Carbonate chemistry of the Dongsha Atoll Lagoon in the northern South China Sea

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ABSTRACT

In this study, we investigated the seawater carbonate chemistry in the Dongsha Atoll Lagoon (DAL) in summer 2015, summer 2016, and autumn 2016. According to the calculation of the total alkalinity anomaly (ΔTA), the DAL is currently maintaining a net calcification status, with higher calcification potential in summer and lower calcification potential in autumn. The calculation of the partial pressure of CO_2 anomaly $(\Delta p CO_2)$ shows that the DAL acts as a CO₂ source for the atmosphere, with higher $\Delta p CO_2$ values in summer and lower values in autumn. In addition to seasonal variation, $\Delta p CO_2$ also exhibits a clear variation between two summer investigations, with higher values in summer 2016 than in summer 2015, which could be associated with the different weather conditions during the sampling periods (2015 vs. 2016: sunny vs. stormy). Moreover, analyzing the salinity-normalized total alkalinity vs. dissolved inorganic carbon relationship reveals that calcification was the dominant process controlling the CO₂ dynamics in summer 2015, while those in summer 2016 were regulated mainly by the combination of calcification and organic respiration. This result further suggests that the change in the organic carbon metabolism induced by the different weather conditions could be the driving force behind the observed variation in pCO_2 between summer 2015 and 2016.

1. INTRODUCTION

The ocean absorbs approximately one-third of the carbon dioxide (CO₂) that is released into the atmosphere (Sabine et al. 2011). When CO₂ is absorbed by seawater, it forms carbonic acid, lowering the pH and carbonate ion concentration and thereby decreasing the saturation state of seawater with respect to carbonate minerals (Ω); this process is referred to as "ocean acidification" (Caldeira and Wickett 2005). Many laboratory and mesocosm studies have shown that coral reefs are some of the most sensitive ecosystems to ocean acidification, where calcification is predicted to decrease (Kleypas and Yates 2009) and dissolution is predicted to increase with declining pH and Ω (Eyre et al. 2018; Chou et al. 2020).

The carbonate chemistry of coral reef waters has long been known to be modified through organic carbon (photosynthesis and respiration) and inorganic carbon (calcifi-

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cation and CaCO₃ dissolution) metabolism. For example, photosynthesis acts to decrease dissolved inorganic carbon (DIC) concentrations and the partial pressure of CO_2 (pCO_2) and increase pH, whereas the total alkalinity (TA) remains largely unaffected; calcification acts to decrease DIC and TA in a ratio of 1:2 and to increase pCO_2 but decrease pH (Bates 2002). Previous studies have demonstrated that coral-dominated reef ecosystems are CO₂ sources for the surrounding waters (Gattuso et al. 1999), while macroalgadominated reef systems are CO₂ sinks (Kraines et al. 1996). These studies indicate that the characteristics of the carbonate chemistry of individual coral reef ecosystems may vary and largely depend on their habitat and community structure (Kleypas et al. 2011). Furthermore, the dependence of organic carbon production and calcium carbonate formation on temperature and light availability suggests that carbonate chemistry in coral reef ecosystems may show substantial temporal variation, e.g., seasonal variation (McNeil et al. 2004; Venti et al. 2014). Consequently, characterizing carbonate chemistry and its variability is critical for better

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predicting the possible effects of ocean acidification on individual coral reef ecosystems.

The Dongsha Atoll is located in the northern South China Sea (SCS, Fig. 1). As a portion of the Coral Triangle, which is the epicenter of coral reef biodiversity, coral reef ecosystems are abundant in the coastal waters of the Dongsha Atoll. Extremely high net ecosystem calcification has been reported in the eastern margin of the Dongsha Atoll (DeCarlo et al. 2017), where the nearshore is shaped by large internal waves (Reid et al. 2019). On the western side of Dongsha Atoll, the coverage of abundant seagrass meadows around Dongsha Island was reported to have important implications for ocean acidification buffering and atmospheric CO₂ sequestration (Chou et al. 2018). However, the carbonate chemistry in the Dongsha Atoll lagoon (DAL) has not yet been reported. As it is the largest component of Dongsha Atoll and connects two studied sites that exhibit distinct CO₂ dynamics (i.e., on the eastern margin and around Dongsha Island), the carbonate chemistry in the DAL is worthy of further investigation. The present study documents the carbonate chemistry in the DAL for the first time. Our purposes here are to report the observed temporal variations in calcification and sink/source status for atmospheric CO₂, examine their controlling processes, and compare our results with those of other studies.

2. MATERIALS AND METHODS

2.1 Study Sites

The Dongsha Atoll (20.88°N, 116.78°E) is a massive circular coral reef emerging from a water depth of \sim 500 m on the continental slope in the northern SCS (Fig. 1); it is directly in the path of some of the world's largest internal

solitary waves (with amplitudes of 100 - 150 m) generated by tidal currents in the Luzon Strait (Hsu and Liu 2000). The living reef flat encircling the lagoon is approximately 46 km long and 2 km in width. The diameter of the atoll lagoon is approximately 25 km, and the average water depth is 10 m, with the deepest part being 22 m deep (Fig. 1). Dongsha Island, located on the western margin of the atoll, is the only part that is higher than sea level. Large seagrass meadows extend from the intertidal to the subtidal zones within the atoll lagoon and around Dongsha Island (Huang et al. 2015). In this study, we investigated the seawater carbonate chemistry throughout the entire DAL in summer 2015 (16 - 18 August), 2016 (22 - 24 August), and autumn 2016 (20 - 21 November). The sampling sites are shown in Fig. 1. There were 24 sites in the interior of the DAL (reef water, R) and 6 - 12 sites in the outer margin of the reef flat. Among the outer margin sites, two sites near the western channels were chosen to serve as the source water end-members (S).

2.2 Measurements of Water Depth, Temperature, Salinity, and Dissolved Oxygen (DO)

The water depth, temperature, salinity, and DO at each site were recorded using a multiparameter probe (Ocean Seven 316 Plus CTD; IDRONAUT S.r.1, Italy). The DO sensor was calibrated with a precision of 0.1 mgL⁻¹ (~3.1 μ M) using the water-saturated air method before deployment.

2.3 Carbonate Chemistry Analysis of Discrete Seawater Samples and Calculation of pCO₂

Discrete seawater samples for TA, DIC, and pH analyses were taken using a 9-L Nalgene[™] HDPE carboy on site



Fig. 1. Locations of sampling sites in the Dongsha Atoll Lagoon, and the inserted map showing the location of the Dongsha Atoll Lagoon in the northern South China Sea. Photo credit: Google Earth Pro V 7.3.3.4507.

and then immediately transferred into 350-mL precleaned borosilicate bottles. These samples were subsequently injected with 200 μ L of saturated HgCl₂ solution to halt biological activity, sealed, and taken back to the laboratory at National Taiwan Ocean University.

The measurements of TA, DIC, and pH followed the standard operating methods described in Dickson et al. (2007) and were consistent with those used in our previous studies (Chou et al. 2005, 2018). TA and DIC were measured using Gran titration on an automatic TA titrator (AS-ALK2, Apollo SciTech Inc.) and the nondispersive infrared method on a DIC analyzer (AS-C3, Apollo SciTech Inc.), respectively. We used certified reference materials (CRMs) obtained from Dr. A. Dickson's laboratory at the Scripps Institution of Oceanography to calibrate and ensure the performance of both the alkalinity titrator and the DIC analyzer. The analytical TA and DIC measurements both had an accuracy and precision of $\pm 0.15\%$ or better. The pH was spectrophotometrically determined at 25°C (pH at 25°C) using unpurified meta-cresol purple (mCP) commercially purchased from TCI, which was reported to have the smallest impurity contribution to spectrophotometric characterizations of seawater pH (Clayton and Byrne 1993; Douglas and Byrne 2017). The pH measurement was based on the total hydrogen ion concentration scale with a precision of 0.005 (Chou et al. 2016).

The seawater pCO_2 was calculated from the DIC, TA, temperature, and salinity using the CO2SYS program (Pelletier et al. 2011). The dissociation constants for carbonic acid for this calculation were obtained from the data of Mehrbach et al. (1973) that were refitted by Dickson and Millero (1987), which has been demonstrated to be able to yield the best results when determining pCO_2 from DIC and TA (Wanninkhof et al. 1999).

2.4 Statistical Analysis

Differences in the means of all parameters among the three sampling seasons, including water temperature, salinity, DO, pH, pCO_2 , DIC, and TA, were assessed using a randomized complete block design (RCBD) to exclude site effects (Montgomery 2012), followed by Tukey's pairwise comparison to determine the significance of differences between each pair of sampling seasons. All statistical analyses were performed with a general linear modeling (GLM) procedure in the SAS 9.4 software package (SAS Institute 2003).

3. RESULTS

The variation ranges, means and stand deviations $(\pm 1\sigma)$ of water temperature, salinity, DO, pH, pCO_2 , DIC, and TA in the DAL in the three sampling periods are summarized in Table 1, and their distributions are shown in Fig. 2.

3.1 Surface Water Properties of the DAL

Water temperature in the DAL ranged from 26.9 to 31.2°C. The water temperature generally decreased from the northeast to the southwest in the lagoon in summer, but no significant spatial variation was found in autumn (Fig. 2a). Salinity in the DAL ranged from 33.2 to 34.1, generally increasing from east to the west in the lagoon in summer and showing no significant pattern in autumn (Fig. 2b).

Both temperature and salinity showed temporal variations in the DAL (Table 1). The temperature in August 2015 was significantly higher than that in August 2016 and higher than that in November 2016 (30.2 ± 0.6 vs. 29.7 ± 0.4 vs. $27.3 \pm 0.3^{\circ}$ C, p < 0.01). The salinity in August 2016 was significantly lower than that in August 2015 and lower than that in November 2016 (33.6 ± 0.3 vs. 33.8 ± 0.1 vs. $34.0 \pm$ 0.04, p < 0.01).

The DO concentration in the DAL ranged from 152 to 236 μ mol kg⁻¹, with higher levels in the western part of the lagoon in August 2015 and November 2016; the opposite pattern was observed in August 2016 (Fig. 2c). The DO values in August 2015 and November 2016 were not significantly different and were both higher than that in August 2016 (201 ± 8 vs. 194 ± 14 vs. 173 ± 13 μ mol kg⁻¹, *p* < 0.01).

3.2 Carbonate Chemistry Parameters in the DAL

The pH and pCO_2 ranged from 7.838 to 8.103 and 348 to 765 µatm, respectively. Spatially, the pH showed higher levels in the western, northern and northeastern parts of the lagoon in August 2015 and 2016 and November 2016, respectively (Fig. 2d). The average pH in the DAL was generally lower than that in the source water (R vs. S: 8.015 vs. 8.065 in summer 2015, 7.974 vs. 8.089 in summer 2016, and 8.051 vs. 8.069 in autumn 2016, Table 1). pCO_2 showed the opposite spatial patterns to pH (Fig. 2e), and the average pCO_2 in the DAL was generally higher than that in the source water (R vs. S: 450 vs. 400 µatm in summer 2015, 545 vs. 420 µatm in summer 2016, and 396 vs. 393 µatm in autumn 2016, Table 1).

DIC and TA ranged from 1796 to 1953 μ mol kg⁻¹ and 2075 to 2238 μ mol kg⁻¹, respectively. Spatially, DIC was higher in the southwestern part of the lagoon in summer and in the southeastern part of the lagoon in autumn (Fig. 2f). The average DIC in the DAL was generally lower than that in the source water (R vs. S: 1868 vs. 1905 μ mol kg⁻¹ in summer 2015, 1887 vs. 1910 μ mol kg⁻¹ in summer 2016, and 1895 vs. 1926 μ mol kg⁻¹ in autumn 2016, Table 1). TA was higher in the northwestern and southwestern parts of the lagoon in summer and in the northeastern parts of the lagoon in autumn (Fig. 2g). The average TA in the DAL was generally lower than that in the source water (R vs. S: 2151 vs. 2217 μ mol kg⁻¹ in summer 2015, 2128 vs. 2215 μ mol kg⁻¹ in summer 2016, and 2188 vs. 2229

Table 1. Summary of temperature, salinity, DO, pH, pCO_2 , DIC, and TA in the Dongsha Atoll lagoon (the variation range and mean \pm SD for the reef water, R, and only the mean value for the source water, S) in different sampling periods: August 2015 (Aug. 2015), August 2016 (Aug. 2016), and November 2016 (Nov. 2016). The significance level (*p*-value) for the RCBD and the corresponding Tukey's pairwise comparison for all parameter means between each pair of sampling periods are shown.

		August 2015	August 2016	November 2016	<i>p</i> -value	Tukey's pairwise comparison
	R	28.5 - 31.2	29.1 - 30.3	26.9 - 27.8	< 0.01	August 15 > August 16 > November 16
Temperature (°C)		30.2 ± 0.6	29.7 ± 0.4	27.3 ± 0.3		
	S	29.4	29.8	27.5		
	R	33.6 - 34.0	33.2 - 34.1	33.9 - 34.1	< 0.01	November 16 > August 15 > August 16
Salinity		33.8 ± 0.1	33.6 ± 0.3	34.0 ± 0.04		
	S	33.9	33.9	34.0		
	R	184 - 226	152 - 195	166 - 236	< 0.01	August 15 = November 16 > August 16
DO (µmol kg-1)		201 ± 8	173 ± 13	194 ± 14		
	S	202	176	183		
	R	7.952 - 8.103	7.838 - 8.086	8.025 - 8.101	< 0.01	November 16 > August 15 > August 16
pH at 25°C		8.015 ± 0.040	7.974 ± 0.063	8.051 ± 0.021		
	S	8.065	8.089	8.069		
	R	368 - 514	414 - 765	348 - 445	< 0.01	August 16 > August 15 > November 16
pCO_2 (µatm)		450 ± 42	545 ± 102	396 ± 23		
	S	400	420	393		
	R	1796 - 1916	1816 - 1985	1866 - 1953	< 0.01	November 16 > August 15*
DIC (µmol kg-1)		1868 ± 29	1887 ± 44	1895 ± 19		
	S	1905	1910	1926		
	R	2084 - 2238	2075 - 2220	2153 - 2238	< 0.01	November 16 > August 15 = August 16
TA (µmol kg ⁻¹)		2151 ± 41	2128 ± 49	2188 ± 19		
	S	2217	2215	2229		

Note: * The DIC in August 16 was less significantly different from those in August 15 and November 16.



Fig. 2. Surface distributions of (a) temperature, (b) salinity, (c) DO, (d) pH, (e) pCO₂, (f) DIC, and (g) TA on the Dongsha Atoll Lagoon in August 2015 and 2016 and November 2016.

 μ mol kg⁻¹ in autumn 2016, Table 1).

Moreover, all of the carbonate chemistry parameters in the DAL showed temporal variations (Table 1). The pH in November 2016 was significantly higher, and the pCO_2 in November 2016 was significantly lower, than those in August 2015 as well as those in August 2016 (8.051 ± 0.021 vs. 8.015 ± 0.040 vs. 7.974 ± 0.063 , p < 0.01; 396 ± 23 vs. 450 ± 42 vs. 545 ± 102 µatm, p < 0.01). The DIC in November 2016 was significantly higher than that in August 2015 (1895 ± 19 vs. 1868 ± 29 µmol kg⁻¹, p < 0.01). However, the TA was significantly higher in November 2016 than in August 2015 and 2016 (2188 ± 19 vs. 2151 ± 41 , $2128 \pm$ 49 µmol kg⁻¹, p < 0.01).

In summary, the observed higher average pCO_2 indicates the overall CO_2 source status of the DAL. The average TA and DIC were both lower in the interior than in the exterior of the lagoon, suggesting the involvement of inorganic and organic metabolic processes in the lagoon carbonate chemistry. In addition, all the carbonate chemistry parameters showed temporal variations. All these issues will be further examined in the discussion section.

4. DISCUSSION

4.1 The Net Calcification Potential of Coral Reefs in the DAL

The TA anomaly (Δ TA) was calculated as the difference between reef TA and source seawater TA values (i.e., reef TA - source water TA), with negative values representing TA depletion and positive values representing TA repletion. Δ TA can provide a direct indication of whether a reef is experiencing net calcification (TA depletion) or dissolution (TA repletion) (Cyronak et al. 2018).

According to Cyronak et al. (2018), most of the coral reefs showed extensive depletion of TA relative to the adjacent open ocean (negative Δ TA) for the majority of observations. A similar result was observed in the DAL (Table 2, Fig. 3). As shown in Table 2, the average Δ TA within the DAL ranged from -87 to -41 µmol kg⁻¹. This is direct evidence that the reefs on the DAL, on average, are currently in a state of net calcification. Moreover, the calcification potential of the DAL was higher in summer than in autumn according to the average Δ TA calculations (-87 and -66 vs. -41 µmol kg⁻¹, Table 2). This result is consistent with the well-established pattern of enhanced summer calcification in tropical corals, mainly as a result of seasonally higher light and temperature conditions (Marshall and Clode 2004; Venti et al. 2014; Vajed Samiei et al. 2015).

It is worth noting that the observed Δ TA in the DAL was apparently lower than that on the eastern margin of the Dongsha Atoll, which was reported to be among the highest values worldwide (DeCarlo et al. 2017); the authors suggested that the high calcification rate on the eastern margin of the Dongsha Atoll could be associated with the large in-

ternal waves colliding with the atoll and delivering nutrient-rich waters that stimulate rapid metabolism. However, with the present results, it is difficult to determine whether internal waves might be transmitted into the lagoon and subsequently affect calcification in the interior of the DAL. In contrast to the negative ΔTA values found on the eastern margin and in the DAL, positive ΔTA values were observed in the seagrass meadows around Dongsha Island; these positive values have been suggested to be the result of TA generated through carbonate dissolution and anaerobic processes in the sediments of the seagrass meadows (Chou et al. 2018). The positive ΔTA in the seagrass meadows around Dongsha Island may at least partially offset the TA depletion in the DAL from calcification. Consequently, these results in the Dongsha Atoll support the recent hypothesis that seagrass meadows may serve as chemical refugia for the associated coral reefs facing future ocean acidification (Manzello et al. 2012; Unsworth et al. 2012; Camp et al. 2016).

4.2 The Sink or Source Status of Atmospheric CO₂ in the DAL

To determine the net effect of reef systems on the airsea CO₂ exchange, the difference in pCO_2 (ΔpCO_2) between the reef water ($pCO_{2,R}$) and the source water ($pCO_{2,O}$) was defined (Gattuso et al. 1993; Suzuki and Kawahata 2003). A mean pCO_2 value of reef water that was higher than that in the source water (i.e., $\Delta pCO_2 > 0$) indicated that the coral reef had the potential to act as a source of atmospheric CO₂ as a whole. By contrast, if $\Delta pCO_2 < 0$, the reef could act as a sink of CO₂.

A previous study indicated that the pCO_2 values in reef waters were generally higher than those in the source water in most of the Indo-Pacific region (Suzuki and Kawahata 2003), and similar results were observed in the DAL (Table 3, Fig. 3). As shown in Table 3, the average $\Delta p CO_2$ within the DAL showed positive values ranging from 3 to 143 µatm. This is direct evidence that the reefs on the DAL, on average, are currently acting as a net CO_2 source. ΔpCO_2 in the DAL showed seasonal variations, with higher average values in summer and a lower average value in autumn (51 and 143 vs. 3 µatm, Table 3). This seasonal fluctuation pattern, with elevated pCO_2 in the warmer, wet season and depressed pCO_2 in the cold, dry season, was reported in other oceanic reefs, e.g., reefs in Bermuda and southeastern Florida (Suzuki and Kawahata 2003; Enochs et al. 2019; Lonbørg et al. 2019). It is possible that the observed seasonal fluctuations in pCO_2 on reefs resulted from seasonal variations in temperature and the calcification rate (Tables 1 and 2, Fig. 3). Increases in temperature and calcification both increase pCO_2 , thereby enhancing the release of CO_2 to the atmosphere in summertime. In contrast, the decrease in temperature and calcification in autumn drive pCO_2 downward.

The high $\Delta p CO_2$ values observed in summer in the

T /·	S*4	G 1. 4.	ΤΑ (μ	mol kg ⁻¹)		NGC St. 4	Df	
Location	Site	Sampling time	Reef water	Source water	$\Delta IA (\mu mol kg^2)$	NCC Status	кетегенсе	
Eastern Margin		June 2014	2128	2241	-113 Calcification		DeCarlo et al. 2017	
Dongsha Island	Inner Lagoon	August 2015	2810	2217	593	Dissolution	Chou et al. 2018	
	North Shore	August 2015	2244	2217	27	Dissolution		
		August 2015	2151	2217	-66	Calcification		
Atoll Lagoon		August 2016	2128	2215	-87	Calcification	This study	
		November 2016	2188	2229	-41	Calcification		

Table 2. Comparison of the TA anomaly (Δ TA, i.e., reef TA - source water TA) and net community calcification (NCC) status in this study and published results from Dongsha Atoll.



Fig. 3. Plots of the mean Δ TA vs. mean pCO₂ for the surface water of the Dongsha Atoll system in this study (blue circle, green triangle, and purple square) and previously published results (gray diamond). AL: Atoll lagoon; EM: eastern margin of Dongsha Atoll; IL: inner lagoon of Dongsha Island; NS: north shore of Dongsha Island.

Table 3. Comparison of ΔpCO_2 (i.e., pCO_2 of the reef water- pCO_2 of the source water) and their sink/source status for atmospheric CO₂ in this study and published results from Dongsha Atoll.

	Site	Sampling time	pCO ₂ (µatm)			$\Delta p \mathrm{CO}_2$ (µatm)		CO ₂ Status			
Location			Reef water	Source water	Air*	Reef- Source	Sea-Air	Reef- Source	Sea-Air	Reference	
Eastern Margin		June 2014	513	423	385	90	128	Source	Source	DeCarlo et al. 2017	
Dongsha Island	Inner Lagoon	August 2015	73	400	382	-327	-309	Sink	Sink	Chou et al. 2018	
	North Shore	August 2015	340	400	382	-60	-42	Sink	Sink		
Atoll Lagoon		August 2015	450	400	382	50	68	Source	Source		
		August 2016	545	421	386	124	159	Source	Source	This study	
		November 2016	396	393	390	3	6	Source	Sink		

Note: * Data from NOAA-ESRL MLO, https://www.co2.earth/, corrected for the saturation vapor pressure of water (Zeebe and Wolf-Gladrow 2001).

DAL were also found on the eastern margin of the Dongsha Atoll, and both of these values were higher than those reported for most Indo-Pacific coral reefs (Table 1, Suzuki and Kawahata 2003). In coastal reef systems such as the Fanning and Canton Atoll, high ΔpCO_2 values were generally related to terrestrial influences from land (Suzuki and Kawahata 2003; Enochs et al. 2019); however, this is not the case for the DAL. In the Dongsha Atoll system, summer internal waves shoaling from the east regularly transport cold, nutrient-rich water shoreward (Reid et al. 2019), which is likely a key factor explaining the unusually high calcification rate and thus ΔpCO_2 in the eastern margin of the Dongsha Atoll and in the DAL (Table 3, DeCarlo et al. 2017). The effect of internal waves on calcification and pCO_2 variation apparently needs more study.

4.3 Relationships Between *p*CO₂ and DO: The Role of Organic Carbon Metabolism

In addition to temperature and inorganic calcification, organic carbon metabolism (i.e., photosynthesis and respiration, P/R) may also play a significant role in regulating the CO₂ dynamics in the DAL. This role was examined by investigating the relationship between the temperature-corrected pCO_2 ($npCO_2$) and the apparent oxygen utilization (AOU). AOU is defined as AOU = $O_{2s} - O_{2m}$, where O_{2m} is the measured O_2 concentration and O_{2s} is its equilib-

rium saturation concentration with the in-situ temperature and salinity, calculated using Benson and Krause's formula (1984). A negative AOU indicates that the system tends to be autotrophic, i.e., the production of O_2 by photosynthesis is greater than the consumption of O_2 by respiration. A positive AOU signifies that the system tends to be heterotrophic, i.e., the consumption of O_2 by respiration surpasses the production of O_2 by photosynthesis. According to this indicator, the organic carbon metabolism of coral reefs in the DAL varied between two years, i.e., it tended to be autotrophic in August 2015 (average AOU = -9.4 µmol kg⁻¹) and heterotrophic in August and November 2016 (20.0 and 7.0 µmol kg⁻¹ for August and November, respectively).

To eliminate the effects of temperature on the pCO_2 variations, pCO_2 was corrected to the average temperature of 29.04°C ($npCO_2$) for the DAL. As shown in Fig. 4, $npCO_2$ and AOU are generally positively correlated, with higher $npCO_2$ and a positive AOU in summer 2016 and lower $npCO_2$ and a negative AOU in summer 2015. These results suggest that the yearly fluctuations in the summer pCO_2 between 2015 and 2016 could be associated with the variations in organic carbon metabolism. We suggest that weather conditions could be one of the possible reasons for these variations (Table 4). Based on the sampling records and weather reports of the Central Weather Bureau, the weather was sunny during the sampling period in summer 2015 but stormy during the sampling period in sum-



Fig. 4. Plots of temperature-normalized pCO_2 ($npCO_2$) vs. apparent oxygen utilization (AOU) in the Dongsha Atoll Lagoon in August 2015 (blue circle), August 2016 (green triangle), and November 2016 (purple square).

Table 4. Summary of wind speed, air temperature, atmosphere pressure, light intensity (the variation range and mean \pm SD for the reef water), and accumulated rainfall in the Dongsha Atoll lagoon during the sampling periods in August (summer) 2015 and 2016.

Sampling period	Wind speed (m s ⁻¹)	Air temperature (°C)	Atmospheric pressure (mbr)	Light intensity (w m ⁻²)	Accumulated rainfall (mm)	
August 2015	1.22 - 4.45	29.6 - 31.3	1007 - 1010	125 - 1036	0	
	3.30 ± 0.05	30.8 ± 0.02	1008 ± 0.1	739 ± 18	0	
August 2016	1.27 - 8.00	25.7 - 31.0	996 - 1004	29 - 1061	20	
	3.82 ± 0.06	29.5 ± 0.1	1002 ± 0.1	628 ± 17	30	

2016. The stormy rainfall diluted and caused lower salinity on the DAL (Table 1). The clouds associated with stormy weather may substantially block sunlight and the weaker light intensity was also recorded (Table 4). Weaker light intensity thus diminish photosynthesis, which would lead the DAL to become less autotrophic or more heterotrophic and thereby elevate pCO_2 . Moreover, it is worth noting that stormy weather could cause a stronger vertical mixing due to stronger wind speed (Table 4), which may transport AOU and pCO_2 -replete subsurface water into the surface layer, and thus could also partially contribute to the observed higher AOU and pCO_2 in August 2016.

4.4 Relationships Between NTA and NDIC: The Net Effect of Inorganic and Organic Carbon Metabolism on *p*CO₂ Variation

As discussed previously, both inorganic (calcification/CaCO₃ dissolution, C/D) and organic (photosynthesis/ aerobic respiration, P/R) carbon metabolism may affect seawater pCO_2 variation on the Dongsha Atoll. Typically, analyzing the relationship between the salinity-normalized TA and DIC (NTA and NDIC) can provide useful insights into the processes controlling the variations in the CO₂ system, as the relative variation in TA and DIC follows a well-established stoichiometric relationship that is specific to the respective biogeochemical processes; the ratios for these processes are: P/R = -0.2 and C/D = 2.0 (Krumins et al. 2013; Sippo et al. 2016). Moreover, a ratio of 0.6 of organic to inorganic carbon metabolism (R_{OI} ratio) represents the balance level at which the effects of organic and inorganic carbon metabolism on pCO_2 variation can offset each other, resulting in a constant pCO_2 level (Ware et al. 1992; Suzuki and Kawahata 2003).

Plots of NTA vs. NDIC for the surface water in the DAL are shown in Fig. 5. The baseline for the R_{OI} ratio of 0.6 is also superimposed as orange arrows. Generally, the variation in NTA and NDIC in summer 2015 is below the baseline of the R_{OI} ratio = 0.6 and close to the predicted stoichiometric relationship for calcification, indicating the dominance of inorganic carbon metabolism driving DIC and TA variations (Fig. 5a). These conditions may lead to



Fig. 5. Plots of NTA vs. NDIC for surface water in August 2015, August 2016, and November 2016 in the Dongsha Atoll Lagoon. Red lines are pCO_2 isoline increments. The black arrows show the predicted theoretical variations in TA and DIC caused by various metabolic processes. The orange arrow shows the variations at a constant R_{OI} ratio of 0.6.

a pCO_2 increase. This result is consistent with the tentative conclusion drawn based on the calculation of ΔpCO_2 and ΔTA (Tables 2 and 3, Fig. 3).

The variation in NTA and NDIC in summer 2016 was also generally below the baseline R_{oI} ratio of 0.6 but apparently deviated from the predicted stoichiometric relationship for calcification (Fig. 5b). Figure 5b further reveals that the covariation of NTA and NDIC during summer 2016 could be explained by the combination of calcification and respiration, supported by the observed negative Δ TA and positive AOU. The additional DIC released from organic respiration can thus further explain why higher Δp CO₂ was recorded in summer 2016 than in summer 2015, although the average Δ TA was not significantly different between the two years (Fig. 3).

Furthermore, the variation in NTA and NDIC in autumn 2016 is very close to the baseline R_{OI} ratio = 0.6 (Fig. 5c), indicating that the effects of inorganic and organic carbon metabolism on ΔpCO_2 variation largely offset each other (Gattuso et al. 1993; Kayanne et al. 1995; Frankignoulle et al. 1996). This result is in good agreement with the observed very low ΔpCO_2 in autumn 2016 (Table 3).

5. CONCLUSIONS

The present study reports the carbonate chemistry in the DAL for the first time. The observed temporal variations in calcification and the sink/source status of the DAL atmospheric CO₂ as well as their controlling processes are summarized in Table 5. First, according to the calculation of ΔTA , the DAL currently maintains a net calcification status, with higher calcification potential in summer and lower calcification potential in autumn. This result is consistent with the well-established pattern of enhanced summer calcification in tropical coral reefs, which occurs mainly due to seasonally higher light and temperature. Second, the calculation of $\Delta p CO_2$ shows that the DAL acts as a CO₂ source for the atmosphere, with higher values in summer and lower values in autumn. This finding is similar to those from other oceanic reefs and primarily reflects the fact that both temperature and calcification are higher in summer. Third, in addition to seasonal variation, $\Delta p CO_2$ also exhibits a clear

variation between two summer investigations, with higher values in summer 2016 than in summer 2015. The analysis of the $npCO_2$ vs AOU relationship suggests that the observed variation in summer pCO_2 could be associated with a change in the organic carbon metabolic status induced by different weather conditions during the sampling periods in summer 2015 and 2016 (sunny vs. stormy). Finally, the analysis of the NTA vs. NDIC relationship reveals that calcification was the dominant process controlling the CO₂ dynamics in summer 2015, while that in summer 2016 was chiefly regulated by the combination of calcification and organic respiration. This result further supports the finding that the change in the organic carbon metabolism could be the driving force behind the variation in pCO_2 between summer 2015 and 2016.

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Table 5. Summary of the observed seasonal and two summer cruises variations in calcification and sink/source status of atmospheric CO_2 and their controlling factors on the Dongsha Atoll Lagoon.

Sampling period	Weather	Temperature (°C)	Calcification potential (ΔTA, μmol kg ⁻¹)	CO ₂ source potential (ΔpCO ₂ , μatm)	Organic metabolism (AOU, µmol kg ⁻¹)	Inorganic vs. organic carbon dynamics (TA-DIC plot)
Summer 2015	Sunny	Medium (28.5)	Medium (-66)	Medium (50)	Autotrophic (-9.4)	Calcification $(R_{oi} < 0.6)$
Summer 2016	Stormy	High (29.1)	Strong (-87)	Strong (124)	Strongly heterotrophic (20.0)	Calcification + respiration $(R_{oi} < 0.6)$
Autumn 2016	Sunny	Low (26.9)	Weak (-41)	Weak (3)	Weakly heterotrophic (7.0)	Balance $(R_{oi} = 0.6)$

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