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Sodium-Calcium Ratios in the Planktic Foraminifera *Trilobatus Sacculifer* as a Proxy for Sea Surface Salinity

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SODIUM-CALCIUM RATIOS IN THE PLANKTIC FORAMINIFERA *TRILOBATUS SACCULIFER* AS A PROXY FOR SEA SURFACE SALINITY

by

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ABSTRACT

SODIUM-CALCIUM RATIOS IN THE PLANKTIC FORAMINIFERA *TRILOBATUS SACCULIFER* AS A PROXY FOR SEA SURFACE SALINITY

Colton Steele Watkins
Old Dominion University, 2020
Director: Dr. Matthew W. Schmidt

Recent culture and field studies have found a significant positive correlation between seawater salinity and the incorporation of sodium into foraminiferal calcite, suggesting a potential new proxy for reconstructing past changes in sea surface salinity (SSS) (Mezger et al., 2016 and Bertlich et al., 2018). In order to test the applicability of this new proxy in an open-ocean setting, Na/Ca ratios in the planktic foraminifera *Trilobatus sacculifer* (*T. sacculifer* Na/Ca) were measured from a suite of sediment core tops spanning a natural salinity gradient from the North Atlantic subtropical gyre to the South Atlantic subtropical gyre. Initial results from nine core tops spanning a salinity range of 1.6 show a positive correlation between upper water column salinity and *T. sacculifer* Na/Ca (R^2 = 0.81, p < 0.005). The data also suggest there is no relationship between *T. sacculifer* Na/Ca and shell weight, shell size, or habitat temperature, indicating that shell Na/Ca may be predominantly controlled by salinity. In addition, we generated a high-resolution downcore record of *T. sacculifer* Na/Ca variability over the last deglaciation from Florida Straits core JPC26. Results show good agreement between our new Na/Ca record with the previously published deglacial $\delta^{18}O_{sw}$ record that is also thought to reflect SSS variability from the same core (Schmidt and Lynch-Stieglitz, 2011). Both records indicate an abrupt increase in SSS during the Younger Dryas (11.7 – 12.9 kyr). Converting our new JPC26 *T. sacculifer* Na/Ca ratios to SSS using our Atlantic core top calibration indicates a maximum salinity change of ~2.2 across the last deglaciation.

This thesis is dedicated to skateboarding.
I do not expect many will understand, but
there are few things more valuable than
knowing how to pick yourself off the ground,
a place that we all find ourselves from time to time.
Thank you for giving me a reason to keep
pushing when I needed one most.

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There are many people who deserve recognition, for I do not think I would have been able to complete this project without the love, support, and encouragement of my friends and family. You know who you are.

First and foremost, however, I would like to thank my advisor and project director, Dr. Matthew W. Schmidt. In the Summer of 2018, I applied to ODUs Ocean, Earth, and Atmospheric Science graduate program. Little did I know, I initially turned in an incomplete application. I, one way or another, missed that big, bold section that instructed all applicants to have selected a potential graduate advisor with whom to work with. A short time later, however, I received an email from Dr. Matthew Schmidt informing me that I had overlooked this (very important) step, and that somehow, despite my inability to follow directions, said brilliant, unbelievably passionate scientist was interested in working with me. I have often struggled with feelings of inadequacy throughout my graduate school experience, as there are so many unbelievably intelligent scientists in our program, but Matthew (as it took me a year to start calling him) has consistently been there to encourage me, pick me off of the ground, and convince me to keep pushing through those thoughts. I will forever be grateful for you taking a chance on me, and I greatly look forward to being able to consider you not just an advisor, but a friend.

Additionally, it would be a criminal offense to not specifically thank Dr. Jennifer E. Hertzberg for her relentless help, encouragement, and instruction. As an undergraduate student in a Geology department, I spent very little time in a true laboratory setting before coming to ODU, and as it turns out, there is a LOT to learn before you can start preforming geochemical trace-metal analysis on foraminifera. I had the absolute privilege of learning these (often very small, seemingly picky) things from Dr. Jennifer E. Hertzberg, someone who I now know is more qualified to teach these things than perhaps anyone else. As a colloquial comparison – it was as if Michael

Phelps taught me how to swim, or if Tony Hawk taught me how to skate. Jennifer, you are an amazing scientist and person, and I will forever be grateful for the things that you have taught me and for the good times that we have had (including our disaster of a flight to San Francisco).

I would also like to acknowledge the fantastic fellow Schmidt Paleo Lab members Brian Close, Lenzie Ward, and Ryan Glaubke that I have had the honor of working with over the course of this experience. I truly cannot think of a better group of people to have had this experience with, and I greatly look forward to seeing the amazing things you all do in life.

Finally, I want to extend one more ‘thank you’ to my friends and family for their unwavering support throughout this entire experience. I am exceptionally blessed to not be able to include all of you by name, but you know who you are, and I am eternally grateful.

Most importantly, though, I would like to think my mother, Colleen Davis. You have been my biggest champion since the day I was born you have sacrificed more than any person should have to for me. You knew I could do this long before I convinced myself that I could, and there are no words to express my gratitude and love for you. I hope and pray I can someday begin to repay you for everything.

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1. INTRODUCTION

Ocean salinity is an important parameter that has implications on the biological, chemical, and physical systems of the ocean. For example, salinity and temperature are the main drivers of the ocean's thermohaline circulation which plays a major role in the redistribution of heat on Earth. In addition, sea surface salinity (SSS) in the open ocean is controlled by the balance between evaporation and precipitation and therefore reflects atmospheric dynamics. Creating accurate paleo-salinity reconstructions is therefore essential for understanding how the ocean-atmosphere system changed in the past and for predicting how it may evolve in the future.

Although measuring salinity in the ocean today is relatively easy using modern instrumentation, methods for reconstructing past salinity change using geochemical proxies remains challenging. The most common method involves combining measured Mg/Ca ratios in planktic foraminifera (a proxy for sea surface temperature (SST) (Nürnberg et al., 1996) with paired $\delta^{18}O_{Calcite}$ ($\delta^{18}O_C$) values on the same species in order to calculate the $\delta^{18}O$ of seawater ($\delta^{18}O_{SW}$) in which the foraminifera lived (Mashiotta, 1999; Elderfield and Ganssen, 2000; Schmidt et al., 2004). After correcting for global ice volume, the ice-volume free $\delta^{18}O_{SW}$ ($\delta^{18}O_{IVF\text{-}SW}$) serves as an indirect proxy for salinity because $\delta^{18}O_{IVF\text{-}sw}$ is predominantly controlled by evaporation/precipitation ratios in the open ocean and is related to salinity in a linear relationship that varies by region and latitude.

This method, although well established, is partially limited by the large compounded error associated with converting $\delta^{18}O_C$ and Mg/Ca ratios into $\delta^{18}O_{SW}$ estimates. For example, a downcore record of $\delta^{18}O_{SW}$ from Florida Straits core KNR166-2-26JPC (JPC26; 24°19.61′N, 83°15.14′W; 546 m depth) derived from *Globigerinoides ruber* $\delta^{18}O_C$ and Mg/Ca ratios had average value of 1.17 ‰ with a considerable uncertainty of ± 0.25 ‰ (Schmidt and Lynch-Stieglitz, 2011). This error includes analytical error on the Mg/Ca and $\delta^{18}O_C$ measurements plus

the calibration error converting these measurements to temperature and $\delta^{18}O_{SW}$. This is in line with other estimates of $\delta^{18}O_{SW}$ error estimates, which typically range within ± 0.20 - 0.25 ‰ (Weldeab et al., 2006 and Schmidt et al., 2004). Furthermore, there is *additional* error introduced in the correction of temporal changes in whole ocean $\delta^{18}O_{SW}$ change due to global ice volume variability and in the conversion of $\delta^{18}O_{SW}$ to salinity. The result is imprecise salinity reconstructions that have an uncertainty of multiple units of salinity.

Another means of estimating paleo salinity involves the use of Ba/Ca ratios in planktonic foraminifera as a proxy for riverine input (Weldeab et al., 2007 and Schmidt and Lynch-Stieglitz, 2011). River water is heavily enriched in Ba compared to seawater, and studies have shown foraminiferal uptake of Ba is directly controlled seawater Ba concentration (Lea and Spero, 1994). Therefore, foraminiferal Ba is positively correlated with river water discharge and negatively correlated with salinity. These properties enable Ba/Ca ratios to be used for paleosalinity reconstructions in coastal areas influenced by riverine discharge (Plewa et al. 2006; Weldeab et al., 2007; Schmidt et al., 2011). Nevertheless, this method also has limitations, the main one being that salinity in the majority of the ocean is controlled by evaporation and precipitation, not river discharge. Additionally, the variation in river Ba/Ca creates the need for river-specific calibration before reliable salinity reconstructions can be produced. The amount of discrepancy and uncertainty in traditional methods demands the need for a more direct proxy for past sea surface salinity variability that is independent of other factors.

Recent studies show a significant, linear relationship between the Na/Ca ratios in planktic foraminiferal calcite and the salinity at which those species lived (**Figure 1**). For example, Bertlich et al. (2018) measured *Trilobatus sacculifer* Na/Ca ratios on numerous individual foraminifera via electron microprobe from cultured samples grown over a large salinity gradient (26 – 45). When Na/Ca ratios from each growth salinity were averaged, they were positively correlated with salinity (*T. sacculifer* Na/Ca = 0.12(S) + 0.97 [R^2 = 0.94, $p < 0.005$]). Additionally, *T. sacculifer* Na/Ca measured on core top sediment from the Caribbean and the Gulf of Guinea using bulk solution

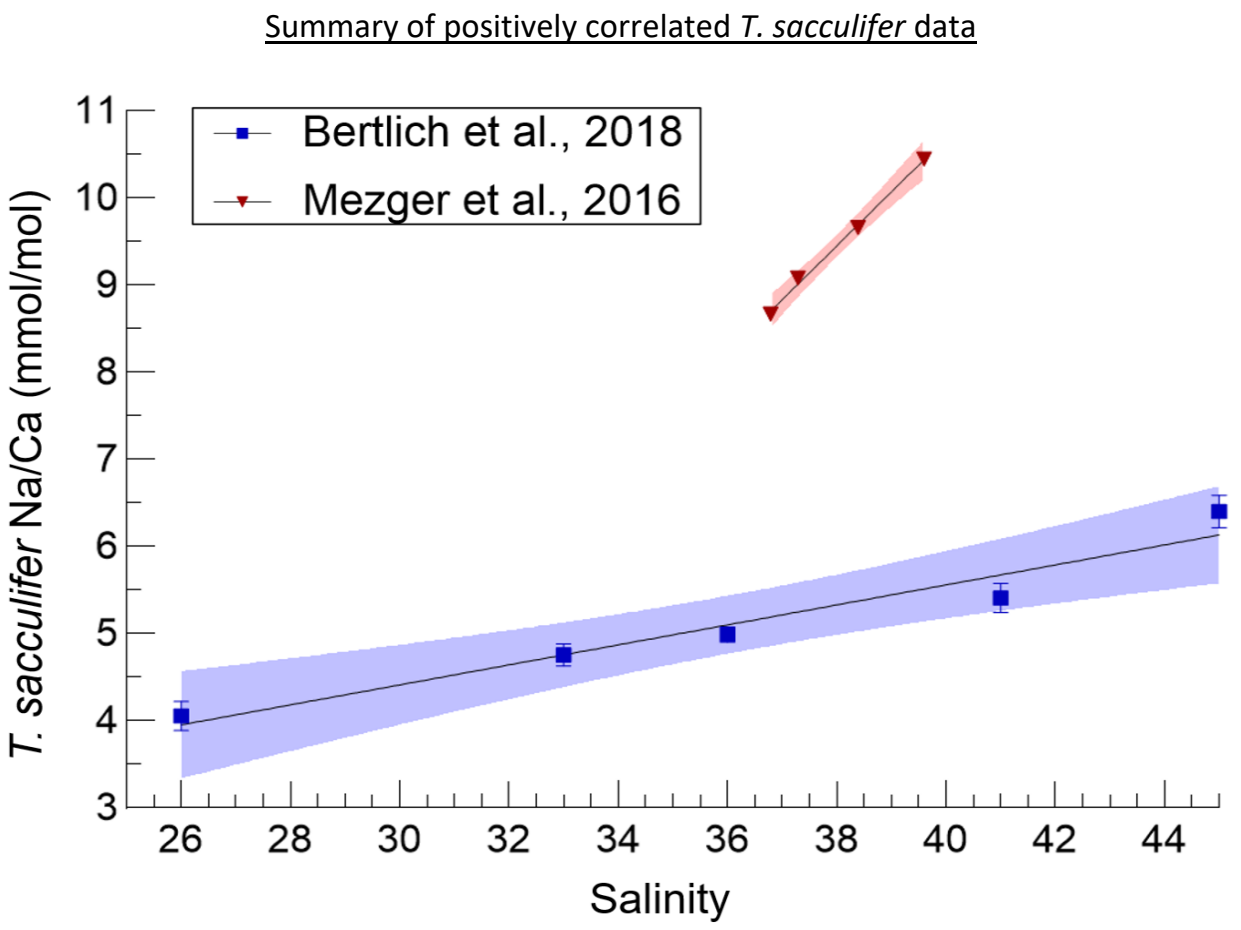


Figure 1. Data from recent studies that have found a significant, positive correlation between *T. sacculifer* Na/Ca and salinity. The top regression consists of *T. sacculifer* Na/Ca ratios measured on Red Sea core tops (red triangles) via ICP-OES (Mezger et al., 2016). The associated regression is *T. sacculifer* Na/Ca = 0.60(S) – 13.49 (R^2 = 0.99, p < 0.001). The lower regression consists of *T. sacculifer* Na/Ca ratios measured via electron microprobe on cultured foraminifera (Bertlich et al., 2018). Averaged *T. sacculifer* Na/Ca ratios from each growth salinity are indicated by blue squares. The associated regression is *T. sacculifer* Na/Ca = 0.12(S)+ 0.97 (R^2 = 0.94, p < 0.005).

mass spectrometry fit well within their regression's 95% confidence interval, suggesting agreement between both field and culturing datasets.

Another study measured a suite of Red Sea *T. sacculifer* and *G. ruber* Na/Ca ratios via laser ablation using a quadrupole ICP-MS on individual foraminifera collected via a plankton pump from six transects covering a salinity gradient of 36.8 - 40.1 (Mezger et al., 2016). When Na/Ca

ratios from each transect were averaged, they also indicated a significant, positive relationship between both *T. sacculifer* and SSS (*T. sacculifer* Na/Ca = 0.60(SSS) – 13.49 [R^2 = 0.99, p < 0.001]; (**Figure 1**).

Although both studies indicated a statistically significant relationship between *T. sacculifer* Na/Ca and SSS, there was discrepancy between the absolute magnitude of *T. sacculifer* Na/Ca ratios in the different studies. Significantly higher *T. sacculifer* Na/Ca ratios were recorded from plankton-pump samples from the Red Sea (8.67 – 10.45 mmol/mol; Bertlich et al., 2018) as compared to either cultured (3.86 – 6.40 mmol/mol) or core top sediment samples (4.64 – 5.68 mmol/mol; Bertlich et al., 2018) across similar salinities (**Figure 1**).

In order to better constrain this developing proxy, I measured *T. sacculifer* Na/Ca ratios from a suite of Atlantic Ocean core tops spanning a natural salinity gradient of 1.6 to explore the relationship between *T. sacculifer* Na/Ca and SSS. I also explored the relationship between measured *T. sacculifer* Na/Ca and other, potentially confounding parameters, such as shell size, weight, and habitat temperature which are known to affect other geochemical paleoceanographic proxies. Next, I created a downcore record of *T. sacculifer* Na/Ca ratios spanning the last 20 kyr from Florida Straits sediment core JPC26 and compared the results to the previously published deglacial $\delta^{18}O_{SW}$ record (derived from the planktic foraminifera *G. ruber*). Finally, I created a Florida Straits sea surface salinity record for the last 20 kyr using the Atlantic core top calibration I generated in the first part of this study. I then compared my new salinity record with the salinity record derived from the previously published $\delta^{18}O_{SW}$ method (Schmidt and Lynch-Stieglitz, 2011) and show that the Na/Ca-based salinity reconstruction using my new calibration yields a more realistic record of past SSS change in the Florida Straits.

2. MATERIALS AND METHODS

2.1. *Trilobatus sacculifer*

T. sacculifer (previously referred to as *Globigerinoides sacculifer*) is a spinose surface-dwelling foraminifera species that bears photosynthetic symbiotic algae (Hemleben et al., 1987; Bijma and Hemleben, 1994; Spezzaferri et al., 2015). Its lifecycle is therefore constrained to the upper photic zone, and its calcite shell (or test) is frequently used for paleoceanographic reconstructions of upper water column conditions (Richey et al., 2007; Groenveld et al., 2006; Coadic et al., 2013). The depth habitat of *T. sacculifer* differs slightly depending on the region in which it is living due to different mixed layer depths. For the purposes of this study, we will focus on those living in the Eastern Atlantic (habitat depth of 25-30 m), Western Atlantic (25-60 m) and the Caribbean (50-90 m) (Steph et al., 2009). *T. sacculifer* are present year-round and their flux to the seafloor shows negligible seasonality in regions with an annual SST ≥ 25 ºC (Bijma et al., 1990; Bijma and Hemleben, 1994; Jonkers and Kucera, 2015). Near the end of its lifecycle, *T. sacculifer* migrate deeper in the water column and calcify a gamete sac, signaling the initiation of reproductive gametogenesis. For the purposes of this study, only specimens without a gamete sac were chosen for analysis, as analysis of individuals with a gamete sac would bias the results to conditions deeper in the water column.

2.2. Sample Collection

2.2.1 Core top calibration

Intact *T. sacculifer* shells (without a gamete sac) selected for analysis were collected from the uppermost portion (<2 cm, the “core tops”) of sediment cores from the Eastern Atlantic, Western Atlantic, and Caribbean basins (**Figure 2**, **Table 1**). These core tops span a natural salinity gradient of 1.6 (35.8 - 37.4) representative of open ocean conditions. *T. sacculifer* shells

Location of cores used in this study

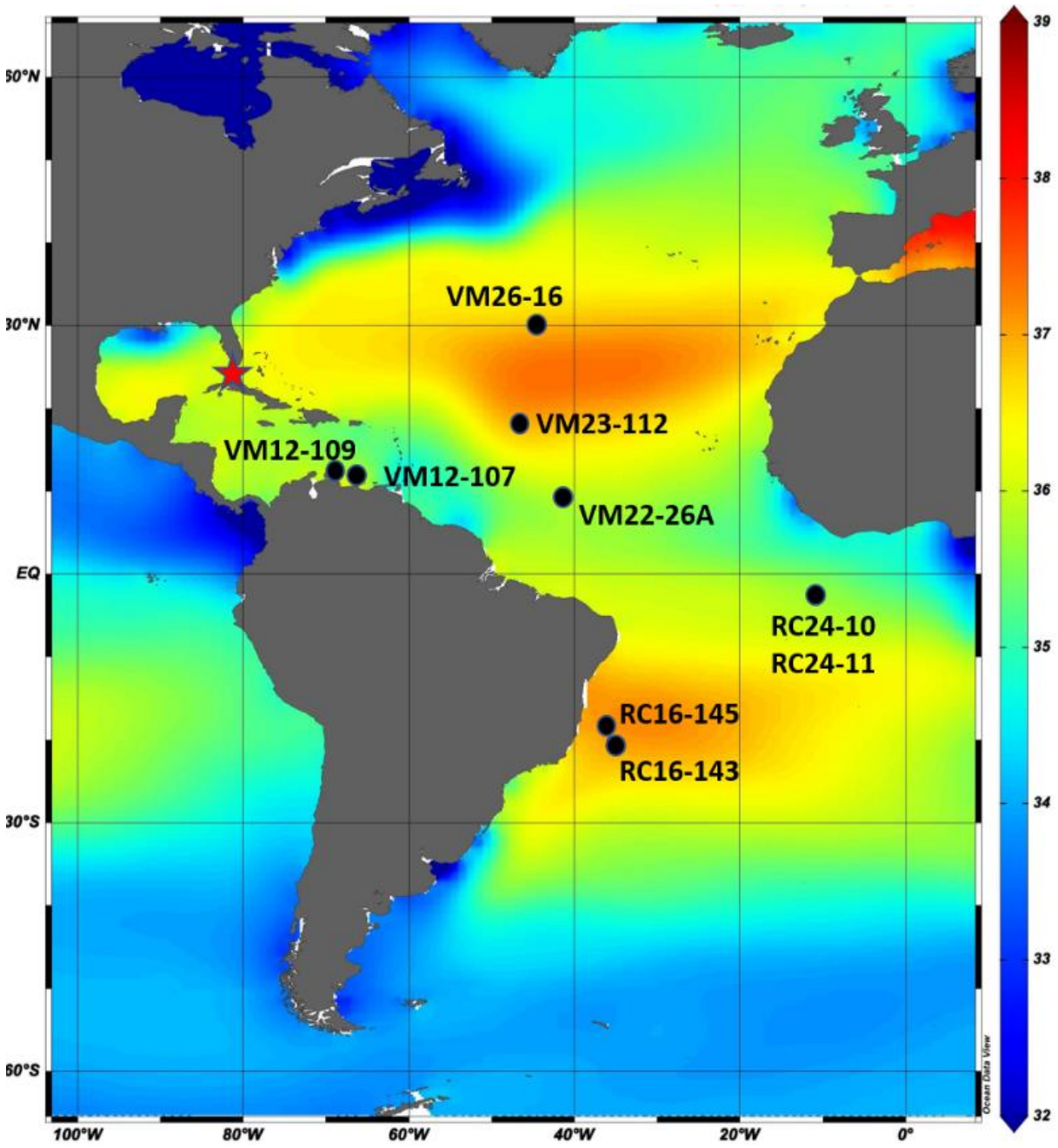


Figure 2. *T. sacculifer* shells were hand-picked from the uppermost interval (<2 cm) of nine Atlantic cores indicated by black circles (**Table 1**) covering a salinity gradient of ~1.6. Florida Straits core JPC26, used to produce my downcore *T. sacculifer* Na/Ca record, is indicated by the red star. Color scales shows surface salinity.

Atlantic core oceanographic information

Core	Lat	Long	SSS	HS	SST	Interval (cm)	Age Constraint (kyr)	Uncertainty (kyr)
RC24-10	-2.18	-11.25	35.71	35.76	25.85	0-1	0.69	0.09
RC24-11	-2.18	-11.25	35.71	35.76	25.85	0-1	0.69	0.09
VM22-26A	8.72	-41.25	35.35	35.82	27.58	0-1	1.95	0.09
VM12-107	11.33	-66.63	36.78	36.56	26.79	0-1	0.69	0.05
VM12-109	11.80	-68.55	36.28	36.69	27.2	0-1	-	-
VM26-16	30.22	-45.10	36.81	36.85	23.35	0-2	-	-
VM23-112	17.27	-46.75	36.75	36.95	25.93	0-1	10	0.16
RC16-143	-19.16	-35.43	37.29	37.30	24.08	1-2	-	-
RC16-145	-17.72	-36.05	37.41	37.40	24.71	0-1	-	-
RC13-189	1.85	-30.00	35.72	35.77	27.33	0-1	3.5	0.15
RC16-77	-12.65	-13.44	36.68	36.71	25.97	0-2	5	-
RC8-19	-24.30	-14.70	36.06	36.11	24.37	0-1	0.5	0.11

Table 1. Cores used for our Atlantic regression. Annual average sea surface salinity (SSS) and sea surface temperature (SST) data was obtained from World Ocean Atlas 2018 (Zweng et al., 2018). Multiple salinity values, also taken from WOA, were averaged across the habitat depth of *T. sacculifer* to produce an average habitat salinity (HS). The portion of the core sampled is indicated by the interval column. Red cores (RC13-189, RC16-77, and RC8-19) indicate data that was not used in the regression (see section 2.6.1).

were handpicked from these samples in four size fractions (250-300 μm, 300-355 μm, 355-425 μm, and >425 μm). Although it is common to pick foraminifera from a single size fraction when performing geochemical analyses in order to negate any ontogenetic bias, initial studies have shown that size fraction choice has a minimal influence on *T. sacculifer* Na/Ca ratios (Mezger et al., 2016). Picking samples from multiple size fractions allowed me to explore this potential relationship in greater detail. For each analysis, 400 μg of sample material was picked (when there was sufficient material in a given core top), crushed, homogenized, and split into two equal aliquots, enabling duplicate analysis. For cores with abundant sample material, additional 400 μg samples of *T. sacculifer* shells were picked in order to provide additional replicate analyses.

2.2.2 Downcore study

A similar protocol was followed on samples from sediment core JPC26 from the Florida Straits to generate a down-core record of past SSS variability over the last deglaciation. *T. sacculifer* shells were picked from the same 2 cm intervals that were previously analyzed for Mg/Ca and $\delta^{18}O_C$ on *G. ruber* by Schmidt and Lynch-Stieglitz (2011). This enabled a direct comparison between our newly measured *T. sacculifer* Na/Ca record with the $\delta^{18}O_{SW}$ record derived from the same depth intervals in the core, both of which are proposed to serve as salinity proxies. The down core samples were typically picked from the 355-425 μm and >425 μm size fractions, as there was a greater abundance of *T. sacculifer* shells in the larger size fraction for most of the core.

2.3. Age Model Development

2.3.1 Core top calibration

Previously published radiocarbon age data (Arbuszewski et al., 2010) was used to confirm that five of the core top sediment samples were Holocene in age, with these core top ages ranging from 0.5 – 10 kyr. Currently, there are no available age data for four of the cores (VM12-109, VM26-16, RC16-143, or RC16-145; **Table 1**).

2.3.2 Downcore study

The age model for JPC26 was previously published by Schmidt and Lynch-Stieglitz (2011) and is based on 21 radiocarbon dates. Radiocarbon ages were measured using accelerator mass spectrometry on both *G. ruber* and *T. sacculifer* at multiple intervals throughout the core, and subsequently converted to calendar age using Calib 6.0 (Stuiver et al., 2011) with the standard marine reservoir correction (Hughen et al., 2004). Linear sedimentation rates were then assumed between ^{14}C dated sample depths.

2.4. Cleaning Procedure

Sample material for both the core tops and down core samples from JPC26 was thoroughly cleaned following the procedure outlined by Schmidt et al. (2012) The cleaning procedure was conducted under trace metal clean conditions in laminar flow benches to prevent contamination. This process includes clay removal via repeated rinsing, sonication, and siphoning of supernatant with ultra-pure water and methanol. Organic matter and metal oxides were removed via hot oxidizing and reducing solutions, respectively. Cleaned samples were then transferred into new acid-leached microcentrifuge vials. Finally, samples were acid leached using a weak ultra-pure nitric acid solution and stored until analysis.

2.5. ICP-MS analysis

Cleaned samples were dissolved in 500 µL of 2% ultra-pure nitric acid just prior to analysis and then analyzed on a Thermo Scientific Element XR high resolution inductively coupled plasma mass spectrometer (HR-ICP-MS) at Old Dominion University's College of Sciences Major Instrument Cluster (COSMIC) lab. A series of trace and minor elements were analyzed and normalized to Ca including Li, Na, Mg, Mn, Al, and Fe. Sample element/calcium ratios were determined from a linear calibration based on a series of calibration standards of known element/calcium ratios analyzed periodically throughout every run. Samples were also blank corrected based on sets of 2% nitric acid blanks analyzed periodically throughout every run. The Mn/Ca, Al/Ca, and Fe/Ca ratios are used to assess the fidelity of the cleaning procedure, with high ratios (>100 mmol/ mol) of any indicating poorly cleaned samples or possible contamination.

2.6. Data Quality Control

The ICP-MS data were assessed post collection for quality control. First, analyses with Mn/Ca, Al/Ca, or Fe/Ca ratios of >100 µmol/mol were rejected. The next steps vary for core top versus downcore JPC26 samples.

2.6.1 Core top samples

For the sediment core top samples, the entire set of *T. sacculifer* Na/Ca ratios from each core was treated as a single data set and assessed to remove bulk data outliers (>1.5σ). This resulted in all analyses from the core top sample of RC8-19 being removed, which had an average *T. sacculifer* Na/Ca ratio of 7.32 as compared to the other core tops with an average *T. sacculifer* Na/Ca ratio between 5.52 and 6.70. The higher than average Na/Ca ratios in this core top may indicate that this sample was contaminated. Next, intra-core top Na/Ca variability was assessed to remove outlier analyses (>1.5σ) within each core top sample. This resulted in the removal of one single *T. sacculifer* Na/Ca measurement from core RC13-189, RC24-10, RC24-11, VM22-26A and VM12-107, as the anomalous *T. sacculifer* Na/Ca measurements may also reflect contamination. Next, each individual *T. sacculifer* Na/Ca measurement in any core top analysis with a coefficient of variation (CV = $[\sigma / \bar{x}] * 100$) of >3% was examined individually and removed if the sample had low recovery (analyzed calcite/sample mass; <10%) or if the mass spectrometer RSD was >10% (indicating poor instrumentation performance). This removed one *T. sacculifer* Na/Ca analysis from core RC13-189, RC24-11, VM22-26A, and VM12-109. Cores with a CV of >5% after these steps were not included in the calibration, as there was too much spread in the data. This removed cores RC13-189 and RC16-77, which had CVs of 5.44 and 5.89%, respectively whereas the remaining core top data sets had an average CV of 2.2 %.

2.6.1 Downcore samples

The downcore JPC26 *T. sacculifer* Na/Ca analyses were also assessed for quality control. *T. sacculifer* Na/Ca ratios within intervals having a duplicate CV of >5% were examined individually and removed if the sample had low recovery (<10%) or if the mass spectrometer RSD was >10% (again, indicating poor instrumentation performance). If an interval had a coefficient of variation of greater than 5%, but neither *T. sacculifer* Na/Ca measurement had sufficient evidence

to reject it, that interval was removed from the reconstruction, as the spread in the data was too considered too significant to include.

2.7. Statistical Analysis

Simple linear regressions were used to determine if any statistically significant relationships existed between *T. sacculifer* Na/Ca and habitat salinity, sea surface salinity (SSS), SST, shell size, and ICP-MS parameters (sample recovery and sample weight). Coefficients of determination (R^2) indicate the amount of variation in *T. sacculifer* Na/Ca that can be explained by each regression, and p values represent the degree of significance (for a given regression a p value < 0.05 indicates significance within a 95% confidence interval). Additionally, regression residuals were tested for normality using a 1-sample Kolmogorov–Smirnov test. This test results in a '0' if the residuals are normally distributed within a 95% significance level, and a '1' if the residuals are not normally distributed. All statistical tests were performed using a combination of Matlab, Prism, and Microsoft Excel.

Because the habitat salinity range between cores RC24-10, RC24-11, and VM22-26A is less than 0.1, the *T. sacculifer* Na/Ca ratios from each size fraction from these three cores were treated as a single dataset and analyzed for statistically different mean values using a simple two-sample t-test. This test results in a '0' if the mean values between two groups are statistically indifferent within a 95% significance level, and a '1' if the mean values between two groups are statistically different.

3. RESULTS

3.1. Core top Na/Ca salinity calibration

Core top *T. sacculifer* Na/Ca ratios are presented in **Figure 3** and **Table 3**. Core top *T. sacculifer* Na/Ca ratios ranged from 5.46 ± 0.10 to 6.66 ± .16 mmol/mol. The habitat salinity was determined for each core location by taking an average of salinity measurements from the World Ocean Atlas 2018 (Zweng et al., 2018) over the range of depths *T. sacculifer* inhabits (Eastern Atlantic: 25-30m; Western Atlantic: 25-60m; and Caribbean: 50-90m (Steph et al. 2009). The resulting core site habitat salinities ranged from 35.8 – 37.4.

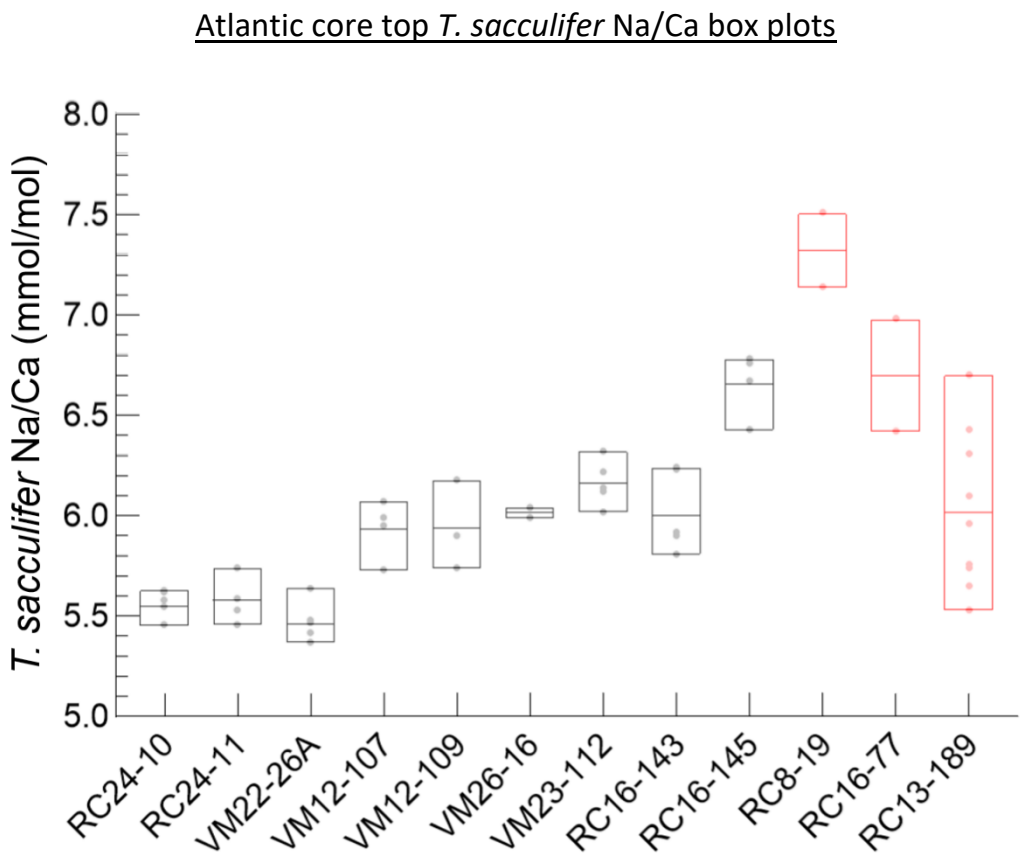


Figure 3. *T. sacculifer* Na/Ca measurements for each Atlantic core top. Individual measurements are indicated by circles within each box plot, and the mean value for each core

(**Figure 3 cont.**) is indicated by the horizontal line. Each sample represents 5-40 individual *T. sacculifer* shells that were homogenized, split into equal aliquots, thoroughly cleaned, dissolved in a nitric acid solution, and analyzed via standard calibrated ICP-MS. Red data represents cores that were not included in analysis, as they were either bulk data set outliers (RC8-19) or had a CV of greater than 5% post processing (RC16-77 and RC13-189).

Atlantic core top *T. sacculifer* Na/Ca data

Core	n	Size Fraction	Na/Ca (mmol/ mol)	Average Na/Ca (mmol/ mol)	STD	CV	HS
RC24-10	16	355-425	5.63	5.55	0.08	1%	35.76
	26	300-355	5.62				
	40	250-300	5.46				
	26	300-355	5.58				
	9	>425	5.45				
	9	>425	5.55				
RC24-11	16	355-425	5.46	5.58	0.12	2%	35.76
	25	300-355	5.59				
	16	355-425	5.74				
	6	>425	5.53				
VM22-26A	24	300-355	5.48	5.46	0.10	2%	35.82
	32	250-300	5.42				
	11	>425	5.64				
	24	300-355	5.47				
	5	>425	5.37				
	5	>425	5.37				
VM12-107	11	355-425	5.73	5.94	0.14	2%	36.56
	11	355-425	5.99				
	7	>425	6.07				
	7	>425	5.95				
VM12-109	16	355-425	5.90	5.94	0.23	4%	36.69
	16	355-425	6.18				
	11	355-425	5.74				
VM26-16	6	>425	6.04	6.01	0.03	1%	36.85
	6	>425	5.99				
VM23-112	30	250-300	6.14	6.16	0.11	2%	36.95
	18	300-355	6.02				
	18	300-355	6.12				
	5	>425	6.32				
	5	>425	6.22				
RC16-143	6	>425	5.90	6.00	0.18	3%	37.30
	6	>425	5.92				
	6	>425	6.24				
	5	>425	5.81				
	6	>425	6.23				

	5	>425	5.91				
RC16-145	5	>425	6.43	6.66	0.16	2%	37.40
	5	>425	6.67				
	6	>425	6.76				
	6	>425	6.78				
RC8-19	5	>425	7.14	7.32	0.26	4%	36.11
	5	>425	7.51				
RC16-77	5	>425	6.42	6.70	0.39	6%	36.68
	5	>425	6.98				
RC13-189	14	355-425	6.70	6.02	0.40	7%	35.77
	14	355-425	5.53				
	14	355-425	6.31				
	23	300-355	6.43				
	14	355-425	5.74				
	23	300-355	6.10				
	34	250-300	5.76				
	5	>425	5.65				
	5	>425	5.96				

Table 2. *T. sacculifer* Na/Ca data for each Atlantic core top analyzed. The number of individual *T. sacculifer* shells homogenized for each measurement is indicated by 'n'. Foraminifera were chosen from four size fractions (250- 300 µm, 300- 355 µm, 355- 425 µm, and >425 µm), with data from the first three cores (RC24-10, RC24-11, and VM22-26A) used for size effect analysis. Core RC8-19, RC16-77, and RC13-189 were not included in our regression.

Na/Ca ratios were then regressed against both habitat salinity and SSS. Results show that *T. sacculifer* Na/Ca increased linearly with habitat salinity according to equation 1 (**Figure 4**):

1. *T. sacculifer* Na/Ca = 0.52 (S) – 12.94; R^2 = 0.81, p < 0.005

This is equivalent to a 9.1% increase of Na incorporation relative to calcium per salinity unit. In addition, there was a similar regression between *T. sacculifer* Na/Ca and SSS for each core location, according to equation 2:

(2) *T. sacculifer* Na/Ca = 0.45 (SSS) – 10.40; R^2 = 0.79, p < .005 (**Figure 5**)

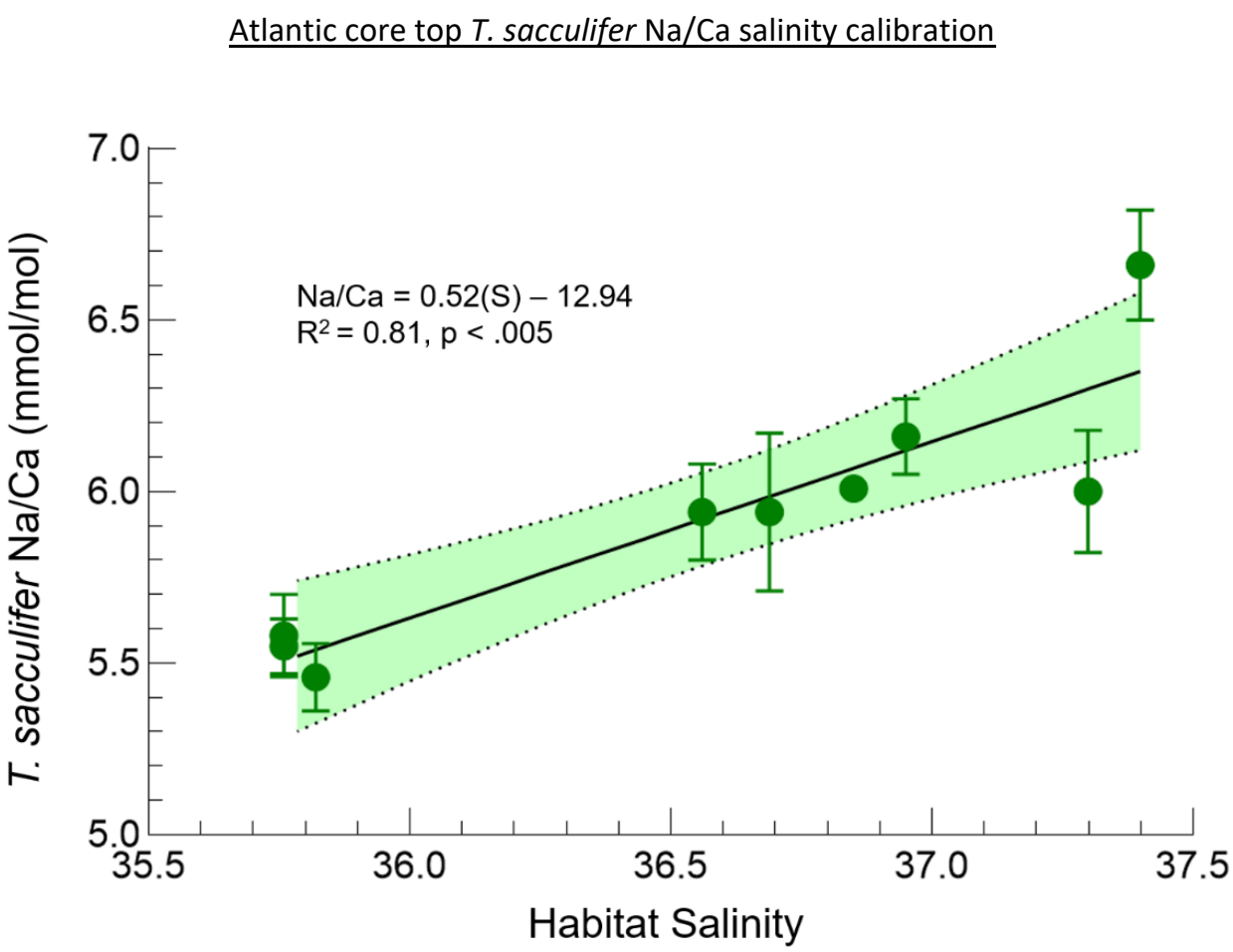


Figure 4. Relationship between *T. sacculifer* habitat salinity and *T. sacculifer* Na/Ca. Results indicate a significant, positive relationship between Na incorporation and salinity. Green circles represent the average *T. sacculifer* Na/Ca ratio for each core, with error bars representing 1-σ standard deviation, and error bands representing the 95% confidence interval of the regression. A Matlab performed Kolmogorov–Smirnov test returned a '0', indicating normality of residuals. *T. sacculifer* Na/Ca ratios were measured via standard calibrated ICP-MS. Habitat salinity was calculated by averaging salinities over the depth range of *T. sacculifer* for each core using data from World Ocean Atlas 2018 (Zweng et al., 2018).

Comparison of regressions between habitat salinity and sea surface salinity

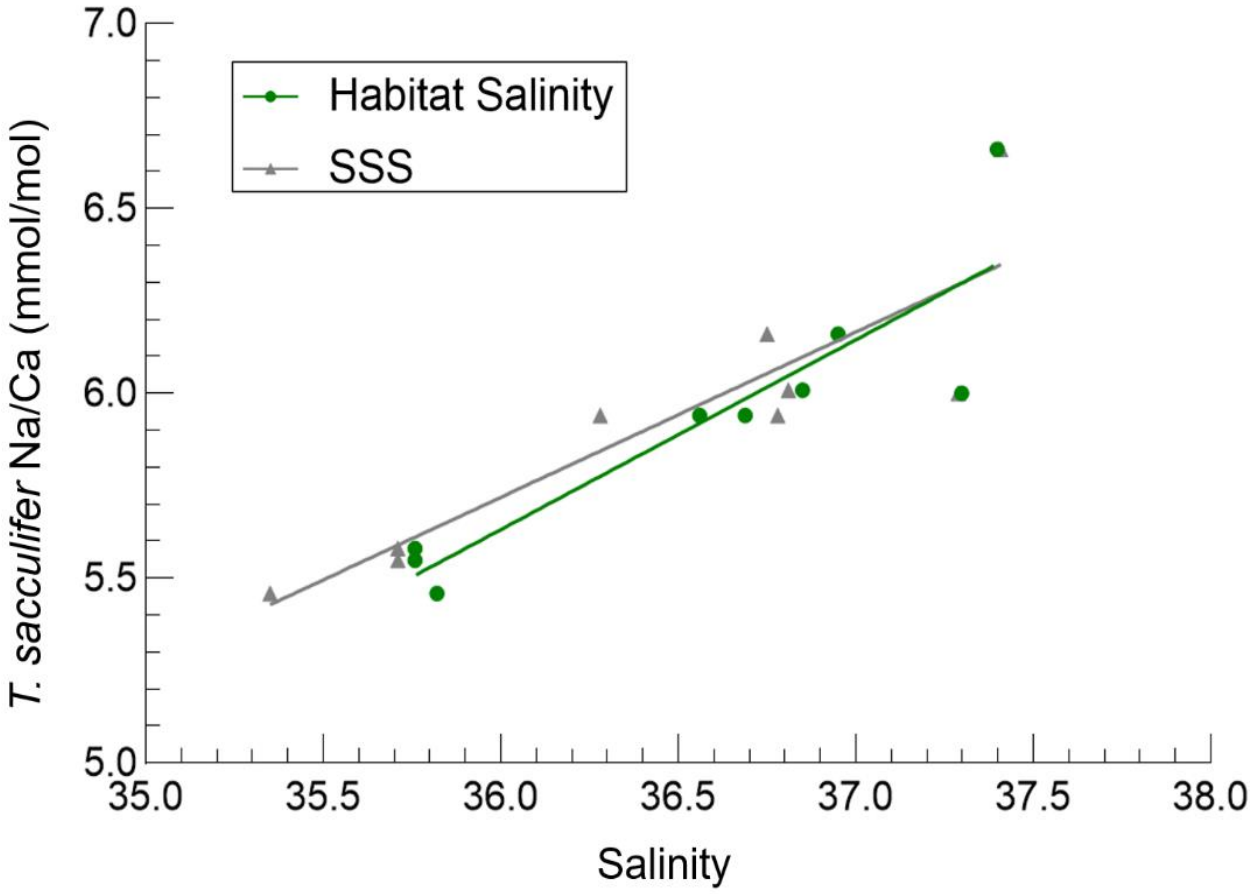
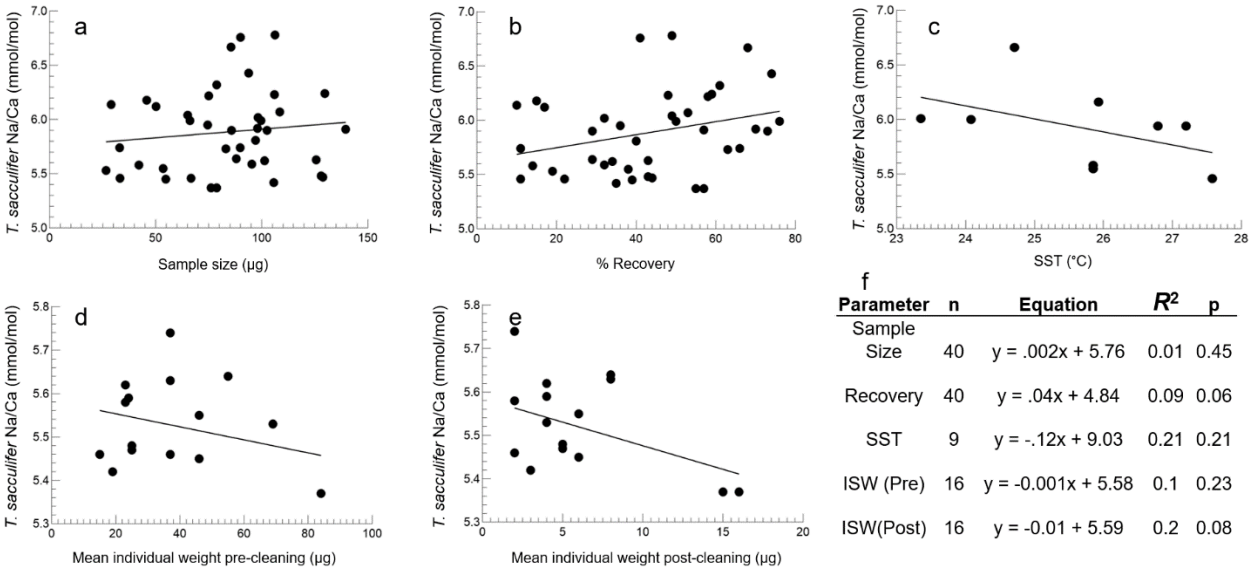


Figure 5. Regressions between habitat salinity *T. sacculifer* Na/Ca (green data) and SSS with *T. sacculifer* Na/Ca (grey data). Habitat salinity had a slightly stronger correlation and more significant relationship (*T. sacculifer* Na/Ca = 0.52 (S) – 12.94; R^2 = 0.81, p < 0.005) compared to SSS (*T. sacculifer* Na/Ca = 0.45 (SSS) – 10.40; R^2 = 0.79, p < .005), but either regression was significant with statistically indifferent slopes. Additionally, a Matlab performed Kolmogorov–Smirnov test returned a '0', for the residuals of either regression, indicating normality of residuals.

The regression of *T. sacculifer* Na/Ca ratios with sample size (**Figure 6a)**, sample recovery ([mass of analyzed calcite/ sample mass]*100; **Figure 6b),** core site SST (**Figure 6c**), mean

Summary of regression statistics for other parameters tested



f

Parameter	n	Equation	R^2	p
Sample Size	40	y = .002x + 5.76	0.01	0.45
Recovery	40	y = .04x + 4.84	0.09	0.06
SST	9	y = -.12x + 9.03	0.21	0.21
ISW (Pre)	16	y = -0.001x + 5.58	0.1	0.23
ISW(Post)	16	y = -0.01 + 5.59	0.2	0.08

Figure 6. Relationship between *T. sacculifer* Na/Ca and other parameters such as sample size (**a**), sample recovery (**b**), SST (**c**), and individual shell weight pre and post cleaning procedure (**d** and **e**). Statistical parameters are summarized (**f**) with provided coefficients of determination (R^2) indicating the amount of variation in *T. sacculifer* Na/Ca that can be explained by each regression, and p values representing the degree of significance. Our data suggests that none of these relationships are statistically significant.

individual shell weight pre-cleaning (**Figure 6d)** or mean individual shell weight post-cleaning **(Figure 6e)** showed no statistically significant relationships. Furthermore, there is no significant difference

in the Na/Ca ratios in the largest of the three size fractions (300-355 µm, 355-425 µm, and >425 µm), with average *T. sacculifer* Na/Ca ratios of 5.55 ± 0.07, 5.61 ± 0.14, and 5.49 ± 0.11 mmol/mol respectively. Because core sites RC24-10, RC24-11, and VM22-26A all had similar habitat salinities (35.68 - 35.72), I combined all *T. sacculifer* analyses (n = 16) from these cores to determine whether the shell size fraction had an impact on Na/Ca ratios. The smallest size fraction (250 - 300 µm) was slightly lower, with a *T. sacculifer* Na/Ca of 5.44 ± .03 (n = 2) **(Figure**

7). Regardless, there is no statistically significant difference in mean Na/Ca values between any of the size fractions.

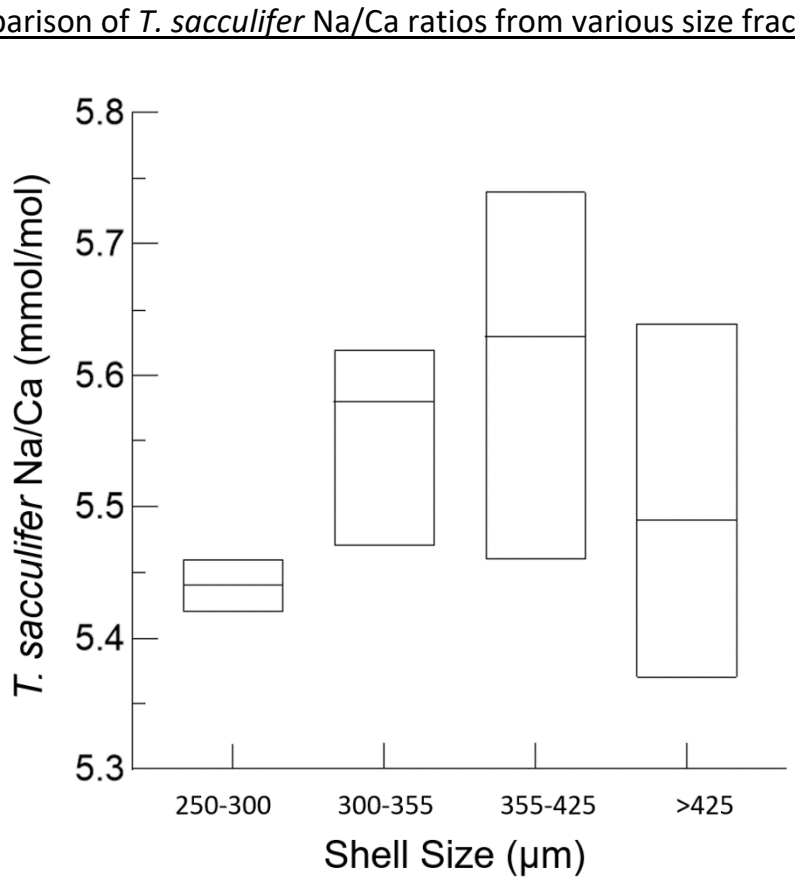


Figure 7. Analysis of *T.* sacculifer Na/Ca variability due to foraminiferal size. Data consists of *T. sacculifer* Na/Ca ratios (n = 16) measured on cores RC24-10, RC24-11, and VM22-26A, which had similar habitat salinities (35.68 - 35.72). The middle bar represents the mean ratio for each size fraction and the upper and lower bars represent the minimum and maximum ratios. A two-sample t-test was performed on Matlab for each core to determine if there were any significant differences in the mean *T. sacculifer* Na/Ca between each size fraction. Each of these tests returned a '0', which indicates no significant difference.

3.2. Error Analysis

Analytical reproducibility of a series of three gravimetrically prepared matrix-matched Na/Ca standards (ranging in Na/Ca from 4.27 to 5.23 mmol mol^{-1}) analyzed during both the Atlantic core top and JPC26 downcore measurements averaged ± 0.7 %. A duplicate error

analysis was also conducted by measuring the coefficient of variance (CV = $[\sigma / \bar{x}] * 100$) between measurements from the same Atlantic core tops or from the same downcore JPC26 intervals. Duplicate error estimates average ± 2.0% (n = 95) based on 9 Atlantic core tops and 86 duplicated JPC26 intervals. Instrumentation error (± 0.7 %) coupled with duplicate analysis error (± 2.0%) yields a propagated uncertainty of ± 2.7% in *T. sacculifer* Na/Ca measurements. For Atlantic core tops (average *T. sacculifer* Na/Ca of 5.92 mmol/mol), this error corresponds to an uncertainty of ± 0.16 mmol/mol. For my downcore JPC26 record (average *T. sacculifer* Na/Ca of 6.43 mmol/mol, n = 92), this error corresponds to an uncertainty of ± 0.17 mmol/mol. This is equivalent to a salinity error of ± 0.34 when converting JPC26 *T. sacculifer* Na/Ca ratios to salinity according to equation (1). Regression calibration error was also calculated for JPC26 *T. sacculifer* Na/Ca ratios that were converted into salinity. Ignoring instrumentation and duplicate error, the average downcore *T. sacculifer* Na/Ca ratio of 6.43 mmol/mol translates to a calculated salinity of 37.55, with a range of 37.20 – 38.40 based off our regressions 95% confidence interval. This is equivalent to a uncertainty of ~ ± 0.60 in salinity reconstructions.

3.3. Downcore record

Downcore JPC26 *T. sacculifer* Na/Ca ratios varied between 6.02 ± .03 and 7.18 ± 0.28 mmol/mol across the last deglaciation with an average of 6.43 ± 0.13 mmol/mol (**Figure 8, Table 3**). Early stages of the last deglaciation are characterized by elevated and variable *T. sacculifer* Na/Ca ratios that generally decrease towards the onset of Heinrich Stadial 1 (H1: 17.5 - 16.5 kyr). H1 had an average *T. sacculifer* Na/Ca ratio of 6.42 ± 0.12 mmol/mol (n = 6). The Bølling-Allerød (B.A) warm period lasting from 14.5 - 13.6 kyr had an average *T. sacculifer* Na/Ca ratio of 6.34 ± 0.12 mmol/mol (n = 4). By 13.23 kyr, *T. sacculifer* Na/Ca ratios reach a minimum (6.08 ± 0.04 mmol/mol), at which point they begin to rapidly increase. This trend continues through the start of the Y.D. (12.9 kyr), and ratios remain somewhat elevated during the remainder of this climate

interval (average Y.D. *T. sacculifer* Na/Ca ratio is 6.45 ± 0.14). The end of the Y.D. is marked by a decrease in Na/Ca ratios (~ 0.1 mmol/mol) until 11.32 kyr. Data from the most recent interval analyzed in the core (8.25 cm; 0.97 kyr) yields an average *T. sacculifer* Na/Ca ratio of 6.21 ± .01 mmol/mol.

3.4. Conversion of *T. sacculifer* Na/Ca ratios to Salinity in JPC26

T. sacculifer Na/Ca ratios analyzed from JPC26 samples were converted to salinity using our Atlantic core top regression according to equation (1). Results show salinity in the Florida Current varied from 36.7 – 39.0 over the last deglaciation, with an average of 37.6 (**Figure 9**).

JPC26 downcore *T. sacculifer* Na/Ca record

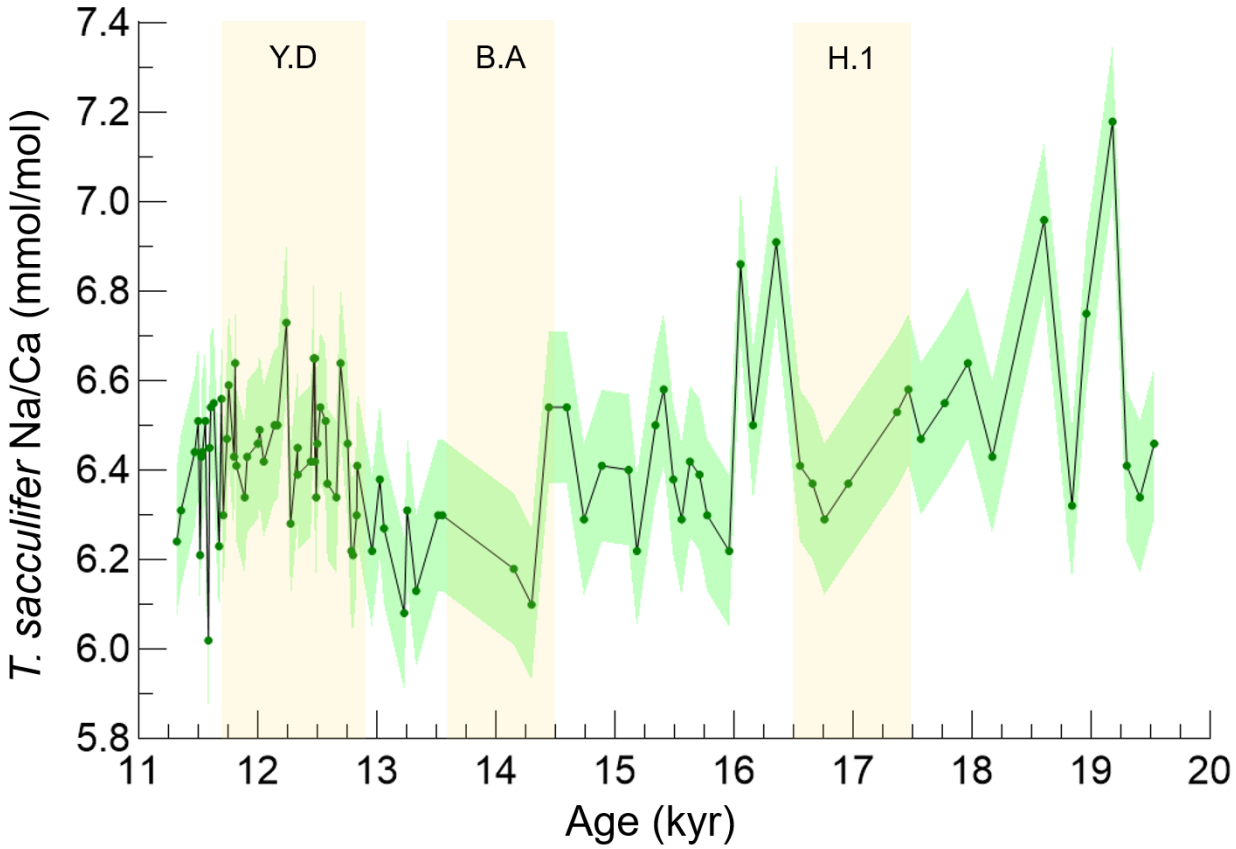


Figure 8. Downcore record of *T. sacculifer* Na/Ca variability across the last deglaciation. Green circles represent the average *T. sacculifer* Na/Ca of two measurements per interval. Green error bands represent the propagated uncertainty (± 0.17 mmol/mol) from my duplicate analysis coupled with instrumentation error.

JPC26 downcore *T. sacculifer* Na/Ca data

Interval (cm)	Age (kyr)	Average Na/Ca (mmol/mol)	STD	CV	Interval (cm)	Age (kyr)	Average Na/Ca (mmol/mol)	STD	CV
8.25	0.97	6.21	0.01	0.2%	590.25	12.84	6.41	0.14	2.2%
312	11.32	6.24	0.07	1.2%	598.25	12.96	6.22	0.02	0.4%
319	11.36	6.31	0.12	1.9%	602.25	13.03	6.38	0.04	0.6%
338	11.47	6.44	0.31	4.8%	604.25	13.06	6.27	0.07	1.2%
344	11.5	6.51	0.16	2.4%	614.25	13.23	6.08	0.04	0.6%
346	11.52	6.21	0.09	1.5%	616.25	13.26	6.31	0.20	3.1%
348	11.53	6.43	0.04	0.6%	620.25	13.33	6.13	0.12	2.0%
350	11.54	6.44	-	-	632.25	13.52	6.30	0.04	0.6%
354	11.56	6.51	0.18	2.8%	634.25	13.55	6.30	0.11	1.7%
358	11.59	6.02	0.03	0.6%	658.25	14.15	6.18	0.12	2.0%
360.25	11.6	6.45	0.25	3.8%	662.25	14.3	6.10	0.00	0.0%
362.25	11.61	6.54	0.04	0.6%	666.25	14.45	6.54	0.29	4.4%
366.25	11.63	6.55	0.07	1.1%	670.25	14.6	6.54	0.07	1.1%
374.25	11.68	6.23	0.06	1.0%	674.25	14.74	6.29	0.07	1.2%
378.25	11.7	6.56	0.08	1.2%	678.25	14.89	6.41	0.08	1.2%
380.25	11.71	6.30	0.10	1.6%	684.25	15.12	6.40	0.08	1.3%
384.25	11.74	6.47	0.16	2.5%	686.25	15.19	6.22	0.01	0.2%
388.25	11.76	6.59	0.29	4.4%	690.25	15.34	6.50	0.31	4.8%
394.25	11.8	6.43	0.21	3.3%	692.25	15.41	6.58	0.17	2.6%
396.25	11.81	6.64	0.02	0.3%	694.25	15.49	6.38	0.15	2.4%
398.25	11.82	6.41	0.15	2.3%	696.25	15.56	6.29	0.15	2.3%
410.25	11.89	6.34	0.09	1.5%	698.25	15.63	6.42	0.08	1.3%
414.25	11.91	6.43	0.25	3.9%	700.25	15.71	6.39	0.13	2.0%
428.25	12	6.46	0.16	2.5%	702.25	15.78	6.30	0.01	0.2%
432.25	12.02	6.49	0.05	0.8%	706.25	15.96	6.22	0.09	1.5%
438.25	12.05	6.42	0.03	0.4%	708.25	16.06	6.86	0.09	1.3%
450.25	12.14	6.50	0.21	3.3%	710.25	16.16	6.50	0.24	3.7%
454.25	12.17	6.50	-	-	714.25	16.36	6.91	0.30	4.3%
462.25	12.24	6.73	0.04	0.5%	718.25	16.56	6.41	0.09	1.5%
472.25	12.28	6.28	0.09	1.4%	720.25	16.66	6.37	0.01	0.1%
490.25	12.34	6.45	0.29	4.5%	722.25	16.76	6.29	0.07	1.0%
492.25	12.34	6.39	0.21	3.3%	726.25	16.96	6.37	0.12	1.9%

524.25	12.45	6.42	0.10	1.5%	734.25	17.37	6.53	0.20	3.0%
530.25	12.47	6.65	0.28	4.2%	736.25	17.47	6.58	0.22	3.3%
532.25	12.48	6.42	0.31	4.9%	738.25	17.57	6.47	-	-
534.25	12.48	6.65	0.17	2.6%	742.25	17.77	6.55	0.06	1.0%
536.25	12.49	6.34	0.16	2.6%	746.25	17.97	6.64	0.10	1.4%
540.25	12.5	6.46	0.22	3.4%	750.25	18.17	6.43	-	-
546.25	12.53	6.54	0.06	1.0%	758.25	18.61	6.96	-	-
552.25	12.57	6.51	0.05	0.7%	762.25	18.84	6.32	0.19	3.0%
554.25	12.59	6.37	0.03	0.5%	764.25	18.96	6.75	0.05	0.7%
564.25	12.66	6.34	0.10	1.5%	768.25	19.18	7.18	0.28	3.9%
570.25	12.7	6.64	0.04	0.7%	770.25	19.3	6.41	-	-
578.25	12.76	6.46	0.17	2.7%	772.25	19.41	6.34	0.05	0.8%
582.25	12.79	6.22	0.17	2.8%	774.25	19.53	6.46	0.14	2.2%
584.25	12.8	6.21	0.05	0.8%			6.43	0.13	2.0%
588.25	12.83	6.30	0.14	2.2%					

Table 3. Downcore record of *T. sacculi*fer Na/Ca (n = 92) variability across the bulk of the last deglaciation (19.53 – 0.97 kyr). Some measurements were removed during data filtering (see 2.6.1.) resulting in 11 intervals without duplicate analysis. The number of shells that were homogenized and split for duplicate analysis is indicated by 'n'.

Salinity was generally higher during the early deglacial period through HS1 and then decreased during the B.A. Salinity then began to rapidly increase at 13.2 kyr (within age model error of the start of the Y.D.) and remained elevated through the cold period (averaged Y.D. salinity 37.6). There is a slight decrease in salinity (~0.5) at the end of the Y.D. transitioning into the Holocene. My study lacks data within the Holocene as I had limited access to sample material from this interval of the core. However, I did analyze the near-modern aged sample from JPC26 from 8.25 cm with an age of 0.97 kyr, and its *T. sacculifer* Na/Ca ratio of 6.21 translates to a salinity of 37.1. For comparison, the modern subsurface salinity over the depth range of *T. sacculifer* in the Florida Straits is about 36.3.

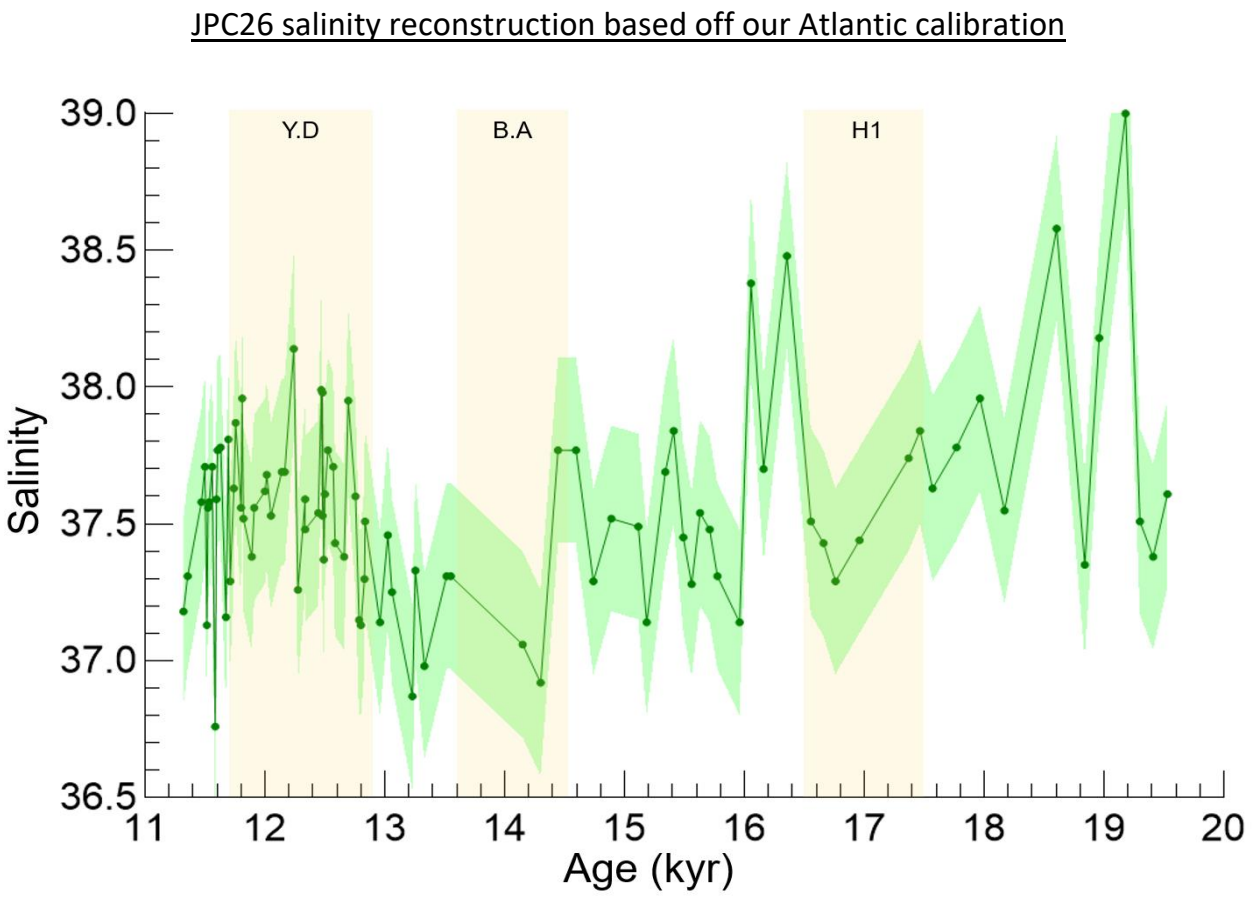


Figure 9. *T. sacculifer* Na/Ca based salinity reconstruction. Ratios were converted to salinity according to equation (1). Results from our duplicate error analysis combined with ICP-MS instrumentation uncertainty yield a compounded error of ± 0.34 in salinity reconstructions. This figure does not include regression calibration uncertainty.

4. DISCUSSION

4.1. Core top calibration

4.1.1 Salinity Na/Ca regression

The results from my Atlantic core top study show the incorporation of Na into the shells of *T. sacculifer* increases significantly ($p < 0.005$) by 9.1% with each unit of habitat salinity (**Figure 4)**. Comparing *T. sacculifer* Na/Ca and habitat salinity versus sea surface salinity results in regressions with slopes and coefficients that are not statistically different (**Figure 5)**. Additionally, either regression demonstrates normality of residuals using a 1-sample Kolmogorov–Smirnov test. This agrees with previous studies that have also found a direct and significant relationship between salinity and *T. sacculifer* Na/Ca ratios. Nevertheless, there is an offset between the magnitude of change that is observed in Na incorporation with increasing salinity between my new data and the two previous studies (**Figure 10a**). For example, my new data suggests a greater increase in Na/Ca per salinity unit increase when compared to previous studies that reported a 2.25% (Bertlich et al., 2018) and 7.40% (Mezger et al., 2016) increase in *T. sacculifer* Na/Ca per salinity unit.

Although the % increase per salinity unit increase in *T. sacculifer* Na/Ca ratios is more similar to what Mezger et al. (2016) reported, the absolute magnitude of *T. sacculifer* Na/Ca ratios measured in my study is more similar to what Bertlich et al. (2018) found. For example, at a salinity of 37, *T. sacculifer* Na/Ca ratios were ~9 mmol/mol in Mezger et al. (2016), but only 5.6 mmol/mol in my results. Bertlich et al. (2018) did not analyze any samples at a salinity of 37, but based on their regression, Na/Ca ratios would be about 5.1 mmol/mol at a salinity of 37 (**Figure 10b**).

Some species of planktic foraminifera are spinose, including *T. sacculifer*, which means they have very thin $CaCO_3$ spines protruding from their shell when they are alive. The spines help the individual foraminifera stabilize in the water and also aid in capture of prey. However,

Comparison of our Atlantic *T. sacculifer* Na/Ca salinity calibration with previously published calibrations

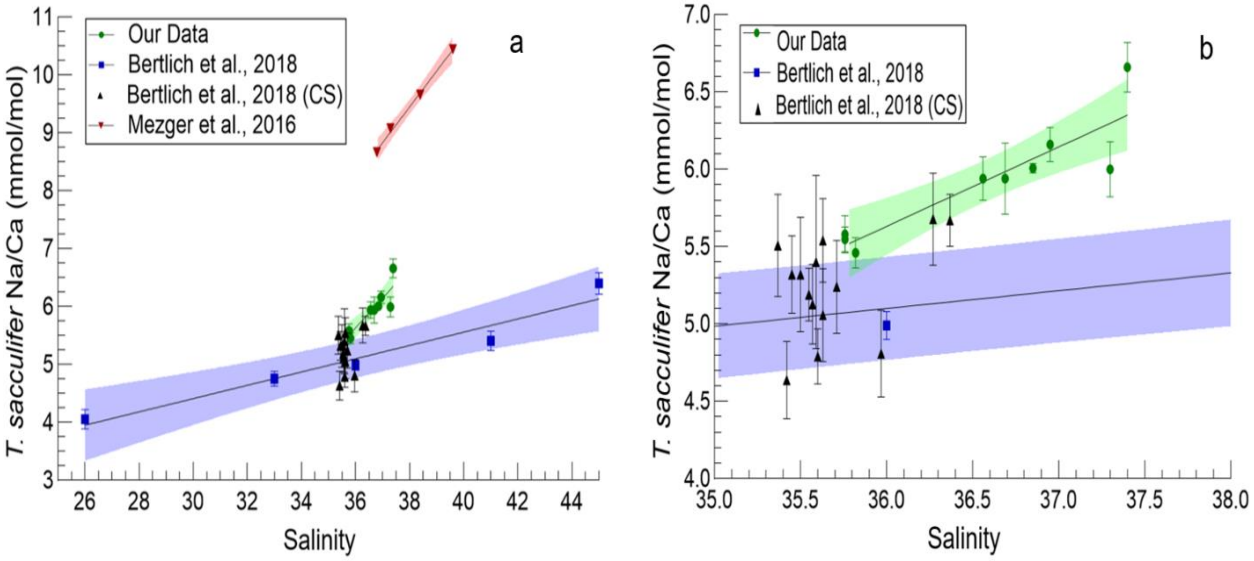


Figure 10a. Comparison of my data with recent studies that have found a significant, positive relationship between *T. sacculifer* Na/Ca and salinity. The uppermost regression consists of *T. sacculifer* Na/Ca measured on Red Sea core tops (red triangles) via LA-Q-ICP-MS (Mezger et al., 2016). The associated regression is *T. sacculifer* Na/Ca = 0..60(S) – 13.49 (R^2 = 0.999, p < 0.001). The lowest regression consists of *T. sacculifer* Na/Ca ratios measured via electron microscopy on cultured foraminifera (Bertlich et al., 2018). Averaged *T. sacculifer* Na/Ca ratios from each growth salinity are indicated by blue squares. The associated regression is *T. sacculifer* Na/Ca = 0.12(S) + 0.97 (R^2 = 0.94, p < 0.005). Our data, measured via ICP-MS, is indicated by green circles. The associated regression is *T. sacculifer* Na/Ca = 0.516(S) – 12.94 (R^2 = .81, p < .005). Finally, Caribbean sediment samples measured via ICP-OES (Bertlich et al., 2018) are indicated by black triangles (**Figure 10b**).

because these spines are so delicate, they dissolve or fall off when the shells are deposited on the seafloor and they are not present in fossil shells. A recent study found that Na is greatly enriched in the calcite forming the spines and spine bases when compared to the chamber shell calcite (Mezger et al., 2019). These authors suggested that the difference in measured *T. sacculifer* Na/Ca ratios between studies could potentially be explained by whether or not analysis are performed via whole-shell analysis which includes measurement of Na-rich spine and spine bases, or partial-shell analysis which do not include these portions (Mezger et al., 2019).

Therefore, this difference may explain why the plankton-pump collected Red Sea samples (containing both spine and spine bases) published by Mezger et al. (2016) had elevated Na/Ca ratios compared to our data and the Bertlich et al. (2018) study. Bertlich et al. (2018) used cultured foraminifera shells in their study, which also contain spines and spine bases, but they used electron microscopy to generate their data and only analyzed portions of the shell without spines or spine bases (**Figure 10**). It is also interesting that whole *T. sacculifer* Na/Ca ratios from sediment samples (as in my study) measured via ICP-MS or ICP-OES are consistently higher than Na/Ca ratios measured on cultured samples via electron microscopy using only partial-shell analysis (avoiding spines and spine bases). Sediment samples, although spineless, still contain spine bases enriched in Na that are included when the whole shell is measured via solution on a MS or OES. This might explain why my Na/Ca ratios were higher than those in the culture portion of the Bertlich et al. (2018) study (**Figure 10**). Furthermore, there is significant agreement between our data and *T. sacculifer* Na/Ca ratios measured on samples collected from Caribbean core tops via ICP-OES (**Figure 10**; Bertlich et al., 2018). For example, their Caribbean samples from core sites with salinities of 36.27 and 36.37 yielded *T. sacculifer* Na/Ca ratios of 5.68 ± 0.30 mmol/mol and 5.67 ± 0.17 mmol/mol, respectively. Although we did not have core top samples from these same salinities, our regression predicts Na/Ca ratios of 5.78 ± 0.17 mmol/mol for a salinity of 36.30.

4.1.2 Testing for other variables that could influence Na/Ca ratios in *T. sacculifer*

Shell size has been shown to have an effect on foraminiferal incorporation of trace metals such as Mg and Sr (Elderfield and Ganssen, 2000, Elderfield et al., 2002). In contrast, my new data show no statistically significant relationships between *T. sacculifer* Na/Ca and shell size when averaging ratios from each size fraction (250-300 µm, 300-355 µm, 355-425 µm, and >425 µm) from cores RC24-10, RC24-11, and VM22-26A (**Figure 7, Table 2**). Although the sample

size of these analyses is smaller (n = 2 for the 250 - 300 µm size fraction), the results agree with previous studies that have also suggested that there is no relationship between foraminiferal shell size and Na incorporation (Mezger et al., 2016). Further, there were no significant relationships between *T. sacculifer* Na/Ca or individual shell weight (both pre and post cleaning procedure; **Figure 6d** and **Figure 6e** respectively).

The *T. sacculifer* Na/Ca ratios were negatively correlated with SST (*T. sacculifer* Na/Ca = -0.12 (SST) + 9.03; R^2 = 0.21, p = 0.21), but this relationship was not significant (**Figure 6c**). This agrees with culture data from Bertlich et al. (2018) in which *T. sacculifer* Na/Ca ratios were measured on foraminifera grown over a temperature gradient of 19.5 - 25.5 ˚C.

4.2. Downcore Record

4.2.1. Downcore Na/Ca record

The SSS in the Florida straits is predominantly controlled by the balance between evaporation and precipitation in the Tropical Atlantic and this relationship over time is influenced by the mean position of the Intertropical Convergence Zone (ITCZ) (Waliser and Gautier, 1993). Schmidt and Lynch-Stieglitz (2011) generated a record of $\delta^{18}O_{SW}$ change in the Florida Straits and showed that as the Atlantic Meridional Overturning Circulation (AMOC) weakened during cold periods of the last deglaciation, a southward shift in the ITCZ caused the E/P balance in the Tropical Atlantic to increase. This resulted in an abrupt increase in SSS in the Florida Straits during the Y.D. and H1.

In order to determine if Na/Ca ratios in *T. sacculifer* show the same pattern of SSS change inferred from $\delta^{18}O_{SW}$ across the deglaciation, I analyzed samples from the same intervals in Florida Straits core JPC26 used in the Schmidt and Lynch-Stieglitz (2011) study. My new record of *T. sacculifer* Na/Ca ratios from JPC26 broadly agrees with the previously published $\delta^{18}O_{SW}$ record in Schmidt and Lynch-Stieglitz (2011) (**Figure 11**). It is worth noting that the $\delta^{18}O_{SW}$ record

was generated using the planktic foraminifera *G. ruber*, a species known to have a slightly shallower habitat depth. Both records span a significant portion of the last deglaciation and show considerable variability. In particular, there is a near synchronous increase in both *T. sacculifer*

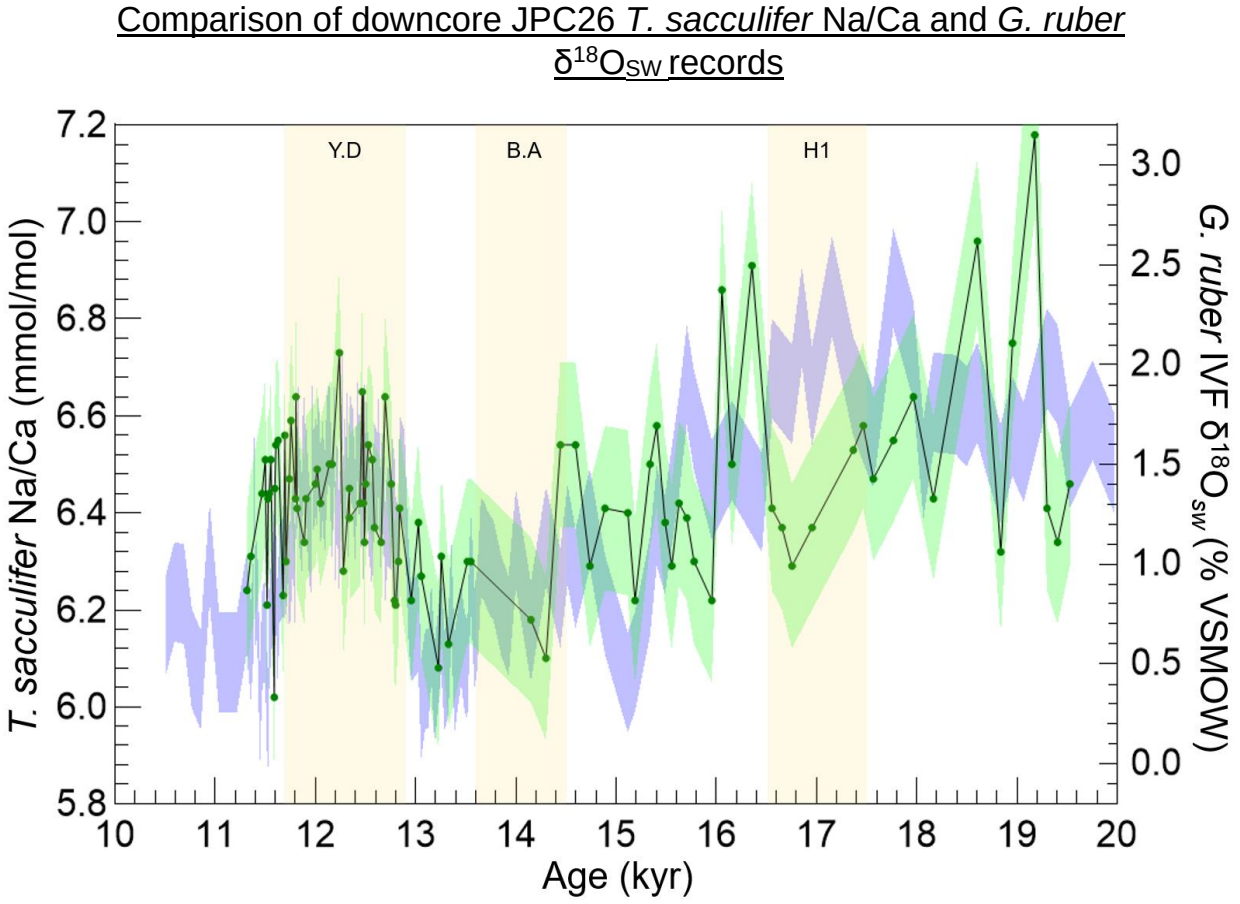


Figure 11. Records of *T. sacculifer* Na/Ca (green) and *G. ruber* ice volume free δ18Osw (blue; Schmidt and Lynch-Stieglitz, 2011) variability across the last deglaciation. Both records show a period of increased salinity during the Younger Dryas (YD; 12.9 – 11.7 kyr).

Na/Ca and *G. ruber* $\delta^{18}O_{sw}$ at the start of the Y.D., indicating a period of elevated SSS. The $\delta^{18}O_{sw}$ record then dramatically decreases into the start of the Holocene at 11.5 ky. Similarly, my *T. sacculifer* Na/Ca ratios begin to decrease at the end of the Y.D. and until 11.32 ky. I also

analyzed a near-modern sample from JPC26 at 8.25 cm core depth with an age of 0.97 kyr. The *T. sacculifer* Na/Ca ratio in this interval of 6.21 ± .01 mmol/mol is significantly lower than those from the Y.D. with an average ratio of 6.45 ± .14 mmol/mol).

4.2.2. Deglacial Salinity Reconstructions for the Florida Straits

Converting my JPC26 *T. sacculifer* Na/Ca ratios into salinity using equation (1) results in a reconstruction with a variability in salinity of 2.3 in the Florida Straits across the last deglaciation (**Figure 12**). Next, I converted the *G. ruber* $\delta^{18}O_{SW}$ record from Schmidt and Lynch-Stieglitz (2011) to salinity using the PSU solver program by Thirumalai et al. (2016). This program converts paired $\delta^{18}O_C$ and Mg/Ca datasets into SSS reconstructions with propagated uncertainty using a bootstrap Monte Carlo simulation.

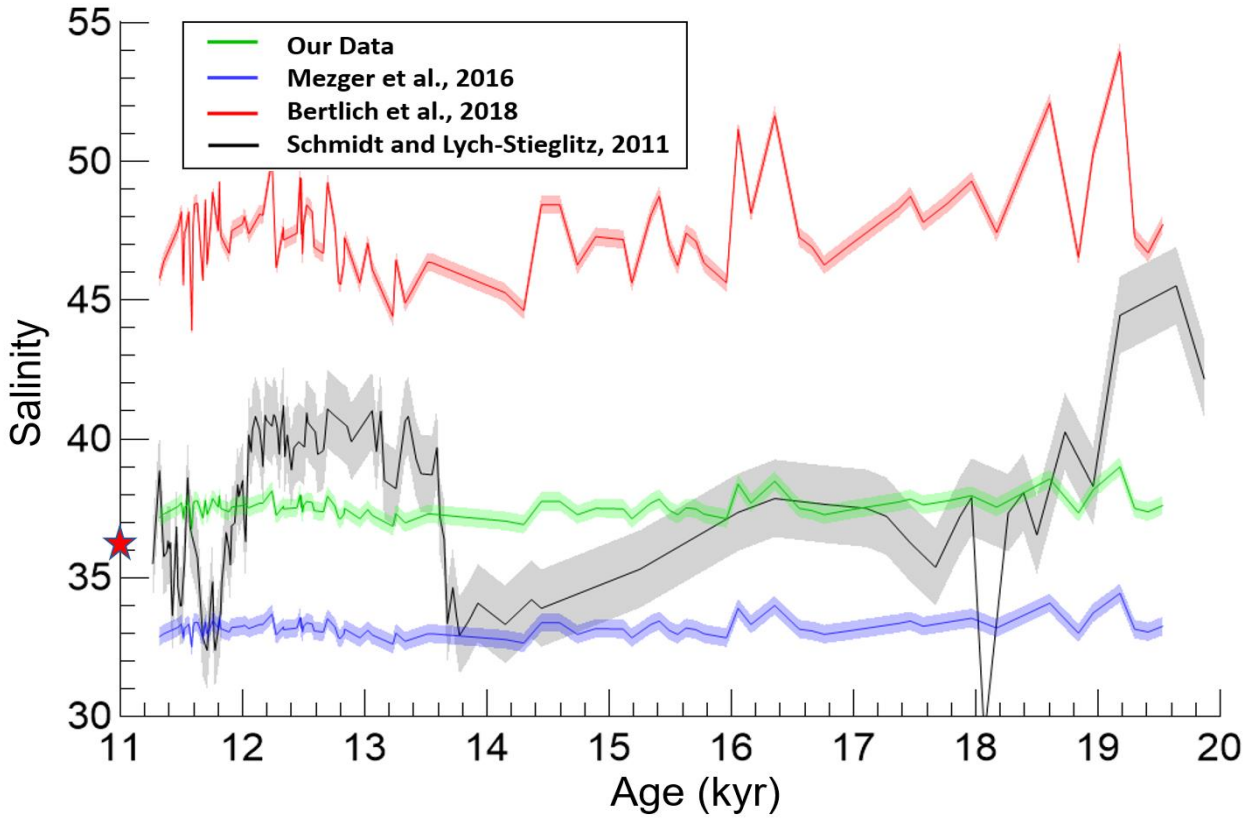


Figure 12. Newly measured downcore JPC26 *T. sacculifer* Na/Ca ratios were converted to salinity using the Atlantic core top calibration from this study (green data), the culture calibration published by Bertlich et al., 2018 (blue data), and the Red Sea field calibration published by Mezger et al., 2016 (red data). The gray band represents the *G. ruber* $\delta^{18}O_{sw}$ record (Schmidt and Lynch-Stieglitz, 2011) converted to salinity using PSU solver (Thirumalai et al., 2016). Error bars for each of the *T. sacculifer* Na/Ca based salinity reconstruction (± 0.34) are based off duplicate error analysis coupled with ICP-MS instrumentation uncertainty. Regression calibration error is not plotted. The red star represents the modern day JPC26 core site SSS of 36.2.

A comparison of these two records shows similar trends, but with significantly smaller magnitude variability in the Na/Ca-based salinity record (**Figure 12**). The Na/Ca-based salinity record suggests a much more reasonable increase in salinity of roughly 0.50 at the start of the Y.D. whereas the reconstruction using *G. ruber* $\delta^{18}O_{SW}$ suggests an increase of nearly 10. Furthermore, results from a tropical Atlantic coupled general circulation model (GCM) experiment

under modern conditions showed that a 50% reduction in AMOC (comparable to the AMOC reduction at the start of the Y.D. resulted in an increase in surface water $\delta^{18}O_{sw}$ of ~0.10‰ (Wan et al., 2010). When converted to salinity using the modern day $\delta^{18}O_{SW}$:SSS relationship for the Florida Straits ($\delta^{18}O_{SW}$ = 0.26(SSS) - 8.44; Schmidt and Lynch-Stieglitz, 2011), this corresponds to an increase in salinity of ~0.4, nearly identical to the salinity changes suggested by my Na/Ca reconstruction. Another coupled GCM experiment modeled an AMOC reduction under glacial boundary conditions and found that this results in a southward shift of the ITCZ and a salinity increase of ~0.5 in the Florida Straits (Lynch-Stieglitz et al., 2014). Agreement between these modeling studies and my proxy data gives additional credence to the applicability of *T. sacculifer* Na/Ca ratios as a means for constructing paleosalinity.

Next, I converted my *T. sacculifer* Na/Ca record from JPC26 to salinity using the calibration of Bertlich et al. (2018). This calibration yields unrealistically high salinity values in the range of 45 to 54 and a salinity increase of 4 at the start of the Y.D. (**Figure 12**). Finally, the Mezger et al. (2016) regression suggests the lowest salinities of all the calibrations, with a Holocene salinity of about 33, much lower than the modern salinity of 36.2 **(Figure 12)**. Nevertheless, this reconstruction is more similar to the one using my calibration, but with an offset of about 4 salinity units. Although the calculated salinity using my regression for the most recent datum (0.97 kyr) overestimates the modern SSS of the region (37.12 ± .34 compared to a modern day annual SSS of 36.20; **Figure 12**), it nonetheless reproduces near-modern salinity better than any of the other calibrations.

It is not surprising that my Atlantic core top calibration using down core *T. sacculifer* Na/Ca ratios from JPC 26 produced the most realistic salinity reconstruction when considering the calibration was developed using sample material taken from cores within the same ocean basin (**Figure 2**) and using identical collection and analytical methodologies. Conversely, the calibration produced by Bertlich et al., (2018) was constructed using cultured samples measured using electron microscopy, and the calibration produced by Mezger et al, (2016) was constructed using

living Red Sea samples collected via plankton pump and measured using ICP-OES. Regardless, it is encouraging that my calibration has been shown to produce a salinity reconstruction that yields realistic salinity changes across the last deglaciation and Holocene salinities that are comparable to modern day conditions.

4.3. Error estimates on salinity reconstructions based on Na/Ca and $\delta^{18}O_{sw}$

Combining standard-calibrated ICP-MS analytical error (± 0.7%) with my bulk Na/Ca data duplicate error (± 2.0%) yields a propagated uncertainty of ± 2.7% in *T. sacculifer* Na/Ca measurements (equal to ± 0.20 mmol/mol for the average JPC26 Na/Ca ratio of 6.43). When converting ratios into salinity, this corresponds to an uncertainty of ± 0.34 salinity units. Including the regression calibration error (± 0.60) for the average JPC26 *T. sacculifer* Na/Ca ratio of 6.43 mmol/mol yields a maximum error of ± 0.94 in resulting salinity reconstructions. It should be noted that this regression calibration error is very likely an over estimation. My regression is lacking sufficient data from cores within the salinity range of what our reconstruction suggests JPC26 averaged across the last deglaciation, which results in greater uncertainty. As a comparison, my regression calibration error associated with converting a ratio similar to that of the mean Atlantic core top data set (5.92 mmol/mol) is ± 0.29. The errors associated with using Mg/Ca and $\delta^{18}O_C$ to reconstruct $\delta^{18}O_{SW}$ results in error estimates that average ± 21% (equal to ± 0.25 ‰ for the average JPC26 $\delta^{18}O_{sw}$ ratio of 1.17 ‰; Schmidt and Lynch-Stieglitz, 2011). When converting these ratios into salinity, this corresponds to an uncertainty of ± 1.4 salinity units, 50% greater than the error estimation for *T. sacculifer* Na/Ca based salinity reconstructions even when including our overestimated calibration error (**Figure 12**).

5. CONCLUSIONS

T. sacculifer Na/Ca is significantly and linearly correlated with salinity according to equation (1). My core top calibration results in an increase in *T. sacculifer* Na/Ca of ~9.1% per unit of salinity, which is higher than previous studies have suggested (2.25%; Mezger et al., 2016 to 7.40%; Bertlich et al., 2018). There was significant overlap in *T. sacculifer* Na/Ca ratios between my data and previous studies, particularly with Caribbean sediment samples (Bertlich et al., 2018). Other parameters (sample size, sample recovery, core site SST, and mean individual shell weight both pre and post-cleaning) showed no significant relationships with *T. sacculifer* Na/Ca, further suggesting Na/Ca ratios are predominantly controlled by salinity. These results are encouraging, and strengthen the growing body of evidence that *T. sacculifer* Na/Ca ratios are a valuable proxy for reconstructing past SSS.

My newly measured JPC26 *T. sacculifer* Na/Ca ratios show good agreement with previously published *G. ruber* $\delta^{18}O_{sw}$ from the same intervals across the majority of the last deglaciation (Schmidt and Lynch-Stieglitz, 2011). Specifically, there is a very clear and abrupt increase in both records at the start of the Y.D., indicating increasing salinity. Additionally, both records suggest elevated salinities through the remainder of this climate event and a decrease in SSS at the end of the Y.D. Converting our downcore *T. sacculifer* Na/Ca ratios into salinity using equation (1), indicates an increase in salinity of ~0.5 during the Y.D. Comparatively, converting $\delta^{18}O_{sw}$ into salinity suggests an increase in salinity of almost 10 over the same time period. Our *T. sacculifer* Na/Ca based salinity reconstruction also predicts a nearly identical increase in salinity during the Y.D. as two GCM studies under both modern day and glacial conditions. Uncertainty in $\delta^{18}O_{sw}$ based salinity reconstructions (± 1.4) is about four times greater than the current error estimation for *T. sacculifer* Na/Ca based salinity reconstructions (± 0.34) when not including regression calibration error, and 50% greater when also including the calibration error (maximum

error of 0.94). Therefore, the Na/Ca proxy may not only provide more realistic reconstructions of SSS change, but significantly reduce errors associated with these estimates.

The results presented here suggest a strong potential for the use of the *T. sacculifer* Na/Ca paleo-salinity proxy to reconstruct past SSS. The calibration presented in this study can be improved upon by measuring additional *T. sacculifer* Na/Ca ratios from Atlantic core tops, specifically ones with *T. sacculifer* habitat salinities that either expand the current gradient, or fall within portions of our gradient that are lacking data (35.82 - 36.56). This will largely aid in reduction of error analysis when including regression calibration uncertainty. Additionally, measuring samples collected from core tops located in different geographic locations would provide a more robust dataset while also providing valuable data regarding the spatial variability in *T. sacculifer* Na/Ca.

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