The Effect of Seawater Carbonate Chemistry on the Stable Isotope Composition of *Cibicidoides wuellerstorfi* and Other *Cibicidoides* Species

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Key Points:

- The offset between the measured and expected $\delta^{13}C$ and $\delta^{18}O$ of *Cibicidoides wuellerstorfi* correlates with seawater carbonate chemistry
- Negative $\Delta^{13}C$ occur mainly in the deep Atlantic due to a combination of low temperature, under-saturation, and low to intermediate [DIC]

Abstract

The $\delta^{13}C$ composition of *Cibicidoides wuellerstorfi* and other *Cibicidoides* spp is an important tool to reconstruct past changes in the deep ocean carbon cycle. The species are expected to match the $\delta^{13}C$ of ambient dissolved inorganic carbon (DIC), although it has been recognised that substantial offsets can occur. Here I present a compilation of modern $\delta^{13}C$ and $\delta^{18}O$ data for named *Cibicidoides* species in combination with fully resolved carbonate chemistry at each core location. The data show for *C. wuellerstorfi* that the offset from the expected value in both carbon ($\Delta^{13}C$) and oxygen ($\Delta^{18}O$) is correlated with seawater carbonate chemistry. The result is comparable to, but not identical with, published culture experiments in which marine organisms were grown under variable pH-conditions. Overall, $\Delta^{13}C$ in *C. wuellerstorfi* correlates positively with carbonate saturation, [DIC], and temperature. The three variables together explain 47.1% of the variation in $\Delta^{13}C$. The trend for $\Delta^{18}O$ is similar, except that the effect of temperature has been removed through correction with a published $\delta^{18}O$-temperature equation. Up to 35% of the remaining variation in $\Delta^{18}O$ can be explained by ambient carbonate chemistry. Data for other named *Cibicidoides* species are broadly similar, but are too sparse for a detailed analysis. The results indicate that strongly negative $\Delta^{13}C$ occurs predominantly in the deep Atlantic in response to a combination of low [DIC], low temperature, and undersaturation within the lysocline. Implications for paleoceanographic reconstructions are discussed.

1 Introduction

The stable carbon isotope composition of dissolved inorganic carbon (DIC) in the deep ocean provides a tracer for ocean circulation and the age of bottom water masses. The $\delta^{13}C$ of DIC ($\delta^{13}C_{DIC}$) in deep water masses initially reflects ocean chemistry at the source location but decreases progressively through remineralisation of sinking organic matter. Epifaunal benthic foraminifera like *Cibicidoides* species are considered to record the $\delta^{13}C$ composition of ambient deep water faithfully and are therefore the preferred material to reconstruct past changes in ocean circulation (Duplessy et al., 1984; Hodell et al., 2003; Peterson et al., 2014; Schmittner et al., 2017).

However, it has been recognised that the $\delta^{13}C$ of *Cibicidoides* spp. ($\delta^{13}C_{Cib}$) can be substantially lower than that of ambient DIC. The effect has been linked to the presence of phytodetritus on the sea floor in areas with seasonally high rain rates of organic matter (Mackensen et al., 1993; Mackensen et al., 2001). However, a subsequent compilation of global $\delta^{13}C_{Cib}$ data shows features that are inconsistent with this explanation. Schmittner et al. (2017) show that the offset between $\delta^{13}C_{Cib}$ and ambient DIC correlates with water depth, with negative offsets occurring preferentially in the deep ocean. In contrast, phytodetritus should be more abundant in shallow water, since the flux of organic matter decreases exponentially with increasing water depth (Armstrong et al., 2002; Martin et al., 1987). Furthermore, the most depleted $\delta^{13}C_{Cib}$ values are essentially restricted to the deep Atlantic Ocean; such values are very rare or absent in the Indian and Pacific Oceans (Schmittner et al., 2017) irrespective of water depth or levels of productivity in the overlying surface waters.

The aim of this paper is to determine if exceptionally low $\delta^{13}C_{Cib}$ can be explained by the carbonate chemistry of ambient water instead. Schmittner et al. (2017) found a weak but significant correlation with carbonate ion concentration ($[CO_3^{2-}]$). The authors estimated $[CO_3^{2-}]$

as the difference between Total Alkalinity (TA) and DIC concentrations, which is a convenient approximation but not accurate enough for any detailed analysis (Broecker & Peng, 1982; Yu et al., 2016) . Yet there is evidence that carbonate chemistry affects the chemical composition of foraminifera. The trace metal composition of benthic foraminifera, including *Cibicidoides*, is sensitive to the carbonate saturation state of ambient sea water (Elderfield et al., 2006; Yu et al., 2007). Both $\delta^{13}C$ and $\delta^{18}O$ of cultured planktonic foraminifera changed substantially when ambient [CO_3^{2-}] was modified (Spero et al., 1997). Additionally, changes in carbonate chemistry could induce vital effects if the habitat of benthic foraminifera is dependent on ambient conditions. Specifically, Wollenburg et al. (2018) found that *Cibicidoides pachyderma* switches between epifaunal and infaunal habitats depending on ambient pH.

To determine if there is a consistent correlation between the stable isotope composition of *Cibicidoides* and ambient deep water carbonate chemistry, I therefore compiled published $\delta^{13}C$ and $\delta^{18}O$ data for named *Cibicidoides* species in conjunction with fully resolved carbonate chemistry at each core location. The main focus is on *Cibicidoides wuellerstorfi* (Schwager), as this is the species that has been analysed the most frequently. Results for other named *Cibicidoides* species are included, where available, but data are too sparse for a detailed analysis..

2 Data Compilation

2.1. *Cibicidoides* stable isotope data

This study is based on a compilation of published stable isotope data for *Cibicidoides* spp from Late Holocene (LH; 0 - ~5 kyr BP) sediment cores and core top samples (Nederbragt, 2023). The $\delta^{18}O$ data were used to screen all records, to ensure that they are representative for LH. Glacial foraminifera can be present at the sediment surface in areas of slow sedimentation, causing $\delta^{18}O$ to be higher than the expected modern value (Matsumoto & Lynch-Stieglitz, 1999). Stratigraphic data were therefore checked for the presence of the expected Holocene plateau in $\delta^{18}O$ and/or ≥1.5 ‰ offset with Last Glacial Maximum (LGM) values (Duplessy et al., 2002; Lisiecki & Raymo, 2005). For undated core top samples, the measured $\delta^{18}O$ was compared to the expected value based on the temperature at the sea floor, and outliers were excluded (Fig. 1). The expected $\delta^{18}O$ value is calculated from an experimental temperature equation for inorganic calcite (Kim & O'Neil, 1997) adjusted to the conventionally used CO_2-calcite fractionation factor (Bohm et al., 2000).

The taxonomic classification of the species included in this study has been discussed elsewhere (Holbourn et al., 2013; Schweizer, 2006). Here, all species are assigned to the genus *Cibicidoides*. Species names are copied as published without adjustment for synonymy. As shown in section 3.1, the $\delta^{13}C$ of *C. wuellerstorfi* is higher than that of other *Cibicidoides* species in the same sample. A large amount of published data has been measured on mixed *Cibicidoides* species without further specification. Such data are not included because changes in the proportion of *C. wuellerstorfi* relative to other species may distort any correlation with ambient sea water chemistry. The abbreviation "Cspp" is here used when discussing single-species results for *Cibicidoides* species other than *C. wuellerstorfi*; the informal term "mixed Cib" is reserved for unnamed mixed species.

106 2.2. Oceanographic data

107 Oceanographic data were compiled from 1° x 1° gridded data sets. Temperature and
108 salinity are taken from the 2013 version of the World Ocean Atlas (WOA13) (Boyer et al., 2013)
109 and DIC and TA from the 2016 version of the Global Ocean Data Analysis Project (Key et al.,
110 2004). Ocean water $\delta^{18}O$ data have been compiled by Schmidt (1999), while a reconstruction of
111 pre-industrial $\delta^{13}C_{DIC}$ ($\delta^{13}C_{DIC\text{-}PI}$) is presented by Eide et al. (2017). The complete set of
112 oceanographic data is limited to the open ocean South of ~62°N, because invasion of
113 anthropogenic CO_2 precludes reconstruction of $\delta^{13}C_{DIC\text{-}PI}$ in the Northern high latitudes (Eide et
114 al., 2017). Marginal seas and silled basins are excluded as well due to sparse oceanographic data
115 availability. For each core locality, oceanographic data were copied from the nearest depth level
116 at the grid-point for the locality. If not available, values were extracted preferably as the mean
117 for surrounding grid points, otherwise the next shallower depth-level was used. In a few cases
118 values are taken from more distant grid points.

119 For illustration purposes, core localities are sub-divided into five ocean regions based on
120 oceanographic characteristics (Fig. 2). The northern boundary of the Antarctic Circumpolar
121 Current at 38°S is used to delineate the Southern Ocean (Talley et al., 2011). Atlantic localities N
122 of 38°S (nAtl) represent low [DIC] and relatively high T, while Indo-Pacific sites N of 38°S
123 (nIPac) have high [DIC] and low T. Most of the deep water localities (>1.5 km) South of 38°S
124 are within the Circumpolar Deep Water (CDW) and, below 4 km, the Antarctic Bottom Water
125 (Emery, 2001). They are split into an Atlantic sector (sAtl) and Indo-Pacific region (sIPac), both
126 of which have intermediate [DIC]. However, the two regions differ in water temperature. Most
127 sAtl sites show very low temperatures (0-1°C) due to mixing of the extremely cold Weddell Sea
128 Bottom Water into CDW (Gill, 1973; Talley et al., 2011). In contrast, values in the sIPac are
129 higher (1-3°C) and similar to temperatures found throughout the deep Indo-Pacific. Most shallow
130 sites (<1.5 km) in the southern Indo-Pacific (shallow sIPac) belong to Antarctic Intermediate
131 Water (AAIW) based on their comparatively low salinities (<34.6 PSU; Emery (2001)).
132 However, the main reason here to group them separately is because they stand out from deeper
133 Indo-Pacific water masses in having lower [DIC] (Fig. 2).

134

135 2.3 Carbonate chemistry

136 Concentrations of dissolved carbonate species were solved iteratively from [DIC] and
137 [TA] using a published macro (Emerson & Hedges, 2008), except that the chemical constants K1
138 and K2 are calculated using functions presented by Millero (1995) and Millero et al. (2006). The
139 degree of carbonate saturation for calcite is expressed either as a ratio:

140 $$\Omega_{cal} = [Ca^{2+}][CO_3^{2-}]/K_{cal} \qquad \text{(Eq. 1)},$$

141 in which K_{cal} is the solubility constant of calcite as a function of temperature, salinity,
142 and pressure (Millero, 1995), or as the offset (in µmol/kg) between measured $[CO_3^{2-}]$ and
143 saturated water:

144 $$\Delta[CO_3^{2-}] = [CO_3^{2-}] - [CO_3^{2-}]_{sat} \qquad \text{(Eq. 2)},$$

145 in which $[CO_3^{2-}]_{sat}$ is calculated from Eq.1 for $\Omega_{cal} = 1$.

146

2.4 Isotope notation

Isotope data are reported in the delta notation (δ), which expresses the isotope composition of a compound as the ‰ (permil) deviation from a standard material. The relevant scales for carbonate $\delta^{18}O$ and $\delta^{13}C$ are the older PDB (Pee Dee Belemnite) scale and its replacement the VPDB (Vienna PDB) scale; the two scales are identical for $\delta^{13}C$ but offset by 0.05‰ for $\delta^{18}O$ (Mook, 2000). However, published $\delta^{18}O$ values for *Cibicidoides* species are used as reported without correction, as it is not always stated clearly in the original publication which scale is used. Offsets between measured isotope data and the expected δ values are denoted by a capital delta (Δ), e.g., $\Delta^{13}C_{Cwue} = \delta^{13}C_{Cwue} - \delta^{13}C_{DIC\text{-}PI}$. The epsilon notation (ε, in ‰) is used here when discussing equilibrium fractionation between two compounds (Mook, 2000) with prefixes 13 and 18 to distinguish between ^{13}C and ^{18}O fractionation factors.

3 Results

3.1 Correlation $\delta^{13}C$ and $\delta^{18}O$

Measured $\delta^{13}C$ and $\delta^{18}O$ for *C. wuellerstorfi* and *Cibicidoides* spp are plotted in Figure 1 against $\delta^{13}C_{DIC\text{-}PI}$ and sea water temperature respectively. Most within-core $\delta^{18}O$ values are within a range of ±0.6 ‰ around the value expected based on ambient temperature. However, core-top data include a high proportion of values that are substantially higher than expected (Fig. 1C). A histogram of $\Delta^{18}O_{Cwue}$ values shows that most values are distributed more or less symmetrically around 0‰ but that there is a long tail of positive values (Fig. 1D). The very high $\Delta^{18}O$ values are interpreted as the result of mixing with glacial specimens in areas with low sedimentation rates. A cut-off level was determined visually based on the shape of histogram of within-core $\Delta^{18}O$, as obvious signs of reworking would have been flagged during pre-screening of the stratigraphic $\delta^{18}O$ time series. Core-top data with $\Delta^{18}O$ >0.6‰ were excluded as most likely affected by inclusion of glacial material. In addition, four data points with $\Delta^{18}O$ <-0.8‰ were excluded as too low, possibly related to down-slope transport. The final $\Delta^{18}O$ data indicate that *C. wuellerstorfi* and *Cibicidoides* spp have the same $\Delta^{18}O$ signature (Fig. 1C, D), with mean and standard deviation of -0.03 ± 0.24‰ (n = 252), and -0.01 ± 0.23 (n = 29) respectively.

In contrast to $\Delta^{18}O$, the results for $\Delta^{13}C$ are not very sensitive to inclusion of reworked or bioturbated material (Fig. 1A, B). The majority of $\delta^{13}C_{Cwue}$ data (168 out of 252 data points) are slightly higher than ambient $\delta^{13}C_{DIC\text{-}PI}$. However, lower than ambient values are common for locations in sAtl and deep nAtl. Data that were excluded based on their $\Delta^{18}O$ do not stand out from other $\delta^{13}C$ data, neither in the cross plot against $\delta^{13}C_{DIC\text{-}PI}$ (Fig. 1A), nor in the histogram of $\Delta^{13}C$ (Fig. 1B). The mean and standard deviation for all $\Delta^{13}C_{Cwue}$ data is 0.04 ± 0.27 ‰. Compared to *C. wuellerstorfi*, other *Cibicidoides* spp are slightly lower, with $\Delta^{13}C$Cspp = -0.24 ± 0.31 ‰ (Fig 1A, B) but the difference is not statistically significant.

A cross-plot of $\Delta^{13}C$ and $\Delta^{18}O$ for all *Cibicidoides* data included here shows that the two isotope offsets are significantly correlated (Fig. 3A). The correlation coefficients for *C. wuellerstorfi* and *Cibicidoides* spp are respectively r = 0.30 (n = 252, $P_{(r=0)} < 10^{-5}$) and r = 0.69 (n = 29, $P_{(r=0)} < 10^{-4}$). The orthogonal regression lines for *C. wuellerstorfi* and *Cibicidoides* spp are nearly parallel but offset by ~0.3‰ in $\Delta^{13}C$ for the same $\Delta^{18}O$. Paired analyses of *C. wuellerstorfi* and *Cibicidoides* spp are available for 13 locations (Fig. 3B, C). Visual inspection of the cross plots indicates that *C. wuellerstorfi* has higher $\Delta^{13}C$ than other *Cibicidoides* spp but

that $\Delta^{18}O$ values are similar. The difference in $\Delta^{13}C$ between paired *C. wuellerstorfi* and *Cibicidoides* spp (0.21 ± 0.26‰) is not statistically significant but it is similar to the offset in the data set as a whole (Figs. 1, 3A.).

A further feature to note is that between-sample variability in $\delta^{13}C_{Cwu}$ is high in areas where $\Delta^{13}C_{Cwue}$ is negative. The standard deviation for multiple analyses of *C. wuellerstorfi* in the same core is shown in Figure 3 D and E. There is a strong negative correlation between $\Delta^{13}C_{Cwue}$ and the between-sample standard deviation ($r = -0.60$, $P_{(r=0)} << 10^{-5}$). That is, in areas where $\Delta^{13}C_{Cwue} < 0$ the reproducibility of repeated $\delta^{13}C$ analyses is poor. In contrast, the variability of $\Delta^{18}O_{Cwue}$ is independent of the measured value ($r = -0.04$).

3.2 stable isotope composition and carbonate chemistry

3.2.1 bivariate correlation patterns

Correlation coefficients for $\Delta^{13}C_{Cwue}$ and $\Delta^{18}O_{Cwue}$ with the oceanographic variables used in this study are shown in Table 1, as well as selected coefficients for oceanographic variables amongst each other. The bivariate correlation between $\Delta^{13}C_{Cwue}$ and all oceanographic variables is significant at the 99% confidence level. For $\Delta^{18}O_{Cwue}$ the correlation is less pronounced. Notably, the correlation between $\Delta^{18}O$ and sea water temperature is not significant. Results here confirm the conclusion of Schmittner et al. (2017), that Δ^{13}_{Cwue} correlates with water depth. Both $\Delta^{13}C$ and $\Delta^{18}O$ correlate significantly with water depth with $r = -0.468$ and $r = -0.381$ respectively; in both cases $P_{(r=0)} << 10^{-5}$. Indeed, the correlation with depth is amongst the strongest in the data set as a whole and is exceeded only by the correlation with $[CO_2]_{aq}$ or fCO_2 (Table 1).

However, the correlation between the isotope offsets and water depth is not a simple global relation. Cross plots of $\Delta^{13}C_{Cwue}$ against selected variables show that the relation depends on geographic location (Fig. 4). Results for $\Delta^{18}O_{Cwue}$ are broadly similar although the correlation is less pronounced (Figure S1). Amongst the oceanographic variables, water depth, temperature and carbonate saturation (Ω_{cal} and $\Delta[CO_3^{2-}]$) correlate strongly with each other, but less so with other variables (Table 1). These variables are here loosely grouped as "depth-related variables". They correlate with $\Delta^{13}C_{Cwue}$ especially when data are split according to ocean region (Fig. 4a-c). Values for the nAtl and nIPac are offset from each other by ~0.3‰ on average. However, the magnitude of change with water depth (0.1‰/km), temperature (0.1‰/°C) and $\Delta[CO_3^{2-}]$ (0.1‰ per 16-20 µmol/kg) is the same in both ocean regions (Fig. 4a-c). Results for southern locations are less well defined.

In contrast to the depth related variables, the concentration of dissolved carbonate species varies between ocean basins (Broecker & Peng, 1982; Key et al., 2004), with high [DIC], [TA], and $[HCO_3^-]$ and low pH and $[CO_3^{2-}]$ in the nIPac compared to the nAtl with little or no overlap between the two regions; intermediate values are confined to the sAtl and sIPac (Fig. 2, 4d, e). . All these variables are all strongly correlated with each other with $|r| \geq 0.9$ as well as with $\Delta^{13}C_{Cwue}$ (Table 1). As a result, there is a positive correlation in the full suite of data between $\Delta^{13}C_{Cwue}$ and [DIC], due to and overall trend from low $\Delta^{13}C_{Cwue}$/low [DIC]in the Atlantic to high $\Delta^{13}C_{Cwue}$/high [DIC]in the Indo-Pacific (Fig. 4d). A similar pattern is found for pH (Fig. 4e) and TA, $[HCO_3^-]$, and $[CO_3^{2-}]$ (not shown). However, within each region separately any correlation between $\Delta^{13}C_{Cwue}$ and these carbonate chemistry variables is not significant (Table 1; Fig. 4).

Of the remaining variables, salinity, $[CO_2]aq$, and fCO_2 show a pattern that is intermediate between the depth-related and carbonate-chemistry variables, in that correlations within the individual ocean regions are mostly weaker than for the data set as a whole but still significant at least in the nAtl. The cross-plot of $\Delta^{13}C_{Cwue}$ with fCO_2 is shown in Figure 4f as an illustration. The data for $\Delta^{18}O_{Cwue}$ follow the same trends as in $\Delta^{13}C_{Cwue}$, with the exception that none of the correlation coefficients for $\Delta^{18}O$ with oceanographic variables within nIPac are significant (Table 1; Figure S1).

3.2.2 multiple linear regression

The presence of an offset between Atlantic and Indo-Pacific data in combination with a depth-related trend in both oceans implies that at least two variables are needed to describe variation in $\Delta^{13}C_{Cwue}$ in the global data. Multiple linear regression was therefore performed with all possible pairs of oceanographic variables as the independent variables, to find which variables are the best suited to describe variation in $\Delta^{13}C_{Cwue}$ and $\Delta^{18}O_{Cwue}$ as the dependent variable. A limited number of combinations with more variables was explored also. The amount of variation explained (R^2) by the various regressions with two independent variables is listed in Table S1. Results are broadly similar for $\Delta^{13}C_{Cwue}$ and $\Delta^{18}O_{Cwue}$, however, in all cases $\Delta^{13}C$ correlates more strongly with ambient conditions than $\Delta^{18}O_{Cwue}$. For $\Delta^{13}C_{Cwue}$, the highest R^2 values are found when the isotope offsets are compared to one of the depth-related variables (depth, temperature, carbonate saturation) in combination with one of the carbonate chemistry variables. Various combinations of two independent variabilities explain more than 35% of the total variance in $\Delta^{13}C_{Cwue}$ ($R^2 \geq 0.35$), up to a maximum of 42.6% for $\Delta^{13}C_{Cwue}$ against temperature and [DIC]. Since different combinations yield broadly similar results, a subjective choice is made here to select [DIC], temperature, and $\Delta[CO_3^{2-}]$ for further analysis.

The regression equation for $\Delta^{13}C_{Cwue}$ against [DIC] and temperature is:

$$\Delta^{13}C_{Cwue} = -6.212 + 0.1217T + 0.0026[DIC] \text{ (eq. 3)},$$

which explains 42.6% of the total variance. The amount of variance explained is slightly lower (39.1%) for the regression for $\Delta^{13}C_{Cwue}$ against $\Delta[CO_3^{2-}]$ and [DIC]:

$$\Delta^{13}C_{Cwue} = -7.283 + 0.0080\Delta[CO_3^{2-}] + 0.0032[DIC] \text{ (eq. 4)}.$$

Equations 3 and 4 are shown as contour plots in Figure 5. The amount of variance explained can be increased further to 47.1% if both temperature and $\Delta[CO_3^{2-}]$ are used in combination with [DIC]:

$$\Delta^{13}C_{Cwue} = -7.424 + 0.0042\Delta[CO_3^{2-}] + 0.0032[DIC] + 0.0815T, \text{ (eq. 5)}.$$

The Standard Error on the estimate (SE) is 0.21 for Eq. 3 and 4 and SE = 0.20 for Eq. 5; the errors on the regression constants vary between 8 - 22%. The maximum amount of explained variance in $\Delta^{13}C_{Cwue}$ is 50.3% when all 12 oceanographic variables are included in the regression analysis simultaneously.

For $\Delta^{18}O_{Cwue}$, the amount of variance explained by ambient conditions is noticeably lower than for $\Delta^{13}C_{Cwue}$ (Table S1). The maximum explained variance is 35.3% when all variables are used in the regression analysis. Regression of $\Delta^{18}O_{Cwue}$ against [DIC] and $\Delta[CO_3^{2-}]$ and against [DIC] and temperature accounts for respectively 19.4% and 18.7% of the total

variation. The equation for $\Delta^{18}O_{Cwue}$ against [DIC] and $\Delta[CO_3^{2-}]$ is shown for illustration purposes to allow comparison with the results for $\Delta^{13}C_{Cwue}$:

$$\Delta^{18}O_{Cwue} = -4.829 + 0.0046\Delta[CO_3^{2-}] + 0.0021[DIC] \quad \text{(eq. 6)},$$

which explains 19.4% of the variation, with SE = 0.22.

Equations 3-6 are applied to LGM reconstructions to illustrate the magnitude of change in $\Delta^{13}C_{Cwue}$ and $\Delta^{18}O_{Cwue}$ that can be expected in response to climate change (Table 2).

3.2.3 Other *Cibicidoides* spp.

Data for named *Cibicidoides* species other than *C. wuellerstorfi* are limited to a few areas in the Atlantic and shallow sIPAC, which have low to intermediate [DIC] (Fig. 6, Nederbragt (2023)). Data from areas with high [DIC] in the Pacific are lacking. As a result, the data cover only a subset of the full range of oceanographic conditions (Fig. 6). Similar to $\Delta^{13}C_{Cwue}$, $\Delta^{13}C_{Cspp}$ correlates positively with $\Delta[CO_3^{2-}]$ ($r = 0.58$; $P_{(r=0)} = 4 \cdot 10^{-4}$) but in contrast the correlation with [DIC] is negative ($r = -0.48$; $P_{(r=0)} = 0.004$). The latter can be attributed to the selection of core localities: paired $\Delta^{13}C_{Cwue}$, which are available for a subset of the data, also show a negative correlation with [DIC] ($r = -0.73$; $n = 16$; $P_{(r=0)} = 0.007$) in contrast to the positive correlation within the data set as a whole (Table 1).

4 Discussion

4.1 Water mass characteristics and *C. wuellerstorfi* isotope composition

Amongst deep water benthic foraminifera the genus *Cibicidoides* has been considered as an accurate recorder of ambient $\delta^{13}C_{DIC}$ (Curry et al., 1988; Duplessy et al., 1984; McCorkle et al., 1990; Schmittner et al., 2017; Zahn et al., 1986). Based on analysis of *C. wuellerstorfi* mainly, but including some data from mixed species, Duplessy et al. (1984) concluded that $\delta^{13}C$ of *Cibicidoides* spp remained in a narrow range around the expected value in a set of 44 globally distributed localities; the authors reported a mean $\Delta^{13}C_{Cib}$ and standard deviation of 0.07 ± 0.15‰. Since then the number of studied sections has increased. The mean value for $\Delta^{13}C_{Cwue}$ in the current compilation of 252 locations remains essentially unchanged; however, the recorded variability is nearly twice as high ($\Delta^{13}C_{Cwue}$ = 0.04‰ ± 0.27‰, section 3.1). The relatively low variability found in early studies appears largely due to the almost complete absence of material from water depths below 4 km and the southern latitudes in the Atlantic Ocean (Duplessy et al., 1984). Subsequent sampling of the deep Atlantic and especially the Atlantic sector of the Southern Ocean revealed that $\Delta^{13}C_{Cib}$ can be substantially lower than expected (Hodell et al., 2003; Mackensen et al., 1993).

Mackensen et al. (1993) first reported the systematic occurrence of negative $\Delta^{13}C_{Cib}$ along a transect South of 35°S in the South Atlantic. The authors suggested that $\delta^{13}C$ of *Cibicidoides* spp was influenced by isotopically light CO_2 from re-mineralisation of organic matter within a seasonal phytodetritus layer. It is indeed well established that infaunal benthic foraminifera can have very low $\delta^{13}C$ due to organic matter decomposition within the sediment (McCorkle et al., 1990). Phytodetritus deposits are an important food source for benthic foraminifera in the deep sea, and may well affect epifaunal benthic organisms. However, phytodetritus deposits are not limited to specific regions or water depths, but can occur anywhere

(Gooday, 2002; Moodley et al., 2005). In contrast, strongly negative $\Delta^{13}C_{Cwue}$ values (<-0.40‰) are common in the sAtl below 2.5 km and the deep Atlantic below 3.5 km, but they occur rarely elsewhere (Fig. 4A) (Schmittner et al., 2017). It is therefore likely that the presence of very low $\Delta^{13}C_{Cwue}$ is linked to a feature that is unique to the southern South Atlantic. In addition, $\Delta^{18}O_{Cwue}$ is affected in tandem with $\Delta^{13}C_{Cwue}$ (Fig. 3). This suggests that there are similarities with other groups of calcifying organisms that show a link between carbonate chemistry and stable isotope composition (Krief et al., 2010; Juranek et al., 2003; McConnaughey, 1989a; Spero et al., 1997; Ziveri et al., 2012). Results found here indicate that the very low temperatures, due to mixing with WSBW, and strong undersaturation are important factors that contribute to strongly negative $\Delta^{13}C_{Cwue}$ values in the deep southern South Atlantic. In the following sections the relative importance of chemical equilibrium reactions versus biological, or vital, effects is discussed. The fact that a large number of locations are situated in the lysocline ($\Delta[CO_3^{2-}]<0$; Fig. 4) suggests that post mortem dissolution may play a role as well. However, there is insufficient published information on the preservation of *Cibicidoides spp* to evaluate its importance.

4.2 Multiple linear regression

Multiple linear regression is used here to illustrate the relation between $\Delta^{13}C_{Cwue}$ and ambient conditions. However, the predictive potential of all regression equations (Eq 3-6) is low. With the relatively low amount of variance explained by Eqs 3-6 (<50%) any confidence intervals around a new observation would be wider than the spread in the entire isotope data set (Sokal & Rohlf, 1994). Furthermore, the presence of collinearity, i.e., the strong correlation between the oceanographic variables used in this study (Table 1), complicates the interpretation of regression coefficients. The explained variance is partitioned more or less arbitrarily between the independent variables when they are intercorrelated (Farrar & Glauber, 1967; Nimon & Oswald, 2013). Although there are various methods to improve the regression model (Nimon & Oswald, 2013), interpretation of the relative importance of the various variables remains somewhat subjective.

The offset between $\Delta^{13}C_{Cwue}$ in the Atlantic and Indo-Pacific Oceans is here described using [DIC] in combination with temperature and/or $\Delta[CO_3^{2-}]$ (Fig. 5). Several studies have found that the isotope composition of biogenic carbonate is dependent on ambient carbonate chemistry. The effect is described variously as a response to changing pH or $[CO_3^{2-}]$ (Spero et al., 1997; Zeebe, 1999; Ziveri et al., 2012). However, in practice pH, $[CO_3^{2-}]$, [DIC] and [TA] are highly correlated in the world oceans (Table 1) such that it is difficult to decide if any specific variable is the underlying cause of the change in isotope composition. The choice here to use [DIC] rather than pH is based on the fact that it is conceptually linked with $\delta^{13}C_{Cwue}$, as aging of bottom waters increases [DIC] but decreases $\delta^{13}C_{DIC}$ through the remineralisation of sinking organic matter in the deep ocean (Broecker & Peng, 1982; Curry et al., 1988; Duplessy et al., 1984). In addition, [DIC] and [TA] are measured directly in the modern ocean (Key et al., 2004), from which all other carbonate chemistry variables (pH, $[HCO_3^-]$, $[CO_3^{2-}]$) are calculated.

The depth-related variables (saturation state, temperature, and water depth or pressure) are also intercorrelated, because saturation state is strongly dependent on ambient temperature and pressure (eq 1, (Millero, 1995)). The correlation between $\Delta^{13}C_{Cwue}$ and water depth, which was previously described by (Schmittner et al., 2017), is here assumed to be indirect, because of

the impact of pressure on saturation state. In contrast, both saturation state and temperature are likely to have a direct impact on the biology of deep sea calcareous organisms. Carbonate saturation state determines the amount of CO_3^{2-} available for calcification, while temperature affects metabolic rates in exothermic organisms (e.g. , Bemis et al., 2000; Gillooly et al., 2001; Juranek et al., 2003; Krief et al., 2010). Of the two saturation state variables, $\Delta[CO_3^{2-}]$ has the practical advantage that it can be reconstructed from fossil material (Yu & Elderfield, 2007). The regression results confirm that temperature and saturation state each have an effect on $\Delta^{13}C_{Cwue}$. Regression equation 5, which relates $\Delta^{13}C_{Cwue}$ to both temperature and $\Delta[CO_3^{2-}]$ with [DIC], explains noticeably more variation (47.1%) than equations 3 and 4 for temperature and $\Delta[CO_3^{2-}]$ separately (42.6% and 39.1% respectively). However, the actual values of the regression coefficients, which describe the magnitude of change in $\Delta^{13}C_{Cwue}$, may not reflect the real contribution of temperature relative to $\Delta[CO_3^{2-}]$ due to the collinearity between the two variables (Farrar & Glauber, 1967; Nimon & Oswald, 2013).

4.3 Stable isotope composition and ambient conditions

4.3.1 Temperature

If taken at face values, the regression coefficients for temperature in Eq. 3 (0.1217) and Eq. 5 (0.0815) imply that $\delta^{13}C$ in *C. wuellerstorfi* is highly sensitive to ambient temperature, with a shift of ~0.1‰ in $\Delta^{13}C_{Cwue}$ per 1°C. Although the $\delta^{13}C$ of various planktonic and benthic foraminiferal species is known to be affected by ambient conditions and physiological processes, the actual role of temperature is poorly constrained. Based on reinterpretation of published precipitation experiments, Mook (2000) estimated that the $\delta^{13}C$ fractionation between solid carbonate and dissolved HCO_3^- ($^{13}\varepsilon_{CaCO3/HCO3-}$) varies with temperature by ~0.05‰/°C. This temperature equation was used to model $\delta^{13}C_{Cwue}$ in response to equilibrium diffusion of DIC around the foraminiferal shell (Hesse et al., 2014). The outcome was that the temperature sensitivity of inorganic carbonate is incorporated into the foraminiferal shell. However, it has to be noted that calcification processes within the foraminiferal cell are not included in the model (Hesse et al., 2014). In contrast to Mook (2000), Romanek et al. (1992) concluded based on another set of carbonate precipitation experiments that $^{13}\varepsilon_{CaCO3/HCO3-}$ remains constant between 10 - 40°C. Indeed, Bemis et al., (2000) found that $\delta^{13}C$ of *Orbulina universa* was not sensitive to changing temperature as long as it was grown under dark conditions to inhibit activity of its symbionts. However, the $\delta^{13}C$ of *O. universa* did change with temperature when grown under light conditions, due to the symbionts contributing isotopically light CO_2. *Globerina bulloides* also showed a correlation between $\delta^{13}C$ and temperature, which was attributed to increased growth rates and enhanced incorporation of metabolic CO_2 at higher temperatures (Bemis et al., 2000). This would suggest that any correlation between foraminiferal $\delta^{13}C$ and temperature is related to vital effects rather than chemical equilibrium.

In contrast to $\delta^{13}C$, the temperature sensitivity of carbonate $\delta^{18}O$ due to chemical equilibrium with ambient H_2O is well established. Numerous experimental and empirical temperature equations have been published, which are offset from each other but show similar temperature dependencies with values of -0.2 - -0.3‰/°C depending on the actual temperature ((Bemis et al., 1998) and references there-in). Here, the $\delta^{18}O_{Cwue}$ data have been corrected for the effect of temperature using an equation established for inorganic calcite precipitation (Bohm et

al., 2000; Kim & O'Neil, 1997). This was an a priori choice, because all variables except temperature can be held constant under experimental conditions. However, it has to be noted that the results may not represent "true" equilibrium precipitation of carbonate, as the specific $\delta^{18}O$ values are dependent on the composition of the reactants and their concentration (Kim & O'Neil, 1997; Watkins et al., 2014; Zeebe, 1999). In contrast, Marchitto et al. (2014) established an empirical equation specifically for *Cibicidoides* spp, which is based mainly on data from the North Atlantic. This equation is therefore potentially biased by regional oceanic conditions. In practice, however, the offset between the two equations is <0.2‰ throughout the observed temperature range (Fig. 1).

Within the data set as a whole, the resultant $\Delta^{18}O_{Cwue}$ values are not significantly correlated with temperature (Table 1). However, any relation between $\Delta^{18}O_{Cwue}$ and temperature is potentially complicated. The equilibrium effect of temperature on $^{18}\varepsilon_{CaCO3/H2O}$ causes a decrease in carbonate $\delta^{18}O$ as temperature increases (Kim & O'Neil, 1997). In contrast, $\Delta^{13}C_{Cwue}$ increases as temperature increases (Fig. 4). Given the positive correlation between $\Delta^{18}O_{Cwue}$ and $\Delta^{13}C_{Cwue}$ (Fig. 3) and assuming that the influence of temperature on $\Delta^{13}C_{Cwue}$ is due to vital effects, the relation between $\Delta^{18}O_{Cwue}$ and temperature is expected to be the inverse of the equilibrium relation between $\delta^{18}O$ and temperature. Indeed, there is a positive correlation between $\Delta^{18}O_{Cwue}$ and temperature within the subset of Atlantic data (Table 1, Fig. S1). The lack of clear correlation in the full suite of data may therefore reflect the presence of noise due to competing equilibrium reactions and vital effects, but for practical purposes $\Delta^{18}O_{Cwue}$ is essentially independent of temperature.

4.3.2 Carbonate chemistry

Several culture experiments have shown that the $\delta^{18}O$ of calcareous organisms is sensitive to a change in the pH, or $[CO_3^{2-}]$, of ambient water (Krief et al., 2010; Spero et al., 1997; Ziveri et al., 2012). Although the exact mechanism is not fully understood, the large isotope contrast between CO_3^{2-} and HCO_3^- is thought to play a role. Values for $^{18}\varepsilon_{CO32-/HCO3-}$ are ~-7‰ in the range of temperatures found in the modern ocean (Beck et al., 2005). As long as calcification involves some form of quantitative precipitation of all available DIC species, the $\delta^{18}O$ of carbonate would decrease when pH increases because isotopically light $[CO_3^{2-}]$ increases (Devriendt et al., 2017; Zeebe, 1999). Indeed, in all three culture experiments it was found that $\delta^{18}O$ decreases when pH (or $[CO_3^{2-}]$) was increased. However, the magnitude of change is species specific (Krief et al., 2010; Spero et al., 1997; Ziveri et al., 2012), suggesting that biological factors, or vital effects, play a role.

The response of skeletal $\delta^{13}C$ to changing pH is more variable. In contrast to $\delta^{18}O$, large changes in carbonate $\delta^{13}C$ in response to ambient pH are not expected as a result of chemical equilibrium reactions. The fractionation $^{13}\varepsilon_{CO32-/HCO3-}$ is too small (~-0.5‰) to allow substantial fractionation due to variation in $[CO_3^{2-}]$ and $[HCO_3^-]$ (Hesse et al., 2014; Mook, 2000). Still, co-variation between $\delta^{13}C$ and $\delta^{18}O$ was observed in two of the culture experiments mentioned (Krief et al., 2010; Spero et al., 1997). Krief et al. (2010) concluded that changes in skeletal $\delta^{13}C$ in corals are mainly due to variation in photosynthesis of the symbionts and uptake of metabolic CO2 under varying pH and pCO2 conditions. In contrast, Spero et al (1997) could exclude the effect of symbiont activity by growing *O. universa* under low light conditions. The authors observed that $\delta^{13}C$ decreased by ~4‰ with increasing $[CO_3^{2-}]$ across a range of pH values

between 7.7 - 8.8, in concert with a decrease in $\delta^{18}O$ of ~1.5 ‰. The magnitude of change in $\delta^{18}O$ is consistent with chemical equilibrium reactions but the much larger shift in $\delta^{13}C$ requires the presence of vital effects (Bijma et al., 1999; Zeebe et al., 1999).

Results here for *C. wuellerstorfi* provide an example that covariation between $\delta^{13}C$ and $\delta^{18}O$ in foraminifera in response to ambient DIC also occurs under natural conditions. However, the correlation between $\Delta^{13}C_{Cwue}$ /$\Delta^{18}O_{Cwue}$ and pH or $[CO_3^{2-}]$ is not the same as that observed in *O. universa.* There is a significant but weak negative correlation between $\Delta^{13}C_{Cwue}$ /$\Delta^{18}O_{Cwue}$ and pH (Table 1), which is similar to the correlation observed by Spero et al (1997). However, a much stronger positive correlation with both [DIC] and $\Delta[CO_3^{2-}]$ is found when multiple variables are considered (equations 4 - 6). The negative correlation with pH is here interpreted as an artefact of the uneven distribution of sample locations across the range of conditions in the oceans (Fig. 4e). Negative $\Delta^{13}C_{Cwue}$ data are most frequent in the deep Atlantic, which has high pH, while $\Delta^{13}C_{Cwue}$ is generally positive in the Pacific, which has low pH. However, there is no significant relation between $\Delta^{13}C_{Cwue}$ /$\Delta^{18}O_{Cwue}$ and pH within either ocean separately (Table 1). Overall, the positive correlation with $\Delta[CO_3^{2-}]$ is taken to mean that undersaturation in the deep ocean is a major factor, with $\Delta^{13}C_{Cwue}$ /$\Delta^{18}O_{Cwue}$ decreasing when $\Delta[CO_3^{2-}]$ decreases.

Given the diverse responses of different organisms it seems likely that species-specific vital effects are important. In the case of *C. wuellerstorfi* and other *Cibicidoides* species such vital effects may well be related to the degree of calcite saturation in the deep ocean, either directly or indirectly.

4.3.3 Habitat and calcite precipitation rates

Benthic foraminiferal habitat is usually discussed in terms of substrate and food supply (e.g., Gottschalk et al., 2016; Jorissen et al., 1998; Lutze & Thiel, 1989; Wollenburg et al., 2018). However, the ability to calcify in undersaturated conditions may well be a another factor. Around half of all localities included in this paper are located within the lysocline, i.e., $\Delta[CO_3^{2-}] < 0$ (Fig. 4). However, foraminifera can create saturated conditions within their cell, because they raise pH internally as part of the calcification process (Bentov et al., 2009). Still, it seems plausible that undersaturated conditions equate to some form of environmental stress, and that this has an effect on the stable isotope signature (Bijma et al., 1999). It is noticeable that the variability in $\delta^{13}C_{Cwue}$ between samples increases when $\Delta^{13}C_{Cwue}<0$ (fig. 3d). The fact that *Cibicidoides* spp can actively seek out a favourable location (Lutze & Thiel, 1989; Wollenburg et al., 2018) suggests that within the lysocline individual specimens are more likely to inhabit a range of different micro-habitats to mitigate adverse conditions in the wider environment.

One of the ways in which *Cibicidoides* species could modify their isotope signature is by alternating between epi- and infaunal habitats. *Cibicidoides pachyderma* (morphotype *C. mundulus*) has been cultured at two different pH-levels in high-pressure cells with artificial sediment (Wollenburg et al., 2018). The authors observed that the foraminifera became infaunal at pH=7.4 while specimens at pH=8.0 actively sought an epifaunal location with active water flow. If *Cibicidoides* species exhibit similar behavior under natural conditions, then the low $\Delta^{13}C$ signature in the deep Atlantic could be acquired from organic matter decay within the sediment rather than from phytodetritus on the sediment surface (Mackensen et al., 1993; Wollenburg et al., 2018). However, the pH-levels applied during the experiment far exceed the range of natural values in the deep ocean (pH 7.79-7.98; Fig. 4). Furthermore, it does not explain why very low $\Delta^{13}C_{Cwue}$ occur in the deep Atlantic but rarely in the deep Pacific (Fig. 4). Lastly, there are

insufficient data to determine if there is a consistent relation between the habitat of *Cibicidoides* species and ambient chemistry under natural conditions. The presence/absence of suitable substrates may also play a role. Where hard substrates are available, *C. wuellerstorfi* is preferentially attached to any solid surface that is elevated above the sea floor (Lutze & Thiel, 1989). In contrast, it has a shallow infaunal habitat in clayey sediments all along a depth transect off Cape Blanc, NW Africa, down to 3010 m water depth (Jorissen et al., 1998). The $\delta^{13}C_{Cwue}$ was not measured in this study. However, data included here from the wider region show that conditions are generally saturated ($\Delta[CO_3^{2-}] > 0$) with $\Delta^{13}C_{Cwue} \geq -0.06$‰ in the relevant depth range (Nederbragt, 2023). For the sediments off Cape Blanc this implies that *C. wuellerstorfi* can be infaunal under saturated conditions without displaying a decrease in $\delta^{13}C$.

As an alternative explanation for the correlation between isotope composition of *Cibicidoides* spp and ambient carbonate chemistry I suggest that variation in saturation state has a direct effect on calcification processes within the foraminiferal test. Reduced calcification rates have been observed in response to lowering of ambient pH in various species of foraminifera (Erez (2003) and references therein; Bijma et al., 1999). A correlation between isotope composition and calcification rates has been observed in corals, although not directly in foraminifera (Bijma et al., 1999; McConnaughey, 1989a). From inorganic carbonate precipitation experiments it is known that at least $\delta^{18}O$ is dependent on the concentration of the reactants (Kim & O'Neil, 1997; Watkins et al., 2014; Zeebe, 1999). As such, the observed variation in $\Delta^{13}C$ and $\Delta^{18}O$ may well represent isotope fractionation due to vital effects within the foraminiferal test rather than variation in ambient $\delta^{13}C_{DIC}$. This does not exclude the possibility that switching between epifaunal and infaunal habitats plays a role. For example, pore water within sediment in the lysocline may have elevated levels of [DIC] or $\Delta[CO_3^{2-}]$ due to carbonate dissolution within the sediment, which would favor an infaunal habitat if ambient undersaturation is a limiting factor.

There may be a parallel with the inorganic calcite precipitation experiments of (Zuddas & Mucci, 1994), who studied calcite precipitation rates in high ionic strength solutions to mimic reactions in sea water. The authors found that precipitation rates increased with increasing pCO_2 as well as increasing Ω_{cal}. That is, similar to the current data, two variables in the carbonate system are required to describe the observed variation. In the precipitation experiment, pCO2 was proportional to [DIC] as pCO_2 was adjusted by adding Na_2CO_3 and $NaHCO_3$ while maintaining constant ionic strength. Zuddas & Mucci (1994) suggested that two variables are needed to predict precipitation rates because both HCO_3^- and CO_3^{2-} contribute to the precipitation reaction. The total range of variation in pCO_2 during the experiment was three orders of magnitude larger than found under natural marine conditions. As such, results are not immediately applicable to biological carbonates formed under natural conditions. Still, it suggests that low $\Delta^{13}C_{Cwue}$ and $\Delta^{18}O_{Cwue}$ may be induced by a decrease in calcification rates in an environment with low [DIC] and $\Delta[CO_3^{2-}]$. The fact that $\Delta^{13}C_{Cwue}$ also correlates with temperature (Fig. 4B; section 4.3.1) is consistent with this hypothesis, since metabolic rates are expected to decrease when temperature decreases (Gillooly et al., 2001). In theory this hypothesis can be tested, by measuring the weight and size of single *Cibicidoides* specimens before analysing their isotope composition. However, any relation, if present, could be complicated by post-mortem dissolution because of the undersaturated environment.

4.3.4 Other *Cibicidoides* spp

Other *Cibicidoides* species are here presented as a group, because there are not enough published data for individual species to substantiate any global trends. Still, the available data suggest that the stable isotope composition of *Cibicidoides* spp correlates with ambient carbonate chemistry similar to *C. wuellerstorfi*, except that $\Delta^{13}C_{Cspp}$ is on average 0.2-0.3‰ lower than $\Delta^{13}C_{Cwue}$ (Fig. 3, 6). However, the data are highly variable while covering only a relatively narrow range of oceanographic conditions. The offset between $\Delta^{13}C_{Cwue}$ and Δ^{13}CCspp is therefore not statistically different from zero, and it is not clear if the offset is constant or depends on oceanographic conditions.

The suggestion that $\delta^{13}C_{Cwue}$ - $\delta^{13}C_{Cspp}$ is dependent on ambient conditions was raised by Gottschalk et al. (2016). The authors observed that the offset between *C. wuellerstorfi* and *C. kullenbergi* changed from ~0.25‰ in the Holocene to ~0.75‰ during the last glacial in a set of sediment cores from the southern South Atlantic. In one of the cores (TTN057-6), the increased glacial offset in $\delta^{13}C$ coincides with lower $\Delta[CO_3^{2-}]$, as indicated by lower carbonate content and increased fragmentation of planktonic foraminifera (Hodell et al., 2003). *Cibicidoides kullenbergi* (or *C. mundulus* depending on the synonomy used) has a habitat ranging from bathyal to abyssal, while *C. wuellerstorfi* is primarily bathyal (Holbourn et al., 2013). This suggests that *C. mundulus/kullenbergi* can withstand more severely undersaturated conditions than *C. wuellerstorfi*. Possibly, the more extreme habitat is accompanied by a further decrease in $\Delta^{13}C_{Cspp}$.

However, it is not clear if there is a consistent correlation between the offset $\delta^{13}C_{Cwue}$ - $\delta^{13}C_{Cspp}$ and saturation state. The glacial deep Atlantic was more undersaturated than the modern ocean (Yu et al., 2013), yet both *C. wuellerstorfi* and mixed-Cib show the same change in $\delta^{13}C$ between LGM and LH values on average. The shift is 0.63 ± 0.35 ‰ for *C. wuellerstorfi* (n = 99) compared to 0.65 ± 0.35 ‰ for mixed-Cib (n = 44) at depths >2.5 km (data from (Hesse et al., 2011; Peterson et al., 2014)). On the other hand, mixed-Cib includes *C. wuellerstorfi* in unknown proportions and may not be representative for *C. mundulus/kullenbergi*. A further complication is that different morphotypes within a given species may have a different isotope signature (Gottschalk et al., 2016), which means that differences in species concept between authors may also play a role. Until further data become available the offset $\delta^{13}C_{Cwue}$ - $\delta^{13}C_{Cspp}$ is best assumed to be variable (0.21 ± 0.26‰, section 3.1) but not dependent on ambient conditions.

5 Conclusions and paleoceanographic implications

Variation in carbonate chemistry in the deep sea explains up to 50.3% and 35.3% of the variance in $\Delta^{13}C_{Cwue}$ and $\Delta^{18}O_{Cwue}$ respectively. Both $\Delta^{13}C_{Cwue}$ and $\Delta^{18}O_{Cwue}$ increase when [DIC] and $\Delta[CO_3^{2-}]$ increase, while only $\Delta^{13}C_{Cwue}$ correlates with temperature. The underlying mechanism is discussed in terms of chemical equilibrium, kinetic effects, and vital effects, but remains essentially unknown. A link with reduced calcification in undersaturated conditions in the deep ocean is suggested. Remaining variation cannot be attributed. It may represent a combination of random noise and analytical error, as well as systematic variation due to environmental factors that are not considered here, like food supply, substrate, or post-mortem dissolution (Corliss et al., 2006; Jorissen et al., 1998; Lutze & Thiel, 1989; Wollenburg et al., 2018).

576 To illustrate the magnitude of change in $\Delta^{13}C_{Cwue}$ and $\Delta^{18}O_{Cwue}$ that can be expected
577 when oceanic conditions change, equations 3-6 have been applied to LGM conditions (Table 2).
578 During LGM, deep oceans everywhere were close to freezing (Adkins et al., 2002; Duplessy et
579 al., 2002). Assuming that both the deep Pacific and Atlantic were around -1 °C implies that
580 temperatures were lower by 2.5°C and 3.5°C respectively compared to LH (Fig. 2). The oceanic
581 carbon budget during LGM is estimated at 38,000 Gt, which is 1.5 Gt, or 2%, higher than the
582 pre-industrial value (Sundquist, 1993). Assuming the increase in carbon to be distributed evenly
583 across all water masses implies that [DIC] during LGM was ~45µmol/kg higher than modern.
584 Lastly, during LGM, $\Delta[CO_3^{2-}]$ was similar to LH values in the Pacific but the Atlantic was more
585 undersaturated by -20µmol/kg (Anderson & Archer, 2002; Yu et al., 2013).

586 The effect on $\Delta^{18}O_{Cwue}$ is minor compared the total variability in the $\delta^{18}O$ data. Overall,
587 $\Delta^{18}O_{Cwue}$ is expected to change by ≤0.1‰ in response to glacial/interglacial variation in [DIC]
588 and $\Delta[CO_3^{2-}]$ (Table 2), a value that is negligible compared to the ~1.5‰ change in $\delta^{18}O_{Cwue}$ due
589 to ice cap effects and changing deep sea temperatures (Duplessy et al., 2002; Lisiecki & Raymo,
590 2005). However, the effect of changing $\Delta[CO_3^{2-}]$ can play a role in the evaluation of coupled
591 Mg/Ca - $\delta^{18}O$ data. $\Delta^{18}O_{Cwue}$ is less sensitive to changes in saturation state than the Mg/Ca
592 composition of *C. wuellerstorfi* but the two reinforce each other. That is, the effect of salinity
593 needed to explain paired Mg/Ca - $\delta^{18}O$ data will be overestimated. A change of -20µmol/kg in
594 $\Delta[CO_3^{2-}]$ for LGM-LH in the deep Atlantic is expected to effect a ~-0.17 mmol/mol change in
595 Mg/Ca, which is equivalent to -1 to -2 °C depending on actual temperature (Elderfield et al.,
596 2006; Yu et al., 2013). The equivalent effect on $\Delta^{18}O_{Cwue}$ is ~-0.09‰ (Table 2), or +0.4 to +0.5
597 °C.

598 By contrast, glacial/interglacial changes in $\Delta^{13}C_{Cwue}$ are potentially a substantial part of
599 the total variation in $\delta^{13}C_{Cwue}$. During LGM $\delta^{13}C_{DIC}$ was lighter than modern, due to reduced
600 storage of terrestrial carbon in combination with changes in water mass circulation (Duplessy et
601 al., 1984; Peterson et al., 2014; Sundquist, 1993). The measured difference in $\delta^{13}C_{Cib}$ between
602 LH-LGM is ~0.35‰ in the deep Pacific and ~0.65‰ in the deep Atlantic (Curry et al., 1988;
603 Duplessy et al., 2002; Hesse et al., 2011; Hodell et al., 2003; Peterson et al., 2014). By
604 comparison, a decrease of up to 0.2‰ and 0.3‰ in $\Delta^{13}C_{Cwue}$ may have occurred in response to
605 changing oceanographic conditions in the deep Pacific and Atlantic respectively (Table 2), which
606 is equivalent to up to half the observed shift in LH-LGM $\delta^{13}C_{Cib}$ in nAtl and nIPac.

607 The largest offset between LH-LGM $\delta^{13}C_{Cib}$ has been found in the Southern Ocean, with
608 LGM values up to 1.3‰ lower than modern (Hodell et al., 2003; Peterson et al., 2014). The low
609 in $\delta^{13}C_{Cib}$ is attributed to the presence of old SCW with high [DIC] (Hodell & Venz-Curtis,
610 2006; Sigman et al., 2010) and/or reduced air-sea exchange in Antarctic surface waters causing
611 lower preformed $\delta^{13}C_{DIC}$ (Broecker & Maier-Reimer, 1992; Mackensen, 2012). Results here
612 suggest a third possibility, that low $\delta^{13}C_{Cwue}$ reflects a further decrease in $\Delta^{13}C_{Cwue}$ under glacial
613 conditions without much change in $\delta^{13}C_{DIC}$ other than the decrease that occurred globally. In the
614 modern ocean, low $\delta^{13}C_{Cwue}$ (≤ 0‰ VPDB) is found both in the Pacific and the deep South
615 Atlantic (Fig. 2). Looking at $\delta^{13}C_{Cwue}$ only, the two ocean regions are distinct in the
616 reproducibility of repeated measurements. In the Pacific, with high [DIC], between-sample
617 reproducibility of $\delta^{13}C_{Cwue}$ is good and $\Delta^{13}C_{Cwue}\geq 0$, while in SAtl sections, which have low to
618 intermediate [DIC], $\delta^{13}C_{Cwue}$ is highly variable and $\Delta^{13}C_{Cwue} < 0$ (Fig. 1, 3). The wide scatter
619 found in modern sAtl data is also apparent in glacial data from this region (Hodell et al., 2003;
620 Ninnemann & Charles, 2002); the analogue with modern data implies that [DIC] during LGM in

SO was not very high, i.e., that SCW water masses were not substantially older than they are currently.

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Open Research

The full compilation of isotope data and oceanographic data has been archived at the world data centre Pangaea (Nederbragt, 2023).

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854

855 **Table 1.** Selected bivariate correlation coefficients for $\Delta^{13}C_{Cwue}$, $\Delta^{18}O_{Cwue}$, and oceanographic
856 variables; ns indicates the correlation is not significantly different from r=0 at the 99%
857 confidence level.

858

	$\Delta^{13}C_{Cwue}$			$\Delta^{18}O_{Cwue}$						
	all	nAtl	nIPac	all	nAtl	nIPac	Depth	T	DIC	pH
n	252	122	76	252	122	76	252	252	252	252
Depth	-0.47	-0.52	-0.48	-0.38	-0.61	ns	-	-0.69	ns	ns
T	0.33	0.56	0.41	ns	0.54	ns	-0.69	-	-0.49	0.42
S	-0.19	0.45	ns	-0.31	0.40	ns	ns	0.28	-0.58	0.63
Ω_{cal}	0.20	0.49	0.47	ns	0.58	ns	-0.78	0.84	-0.65	0.69
$\Delta[CO_3^{=}]$	0.19	0.47	0.46	ns	0.52	ns	-0.77	0.76	-0.65	0.73
DIC	0.33	ns	ns	0.28	ns	ns	ns	-0.49	-	-0.94
TA	0.26	ns	ns	ns	-0.44	ns	0.33	-0.56	0.95	-0.82
pH	-0.27	ns	ns	-0.30	ns	ns	ns	0.42	-0.94	-
$[HCO_3^{-}]$	0.32	ns	ns	0.29	ns	ns	ns	-0.50	1.00	-0.95
$[CO_3^{=}]$	-0.30	ns	ns	-0.37	ns	ns	ns	0.41	-0.92	0.96
$[CO_2]aq$	0.43	0.29	ns	0.41	ns	ns	-0.24	-0.22	0.89	-0.91
fCO_2	0.51	0.42	0.34	0.45	0.44	ns	-0.39	ns	0.79	-0.84

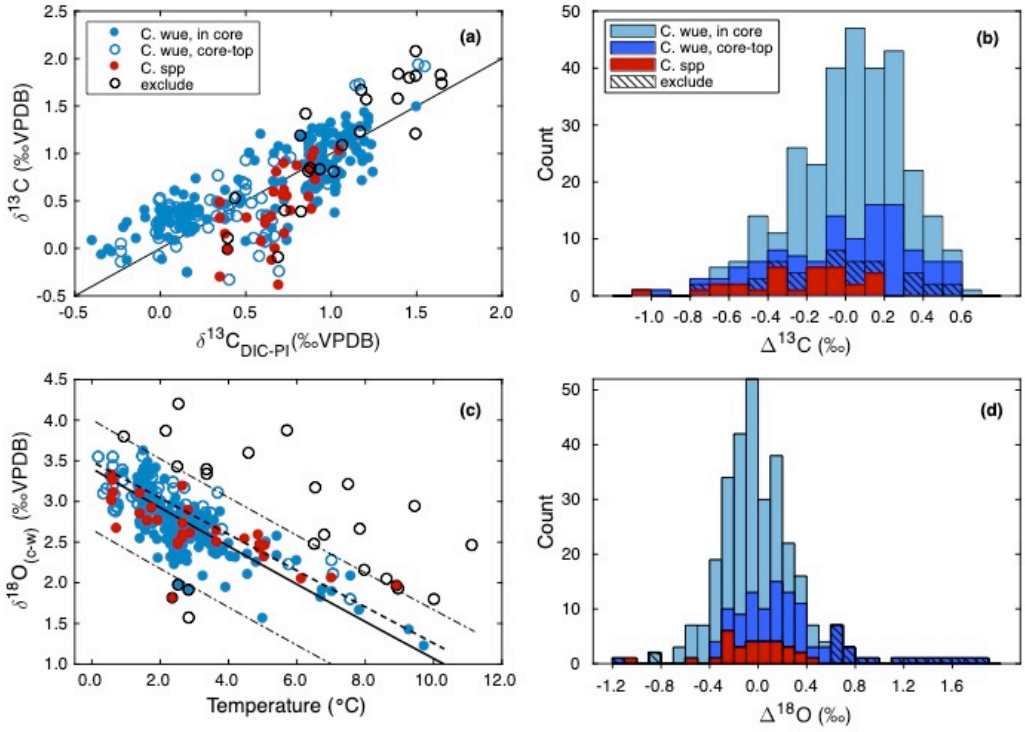
859

860

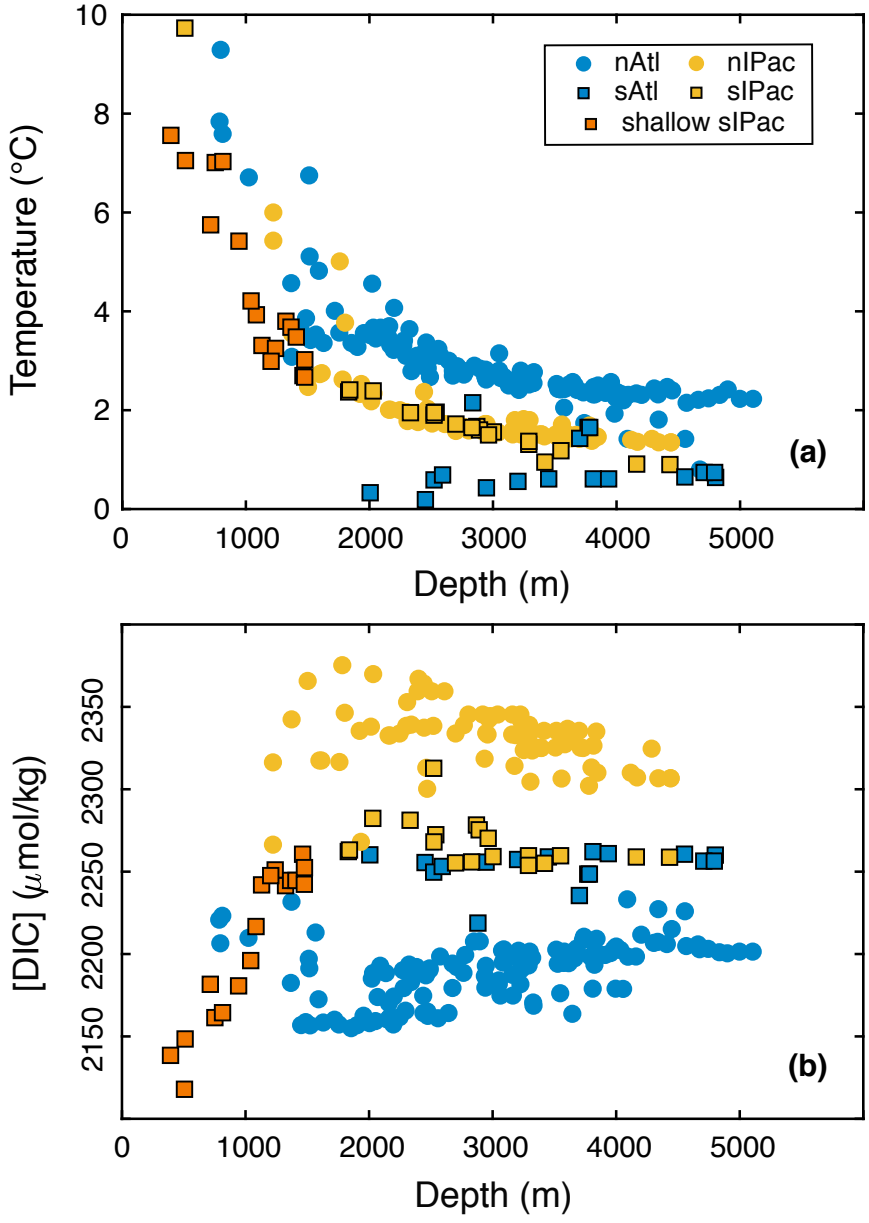
Table 2. Shift in $\Delta^{13}C_{Cwue}$ and $\Delta^{18}O_{Cwue}$ between LGM-LH expected from Eqs 3-6 and published estimates for ocean temperature (Adkins et al., 2002; Duplessy et al., 2002), [DIC] (Sundquist, 1993), and $\Delta[CO_3^{2-}]$ (Anderson & Archer, 2002; Yu et al., 2013).

	Pacific					Atlantic (deep)				
	LGM-LH	$\Delta^{13}C$ (‰)			$\Delta^{18}O$ (‰)	LGM-LH	$\Delta^{13}C$ (‰)			$\Delta^{18}O$ (‰)
		eq. 3	eq. 4	eq. 5	eq. 6		eq. 3	eq. 4	eq. 5	eq. 6
ΔDIC	45 µmol/kg	0.12	0.14	0.14	0.09	45 µmol/kg	0.12	0.14	0.14	0.09
ΔT	-2.5°C	-0.30	-	-0.20	-	-3.5°C	-0.43	-	-0.28	-
$\Delta[CO_3^{2-}]$	0 µmol/kg	-	0.00	0.00	0.00	-20 µmol/kg	-	-0.16	-0.08	-0.09
total		-0.19	0.14	-0.06	0.09		-0.31	-0.02	-0.22	0.00

Figure 1. (a) Plot of $\delta^{13}C$ of *C. wuellerstorfi* and *Cibicidoides* spp against $\delta^{13}C_{DIC\text{-}PI}$, black line denotes the 1:1 relationship. Black circles denote data that are excluded based on outlying $\delta^{18}O$ values as shown in (c); (b) Histogram of $\Delta^{13}C$ for data in (a); (c) Plot of $\delta^{18}O_{(c\text{-}w)}$ against temperature with symbols as in (a), the subscript (c-w) refers to the measured value corrected for ambient $\delta^{18}O_{water}$. Black line indicates expected values based on the temperature equation of Kim & O'Neil (1997) as adjusted by Bohm et al. (2000), dashed line represents the empirical temperature equation for *Cibicidoides* spp (Marchitto et al., 2014). Dash-dot lines represent cut-off levels used to define outliers; (d) Histogram of $\Delta^{18}O$ for data in (c) with symbols as in (b). For further description see section 3.1.



877 **Figure 2.** (a) Temperature and (b) [DIC] for all *C. wuellerstorfi* localities plotted against water
878 depth, to illustrate differences between core localities grouped by ocean region; for further
879 description see section 2.2.



880

881 **Figure 3.** Correlation between $\Delta^{18}O$ and $\Delta^{13}C$. (a) Cross plot of $\Delta^{18}O$ against $\Delta^{13}C$ for all
882 *Cibicidoides* data; black and red lines represent orthogonal regression lines for *C. wuellerstorfi*
883 and *Cibicidoides* spp respectively; (b) and (c) show cross plots of $\Delta^{13}C$ and $\Delta^{18}O$ data
884 respectively paired *Cibicidoides* spp and *C. wuellerstorfi* data; black lines indicate the 1:1
885 relationship; (d) and (e) show the standard deviation (s) for $\Delta^{13}C_{Cwue}$ and $\Delta^{18}O_{Cwue}$ respectively
886 for multiple analyses ($n \geq 3$) from a single locality. Note that for $\Delta^{13}C$ the between-sample
887 variability increases as $\Delta^{13}C_{Cwue}$ decreases, while the variability of $\Delta^{18}O_{Cwue}$ is independent of the
888 measured value.

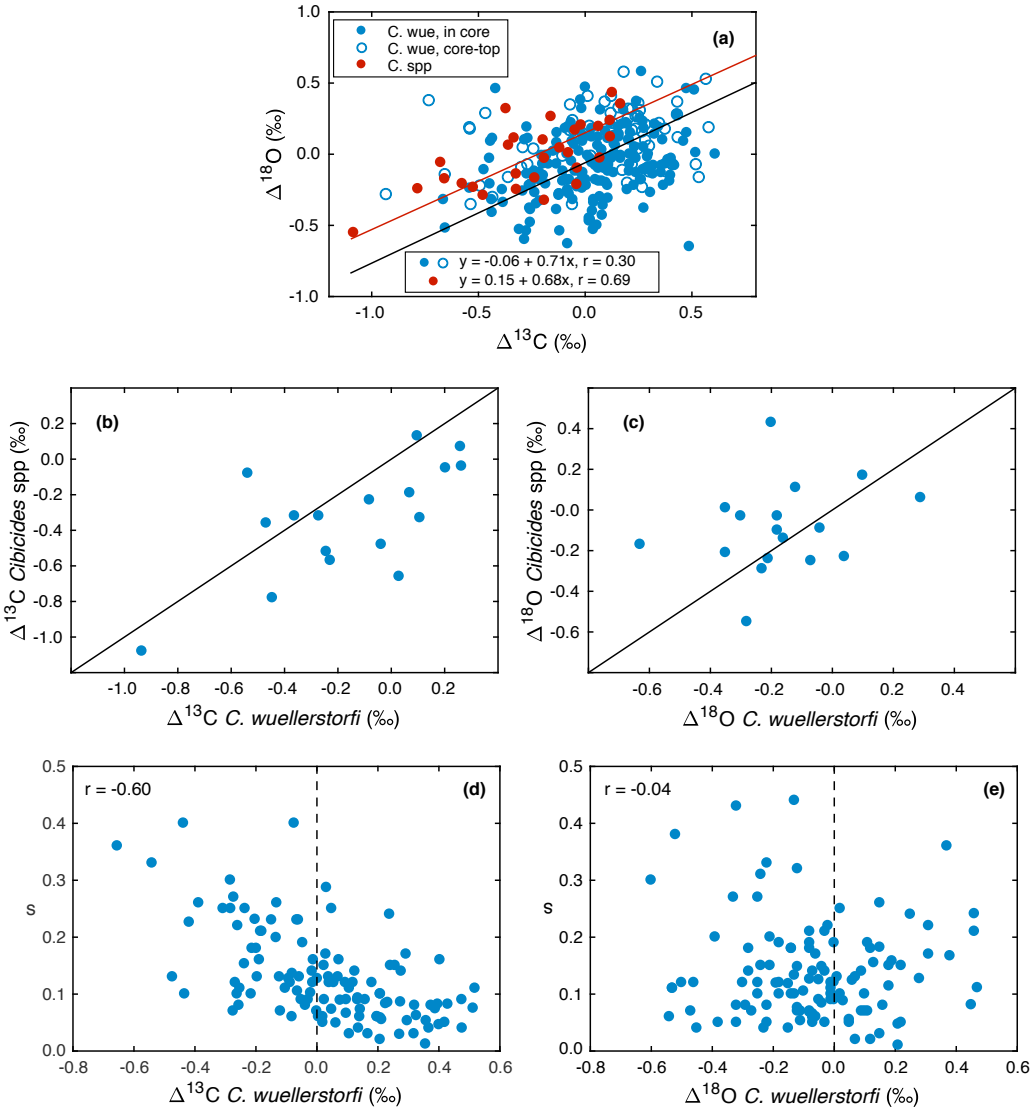


Figure 3

889

890

Figure 4. Plots of $\Delta^{13}C_{Cwue}$ against selected oceanographic variables with data separated by ocean region as shown in Fig. 2. Black lines represent regression lines for Atlantic (i) and Indo-Pacific data (ii) separately, dashed lines indicate that the correlation is not significant at the 99% confidence level.

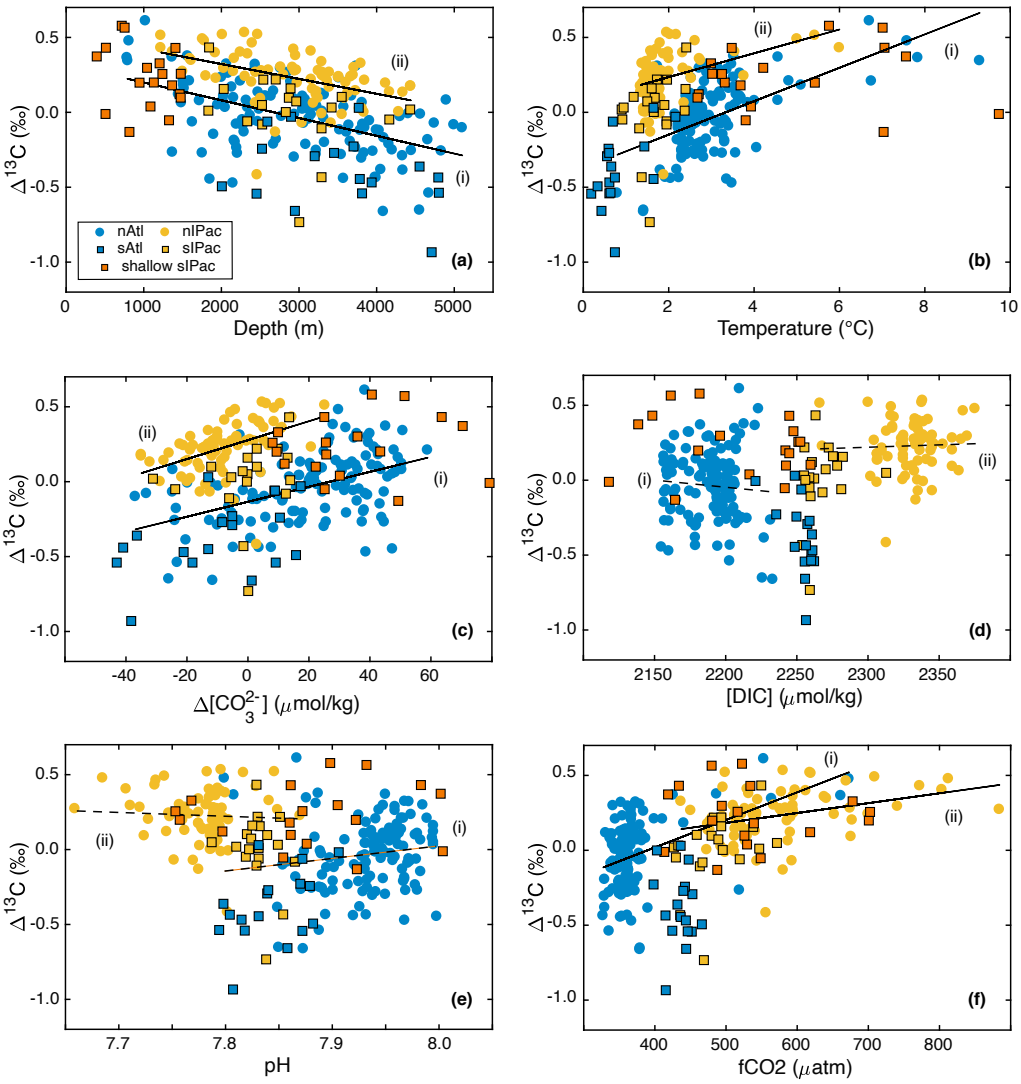


Figure 4

Figure 5. Contour plots of $\Delta^{13}C_{Cwue}$ to illustrate multilinear relation with oceanographic conditions. (a) scatter plot of temperature and [DIC] showing distribution of data points, and (b) contour plot of $\Delta^{13}C_{Cwue}$ as a function of temperature and [DIC], thick lines indicate iso-plane described by equation 4; (c) scatter plot as in (a) but for $\Delta[CO_3^{2-}]$ and [DIC] and (d) contour plot of $\Delta^{13}C_{Cwue}$ against $\Delta[CO_3^{2-}]$ and [DIC] with lines calculated from equation 5.

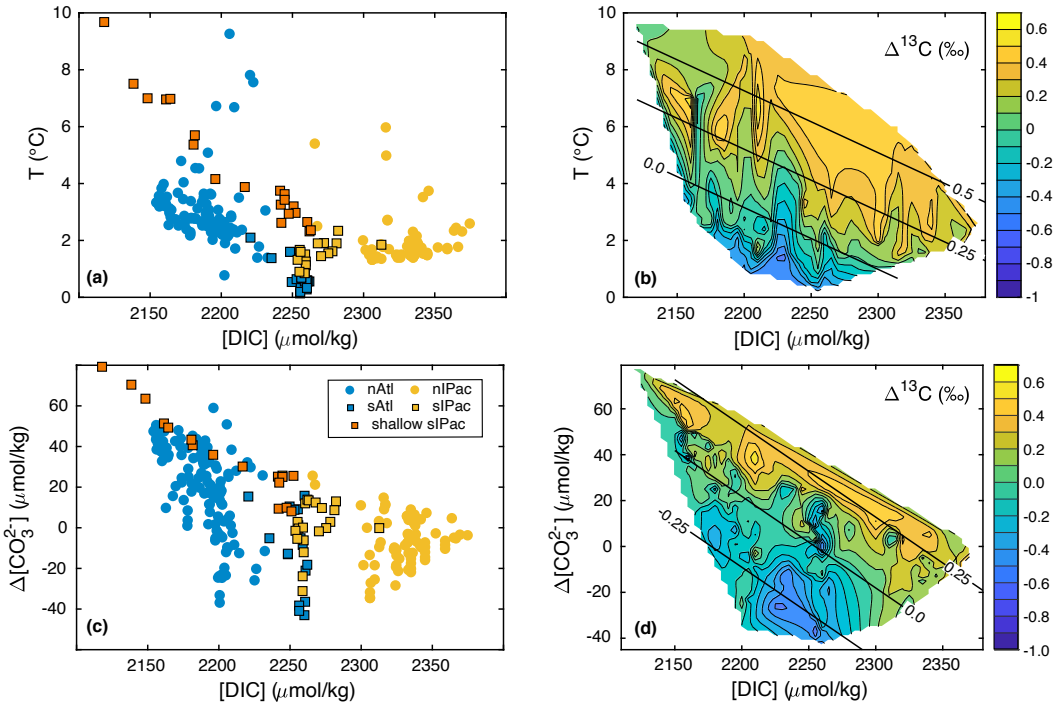
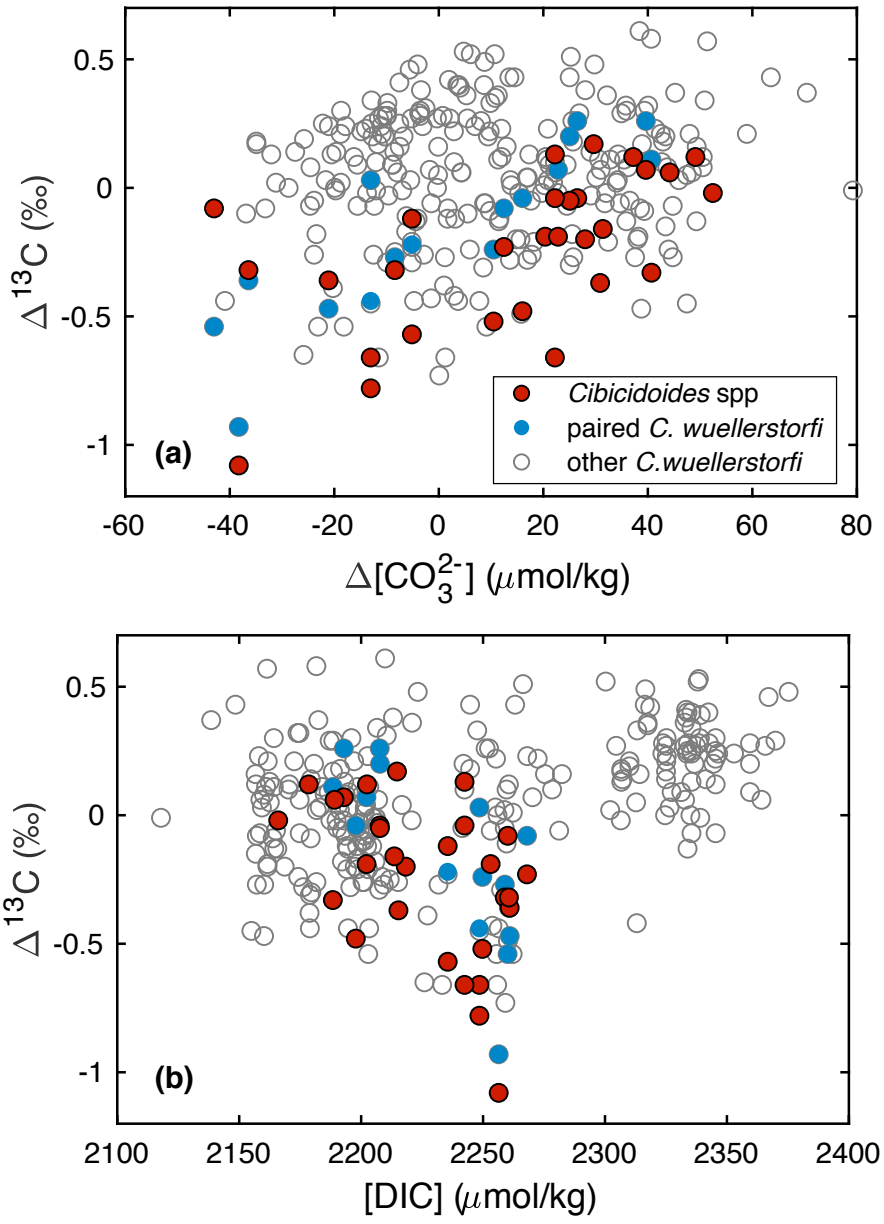


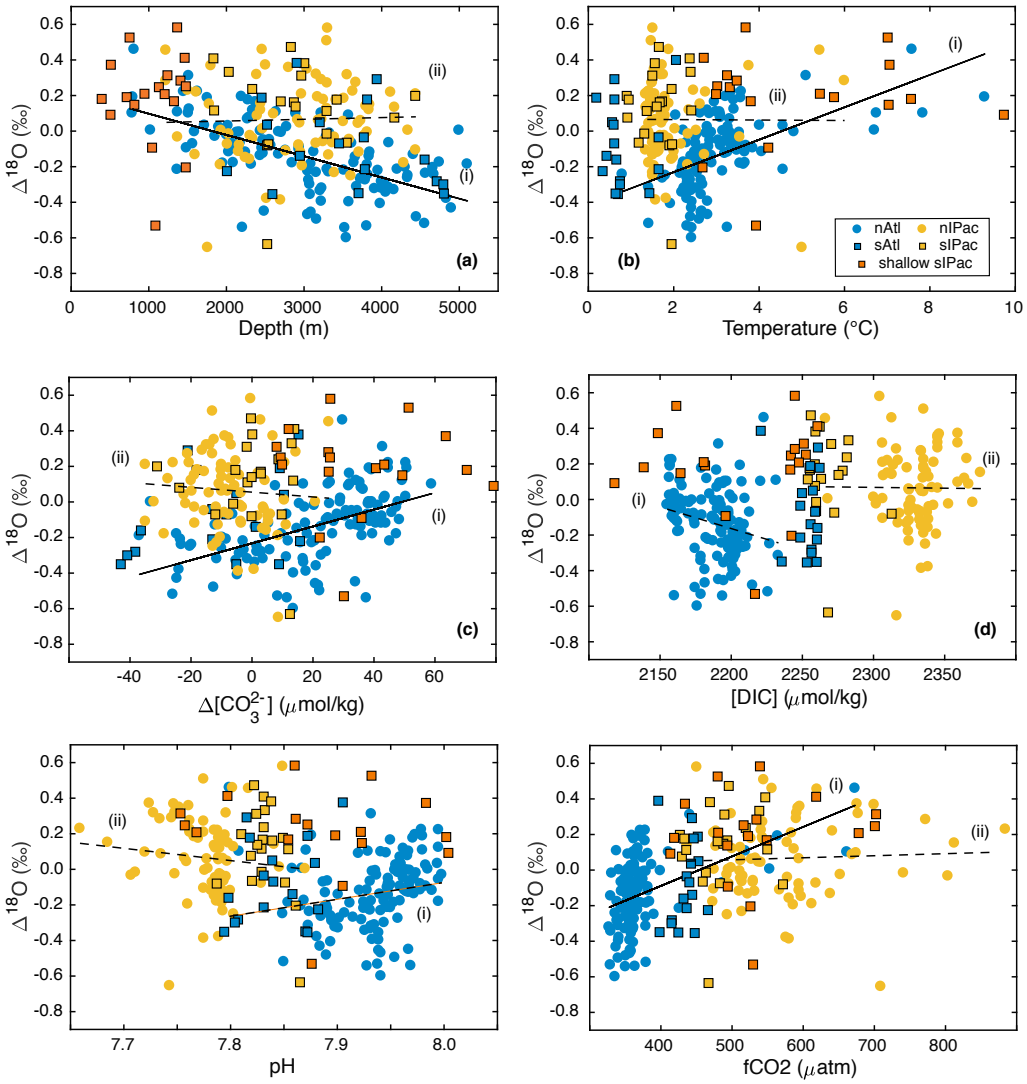
Figure 5

Figure 6. Scatter plot of $\Delta^{13}C_{Cspp}$ against (a) $\Delta[CO_3^{2-}]$ and (b) [DIC] with data for *C. wuellerstorfi* shown for comparison. Note that $\Delta^{13}C_{Cspp}$ is lower on average than $\Delta^{13}C_{Cwue}$ from the same core as shown in Fig. 3B.



Supplementary Tables and Figures

Figure S1. Plots of $\Delta^{18}O_{Cwue}$ against selected oceanographic variables with data split by ocean region. Black lines represent regression lines for Atlantic (i) and Indo-Pacific data (ii) separately, dashed lines indicate that the correlation is not significant at the 99% confidence level. Note that the distribution pattern of $\Delta^{18}O_{Cwue}$ with all variables is similar to that of $\Delta^{13}C_{Cwue}$ but that correlation coefficients are consistently weaker.



916 **Table S1.** Amount of variation explained by multiple linear regression of $\Delta^{13}C_{Cwue}$ and $\Delta^{18}O_{Cwue}$
917 against pairs of two independent variables. Bold values indicate R^2 >0.35 for $\Delta^{13}C_{Cwue}$ and R^2 >
918 0.25 for $\Delta^{18}O_{Cwue}$; ns indicates values that are not significant at the 99% confidence level.

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Δ13C	T	S	Depth	DIC	TA	pH	$[HCO_3^-]$	$[CO_3^{=}]$	$[CO_2]aq$	fCO_2	Ω_{cal}	$\Delta[CO_3^{=}]$
T	-											
S	0.200	-										
Depth	0.219	0.239	-									
DIC	**0.426**	0.109	**0.372**	-								
TA	**0.397**	0.075	**0.407**	0.137	-							
pH	0.309	0.072	0.335	0.124	0.075	-						
$[HCO_3^-]$	**0.418**	0.100	**0.361**	0.161	0.111	0.112	-					
$[CO_3^{=}]$	0.335	0.090	0.298	0.109	0.091	0.094	0.100	-				
$[CO_2]aq$	**0.374**	0.199	0.326	0.195	0.187	0.276	0.207	0.345	-			
fCO_2	**0.370**	0.283	0.346	0.276	0.263	**0.354**	0.285	**0.384**	**0.353**	-		
Ω_{cal}	0.133	0.108	0.293	**0.399**	0.349	0.344	**0.389**	0.287	0.341	**0.361**	-	
$\Delta[CO_3^{=}]$	0.119	0.117	0.294	**0.391**	0.322	**0.383**	**0.384**	0.294	0.342	**0.369**	0.038	-

Δ18O	T	S	Depth	DIC	TA	pH	$[HCO_3^-]$	$[CO_3^{=}]$	$[CO_2]aq$	fCO_2	Ω_{cal}	$\Delta[CO_3^{=}]$
T	-											
S	0.158	-										
Depth	0.171	0.219	-									
DIC	0.187	0.114	**0.257**	-								
TA	0.099	0.099	0.229	0.214	-							
pH	0.176	0.114	**0.272**	0.087	0.113	-						
$[HCO_3^-]$	0.198	0.115	**0.262**	0.103	0.197	0.088	-					
$[CO_3^{=}]$	0.243	0.141	**0.272**	0.155	0.171	0.183	0.159	-				
$[CO_2]aq$	0.231	0.174	**0.256**	0.203	0.209	0.211	0.203	0.181	-			
fCO_2	0.224	0.205	**0.252**	0.217	0.222	0.227	0.216	0.208	0.214	-		
Ω_{cal}	n.s.	0.148	0.226	0.241	0.124	**0.287**	**0.258**	**0.300**	**0.266**	**0.254**	-	
$\Delta[CO_3^{=}]$	n.s.	0.140	**0.270**	0.194	0.080	**0.262**	0.211	**0.266**	0.240	0.239	0.047	-

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