Old and new climate proxies with foraminifera: Providing geochemical evidence for porosity as a proxy for metabolism, and investigating the validity of I/Ca as a new redox proxy

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Contents

Chapter 1: Porosity of Planktonic Foraminifera through a Geochemical Lens

ABSTRACT

This study investigates the biological response of planktonic foraminifera (or "forams") to environmental conditions via the morphology of foram tests and geochemical data from 11 species and 5 sieve size fractions. The purpose of this research is to test the effectiveness of porosity as a proxy so that it might be used in future studies to assess paleoenvironments, examining foram metabolism in relation to the features of their habitat, particularly the temperature and oxygenation of seawater. As this study reveals a strong correlation between porosity and both δ13C and δ18O, a question it raises is whether there is bidirectionality in the geochemical signatures. To what degree do forams serve as paleothermometers and passive tracers as compared with recording their own biological conditions and metabolic effects? Geochemical data (δ18O and δ13C) on two modern core-top samples has been collected and compared with porosity data (from the unpublished thesis work of Janet Burke) and considered in light of biological and environmental conditions. The results suggest that porosity is influenced by both temperature and metabolism, and the interconnected nature of these driving forces suggest that forams can provide information as to seawater conditions while also reporting on their own physiological and morphological responses.

1 INTRODUCTION

In light of current concerns around climate change, developing a clear understanding of paleoceanographic conditions, especially during periods of warming, can provide insight into future change and its potential impacts on life in the ocean. Planktonic forams are protists with multi-chambered $CaCO_3$ shells (tests), and due to their abundance in the fossil record, are commonly used in reconstructing paleoceanographic records (Ravelo and Hillaire-Marcel, 2007). They live in the upper zone of the open ocean, and passively incorporate geochemical signatures of their environment during their growth and test development (Kucera, 2007). Planktonic forams are widely used in paleoclimate research, because their high preservation potential, rich

fossil record and temporal resolution, in conjunction with their integrated geochemical signatures, can provide valuable information on ocean productivity and temperature (Ravelo and Fairbanks, 1995, 1992)

Though trends in porosity have been recorded for decades, less is known about the direct drivers of this physiological trend. My multi-species study utilizes morphological variation in order to observe geochemical variation in relation to porosity, seeking to examine the causes of the observed patterns. Forams have been widely used in geochemical research and paleoclimatic reconstructions, and a developing body of literature is now beginning to explore a direct, measured correlation between the biological responses of the forams themselves to climate change. Past studies have suggested that the shell walls of forams reflect this response, with higher "porosity," – percent test wall area occupied by pores (Bé, 1968) – linked to higher temperatures (Bijma, Faber, & Hemleben, 1990; Fischer, 2003) and lower oxygen concentrations (Kundt et al., 2014). Recent work demonstrates the sensitivity of foram metabolism to temperature and primary productivity, features that could be deduced by examining δ13C and δ18O (John et al., 2013). Higher temperatures would result in higher metabolic rates, and a tentative link has been posed between porosity and metabolism (Bijma et al., 1990).

For this study, I have measured δ18O and δ13C across 11 species in two modern core-top samples (KC78, located at +5.26, -44.13 and one sample from CH82, located at +43.5, -29.8). The species live across a range of depth habitats, including mixed layer, thermocline and subthermocline depths, and were from five sieve size fractions, ranging from 250-850 um. The sample range also included both symbiont-bearing and non-symbiotic taxa. The species examined were *Globorotalia menardii, Pulleniatina obliquiloculata, Globigerinella siphonifera, Globorotalia tumida, Globigerinoides ruber, Neogloboquadrina dutertrei, Globigerinoides sacculifer, Orbulina universa, Globorotalia truncatulinoides, Globigerinoides conglobatus and Sphaeroidinella dehiscens.*

The geochemistry of foraminiferal calcite records surface water conditions such as water temperature and productivity while providing evidence of metabolically- or kinetically-mediated fractionations, and as such are used for seawater proxy measurements (Bijma et al., 1999). Metabolic effects on δ13C are common, with size-dependent differences in isotopic carbon integration, as will be explored in Section 2.2.1 (Elderfield et al., 2002).

However, it is essential to understand the ecological side of this process and how these factors are recorded by their linked fractionations. Habitat (specifically temperature, light and nutrient availability) impacts metabolic rate and therefore growth rate, dynamics that would appear to impact the chemical signals recorded by foram tests (Brown et al., 2004; Kucera, 2007; John et al., 2013). Vital effects should also be considered, as life processes can lead to discrepancies in isotopic and geochemical results (Zeebe et al., 2008). A change in the depositional environment, season, depth of calcification or vertical migration pattern can all alter the isotopic values. The recorded geochemical signatures alter seasonally, with lighter δ18O values occurring in the winter and peak values in spring and fall (Kuroyanagi et al., 2011), while δ13C values recorded are richest in the winter when a reduction in vertical mixing results in less nutrient-rich and δ13C-depleted water reaching the surface (King and Howard, 2004). Vertical mixing patterns affect signals as well – in particular, δ13C records the dissolved inorganic carbon (DIC) of seawater, which will be reported differently depending on where a given taxa lives. Below the thermocline, δ13C is depleted, because in the deeper waters below this zone, the water is cooler and more nutrient-rich in comparison with the overlying warm and well-lit surface waters, and as a result primary productivity differs across this boundary (Kuroyanagi et al., 2011; Ravelo and Hillaire-Marcel, 2007; King and Howard, 2004). The isotopic information of foraminiferal calcite has the potential to assist in the reconstruction of paleoceanographic variation and the abiotic habitat of a given species (Kucera, 2007).

δ18O and δ13C provide different information on ocean conditions. δ18O is a temperature proxy, reflecting (at the surface) the balance between evaporation and precipitation and changes in ice volume in addition to the mixing and distribution of water masses (in deep ocean data) (Spero et al., 1997). The overall δ18O value of the oceans is higher both during glacial periods and at lower latitiudes (Ravelo and Hillaire-Marcel, 2007). δ13C broadly reflects the dissolved inorganic carbon (DIC) of the water, but the signal can be complicated by biological controls like respiration and photosynthesis (Kucera, 2007; Spero et al., 1997). In this study, I analyzed δ13C and δ18O values in relation to porosity. As the behavior of forams is still not fully understood, the function of pores is not confirmed but it would appear that they support respiration, functioning for gas exchange (Gupta & Castillo, 1992). This theory is supported by the presence of mitochondrial clusters around pores, suggesting a respiratory function (Leutenegger and Hansen, 1979). Higher porosity has been correlated with larger body size, lower oxygen

conditions, and lower latitudes (Bé, 1968; Hemleben et al., 1989; Frerichs et al., 1972). This would then suggest a metabolism-driven change in porosity (Bijma et al., 1990). To fill a gap in the literature, my study aims to investigate the relationship between porosity, the environment and geochemical proxies (δ13C and δ18O) in order to better understand the (not necessarily independent) factors that drive the observed trends in porosity, and whether metabolism could be the link that ties these factors together.

2 BACKGROUND

There is a large body of research that has established the relationship between δ13C and δ18O and the environmental, ecological, and taxonomic identity of species (Kucera, 2007; Ravelo and Hillaire-Marcel, 2007). Porosity has been demonstrated to vary with latitude, oxygenation, temperature and foram size, factors which could perhaps be connected by metabolism (Kundt et al., 2014; Fisher, 2003; Bijma et al., 1990).

2.1 Porosity

The studies exploring the link between porosity and oxygenation have shown an inverse relationship between porosity and bottom water oxygen content, with an increase in porosity a survival response to low oxygen conditions (Kundt et al., 2014; Kuroyanagi et al., 2013). Porosity has been determined to be superior to pore concentration in serving as a paleothermometer. (Fischer et al., 2003). Higher temperatures not only lead to higher rates of respiration, but also an increase in metabolic and growth rates, leading to higher oxygen demands. It has been inferred that higher oxygen demand could necessitate these morphological and physiological changes; for example, increased porosity could facilitate the higher oxygen consumption needed in a warmer habitat (Bijma et al., 1990). In fact, Bé et al. (1968) demonstrated that porosity is highest in species living in warmer, near-surface waters. It has also been suggested that lower gas solubility resulting from higher temperatures leads to the development of larger pores. There is more specific knowledge to be acquired in this area, as changes in porosity have been suggested to correlate with dissolved oxygen availability, as well as influenced by temperature and nitrogen levels (Bé 1968; Fischer 2003; Kundt 2014).

Several concerns have been raised about using porosity as a proxy. One is that porosity is reported to change during ontogeny, as surface area to volume ratios change and cause different metabolic processes to take precedence at various stages, which would necessitate comparing species of the same maturity (Huber et al., 1997; Caromel et al., 2015). Also, calcite dissolution appears to result in increased pore diameter (though increase in overall porosity usually occurs through increase in pore area and decrease in pore density) (Be et al, 1975). Still, there is a clear link between temperature and porosity (Bijma et al., 1990).

The results observed by Janet Burke suggest a correlation between porosity and oxygen content, and a weaker correlation between porosity and temperature (Burke, 2016). But, as the temperature and oxygen data in the study were based on assumptions of depth habitat, it was difficult to tell whether the relationships were just an artifact of uncertainty about where each species resides in the water column. Core-tops can present challenges, as there can be inter-test variability in geochemical signatures within a given species, uncertainty that can result from calcification temperature differences (perhaps due to unspecific habitat depth or seasonal variations) (Sadekov et al., 2008). The results of the Burke study began to reveal a potential metabolic framework for porosity, and my geochemical investigation provides insight into potential causes for the trends observed between porosity and seawater conditions. In doing so, it aims to help elucidate what porosity means as a proxy, and what causes the observed morphological response.

2.2 δ18O and δ13C

Important distinctions between δ18O and δ13C as proxies are that only δ18O is at isotopic equilibrium with the seawater (due to larger available reserves of equilibrating oxygen), while δ13C is not globally uniform, nor does it vary consistently over time. As these proxies inform about seawater conditions, when examined in conjunction with porosity they can provide information about the environment that induced a morphological response, and so are beneficial in analyzing foram biotic response to climate change (Ravelo and Hillaire-Marcel, 2007; Ravelo and Fairbanks, 1995, 1992). This is particularly useful as these isotopic values do not just reflect the state of the forams' microenvironment; a biotic response is added through vital effects, size specificity and seasonal patterns (Ezard et al., 2015; Kuroyanagi et al., 2011; Spero et al., 1991). In addition, this is the first study to look at foram porosity in conjunction with δ18O and δ13C,

and there is still more to be learned about how δ18O and δ13C interrelate (Janet Burke, personal correspondence).

2.2.1 δ13C

δ13C reflects the dissolved inorganic carbon (DIC) of the water in which the foram shell calcified (Spero et al., 1997). This record is affected by perturbations in the isotopic composition of the ocean and the balance between photosynthesis and respiration, photosynthetic symbiont presence, mixing of water masses, and the $\delta 13C_{DIC}$ reaching the site, with changes in the amount of carbon stored on land affecting the global reading (ocean levels of this isotope increase with increased terrestrial vegetation) (Ravelo and Hillaire-Marcel, 2007; Spero et al., 1997). Particularly relevant here is the thermocline effect described earlier, with different DIC levels dependent on foram location within the water column (Kuroyanagi et al., 2011; Ravelo and Hillaire-Marcel, 2007; King and Howard, 2004). Species-specific calibration is needed due to differences in habitat preferences and therefore the recorded seawater $\delta 13C_{DIC}$. Additionally, different species have varying light, temperature and nutrient needs, resulting in different vertical depths and seasonality recorded (Ravelo and Hillaire-Marcel, 2007).

Size seems to play a key role in δ13C records. Isotopic composition can differ between small and large forams, perhaps due to vital effects, habitat change, seasonal patterns, or differences in dissolution due to shell thickness (Ravelo and Hillaire-Marcel, 2007). Size-driven variation in δ13C, with smaller specimens depleted in ^{13}C in comparison with their larger counterparts, could suggest a growth-related pattern (Elderfield et al., 2002; Spero et al., 1997). This is significant, as our study considers δ13C as representative of metabolism. With an increase in growth (therefore increased size) comes a decrease in growth rate, leading to one of three things occurring: A decrease in kinetic fractionation due to transfer of carbon during biological processes, a decrease in the incorporation of metabolic CO2 (low $^{12}C/^{12}C$) which contaminates the carbon pool from which calcite precipitates, or an increase in photosynthetically-fractionated CO_2 uptake (more ^{13}C is available for calcification when low $^{13}C/^{12}C$ carbon is used for photosynthesis) (Elderfield et al., 2002; Ravelo and Fairbanks, 1995). All of these aspects could affect the recorded isotopic values, and result in this size-based pattern.

2.2.2 δ18O

Local variations in the δ18O of surface water are a reflection of overall oceanic δ18O affected by changes in ice volume and the balance between evaporation and precipitation, while deep ocean δ18O is a reflection of mixing and the distribution of water masses (Spero et al., 1997). While the δ18O of the foram calcite is at isotopic equilibrium with the seawater, it does not provide an identical signal, the offset resulting from fractionation during calcite precipitation (Ravelo and Hillaire-Marcel, 2007; Erez and Luz, 1982). There is a decrease in δ18O of calcite with an increase in ambient seawater temperature. As a result, if the δ18O of seawater is known, this can be compared to foram δ18O to construct a temperature record (Farmer et al., 2007). The signal recorded in the foraminiferal calcite can serve as a "paleothermometer," with its oxygen isotope directly linked to temperature changes (Kucera, 2007). In general, higher δ18O measurements reflect a lower temperature. Once again, this must be interpreted in conjunction with habitat analysis, as seasonal and depth preferences impact results and metabolism is temperature-sensitive (Ravelo and Hillaire-Marcel, 2007; Ravelo and Fairbanks, 1992).

δ18O can be used as an indicator of temperature and density stratification for a given locality, when this information is not known for a given point in time. In this process however, inferences are made regarding seasonality, density stratification, and percentage abundance of each size within a species for a given depth, all based on expected and relative isotopic values (Ezard et al., 2015; Ravelo and Hillaire-Marcel, 2007; Ravelo and Fairbanks, 1992). In modern oceans with readily available data on ocean conditions, δ18O measurements can provide insight into the depth habitats for different species for which this data is unknown (Farmer et al., 2007).

2.3 Metabolism

Body size increases with ontogeny, while surface area to volume ratios decrease throughout ontogeny (Caromel et al., 2015; Elderfield et al., 2002). With an increase in body size, there is an increase in gross metabolism and a decrease in weight-specific metabolic rate (Brown et al., 2004). As a result, forams of the same maturity level must be compared when examining porosity, as the relevant metabolic effects should be controlled (Caromel et al., 2015). Based on δ13C and δ18O studies, it would seem that vital effects are driven by the

environmental factors affecting the organism size, rather than just ontogeny (Ezard et al., 2015; Spero et al., 1991). The environmental factor driving size-specific δ18O trends was the type of symbiont hosted, whereas for δ13C trends, depth habitat in addition to the symbionts became integral factors (Ezard et al, 2015). As metabolism is inextricably linked to body size and temperature, and we wanted to test how these factors relate to porosity, it was important to assess temperature at the different assumed depth habitats to better understand metabolism (John et al., 2013; Brown et al., 2004). This involved comparing δ13C and δ18O to gauge how these factors changed in relation to porosity.

Many porosity studies only examine one or two species, which proves to be limiting in discerning overall trends, and so the data used here (compiled by Janet Burke) compares multiple species. Isotopic studies reveal that shallow-dwelling species are more likely to have low δ18O and high δ13C relative to deeper-dwelling ones, reflecting that warmer surface waters should have these isotopic values as well as compared to the nutrient-rich, cooler waters lying below; multi-species studies thereby allow for an isotopic reconstruction of the water column (Ravelo and Fairbanks, 1992, 1995). However, many factors can complicate depth habitat identification for species, whether effects of seasonality, differential dissolution, metabolic rates, or preservational elements (Ezard et al., 2015; Zeebe et al., 2008).

2.4 Symbionts

In tropical euphotic waters, likely due to the high degree of competition for resources in combination with the abundance of sunlight, some planktonic forams have evolved to be symbiont-bearers. Symbionts provide energy from photosynthesis, and also assist with calcification (Hemleben et al., 1989; Bé et al., 1982). In the species examined in my study, the two photoautotrophs hosted were dinoflagellates and chrysophytes. Because of the scope of endosymbionts hosted by forams, there is a variety of photopigments available for photosynthesis, allowing these surface-dwelling forams to inhabit a broader depth range and also use a greater percentage of the light spectrum (Hallock, 2016; Uhle et al., 1997). Symbionts produce organic matter in excess of what is necessary for both their own and their host foram's growth. This is a complicating factor in terms of recorded δ13C, as a part of this organic carbon could be used for growth, and in doing so add another isotopic component to the carbon signature recorded in the foram test (Uhle et al., 1997).

3 METHODS

This study used two modern core top samples for which the environmental conditions of the locality are already known (ten samples from KC78, located at +5.26, -44.13 and one sample from CH82, located at +43.5, -29.8). The species varied in depth habitat and symbiont-presence, and represented a range of size fractions (250-850 um). The goal was to test our method as a manner by which to compare the physical characteristics of the forams with sea surface temperature and oxygenation, in the hopes of applying it in future studies of the biotic response to past paleoceanographic change.

3.1 Porosity

The geochemical work in this study was analyzed in conjunction with unpublished data compiled by Janet Burke. She measured size, structure, porosity, surface area, volume and shell thickness for the species and size fractions within the two core-top samples. The process began by washing the samples, and then separating them by sieve size fraction (150-200um, 200-300um, 300-425um, 425-600um, 600-710um and 710-800um). A split of 50-100 forams from each size fraction was then sorted by species. Each specimen was imaged, and after a dissection, the smooth inner wall of the penultimate chamber was imaged with a Scanning Electron Microscope (SEM). The full specimen images were used to obtain surface area and volume measurements, using Hull lab Automorph code (Hsiang et al., 2016). The SEM images allowed for porosity of the chamber to be determined, as measurements of the penultimate chamber inner wall are the accepted way of obtaining porosity measurements (Bé, 1969). Porosity measurements were estimated using ImageJ software, where an image of a flat section of the test wall was converted so that negative space was shown in black, the area of which was then recorded as a quantitative metric of porosity (Burke, 2016).

3.2 δ13C and δ18O

The core-top samples were sorted by species and size (See Appendix 1). Next, each species sample in each sieve size fraction was weighed, imaged and crushed between two glass slides to open the chambers in order to ensure maximum removal of clays trapped within. The samples were then sonicated for 15 seconds each, and excess water was pipetted out. They were then left in a 50 degree C heating oven overnight to allow for full evaporation.

The δ18O and δ13C tests were conducted at the Yale Analytical and Stable Isotope Center, using a Thermo MAT 253 with KIEL IV Carbonate Device. The crushed forams in each tube were first dissolved in orthophosphoric acid to produce CO_2, and then a mass spectrometer ionized the CO_2(g) and provided ratios of the samples, in addition to the ratios for a recommended reference sample. From here, the δ18O and δ13C values were calculated in comparison to a standard (VPDB, VSMOW) (Ravelo and Hillaire-Marcel, 2007).

4 RESULTS AND DISCUSSION OF TRENDS

The results demonstrate a notable trend between both porosity and δ13C as well as with δ18O. When looking at the data in statistical frameworks, these two factors were primary drivers of the porosity trend observed.

The results observed by Janet Burke and Dr. Pincelli Hull suggest a correlation between porosity and oxygen content, and a weaker correlation between porosity and temperature (See Figure 1).

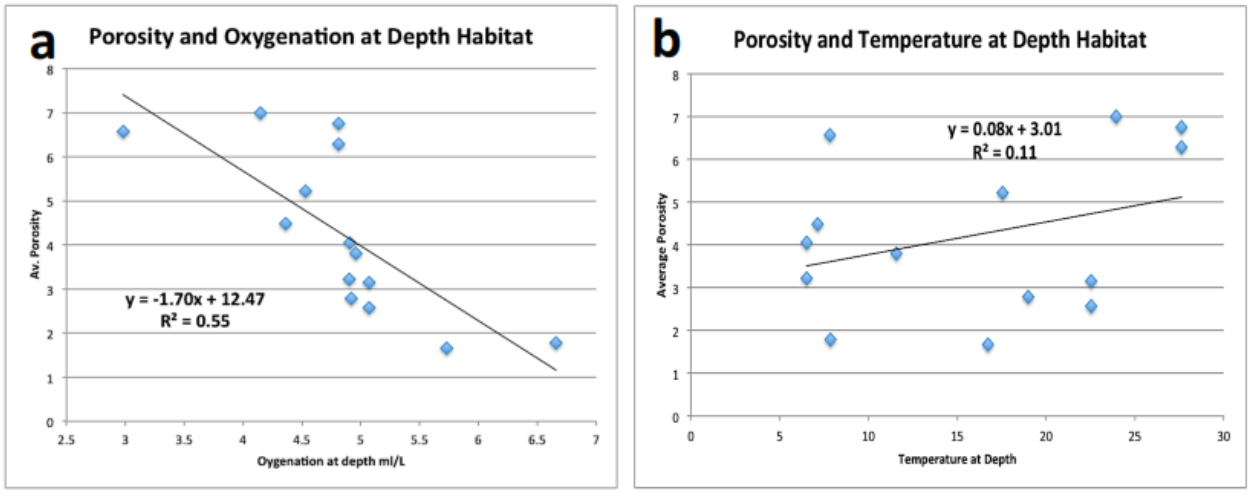

Figure 1: "Average species porosity plotted with oxygenation (1a) and temperature (1b)" (Burke & Hull, 2015)

However, in the geochemical research conducted this year, strong trends (See Figure 2) were seen for porosity with both δ18O (R^2 = 0.5217, p<0.0001) and δ13C (R^2 = 0.5336, p<0.0001), which was surprising as it was hypothesized that the trend would be only apparent for δ18O. δ18O reflects the temperature effect on porosity, while having a trend with δ13C as well suggests a metabolic driver. Though this demonstrates the overall observed trend, further plots attempt to show the most influential factors in determining this pattern.

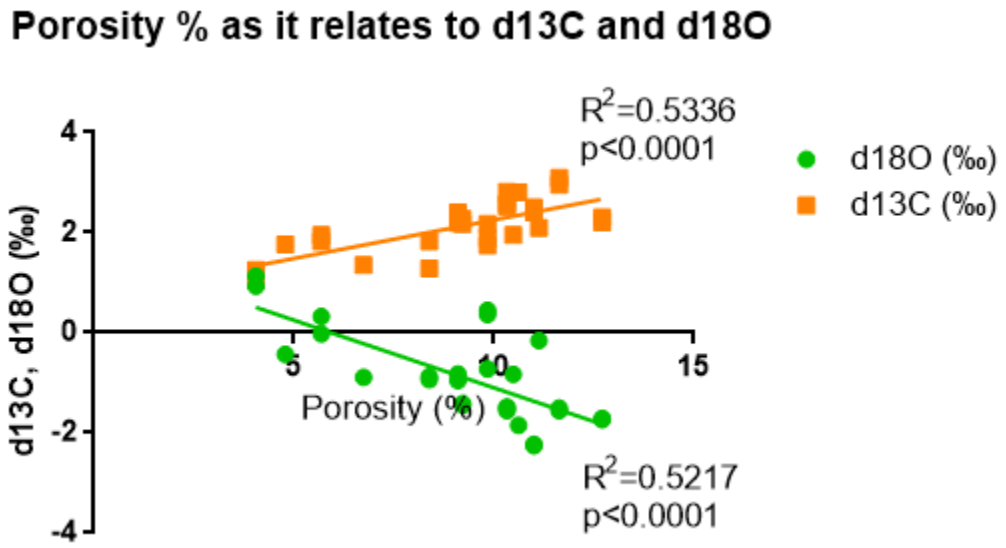

Figure 2: Overall patterns between porosity, δ13C and δ18O

The data was examined with a general linear model (GLM) (using glmfit in MATLAB). The fit of different distributions was evaluated for the GLM regression. For the continuous data investigated, normal, gamma and inverse Gaussian distributions were tested. Normal distributions were found to most accurately represent the data. This statistical framework suggested that the most prominent driver of the porosity trend is δ13C, with size and δ18O also having a degree of correlation; however none of the factors are statistically significant (See Figure 3). Size was expected to be a main contributing factor to the trend, based on past studies (See Figure 4a). This can be related more broadly to Janet Burke's findings in that porosity varied with size fraction within species from the same locality, with an overall pattern of larger forams having higher percent porosity than smaller ones of the same species (See Figure 4b).

On the other hand, the effect of species type on porosity was weak. Much of the existing literature examines very few species at a time, so with this wide sampling base it is notable that there is an overarching trend in porosity across individual species boundaries (See Figure 5).

FACTOR	P-VALUE
δ13C	0.1298
Size	0.2815
δ18O	0.3324
Symbiont presence	0.4777
Depth habitat	0.7135
Species	0.8231

Figure 3: GLM for porosity

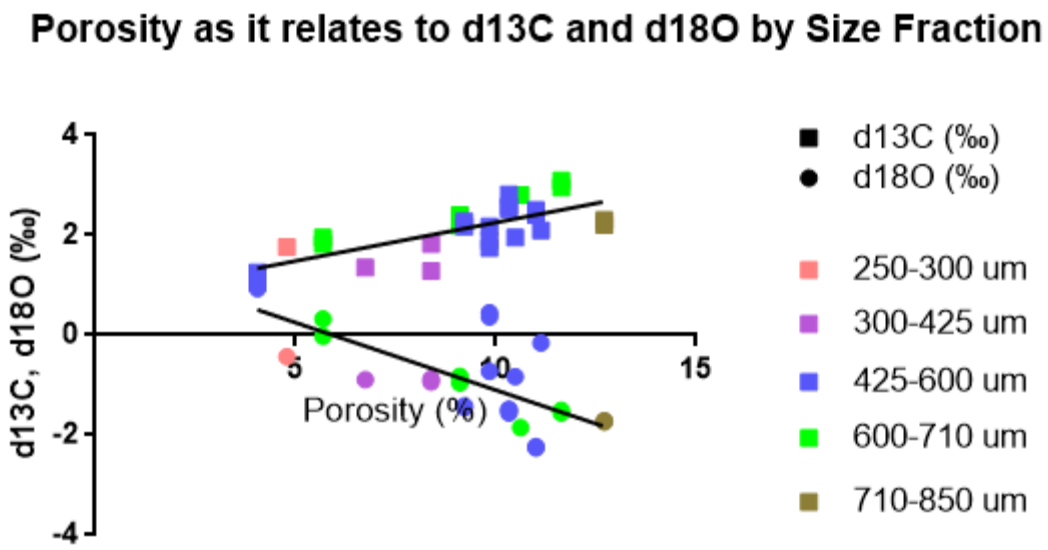

Figure 4a: same R^2 and p-values as in Figure 2

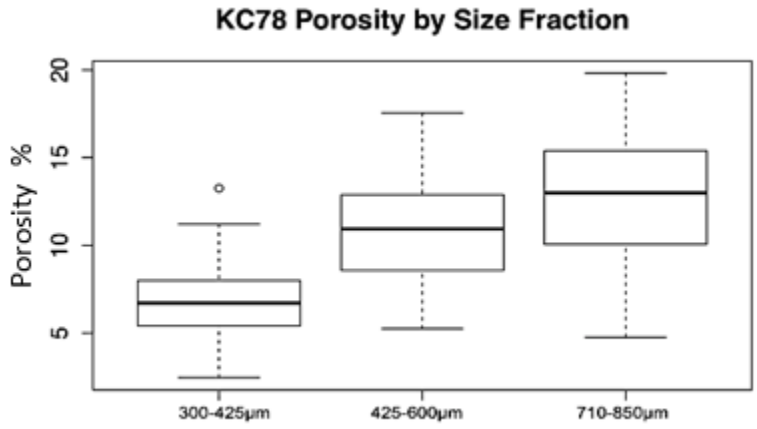

Figure 4b: (Burke, 2016)

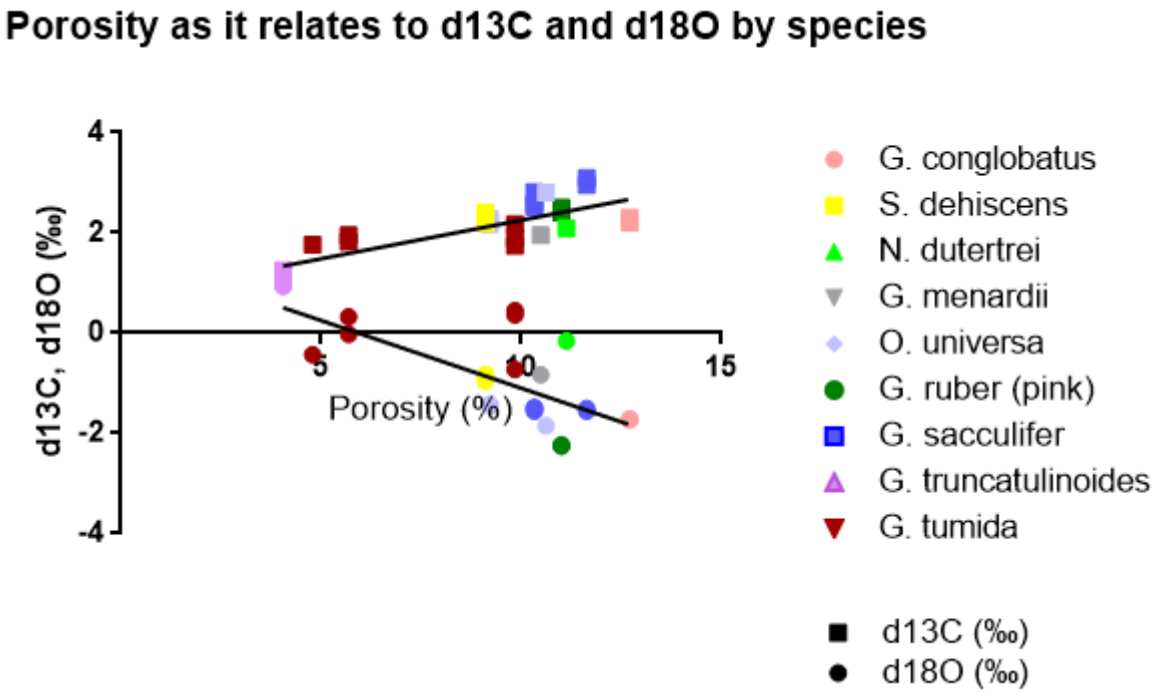

Figure 5: Same R^2 and p-values as in Figure 2

A GLM framework was also used to determine which factors most influenced δ13C, where δ13C was used to represent some combination of environmental signal (depth-specific DIC as measured by depth habitat) and various metabolic factors (species, size, temperature (δ18O serves as a proxy) and symbiont ecology). The results are as follows, with the most significant factors at the top, and correlation represented by p-values (See Figure 6a). It would appear that metabolism varies by species and scales with size, and that temperature (as represented by δ18O) could drive metabolism, although the p-value for δ18O is not significant in this study. The small sample size may have limited the ability of the GLM to show significance, and it is possible that for a larger sample size, both δ18O and porosity could be significant.

In terms of δ18O, the GLM results suggest that size and symbiont presence could be the most influential factors in determining this value (though neither was statistically significant). Depth is significant, but this is not surprising as δ18O reflects temperature and is based on depth habitat assumptions (See Figure 6b).

FACTOR	P-VALUE
Species	0.0327
Size	0.0950
Porosity	0.1298
δ18O	0.1459
Symbionts	0.3329
Depth Habitat	0.4510

Figure 6a: GLM for δ13C

FACTOR	P-VALUE
Depth	0.0006
Size	0.0643
Symbionts	0.0755
δ13C	0.1459
Species	0.2011
Porosity	0.3324

Figure 6b: GLM for δ18O

The presence of symbionts was considered as a potentially influential factor, and so the various symbiont types are presented below on the same observed porosity trend line (See Figure 7a). Dinoflagellates are suspected to have an impact on isotopic ratios, particularly for δ13C, while chrysophytes have not been seen to have a notable influence (Hallock, 2016; Uhle et al.,

1997). While sorting based on two categories, Dinoflagellates and No symbionts/Chrysophytes, trend lines within these groups appear less striking, however this is a small data set and other factors, as will be further discussed below, can also have an effect on this observation (See Figure 7b). In addition, an ANCOVA was conducted to determine whether there is a statistically significant difference between the No symbionts/Chrysophytes category and the Dinoflagellates category on the isotopic values recorded, controlling for porosity, set here as the covariate. One ANCOVA test focused on δ13C, and a second on δ18O. There does not appear to be a statistically significant effect of symbionts on δ13C after controlling for porosity; $F(1,22)=0.07$, $p>0.05$. There also does not seem to be a significant effect of symbionts on δ18O following this same method, $F(1,22)=0.1$, $p>0.05$.

The problem with presenting symbionts in this way given the inputted samples is that the No symbionts/Chrysophytes category is comprised solely of samples that are sub-thermocline and thermocline dwelling species, while the Dinoflagellates category is primarily mixed layer ones (with the exception of two samples). These photosynthetic symbionts would also be depth dependent. Depth habitat can also fluctuate seasonally. Depth habitat is also plotted in relation to porosity to visualize its effect on the trend, though based on the GLM analysis, it has a more minor influence (See Figure 8).

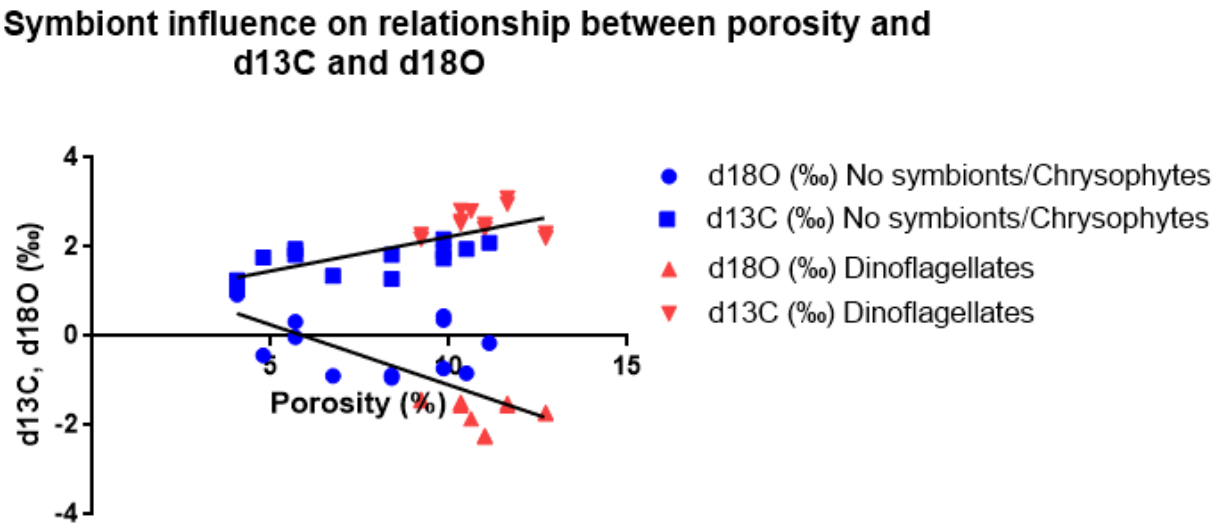

Figure 7a: same R^2 and p-values as in Figure 2

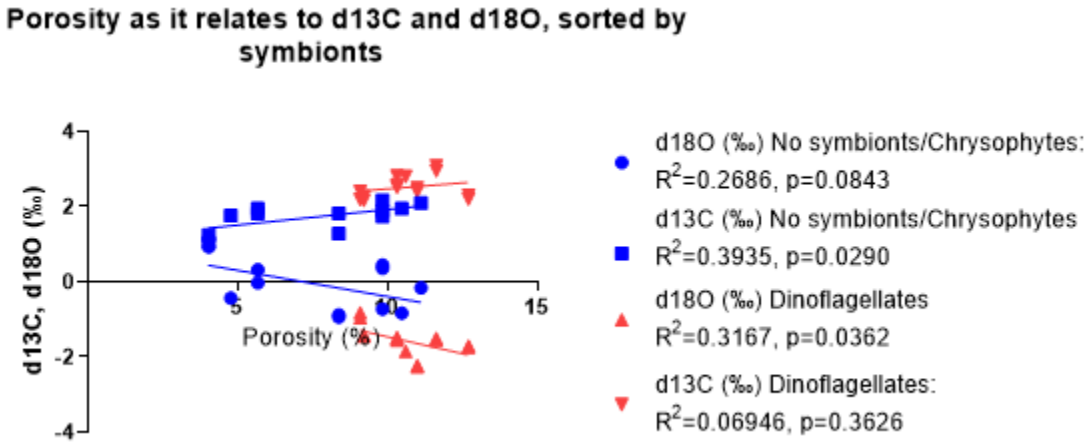

Figure 7b

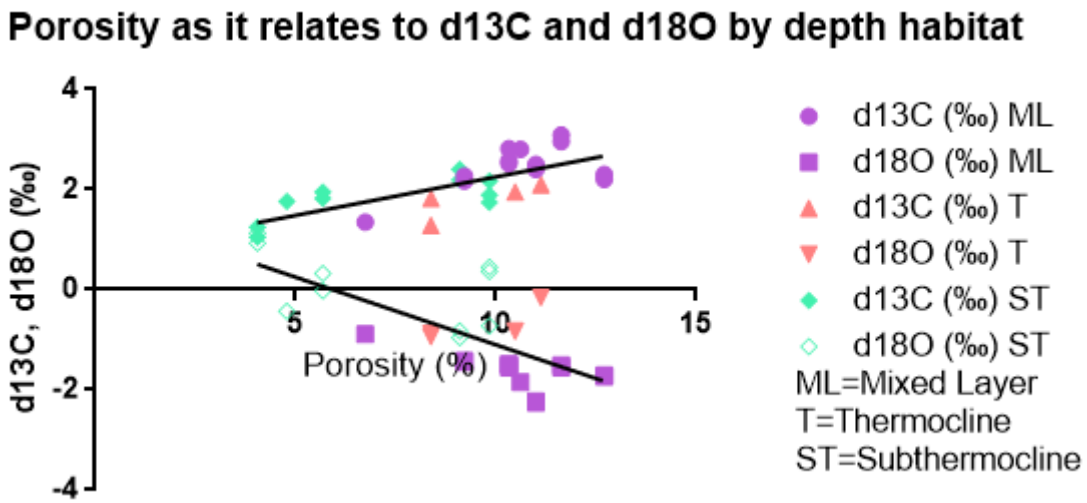

Figure 8: same R^2 and p-values as in Figure 2

5 DISCUSSION OF BROADER IMPLICATIONS

This research raises questions as to what is driving porosity, and more generally, what forams are recording through their geochemical signatures; to what degree are they reporting on their microenvironment or are the signals more indicative of biological response? There are different ways to interpret the observed trends – a traditional view of temperature being the driver, or instead it can be viewed in a metabolic framework. These two factors are interconnected, as metabolism is strongly influenced by temperature, in addition to body size. Though another driver could be a symbiotic effect, symbiont presence does not seem to drastically alter the observed trends. pH is posed as an influencing factor, though there is not enough evidence to support its effect here.

5.1 Metabolism

There is evidence to demonstrate the connection between porosity and temperature, and as a result, porosity appears to be a promising manner by which to trace past climate cycles (Hecht, Bé, and Lott, 1976; Bé, 1968).This is supported by my results, with δ18O representing temperature and the regression between porosity and δ18O having a highly significant p-value of <0.0001. But in addition, our data would suggest that metabolism plays a prominent role in influencing porosity; although there is no significant predictor of porosity in the GLM results, the closest one is δ13C. δ13C (representing metabolism) is shown here to be strongly correlated with porosity, and also has a significant p-value of <0.0001. As the forams experience warmer water temperatures, their metabolism increases (though this should be viewed in a relative scale as basal metabolism can differ between species and sizes) (Brown et al., 2004; King and Howard, 2004). This metabolic change is recorded by δ13C, whereas temperature is recorded by δ18O (Spero et al., 1997). Larger foram size has been connected to warmer habitats, as recorded by the wider size range of foram species living near the equator as compared to the polar regions (Schmidt et al., 2004). With these multiple confounding and interrelated factors, it is difficult to determine the core driving causes behind the trend in recorded isotopic signatures and porosity. Faster metabolic rates have a strong influence, but there is also higher carbonate saturation in warmer waters, and also greater light intensity (with possible benefits, but also the potential for

isotopic contamination from the photosynthetic activity of algal symbionts) (Kucera 2007; Schmidt et al., 2004).

In general, growth rate scales with metabolism (Glazier, 2009), and this scaling is linear for protists (Brown et al., 2004). Growth can be generally defined as the difference between inputs (nutrients or photosynthetic products from symbionts) and outputs (from excretion or respiration) (Lombard et al., 2009). Temperature strongly influences foram growth rate (Bijma et al., 1990), and as a result influences the isotopic composition of foram tests (Erez and Luz, 1982). Temperature intensifies respiration and photosynthesis, and faster metabolism at warmer temperatures results in increased incorporation of respired ^{12}C into foram tests (Bemis et al., 2000). Broad research conducted in the past has suggested that the growth rate of unicellular protists can react in varying manners in response to temperature change, but it would appear that there is a clear correlation for the foram species we investigated (See Figure 4a) (Glazier, 2009). In general, there is a direct correlation between higher metabolisms at larger sizes and at higher temperatures, which appears to be the driving principle behind the geochemical signatures recorded in my study (Brown et al., 2004). This trend is evident in the GLM results, which gives some indication that δ13C (used here as a metabolic proxy), followed by size and δ18O (temperature proxy) drive the porosity trend (See Figure 3) and that δ13C is most influenced by size and temperature (See Figure 6).

Based on this, it might appear that our data reflects a temperature-driven metabolic trend, with warm water increasing metabolism, leading to a biotic response of increase porosity as recorded by the isotopic trends observed (See Figure 2). However, because the order of the correlates are δ13C, followed by size and δ18O, the results could also suggest that there are basal offsets between taxa or groups of taxa that affect δ13C and porosity, and that metabolic factors related to body size contribute as well. δ18O, as the third correlate, may be the least important of these three, and yet because it represents temperature it could be the driving force that ties these other factors together, as temperature impacts metabolism and growth rate (King and Howard, 2004; Elderfield et al., 2002).

It might then logically follow that porosity could be a strong metabolic proxy, providing information on multiple biotic responses, signs which could also be used as climate indicators. Using porosity as a climate proxy would be contingent on running a more geographically diverse sample set, with more definitive depth habitat constraints. In doing so, it would also be important

to run a larger data set to better determine which factors are statistically significant, as the high p-values in the GLM results may have been a function of this small sample size.

5.1.1 Drivers of Metabolism

As δ18O and δ13C are the closest correlates with porosity, this would seem to suggest that porosity is driven by both temperature and metabolism, but a GLM framework helped to better understand this trend. The main correlates with δ13C (where δ13C is considered as representative of metabolism) were size (p=0.0950) and δ18O (p=0.1459) (See Figure 6a), though neither is statistically significant. Size is closely tied as metabolism is known to scale with size (Brown et al., 2004), with larger forams having faster metabolisms, a trend that would be recorded in their δ13C values. As δ18O also has a strong effect on δ13C, this would suggest that temperature affects metabolism, meaning that the recorded δ13C signature is not independent of δ18O, and therefore as porosity is most strongly correlated with δ13C, this is closely tied with δ18O.

And still, based on the results of this study it would appear that metabolism is the central, unifying biological mechanism driving the trends apparent in this data set. Though the metabolic component could be altering the interpretation of porosity, this aspect is still temperature-driven. Size-specific scaling can help hone the accuracy of porosity as a proxy, as it would seem that metabolism (and porosity to a lesser scale) is influenced by size. Also, even if the forams are also recording their own biological response, geochemistry is still likely reflecting their microenvironment, which is closely, if not linearly, related to the wider environment. The literature does not provide strong evidence to suggest that other signals or trends are drastically affecting interpretation, with the exception of pH, a factor which will be discussed below.

5.2 pH

Although δ18O is usually used as a temperature proxy, some research has suggested that it may also be influenced by pH. The δ18O and δ13C of foram tests have been recorded as becoming isotopically heavier with lower seawater pH (Uchikawa and Zeebe, 2010). Culture experiments reveal an increase in δ18O and δ13C when $[CO_3^{2-}]$ is decreased, a relationship seen in *O. universa, G. bulloides, G. sacculifer, and G. ruber* (Spero et al., 1997; Bijma et al., 1999).

As [CO_3^{2-}] and pH are known to co-vary, a pH effect is put forward here. It can be further suggested that pH controls the observed isotopic trend, as it is pH rather than [CO_3^{2-}] which controls seawater DIC levels. Experimental evidence from *O. universa* (symbiotic) and *G. bulloides* (non-symbiotic) can support this claim, and also demonstrate that the trend is not the result of temperature or symbiont presence (Bijma et al., 1999).

Another question is whether carbonate ion availability could affect pore size. It is known that pH affects wall thickness in forams (Uchikawa and Zeebe, 2010). Perhaps then if the forams are finding it harder to calcify they could compensate by altering their pore size in order to optimize chamber formation. Though δ18O in relation to pH would reflect precipitation temperature and salinity, it would still appear that large inputs of carbon into the seawater could cause an increase in δ18O values recorded locally, indicating that temperatures interpolated from those signatures could be too low (Uchikawa and Zeebe, 2010; Spero et al., 1997). The pH effect involving δ18O is believed to be a result of the thermodynamic isotope influence, causing HCO^{3-} ions to be richer in δ18O in comparison with CO_3^{2-} ions (Uchikawa and Zeebe, 2010). However, this does not explain the pH effect on δ13C. It is generally thought that the changes that varying pH levels induce on local carbonate chemistry, in addition to vital effects, are the cause of this relationship (Spero et al., 1997).

In general, the uptake of respired CO_2 does not impact δ18O values in foram tests, though it will significantly decrease the δ13C signature. Photosynthetic surface dwellers preferentially fix $^{12}CO_2$ and so these waters are depleted in ^{12}C (Ezard et al., 2015). When a symbiont is involved, the host's respiration will deplete the isotopic composition of the shell, observed by the addition of $^{12}CO_2$ to the environment, a metabolic byproduct (Uhle et al., 1997). This ties into the primary complication for interpreting δ13C records: the vital effect involved. The uptake of metabolic CO_2 results in a less direct correlation between δ13C records in the foram tests and that of the CO_2 in the forams' microenvironment (Spero et al., 1991). Perhaps a correlation could become apparent, where directional depletion of the carbon pool could be reflected in pH and subsequently in δ13C and porosity (Bijma et al., 1999; Spero et al., 1997). Further studies could examine whether there is an equally strong relationship between δ18O and pH, and whether metabolism could impact both signatures. It would also be interesting to consider whether there

could be direct depletion of the carbon pool and of the acidifying environment around it, and how this might be reflected in pH, and subsequently in δ13C and porosity.

5.3 Symbionts

Symbiont-bearing planktonic foram species are recorded as having higher δ18O and δ13C values than non-symbiont bearers because they are more likely to live in shallower (and likely warmer) depths because of the sunlight availability there (Hallock, 2016). This trend was examined here, and in addition to the impact that dinoflagellates had on porosity and isotopic records, as past research has suggested size-driven δ13C trends, likely resulting from preferential uptake of ^{12}C by the symbiont with increased symbiont density (Ezard et al., 2015).

However, based on the ANCOVA results and observed trends (Figures 7a, 7b) it would appear that our results are not simply skewed by the effects of symbiont photosynthetic activity. To fully understand this trend, more samples would be required. Currently these results are too closely tied to depth habitat, as the No symbionts/Chrysophytes category is just comprised of subthermocline and thermocline dwellers, while the Dinoflagellates category is almost entirely mixed layer. It cannot be confidently stated whether the symbiont effect is in fact present, or whether what is observed is simply the result of larger forams living in warmer surface waters (thus in a position to benefit from symbiont presence); it is difficult to pinpoint which aspect drives the trend.

Simply having a higher number of samples could help distinguish whether trends exist within each symbiont category. Depth habitat, though an unreliable category (as it is generally estimated off of isotopic values and also varies seasonally), did not appear to be closely tied to porosity in our study (based on the GLM data), though symbiont presence appeared to be a contributing factor. Further research and a larger sample size could provide more information on the degree of interrelation between these factors. Additionally, incorporating taxa that do not meet general expectations for symbiont presence based on their depth habitat would aid in answering this question. For example, *G. bulloides* is a surface dwelling taxa that is not a symbiont-bearer, and testing such species could help separate the two factors and see whether the observed pattern can be sustained.

6 SUMMARY

Based on this study, it appears that porosity has considerable promise as a biological proxy, and could be useful in future studies of the biotic response to past paleoceanographic change. The primary drivers of the observed trends in porosity are δ13C, size and δ18O, suggesting that porosity can provide information into water temperature while also providing information as to foram biological activity. As the statistical evaluation of the data set revealed that δ18O has some effect on δ13C, the results exhibit the effect of temperature on metabolism, signifying that the recorded δ13C signature is likely not independent of δ18O. As porosity is most correlated with δ13C (metabolism), it is also tied to δ18O (temperature), and it appears that metabolism (influenced by temperature) would be a likely link that ties together the factors that influence porosity. The interconnected nature of the drivers of porosity demonstrates that forams likely are able to inform as to past seawater conditions while also recording their own physiological responses.

Chapter 2: Investigating I/Ca as a novel proxy for ocean oxygenation

ABSTRACT

The ratio of iodine to calcium (I/Ca) in foraminiferal carbonate has been recently proposed as a proxy for ambient redox conditions (Zhou et al., 2014). An I/Ca proxy has the potential to fill in gaps in our understanding, whether in considering how future ocean deoxygenation could affect marine life or to gain a glimpse into oxygen levels in the surface waters of ancient oceans. As I/Ca is a newer proxy, this study has attempted to provide some preliminary data on a range of species and size fractions of planktonic foraminifera, helping to lay the groundwork for further investigation. Unexpectedly, trends appeared within this small depth range that suggested a correlation between low oxygen levels and low I/Ca values, as well as a correlation between δ13C and I/Ca, trends which would only have been expected over a depth profile which involved significant oxygen depletion. Since above a given O_2 level, $[IO_3^-]$ is not dependent on O_2, I/Ca should not be able to record $[O_2]$ within oxygen-rich waters, as I/Ca tracks $[IO_3^-]$ (Rue et al., 1997). The sample size in this study is too small and is restricted to well-oxygenated waters; this data range is not able to provide reliable information on the ability of I/Ca to serve as an indicator of an OMZ or of redox conditions. A more detailed data set, spanning a wider depth range and with more samples per size fraction, will be needed to further explore this in the future.

1 INTRODUCTION

Recent studies indicate a correlation between bottom water oxygenation and the I/Ca ratio, presenting it as a proxy for fluctuations in ambient redox conditions (Glock et al., 2014). There is a positive trend in the ratio with higher oxygen concentrations (Glock et al., 2014; Zhou et al., 2014). In addition to further exploring I/Ca as a proxy, this is a useful point of inquiry in light of the larger study's examination of the link between porosity and seawater oxygenation, as described in Chapter 1.

To consider the potential of I/Ca as a potential proxy, it is first essential to understand the nature of iodine in seawater. Iodine is a biophilic halogen and is redox-sensitive. Under anoxic

conditions, iodate (the iodized form, IO_3^-) converts to iodide (the reduced form, I^-). It has been seen that iodate, rather than iodide, can be incorporated into the carbonate structure (likely substituting for CO_3^{2-}) in calcareous foram tests. Therefore, it might appear that I/Ca ratios in foram tests could reflect paleo-redox conditions through recording changes in the iodate/iodide ratio in seawater over time. The incorporation of IO_3^- into carbonates follows a linear scale, and I/Ca also linearly tracks IO_3^-. This would seem to demonstrate that I/Ca provides information on the presence of IO_3^- in the water, thereby showing whether there is oxygen present, as IO_3^- and O_2 values follow I/Ca values (Hardisty et al., 2014; Zhou et al., 2014). The ratio could also be altered as a response to accelerated organic matter burial, which would result in a drawdown of global iodine, reflecting productivity at a given time (Lu et al., 2010; Lu et al., 2013).

Iodate concentration in seawater is most strongly affected by primary productivity and oxygen levels (Zhou et al., 2014). As foram tests reflect seawater iodate/iodide ratios, it follows that these are also the main controls on I/Ca ratios for the foram tests themselves. It would appear that subtle elements of deoxygenation can be picked up by this proxy (Lu et al., 2016). Additionally, decreased productivity will lead to an increase in foram I/Ca (Zhou et al., 2014). This appears to be a sensitive proxy, and should this be fully verified to be the case, it will be useful in piecing together characteristics of the water column (Lu et al., 2013; Zhou et al., 2014).

Iodate concentration can assist in determining local paleoceanographic features. Iodate loss at the surface is the result of primary productivity in addition to the decomposition of organic matter (Zhou et al., 2014). It is also influenced by iodide production farther down in the water column. Iodate is more prevalent in oxic bottom waters, whereas iodine occurs mostly as iodide in anoxic waters below more oxygenated water closer to the surface (Hardisty et al., 2014).

Productivity levels and the presence or absence of an OMZ influence the profile that can be reconstructed with I/Ca (Zhou et al., 2014). Three scenarios help to illustrate this. If there is no OMZ, iodate concentration will increase downwards, as oxygen concentration decreases with depth (note that this is a result of respiration, and only after oxygen is entirely consumed will iodate be used as an oxidant). In a second scenario, if the OMZ is higher in the water column, iodate concentration will decrease to the upper part of the OMZ from the mixed layer of primary productivity. For a third scenario, if the OMZ is found deep in the water column, iodate

concentration will increase with depth from the mixed layer, and decrease to zero in the OMZ. These factors are important to consider when analyzing I/Ca data retrieved from forams, and also in identifying plausible foram depth habitats based on I/Ca ratios (Hardisty et al., 2014; Zhou et al., 2014).

In my study, I also compare I/Ca to δ13C values. δ13C interpretation in planktonic forams is complex (as discussed in Chapter 1), as the recorded signals are often at disequilibrium with seawater δ13C values, and yet this isotopic measurement can still be used to generally reflect oceanic DIC levels and productivity (Kuroyanagi et al., 2011; King and Howard, 2004). In relation to I/Ca, δ13C also could serve as an O_2 proxy; for example, it could reflect greater oceanic storage of respired CO_2 as a result of decreased ventilation and altered upwelling patterns during glacial periods (Lu et al., 2016; Archer, 2003).

2 METHODS

The cleaning procedure followed was based on the protocol outlined in Barker et al. (2003). The crushed samples underwent between five and seven cycles of MilliQ ultrapure water rinses (18.2 MΩ) and 30 seconds of ultrasonication, the number of repetitions determined by when the samples appeared white. The samples were then treated with an oxidative solution (1% H_2O_2 in 0.1 *M* NH_4OH buffer) and then heated in a boiling water bath for three five-minute intervals. The oxidative solution was then diluted and pipetted out. This was followed by a weak acid leach stage (in 5 x 10^{-4} *M* HNO_3) for 30 seconds per sample (Barker et al., 2003; Henehen et al., 2015). Following this step, the samples were rinsed and sonicated once again. The samples were then split, with a small fraction (about the material equivalent of 1-3 forams depending on size) set aside for δ18O and δ13C testing, and the rest allocated to I/Ca.

The I/Ca testing was completed by Dalton Hardisty at the University of California, Riverside. An inductively coupled plasma mass spectrometer was used to obtain results (an Agilent 7900 ICP-MS), following the method of Lu et al. (2010). Acceptable levels of precision as well as standard deviations (in counts per second) for blanks and standards for this method are based on Hardisty et al. (2014). In general the detection limit for the target ratio is better than 0.1 umol/mol, which correlates to 10 nM IO_3^- (Hardisty et al., 2014). Consistency standards (JCP-1

and Sohl) were included as well to verify proper machine performance and to provide a basis for correction. (Barker et al., 2003; Dalton Hardisty, personal correspondence). The samples were corrected based on blanks, and the values were corrected so as to only account for I/Ca, rather than I/(Ca+Mg).

In analyzing the data, I controlled for variation due to varying size fractions (as the range tested was from 250-850 um) by examining results within comparable size ranges, as this proxy appears to by size-sensitive (Ellen Thomas, personal correspondence). The I/Ca values obtained were compared to known δ13C values for the samples (Ravelo and Fairbanks, 1992, 1995), using a regression to evaluate how strong of a predictor I/Ca is of δ13C. I/Ca values were also compared to O_2 values (inferred based on depth habitats). The oxygen values are from World Ocean Atlas 2009 data, obtained using Ocean Data View (Baranova, 2009). The depth habitats from which our oxygen data is derived are from Farmer et al. (2007), which roughly reflects the tropical Atlantic waters from which our study's species originate. Particularly for the comparison between the shallowest species, there is only limited confidence as to the depth habitats, as they can be affected by seasonality and size, among other factors, and this uncertainty could be magnified at a small scale.

3 RESULTS AND OVERALL TRENDS

This was a small study, incorporating 26 samples from 5 size fractions and 9 taxa (same as for the porosity study, except without *S. dehiscens* and *G. truncatulinoides)*. Once again, these are all from the upper ocean, with depth habitats as follows: 5 mixed layer, 3 thermocline and 1 subthermocline. All of the samples are from well-oxygenated waters, and the I/Ca trend based on O_2 levels is comparable to that of current studies on planktonic forams in well-oxygenated waters, allowing for greater confidence in the interpretation of our results (See Figure 2.1) (Lu et al., 2016). Unfortunately, 4 of the 26 samples were discarded due to concerns about the accuracy of the data; calcium levels below 50 ppm suggested an error in dilution during sample preparation, and these samples had I/Ca ratios closer to 2 umol/mol (regardless of species, when O_2 levels are above 100 umol/kg, I/Ca ratios are expected to be closer to 4 umol/mol or higher) (Dalton Hardisty, personal correspondence; Lu et al., 2016).

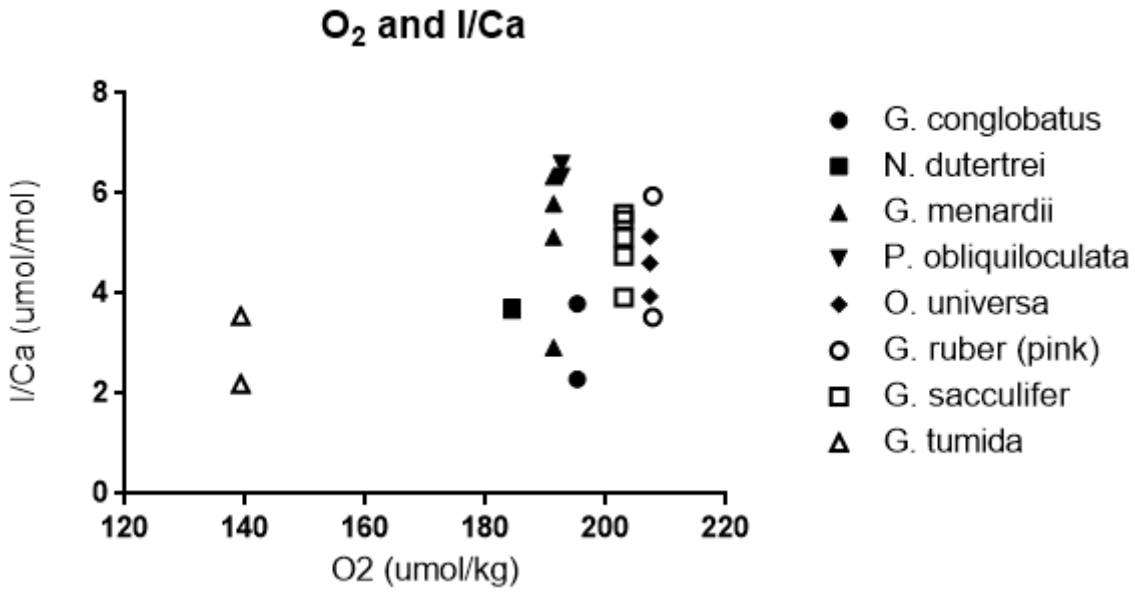

Figure 2.1: p=0.0576 (though this is only slightly above 0.05 and the range of significance, there are not enough species living in subthermocline and thermocline waters to infer a level of significance). Primarily this graph just aims to demonstrate that the results from our small study are within the realm of expected data (Lu et al., 2016).

Although all species are from well-oxygenated waters (considered here to be above 100 umol/kg, based on Lu et al., 2016), comparing the shallowest-dwelling samples to the deepest (as determined by Farmer et al., 2007), and including a thermocline taxa as well, allowed for a clearer sense of how O_2 impacted I/Ca within our oxygenated upper ocean sampling range. Size was controlled, as per standard protocol (Zhou et al., 2014; Lu et al., 2016). There was a trend (R^2=0.6062) between oxygenation of the seawater and the I/Ca value recorded in the foram tests, as expected (See Figure 2.2), though this trend was just slightly out of the range of significance (p=0.0681) (Zhou et al., 2014). A trend also emerged at a micro-scale when comparing species within larger size fractions at the shallowest depths in our sample set. Again, the data set is small, and so the size range is larger than ideal; however, a positive correlation is apparent between O_2 and I/Ca, even within this smaller depth range (See Figure 2.3). However, here R^2=0.3605 and p=0.1155, reflecting that this trend is not significant.

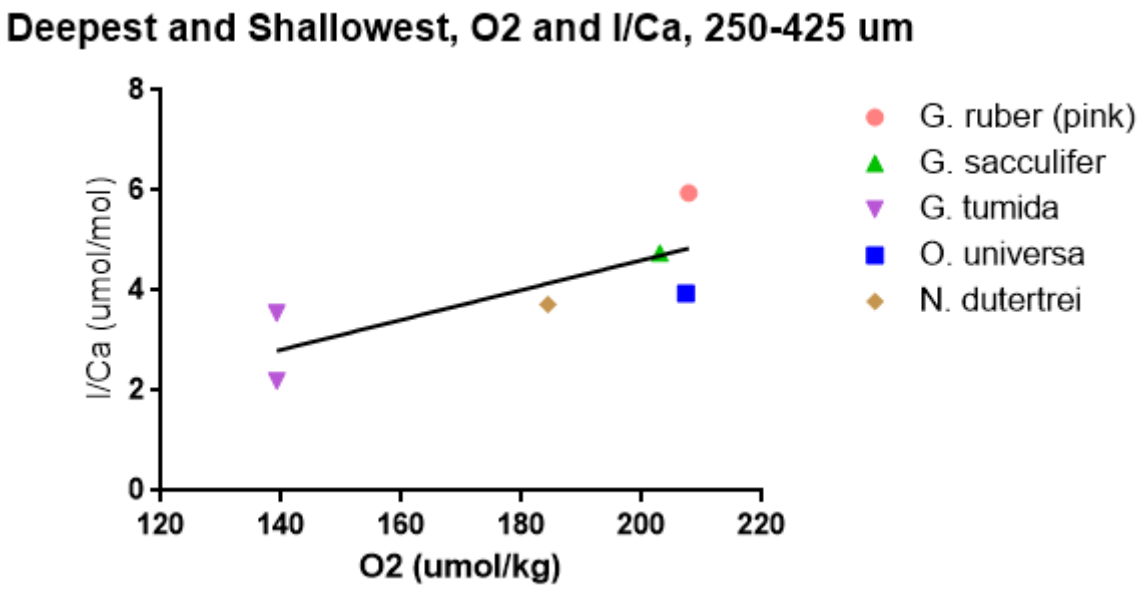

Figure 2.2: R^2=0.6062, p=0.0681

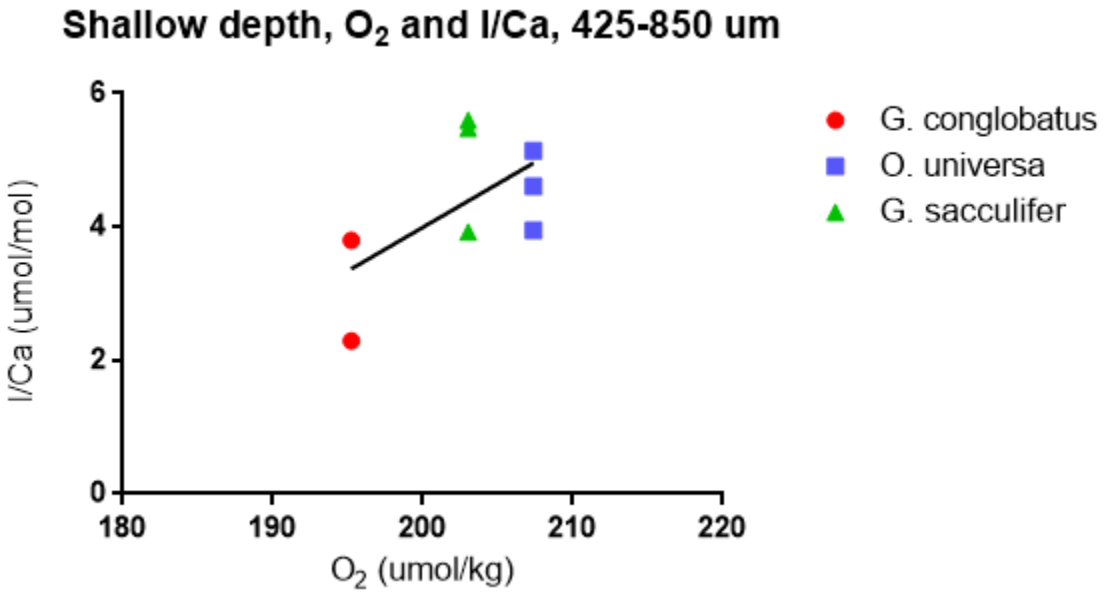

Figure 2.3: R^2=0.3605, p=0.1155

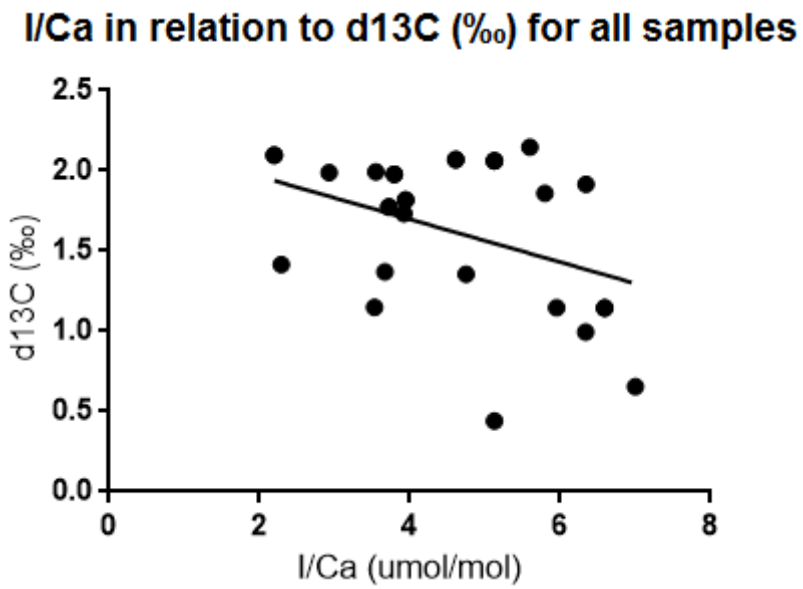

Figure 2.4: R^2=0.1637, p=0.0266

It appears that I/Ca is correlated with δ13C values (p=0.0266), an element which has yet to be described thoroughly in the literature. There is a trend towards higher I/Ca with lower δ13C, which is consistent with past observations (see Figure 2.4) (Lu et al., 2016; Zhou et al., 2014).

4 DISCUSSION OF BROADER IMPLICATIONS AND UNCERTAINTY

Though there is still uncertainty surrounding the strength of I/Ca as a proxy, the range of research conducted so far suggests that it is a good indicator of the presence or absence of an OMZ, and more generally, of low-oxygen conditions in seawater (Zhou et al., 2014; Lu et al., 2016). Though our study provides additional insight into a new field of inquiry, it should be noted that many of the trends described below could be entirely due to chance, as the sample size is very small, the depth range is insufficient and there are only samples within well-oxygenated waters (so no trends should have been evident because of the lack of redox effect), and there is a large range of size fractions presented without a detailed resolution for any given one.

Oxygen depletion in the upper ocean would seem to suggest poor ventilation and respired carbon storage, factors which likely correlate with atmospheric CO_2 levels (Zhou et al., 2014). Recent research has suggested that I/Ca values below 2.5 umol/mol serve as an indicator of low oxygen conditions in the water column (Lu et al., 2016). In interpreting this data set it is essential to consider that while I/Ca is a strong proxy for demonstrating deoxygenated seawater, I/Ca does not appear to be a linear proxy for [O_2]. The reason for this is that IO_3^- reduction only occurs once [O_2] is low enough for nitrate reduction to take place (Rue et al., 1997). Without reaching depths where a IO_3^- reduction zone would be likely, or without an apparent record of an OMZ in the data set, these results cannot speak to the potential for I/Ca to serve as a redox proxy, although there is no clear explanation for the trends that appear here.

The surface water [IO_3^-] is influenced by the productivity of the waters as well as by the presence or absence of an OMZ. It would appear that higher [IO_3^-] correlates with lower productivity, aligning with lower iodine uptake in the surface waters and less O_2 consumption through organic matter decomposition lower down in the water column. Planktonic forams record the IO_3^- mixing gradient in these surface waters. On a broader ocean scale, a decrease in I/Ca should correlate with a decrease in [O_2] and an increase in productivity. In general, productivity and I/Ca are negatively correlated (it is worth noting that productivity and [O_2] have opposite effects on I/Ca, so the impact that they have on I/Ca depends on the balance and net effect of the two). This trend (though not a statistically significant one) is observed in the data set, for both the larger depth range (See Figure 2.2) and the micro-range in shallow waters (See Figure 2.3, weaker correlation). Various factors are thought to affect the relationship between I/Ca, [O_2] and productivity; decreased [O_2] (reflected by decreased I/Ca) could be the result of warmer waters causing ocean stratification, or could represent higher respiration rates under these warmer conditions (Zhou et al., 2014).

To better assess productivity, δ13C was compared with I/Ca. The data supports the negative correlation between I/Ca and δ13C ($p=0.0266$) that should be expected based on the chemistry involved in the relationship between the two variables (See Figure 2.4) (Zhou et al., 2014). If there is an increase in the rate of organic matter production and burial, it could lead to the release of O_2. The iodine ratio in a region with enhanced organic matter burial could then

control the observed I/Ca, suggesting that higher I/Ca ratios would pair with lower δ13C values (Hardisty et al., 2014).

Importantly, though trends emerged here, this data set is far from ideal in analyzing I/Ca as a proxy because it is limited to well-oxygenated waters. The lowest [O_2] level included in the data set (based on the deepest dwelling species included) is 139.26 umol/kg, and for Atlantic oceans, an OMZ is defined as [O_2]<50 umol/kg. Calcareous foram tests that precipitated closer to an OMZ will have lower I/Ca values, as iodine speciation is highly redox-sensitive, and I/Ca represents IO_3^-, which is the only form of iodine that calcareous organisms can incorporate (Lu et al., 2016). It could be a logical conclusion that any trend in the data set from our study will likely reflect a chance observation, as none of the specimens developed under sufficiently low oxygen conditions to reflect the redox effect that would cause I/Ca to represent O_2 levels.

5 SUMMARY

Despite the non-linear nature of I/Ca as a redox proxy, it still is valuable in recording the presence or absence of an OMZ for a particular region and giving information about the dynamics of a given water column. Although the plots appear to reveal relationships, based on what is known about how I/Ca would reflect ocean redox chemistry, it is possible that our results could just be due to chance. The scope of the data set is not sufficient to draw conclusions. The chemistry of this reasoning can be summarized as follows: Above a given O_2 threshold, [IO_3^-] is not dependent on O_2 (Rue et al., 1997). Based on this, since I/Ca tracks IO_3^-, it should not be expected that I/Ca records [O_2] within well-oxygenated waters. To better understand what is occurring, more research will be required, using a broader scope of foram samples that encompasses a range of depth habitats (and oxygenation levels) and greater richness within size fractions. Detailed records within the shallowest depth profile and within a set size range could also work to understand or disprove the correlations that emerged between I/Ca and δ13C and I/Ca and [O_2] in this well-oxygenated part of the water column.

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Very few papers have been published on I/Ca, and I was fortunate enough to receive an incredible amount of assistance from three of the scientists who were involved in these publications. Noah Planavsky, Dalton Hardisty (University of California – Riverside) and Ellen Thomas were instrumental in making the I/Ca portion of the study possible. Noah's eagerness to pursue new and exciting projects created this as an opportunity. Dalton Hardisty completed the I/Ca work at UCA-Riverside and was incredibly helpful in answering questions, reviewing data, and helping me understand this newer field. Ellen Thomas co-authored nearly all of the papers currently written on I/Ca and was conveniently located on the third floor of KGL, and she redirected my way of analyzing the data.

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Appendices

Appendix 1

				TEST(S) RUN	
Species	**Sieve Size (um)**	**Amt of material (mg)**	**Locality**	**I/Ca**	**Kiel**
Globigerinella siphonifera	250-300		KC78		
Globigerinella siphonifera	300-425		KC78		
Globigerinella siphonifera	425-600		KC78		
Globigerinoides conglobatus	300-425	0.446666667	KC78		
Globigerinoides conglobatus	425-600	1.664	KC78		
Globigerinoides conglobatus	600-710	0.292	KC78		
Globigerinoides conglobatus	710-850		KC78		
Globigerinoides ruber	250-300	0.28	KC78		
Globigerinoides ruber	300-425	0.612	KC78		
Globigerinoides ruber	425-600	0.966	KC78		
Globigerinoides sacculifer	250-300	0.32	KC78		
Globigerinoides sacculifer	300-425	0.99	KC78		
Globigerinoides sacculifer	425-600	2.154	KC78		
Globigerinoides sacculifer	600-710	1.94	KC78		
Globigerinoides sacculifer	710-850	1.494	KC78		
Globorotalia menardii	250-300	0.152	KC78		
Globorotalia menardii	300-425	1.158	KC78		
Globorotalia menardii	425-600	3.018	KC78		
Globorotalia menardii	600-710	2.23125	KC78		
Globorotalia menardii	710-850	2.58	KC78		
Globorotalia truncatulinoides	300-425		CH82		
Globorotalia truncatulinoides	425-600		CH82		
Globorotalia tumida	250-300	0.315	KC78		
Globorotalia tumida	300-425	1.692	KC78		
Globorotalia tumida	425-600	5.67	KC78		
Globorotalia tumida	600-710	4.712	KC78		
Neogloboquadrina dutertrei	250-300	0.164	KC78		
Neogloboquadrina dutertrei	300-425	1.344	KC78		
Neogloboquadrina dutertrei	425-600	1.884	KC78		
Orbulina universa	250-300		KC78		
Orbulina universa	300-425	0.285	KC78		
Orbulina universa	425-600	1.266	KC78		
Orbulina universa	600-710	1.385	KC78		
Orbulina universa	710-850	2.312	KC78		
Pulleniatina obliquiloculata	250-300	0.304	KC78		
Pulleniatina obliquiloculata	300-425	1.116	KC78		
Pulleniatina obliquiloculata	425-600	1.46	KC78		
Sphaeroidinella dehiscens	425-600	0.638	KC78		
Sphaeroidinella dehiscens	600-710	0.688	KC78		
Sphaeroidinella dehiscens	710-850	0.984	KC78		