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Using the Stable Isotopic Composition of *Heliconoides inflatus* Pteropod Shells to Determine Calcification Depth in the Cariaco Basin

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Pteropods have been hailed as the "canary in the coal mine" for ocean acidification, however, questions remain about their life history, habitat, and the environmental parameters that the isotopic composition of their shells reflect. In order to use pteropods as recorders of ocean chemistry, it is first necessary to understand where they calcify and how this may change through the year, whether this signal is affected by dissolution, and if shells are retained in the subfossil, and eventually fossil, record. Here we create the first annual record of the stable isotopic composition of shells of the pteropod *Heliconoides inflatus* in the Cariaco Basin, Venezuela utilizing samples and data from the CARIACO time series. Sixty-four *H. inflatus* specimens from 17 sediment trap samples between November 1996 and April 1998, and 22 specimens from the late Holocene-aged CAR2000-MC-2 core were analyzed for shell condition (an assessment of the amount of dissolution that a shell has experienced), size, and carbon and oxygen isotopic composition. Carbon isotopic measurements of juveniles (< 1mm) were more variable than those in adults (>1 mm), suggesting juvenile pteropods likely have a higher growth rate, and therefore different metabolic vital effects, and a more varied diet than adult pteropods. *H. inflatus* was found to have an apparent calcification depth of 51.2 ± 34.0 m, suggesting they calcify at the shallowest part of their diurnal migration in the mixed layer (10–35 m in the Cariaco Basin). *H. inflatus* shell calcification will therefore only be impacted by changes in water chemistry at mixed layer depths. The shell condition did not impact the stable isotopic composition of the shells in either the sediment trap or core sample, suggesting the potential for using the isotopic composition of pteropod shells as oceanographic proxies when they are preserved. Comparisons between sediment trap and core sample show a 0.5°C warming that is marginally significant and a significant 0.45‰ decrease in $\delta^{13}C$ between the late Holocene and the late 1990's. These measurements reflect changes in oceanic conditions linked to anthropogenic fossil fuel emissions known as the Suess effect, and lay the groundwork for establishing pteropods as paleoceanographic proxies in the future.

Keywords: pteropoda, stable isotopes, calcification, plankton, CARIACO, proxy

INTRODUCTION

Understanding the impact of ocean acidification on epipelagic ecosystems is inherently difficult. This ∼100 m deep layer spans over 360-million square kilometers in area, from the poles to the equator, and is changing at rates unprecedented in the geologic record. Ocean chemistry and hydrographic properties are monitored at fixed mooring sites (e.g., Bailey et al., 2019) and using automated gliders [e.g., Argo floats (*argo.ucsd.edu*)]. However, these methods are designed to measure abiotic changes in ocean chemistry at a fixed location over time, or at random locations in the ocean at a designated time. To gain a more holistic view of the impact of ocean acidification on marine biota, recent studies have proposed the development of organisms as biological indicators of human-induced changes to ocean chemistry (Bednaršek et al., 2017, 2019; Gaylord et al., 2018; Marshall et al., 2019).

Marine calcifiers, such as foraminifera and mollusks, are widely used as proxies for ocean chemistry. The shell chemistry of foraminifera and mollusks, such as mussels and oysters, record seawater conditions (e.g., Epstein et al., 1953; Anderson and Arthur, 1983; Grossman and Ku, 1986; Kucera, 2007; McConnaughey and Gillikin, 2008; Katz et al., 2010). However, despite the wealth of information drawn from these groups, they have their limitations, especially for interpreting conditions in the mixed layer. Planktic foraminifera have lifespans on the scale of weeks to months, and their blooms are often seasonal (Tedesco and Thunell, 2003; Jonkers and Kučera, 2015). The chemistry of their shells therefore records a snapshot of ocean conditions. Benthic marine mollusks are most abundant in coastal settings, and although their larvae are found in surface waters, their lack of larval diagnostic features and the limited understanding of their early life stages restricts their utility for deciphering upper ocean conditions (Parker et al., 2013; León et al., 2019).

Pteropods are a group of planktonic gastropods that, despite their abundance and global distribution (Bednaršek et al., 2012), are underdeveloped as oceanographic proxies. They form their thin shells from aragonite, a polymorph of calcium carbonate that is 1.5 times more soluble than calcite (Mucci, 1983). For this reason, they have been used as biological indicators of ocean acidification linked to anthropogenic (Busch et al., 2014; Bednaršek et al., 2019) and natural (Manno et al., 2019) forcings, and to assess seasonal and multi-decadal climatic shifts (Mohan et al., 2006; Thibodeau and Steinberg, 2018). Pteropods are more abundant in open ocean settings than other mollusks and it has been hypothesized that the pteropod *Heliconoides inflatus* could be the most abundant gastropod species in the world (Lalli and Gilmer, 1989). Pteropods live for about 1 year, a relatively long lifespan compared to other planktonic calcifiers (Wells, 1976; Gannefors et al., 2005; Wang et al., 2017). Like most mollusks (e.g., Grossman and Ku, 1986; Wefer and Berger, 1991; Schöne and Surge, 2012; Steinhardt et al., 2016; García-Escárzaga et al., 2019), pteropods, and specifically the group Limacinidae, have been found to calcify in near oxygen isotopic equilibrium with seawater (Grossman et al., 1986; Fabry and Deuser, 1992; Juranek et al., 2003), at depths of between 50 and 650 m (Fabry and Deuser, 1992; Jasper and Deuser, 1993; Fischer et al., 1999; Juranek et al., 2003; Keul et al., 2017). There have been no studies on the average or seasonal isotopic variability of *H. inflatus* shells in the Cariaco Basin. Furthermore, none of the pteropod isotope studies to date have assessed the impact of shell dissolution on isotopic composition of shell material, an essential variable to understand if pteropods are to be used as oceanographic proxies. Developing pteropods as oceanographic proxies would give new insights into the response of multicellular planktonic organisms, a previously understudied group. Pteropods contribute substantially to carbon cycling and carbonate biomass (Hunt et al., 2008; Bednaršek et al., 2012), with pteropod shells contributing 33% to shallow calcium carbonate export, and 1% to $CaCO_3$ export at 4,000 m (Buitenhuis et al., 2019). Changes in pteropod populations therefore have the potential to affect the marine carbon cycle as a whole.

The Cariaco Basin is a tectonic depression on the Venezuelan shelf in the southwest Caribbean Sea. Seasonal changes in basin hydrography are controlled by the position of the Inter Tropical Convergence Zone (ITCZ). From December to April, the ITCZ moves south and Ekman transport, triggered by the strengthening of easterly trade winds, causes the upwelling of cold, nutrient rich waters to the surface. From August to November, the ITCZ moves north, rainy conditions prevail, and surface waters become warm and oligotrophic (Astor et al., 2013; Muller-Karger et al., 2019) (**Supplementary Figure 1**). The CARIACO (CArbon Retention In A Colored Ocean) program ran from 1995–2017 with the aim to monitor and document the physical and biological processes occurring in this unique basin. Sediment trap samples were collected every 2 weeks, supplemented by measurements of hydrography and water chemistry on monthly oceanographic cruises. The planktic foraminifera from the CARIACO timeseries have been used extensively to study seasonal and interannual population changes, and changes in the isotopic composition, temperature, and carbonate concentration of seawater (e.g., Black et al., 2001; Tedesco and Thunell, 2003; Tedesco et al., 2007; McConnell et al., 2009; Marshall et al., 2013, 2015; Davis et al., 2019), however, there has only been one study on pteropods from the Cariaco Basin (Oakes and Sessa, 2020). The wealth of samples, hydrographic measurements, and previous studies of calcareous plankton, makes the Cariaco Basin the ideal place to develop pteropods as oceanographic proxies.

Here we establish an annual record of the stable isotopes of oxygen and carbon in the shells of *H. inflatus* pteropods in the Cariaco Basin. These data are compared to established oxygen isotopic records of six planktic foraminifera species from the same sediment trap cups the pteropods were collected from Tedesco et al. (2007). Average stable isotopic values of specimens from the sediment trap samples are compared to specimens from a nearby core to assess the viability of using isotopes from pteropod shells from subfossil sediments as recorders of oceanographic conditions (**Figure 1**). This study is the first to establish an annual record of stable isotopic composition of pteropod shells in the Cariaco Basin, and to compare pteropod shells from sediment traps to those from surficial sediment samples.

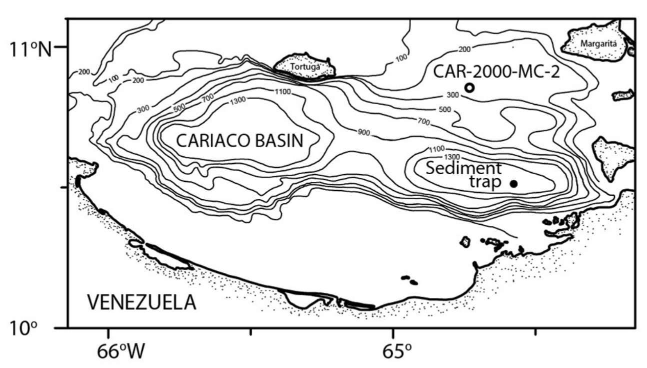

FIGURE 1 | Location of the sediment trap (filled circle) and the CAR2000-MC-2 core (open circle) where specimens from this study were collected.

MATERIALS AND METHODS

Sediment Trap Collection

The samples in this study came from a sediment trap deployed in the Cariaco Basin, off the coast of Venezuela (10° 30′ N, 64° 38.5′ W) as part of the CARIACO Time Series (**Figure 1**). The trap was at 150 m water depth (also known as the A trap) and samples were collected continuously for two-week intervals. Trap cups were filled with borate-buffered formalin prior to deployment to prevent degradation of the material after collection (Thunell et al., 2000). Sediment trap cups from between November 1996 and April 1998 were processed as described in Thunell et al. (2000) and Tedesco and Thunell (2003). Unfortunately samples were not collected from late March-April 1997 as the sediment trap was clogged (Tedesco et al., 2007). A quarter split was washed with deionized water over a 150-micron sieve and calcareous plankton were wet picked and then dried in an oven at 40°C for 24 h, before being stored for faunal analysis.

Core

Multicore CAR2000-MC-2 was taken on October 31, 2000 from the Cariaco Basin (10° 51′ N, 64° 44′ W; 192 m water depth). Pteropod specimens were picked from the 0.5–1.0 cm interval and later identified to the species level. Whole shells of the planktic foraminifera *Globigerinoides sacculifer* were also picked from this interval for carbon dating (see section Carbon Dating).

Specimen Selection

Pteropod shells were present in 17 out of 36 trap samples. We sampled 64 *H. inflatus* specimens from 17 trap samples collected between November 1996 and April 1998 (**Table 1**). A further 66 *H. inflatus* specimens were sampled from the CAR2000-MC-2 core: 22 for carbon and oxygen isotopic analysis, and 44 for carbon dating.

Light Microscopy

Light Microscopy Image Collection

All 64 specimens from the sediment trap, and the 22 specimens from the core that were analyzed for stable isotopes, were imaged in the Malacology Imaging Center at the Academy of Natural Sciences of Drexel University, Philadelphia. Pteropods were positioned in apical view in a well slide with a black base. Images were taken using a circa 1950 Bausch & Lomb compound microscope attached via an eyepiece adaptor to a Nikon D5100 DSLR camera. Specimens were lit by a DynaLite 500XL power pack with two reversed studio heads and diffusers. A Carl Zeiss calibrated slide was photographed at the same magnification as the images in order to create a scale bar. Focus stacking was used to create an image with more depth of focus than is possible with a single exposure. The focus stack was created manually by taking 15–30 images per specimen at different depths of focus depending on the z-height of the shell. Images were compiled into a focus stack using the software Helicon Focus v. 6.7.2 with the pyramid rendering method (method C). All light microscope images of specimens from the sediment trap and the core are available in the Supplementary Materials (**Supplementary Figure 2**).

TABLE 1 | Sample information about the specimens from the sediment trap and the core top used in this study.

Trap deployment	Cup #	Date	Number of specimens	Number light microscope imaged	Number of isotope analyses
3A	1	08-Nov-96	7	7	3
3A	2	22-Nov-96	4	4	1
3A	3	06-Dec-96	2	2	2
3A	7	31-Jan-97	1	1	0
3A	8	14-Feb-97	1	1	0
4A	2	22-May-97	6	6	2
4A	3	05-Jun-97	6	6	4
4A	5	03-Jul-97	3	3	3
4A	6	17-Jul-97	3	3	2
4A	7	31-Jul-97	6	6	4
4A	8	14-Aug-97	1	1	1
4A	10	11-Sep-97	3	3	2
4A	11	25-Sep-97	5	5	5
4A	12	09-Oct-97	4	4	3
5A	2	20-Nov-97	1	1	1
5A	3	04-Dec-97	10	10	8
5A	13	23-Apr-98	1	1	1
			64	**64**	**42**

Core	Core depth (cm)	Water depth (m)	Number of specimens	Number Light MS imaged	Number of isotope analyses
MC-2	0.5-1.0	192	22	22	21

The numbers in bold are the totals for the sediment trap samples.

Assessment of Shell Condition and Life Stage

The condition of pteropod shells is used as an indicator of the amount of dissolution the shell has undergone; pristine shells are glassy and transparent, and highly dissolved shells are white and lusterless (Almogi-Labin et al., 1986; Gerhardt and Henrich, 2001). All shells from the sediment trap and the core were assessed using the Limacina Dissolution Index (LDX) (Gerhardt and Henrich, 2001) following the findings of Oakes and Sessa (2020) [Data in **Supplementary Table 1** (sediment trap), and **Supplementary Table 2** (core)].

To assess whether life stage affected isotopic composition, shells were split into juvenile (<1 mm) and adult (>1 mm) specimens based on the size differences found in these *H. inflatus* life stages off Barbados (Lalli and Wells, 1978). Shell size was assessed using shell diameter, measured in pixels at the widest part of the shell (Lischka et al., 2011) in ImageJ (Schneider et al., 2012). The image of the scale bar was used to convert the number of pixels to length.

Measurement of Stable Isotopic Composition ($\delta^{18}O$ and $\delta^{13}C$) of Pteropod Shells

Pteropod shells were gently crushed with tweezers and any residual organic (sediment trap) or sediment (core) material was removed. Shell fragments were triple washed in borate-buffered deionized water. Oxygen and carbon isotopes were analyzed on a GV IsoPrime ratio mass spectrometer at the University of South Carolina. All results are reported relative to Vienna Pee Dee Belemnite (VPDB), and precision based on replicate analyses of an in-house Carrera marble standard during these analyses was 0.05‰ (1σ) for $\delta^{18}O$ and 0.03‰ (1σ) for $\delta^{13}C$. In most cases, single pteropod specimens were analyzed, however when individual masses were below 12 µg, smaller shells were combined to meet a minimum mass for analysis of 12 µg. The number of specimens per analysis is clearly marked on all figures. All data are presented in **Table 2**. All $\delta^{18}O$ terms used in this study are summarized in **Table 3**.

Seawater Composition

Contemporaneous measurements of the stable isotopic composition of seawater ($\delta^{13}C_{SW}$, $\delta^{18}O_{SW}$) are not available. The oxygen isotopic composition of seawater was therefore calculated from seawater salinity measurements (S) from discrete bottle samples collected between September 1996 and June 1998. Hydrographic measurements were made on monthly cruises at 19 discrete depths (1, 7, 15, 25, 35, 55, 75, 100, 130, 160, 200, 250, 300, 350, 400, 500, 750, 1,000, 1,200 m): data are publicly available at http://imars.marine.usf.edu/WebPageData_CARIACO/Master_Hydrography/. The salinity data were input into three formulas: the LeGrande and Schmidt (2006) Tropical Atlantic calibration ($\delta^{18}O_{SW} = 0.15{*}S{-}4.61$), the McConnell et al. (2009) Cariaco Basin monthly calibrations (see **Supplementary Table 3** for full list of equations), and the McConnell et al. (2009) Cariaco Basin annual calibration ($\delta^{18}O_{SW} = 0.34{*}S{-}11.48$). The LeGrande and Schmidt (2006) equation is used throughout the study (see section Oxygen Isotopes) and has a $\delta^{18}O_{SW}$ error of ± 0.164‰.

Discrete bottle samples were also analyzed for nutrient concentrations and carbonate chemistry parameters (Astor et al., 2011). Water column properties were interpolated between sample days, and between bottle sample depths, using the interp function in the "akima" package (Akima and Gebhardt, 2016) in the computing language R, version 3.6.0 (R. Core Team, 2019), using RStudio (RStudio Team, 2016). The depth and date of sampling are clearly marked on **Figures 5**, **9**.

Pteropod Calcification Depths

The apparent calcification depth (ACD) of pteropods was calculated following the findings of other studies that pteropods calcify in near equilibrium with the $\delta^{18}O$ of seawater (Grossman et al., 1986; Fabry and Deuser, 1992; Jasper and Deuser, 1993). In *H. inflatus*, the majority of the shell volume is comprised of the final, or body, whorl, which represents the most recently calcified material (Fabry and Deuser, 1992). Shell isotopic measurements will therefore be dominated by this most recently calcified whorl (Keul et al., 2017). The $\delta^{18}O$ of seawater, $\delta^{18}O_{SW}$, for each discrete bottle sample was calculated using the LeGrande and Schmidt (2006) calibration. The theoretical $\delta^{18}O$ of an aragonitic shell calcified in equilibrium with $\delta^{18}O_{SW}$ was determined from these calculated $\delta^{18}O$ seawater values and CTD-derived temperature measurements (T) following the equation from Böhm et al. (2000) ($\delta^{18}O_{arag} = (T\text{-}20)/(-4.42) + \delta^{18}O_{SW}$). Measured $\delta^{18}O$ of pteropod shells ($\delta^{18}O_{ptero}$) were compared to full water column $\delta^{18}O$ ($\delta^{18}O_{arag}$) (i.e., 0–1,300 m); the ACD was assigned as the depth in the water column on the date the sediment trap opened where $\delta^{18}O_{ptero}$ and $\delta^{18}O_{arag}$ were equal. As all pteropods were found to calcify in the top 200 m, the figures only present the top 200 m of the water column.

Carbon Dating

In order to determine the age of the core samples, 3.1 mg of pteropod (*H. inflatus*) shells and 8.1 mg of whole planktic foraminifera (*Globigerinoides sacculifer*) tests from core CAR2000-MC-2 were carbon dated at the Keck-Carbon Cycle AMS facility at the University of California, Irvine. Both pteropods and foraminifera were measured since the carbon ages of foraminifera tests are commonly analyzed in oceanographic and paleoceanographic work whereas pteropods are less well-studied. The foraminifera *G. sacculifer* has an average calcification depth of 25 m in the Cariaco Basin (Wejnert et al., 2013) so will be affected by similar water column properties as *H. inflatus*. Samples were leached 10% with dilute HCl prior to hydrolysis with 85% phosphoric acid. Measurements have been corrected for isotopic fractionation according to the conventions of Stuiver and Polach (1977), with $\delta^{13}C$ values measured on prepared graphite using the AMS spectrometer.

Statistical Methods

Simple linear models were used to test the relationship between two parameters. Normality was tested using a Shapiro-Wilks test. The difference in variance between two normally distributed groups was tested using an F-test, and between two non-normally distributed groups using a Fligner-Killeen's test. The difference in means between two normally distributed groups was tested using Welch's *t*-test and between two non-normally distributed groups using the Wilcoxon rank-sum test. All statistical analyses were performed in R version 3.6.0 (R. Core Team, 2019) using the RStudio Interface (RStudio Team, 2016).

TABLE 2 | Carbon and oxygen isotope measurements of pteropod shells from the sediment trap.

Trap deployment	Cup #	Date (mm/dd/yyyy)	Sample #	δ^{13}C (‰VPBD)	δ^{18}O (‰VPBD)	# Specimens/analysis	Length (mm)
3A	1	11/08/1996	1	0.695	0.130	1	1.021
3A	1	11/08/1996	02a	1.269	0.188	1	0.764
3A	1	11/08/1996	02b	1.089	0.526	1	0.720
3A	2	11/22/1996	1	0.536	−0.076	1	1.210
3A	3	12/06/1996	1	0.706	0.207	1	1.304
3A	3	12/06/1996	2	0.940	0.010	1	0.829
4A	2	05/22/1997	11	1.352	0.367	4	0.548
4A	2	05/22/1997	4	0.787	0.015	3	0.656
4A	3	06/05/1997	1	1.466	0.564	1	0.800
4A	3	06/05/1997	2	0.799	0.181	1	1.123
4A	3	06/05/1997	3	0.683	0.205	1	0.950
4A	3	06/05/1997	7	0.632	−0.124	3	0.415
4A	5	07/03/1997	1	0.501	0.802	1	0.732
4A	5	07/03/1997	2	0.996	0.346	1	1.093
4A	5	07/03/1997	3	0.494	0.354	1	1.538
4A	6	07/17/1997	1	0.575	0.558	1	1.473
4A	6	07/17/1997	2	0.956	0.788	1	1.423
4A	7	07/31/1997	1	1.407	0.358	1	0.885
4A	7	07/31/1997	2	0.725	0.686	1	1.405
4A	7	07/31/1997	3	0.455	0.458	1	0.800
4A	7	07/31/1997	4	0.911	0.484	1	0.844
4A	8	08/14/1997	1	0.919	0.754	1	1.421
4A	10	09/11/1997	1	0.932	0.485	1	0.708
4A	10	09/11/1997	2	1.059	0.504	1	0.944
4A	11	09/25/1997	1	0.492	0.641	1	1.565
4A	11	09/25/1997	2	1.045	0.592	1	1.257
4A	11	09/25/1997	3	0.882	0.227	1	0.917
4A	11	09/25/1997	4	1.555	0.223	1	0.785
4A	11	09/25/1997	5	1.527	1.133	1	0.786
4A	12	10/09/1997	1	0.752	0.019	1	1.231
4A	12	10/09/1997	2	1.056	0.758	1	1.460
4A	12	10/09/1997	5	0.779	−0.320	1	0.888
5A	2	11/20/1997	1	0.755	0.079	1	1.068
5A	3	12/04/1997	10	0.856	−0.169	3	0.645
5A	3	12/04/1997	1	0.796	0.225	1	0.855
5A	3	12/04/1997	2	1.028	0.413	1	1.012
5A	3	12/04/1997	3	1.913	0.601	1	0.727
5A	3	12/04/1997	4	0.880	0.495	1	1.168
5A	3	12/04/1997	5	0.986	0.439	1	0.804
5A	3	12/04/1997	6	1.042	0.478	1	0.828
5A	3	12/04/1997	7	0.999	0.469	1	0.727
5A	13	04/23/1998	1	0.752	0.496	1	1.519

RESULTS

Pteropod Shell Condition

Pteropod shell condition, ranked using the LDX (Gerhardt and Henrich, 2001), varied between 0 (pristine, transparent shell with smooth surface) and 2.5 (opaque, white shell that is beginning to lose surface sheen) in specimens from the sediment trap (**Figure 2**, **Supplementary Table 1**) and between 0.5 and 2.5 in specimens from the core (**Supplementary Figure 4**, **Supplementary Table 2**). There was no correlation between the amount of time pteropod shells spent in the collecting cups and their shell condition ($p = 0.507$, $R^2 = 0.011$) (**Supplementary Figure 3**), similar to the findings of another sediment trap study in the Cariaco Basin (Oakes and Sessa, 2020). Similarly, there was no correlation between the shell condition of the pteropods from the sediment trap or the core and the δ^{18}O or

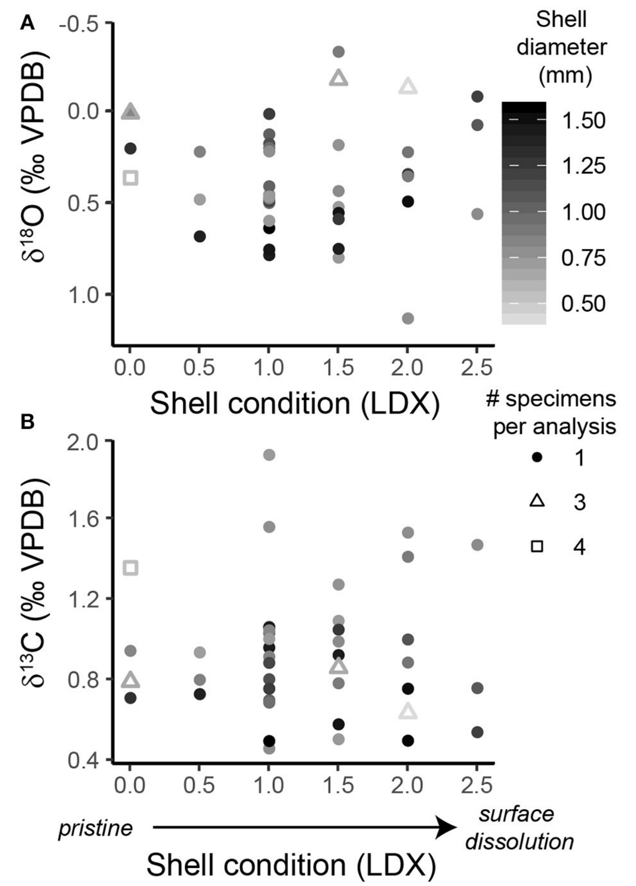

FIGURE 2 | Scatter plots of the shell condition of *H. inflatus* shells from the sediment trap, assessed using the *Limacina* Dissolution Index (LDX: 0 = pristine, 5 = highly altered), and **(A)** the $\delta^{18}O$ and **(B)** $\delta^{13}C$ of the shells. Following convention, the $\delta^{18}O$ axis is inverted. The color of the points corresponds to the shell diameter. The shape of the point represents the number of specimens pooled per isotopic analysis (see key in figure).

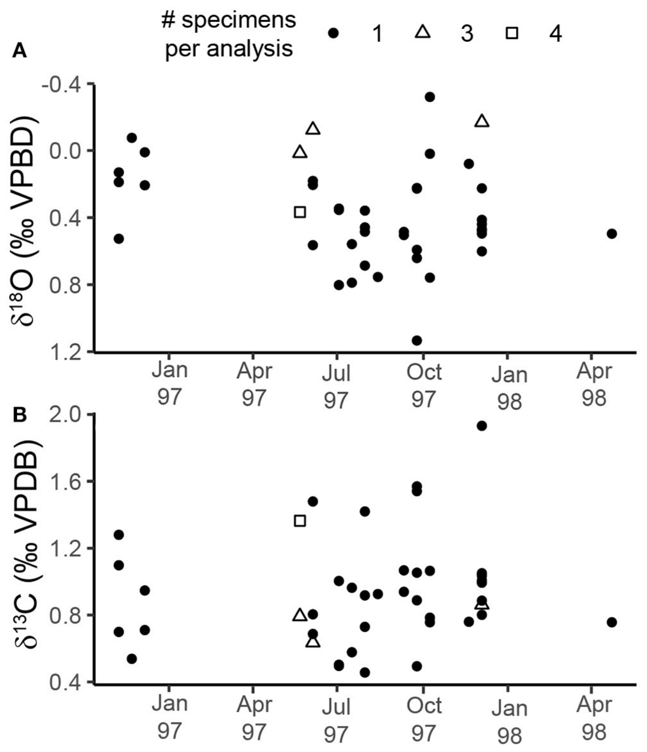

FIGURE 3 | Scatter plots showing the changes in: **(A)** $\delta^{18}O$, and **(B)** $\delta^{13}C$ throughout the study period for the sediment trap. The shape of the point represents the number of specimens pooled per isotopic analysis (see key at top of figure). Following convention, the $\delta^{18}O$ axis is inverted. The breaks in the record correspond to times when pteropods were not found in the faunal splits from the sediment trap samples.

TABLE 3 | Definitions of the $\delta^{18}O$ values used in this study.

$\delta^{18}O_{SW}$	$\delta^{18}O$ of seawater
$\delta^{18}O_{arag}$	theoretical $\delta^{18}O$ of aragonite precipitated in equilibrium with seawater
$\delta^{18}O_{ptero}$	measured $\delta^{18}O$ of a pteropod shell
$\delta^{18}O_{trap}$	measured $\delta^{18}O$ of pteropod shells from the sediment trap
$\delta^{18}O_{core}$	measured $\delta^{18}O$ of pteropod shells from the sediment core

$\delta^{13}C$ of shell material ($\delta^{18}O_{trap}$: $p = 0.791$, $R^2 = 0.002$; $\delta^{13}C_{trap}$: $p = 0.944$, $R^2 = 0.0001$; $\delta^{18}O_{core}$: $p = 0.742$, $R^2 = 0.006$; $\delta^{13}C_{core}$: $p = 0.309$, $R^2 = 0.054$) (**Figure 2**, **Supplementary Figure 4**).

To further explore whether the extent of dissolution affected shell isotopic composition, specimens were split into two groups: those that had undergone minor dissolution (LDX 0–1.5), and those that had undergone moderate dissolution (LDX 2-3). This threshold was chosen because shells with an LDX of 2 and higher have become fully opaque and therefore have, "truly experienced initial dissolution on the surface" (Gerhardt and Henrich, 2001, p. 2059). The $\delta^{18}O$ and $\delta^{13}C$ measurements were not significantly different between shells which had experienced minor vs. moderate dissolution, in either the sediment trap or core samples ($\delta^{18}O_{trap}$: $p = 0.458$, $W = 186$; $\delta^{13}C_{trap}$: $p = 0.836$, $W = 167$; $\delta^{18}O_{core}$: $p = 0.689$, $W = 43$; $\delta^{13}C_{core}$: $p = 0.197$, $W = 67$) (**Figure 2**; **Supplementary Figure 4**).

Sediment Trap

Oxygen Isotopes

Oxygen isotope measurements of specimens from the sediment trap samples ranged from −0.32 to 1.13‰ (1.45‰ range) with a median value of 0.44‰ (**Figure 3A**, **Table 2**). The highest values were measured in specimens sampled during the summer (July–September 1997), and the lowest values were measured in specimens from October and November 1997 (**Figure 3A**). The range in ACDs for pteropod shells measured from the same sediment trap cup varies between 2 and 90 m with greater variability occurring in the non-upwelling conditions (**Figure 5**, **Supplementary Table 4**). There was not a significant relationship between the oxygen isotopic composition of pteropod shells and their shell diameter ($p = 0.068$, $R^2 = 0.081$) (**Figure 4A**). The variability in $\delta^{18}O_{ptero}$ measurements of adult (>1 mm diameter) and juvenile (<1 mm diameter) shells, corresponding to the transition from juvenile to male for this species (Lalli and Wells, 1978), were not significantly different ($F = 1.334$, $p = 0.547$) (**Figure 4A**).

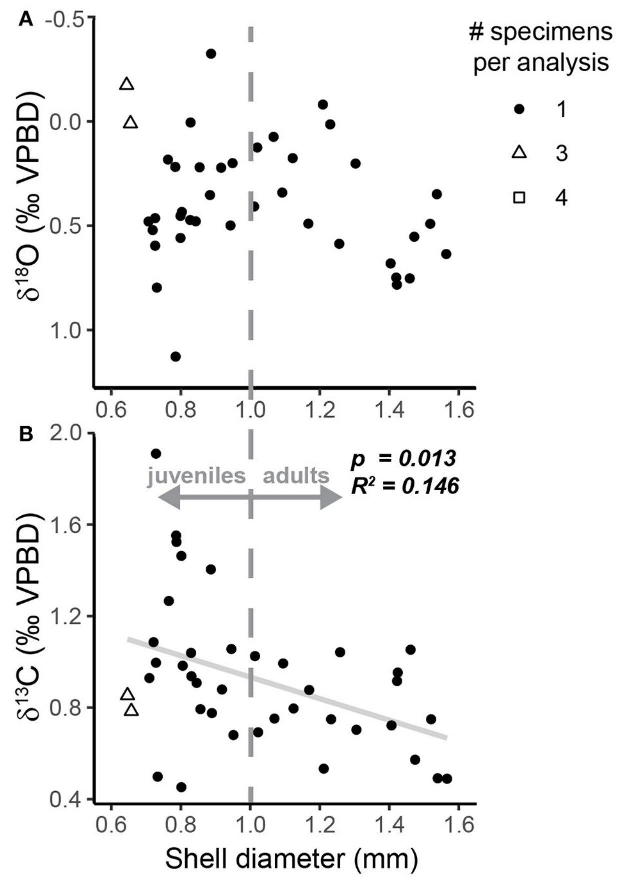

FIGURE 4 | Scatter plots of *H. inflatus* shell diameter relative to the **(A)** $\delta^{18}O$ and **(B)** $\delta^{13}C$ of shells from the sediment trap. Following convention, the $\delta^{18}O$ axis is inverted. The shape of the point represents the number of specimens pooled per isotopic analysis (see key in figure). The gray dashed line represents the break between juvenile and adult pteropod shells following the work of Lalli and Wells (1978). The relationship between $\delta^{18}O$ and shell diameter is not significant ($p = 0.068$, $R^2 = 0.081$). The relationship between $\delta^{13}C$ and shell diameter is significant ($p = 0.013$, $R^2 = 0.146$; trendline plotted in gray solid line), and $\delta^{13}C$ measurements of adult shells (>1.0 mm) are significantly less variable ($F = 3.60$, $p = 0.009$) than those in juvenile shells (<1.0 mm).

H. inflatus pteropods were found to calcify at an average ACD of 51.2 ± 34.0 m using the LeGrande and Schmidt (2006) calibration (1 standard deviation (s.d.) range = 1–153 m) (**Figure 5**). If we were to apply the month-specific (**Supplementary Table 3**), and yearly average calibrations from McConnell et al. (2009) average ACDs would be 38.5 ± 33.2 m (1 s.d.) and 40.3 ± 31.9 m (1 s.d.) respectively (**Supplementary Figure 5**). The relevant calibrations from McConnell et al. (2009) are sometimes limited to 100 m depth, rather than covering the full range of pteropod ACDs, and are therefore likely to be less reliable. The calibration from LeGrande and Schmidt (2006) has therefore been used in all following calculations.

Carbon Isotopes

Carbon isotope measurements of sediment trap specimens ranged from 0.46 to 1.91‰ (1.45‰ range) with a median value of 0.88‰ (**Figure 3B**, **Table 2**). The highest values were measured in specimens from September and December 1997 and the lowest values were measured in specimens from July 1997 (**Figure 3B**). There is a significant relationship between the carbon isotopic composition of pteropods shells and their shell diameter ($p = 0.013$, $R^2 = 0.146$) (**Figure 4B**). The variability of $\delta^{13}C_{\mathrm{ptero}}$ in juvenile shells (<1 mm diameter) is significantly higher than in adult shells (>1 mm diameter) ($p = 0.009$, $F = 3.60$), however there is not a significant relationship between the ACD and $\delta^{13}C$ ($p = 0.215$, $R^2 = 0.038$). There is not a strong or significant relationship between the $\delta^{18}O$ and $\delta^{13}C$ of the shell material ($p = 0.074$, $R^2 = 0.077$) (**Figure 6**).

Core

The radiocarbon dates from foraminifera (*G. sacculifer*) and pteropods (*H. inflatus*) varied greatly: planktic foraminifera yielded a date of 1740 ± 15 BP, while pteropods gave a date of 860 ± 15 BP, a difference of 880 years (**Table 4**). Applying a marine surface reservoir correction for the Cariaco Basin of 420 years (Hughen et al., 1996), the sediment core is dated to either 1,340 ± 15 BP if *G. sacculifer* is used and 440 ± 15 BP if *H. inflatus* is used.

Oxygen isotope measurements of specimens from the core samples were higher than those from the sediment trap, ranging from 0.13 to 1.36‰ (1.23‰ range) with a median value of 0.51‰ (**Figure 7A**, **Supplementary Table 5**). Using the temperature calibration from Keul et al. (2017), this offset represents a 0.5°C difference between the median values of samples from the core and the sediment trap, however the difference was only significant at $p = 0.071$. Carbon isotope measurements of specimens from the core were higher than the specimens from the sediment trap sample, ranging from 0.80 to 1.75‰ (0.95‰ range) with a median value of 1.33‰ (**Figure 7B**, **Supplementary Table 5**). The median core $\delta^{13}C$ is 0.45‰ higher than the median sediment trap value, which represents a statistically significant difference ($p = 1.91 \times 10^{-5}$).

DISCUSSION

Fidelity of $\delta^{13}C$ and $\delta^{18}O$ Records From Pteropod Shells

Pteropods' fragile, aragonitic shells make them susceptible to dissolution, a concern when developing a proxy. The Cariaco Basin is anoxic below 300 m depth due to a shallow sill restricting exchange with other ocean basins (Hughen et al., 1996). The carbonate-rich waters in this shallow basin are supersaturated with respect to aragonite, even in the deepest part of the basin (1,300 m; **Figure 1**). The combination of anoxia and aragonite supersaturated seawater creates an ideal environment for the preservation of calcareous and siliceous microfossils, including pteropod shells (Peterson et al., 1991).

The chemical composition of mollusk shells, when sufficiently preserved, have been found to record the physical and chemical

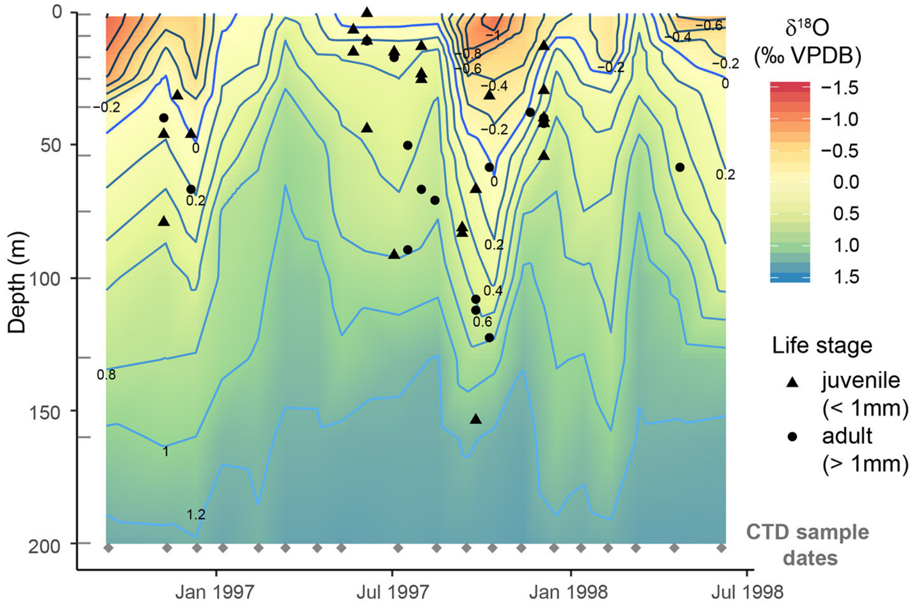

FIGURE 5 | Calcification depths of *H. inflatus* determined by comparing δ^{18}O measurements of shells to δ^{18}O of the water column calculated from CTD sampled bottle measurements of salinity using the LeGrande and Schmidt (2006) Tropical Atlantic calibration (two additional calibrations are presented in **Supplementary Figure 4**). The average calcification depth was 50.2 ± 33.5 m (1 s.d.). The shape of the point represents the life stage of the individual: juveniles (<1 mm), adults >1 mm (Lalli and Wells, 1978). There is not a significant correlation between calcification depth and shell size ($p = 0.090$, $R^2 = 0.067$). CTD collection dates are marked by gray diamonds and CTD bottle depths are marked by gray lines; $\delta^{18}O_{SW}$ values between these points have been interpolated.

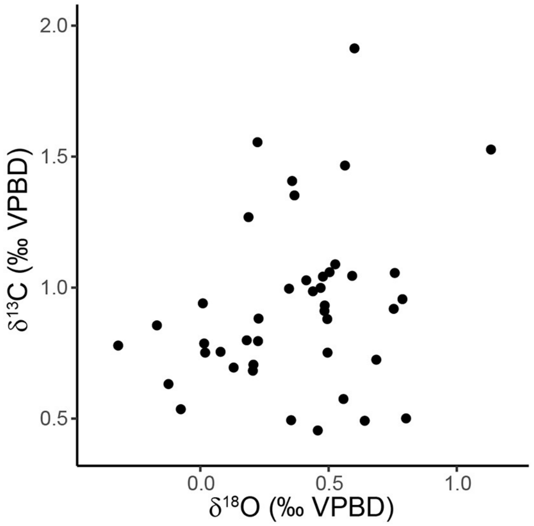

FIGURE 6 | Scatter plot showing the relationship between δ^{18}O and δ^{13}C of *H. inflatus* shells from the sediment trap samples ($p = 0.074$, $R^2 = 0.077$).

environmental conditions at the time of shell formation (e.g., Epstein et al., 1953; Anderson and Arthur, 1983; Grossman and Ku, 1986; McConnaughey and Gillikin, 2008). No previous studies have specifically investigated the relationship between pteropod shell condition and stable isotopic composition. Fabry and Deuser (1992) found that there was no change in the isotopic composition of pteropod shells between sediment trap samples from 500 to 3,200 m, implying minimal isotopic exchange occurred in the water column. In this study, there was no correlation between shell condition and δ^{13}C or δ^{18}O of shell material, despite visible alteration of pteropod shells from both sediment trap and core materials (**Figure 2**, **Supplementary Figure 4**). This demonstrates that in aragonite-supersaturated waters and in shallow subfossil sediment, the isotopic composition of *H. inflatus* pteropod shells is not altered during initial dissolution (at least up to an LDX score of 2.5), and shells in this preservational range are well-suited for use as oceanographic proxies.

Calculating Calcification Depth From δ^{18}O

Based on comparison between the calculated $\delta^{18}O_{arag}$ of seawater (LeGrande and Schmidt, 2006) and measured δ^{18}O of pteropod shells, we found an ACD of 51.2 ± 34.0 m for *H. inflatus* in the Cariaco Basin (**Figure 5**). This falls within error of previously reported calcification depths of other pteropods within the same superfamily as *H. inflatus; Limacina helicina* from the Sargasso Sea (50 m, Fabry and Deuser, 1992), *L. bulimoides* from the North Pacific (75–125 m for large specimens, Grossman et al., 1986), and *H. inflatus* from the Atlantic Ocean (75 m, Keul et al., 2017), and is at the shallow end of the range proposed by Juranek et al. (2003) for *H. inflatus* from the Sargasso Sea (50–650 m). Unlike in *L. bulimoides* from the North Pacific (Grossman et al., 1986), we found no significant difference in the ACD of juvenile and adult specimens of *H. inflatus* in the Cariaco Basin.

TABLE 4 | ^{14}C ages of *Globigerinoides sacculifer* (planktic foraminifera), and *Heliconoides inflatus* (pteropod) from the CAR2000-MC-2 core in the Cariaco Basin.

Sample	fraction modern	±	$D^{14}C$ (‰)	±	^{14}C age (BP)	±
G. sacculifer (foraminifera)	0.8053	0.0014	−194.7	1.4	1740	15
H. inflatus (pteropod)	0.8982	0.0016	−101.8	1.6	860	15

Radiocarbon concentrations are given as the fractions of the Modern standard $D^{14}C$, and conventional radiocarbon age. BP = years before present.

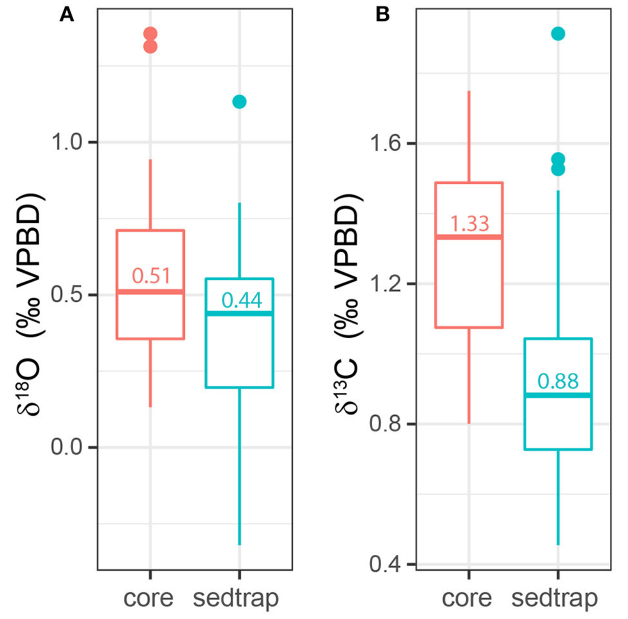

FIGURE 7 | Box and whisker plots showing the difference between **(A)** the $\delta^{18}O$ and **(B)** $\delta^{13}C$ measurements of *H. inflatus* specimens from the sediment trap (blue) and the core (red). Both $\delta^{18}O$ and $\delta^{13}C$ values are higher in the core material than in the sediment trap. Median values are written inside each box.

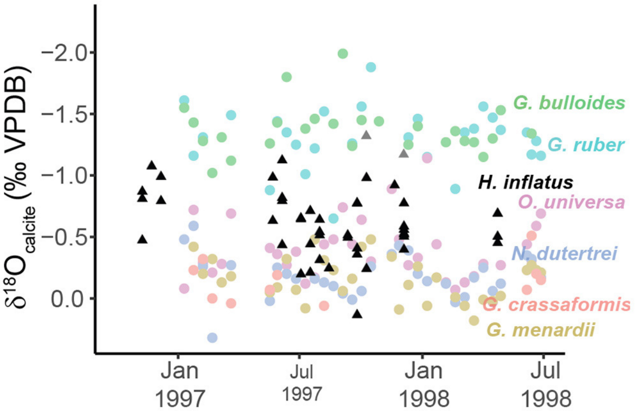

FIGURE 8 | Scatter plot showing the oxygen isotopic composition of six species of foraminifera (colored circles) (Tedesco et al., 2007) and one species of pteropod (black triangles) (this study) from CARIACO sediment trap A (150 m water depth) between October 1996 and July 1998. Because aragonite and calcite have different fractionation factors relative to ambient seawater, the oxygen isotopic composition of pteropods (aragonite) are adjusted using the calibration from Böhm et al. (2000) (black triangles, 1‰ offset) to plot in calcite space.

Shell isotopic composition was compared to water chemistry on the day the sediment trap opened. Pteropods live for about a year (Wells, 1976; Fabry and Deuser, 1992), and although early studies on this species proposed constant growth rates over time (Wells, 1976), studies on other groups from the same superfamily have found that shell growth rates vary substantially depending on season, geographical region, and food availability (Dadon and de Cidre, 1992; Wang et al., 2017). Shell growth of *H. inflatus* in the Cariaco Basin has been found to vary associated with changes in upwelling, with larger, thicker shells forming during periods of wind-driven upwelling when nutrient concentrations, and food availability are higher (Oakes and Sessa, 2020). It is therefore likely that the individuals in this study experienced different water column conditions and therefore had different growth rates. As the growth rates of these specimens are unknown and there is not enough material to perform incremental isotopic measurements through the shell, the sediment trap opening date water chemistry is used as water chemistry at the time of calcification.

Tedesco et al. (2007) studied the seasonal and interannual variability of oxygen isotopes in six species of foraminifera from 1997 to 1999, sampled from the same sediment trap as this study. In order for the oxygen isotopic composition of aragonitic pteropods and calcitic planktic foraminifera to be compared, the aragonitic values are adjusted by 1.0‰ to account for the different fractionation factors between ambient seawater and calcite and aragonite (Böhm et al., 2000). When plotted in $\delta^{18}O_{calcite}$ space, *H. inflatus* fall in a similar range (−1.3 to 0.13‰, average −0.63‰) to the planktic foraminifera *Orbulina universa* (−0.14 to 0.03‰, average −0.37‰), a mixed-layer to thermocline dwelling organism which reaches its highest abundances at ∼50 m in the east tropical Atlantic (Ravelo and Fairbanks, 1992; Tedesco et al., 2007) (**Figure 8**). The similarity of *O. universa* and *H. inflatus* oxygen isotopic values supports the calculated ACD for *H. inflatus* in the Cariaco Basin (51.2 ± 34.0 m).

The range of pteropod ACDs measured within one sample varies throughout the year, with smaller depth ranges during times of upwelling, and more varied ACDs during non-upwelling conditions (**Figure 5**, **Supplementary Table 4**). A greater range between minimum and maximum ACD can be interpreted as signifying an expanded vertical habitat, and likely intervals with a deeper mixed layer. We hypothesize that pteropods are recording

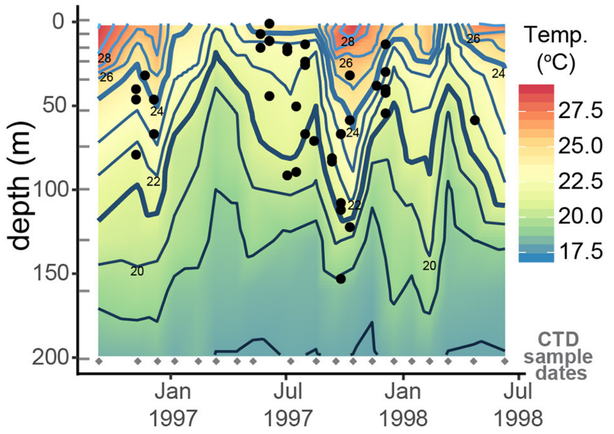

FIGURE 9 | Apparent calcification depths of *H. inflatus* plotted relative to the seawater temperatures from CTD casts. CTD sampling days are marked by gray diamonds and depths are marked by gray dashes; δ^{18}O values in between these points are interpolated. Over eighty percent of *H. inflatus* apparent calcification depths fall between the 21 and 24°C contours (bold lines), suggesting that *H. inflatus* is tracking this habitat throughout the year rather than calcifying at a fixed depth.

this change in hydrography. The number of pteropods which reach the sediment trap cups varies with time, with some cups containing no pteropod shells. This could be the result of the inherent patchiness of pteropod distributions (Bednaršek et al., 2012; Thibodeau and Steinberg, 2018), or could reflect seasonality in the flux of shells, a hypothesis which could be tested with examination of a longer timeseries.

Previous studies have found that there are only small annual changes in the salinity in the Cariaco Basin [equivalent to $\sim$0.10‰ δ^{18}O (Tedesco et al., 2007)] therefore the majority of variation $\delta^{18}O_{SW}$ can be attributed changes in temperature. Using the only established palaeothermometry equation for *H. inflatus* (Keul et al., 2017) and CTD temperature profiles yields an average calcification depth of 15.9 ± 25.9 m (1 s.d.) (**Supplementary Figure 6**). This estimate is shallower than the ACD's calculated from seawater δ^{18}O and comparisons with planktic foraminifera in this study, and shallower than previously published calcification estimates of *H. inflatus* (Fabry and Deuser, 1992; Juranek et al., 2003; Keul et al., 2017). In terms of $\delta^{18}O_{ptero}$, values are lower than would be expected if specimens had calcified at 50 m, the depth at which the paleothermometer was calibrated (Keul et al., 2017). One explanation for this offset could be that the specimens in this study span the whole year, whereas the specimens and water chemistry samples used to calibrate the paleothermometer were from single net samples taken between October and November 2012 (Keul et al., 2017), skewing the calibration toward cooler values.

Comparing ACDs to temperature profiles from CTD casts reveals 78% of individual *H. inflatus* calcify in water between 21 and 24°C, rather than calcifying at a fixed depth throughout the year (**Figure 9**). Calcification rates in other groups of marine calcifiers, such as bivalves (Kennish and Olsson, 1975; Jones et al., 1989), corals (Clausen and Roth, 1975; Bessat and Buigues, 2001), and coccolithophores (Buitenhuis et al., 2008), are temperature sensitive. *H. inflatus* in the Cariaco Basin may, therefore, be tracking their optimal temperature range for shell precipitation. Temperature can co-vary with other important parameters such as food and nutrient availability, light, and salinity, and therefore their calcification depth distribution may be controlled by a combination of these factors (Jonkers and Kučera, 2015).

Pteropods migrate diurnally, and in the Florida Strait *H. inflatus* have an average daytime depth of 230 m (spread = 177 m), and migrate upwards at night (Wormelle, 1962). If we assume that *H. inflatus* in the Cariaco Basin has a similar migratory pattern, the $\delta^{18}O_{ptero}$ suggests that the majority of calcification occurs at night when *H. inflatus* reach the shallowest part of their migration. Night-time calcification, at the shallowest part of a pteropods diurnal migration, has been proposed in previous studies (Fabry and Deuser, 1992; Keul et al., 2017), hypothesized to be due to the lower energy requirements for calcification in warmer, more aragonite saturated, shallow waters.

Deciphering Pteropod δ^{13}C

The δ^{13}C of the shells of mollusks incorporate both respired CO_2, derived from dietary organic carbon, and dissolved inorganic carbon (DIC) (e.g., Tanaka et al., 1986; McConnaughey, 1989; McConnaughey et al., 1997; Owen et al., 2002; Lorrain et al., 2004; McConnaughey and Gillikin, 2008; Butler et al., 2011). Carbon isotopes derived from a mixture of these sources (and of the intermediate calcification steps) can be difficult to disentangle (McConnaughey and Gillikin, 2008), but the proportion of respired carbon incorporated into the shells of aquatic (marine and freshwater) mollusks ranges between $<$10 and 90% (McConnaughey and Gillikin, 2008; Butler et al., 2011). Studies specifically focusing on δ^{13}C in pteropod shells have investigated the effects of dissolved inorganic carbon and respired CO_2 on $\delta^{13}C_{ptero}$. In a study of six species of pteropods, including *Limacina bulimoides*, in the North Pacific Ocean, Grossman et al. (1986) found no shells precipitated in ^{13}C equilibrium with dissolved bicarbonate. A study of "*Limacina inflata*" (now *H. inflatus*) from Bermuda concluded that $\delta^{13}C_{ptero}$ is influenced by metabolic incorporation of CO_2 during shell growth as well as ambient seawater [CO_3^{2-}] (Juranek et al., 2003). The carbon isotopic composition of pteropod shells in this study is discussed in the context of DIC, metabolic vital effects, and diet.

The δ^{13}C of pteropod shells has been shown to record the concentration of carbonate ions in seawater (Keul et al., 2017). The calibration presented in Keul et al. (2017) is valid for δ^{13}C of $<$1‰, equivalent to minimum carbonate ion concentrations of $>$200 µmol/ kgSW. These conditions are only found in the upper 50 m of the water column in the Cariaco Basin, shallower than the ACD of most pteropods. Despite the limitations, if the equation of Keul et al. (2017) is applied to this dataset, the ACD would be 38 ± 38 m (**Supplementary Figure 7**), within error of the ACD assessed by δ^{18}O.

There are significant differences in δ^{13}C variability between juvenile ($<$1 mm) and ($>$1 mm) adult pteropod shells ($F = 3.60$, $p = 0.0087$) which may indicate the presence of a metabolic vital effect (**Figure 4B**). The isotopic composition of scallop specimens displaying high growth rates has been found to deviate more from isotopic equilibrium than specimens with slower growth rates (Owen et al., 2002), and several studies have found that growth rates decrease and become less variable with age (Schöne et al., 2005; Butler et al., 2010; Mancuso et al., 2019). Assuming similar relationships occur in pteropods, the increased variability in δ^{13}C of juvenile pteropods relative to adults could be attributed to higher growth rates in smaller specimens. Alternatively, Grossman et al. (1986) found two other species of pteropod, *Cuvieria columnella* and *Diacria trispinosa*, incorporated more metabolic carbon with age, which would cause the δ^{13}C of adult shells to be less variable than juvenile shells.

Studies of other groups of planktonic calcifiers (Uhle et al., 1997; Doi et al., 2010) pelagic nekton (Gorokhova and Hansson, 1999), and mollusks (McConnaughey and Gillikin, 2008) have found that organism δ^{13}C is linked to diet, and that diet can change with growth (Doi et al., 2010). There is not a significant relationship between δ^{13}C and ACD, suggesting that *H. inflatus* of all sizes in this study (0.67–1.52 mm) were calcifying in the same water mass (**Figure 5**). The difference in δ^{13}C variability between juvenile and adult pteropods suggests that pteropods may target different food sources dependent on their life stage. Pteropods feed on small crustaceans, amphipods, copepods, and phytoplankton (Lalli and Gilmer, 1989; Gilmer and Harbison, 1991). Gilmer and Harbison (1986, 1991) found that over 40% of the diet of large (i.e., adult) *Limacina helicina* pteropods in the Arctic Ocean was composed of juvenile pteropods and crustaceans, but suggested smaller *L. helicina* (i.e., those at an earlier lifestage) may be herbivorous, transitioning to omnivory as they grow. The lower variability in δ^{13}C of adult pteropods may, therefore, be due to their diet being composed of few, large zooplankton while juvenile pteropods would need to consume a large number of smaller planktonic organisms such as diatoms, algae, and dinoflagellates to gain their energy. These smaller planktonic organisms span a wide range of δ^{13}C values (Hansman and Sessions, 2016; Tiselius and Fransson, 2016) which would cause the δ^{13}C of juvenile pteropod shells to be more variable than adults.

Using Pteropods as Proxies in the Shallow Sedimentary Record

Core specimens of *H. inflatus* were dated to 440 years BP. Interestingly, planktic foraminifera (*G. sacculifer*) from the same sample were dated to 1,340 years BP. Incongruent ^{14}C ages from planktic foraminifera and pteropods have been documented in previous studies (Price et al., 1985; Ganssen et al., 1991; Mekik, 2014) and this offset has been attributed to differences in sedimentation rates, bioturbation, and winnowing between the two groups. In contrast to previous findings, the pteropods from the MC-2 core record a younger age than the planktic foraminifera sampled at the same stratigraphic level. Regardless of which date is correct, specimens are late Holocene in age, and therefore record δ^{13}C marine reservoir and seawater temperatures from pre-1850 (i.e., prior to changes related to anthropogenic emissions) (Beveridge and Shackleton, 1994). Both the oxygen and carbon isotopic values of pteropod shells from the core material are higher than specimens from the sediment trap, although the change in $\delta^{18}O_{ptero}$ is only significant at $p = 0.071$ ($\Delta^{18}O = 0.07‰$, $\Delta^{13}C = 0.45‰$) (**Figure 7**, **Supplementary Table 5**). Applying the calibration from Keul et al. (2017), the offset in δ^{18}O represents an increase in median seawater temperatures recorded by pteropods of 0.5°C between the late Holocene and 1997. This is comparable to the amount of warming recorded by planktic foraminifera from the same basin between 1850 and 1990 (Black et al., 2007).

The 0.45‰ decrease in δ^{13}C is of similar magnitude to the changes recorded in the planktic foraminifera *Globigerinoides ruber* (pink) from the same basin between 1750 and 1998 (0.5–0.6‰) (Black et al., 2011). The δ^{13}C of marine carbonates, such as corals (Swart et al., 2010) and planktic foraminifera (Beveridge and Shackleton, 1994), have been shown to record the change in atmospheric and oceanic reservoirs of ^{13}C associated with the combustion of ^{13}C poor fossil fuels known as the ^{13}C Suess Effect (Suess, 1955; Keeling, 1979). The 0.07‰ decrease in δ^{18}O, and 0.45‰ decrease in δ^{13}C between late Holocene samples and sediment trap samples from 1997 show that the *H. inflatus* shells from Cariaco Basin surface sediments record both the warming, and the ^{13}C Suess Effect caused by increased combustion of fossil fuels since the industrial revolution.

Implication of Establishing Pteropods as Proxies

The shells of *H. inflatus* record seawater chemistry from mixed layer depths (51 ± 34 m), tracking a 21–24°C temperature range throughout the year. Understanding where this ocean acidification-susceptible species calcifies delineates a critical depth range for monitoring with regards to ocean acidification. Although the shells of other marine calcifiers, such as foraminifera and benthic mollusks, have been traditionally used for oceanographic analyses (see Urey et al., 1951; McConnaughey and Gillikin, 2008; Pearson, 2012), foraminifera are short-lived and influenced by seasonality, while benthic mollusks are orders of magnitude less common than pteropods in ocean cores. The development of proxies from pteropod shells gives a new insight into how these abundant, multicellular calcifying plankton respond to ocean chemistry, both on seasonal and annual time scales in the modern ocean, and potentially over decadal to millennial time scales in the fossil record.

Because of their size, pteropod shells settle relatively quickly through the water column at rates of 850–1,700 m/day (Bergan et al., 2017). Pteropod shells are therefore less likely to be transported post-mortem than smaller planktonic calcifiers (Kalberer et al., 1993), however, their delicate, aragonitic shells mean they are not well-preserved in all oceanographic settings, which has likely limited their development as oceanographic proxies. The pteropod fossil record reflects the specialized nature of their preservation: the oldest known pteropod is a single specimen preserved as a mold in Campanian (~82 Ma) sediments; there is then a 20 million year gap in their fossil record (Janssen and Goedert, 2016). Molds are the dominant preservation style, until the Late Oligocene (∼27 Ma) when shell material is more commonly preserved (Janssen, 1990, 2012). We predict that pteropod fossils retaining original shell material will be found in ocean basins which have experienced aragonite-supersaturated conditions at depth, such as the Red Sea (Almogi-Labin et al., 1991) and the Cariaco Basin. Despite the geographically restricted nature of the pteropod fossil record, the promise of pteropods as oceanographic proxies, as outlined in this study, suggests there is a need for exploration of the pteropod fossil record in other ocean basins.

CONCLUSIONS

Pteropods' importance for monitoring ongoing changes in ocean chemistry positions them well to be developed as oceanographic proxies. Shells of *H. inflatus* record the stable isotopic composition at ∼50 m depth, the shallow part of their diurnal migration. They appear to track a temperature range of 21–24°C. This delineates a focused range of water conditions that should be monitored to understand the impact of changing ocean chemistry on this ecologically relevant species. The isotopic composition of pteropod shells is not affected by moderate dissolution in this aragonite-supersaturated basin. Comparing pteropod shells from the sediment trap to surface sediment samples reveals a 0.5°C increase in temperature and 0.45‰ decrease in δ^{13}C since the late Holocene, recording the warming and changing isotopic composition of carbon reservoirs associated with anthropogenic combustion of fossil fuels known as the Suess Effect. The data presented in this study highlight that pteropods are viable candidates to be developed as oceanographic and paleoceanographic proxies in environments where their shells are preserved. Developing this new proxy will enable investigations into how multicellular planktonic organisms have been impacted by past climatic changes on timescales from weeks to millennia.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/**Supplementary Material**, further inquiries can be directed to the corresponding author/s.

AUTHOR CONTRIBUTIONS

RO, CD, and JS conceived the idea. RO identified specimens, took light microscope images, performed statistical analyses, made figures, and wrote the initial manuscript draft. CD ran isotopic analyses. RO and CD ran initial data analyses and drafted the manuscript. All authors read and edited the manuscript and approved the submitted version.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fmars.2020.553104/full#supplementary-material

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