

TITLE: Oceanographic patterns and carbonate chemistry in the vicinity of cold-water coral reefs in the Gulf of Mexico: Implications for resilience in a changing ocean

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ABSTRACT:

Limnology and Oceanography Volume 61, Issue 2 p. 648-665 ArticleFree Access Oceanographic patterns and carbonate chemistry in the vicinity of cold-water coral reefs in the Gulf of Mexico: Implications for resilience in a changing ocean Samuel E. Georgian, Corresponding Author Samuel E. Georgian Center for Biodiversity, Department of Biology, Temple University, Philadelphia, PennsylvaniaCorrespondence: georgian@temple.eduSearch for more papers by this authorDanielle DeLeo, Danielle DeLeo Center for Biodiversity, Department of Biology, Temple University, Philadelphia, PennsylvaniaSearch for more papers by this authorAlanna Durkin, Alanna Durkin Center for Biodiversity, Department of Biology, Temple University, Philadelphia, PennsylvaniaSearch for more papers by this authorCarlos E. Gomez, Carlos E. 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Cordes Center for Biodiversity, Department of Biology, Temple University, Philadelphia, PennsylvaniaSearch for more papers by this author First published: 21 December 2015 <https://doi.org/10.1002/lno.10242>Citations: 31AboutSectionsPDF ToolsRequest permissionExport citationAdd to favoritesTrack citation ShareShare Give accessShare full text accessShare full-text accessPlease review our Terms and Conditions of Use and check box below to share full-text version of article.I have read and accept the Wiley Online Library Terms and Conditions of UseShareable LinkUse the link below to share a full-text version of this article with your friends and colleagues. Learn more.Copy URL Share a linkShare onFacebookTwitterLinkedInRedditWechat Abstract To accurately assess the threat that global climate change poses to marine systems, a detailed baseline of the current carbonate chemistry and other oceanographic conditions is required. Despite the heightened vulnerability of deep-sea communities to ocean acidification, there have been relatively few studies investigating the carbonate chemistry immediately above cold-water coral reefs. Here, we present data collected during five cruises from 2010 to 2014 in the northern Gulf of Mexico and quantify the carbonate system and other oceanographic parameters in offshore surface-waters, the water column, and at deep benthic sites. Benthic sites containing the scleractinian cold-water coral *L. pertusa* occurred in waters with a relatively wide temperature range ($6.8\text{--}13.6^\circ\text{C}$), low potential density ($\sigma_t = 26.9 \pm 0.3 \text{ kg m}^{-3}$), low dissolved oxygen concentration ($111.3 \pm 2.0 \text{ } \mu\text{mol kg}^{-1}$), low pHT (7.87 ± 0.04), low ΔARAG (1.31 ± 0.14), and a low availability of carbonate ions ($94.4 \pm 9.2 \text{ } \mu\text{mol kg}^{-1}$) compared with *L. pertusa* habitats in other regions. Based on previous modelling and experimental results, these values place *L. pertusa* at the edge of its viable niche in the deep Gulf of Mexico. However, significantly elevated total alkalinity ($+39\text{--}44 \text{ } \mu\text{mol kg}^{-1}$) was detected above large *L. pertusa* mounds, suggesting that carbonate dissolution within the mounds may be partially ameliorating the direct effects of ocean acidification. Together, these results provide an important baseline for assessing future oceanographic changes in the Gulf of Mexico and for predicting the resilience of cold-water coral reefs to global climate and ocean change. Global climate change, a consequence of increasing anthropogenic emissions, is inducing alarming changes in marine

ecosystems around the world, even in the relatively isolated deep-sea environment. Despite its apparent remoteness, the deep sea is already subjected to a large number of anthropogenic stresses including commercial fishing (Koslow et al. 2000; Gage et al. 2005), oil and natural gas extraction (White et al. 2012a), reductions in food availability (Ruhl and Smith 2004), and waste disposal (see Ramirez-Llodra et al. 2011). In the near future however, climate change is expected to become a more pervasive threat to deep-sea ecosystems with potentially irrevocable damage caused by predicted levels of ocean warming, deoxygenation, and acidification (Mora et al. 2013). These changes will likely outpace the ability of marine ecosystems to respond effectively through plasticity, acclimatization, or adaptation (Hoegh-Guldberg 2014). The ocean is a global sink for the heat building up in the atmosphere, with an estimated 80% of atmospheric heat ultimately being stored in the oceans (Levitus et al. 2005). Over the last 100 yr, this has caused a mean temperature increase of 0.7°C in surface waters (Trenberth et al. 2007), which are predicted to increase by a further 2–3°C by 2100 under a business-as-usual greenhouse gas emission scenario (Cocco et al. 2013). Associated increases in deep-sea temperatures have been estimated on the order of 0.2–0.3°C (Mora et al. 2013). Due to long equilibrium times, water temperatures in the deep sea will continue to rise for centuries after atmospheric temperatures stabilize or are even reduced (Hansen et al. 2005; Purkey and Johnson 2010). Ocean warming will also drive ocean deoxygenation due to the lower solubility of O₂ in warmer seawater and increases in upper ocean stratification that reduce oxygen transport to deeper waters (Keeling et al. 2010). Deoxygenation will be locally exacerbated by fertilizer runoff and subsequent eutrophication of surface waters that results in the formation or expansion of ‘dead zones’ in regions with large terrestrial inputs, including the Gulf of Mexico (Rabouille et al. 2008). Surface waters are predicted to experience 2–4% reductions in dissolved oxygen by 2100, with similar decreases expected in the deep sea (Cocco et al. 2013). In concert with these changes, oxygen minimum zones are expected to both expand spatially and exhibit lower minima in the near future (Keeling et al. 2010), with measurable reductions already observed in some North Pacific and tropical regions (e.g., Ono et al. 2001; Whitney et al. 2007). Over long time periods, the ocean is the major net sink for anthropogenic CO₂, which mediates the buildup of atmospheric concentrations but will ultimately cause extensive damage to marine ecosystems (IPCC 2013; Wittmann and Pörtner 2013). Approximately 26% of anthropogenic CO₂ emissions are currently absorbed by the world's oceans (Le Quere et al. 2009), with a total global oceanic uptake of 118 ± 19 petagrams of carbon between 1800 and 1994 (Sabine et al. 2002). The dissolution of CO₂ at the air–sea interface induces a series of chemical reactions that decrease seawater pH and drive the conversion of carbonate ions (CO₃²⁻) to bicarbonate ions (HCO₃⁻), lowering the saturation state of the calcium carbonate polymorphs aragonite (ARAG) and calcite (CAL) that are secreted by calcifying organisms (Doney et al. 2009; Orr 2011). Anthropogenic emissions have already reduced global mean surface water pH by 0.1 units since the Industrial Revolution, and reductions of 0.3–0.5 units are expected by the year 2100 under a business-as-usual emission scenario (Brewer 1997; Caldeira and Wickett 2005; IPCC 2013). The deep sea will ultimately be the final sink for the vast majority (up to 90%) of CO₂ emissions, resulting in considerable alterations to the deep-water carbonate system (Sabine et al. 2002). While much of the deep sea is shielded from anthropogenic CO₂ in surface waters due to strong vertical stratification, areas with sufficient mixing and downwelling (see Findlay et al. 2013) may experience rapid deep-water acidification due to cold temperatures and a low buffering capacity (Sabine et al. 2002). Once the acidification of deep waters occurs, the long circulation time and limited mixing with surface waters will likely prevent the full return of these habitats to a pre-industrial state for thousands of years (Cao et al. 2014). Numerous lines of evidence from field, experimental, and modelling studies suggests that deep-sea corals are among the most susceptible groups to ongoing and predicted ocean acidification (e.g., Guinotte et al. 2006; Tittensor et al. 2010; Lunden et al. 2014), even though they currently persist at low saturation states (e.g., Thresher et al. 2011) and have demonstrated a tolerance to low pH in some experimental studies (Form and Riebesell 2012; Hennige et al. 2014). One of the most widespread and common scleractinian cold-water corals is *Lophelia pertusa*, which has a near global distribution and occupies a wide range of habitats ranging from deep-sea canyons, seamounts, carbonate mounds, and shallow-water fjords (Roberts et al. 2009). Throughout these locations, *L. pertusa* supports high levels of biodiversity by creating complex three-dimensional structures used as habitat by a large number of associated fauna (Henry and Roberts 2007; Cordes et al. 2008). Diversity within these reefs and proximal sediments has been found to be orders of magnitude higher than in the surrounding seafloor and in some locations rivals that of shallow-water reefs (Rogers 1999; Henry and Roberts 2007; Demopoulos et al. 2014). Despite having a relatively low growth rate (5–34 mm yr⁻¹; see Roberts et al. 2009) compared with shallow-water scleractinian species, *L. pertusa* forms extensive calcium carbonate skeletal structures which range from small isolated colonies centimeters tall to coalescing thickets several meters across or to large mounds and reefs hundreds of meters wide (Riding 2002). The largest reef structures built by *L. pertusa* cover areas on the order of square kilometers and tens of meters high (De Mol et al. 2002), supporting the concept that this species represents an important carbon sink in the deep sea (van Weering et al. 2003). Therefore, the loss or significant reduction of

cold-water coral populations would remove a significant carbon sink in the deep sea and result in a considerable decline in biodiversity along continental margins worldwide (White et al. 2012b). In the Gulf of Mexico (GoM), *L. pertusa* commonly occurs on the continental slope within a depth range of approximately 300–600 m (Schroeder 2002; Georgian et al. 2014). Its distribution is largely determined by temperature (4–12°C; Freiwald 2002), supersaturated Δ ARAG conditions (Guinotte et al. 2006; Davies et al. 2008), and the presence of local topographic highs with hard substrata for recruitment (Georgian et al. 2014). The GoM has a complex and variable current system that also likely influences cold-water coral growth and distribution. The dominant circulation is driven by the Loop Current, which enters the GoM through the Straits of Yucatan, loops clockwise while extending a varying distance into the GoM, and exits through the Straits of Florida to form the Gulf Stream. Both anticyclonic and cyclonic eddies periodically detach from the Loop Current and travel into the northern and western regions of the GoM (Sturges et al. 2010). Finally, the Mississippi–Atchafalaya River System (MARS) strongly influences the northern GoM by discharging large amounts of freshwater ($530 \times 10^9 \text{ m}^3 \text{ yr}^{-1}$; Milliman and Meade 1983) as well as sediment, organic matter, and nutrients (Balsam and Beeson 2003) which either directly sink to benthic environments or alternatively influence export productivity to the seafloor by modifying surface primary productivity patterns (Jochens and DiMarco 2008). In this study, we characterize the oceanographic conditions in the northern GoM over a 5 yr period with a focus on the water mass properties and carbonate chemistry dynamics surrounding cold-water coral mounds. Specifically, we assess the temperature, salinity, dissolved oxygen concentration, pH, and alkalinity of near-surface, water column, and benthic sites in the northern GoM to characterize the water masses in the vicinity of cold-water coral habitats and evaluate the potential for large *L. pertusa* mound structures to influence local carbonate chemistry.

Methods

Sample collection The GoM is a semi-enclosed basin with a total area of approximately $1.5 \times 10^6 \text{ km}^2$. In this study, we focused on a region of the upper continental slope in the northern GoM covering an area of approximately 38,000 km^2 (Fig. 1). Site names are listed in accordance with the lease block naming scheme established by the U.S. Bureau of Ocean Energy Management (BOEM): Viosca Knoll (VK), Mississippi Canyon (MC), Desoto Canyon (DC), Green Canyon (GC), Garden Banks (GB), and Atwater Valley (AT). A total of 316 water samples (sampling locations given in Table 1; Fig. 1) were collected over a series of four cruises in the northern GoM: a Schmidt Ocean Institute cruise aboard the R/V Falkor in August–September 2012, an ECOGIG (a GoM Research Initiative funded consortium) cruise aboard the R/V Falkor in November 2012, an ECOGIG cruise aboard the R/V Nautilus in June–July 2013, and an NSF Ocean Acidification Program funded cruise on the R/V Atlantis in April–May 2014. Previously collected data were included from a 2010 cruise aboard the NOAA Ship Ronald H. Brown (originally published in Lunden et al. 2013), increasing the total number of water samples to 457. Total alkalinity and pH were measured for water samples collected during the 2010 and 2014 cruises, but only total alkalinity values were available from the samples acquired in 2012 and 2013. CTD data (temperature, salinity, pressure, and dissolved oxygen) were collected both as water column data from ship deployments and as bottom-water data from a vehicle-mounted CTD. In all years, a SBE 9/11+ CTD was used for water column measurements, while vehicle-mounted CTD usage varied by year: SBE 19 (2010), SBE 37-SI (2012), and SBE 49 (2013, 2014). All dissolved oxygen measurements were collected using a SBE 43 dissolved oxygen sensor. CTD and dissolved oxygen measurements were vertically binned every meter to smooth water column profiles prior to additional analyses. Long-term temperature probes (HOBO U12 Deep Ocean Data Logger, Onset Computer Corporation) were deployed for approximately 1 yr at GC354 and VK862 in 2004 (data logged every 5 h), and at VK906 in 2009 (data logged every 9 min and binned hourly). Water column samples ($n = 309$) were collected using a standard CTD rosette, and bottom-water samples ($n = 147$) were collected using vehicle-mounted Niskin bottles that allowed for precise sampling directly ($< 2 \text{ m}$) above reefs and sediments. Each water sample was transferred to 500 mL high-density polyethylene (HDPE) Nalgene-brand bottles using silicone or Tygon® tubing to prevent atmospheric gas exchange. HDPE bottles have been shown to be adequate for the long-term storage of water samples for the analysis of total alkalinity (Huang et al. 2012). While these bottles are permeable to CO_2 , pH was always measured within 1 h after samples reached the surface. Immediately following the measurement of pH, samples were poisoned with 100 μL of saturated mercuric chloride to prevent changes in total alkalinity (Dickson et al. 2007). After being poisoned, samples were stored in a cool, dark location and returned to Temple University for further analysis.

Figure 1 Open in figure viewer PowerPoint Map of sampling locations (black triangles) in the northern Gulf of Mexico with depth ranges indicated (color breaks at depths of: 100 m, 500 m, 1000 m, 2000 m, 3000 m, and 3700 m). Blue lines indicate the major Mississippi–Atchafalaya River System influxes to the Gulf of Mexico.

Figure 2 Open in figure viewer PowerPoint Water column profiles of carbonate parameters in the northern Gulf of Mexico. A = pH_T, B = nTA ($\mu\text{mol kg}^{-1}$), C = Δ ARAG, D = TA: DIC ratio, E = $[\text{CO}_2]$ ($\mu\text{mol kg}^{-1}$), and F = nDIC ($\mu\text{mol kg}^{-1}$). Dashed line in Panel C indicates the aragonite saturation horizon (Δ ARAG = 1). Solid line in Panel C indicates the exponential depth-decay function used to model Δ ARAG.

Table 1. Sampling locations and mean (\pm SD) seawater parameters for bottom-water sites and surface waters.

Asterisk denotes sites with live *L. pertusa* colonies. n = total number of bottom water or surface samples at each site. Depths are approximate. Site n Depth (m) Lat. (DD) Long. (DD) Salinity (psu) Temp. (°C) pHT nTA (?mol kg⁻¹) ?ARAG [CO ?] (?mol kg⁻¹) nDIC (?mol kg⁻¹) AT357 14 1050 27.58 ?89.71 34.66 ± 0.37 4.9 ± 0.3 7.93 ± 0.00 2362 ± 37 1.17 ± 0.00 94.6 ± 0.3 2270 ± 2 DC1 2 2110 28.25 ?87.41 34.95 ± 0.00 4.3 ± 0.0 n.d. 2349 ± 11 n.d. n.d. n.d. DC673 7 2600 28.01 ?87.31 34.95 ± 0.02 4.3 ± 0.0 7.96 ± 0.01 2339 ± 8 1.04 ± 0.07 107.8 ± 1.4 2192 ± 4 GB535* 10 510 27.69 ?92.23 34.73 ± 0.45 8.7 ± 1.0 7.88 ± 0.04 2352 ± 28 1.31 ± 0.15 91.6 ± 1.1 2235 ± 45 GB903 3 1070 27.42 ?93.60 34.20 ± 0.00 4.9 ± 0.0 7.92 ± 0.01 2385 ± 5 1.13 ± 0.01 109.4 ± 3.3 2266 ± 8 GC140 4 310 27.08 ?92.82 35.40 ± 0.05 11.8 ± 0.4 7.90 ± 0.01 2305 ± 7 1.57 ± 0.05 89.7 ± 3.2 2165 ± 12 GC234* 11 510 27.80 ?91.54 34.36 ± 0.05 9.6 ± 0.5 7.84 ± 0.02 2379 ± 5 1.24 ± 0.04 100.8 ± 5.4 2270 ± 8 GC249 7 1380 27.75 ?91.22 34.94 ± 0.10 6.5 ± 1.5 n.d. 2357 ± 6 n.d. n.d. 2227 ± 13 GC354* 10 540 27.70 ?90.65 34.23 ± 0.01 8.3 ± 0.2 7.83 ± 0.02 2379 ± 5 1.15 ± 0.05 83.3 ± 3.4 2280 ± 9 MC751* 6 460 28.63 ?88.17 34.91 ± 0.27 9.4 ± 0.5 7.86 ± 0.03 2372 ± 17 1.29 ± 0.06 92.0 ± 4.7 2259 ± 25 MC885* 5 640 28.47 ?88.23 34.28 ± 0.32 7.2 ± 0.2 7.89 ± 0.02 2383 ± 12 1.24 ± 0.06 91.7 ± 4.1 2268 ± 18 VK826* 34 480 28.03 ?89.73 34.85 ± 0.29 8.9 ± 0.7 7.89 ± 0.05 2344 ± 36 1.37 ± 0.11 98.7 ± 8.7 2243 ± 26 VK906* 23 400 25.31 ?84.82 35.02 ± 0.37 10.1 ± 0.6 7.90 ± 0.03 2332 ± 25 1.44 ± 0.11 102.1 ± 7.7 2204 ± 34 Surface 39 <25 ? ? 35.40 ± 1.30 24.9 ± 2.1 8.11 ± 0.04 2352 ± 61 3.88 ± 0.31 245.3 ± 17.7 2008 ± 53 Carbonate chemistry pH was measured on the total hydrogen scale (pHT) within 1 h of sample collection. Each water sample was placed in a 25°C water bath for 10?20 min to standardize temperature (mean temperature over all pH measurements of 22.2 ± 2.6°C). pHT was then measured in duplicate using the Orion 5 Star pH meter and glass electrode (ROSS Ultra pH/ATC Triode 8107BNUMD) calibrated with Tris?HCL buffer solution obtained from the Dickson Lab (Batch 22). Electrode performance was regularly checked against standard Tris?HCl and AMP-HCl buffers in artificial seawater (Nemzer et al. 2005; Dickson et al. 2007). Temperature was measured using the integrated temperature sensor on the ROSS Ultra pH/ATC Triode from 2010 to 2013, and using a handheld thermocouple (Omega® HH81A) in 2014. Figure 3Open in figure viewerPowerPoint Cross-sectional profiles of pHT, nTA (?mol kg⁻¹), ?ARAG, and [CO ?] (?mol kg⁻¹) in the northern Gulf of Mexico. Transect line generally follows deeper, offshore sites and is indicated in the bottom panel. Black circles indicate sampling locations. Figure 4Open in figure viewerPowerPoint Measured surface-water TA values against TA values predicted by the North Atlantic SST?SSS?TA relationship (Lee et al. 2006). Measured TA values were significantly correlated with predicted model values (Linear regression, r² = 0.51, p < 0.001). Colors (green to blue) correspond to the linear distance (km) of sampling locations from the outflow of the Mississippi River. Dashed lines indicate the linear regression fit with 95% confidence intervals. Solid line indicates a theoretical 1 : 1 relationship between modelled and measured TA values. Total alkalinity (TA) was measured in triplicate by acid titration on a Mettler?Toledo DL15 autotitrator using 0.1 mol L⁻¹ HCl buffered in 0.6 mol L⁻¹ NaCl (modified from SOP 3b, Dickson et al. 2007). The autotitrator was calibrated daily on the NBS scale using certified reference buffers (Orion), and certified reference materials (Dickson Lab, batches 138 and 141) were measured periodically to ensure accuracy (within ± 10 ?mol kg⁻¹). CO2SYS software (Pierrot et al. 2006) was used to correct pHT values for in situ temperature and pressure, and to calculate the entire carbonate system from TA, pHT, temperature, salinity, and pressure. For all calculations, we used the carbonic acid constants (K1 and K2) of Mehrbach et al. (1973) refitted by Dickson and Millero (1987), and the aragonite solubility product (Ksp) from Mucci (1983). The effects of nutrients (phosphate and silicate) on the carbonate system were assumed to be negligible (e.g., Cai 2003; Yates and Halley 2006). TA and dissolved inorganic carbon (DIC) values were corrected for in situ salinity values using the mean salinity of all sites (35.3 psu) to yield salinity-normalized TA (nTA) and DIC (nDIC). Figure 5Open in figure viewerPowerPoint Spatial distribution of ?ARAG, nTA (?mol kg⁻¹), pHT, and [CO ?] (?mol kg⁻¹) in surface waters (panel A) and in the depth range of *L. pertusa* sites (300?640 m, panel B). LA, Louisiana. Note differences in the y-axis between corresponding plots in panel A and panel B. Figure 6Open in figure viewerPowerPoint Temperature vs. salinity plots of CTD casts over *L. pertusa* sites. SUW, Subtropical Underwater; NACW, North Atlantic Central Water; AAIW, Antarctic Intermediate Water. Blue lines indicate data from 2014, green lines indicate data from 2013, and red lines indicate data from 2010. Grey lines indicate potential density (??; kg m⁻³) isopycnals plotted every 1.0 units. Bottom-water TA analysis TA and DIC measured directly over coral communities were compared with off-site TA and DIC values at the same depths. To calculate the expected value at the exact depth of bottom-water samples based on nearby CTD casts, polynomial curves were fitted to water column TA and DIC depth profiles (see Fig. 7). These expected values were subtracted from the values measured directly over corals from the vehicle-mounted Niskin bottles to calculate the change in TA and DIC in near-bottom water samples, reported as ?TA and ?DIC (?mol kg⁻¹). Figure 7Open in figure viewerPowerPoint Total alkalinity of bottom water samples (circles) collected directly over the VK906 (red) and VK826 (blue) reefs compared with off-reef water column profiles (triangles). Dashed lines indicate the best-fit polynomial curve for each CTD cast. WC, water column sample. BW, bottom water sampled collected by vehicle-mounted Niskin bottles. Statistical analysis A Student's t-test was used

to determine if near-bottom TA and DIC measurements were significantly different from the predicted TA and DIC values modelled from water column values at the same depth. Measured surface TA values were compared with the regional SST-SSS-TA models given in Lee et al. (2006) using a linear regression analysis to compare predicted model outputs to measured values. To investigate the relationship between Δ ARAG and depth we compared the fit of various exponential-decay functions and chose the model with the lowest sample-size corrected Akaike information criterion (AICC score). A stepwise reverse elimination regression using minimum AICc values was used to model Δ ARAG based on temperature, salinity, dissolved oxygen, and pressure data. This analysis was limited to water column samples with both dissolved oxygen and Δ ARAG measurements, reducing the sample size to 174. Models were also calculated using data from 2010 to 2014 and the relationship between modelled and predicted Δ ARAG was compared between years using the multiple regression comparison in Zar (1984). All data are given as mean \pm standard deviation unless otherwise stated. An alpha level of 0.05 was used for all tests. Results Surface waters had a mean pHT of 8.11 ± 0.04 , nTA of 2352.4 ± 61.2 $\mu\text{mol kg}^{-1}$, Δ ARAG of 3.88 ± 0.31 , nDIC of 2008.5 ± 52.6 $\mu\text{mol kg}^{-1}$, and $[\text{CO}_2]$ of 245.3 ± 17.7 $\mu\text{mol kg}^{-1}$ (Table 1). Salinity was positively correlated with both TA (linear regression, $r^2 = 0.52$, $df = 38$, $p < 0.001$) and DIC (linear regression, $r^2 = 0.53$, $df = 34$, $p < 0.001$). All surface samples were supersaturated with respect to aragonite, with Δ ARAG values ranging from 3.17 to 4.43 (Figs. 2, 3, and 5a). There was a marked increase in surface nTA compared with oceanic values in the area surrounding the influx of the MARS (> 100 $\mu\text{mol kg}^{-1}$; Fig. 5a), a pattern not observed at depths below 300 m (Fig. 5b). In the same region, there was also a slight increase in Δ ARAG and $[\text{CO}_2]$ concentrations (Fig. 5a). TA in surface waters significantly fit the salinity-temperature relationship modelled for North Atlantic surface waters (Lee et al. 2006; linear regression, $r^2 = 0.51$, $df = 38$, $p < 0.001$) (Fig. 4). However, the residuals of the fit of our data to this model revealed a bias toward higher than expected values, with a mean difference of $+33.0 \pm 44.9$ $\mu\text{mol kg}^{-1}$, and a maximum difference of $+131.2$ $\mu\text{mol kg}^{-1}$. Residual TA values were not significantly correlated with the distance between the sampling location and the Mississippi River output (linear regression, $r^2 = 0.01$, $df = 38$, $p = 0.56$) (see Fig. 4). General carbonate chemistry patterns in the water column were primarily influenced by depth (see Figs. 2, 3). Minimum values of pHT and $[\text{CO}_2]$ occurred at a depth of approximately 500 m (Fig. 2), with minor spatial disparities at that depth (Fig. 3). nDIC increased with depth through the upper water column, reaching a maximum of 2265.8 $\mu\text{mol kg}^{-1}$ at a depth of 625 m at MC885 (Fig. 2f), and showing a slight decline in deeper waters. The TA: DIC ratio, which signifies the increased buffering capacity of seawater at higher values and a minimum capacity when TA: DIC equals one (Egleston et al. 2010), had a mean of 1.17 ± 0.02 in surface waters, and generally decreased with depth, reaching a minimum of 1.05 at approximately 500 m (Fig. 2d). The Revelle factor, a measure inversely proportional to the capacity for seawater to absorb atmospheric CO_2 (Sabine et al. 2002), was lowest in surface waters (9.05 ± 0.37) and gradually increased with depth, reaching a maximum of 16.1 at approximately 500 m. Δ ARAG decreased rapidly with depth until approximately 500 m after which it decreased more gradually (Figs. 2, 3). Undersaturation of Δ ARAG (< 1) was only observed in benthic samples collected at the deepest site (DC673, 2600 m), which had a mean pHT of 7.96 ± 0.01 , nTA of 2339.1 ± 77 $\mu\text{mol kg}^{-1}$, Δ ARAG of 1.04 ± 0.07 $\mu\text{mol kg}^{-1}$ (Δ ARAG ranged from 0.99 to 1.13), and a carbonate ion concentration of 107.8 ± 1.4 $\mu\text{mol kg}^{-1}$ (Table 1). Δ ARAG closely followed a third-order exponential depth-decay model: Δ ARAG = $a e^{(b \times \text{depth})} + c$, where $a = 2.9330$, $b = -0.0055$, and $c = 1.1156$ ($r^2 = 0.97$; Fig. 2c). It was possible to accurately predict Δ ARAG values in the water column based on temperature, pressure, and dissolved oxygen data as given by the following formula: Δ ARAG = $(0.16794559 \times t) + (0.00079128 \times p) + (0.00401013 \times \text{do}) - 1.0744794$, where t = temperature ($^{\circ}\text{C}$), p = pressure (dbar), and do = dissolved oxygen ($\mu\text{mol kg}^{-1}$) (Stepwise reverse regression, $r^2 = 0.968$, $df = 170$, $p < 0.001$) (Supporting Information Fig. S1). Salinity was not a significant predictor for Δ ARAG and was eliminated as a variable in the step-wise selection process ($p = 0.18$). To determine if this relationship changed over time, models were calculated separately for the 2010 and 2014 sampling years, but there was no significant difference between the slope (Multiple regression comparison, $F = 1.39$, $p = 0.24$) or intercept (Multiple regression comparison, $F = 0.06$, $p = 0.81$) of the 2010 and 2014 regressions (Supporting Information Fig. S1). Benthic habitats with live *L. pertusa* colonies (occurring between 300 m and 640 m depth) had a mean pHT of 7.87 ± 0.04 , mean nTA of 2253.1 ± 32.1 $\mu\text{mol kg}^{-1}$, and mean Δ ARAG of 1.31 ± 0.14 (Table 1; Fig. 5b). There was low CO_2 availability at *L. pertusa* sites, with a mean concentration of 94.4 ± 9.1 $\mu\text{mol kg}^{-1}$ (Table 1; Fig. 5b). Bottom-water temperatures measured via vehicle-mounted CTDs had a mean of $9.1 \pm 0.96^{\circ}\text{C}$ with a wide spatial range of 6.79 – 11.98°C across sites at different depths (Table 2). Year-long temperature probe deployments revealed large temperature variations within sites as well (Supporting Information Fig. S2), with temperatures ranging from 8.6 – 13.6°C at VK862 (310 m), 7.9 – 11.9°C at VK906 (400 m), and 6.6 – 9.1°C at GC354 (540 m). Salinity ranged from 34.1 to 35.5 psu with a mean of 34.7 ± 0.4 psu (Table 2). The mean dissolved oxygen concentration across all *L. pertusa* sites was 111.3 ± 2.0 $\mu\text{mol kg}^{-1}$ (2.53 ± 0.05 mL L^{-1}) (Table 2; Supporting Information Fig. S3). Mean dissolved oxygen at *L. pertusa* sites ranged from a low of 88.1 ± 4.7 $\mu\text{mol kg}^{-1}$ (2.02 ± 0.01 mL L^{-1}) at MC751 (46

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