

The Importance of Natural Acidified Systems in the Study of Ocean Acidification: What Have We Learned?

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Abstract

Human activity is generating an excess of atmospheric CO₂, resulting in what we know as ocean acidification, which produces changes in marine ecosystems. Until recently, most of the research in this area had been done under small-scale, laboratory conditions, using few variables, few species and few life cycle stages. These limitations raise questions about the reproducibility of the environment and about the importance of

indirect effects and synergies in the final results of these experiments. One way to address these experimental problems is by conducting studies *in situ*, in natural areas where expected future pH conditions already occur, such as CO₂ vent systems. In the present work, we compile and discuss the latest research carried out in these natural laboratories, with the objective to summarize their advantages and disadvantages for research to improve these investigations so they can better help us understand how the oceans of the future will change.



1. THE QUESTION

Since the industrial revolution, human activity has produced an excess of atmospheric carbon dioxide (CO₂) due to the use of fossil fuels. One-third of this anthropogenic gas has been absorbed by the oceans, helping to mitigate the harmful effects of climate change in the atmosphere (Sabine et al., 2004), but the resulting changes in the carbon (C) chemistry of seawater have triggered a decrease in pH of up to 0.1 units in recent years, causing ocean acidification (OA) (Feely et al., 2004; IPCC, 2014). Acidification occurs when CO₂ is dissolved in seawater, forming carbonic acid (H₂CO₃) that rapidly dissociates into bicarbonate (HCO₃⁻) and hydrogen atoms (H⁺), lowering the pH of the water. The protons can combine with carbonate ion molecules (CO₃²⁻), which are normally free in water, to produce more (HCO₃⁻) and decrease the formation of calcium carbonate (CaCO₃). This chemical imbalance generates a series of direct and indirect negative consequences for marine life, of which organisms with external skeletons or protective shells, such as corals, crustaceans, molluscs and single-celled organisms, or those with endoskeletons, such as echinoderms, are the most affected because obtaining the CaCO₃ they need to form these structures becomes more difficult (Doney et al., 2012; Gattuso et al., 2013; Kroeker et al., 2010; Orr et al., 2005).

The problem is exacerbated by the continuous emission of anthropogenic gases into the atmosphere. According to recent predictions, an increase in *p*CO₂ between 750 and 900 ppm is expected by the year 2100 (Meinshausen et al., 2011), which implies a drop in seawater pH by 0.2–0.6 units in addition to a decrease in the aragonite and calcite saturation states (Ω) between 1.5 and 4 units (IPCC, 2014). Preventing these changes will depend on our capacity to replace fossil fuels with renewable energy (Feely et al., 2004).

Predicting the effects of these changes in future oceans is one of the most important questions facing researchers today. Studying the effects of

OA poses a great challenge because predicting future conditions is quite complex. Experimental studies carried out to date have helped us predict the possible responses of many organisms to the chemical changes produced by seawater acidification, so we have been able to estimate the likely negative effects on communities and species as well as their different life stages (Byrne et al., 2013; Dupont and Thorndyke, 2008; Hendriks et al., 2010; Kroeker et al., 2010). The most recent studies have also accounted for the interaction between OA and global warming (Byrne and Przeslawski, 2013; García et al., 2015; Harvey et al., 2013; Hernández et al., 2018a,b).

However, most results have so far come from experimental manipulations under laboratory conditions, i.e., in tanks or aquariums, which limits the inferences that can be drawn. The greatest challenges when predicting the effects of acidification include performing studies over large temporal or spatial scales, such as with increasing the number of studied species and the different stages of their life cycles, with studying whole populations or communities, and by including the natural variability inherent to the studied systems (Garrard et al., 2012; Hernández et al., 2016). Therefore, many questions have been raised about the reproducibility of natural conditions, about several important indirect effects such as natural variability, and about the ecological interactions between different species. Addressing these issues would ensure a more realistic prediction of the effects of acidification on marine ecosystems.

One approach to address these problems is to conduct studies in natural environments characterized by the expected future conditions, such as lower pH and lower concentrations of aragonite and calcite, which can be achieved by two methods: artificially pumping CO₂ into natural environments and creating mesocosms (Liu et al., 2017) or, perhaps more realistically, using areas with permanent volcanic activity that produce excess CO₂ known as acidification systems to study ocean acidification (AS). The first study using an AS was carried out by Hall-Spencer et al. (2008) and was widely accepted by the climate change research community. Since then, an increasing number of published studies have been performed in these areas.

With this review, we intend to produce an exhaustive compilation of the works published to date that have been carried out in AS. We intend to compare the characteristics of the studied areas, organisms and communities and discuss the main impacts that have been found. Thus, we summarize the advantages and disadvantages of AS as well as the studied biological and ecological processes to offer a global and detailed view of the current research and provide recommendations for future studies. This review will be useful for researchers studying the impact of climate change, especially OA, on the oceans.



2. 'NATURAL LABORATORIES' IN THE STUDY OF OCEAN ACIDIFICATION

For the purposes of this review, we define an AS to be an area with a higher-than-normal CO_2 input that is of natural origin and sufficient to acidify the surrounding marine environment. We have selected coastal and shallow areas, not more than 200m deep, in the euphotic zone, where the diversity of marine habitats is greatest. We have found a total of 30 AS matching this definition in different biogeographic regions (temperate, subtropical and tropical) whose origins are usually volcanic (CO_2 vents, seeps), although the origin might also be karstic (acid lagoons), biological or even generated by the upwelling of nutrient-rich water (Fig. 1).

2.1 Carbon Dioxide Vent Systems of Volcanic Origin

Natural CO_2 vent or seep systems are subtidal areas affected by the emission of gases of volcanic origin, and they are rich in CO_2 . They can be found where there is or has been recent underwater volcanic activity, such as mid-oceanic ridges or island arcs, or intra-plate magmatism (Tarasov et al., 2005). These active zones can be found in several areas of the planet; we have identified 23 such CO_2 vent systems where research has occurred (Fig. 1).

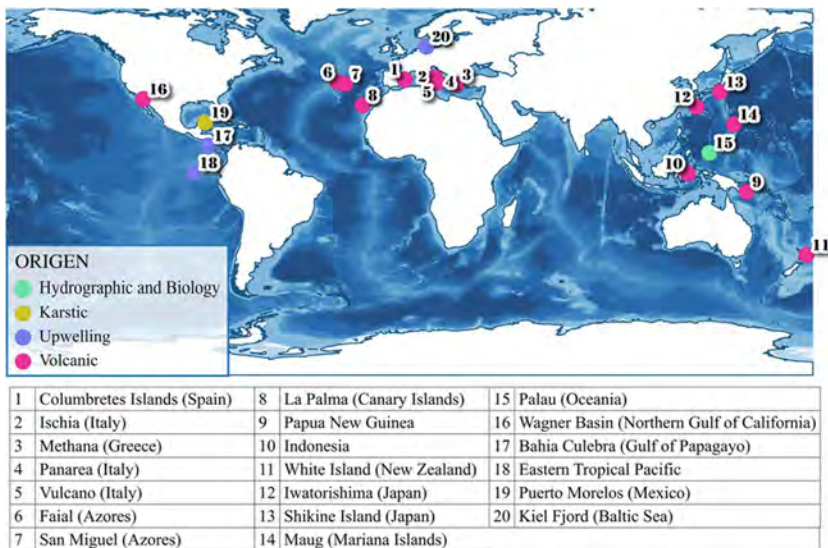


Fig. 1 Locations in the ocean, or 'Natural laboratories' to study ocean acidification (AS) that have been included in this study. Colours indicate the origin of each AS.

Because it is the focus of most publications, we consider the *Mediterranean Sea* to be the starting point for the development of this new line of research (Fig. 1). The pioneering work on the Ischia (Castello d'Aragonese) vent system was published by Hall-Spencer et al. (2008), and numerous studies have been conducted in this area since then, and even before (but see Foo et al., 2018b; Hall-Spencer and Rodolfo-Metalpa, 2012 for a more detailed information), followed by studies on the island of Vulcano (Bahia de Levante), the Panarea Islands (also Italian), Methana, in Greece and in an area near the Columbretes Islands in Spain (Fig. 1). All these vent systems are in temperate areas and are characteristic of the Mediterranean, but they differ in their physico-chemical conditions (Table 1) and can be divided into two groups: one group consisting of the area near the Columbretes Islands and the Panarea Islands, which would include vents between 5 and 40 m deep with a small variation in pH of no more than 0.7 units (Linares et al., 2015; Prada et al., 2017), and a second group including all other Mediterranean vent systems, where the emissions occur less than 3 m deep but with variations in the ambient pH as well as the dissolved inorganic C (DIC) and the percent saturation (Ω) of aragonite and calcite of more than 1.5 units (Table 1).

The vent systems in the Atlantic Ocean include the Sao Miguel and Faial system in the Azores and the most recently discovered system on the island of La Palma in the Canary Islands, all of which are in the Macaronesian Region (Fig. 1). The pH levels in these vent systems are not as low as those in the Mediterranean and are always above pH 7 (Table 1). In particular, the pH does not decrease by more than 0.2 units in the Faial vent system, and acidification only occurs below 15 m in depth (Campoy, 2015). In contrast, although more shallow (changes can already be detected on the surface), the other two vent systems show greater variations in aragonite Ω , especially the island of La Palma, and in calcite Ω in both La Palma and Sao Miguel (Campoy, 2015; Hernández et al., 2016) (Table 1).

In the Pacific Ocean, a large number of natural vent systems have been studied that are characterized by high tectonic and volcanic activity (see Fig. 1). The first three systems studied in this part of the world are in the province of Milne Bay, Papua New Guinea (PNG) (Dobu, Esá Ala and Upa-Upasina) that were also the first locations for the study of CO₂ emissions in tropical ecosystems supporting prolific coral reefs (Fabricius et al., 2011). We have found up to seven areas with vent systems of volcanic origin with favourable conditions for the study of OA in the Pacific Ocean

Table 1 Comparison of the Physicochemical Properties of All Known 'Natural Laboratories' in the Sea to Study Ocean Acidification (AS), Located in Different Parts of the World: Range of Depth in *m* (*D(m)*); Temperature of the Affected Area (*T^a*), Where 'Warmer' Indicates Temperatures 0.2–0.3 °C Higher Than Normal and 'Colder' Indicates 1–5 °C Lower Than Normal; and Aragonite Saturation State (*ΩAra*) and Calcite Saturation State (*ΩCal*)

	<i>D(m)</i>	<i>T^a</i>	<i>pH am</i>	<i>G pH</i>	<i>DIC</i>	<i>ΩAra</i>	<i>ΩCal</i>
<i>Mediterranean Sea</i>							
Columbretes Islands (Spain) ¹	5–40	Normal	8.1	7.95–7.8	2.3–2.4	2.26–1.78	3.51–2.77
² Ischia (Italy)	0–5	Normal	8.2	8.1–6.6	1.77–3.16	3.66–0.19	5.63–0.3
Methana (Greece) ³	0–2	Normal	8.1	8.1–6.53	2.56–3.21	4.18–0.09	6.29–0.13
⁴ Panarea (Italy)	8–23	Normal	8.2	8.17–7.41	2.11–2.32	3.6–1.4	5.1–1.29
Vulcano (Italy) ⁵	0–3	Normal	8.2	8.2–6.8	2.23–2.66	4.65–1.49	7–2.28
<i>Atlantic Ocean</i>							
Faial (Azores) ⁶	15–38	Normal	8.1	8.1–7.88	2.02–2.17	4.5–3.54	5.57–2.78
San Miguel (Azores) ⁷	0–10	Normal	8.1	8.1–7.75	2.06–2.27	3.13–1.83	5.3–2.83
La Palma (Canary Islands) ⁸	0–5	Normal	8.1	8.0–7.6	2.81–3.15	4.35–1.73	6.65–2.64
<i>Pacific Ocean</i>							
⁹ Papua New Guinea	0–5	Normal	8.0	7.98–7.29	1.97–2.44	3.4–1.2	5.12–1.36
Indonesia ¹⁰	0–4	Normal	8.2	8.01–7.8	1.90–1.99	4.85–2.48	7.29–3.73
White Island (New Zealand) ¹¹	8–10	Warmer	8.1	8.06–7.86	2.05–2.13	2.7–1.85	4.17–2.86
Iwatorishima (Japan) ¹²	0–3	Normal	8.3	7.81–7.4	2.14–2.25	2.25–1.12	3.4–1.69

^a Shikine Island (Japan) ¹³	0–20	Normal	8.1	8.1–6.8	2.03–2.54	2.22–0.2	3.45–0.3
Maug (Mariana Islands) ¹⁴	0–5	Normal	8.0	8.07–7.7	1.94–2.05	4.00–2.7	6.1–3.11
Palau (Oceania) ¹⁵	0–10	Normal	8.1	8.05–7.84	1.77–1.85	3.73–2.34	5.51–3.43
Wagner Basin (Northern Gulf of California) ¹⁶	74–207	Normal	8.2	7.94–7.56	2.29–2.33	3.23–1.19	4.87–1.83
Bahía Culebra (Gulf of Papagayo, Costa Rica) ¹⁷	> 0.3	Colder	8.2	8.02–7.91	1.8–2.10	3.41–2.71	—
^a Eastern Tropical Pacific ¹⁸	0–5	Colder	8.1	8.07–7.65	1.61–2.1	3.09–2.46	4.26–3.64
<i>Caribbean Sea</i>							
Puerto Morelos (Mexico) ¹⁹	4–7	Colder	8.0	7.29–6.61	3.18–3.33	0.87–0.50	1.32–0.77
<i>Baltic Sea</i>							
Kiel Fjord (Central Europe) ²⁰	1–20	Colder	8.2	8.1–7.49	2.04–2.07	0.79–0.47	1.36–0.79
<i>In the Future 2100²¹</i>	Surface	Warmer	7.8–7.4	—	—	<3–2	<4–3

^aThis area include several vent systems or upwellings spots in that particular location (Agostini et al., 2015; Fabricius et al., 2011; Gambi, 2014; Gambi and Teixido, 2016; Manzello, 2010; Molari et al., 2018).

The bottom row of the table includes predicted values according to the IPCC (2014), to compare with the predictive framework of each AS.

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Table 1 Comparison of the Physicochemical Properties of All Known ‘Natural Laboratories’ in the Sea to Study Ocean Acidification (AS), Located in Different Parts of the World: Range of Depth in *m* (*D(m)*); Temperature of the Affected Area (7%), Where ‘Warmer’ Indicates Temperatures 0.2–0.3 °C Higher Than Normal and ‘Colder’ Indicates 1–5 °C Lower Than Normal; and Aragonite Saturation State (Ω_{Ar}) and Calcite Saturation State (Ω_{Ca})—cont’d

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(Table 1 and Fig. 1), but except for PNG with more than 30 published articles and the White Islands of New Zealand with eight published articles, the other vent systems have not been used in more than one or two studies, to our knowledge. However, some of these studies were quite comprehensive and of great relevance, such as those conducted in the Marianas Islands (Enochs et al., 2015) and at Iwa Torishima in Japan (Inoue et al., 2013). The other two studies, which have gone largely unnoticed, were based in a system in Indonesia (Januar et al., 2016) and on the Mikama and Ashitsuke vent systems on Shikine Island, Japan, where only water chemistry has been studied (Agostini et al., 2015) (see Fig. 1). We also recently became aware of a vent system in Mainit, the Philippines (Dr Michael Roleda, personal communication) and in Roca Redonda, the Galapagos Islands, Ecuador (OA-ICC, 2018).

Lower pH, and thus differences in other chemical parameters, has been detected in the vent systems of PNG and the island of Shikine, where the ambient pH is decreased by 1.3 units (Table 1). In contrast, the emissions at the White Islands, New Zealand, are distinguished by the depths that they affect. The emissions do not reach the surface, but acidic conditions are present from 8 to 10 m below the surface. In addition, the location is one of the few natural CO₂ vent systems where an increase in ambient temperature, between 0.2 and 0.3 °C, has been detected (Brinkman and Smith, 2015) (Table 1). Therefore, the vent system in New Zealand is the only known AS to date that would allow the study of the combined effects of acidification and global warming. However, vents with the appropriate combined features and with no toxic gases nor higher concentrations of trace elements are very limited in extension (Tarasov, 2006).

Finally, an exceptional case of a vent system of the Gulf of California is currently the only AS at deeper levels of the euphotic layer (70 m), as it has a pH of up to 7.56 and variations in aragonite and calcite Ω values of up to 2–3 units (Prol-ledesma et al., 2013) (Table 1). Another interesting deep vent system that deserves further attention is the young submarine volcano of El Hierro, where significant discharge of CO₂ has been recently detected (Santana-Casiano et al., 2016).

2.2 Natural Laboratories of Non-Volcanic Origin

The karstic or acidic lagoons of Puerto Morelos, in the Gulf of Mexico, are other areas that can be considered AS (Crook et al., 2016). They owe their origin to the chemical phenomenon of karstification, which essentially consists of the dissolution of karstic limestone by the slightly acidic rainwater that

flows through caves and underground fractures into the ocean (Beddows et al., 2007). This underground acidic water is increasingly mixed with seawater in aquifers, resulting in salinity and temperature almost identical to that of the sea but with a higher DIC content and thus high alkalinity and low pH (Paytan et al., 2014). These lagoons, also called ‘ojos’ (eyes) by Crook et al. (2012), are located in the coral reef of the Maritime National Park of the Yucatan Peninsula, so they represent a unique location for studying these habitats in the Caribbean Sea (Fig. 1). However, due to the origin of its groundwater, the results of studies in this system must be interpreted with caution because both the present pH and CaCO_3 saturation values are not comparable to those expected in the future (Table 1), as well as the detected changes in salinity (Crook et al., 2012).

Another AS has been found in the Rocas Islands of Palau (Oceania), and it originated due to hydrographic-biological processes. Its cause is similar to that of acidic lagoons; that is, the system forms due to changes in water chemistry caused by rainwater combined with the high rate of respiration in the coral bay and the discharge of groundwater with high CO_2 levels (Shamberger et al., 2014). This area stands out for having a pH of approximately 7.8 without temporal fluctuations (Table 1).

Finally, other areas we consider to be AS are those affected by cold-water upwellings that are rich in inorganic C. To date, four such upwelling systems have been studied in very different habitats: three areas in the Eastern Tropical Pacific (ETP), i.e., the Galapagos, the Gulf of Panama and the Gulf of Chiriqui (Manzello et al., 2008), the Bay of Kiel in the Baltic Sea (Thomsen et al., 2010), as well as the Papagayo upwelling system in the north Pacific Costa Rica (Sánchez-Noguera et al., 2018) (Fig. 1). Due to their deep origin, the water in these systems is acidic but also colder than the ambient temperature, which can cause a decrease in environmental temperature of up to 5°C (Table 1). Furthermore, there are many temporal and spatial variations that are mainly due to ocean currents, the bathymetry of the area and wind force (Manzello, 2010; Sánchez-Noguera et al., 2018; Thomsen et al., 2013).

2.3 Caveats

Due to the nature of CO_2 emissions, there are factors in most AS that can affect OA research to a greater or lesser extent. These factors include pH fluctuations and thus fluctuations of the calcite and aragonite Ω values (Table 1), which depend on the amount of CO_2 and other gases emitted, the concentration of nutrients and the presence of bubbling, which can affect the AS environment both mechanically and acoustically (Table 2).

Table 2 Comparison of the Physicochemical Characteristics of All Known AS

	Origin	%CO ₂	Other Gas E	Bubbles	¹ [Nu]	Y. ex
<i>Mediterranean Sea</i>						
	Volcanic	90	N ₂ , O ₂ , CH ₄	YES	NO	-
	Volcanic	90.1–95.3	N ₂ , O ₂ , Ar, CH ₄	YES	-	188
³ Ischia (Italy) ²	Volcanic	97–99.1	N ₂ , O ₂ , He, H ₂ , CH ₄	YES	NO	2200
Methana (Greece) ³	Volcanic	98–99	N ₂ , O ₂ , Ar, CH ₄ , H ₂ S	YES	YES	10
⁴ Panarea (Italy) ⁴	Volcanic	98	N ₂ , O ₂ , H ₂ , CH ₄ , H ₂ S	YES	YES	10000
Vulcano (Italy) ⁵	Volcanic	98	N ₂ , O ₂ , H ₂ , CH ₄ , H ₂ S	YES	YES	10000
<i>Atlantic Ocean</i>						
	Volcanic	98.6–99.3	N ₂ , He, O ₂ + Ar	YES	YES	-
Faial (Azores) ⁶	Volcanic	99.9–99.5	N ₂ , He, O ₂ + Ar, CH ₄ , H ₂ S	YES	-	-
San Miguel (Azores) ⁷	Volcanic	99	Si	NO	NO	45
La Palma (Canary Islands) ⁸	Volcanic	99	Si	NO	NO	45
<i>Pacific Ocean</i>						
	Volcanic	99–98	N ₂ , O ₂ , CH ₄ , H ₂ S	YES	YES	80
⁴ Papua New Guinea ⁹	Volcanic	-	H ₂ S	YES	YES	29
Indonesia (Pacific) ¹⁰	Volcanic	99	N ₂ , Hg, CH ₄ , SO ₂	YES	NO	-
White Island (New Zealand) ¹¹	Volcanic	-	H ₂ S	-	-	50
Iwatorishima (Japan) ¹²	Volcanic	98	H ₂ S	YES	-	-
⁴ Shikine Island (Japan) ¹³	Volcanic	98	H ₂ S	YES	-	-

Continued

Table 2 Comparison of the Physicochemical Characteristics of All Known AS—cont'd

	Origin	%CO ₂	Other Gas E	Bubbles	↑[Nu]	Y. ex
Maug (Mariana Islands) ¹⁴	Volcanic	61.1	N ₂ , Ar, CH ₄ , S	YES	—	—
Palau (Oceania) ¹⁵	Hydrographic and biology			NO	NO	—
Wagner Basin (Northern Gulf of California) ¹⁶	Volcanic	78	CH ₄	YES	—	—
Bahía Culebra (Gulf of Papagayo, Costa Rica) ¹⁷	Upwelling			NO	YES	—
^a Eastern Tropical Pacific ¹⁸	Upwelling			NO	YES	—
<i>Caribbean Sea</i>						
Puerto Morelos (Mexico) ¹⁹	Karstic			NO	YES	18,000
<i>Baltic Sea</i>						
Kiel Fjord (Central Europe) ²⁰	Upwelling			NO	YES	—

^aThis area include several vent systems or upwellings spots in that particular location (Agostini et al., 2015; Fabricius et al., 2011; Gambi, 2014; Gambi and Teixido, 2016; Manzello, 2010; Molari et al., 2018).

Location of the natural laboratories; %CO₂: other elements that accompany the gas emissions (*other gas E*); presence of bubbling in the vent zone (*bubbles*); high concentrations of nutrients (\uparrow [Nu]); and minimum exposure time in years (*Y. ex*).

¹Linares, C., Vidal, M., Canals, M., Kersting, D.K., Amblas, D., Aspillaga, E., Cebrián, E., Delgado-Huertas, A., Díaz, D., Garrabou, J., Hereu, B., Navarro, L., Teixido, N., Ballesteros, E., 2015. Persistent natural acidification drives major distribution shifts in marine benthic ecosystems. *Proc. R. Soc. B* 282 (1818), 20150587; ²Hall-Spencer, J.M., Rodolfo-Metalpa, R., Martin, S., Ransome, E., Fine, M., Turner, S.M., Rowley, S.J., Tedesco, D., Buia, M.C., 2008. Volcanic carbon dioxide vents show ecosystem effects of ocean acidification. *Nature* 454 (7200), 96–99; Kroeker, K.J., Micheli, F., Gambi, M.C., Martz, T.R., 2011. Divergent ecosystem responses within a benthic marine community to ocean acidification. *Nature* 474 (7200), 108–111; Lombardi, C., Gambi, M.C., Vasapollo, C., Taylor, P., Cocito S., 2011. Skeletal alterations and polymorphism in a Mediterranean bryozoan at natural CO₂ vents. *Zoomorphology* 130 (2), 135–145; Foo, S.A., Byrne, M., Rivevuto, E., Gambi, M.C. (2018b). The carbon dioxide vents of Ischia, Italy, a natural laboratory to assess impacts of ocean acidification on marine ecosystems: an overview of research and comparisons with other vent systems. *Oceanogr. Mar. Biol. Annu. Rev.* 56 (in press); ³Baggini, C., Salomidi, M., Voutsinas, E., Bray, L., Krasakopoulou, E., Hall-Spencer, J. M., 2014. Seasonality affects macroalgal community response to increases in pCO₂. *PLoS One* 9 (9), e106520; ⁴Goffredo, S., Prada, F., Caroselli, E., Capaccioni, B., Zaccanti, F., Pasquini, L., Fantazzini, P., Fermani, S., Reggi, M., Levy, O., Fabricius, K.E., Dubinsky, Z., Falini, G., 2014. Biomining control related to population

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Biol.* 160 (8), 1813–1824; ⁶Campoy, A.N., 2015. Assemblage structure and secondary production of mesozooplankton in shallow water volcanic CO₂ vents of the Azores. (Doctoral dissertation, University of Algarve); ⁸Hernández, C.A., Sangil, C., Hernández, J.C., 2016. A new CO₂ vent for the study of ocean acidification in the Atlantic. *Mar. Pollut. Bull.* 109 (1), 419–426; ⁹Fabricius, K.E., Langdon, C., Uthicke, S., Humphrey, C., Noonan, S., De'ath, G., Okazaki, R., Muehllehner, N., Glas, M.S., Lough, J.M., 2011. Losers and winners in coral reefs acclimated to elevated carbon dioxide concentrations. *Nat. Clim. Chang.* 1 (3), 165–169; Takahashi, M., Noonan, S.H.C., Fabricius, K.E., Collier, C.J., 2016. The effects of long-term in situ CO₂ enrichment on tropical seagrass communities at volcanic vents. *ICES J. Mar. Sci.* 73 (3), 876–886; ¹⁰Januar, H.I., Zamani, N.P., Soedarma, D., Chasanah, E., Wright, A.D., 2017. 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Calcifying invertebrates succeed in a naturally CO₂-rich coastal habitat but are threatened by high levels of future acidification. *Biogeosciences* 7 (11), 3879; Thomsen, J., Casties, I., Pansch, C., Körzinger, A., Melzner, F., 2013. Food availability outweighs ocean acidification effects in juvenile *Mytilus edulis*: laboratory and field experiments. *Glob. Chang. Biol.* 19 (4), 1017–1027.

On the other hand, vent systems and acidic lagoons trend towards intense temporary fluctuations in pH due to coastal dynamics (Crook et al., 2012; Kerrison et al., 2011). Tides, currents or thermoclines can temporarily dissipate the emitted CO₂, thus affecting the overall water chemistry. In the case of upwelling systems, punctuated, discontinuous emissions can also produce very marked fluctuations (Sánchez-Noguera et al., 2018).

One of the most important disadvantages of using AS of volcanic origin is the presence of undesirable associated chemicals. Surge emissions are composed of 90–99% CO₂, with the known exceptions of the Gulf of California (78%) and Maug (61.1%) (Table 2). Volcanic emissions are always associated with other gases or elements, such as nitrogen (N₂), oxygen (O₂), argon (Ar), dihydrogen (H₂), helium (He), mercury (Hg), methane (CH₄), hydrogen sulphide (H₂S) and others, which usually make up 1–20% of the remaining volume (Table 2). These gases, although present in small quantities, could affect research results, especially in the case of sulphides or CH₄. Therefore, special attention must be paid to these aspects when choosing the AS for particulate OA studies. For example, in the case of Vulcano, Italy (Boatta et al., 2013) and Greece (Baggini et al., 2014), no negative effects have been observed to be associated with these elements, but in the Shikine Islands of Japan (Agostini et al., 2015), the toxic concentrations of H₂S definitely affect organisms and cannot be used for certain OA studies. Moreover, complex spatial dynamics of trace elements occur in the CO₂ vents that can also bias the use of CO₂ vents as analogues future oceans (Vizzini et al., 2013). Nevertheless, careful monitoring of such toxic emissions and elements throughout an investigation is always desirable.

Another factor to emphasize that has normally been disregarded is bubbling. The gases dissolved in seawater come from continuous bubbling in areas with volcanic activity (Fig. 2), which is a clear environmental change that is not considered in future ocean acidification scenarios and can interfere with experiments, thus affecting the results obtained in these AS. For example, continuous bubbling can both prevent the establishment of some organisms as well as generate acoustic turbulence that can alter the perception of the surrounding environment by some animals, thus affecting the development and behaviour of larvae and juveniles seeking refuge or food (Aguilar De Soto et al., 2013; Montgomery and Radford, 2017). Therefore, it is necessary to avoid this negative factor when searching for an AS. To our knowledge, the only natural vent system of volcanic origin discovered so far that does not present bubbling is south of the island of La Palma (Hernández et al., 2016) (Fig. 2). Of course, there are also non-volcanic AS (Table 2).

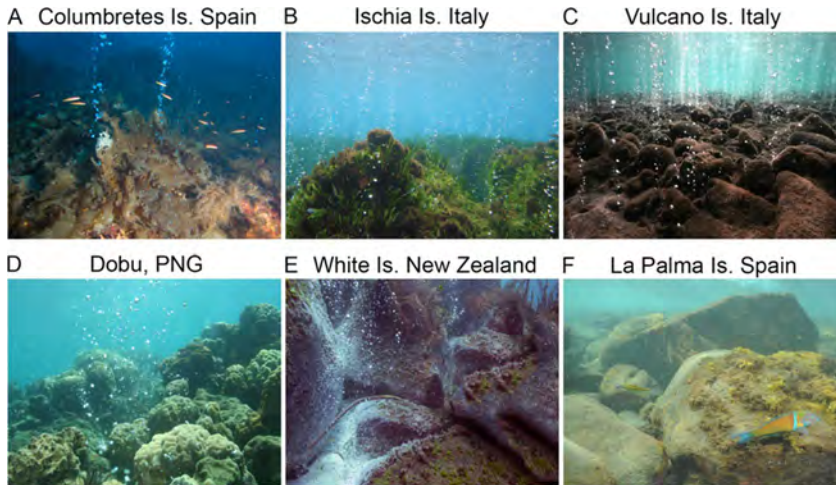


Fig. 2 General view of different natural CO₂ vent systems: (A) Laminaria beds at Columbretes Islands, Spain. (B) Macroalgae and Seagrasses at Castello, Ischia, Italy. (C) Rocky bottom in Vulcano, Italy. (D) Porite's coral reef in Dobu, Papua New Guinea, Pacific. (E) Macroalgae beds at White Island, New Zealand. (F) Macroalgae assemblages in La Palma Island, Atlantic Ocean, Spain. *Panel (A): Photo: D. Kersting. Panel (B): Photo: R. Rodolfo-Metalpa. Panel (C): Photo: Maarten van Rouveroy; Panel (D): Photo: K. Fabricius. Panel (E): Photo: N. Bennett. Panel (F): Photo: J.C. Hernández.*

Finally, increased nutrient concentrations have also been detected in some vent systems and in acidic lagoons, as is generally expected in areas affected by upwelling events (Table 2). In these cases, most authors argue that these elements do not influence investigations because they are present in very low concentrations and/or in very specific areas, such as in Ischia, Italy (Ravaglioli et al., 2017), PNG (Fabricius et al., 2015) or in Iwa Torishima (Inoue et al., 2013), among others. However, conflicting responses of different organisms, such as the excessive proliferation of *Padina pavonica* in the Vulcano vent system (Celis-Plá et al., 2015) or the complete disappearance of coral reefs in ETP (Manzello et al., 2014), may be favoured by the increase in nutrients, so this factor also should be taken into account.



3. RESEARCH IN ACIDIFIED SYSTEMS

Early research in AS focused on the effects of acidification on species abundance and diversity and, therefore, on changes in the distribution and structure of benthic (Crook et al., 2016; Enochs et al., 2015; Fabricius et al., 2011, 2014; Hall-Spencer et al., 2008; Inoue et al., 2013; Kroeker et al., 2011; Linares et al., 2015) and planktonic communities

(Smith et al., 2016; Ziveri et al., 2014) as well as microorganisms (Burrell et al., 2015; Enochs et al., 2016; Kerfahi et al., 2014; Uthicke et al., 2013). Subsequent studies focused on physiological changes in calcification (e.g. Rodolfo-Metalpa et al., 2010), photosynthesis (e.g. Russell et al., 2013), biomineralization (e.g. Collard et al., 2016; Duquette et al., 2017; Kamenos et al., 2016) and other metabolic processes (e.g. Celis-Plá et al., 2015; Kumar et al., 2017a,b; Uthicke and Fabricius, 2012). There have also been several studies on changes in intraspecific ecological interactions, such as herbivory (e.g. Johnson et al., 2012) and competition (e.g. Inoue et al., 2013; Kroeker et al., 2013b). Finally, studies have focused on early life cycle stages and reproduction, such as recruitment, colonization or juveniles (e.g. Fabricius et al., 2011; Munday et al., 2014; Porzio et al., 2013; Ricevuto et al., 2014), on ecological succession (Brown et al., 2017; Kroeker et al., 2013a,b) and on changes in species reproduction (Milazzo et al., 2016) in addition to impacts on larvae (e.g. Lamare et al., 2016) (Fig. 3; Table S1 in the online version at <https://doi.org/10.1016/bs.amb.2018.08.001>).

3.1 Main Changes in Marine Communities

The results obtained in the AS from temperate, tropical and subtropical regions have been consistent with expectations with some interesting exceptions.

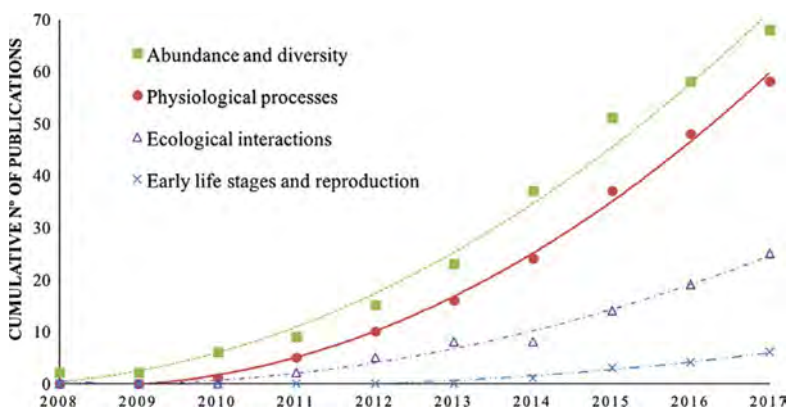


Fig. 3 Cumulative number of published articles in the last 9 years showing research topic. See supplementary material (Table S1 in the online version at <https://doi.org/10.1016/bs.amb.2018.08.001>).

3.2 Algae

Populations of calcifying red algae, especially crustose coralline algae (CCA), which form calcite crystals with Mg content, decrease and even disappear from the AS and are therefore the species most affected by acidification (e.g. Enochs et al., 2015; Fabricius et al., 2011; Johnson et al., 2013; Kamenos et al., 2016; Linares et al., 2015). In contrast, calcifying algae that form aragonite crystals, such as CCA species of the genus *Peyssonnelia* (e.g. Linares et al., 2015), brown algae (*Padina* spp.) (e.g. Celis-Plá et al., 2015; Goffredo et al., 2014; Johnson et al., 2012) or green algae such as *Halimeda* and *Acetabularia* (e.g. Enochs et al., 2015; Newcomb et al., 2015; Vogel et al., 2015), are more tolerant to the decrease in pH, and in many cases, with the exception of AS with large variations in aragonite Ω (such as Ischia, Methana and, to a lesser extent, Vulcano, Table 1), they are able to adapt and proliferate in acidified environments but with some negative cost in mineralization (Goffredo et al., 2014) (Table 3). This is because although aragonite is more soluble than calcite, the presence of other components, such as Mg, in the mineralization favours the dissolution of the latter in acidified environments, making calcite structures with high Mg contents more vulnerable than aragonite (Koch et al., 2013). Certain brown algae, such as the genera *Lobophora* (Goffredo et al., 2014), *Dictyota* (e.g. Porzio et al., 2011), *Cystoseira* (e.g. Baggini et al., 2014; Celis-Plá et al., 2015), *Sargassum* (e.g. Porzio et al., 2011, 2017), *Halopteris* and *Laminaria* (e.g. Hall-Spencer et al., 2008; Linares et al., 2015; Pérez, 2017) as well as some cespitose algae (e.g. Enochs et al., 2015; Pérez, 2017; Porzio et al., 2011, 2013) and marine phanerogams, such as *Posidonia oceanica* (e.g. Guilini et al., 2017; Lauritano et al., 2015; Scartazza et al., 2017) or *Cymodocea* spp. (e.g. Russell et al., 2013; Takahashi et al., 2016), are also clearly favoured by the increase in $p\text{CO}_2$ and are thus more abundant in areas most affected by CO_2 emissions (Table 3).

3.3 Benthic Invertebrates

Most changes in the abundance and diversity of benthic invertebrate communities are caused by a noticeable reduction in the number of species of sponges (Goodwin et al., 2014), decapods, calcifying polychaetes, some molluscs (e.g. Allen et al., 2016; Cigliano et al., 2010; Gambi et al., 2016; Kroeker et al., 2011) and echinoderms (e.g. Bray et al., 2014; Calosi et al., 2013a) (Table 4), but the reported changes are not as drastic as those in plant communities. In most groups, there are species that are able to tolerate these extreme pH conditions, such as bryozoans (Rodolfo-Metalpa et al., 2010),

Table 3 Summary of Documented Responses to the Impact of Acidification on Macroalgae and Seagrass Communities According to Studies in AS

	Mediterranean			Atlantic			Pacific			
	Columbretes ¹	Ischia ²	Panarea ³	Methana ⁴	Vulcano ⁵	Canaries ⁶	Azores ⁷	PNG ⁸	White Island ⁹	Maug ¹⁰
<i>Red Calcareous algae</i>										
Corallinaceae	-	=	-	-	-	-	-	-	-	-
CCA	-	-	-	-	-	-	-	-	-	-
<i>Peyssonmelia</i> spp.	+	+	-	-	-	=	=	=	=	=
<i>Non-calcareous</i>										
Cespitose and erect fleshy algae										
<i>Brown Calcareous algae</i>										
<i>Padina</i> spp.	-	-	-	-	+	+	+	+	+	-
<i>Non-calcareous</i>										
<i>Cystoseira</i> spp.	-	=	+	+	+	+	+	+	+	-
<i>Sargassum</i> spp.	+	+	+	+	+	+	+	+	+	-
<i>Dyctiota</i> spp.	-	+	+	+	+	=	=	=	=	-

<i>Laminaria rodriguezii</i>	+							
<i>Halopetis</i> spp.	+	+	-	+				+
Cespitose algae		+	+					+
<i>Calcareous green algae</i>								
Chlorophyta	-	-	+					=
Phanerogams		+	+					+

Symbols and abbreviations: (+) positive effect; (-) negative effect; (=) no apparent effect; CCA, crusty coralline algae; PNG, Papua New Guinea.

- ¹Linares, C., Vidal, M., Canals, M., Kersting, D.K., Ambias, D., Aspillaga, E., Cebrían, E., Delgado-Huertas, A., Díaz, D., Garrabou, J., Hereu, B., Navarro, L., Teixidó, N., Ballesteros, E., 2015. Persistent natural acidification drives major distribution shifts in marine benthic ecosystems. *Proc. R. Soc. B* 282 (1818), 20150587; ²Hall-Spencer, J.M., Rodolfo-Metalpa, R., Martin, S., Ransome, E., Fine, M., Turner, S.M., Rowley, S.J., Tedesco, D., Buia, M.C., 2008. Volcanic carbon dioxide vents show ecosystem effects of ocean acidification. *Nature* 454 (7200), 96–99; Martin, S., Rodolfo-Metalpa, R., Ransome, E., Rowley, S., Buia, M.C., Gattuso, J.P., Hall-Spencer, J., 2008. Effects of naturally acidified seawater on seagrass calcareous epibionts. *Biol. Lett.* 4 (6), 689–692; Porzio, L., Buia, M.C., Hall-Spencer, J.M., 2011. Effects of ocean acidification on macroalgal communities. *J. Exp. Mar. Biol. Ecol.* 400 (1), 278–287; Johnson, V.R., Russell, B.D., Fabricius, K.E., Brownlee, C., Hall-Spencer, J.M., 2012. Temperate and tropical brown macroalgae thrive, despite decalcification, along natural CO₂ gradients. *Glob. Chang. Biol.* 18 (9), 2792–2803; Kroeker, K.J., Gambi, M.C., Micheli, F., 2013. Community dynamics and ecosystem simplification in a high-CO₂ ocean. *Proc. Natl. Acad. Sci. U.S.A.* 110 (31), 12721–12726; Kroeker, K.J., Micheli, F., Gambi, M.C., 2013. Ocean acidification causes ecosystem shifts via altered competitive interactions. *Nat. Clim. Chang.* 3, 156–159; Porzio, L., Garrard, S.L., Buia, M.C., 2013. The effect of ocean acidification on early algal colonization stages at natural CO₂ vents. *Mar. Biol.* 160 (8), 2247–2259; Porzio, L., Buia, M.C., Lorenti, M., De Maio, A., Arena, C., 2017. Physiological responses of a population of *Sargassum vulgare* (Phaeophyceae) to high pCO₂/low pH: implications for its long-term distribution. *Sci. Total Environ.* 576, 917–925; ³Goffredo, S., Prada, F., Caroselli, E., Capaccioni, B., Zaccanti, F., Pasquini, L., Fantazzini, P., Fermiani, S., Reggi, M., Levy, O., Fabricius, K.E., Dubinsky, Z., Falini, G., 2014. Biomimetalization control related to population density under ocean acidification. *Nat. Clim. Chang.* 4 (7), 593; Lauritano, C., Ruocco, M., Dattolo, E., Buia, M.C., Silva, J., Santos, R., Olivé, I., Costa, M.M., Procaccini G., 2015. Response of key stress-related genes of the seagrass *Posidonia oceanica* in the vicinity of submarine volcanic vents. *Biogeosciences* 12 (13), 4185–4194; Guilini, K., Weber, M., de Beer, D., Schneider, M., Molari, M., Lott, C., Bodnar, W., Mascart, T., De Troch, M., Vanreusel, A., 2017. Response of *Posidonia oceanica* seagrass and its epibiont communities to ocean acidification. *PLoS One* 12 (8), e0181531; ⁴Baggini, C., Salomidi, M., Voutsinas, E., Bray, L., Krasakopoulou, E., Hall-Spencer, J.M., 2014. Seasonality affects macroalgal community response to increases in pCO₂. *PLoS One* 9 (9), e106520; Baggini, C., Issaris, Y., Salomidi, M., Hall-Spencer, J., 2015. Herbivore diversity improves benthic community resilience to ocean acidification. *J. Exp. Mar. Biol. Ecol.* 469, 98–104; ⁵Apostolaki, E.T., Vizzini, S., Hendriks, I.E., Olsen, Y.S., 2014. Seagrass ecosystem response to long-term high CO₂ in a

Continued

Table 3 Summary of Documented Responses to the Impact of Acidification on Macroalgae and Seagrass Communities According to Studies in AS—cont'd

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Table 4 Summary of Documented Responses to the Impact of Acidification on Invertebrate Communities According to Studies in AS

	Mediterranean			Atlantic		Pacific		Baltic
	Ischia ¹	Panarea ²	Methana ³	Vulcano ⁴	Canaries ⁵	PNG ⁶	White Island ⁷	
<i>Porifera</i>	-					-		
<i>Bryozoa</i>	= +							
<i>Polychaeta</i>								
No calcifying	= +	=				=		
Calcifying	- =	-				-		
<i>Echinodermata</i>								
<i>Paracentrotus lividus</i>	-		-	=	=			
<i>Arbacia lixula</i>	-		=	+ +	+ +			
<i>Echinometra</i> sp.						+ +		
<i>Evechinus chloroticus</i>							= =	
<i>Mollusca</i>	- =	-		- =		= =	= =	
<i>Crustacea</i>								
Decapoda	-					-		
Amphipoda	+ +	+ +				-		
Tanaidacea	+ +					+ +		
Isopoda	=							
<i>Cnidaria</i>								
<i>Anemonia</i> spp.	+ +			+ +	+ +			
<i>Balanophyllia europaea</i>							=	

Continued

Table 4 Summary of Documented Responses to the Impact of Acidification on Invertebrate Communities According to Studies in AS—cont'd

Symbols and abbreviations: (+) positive effect; (−) negative effect; (=) no apparent effect; PNG, Papua New Guinea.

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some species of sea urchins (e.g. Calosi et al., 2013a; Uthicke et al., 2016) or small crustaceans (e.g. Allen et al., 2016; Cigliano et al., 2010; Kroeker et al., 2011), in addition to non-calcifying species, such as some cnidarians as *Anemonia* spp. (e.g. Borell et al., 2014; Januar et al., 2016; Suggett et al., 2012) (Table 4). Furthermore, among the most affected groups, such as molluscs, acidification-tolerant species are still being found, such as the bivalve *Mytilus* spp. in the Mediterranean and Baltic Seas (Ricevuto et al., 2012; Thomsen et al., 2010, 2013), the endemic Mediterranean species *Pinna nobilis* (Basso et al., 2015), the limpets *Patella* spp. (Duquette et al., 2017; Langer et al., 2014) and the gastropod *Eatoniella mortoni* (Connell et al., 2017). These organisms are interesting because they have demonstrated some resistance to decreasing pH.

3.4 Corals

Corals are the most studied invertebrates in such studies due to their role as habitat formers that build entire ecosystems, such as the coral reefs of tropical regions. Because they are sessile and calcifying, they are highly sensitive to changes in seawater pH. According to the results obtained in different tropical AS, coral reefs tend to lose their composition and their characteristic high degree of heterogeneity (Table 5), especially in those environments where the pH is lower than 7.8 (Table 1). Hard corals, which are considered habitat-structuring or habitat-transforming organisms, tend to disappear from acidic areas, being replaced by coral species that are more resistant to acidification, such as *Porites* spp., or by soft corals that are capable of tolerating such conditions (e.g. Barkley et al., 2015; Crook et al., 2012, 2013, 2016; Enochs et al., 2015; Fabricius et al., 2011, 2017; Noonan et al., 2018) (Table 5). In broad terms, the diversity of hard corals is lost and replaced by a few species of resistant soft corals.

3.5 Planktonic Invertebrates

With regard to planktonic communities, changes are only known in phytoplankton (coccolithophorids) and coastal zooplankton communities (Table 6). More specifically, coccolithophorid communities decrease in abundance and diversity with acidification, and some species are further harmed by malformation and corrosion of their calcite skeletons (Ziveri et al., 2014). Similarly, coastal zooplankton also present lower abundance, as seen in both the Azores (Campoy, 2015) and PNG (Smith et al., 2016, 2017), mainly due to the decreased abundance of crustaceans.

The foraminifera are another group of small organisms that have been considered important due to their calcifying ability (Table 6). Although this

Table 5 Summary of Documented Responses to the Impact of Acidification on Coral Reef Communities According to Studies in AS

	Pacific						Caribbean sea
	PNG ¹	Indonesia ²	Iwatorishima ³	Maug ⁴	Palau ⁵	ETP ⁶	Puerto Morelos ⁷
<i>No framework-building</i>							
Soft-coral	–	=	=				
Hard-coral	+			=	+	–	=
<i>Framework-building</i>							
Framework-building	–	=	–	–	=	–	–

Symbols and abbreviations: (+), positive effect; (–) negative effect; (=) no apparent effect; PNG, Papua New Guinea; ETP Eastern Tropical Pacific.

¹Fabricius, K.E., Langdon, C., Uthicke, S., Humphrey, C., Noonan, S., De'ath, G., Okazaki, R., Muehlehner, N., Glas, M.S., Lough, J.M., 2011. Losers and winners in coral reefs acclimatized to elevated carbon dioxide concentrations. *Nat. Clim. Chang.* 1 (3), 165–169; Wall, M., Fietzke, J., Schmidt, G.M., Fink, A., Hofmann, L.C., De Beer, D., Fabricius, K.E., 2016. Internal pH regulation facilitates in situ long-term acclimation of massive corals to end-of-century carbon dioxide conditions. *Sci. Rep.* 6, 30688; Brown, N.E., Milazzo, M., Rastrick, S.P., Hall-Spencer, J.M., Theriault, T.W., Harley, C.G., 2017. Natural acidification changes the timing and rate of succession, alters community structure, and increases homogeneity in marine biofouling communities. *Glob. Chang. Biol.* 24, e112–e127; Fabricius, K.E., Noonan, S.H., Abrego, D., Harrington, L., De'ath, G., 2017. Low recruitment due to altered settlement substrata as primary constraint for coral communities under ocean acidification. *Proc. R. Soc. B* 284 (1862), 20171536; ²Januar, H.I., Zamani, N.P., Soedarma, D., Chasanah, E., 2016. Changes in soft coral Sarcophyton sp. abundance and cytotoxicity at volcanic CO₂ seeps in Indonesia. *AIMS Environ. Sci.* 3 (2), 239–248; Januar, H.I., Zamani, N.P., Soedarma, D., Chasanah, E., Wright, A.D., 2017. Tropical coral reef coral patterns in Indonesian shallow water areas close to underwater volcanic vents at Minahasa Seashore, and Mahengetang and Gunung Api Islands. *Mar. Ecol.* 38, e12415; ³Inoue, S., Kayanne, H., Yamamoto, S., Kurihara, H., 2013. Spatial community shift from hard to soft corals in acidified water. *Nat. Clim. Chang.* 3 (7), 683–687; ⁴Enochs, I.C., Manzello, D.P., Donham, E.M., Kolodziej, G., Okano, R., Johnston, L., Young, C., Iguel, J., Edwards, C.B., Fox, M.D., Valentino, L., Johnson, S., Benavente, D., Clark, S.J., Carlton, R., Burton, T., Eynaud, Y., Price, N.N., 2015. Shift from coral to macroalgae dominance on a volcanically acidified reef. *Nat. Clim. Chang.* 5 (12), 1083–1088; ⁵Barkley, H.C., Cohen, A.L., Golbuu, Y., Starczak, V.R., DeCarlo, T.M., Shamberger, K.E., 2015. Changes in coral reef communities across a natural gradient in seawater pH. *Sci. Adv.* 1 (5), e1500328; ⁶Manzello, D.P., Enochs, I.C., Bruckner, A., Renaud, P.G., Kolodziej, G., Budd, D.A., Carlton, R., Glynn, P.W., 2014. Galápagos coral reef persistence after ENSO warming across an acidification gradient. *Geophys. Res. Lett.* 41 (24), 9001–9008; ⁷Crook, E.D., Potts, D., Rebolledo-Vieyra, M., Hernandez, L., Paytan, A., 2012. Calcifying coral abundance near low-pH springs: implications for future ocean acidification. *Coral Reefs* 31 (1), 239–245; Crook, E.D., Cohen, A.L., Rebolledo-Vieyra, M., Hernandez, L., Paytan, A., 2013. Reduced calcification and lack of acclimatization by coral colonies growing in areas of persistent natural acidification. *Proc. Natl. Acad. Sci. U.S.A.* 110 (27), 11044–11049; Crook, E.D., Kroecker, K.J., Potts, D.C., Rebolledo-Vieyra, M., Hernandez-Terrones, L.M., Paytan, A., 2016. Recruitment and succession in a tropical benthic community in response to in-situ ocean acidification. *PLoS One* 11 (1), e0146707.

group has become practically extinct in many acidified areas (e.g. Cigliano et al., 2010; Dias et al., 2010; Uthicke et al., 2013), species have also been found that are able to adapt to extreme pH conditions (pH 7.6), such as in the deep waters of the Northern Gulf of California (Pettit et al., 2013).

Table 6 Summary of Documented Responses to the Impact of Acidification on Microorganisms According to Studies in AS

	Mediterranean		Atlantic		Pacific		
	Ischia ¹	Vulcano ²	Azores ³	NGC ⁴	PNG ⁵	White Island ⁶	Maug ⁷
<i>Plankton</i>							
Zooplankton			=	=	-		
Phytoplankton	+	-					
<i>Others</i>							
Foraminifera	-			=	-		
Microorganisms	=	+			+	+	+

Symbols and abbreviations: (+) positive effect; (-) negative effect; (=) no apparent effect; PNG, Papua New Guinea; NGC, Northern Gulf of California.

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3.6 Microorganisms

The groups of organisms that are most favoured by OA include the biofilm-forming microorganisms (Table 6). These biofilms, which are mainly composed of bacteria, cyanobacteria and microalgae, increase in both species abundance and diversity (Chauhan et al., 2015; Hassenrück et al., 2017; Johnson et al., 2015; Kerfahi et al., 2014; Lidbury et al., 2012; Morrow et al., 2015), especially those species that degrade organic matter (Taylor et al., 2014). In tropical regions, this increase is worrisome because it can amplify the negative effects of acidification on other organisms, as has been observed by Enochs et al. (2016) in the vent system of the Mariana Islands, where the increase in bacterial populations that compose the coral microbiota magnifies the erosion of coral reefs.

3.7 Changes in the Physiological Responses of Organisms in Natural Laboratories

Thanks to AS, we now know many of the physiological responses of organisms after exposure to an acidified environment for an extended period of time. The AS studied thus far date from at least between 10 and 18,000 years old (Table 2), which allows us to identify species that are already adapted to these putative future conditions and compare their ability to adapt to their ability to acclimatize through organism transplant experiments (e.g. Kumar et al., 2017b; Olivé et al., 2017).

Brown algae and phanerogams seem to thrive in acidified waters due to the extra DIC (Table 1) that allows them to increase their photosynthetic rate and growth (Koch et al., 2013) by overcoming their physiological C limitations; they usually present a C concentration mechanism (CCM) with low affinity for DIC (Cornwall et al., 2017). The physiology of the seaweed *Sargassum vulgare* has been one of the most studied in CO₂ vent systems (Kumar et al., 2017a,b; Porzio et al., 2017) in addition to the marine phanerogam *P. oceanica* (Hall-Spencer et al., 2008; Lauritano et al., 2015; Ravaglioli et al., 2017; Scartazza et al., 2017) and several species of *Cymodocea* (Apostolaki et al., 2014; Arnold et al., 2012; Olivé et al., 2017; Russell et al., 2013; Takahashi et al., 2016). These species have favourably adapted to acidified environments and have increased their photosynthetic activities and energetic metabolism, which, among other changes, allows them to control ionic homeostasis and allocate resources for increased growth and cell development. The only exception is *Cymodocea nodosa* in the Mediterranean Sea, which does not present increased net productivity. This responds differently

to other phanerogams and has not increased in abundance in the case of the Vulcano vent system (Olivé et al., 2017). Its response is likely influenced by other factors such as the loss of its epiphytic species, which reduces protection in eutrophic conditions (Arnold et al., 2012), or the appearance of toxic compounds of volcanic origin (Vizzini et al., 2013).

The regulation of calcification can also play a very important role in the survival of calcifying species. For example, extraordinary adaptation with no compromise to its calcified structures has been observed by the red algae *Peyssonnelia* spp. in AS (Linares et al., 2015), and in extreme cases (Ischia—pH below 7.4) for other algae, aragonite concentrations have been replaced with gypsum (Kamenos et al., 2016).

Invertebrates that are resistant to changes in seawater pH have also developed different strategies to survive and adapt to these environments. They also have a great capacity to regulate extracellular ionic homeostasis or exert acid-base regulation, as demonstrated by the polychaete *Platynereis dumerilii* (Calosi et al., 2013b), the sea urchin *Arbacia lixula* (Calosi et al., 2013a; Small et al., 2015), the fan worm *Sabella spallanzanii* (Ricevuto et al., 2016) and the isopod *Dynamene torelliae* (Turner et al., 2016). In contrast, many species can redirect their metabolic energy to compensate for the problems caused by increased acidity. For example, hard corals of the genus *Porites* are able to regulate and maintain net calcification at low pH levels due to an increase in photosynthetic rates (Crook et al., 2013; Strahl et al., 2015), and the bryozoan *Schizoporella errata* increases its energy available for calcification processes by decreasing its defensive structures so as not to harm its somatic growth (Lombardi et al., 2011). There are also some species of gastropods that obtain the energy necessary to calcify in these acidic environments by decreasing the size of their shell (Garilli et al., 2015; Harvey et al., 2016). Decreases in body size and spines have also been observed in polychaetes (Gambi et al., 2016; Lucey et al., 2015) and in the sea urchin *A. lixula*, which even allows the sea urchin to grow a more resistant skeleton (Hernández et al., 2018b).

The presence of external protective layers, such as in the bryozoan *Myriapora truncata* (Rodolfo-Metalpa et al., 2010) and expansion of organic layers in the mussel *Mytilus galloprovincialis* or the coral *Balanophyllia* spp. (Rodolfo-Metalpa et al., 2011) is another defence against low pH levels. Finally, some gastropods stand out for their ability to alter their mineralization processes, increasing the thickness of their shells (Langer et al., 2014; Rodolfo-Metalpa et al., 2011) or even replacing the aragonite crystals, which are more soluble under low pH, with calcite, as observed by Duquette et al. (2017) in *Patella rustica*.

3.8 Intraspecific Ecological Interactions

One of the most important advantages offered by experimentation in AS is the opportunity to observe potential changes in ecosystem function. Acidification has been demonstrated to influence herbivory dynamics (Connell et al., 2013; Nogueira et al., 2017; Ricevuto et al., 2015a,b). The relationships between producers (in this case, algae) and their herbivores, such as sea urchins, molluscs or fish, have been found to be indirectly altered in acidified ecosystems. In the Mediterranean, increased browsing by herbivores has been associated with the survival of species such as *P. pavonica* (Baggini et al., 2015; Johnson et al., 2012). Likewise, the increase in the abundance of herbivorous gastropods in vent systems has been attributed to increased quantities of cespitose algae (Connell et al., 2017) or to the seagrasses buffering effect on low pH (Garrard et al., 2014; Zupo et al., 2015).

Acidified natural environments also offer the opportunity to observe changes in the recruitment phase. There have been several studies in this regard, in both the Mediterranean (Cigliano et al., 2010; Kroeker et al., 2013b; Ricevuto et al., 2012) and tropical systems (Allen et al., 2016; Crook et al., 2016; Fabricius et al., 2015), where acidified environments have been shown to negatively alter the recruitment success of calcifying species (especially CCA and corals) and indirectly alter the recruitment success of other species that might lose their substrates in the absence of calcifying species. Changes in succession and colonization dynamics have also been studied recently (Brown et al., 2017) as have metabolic rate variations during these processes (Noonan et al., 2018). Acidification alters succession rates and influences colonization by favouring some species (e.g. biofilm-forming microorganisms) over others, which results in more homogeneous, less diverse environments in addition to a possible imbalance in the flow of energy through trophic chains (Brown et al., 2017; Vizzini et al., 2017).

Many organisms, such as fleshy algae (Kroeker et al., 2013b), phanerogams (Takahashi et al., 2016) or the corals of the genus *Porites* (Inoue et al., 2013), exhibit competitive advantages in acidified environments. In extreme cases, the favoured species can completely transform a habitat, as observed in the Maug vent system where macroalgae have completely dominated the ecosystem and replaced coral reefs (Enochs et al., 2015). In turn, these changes have indirect effects on other organisms, as observed in demersal zooplankton communities associated with coral reefs that lose their places of settlement and refuge in the absence of corals (Smith et al., 2016, 2017).

Species are expected to compete with each other for resources, such as space and food, but in altered environments, such as AS, the biotic and abiotic relationships between species change markedly (Nagelkerken et al., 2016; Sunday et al., 2016). Knowing these future changes is one of the objectives of OA investigations, and although it is extremely difficult to identify the indirect, global effects of OA due to their magnitude, interesting answers are increasingly being obtained at the local level. All indications are that the changes observed in the AS will generate communities with less diversity and structural complexity, in which the primary producers will directly increase along with the herbivore populations while the predators will not be affected, thus creating decompensation in the trophic chain (Nagelkerken et al., 2016; Vizzini et al., 2017).

3.9 Reproduction and Early Life Stages

There have been numerous laboratory studies of the effects of acidification on the early life stages of organisms. The best studied are changes in the reproduction and development of sea urchin larvae (Dupont and Thorndyke, 2013; García, 2014), but even here there have been only a few publications on this line of research in AS. In a recent study, Lamare et al. (2016) observed the effects of CO₂ vents in echinoderm larvae in a short-term *in situ* experiment, and although they did not observe significant differences in the abundance of individuals, they did observe atrophied development and morphological anomalies in the larvae in laboratory experiments. Additionally, fish larvae exhibited changes in behaviour in acidified areas due to the loss of acoustic signals from the habitat that the species used for orientation. This effect is mainly caused by the loss of structural complexity as well as by loss of the organisms that generate environmental noise (Mirasole et al., 2017; Nagelkerken et al., 2016; Rossi et al., 2016a,b).

Another discovery made possible through *in situ* studies in AS was of changes in life strategies related to parental care. The larval stages of some free-swimming invertebrates, such as some polychaetes, are more sensitive to acidification, while species with parental care and whose offspring are more protected are favoured (Gambi et al., 2016; Lucey et al., 2015; Wäge et al., 2017).

Only three studies have yielded information about impacts on reproduction. The first was carried out in Vulcano, where an increase in reproductive activity was reported for dominant fish males of acidified zones, which was contrary to expectations (Milazzo et al., 2016), and the other study,

in Panarea, showed no negative effects on gametogenesis nor on embryogenesis in the scleractinian coral *Leptopsammia pruvoti* (Gizzi et al., 2017). And a third recently published paper, on *A. lixula* egg development, has shown a plastic response to low pH conditions of the jelly coat size of sea urchins from the vent site. This could be a strategy to facilitate the maintenance of gamete function, facilitating fertilization success in a low pH ocean (Foo et al., 2018a).



4. CONCLUSION AND RECOMMENDATIONS

The above presents most of the known AS to date. A summary of the negative and positive inclination of different marine organisms due to a natural decreasing of pH is shown in Fig. 4. The evidence strongly indicates that these systems are useful for examining the direct, and more interestingly, unexpected indirect effects (e.g. community wide-effects) of OA.

Despite the evident usefulness of the AS, it is necessary to carefully control certain chemical and physical variables before conducting research in these areas. Therefore, we recommend (1) thoroughly studying the area before and during the investigation to better understand the fluctuations in the venting intensity, the chemical composition of the water, not only in the concentrations of C but those of other chemical compounds, nutrients and contaminants; (2) choosing the area of interest according to the pH levels, temperature (when possible) and levels of aragonite and calcite Ω that are expected in the future to achieve the best possible predictions; and (3) complementing *in situ* studies with *in vitro* experiments that help demonstrate the causality of patterns observed in the AS.

Presently, the most abundant AS are those of volcanic origin, so we recommend continuing to search for this type of vent system, which will help expand the number of biogeographic areas and represented habitats to create a worldwide network of laboratories that can share results. Maps of volcanic arcs, faults and other areas with volcanic activity can be used to locate new potential AS. However, in this search for new areas, we must bear in mind that an appropriate AS for the study of acidification must have a constant C input that maintains the average pH levels below 8 but never lower than 7.4 to more realistically represent the putative future conditions predicted by the IPCC (2014), with aragonite Ω below 3 (tropical zones) or 2 (temperate zones) and calcite Ω below 4 (tropical zones) or 3 (temperate zones).

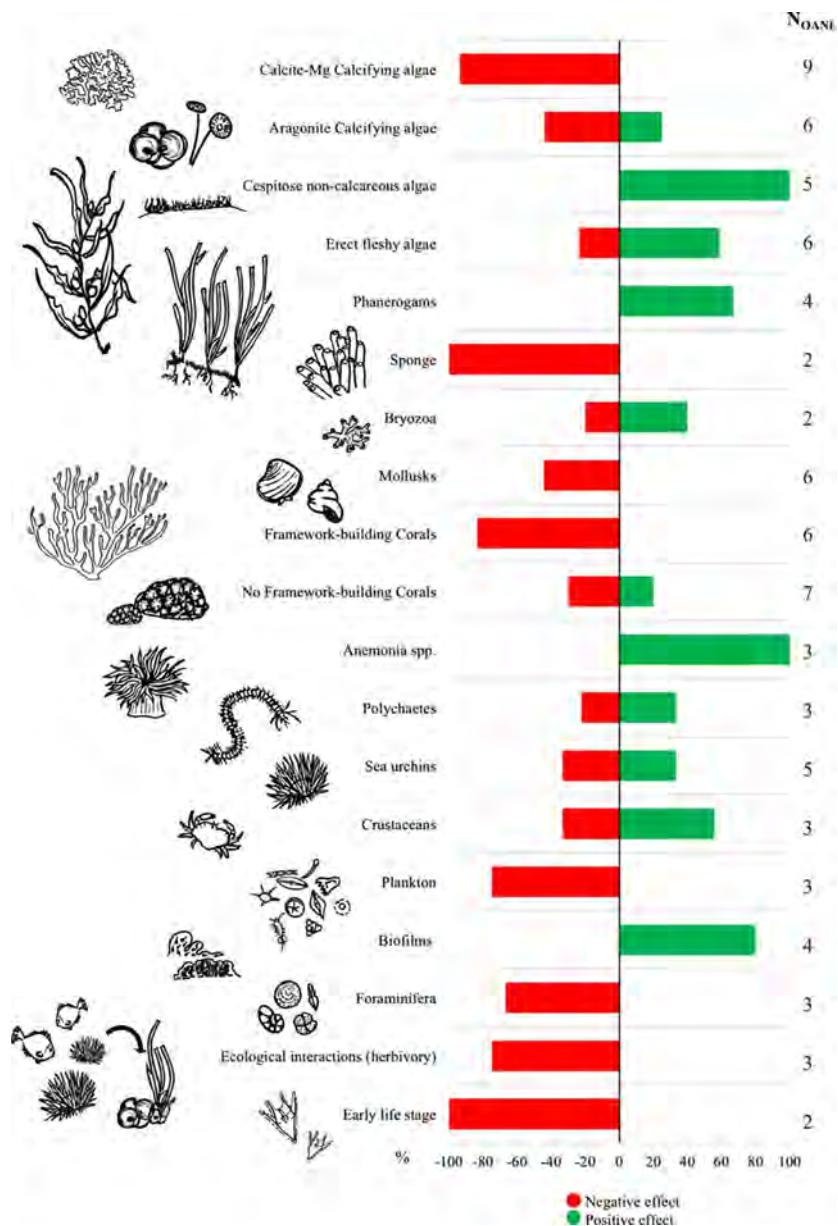


Fig. 4 Summary of the positive and negative effects of OA on different organisms. Percentages have been calculated based on the studies conducted at naturally acidified areas. N_{AS} is the number of natural laboratories where the organism has been studied.

Another important consideration is that the system should not be subject to the influence of other chemical compounds, such as sulphur from gases of volcanic origin, nutrient-rich water, or freshwater and, if possible, mechanical-acoustic contamination due to bubbling should be avoided. In addition, the AS would ideally be located in shallow coastal areas with the greatest possible representation of habitats that are easily accessible for study.

Many questions remain about the changes that are taking place in these acidified areas that can help us understand the oceans of the future. We need more information about changes at the ecosystem level as well as ecological processes and species interactions, and we must also emphasize the importance of understanding the evolutionary processes leading to adaptation in many of the organisms that live in these environments. Finally, we must strive to work in an integrative way, studying the greatest number of geographical areas and habitats; this will help us create a worldwide network of AS for studying and understanding of the oceans of the future.

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