

Aragonite saturation states and nutrient fluxes in coral reef sediments in Biscayne National Park, FL, USA

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ABSTRACT: Some coral reefs, such as patch reefs along the Florida Keys reef tract, are not showing significant reductions in calcification rates in response to ocean acidification. It has been hypothesized that this recalcitrance is due to local buffering effects from biogeochemical processes driven by seagrasses. We investigated the influence that pore water nutrients, dissolved inorganic carbon (DIC) and total alkalinity (TA) have on aragonite saturation states ($\Omega_{\text{aragonite}}$) in the sediments and waters overlying the sediment surfaces of sand halos and seagrass beds that encircle Alinas and Anniversary reefs in Biscayne National Park. Throughout the sampling period, sediment pore waters from both bottom types had lower oxidation/reduction potentials (ORP), with lower pH relative to the sediment surface waters. The majority (86.5%) of flux rates ($n = 96$) for ΣNO_x^- , PO_4^{3-} , NH_4^+ , SiO_2 , DIC and TA were positive, sometimes contributing significant concentrations of the respective constituents to the sediment surface waters. The $\Omega_{\text{aragonite}}$ values in the pore waters (range: 0.18 to 4.78) were always lower than those in the overlying waters (2.40 to 4.46), and 52% ($n = 48$) of the values were <2.0 . The DIC and TA fluxes at the sediment–water interface reduced $\Omega_{\text{aragonite}}$ in 75% ($n = 16$) of the samples, but increased it in the remainder. The elevated fluxes of nutrients, DIC and TA into the sediment–water interface layer negatively alters the suitability of this zone for the settlement and development of calcifying larvae, while enhancing the establishment of algal communities.

KEY WORDS: Reef sediments · Aragonite saturation state · Nutrient flux · Pore water · Seagrass

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INTRODUCTION

Ocean acidification is the reduction in pH of marine waters resulting from the uptake of atmospheric carbon dioxide (CO_2) (Solomon et al. 2007). Atmospheric CO_2 has increased as a result of the combustion of fossil fuels, which in turn has increased the concentration of CO_2 dissolved into marine waters and negatively influenced the carbonate chemistry responsible for buffering the ocean system (e.g. Solomon et al. 2007, Andersson et al. 2011). Coastal and shelf ecosystems may be more susceptible to ocean acidification because of the input of additional carbon from terrestrial sources and benthic processes, especially in shallow and nearshore regions like the Florida Keys reef tract (Walter & Burton 1990, Ander-

sson et al. 2005, Manzello et al. 2012) and the Great Bahama Bank (Burdige & Zimmerman 2002, Hu & Burdige 2007, Burdige et al. 2008). The sediments in both of these regions are composed of carbonate sands and support productive coral reef and seagrass communities.

Recent studies have assessed the influence of ocean acidification on coral reef ecosystems. In the Florida Keys reef tract, Helmle et al. (2011) and Manzello et al. (2012) found that seagrasses remove CO_2 from the water column through CO_2 fixation during photosynthesis, thereby partially offsetting the effects of ocean acidification. Additionally, the dissolution of carbonate sediments of the Great Bahama Bank is shown to be enhanced in the sediments that underlie seagrass beds, and the flux of

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these dissolution products (i.e. dissolved inorganic carbon [DIC] and total alkalinity [TA]) are proposed to have a minor buffering effect on ocean acidification (Burdige & Zimmerman 2002, Hu & Burdige 2007, Burdige et al. 2008). In support of this conclusion, a predictive model by Andersson et al. (2003) showed that carbonate sediments do dissolve under normal conditions in pore waters, but the production and flux of TA into the waters overlying the sediment surface would be insufficient to completely buffer the predicted decrease in pH resulting from the increased absorption of atmospheric CO₂.

The cited studies confirm that geochemical conditions in carbonate sediments promote the dissolution of those sediments, thereby establishing vertical concentration gradients that enhance the flux of DIC and TA into the waters overlying the sediment surface. Although the flux of these constituents may not be large enough to counter the effects of ocean acidification in the much larger volume of overlying waters, the flux of DIC and TA into the sediment–water interface, or benthic boundary layer, may depress the saturation state for calcium carbonate in this zone. Depressed saturation states for calcium carbonate decrease calcification rates in a wide variety of organisms (Fabry et al. 2008). The majority of these organisms live as adults or initiate their life cycles in the benthic boundary layer. The objective of this study was to determine if biogeochemical processes within the carbonate sediments of the sand halos and seagrass beds that surround coral reefs alter the carbonate saturation states in the benthic boundary layers. This was achieved by obtaining overlying water and vertical pore water profiles of nutrients and carbonate chemistry parameters from both substrate types during the spring and summer at 2 coral patch reefs in Biscayne National Park.

MATERIALS AND METHODS

Site description, sampling methods and sample dates

Samples of sediment pore water and of water overlying the sediment surface (hereafter referred to as sediment surface water) were collected from 2 reef sites within Biscayne National Park during April, June, July and August 2007 (Fig. 1). Samples were collected during the late morning on each sampling date, with a sampling event duration of ~1 h per reef.

The 2 sites, Alinas (25.3862° N, 80.1629° W) and Anniversary (25.3874° N, 80.1623° W) reefs, are lo-

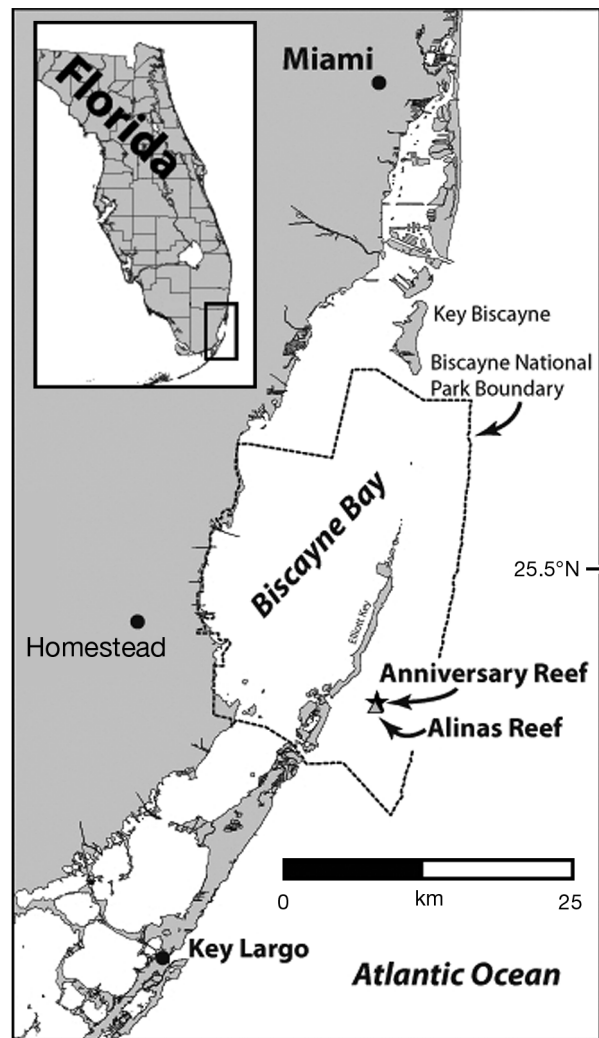


Fig. 1. Location of Alinas and Anniversary reefs, Biscayne National Park

cated ~20 km off the east coast of southern Florida. Both reefs reside in ~5.0 m of water, are not sub-aerially exposed during any point in the tidal cycle and have high wave energies except during tropical storms. At each reef, one sampling site was located within the sand halo and 2.0 m from the base of each reef, and a second site was located within the seagrass beds that grow adjacent to the sand halos and ~5.0 m from the base of the reef.

Reef sediments are produced through erosion of the reef framework and direct sedimentation from calcifying green and red algae. Marine grasses in the seagrass beds at both reefs occupy ~20% of the carbonate sand surfaces and are dominated by species of *Thalassia* and *Syringodium* (Yates & Halley 2003). The sediments in this area of Biscayne National Park are generally 10% high-Mg calcite, 87% aragonite

and 3% low-Mg calcite (Stehli & Hower 1961). The average porosity of these sediments is 0.47 (Enos & Sawatsky 1981).

Using SCUBA, divers collected pore water samples through stainless-steel PushPoint samplers (MHE Products). These samplers are 35.56 cm long and have an o.d. and i.d. of 0.32 and 0.16 cm, respectively. The sample collection interval at the tips of the samplers is 0.64 cm. The void volume of the sampler is approximately 750 μl . Pore water samples were collected from 3 depths below the sediment surface (1.27, 12.70 and 27.31 cm) at each site by first positioning a weighted stabilization plate (Komatex[®]; 26.50 cm in diameter, 1.30 cm thick) at the sampling sites and then inserting 3 samplers to the pre-determined depths (Lisle & Reich 2006). The samplers were positioned so that each was located 18.5 cm from the other samplers and the edge of the stabilization plate. Images of the sampling devices can be accessed at <http://pubs.usgs.gov/fs/2006/3052/>.

Pore waters were collected by attaching a short length of silicone tubing (0.64 cm o.d., 0.32 cm i.d.) and a polycarbonate 3-way valve to an acid-cleaned and reagent-grade-water-rinsed polyethylene/polypropylene 50.0 ml syringe. The end of the silicone tubing was then attached to the samplers while underwater immediately prior to sampling. Using the 3-way valve to flush the sampler without forcing water back into the sediments, 20 to 30 sampler void volumes were flushed from the samplers 3 times prior to taking the pore water samples from the respective depths. At each sediment depth, ~250 ml (5 syringes) were collected. Because of the relatively large sample volumes required for the analyses, the vertical sample collection zones around each pore water sampler may have overlapped to some degree (Seeberg-Elverfeldt et al. 2005). The sample collection depth (i.e. 1.27 cm) most susceptible to mixing with the sediment surface water, was isolated from the water by the stabilization plate during each sample collection event. Although the possibility of mixing pore water from the different vertical sample depths during sample collection is acknowledged by the authors, the degree to which this mixing occurred is not assumed to have made the samples homogeneous. This is supported by the geochemistry from each sample site and event, which does show distinct vertical zonation.

Sediment surface waters were sampled within 30.0 cm above the sediment surface at each of the reef sites by opening an evacuated 1.0 l polypropylene bottle. Once on deck, all syringes and bottles were placed in a cooler that maintained the samples in the dark and at *in situ* temperatures.

Field data

On deck, an aliquot of each sample was transferred to a separate container and analyzed for salinity and oxidation-reduction potential (ORP) using an Ultrameter (model 6P; Myron L Company). ORP, instead of dissolved oxygen, was used as an indicator of vertical stratification of microbial processes within the sediments. Temperature data were collected from a Sea-Bird SBE 16*plus* SeaCAT (Sea-Bird Electronics) that was permanently anchored to the seabed close to the Alinas Reef sample site. The sensor was ~15 cm above the surface of the sediments.

pH analysis was performed on each sample using a temperature-compensated, high-resolution pH probe (± 0.03 pH unit) (model 815600; Orion ROSS combination electrode) with a sensION2 pH meter (Hach). The sensION2 pH meter was calibrated with Tris seawater buffers as described by Yates et al. (2007).

Nutrient sample processing and analyses

Nutrient samples were filtered through a syringe filter (0.45 μm , Supor[®] membrane) into acid-cleaned and reagent-grade-water-rinsed low-density polyethylene bottles and stored at 4.0°C. Samples for NH_4^+ , SiO_2 and $\text{NO}_3^- + \text{NO}_2^-$ (ΣNO_x^-) analysis were filtered only, whereas samples for PO_4^{3-} analysis were filtered and acidified by adding ~0.1 ml of concentrated HCl. All nutrient samples were appropriately packed and shipped via overnight carrier to the Woods Hole Oceanographic Institute Nutrient Analytical Facility. All analyses were performed on a QuickChem 8000 (Lachat Instruments) 4-channel continuous flow injection system.

TA and DIC sample processing and analyses

Samples for the analysis of TA and DIC were filtered through a syringe filter (0.45 μm , Supor[®] membrane) into borosilicate glass serum bottles that were acid washed, rinsed with reagent-grade water and combusted in a muffle furnace. Samples were preserved by adding saturated HgCl_2 to a final concentration of 0.02% (v/v) and immediately inserting butyl rubber stoppers that were secured using aluminum caps crimped in place. Samples were stored at 4.0°C until analysis. All TA ($\pm 1 \mu\text{M kg}^{-1}$) and DIC ($\pm 2 \mu\text{M kg}^{-1}$) analyses were conducted at the US Geological Survey (USGS) Coastal and Marine Sci-

ence Center in St. Petersburg, FL, following the analytical methods described by Yates et al. (2007).

Benthic flux rate calculations

Flux rates (J ; $\text{mM m}^{-2} \text{d}^{-1}$) were calculated using Fick's first law of diffusion:

$$J = -\Phi D_s (\Delta C / \Delta z) \quad (1)$$

where Φ is the sediment porosity, D_s is the appropriate diffusion coefficient ($\text{m}^2 \text{d}^{-1}$), ΔC (mol l^{-1}) is the difference between the concentration of each nutrient in the sediment surface and pore waters at that sediment depth where the nutrient had the greatest concentration, and Δz (m) is the distance between the sediment–water interface and the respective sediment depths at which the greatest concentrations of the respective nutrients occurred. Since advective forces are not accounted for in the flux calculations, the resulting flux rates should be considered as representative of the minimum rates for the movement of dissolved constituents in the pore waters into the overlying surface waters. For the nutrients, the following diffusion coefficients ($\text{m}^2 \text{d}^{-1}$) were used: NH_4^+ , 8.85×10^{-5} ; ΣNO_x^- , 6.65×10^{-5} ; PO_4^{3-} , 2.97×10^{-5} ; and SiO_2 , 5.89×10^{-5} (Rasheed et al. 2002). The diffusion coefficient for DIC (1.34×10^{-5}) was taken from Komada et al. (1998). The diffusion coefficient for DIC was also used for alkalinity, as the majority of alkalinity (i.e. HCO_3^- , CO_3^{2-}) is accounted for by DIC in marine water (Wolf-Gladrow et al. 2007).

Aragonite saturation index calculations

The aragonite saturation state ($\Omega_{\text{aragonite}}$) was calculated using the CO2SYS (Pierrot et al. 2006) or CO2calc (Robbins et al. 2010) program and is expressed as:

$$\Omega_{\text{aragonite}} = ([\text{CO}_3^{2-}] [\text{Ca}^{2+}]) / K_{\text{sp}} \quad (2)$$

where K_{sp} is the solubility product for aragonite as given by Mucci (1983). The following program options were selected prior to running the analyses: dissociation constants K_1 and K_2 were those recommended by Mehrbach et al. (1973) as refit by Dickson & Millero (1987), the dissociation constant K_{SO_4} was that of Dickson (1990) and the selected pH scale was the seawater scale.

Measured TA, DIC and pH values; water temperatures; salinities; and relevant nutrient concentrations were used as input data to calculate $\Omega_{\text{aragonite}}$ values,

except for TA for the following pore water samples: Alinas Reef sand halo in August (1.27 cm) and seagrass bed in July (27.31 cm) and August (1.27 and 27.31 cm), and Anniversary Reef seagrass bed (all sample depths) in August. These samples for TA analysis had varying quantities of sulfide precipitates following the addition of HgCl_2 . Sulfide precipitates artificially reduce measurable TA (Goyet et al. 1991, Hiscock & Millero 2006, Andersson et al. 2007). Accordingly, the DIC and pH values were used to calculate the TA for each of the sulfide affected samples. These calculated TA values were then used in conjunction with the original DIC values to calculate the respective Ω aragonite values.

Statistical analyses

Pearson product moment correlation coefficients (r) and the associated p-values were calculated for selected data variables using $\alpha = 0.05$. Tests of significant differences between 2 data variables were performed using the Mann-Whitney rank sum test and between 3 or more variables using the Kruskal-Wallis ANOVA on ranks with multiple comparisons using Dunn's test. Non-parametric data analysis tests were chosen because all data sets, pooled or not, failed the Shapiro-Wilks test for normality. Data below the detection limit of the method and expressed as censored data were included in all analyses after adjusting each value to one-half of the detection limit. All statistical analyses were performed using Minitab® ver. 15.

RESULTS

Sediment surface waters

Sediment surface water temperature (median: 29.4, range: 25.1 to 30.0°C), salinity (36.1, 35.9 to 36.4‰), pH (8.05, 7.92 to 8.23) and ORP (79.7, 42.0 to 243.0 mV) data were similar at both reefs and bottom types for the respective sampling dates (Table 1). Sediment surface water temperatures, which increased during the study period, were significantly and positively correlated with SiO_2 ($r = 0.614$, $p = 0.011$), TA ($r = 0.627$, $p = 0.009$) and DIC ($r = 0.978$, $p < 0.001$) and negatively correlated with ORP ($r = -0.816$, $p < 0.001$) (Table 2). Comparing the pooled sediment surface- ($n = 16$) and pore-water data from both bottom types ($n = 24$ per type), the pH and ORP data were significantly different ($p = 0.001$) and greater in the sediment surface waters and were significantly lower

Table 1. pH and oxidation-reduction potential (ORP) data for sediment surface (SSW) and pore waters (3 sediment depths) of 2 bottom types (sand halos and seagrass beds) at Alinas and Anniversary reefs, Biscayne National Park. SSW = sediment surface water

Reef and month	Depth (cm)	pH		ORP (mV)	
		Sand	Seagrass	Sand	Seagrass
Alinas					
April	SSW	8.03	8.03	167.0	167.0
	1.27	8.00	8.00	279.0	280.0
	12.70	7.62	7.62	208.0	180.0
	27.31	7.66	7.66	210.0	240.0
June	SSW	7.92	7.92	53.3	53.3
	1.27	7.73	7.80	-35.0	6.0
	12.70	7.50	7.46	-119.0	-154.0
	27.31	7.62	7.68	-30.0	-73.0
July	SSW	8.03	8.03	50.0	50.0
	1.27	8.11	8.12	-32.0	-31.0
	12.70	7.84	7.60	-79.0	-133.0
	27.31	7.82	7.44	-30.0	-197.0
August	SSW	8.23	8.23	112.0	112.0
	1.27	7.73	7.94	-113.0	-50.0
	12.70	7.83	7.46	-20.0	-129.0
	27.31	7.84	7.30	-5.0	-201.0
Anniversary					
April	SSW	8.16	8.16	243.0	243.0
	1.27	8.05	8.05	318.0	277.0
	12.70	7.72	7.72	252.0	-94.0
	27.31	7.68	7.68	236.0	-60.0
June	SSW	7.92	7.92	53.3	53.3
	1.27	7.87	7.70	30.0	-148.0
	12.70	7.56	7.32	32.0	-167.0
	27.31	7.44	7.31	-96.0	-173.0
July	SSW	8.07	8.07	42.0	42.0
	1.27	8.07	8.20	-86.0	-55.0
	12.70	7.87	7.67	-54.0	-113.0
	27.31	7.77	7.67	-139.0	-125.0
August	SSW	8.20	8.20	106.0	106.0
	1.27	7.85	7.76	20.0	-115.0
	12.70	7.81	7.32	29.0	-202.0
	27.31	8.03	7.40	44.0	-169.0

for ΣNO_x^- , NH_4^+ (sand halo only), SiO_2 , DIC and TA (seagrass beds only) (Tables 1 & 2). There were no significant differences between the sediment surface and pore water concentrations of PO_4^{3-} in both bottom types, NH_4^+ in the seagrass beds and TA in the sand halos.

Pore waters

There were significant trends between pore water variables, but these trends were not consistent within and between bottom types. ORP and pH were negatively correlated with temperature and sample depth, respectively, in both bottom types. Concentrations of

PO_4^{3-} , SiO_2 and NH_4^+ were all positively correlated with each other in the sand halo pore waters but not in the seagrass beds, while ΣNO_x^- concentrations were positively correlated with DIC concentrations in the sand halos and ORP data in the seagrass beds. None of the nutrient concentrations were significantly correlated with sample depth or temperature in either bottom type.

For the carbonate chemistry, pH was negatively correlated with DIC and positively correlated with ORP in the seagrass pore waters only. The $\Omega_{\text{aragonite}}$ data were negatively correlated with DIC concentrations in the sand halos and positively correlated with ORP in the seagrass beds.

When comparing the pore water data for all variables measured, there were no significant differences between the reefs for the same bottom type (e.g. sand halo vs. sand halo). The data were then pooled based on bottom type (i.e. sand halos vs. seagrass beds). The pore-water pH data in both bottom types (sand halo: median 7.82, range 7.44 to 8.11; seagrass: 7.67, 7.30 to 8.20) were significantly different ($p = 0.001$), as were the ORP data ($p = 0.003$) (sand halo: -12.5, -139.0 to 318.0 mV; seagrass: -14.0, -202.0 to 280.0 mV) (Table 1).

There was a general trend of increasing ΣNO_x^- concentrations with pore water depth in both bottom types at both reefs per sampling event, with intermediate depths containing the highest concentrations (Table 2). There was no significant difference between concentrations of these nitrogen species when comparing the sand halos (0.08, <0.05 to 2.46 μM) to seagrass beds (0.07, <0.05 to 1.67 μM). The ΣNO_x^- flux rates from the sand halos and seagrass beds around both reefs were similar within each site, except during the April (Alinas Reef) and June (Anniversary Reef) sampling events, when the fluxes from the seagrass beds were approximately 45- and 10-fold greater, respectively, than those from the sand halos (Table 3).

The pore waters at both reef sites were enriched for PO_4^{3-} for the April, July and August sampling events and were significantly different ($p = 0.012$) between the sand halos (0.13, <0.05 to 0.86 μM) and seagrass beds (0.06, <0.05 to 0.57 μM) (Table 2). The flux rates for this nutrient around both reefs were greatest during the April sampling event and remained relatively low during the remainder of the project. The exception was the June sampling event, when the PO_4^{3-} demands in the sand halo and seagrass bed sediments were between 1 and 2 orders of magnitude greater than the respective flux rates for the other sampling events (Table 3).

Table 2. Sediment surface water (SSW) and pore water (3 sediment depths) nutrient, dissolved inorganic carbon (DIC), and total alkalinity (TA) values of 2 bottom types (sand halos and seagrass beds) at Alinas and Anniversary reefs, Biscayne National Park

Reef and month	Depth (cm)	Sand						Seagrass					
		ΣNO_x^- (μM)	PO_4^{3-} (μM)	NH_4^+ (μM)	SiO_2 (μM)	DIC (μM)	TA (μM)	ΣNO_x^- (μM)	PO_4^{3-} (μM)	NH_4^+ (μM)	SiO_2 (μM)	DIC (μM)	TA (μM)
Alinas													
April	SSW	0.06	<0.05	<0.05	2.08	1876.9	2164.5	0.06	<0.05	<0.05	2.08	1876.9	2164.5
	1.27	0.10	0.08	3.18	10.64	1975.7	2265.7	1.67	<0.05	0.27	3.53	1975.7	2254.0
	12.70	0.06	0.86	19.64	36.35	2173.7	2279.9	0.24	0.57	0.20	8.90	2173.7	2278.9
	27.3	0.83	0.44	8.30	11.23	2187.0	2307.2	0.68	0.21	0.70	2.88	2187.0	2302.9
June	SSW	<0.05	2.63	1.50	2.13	1964.2	2180.3	<0.05	2.63	1.50	2.13	1964.2	2172.0
	1.27	0.31	<0.05	1.61	4.38	2040.6	2257.6	0.06	<0.05	1.05	6.02	2061.7	2331.2
	12.70	0.15	0.21	1.13	9.60	2154.1	2239.7	0.19	0.05	1.14	9.88	2253.7	2380.2
	27.31	0.43	0.06	0.53	7.60	2063.0	2179.5	0.48	<0.05	0.71	5.68	2131.2	2306.8
July	SSW	0.05	0.07	2.28	2.48	1975.1	2297.6	0.05	0.07	2.28	2.48	1975.1	2297.6
	1.27	0.07	0.06	0.06	4.14	2026.8	2292.1	<0.05	0.06	0.24	4.08	2002.0	2266.4
	12.70	0.05	0.13	0.50	10.70	2087.9	2228.9	0.05	<0.05	0.64	10.70	2341.0	2391.2
	27.31	0.09	0.31	16.50	21.70	2227.3	2422.9	0.06	<0.05	0.88	11.90	2763.6	2669.0
August	SSW	0.05	<0.05	<0.05	2.14	1976.6	2368.5	0.05	<0.05	<0.05	2.14	1976.6	2368.5
	1.27	0.08	0.05	9.88	40.20	2894.0	2565.0	<0.05	<0.05	<0.05	7.86	2047.1	2378.3
	12.70	0.10	0.11	8.17	13.30	2171.9	2342.7	0.14	0.07	0.61	9.78	2704.4	2677.6
	27.31	<0.05	0.13	4.68	9.59	2146.0	2279.5	0.11	0.11	<0.05	12.00	3984.2	3885.3
Anniversary													
April	SSW	0.08	<0.05	<0.05	2.00	1876.9	2249.0	0.08	<0.05	<0.05	2.00	1876.9	2249.0
	1.27	0.06	<0.05	0.06	4.54	1958.2	2264.5	0.06	0.20	0.10	3.38	2675.3	3040.1
	12.70	0.07	0.35	15.44	19.21	2205.0	2351.1	<0.05	0.12	0.31	30.93	2741.8	2910.3
	27.31	0.06	0.45	7.50	14.97	2190.0	2321.8	0.05	<0.05	7.84	9.20	2389.1	2526.8
June	SSW	<0.05	2.63	1.50	2.13	1956.4	2172.0	<0.05	2.63	1.50	2.13	1956.4	2172.0
	1.27	0.16	0.08	1.35	3.64	2032.8	2314.8	0.06	0.06	1.17	3.85	2121.1	2413.8
	12.70	<0.05	0.25	0.74	7.56	2008.7	2198.1	0.09	0.13	0.77	7.20	2441.9	2556.7
	27.31	<0.05	0.19	1.74	7.80	2389.2	2519.9	0.94	0.08	1.58	7.21	2246.5	2347.0
July	SSW	0.06	<0.05	<0.05	2.46	1975.4	2304.1	0.06	<0.05	<0.05	2.46	1975.4	2382.4
	1.27	0.08	<0.05	0.97	4.09	2002.5	2248.0	0.09	<0.05	0.23	3.29	1992.2	2302.3
	12.70	<0.05	0.14	1.60	12.20	2158.0	2331.9	0.06	0.06	1.01	10.70	2182.0	2242.5
	27.31	<0.05	0.20	1.20	8.80	2307.1	2382.4	<0.05	0.05	1.61	8.50	2187.2	2270.3
August	SSW	0.05	0.06	<0.05	2.07	1998.4	2367.8	0.05	0.06	<0.05	2.07	1998.4	2367.8
	1.27	0.09	0.12	0.96	5.51	2042.0	2234.7	0.05	0.06	3.97	14.60	2441.2	2660.4
	12.70	0.86	0.05	3.39	8.43	2078.8	2302.3	0.73	0.08	2.12	13.90	3459.4	3480.9
	27.31	2.46	0.07	0.71	4.23	2731.3	2334.6	0.07	0.05	0.58	15.90	2027.9	2076.7

The NH_4^+ concentrations in the sand halos (1.61, <0.05 to 19.64 μM) were significantly greater ($p = 0.004$) than those in the seagrass beds (0.71 μM ; <0.05 to 7.84 μM) (Table 2). The NH_4^+ flux rates from the sand halo sediments at Alinas Reef were greater than those from the seagrass bed, while the reverse was generally shown for Anniversary Reef (Table 3). There were relatively low NH_4^+ demands in the sand halo sediments during the June sampling event at both reefs and in the seagrass beds at Alinas Reef during June and July.

Pore water SiO_2 concentrations were also enriched relative to those in the sediment surface waters, al-

though there were no significant differences between sand halos (9.20, 3.64 to 40.20 μM) and seagrass beds (8.70, 2.88 to 30.93 μM) (Table 2). The greatest concentrations of SiO_2 in the pore waters at both reefs were recorded during the August sampling event and were similar between reefs and bottom types (Table 2). The SiO_2 flux rates at both reefs and bottom types were similar in magnitude for each sampling event, with April having the overall highest flux rates (Table 3). The exception to this trend was from the sand halo at Alinas Reef in August, when the flux rate was 82.96 $\mu\text{M m}^{-2} \text{d}^{-1}$, ~80-fold greater than the other flux rates for the same sampling event (Table 3).

The DIC concentrations in pore waters from the sand halos (2150.0, 1958.2 to 2894.0 μM) and seagrass beds (2216.9, 1975.7 to 3984.2 μM) were similar and increased slightly with temperature (Table 2). There was no trend in the DIC flux rates from either reef or bottom type (Table 3). The DIC flux rates during the August sampling event were collectively the highest of the study period, with the rate from the sand halo at Alinas Reef being 25- to 80-fold greater than the other DIC flux rates from this bottom type (Table 3).

The TA concentrations in the pore waters at both reefs and bottom types followed a trend similar to the DIC data, with increasing concentrations in the lower depths as the study progressed (Table 2). The TA concentrations in the seagrass beds (2379.3, 2076.7 to 3885.3 μM) were significantly greater ($p = 0.015$) than those in the sand halos (2297.2, 2179.5 to 2565.0 μM). As with the DIC flux data, there was no consistent trend in TA flux rates between reefs or bottom types, with the highest flux rate occurring during the first sampling event in April (Table 3). Unlike the DIC data, however, there was no TA flux from the sand halo at Anniversary Reef or the seagrass bed at Alinas Reef during the August and July sampling events, respectively (Table 3).

Aragonite saturation

Measured pH, DIC and alkalinity data were used to calculate the $\Omega_{\text{aragonite}}$ of the sediment surface- and pore-water samples collected at both reef sites. The average $\Omega_{\text{aragonite}}$ for calcification processes in tropi-

cal waters varies between 3.0 and 4.0, with values below 1.0 representing undersaturated conditions where aragonite dissolution occurs (Kleypas et al. 1999). Collectively, 77.1% of the pore water samples collected ($n = 48$; Table 4) at both reefs were below the average $\Omega_{\text{aragonite}}$ range for calcification in tropical waters (Fig. 2).

The $\Omega_{\text{aragonite}}$ values for the sediment surface waters at Alinas (median 3.45, range 2.40 to 4.46) and Anniversary (4.17, 2.48 to 4.60) reefs were relatively consistent between sample sites and bottom types per sampling event (Table 4). The pore water $\Omega_{\text{aragonite}}$ values in the seagrass bed at Alinas Reef (1.73, 0.62 to 3.83) and both bottom types at Anniversary Reef (sand halo: 2.23, 0.18 to 3.50; seagrass bed: 1.86, 1.04 to 4.78) showed similar decreasing trends with increasing depth as the study progressed (Fig. 2, Table 4). The $\Omega_{\text{aragonite}}$ values from the sand halo at Alinas Reef (1.84; 0.25 to 3.19) decreased relative to the surface water values but did not decrease with time and depth as at the other 3 sites (Fig. 2, Table 4). The pooled $\Omega_{\text{aragonite}}$ values for pore waters from both bottom types were similar to those of the respective sediment surface water values for the April and June sampling events. During the July sampling event, only the pore water $\Omega_{\text{aragonite}}$ values from the seagrass beds were significantly different from those of the sediment surface waters, whereas both bottom types were significantly different from the sediment surface water values for the August samples. There were no significant differences between the $\Omega_{\text{aragonite}}$ values for the sand halo and seagrass bed pore waters throughout the project.

Table 3. Nutrient, dissolved inorganic carbon (DIC) and total alkalinity (TA) flux rates ($\text{mM m}^{-2} \text{d}^{-1}$) in the sediments of 2 bottom types (sand halos and seagrass beds) at Alinas and Anniversary reefs, Biscayne National Park. Diffusion coefficients ($\text{m}^2 \text{d}^{-1}$) are as follows: NH_4^+ , 8.85×10^{-5} ; NO_x^- , 6.65×10^{-5} ; PO_4^{3-} , 2.97×10^{-5} ; SiO_2 , 5.89×10^{-5} ; DIC, 1.34×10^{-5} ; TA, 1.34×10^{-5} . Porosity assumed to be, on average, 0.47

Month and reef	ΣNO_x^-		PO_4^{3-}		NH_4^+		SiO_2		DIC		TA	
	Sand	Seagrass	Sand	Seagrass	Sand	Seagrass	Sand	Seagrass	Sand	Seagrass	Sand	Seagrass
April												
Alinas	0.088	3.94	0.089	0.057	6.42	0.099	7.47	1.49	7.31	15.03	3.36	5.80
Anniversary	-0.002	-0.006	0.021	0.165	5.04	2.55	3.75	6.31	16.62	43.80	5.17	400.10
June												
Alinas	0.044	0.049	-0.266	-0.132	-0.148	-0.120	1.63	1.69	9.62	14.66	3.01	10.54
Anniversary	0.028	0.278	-0.280	-0.282	-0.248	0.723	0.575	0.515	10.20	10.20	8.20	19.48
July												
Alinas	0.004	0.001	0.012	-0.001	2.17	-0.213	1.95	0.955	5.94	18.58	32.00	8.75
Anniversary	0.066	0.088	0.008	0.001	0.508	5.10	2.12	1.80	7.81	4.99	1.84	-40.56
August												
Alinas	0.012	0.022	0.004	0.003	3.22	0.184	82.96	1.00	464.54	47.30	99.51	35.73
Anniversary	0.276	0.166	0.068	0.002	1.09	12.84	1.39	1.40	17.26	73.99	-67.36	56.40

Table 4. Aragonite saturation states ($\Omega_{\text{aragonite}}$) in the sediment surface (SSW) and pore water (3 sediment depths) of 2 bottom types (sand halos and seagrass beds) at Alinas and Anniversary reefs, Biscayne National Park

Reef and site	Depth (cm)	$\Omega_{\text{aragonite}}$			
		April	June	July	August
Alinas					
Sand	SSW	3.23	2.49	3.67	4.46
	1.27	3.19	2.57	3.08	0.25
	12.70	1.54	1.37	1.85	2.19
	27.31	1.68	1.60	2.45	1.82
Seagrass	SSW	3.23	2.40	3.67	4.46
	1.27	3.19	3.13	3.06	3.83
	12.70	1.54	1.78	1.19	0.87
	27.31	1.68	2.19	0.62	1.05
Anniversary					
Sand	SSW	4.17	2.48	3.73	4.23
	1.27	3.50	3.25	2.86	2.35
	12.70	1.94	2.26	2.20	2.69
	27.31	1.78	1.88	1.37	0.18
Seagrass	SSW	4.17	2.48	4.60	4.23
	1.27	4.78	3.41	3.54	2.83
	12.70	2.41	1.76	1.20	1.49
	27.31	1.95	1.54	1.38	1.04

DISCUSSION

Coastal marine systems receive ~20 terramoles C yr⁻¹ from the overlying air, ~80 terramoles C yr⁻¹ from terrestrial sources, and retain ~40% of that total carbon loading in the sediment systems of these relatively shallow coastal zones (Andersson et al. 2005, 2011, Solomon et al. 2007). The retention and mineralization of organic and inorganic carbon and nutrients are especially enhanced in permeable carbonate sands and seagrass beds like those described in this study (Falter & Sansone 2000, Wild et al. 2004, Unsworth et al. 2012). Mineralization rates are directly influenced by transport processes between the pore waters and overlying surface waters (Huettel et al. 2003, King et al. 2009, Santos et al. 2012). These transport processes are responsible for both the delivery of dissolved and particulate organic and inorganic carbon and dissolved oxygen into the sediments and the vertical and horizontal transport of dissolved organic matter released from seagrass roots and rhizomes (Holmer et al. 2001). The mineralization and cycling of carbon substrates and nutrients are driven by microbial communities associated with the surfaces of the sediment particles and seagrass rhizomes and suspended in the pore waters.

Microbial communities in shallow marine sediment systems can drive the development of relatively steep gradients in pore water geochemistry profiles (Huet-

tel et al. 1998, Precht et al. 2004). Characterizations of these microbial communities have shown them to possess diverse physiological capabilities, including photosynthesis, aerobic and anaerobic heterotrophy, fermentation and chemolithotrophy (Sander & Kalff 1993, Sorensen et al. 2007, Rusch et al. 2009, Schöttner et al. 2011, Gobet et al. 2012). Studies of microbial activities in marine sediments commonly follow dissolved oxygen concentrations as a metric for predicting biogeochemical processes. Our decision to use ORP instead of dissolved oxygen was based on the fundamental principle that activities of biogeochemical pathways in microbial communities are constrained by the respective redox environments within those communities (Walter & Burton 1990, Van Cappellen & Gaillard 1996, Thullner et al. 2005). The relative changes in ORP values in surface waters and vertically within the pore waters can be used as a generally applied metric for assessing the likelihood of oxygenic (>25 mV), nitrogen cycling and anaerobic ammonium oxidation (50 to -50 mV), fermentative (-100 to -225 mV), sulfate-reducing (-50 to -250 mV), acetogenic and methanogenic (-175 to -400 mV) microbial processes occurring in the sediments (Stumm & Morgan 1981b). Therefore, knowing if fermentative and anaerobic biogeochemical processes are likely to proceed in marine sediments, as shown in this study (Table 1), was important, as these processes commonly produce bicarbonate (HCO₃⁻), CO₂, organic acids and protons, all of which influence TA, DIC and pH and, thereby, $\Omega_{\text{aragonite}}$ in the pore waters (Stumm & Morgan 1981a, Burdige 2006a, Hu & Burdige 2007, Soetaert et al. 2007, Walter et al. 2007, Hofmann et al. 2009).

TA and DIC concentrations are generally assumed to covary at a 1:1 ratio in carbonate sediment pore water and the overlying sediment surface water, in the tropics (Burdige & Zimmerman 2002, Hu & Burdige 2007, Burdige et al. 2008). In this study, the TA:DIC ratio (i.e. the inverse of the slopes of the regression lines) for the sediment surface water (1:0.9) approximates 1:1; however, the pore water ratio (1:1.3) indicates a relatively greater net production of DIC than TA, with generally higher concentrations of both variables occurring in the seagrass bed sediments (Fig. 3). The distribution of TA:DIC ratios along the regression line in Fig. 3 shows generally greater concentrations of the 2 variables in seagrass beds than in sand halos, although 15 of the 24 (62.5%) data points from the seagrass beds were similar to those from the sand halos. Plotting the data from Fig. 3 by sampling date and depth of the pore water sample shows that the groupings of TA:DIC

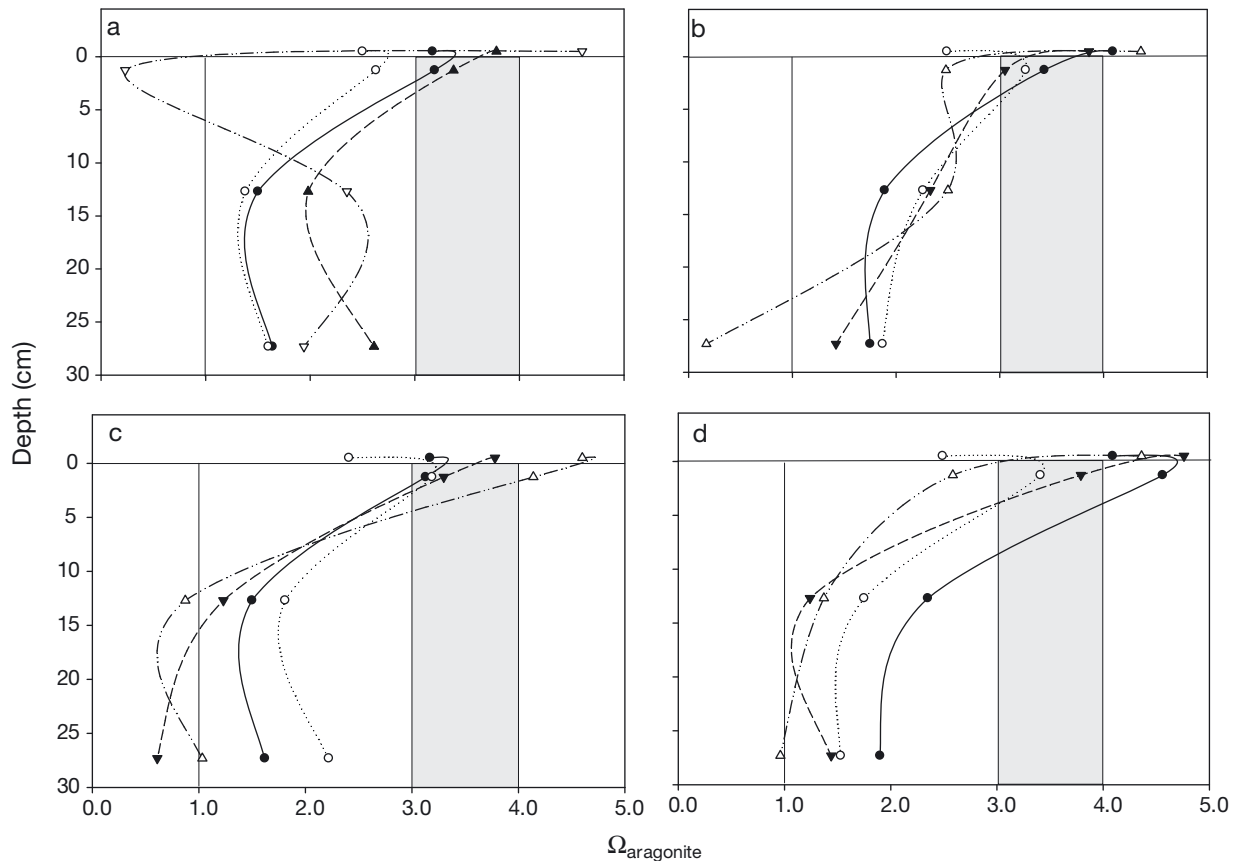


Fig. 2. Aragonite saturation states ($\Omega_{\text{aragonite}}$) of sediment surface and pore waters in the Alinas Reef (a) sand halos and (b) seagrass beds and Anniversary Reef (c) sand halo and (d) seagrass bed for sample dates in April (●), June (○), July (▼) and August (Δ). The vertical line at $\Omega_{\text{aragonite}} = 1.0$ and the range from 3.0 to 4.0 (grey) represents the point of undersaturation and consensus surface water range in tropical waters, respectively (Kleypas et al. 1999)

ratios generally decrease and disperse relative to the date of the sampling event (i.e. increasing temperature) and sample depth (Fig. 4). When assessed in the context of decreasing ORP and pH values with depth (Table 2), the higher DIC concentrations indicate that aerobic, fermentative and anaerobic microbial activities in the sediments are producing excess DIC. Although there were no consistent trends in the relationships between the geochemical variables and nutrient, DIC and TA data, the vertical pore water data (Table 2) do show active nitrogen cycling (i.e. ΣNO_x^- and NH_4^+) and the release and/or production of PO_4^{3-} and SiO_2 due to decreased pH or mineralization of organic matter, respectively, at one or more depths in both bottom types throughout the sampling period (Canfield et al. 2005a,b,c).

The lack of significant correlations between these data is attributed to the variability on vertical and temporal scales and, most likely, the quality and quantity of organic matter in the surface and pore waters, which has been shown to dramatically influ-

ence microbial mineralization processes and their by-products (e.g. protons, DIC, TA, reduced forms of nutrients) (Paulmier et al. 2009). For example, the seemingly random occurrence of elevated ΣNO_x^- flux rates in the seagrass beds in April (Alinas Reef) and June (Anniversary Reef) (Table 3) are most likely responses to episodic input of seagrass detritus and/or post-bloom phytoplankton biomass, which have been shown to increase nutrient fluxes from sediments in general and ΣNO_x^- specifically (Jensen et al. 1990, Capone et al. 1992, Charpy-Roubaud et al. 1996, McGlathery et al. 2001, Hu & Burdige 2007). Additionally, recent studies have shown that anaerobic mineralization of organic matter, especially nitrogen cycling, not only depresses pH values (Soetaert et al. 2007, Paulmier et al. 2009, Hofmann et al. 2010) but also produces concentrations of DIC (i.e. pCO_2) that can far exceed the concomitant production of TA (Hu & Cai 2011a,b).

The decreasing pH and increasing DIC concentrations in the pore waters contribute to a reduced

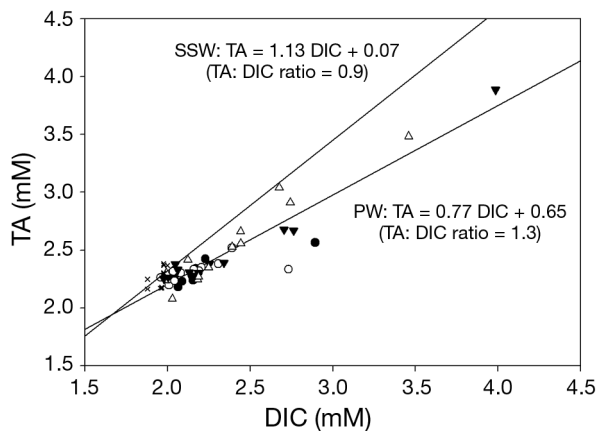


Fig. 3. Relationship between dissolved inorganic carbon (DIC) and total alkalinity (TA) in the sediment surface (\times , SSW) and pore waters (PW) at Alinas Reef (\bullet , sand halo; \blacktriangledown , seagrass) and Anniversary Reef (\circ , sand halo; Δ , seagrass). The lines represent the best-fit linear regression, derived from the equations

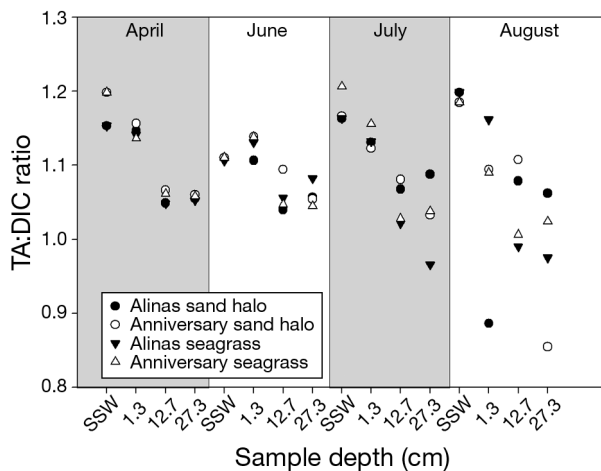


Fig. 4. Total alkalinity:dissolved inorganic carbon (TA:DIC) ratios in the sediment surface water (SSW) and the 3 pore water depths at Alinas Reef (\bullet , sand halo; \blacktriangledown , seagrass) and Anniversary Reef (\circ , sand halo; Δ , seagrass) for each sampling event

$\Omega_{\text{aragonite}}$ promoting the dissolution of the carbonate sediments. Carbonate dissolution and precipitation are dynamic processes in sediment diagenesis (Berner 1980, Burdige 2006b) and are enhanced in coastal sediments at tropical latitudes, especially in those that support seagrasses (Burdige & Zimmerman 2002, Hu & Burdige 2007). The general explanation for dissolution in these types of carbonate sediments is the aerobic microbial mineralization and remineralization of organic and inorganic carbon and sulfate reduction within the sediments (Walter & Burton 1990, Burdige & Zimmerman 2002, Hu & Burdige 2007, Walter et al. 2007, Burdige et al. 2008).

Although these cited studies acknowledge that an anaerobic process that proceeds under reduced conditions (i.e. sulfate reduction) occurs and is the major carbon cycling process in marine sediments, there is an implicit assumption that coastal pore waters are also generally aerobic and oxidized. The assumption of oxidized pore water and sulfate cycling may be uniformly applied to the reef systems of those studies, but it does not generally apply to the pore waters sampled during this study, as shown by the ORP and supported by the nutrient data (Tables 1 & 2). Collectively, these data indicate that a consortium of aerobic, fermentative and anaerobic microbial processes, including sulfate reduction, is establishing steep geochemical gradients in the pore water.

Regarding $\Omega_{\text{aragonite}}$, only 22.9% of the pore water samples ($n = 48$) fall within the current range ($\Omega_{\text{aragonite}} = 3.0$ to 4.0) for tropical waters (Kleypas et al. 1999), 12.5% are in an undersaturated state ($\Omega_{\text{aragonite}} < 1.0$) and 77.1% fall between these limits. Although the carbonate sediments in contact with the undersaturated pore water would be predicted to dissolve, it is less clear how $\Omega_{\text{aragonite}}$ values between 1.0 and 3.0 influence carbonate dissolution or precipitation. Burdige & Zimmerman (2002) used salinity-normalized changes in pore water DIC (ΔDIC) and TA (ΔTA), relative to the values in the overlying surface waters, to detect the occurrence of carbonate dissolution. Assuming carbonate dissolution to be the main process through which inorganic carbon is released into the pore water, the slope of a best-fit regression line through the ΔTA and ΔDIC should be 2.0. Fig. 5 shows the linear regression plot of the ΔTA and ΔDIC pore water data, from which a slope of 0.739 is derived, indicating an excess production of DIC relative to TA. A $\Delta\text{TA}:\Delta\text{DIC}$ relationship less than 2.0 has been attributed to a combination of carbonate dissolution and aerobic and anaerobic mineralization of organic matter that results in the production of CO_2 , thereby increasing the DIC concentration without increasing TA (Brasse et al. 1999, Burdige & Zimmerman 2002, Hu & Burdige 2007, Hu & Cai 2011a).

The pore water geochemical and nutrient gradients promote the flux of pore water constituents into the overlying surface waters (Table 3). The positive flux rate data for the nutrients (Table 3) were used to calculate N:P and N:Si molar ratios at the sediment–water interface. This interface is considered a benthic boundary layer in which molecular diffusion is the dominant transport process (Jorgensen 2001). The C:N:P molar ratio of 106:16:1 for plankton and algae (Redfield 1958, Geider & La Roche 2002,

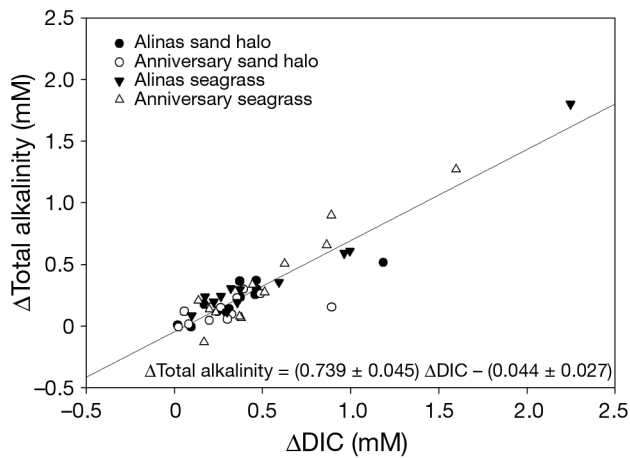


Fig. 5. Relationship between the salinity-normalized changes in pore water dissolved inorganic carbon (Δ DIC) and total alkalinity (Δ TA) at Alinas Reef (\bullet , sand halo; \blacktriangledown , seagrass) and Anniversary Reef (\circ , sand halo; Δ , seagrass). The line represents the best-fit linear regression, derived from the equation

Weber & Deutsch 2010) and the C:N:Si:P ratio of 106:16:15:1 for diatoms (Brzezinski 1985) were used as average elemental concentration requirements for optimal metabolic activities in the sediment surface water and pore water flux into the benthic boundary layer (Table 5). The sediment surface water N:P (range: 1.4 to 3.4) and N:Si (range: 0.045 to 1.539) ratios were significantly below the optimal ratios of 16:1 and 15:1, respectively, indicating a general nitrogen limitation for plankton, algae and diatoms. The only exception was the July sampling event at Alinas Reef, where the N:P ratio (i.e. 74.8) indicated a nitrogen concentration that was \sim 5-fold greater than the optimal stoichiometric ratio (Table 5). However, the N:P ratios at the benthic boundary layer in the sand halos and seagrass beds ranged from a fewfold to orders of magnitude greater than the optimal ratio of 16:1, with generally greater ratios associated with the seagrass beds, although this association was not consistent over the study period (Table 5). These elevated N:P ratios are due to the relatively high total nitrogen (predominantly from NH_4^+) concentrations from microbial activities and very low PO_4^{3-} concentrations in the pore waters. On the other hand, the N:Si ratios in the benthic boundary layer above both bot-

tom types did not approach the 15:1 ratio, except for a single sampling event in August in the seagrass bed at Anniversary Reef (Table 5). The higher Si flux rates from both bottom types can be attributed to the dissolution of biogenic silica (e.g. diatoms) in the sediments. This process has been shown to be enhanced by increasing temperatures and/or decreasing pH at the levels recorded during this study (Canfield et al. 2005c).

The DIC and TA flux data (Table 3) were used to recalculate the $\Omega_{\text{aragonite}}$ values in the benthic boundary layer. When compared to the surface water $\Omega_{\text{aragonite}}$ in Table 4, 75.0% ($n = 16$) of the pore water values decreased between 0.03 and 0.88 units (Table 6). The August $\Omega_{\text{aragonite}}$ from the sand halo at Alinas Reef was the exception, being reduced by 3.36 units and making the water in the benthic boundary layer undersaturated, promoting carbonate dissolution. The remainder of the recalculated $\Omega_{\text{aragonite}}$ values increased by 0.04 to 0.31 units, except for the April sampling event at the Anniversary Reef seagrass bed, where the benthic boundary layer value increased by 3.88 units, making the water supersaturated (Table 6). These changes in $\Omega_{\text{aragonite}}$ within the benthic boundary layer will have an influence on calcifying organisms, as a significant positive correlation has been shown between saturation state and calcification rates, although this relationship is not always linear (Gattuso et al. 1998, Kleypas et al. 1999, Silverman et al. 2007, Fabry et al. 2008, Kleypas & Yates 2009, Andersson et al. 2011, Comeau et al. 2012). Although these $\Omega_{\text{aragonite}}$ values are not ≤ 1.0 , the threshold for carbonate dissolution, a reduc-

Table 5. Stoichiometric nutrient ratios at the sediment–water interface at Alinas and Anniversary reefs, Biscayne National Park. NA = ratio not applicable, as one or both of the nutrients were not fluxed from the sediments; SSW = sediment surface water

Month and reef	N:P ratio			N:Si ratio		
	SW	Sand	Seagrass	SW	Sand	Seagrass
April						
Alinas	3.3	172.9	51.8	0.055	1.433	1.394
Anniversary	3.4	581.4	36.8	0.060	2.233	0.673
June						
Alinas	1.4	1.2	1.9	1.182	NA	NA
Anniversary	1.4	2.0	NA	1.182	NA	2.594
July						
Alinas	74.8	426.0	428.9	1.539	1.849	NA
Anniversary	3.2	159.2	10688.1	0.045	0.412	4.740
August						
Alinas	3.1	1923.9	149.8	0.050	0.065	0.316
Anniversary	2.5	41.3	12573.1	0.052	1.408	15.278

Table 6. Recalculated aragonite saturation states ($\Omega_{\text{aragonite}}$) in sediment surface waters affected by dissolved inorganic carbon and total alkalinity fluxes at Alinas and Anniversary reefs, Biscayne National Park. Values in parentheses are differences from surface water $\Omega_{\text{aragonite}}$ values in Table 4

Reef and site	April	June	July	August
Alinas				
Sand	3.08 (−0.15)	2.38 (−0.11)	3.98 (+0.31)	1.10 (−3.36)
Seagrass	3.03 (−0.20)	2.32 (−0.08)	3.60 (−0.07)	4.42 (−0.04)
Anniversary				
Sand	3.90 (−0.27)	2.41 (−0.07)	3.70 (−0.03)	3.35 (−0.88)
Seagrass	8.05 (+3.88)	2.52 (+0.04)	4.68 (+0.08)	3.90 (−0.33)

tion in calcification rates, would still occur, leading to weaker skeletons, reductions in extension rates and increased susceptibility to erosion and bioerosion (Kleypas et al. 1999).

CONCLUSIONS

Our data indicate that carbonate sediments associated with coral reefs, whether they are sand halos or seagrass beds, contribute concentrations of nutrients that are orders of magnitude greater than those in the overlying water, via pore water fluxes to the benthic boundary layer. The microbial processes that drive the establishment of these nutrient gradients also promote an increase in DIC and TA concentrations in the pore water while lowering pH, establishing a zone of aragonite undersaturation in the benthic boundary layer. The prevalence and rates of these aerobic and anaerobic microbial processes are dependent on the quality and quantity of carbon that is either generated within the pore water compartment and/or transported into the sediments from the overlying water (Canfield et al. 2005d). It is likely that the variability within and between the concentrations and flux rates of the nutrients and carbonate chemistry constituents in the sand halos and seagrass beds led to variations in the quality and quantity of the particulate organic carbon (POC) (e.g. seagrass detritus, phytoplankton biomass) and/or dissolved organic carbon (DOC) (e.g. seagrass root exudates, mineralization of phytoplankton biomass following bloom collapse) that entered the sediments.

The stoichiometric ratios of nitrogen, phosphorus and silica in the benthic boundary layer show that this zone can promote the establishment and growth of attached autotrophic organisms (e.g. algae, diatoms). In fact, the calculated N:P ratios in this study were sufficient to support the growth and establish-

ment of heterotrophic bacterial communities (C:N:P = 400:62:1) (Grob et al. 2013, Steenbergh et al. 2013).

Additionally, the flux of DIC and TA into the benthic boundary layer resulted in a systematic decrease of $\Omega_{\text{aragonite}}$. This level of decrease in saturation state has been proposed as having a negative effect on the calcification and settlement, survival and development of a wide range of larval and mature calcifying organisms (Fabry et al. 2008, Albright 2011, Andersson et al. 2011, Anlauf et al. 2011, Anthony et al. 2011, Arnold & Steneck 2011, Ross et al. 2011, Doropoulos et al. 2012, Waldbusser & Salisbury 2014).

Collectively, the data from this study suggest that the sand halo and seagrass sediment systems that surround a coral reef should enhance the autotrophic and heterotrophic productivity while depressing the carbonate chemistry saturation state of the sediment surface water. However, this has not been observed in coral reef ecosystems to date. The absence of this ecosystem-level effect has been attributed to the TA flux not being adequate to buffer pH changes or carbonate saturation state (Andersson et al. 2003) and DIC fixation by seagrasses (e.g. Manzello et al. 2012, Unsworth et al. 2012). We propose that nutrient and saturation state conditions in the benthic boundary layer are missed because of sampling depth (i.e. meters vs. centimeters above the sediment surface); differences between the benthic boundary layer and overlying water column volumes; and the photoautotrophic, autotrophic and heterotrophic demand for the nutrients, DIC and TA in the overlying water.

As global climate change is predicted to increase POC and DOC in coastal waters (Riebesell & Tortell 2011) and thereby in the sediments, the rates and durations of the biogeochemical processes we have described would also be predicted to increase. The increased flux of nutrients and depressed $\Omega_{\text{aragonite}}$ could have a dual effect of promoting the establishment and persistence of benthic algal and microbial communities while inhibiting the settlement and development of calcifying coral larvae and other calcifying benthic organisms. Although changes in the structure and diversity in benthic communities may be incremental, the responses at the species level will become amplified over successive generations and drive major shifts in the benthos that could significantly influence the productivity of adjacent coral reefs (Doney et al. 2009, Krumins et al. 2013).

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LITERATURE CITED

- Albright R (2011) Reviewing the effects of ocean acidification on sexual reproduction and early life history stages of reef-building corals. *J Mar Biol* 2011:473615
- Andersson AJ, Mackenzie FT, Ver LM (2003) Solution of shallow-water carbonates: an insignificant buffer against rising atmospheric CO₂. *Geology* 31:513–516
- Andersson AJ, Mackenzie FT, Lerman A (2005) Coastal ocean and carbonate systems in the high CO₂ world of the Anthropocene. *Am J Sci* 305:875–918
- Andersson AJ, Bates NR, Mackenzie FT (2007) Dissolution of carbonate sediments under rising pCO₂ and ocean acidification: observations from Devil's Hole, Bermuda. *Aquat Geochem* 13:237–264
- Andersson AJ, Mackenzie FT, Gattuso JP (2011) Effects of ocean acidification on benthic processes, organisms, and ecosystems. In: Gattuso JP, Hansson L (eds) *Ocean acidification*. Oxford University Press, New York, NY, p 122–153
- Anlauf H, D'Croz L, O'Dea A (2011) A corrosive concoction: the combined effects of ocean warming and acidification on the early growth of a stony coral are multiplicative. *J Exp Mar Biol Ecol* 397:13–20
- Anthony KRN, Kleypas JA, Gattuso JP (2011) Coral reefs modify their seawater carbon chemistry—implications for impacts of ocean acidification. *Glob Change Biol* 17:3655–3666
- Arnold SN, Steneck RS (2011) Settling into an increasingly hostile world: the rapidly closing 'recruitment window' for corals. *PLoS ONE* 6:e28681
- Berner RA (1980) *Early diagenesis: a theoretical approach*. Princeton University Press, Princeton, NJ
- Brasse S, Reimer A, Seifert R, Michaelis W (1999) The influence of intertidal mudflats on the dissolved inorganic carbon and total alkalinity distribution in the German Bight, southeastern North Sea. *J Sea Res* 42:93–103
- Brzezinski MA (1985) The Si:C:N ratio of marine diatoms: interspecific variability and the effects of some environmental variables. *J Phycol* 21:347–357
- Burdige DJ (2006a) Biogeochemical processes in sediments. In: *Geochemistry of marine sediments*. Princeton University Press, Princeton, NJ, p 97–141
- Burdige DJ (2006b) Models of sediment diagenesis. In: *Geochemistry of marine sediments*. Princeton University Press, Princeton, NJ, p 72–96
- Burdige DJ, Zimmerman RC (2002) Impact of sea grass density on carbonate dissolution in Bahamian sediments. *Limnol Oceanogr* 47:1751–1763
- Burdige DJ, Zimmerman R, Hu X (2008) Rates of carbonate dissolution in permeable sediments estimated from pore-water profiles: the role of sea grasses. *Limnol Oceanogr* 53:549–565
- Canfield DE, Thamdrup B, Kristensen E (2005a) The nitrogen cycle. In: *Aquatic geomicrobiology*. Elsevier Academic Press, London, p 205–268
- Canfield DE, Thamdrup B, Kristensen E (2005b) The phosphorus cycle. In: *Aquatic geomicrobiology*. Elsevier Academic Press, London, p 419–440
- Canfield DE, Thamdrup B, Kristensen E (2005c) The silicon cycle. In: *Aquatic geomicrobiology*. Elsevier Academic Press, London, p 441–464
- Canfield DE, Thamdrup B, Kristensen E (2005d) Heterotrophic carbon metabolism. In: *Aquatic geomicrobiology*. Elsevier Academic Press, London, p 95–128
- Capone DG, Dunham SE, Horrigan SG, Duguay LE (1992) Microbial nitrogen transformations in unconsolidated coral reef sediments. *Mar Ecol Prog Ser* 80:75–88
- Charpy-Roubaud C, Charpy L, Sarazin G (1996) Diffusional nutrient fluxes at the sediment-water interface and organic matter mineralization in an atoll lagoon (Tikehau, Tuamatu Archipelago, French Polynesia). *Mar Ecol Prog Ser* 132:181–190
- Comeau S, Gattuso JP, Jeffree R, Gazeau F (2012) Effect of carbonate chemistry manipulations on calcification, respiration, and excretion of a Mediterranean pteropod. *Biogeosci Discuss* 9:6169–6189
- Dickson AG (1990) Standard potential of the reaction: AgCl(s) + ½H₂(g) = Ag(s) + HCl(aq), and the standard acidity constant of the ion HSO₄⁻ in synthetic sea water from 273.15 to 318.15 K. *J Chem Thermodyn* 22:113–127
- 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
- Doney SC, Fabry VJ, Feely RA, Kleypas JA (2009) Ocean acidification: the other CO₂ problem. *Annu Rev Mar Sci* 1:169–192
- Doropoulos C, Ward S, Diaz-Pulido G, Hoegh-Guldberg O, Mumby PJ (2012) Ocean acidification reduces coral recruitment by disrupting intimate larval-algal settlement interactions. *Ecol Lett* 15:338–346
- Enos P, Sawatsky LH (1981) Pore networks in Holocene carbonate sediments. *J Sediment Res* 51:961–985
- Fabry VJ, Seibel BA, Feely RA, Orr JC (2008) Impacts of ocean acidification on marine fauna and ecosystem processes. *ICES J Mar Sci* 65:414–432
- Falter JL, Sansone FJ (2000) Hydraulic control of pore water geochemistry within the oxic-suboxic zone of a permeable sediment. *Limnol Oceanogr* 45:550–557
- Gattuso JP, Frankignoulle M, Bourge I, Romaine S, Budde-meier RW (1998) Effect of calcium carbonate saturation of seawater on coral calcification. *Global Planet Change* 18:37–46
- Geider R, La Roche J (2002) Redfield revisited: variability of C:N:P in marine microalgae and its biochemical basis. *Eur J Phycol* 37:1–17
- Gobet A, Boer SI, Huse SM, van Beusekom JEE and others (2012) Diversity and dynamics of rare and of resident bacterial populations in coastal sands. *ISME J* 6:542–553
- Goyet C, Bradshaw AL, Brewer PG (1991) The carbonate system in the Black Sea. *Deep-Sea Res A* 38:S1049–S1068
- Grob C, Ostrowski M, Holland RJ, Heldal M and others (2013) Elemental composition of natural populations of key microbial groups in Atlantic waters. *Environ Microbiol* 15:3054–3064
- Helmle KP, Dodge RE, Swart PK, Gledhill DK, Eakin CM (2011) Growth rates of Florida corals from 1937 to 1996 and their response to climate change. *Nature Commun* 2: 215

- Hiscock WT, Millero FJ (2006) Alkalinity of the anoxic waters in the Western Black Sea. *Deep-Sea Res II* 53: 1787–1801
- Hofmann AF, Middelburg JJ, Soetaert K, Meysman FJR (2009) pH modelling in aquatic systems with time-variable acid-base dissociation constants applied to the turbid, tidal Scheldt estuary. *Biogeosciences* 6: 1539–1561
- Hofmann AF, Middelburg JJ, Soetaert K, Wolf-Gladrow DA, Meysman FJR (2010) Proton cycling, buffering, and reaction stoichiometry in natural waters. *Mar Chem* 121: 246–255
- Holmer M, Andersen FO, Nielsen SL, Boschker HTS (2001) The importance of mineralization based on sulfate reduction for nutrient regeneration in tropical seagrass sediments. *Aquat Bot* 71:1–17
- Hu X, Burdige DJ (2007) Enriched stable carbon isotopes in the pore waters of carbonate sediments dominated by seagrasses: evidence for coupled carbonate dissolution and reprecipitation. *Geochim Cosmochim Acta* 71: 129–144
- Hu X, Cai WJ (2011a) An assessment of ocean margin anaerobic processes on oceanic alkalinity budget. *Global Biogeochem Cycles* 25:GB3003, doi:10.1029/2010-GB003859
- Hu X, Cai WJ (2011b) The impact of denitrification on the atmospheric CO₂ uptake potential of seawater. *Mar Chem* 127:192–198
- Huettel M, Ziebis W, Forster S, Luther GW III (1998) Advective transport affecting metal and nutrient distributions and interfacial fluxes in permeable sediments. *Geochim Cosmochim Acta* 62:613–631
- Huettel M, Roy H, Precht E, Ehrenhauss S (2003) Hydrodynamical impact on biogeochemical processes in aquatic sediments. *Hydrobiologia* 494:231–236
- Jensen MH, Lomstein E, Sorensen J (1990) Benthic NH₄⁺ and NO₃⁻ flux following sedimentation of a spring phytoplankton bloom in Aarhus Bight, Denmark. *Mar Ecol Prog Ser* 61:87–96
- Jorgensen BB (2001) Life in the diffusive boundary layer. In: Boudreau BP, Jorgensen BB (eds) *The benthic boundary layer: transport processes and biogeochemistry*. Oxford University Press, New York, NY, p 348–373
- King JN, Mehta AJ, Dean RG (2009) Generalized analytical model for benthic water flux forced by surface gravity waves. *J Geophys Res* 114:C04004, doi:10.1029/2008JC-005116
- Kleypas JA, Yates KK (2009) Coral reefs and ocean acidification. *Oceanography (Wash DC)* 22:108–117
- Kleypas JA, Buddemeier RW, Archer D, Gattuso JP, Langdon C, Opdyke BN (1999) Geochemical consequences of increased atmospheric carbon dioxide on coral reefs. *Science* 284:118–120
- Komada T, Reimers CE, Boehme SE (1998) Dissolved inorganic carbon profiles and fluxes determined using pH and P_{CO2} microelectrodes. *Limnol Oceanogr* 43:769–781
- Krumins V, Gehlen M, Arndt S, Van Cappellen P, Regnier P (2013) Dissolved inorganic carbon and alkalinity fluxes from coastal marine sediments: model estimates for different shelf environments and sensitivity to global change. *Biogeosciences* 10:371–398
- Lisle J, Reich C (2006) Microbial ecology in reef sediments of Biscayne National Park. USGS Fact Sheet 2006-3052, US Geological Survey, Reston, VA
- Manzello DP, Enochs IC, Melo N, Gledhill DK, Johns EM (2012) Ocean acidification refugia of the Florida reef tract. *PLoS ONE* 7:e41715
- McGlathery KJ, Berg P, Marino R (2001) Using porewater profiles to assess nutrient availability in seagrass-vegetated carbonate sediments. *Biogeochemistry* 56: 239–263
- Mehrbach C, Culberson CH, Hawley JE, Pytkowicz RM (1973) Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. *Limnol Oceanogr* 18:897–907
- Mucci A (1983) The solubility of calcite and aragonite in seawater at various salinities, temperatures, and one atmosphere total pressure. *Am J Sci* 283:780–799
- Paulmier A, Kriest I, Oschlies A (2009) Stoichiometries of remineralisation and denitrification in global biogeochemical ocean models. *Biogeosciences* 6:923–935
- Pierrot D, Lewis E, Wallace DWR (2006) MS Excel program developed for CO₂ system calculations. ORNL/CDIAC-105, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Washington, DC
- Precht E, Franke U, Polerecky L, Huettel M (2004) Oxygen dynamics in permeable sediments with wave-driven pore water exchange. *Limnol Oceanogr* 49:693–705
- Rasheed M, Badran MI, Richter C, Huettel M (2002) Effect of reef framework and bottom sediment on nutrient enrichment in a coral reef of the Gulf of Aqaba, Red Sea. *Mar Ecol Prog Ser* 239:277–285
- Redfield AC (1958) The biological control of chemical factors in the environment. *Am Sci* 46:205–221
- Riebesell U, Tortell PD (2011) Effects of ocean acidification on pelagic organisms and ecosystems. In: Gattuso JP, Hansson L (eds) *Ocean acidification*. Oxford University Press, New York, NY, p 99–121
- Robbins LL, Hansen ME, Kleypas JA, Meylan SC (2010) CO₂calc: a user-friendly seawater carbon calculator for Windows, Max OS X, and iOS (iPhone). USGS Open File Report 2010-1280, US Geological Survey, Reston, VA
- Ross PM, Parker L, O'Connor WA, Bailey EA (2011) The impact of ocean acidification on reproduction, early development and settlement of marine organisms. *Water* 3:1005–1030
- Rusch A, Hannides AK, Gaidos E (2009) Diverse communities of active Bacteria and Archaea along oxygen gradients in coral reef sediments. *Coral Reefs* 28:15–26
- Sander BC, Kalf J (1993) Factors controlling bacterial production in marine and freshwater sediments. *Microb Ecol* 26:79–99
- Santos IR, Eyre BD, Huettel M (2012) The driving forces of porewater and groundwater flow in permeable coastal sediments: a review. *Estuar Coast Shelf Sci* 98:1–15
- Schöttner S, Pfitzner B, Grünke S, Rasheed M, Wild C, Ramette A (2011) Drivers of bacterial diversity dynamics in permeable carbonate and silicate coral reef sands from the Red Sea. *Environ Microbiol* 13:1815–1826
- Seeberg-Elverfeldt J, Schluter M, Feseker T, Kolling M (2005) Rhizon sampling of porewaters near the sediment-water interface of aquatic systems. *Limnol Oceanogr Methods* 3:361–371
- Silverman J, Lazar B, Erez J (2007) Effect of aragonite saturation, temperature, and nutrients on the community calcification rate of a coral reef. *J Geophys Res* 112:C05004, doi:10.1029/2006JC003770
- Soetaert K, Hofmann AF, Middelburg JJ, Meysman FJR, Greenwood J (2007) The effect of biogeochemical pro-

- cesses on pH. *Mar Chem* 105:30–51
- Solomon S, Qin D, Manning M, Chen Z and others (eds) (2007) *Climate change 2007: the physical science basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC)*. Cambridge University Press, New York, NY, p 235–337
- Sorensen KB, Glazer B, Hannides A, Gaidos E (2007) Spatial structure of the microbial community in sandy carbonate sediment. *Mar Ecol Prog Ser* 346:61–74
- Steenbergh AK, Bodelier PLE, Heldal M, Slomp CP, Laanbroek HJ (2013) Does microbial stoichiometry modulate eutrophication of aquatic ecosystems? *Environ Microbiol* 15:1572–1579
- Stehli FG, Hower J (1961) Mineralogy and early diagenesis of carbonate sediments. *J Sediment Res* 31:358–371
- Stumm W, Morgan JJ (1981a) Dissolved carbon dioxide. In: *Aquatic chemistry: an introduction emphasizing chemical equilibria in natural waters*. John Wiley & Sons, New York, NY, p 171–229
- Stumm W, Morgan JJ (1981b) Oxidation and reduction. In: *Aquatic chemistry: an introduction emphasizing chemical equilibria in natural waters*. John Wiley & Sons, New York, NY, p 418–503
- Thullner M, Van Cappellen P, Regnier P (2005) Modeling the impact of microbial activity on redox dynamics in porous media. *Geochim Cosmochim Acta* 69:5005–5019
- Unsworth RKF, Collier CJ, Henderson GM, McKenzie LJ (2012) Tropical seagrass meadows modify seawater carbon chemistry: implications for coral reefs impacted by ocean acidification. *Environ Res Lett* 7:024026
- Van Cappellen P, Gaillard JF (1996) Biogeochemical dynamics in aquatic sediments. *Rev Mineral Geochem* 34:335–376
- Waldbusser GG, Salisbury JE (2014) Ocean acidification in the coastal zone from an organism's perspective: multiple system parameters, frequency domains, and habitats. *Annu Rev Mar Sci* 6:221–247
- Walter LM, Burton EA (1990) Dissolution of Recent platform carbonate sediments in marine pore fluids. *Am J Sci* 290:601–643
- Walter LM, Ku TCW, Muehlenbachs K, Patterson WP, Bonnell L (2007) Controls on the $\delta^{13}\text{C}$ of dissolved inorganic carbon in marine pore waters: an integrated case study of isotope exchange during syndepositional recrystallization of biogenic carbonate sediments (South Florida Platform, USA). *Deep-Sea Res II* 54:1163–1200
- Weber TS, Deutsch C (2010) Ocean nutrient ratios governed by plankton biogeography. *Nature* 467:550–554
- Wild C, Huettel M, Klueter A, Kremb SG, Rasheed MY, Jørgensen BB (2004) Coral mucus functions as an energy carrier and particle trap in the reef ecosystem. *Nature* 428:66–70
- Wolf-Gladrow DA, Zeebe RE, Klaas C, Kortzinger A, Dickson AG (2007) Total alkalinity: the explicit conservative expression and its application to biogeochemical processes. *Mar Chem* 106:287–300
- Yates KK, Halley RB (2003) Measuring coral reef community metabolism using new benthic chamber technology. *Coral Reefs* 22:247–255
- Yates KK, Dufore C, Smiley N, Jackson C, Halley RB (2007) Diurnal variation of oxygen and carbonate system parameters in Tampa Bay and Florida Bay. *Mar Chem* 104:110–124

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