Coral persistence despite extreme periodic pH fluctuations at a volcanically acidified Caribbean reef

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Abstract

Naturally acidified environments, such as those caused by volcanic CO_2 venting, reveal how complex coral reef ecosystems may respond to future ocean acidification conditions. Few of these sites have been described worldwide, and only a single such site is known from the Caribbean. Herein, we have characterized an area of volcanic acidification at Mayreau Island, St. Vincent and the Grenadines. Despite localized CO_2 enrichment and gas venting, the surrounding area has high hard and soft coral cover, as well as extensive carbonate frameworks. Twice daily extremes in acidification, in some cases leading to undersaturation of aragonite, are correlated with tidal fluctuations and are likely related to water flow. Corals persisting despite this periodic acidification can provide insights into mechanisms of resilience and the importance of natural pH variability on coral reefs.

Keywords: ocean acidification, vent, variability, coral resilience

Introduction

Oceanic acidification (OA) resulting from the absorption of atmospheric carbon dioxide into seawater is presently occurring at a rate faster than in the past 300 million yr (Honisch et al. 2012). This remarkable rate of change will have profound ramifications for marine organisms. Coral reef ecosystems are particularly sensitive to OA owing to both habitat-forming (Chan and Connolly 2013) and habitat-eroding processes (Tribollet et al. 2009) that are closely tied to seawater carbonate chemistry. Much of what we know about reef species responses to OA has come from laboratory experiments, which by design represent a simplification of environmental conditions and ecological interactions. While these data are critical, incorporation of real-world complexity into OA research is necessary for understanding and predicting reef ecosystem responses.

Naturally acidified coral reef ecosystems represent a valuable tool in this pursuit. These environments expand brief, single-taxon experiments to the ecosystem scale, where diverse organisms in numerous phyla have been interacting within acidified conditions for decades. To date, natural acidification hotspots have been identified corresponding to upwelling (Manzello 2010), submarine groundwater discharge (Crook et al. 2013), and biological activity (Shamberger et al. 2014), as well as volcanic CO_2 seeps.

In the latter case, persistent venting of subterranean CO_2 gases or acidified vent fluids directly lowers pH, providing a localized means of investigating the influence of global OA. As with other natural ecosystems, careful characterization is necessary to factor out the influence of co-occurring factors and infer the cause of observed community responses (Oprandi et al. 2019; Pichler et al. 2019). Few such systems have been described and fewer still have been found in close association with coral reefs. Those that have include multiple locations within Papua New Guinea (Fabricius et al. 2011), as well as a singles sites off Japan (Inoue et al. 2013) and the

Mariana Islands (Enochs et al. 2015). Data from these sites have identified resilient coral species (Fabricius et al. 2011), and have demonstrated ecosystem shifts from coral to algae (Enochs et al. 2015), or soft-coral-dominated states (Inoue et al. 2013). At these sites, bioerosion by multispecies assemblages of organisms is accelerated and calcification is impeded, leading to the loss of critical reef habitat (Enochs et al. 2016) and associated fauna (Fabricius et al. 2014).

To date, a single geothermal venting site has been documented from the Caribbean at the island of Dominica (McCarthy et al. 2005), but ecological assessment of community responses remains preliminary compared with the Pacific (Graham et al. 2016). As OA research moves towards understanding long-term, ecosystem-scale impacts, identification of further marginal acidified sites, especially in underrepresented regions, is of great importance. Here, we describe a volcanic CO_2 vent associated with a Caribbean coral reef at Mayreau, St. Vincent and the Grenadines.

Materials and Methods

Active venting of subterranean gases was observed at multiple locations throughout Mayreau Gardens. This study was conducted at an area of particularly active venting (12°37'42.0"N, 61°22'41.6"W). A high-resolution photomosaic was constructed in order to provide spatial context for discrete water samples and to document the existence of coral communities in close proximity to the vent. Briefly, photos were taken using two cameras (Hero 6 Black, GoPro) affixed in parallel (~ 60 cm apart) on an aluminum rod. Images were imported into Photoscan (Agisoft), where they were aligned on a PC (Genesis II, Puget Systems).

Water samples for spatial characterization of carbonate chemistry were collected on SCUBA in borosilicate glass bottles immediately above the benthos, as well as at the surface at a nearby unaffected shallow reef site and a deeper offshore site (each ~400 m away). All samples were fixed with $HgCl_2$ at the surface within an hour of collection and sealed with rubber bands and Apiezon grease. Water sample locations were superimposed on the aforementioned site photomosaic. Total alkalinity (TA) and dissolved inorganic carbon (DIC) were determined using Apollo SciTech autotitrators (AS-ALK2 and AS-C3, respectively). All values were measured twice, averaged, and corrected using certified reference materials following Dickson et al. (2007). The remaining carbonate parameters were calculated using CO2SYS (Lewis and Wallace 1998) and the dissociation constants for carbonic and boric acid of Dickson and Millero (1987) and Dickson (1990), respectively. Salinity was measured by a densitometer (DMA 5000 M, Anton Paar).

Temperature and pH (total scale) were recorded every 15 min from May 1 to July 23, 2018, using a SeaFET (Seabird). Higher frequency (5-min) pH characterization was conducted from September 27 to October 1, 2019. During this time, "Subsurface Automatic Samplers" (SAS, Enochs et al., in review) were deployed at a site roughly five meters away from the SeaFET and

were programmed to collect water samples every 3 h. Carbonate chemistry of these samples was measured and calculated as above. All SeaFET data were calibrated to CO2SYS-calculated pH from water samples taken during deployment. Temperature was logged from September 29 through October 1, 2019, within the area of active venting using high-accuracy thermistors (SBE56, Seabird). Instruments were deployed immediately on top of the benthos to reflect what benthic organisms would experience, as well as roughly five cm underneath the sediment to record geothermal activity.

In order to evaluate the synchronicity of tidal flow and extreme pH events, tide data (radar) were taken from the closest (~ 81 km) accurate sea-level station at Prickly Bay, Grenada (IOC 2018), and monthly-derived depth offsets were used to calculate the relative tidal deviation. pH data were smoothed before graphical interpretation with coincident tidal state by calculating a 2-h running mean (1 h before and 1 h after each time point).

Results and Discussion

Strong venting was observed originating from a patch of rocky rubble (primarily of volcanic origin), covering roughly 5 × 5 m (Fig. 1). Nearby carbonate sediment patches and reef frameworks were also observed to be releasing bubbles, though not to the extent of the study site described here. Bottle samples collected over the extent of the study site revealed localized CO_2 enrichment, leading to extreme acidification with pH levels as low as 6.540 and undersaturation of aragonite (Fig. 1 and Table S1). DIC enrichment was higher than TA (DIC = 2.9515*TA − 4738, R^2 = 0.996), though in the most acidified sample TA was 399.2 µequiv kg^{-1} higher than the offsite control, potentially reflecting dissolution. Acidification was intermittent or patchy in nature, as evidenced by markedly different acidification levels measured in closely located bottles (Fig.1 and Table S1).

Whereas prior studies have compared the ecology of acidified sites to that of controls (e.g., Fabricius et al. 2011; Inoue et al. 2013; Enochs et al. 2015) or quantified community responses relative to exposure (e.g., vent proximity, Enochs et al. 2015; pH, Enochs et al. 2016), it is difficult to apply either approach at the Mayreau vent. Temporally and spatially heterogeneous acidification, coupled with a relatively small site footprint, render attribution of community-scale responses to acidification tenuous. That said, at least three species of corals (*Orbicella faveolata*, *Montastraea cavernosa*, *Porites astreoides*) were observed living in areas that periodically experienced vent-associated acidification (Fig. 1, Table S1). More diverse assemblages were observed within five meters (Fig. 1), which qualitatively are more reflective of the communities present throughout the wider >1-hectare extent of the Mayreau Gardens reef.

Long-term, high-frequency monitoring of the pH at Site 1 (Fig.1) revealed relative stability followed by periodic drops to extreme lows in pH (Fig. 2a). Data from sequential water sample collection at the same location (Fig. S2 and Table S2) as well as higher-frequency pH logging at location 2 (Fig. S2) reflected similar variability. In both cases, SeaFET pH loggers were secured

to carbonate frameworks, and data are representative of the conditions experienced by the live coral colonies in the immediate vicinity. In addition to periodic draw-downs in pH, the carbonate chemistry of the water samples showed consistent baseline acidification versus offsite controls and contemporary oceanic CO_2 levels (Table S2 vs offsite in Table S1). Extreme acidification events were strongly correlated with tidal state as determined from the Grenada sea level station (Fig. S3). While the tidal range is less than one meter, strong tidally driven currents were experienced during diving operations. Reduced water exchange during slack tide would lead to greater acidification, even with consistent venting output, and it is likely that depressed flow during slack tide is responsible for the periodic pH depression at Mayreau.

Tidally-driven fluctuations in seawater pH have also been observed at volcanically acidified reef sites in Iwotorishima, Japan, where they contributed to a community shift from hard to soft coral species (Inoue et al. 2013). Similar patterns have also been recorded within sheltered mangrove-lined bays in New Caledonia, though pH depression was accompanied by dissolved oxygen fluctuations and was likely driven by biological activity (Camp et al. 2017).

At Mayreau, as with the sites in New Caledonia, corals were observed to persist within acidified waters, potentially indicating mechanisms of resilience to extreme acidification stress. These mechanisms may be molecular in nature and are therefore important for informing biological and ecological forecasting, as well as OA-resistant reef restoration efforts. Extreme sites may serve as a means of selecting/concentrating resilient species and genotypes, providing important biological repositories (sensu Camp et al. 2017). Additionally, temperature variability can confer resistance to thermal anomalies (Palumbi et al. 2014), and it is possible that similar processes may apply to pH variability and subsequent OA stress tolerance (Rivest et al. 2017).

Shallow-water benthic communities, especially those with restricted water exchange, influence local carbonate chemistry through calcification, dissolution, photosynthesis, and respiration. As such, coral reefs often experience natural cyclical oscillations in carbonate chemistry on scales ranging from seasonal to daily, as mediated by the relative contribution of the aforementioned biological processes. The magnitude of these oscillations will likely increase due to OA, meaning that coral reefs will experience periodic extremes in OA in addition to a depressed mean pH (Shaw et al. 2012). These oscillations will have biological ramifications for calcifying taxa and may be important in influencing ecosystem structure in their own right (Price et al. 2012). Regardless, the direct impacts of carbonate chemistry variability on the biology and ecology of reef organisms remain poorly understood. Daytime pH elevation due to photosynthetic activity may drive enhanced calcification, as has been observed with Caribbean *Acropora cervicornis* populations (Enochs et al. 2018). Conversely, nighttime depressions in pH could favor both biological (Enochs et al. 2016), as well as abiotic dissolution if acidification is strong enough. The Mayreau site is particularly informative to the latter example since periodic pH depressions are not balanced by enhancement.

The presence of reef frameworks and coral skeletons at the Mayreau vent site is interesting in that the persistence of these carbonates can only occur if net calcification is sustained at levels equal to or greater than zero over a protracted period of time. Aragonitic conch shells placed within the vent field were observed to experience extensive degradation in <1 yr, indicating saturation states lower than one, favoring dissolution (Figs.1, S1B). At the organismal level, corals were observed within acidified waters and in close proximity to the dissolving conch shell (Fig. S1). This supports up-regulation of pH at the site of calcification (McCulloch et al. 2012) and/or intermittent calcification at ambient pH levels contributing to carbonate precipitation at a rate equal to or exceeding dissolution. Anecdotally, however, corals persisting on venting rubble exhibited poorly developed, thin skeletons (Figs.1, S1).

With respect to larger-scale reef habitats, dissolution already occurs naturally within sediments (Cyronak and Eyre 2016) or during episodic stress events such as storms (Manzello et al. 2013). Global OA will favor this process (Eyre et al. 2018), further depressing calcification and enhancing bioerosion (Albright et al. 2018; Enochs et al. 2016). Developed frameworks evident at the peripheral margins of the vent site in Fig. 1 may therefore indicate a threshold in the localized acidification gradient where positive net ecosystem calcification is possible. Alternatively, framework accumulation may simply have occurred prior to the formation of the vent. These two hypotheses, however, should be considered within the context of the intermittent nature of the acidification, and more prolonged exposure may lead to OA-accelerated dissolution manifesting differently. Further investigation is necessary to identify which factors contribute to carbonate persistence at the site.

Co-occurring stressors such as elevated sea temperature due to geothermal activity (McCarthy et al. 2005) or simply flushing (Camp et al. 2017) can potentially drive community shifts at naturally high-CO_2 sites. At Mayreau, the surface temperatures measured at two sites within the vent field were roughly the same (29.18°C ± 0.288 and 29.15°C ± 0.263 [mean ± SD]) as the adjacent carbonate framework (29.07°C ± 0.237), though interstitial water and rocks were warmer roughly five cm below the surface (34.51°C ± 0.586). Corals observed growing directly on the sediments were not bleached, and temperature-driven community structuring are not consistent with the data recorded here. Episodic extreme temperature anomalies, however, cannot be completely ruled out.

Volcanically acidified corals and reefs at Mayreau can provide valuable insights into the impacts of global ocean acidification. This site is of particular importance given the paucity of described naturally acidified Caribbean ecosystems relative to the Pacific. The periodic brief exposure to acidification extremes, coupled with the close proximity of scleractinian corals, is apparently incongruous. Both endogenous and exogenous factors contributing to coral and reef persistence should be investigated further.

Conflict of Interest Statement

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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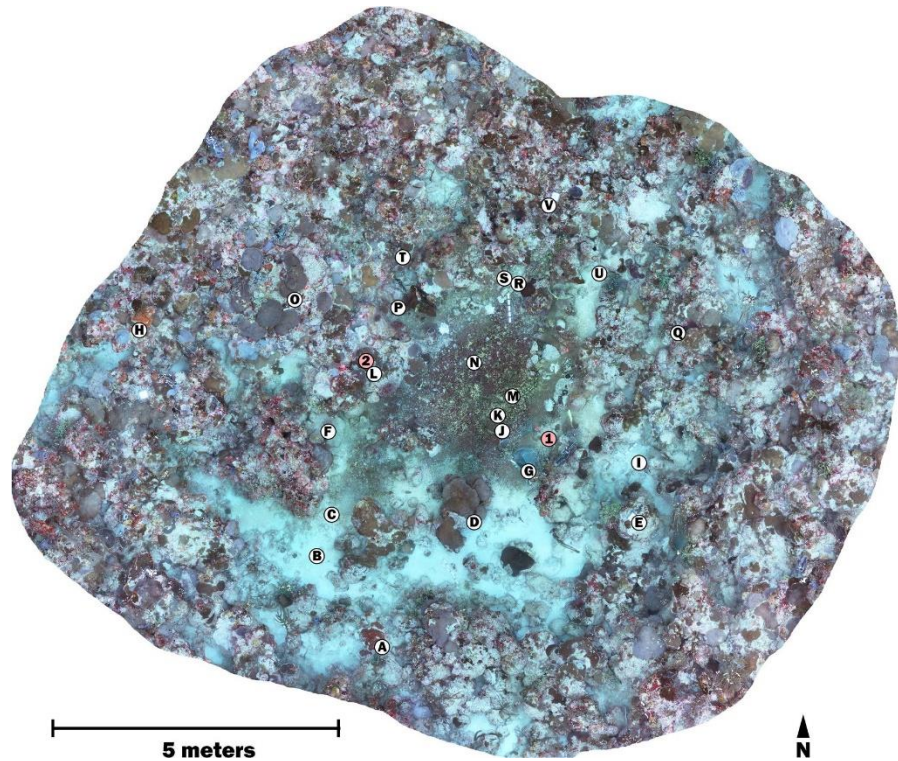
Figure 1. Photomosaic of the Mayreau vent site with area of most active venting in center, surrounded by corals and reef carbonate frameworks. Letters denote sites of seawater samples analyzed for carbonate chemistry in Table S1. Site 1 denotes the location of the long-term SeaFET deployment and collection of water samples for temporal characterization. A second, short-term SeaFET deployment took place at site 2. Striped white bars present near sites I, S, R, and O are 0.5 m pieces of pipe with 10 cm segments marked using black electrical tape. The grey section next to site G is a mesh gear bag captured during mosaic collection.
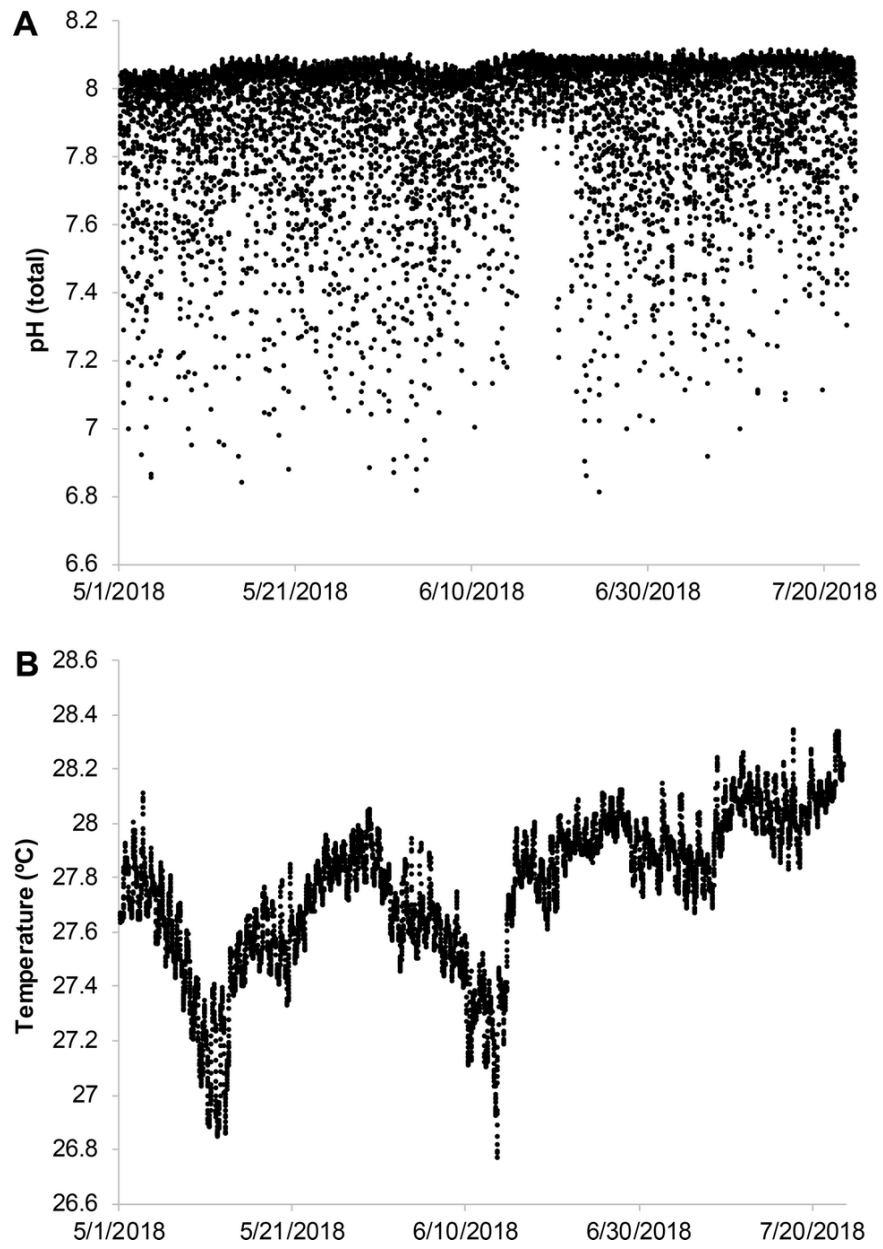
Figure 2. The pH (**a**) and temperature (**b**) at the Mayreau vent site (location 1, Fig. 1).