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Global Review of the impact of naturally occurring shallow water CO2 seeps

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ABSTRACT

Studying the local impacts of natural marine discharges can help in understanding the local impacts of large-scale restoration programs. This paper reviews studies of naturally occurring CO_2 rich hydrothermal vents to understand how nature responds. Venting CO_2 raises both total DIC, and the CO_2 partial pressure by a factor of 10 or 20 times, lowering the pH and the saturation state of calcium carbonate, impeding calcification by calcifying organisms.

The ocean is a relatively stable environment and significant changes to water chemistry caused by high levels of CO_2 input impacts marine organisms. Many algae are able to survive and photosynthesise at low pH levels, and some may actually benefit from an increase in dissolved CO_2. However, coralline and calcareous algae that form carbonate skeletons are negatively impacted at low pH. Ecologically and economically valuable marine flora such as kelp, seagrass and certain seaweeds can benefit from increased DIC, exhibiting increases in photosynthetic and growth rates. Kelp and seagrass may also increase local pH levels, creating refuges for calcifying marine species.

The calcification rates of Many marine invertebrates decrease with increasing pCO_2. At sites closer to vent openings, with lower pH, the abundance and diversity of invertebrates is significantly reduced. This can impact species valuable to the fishery and aquaculture industry by directly affecting recruitment, growth and survivorship of species such as mussels and oysters and indirectly through reduced abundance of invertebrate prey for herring and mackerel. Corals are also negatively impacted by declining pH and calcium carbonate saturation, yet not all hard corals respond evenly. More resilient genera such as Porites can survive pH drops to approximately 7.8, however below this value reef development is virtually absent and the habitat is dominated by algae and soft corals.

Naturally occurring low pH sites are relatively common in the marine environment and though they clearly alter species composition and abundance, the locally lower pH does not kill marine life, and beyond dispersion zones species are unaffected. Global ocean acidification is a serious problem, however the impacts of local releases of CO_2 are relatively limited, resulting in community shifts towards low pH tolerant species. Reversal of global ocean acidification is essential, and restoration of the oceans will require huge carbon dioxide removal (CDR) processes.

KEY WORDS

- Ocean acidification
- Carbon dioxide
- Volcanic vents
- Calcifying species
- Natural analogues
- Marine invertebrates
- Marine communities

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1 Shallow water CO_2 seeps as study sites

This paper is the first in a series looking at the local impacts of marine discharges. The question is how does nature manage extreme variations and recover from them locally? How large are the affected zones? Which species are displaced and what takes over in these areas?

This paper reviews studies examining naturally occurring shallow water seeps of carbon dioxide (CO_2) that have the effect of lowering the pH of water in the close vicinity of the release sites.

The reader should note that there is no suggestion that we should contemplate deliberate acidification of the oceans from industrial discharges just because the oceans manage to dissipate the impacts of natural acidifying releases. Far from it.

The purpose is to shed light on how the oceans adapt to local extreme variances and learn from these occurrences so that when developing ways to apply ocean CDR we can stay within the limits of what nature can manage.

A number of carbon dioxide rich areas exist in the shallow seas throughout the world, of which at least 60 have been studied, and these are important areas of study for predicting future impacts of anthropogenic CO_2 emissions on the oceans [1]. Sources of high CO_2 include karstic groundwater inflow (e.g. Yucatan, Gulf of Mexico; Crook et al., 2016), high respiration of living organisms (e.g. Rocas Islands, Palau; Shamberger et al., 2014), upwelling of deep ocean water rich in inorganic carbon (e.g. Kiel Bay, Baltic sea; Thomsen et al., 2010), and discharge of CO_2 rich fluids from volcanic hydrothermal vents (e.g. Levante bay, Italy; Hall-Spencer et al., 2008).

The latter category, hydrothermal vents exist around active marine, coastal and island volcanoes [1]. Many are found in shallow coastal waters, making them relatively accessible study sites. Chemical and biological information currently exists for approximately 60 of these shallow water vents sites globally (Figure 1).

2 Chemical impact of hydrothermal CO_2 venting on the seawater column

Upon exiting vents, CO_2 dissolves into seawater, raising total dissolved inorganic carbon (DIC) and CO_2 partial pressure (pCO_2) (Figure 2). At the vent areas pCO_2 transitions from normal seawater pCO_2 ~ 400 ppm to intermediate partial pressures ~ 1000 ppm in the range of meters to 10s of metres from vents to above 10,000 ppm in near vent conditions.

Dissolution of CO_2 at vents lowers the pH as the carbonic acid molecule splits into hydrogen ions (H^+) and bicarbonate ions (HCO_3^-). It is the free hydrogen ions (H^+) that make it acidic. The existing carbonate ions (CO_3^{2-}) in the water buffer the pH by combining with the extra hydrogen ions (H^+) to form bicarbonate (HCO_3^-). The result of this is that the pH of the water. is lowered, in turn lowering the amount of carbonate in the seawater, thus lowering the saturation state of calcium carbonate minerals (Box 1) and potentially impeding calcification by calcifying organisms. At intermediate sites (m's to 10s of m's from vents) pH is typically 0.2 – 1 log units lower than the ambient pH and calcite/aragonite saturation indexes drop from ~ 4 – 6 Ω_{arag} to ~ 1 – 2 Ω_{arag}. These transitions in water properties can be used as a gradient along which to study effects of CO_2 and pH on marine communities. pCO2 gradients from 300 – 1000 ppm are typically used for biological research into response of communities to enhanced CO_2 levels.

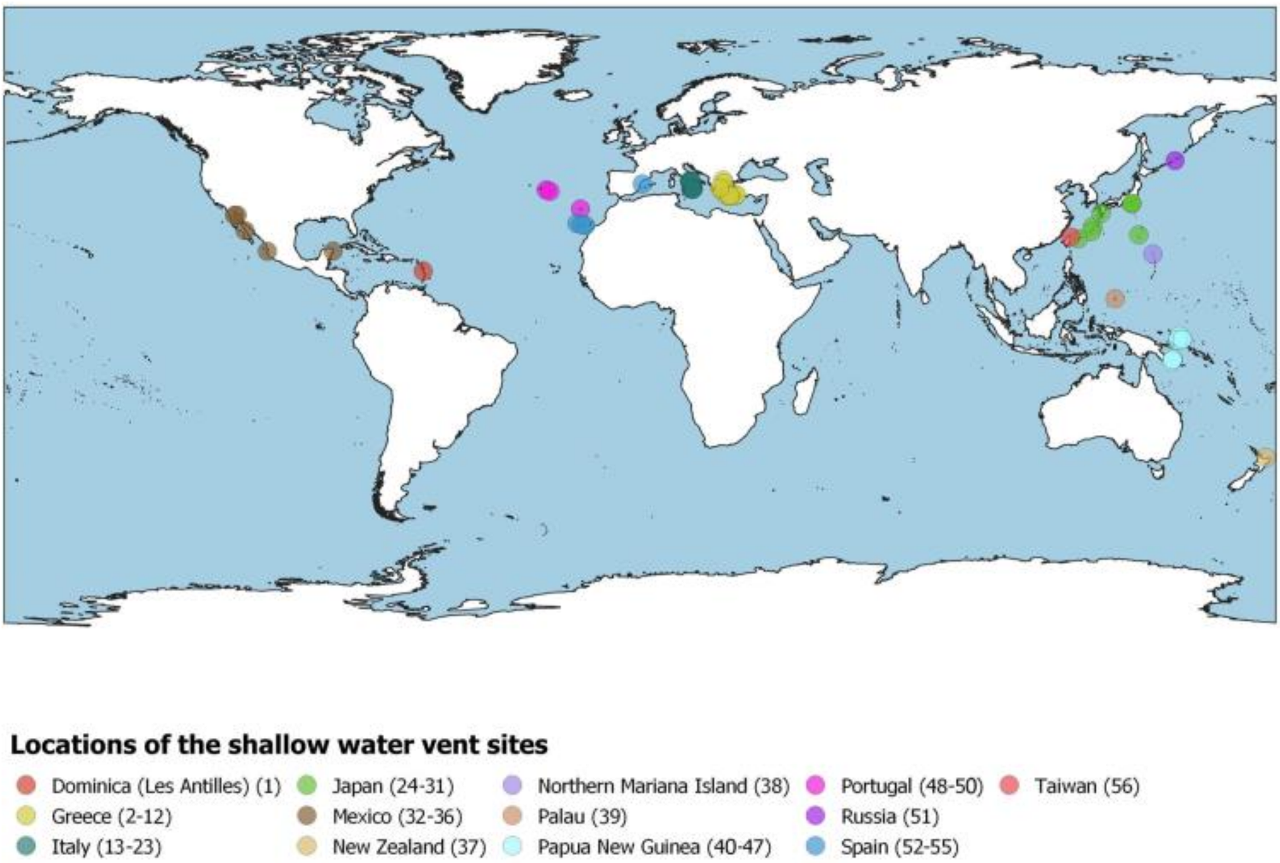

Figure 1 - Map from Aiuppa et al. 2020 showing the locations of shallow water vent sites.

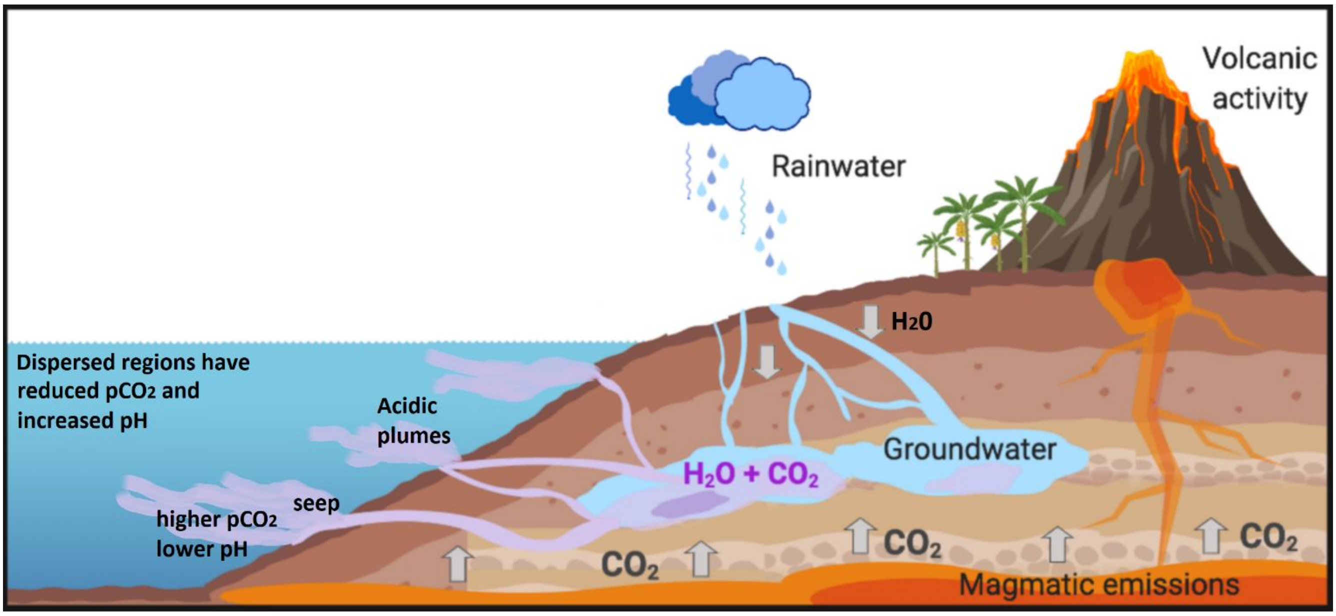

Figure 2 - Geological sketch (not to scale) illustrating the chemistry of CO_2 hydrothermal seeps at shallow coastal vent sites. There is reduced pH and increased DIC and pCO_2 closer to vent sites and dilution occurring further from the vent sites reversing these changes. Figure copied from González-Delgado et al. (2020).

BOX 1. CALCIUM CARBONATE MINERAL SATURATION

Surface seawater is typically supersaturated with respect to calcium carbonate minerals. This means the concentration of these minerals is greater than the concentration required for biogenic precipitation to occur. The aragonite saturation state (Ω_{arag}) is commonly used to understand the impacts of pH changes because it is a measure of carbonate ion concentration and aragonite is widely used by marine calcifiers (e.g. corals and molluscs) to build their skeletons and shells. These calcifiers are generally able to survive and prosper when the Ω_{arag} is greater than 3, below this these organisms typically become stressed and when Ω_{arag} falls below 1 the aragonite structures begin to dissolve.

3 Biological experiments at seeps

To understand the impacts of pCO_2 and pH changes at vent sites, two types of experiment are typically employed 1) in-situ observations and 2) transplantations. Observations assess species responses along natural gradients. Transplantations use single or multispecies assemblages under short or long term acidified and control conditions to attempt to identify cause and effect mechanisms.

Both approaches typically focus on organisms attached to seabed or species with little movement during one or more stages of their life. These species will experience prolonged exposure to the local vent conditions and their presence or absence, and general condition will reflect this exposure. Studies at vents include investigation of processes such as:

- calcification/dissolution
- growth
- survival

- settlement
- reproduction
- metabolic performance
- behaviour
- species interactions and community shifts in relation to pH, pCO_2 and calcite/aragonite
- saturation levels

3.1 Algae

Algal communities perform a range of ecosystem services in shallow coastal systems such as providing food, forming substrate for settlement, offering protection from predators and shelter from disturbances. Macroalgal communities are sensitive to disturbances and so are commonly used to assess the status of coastal ecosystems. There is compelling evidence that many species of red, green and brown algae are able to survive and photosynthesise at pH levels below 7.8 [6].

It is likely that algal communities will have mixed relationship(s) with increasing CO_2. Some algae will benefit from increased CO_2 through enhanced growth [7] while others will suffer due to reduced calcification [8] and general conclusions can be hard to determine. Affects can even vary between closely related algae species [9]. In general, turf and macroalgae's seem to thrive while coralline algae are amongst the most negatively impacted [10] and it is likely that macroalgae and turf algae have a competitive edge over calcifying algae's in lower pH systems due to changes in DIC concentrations and Ω_{arag} saturation states.

As a group, calcareous algae tend to exhibit a decline in abundance as pH declines. One experiment examined the colonisation of limestone tiles deployed at sites with a range of Ω_{arag} saturation states in Mexico [2]. Low Ω_{arag} zones had significantly less cover of calcifying algae's and 42% more fleshy algae than the controls and the percent cover of turf algae was also notably higher [2]. However, there appears to be a division in susceptibility between species. Those that form with a skeleton made of calcite crystals with magnesium content decrease in abundance and may even disappear from acidified systems [11,12]. In contrast, species that form aragonite crystals appear more tolerant to a decrease in pH and appear capable of adapting and even thriving in acidified environments [11,13,14]. This is because the magnesium in the mineralisation increases the rate of dissolution in acidified environments, making species with higher magnesium content more vulnerable [15].

Resilience of a range of brown seaweeds (Ochrophyta) observed at vents [6,14] suggests that this group, which includes ecologically and commercially important genera of kelp (e.g. *Laminaria)* and fleshy algae (e.g. *Sargassum*) may be able to survive some level of seawater acidification. In fact several genera, including both *Laminaria* and *Sargassum* have actually been found to favour the increased pCO_2 environment at vent sites and had higher abundance at these areas (González-Delgado et al., 2018; Table 1).

3.2 Seagrass

Potential beneficiaries of increased pCO_2 and DIC include ecologically valuable seagrasses and kelps as well as economically valuable seaweeds.

Exposure to increased pCO_2 leads to increases in the photosynthetic rates, shoot productivity, density, leaf growth rates, flowering frequency, and biomass of seagrasses [17–21]. In some cases seagrass can increase the pH within nearby areas which can help provide a refuge to more susceptible calcifying algae, increasing the resilience of these species to lower pH [22]. Seagrass beds may also have the potential to increase Ω_{arag} locally, resulting in greater hard coral calcification rates downstream of seagrass beds [23].

However, increasing pCO_2 can also lower the pH compensation point, suggesting it would reduce the ability of seagrass to use HCO_3^- [24]. Therefore, species which favour uptake of dissolved CO_2 may experience greater benefits than those with efficient HCO_3^- uptake systems.

Coralline algae were the dominant contributors to calcium carbonate mass on seagrass blades at normal pH but were absent from the system at mean pH 7.7

and were dissolved in aquaria enriched with CO_2 [26]. This suggests that declining pH may have dramatic effects on the diversity of seagrass habitats and lead to a shift in the biogeochemical cycling of both carbon and carbonate in coastal ecosystems dominated by seagrass beds [26].

While seagrasses can be carbon-limited and productivity can respond positively to CO_2 enrichment, varying carbon allocation strategies amongst species suggest differential growth response between species. Thus, future increase in seawater CO_2 concentration may lead to an overall increase in seagrass biomass and productivity, as well as community changes in seagrass meadows [18]. Therefore, seagrass communities may be good candidates to mitigate CO_2 inputs into the ocean while also forming long-term carbon sinks [25].

3.3 Kelp

Kelp (order Laminariales), like seagrass can modify the pH and carbonate of the surrounding seawater through photosynthesis and respiration which increase and decrease seawater pH respectively [27,28]. These pH fluctuations are beneficial for kelp growth, however a reduction in mean pH can have negative impacts on kelp photosynthesis [29].

Kelp are known to be mixed CO_2/HCO_3^- users and can alter their preferred CO_2 pathway depending on the relative concentration in the surrounding water [30].

Declining pH has been found to have mixed effects for early stages of the giant kelp, *Macrocystis pyrifera*, in one study it was found a drop in pH negatively impact germination [31], however in a second, pH as low as 7.2 was not found to affect germination of either *M. pyrifera* or another kelp species *Undaria pinnatifida* [32]. The difference between studies has been attributed to seasonal variations. The addition of DIC in the first study was found to reduce or even reverse physiological stress [33].

The growth rate of kelp germlings may increase at lower pH, likely due to high pCO_2 [32]. As a result kelp species will likely be positively/neutrally affected by declines in pH, at least during early life history stages [32]

The ability of kelp to persist in the face of declining pH and increasing DIC, while also ameliorating these changes for the local area, could mean that kelp beds may be important refugia for associated organisms in a changing environment.

Table 1. Summary of Documented Responses to the Impact of Acidification on Macroalgae and Seagrass Communities According to Studies in acidified systems from Gonzalez-Delgado and Hernandez (2018). Symbols and abbreviations: (+) positive effect; (–) negative effect; (=) no apparent effect; CCA, crustose coralline algae; PNG, Papua New Guinea

		Mediterranean					Atlantic		Pacific		
		Columbretes	Ischia	Panarea	Methana	Vulcano	Canaries	Azores	PNG	White Island	Maug
Red Algae											
Calcareous	Corallinaceae	+	-/=		-		-	-	-		-
	CCA	-	-		-	-	-		-	-	-
Peyssonnelia spp.		+	+			-			=		
Non-calcareous	Algae mats and erect fleshy algae		+			+	+			+	+
Brown algae											
Calcareous	*Padina* spp.		-	-	-	+			+		-
Non-calcareous	*Cystoseira* spp.	-	=		+	+					
	Sargassum spp.		+			+					
	Dictyota spp.	-	+		+		=				-
	Laminaria rodriguezii	+									
	Halopeteris spp.	+	+			-	+				
	Algae mats		+			+	+			+	+
Green algae											
Calcareous	*Chlorophyta*	-	-	+		=			=		=
Seagrass			+	+		=			+		

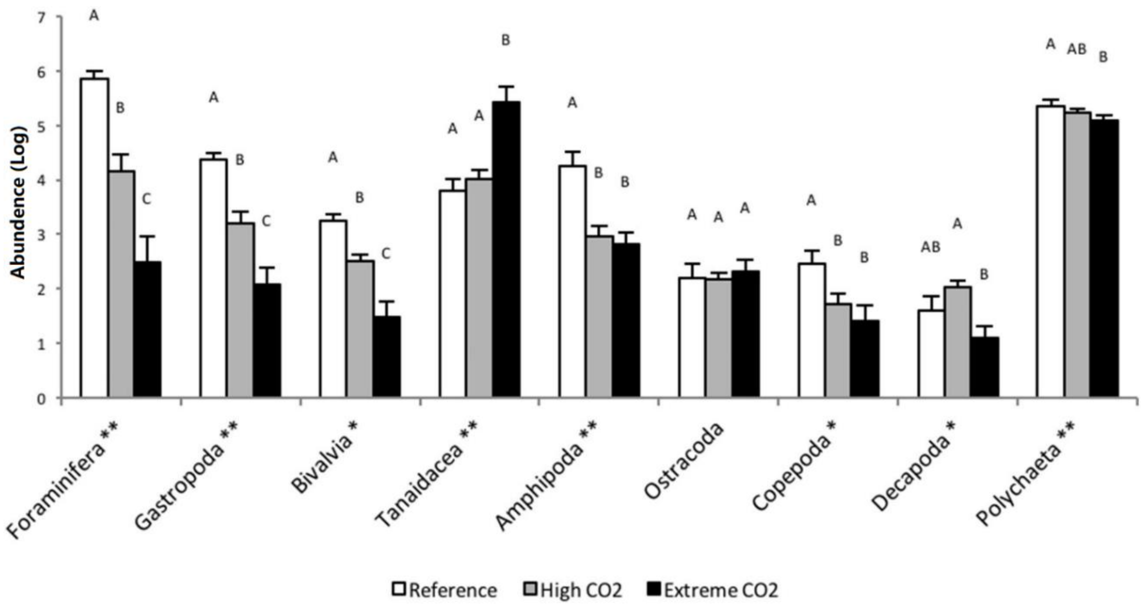

Figure 3 - Abundance of invertebrates from extreme and high CO_2 sites compared to control sites. From Allen et al. [34].

3.4 Invertebrates

Invertebrates are a key component of marine ecosystems; they create habitat, many are first level consumers, and they have a high fishery and aquaculture value. Many invertebrates create calcified shells or exoskeletons and studies have shown that the calcification rate of these organisms decreases with increasing pCO2, even when seawater is supersaturated with $CaCO_3$ [35–37].

At natural low pH sites, changes in the abundance and diversity of invertebrate communities are driven by a significant reduction in the number of calcifying species. There appears to be a clear decrease as pH declines due to the disappearance or strong reduction including the majority of Bivalves, Foraminifera, many Gastropods and many polychaetes and decapods [34,38,39]. Low pH adversely impacts recruitment of calcareous invertebrates in a similar manner to low nutrient conditions [34].

Early life stages, including fertilisation, hatching and larval development (survival and growth), of both oysters [40] and mussels [41] are negatively impacted by declines in the pH. The probability that other bivalves may suffer similar effects is high, since the larval stage is similar among different species of his group.

Amphipods and copepods were significantly less abundant in recruitment communities under near-future elevated CO_2 conditions [34,38]. These small zooplankton crustacea are an important link in the food chain, with species feeding on items including single-celled plankton, planktonic algae (phytoplankton) and other zooplankton. They are a key food source for many fish species, including herring and mackerel. Coastal zooplankton communities appear to have lower abundances in low pH conditions [42,43], primarily due to the loss of these crustaceans.

However, there appears to be some variability even within these calcifying invertebrate groups. Some studies have found that species of echinoderms, molluscs and crustaceans. **[34,44]** either increased or maintained the same levels of calcification under moderate elevation in pCO_2 (400–1,000 ppm pCO_2).

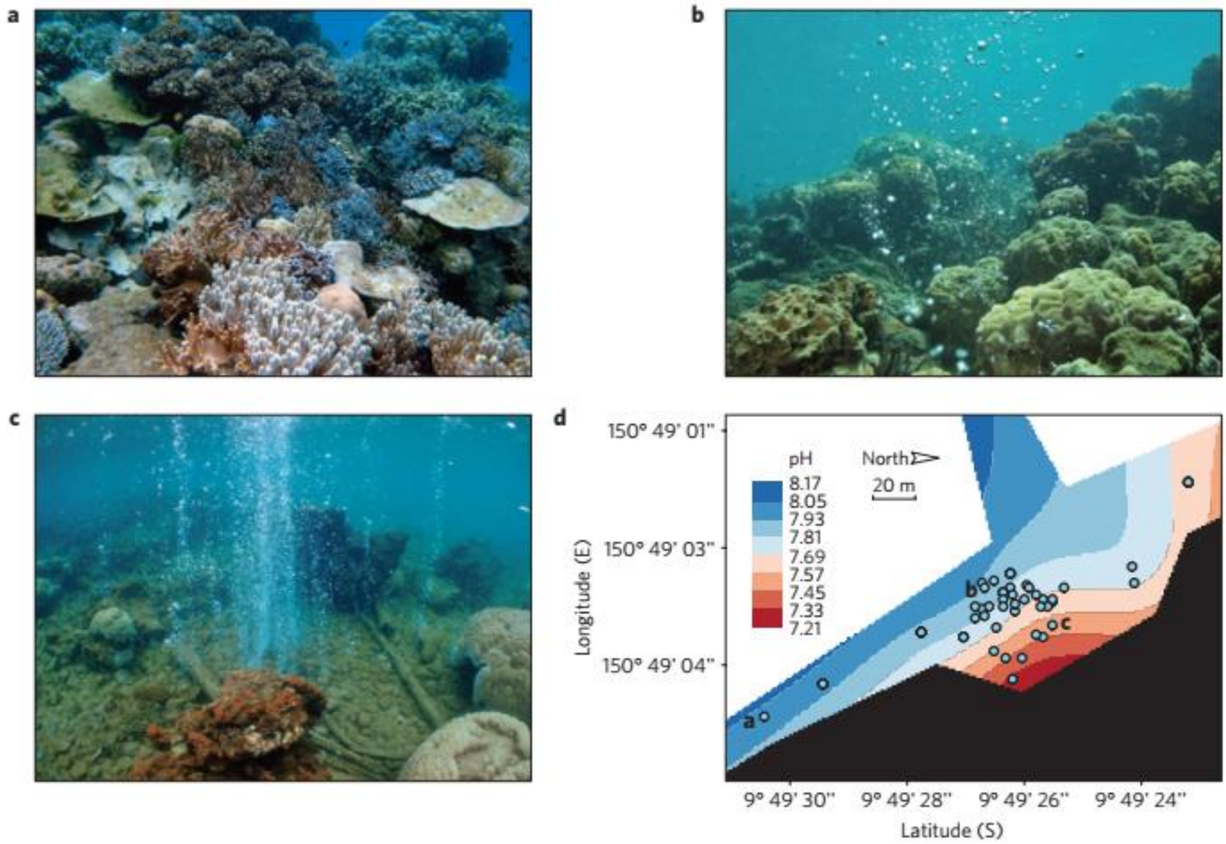

Figure 4 - Hydrothermal vent sites at Milne Bay, Papua New Guinea. Images showing progressive loss of diversity and structural complexity with increasing pCO2 and decreasing pH from: a. control site ("low pCO2", pH ~ 8.1), b. moderate seeps ("high pCO2", pH 7.8 – 8.0) and c. the most intense vents (pH < 7.7). d. Shows map of the main vent site surveyed in the study. Colour contours indicate seawater pH, and the letters show the proximate locations of images a – c. Figure taken from Fabrcius et al. [45]

There are also examples of calcareous organisms, such as Tanaid crustaceans [34] and the barnacle *Chthamalus stellatus* [5] thriving in close proximity to vent sites with extremely low pH and high pCO_2.

Non-calcifying taxa actually appear to be relatively resilient to high pCO_2 and low pH [34].

3.5 Corals

Corals play a vital role in the tropical marine coastal environment. They are the building blocks of vast, diverse ecosystems with incredibly high ecological, social, and economic value. Because they are both fixed to the bottom (sessile) and calcifying they are extremely sensitive changes to surrounding conditions including pCO_2 and pH.

At a vent site in Papua New Guinea (PNG), areas with lower pH had lower coral diversity, recruitment and abundance. This was especially true for structurally complex species which build the 3-dimensional framework vital for high diversity coral reefs [45]. This shift was gradual along a gradient of pH without a clear threshold. Coral cover however, remained constant along a gradient from pH 8.1 to approximately 7.8 as less complex, more resilient massive *Porites* corals dominated the habitat and calcification rates of this genus appeared insensitive to pH changes as low as pH 7.8. Below pH 7.7 reef development was virtually absent, even for the most resilient corals.

In Japan, high pCO_2 conditions close to a vent site where the pH is approximately 7.8, the reef community was dominated by non-calcifying soft corals, whereas in normal pCO_2 and pH conditions nearby the reefs are dominated by hard corals [46].

At a vent site in Maug, Commonwealth of the Northern Mariana Islands, the community shifted from one dominated by hard corals to macroalgae [11]. There was also a lower diversity of coral and calcifying algae at surveys closer to the vent site. The change is attributed to increasing pCO_2 and decreasing pH which resulted in suppressed calcification of relatively resilient massive *Porites* corals. Unlike in the PNG study calcification rates for the *Porites* corals began to decline at pH 7.98.

It is apparent that high pCO_2, low pH seawater negatively impacts coral reefs. Structurally complex hard coral areas shift first to areas of less complex coral development and ultimately to areas dominated by non-calcifying organisms such as macroalgae or soft corals. These changes to coral reef habitat caused by high pCO_2 and declines in pH will have significant impacts on associated communities likely leading to declines in abundance, diversity and resilience of these high value ecosystems.

4 Conclusions

1. There are many naturally formed significantly acidic locations in our oceans. They are relatively common, and we continue to discover more and more of these sites.
2. Life goes on. Having locally different water chemistry does not kill marine life, rather it changes the composition of species and abundances at those sites, and beyond the dispersion zones life remains the same as the locations that are completely unaffected (e.g. permanently upstream). This should not be used to undermine the point that overall ocean acidification is a significant problem because the impacts of overall acidification are unavoidable - there would be no unaffected locations.
3. Lowering the pH alters the competitive dynamics within these systems leading to shifts in the communities of species. Low pH in highly localised areas does not create barren deserts, rather it stimulates the growth of species and suppresses others.
4. There are species of kelp, seagrass and seaweed that can significantly raise pH in shallow waters, and this has the potential for local benefits for marine calcifiers and even for coral reefs downstream of these areas.
5. The lower pH found at vent sites significantly impacts coral reefs exposed to the dispersion plume. A small drop in pH results in less complex and diverse coral communities, while a pH below approximately 7.8 appears to completely inhibit coral growth.
6. It is not clear from the vent studies what proportion of the motile marine animals have travelled to the site to temporarily take advantage of the site rather than adapting in situ [47].
7. The vent studies don’t report any estimates of the vent flowrates or the local ocean currents such that it is difficult to relate the size of affected zones to other point ocean releases and the size of their affected zones.
8. Though localised acidification by vents is a natural occurrence with limited impacts, ocean acidification caused by rising carbon dioxide concentrations is a huge problem. Restoration of the oceans at a global scale will require carbon dioxide removal (CDR) and whatever methods are used they will be very large and impactful.

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