Marine Pollution Bulletin 109 (2016) 419–426

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

A new CO_2 vent for the study of ocean acidification in the Atlantic

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ARTICLE INFO

Article history:
Received 10 March 2016
Received in revised form 9 May 2016
Accepted 14 May 2016
Available online 20 May 2016

Keywords:
CO_2 vent
Ocean acidification
Natural laboratory
Carbon system
Nutrients

ABSTRACT

Natural CO_2 vents are considered the gold standard of ocean acidification (OA) studies. In coastal areas these rare vents have only been investigated at the Mediterranean temperate rocky reefs and at Indo-Pacific coral reefs, although there should be more at other volcanic shores around the world. Substantial scientific efforts on investigating OA effects have been mostly performed by laboratory experiments. However, there is a debate on how acute this kind of approach truly represents the responses to OA scenarios, since it generally involves short-term, rapid perturbation and single variable and species experiments. Due to these limitations, world areas with natural CO_2 vents are essential to understand long-term marine ecosystem responses to rising human derived atmospheric CO_2 concentrations. Here, we presented a new vent found in the subtropical North East Atlantic reefs (28°N, La Palma Island) that shows moderate CO_2 emission (900 ppm), reducing pH values to an annual average of 7.86 ± 0.16.

1. Introduction

Humans have released huge quantities of pollutant gases into the atmosphere since the beginning of the industrial period. Among these gases, the carbon dioxide (CO_2) is considered one of the most important, not only because its greenhouse effect but also because it is acidifying the oceans (Feely et al., 2004). Oceans have taken up about 25% of the carbon generated by human activities since 1800 (Sabine et al., 2004). By the end of this century, CO_2 absorbed by the oceans will decrease ocean pH by 0.2–0.4 units, and increase pCO_2 content about 750–900 ppm (Meinshausen et al., 2011). As a consequence of these changes decrease the saturation state of the carbonate ions (CO_3^{-2}) in seawater, assuming that calcifying organisms to be most severely affected (Orr et al., 2005; Kroeker et al., 2011; Doney et al., 2012; Gattuso et al., 2013). However, ecological consequences of ocean acidification (OA) remain unexplored and, until now, the vast majority of studies have been performed in laboratories and are characterized by short-term and univariate experimental approaches.

Although, laboratory manipulation experiments simulating current and future pCO_2 concentrations are a crucial tool to ensure causality, a great proportion of them, 95%, do not make use of the appropriate experimental design (Cornwall and Hurd, 2015). Other problem of these experimental approaches is that they do not incorporate the understanding of the carbon chemistry environment that is naturally experienced by the study organism (McElhany and Busch, 2013; Hernández et al., 2015). All these make it very difficult to draw an ecological relevant interpretation from some of the current data, and the need for truly rigorous experimental designs has been recently highlighted (Cressey, 2015). Experimental approaches dealing with OA are very important but future studies should improve the environmental realism, including natural pH ranges and pH variability in the studied local habitats combined with relevant variables such us temperature, and follow the "Guide to Best Practices for Ocean Acidification Research and Data Reporting" (Riebesell, 2008).

An alternative way to improve results of laboratory experiments is to study naturally occurring CO_2 vents, however field observations at such spots are scarce and very few studies investigating the biological effects of these natural experiments have been performed to date. As a summary, there are three studies on the effects of *in situ* CO_2 leakage on benthic community (Hall-Spencer et al., 2008; Fabricius et al., 2011; Enochs et al., 2015; Linares et al., 2015) and five more specific on calcareous species (Martin et al., 2008; Crook et al., 2012; Pettit et al., 2013; Inoue et al., 2013; Fabricius et al., 2015) and one on macroinvertebrates (Fabricius et al., 2013). Most of these studies, six out of nine, have been performed in the Mediterranean Sea (Ischia Island, Italy) and Papua New Guinea (Dobu, Esa'Ala and Upa Upasina). Recently other shallow areas are being explored off Vulcano Island, Italy (Boatta et al., 2013) and Northern Mariana Islands (Enochs et al., 2015), as well as a deep bottom area in the northern Gulf of California, with several natural CO_2 vents (Prol-Ledesma et al., 2013).

These vent sites occurred over different habitats, including shallow coral reefs in Papua New Guinea, Japan and Northern Mariana Islands; seagrass meadows, macroalgae stands and coralligenous in the Mediterranean Sea; as well as deep sedimentary bottoms in the Gulf of

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http://dx.doi.org/10.1016/j.marpolbul.2016.05.040
0025-326X/

California. However, a larger representation of environments is needed covering other oceans, latitudes and habitats and creating a CO_2 vent network around the world oceans to predict biological and ecological consequences of OA.

Our study explores a new underwater CO_2 vent discovered in the south east of La Palma Island between 1 and 5 meter depth. The southern tip of the island, called Cumbre Vieja, is a complex volcano with disperse eruptive vents and craters along the North-South rift zone, and it has experienced an extremely fast growth in the last few thousand years (Carracedo, 1994; Carracedo et al., 2001). Cumbre Vieja volcano is considered the most active basaltic volcano in the Canary Islands (Padrón et al., 2015). For instance, latest swath bathymetry around the Island has revealed the presence of very recent seamounts, forming the offshore prolongation of the rift (Masson et al., 2002). Along the off water rift there has been also several historical eruptions recorded since the 15th century, which generated lava flows: Tacande (1480), Tahuya (1585), Martín (1646), San Antonio (1677), El Charco (1712), San Juan (1949), and Teneguía (1971).

The recent history of volcanic activity in La Palma together with our new finding makes this area of the Atlantic a hotspot for OA studies. With this study we aims to (1) characterize most prominent geochemical parameters at the new vent site found compared to nearby and other contrasting areas; (2) to provide a spatio-temporal variability of pH/CO_2 at the vent site and other studied locations; and (3) to explore its nutrients composition.

2. Methods

2.1. Study areas and temporality

The vent site is located in the southeast coast of La Palma Island, Canary Islands; in a location called "Las Cabras" (Figs. 1 and 2). Besides the vent site and the nearby area, we also selected four more control locations, representing the most common and characteristic coastal ecosystems of the subtropical Eastern Atlantic Archipelagos. Each location was studied periodically to characterize the coastal seawater carbonate system and nutrients concentration, with three to four sampling times spanning different seasons during the years 2011 and 2012. Two locations were situated in the north of Tenerife Island, characterized by large extensions of canopy-forming seaweeds and another two locations in the southeast at a sea urchin barren ground with reduced seaweed cover. The selection of the study areas and the sampling times was not haphazardly; control sites were chosen to include very contrasting habitats with and without macroalgae, which can alter pCO_2; and we sampled seasons with and without thermocline to control possible interferences on pCO_2 concentrations due to phytoplankton productivity. In the north of Tenerife the study site was characterized by *Cystoseira abies-marina* bed; and the south site was a sea urchin barren ground dominated by crustose algae due to the grazing activity of the sea urchin *Diadema africanum* (Hernández et al., 2008). In La Palma, extensive beds of the algae *Lobophora variegata* surround the vent site.

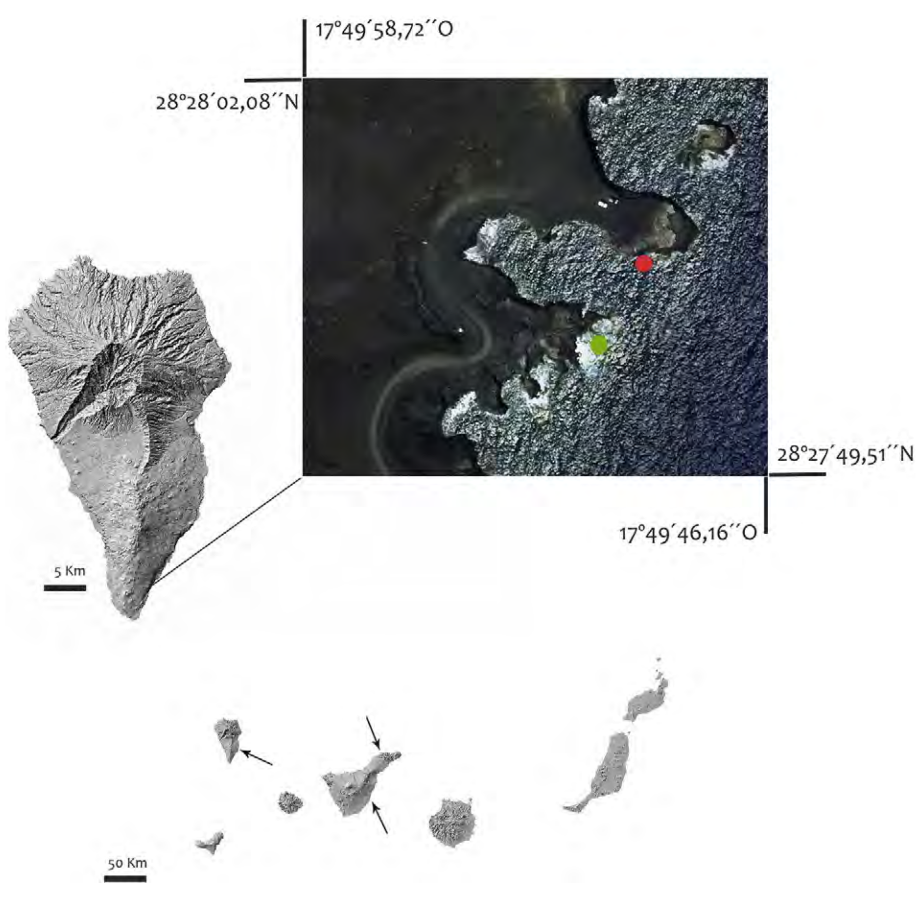

Fig. 1. Location of the studied areas in Tenerife and La Palma, Canary Islands. In Tenerife, arrows show Tenerife South (sites 1–2) and Tenerife North (sites 3–4). In La Palma, the red circle shows the CO_2 vent site (site 6) and the green one is site 5. Site's coordinates: (1) 28°08′33.80″N/16°25′56.31″W; (2) 28°08′29.06″N/16°26′10.44″W; (3) 28°34′06.79″N/16°19′59.96″W; (4) 28°34′29.11″N/16°19′48.15″W; (5) 28°27′54.8″N/17°49′51.37″W; (6) 28°27′56.10″N/17°49′50.92″W.

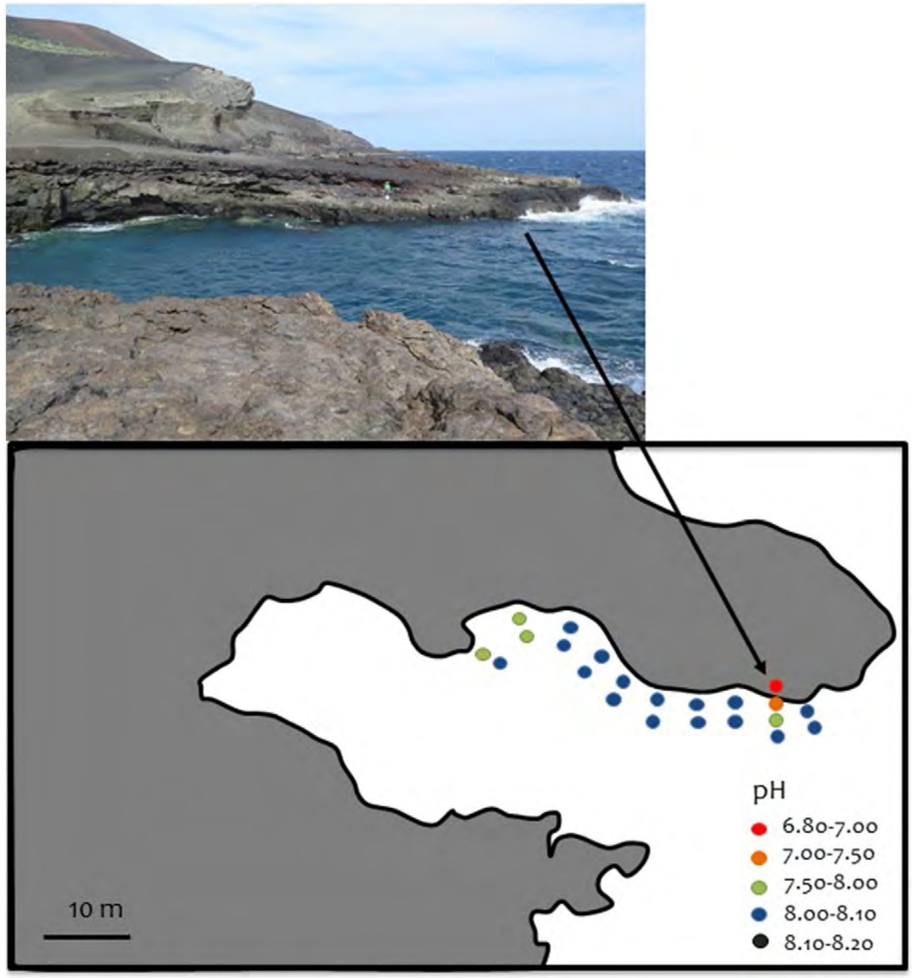

Fig. 2. Photography of site 6 at Las Cabras, La Palma, showing the exact spot of the CO_2 vent. On the map, circles show the location of the seawater sampling for pH measurements. At the vent site more samples were taken to determine the pH gradient from the emission crack to the surroundings.

2.2. Carbonate system parameters

At each site, salinity and sea surface temperature were measured *in situ* using a (handheld conductivity meter WTW COND 315i). Three replicated water samples were taken at two different depth levels: sea surface and bottom, at approximately 5 meter depth. The samples were stored in borosilicate bottles and hermetically sealed with a plastic cap. pH_{NBS} was measured just after sampling from each replicate bottle with a pH meter (Metrohm mobile meter with a combined electrode: Primatrode NTC IP pH electrode and temperature sensor). The pH meter was calibrated using a three-point calibration program against NIST buffer solutions (pH 4, 7 and 9 $\pm$ 0.02). Seawater total alkalinity (TA) was measured using an open cell potentiometric titration with a Metrohm Dosimat 665 titrator using 0.1 N HCl with a salinity of about 35 and following the Standard Operation Procedure 3b (Dickson et al., 2007). Alkalinity measurements took place 2–3 h after sampling, so there was no need of poisoning the samples. The rest of the carbonate chemistry parameters were calculated salinity, temperature, TA and pH using the package SEACARB 3.08 for R (https://cran.r-project.org/web/packages/seacarb/). Calculations were based on a set of constants, K1 and K2, taken from Lueker et al. (2000).

2.3. Nutrients measurements

Ten-milliliter samples were collected in sterile plastic tubes from sampling sites with the same temporality to measure nutrients (nitrate, phosphate and silicate) concentration on seawater. Samples were immediately frozen at −20 °C until being analyzed using a *Technicon* AutoAnalyzer II at the Instituto Español de Oceanografía (Santa Cruz de Tenerife) and by the company OCEOMIC SA. The methodology described by Tréguer and Le Corre (1975) was used for nitrite, nitrate and phosphate and by Kirkwood (1989) for silicate.

2.4. Statistical analysis

Statistical analyses were carried out using PRIMER 6 with PERMANOVA v.1.0.1 software. In order to assess the effect of the contrasting location, sites and thermocline data were analyzed by 3-ways permutational analysis of variance (Anderson, 2001). For each carbon system parameter the same three ways ANOVA design was applied, location was treated as a fixed factor with three levels (Tenerife South-no macroalgae, Tenerife North-macroalgae and La Palma (vent site)), thermocline as a fixed factor with two levels (1. presence of thermocline; 2. no thermocline) and site as a random factor, nested in location with six levels.

Principal Component Analysis (PCA) ordination was used to identify similarities between sampled locations and sites according to their nutrient concentrations.

3. Results

3.1. Seawater chemistry

Significant differences were detected in the carbonate chemistry of the different sites, with a substantial increase in pCO_2 concentration at

Table 1
Seawater chemistry of study sites. Summary of the seawater chemistry at the different studied locations in the Canary Islands.

Study area	Loc	Ωcalcite				Ωaragonite				pH_{NBS}				pCO_2				Ta				S			
		Min	Max	Av	SD	Min	Max	Av	SD	Min	Max	Av	SD	Min	Max	Av	SD	Min	Max	Av	SD	Min	Max	Av	SD
SE. Tenerife	1	5.92	7.93	6.63	0.54	3.85	5.15	4.33	0.35	8.14	8.35	8.22	0.05	177.42	317.53	259.47	36.96	2358.24	2521.60	2439.15	43.61	36.5	37.0	36.8	0.2
	2	6.17	7.51	6.72	0.40	4.01	4.94	4.39	0.27	8.16	8.31	8.22	0.04	199.47	299.00	252.88	24.71	2394.03	2511.89	2438.79	34.19	36.6	37.0	36.8	0.1
N. Tenerife	3	5.41	7.60	6.20	0.60	3.52	4.99	4.06	0.40	8.09	8.28	8.18	0.05	208.13	368.01	289.13	45.56	2341.59	2448.86	2417.32	30.97	36.4	36.8	36.7	0.1
	4	5.67	8.07	6.39	0.68	3.69	5.26	4.18	0.44	8.11	8.34	8.19	0.06	183.13	351.36	279.52	45.58	2348.19	2503.02	2420.66	45.30	36.7	36.8	36.8	0.1
SE. La Palma	5	3.64	6.65	5.61	0.78	2.36	4.35	3.66	0.52	7.81	8.20	8.09	0.10	276.39	1018.57	427.50	204.07	2423.19	3136.71	2616.04	202.86	36.8	37.0	36.8	0.1
	6	2.64	5.91	4.26	1.06	1.73	3.87	2.79	0.70	7.59	8.12	7.86	0.16	349.97	1746.81	913.21	444.82	2495.68	3253.47	2871.88	277.08	36.6	36.9	36.7	0.1

the vent site with an average of 913.21 ± 444.82 μatm (Table 1). Nearby site 5 showed some influence of the vent with mean pCO_2 of 427.50 ± 204.7 μatm higher than the rest of the studied sites (mean pCO_2 < 400 μatm, but see Table 1). The vent also produced a decrease in calcite and aragonite saturation states at both sites (Fig. 3, Table 1). Ωcalcite mean values were lower than 6.00 with the lowest values at the vent site (mean Ωcalcite = 4.26 ± 1.06). Ωaragonite got lower than 4 at both sites, with the lower values at the vent (mean Ωaragonite = 2.79 ± 0.70) (Table 1). pH_{NBS} was significantly different at the vent site, with lower values when compared with the other sites (Tables 1, 2). Mean pH_{NBS} was of 7.86 ± 0.16 at this site, while the other sites showed mean pH_{NBS} values in the range of 8.18 ± 0.05 and 8.22 ± 0.05. Site 5, located nearby the vent site had a mean pH_{NBS} that was comparatively low too (pH_{NBS} 8.09 ± 0.1) (Fig. 3). Extreme values were also measured at the vent site; reaching low pH_{NBS} of 7.59 during June 2012 (Table 1).

3.2. Salinity and seawater temperature

Salinity and seawater temperature parameters showed a significant interaction of factors site and thermocline (Tables 1, 2). Although, higher salinities and temperature were detected when the seasonal thermocline exists some site to site slight variations do exist. Sites 5 and 6 mean temperature during the thermocline period was 21.7 °C and 21.9 °C respectively. During the no-thermocline period, mean temperature at these sites lowered to 17.5 °C at site 5 and 17.9 °C at site 6. At the rest of the sites mean temperature period ranged from 22.2 °C to 23 °C during the thermocline period, and from 19.1 °C to 19.7 °C during the colder period without seasonal thermocline (Fig. 3).

3.3. Nutrients

PC1 and PC2 explained the 82.7% of total variation of the collected seawater samples. PC1 (50.5% of variation explained, horizontal) was mainly defined by the presence of Si-SO_4 (−0.965 eigenvector coefficient) and clearly shows that the vent site was characterized by higher contents of this nutrient. PC2 (32.2% of variation explained, vertical) was mainly defined by N-NO_3 (0.976 eigenvector coefficient) and only a group of samples collected at one site of the North side of Tenerife showed higher concentrations of this nutrient (Fig. 4).

4. Discussion

To our knowledge this is the first CO_2 shallow vent discovered in the Atlantic and can be used as proxy for ocean acidification studies. Here we provide accurate measurements of the carbon systems and nutrients at the vent site and other contrasting sites in the Canary Islands that were used as controls. This vent occurs in the North East Atlantic region in a near shore shallow rocky area, where the macroalgae *Lobophora variegata* is the main ecosystem engineer (Sangil et al., 2014; Hernández et al., 2015). Although, we have only characterized one vent in the area, a preliminary exploration has revealed more spots with low pH values that should be explored. Habitats affected by these vents are saline lagoons, intertidal benches and subtidal caves and rocky bottoms. The mean values of emitted pCO_2 are around 900 ppm reducing pH values to an annual average of 7.86 ± 0.16. This pH reduction is predicted to occur over the next 70 years in the world ocean. However, extreme averaged values as low as 7.59 were also observed, exceeding the mean seawater pH predicted for the next 100 years, in a global change scenario with business as usual.

For the Canary Islands benthic assemblages, it has been previously demonstrated that the highest daily and seasonal variation in pH values occurred in macroalgae beds (Hernández et al., 2015). In these vegetated assemblages, included here as a control location (sites 3–4), pH values were higher (8.09 and 8.34 pH units) than the observed range at the vent site 7.59 and 8.12. At this latitude, another source of pH

Table 2
Permutational ANOVA for comparing seawater chemistry among study sites. pCO_2, pHNBS, total alkalinity, salinity, temperature, Ω-calcite and Ω-aragonite were compared.

Source	df	MS	Pseudo-F	P(perm)
pCO_2				
Loc	2	1.3064E6	2.5004	0.2122
Thermocline	1	64,730	2.0753	0.2194
Site (loc)	**3**	**5.3774E5**	**20.559**	**0.0002**
Loc × thermocline	2	8855.3	0.28187	0.7752
Site (loc) × thermocline	3	31,578	1.2073	0.3228
Res	145	26,155		
pH_{NBS}				
Loc	2	0.48684	4.2235	0.1212
Thermocline	1	6.2808E−2	5.4025	0.0798
Site (loc)	**3**	**0.11865**	**22.172**	**0.0002**
Loc × thermocline	2	2.8566E−3	0.23992	0.7966
Site (loc) × thermocline	3	1.2108E−2	2.2627	0.082
Res	145	5.3513E−3		
Total	156			
Ta				
Loc	2	1.1519E6	4.499	0.118
Thermocline	**1**	**73,891**	**15.511**	**0.012**
Site (loc)	**3**	**2.6354E5**	**21.564**	**0.0002**
Loc × thermocline	2	19,887	4.4888	0.1074
Site (loc) × thermocline	3	4190.4	0.34287	0.7892
Res	145	12,222		
Total	156			
Salinity				
Loc	2	9.8754E−2	0.33439	0.7462
Thermocline	1	0.28579	2.8947	0.1728
Site (loc)	3	0.3041	29.555	0.0002
Loc × thermocline	2	0.27425	2.6708	0.2084
Site (loc) × thermocline	**3**	**0.10553**	**10.256**	**0.0002**
Res	145	1.0289E−2		
Total	156			
Temperature				
Loc	2	9.8754E−2	0.33439	0.7462
Thermocline	1	0.28579	2.8947	0.1728
Site (loc)	3	0.3041	29.555	0.0002
Loc × thermocline	2	0.27425	2.6708	0.2084
Site (loc) × thermocline	**3**	**0.10553**	**10.256**	**0.0002**
Res	145	1.0289E−2		
Total	156			
Ω-calcite				
Loc	2	27.148	5.8142	0.079
Thermocline	1	0.11634	0.10011	0.7764
Site (loc)	3	4.8011	12.345	0.0002
Loc × thermocline	2	0.18091	0.15117	0.874
Site (loc) × thermocline	**3**	**1.2216**	**3.1412**	**0.0326**
Res	145	0.38891		
Total	156			
Ω-aragonite				
Loc	2	11.758	5.9143	0.0858
Thermocline	1	0.18864	0.37678	0.588
Site (loc)	3	2.0441	12.227	0.0002
Loc × thermocline	2	7.6358E-2	0.1481	0.868
Site (loc) × thermocline	**3**	**0.5263**	**3.148**	**0.0332**
Res	145	0.16718		
Total	156			

Significant source of variations are highlighted in bold.

variation is the breakdown of the seasonal thermocline in spring. During this period, there is an increment in the photosynthetic activity due to the cold nutrient-rich deep waters that mix with the upper, nutrient depleted waters, which coincide with the availability of more daylight hours. Our results showed that the breakdown of the thermocline generates lower salinities and temperatures. pCO_2, pH, total alkalinity and calcite and aragonite saturation states were more variable between sites but clearly affected by the CO_2 vent. The higher pCO_2 at the vent site, double than the rest of the studied sites, reduced pH and the saturation states of calcite and aragonite.

Higher concentrations of Si-SO_4 at the vent site can only be explained by remnant underwater volcanic activity at this location in La Palma since no soft water input was detected. Recent volcanism in the south tip of this (Carracedo et al., 2001; Masson et al., 2002) and El Hierro Islands (Santana-Casiano et al., 2013) makes it an incredible spot for future expeditions to find more CO_2 vents for ocean acidification studies.

Predicting future consequences of OA on marine environments is a difficult task, and requires rigorous experimental designs to avoid artifacts related to inappropriate replication and randomization. The same

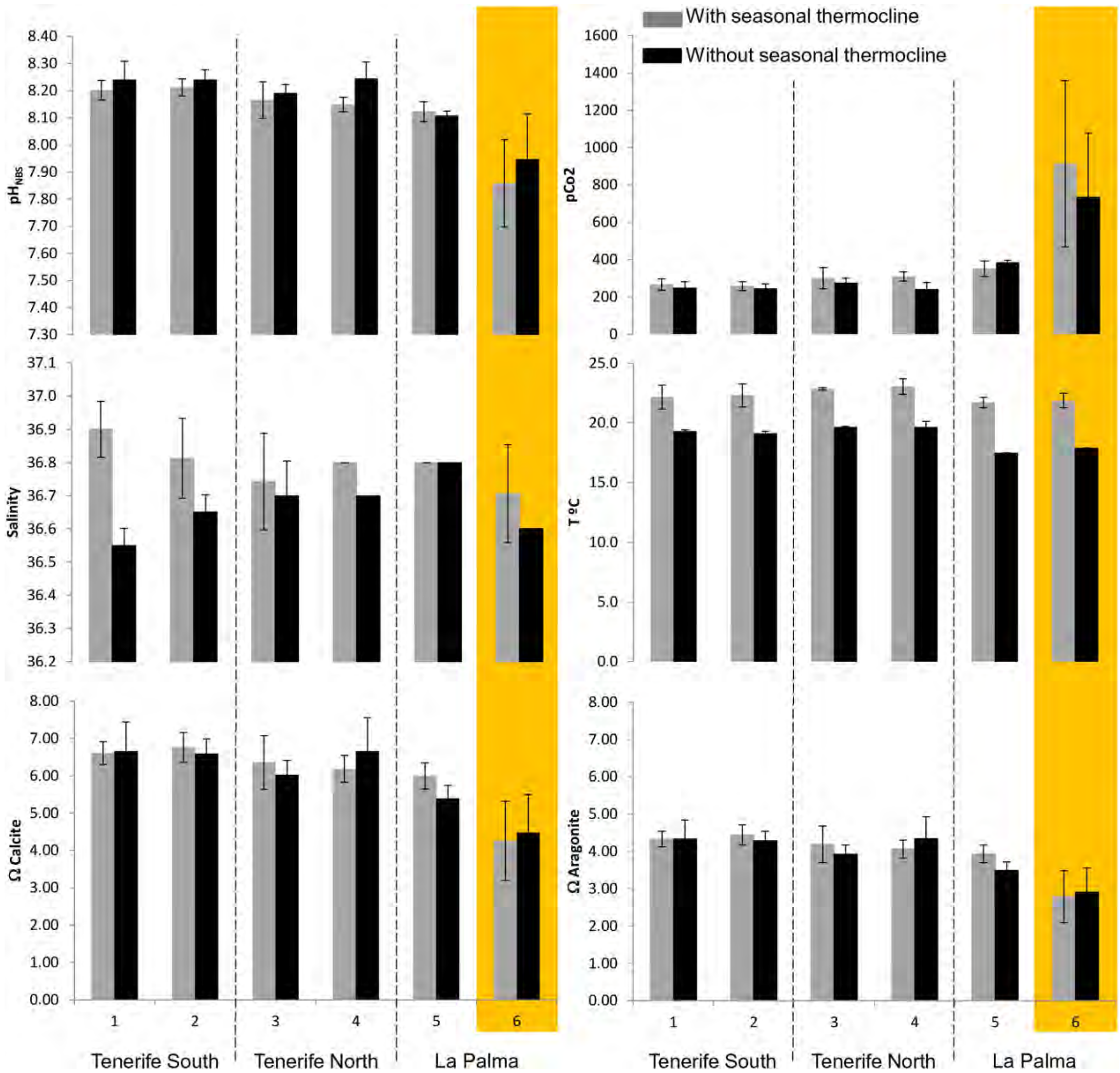

Fig. 3. Sea water chemistry. pHNBS, pCO_2 concentration, salinity, temperature, Ωcalcite and Ωaragonite (mean ± SE) measured at vent (yellow band) and other locations. Averages have been calculated across studied month with or without seasonal thermocline.

is applicable for manipulating seawater carbonate chemistry. On top of these important issues there are also intrinsic limitation of laboratory experiments such as short-term duration, *in vitro* conditions which means limited number of environmental variables, species and interactions tested, and other unexpected indirect effects of OA like changes in habitat properties, food webs, competition, diseases that could alter the final physiological and ecological responses of organisms to OA (Connell and Russell, 2010; Fabricius et al., 2011; Kroeker et al., 2011; Calosi et al., 2013; Uthicke et al., 2016). This is the main argument to use submarine volcanic vents as natural laboratories for the study of the effects of elevated pCO_2 over long periods. These areas are the perfect natural environments to study the acclimation of species to OA and to corroborate models and mesocosms experiments.

Investigations on vents have mainly focuses on distribution shifts of the species along a carbon dioxide gradient. Among its effects there is a clear reduction in diversity, biomass and trophic complexity of benthic marine assemblages, major declines in the number of many calcifying organisms and increased abundances of erect macroalgae, seagrass and soft-corals (Hall-Spencer et al., 2008; Inoue et al., 2013; Linares et al., 2015; Enochs et al., 2015). Other authors have also demonstrated, using natural vents, the capacity of adaptation of calcifying organisms (Johnson et al., 2012; Uthicke et al., 2016) and the important role that non-calcifying ones would play in future conditions (Russell et al., 2013). However, potential secondary ecological consequences of OA, such as habitat modification and altered food supply are not usually investigated (Nagelkerken et al., 2015) and only one paper has link the distribution shift to physiological abilities of species (Calosi et al., 2013).

More vents systems are necessary to represent more oceans and environments. However, these natural experiments are not perfect predictors of future ocean ecology so caution is required (Riebesell et al., 2010). Coastal pH is highly variable (Hofmann et al., 2011; Hernández et al., 2015) and vent pH values could be more constant; only affects relatively small areas of the benthic systems and their ecology can be affected by surrounding areas; and other non-measured effects, for

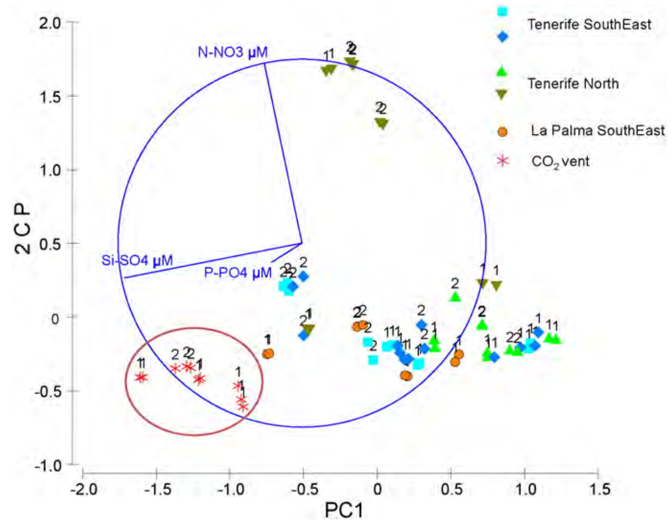

Fig. 4. Nutrients. PCA ordination analysis showing the effect of nutrients concentration (N-NO_3, P-PO_4 and Si-SO_4 µmol) on the distribution of the seawater samples collected at the vent sites and other locations (1. with seasonal thermocline and 2. without seasonal thermocline).

instance the disturbance that may cause the noise originated by CO_2 bubbling. Although not perfect, natural vents are incredible spots to poke our goggles into the future ocean.

Author contributions

CAH and JCH design the study and JCH, CAH, CS carried them out. JCH prepared the manuscript with contributions from all co-authors.

Acknowledgements

This manuscript was written within the framework of the project Plan Nacional de Investigación of the Spanish Ministerio de Economía y Competitividad, BLUEROCK, CGL17 2013_43908_R. Thanks to T. Ebert who improved earlier versions of the manuscript. We also thank B. Alfonso who helped during the seawater sampling and for the picture used in Fig. 2.

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