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ORIGINAL PAPER

# Latitudinal Trends and Drivers in the $CO_2$–Carbonic Acid System of Papahānaumokuākea Marine National Monument

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**Abstract** Emissions of anthropogenic carbon dioxide ($CO_2$) to the atmosphere and the consequent effects of climate change and ocean acidification on coral reef ecosystems have motivated significant interest in describing and understanding the $CO_2$–carbonic acid system of diverse coral reef environments. Although numerous studies have been successful in monitoring reef metabolism both in the field and in the laboratory, physical and biological forcings produce distinct conditions among environments. Due to the geographic isolation and associated difficulties with measuring marine carbon chemistry in waters of the Papahānaumokuākea Marine National Monument (PMNM), relatively few studies have described the $CO_2$–carbonic acid system and carbonate saturation state gradients of these waters. Yet, PMNM remains one of the largest conservation areas in the world with extensive and diverse coral reef ecosystems that could offer valuable insight into our current and future understanding about regional and global impacts of ocean acidification. In order to provide a broad overview of latitudinal trends and features of the marine carbon system in PMNM waters, continuous measurements for surface seawater fugacity of $CO_2$ ($fCO_2$) and pH were collected during August 2011 and July 2012 cruises of the NOAA Ship *Hi'ialakai*. These

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measurements indicate that pH and $f\mathrm{CO_2}$ are three times more variable in nearshore monument waters relative to open ocean transect measurements. This variability can be observed up to 50 km away from the nearest reef and is likely the result of the direct and significant impact of coral reef metabolism on marine carbon chemistry around the islands and atolls. The relationship between total alkalinity and dissolved inorganic carbon is consistent with net calcification which creates an alkalinity sink throughout PMNM waters. Additionally, our measurements show clear latitudinal trends in $f\mathrm{CO_2}$, pH, and aragonite saturation state that are influenced by environmental forcings, including temperature, wind speed, and residence time of the water. Collectively, our results suggest that coral reefs located at the northernmost atolls of PMNM may be the most susceptible to the adverse impacts of climate change and ocean acidification.

**Keywords**  Carbon · Ocean acidification · Coral reef · Papahānaumokuākea Marine National Monument

# 1 Introduction

Papahānaumokuākea Marine National Monument (PMNM), encompassing the Northwestern Hawaiian Islands (NWHI), is home to a diverse array of biological, ecological, and cultural resources. The islands and coral reef atolls that make up this unique archipelago comprise one of the largest marine reserves in the world, encompassing nearly 140,000 square miles. In addition to serving as a biodiversity hotspot (DeMartini and Friedlander 2004; Kane et al. 2013) and important habitat to protected species, such as the critically endangered Hawaiian monk seal and threatened green sea turtle, the nearly uninhabited monument is in relatively pristine condition and exhibits a predator-dominated ecosystem structure observed in few places around the world (Friedlander and DeMartini 2002). Although conservation efforts in the monument are ongoing, the risks associated with climate change, including seawater acidification, sea level rise, and ocean warming, are considered threats to the health and abundance of resources in this important marine ecosystem (Selkoe et al. 2008).

Relatively few studies describing the trends and dynamics of the $\mathrm{CO_2}$–carbonic acid system in marine waters of the NWHI have been published (Sabine and Mackenzie 1995; Thompson et al. 2014). Although Grigg (1982) quantified reef accretion rates as a function of latitude by measuring the linear growth rate of corals, there have been no recent publications describing the latitudinal gradients and features of the marine carbon system along the archipelago. The goal of this study is to provide a current baseline understanding of the $\mathrm{CO_2}$–carbonic acid system of the NWHI, identify latitudinal gradients and features, and describe the processes and mechanisms that are responsible for these patterns. These measurements may provide some insight into the resilience and/or vulnerability of reef habitats in the monument waters undergoing the effects of climatic change, as well as assess the potential biological impacts in response to ocean acidification (OA).

# 2 Climate Change and Ocean Acidification

Oceanic uptake of $\mathrm{CO_2}$ decreases pH and shifts the distribution of dissolved inorganic carbon (DIC) species by increasing the partial pressure of carbon dioxide ($p\mathrm{CO_2}$) and decreasing carbonate ($\mathrm{CO_3}^{2-}$) ion concentration and aragonite saturation state ($\Omega_{\mathrm{ar}}$), a

process known as OA (Caldeira and Wickett 2003; Raven et al. 2005). Given the $CO_2$ emission scenarios described by the IPCC, surface ocean pH is expected to decline by 0.07–0.33 pH units by the end of the twenty-first century (Bopp et al. 2013). The maximum projected drop in pH is equivalent to an approximate 150 % increase in [$H^+$] and 50 % decrease in [$CO_3^{2-}$] (Orr et al. 2005). A decrease in [$CO_3^{2-}$] may decrease the rate at which marine calcifying organisms form calcium carbonate shells and tests ($CaCO_3$) (e.g., Broecker 1971; Kleypas et al. 1999a, b).

At the present time, $CaCO_3$ saturation states are highest in shallow, warm tropical waters and lowest in cold, high-latitude regions and at depth in the sea, reflecting the influence of temperature and pressure on $CaCO_3$ solubility (Morse and Mackenzie 1990; Feely et al. 2003; Doney et al. 2009). However, the $\Omega_{ar}$ of the global ocean is projected to decline by 2.8 by the year 2100, which reflects a 17–35 % decrease in calcification since preindustrial times. Additionally, the isolines of high $\Omega_{ar}$ will shift equatorward, narrowing the latitudinal boundaries for optimal reef growth (Kleypas et al. 1999a, b). Although some species of corals may be resilient to certain environmental conditions that inhibit calcification (Jokiel et al. 2008; Cohen and Holcomb 2009), seasonally extreme temperature, and low-light conditions, combined with a decrease in $\Omega_{ar}$ may put calcifying organisms in the high-latitude regions as the first to experience the adverse impacts of OA (Grigg 1982; Kleypas et al. 1999a, b; Andersson and Mackenzie 2004; Andersson et al. 2005; Orr et al. 2005).

The relative abundance of calcifying organisms such as bryozoans and crustose coralline algae (CCA) increases toward the northwest in the Hawaiian Archipelago (Chave 1954; Schlanger and Konishi 1975; Agegian and Mackenzie 1989). These organisms contain a higher percentage of Mg calcite, the most soluble phase of $CaCO_3$. CCA are an important component for the framework of coral reefs and facilitate the growth of larger structures by acting like cement that glues the reef together. The increased susceptibility of CCA–OA has been demonstrated in numerous studies (Anthony et al. 2008; Manzello et al. 2008; Fabricius et al. 2011), and a loss of these sensitive reef-building species could result in a decline in the overall health of a coral reef.

# 3 Seasonal Trends in $CO_2$–Carbonic Acid System Variability in the North Pacific Subtropical Ocean

Oceanographic conditions and carbon chemistry trends in the North Pacific subtropical region are well characterized (Takahashi et al. 2009; Nakano and Watanabe 2005; http://www.socat.info/). Summer latitudinal (15°–35°N) gradients in sea surface temperature (SST) are relatively small (24–28 °C), whereas winter temperatures (15–25 °C) decrease rapidly with increasing latitude. Wind speed in the summer lacks a defined latitudinal gradient, while during the winter, wind speed increases in the north. (http://www.socat.info/). The average peak-to-peak $\Delta pCO_2$ ($pCO_{2sw} - pCO_{2air}$) is approximately 40 µatm and reflects the influence of temperature on $CO_2$ solubility. The spatiotemporal distribution of pH below 40°N is small (<0.03) (Nakano and Watanabe 2005). These seasonal and geographic trends cause the northern ocean region to switch from a source of $CO_2$ in the summer to a $CO_2$ sink in the winter (Takahashi et al. 2009).

At the Hawai'i Ocean Time-Series (HOT) station A Long-term Oligotrophic Habitat Assessment (ALOHA), 100 km north of Oahu, $pCO_2$ in the surface seawater is monitored by time series observations. Since these waters are oligotrophic and average peak-

to-peak SSTs are 23–27 °C, annual variations in surface $p$CO$_2$ (350–390 µatm), pH (8.055–8.082), and total alkalinity (TA) (2305–2335 µeq kg$^{-1}$) are relatively small. Similarly, daily temperature only varies by about ±0.07 °C (Church et al. [2009]), producing a diel $p$CO$_2$ signal of ±1.5 ppm (Karl [1999]; Takahashi et al. [2002]; Sarmiento and Gruber [2006]; Dore et al. [2003]; Sutton et al. [2010]; http://hahana.soest.hawaii.edu/hot/hot-dogs/bseries.html).

Although time series data collected at station ALOHA reveal that open ocean waters surrounding the Hawaiian Islands currently act as a net sink for CO$_2$ (Dore [2009]), monitoring studies have observed concurrent increases in atmospheric CO$_2$, surface seawater $p$CO$_2$, and DIC at station ALOHA (Winn et al. [1998]; Takahashi et al. [2006]). The uptake of anthropogenic CO$_2$ is likely the cause for both long-term increases in DIC and decreases in CaCO$_3$ saturation state and pH (−0.02 units per decade) (Dore et al. [2003]). Over time, this shift in the distribution of DIC species will decrease the buffering capacity and the ability of the ocean to absorb anthropogenic CO$_2$ (Revelle and Suess [1957]).

# 4 Coral Reef Metabolism in Coastal Environments

Shallow-water environments play an important role in the global carbon cycle (Andersson and Mackenzie [2004]; Andersson et al. [2005]) and display complex carbon system dynamics, particularly in tropical and subtropical coral reef ecosystems. Because of the great physical and biological heterogeneity of these environments (Gattuso et al. [1996]; Lantz et al. [2013]), spatial and temporal variations in the parameters of the CO$_2$–carbonic acid system are large and often difficult to assess accurately over time (Drupp et al. [2013]). In addition to physical and environmental forcings, organic and inorganic metabolic processes significantly alter the chemical properties of the water. Photosynthesis and respiration and calcification and dissolution are opposing forces for changes in $p$CO$_2$ (Smith and Key [1975]) and other components of the carbonate system (Morse and Mackenzie [1990]; Gattuso et al. [1993], [1996]; Yates and Halley [2006]). Thus, determination of the physical and biological forcings driving changes is often difficult.

The effect of increased marine productivity near islands, or downstream from an island, is termed the 'island mass effect' (Doty and Oguri [1956]). This effect refers to an upwelling-induced, biological enhancement around oceanic islands (Barton [2001]). The topographic disturbance of an island assists in the formation of eddies downstream. These eddies can enhance the supply of nutrients into the euphotic zone and increase surface seawater productivity, stimulating higher biological carbon uptake and strengthening the flux of CO$_2$ into the ocean (Caldeira et al. [2002]; Bakker et al. [2007]).

Lack of freshwater, nutrient and suspended solid inputs by rivers, and human discharge make the NWHI an ideal location to study the natural physical, biological, and chemical forcings that influence variability in the CO$_2$–carbonic acid system across the archipelago. Furthermore, studies describing this chemical system in the NWHI are relatively scarce, despite the critical need to characterize such environments for future time series observations tracking the long-term impacts of OA. In order to understand the processes that influence the marine carbon system and quantify the magnitude of variability in carbon parameters both spatially and temporally within coral reef ecosystems and adjacent waters of the NWHI, continuous high-resolution measurements of surface seawater $f$CO$_2$ and pH were made during oceanographic cruises in the summer seasons of 2011 and 2012 around the islands and atolls of the NWHI.

## 5 Description of Northwestern Hawaiian Islands Area

PMNM (Fig. 1) is comprised of a number of islands and coral reef atolls in a relatively pristine environment undisturbed by local anthropogenic activity (Desch et al. 2009). The NWHI chain extends from the island of Nihoa (23°N, 161°W) in the south to Kure atoll (28°N, 178°W) in the north. Due to the large expanse of the Monument, various natural factors play a role in influencing the structure of NWHI reef ecosystems. While SSTs at the southern end of the chain vary annually by 4 °C ($\sim$23–27 °C), SSTs at the northern end may vary annually by up to 10 °C (18–29 °C) (Friedlander et al. 2005; Desch et al. 2009). Surface currents in the NWHI are highly variable in both speed and direction (Firing et al. 2006). In the mean, surface currents at the southern end of the chain flow eastward, while the northern atolls experience predominantly southwestward flow. Winter storms in the North Pacific also affect the spatial distribution of benthic organisms, as some corals and/or algae are sensitive to high-wave-energy events generated by these storms (Grigg et al. 2008; Desch et al. 2009; Rooney et al. 2008). Additionally, internal tidal-driven waves have been observed along the Hawaiian Ridge and have the potential to cause turbulent mixing near island boundaries, bringing up waters that have different chemical characteristics than those of the overlying surface seawaters (Rudnick et al. 2003). Collectively, these oceanographic influences can affect the formation and distribution of coral reef communities in the NWHI (Polovina et al. 2001; Rudnick et al. 2003; Firing et al. 2006; Friedlander et al. 2005; Grigg et al. 2008; Rooney et al. 2008; Desch et al. 2009).
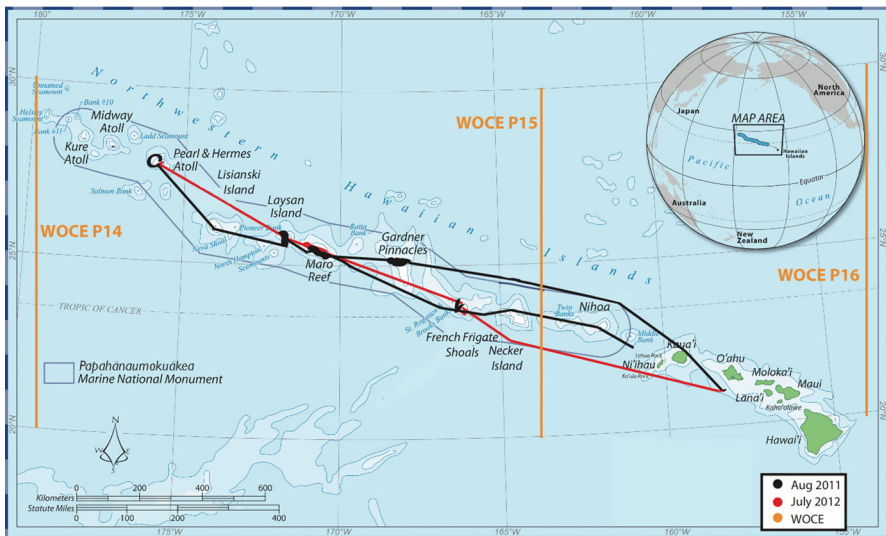


**Fig. 1** Map with boundaries of the PMNM (NOAA PMNM) and track of ship for August 2011 (*black*) and July 2012 (*red*) research cruises. Sections (20°–30°N) of WOCE legs P14, P15, and P16 are given in *white*

# 6 Data Collected and Quality Control

Continuous underway measurements of oceanic $f{CO_2}$, atmospheric $f{CO_2}$, pH, salinity, temperature, and oxygen were collected in surface seawaters of PMNM during August 2011 (7/24–8/21) and July 2012 (7/5–7/13) (see Fig. 1 for ship track). Meteorological data including wind speed and direction were recorded by the ship's instruments and are available on the National Oceanographic Data Center (NODC) website (http://www.nodc.noaa.gov/access/ accession numbers: 0075826, 0104266). Because the various instruments were sampled at different time intervals, the data were binned into the approximate 2-min sampling interval used by the underway system. These data include measurements in offshore waters throughout the monument, as well as shallow waters surrounding the islands and atolls.

Atmospheric and surface seawater $f{CO_2}$ were collected with a General Oceanics Model 8050 underway $p{CO_2}$ system with a LI-COR, Inc., 7000 Infrared Gas ($CO_2/H_2O$) Analyzer (IRGA) located in the wet lab of the NOAA Ship *Hi'ialakai*. The instrument sampled air collected from the bridge and air equilibrated with seawater. Air samples were drawn in from both sides of the bridge where a sensor located 10 m above sea level analyzed wind speed and direction and used air from the upwind side least contaminated by the ship's stack gases. Seawater samples were collected approximately every 2 min from an intake port 5 m below the ship's waterline. These samples were collected with a ratio of 60 equilibrator samples to six atmospheric boundary layer samples (Pierrot et al. 2009). In order to calibrate the IRGA, the underway $p{CO_2}$ system measures four $CO_2$ standard gases every 2.5–3 h, and the differences between the certified values and the measured values are used to correct seawater and atmospheric $CO_2$ measurements. Offsets between certified and measured values for July 2012 indicate that on average the system was accurate to within ±2 μatm.

In order to calculate sea surface $f{CO_2}$ using mixing ratios determined by the IRGA, temperature and pressure inside the equilibrator, as well as SST, are required. Atmospheric pressure is also required to convert mixing ratios to partial pressures. Pressure inside the infrared analyzer is used to correct the signal for pressure effects. Temperature (within ±0.01 °C) and pressures (within ±0.2 mbars) were measured in order to achieve an accuracy of 0.2 μatm for atmospheric measurements and 2 μatm for surface seawater measurements (Dickson et al. 2007; Pierrot et al. 2009).

Measurements of SST were made using a digital oceanographic thermometer, Sea-Bird Electronic (SBE) 38, which is located at the intake port for the $p{CO_2}$ system. Sea surface salinity was measured and recorded by a SBE 21, and dissolved oxygen concentrations were determined using an Aanderra Optode 4330F, corrected for the influences of temperature and salinity. Both the salinity and oxygen sensors were located in the ship's wet lab.

pH was measured using a Honeywell Durafet (see Martz et al. 2010 for performance evaluation) pH electrode with a 2-min sampling interval. Duplicate water samples were collected daily for electrode calibration. Samples were collected in the ship's wet lab from the same inflow pipe used to measure $CO_2$ and kept in 250-ml and 500-ml borosilicate glass bottles, which were allowed to overflow twice. Samples were then poisoned with 100–200 μl of saturated mercuric chloride ($HgCl_2$) solution to prevent further biological activity, and sealed with Apiezon grease. Rubber bands were affixed to ensure a tight seal. The samples were analyzed using spectrophotometric techniques (Clayton and Byrne 1993) and purified m-cresol purple dye (Liu et al. 2011) at 25 °C. A Lambda EZ210 spectrophotometer equipped with a temperature-controlled sample chamber was used for these analyses.

To test the accuracy of our laboratory measurements, certified reference materials (CRM) of a known TA, salinity, and DIC (Dickson et al. 2003) were used. Although CRMs are not available for pH, we calculated pH in $CO_2$ sys using the certified TA and DIC values (Pierrot et al. 2006). In order to limit $CO_2$ exchange, spectrophotometric pH was measured immediately after opening each bottle. Based on the offset between the calculated pH from the CRMs and our measured pH, the average difference was 0.006 pH unit with a standard deviation (SD) of 0.003 pH unit (Table S1). Thirty-three sets of duplicates were also analyzed for reproducibility and indicate the average difference between samples was 0.0002 pH unit (SD = 0.007) (Figure S1) (Dickson et al. 2007).

A total of 17 discrete samples were used for electrode calibration during July 2012. An average standard electrode potential ($E_0$) was calculated from spectrophotometric pH measurements on discrete samples corrected to in situ temperature. The average $E_0$ for July was −0.43485. This value, along with the voltage output from the electrode, was then applied in the calculation for pH over the entire transect.

# 7 Results and Discussion

## 7.1 Coral Reef Metabolism and the Island Mass Effect

Net ecosystem calcification (NEC) over most coral reef environments is positive (i.e., NEC >0), while net organic production (NP) is near zero (Falter et al. 2011; Shamberger et al. 2011; Lantz et al. 2013). The resulting combination for net ecosystem production (NEP) causes coral reef environments to act as net sources of $CO_2$ to the atmosphere (Suzuki and Kawahata 2003). High-frequency carbon measurements collected during our study display more variability and consistently higher $fCO_2$ and lower pH values in surface seawaters than nearby transects in the open ocean, indicating the influence of coral reef metabolism and suggesting net calcification (i.e., net source of $CO_2$) over these reefs (Suzuki and Kawahata 1999; Borges et al. 2005; Fagan and Mackenzie 2007; Hofmann et al. 2011; Drupp et al. 2011, 2013). In order to describe quantitatively the magnitude of variability within our transects, we compared our underway $fCO_2$ and pH to the underway $pCO_2$ and discrete pH data collected on the World Ocean Circulation Experiment (WOCE) transects located both west and east of the NWHI. The WOCE lines used for comparison here are P14 conducted in November–December 2007 (Fukasawa et al. 2008) and P16 conducted in February–March 2006 (Feely et al. 2008) (see Fig. 1).

### 7.1.1 August 2011 Transects

Although pH measurements were not made during the August 2011 cruise, these transects provided the greatest opportunity to examine latitudinal gradients in $fCO_2$ near the atolls. On the first transect traveling north, the surface seawaters of Nihoa, French Frigate Shoals (FFS), and Pearl and Hermes (P&H) were sampled. Traveling back south toward the main Hawaiian Islands (MHI), the Lisianski, Laysan, and Gardner Pinnacles surface seawaters was sampled. The $fCO_2$ data collected during the August 2011 transects clearly show an increase in the magnitude and variability of $fCO_2$ in shallow surface seawaters (denoted by the red circles) near the islands and atolls (Figs. 2, S6), while at further distances (denoted by the blue and green circles), lower values and less variability in $fCO_2$ is observed. The coefficient of variation (CV) was calculated for WOCE P16 (0.012), WOCE P14 (0.017), and NWHI August 2011 (0.034) and indicates two to three times higher variability in the NWHI measurements.
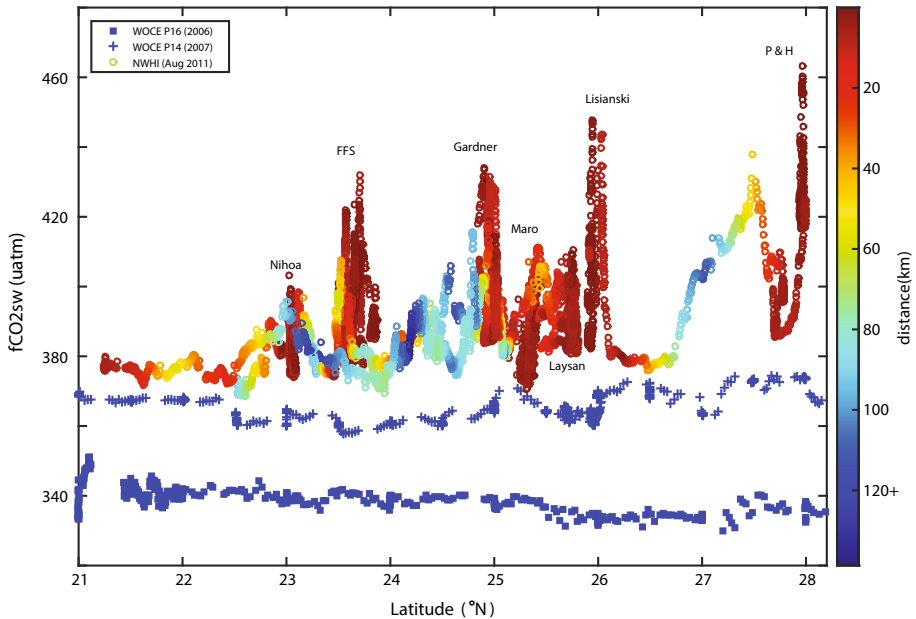
**Fig. 2** Underway surface seawater $f$CO$_2$ (at in situ $T$) during August 2011 (*circles*), WOCE P16 (*squares*), and WOCE P14 (*crosses*). The *colors* represent distance (km) from the nearest island or atoll

Whereas $f$CO$_2$ is relatively constant in surface seawaters of the WOCE transects, much more variability exists in our measurements within the monument waters, even while transiting between islands and at distances >50 km from the nearest reef (e.g., between 26°N and 28°N). Although this variability could be explained by turbulent mixing induced by eddies (Lumpkin 1998; Calil et al. 2008) or internal wave and tidal action along the island slope (Garrett and Munk 1979; Rudnick et al. 2003), surface seawaters would need to mix with waters at least 300 m below the surface (assuming a 50 % mixing ratio) to produce a 20–60 ppm $f$CO$_2$ increase in the open ocean near our transects. CTD profiles collected during our NWHI research cruises show that temperature and salinity at 300 m depth are generally lower by ~14 °C and 1.0 ppt, respectively, than in the surface seawater. These changes in salinity and temperature do not coincide with the $f$CO$_2$ increases observed on the NWHI transect. The increase in $f$CO$_2$ variability observed in our measurements throughout Monument waters therefore is probably primarily a result of photosynthesis/respiration and calcification/dissolution that occurs over and around the atolls within Papahānaumokuākea. The variability observed in our $f$CO$_2$ and pH measurements collected farther away from the islands is hypothesized to be a result of water parcels moving away from the reefs and not fully mixing with open ocean water.

There also appears to be an underlying trend in $f$CO$_2$ during the August 2011 cruises, with $f$CO$_2$ increasing with latitude near the atolls. Most coral reefs are balanced in terms of the uptake or contribution of DIC for photosynthesis and respiration (Falter et al. 2011; Shamberger et al. 2011; Lantz et al. 2013), respectively, and we can assume that organic metabolism in reefs of the NWHI are also balanced (Falter et al. 2011), since there is no land-derived inputs or evidence of upwelling in the northern region during the time of our study that would drive excess metabolism. If the latitudinal $f$CO$_2$ increase is not driven by net respiration, and net calcification

produces $CO_2$, our 2011 data suggest that the northern reefs could be calcifying at a higher rate than reefs located at the southern end of the chain. Grigg (1982) found that net reef accretion of corals in the NWHI decreases with increasing latitude due to high-intensity storm events in the north, cooler water temperatures, less light availability, and subsidence of the Pacific plate. Therefore, other possible explanations for this trend were explored.

We have identified two main environmental factors that may contribute to the latitudinal increase in $f$CO$_2$ during August 2011. First, there is a latitudinal increase in temperature (Figure S2). Normalizing $f$CO$_2$ with respect to temperature according to Takahashi et al. (1993, 2002) removes the effect of temperature on $f$CO$_2$ for any given water sample (Fig. 3). Independent of temperature, $f$CO$_2$ at P&H is still ∼20 μatm higher than $f$CO$_2$ data measured in waters at lower latitudes indicating that temperature alone cannot account for all of the variability observed. Second, trade wind intensity and residence time of reef water also appear to play an important role in latitudinal carbon gradients.

The increase in $f$CO$_2$ of reef-associated surface seawaters over that of the open ocean during the cruise of August 2011 was coincident with a latitudinal decrease in trade wind intensity (Fig. 4) and a slight decrease in the flux of $CO_2$ to the atmosphere (Figure S5). Decreases in wind speed suppress air–sea exchange (Wanninkhof 1992; Fagan and Mackenzie 2007) and could decrease surface current velocities, which in turn may reduce the flushing of reef ecosystems and increase the residence time of waters within the lagoon. Additionally, islands located at the southern end of the chain (e.g., Nihoa and Gardner) and open atolls such as FFS and Maro Reef, are more exposed to flushing with the open ocean. The semi-enclosed northern atolls, including P&H and Midway, experience limited exchange between the lagoon and open ocean waters. Therefore, semi-enclosed bays and lagoons typically have longer residence times than fringing reef systems (Delesalle and Sournia 1992; Lowe et al. 2009), which contributes to greater magnitudes of change in
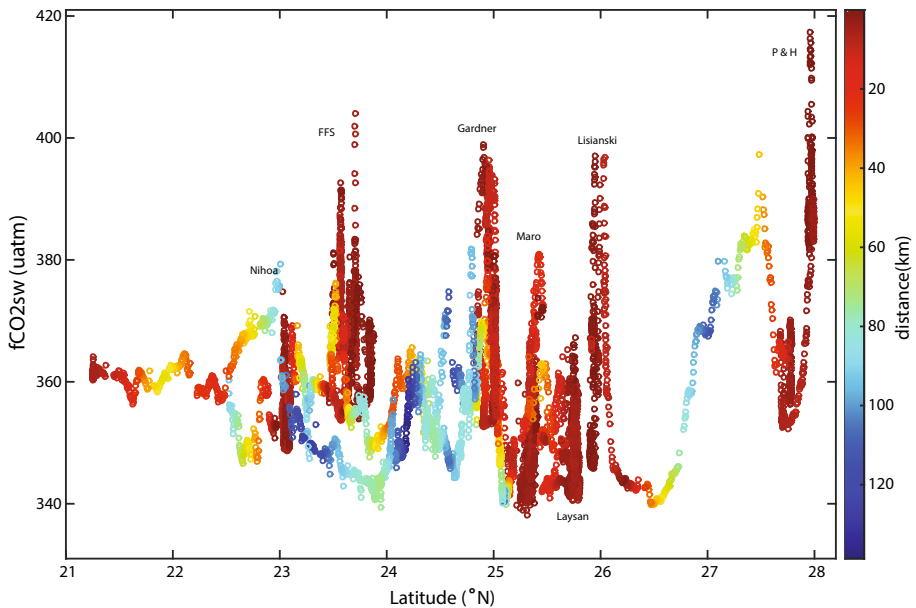


**Fig. 3** Underway surface seawater-normalized $f$CO$_2$ (at 25 °C) during August 2011. The *colors* represent distance (km) from the nearest island or atoll
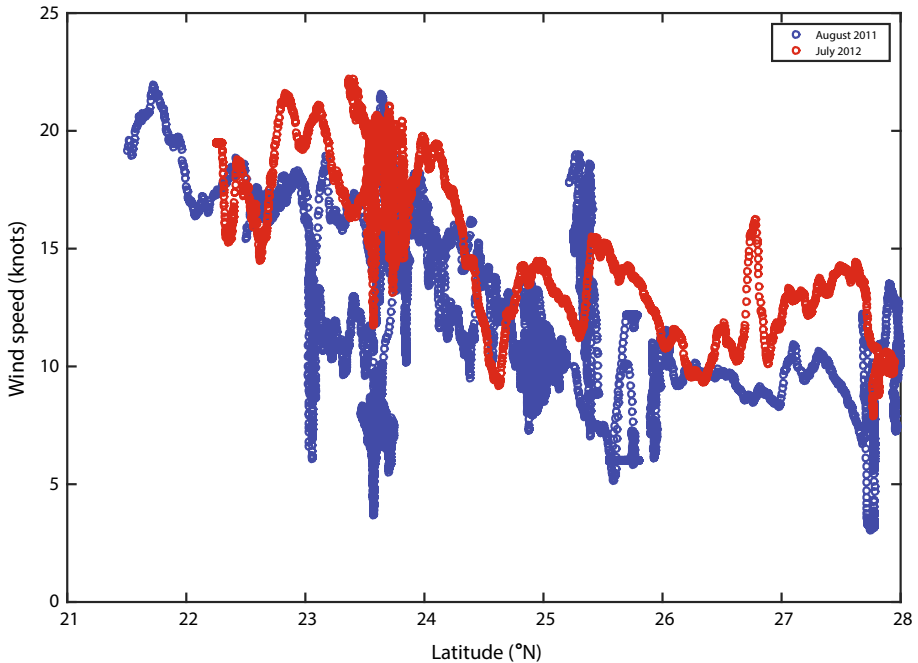
**Fig. 4** Wind speed (*knots*) as a function of latitude during August 2011 (*blue circles*) and July 2012 (*red circles*)

carbon parameters (Shamberger et al. 2011) and increases $fCO_2$ through the processes of calcification and organic matter decomposition (Gattuso et al. 1996; Suzuki and Kawahata 1999; Kayanne et al. 2005).

### 7.1.2 July 2012 Transect

Both $fCO_2$ and pH data for surface seawaters were collected during the July 2012 cruise. July measurements indicated an increase in the variability (CV = 0.031) and magnitude of $fCO_2$ and pH in both nearshore and offshore waters of reef ecosystems (Fig. 5), relative to the WOCE transects. pH declined markedly (−0.06) in nearshore waters around FFS and also displayed a decreasing trend with increasing latitude. The latitudinal gradients in $fCO_2$, wind speed (Fig. 4) and $CO_2$ flux (Figure S5) are weak, in part, because only FFS and P&H were sampled. This increases our confidence that while biological processes are the dominant control on island-to-open ocean carbon gradients, latitudinal trends in wind speed and reef water residence time indirectly contribute to the build-up (or lack thereof) of $CO_2$.

## 7.2 TA/DIC Relationship

Because both pH and $pCO_2$ were measured during the July cruise, we used these data to examine the latitudinal gradients in the TA/DIC ratio as well as in $\Omega_{ar}$. Although TA and DIC can be computed from the $fCO_2$–pH pair, there are potentially significant errors associated with this calculation (Millero 2007). These errors are attributed to the strong

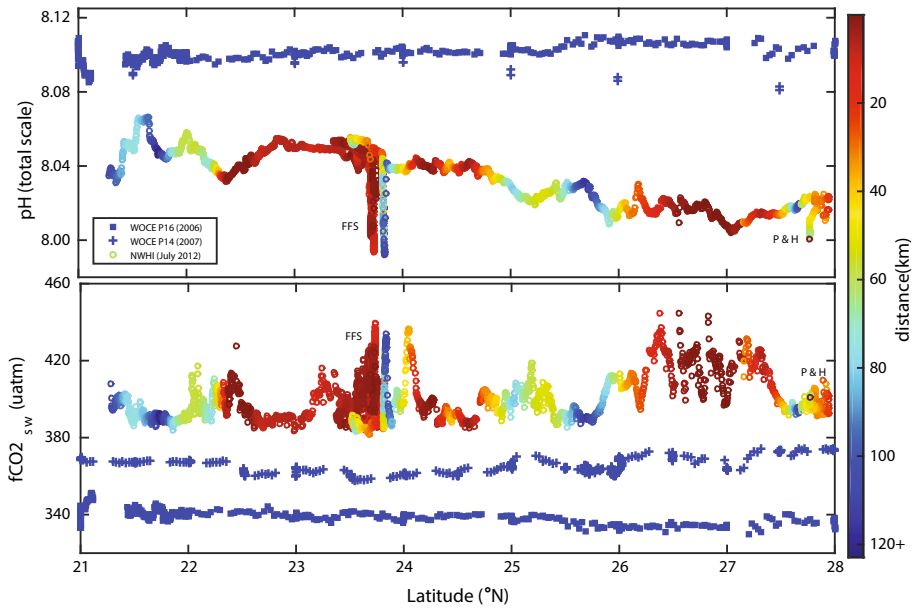**Fig. 5** Underway surface seawater pH (*top*) and $fCO_2$ (*bottom*) during July 2012 (*circles*), WOCE P16 (*squares*) and WOCE P14 (*crosses*). Discrete pH samples were collected during the WOCE transects. The *colors* represent distance (km) from the nearest island or atoll. All values are measured at in situ temperature

covariance between pH and $fCO_2$ (Dickson and Riley 1978; Gray et al. 2011). The uncertainty for our $fCO_2$ and our spectrophotometric pH calibration measurements was ±2 μatm and ±0.003 pH units, respectively. This combination of uncertainties can produce inaccuracies of 15–30 μmol/kg for DIC and alkalinity, respectively. However, since the calculation of both alkalinity and DIC is similarly affected by the covariance of pH and $fCO_2$, considerably greater confidence can be attributed to the TA/DIC ratio. In fact, doubling the uncertainties in both $fCO_2$ and pH described above yields a potential error of only 0.2 % in the ratio of these parameters.

The TA/DIC ratios computed from our underway data varied between 1.144 and 1.160 (Fig. 6), with the lowest values observed at FFS. The TA/DIC at station ALOHA during summer months, as well as the ratios on the available WOCE lines east and west of the island, are generally higher than the ratios we observed (Table 1). The relatively low TA/DIC ratios observed on the July transect are consistent with the higher $fCO_2$ and lower pH within the archipelago (Fig. 5), and are produced by TA decreasing at a higher rate than DIC. This pattern is consistent with net calcification that intensifies near the reefs and creates an alkalinity sink in the coastal waters surrounding the NWHI. A net increase in nDIC in the waters surrounding the NWHI is unlikely given that it would require net heterotrophy or net air–sea invasion of $CO_2$. Given the late summer timing of the NWHI surveys, these scenarios are implausible.

Plotting changes in the TA relative to DIC can provide some insight into the relative impact of organic photosynthesis/respiration and $CaCO_3$ calcification/dissolution on the marine carbon system (Moulin et al. 1985; Morse and Mackenzie 1990; Andersson and Gledhill 2013). Typical coral reef environments exhibit a slope of 0.95 when changes in TA are plotted versus changes in DIC (Andersson and Gledhill 2013; Andersson et al.
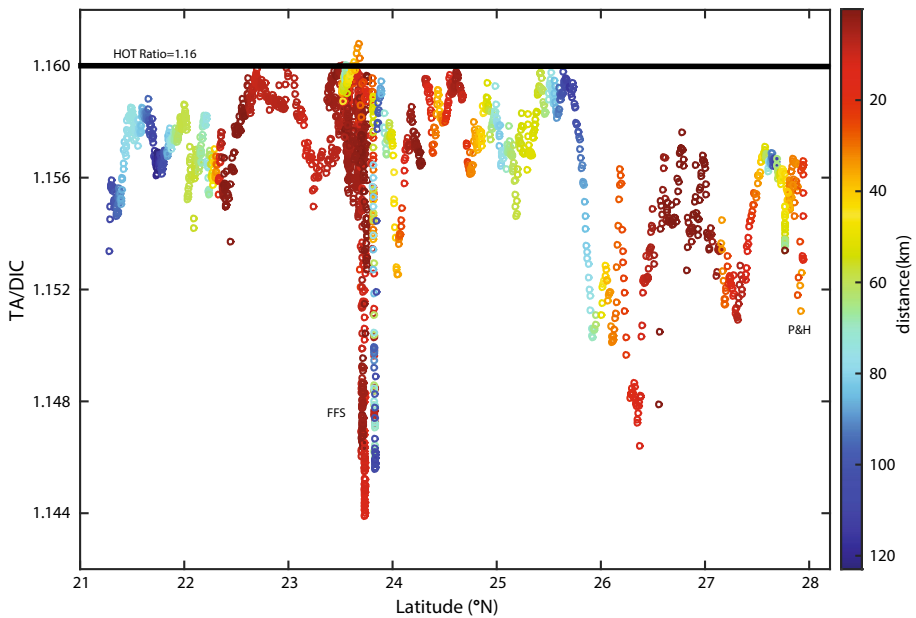
**Fig. 6** Relationship between calculated TA and DIC with latitude during July 2012. The *black line* is the average TA/DIC over 1998–2012 at the Hawaii Ocean Time series station ALOHA. The *colors* represent distance (km) from the nearest island or atoll

**Table 1** Temperature, average normalized alkalinity, average normalized DIC, and average nTA/nDIC for WOCE P14 (1993, 2007), WOCE P15 (1994), WOCE P16 (1997, 2006), and this NWHI study (2012)

| Program | Sample period | Temperature range | Average nTA | Average nDIC | Average nTA/nDIC |
|---|---|---|---|---|---|
| WOCE P14 1993 | July | 20.1–28.1 | 2298.0 | 1958 | 1.1736 |
| WOCE P15 1994 | October | 21.3–27.8 | 2302.3 | 1962 | 1.1734 |
| WOCE P16 1997 | November | 24.2–25.8 | 2301.5 | 1974.8 | 1.1654 |
| WOCE P16 2006 | March 2006 | 19.9–23.2 | 2302.2 | 1979.6 | 1.1630 |
| WOCE P14 2007 | October–November 2007 | 25.6–26.9 | 2300.6 | 1962 | 1.1726 |
| Average | | | 2300.9 | 1967.3 | 1.1696 |
| This study | July 2012 | 25.1–27.3 | 2227.1 | 1926.3 | 1.1562 |
| Difference | | | −73.8 | −41.0 | 1.80 |

2014). However, studies have reported slopes ranging from 0.26 to 2.02 (Suzuki and Kawahata 2003; Lantz et al. 2013). A scatterplot of nTA versus nDIC for all of the data collected within the archipelago in July displays a remarkably consistent relationship with a least squares slope of 1.17 (Fig. 7). At the temperatures and salinities observed during the July transect, a slope of 1.22 is expected if the ocean remains in equilibrium with the atmosphere. The slightly lower slope observed through the NWHI suggests that the reaction pathway of the carbon system within the surface seawaters of the archipelago is predominantly governed by calcification and dissolution.
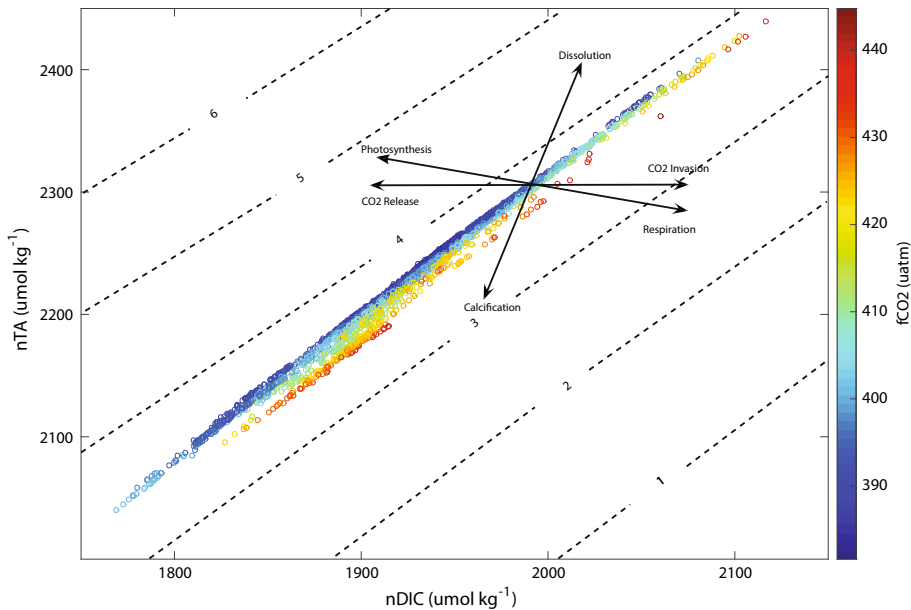
**Fig. 7** TA plotted against DIC (slope = 1.17) for all data collected during July 2012. The *colors of the circles* represent *f*CO$_2$ concentration, and *dotted lines* represent $\Omega_{arag}$

The net effect of the NWHI reef metabolism on the waters of the North Pacific Subtropical Gyre (NPSG) can be illustrated by comparing the average nTA and nDIC values for WOCE P-14 and P-16 (2300.9 and 1967.3, respectively) to the overall average for the NWHI (2227.1 and 1926.3, respectively) (Table 1). Assuming the WOCE data are representative of NPSG water unaffected by the Hawaiian Archipelago, the overall difference reveals a nTA/nDIC slope of approximately 1.80 which is close to the theoretical 2.00 value expected solely from net calcification without exchange with the overlying atmosphere.

### 7.3 Aragonite Saturation

As expected, $\Omega_{ar}$ showed the greatest range within the waters surrounding FFS, decreasing in shallow water near the reef due to calcification and increasing further away from the atoll as a result of dissolution and likely some mixing with open ocean water (Fig. 8). The decrease in pH with latitude also forces a latitudinal decrease in $\Omega_{ar}$. Previous studies have reported average near-surface ($\sim$20 m depth) $\Omega_{ar}$ of 4.80 (Sabine 1992; Sabine and Mackenzie 1995) and 3.61 (Thompson et al. 2014). Here, we report aragonite saturation levels ranging from 3.03 to 3.82 (mean = 3.44), with the lowest values measured in nearshore waters around FFS and in the northern end of the NWHI chain. Although our measurements provide greater coverage and data closer to shore, an overall decrease (1.36) in the mean value of $\Omega_{ar}$ over the past 20 years may be an indication of long-term change as a consequence of OA.

Laboratory-derived studies have found that the calcification rate of corals decreases as carbonate saturation states decline (Gattuso et al. 1998), and previous research has shown that most coral reef communities exist in waters with $\Omega_{ar} > 3.3$ (Kleypas et al. 1999a, b). From a thermodynamic perspective, organisms expend more energy to calcify at lower

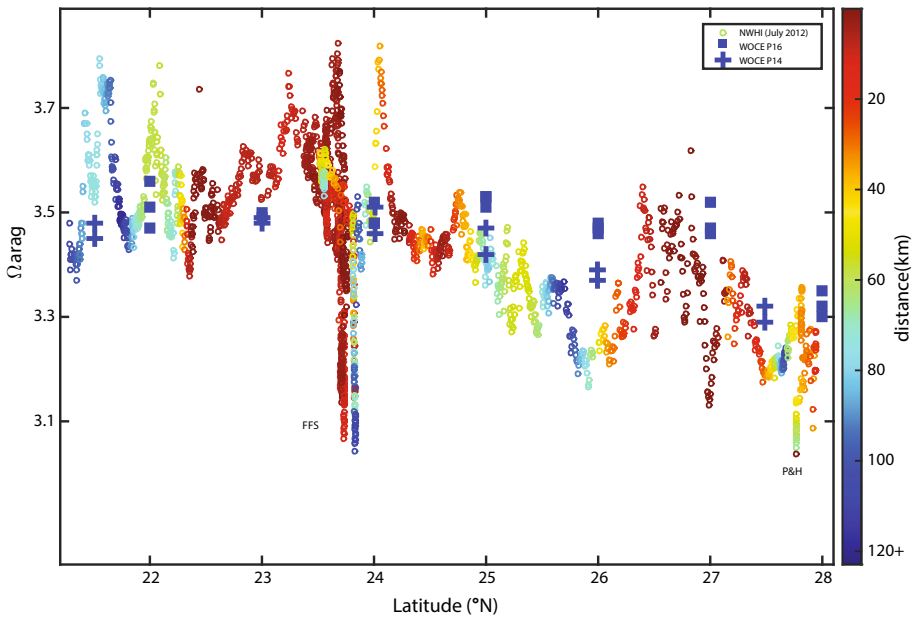**Fig. 8** Aragonite saturation state during July 2012 (*blue circles*) calculated from underway $f$CO$_2$ and pH. WOCE P14 (*red triangles*) and WOCE P16 (*black boxes*) data are also shown. *Colors* represent distance (km) from the nearest island or atoll

saturation states, and at undersaturation, dissolution of CaCO$_3$ may exceed precipitation (Andersson et al. 2011; Mackenzie and Andersson 2013). A recent study by Shamberger et al. (2014) found that coral cover, diversity, and richness were maintained in waters with $\Omega_{ar} < 2.7$ at Rock Island, Palau. While this observation may have hopeful implications for some reefs in an OA world, northern reefs in the NWHI experience a combination of growth-inhibiting environmental factors (e.g., high temperature variability, strong storm events, less light availability) (Grigg 1982), in addition to low aragonite saturation states. Although the July 2012 transect only extended to P&H, a linear regression of the data yielded $-0.054$ $\Omega_{ar}$ deg$^{-1}$ °N, which would mean that reefs at Midway and Kure may experience average aragonite saturation states of 3.01 and 3.00, and chronically lower than those at P&H. The reef ecosystems at Midway and Kure may not have the capacity to maintain their growth rates under current or future OA conditions.

# 8 Conclusions

The observations presented in this study suggest that biological processes occurring within the coral reef ecosystems that comprise the NWHI significantly influence the CO$_2$–carbonic acid system in the surrounding coastal and open ocean environment. Our data demonstrate that considerably more variability in the seawater carbon system exists in and around the archipelago than in the surrounding open ocean. We interpret this spatial variability as being a consequence of the mixing of waters directly impacted by the coral reef ecosystem with open ocean waters being advected generally east to west across the NPSG. Our data also show that the impact of reef metabolism is not restricted to nearshore

waters within the archipelago, but that the impact can be observed at distances up to 50 km from the nearest shallow water environments. In addition, our observations suggest that metabolic processes generate a significant decrease in the ratio of alkalinity to DIC relative to the open ocean waters both east and west of the archipelago. The change in this ratio is consistent with net calcification that decreases both alkalinity and DIC. These data taken together suggest that the reef ecosystems within the Pahapahānaumokuākea Marine National Monument have substantial impact on the inorganic carbon system in relatively vast regions (at least 10s of kilometers) around the archipelago.

Our data also show latitudinal variability within monument waters. There appeared to be gradients in $f$CO$_2$ and pH that can be linked to latitudinal gradients in environmental factors, such as temperature, wind speed, and assumed atoll residence times that are produced, in part, by the configuration of the islands geomorphology. In addition, seawater aragonite saturation state values calculated from $f$CO$_2$ and pH during July 2012 reveal a decrease in nearshore waters as well as a latitudinal decrease in the surrounding open ocean. In addition to the lower $\Omega_{ar}$ values observed in this study, coral reefs of the northern atolls are subject to conditions less favorable for reef accretion due to higher wave energy during the winters, extreme seasonal variability in water temperatures, and lower solar insolation (Grigg [1982]; Andersson and Mackenzie [2004]; Andersson et al. [2005]; Orr et al. [2005]; Rooney et al. [2008]; Doney et al. [2009]; Gove et al. [2013]), relative to the southern reefs. Although we do not have winter carbon data in the NWHI, the environmental conditions of the North Pacific subtropical ocean would likely drive $\Omega_{ar}$ approximately one unit lower than the summer values observed in this study. Furthermore, the abundance of high-Mg-calcite-secreting organisms (i.e., coralline algae and bryozoa) increases in the northern Hawaiian waters (Chave [1954]; Schlanger and Konishi [1975]). These mineral compositions are more soluble than those of calcite and even aragonite. At the lower carbonate saturation states of northern waters, as anthropogenic CO$_2$ is added to surface ocean water, Mg calcite mineral phases are probably most at risk of dissolution, relative to organisms with primarily calcite and aragonite mineral compositions (Bischoff et al. [1987]; Morse et al. [2006]; Andersson et al. [2008]; Manzello et al. [2008]). Thus, the coral reef ecosystems of these northern atolls may be most susceptible to the adverse effects of climate change and OA. Additional surveying and monitoring of underway $f$CO$_2$ and pH in the Monument waters may help to quantify net calcification rates across the archipelago, measure the long-term effects of OA, and assist in the development of effective and informed management plans.

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