. Levin *et al.* 2016; Boyd *et al.* 2018; Hawkins *et al.* 2018), which hampers the ability to use these sites to determine whether dispersive populations could adapt to environmental stressors over multiple generations
- the eventuality that some organisms that live at CO_2 vents could have higher tolerance thresholds for environmental stressors owing to the possibility of evolving and genetically adapting over long timescales to extreme physicochemical conditions (e.g. Hall-Spencer *et al.* 2008)
- the chemical composition of hydrothermal fluids at many vent sites (i.e. the potential presence at toxic concentrations of elements and gases), which may have confounding effects on vent biota (e.g. Cunha *et al.* 2008; Chen *et al.* 2018; Dahms *et al.* 2018; González-Delgado and Hernández 2018; Hawkins *et al.* 2018; Pichler *et al.* 2019).

Most CO_2 vent studies to date have focused on the ecological consequences of lower pH, lower carbonate saturation state or higher CO_2 (e.g. Hall-Spencer *et al.* 2008; Fabricius *et al.* 2011, 2014; Brinkman and Smith 2015; Nagelkerken *et al.* 2016), whereas elevated levels of heavy metals in vent fluids compared with non-hydrothermal environments and their potential effects on the local environment (Chen *et al.* 2018; Hawkins *et al.* 2018) have either largely been overlooked, dismissed as insignificant or were studied using methods unable to detect bioactive trace metals with necessary sensitivity. Emanating fluids of many volcanic submarine CO_2 vents are typically characterised by high concentrations of toxic metals such as Pb, Cd, Zn, Hg, Cu, Co, Mo and Sr (Cunha *et al.* 2008; Chen *et al.* 2018; Hawkins *et al.* 2018; Burger and Lichtscheidl 2019). These metal-rich fluids contaminate the surrounding water column, and potentially adversely affect the physiology of vent biota (Cunha *et al.* 2008; Chen *et al.* 2018; Hawkins *et al.* 2018). Thus, it is surprising that so far most shallow vent studies of biological nature limited their element measurements to gases (e.g. CO_2, H_2S, CH_4, N_2, O_2; Pichler *et al.* 2019) and sediments (e.g. Vizzini *et al.* 2013), despite elements in solution being potentially key factors for the assessment of the suitability of vent systems for the study of climate change effects on marine biota (Vizzini *et al.* 2013). Consequently, an integrated picture of the carbonate chemistry, biology and, in particular, the geochemistry (i.e. element composition, metal speciation and bioavailability) of shallow submarine vents is required to simulate and investigate OA at CO_2 vents.

The most well-studied shallow submarine CO_2 vents in the context of climate change are in the warm temperate Mediterranean Sea (e.g. Hall-Spencer *et al.* 2008; Kroeker *et al.* 2011; Lidbury *et al.* 2012; Vizzini *et al.* 2013; Baggini *et al.* 2014; Ziveri *et al.* 2014; Cornwall *et al.* 2017a; Hawkins *et al.* 2018), in deep water (e.g. Rossi and Tunnicliffe 2017) or in tropical to subtropical coral reef environments in Papua New Guinea (e.g. Fabricius *et al.* 2011; Morrow *et al.* 2015; Takahashi *et al.* 2016;
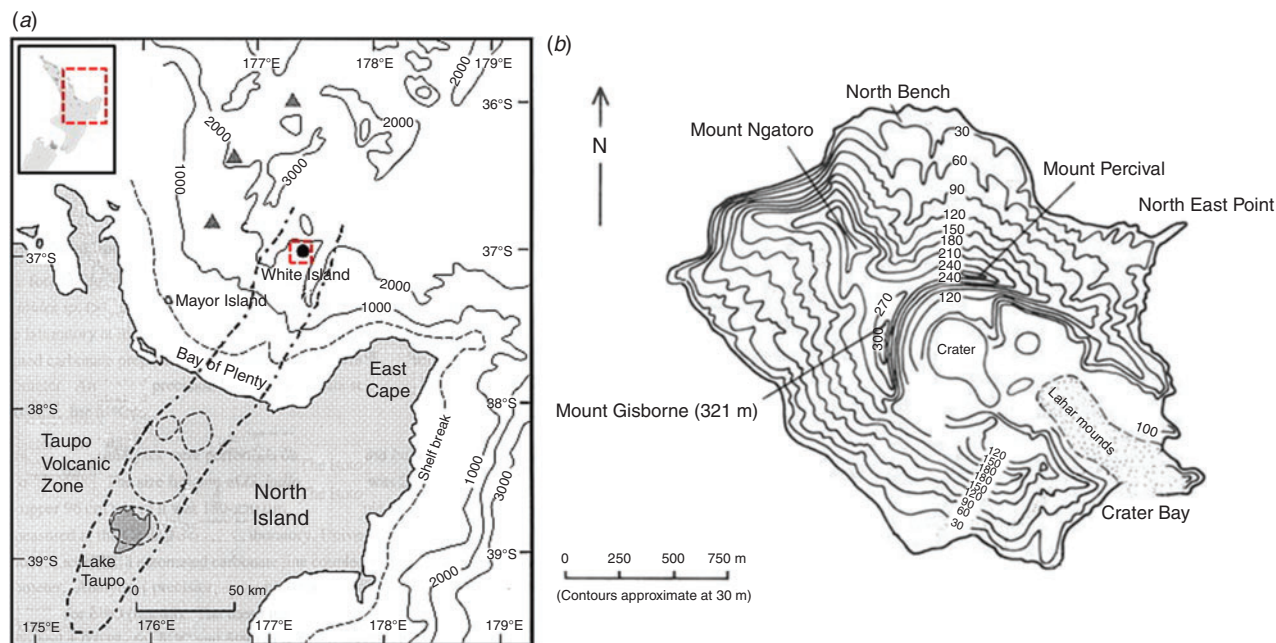
Fig. 1. (*a*) Bathymetric map of the Taupo Volcanic Zone in the Bay of Plenty, North Island, New Zealand (after Samson *et al.* 2005). (*b*) Geomorphic map of White Island (after Clarkson and Clarkson 1994).

Pichler *et al.* 2019), Japan (Inoue *et al.* 2013; Agostini *et al.* 2015), Canary Islands (Hernández *et al.* 2016) and Mariana Islands (Enochs *et al.* 2015). OA studies of shallow vents in cooler waters of the Southern Hemisphere are still scarce. Therefore, the present study focused on volcanic submarine CO_2 vents off Whakaari–White Island in New Zealand's Bay of Plenty, in a temperate location for OA research (Brinkman and Smith 2015; Nagelkerken *et al.* 2016). Seawater immediately adjacent to the vents is lower in pH and higher in temperature than the ambient seawater, even given the natural diurnal variation typical of rocky kelp-dominated ecosystems (Cornwall *et al.* 2013). Nevertheless, the working area is home to a variety of calcified and non-calcified marine biota and is accessible by SCUBA, highlighting its potential for OA research. The results of previous surveys (Grace 1975; Brinkman and Smith 2015; Nagelkerken *et al.* 2016; Connell *et al.* 2018) suggested that these cool temperate CO_2 vents can offer a natural laboratory for studying the response of temperate communities to future pH and temperature projections for the year 2100 (Gattuso *et al.* 2015). However, in some studies the effect of clearly enriched heavy metals and elements, such as Hg and sulfide, in the water column around the vents was either omitted in their overall conclusions or was thought to have negligible effects on prevalent marine biota (Brinkman and Smith 2015). Consequently, this study aimed to combine carbonate chemistry, biology and, in particular, geochemical data to evaluate the suitability of the Whakaari vents as potential natural study sites of OA in the Southern Hemisphere. To conclusively confirm the potential of these shallow vent areas for OA research, any possible effects of elevated trace element concentrations must be precluded (Vizzini *et al.* 2013).

Grange *et al.* (1992) and Tarasov (2006) described Whakaari–White Island as 'possibly unique'. Certainly its

accessibility, its continuous production of ash and steam (but not lava) and the proximity of a temperate kelp forest community to CO_2 vents are special and unusual features, which could make Whakaari's vents a valuable addition to current OA research so long as any geochemical parameters are within acceptable limits. In order to establish basic biogeochemical information and examine Whakaari's potential for further study as a natural analogue for future climate change effects, a group of scientists converged on the island in December 2015. In a single week, physical, geochemical and biological characteristics were measured at three vent sites, three control sites near the volcano and one coastal control to provide a cross-disciplinary snapshot of the seawater chemistry and ecology around Whakaari in early summer. Here we report on the preliminary results of the 'White Island Blitz' expedition and evaluate the future utility and potential of Whakaari as a 'living laboratory' for climate change science.

Materials and methods

Ethics

This study does not report on animal work and thus did not require any animal ethics approval. Biological (i.e. algae) and water samples were collected under a Special Collection Permit from the Ministry of Primary Industries (number 644-2).

Study location

Whakaari–White Island is an active andesite stratovolcano located ~50 km offshore in the Bay of Plenty, North Island, New Zealand (37°31.19′S, 117°10.85′E; Fig. 1). The island is part of the Taupo Volcanic Zone in the back-arc basin of the Kermadec–Tonga subduction zone. The island is approximately circular, covering 238 ha, ~2 km in diameter (Fig. 1).

The highest point of the crater wall, Mount Gisborne, is 321 m above sea level (Clarkson and Clarkson 1994) and ~1600 m above the sea floor (Fig. 1). White Island is New Zealand's most active cone volcano, and has probably been active for at least 16 000 years (Grange *et al.* 1992). There have been periods of fairly quiet steaming, during which scrubby forests were able to develop, but then periods of heightened activity (e.g. 1976–90; Clarkson and Clarkson 1994), with nearly continuous outpouring of ash, steam and gas, killing trees and shrubs and resulting in a fairly barren landscape (Clarkson and Clarkson 1994). Nevertheless, the island presently supports a breeding colony of gannets and areas of vegetation. Eruptions, which are infrequent, can be quite violent, with andesite blocks and ash being hurled into the sea.

The island has a well-developed terrestrial hydrothermal system, consisting of saline fluids around the active vents (Giggenbach 1987). These magmatic fluids interact with meteoric fluids, magmatic gases (70 : 29 : 1 C : S : Cl; Giggenbach 1975), host rocks and metalliferous deposits (rich in V, Cr, Fe, Co, Ni, Rb, Mg, Al, Mn, Zn and Cu; Cole *et al.* 2000) to produce hot springs and fumaroles (fumarole gases are normally 100–300°C but rise to 1000°C during strong activity; Sarano *et al.* 1989). The composition of gas fumaroles around Whakaari varies with temperature (Giggenbach 1975), but in all cases the dominant component, besides water vapour, is CO_2, followed by SO_2, H_2S and HCl. Dissolved volcanic gases in hydrothermal fluids give rise to strongly acidic (~1.7 pH) and thus metal-rich surface waters (Donachie *et al.* 2002) that drain into the surrounding sea, particularly at Crater Bay (Fig. 1), to the south-east of the island (Grace 1975).

Diffuse fluid sources and gas vents occur also in the shallow waters (10–30 m) north and east of the island (e.g. 'Champagne Bay'; Sarano *et al.* 1989) with warm water (18–55°C; Tarasov 2006) and gas bubbles (containing CO_2, N_2, CH_4, C_2H_6, H_2, H_2S; Propp *et al.* 1992; Tarasov *et al.* 1999; Hocking *et al.* 2010; Brinkman and Smith 2015) emerging from among boulders or out of the sand. Measurements of the emanating fluids showed pH values as low as 7.5 (Brinkman and Smith 2015) and high concentrations of elements and metals, such as S, K, Hg, Rb, Mg and Ca (Brinkman and Smith 2015).

Intertidal fauna are low in abundance and diversity (Grange *et al.* 1992) and exhibit shell pitting and staining, perhaps due to acidified rain or ashfall (Grace 1975). Subtidally, fish are plentiful and macroalgae (i.e. kelp *Ecklonia radiata* forests) are abundant, but species composition is different from and diversity is lower than nearby Mayor Island or other coastal islands around north-eastern New Zealand (Grange *et al.* 1992). Submarine invertebrates are neither diverse nor abundant around the vent sites, whereas bacterial biomass is noticeably greater around the CO_2 vents (Grange *et al.* 1992). Subtropical marine species are sometimes found here because of the warm East Auckland Current (Grace 1975), which brings clear subtropical waters from the north-east of the North Island into the Bay of Plenty. Geostrophic currents flow across the Bay of Plenty from west to east, at an average speed of 0.14 m s^{-1} (Ridgway and Greig 1986). Mean sea surface temperature in the area is 21°C in summer and 15°C in winter, and surface salinity is typically 35.0–35.7 (Ridgway and Greig 1986).

Sampling sites

Collection of seawater and biological samples occurred during New Zealand's summer in 2015 over three consecutive days in early December. Sampling was conducted during severe weather with heavy surge and strong winds resulting in challenging sampling conditions for divers and the boat crew. Sampling resolution was consequently lower than planned.

Three natural CO_2 vents (V1, V2 and V3) and four control sites (C1, C2, C3 and C4) were sampled near White Island and in the Bay of Plenty (Fig. 2; Table 1). The seven sites were chosen based on their variety of vent activity and their biological diversity (i.e. calcified and non-calcified macroalgae, as well as numerous species of invertebrates and fish). The vent locations were chosen based on previous studies and included one large vent (V1; previously examined by Brinkman and Smith 2015), a smaller vent (V2) and a moderate vent (V3). Vent sites V1 and V2 were located 8–10 m below the surface at the northeastern tip of the island, whereas V3 was on the western side at a depth of 14.5 m. Control sites were chosen, based on accessibility and weather conditions during sampling, with at a distance of at least 25–30 m from visible vent activity. Prevailing water flow in New Zealand's Bay of Plenty is west to east as part of the East Auckland Current (Ridgway and Greig 1986), and thus control sites C3 and C4 experience flow regimes most similar to the sampled vent sites on the east side of the island. The control site C4 was located midway between V1 and V2 and was referred to as a 'vent control', whereas C3 was established in the outer part of the bay, north of the vent field, and was expected to be more representative of pH around the island with less influence from the vent field. The control site C2 located on the western site of the Island was established outside the influence of the Whakaari vent field and was thus expected to be more representative of ambient seawater conditions. The open ocean control sample (C1) was taken approximately mid-way between White Island and mainland New Zealand over the continental shelf, thus giving a regional context.

Sample collection and sampling procedure

Sampling – water chemistry. Temperature, conductivity (salinity) and depth were measured *in situ* at the study sites using an RBR CTD XR 620 (RBR Ltd, Stadhampton, UK) alongside water sampling. In addition, seawater pH (on the total scale, hereafter pH_T) and temperature were monitored half hourly from 13 to 27 November using SeaFET pH sensors (Sea Bird Scientific, Bellevue, WA, USA) placed on the reef within V1 and V2 and at two nearby control locations (C3 and C4; Fig. 2). The SeaFET sensors were deployed to investigate the temporal variability of pH_T and temperature around Whakaari. Unfortunately, there was an unknown problem with the SeaFET sensor at C3, and the data were deemed unreliable. However, additional data are available from C3 and C4 from before and after the long-term deployment, which allows some comparison in pH_T between the two controls.

Vent samples for total dissolved trace metal concentrations, Cu speciation, total mercury (Hg_T), sulfide (the term 'sulfide' used in this study refers to total reduced sulfur; i.e. the sum of H_2S, HS^- and S^{2-}) and nutrient (ammonium, nitrogen oxides (NO_x) and phosphate) concentrations were taken by SCUBA divers directly at the vent outflow (which, for the larger vents,
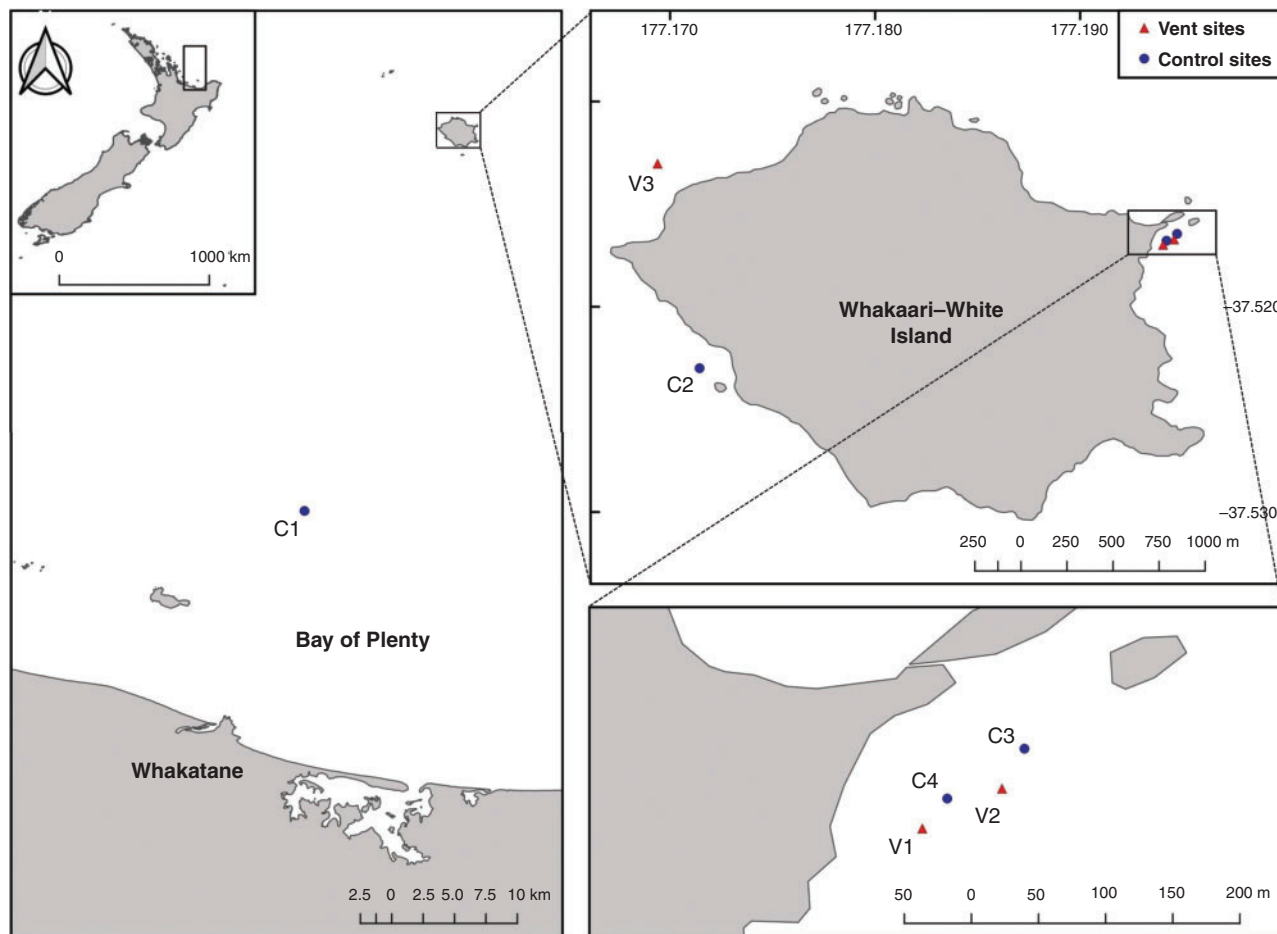
Fig. 2. Map of sites sampled during the 'White Island Blitz' in December 2015 near Whakaari–White Island in New Zealand's Bay of Plenty. V1, large vent site; V2, small vent site; V3, an active vent on the western side of White Island; C1, open ocean control; C2, White Island control; C3, Champagne Bay control; C4, 'vent control' site sampled with SeaFET pH sensors (Sea Bird Scientific, Bellevue, WA, USA).

was beneath the reef surface), and at a distance of 2 m from the emanating vent fluid at ~1 m from the bottom using acid-cleaned 5-L collapsible containers. Surface and subsurface samples at the vent and control sites were taken from the research vessel for the same parameters using a peristaltic pump connected to acid-cleaned polyethylene tubing, which was rinsed with 1 L of sample seawater before sample collection, except for sample C3 SW, which was taken manually by submersing a sample bottle from aboard ship because of the huge swell. After recovery, sample aliquots reserved for trace metal, Cu speciation, Hg_T, sulfide and nutrient analysis were subsequently filtered in-line through a 0.2-µm polycarbonate cartridge filter (Acropak, Pall Corporation, Port Washington, NY, USA; one filter per site) and individually stored in pre-cleaned and rinsed low-density polyethylene (LDPE) bottles. Total dissolved trace metal samples were stored in the dark at room temperature in two plastic bags until they were acidified to pH_{NBS} 2 using quartz distilled HCl (analytical grade; Scharlau, Scharlab, Barcelona, Spain; 37%) in the laboratory of the University of Otago (Dunedin, New Zealand). Sample bottles for Cu speciation analysis were double-bagged and immediately frozen ($-20°C$) and kept frozen until analysis. Bottles reserved

for nutrient and Hg_T analysis were placed into two resealable plastic bags, refrigerated (4°C) and stored in the dark until analysed in the laboratory. Hg_T samples were acidified in the laboratory of the University of Otago with 0.5% (v/v) HCl and subsequently sent to the University of California (Santa Cruz, CA, USA) for analysis. Sample analysis for sulfide was conducted on board. Equipment and sample bottles used for total dissolved trace metals, Hg_T and Cu speciation analysis had been cleaned according to conventional trace metal clean protocols (Sander *et al.* 2009; Leal *et al.* 2016).

Dissolved inorganic carbon (C_T) and total alkalinity (A_T) samples were collected following the method prescribed by Dickson *et al.* (2007). Vent samples were collected in 1-L Schott glass bottles without headspace by SCUBA divers, and surface samples were collected by hand off the side of the boat. Two samples were collected at each site and each sample was analysed for both C_T and A_T. Immediately after sample recovery, 5 mL of each sample was discarded and 0.5 mL of saturated $HgCl_2$ solution was added to poison and preserve the samples (i.e. to avoid biological alteration) for later analysis at the National Institute for Water and Atmospheric (NIWA)/University of Otago Research Centre for Oceanography.

Table 1.   Sampling sites near Whakaari–White Island in New Zealand's Bay of Plenty

Zooplankton samples were collected from a depth of 10 m. The sampling depth for all other parameters is stated in the table. SeaFET pH sensors (Sea Bird Scientific, Bellevue, WA, USA) were deployed between 13 and 27 November 2015. The Champagne Bay control surface water (C3 SW) sample was taken manually by submersing a sample bottle from on board the ship. Sample sites are shown in Fig. 2. V1, large vent site; V2, small vent site; V3, an active vent on the western side of White Island; '-2m', vents sampled at a distance of 2 m from the vent outflow; C1, open ocean control; C2, White Island control; C3, Champagne Bay control; C4, 'vent control'; T, temperature; S, salinity

Site	Date	Latitude	Longitude	Sampling depth (m)	T, S, carbonate chemistry	SeaFET	Elements	Speciation	Coralline algae	Zooplankton	Phytoplankton
C1	3 Dec. 2015	37°47.483′S	177°04.272′E	2.0	X		X[A]			X	X
C2	2 Dec. 2015	37°31.379′S	177°10.286′E	2.0	X		X		X		X
C3 SW	3 Dec. 2015	37°31.00′S	177°11.647′E	0.3	X		X				X
C3	2 Dec. 2015	37°30.997′S	177°11.685′E	5.8	X	X	X			X	
	3 Dec. 2015							X			
C4		37° 31.007′S	177° 11.653′E	9.0		X	X	X			
V1	2 Dec. 2015	37°30.994′S	177°11.682′E	8.6	X	X	X	X	X	X	X
	3 Dec. 2015				X						
V1-2m	2 Dec. 2015	37°30.994′S	177°11.682′E	8.6	X		X	X			
	3 Dec. 2015				X						
V2	2 Dec. 2015	37°31.002′S	177°11.731′E	9.9	X	X	X	X	X		
	3 Dec. 2015				X						
V2-2m	2 Dec. 2015	37°31.002′S	177°11.731′E	9.9	X		X				
	3 Dec. 2015				X						
V3	2 Dec. 2015	37°30.781′S	177°10.163′E	14.5	X		X				
	3 Dec. 2015										
V3-2m	2 Dec. 2015	37°30.781′S	177°10.163′E	14.5	X		X				X
	3 Dec. 2015										

[A]Station not sampled for Li, Rb, Sr, Mo, Cs, Ba and U.

Sampling – biological samples. Samples for phytoplankton species composition were collected at five different stations (Table 1). Surface samples at Champagne Bay (C3 SW) were taken off the side of the boat, whereas the other deeper samples were pumped on board using a peristaltic pump set-up. Samples for larger phytoplankton cells ($>20\,\mu m$) were stored in 200-mL brown borosilicate glass bottles and preserved with 0.5 mL of Lugol's solution. Samples for analysis of small phytoplankton species ($<20\,\mu m$) by flow cytometry were snap frozen in liquid nitrogen until analysis in the home laboratory at the University of Otago.

Zooplankton samples were collected using a vertical haul of a 0.5-m diameter, 150-µm plankton net from a depth of 10 m at C1, C3 and V1. Three replicate zooplankton hauls were taken at each location (total $n = 9$), which, assuming 100% efficiency, filtered $1.95\,m^3$ of seawater. Samples were subsequently fixed with 2–4% formalin. Unfortunately, poor weather prevented a representative zooplankton sampling haul at V1 at a depth of 10 m. In addition, extreme mixing within Champagne Bay meant that the V1 sample was contaminated with benthic crustaceans and coralline algae.

Seven individuals of the two most abundant species of coralline alga (i.e. *Corallina officinalis*, $n = 5$; and *Amphiroa anceps*, $n = 2$) around the study sites were collected by SCUBA divers from V1 ($n = 1$), V2 ($n = 2$) and C2 ($n = 4$) using hammer and chisel. Specimens were stored on silica gel for analyses of $\delta^{11}B$ at the University of Western Australia (Crawley, WA, Australia) to subsequently determine the pH in the calcifying fluid (pH_{cf}) of the collected coralline alga (Cornwall *et al.* 2017b).

Analysis of water chemistry

Analysis of physicochemical parameters

Nutrient samples were analysed in duplicate at the University of Otago using a Lachat QuikChem 8500 Series 2 flame ionisation auto analyser (Hach, Auckland, New Zealand). C_T and A_T were both measured at the NIWA/University of Otago Research Centre for Oceanography. A_T was measured by potentiometric titration in a closed cell using a custom-built system (Metrohm Dosimat 765, Metrohm AG, Herisau, Switzerland; Fluke high-precision voltmeter, Fluke Calibration, Everett, WA, USA; in-house-built closed cell and custom-written software) following the method of Dickson *et al.* (2007). C_T was determined on a custom-built system (following the Guide to Best Practices SOP2; Dickson *et al.* 2007) by coulometric analysis (UIC Model 5011, UIC Inc., Joliet, IL, USA) of evolved gas (single-operator multi-parameter metabolic analyser (SOMMA) style CO_2 extraction system). The accuracy of both methods, as determined by analysis of certified reference materials (provided by Andrew Dickson, Scripps Institution of Oceanography, San Diego, CA, USA), is estimated to be $\pm 2\,\mu mol\,kg^{-1}$ for A_T and $\pm 1\,\mu mol\,kg^{-1}$ for C_T. C_T and A_T data were used to calculate pH_T (total scale), pCO_2, CO_3^{2-} concentration and calcite and aragonite saturation states ($\Omega_{calcite}$ and $\Omega_{aragonite}$ respectively) of each sample at the *in situ* temperature, salinity and pressure (CTD XR 620 values) using the refitted Mehrbach CO_2 equilibrium constants (Mehrbach *et al.* 1973; Dickson *et al.* 2007). Stored C_T and A_T samples were analysed within 3 months of collection.

Analysis of total dissolved trace metals, Hg_T, sulfide and Cu speciation

Total dissolved trace metal measurements for Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb were made at the Centre for Trace Metal Analysis at the University of Otago using an automated off-line SeaFAST (Elemental Scientific Instruments, Omaha, NE, USA) preconcentration system (Biller and Bruland 2012; Middag *et al.* 2015) combined with a subsequent trace metal analysis by a Nu Attom high-resolution sector field inductively coupled plasma mass spectrometer (HR-SF-ICP-MS; Nu Instruments Ltd, Wrexham, UK). A detailed description of the method and sample preparation procedure is provided elsewhere (Biller and Bruland 2012; Bown *et al.* 2017; Rapp *et al.* 2017). Quantitative resin (Nobias-chelate PA1) recovery was within an acceptable range for the trace metals of interest and the accuracy of the method, verified by multiple measurements of certified reference material (SLEW-3; National Research Council (NRC), Ottawa, ON, Canada), was within $\pm 7\%$ (s.d.) of the certified values for Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb (for more detail, see Table S1, available as Supplementary material to this paper).

Trace metal concentrations for Li, Rb, Sr, Mo, Cs, Ba and U were determined by ICP-MS (NexION; Perkin Elmer, Foster City, CA, USA) at the Jacobs University (Bremen, Germany). For quality control, the seawater reference material NASS-7 (NRC) and an in-house standard were measured along with the samples. The analytical error was within $\pm 8\%$ (s.d.) of the reference values for the trace metals of interest (for more detail, see Table S2).

Hg_T was measured at the University of California by cold vapour atomic fluorescence spectrometry using the methods of Bloom and Crecelius (1983) and Balcom *et al.* (2004). Samples were measured in duplicate for quality assurance.

Sulfide (H_2S, HS^- and S^{2-}) was measured on board using a vibrating, mercury-coated, gold microwire electrode in conjunction with rapid electrochemical cathodic stripping square wave voltammetry (IviumStat electrochemical analyser, Ivium Technologies B.V., Eindhoven, Netherlands) following a procedure adapted from Bi *et al.* (2013) and Al-Farawati and van den Berg (1997). The electrode was precoated with mercury and calibrated in the field using thiourea, which was found to give a similar sensitivity to that of free sulfide. Samples were measured in duplicate. The concentration of hydrogen sulfide (H_2S) in the samples was estimated using the calculation described by Boyd (2014).

Cu speciation parameters (i.e. binding strength of the organic Cu-complexing ligands ($\log(K)$), concentration of organic ligands ($[L]$) and concentration of bioavailable Cu ($[Cu']$; sum of the concentration of free hydrated Cu ions ($[Cu^{2+}]$) and the concentration of Cu weakly bound to inorganic ligands ($[CuX_{IN}]$)) were determined using adsorptive cathodic stripping voltammetry (AdCSV) with salicylaldoxime as the complexing agent (Lucia *et al.* 1994; Kleint *et al.* 2015; Cotte *et al.* 2018) at the University of Otago on a Metrohm 663 VA stand (Metrohm Autolab B.V., Utrecht, Netherlands). A description of the instrumental set-up is given in Zitoun *et al.* (2018). Samples underwent pretreatment to remove acid volatile sulfides from the sample solutions, which enabled the electrochemical measurement of Cu' in sulfide-rich vent samples (Sander *et al.* 2007;

Kleint *et al.* 2015; Cotte *et al.* 2018). For comparison purposes, sample aliquots were measured before the acid pretreatment as well as after the acid pretreatment with subsequent filtration (0.2 μm) of the samples to remove potential metal precipitates formed during the pretreatment (Sander *et al.* 2007). For detailed information on removal of acid volatile sulfides, sample preparation and operating conditions of the instrument, see Sander *et al.* (2007) and Kleint *et al.* (2015). Samples were then analysed with the AdCSV method and every measurement was repeated three times. After completion of the titration, Cu speciation parameters of each sample were obtained using the one- or two-ligand complete complexation-fitting model incorporated in the ProMCC software (https://sites.google.com/site/mccprosece/download, accessed 14 August 2019; Omanović *et al.* 2010). Fitting of the titration data for a two-ligand-system failed with the ProMCC software, and thus samples were fitted to a one-ligand model.

Analysis of biological samples

Analysis of phytoplankton

Larger phytoplankton cells (>20 μm) of each station were counted and identified after the Utermöhl method in Utermöhl chambers (HYDRO-BIOS Apparatebau GmbH, Kiel-Altenholz, Germany) following procedures recommended in Karlson *et al.* (2011). An Accu-Scope inverted microscope (Olympus, Auckland, New Zealand) was used for counting. Phytoplankton was identified to genus level and down to species level when possible. Samples of small phytoplankton species (<20 μm) were analysed without the addition of preservative immediately after returning to the home laboratory at the University of Otago (within 10 days of sampling). Samples were analysed on an Accuri C6 (BD Biosciences, San Jose, CA, USA). Cryptophytes were identified and counted on the plots of phycoerythrin (PE) *v.* chlorophyll (CHL) fluorescence. After exclusion of this group, picoeukaryotes, nanoeukaryotes and coccolithophores were identified based on side scatter (SSC) *v.* CHL fluorescence. The different phytoplankton groups were identified as described in Tarran and Bruun (2015).

Analysis of zooplankton

Zooplankton samples of the three sampled sites were compared at the University of Auckland using a binocular microscope and a Bogoroy tray in a semiquantitative manner, identifying abundant (>10 individuals per sample) and rare categories of both holoplankton and meroplankton.

Analysis of coralline algae

Recent analysis of $\delta^{11}B$ has implied that these values can be used as proxies for determining pH in the fluid (pH_{cf}) where coralline algal calcite is formed (Cornwall *et al.* 2017*b*, 2018; Comeau *et al.* 2018). This finding enables us to understand how the vent systems can alter the calcification physiology of these species. Coralline algae collected around Whakaari were processed in the clean laboratory of the Advanced Geochemical Facility for Indian Ocean Research (AGFIOR), University of Western Australia). Sample analysis and preparation followed that of Cornwall *et al.* (2017*b*). Boron was quantitatively separated on ion exchange columns according to McCulloch

et al. (2014) and boron isotopes were subsequently measured using the NU Plasma II multicollector ICP-MS (Nu Instruments, Charlestown, MA, USA). Boron isotopes were transformed to pH_{cf} using the calculations of Trotter *et al.* (2011) assuming all primary boron uptake was as the borate species at a temperature of 17.5°C and salinity of 35.0.

Results

Water chemistry

Physicochemical parameters

Mean (±s.d.) temperature and salinity values obtained with the CTD XR 620 were $17.68 \pm 0.43°C$ and 34.39 ± 0.91 ppt (Fig. 3; Table 2) during the observation period with rough weather conditions. The highest mean temperatures were recorded at the vent shafts, followed by control sites and then vent 2-m sites. Mean salinities followed the order of control sites > vent 2-m sites > vent shafts (Fig. 3; Table 2). Temperature and salinity values showed some temporal variability of up to ±1.2°C and ±2.59 ppt at the vent sites. Calculated mean (±s.d.) sample pH_T for the control stations was consistent with normal present-day pH of seawater (8.06 ± 0.01), whereas vent fluids showed lower mean pH_T values of 7.43 ± 0.43 within the vents and 7.94 ± 0.25 at a distance of 2 m from the vent outflow (Fig. 3; Table 2). As expected, because of dilution and mixing processes of the vent fluid with seawater, calculated pH_T values commonly increased to ambient seawater pH levels with 2-m distance from the vent outflow. Calculated pH_T values showed some temporal variability of up to ±0.71 at the vent sites for samples taken on the same day ($n = 2$) and up to ±0.77 for samples collected on the two different sampling occasions (Fig. 3; Table 2). The temporal variability of pH_T and temperature is more obvious in the SeaFET data. It is worth noting that the CTD XR 620 data were collected during large swells, which possibly resulted in mixing around the sites where measurements were taken, whereas the SeaFET operated from 13 to 27 November under reasonably calm conditions.

The water temperature obtained with the SeaFET within V1 and V2 was consistently higher than at the vent control site (i.e. C4; Fig. 4*a*). On average, the water temperature at V1 and V2 was 1.19 and 0.95°C higher than at C4. Consistent with the CTD XR 620 data, temperature was most variable at V1, and this appears to be related to tidal height, with warmest temperatures within the vent consistently associated with low tide (Fig. 4*a*). Temperatures at V2 did not appear related to tidal height and were positively correlated with temperatures at C4 ($r^2 = 0.79$). Temperature at C4, and to a lesser extent at V2, exhibited diel variation, peaking between 1300 and 1700 hours and lowest from 0200 to 0700 hours (for more detail, see Fig. S1).

Seawater pH_T obtained with the SeaFET within the vents was highly variable and was, on average 0.54 (V2) and 1.19 (V1) pH units lower than seawater at C4 (Fig. 4*b*), which is consistent with the CTD XR 620 data. In addition, diel variation was evident at the two vents. Similarly, at C4 mean pH was 7.95 and showed periodic drops in pH to ~7.5. These drops in pH at C4 typically coincided with low tide, particularly at night-time. Overall pH at C4 was weakly correlated with pH at V1 and V2 ($r^2 = ~0.33$ and 0.38 respectively), but many of the large drops in pH at C4 coincided with drops in pH at the vents, suggesting

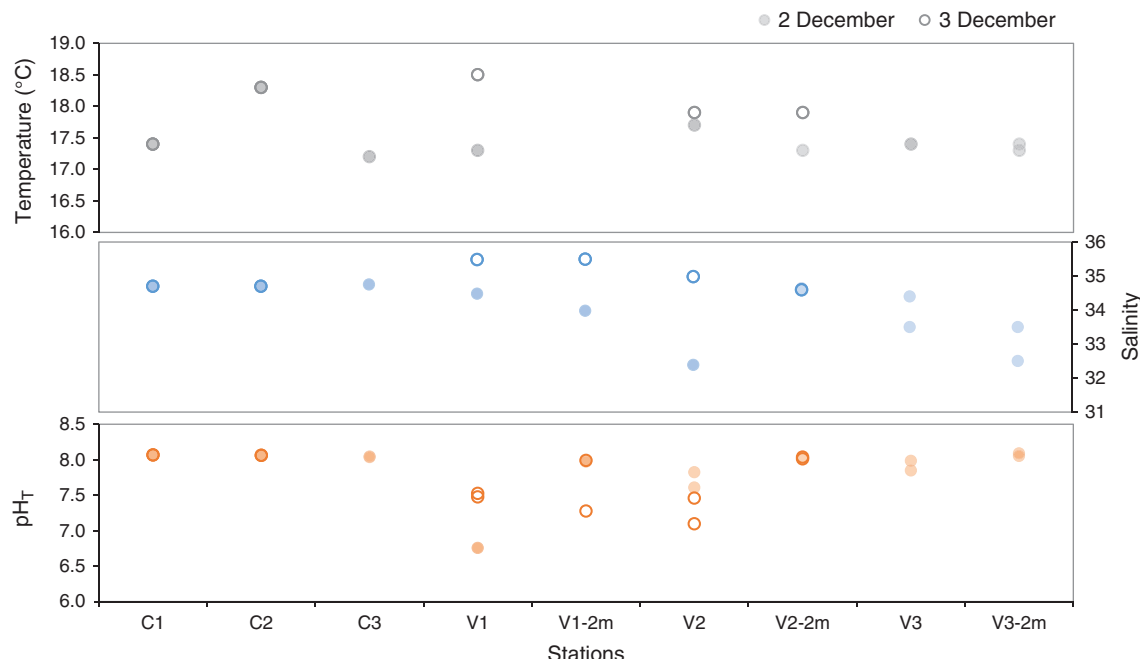**Fig. 3.** Temperature, salinity and seawater pH on the total scale (pH$_T$) values from nine stations around Whakaari–White Island in the Bay of Plenty, New Zealand. Salinity and temperature values are averaged readings (90 s) from the CTD XR 620 (RBR Ltd, Stadhampton, UK) and were used together with dissolved inorganic carbon and total alkalinity values to calculate pH$_T$ of each discrete sample using the refitted Mehrbach CO₂ equilibrium constants (Mehrbach *et al.* 1973; Dickson *et al.* 2007). Note that data were collected during a large swell, resulting in a lot of mixing around the sites where measurements were taken. There is no temperature data available for V1-2 m. Sample sites are shown in Fig. 2. V1, large vent site; V2, small vent site; V3, an active vent on the western side of White Island; '-2m', samples taken at a distance of 2 m from the vent outflow; C1, open ocean control; C2, White Island control; C3, Champagne Bay control.

some effect of the vents on pH at C4. The pH at V1 and V2 was more strongly correlated ($r^2 = 0.54$; Fig. 4*b*). Diel variation in pH was most evident at C4, with lowest pH between midnight and 0700 hours, a steady increase throughout the day and a decline after ~1700 hours (for more detail, see Fig. S1). Additional pH data collected at C3 and C4 suggested pH at C3 was consistently higher (typically >8), with less variation in pH than seen at C4 (Fig. S2). Drops in pH were evident at C3, but they were not as large as those observed at C4.

Nutrient concentrations in the study area were in the range of 0.29–11.66 µM for ammonium, 0.03–0.53 µM for NO$_x$ and 2.26–17.71 nM for phosphate. Ammonium and NO$_x$ concentrations decreased with distance from the vent outflow, following the order of vent fluids > vent 2-m sites > control sites, whereas phosphate concentrations followed the order of vent 2-m sites > vent fluids > control sites (Table 2).

Values of C$_T$, A$_T$ and pCO₂ declined from vent fluids to vent 2-m sites to control sites, whereas CO$_3^{2-}$ concentrations and Ω$_{calcite}$ and Ω$_{aragonite}$ levels increased along this gradient (control sites > vent 2-m sites > vent fluids). Carbonate chemistry samples collected with distance from the vent fluids (i.e. 2 m from V1, V2 and V3) did not differ significantly from data obtained at the control sites (C1, C2 and C3). Undersaturation with respect to aragonite was observed for V1 during both sampling periods and for V1-2m and V2 on 3 December. Values of Ω$_{calcite}$ < 1 were calculated for V1 on 2 December and for V1-2m and V2 on 3 December. Values of C$_T$, A$_T$, pCO₂, CO$_3^{2-}$ concentration,

Ω$_{calcite}$ and Ω$_{aragonite}$ suggest large temporal (i.e. samples taken on 2 and 3 December) and environmental (i.e. samples taken on the same day; $n = 2$) variability in the carbonate chemistry of the vent sites.

Total dissolved trace metals, Hg$_T$ and sulfide

Trace element and metal concentrations of Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb, Hg$_T$ and sulfide were between ~2 to 70 000-fold higher at all nine study sites than values commonly measured in open ocean seawater samples around New Zealand (TAN1604, Station CS19, depth 25 m, Hauraki Gulf; R. Middag, C. Stirling, M. Reid, and K. Seyitmuhammedov, unpubl. data; Table 3). Mn, Fe and Cs concentrations declined from vent fluids to vent 2-m sites to control sites, whereas Zn, Cu, Hg$_T$, Sr and Rb concentrations were in the order control sites > vent fluids > vent 2-m sites (Table 3). Concentrations of Ba, Li, Co, Pb and Ni were in the order vent fluids > control sites > vent 2-m sites, whereas sulfide concentrations were in the order vent 2-m sites > vent fluids > control sites (Table 3). Cd, Mo, and U concentrations were higher at the control sites, followed by vent 2-m sites and then vent fluids (Table 3). However, Li, Rb, Sr, Mo, Ba and U concentrations did not vary considerably between vent and control sites (difference between the maximum and minimum concentration <5%; Table 3). Concentrations of Ni, Zn, Cd, Pb, Co and Cu at all nine study sites at Whakaari were well below the Australian and New Zealand Environment and Conservation Council (2000) guidelines for a 95% level of protection for biota

Table 2. Physicochemical parameters from the sampling sites at Whakaari–White Island in the Bay of Plenty, New Zealand

Nutrient measurements are given as the mean ± s.d. ($n = 2$). Values for seawater pH on the total scale (pH_T) ($n = 2$) and carbonate chemistry parameters ($n = 2$) of the sampling sites are given as ranges. Salinity and temperature values are averaged readings (90s) from the CTD XR 620 (RBR Ltd, Stadhampton, UK) and were used together with dissolved inorganic carbon (C_T) and total alkalinity (A_T) to calculate pH_T and the carbonate chemistry parameters of each discrete sample using the refitted Mehrbach CO_2 equilibrium constants (Mehrbach *et al.* 1973; Dickson *et al.* 2007). Saturation states <1 are in bold and italic. Sample sites are shown in Fig. 2. –, not sampled or not enough sample for analysis; T, temperature; NO_x, nitrogen oxides; $\Omega_{aragonite}$, aragonite saturation state; $\Omega_{calcite}$, calcite saturation state; V1, large vent site; V2, small vent site; V3, an active vent on the western side of White Island; '-2m', vents sampled at a distance of 2 m from the vent outflow; C1, open ocean control; C2, White Island control; C3, Champagne Bay control; SW, surface water

Site	Date	T (°C)	Salinity	Ammonium (µM)	NO_x (µM)	Phosphate (nM)	pH_T	C_T (µmol kg⁻¹)	A_T (µmol kg⁻¹)	pCO_2 (µatm)	$[CO_3^{2-}]$ (µmol kg⁻¹)	$\Omega_{aragonite}$	$\Omega_{calcite}$
C1	3 Dec. 15	18.3	34.7	0.29 ± 0.02	0.30 ± 0.02	10.53 ± 4.44	8.06–8.07	2058.0–2058.8	2309.8–2312.0	372.5–285.8	180.3–181.5	2.79–2.83	4.32–4.37
C2	2 Dec. 15	17.4	34.7	0.71 ± 0.42	0.03 ± 0.03	15.42 ± 0.16	8.06–8.08	2062.9–2067.6	2312.5–2314.8	372.5–385.8	176.1–180.7	2.72–2.79	4.21–4.32
C3 SW	3 Dec. 15	–	–	0.40 ± 0.08	0.09 ± 0.03	2.26 ± 1.73	–	–	–	–	–	–	–
C3	2 Dec. 15	17.2	34.7	0.44 ± 0.06	0.23 ± 0.15	12.47 ± 1.21	8.04–8.05	2079.7–2081.3	2312.1–2317.7	403.1–409.9	168.1–170.8	2.59–2.63	4.01–4.08
V1	2 Dec. 15	17.3	34.5	11.66 ± 0.13	0.53 ± 0.04	17.51 ± 4.98	6.76	2586.0–2591.3	2249.4–2280.1	9328.9–10015.9	9.4–10.4	***0.15–0.16***	***0.23–0.25***
V1	3 Dec. 15	18.5	35.5	–	–	–	7.48–7.53	2252.8–2274.9	2292.6–2299.4	1520.43–1714.7	55.9–61.8	***0.86–0.95***	1.33–1.47
V1-2m	2 Dec. 15	–	–	0.66 ± 0.06	0.27 ± 0.15	15.19 ± 3.06	7.97–8.00	2080.7–2091.9	2315.0–2315.4	462.7–492.4	164.5–171.9	2.58–2.69	3.96–4.14
V1-2m	3 Dec. 15	–	–	–	–	–	7.28–8.00	2086.4–2319.4	2283.1–2314.9	465.6–2763.9	37.0–166.1	***0.57–2.56***	***0.88–3.95***
V2	2 Dec. 15	17.7	32.4	–	–	–	7.61–7.83	2193.8–2424.5	2323.2–2480.6	634.8–1351.5	73.1–107.5	1.14–1.68	1.77–2.61
V2	3 Dec. 15	17.9	35.0	2.20 ± 0.04	0.18 ± 0.01	5.97 ± 5.08	7.10–7.46	2319.1 – 2435.0	2322–2334.1	1816.2–4298.9	23.6–52.9	***0.36–0.82***	***0.56–1.26***
V2-2m	3 Dec. 15	17.3	34.6	–	–	–	8.03[A]	2086.5[A]	2315.8[A]	417.3[A]	166.5[A]	2.57[A]	3.98[A]
V2-2m	3 Dec. 15	17.9	34.6	–	–	–	8.01–8.04	2077.2–2090.3	2313.2–2314.0	2313.2–2314.0	162.6–171.4	2.51–2.65	3.89–4.1
V3	2 Dec. 15	17.4	34.4	0.32 ± 0.05	0.17 ± 0.04	15.46 ± 5.67	7.85–7.98	2134.3–2212.7	2334.8–2360.4	484.9–693.7	118.3–150.0	1.82–2.32	2.83–3.61
V3-2m	2 Dec. 15	17.3	32.5	0.79 ± 0.01	0.36 ± 0.05	17.71 ± 6.60	8.05–8.09	2079.3–2088.7	2322.6–2324.9	364.7–399.3	170.6–179.1	2.64–2.79	4.11–4.34

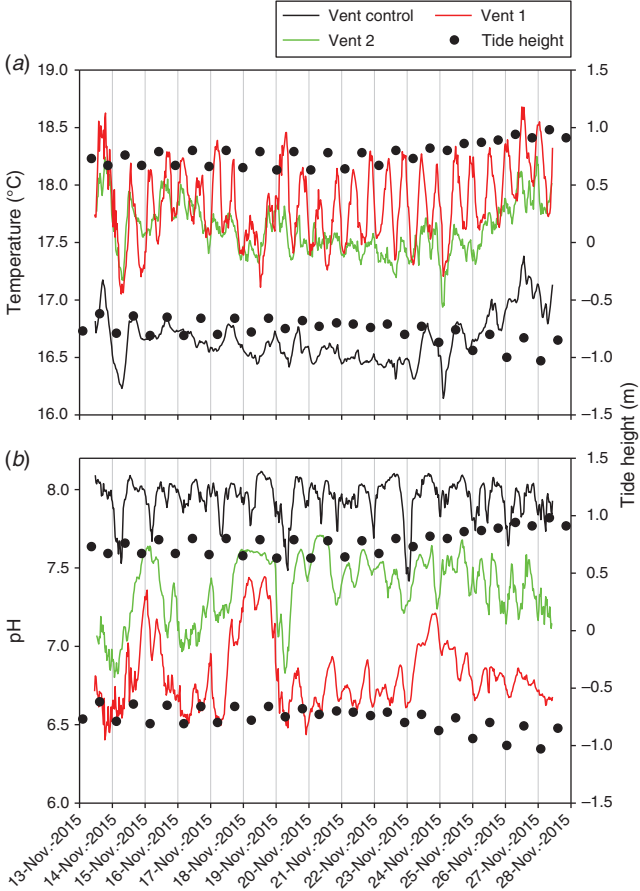[A]Sampling sites with $n = 1$.

Fig. 4. Variation in (*a*) seawater pH on the total scale (pH_T) and (*b*) temperature of seawater in the CO_2 vents sampled (V1, large vent site; V2, small vent site) and the nearby 'vent control' (C4) at Champagne Bay, White Island (New Zealand) in November 2015, obtained using SeaFET pH sensors (Sea Bird Scientific). Black dots show the timing and height of high and low tides.

in saltwater systems, whereas the concentration of Hg_T far exceeded the guideline threshold by up to two orders of magnitude (Table 3).

Copper speciation

Titration data demonstrated the presence of one ligand class with uniform Cu-binding capacities ($\log(K)$) of 11.9 ± 0.2 (mean ± s.d.) for sulfide-containing samples and 12.6 ± 0.6 for sulfide-free samples (Table 4). Ligand concentrations ([L]) were higher in the sulfide-containing vent samples (i.e. V1, V2 and V1-2m; Table 3), before the pretreatment compared with [L] in pretreated samples (Table 4). By contrast, the change in [L] between the untreated and pretreated control sample (C3) that had fairly moderate sulfide concentrations was negligible. This trend highlights the important role of sulfide as an inorganic ligand around the CO_2 vents at Whakaari.

In pretreated samples, mean (±s.d.) [L] ranged from as low as 3.9 ± 0.9 nM for the V1-2m station to 29.4 ± 8.4 nM for the C3 station. The highest [L] was found at C3, followed by V1, V2 and then V1-2m. At V1, [L] decreased with distance from the

Table 3. Total dissolved trace metal and element concentrations for the nine sites sampled around Whakaari–White Island in the Bay of Plenty, New Zealand

Total mercury and sulfide are presented as the mean ± s.d. of sample duplicates ($n = 2$). Metal and element values of an open ocean seawater sample (TAN1604, Station CS19, depth 25 m, Hauraki Gulf, New Zealand; R. Middag, C. Stirling, M. Reid, and K. Seyitmuhammedov, unpubl. data), including s.d., and the Australian and New Zealand Environment and Conservation Council (2000) trigger values for toxicants at a 95% level of protection in marine waters were added for comparison purposes. The open ocean seawater sample TAN1604 – CS19 (–34°48.40, 175°45.31) was collected during a cross-shelf transect from the Hauraki Gulf to the open ocean (north-eastern New Zealand) during a cruise led by the National Institute for Water and Atmospheric Research (NIWA) on the *RV Tangaroa* in April 2016 (Middag *et al.*, unpubl. data). Concentrations in bold and italic are enriched compared with the CS19 sample, whereas non-formatted values are impoverished relative to the CS19 sample. Underlined values are above the Australian and New Zealand Environment and Conservation Council (2000) 95% trigger value. Hydrogen sulfide concentrations (H₂S) were estimated from the sulfide concentrations following Boyd (2014). Sample sites shown in Fig. 2. –, not sampled or not enough sample for analysis; *, insufficient data to derive a reliable trigger value (Australian and New Zealand Environment and Conservation Council 2000); #, sample was analysed with a 1-day delay and thus may not be representative owing to potential oxidation processes; V1, large vent site; V2, small vent site; V3, an active vent on the western side of White Island; '-2m', vents sampled at a distance of 2 m from the vent outflow; C1, open ocean control; C2, White Island control; C3, Champagne Bay control; SW, surface water; HgT, total mercury

Element	C1	C2	C3 SW	C3	V1	V1-2m	V2	V3	V3-2m	TAN1604 CS19	ANZECC 95%
Mn (nM)	*36.05*	*20.55*	*31.45*	*26.78*	*99.31*	*29.33*	*79.07*	*168.57*	*31.16*	0.87 ± 0.27	*
Fe (nM)	*34.47*	*11.83*	*26.59*	*14.64*	*125.18*	*24.41*	*34.31*	*175.24*	*29.94*	0.23 ± 0.01	*
Co (nM)	*0.13*	*0.08*	*0.18*	*0.10*	*0.39*	*0.14*	*0.09*	*0.11*	*0.09*	0.0062 ± 0.0004	16.97
Ni (nM)	*4.62*	*4.54*	*4.57*	*4.69*	*6.64*	*3.62*	*5.05*	*5.22*	*4.50*	2.23 ± 0.08	1192.30
Cu (nM)	*1.83*	*1.01*	*3.13*	*1.72*	*2.04*	*0.82*	*1.29*	*1.74*	*1.11*	0.39 ± 0.02	20.46
Zn (nM)	*5.29*	*5.24*	*7.04*	*18.19*	*7.71*	*6.62*	*7.61*	*10.07*	*6.92*	0.44 ± 0.04	229.46
Cd (nM)	*0.03*	*0.02*	*0.04*	*0.23*	*0.02*	*0.05*	*0.02*	*0.06*	*0.03*	0.0026 ± 0.0001	48.93
Pb (nM)	*0.03*	*0.03*	*0.06*	*0.23*	*0.13*	*0.04*	*0.13*	*0.25*	*0.06*	0.0174 ± 0.0007	21.24
HgT (pM)	*80.3 ± 3.5*	*97.7 ± 2.5*	*664.0 ± 49.4*	*72.8 ± 5.1*	*283.7 ± 8.0*	*189.1 ± 16.5*	*263.1 ± 20.9*	*83.5 ± 6.4*	*82.0 ± 1.1*	<1.5[A]	1.99
Sulfide (nM)	*7.2 ± 0.1*	*400.0 ± 17.2*	*1.7 ± 0.9*	*200 ± 9.1#*	*6957.0 ± 146.0*	*138.8 ± 11.8*	*24.0 ± 0.8*	*0.0*	*3.1 ± 0.1*	0.1[B]	*
H₂S (nM)	0.7 ± 0.1	41.0 ± 1.8	0.2 ± 0.1	20.5 ± 0.9#	5021.6 ± 105.4	13.4 ± 1.1	6.2 ± 0.2	0.0	0.3 ± 0.01	–	*
Li (µM)	–	25.28	27.24	26.57 ± 0.23	28.66 ± 5.89	27.36	28.15	23.68	24.49	–	*
Rb (µM)	–	1.27	1.32	1.24 ± 0.10	1.14 ± 0.11	1.13	1.09	1.32	1.27	–	*
Sr (µM)	–	90.47	95.81	93.93 ± 9.12	88.54 ± 9.24	76.76	83.23	89.32	95.61	–	*
Mo (nM)	–	120.87	123.85	120.12 ± 10.12	111.59 ± 14.30	105.61	101.23	123.71	123.59	–	*
Cs (nM)	–	2.30	3.63	3.17 ± 0.04	3.69 ± 0.13	3.44	5.89	5.55	2.97	–	*
Ba (nM)	–	34.69	31.49	31.17 ± 0.67	31.76 ± 0.32	30.96	33.14	34.96	30.84	–	*
U (nM)	–	13.20	13.44	12.91 ± 0.44	11.84 ± 1.45	12.33	12.12	13.51	13.44	–	*

[A] Value from Lamborg *et al.* (2014) and Gworek *et al.* (2016).
[B] Value from Radford-Knęry and Cutter (1994).

vent outflow (Table 4), which appears reasonable considering prevailing fluid–seawater mixing and dilution processes. [L] after the pretreatment was always in excess of the total dissolved Cu concentration ([Cu$_T$]; Tables 3, 4), with the consequence that [Cu^{2+}] was low in the sampling area. Bioavailable Cu concentrations ([Cu′]) ranged from 0.6 to 2.6 pM, with highest [Cu′] found at C3, followed by V2, V1-2m and then V1.

Biological samples

Phytoplankton community

The larger phytoplankton community in the working area was reasonably similar and showed no major differences in either cell concentrations or the number of phytoplankton species between the vent and control sites in the direct vicinity of Whakaari (Fig. 5; Table 5). However, the number of larger phytoplankton species at C1, halfway between White Island and the main coast, was approximately half that of all other sites close to Whakaari (12 *v.* 21–30; Table 5).

Further, there were distinct differences in the relative phytoplankton composition of the larger phytoplankton community around Whakaari, with diatoms accounting for 42.9–73.9% of the phytoplankton community at sites in the direct vicinity of Whakaari (i.e. C2, C3 SW, V1 and V3-2m), but only 2.65% at C1 (Fig. 5). At the same time, the relative contribution of dinoflagellates and flagellates to the larger phytoplankton community was fairly stable (at 24.0–39.6 and 0.5–7.5% respectively) in the whole working area (Fig. 5).

At C1, total cell numbers for large phytoplankton were up to twofold higher compared with stations around the island (Table 6). At the same time, at C1 we found less than half the large phytoplankton species compared with the Whakaari stations (Table 5). A large difference was again observed for heterotrophic plankton species, which accounted for 60.0% of total cell numbers at C1 but for only 12.0–22.2% at the four sites (C2, V3-2m, V1 and C3 SW; Fig. 5) in the direct vicinity of Whakaari.

The picoeukaryote species (i.e. small phytoplankton groups), as identified by flow cytometry, showed a similar trend, with total cell numbers being approximately twofold higher and only three groups of picoeukaryotes identified at C1 compared with four

groups of picoeukaryotes identified at the four sites in the direct vicinity of Whakaari (Fig. 5; Table 6). In addition, the picoeukaryote community showed differences in relative group composition. Although four distinct groups could be identified by
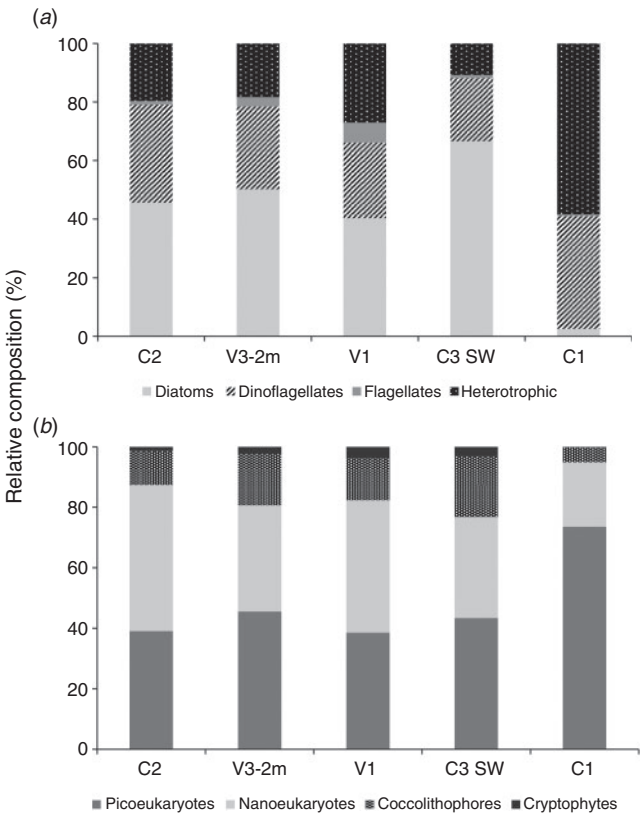

Fig. 5. Relative composition of (*a*) phytoplankton species >20 μm and heterotrophic dinoflagellates and (*b*) the different small phytoplankton groups identified by flow cytometry at the five stations at Whakaari–White Island in the Bay of Plenty, New Zealand. Sample sites are shown in Fig. 2. V1, large vent site; V3-2m, an active vent on the western side of White Island, sampled at a distance of 2 m from the vent outflow; C1, open ocean control; C2, White Island control; C3 SW, Champagne Bay control surface water.

Table 4. Copper speciation parameters for four stations sampled at Whakaari–White Island in the Bay of Plenty, New Zealand

Cu speciation parameters were computed using the complete complexation-fitting model embedded in the ProMCC software (D. Omanović, Ruđer Bošković Institute, Center for Marine and Environmental Research, Laboratory for Physical Chemistry of Traces, Zagreb, Croatia; Omanović *et al.* 2010). Ligand concentrations ([L]) and conditional stability constants (log(*K*)) are shown for samples before and after the acid pretreatment (PT) to remove acid volatile sulfides (AVS) in the sample solutions. The errors for [L] and log(*K*) values are the fitting errors of the complete complexation-fitting model used to calculate Cu speciation parameters in the ProMCC software. Sample sites are shown in Fig. 2. [CuX$_{IN}$], concentration of inorganic Cu complexes; [Cu^{2+}], free Cu ion concentration; [Cu′], bioavailable Cu concentration (sum of [CuX$_{IN}$] and [Cu^{2+}]); C3, Champagne Bay control; V1, large vent site; V1-2m, vent 1 sampled at a distance of 2 m from the vent outflow; V2, small vent site

Site	Before AVS PT		After AVS PT		[CuX$_{IN}$] (pM)	[Cu^{2+}] (pM)	[Cu′] (pM)
	[L] (nM)	log(*K*)	[L] (nM)	log(*K*)			
C3	33.6 ± 8.8	12.0 ± 0.2	29.4 ± 8.4	11.8 ± 0.2	2.52	0.1	2.62
V1	30.5 ± 4.0	11.9 ± 0.2	6.9 ± 1.1	13.2 ± 0.2	0.61	0.03	0.64
V1-2m	18.2 ± 5.2	11.6 ± 0.2	3.9 ± 0.9	12.8 ± 0.2	0.97	0.04	1.01
V2	13.0 ± 1.9	11.9 ± 0.1	5.8 ± 1.8	12.5 ± 0.3	2.2	0.09	2.28

flow cytometry at the four sites close to Whakaari, with picoeukaryotes accounting for 38.6–45.5%, nanoeukaryotes accounting for 33.4–48.3%, coccolithophores accounting for 11.2–20.0% and cryptophytes accounting for 1.4–3.8%, only three groups were identified at C1 (Fig. 5). At C1, picoeukaryotes clearly dominated the small phytoplankton community (accounting for 73.6%), whereas nanoeukaryotes and coccolithophores accounted for 21.2 and 5.2% respectively.

Zooplankton community

The zooplankton samples of C1 were more than 20-fold the volume of samples collected at the two stations close to Whakaari (C3 and V1) because of the dominance of salps. Calanoid copepods and pericarid larvae were the dominant zooplankton component at C1 (Table 7). Zooplankton samples collected in the direct vicinity of White Island (C3 and V1) contained the same abundant taxa as C1 within a very small plankton volume (<5 mL), with a slightly higher diversity of meroplankton (Table 7). Overall, there was no compositional difference in the abundant zooplankton taxa between vent and control sites.

Benthic algae, especially corallines

Articulate and crustose coralline algae were present in reasonably high abundances at Whakaari, both near active venting locations (i.e. V1 and V2) and control locations (i.e. C2; C. Cornwall, pers. obs.). The articulate coralline alga *C. officinalis* maintained a mean (±s.d.) pH$_{cf}$ of 8.66 ± 0.04

Table 5. Number of phytoplankton species >20 µm, Shannon diversity index (H) and Shannon equitability index (E) for the five stations sampled at Whakaari–White Island in the Bay of Plenty, New Zealand
Sample sites are shown in Fig. 2. V1, large vent site; V3-2m, an active vent on the western side of White Island, which was sampled at a distance of 2 m from the vent outflow; C1, open ocean control; C2, White Island control; C3 SW, Champagne Bay control surface water

Site	Number of species	H	E
C1	12	1.30	0.11
C2	21	2.31	0.12
C3 SW	28	2.76	0.10
V1	30	2.78	0.09
V3-2m	26	2.65	0.12

Table 6. Total cell numbers for phytoplankton species >20 µm and heterotrophic dinoflagellates as identified by microscopy and total cell numbers for picoeukaryotes (small phytoplankton) as identified by flow cytometry (duplicate measurements) at the five sampling stations at Whakaari–White Island in the Bay of Plenty
Sample sites are shown in Fig. 2. V1, large vent site; V3-2m, an active vent on the western side of White Island, sampled at a distance of 2 m from the vent outflow; C1, open ocean control; C2, White Island control; C3 SW, Champagne Bay control surface water

Site	Heterotrophic dinoflagellates (cells mL^{-1})	Phytoplankton (cells mL^{-1})	Picoeukaryotes (cells mL^{-1})
C1	66.58	44.44	4699.387–5699.387
C2	5.36	18.80	2104.294–2108.571
C3 SW	3.24	28.68	2024.540–2122.699
V1	12.80	31.64	1797.546–2226.994
V3-2m	6.22	24.64	2570.552–3079.755

Table 7. Summary of abundant (>10 individuals per sample) and rare (0–10 individuals per sample) zooplankton taxa at three stations sampled at Whakaari–White Island in the Bay of Plenty, New Zealand
Note that the White Island vent sample (V1) was contaminated with large amounts of benthic material that is not recorded in the table. Zooplankton taxa were classed into abundant and rare categories based on three replicate samples. Dominant taxa are shown in bold. Sample sites are shown in Fig. 2. C1, open ocean control; C3, Champagne Bay control; V1, large vent site

Site	Plankton sample volume (mL)	Holoplankton		Meroplankton	
		Abundant	Rare	Abundant	Rare
C1	106	**Salps**	Chaetognath	Pericarid larvae	Mysid larvae
	208	**Calanoid Copepod**	Doliolid		
	172	Cyclopoid Copepod	Hydrozoan medusae		
			Ctenophore		
			Amphipod		
C3	<5	**Calanoid Copepod**	Oikopleura		Mysid larvae
	<5	Cyclopoid Copepod	Chaetognath		Fish egg
	<5	Salps	Harpacticoid copepod		Crab larvae
			Amphipod		
V1	<5	**Calanoid Copepod**	Hydrozoan medusae		Ascidian tadpole
	<5	Cyclopoid Copepod			Fish egg
	<5	Salps			Polychaete nectochaete

at the venting site and 8.75 ± 0.07 at the control site. *A. anceps* had a mean ($\pm$s.d.) pH_{cf} of 8.67 ± 0.06 at the control site, but was unfortunately not sampled at the vent location (Table S3). Although pH_{cf} is affected by external seawater pH, it was still elevated at the venting location.

Discussion

Even though shallow submarine CO_2 vents are not exact analogues of future ocean conditions, they are commonly used as the best natural settings to investigate community composition shifts and ecosystem-scale effects of OA, over long timescales (Hall-Spencer *et al.* 2008; Fabricius *et al.* 2011; Pichler *et al.* 2019). The suitability of the unique rocky coastal temperate submarine CO_2 vents around Whakaari–White Island in the Bay of Plenty (New Zealand) as a 'living laboratory' for OA science is discussed below. However, it has to be noted that the research findings of this study are limited by the short sampling period and the low sampling resolution, which prohibited statistical analysis. These limitations add a level of uncertainty to data interpretation.

Overall water chemistry

Physicochemical parameters

At Whakaari–White Island, vent sites were strongly influenced by the tides and the volcanic CO_2 seeps resulting in localised acidification of seawater (i.e. decreased mean pH_T), large pH_T fluctuations and a mean decrease in $\Omega_{calcite}$ and $\Omega_{aragonite}$ relative to control sites (Fig. 3, 4; Table 2). In the proximity of the vents (i.e. V1, V2 and V3), pCO_2 levels were high, ranging between 484 and 10015 µatm, and calculated seawater pH_T values were constantly lower than 7.98, which are projected average global sea surface pH values for the year 2100 and beyond (e.g. Caldeira and Wickett 2003; Gattuso and Lavigne 2009). As a result, $\Omega_{calcite}$ and $\Omega_{aragonite}$ at the vent sites (V1 and V2) substantially decreased to values <1, producing progressively lower saturation states for prevalent calcifying organisms. In addition, the water temperature at V1 and V2 was consistently higher than at the control site C4 (Fig. 4*a*), which makes the White Island CO_2 vents also useful analogues for the effect of ocean warming on marine biota (González-Delgado and Hernández 2018). As expected, the effects of volcanic vent emissions on pCO_2, pH_T and carbonate chemistry drop off quickly with distance from the vent outflow (Brinkman and Smith 2015; Pichler *et al.* 2019), creating close to ambient seawater conditions for biota at a distance of 2 m from the active vent sites on the dates sampled for this study during rough weather.

Even though the SeaFET data of Whakaari demonstrate a well-mixed water column during the 'White Island Blitz' due to the large swell (Fig. S2), pH_T values and other carbonate chemistry parameters still showed large temporal variability at the vent sites during the 3-day sampling trip (Table 2). SeaFET data taken during an earlier study in the working area in November 2015 (see Fig. 4, S2) show more intense sudden changes, extreme variations and irregular fluctuations in pH_T at Champagne Bay, which is in accordance with pH data recorded at other CO_2 vent settings off Ischia (Italy; Kerrison *et al.* 2011) and Ambitle Island (Papua New Guinea; Pichler *et al.* 2019). This variability is typical for dynamic CO_2 vent systems that can

undergo short-term changes in physicochemical conditions due to changes in geological conditions (e.g. German and Von Damm 2003), volcanic activity (Chiodini *et al.* 2006), discharge rates, chemical composition of hydrothermal fluids and gases (Pichler *et al.* 2019) and hydrodynamic conditions (i.e. tidal cycle, storms, wind, stratification, currents) of the surrounding water column. Hence, as suggested by Pichler *et al.* (2019), it is important to describe hydrothermal study sites using either continuous or multiple discrete measurements over time of abiotic parameters (i.e. temperature, salinity, pH, C_T, A_T, pH_T, pCO_2, $[CO_3^{2-}]$, $\Omega_{calcite}$ and $\Omega_{aragonite}$) to better quantify means and variability, as well as to account for short-term fluctuations that can affect the biological responses of prevalent biota. This is particularly important for calcifying organisms when undersaturated conditions for aragonite and calcite continue for a long time, affecting their calcification rates and acid–base regulation processes in the absence of protective mechanisms (Fabry *et al.* 2008). However, the biological implications of natural physical and chemical fluctuations for flora and fauna adjacent to vent sites are so far scarce (e.g. Kerrison *et al.* 2011), and their effects are difficult to reproduce in laboratory experiments (Rivest *et al.* 2017). Nevertheless, with seawater pH, temperature and pCO_2 variability expected to intensify in the future global ocean, considerations of the natural environmental variability of abiotic parameters are essential to understand species susceptibilities to future ocean conditions and to predict future organism responses at physiological, ecological and evolutionary levels.

In the marine environment, nitrogen and phosphorous are important nutrients affecting primary production, aquatic plant growth and the community composition of phytoplankton, macroalgae and vascular plants (e.g. Ngatia *et al.* 2019). The Redfield ratio (N : P) in the working area of Whakaari ranged between 31 and 695, and was thus above the optimal N : P ratio for marine biota of 16 (Redfield *et al.* 1963). However, an N : P ratio >16 suggest a P limitation of the study area (Redfield *et al.* 1963). The Australian and New Zealand Environment and Conservation Council (1992) recommends that marine (coastal) nitrogen and phosphorus concentrations should not exceed PO_4-P values of 10 µg L^{-1}, and NO_3-N values of 60 µg L^{-1}, and should not fall short of NH_4-N values of 5 µg L^{-1} to prevent adverse effects on the ecosystem (i.e. eutrophication leading to hypoxia and anoxia, reduced water quality, changes in food web structure, habitat degradation, loss of biodiversity and noxious and harmful algal blooms; Ngatia *et al.* 2019). All nutrient samples measured around Whakaari– White Island were within these Australian and New Zealand Environment and Conservation Council (1992) guidelines, suggesting that the nutrient composition of the study area is suited to the requirements of prevalent biota.

Total dissolved trace metals, Hg_T and sulfide

Elements are naturally present in seawater and are either enriched or impoverished in hydrothermal fluids relative to their background content in ambient seawater (e.g. German and Von Damm 2003; Tarasov 2006; Kleint *et al.* 2015; Pichler *et al.* 2019). The main processes affecting the concentration, speciation and bioavailability of elements in the water column around CO_2 vents are precipitation as sulfides, sediment resuspension, complexation with ligands and biological uptake (e.g. Bruland *et al.*

2014; Sander and Koschinsky 2011). Therefore, the enrichment of trace metals in the hydrothermal fluids of the working area relative to their concentrations in open ocean seawater samples around New Zealand (TAN1604, Station CS19, depth 25 m, Hauraki Gulf; R. Middag *et al.*, unpubl. data; Table 3) may be explained by ligand complexation, which stabilises dissolved metals in solution, or by the resuspension of metal-rich sediments within the dynamic Taupo Volcanic Zone (Sarano *et al.* 1989). Zn, Cu, Cd, Sr, Rb, Mo, U and Hg$_T$ concentrations were highest at the control sites, suggesting a terrestrial input of these metals, whereas Ba, Cs, Li, Mn, Fe, Ni, Pb and Co concentrations were highest at the vent shafts, which hints towards a hydrothermal source of these metals. However, Li, Rb, Sr, Mo, Ba and U concentrations were quite uniformly mixed in the working area due to the large swell experienced during sampling, which high-lights the difficulties in finding suitable control sites in the Bay of Plenty, at least during bad weather conditions. Because sulfide is a common low-temperature product of hydrothermal activity (Boatta *et al.* 2013), we expected enriched sulfide concentrations in the working area, except for V3, particularly because Whakaari has large terrestrial sulfur deposits (Nairn *et al.* 1996). Future studies are needed to assess bioaccumulation and the importance of biological uptake of these elements and metals in the working area.

Some trace metals, such as Mn, Fe, Co and Zn, are essential elements for the metabolism of organisms, whereas other metals, such as Cd, Pb and Hg, have no biological function and are entirely toxic to marine organisms, even at low con-centrations (Rainbow 2002; Jakimska *et al.* 2011; Tercier-Waeber *et al.* 2012), or, in the case of Cu, are both essential and toxic depending on the concentration (Bruland *et al.* 1991; Kleint *et al.* 2015). Concentrations of Zn, Cu, Co, Cd, Pb and Ni around Whakaari were well below the Australian and New Zealand Environment and Conservation Council (2000) guide-lines for a 95% level of protection for biota in saltwater systems, whereas the concentration of Hg$_T$ far exceeded the guideline threshold at all sites, including the open ocean control site C1 ~40 km away from White Island, by up to two orders of magnitude. High Hg concentrations around White Island were also reported by Brinkman and Smith (2015). As a result of the high Hg$_T$ concentrations in the water column around White Island, there is a risk of its accumulation in aquatic organisms, which is not only a threat for the organisms themselves, but also a concern for human health following the consumption of locally caught seafood from this area (e.g. Mousavi *et al.* 2011; Gworek *et al.* 2016). However, understanding Hg toxicity requires an understanding of its speciation, because different forms of Hg are variously toxic to aquatic biota and humans (Mousavi *et al.* 2011). In light of addressing the toxicological concerns of Hg around White Island, future studies need to investigate the occurrence and speciation of Hg at the vent sites, and quantify the degree of methylation and the adsorption and accumulation levels of Hg in local biota. Owing to bioaccumu-lation, the more toxic organic Hg species are usually elevated in higher trophic levels of fish, which may be a concern for human health at this popular recreational fishing spot. Similarly, macroalgae accumulate contaminants in proportion to their environmental concentrations (e.g. Karthick *et al.* 2012), and thus future studies could include macroalgae to monitor and

characterise the status of environmental risk and water quality in the shallow waters around Whakaari.

Trigger values for Li, Rb, Sr, Mo, Cs, Ba, U, Mn, Fe and sulfide are not given in the Australian and New Zealand Environment and Conservation Council (2000) guidelines. However, H$_2$S is a known toxicant in the marine environment because it imposes severe respiratory stress to aquatic biota even at low concentrations, and thus affects the health, survival, productivity and distribution of various organisms (Jahn and Theede 1997; Boyd 2014). HS$^-$ anions may also contribute to toxicity at high sulfide concentrations (Jahn and Theede 1997; Boyd 2014), whereas S^{2-} ions are not an issue because they only occur in the water column at pH values >12 (Boyd 2014). The 96-h LC$_{50}$ values of H$_2$S to marine species range from 1.5 to 14.7 μM, but should not exceed 146.6 nM in aquaculture (Boyd 2014). According to these values, the water column around V1 is considered harmful for local biota. Nevertheless, vent organ-isms could be ecologically adapted to high sulfide concentra-tions in their environment (Dahms *et al.* 2018), but more research is needed to validate this assumption.

The elevated Hg$_T$ and sulfide concentrations, among other elements, found at the control sites, especially the open ocean control site C1, suggest that other sites in the Bay of Plenty are affected by extensive hydrothermal activity, which accords with earlier findings of Sarano *et al.* (1989) and Kleint *et al.* (2015). These two studies concluded that hydrothermal activity and element signatures are not confined to the vicinity of the White Island CO$_2$ vents, but result from the positioning of various other submarine CO$_2$ vents and gas seeps in the Bay of Plenty that extend along the whole Taupo Volcanic Zone (mainly between Whale Island and White Islands). Therefore, there are no 'real' experimental control sites in the Bay of Plenty with regard to the element and metal composition of the water column. However, there may be a possible bias in the hydrothermal element signature collected during the 'White Island Blitz' due to the influence of large swells, which likely magnified the spatial distribution of the elements in the water column around the working area. That is, if the regional context of water chemistry is to be understood, there is a need to understand the temporal variability of the element and metal composition in the Bay of Plenty during both calm and well-mixed periods.

For the shallow CO$_2$ vents around Whakaari sampled in this study, high amounts of Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb, Hg$_T$ and sulfide were observed, which could confound the effects of pCO$_2$ and low pH on the ecosystem in isolation. However, we emphasise that this study does not establish such confounding effects. We suggest that scientists should be cautious when relating ecosystem-scale effects and biological responses of prevalent biota along pH gradients in the working area to the unifactorial and direct effect of pH, because interactions with concurrent, multiple simultaneous stressors, including bioactive metals, high sulfide concentrations and fluctuation of carbonate chemistry, may occur (Boyd 2010; Vizzini *et al.* 2013; Chen *et al.* 2018; Dahms *et al.* 2018). Knowledge of whether these stressors will have synergistic, antagonistic or additive effects is limited because of the scarcity of published research, but multiple stressors have the potential to affect the environment of Whakaari at multiple scales (e.g. Ivanina and Sokolova 2015; Boyd *et al.* 2018). To progress an understanding of the

individual and interactive effects of these multiple stressors, both laboratory and field studies are needed so that the effects of these stressors on biotic responses can be understood when using vents as a natural laboratory for studying biotic responses to projections of future climate.

Copper speciation

Chemical speciation is the driving factor for understanding metal bioavailability and toxicity to marine organisms (Van Briesen *et al.* 2010). According to the literature (e.g. Morel 1983; Kozelka and Bruland 1998; Paquin *et al.* 2000), metal toxicity is primarily related to the labile inorganic metal fraction, consisting of free hydrated trace metal ions and trace metals weakly complexed to inorganic ligands, rather than the total dissolved metal concentration in a system. However, some forms of organically complexed metals are also considered bioavailable (Lorenzo *et al.* 2005; Semeniuk *et al.* 2015), but it is generally accepted that the labile inorganic metal fraction represents the most readily bioavailable, and thus toxic, form of metals to marine organisms. Organic ligands generally increase the stability and effective solubility of trace metals in the water column, and thereby decrease the biologically available metal fraction in the surrounding water and the metal toxicity to marine biota (e.g. Laglera and Van den Berg 2009; Bundy *et al.* 2015; Whitby *et al.* 2018).

The voltametric data of the present study demonstrated the presence of stable organic and inorganic (i.e. thiols and sulfide) Cu complexes in the hydrothermal vent fluids around Whakaari. Values of [L] in analysed samples were consistently in excess of the measured [Cu_T], suggesting that most of the Cu_T in the water column was complexed and stabilised by ligands ($\sim$99.9%), thereby reducing the concentration of the bioavailable free Cu^{2+} ion to optimal levels between Cu^{2+} deficiency ($\leq$10 fM; Peers *et al.* 2005; Maldonado *et al.* 2006; Annett *et al.* 2008; Amin *et al.* 2013; Jacquot *et al.* 2014) and Cu^{2+} toxicity ($>$1 pM; Brand *et al.* 1986) for prevalent marine microorganisms (Kiaune and Singhasemanon 2011; Tercier-Waeber *et al.* 2012). Further, [L] exceeded [Cu_T] and the [Cu_T] was significantly higher at C3 and the [L] followed that trend, which strongly hints towards an active biological ligand production by local biota to mitigate the toxic effects of elevated Cu^{2+} concentrations around C3. This theory is further supported by the mean $\log(K)$ value of 12.6 ± 0.6 for sulfide-free samples around Whakaari, because $\log(K)$ values in the range of 10–13 are predominantly attributed to marine-derived humic substances or thiols (Whitby *et al.* 2018) produced by bacteria (e.g. Shimotori *et al.* 2009; Romera-Castillo *et al.* 2011), decaying phytoplankton (e.g. diatoms; Lorenzo *et al.* 2007), mussel embryos (*Mytilus galloprovincialis*; Zitoun *et al.* 2018) and other microorganisms (e.g. *Synechococcus*, *Fucus vesiculosus* and *Emiliania huxleyi*; Brand *et al.* 1986; Moffett *et al.* 1990; Moffett and Brand 1996; Gledhill *et al.* 1999; Leal *et al.* 1999; Klevenz *et al.* 2012; Echeveste *et al.* 2018) during Cu^{2+} stress, which adds an additional cost for their fitness (e.g. growth, development and reproduction; Ivanina and Sokolova 2015) but provides an advantage when exposed to potentially harmful Cu loads. All in all, ligands play an important role in controlling the solubility, bioavailability and toxicity of Cu_T around the shallow CO_2 vents of White Island.

The active production of ligands may be a general survival strategy of prevalent biota around Whakaari, and some of these ligands may have binding affinities for multiple metals (Kogut and Voelker 2001) and thus ameliorate the potential toxicities of several free metal ions by the formation of metal–ligand complexes. As a result, the importance of ligands in the working area may not be confined to Cu, and may be conferred to other bioactive metals that are enriched in the water column, including Mn, Fe, Ni, Zn and Hg (e.g. Lamborg *et al.* 2003; Vraspir and Butler 2009; Oldham *et al.* 2015). Consequently, ligand complexation of bioactive metals around Whakaari may allow biota to tolerate otherwise toxic metal concentrations in their environment, and hence may play a critical role in shaping the environmental niches and survival strategies of vent organisms. Nevertheless, more speciation research is necessary to evaluate the importance of organic and inorganic ligands in lowering the lethal and sublethal effects of elevated metal concentrations, especially Hg, to the local communities around White Island.

Ecological responses
Phytoplankton and zooplankton

The phytoplankton community structure at all stations around Whakaari (including the control stations) was very similar, which is not surprising given the strong water mixing in the area. However, it was surprising to see higher absolute cell numbers and lower diversity of the phytoplankton community at C1, the control station further away from the island. The C1 station showed the lowest ammonia level and a moderate NO_x concentration, which could indicate that there has been elevated phytoplankton growth in this region for a longer time, resulting in the higher cell numbers and lower nutrient concentrations observed. The difference in phytoplankton biomass and diversity between the control station and all stations around the island could be caused by differences in concentrations of potentially toxic trace metals such as Hg, Pb and Cd (Thomas and Seibert 1977; Thomas *et al.* 1980; Tortell and Price 1996). The much higher relative concentration of diatoms around the island compared with C1 could be explained by the high ratio of Mn : Cd, Mn : Cu and Mn : Zn in the water column because all four metals are taken up by the same membrane uptake system in diatoms and high Mn concentrations are known to block the biological uptake of toxic metals (Sunda *et al.* 1981; Sunda and Huntsman 1996, 1998*a*, 1998*b*, 1998*c*). Therefore, diatoms are able to tolerate higher concentrations of toxic metals released by volcanic material that also release high Mn concentrations compared with other phytoplankton groups (Hoffmann *et al.* 2012). In addition, diatoms and coccolithophores are known to have a high metal tolerance because of the production of metal-binding ligands (e.g. Lorenzo *et al.* 2007; Echeveste *et al.* 2018). This statement is supported by our data, showing a greater [L] at C3 relative to V1 (Table 4) accompanied by a higher abundance of these two species at C3 SW (Fig. 5).

The zooplankton community showed parallel patterns to the phytoplankton, with a lower abundance at White Island compared with C1 in the Bay of Plenty. Chavtur (1992) also identified abundant holoplanktonic and meroplanktonic species at White Island with overlapping composition to the 'White Island Blitz' sampling (e.g. *Oikopleura* sp., calanoid and

cyclopoid copepods), but also noting lower densities compared with the Hauraki Gulf. In the present study, sampling at the vent and control sites focused on the water column, and thus future sampling could also include waters in the immediate vicinity of the vent outlets, where high numbers of harpacticoid copepods are found (Tarasov *et al.* 1986).

Macroalgae

The natural history of Whakaari–White Island is broadly typical of subtidal temperate rocky coasts of Australia (Connell and Irving 2008) and northern New Zealand (Shears and Babcock 2007). It comprises mosaics of kelp (*E. radiata*), infrequent and small patches of turf-forming macroalgae (<10 cm in height) and urchin barrens (i.e. hard substratum sea urchin barrens devoid of vegetation). Turf-forming algae at the vents appear to be more productive and have a greater biomass at vents (Connell *et al.* 2017), which is comparable to algae raised under similar conditions in controlled laboratory and mesocosm experiments (Connell and Russell 2010; Connell *et al.* 2013). Such concurrence between experimental field and laboratory observations across a wide variety of conditions provides the kind of investigative approaches needed to illustrate CO$_2$ as a driver of ecological responses in nature (Connell *et al.* 2013). The most conspicuous herbivores were damselfishes (*Parma alboscapularis*) and sparse densities of urchins common to Australia (*Centrostephanus rodgersii*) and moderate densities of urchins common to New Zealand (*Evechinus chloroticus*; Connell *et al.* 2018; Ferreira *et al.* 2018). Where a species has a positive association with turfs, its density can be substantially greater near vents (Connell *et al.* 2017). It is worth noting that the differences between these biological studies and the present study may be due to the fact that the studies were conducted in different locations, with the biological studies done at greater distances from vents (~25 m) than the sampling undertaken in the present study (i.e. within the vent fluids and 2 m from the vents).

Coralline algae

Evidence supports the hypothesis that those coralline algae that are capable of regulating pH at the site of calcification in their internal calcifying fluid (pH$_{cf}$) under OA demonstrate more robust responses to lower pH conditions (Cornwall *et al.* 2017*b*). The articulate coralline alga *C. officinalis* maintained mean (±s.d.) pH$_{cf}$ of 8.66 ± 0.04 at the venting site and 8.75 ± 0.07 at the control site. Although pH$_{cf}$ is affected by external seawater pH, it is still elevated at the venting location relative to the surrounding seawater. The capacity of *C. officinalis* to maintain elevated pH in the calcifying fluid under OA could explain why this species of coralline algae is still in such high abundance near the high-CO$_2$ locations at Whakaari. This mechanism of resistance could enable some species of coralline algae to persist in the future under OA, despite past conclusions that they are, in general, among the most susceptible taxa to OA (Fabricius *et al.* 2011).

Articulate and crustose coralline algae were present in seemingly high abundances at Whakaari, both near active venting sites and at control sites. This is in contrast with other vents sites studied off Vulcano (Italy; Cornwall *et al.* 2017*a*), Ischia Island (Italy; Hall-Spencer *et al.* 2008) and Milne Bay

(Papua New Guinea; Fabricius *et al.* 2015), where coralline algae are nearly absent. Other coralline algae from New Zealand have shown similar robust responses to OA (Cornwall *et al.* 2013, 2014; James *et al.* 2014) compared with large declines in calcification observed in other coralline algal species (Anthony *et al.* 2008; Fabricius *et al.* 2015). The high abundance of coralline algae around the vents at Whakaari could include the fact that mean pH is higher or variability in pH lower at the study site relative to other shallow CO$_2$ vent sites in the Mediterranean (Hall-Spencer *et al.* 2008; Cornwall *et al.* 2017*a*) and Papua New Guinea (Fabricius *et al.* 2015), which would elicit different responses. Some coralline algae are particularly susceptible to both increased variability in pH and abrupt changes in pH (Cornwall *et al.* 2013; Kamenos *et al.* 2013; Roleda *et al.* 2015). However, pH$_{cf}$ usually responds to changes in seawater mean pH rather than pH variability (Cornwall *et al.* 2018). This is most likely also occurring at White Island. Further research is required to understand the comparatively high coralline algal abundance here compared with other CO$_2$ seep locations.

Conclusions

Findings of the 'White Island Blitz' suggest that the CO$_2$ system of Whakaari–White Island represents one of many globally distributed vent systems that require care in their use as modern models of the 'future ocean'. Although they create a pH and carbonate chemistry environment suitable for OA research (e.g. for predictions of 2100 and beyond), they also have several caveats, some of which have the potential to co-vary with scales of biological sampling, although this was not observed in this study. First, seawater carbonate chemistry was altered in only quite small areas around the vents, preventing a study of potential responses of pelagic and wide-ranging mobile organisms. Second, as around most other natural vents, the carbonate chemistry showed substantial variability, with unknown physiological and ecological consequences. Third, Hg$_T$ concentrations at both vent and control sites reached concentrations that are considered biologically toxic (Australian and New Zealand Environment and Conservation Council 2000). Finally, even though concentrations of most elements and metals around the study site were within acceptable ranges, some (Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and sulfide) were elevated at both the vent and control sites, potentially affecting the metabolic rates of sensitive taxa.

Our results provide particular warning for the ability of metals and elements to confound studies of CO$_2$ research at this hydrothermal vent system. The inconsistent variation of elements and dissolved metals in the working area across such small spatial scales suggests that these non-CO$_2$ effects need to be measured and understood, along with CO$_2$ concentrations, to improve our ability to reliably predict and manage for further ocean changes. It is possible that the ecology of Whakaari is different from assemblages elsewhere because of the general and variable chemical environment that envelops the broader coast of the Bay of Plenty. Therefore, the reporting of biological responses needs greater attention to potential prevalent multiple environmental stressors.

Our initial interdisciplinary results highlight that considerably more work is needed to better understand the biological

responses to and ecosystem-scale effects of the environmental factors around White Island and vent systems worldwide. To tackle the lack of information and to better quantify the suitability of the temperate CO_2 vents at White Island, or any other marine CO_2 vent system, as a climate change analogue, future studies are encouraged to include the following steps and practices:

- map the spatial and temporal changes in pH and other parameters of seawater carbonate chemistry during calm and well-mixed periods
- consider the location of suitable control sites outside the influence of the hydrothermal signatures of the numerous CO_2 vents at the study site to provide a regional context for biotic and abiotic interpretations
- make detailed *a priori* investigations of the temporal and spatial trace element distribution and speciation of bioactive trace metals (e.g. Cu, Hg, Cd and Pb) at both vent and control sites
- characterise the effects of OA on metal speciation, bioavailability and toxicity (Future decreases in OH^- and CO_3^{2-} concentrations will directly affect the solubility, distribution and speciation of metals in natural waters (Millero *et al.* 2009). Trace metals that form inorganic complexes with OH^- and CO_3^{2-} will undergo significant changes in speciation as the pH of seawater decreases, resulting in elevated levels of the bioavailable free ionic form of these metals (e.g. Millero *et al.* 2009; Ivanina and Sokolova 2015; Stockdale *et al.* 2016). Although some OA-induced changes in metal speciation will be beneficial (e.g. in the open ocean and in deep waters where productivity is limited by the low availability of micronutrients), others will exacerbate the harmful effects of bioactive metals to marine organisms (Ivanina and Sokolova 2015). Lower pH will also affect the adsorption of metals to organic ligands (Millero *et al.* 2009; Stockdale *et al.* 2016). However, the effect of pH on organic metal complexation in the marine environment is so far not well characterised and future studies are needed to examine the effect of OA on organic metal complexation and associated effects on marine organisms (e.g. Millero *et al.* 2009; Ivanina and Sokolova 2015; Stockdale *et al.* 2016).)
- understand the interaction between CO_2 and heavy metal concentrations, especially Hg, on biological responses (Based on published research, OA can change the toxicity, accumulation and intracellular binding processes of metals in several marine organisms, thereby affecting key physiological functions, including acid–base regulation, protein synthesis and energy homeostasis (e.g. Ivanina and Sokolova 2015; Zeng *et al.* 2015). Nevertheless, because of the scarcity of published research on OA–metal interactions, it is difficult to assess the degree to which both stressors are likely to affect the survival, performance and fitness-related functions (e.g. reproduction and growth) of marine organisms in the future ocean (Ivanina and Sokolova 2015).)
- improve understanding of biological responses to sulfide, particularly at the scales of biological observation and experimentation
- distinguish and quantify the individual and interactive effects of multiple stressors in the field and in the laboratory (e.g. laboratory-based experimental studies could be used to tease apart the effects of the increased CO_2 and Hg on vent biota)
- improve understanding regarding the biological and ecosystem-scale effects of the environmental variability around the vent sites
- perform detailed laboratory investigations of the effects of CO_2 on target taxa so that variation in response among taxa at vents can be better interpreted; calcareous organisms, such as mussels and coralline algae, may be investigated for their capacity to integrate CO_2 exposure over time in their skeletons
- focus on benthic sessile organisms because these communities integrate environmental conditions around the vent sites and thus provide a good proxy for the investigation of ecosystem processes (e.g. Pichler *et al.* 2019)
- compare broad-scale and long-term OA and climate change studies in the field with laboratory-based experiments to validate findings and associated conclusions (González-Delgado and Hernández 2018)

Although research of CO_2 vents was intended to improve the realism of OA research, which relies heavily on laboratory and mesocosm experiments, we acknowledge that CO_2 vents are not perfect analogues for forecasts of OA, and Whakaari–White Island is no exception. Indeed, there are few study sites or methods that can be relied upon to progress an entire discipline. Multiple approaches are needed, and each method needs constant reflection and refinement as to whether they establish the cause (abiotic change) and effect (biological response) for the chemical parameters of concern. Do ecological studies of volcanic vents measure the consequences of CO_2 enrichment? The 'White Island Blitz' shows that care is needed in the use of this particular multivariate site in New Zealand as a natural laboratory for studying temperate communities in future pH projections. The 'White Island Blitz' points to the need for validation by intensive laboratory and field investigations. Although laboratory investigations (e.g. mesocosms) tend to oversimplify and exaggerate their measured effects of OA and obscure important natural processes (Goldenberg *et al.* 2018), they provide insight into the types of responses and their mechanisms and causes. Although field investigations of naturally complex ecological systems incorporate a multitude of drivers, and thus reflect a more environmentally realistic scenario than laboratory-based experiments, they make any one driver or even multiple stressors challenging to isolate (Sommer 2012; Ivanina and Sokolova 2015; Boyd *et al.* 2018). If research into OA is not to stagnate, we need to understand biological or ecological responses to OA, as well as the sensitivity and legitimacy of our tests of OA.

Conflicts of interest

The authors declare that they have no conflicts of interest.

Declaration of funding

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