



# A review of benthic foraminiferal oxygen and carbon isotopes

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## ABSTRACT

Stable isotopes in the calcium carbonate of benthic foraminifera provide important paleoenvironmental information about seawater/sedimentary porewaters that these foraminifera live in. Oxygen isotopes provide essential insights about variations in deep water temperatures and sea-level/ice volume changes, while carbon isotopes provide information about sea-water carbon/nutrient cycling. In this review we look into detail at the direct and indirect mechanisms that contribute to stable oxygen and carbon isotope signals in Rotaliid benthic foraminifera. This includes effects from ontogenetic- and calcification mechanisms, and the impact of methane seeps and post-depositional diagenesis. We conclude our review with an overview of current challenges and provide recommendations for future research endeavors aimed at outstanding knowledge gaps in understanding how these biomineralizers control their stable isotopes.

## 1. Introduction

The chemical composition of biogenic carbonates (foraminifera, corals, bivalves, fish otoliths) can reflect the environmental conditions in which they were formed. Conditions reflecting the water-column, bottom waters, pore-waters and sediments may thus be recorded in the fossil material buried within the sediments. The stable isotopic composition of oxygen ( $\delta^{18}\text{O}$ ) and carbon ( $\delta^{13}\text{C}$ ) in marine carbonates are widely used tools to make inferences about past seawater temperatures, ice volume, stratigraphy, seawater nutrients, and ocean circulation (Zachos et al., 2001; Waelbroeck et al., 2002; Curry and Oppo, 2005; Lisiecki and Raymo, 2005; Völpe et al., 2018; Dentith et al., 2020). Foraminifera are particularly useful for these reconstructions as they can be found across the various ocean basins and seas, occur in vast numbers, and span multiple geological eras. Stacked benthic foraminifera  $\delta^{18}\text{O}$  from the Pliocene-Pleistocene are important in understanding the evolution of deep water temperature and ice volume during the intensification of Northern Hemisphere glaciations, the mid-Pleistocene climate transition and for stratigraphic purposes (Lisiecki and Raymo, 2005; Elderfield et al., 2012; Ahn et al., 2017; McClymont et al., 2023). For the Pliocene the variance associated with the stacks however contains considerable uncertainties (Ahn et al., 2017). Stable carbon isotope records of deep-sea benthic foraminifera provide a wealth of information on past changes in deep-water

circulation and related carbon storage and cycling in the deep ocean (Zachos et al., 2001; Friedrich et al., 2012; Mackensen and Schmiedl, 2019). The majority of applications address changes in deep-water circulation, air-sea gas exchange, and biosphere carbon cycling during the Quaternary (Oliver et al., 2010; Mackensen and Schmiedl, 2019).  $\delta^{13}\text{C}$  records from different ocean basins suggest substantial changes in deep-water circulation during the late Quaternary responding to both glacial-interglacial and millennial-scale climate variability (Bickert and Mackensen, 2004; Gebbie, 2014; Mackensen et al., 2001; Sikes et al., 2017). Differences in carbon isotopes of contemporary species of benthic foraminifera furthermore have provided insights in the dynamics of respired carbon reservoirs and oxygen-depletion in bottom water masses (Schmiedl and Mackensen, 2006; Hoogakker et al., 2015, 2018; Jacobel et al., 2020).

Foraminifera represent a highly diverse group of protists and are distributed in a wide range of shallow to deep marine environments (Murray, 1991; Sen Gupta, 1999). The vast majority of foraminifera species are benthic, with an estimated number of 10,000 modern species (Vickerman, 1992). Molecular phylogenetic studies place the origin of benthic foraminifera in the Neoproterozoic (Pawlowski et al., 2003), but calcifying orders first occurred in the Paleozoic (Ross and Ross, 1991; De Nooijer et al., 2023). Within the class of Globobulimina, the order Rotaliida with multi-chambered tests of low-Mg/Ca calcite, diverged in the Cretaceous and Cenozoic and represents the most diverse group in

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modern benthic foraminiferal assemblages (Tappan and Loeblich, 1988; Groussin et al., 2011; Pawlowski et al., 2013; de Nooijer et al., 2023). Despite taphonomic processes, the calcium carbonate tests are commonly preserved in the sediment archive, and can be used for ecological, morphological and geochemical analyses.

Benthic foraminifera are ubiquitous throughout the world's seafloor habitats, from intertidal flats to deep ocean trenches (Gooday, 2019). Populations of benthic foraminifera live within, on, and above seafloor sediments, ranging from several centimeters below the sediment-water interface to hard surfaces elevated above the seafloor (Corliss, 1985; Jorissen et al., 1995; Burkett et al., 2018). Species distribution patterns within this vertical range of microhabitats show that some species have maximum abundances at different sediment depths than others (Rathburn and Corliss, 1994; Jorissen et al., 1995). A number of terms have been proposed to describe where groups of foraminiferal species live in the sediments. The term "epifaunal" typically refers to taxa that live at or near the sediment-water interface, while "infaunal" refers to species that are able to live within seafloor sediments (Corliss, 1985). Although definitions of terms vary, infaunal taxa are often divided into "shallow infaunal" and "deep infaunal" groups (Corliss and Emerson, 1990; Jorissen et al., 1995). Epifaunal species that live above the sediment-water interface have been referred to as "epibenthic" (Burkett et al., 2018). Most benthic foraminifera are mobile, and can adjust distributions within the sediments (Gross, 2000; Ernst et al., 2008; Wollenburg et al., 2018). Density differences in vertical profiles are thought to reflect species-specific ecological preferences and responses to ambient conditions such as food and dissolved oxygen availability (e.g., Jorissen et al., 1995; Gooday and Rathburn, 1999; Fontanier et al., 2002).

In addition to providing clues about ecological, biological, morphological, and biogeochemical differences between taxa (Gooday, 2019) an understanding of foraminiferal microhabitat preferences and responses to ambient conditions also enables paleoceanographers to use fossil foraminifera and the biogeochemistry of their calcareous tests to assess changes in ancient ocean conditions (Jorissen et al., 2007; Gooday, 2003). Illustrations of some of the more commonly used epifaunal and infaunal taxa in their depth habitats are shown in Fig. 1.

## 2. Stable isotopes of benthic foraminifera

### 2.1. Oxygen isotopes ( $\delta^{18}\text{O}$ )

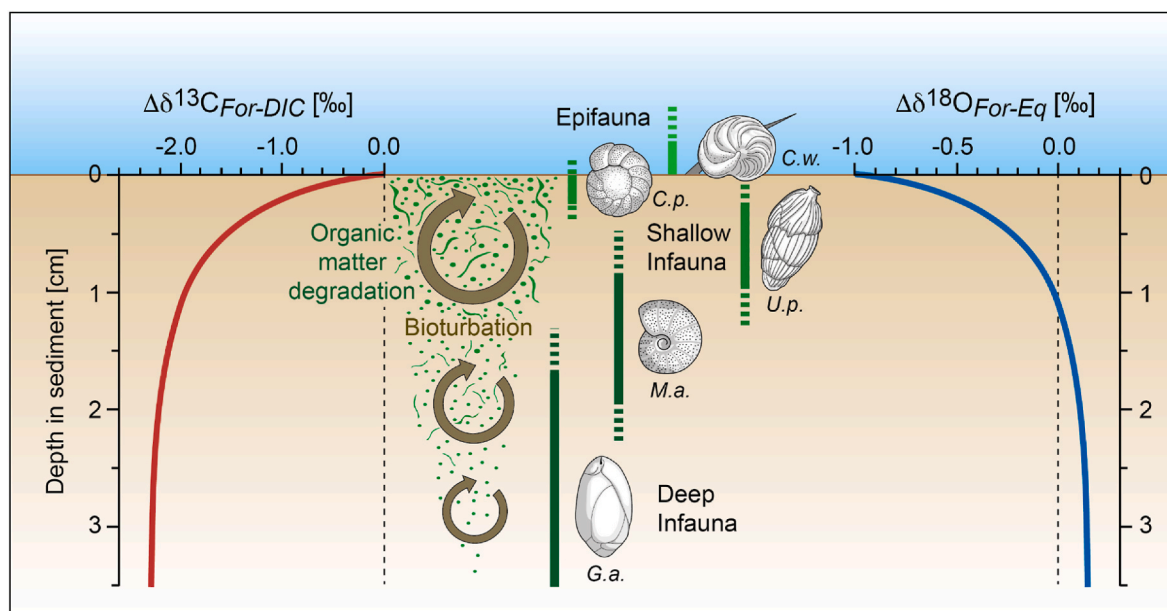
Oxygen isotopes in carbonates are a function of the oxygen isotopic composition of seawater, and temperature, and as such they have been instrumental in estimating changes in global ice sheet volumes and determining ages through identification of glacial and interglacial marine isotopes stages (Zachos et al., 2001; Lisiecki and Raymo, 2005). In the majority of studies, the  $\delta^{18}\text{O}$  of epifaunal species are lighter (i.e. isotopically depleted) compared with infaunal benthic foraminifera (for example see Schmiedl and Mackensen, 2006; Fontanier et al., 2008; Hoogakker et al., 2010; Jöhnck et al., 2021). It has been speculated that this may relate to fractionation during metabolism, where epifaunal taxa have sufficient access to oxygen and preferentially take up the lighter isotope, while infaunal microhabitats have lower oxygen contents, causing equilibrium calcite precipitation (Theodor et al., 2016a). Others primarily ascribed this effect to changes in  $[\text{CO}_3^{2-}]$  with sediment depth. Since changes in inorganic carbon chemistry are most variable in the shallowest sediment layers, epifaunal taxa may have a more variable  $\delta^{18}\text{O}$  (Jahnke et al., 1994).

Furthermore, dissolution of carbonates at and within the seafloor may affect the foraminiferal oxygen isotopic composition. The rotaliid shell consists of consecutive layers formed over the course of an individual's life. Therefore, migration over a specimen's lifetime may result in a layered  $\delta^{18}\text{O}$ ; if dissolution only removes the outer layer(s) of calcite, the average stable isotope composition may thus be affected (e.g. Wu and Berger, 1989). Due to differences in morphology and shell microstructures, this may also introduce inter-species variability in isotopic signatures. For both processes, it is important to consider that the depth at which the foraminiferal shell (test) forms may not necessarily align with the entire depth range of its habitat (see section 4.1.1).

### 2.2. Carbon isotopes ( $\delta^{13}\text{C}$ )

The  $\delta^{13}\text{C}$  value of biogenic carbonate is predominantly influenced by dissolved inorganic carbon (DIC) in the surrounding sea- or pore-water. Several authors have suggested that epifaunal species may form their calcite in equilibrium with the surrounding bottom water, adopting a 1:1 relationship between  $\delta^{13}\text{C}$  of DIC and  $\delta^{13}\text{C}$  of epifaunal benthic foraminifera calcite (Mackensen, 2008). Of the epifaunal species investigated, *Cibicides wuellerstorfi* and *Planulina ariminensis*, which prefer an elevated microhabitat, seem to correlate most closely to  $\delta^{13}\text{C}$  of DIC (Lutze and Thiel, 1987; Schmittner et al., 2017). Other epifaunal species, such as *C. mundulus* and *C. pachyderma*, have been observed to migrate within sediments and thus record the signal of a mixed epi- and in-faunal habitat (Wollenburg et al., 2018). Infaunal benthic foraminifera  $\delta^{13}\text{C}$  is thought to reflect  $\delta^{13}\text{C}$  of the surrounding pore-waters. Pore-water studies have shown that pore-water  $\delta^{13}\text{C}$  decreases with increasing depth in sediment (McCorkle and Emerson, 1988). The reason for depletion of  $\delta^{13}\text{C}$  in pore-water is due to decomposition of organic material. Marine organic matter ( $\text{C}_{\text{org}}$ ), such as phytodetritus, is depleted in  $^{13}\text{C}$  with  $\delta^{13}\text{C}_{\text{org}}$  values between  $-31$  and  $-19$ ‰ (Rau et al., 1989; Mackensen and Schmiedl, 2019). Accordingly, the microbial decomposition of phytodetritus on and within the upper few centimeters of the sediment and the associated release of  $^{12}\text{C}$  results in steep  $\delta^{13}\text{C}$  gradients of pore water DIC with up to  $1.0$ ‰ per cm (McCorkle et al., 1985, Fig. 1). The pore water  $\delta^{13}\text{C}$  gradient depends on the combined influences of organic matter fluxes and remineralization rates, and, thus, is also related to the ventilation state of the bottom water mass (McCorkle and Emerson, 1988; McCorkle et al., 1990; Stott et al., 2000; Holsten et al., 2004).

Because the  $\delta^{13}\text{C}$  of epifaunal species is closely related to bottom water DIC, these are suitable taxa for reconstructing sea-water nutrient/water mass changes. Infaunal taxa, such as species of the genera *Uvigerina*, *Melonis*, *Bulimina*, and *Globobulimina* contain strong pore water signals (e.g., Grossman, 1984b; Schmiedl et al., 2004). Differences in  $\delta^{13}\text{C}$  between epifaunal and shallow infaunal taxa (e.g., *Uvigerina* species) can be used as a proxy for organic matter flux rates, since the pore water  $\delta^{13}\text{C}_{\text{DIC}}$  gradient in the uppermost centimeter of the surface sediment is mainly controlled by the organic matter flux rates (McCorkle et al., 1990; Zahn et al., 1986; Theodor et al., 2016a, 2016b), although it is noted that lateral organic matter fluxes may obscure this signal in marginal basins (Theodor et al., 2016b). Differences in  $\delta^{13}\text{C}$  between epifaunal and deep infaunal taxa (*Globobulimina* species) have been shown to be driven mainly by bottom water oxygen contents, reflecting the difference between bottom water  $\delta^{13}\text{C}$  and  $\delta^{13}\text{C}$  of pore waters near the anoxic boundary in sediments, and can be used as a bottom-water oxygen proxy (McCorkle et al., 1990, 1997; Schmiedl and Mackensen, 2006; Hoogakker et al., 2015).



**Fig. 1.** Schematic shape and magnitude of observed differences between foraminiferal test  $\delta^{13}\text{C}$  and ambient bottom water  $\delta^{13}\text{C}_{\text{DIC}}$  (left), and difference between test  $\delta^{18}\text{O}$  and equilibrium calcite  $\delta^{18}\text{O}_{\text{Eq}}$  (right) in the upper few centimeters of the surface sediment. The magnitude of effects is based on observations from the northwestern Mediterranean Sea (Schmiedl et al., 2004) and it can vary in different environments, depending on organic matter fluxes and degradation rates, and bioturbation. The bars next to foraminiferal drawings indicate the specific microhabitat ranges. C.w. = *Cibicoides wuellerstorfi*, C.p. = *Cibicides pachyderma*, U.p. = *Uvigerina peregrina*, M.a. = *Melonis affinis*, G.a. = *Globobulimina affinis*. Processes after Ishimura (2021). Note that isotopic equilibrium values of  $\delta^{18}\text{O}$  vary depending on the reported equation (e.g., Friedman and O'Neil, 1977; Kim and O'Neil, 1997; see Fig. 5).

### 3. Analyses of stable isotopes

Analyses of biogenic calcites, including foraminifera shells, started in the mid 20th century, facilitated by the pioneering work of Urey (1947), McCrea (1950), Epstein et al., 1951 and Emiliani (1955).

Stable oxygen and carbon isotopes are commonly measured from the  $\text{CO}_2$  gas generated following reaction of the carbonate tests with phosphoric acid ( $\text{CaCO}_3 + \text{H}_3\text{PO}_4 \rightarrow \text{CaHPO}_4 + \text{H}_2\text{O} + \text{CO}_2$ ). The  $\text{CO}_2$  gas

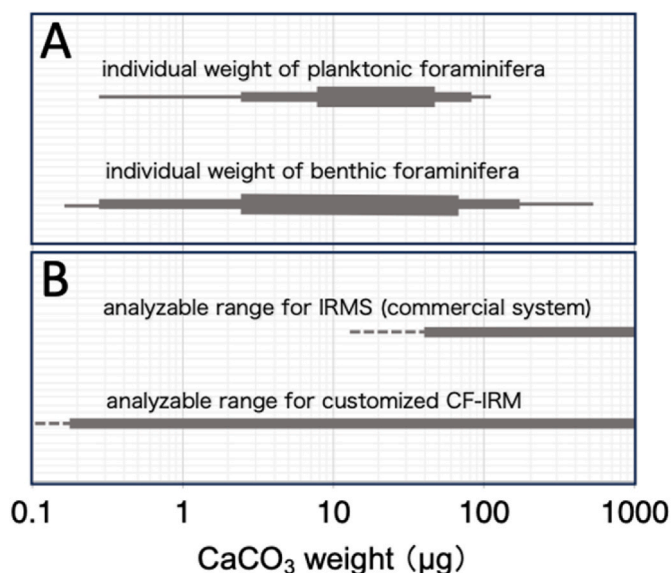
generated is analyzed using a magnetic sector stable isotope ratio mass spectrometer (IRMS). The reported data are commonly presented using standard delta ( $\delta$ ) notations ( $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ ) relative to the Vienna Pee Dee belemnite (VPDB) standard scale, and typically reported as deviations in parts per thousand (‰). While minimal isotopic fractionation occurs around temperatures of 25 °C (e.g., Coplen et al., 1983), systems are commonly set up with reaction temperatures varying between 60 and 90 °C to reduce reaction time and enhance analysis efficiency.

A 4 °C increase in seawater temperature results in an about 1 ‰ depletion in  $\delta^{18}\text{O}$  of carbonate minerals formed in that seawater (e.g. Kim and O'Neil, 1997). To accurately reconstruct past environmental changes an analytical precision (external precision) of typically  $\pm 0.1$  ‰ (1 $\sigma$ ) is necessary (this would give a 0.5 °C precision in temperature, provided there was no change in  $\delta^{18}\text{O}$  of seawater).

Traditional IRMS analysis commonly uses sample sizes with weights of around 40–80  $\mu\text{g}$ . The weight of individual benthic foraminifera varies between 0.1  $\mu\text{g}$  to  $\gg 100$   $\mu\text{g}$  (Fig. 2). To get meaningful results this would mean 100s of smaller specimens are necessary, although for some species, one large specimen may suffice. The latter has the disadvantage that any inter-specimen variability in isotopic signature is not accounted for. Benthic foraminifera stable isotope analyses and environmental reconstructions generally focus on deeper (<500/1000 m) settings and commonly occurring species. As a result, only a handful of extant species have been analyzed, with individual analyses generally limited to the larger size fractions (e.g. Oba, 1990; Billups et al., 1996). Therefore, our current understanding of foraminifera isotopes is constrained by information, mainly focusing on larger individuals and groups of individuals analyzed together, and a comprehensive understanding has not yet been attained, although there are now systems available that can deal with smaller sample weights (see section 3.1 and Fig. 5).

#### 3.1. Techniques

Dual Inlet Isotope Ratio Mass Spectrometry (DI-IRMS) is a commonly used technique to measure stable isotopes in carbonates. Concentrated sample gas and a standard gas with a known isotope composition are



**Fig. 2.** (A)  $\text{CaCO}_3$  weight of individual benthic and planktonic foraminifera larger than 63  $\mu\text{m}$  (data from Takagi et al., 2015, 2016; Kimoto et al., 2009; Ujiie et al., 2019; Ishimura et al., 2012; Kinoshita et al., 2021, 2023). The width of the bar indicates their abundance in the sediment. (B) Analyzable weight of  $\text{CaCO}_3$  of commercial DI-/CF-IRMS systems and a customized CF-IRMS system (Ishimura et al., 2004, 2008).

alternately introduced to the mass spectrometer through diffusion, averaging the measurements for precise isotopic analysis.

A Continuous Flow Isotope Ratio Mass Spectrometry (CF-IRMS) method quantifies the stable isotope composition of light element gases. It employs capillary separation columns to purify and separate sample gases carried by a carrier gases like helium, introducing them into the mass spectrometer in a pulsed manner. Required sample size is substantially reduced. However, due to the small volume of CO<sub>2</sub> introduced, the risk of atmospheric CO<sub>2</sub> contamination, and isotopic exchange with trace H<sub>2</sub>O may introduce substantial uncertainties, as well as cumulative minor isotopic fractionation during sample introduction (Ishimura et al., 2004). To keep precision high, CF-IRMS systems operate with larger sample amounts, similar to DI-IRMS.

Various authors have applied custom adjustments/improvements that allowed them to analyze smaller samples using a GasBench II or original devices (Velivetskaya et al., 2009, 10–30 µg; Breitenbach and Bernasconi, 2011, 20–100 µg; Vonhof et al., 2020, 3–10 µg). A technique to measure ultra small samples was developed by Ishimura et al. (2004, 2008). This technique employs the high-sensitivity CF-IRMS analysis while maintaining analytical precision at the level of DI-IRMS and can be used to measure samples with minimum of 2 nmol CO<sub>2</sub> (=0.2 µg CaCO<sub>3</sub>). Secondary Ion Mass Spectrometry (SIMS) is a technique for ultra-small scale isotope analysis, with its application to carbonate isotope research gaining traction. SIMS irradiates the target with a primary ion beam such as Cs ions, detecting secondary ions, generated by sputtering from the sample surface, with a mass spectrometer. This technique is limited in precision in comparison with IRMS due to sample heterogeneity and influence of impurities. Despite such limitations, Kozdon et al. (2009) showed variability in δ<sup>18</sup>O across chamber walls in the planktonic *Neoglobobadrina pachyderma*. Recently Balestra et al. (2020) suggest a correction factor of 1‰ is needed for SIMS measurements for infaunal *Uvigerina* spp.

## 4. Discussion

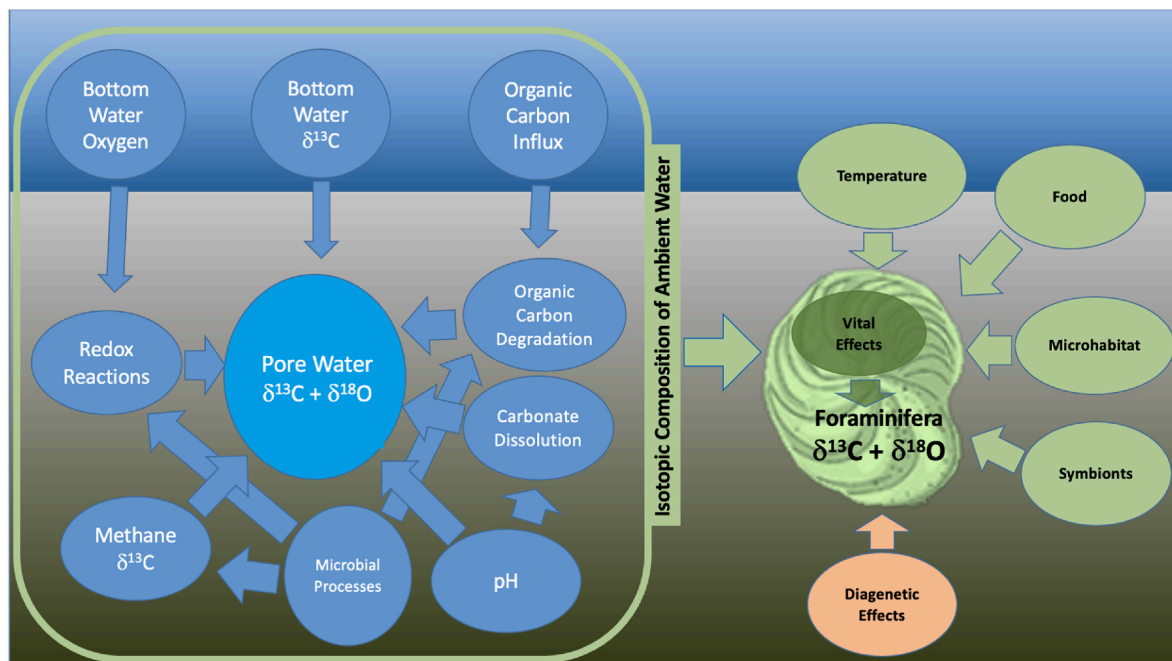
In section 2 the general environmental effects that influence the stable isotopic composition of benthic foraminiferal calcite were discussed. In section 4.1 we delve deeper into several other effects, some of which occur in specific environments. Fig. 3 provides a generalized overview of the variables that can influence the stable isotopic signatures of foraminiferal carbonates. In sections 4.2 we make recommendations for future research directions, suitable for biological, chemical and paleo applications.

### 4.1. Other influences on the stable isotopic composition of benthic foraminifera

#### 4.1.1. Foraminifera mobility

The isotopic geochemistry of benthic foraminifera is influenced by ambient conditions, particularly as the δ<sup>13</sup>C and carbonate chemistry of pore waters vary with sediment depth. The mobility of foraminifera implies that despite changes in vertical geochemical profiles, they could maintain favorable ambient conditions by moving with them. Through their movements, they could be exposed to different ambient conditions at different times. Some species of epifaunal foraminifera live attached to substrates at or above the sediment-water interface (Linke and Lutze, 1993; Burkett et al., 2016, 2020), while most infaunal taxa living within the sediments are considered to be mobile (Alve and Bernard, 1995). Moving within sediment requires a significant amount of energy, and the ability of taxa to move within sediments implies that it is beneficial to change position. Taxa that are able to adjust their position in the sediments can potentially respond to changes in their ambient environment and track favorable microenvironments or at least escape from unfavorable conditions (Wollenburg et al., 2015).

In addition to changes in oxygen availability, food acquisition



**Fig. 3.** Schematic overview of variables that can influence the stable isotopic values of benthic foraminifera. On the left variables that influence sediment pore water (interstitial water) are shown, which will influence the stable isotopic composition of benthic foraminifera that have an infaunal habitat at some point in their life. While external processes play a primary role in influencing the stable isotopic composition of foraminiferal carbonate, vital effects may also cause different species to have different isotopic signatures. Vital effects (biomineralization processes) are considered to be those factors that are intrinsic to the biology of a species (e.g., metabolism, biomineralization fractionation, changes in ontogenetic kinetics, etc.), but do not include ecological variables, such as geographic or microhabitat preferences. Food can directly, and indirectly affect stable isotopes. As a result of the intricate network of linkages between various factors influencing the stable isotopic values of benthic foraminifera, it is challenging to separate the isotopic consequences caused by each variable. Note that diagenetic effects (e.g., post-depositional dissolution, authigenic precipitates, mineralogical changes, etc.) influence dead/fossil foraminifera. See the text for details.



(phytodetritus, bacteria, organic matter) is one of the prime motivators for foraminifera to relocate within sediments (e.g., Gooday and Rathburn, 1999; Heinz et al., 2001). As mentioned in section 2.2, organic matter degradation in seafloor sediments has a direct impact on the carbon isotopic composition of pore water. By changing ambient isotopic values, foraminiferal food in the form of organic matter in various forms can indirectly influence foraminiferal  $\delta^{13}\text{C}$  signatures (e.g., Wollenburg et al., 2018; Mackensen and Schmiedl, 2019). Foraminiferal tests are internal (enveloped in protoplasm), and some workers have suggested that after consumption, food may have a direct influence on foraminiferal test carbonate  $\delta^{13}\text{C}$  (e.g., Rathburn et al., 1996), as is the case with soft and hard macrofaunal tissues (e.g., Levin et al., 2015) and vertebrate bones (e.g., Zhao et al., 2021). In addition to potential effects of consumed food on metabolism (which is known to influence  $\delta^{13}\text{C}$  carbonate signatures), the isotopic composition of food consumed would directly alter the  $\delta^{13}\text{C}$  of the protoplasm whose influence on  $\delta^{13}\text{C}$  of the test is possible, but currently unknown. Documenting any direct influences of food on the  $\delta^{13}\text{C}$  of foraminiferal carbonate needs detailed laboratory biomineralization analyses.

Benthic foraminifera are among the first to colonize new marine habitats (Hess et al., 2001; Burkett et al., 2016, 2020), and self-locomotion is a means to invade new microhabitats over short (i.e. centimeter-scale) distances (Alve, 1999), or recover from burial or repositioning due to macrofaunal bioturbation (Severin et al., 1982; Wetmore, 1988; Bornmalm et al., 1997). Laboratory observations have recorded the movements of individual foraminifera within the sediments in response to changing conditions (Alve and Bernard, 1995; Wollenburg et al., 2015). Seasonal studies of deep-sea microhabitats reveal differences in population dynamics over time that reflect changes in ambient conditions, such as phytodetrital flux and food availability (reviewed in Gooday and Rathburn, 1999). These lines of evidence all suggest that mobile foraminifera may be exposed to changing ambient isotopic conditions that, if they calcify under these conditions, could alter the isotopic signatures of their calcareous test (Mackensen and Licari, 2003; Schmiedl et al., 2004; Gotschalk et al., 2016).

As a result of the disequilibrium between the stable isotope values of ambient water and those of foraminiferal carbonate, it has been suggested by some workers that benthic foraminifera may calcify in microhabitats that are different from where they are found living in the sediments. This is unlikely for a number of reasons. After decades of studies examining vertical distribution patterns of benthic foraminifera living in seafloor microhabitats from shallow water to the deep-sea, consistent patterns have emerged for cosmopolitan species (e.g., Gooday and Jorissen, 2012). This strongly suggests that at least most taxa are not calcifying in one place, then migrating vertically to spend the rest of their lives in another microhabitat with different isotopic characteristics. The postulate that deep-sea foraminifera move to different microhabitats during recovery of multicores is also not supported by movement rate experiments (e.g., Bornmalm et al., 1997), and the absence of vertical foraminiferal trails in multicore sediments (A. Rathburn, personal observations). In situ deep-sea observations of foraminiferal distributions and movements are needed, but currently here is no physical evidence to suggest that foraminifera move significantly during the transit from the seafloor to the ship as part of the recovery of multicores. Laboratory observations from a number of studies of a wide variety of species report foraminifera moving at speeds in sediment of up to 4.9 mm/h for shallow water species (Wetmore, 1988; Kitazato, 1988; Jauffrais et al., 2016; Guihermic et al., 2023 and references therein) with deep water species moving much slower, up to 1.3 mm/h (Hemleben and Kitazato, 1995; Bornmalm et al., 1997 and references therein). These movement rates and the general absence of observable foraminifera trails along the inside edge of multicores suggest that foraminifera don't change vertical position during the trip from the deep ocean. Geochemical profiles also are not likely to change dramatically in multicore sediments on the trip to the surface, so there is no incentive for foraminifera to move with geochemical changes.

Additional, detailed work is needed to examine species-specific biomineralization processes and further *in situ* and laboratory studies to determine biological and ecological influences on the stable isotopic compositions of foraminiferal carbonate.

#### 4.1.2. Ontogenetic effects

Field and laboratory studies have documented size-related (i.e. ontogenetic) trends in the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  signals of various foraminifera groups and species. While ontogenetic effects are common in planktic foraminiferal species (Berger et al., 1978; Spero and Lea, 1996), the available stable isotope data for deep-sea benthic foraminifera provide an inconclusive picture. Based on test size-related studies, the majority of deep-sea benthic foraminiferal species seem to lack clear ontogenetic trends (Vincent et al., 1981; Grossman, 1984a; Wefer and Berger, 1991; Loubere et al., 1995; Corliss et al., 2002).

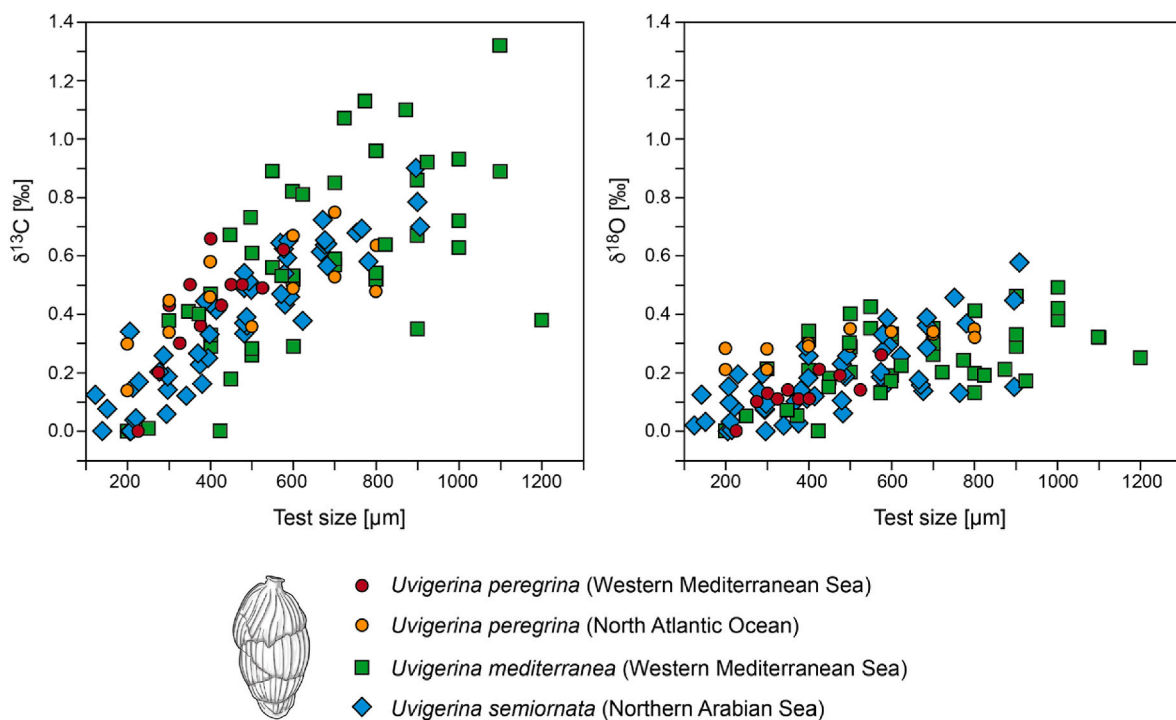
Negligible size-related (ontogenetic) effects are observed in certain epifaunal taxa, such as *Cibicides wuellerstorfi* (Franco-Fraguas et al., 2011), and *C. pachydermus* and *Lobatula lobatula* (Theodor et al., 2016a; Jöhnck et al., 2021), which is advantageous in paleoceanographic applications. Significant test size-related effects are however observed in different infaunal taxa, including species of the genera *Uvigerina*, *Bolivina*, *Bulimina*, and *Globobulimina*. For example, enrichments of 0.3–0.5 ‰ in  $\delta^{18}\text{O}$  and 0.8–1.5 ‰ in  $\delta^{13}\text{C}$  over a size range of 175–1250  $\mu\text{m}$  were documented in *U. mediterranea* from the Mediterranean Sea (Schmiedl et al., 2004; Fontanier et al., 2006; Theodor et al., 2016a) (Fig. 4). Size-related enrichments of similar magnitude were also observed for *U. peregrina* (Dunbar and Wefer, 1984) but with variable ontogenetic slopes under contrasting trophic regimes (Theodor et al., 2016a, 2016b).

Contrasts in size-related stable isotope trends in different populations of the same species demonstrate that differences in test size and/or weight may not necessarily represent different ontogenetic stages. Instead, they may also reflect contrasting environmental conditions, such as differences in food fluxes, oxygen concentrations, or stress due to pollution (e.g., Yanko et al., 1994; Davis et al., 2016; Belanger, 2022). However, as long as the observed population of a certain species grew under comparable environmental conditions, trends in test size and/or weight represent, to a first approximation, ontogenetic trends.

Size-related isotopic effects have also been observed in *U. proboscidea* from the South China Sea (Jöhnck et al., 2021). Similar ontogenetic trends, although usually of lower magnitude were documented for *Bolivina subavena* (Staines-Urías and Douglas, 2009), *Bulimina aculeata* (McCorkle et al., 2008; Filipsson et al., 2010), and various *Globobulimina* species (Theodor et al., 2016a). Changes in microhabitat are unlikely the cause for isotope offsets between different size fractions, as for the Sulu Sea and off California microhabitat preferences of smaller (e.g., 63–150  $\mu\text{m}$ ) and larger (>150  $\mu\text{m}$ ) specimens were similar (Rathburn and Corliss, 1994; Silva et al., 1996). Ontogenetic enrichment can sometimes be more prominent in the smaller size fractions and seems to slow down in the adult stages, and more likely reflects differences in metabolic activity during different life stages (Schmiedl et al., 2004). It is noteworthy that trace element analyses of individual chambers of planktonic (e.g., Davis et al., 2023) and benthic foraminifera (e.g., Raitzsch et al., 2011) have shown ontogenetic heterogeneity between chambers of individuals. Until we can analyze stable isotopes in individual chambers, it will be difficult to be more certain about ontogenetic influences on isotopic signatures within individual tests. Recently, using microscale isotopic analytical techniques, ontogenetic size effects were recognized in some deep-sea infaunal benthic foraminifera, with heavier foraminifera exhibiting more positive  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values (Fig. 5, Ishimura et al., 2012). Mechanisms to explain these effects are discussed later in section 4.1.3.1. and 4.1.3.2.

#### 4.1.3. Calcification mechanism

Calcification by foraminifera (as by other marine calcifiers) involves 1) the uptake of calcium ions ( $\text{Ca}^{2+}$ ) and inorganic carbon, and 2) combining them in a controlled microenvironment to promote calcite



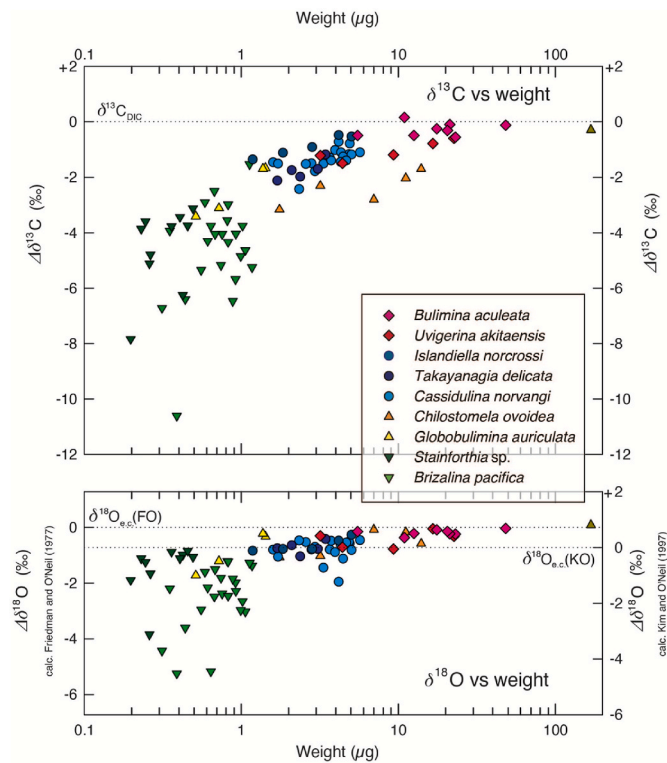
**Fig. 4.** Mean values of stable carbon and oxygen isotope signals plotted against test size of different *Uvigerina* species from the western Mediterranean Sea (Schmiedl et al., 2004; Theodor et al., 2016a), North Atlantic Ocean (Corliss et al., 2002), and northern Arabian Sea (Schumacher et al., 2010). For better comparison, the lowest value of each data series has been referred to zero. Note that ontogenetic trends are stronger in the  $\delta^{13}\text{C}$  signal than in the  $\delta^{18}\text{O}$  signal.

precipitation. In both of these steps, isotopic fractionation may occur (of C and O, but also of Ca and Mg ions) and together they set the overall fractionation ( $\epsilon$ ) between the surrounding seawater and the calcite. Therefore, the biological controls on the uptake of the ions and on the chemical conditions at the site of calcification will affect the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of the foraminiferal calcite. Such controls are often abbreviated as the ‘vital effect’, but an informal use of this term means that it can refer to any biological process. We suggest referring to ‘microhabitat-effects’ whenever vertical movement (either throughout the water column by planktonic species or within the sediment by benthics) causes variability in calcite chemistry. Processes that are related to cellular processes promoting the nucleation and growth of foraminiferal  $\text{CaCO}_3$  (including the effects of metabolism) may be better referred to as calcification- or biomineralization-related processes.

Perhaps the largest effect on C- and O-isotopic fractionation is caused by changes in the inorganic carbon chemistry, both inside and outside the foraminiferal cell. Such changes can be caused by two processes. First, proton pumping due to calcification lowers the pH outside rotaliid, low-Mg/Ca species and hence changes the balance between the three dissolved inorganic carbon (DIC) species (i.e.  $\text{CO}_2$ ,  $\text{HCO}_3^-$  and  $\text{HCO}_3^{2-}$ ). Such modulation of the pH during calcification in benthic species (Bentov et al., 2009; Glas et al., 2012; Toyofuku et al., 2017) shifts the balance from bicarbonate ( $\text{HCO}_3^-$ ) to carbon dioxide ( $\text{CO}_2$ ) outside the foraminiferal cell. Inside the foraminifer, the opposite happens, with a transformation of  $\text{CO}_2$  and  $\text{HCO}_3^-$  to  $\text{CO}_3^{2-}$ , as a consequence of the removal of protons (e.g. De Nooijer et al., 2009, Fig. 6). Due to the considerable fractionation of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  between these chemical species (Zhang et al., 1995; Zeebe, 1999; Zeebe and Wolf-Gladrow, 2001; DeVriendt et al., 2017), even small changes in the pH outside the foraminifer will affect the isotopic composition of these three inorganic carbon species. This in turn, is crucial for the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of the inorganic carbon species that is taken up for calcification, which is suggested to be  $\text{CO}_2$  through diffusion (Toyofuku et al., 2017) and/or  $\text{HCO}_3^-$  through transmembrane transporters (Erez, 2003; Ujiie et al., 2023).

Secondly, shifts in the outside pH due to algal photosynthesis and/or respiration (Erez, 1983; Spero et al., 1991) also shifts the balance of the inorganic species and hence, their isotopic composition. These two processes have an opposite effect on the total inorganic carbon concentration (which is lowered by the uptake by photosynthetic symbionts and increases due to the addition of respired  $\text{CO}_2$ ), but shift the isotopic signature in the same direction since photosynthesis takes up the isotopically light  $\text{CO}_2$  while respiration by the foraminifer adds isotopically light  $\text{CO}_2$ . The effect of both these processes have been quantified in both planktonic foraminifera (Rink et al., 1998; Köhler-Rink and Köhl, 2005) and larger, symbiont-bearing benthic foraminifera (Köhler-Rink and Köhl, 2000). The observed gradients in pH have been used to develop a model for foraminiferal calcification that is able to explain changes in calcite  $\delta^{13}\text{C}$  as a function of light intensity and seawater inorganic carbon chemistry (Zeebe et al., 1999). Such sensitivities, in turn, can be used to explain the carbon- and oxygen isotopic fractionation in planktonic species (e.g. Spero et al., 1997) when cultured at a range of seawater pH's or [DIC].

Besides the shift in balance between the inorganic carbon species outside the foraminifer, the uptake of carbon into the cell introduces another isotopic fractionation step. The uptake could be through seawater vacuolization (Erez, 2003; Bentov and Erez, 2006), which transports all inorganic carbon species into the foraminifer. Preferential uptake of  $\text{CO}_2$  through diffusion resulting from the steep internal-external pH gradient is also suggested (Toyofuku et al., 2017) and specific bicarbonate ion transporters have been hypothesized (Erez, 2003) and found to be genetically coded for in *Ammonia beccarii* (Ujiie et al., 2023). Determining whether foraminifera rely on  $\text{CO}_2$  and/or  $\text{HCO}_3^-$  uptake is essential in explaining the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  composition of the DIC at the site of calcification. The uptake mechanism itself likely isotopically fractionates the inorganic carbon. For  $\text{CO}_2$  uptake, diffusion over the cell membrane discriminates against  $^{13}\text{C}$ , resulting in an internal  $\text{CO}_2$  that is depleted relative to that outside the foraminifer. Such carbon isotope fractionation is reported to be  $\sim 4\%$  for cell membranes in plants (O'Leary, 1988), but cell membranes in other organisms, as

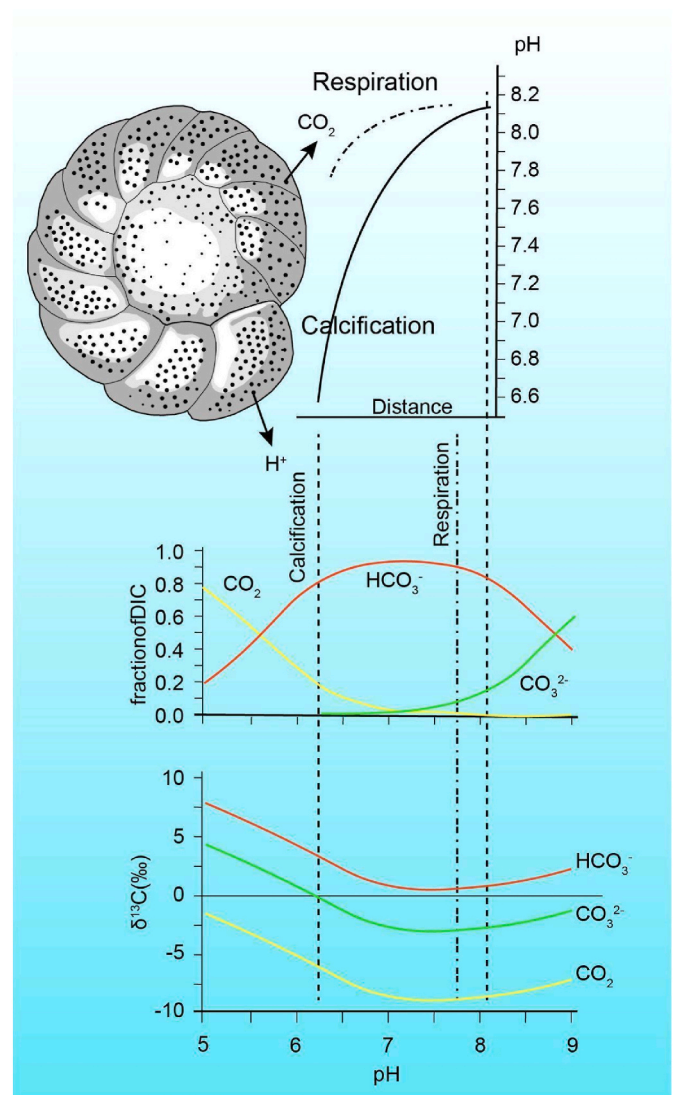


**Fig. 5.**  $\Delta\delta^{13}\text{C}$  and  $\Delta\delta^{18}\text{O}$  values plotted with calcite weight of individual foraminifera.  $\Delta\delta^{13}\text{C}$  is the difference between the  $\delta^{13}\text{C}$  of foraminiferal shells and the  $\delta^{13}\text{C}$  of dissolved inorganic carbon (DIC) in bottom water ( $\delta^{13}\text{C}_{\text{DIC}}$ ).  $\Delta\delta^{18}\text{O}$  is the difference between the  $\delta^{18}\text{O}$  of foraminifera and the  $\delta^{18}\text{O}$  of calcite in equilibrium with bottom water ( $\delta^{18}\text{O}$  e.c. FO). Dotted lines in the graph indicate the  $\delta^{13}\text{C}$  values of DIC in bottom water ( $\delta^{13}\text{C}_{\text{DIC}}$ ) and the  $\delta^{18}\text{O}$  values of calcite in equilibrium with bottom water ( $\delta^{18}\text{O}$  e.c. FO), calculated using the equation proposed by Friedman and O'Neil (1977). Additionally, the  $\delta^{18}\text{O}$  e.c. (KO) values according to the equation proposed by Kim and O'Neil, 1997 are also shown as dotted lines. The data used for this graph are sourced from Ishimura et al. (2012).

well as the diffusion rate may affect this fractionation factor. Alternatively, the foraminifer's cell membranes may also contain the specialized membrane proteins that transport  $\text{CO}_2$  as found in higher animals (Nakhoul et al., 1998; Michenkova et al., 2021): the  $^{12}\text{C}/^{13}\text{C}$  fractionation associated with such transmembrane proteins, however, is currently unknown.

Once inorganic carbon is taken up, whether through  $\text{CO}_2$  diffusion or specialized  $\text{HCO}_3^-$  transporters, the conditions at the site of calcification provide a final step in the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  fractionation. Crystal growth rate can cause additional C- and O-isotopic fractionation (Gabitov et al., 2012; Gabitov, 2013; Watkins et al., 2013), reflecting kinetic isotope effects (KIE) during precipitation (Watkins et al., 2014). With the relatively high crystal precipitation rates found in foraminifera (e.g. Geerken et al., 2022), these KIE have a significant impact on the overall isotope fractionation and show that any variability in the precipitation rate may account for much of the variability in  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ . The presence of the enzyme carbonic anhydrase (CA) may enhance the conversion between inorganic carbon species and hence have an impact on the precipitation rates and the KIE (DeVriendt et al., 2017; Chen et al., 2018). This enzyme was found to be vital for calcification in foraminifera (De Goeysse et al., 2021) and a full understanding of the biological effects on C- and O-isotopes in foraminiferal calcite should therefore include the activity of CA.

#### 4.1.3.1. Can ontogenetic or size effects be explained by varying pH regulation with size? Ontogenetic effects on the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ could be



**Fig. 6.** pH regulation and its effect on the inorganic carbon speciation and isotopic fractionation outside the calcifying specimen. The magnitude of pH regulation is arbitrary, but follows what is reported for *Ammonia* spp. (Toyofuku et al., 2017; Glas et al., 2012). The effect of respiration on ambient pH is also indicated and generally much smaller (Köhler-Rink and Kühl, 2000, 2005) than that of active pH regulation due to calcification.

related to pH manipulation by the foraminifer. The reported stronger effect in smaller-sized specimens (Schmiedl et al., 2004; Filipsson et al., 2010; Ishimura et al., 2012, section 4.1.2), may indicate that the surface-to-volume ratio of specimens causes the observed ontogenetic trends in isotopes. The pH regulation in (low-Mg/Ca) rotaliid foraminifers scales with size (Glas et al., 2012), with a stronger decrease in pH outside the larger specimens, and could help explain the ontogenetic trends in stable isotopes. The magnitude of pH decrease outside the newly formed chamber determines the ratio of the inorganic carbon species, as well as on their carbon and oxygen isotopic composition (Fig. 6).

Stronger pH regulation in larger specimens will increase the  $[\text{CO}_2]$  close to the foraminifer and decrease  $[\text{HCO}_3^-]$ . At pH  $\sim 5.5$ , these chemical species are present in equal concentrations. Through the relatively large ( $\sim 9\%$ ) difference in  $\delta^{13}\text{C}$  between these two inorganic carbon species (Fig. 6) it is clear that the isotopic signature of the inorganic carbon that is taken up and incorporated into the shell depends on the inorganic carbon species taken up (i.e.  $\text{CO}_2$ ,  $\text{HCO}_3^-$  or  $\text{CO}_3^{2-}$ ) and in which ratio they are utilized. The trend and magnitude of



more enriched  $\delta^{13}\text{C}$  (and  $\delta^{18}\text{O}$ ) in larger specimens (Figs. 4 and 5), is in line with the hypothesis that pH regulation determines the isotopic composition of the shell.

The  $\delta^{18}\text{O}$  of the various inorganic carbon species (i.e.  $\text{CO}_2$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ ) does not depend on pH, but changes in the relative contribution of them are used to explain differences in oxygen isotopic composition of planktonic species cultured at different carbon chemistries (Spero et al., 1997; Zeebe, 1999). This explanation did not take into account active pH manipulation by the foraminifera, but the relatively large pH changes in some benthic foraminifera (Glas et al., 2012; Toyofuku et al., 2017) would result in a large impact on the  $\delta^{18}\text{O}$  if they take the inorganic carbon in the ratio that they are present in the direct vicinity of the specimen. To explain the effect of ontogeny on foraminiferal  $\delta^{18}\text{O}$  in terms of pH manipulation during calcification, it is necessary to assume that the effect of the extracellular pH on the  $\text{CO}_2/\text{HCO}_3^-$  ratio affects the uptake ratio, but not with the same magnitude. For example, the external  $\text{CO}_2/\text{HCO}_3^-$  may be 50:50, and due to a stronger pH regulation, shift to 90:10. This could explain the changes in  $\delta^{18}\text{O}$ , but only if the ratio of  $\text{CO}_2$  versus  $\text{HCO}_3^-$  uptake changes to 60:40 (these ratios are purely hypothetical and only serve to outline the principle).

**4.1.3.2. Can different carbon uptake mechanisms (through internal pH regulation) explain inter-/intra-species isotopic variations in  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ ?** The influence of the foraminifera's biology on the stable isotopic composition of their calcite is widely recognized and arises due to biomineralization-related processes and ecological activity (e.g. migration; see e.g. 4.1.1). To account for the effect of these biological processes when reconstructing paleo-environments and - climates, it is either necessary to precisely quantify these effects or identify species in which these offsets are minimal and respond to one or more environmental parameters only.

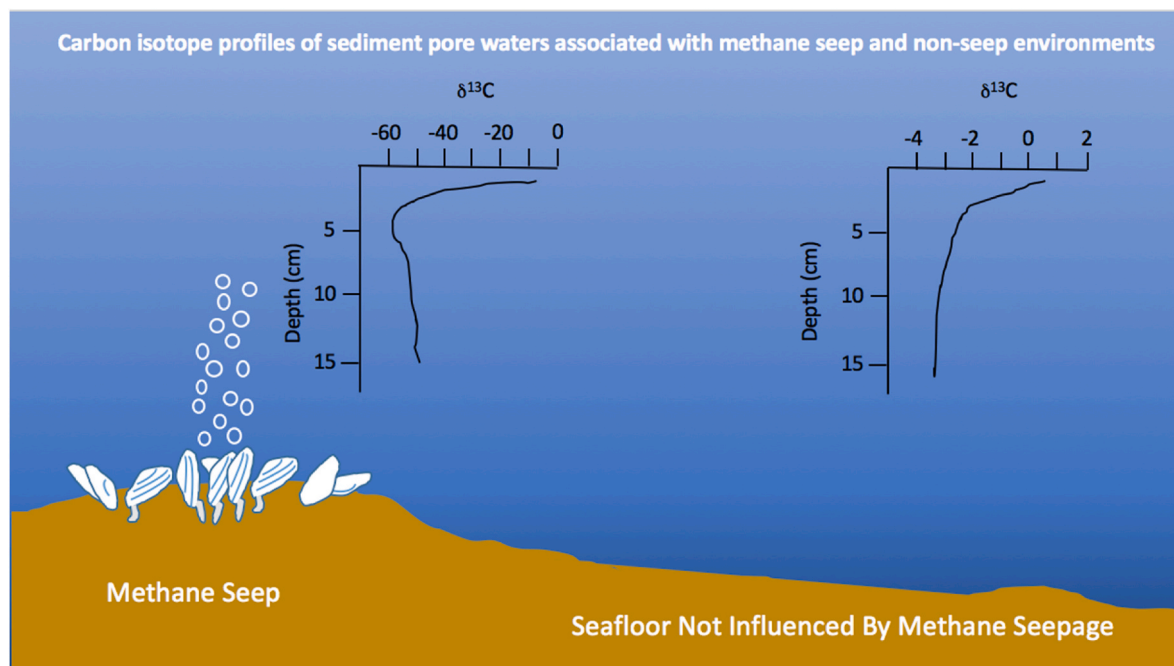
The most obvious potential source of biological-introduced variability in calcite chemistry is vertical movement by benthic foraminifera. Amongst others, this complicates an accurate quantification of the 'vital effect' in field studies. With the vertical, within-sediment

movement of foraminifera through a variety of pore-water chemistries exist in which they calcify. Such movements are unlikely uniform among specimens, and therefore may result in (large) inter-specimen variability in  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ . Moreover, species may differ in their vertical migration behaviour and thus explain inter-species differences in  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ , even when collected from the same sediment depth. Heterogeneity of microenvironments within a given sediment depth could also play a role in creating isotopic differences among individual foraminifera living at the same sediment depth. Finally, changes in depth habitat preferences during the life of a given species may explain (part of) the size-related patterns in the shells'  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ . However, available data suggest that at least some species don't change habitats during their lifetime (see section 4.1.2 for discussion). More work is needed to quantify and differentiate ecological and biological influences on inter- and intra-species isotopic variations.

When inter-individual isotopic variability is minimal, species can be regarded as 'environmental indicator species'. Particularly when shell weights and  $\delta^{13}\text{C}/\delta^{18}\text{O}$  correlate and converge towards the isotopic composition of inorganically precipitated calcite (Ishimura et al., 2012), the offsets from equilibrium can be accounted for when using specimens of this species for paleo-reconstructions.

#### 4.1.4. Impact of methane seeps on $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$

Seafloor methane seeps are inhabited by benthic foraminifera, and exposure to the extreme conditions in these habitats provide interesting clues about the tolerances and isotopic biogeochemistry of taxa that live there (Rathburn et al., 2003; Heinz et al., 2005; reviewed in Lu et al., 2023). Benthic foraminifera can be abundant at methane seeps (Rathburn et al., 2003), although populations may also succumb to changes in the toxicity of methane fluxes (Melaniuk et al., 2022). Marine methane seeps are areas of the seafloor where methane escapes into the water column from sediments and are relatively common (see Levin et al., 2016 for a review). Under the right pressure, temperature and gas concentrations, methane is trapped in large accumulations of methane clathrates beneath seafloor sediments of continental margins (Paull



**Fig. 7.** Examples of carbon isotopic profiles of interstitial water in sediments from seafloor environments influenced (left) and not influenced (right) by methane seeps. Note the difference in scale for  $\delta^{13}\text{C}$  values between the two graphs. Pore-water isotope profiles can change depending upon local conditions, and the graphs in this figure serve to illustrate common trends in  $\delta^{13}\text{C}$  values of pore waters with depth within sediments from seep and non-seep environments. The decrease in pore water  $\delta^{13}\text{C}$  values with depth in the sediment reflects the release of  $^{13}\text{C}$ -depleted  $\text{CO}_2$  during the progressive degradation of organic matter. Methane seep pore waters are influenced by the very negative  $\delta^{13}\text{C}$  values of methane. See the text for more details.



et al., 1996). The source of clathrate methane is buried organic material that has been altered by microbial or thermal processes. Clathrates have  $\delta^{13}\text{C}$  values between  $-40\text{‰}$  and  $-94\text{‰}$ , with the majority having values more negative than  $-60\text{‰}$  (Kvenvolden, 1993). Seep sediment pore waters also reflect these very negative  $\delta^{13}\text{C}$  values (Fig. 7, Rathburn et al., 2003; Torres et al., 2003; Ussler and Paull, 2008; Gieskes et al., 2011). Carbon isotope values of benthic foraminifera are directly or indirectly influenced by ambient conditions (the bottom waters or pore waters they are exposed to), biological factors, and ecological preferences (e.g., Gooday, 1994). It therefore stands to reason that benthic foraminiferal carbonate generated in ambient seep pore waters with negative  $\delta^{13}\text{C}$  values would have more negative  $\delta^{13}\text{C}$  values than their non-seep counterparts, but this is not necessarily the case (Rathburn et al., 2001, 2003; Torres et al., 2003; Melaniuk et al., 2022).

On the basis of fossil data, Wefer et al. (1994) suggested that the carbon isotopic geochemistry of calcareous benthic foraminifera might provide a quantitative means to evaluate the regional history of methane fluxes. Alterations of about 5 ‰ in fossil benthic foraminiferal carbon isotopes over the past 60,000 years led Kennett et al. (2000; 2003) to propose that temperature fluctuations in ocean waters alternatively promoted the accumulation and then release of methane from the upper continental slope of California. This “clathrate gun hypothesis” suggested that the dissociation of seafloor methane clathrates influenced climate changes in the Quaternary (Kennett et al., 2003). In efforts to evaluate and calibrate stable isotopic signatures from foraminifera living at methane seeps, several subsequent studies examined the stable isotopic signatures of living benthic foraminifera (Rathburn et al., 2000, 2003; Torres et al., 2003; Martin et al., 2004; Herguera et al., 2014; Melaniuk et al., 2022). Although authigenic carbonates produced in methane seep environments typically have  $\delta^{13}\text{C}$  values of around  $-40\text{‰}$  (Whiticar, 1999; Naehr et al., 2000; also see 4.1.5), the carbonate tests of living benthic foraminifera recovered from methane seeps typically have  $\delta^{13}\text{C}$  values that are an order of magnitude more positive, similar to those found in non-seep environments (Rathburn et al., 2000, 2003). However, while species of benthic foraminifera from non-seep environments have relatively narrow  $\delta^{13}\text{C}$  values, those from methane seeps are much more variable and on average, slightly more negative (Rathburn et al., 2003; Gieskes et al., 2011; Melaniuk et al., 2022). In laboratory culture experiments, Wollenburg et al. (2015) demonstrated that the  $\delta^{13}\text{C}$  values of benthic foraminifera can be influenced by  $^{13}\text{C}$ -altered methane conditions. The presence of symbionts can influence the carbon isotopic composition of planktonic foraminifera (e.g., Spero and Deniro, 1987), and it is possible that ecto- or endosymbionts may influence the  $\delta^{13}\text{C}$  values of benthic foraminifera at seeps, although this has not been confirmed (Bernhard et al., 2010).

It is clear that microhabitat preferences and consequent exposure to different ambient conditions play a role in accounting for differences in carbon isotopic signatures of different species of benthic foraminifera at seeps and non-seeps (Rathburn et al., 2003; Wollenburg et al., 2015; Melaniuk et al., 2022). However, the reasons for the disequilibrium between  $\delta^{13}\text{C}$  values of seep and non-seep foraminifera remain unclear. Proposed explanations for at least some of the carbon isotopic disequilibrium at seeps include: the influence of the degradation of photosynthetically derived organic material rather than methane (Stott et al., 2002); calcification only under conditions when methane flux is absent (Torres et al., 2003; Herguera et al., 2014); inherent biological/ecological aspects where the biology or behavior of a species control the isotopic fractionation during calcification (Rathburn et al., 2003); food preferences where foraminifera are consuming isotopically light microbes and/or degraded organic material which influence  $\delta^{13}\text{C}$  values of the test (Rathburn et al., 2003; Wollenburg et al., 2015; Melaniuk et al., 2022; Schmidt et al., 2022). Despite these uncertainties, benthic foraminiferal isotopic signatures play a significant role in assessments of ancient methane seepage and paleoclimate change (Panieri et al., 2023). The reasons for the pronounced disequilibrium between  $\delta^{13}\text{C}$  values of carbonate tests calcified by foraminiferal carbonate living

in ambient seep fluids remain unclear.

Methane seep environments can influence  $\delta^{18}\text{O}$  signatures of benthic foraminiferal carbonate, but the influence on living foraminifera is typically small or non-existent, and may be influenced by changes in ambient fluid temperatures in hydrothermal methane seeps whose fluid fluxes have elevated temperatures compared to ambient ocean water (Burkett et al., 2018).

#### 4.1.5. Diagenesis

Diagenetic processes can further influence benthic foraminifera stable isotopes. Processes include the dissolution of carbonate tests under low carbonate saturation conditions, secondary calcite precipitation, and recrystallization. Scanning Electron Microscopy (SEM) is an ideal method to assess foraminiferal tests for such effects. Dissolution can cause etching and pitting of the foraminifera test, loss of wall layers and chambers (Murray and Alve, 1999) and especially (but not exclusively) affects foraminifera from environments with low pH/carbonate undersaturated conditions, such as the deep sea, and areas with high primary productivity. Under low pH/carbonate undersaturated conditions, partial dissolution of foraminifera tests may lead to oxygen isotope enrichment (Pearson, 2012). Dissolution through carbonate undersaturation can occur in seawater, or in sediments. Most observations of secondary calcite precipitation and especially recrystallization, are from cores that are from older geological strata. The effects of diagenetic calcite on stable isotopes have been mainly reported for bulk sediments (Killingley, 1983; Schrag, 1999) and planktonic foraminifera (Kozdon et al., 2013; Sexton et al., 2006; Edgar et al., 2015). Secondary precipitation can have no or negligible effects on benthic foraminifera  $\delta^{18}\text{O}$ , in cases where the conditions ( $\delta^{18}\text{O}$  seawater and bottom water temperature) are similar to that of the time of primary calcification of the tests, or it can cause depletion (in case of pore waters being warmer, and/or enriched  $\delta^{18}\text{O}$  seawater), or it can cause enrichment (in case of pore waters being cooler, and/or  $\delta^{18}\text{O}$  seawater being depleted) (Pearson, 2012). Secondary precipitation can also affect  $\delta^{13}\text{C}$ , with diagenetic ‘frosty’ calcite causing an enrichment in planktic foraminifera from Eocene sediments in the central Pacific (Edgar et al., 2015). Precipitation of authigenic carbonates on fossil foraminifera also occurs in sedimentary porewaters containing methane gas; with high levels of detected methane tending to coincide with sedimentary strata that contain high levels of organic material. Fossil benthic foraminiferal carbonate from ancient methane seeps can show positive  $\delta^{18}\text{O}$  signatures due to the precipitation of secondary carbonate (Dessandier et al., 2020). Authigenic carbonate is one of the confounding aspects of using the stable isotopic signatures of fossil foraminifera to assess ancient methane seepage (Rathburn et al., 2000; Martin et al., 2004; Panieri et al., 2017). As a result of the very negative (around  $-40\text{‰}$ )  $\delta^{13}\text{C}$  of authigenic carbonate, even a light coating on fossil foraminiferal tests would significantly skew the isotopic analyses of the test, for example, shifting  $\delta^{13}\text{C}$  values to be much more negative than the original test (Rathburn et al., 2001, 2003; Melaniuk et al., 2022). Due to the potential influence of seafloor methane seepage on paleoceanographic records and past, present and future climate change, it is important to understand the regional history of subsurface methane gasses. Isotopic analyses of living and fossil foraminifera from expected seep environments offer one of the best tools to assess the biogeochemical and paleo-environmental influences of modern and ancient methane seepage.

Pressure, induced by burial, has the potential to alter the  $\delta^{18}\text{O}$  of foraminifera through oxygen-isotope re-equilibration (Bernard et al., 2017). These authors suggest that late Cretaceous and Paleogene deep-ocean temperatures, inferred from benthic foraminifera  $\delta^{18}\text{O}$ , may be significantly overestimated as a result of this effect. Finally, it has been shown that incubation of foraminifera with significantly  $^{18}\text{O}$ -enriched artificial seawater can affect oxygen isotopes in foraminifera through rapid grain boundary diffusion (Adams et al., 2023).

#### 4.2. Challenges and future research directions

There is a broad array of important questions and research directions that are needed to fully understand stable isotopic compositions in benthic foraminifera. While work on shallow-water species has provided significant insight into the origins and influences of isotopic signatures in benthic foraminifera, it is clear that more work needs to focus on the deep-sea taxa that are used extensively to assess characteristics of ancient oceans. Specifically, more work on the isotopic biogeochemistry of living deep-sea foraminifera (rather than the mixed living/dead/fossil assemblage found in core tops) is needed to clearly understand the multitude of processes affecting isotopic compositions of those taxa whose fossils are commonly used to evaluate paleoceanographic conditions. This work requires use of the appropriate methods and advanced techniques to answer long-standing questions that currently hinder interpretations of isotopic data from foraminiferal carbonate. This includes taking advantage of recent methodological advances as described in section 3.1. Laboratory culturing work, *in-situ* measurements, and comparisons of data from populations living in different environments (natural experiments) are among the procedures that will help elucidate processes that affect isotopic signatures in deep-sea benthic foraminifera.

**Mobility.** Studies have shown that benthic foraminifera can move to different microhabitats over seasons and in response to changing conditions. Since ambient conditions can significantly influence the biogeochemistry of foraminiferal calcium carbonate (Fig. 2), it is important to understand: 1) what environmental variables might cause individual foraminifera of a given species to move during their lifespan; 2) migration of populations according to seasonal food availability and/or the consequent changes in their microhabitat; 3) how much of the temporal changes observed in populations result from individual mobility and how much results from changes in population (reproduction) or colonization dynamics; 4) whether foraminifera calcify at the depths they live/are found; 5) basic knowledge of life span for important species; 6) how are deep-sea benthic foraminifera able to maintain global populations genetically, with similar biological and biogeochemical characteristics (propagule longevity and colonization potential); 7) basic ecological aspects, including competition-driven changes in population/assemblages (that influence which species are available for isotopic and/or trace element analyses)?

**Ontogeny.** Most rotalid foraminifera retain earlier chambers throughout their life span, making it possible, with emerging and future technologies that can analyze individual chambers, to evaluate ontogenetic changes in biogeochemical signatures. A number of questions emerge from comparisons of smaller tests versus larger tests and initial evaluations of individual test chamber biogeochemistry. These questions include: 1) are ontogenetic differences in isotopic signatures of some species due to lifespan changes in microhabitat or to changes in kinetics/fractionation during the lifespan of individuals; 2) do apparent ontogenetic differences between some infaunal and epifaunal species result from biological or ecological (microhabitat) influences, or both; 3) does the addition of calcium carbonate to earlier chambers significantly influence the isotopic composition of early chambers (effectively diluting or muting the original chamber's isotopic signature); 4) are ontogenetic changes in biogeochemical signatures gradual through the lifespan of an individual or are there abrupt changes at particular stages of development; 5) what is the role, if any, of internal and/or external symbionts on stable isotopic signatures of deep-sea foraminifera, and do these influences change during the lifespan of an individual; 6) do changes in diet during the lifespan of an individual contribute to changes in isotopic signatures?

**Biology.** The isotopic influences of calcification processes remain largely unknown. Some frustrating questions that need to be addressed include: 1) Why do different species have inherently different isotopic signatures (why don't they all calcify similarly, and if living in the same microenvironment, have the same carbon isotopic signature); 2) What is

the relationship, if any, between the carbon isotopic composition of the protoplasm and the  $\delta^{13}\text{C}$  of the calcareous test; 3) why are there differences between the wall structure of different groups of foraminifera, such as porcellaneous and hyaline (is there an advantage related to the environment, or is this an evolutionary difference between taxa), and how do these differences influence isotopic composition.

**Calcification mechanism.** Determining which carbonate species ( $\text{CO}_2$  and/or  $\text{HCO}_3^-$ ) foraminifera calcification relies is essential in explaining the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  composition of the DIC at the site of calcification (Zeebe et al., 1999; Toyofuku et al., 2017). Uptake of carbon and modification of the internal and external pH (and thus inorganic carbon speciation) during calcification need to be quantified to understand the effect of biomineralization on the C- and O-isotopic fractionation (e.g. De Nooijer et al., 2009; Bentov et al., 2009). As the controls on calcification likely vary among species and may scale with size (e.g. through changes in surface-to-volume ratios), unlocking the exact routes by which inorganic carbon is taken up, may increase our understanding of foraminiferal isotope signatures significantly. More specifically, it is crucial to quantify the uptake through  $\text{CO}_2$  diffusion versus transmembrane  $\text{HCO}_3^-$  uptake versus seawater vacuolization (e.g. Ujiie et al., 2023). Secondly, it is necessary to assess the chemical conditions during calcification, including the  $\text{CaCO}_3$  phases that are formed (Jacob et al., 2017; Evans et al., 2020) and the involvement of enzymes, as together they determine the isotopic fractionation between the fluid of the calcifying fluid and the shell's calcium carbonate.

Since the scale at which the inorganic carbon chemistry changes is very small ( $\mu\text{meters}$ ), it is necessary to model the oxygen- and carbon isotope composition in the foraminiferal microenvironment, as well as at the site of calcification (Köhler-Rink and Köhl, 2005). The rate of calcification (i.e. of  $\text{CaCO}_3$  crystal precipitation) by foraminifera is poorly constrained, but first reports show rates that are relatively high (Geerken et al., 2022), suggesting high rates of inorganic carbon uptake and fast transformation of inorganic carbon species. This may have important consequences for the isotopic fractionation and thus likely affects the calcite's  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ . Accurate determination of precipitation rates,  $\text{CO}_2$  diffusion rates, bicarbonate transport and active pH modulation will need to be combined to model the net effect of these processes on the stable isotope fractionation.

**Methane seeps.** The history of seafloor methane seepage is important to understand the relationships of this source of greenhouse gas emissions with climate change of the past, present, and future. Use of isotopic signatures of benthic foraminifera have been useful to evaluate ancient seafloor methane seepage and its consequent effects, but work on living Rotalid foraminifera from active methane seeps has raised a number of questions. These include: 1) What carbon species do foraminifera use to calcify, and where is this carbon derived from; 2) Is it the mechanism ecological (e.g., avoidance), or biological (e.g., calcification process, or manipulation of the nanohabitat), or both that results in the extreme offset between foraminiferal  $\delta^{13}\text{C}$  and that of ambient methane seep porewater. Recent research has shown that  $\delta^{13}\text{C}$  of fossil Miliolida species may potentially capture methane hydrate dissociation (Clemens et al., 2023), which raises further questions about the extent the various effects discussed in this review affect different calcification mechanisms. How are Rotalid benthic foraminifera apparently capable of discriminating against the heavily depleted carbon (and why do they do this?), and Miliolids apparently not?

**Diagenesis.** It is currently unclear when, if, and by how much benthic foraminifera stable isotopes become affected by diagenesis through secondary precipitation and dissolution. Are thin-walled species and/or smaller specimens more affected compared with thick walled/heavy calcified ones? In carbonate undersaturated seawaters, are infaunal species potentially less affected by dissolution effects compared to epifaunals, as has been proposed for Mg/Ca temperature reconstructions (Elderfield et al., 2012)? In populations, why do we sometimes observe well preserved and poorly preserved specimens in the sample? Does dissolution have a similar effect on benthic foraminifera as it has on

planktic foraminifera (e.g. enrichment)?

To answer the questions posed above dedicated research programs are required. In order to thoroughly assess potential early diagenetic effects on recent faunas it is important to compare results from living and dead assemblages, and make assessment of benthic foraminifera preservation (SEM), weights, shell thickness, stable isotopes. With advancements in IRMS techniques (e.g. Ishimura et al., 2004, 2008) and potentially SIMS (we need to better understand the matrix effect, caused by differences in the chemical composition or structure of carbonate that shift the measured isotopic values) we will now be able to make significant advances in our understanding of natural stable isotope variability in benthic populations, including individual and smaller specimens. In combination with measurements of in-situ environmental variables, such as amount, quality and stable isotopes of food, carbon isotopes of bottom and pore waters, and carbonate chemistry, we can assess potential causes for observed trends. It is also imperative that modern/recent epifaunal foraminifera are thoroughly calibrated using real core-tops (living and dead specimens) and databases and compared with seawater and modern analyses. Epifaunal benthic  $\delta^{13}\text{C}$  need to be thoroughly calibrated with in-situ bottom water  $\delta^{13}\text{C}$  of DIC measurements. In a recent study, Reyes Macaya et al. (2021) revealed significant differences in the distribution of water masses in the upper ~1000 m of the water column, as inferred from  $\delta^{13}\text{C}$  of DIC, along the continental slope and shelf of the Southeast Pacific, and the open ocean. It is also important that taxonomic references are included in publications that present isotopic analyses. Use of mixed species analyzed together for isotopic measurements should be avoided. It is recommended to keep images of specimens analyzed and to publish representative images of species analyzed. Furthermore, key questions from above may be addressed using incubations (*in situ* pressure and temperature experiments, following Wollenburg et al., 2018) and field (landers), lab-culturing, and modeling studies.

## 5. Conclusions

Benthic foraminifera stable isotopes are crucial in creating an understanding of past paleoenvironmental in ocean temperatures, sea-level and carbon and nutrient changes. In this review the direct and indirect mechanisms that contribute to stable oxygen and carbon signals in benthic foraminifera are discussed. Our review highlights that several questions remain with regards to how benthic foraminifera calcite acquires its isotopic composition, and provides ample concepts to fuel future research endeavors to address these knowledge gaps.

## CRedit authorship contribution statement

All authors contributed equally to this manuscript; Babette Hoogakker: abstract, introduction, discussion (4.1.5; 4.2), conclusion; overall formatting etc; Toyoho Ishimura: Stable isotopes of foraminifera, analyses of isotopes, discussion (4.1.2; 4.2); Lennart de Nooijer: introduction, discussion (4.1.3; 4.2); Gerard Schmiedl: introduction, discussion (4.1.1; 4.1.2; 4.2); Anthony Rathburn: introduction, discussion (4.1.1; 4.1.4; 4.2).

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

No new data, appropriate references are made.

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