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Drivers of carbon isotopic fractionation in a coral reef lagoon: Predominance of demand over supply

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Abstract

The carbon isotopic signature ($\delta^{13}C$) of coral skeletons is influenced by isotopic fractionation (ε_{org}) during photosynthetic dissolved inorganic carbon (DIC) fixation, but only a few direct ε_{org} measurements are available in coral communities. In particular, observations of ε_{org} at the ecosystem scale are lacking. Here we present high frequency (hourly) measurements of DIC and its $\delta^{13}C$ in the water column and benthic chambers in a highly productive coral reef lagoon (Heron Island, Great Barrier Reef, Australia) and apply simple molar balance calculations to infer community ε_{org}. Variation in ε_{org} was between 3.7‰ and 25.2‰ in the open lagoon, with lower values during the mid-afternoon and higher values in early morning and evening. The ε_{org} range was broader (0.3–30.1‰) in enclosed benthic chambers with a similar diel pattern. There was a strong correlation between carbon uptake rates and ε_{org} in closed incubations, suggesting that C demand largely controlled ε_{org}. Benthic chamber incubations revealed increased ε_{org} as water circulation increased, implying that C supply to photosynthesizing algae on the sediment also influenced ε_{org}. Hysteresis in carbon uptake through the day complicated the expected straightforward influence of irradiance on C demand, and consequently on ε_{org}. These results highlight the need for more in depth understanding on carbon uptake rates to fully understand $\delta^{13}C$ variation in coral paleo-records.

1. INTRODUCTION

The proportion of ^{13}C to ^{12}C relative to a standard (symbolized by $\delta^{13}C$) in organic substances is usually much lower than that in inorganic substances. This is due to the phenomenon of isotopic fractionation (symbolized by ε_{org}) during organic matter production (Park and Epstein, 1961). In some cases, inorganic compounds can also have their $\delta^{13}C$ affected by ε_{org}, as in the case of corals due to their symbiosis with microalgae which generates a partitioning of inorganic carbon for photosynthesis or coral skeleton building (Swart, 1983). Therefore, understanding variability in ε_{org} is fundamental to fully understand $\delta^{13}C$ in materials of biological origin, such as coral skeletons, which, in turn, are useful to reconstruct past climatic and oceanographic conditions (McConnaughey et al., 1997; Sun et al., 2008; Swart et al., 2010).

In aquatic photosynthesis, ε_{org} can be defined as the approximate difference between $\delta^{13}C$ DIC (dissolved inorganic carbon) and $\delta^{13}C$ in organic matter produced in photosynthesis. The chemical reaction that yields the highest fractionation in photosynthesis is the fixation of CO_2 by RUBISCO (Ribulose-1,5-bisphosphate carboxylase/oxygenase), with a value of 30‰ (Raven et al., 1994), meaning that ^{12}C is fixed 30‰ faster than ^{13}C. However, intricacies

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in DIC uptake and assimilation (Sharkey and Berry, 1985; Raven et al., 2002; Schulz et al., 2007) lead to very different ε_{org}, resulting in a very wide variation in $\delta^{13}C$ in marine primary producers, between −3‰ and −35‰ (Raven et al., 2002). Variation in seawater $\delta^{13}C$ DIC is much smaller, between −1‰ and 2‰ (Kroopnick, 1985).

The combined influence of photosynthetic rates and substrate availability on ε_{org} is understood with the concept of demand–supply control: higher demand at constant supply will decrease ε_{org}, while higher supply at constant demand will increase ε_{org} (Sharkey and Berry, 1985). For example, higher photosynthetic rates (i.e., high demand) will result in lower ε_{org} (Carvalho et al., 2009), while higher supply, driven by higher concentrations of DIC and CO_2/lower pH (Erez et al., 1998) or higher velocity of water circulation (Raven et al., 1982) can increase ε_{org} at constant photosynthetic rates. The combination of these multiple factors lead to complex scenarios: for example, higher temperature causes photosynthesis to increase, which means more demand, thus reducing ε_{org}, but at the same time also facilitates DIC supply by means of enhanced diffusion, which increases ε_{org} (Carvalho et al., 2010). Hence, to understand the effect of supply on ε_{org}, it is important to normalize supply to carbon demand.

These subtle aspects of ε_{org} can be conveniently observed if this parameter is measured based on changes in dissolved inorganic C concentration and stable isotope composition in incubated water (Carvalho et al., 2009). Investigations from the molecular (McNevin et al., 2006) to the ecosystem (Smith and Kroopnick, 1981) scale are possible with this approach, but it has hardly ever been applied to aquatic communities. In two coral reef studies that employed DIC based measurements of ε_{org}, data was pooled to obtain integrated temporal rates on time scales of weeks to months with no insight into short term (i.e., diel) processes (Smith and Kroopnick, 1981; Swart et al., 2005). Data on the scale of minutes to hours are virtually absent. This is also a problem because ε_{org} is a factor directly related to photosynthetic rates (Carvalho et al., 2009, 2010), which can quickly change responding to environmental conditions in dynamic environments such as coral reef lagoons (Cyronak et al., 2013; Eyre et al., 2013).

Considering the dramatic diel variations in carbonate chemistry, and photosynthetic and calcification rates often observed in coral reefs (Weber and Woodhead, 1971; Shaw et al., 2012; Cyronak et al., 2014a,b), high resolution, short term studies may provide new insight into the main controls of ε_{org} on a community scale. We performed detailed field observations to assess how diel variability in photosynthetic rates, irradiance, water carbonate chemistry, and temperature may influence ε_{org}.

2. MATERIALS AND METHODS

2.1. Experiments

Field investigations were performed in Heron Island, a coral cay in the Great Barrier Reef, Australia, (23°27′S, 151°55′E; Fig. 1). The island is surrounded by a highly productive reef lagoon (26 km^2 in area, 1.7 m of average depth). This study builds on work at the same site using the DIC (but not $\delta^{13}C$) concentrations to estimate sediment metabolic rates enclosed in incubation chambers (Cyronak et al., 2013) and low tide water column observations to estimate net ecosystem metabolic rates (McMahon et al., 2013). Thus, two sets of experiments were performed with the objective of measuring the metabolism (photosynthesis, respiration, calcification and dissolution) of the lagoon. Although the experiments were done during two different seasons, diel variation in carbonate parameters is typically much larger than seasonal variation in ecosystems like Heron Island Lagoon (Cyronak et al., 2014a,b). As such, seasonality should not have greatly influenced the results.

Incubations were performed in closed benthic chambers at three different stirring rates (0, 40 and 80 rpm; RPM) on 9 and 10 October 2011. The chambers were cylindrical in shape with a volume of 4 L, and were affixed to a sandy bottom. The unstirred chamber induces no porewater flow and the 40 and 80 RPM induce flows of approximately 43 and 217 L m^{-2} d^{-1}, respectively (Eyre et al., 2008; Glud et al., 2008). Water for $\delta^{13}C$ DIC measurements was sampled every 2 h over a 24-h diel cycle. Forty milliliter of filtered water (0.45 μm) was stored in pre-combusted glass vials containing 50 μL of $HgCl_2$. Full details on the benthic incubations are provided elsewhere (Cyronak et al., 2013). Benthic chamber treatments were not replicated, and thus it was not possible to compare them statistically. Nevertheless, trends between treatments were consistent with theoretical expectations, making it worthwhile to compare with open water results.

Open water "incubations" taking advantage of the characteristics of the lagoon (Kinsey, 1978) conducted between 4 April 2012 and 1 May 2012. The lagoon becomes isolated from the open sea at low tide and behaves as a closed system for 1–4 h (Santos et al., 2010). Lagoon water samples were collected 1–2 h each side of low tides every 30–40 min (total of 47 low tides throughout the experiment). Sample processing was the same as for the closed incubations. Details on open water incubations are provided elsewhere (McMahon et al., 2013).

2.2. Measurements

Analysis of $\delta^{13}C$ DIC were done using an Aurora 1030 TOC (total organic carbon) analyzer (OI instruments, College Station, USA) coupled to a Delta V plus IRMS (stable isotope ratio mass spectrometer, Thermo Fisher, Sydney, Australia; (Oakes et al., 2010). A 2 mL aliquot of the sample in the vial was transferred to the TOC analyzer, where it was mixed with a 5% H_3PO_4 acid solution. The mixture was bubbled with He in a closed chamber and the extracted CO_2 was carried by the He stream to the IRMS. Isotope measurements were done in relation to the VPDB standard. Each sequence consisted of nearly 40 samples interspaced with 4–5 runs of an in house standard (sodium bicarbonate solution, concentration between 1 and 3 mM $\delta^{13}C = -5.1 \pm 0.1$‰; determined previously by running it together with NBS19 and NIST 8542 on an elemental analyzer coupled to the IRMS; error in $\delta^{13}C$ measurement was ±0.1‰). Photosynthetically active radiance (PAR, ±5%), pH