Carbonate Chemistry Report for Water Samples from Southeast Deep Coral Initiative Expedition aboard NOAA ship *Nancy Foster* (NF1708) in 2017

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Date: November 20, 2019

Introduction

A research expedition was conducted by NOAA in 2017 entitled 'Southeast Deep Coral Initiative: Exploring Deep-Sea Corals Ecosystems of the Southeast US'. The survey explored deep-sea coral habitat along West Florida shelf, using the remotely operated vehicle (ROV) Odysseus aboard NOAA ship *Nancy Foster*. The survey made 13 ROV dives over coral mounds, rocky ridge, and flat seafloor, comparing coral abundance and diversity in each of these environments. The reef-forming scleractinian coral *Lophelia pertusa* (= *Desmophyllum pertusum*) was present in several areas (Wagner et al., 2018).

Deep-water stony corals are sensitive to carbonate chemistry (Georgian et al., 2016). The skeletons of scleractinian corals are aragonitic, made of a form of calcium carbonate. The health and condition of the colonies are correlated with aragonite saturation, or omega (Ω), a measure of the tendency for aragonite to dissolve in seawater. Values of aragonite saturation lower than Ω = 1 are considered detrimental to coral growth and condition, whereas values higher than 1 are generally conducive to coral growth.

In the northern Gulf of Mexico, *L. pertusa* reefs are typically found in the depth range from 300 to 600 meters, at temperatures of 8–12°C and relatively low aragonite saturation states of 1.2–1.5 and pH of 7.85 to 8.0 (Lunden et al., 2013). In contrast, omega (Ω) on a shallow South Pacific coral reef ranges from 2.4 to 3.7, and the pH can range from 7.2 to 8.2 (Mollica et al., 2019).

In order to understand the carbonate chemistry along West Florida slope, and how it varied with depth, a CTD-rosette was deployed from *Nancy Foster* a total of 17 times in the vicinity of deep coral reefs over the course of 13 days, mostly to 400-500 meters depth, but as deep as 1,000 meters. Aragonite saturation state values were calculated from bottle samples ranging from 20 m to 1000 m water depth. A total of 69 water samples were collected for carbonate chemistry analyses. The results of these analyses are presented here.

Methods

A total of 68 bottle samples were analyzed for TCO2 and TA by Dr. Kim Yates at the United States Geological Survey (USGS) laboratory facility in Gainesville, Florida. One bottle arrived at testing facility broken and was unable to be analyzed. The lab used a closed cell acidification module and procedure to convert all dissolved TCO2 in the sample to CO2 gas which was then analyzed in a UIC coulometer. This measurement is independent of temperature.

The aragonite saturation state (omega aragonite) for all bottle samples was calculated using the program CO2calc (v.1.0) with data provided by USGS data analysis and NOAA cruise report for the expedition (Wagner et al. 2018). Input parameters for aragonite saturation calculations included the following data collected from the CTD: in situ temperature (°C), salinity (PSU), and pressure (decibars). Pressure was converted from depth in meters using an algorithm provided by Seabird Electronics, see SBE App. Note 69 for reference. Additional input parameters for aragonite saturation calculation included total alkalinity (TA, $\mu mol \cdot kg^{-1}$) and total carbon dioxide (TCO2, $\mu mol \cdot kg^{-1}$) measured from preserved bottle samples at the St. Petersburg Coastal and Marine Science Center. The following constants were used in all omega aragonite calculations: K1, K2 from Mehrbach et al. 1973 as refit by Dickson and Millero 1987; KHSO4 from Dickson 1990, and air-sea flux from Wanninkhof 1992.

Results

Aragonite saturation state values ranged from a high of 4.16 at 20 m water depth at the Many Mounds site to a low of 1.12 at 800 m water depth at the North Wall site. Generally, aragonite saturation decreased rapidly as depth increased, as expected. The high rate of change coincided with occurrence of the thermocline (20-200 m) at each site, and approaches a soft asymptote of ~1.3-1.4 at approximately 400 m (see Fig 1).

The scleractinian cold-water coral *Lophelia pertusa* was collected from the North Reed (500 m), Many Mounds (430-480 m), and Okeanos Ridge (521 m) sites, where the aragonite saturation state is roughly 1.2-1.3. Differences in aragonite saturation state from bottles collected at day vs. night were minimal, but highest in samples near the surface, where there was difference of 0.1 to 0.2 in aragonite saturation at 20 m depth.

Discussion/Future Directions

Generally, the values of aragonite saturation in *Lophelia pertusa* habitats sampled during the expedition were $\Omega = 1.2 – 1.3$ between 430-520 meters depth. These values are similar to those reported from other published studies in the region and broader area. At similar depths throughout the Gulf of Mexico, *Lophelia pertusa* is found to occur at aragonite saturation states ranging from 1.24 to 1.69 (Georgian et al. 2016, Lunden et al. 2013). At canyon sites along the U.S. Atlantic margin, *Lophelia* was observed at aragonite saturation states ranging from 1.41 to 1.44 (Brooke and Ross, 2014). These results suggest that *Lophelia* along the west coast of Florida experiences similar carbonate chemistry regimes as *Lophelia* along the U.S. Atlantic margin. However, the values reported here are relatively low, compared to the range observed in other regions of the Southeast US.

The study could be improved upon by replicating bottle sample collections at depth, and by increased sampling periodicity over daily/seasonal scales. With an enhanced sample size and replicated design, testing for statistical significance between day and night samples would be possible, which would aid in identifying any contributions from photosynthesis and respiration at the surface to the carbon dynamics of cold-water coral habitats at depth.

References

Brooke S & Ross SW (2014). First observations of the cold-water coral *Lophelia pertusa* in mid-Atlantic canyons of the USA. *Deep-Sea Res. Pt. II* 104:245-251.

Dickson AG & Millero FJ (1987). A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. *Deep-Sea Res. A* 34:1733-1743

Dickson AG (1990). Thermodynamics of the dissociation of boric acid in synthetic seawater from 273.15 to 318.15 K. *Deep-Sea Res.* 37:755-766.

Georgian SE, DeLeo D, Durkin A, Gomez CE, Kurman M, Lunden JJ, & Cordes EE (2016). 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. *Limnol. Oceanogr.* 61:648-665.

Lunden JJ, Georgian SE, & Cordes EE (2013). Aragonite saturation states at cold-water coral reefs structured by *Lophelia pertusa* in the Gulf of Mexico. *Limnol. Oceanogr.* 58:354-362.

Mehrbach C, Culberson CH, Hawley JE, & Pytkowicx RM (1973). Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. *Limnol. Oceanogr.* 18:897-907.

Mollica, NR, W Guo, AL Cohen, K-F Huang, GL Foster, HK Donald, AR Solow. (2019) OA affects coral growth by reducing density. Proc Nat Acad Sci. 115 (8) 1754-1759.

Wagner D, Kilgour M, & Etnoyer PJ (2018). Expedition Report: 2017 Southeast Deep Coral Initiative (SEDCI) expedition aboard NOAA Ship *Nancy Foster* (NF-17-08: August 12-31, 2017). NOAA Technical Memorandum NOS NCCOS 244. Silver Spring, MD.

Wanninkhof R (1992). Relationship between wind speed and gas exchange over the ocean. *J. Geophys. Res.* 97:7373-7382.

Table 1. Water samples by depth bin from NF17-08 at West Florida Slope sites.

Depth bin (m)	# of samples	Mean Total Alkalinity (µmol·kg^{-1}) ± S.D.	Mean TCO2 (µmol·kg^{-1}) ± S.D.	Mean Ω_{arag} ± S.D.
0-49	9	2379.7 ± 13.7	2030.6 ± 16.6	3.99 ± 0.08
50-99	0	n/a	n/a	n/a
100-149	9	2392.5 ± 8.1	2159.7 ± 12.4	2.57 ± 0.22
150-199	1	2352.7	2180.4	1.94
200-249	7	2353.0 ± 11.9	2175.2 ± 7.6	1.96 ± 0.18
250-299	4	2344.8 ± 22.3	2184.5 ± 14.5	1.79 ± 0.35
300-349	5	2333.4 ± 12.1	2190.6 ± 8.6	1.61 ± 0.18
350-399	6	2325.7 ± 8.2	2195.9 ± 7.3	1.48 ± 0.13
400-499	8	2317.2 ± 11.0	2202.0 ± 4.3	1.33 ± 0.11
500-699	5	2311.7 ± 1.5	2211.5 ± 2.8	1.17 ± 0.03
700-1000	4	2319.2 ± 2.6	2209.5 ± 3.5	1.14 ± 0.01

Figure 1. Water column profile showing average omega aragonite with depth. Data points are average omega aragonite within each depth bin, error bars are standard deviation of the mean. The black dotted line represents Ω_{arag} = 1.0, and the shaded gray box represents the depth range of *Lophelia pertusa* in this region (438-693 m).