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Expression of Global Stadial Events Captured in a High Deposition Rate Marine Sedimentary Sequence off the Zambezi River Delta

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Expression of Global Stadial Events Captured in a High Deposition Rate Marine Sedimentary Sequence off the Zambezi River Delta

A thesis submitted in partial satisfaction of the
requirements for the degree
Master of Science

in

Earth Sciences

by

Gregory Vartan Mamikunian

Committee in charge:

Professor Christopher Charles, Chair
Professor Neal Driscoll
Professor Richard Norris

2019

The thesis of Gregory Vartan Mamikunian is approved, and it is acceptable in quality and form for publication on microfilm and electronically:

Chair

University of California San Diego

2019

DEDICATION

To my parents.

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I acknowledge my Advisor Chris Charles for his continued guidance and support these past two years. While working in his lab, he let me the freedom to think and act independently while offering his guidance and insight whenever I needed it. I acknowledge my committee members Neal Driscoll and Richard Norris for their guidance and support in writing and defending my thesis. I acknowledge Sara Sanchez for her help with the SODA anomaly data. I would also like to thank my parents, brothers and sister for their continued support and motivation. This research would not be possible without International Ocean Discovery Program Expedition 361 which was funded by the National Science Foundation.

The work in thesis is currently being prepared for submission for publication of the material.

ABSTRACT OF THE THESIS

Expression of Global Stadial Events Captured in a High Deposition Rate Marine Sedimentary Sequence off the Zambezi River Delta

by

Gregory Vartan Mamikunian

Master of Science in Earth Sciences

University of California San Diego, 2019

Professor Christopher Charles, Chair

The progression of a geographically specific hydroclimate system over the course of global climatic anomalies and shifts like the Last Glacial Maximum (LGM) and Heinrich Stadial (HS) events gives rise to the strength and impact of these paleoclimate events on the worlds oceans and atmospheric conditions. The interplay of the Intertropical Convergence Zone (ITCZ) location in response to positive feedback loops derived from high latitude hemispheric specific aberrations (HS events) causes shifts in the intensity and spatial variability of global precipitation belts. Here, we show the implications of HS1, HS4, and the LGM on the hydroclimate variability of South Central Africa using barium ratios and the $\delta^{18}O$ of individual planktonic foraminifera

captured in an ultra-high deposition sequence drilled off the Mozambique Margin at the output of the Zambezi River. In addition to sea surface measurements, a high resolution benthic $\delta^{18}O$ record was constructed to locate and observe the expression of these events in the Southern Hemisphere. We find abrupt excursions to low $\delta^{18}O$ values in line with HS events indicating these events are characterized by a warming of sub-Antarctic surface waters. In addition, we find that during HS events and the LGM there is evidence for southern shifts in the ITCZ documented by increased precipitation and freshwater discharge into the Mozambique Channel captured by elevated barium levels and negative shifts in $\delta^{18}O$ of planktonic foraminifera.

Chapter 1

Introduction and Background

1.1 Introduction

Heinrich Stadial (HS) events are extreme ocean-climate events that have global implications and cause drastic changes from sea-surface waters to deep bottom waters. There are six prominent HS events since the last interglacial period 125kya (Bond et al., 1992). These events occur with varying intensity and frequency in the Pleistocene and are associated with elevated glacial discharge from the Hudson Straight (Goldstein et al., 2014). Evidence of these glacial discharge events comes from the presence of ice rafted detritus observed in the North Atlantic Ocean and it is hypothesized to be accompanied by large freshwater generation which may have disrupted North Atlantic Deep Water (NADW) formation (Broecker et al., 1994). This disruption of major ocean circulation pathways may have had an impact on global climates via ocean-atmospheric heat transfer, distribution, and regulation. Consequentially, these HS events have an impact on air masses interactions leading to shifts and divergence of the Intertropical Convergence Zone (ITCZ) leading to spatial shifts in tropical and subtropical evaporation and precipitation trends. Studies have shown that the ITCZ responds to extratropical changes in hemispheric energy balance like that observed during Last Glacial Maximum (LGM) and HS events (Kang et al., 2008).

This study aims to elucidate the interannual hydroclimate variability (El Niño teleconnections) throughout the duration of paleoclimatic events like Heinrich Stadials and glacial to interglacial transitions with regards to the modern hydroclimate of S. Central Africa. In this study, we are analyzing a sediment core drilled off the continental slope at the output of the Zambezi River Delta. The uniqueness and ultra-high resolution of this sediment core leads to the possibility of investigating multiple climatic events in the last 100,000 years in quasi-decadal resolution. The transitions from glacial to interglacial and well-documented climatic events like the LGM, and HS1 and HS4 are targets for investigating the evolving hydrology in terms of frequency and intensity of Zambezi flood events. To achieve this, a high resolution $\delta^{18}O$ record was created using benthic foraminifera to locate and observe the expression of these paleoclimate events in the Southern Hemisphere. Next, individual planktonic foraminifera were analyzed at depth for their oxygen isotope ratios to elucidate changes in sea surface conditions during the duration of these events. In addition, minor and trace elemental concentratins (ppm) were measured in the planktonic foraminifera carbonate tests to correlate changes in seawater chemistry at the study site via large discharge events from the Zambezi River in Africa.

1.2 Study Site and Background

1.2.1 Geologic and Oceanographic Context

This study takes place on the upper continental slope within the Mozambique Channel, a north-south trending channel that lies between Madagascar and Eastern Africa. The sediment core was drilled at the output of the Zambezi, the largest river in southern Africa. In the channel, there is a dominant southward surface flow accompanied by multiple quasi-stationary counterclockwise eddies (Wiles et al., 2017).

The catchment area of the Zambezi River is encompassing of the hydroclimate variability as the catchment area is the largest in southern Africa with a total area of 1.37 million km^2, mean annual rainfall of 95cm, and an average annual discharge of 103 km^3 or (103 billion m^3) (Euroconsult Mott MacDonald, 2008). This study site is relevant to hydrological changes because total catchment discharge is released at a singular point, elucidating potential hydrological changes of the entire southern Africa region in a single sediment core.

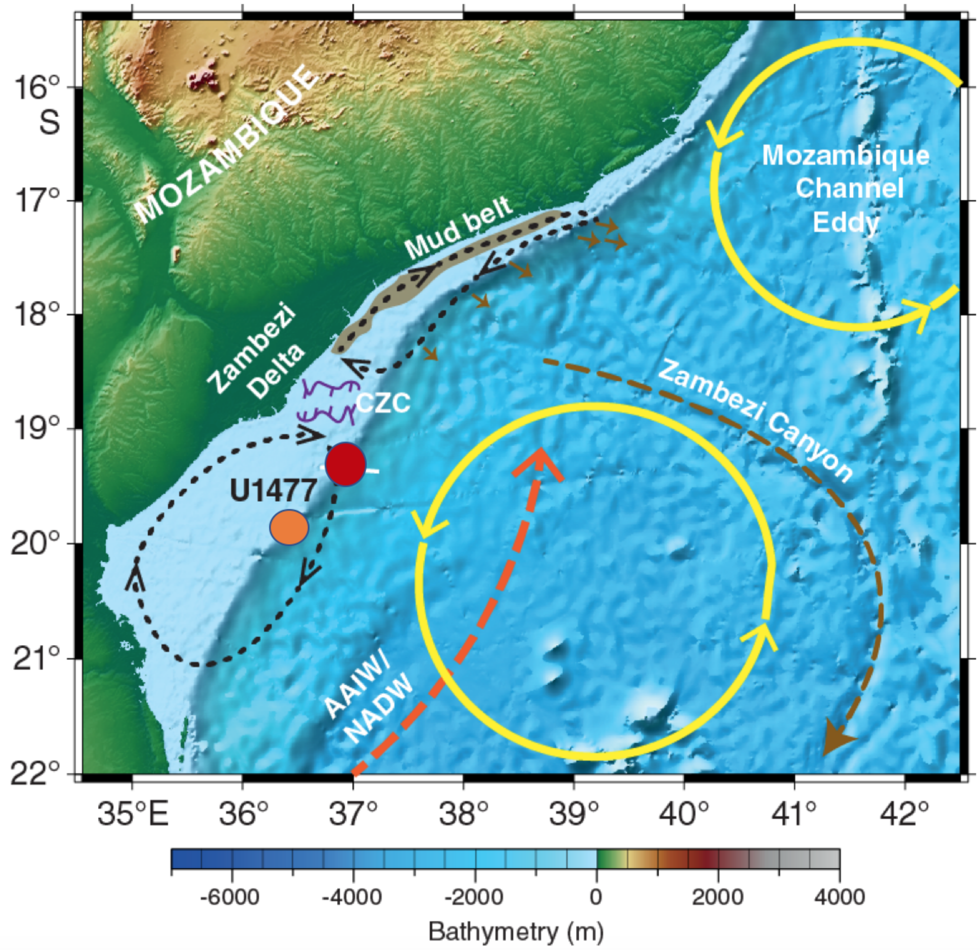

Figure 1.1: Study site location and location of core drilling denoted by red circle (19°49.25S; 36°46.12E). The orange circle denotes location of well log used for conversion of TWT to depth. The yellow arrows denote positions of quasi-stationary eddies observed in the Mozambique Channel. Black dotted lines denote sediment suspension and transport pathways from the Zambezi River Delta to seafloor deposition. Orange dotted line denotes location and direction of Antarctic Intermediate Water/North Atlantic Deep Water (AAIW/NADW). Figure modified from (Hall et al., 2016).

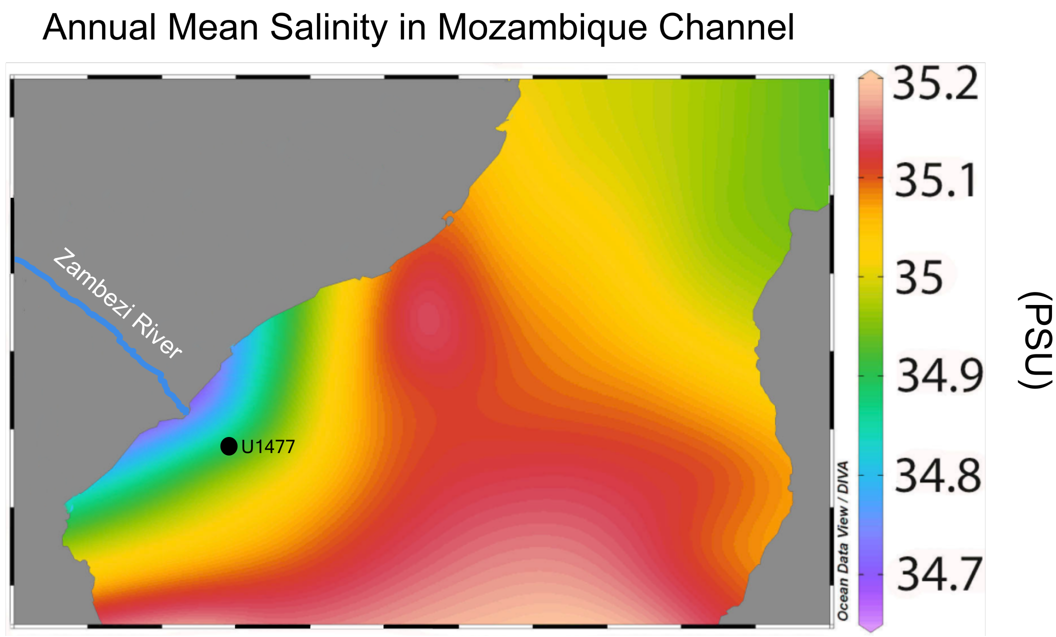

Figure 1.2: Annual mean salinity (psu) in the Mozambique Channel. Figure emphasizes the influence of freshwater discharge from the Zambezi River. This freshwater influence has a direct effect on the $\delta^{18}O$ ratio of the planktonic foraminifera, with flood events resulting in negative $\delta^{18}O$ excursions. Figure modified from (Lattaud et al., 2017)

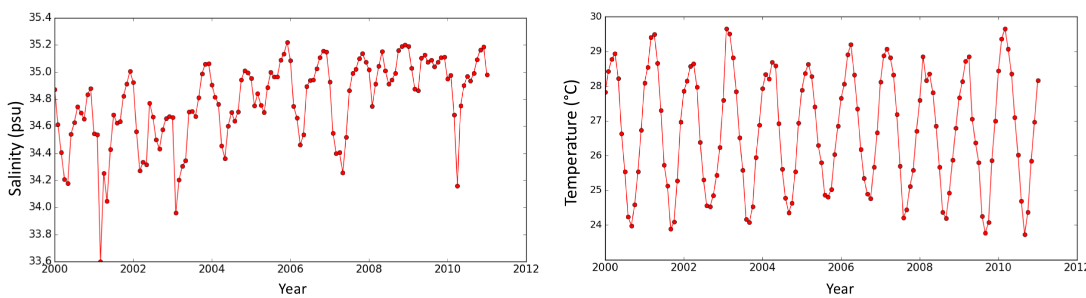

Figure 1.3: Sea surface salinity (left) and sea surface temperature (right) modeled data from SODA (Simple Ocean Data Assimilation) (Carton and Giese, 2008) from Jan. 2000-Dec 2010, 19°5S;36°5E. This gives a true sense to the annual variability or seasonality of the Mozambique Channel in a given decade. One can see various and intermittent drops in salinity in the Mozambique Chanel due to various flood/discharge events in the austral summer.

At the study location, ENSO events are deciphered by either drought conditions which lead to positive $\delta^{18}O$ excursions (El Niño event) or flood events which lead to negative $\delta^{18}O$ excursions (La Niña event). Stronger variability results in a longer tailed distribution of $\delta^{18}O$

values, where the tails (extremes) of the histogram coincide with extreme hydroclimate/discharge events (drought or flood) with a higher deviation from the mean. This is due to the ratio of the heavy oxygen isotope ^{18}O to the lighter ^{16}O. As the flux of freshwater from river runoff enters the Zambezi Channel, it will be heavily enriched in the lighter ^{16}O as evaporation and precipitation separate the light $H_2{}^{16}O$ from the heavy $H_2{}^{18}O$. The terrestrial runoff from the Zambezi river system will be low in the heavy $H_2{}^{18}O$ and this is subsequently incorporated and captured in the sea surface residing planktonic forams. Where $\delta^{18}O$ is:

$$\delta^{18}O = \left(\frac{(\frac{^{18}O}{^{16}O})_{sample}}{(\frac{^{18}O}{^{16}O})_{standard}} - 1 \right) * 1000‰ \tag{1.1}$$

The incorporation of oxygen isotopes during the formation and growth of a foraminiferas calcareous test, which is composed of calcium carbonate ($CaCO_3$), is temperature dependent and the lower the temperature (at the time of calcite precipitation), the more ^{18}O will go into $CaCO_3$. The effect has been determined empirically by a shift of -0.22 +/-0.1 per °C (Mulitza et al., 2003). Note that there is a 5 °C seasonal shift in sea surface temperature at the study site which is influenced by the changing seasonal influence of northward and southward surface currents along with the seasonal heat flux in the subtropical western Indian Ocean. Additionally, a eustatic drop in sea level of roughly 100 meters leads to a shift by +1.0 shift in $\delta^{18}O$ (Urey, 1947) based on the mass balance of glacial ice formation to ocean volume reduction. This leads to the assumption that a lowering in sea level of 100 meters will increase global ocean salinity by ∼3%.

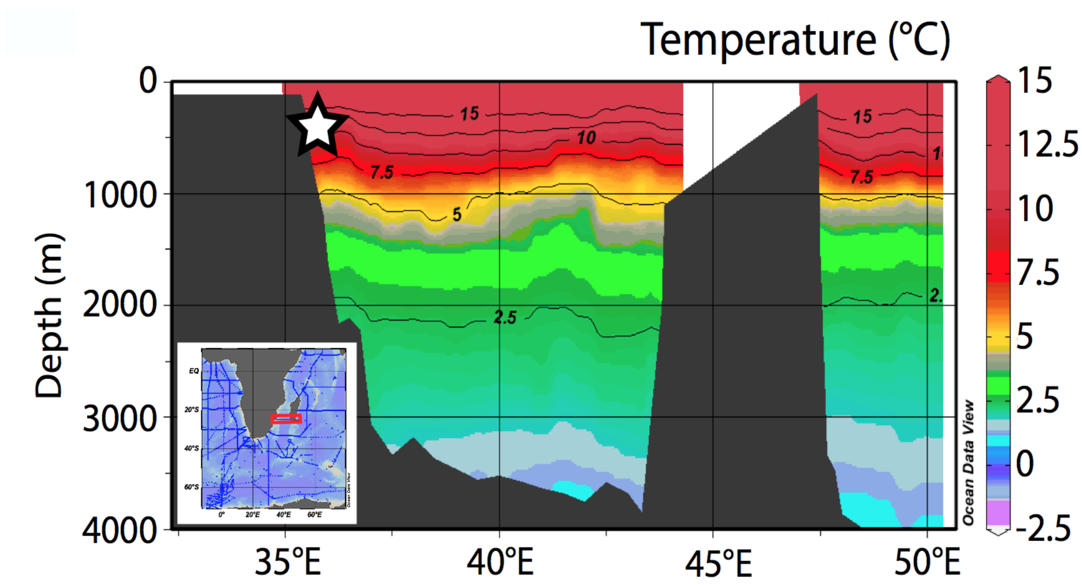

Figure 1.4: West to east longitudinal temperature cross section of Mozambique Channel with the East African continental margin (left) and Madagascar (right). The star denotes the location of drilling. Figure shows the stratification of water masses at depth. Figure sets context of sediment core characteristics as sedimentary sequence records stable bottom water conditions (*uvigerina*) and surface conditions (*G. ruber* and *G. sacculifer*) giving a proper sense of past ocean conditions. Figure courtesy of Sophia Hines.

To properly assess climatic events in the benthic record, one must look at where the ocean water mass at depth of coring is derived. At the study site, following isopycnals, or lines of constant density, from the coring location to the surface, one can see the origin of ocean waters at depth. South of the coring location, wind-driven convergence and wintertime cooling of surface water in the northern subantarctic pumps water into the sub-thermocline depths.

Looking at the latitudinal cross section of oxygen (fig. 1.5a), one can see that bottom waters at location of coring are derived by subantarctic surface waters sinking just south of the Subtropical Convergence Zone. Ocean water readily mixes along lines of constant density and if one follows the bolded isopycnal (fig. 1.5b) one can see its spatial origin. This water should be representative of subantarctic surface waters in terms of its temperature and salinity.

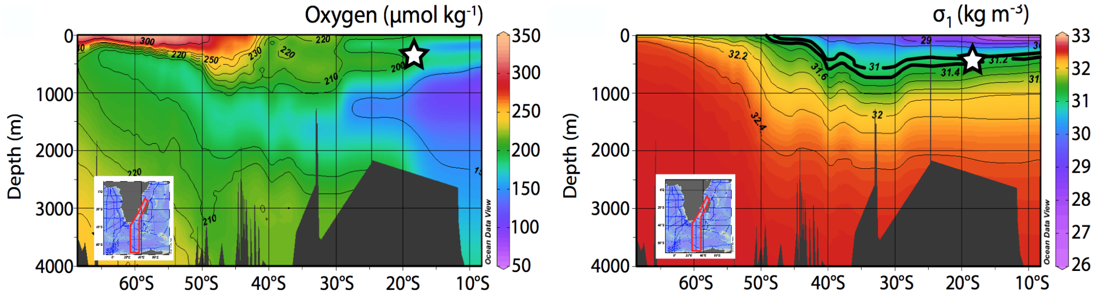

Figure 1.5: South to north latitudinal cross section of oxygen (μmol/kg) (left) and ocean water density (kg/m^3) (right). The star denotes the location of drilling. Plot emphasizes the relatively direct influence of sub-Antarctic surface water being "pumped" to depths of sediment core drilling. This provides confidence that the benthic foraminifera recovered from the core provides a proxy for past global ocean conditions. It should be noted that the benthic record records sub-Antarctic surface temperature fluctuations and is not affected by salinity changes from discharge events. Figure courtesy of Sophia Hines.

1.2.2 Sedimentation and Sediment Characteristics

Sedimentation at the study site is on the order of $\sim$1m/kyr or ($\sim$1cm/10yrs). Sediment is predominantly fine-grained fluvial siliciclastic sediments derived from the Zambezi River Basin Catchment. This characterizes the Mozambique margin deposits as a mix of river-borne sediment ($\sim$75%), eddy current transported sediment ($\sim$15%) and biogenic material ($\sim$6-8%) (Hall et. al, 2017).

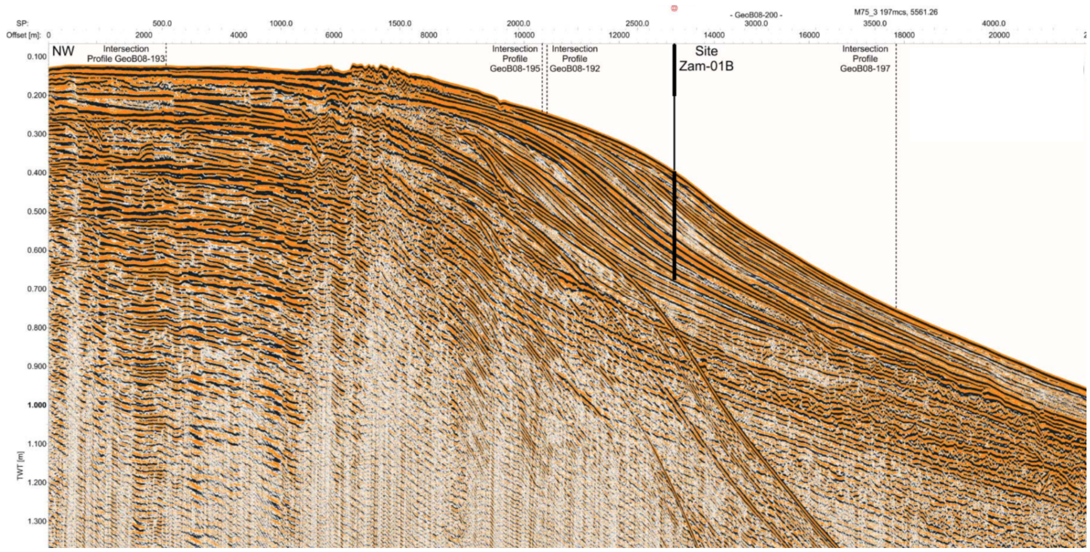

Figure 1.6: Multi-channel seismic section (TWT) of the Mozambique shelf to margin using a GI (Generated Injected) Air gun with a volumetric displacement of 90 cubic meters. The seismic section shows the mostly flat lying continental shelf to the NW. A carbonate reef begins at 6000m offset, indicated by the rougher seafloor topography. On the downslope of the continental shelf one can see prograding stratal packages and clinoforms consistent with the accommodation created by sea level rise observed in the Holocene and Late Pleistocene. At 16,000m offset, between 0.7s and 1.0s TWT, rough topography reflectors begin under the seafloor consistent with past continental shelf collapse events. It should be noted that there are artifacts in the seismic section that are consistent with multiples or ringing due to impedance contrast of air to water. One can see this as the reflection multiples are consistent with twice the water depth and twice the slope of topography. One can also see that these reflections cut across continuous sedimentary sequence reflections, instilling confidence that they are artifacts and not a part of the geologic interpretation. Figure modified from (Hall et al., 2016).

Basin area and topographic relief are the primary controlling factors on sediment load and sediment yield at the output of major river systems (Milliman et al., 1992). Another study suggests that rate of uplift and drainage area are the primary factors controlling sediment yield. (Hovious et al., 1998). The extensive rate of uplift and the doubling of the drainage area of the Zambezi River Basin in the Pleistocene has allowed for increased sedimentation in the Mozambique Channel (Walford et al., 2005). Currently the Zambezi catchment relief is >2500m and the Zambezi river travels for roughly 2500km from Northern Zambia in a general SE direction until it outflows into the Mozambique Channel through a substantial delta system. This increase in sedimentation has allowed for the potential to investigate possible hydrological changes in sub-decadal resolution during the Pleistocene.

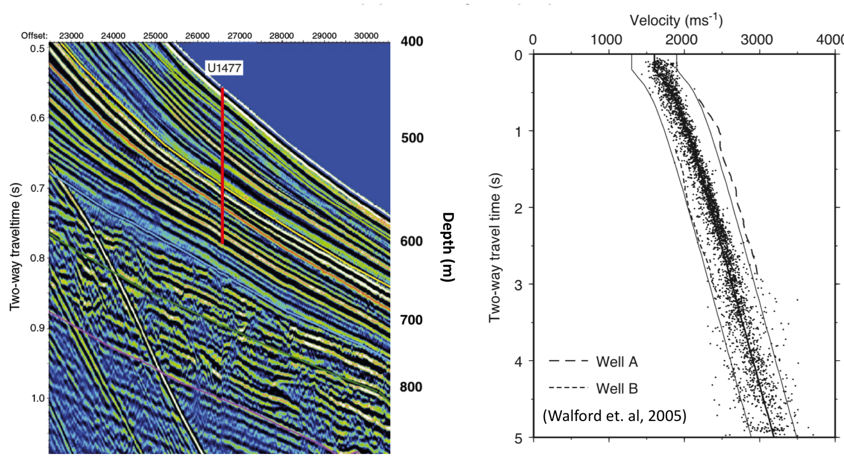

Figure 1.7: Using an exploration well drilled by British Petroleum we are able to convert two-way travel time to depth in meters if we extrapolate the velocity of the sediment by using the uncalibrated, integrated sonic times and the interval velocities. Doing so allows for an estimate of TWT to depth. To covert TWT to depth, 12 different tie points were chosen between the well log and the seismic line. Uncertainty lies in the fact the well log location is offset by ∼60km to the south but it is at the same approximate distance from the delta system with similar slope and geometry of the coring site with respect to the continental margin. The assumption made here is that the general geology and depositional environments are the same at the coring site and well log location and a constant velocity of 1500m/s was implemented for the value of seawater. Well log figure modified from (Walford et al., 2005). Figure modified from (Hall et al., 2016).

Chapter 2

Methodology

2.1 Sampling and Biogeochemical Analysis

Sediment cores were drilled by the JOIDES Resolution on IODP Expedition 361 at site U1477 (19°49.25S; 36°46.12E). The location of coring began at a water depth of 429 m below sea level in the western Mozambique Channel on the upper continental slope, ~120km east of the Zambezi River delta region. There were three holes drilled at core site U1477A, U1477B, and U1477C. The three cores were spliced together to create a composite depth using distinct magnetic susceptibility, lithological trends and $\delta^{18}O$ values observed in all three cores.

Sediment cores were cut at 20cm intervals and each sample was cut at 20mm which was then washed through a set of screen filters using deionized water for the chemical analysis of the foraminifera. Once the fine-grained sediment less than 63 microns were removed, foraminifera between 250-315 micron range were handpicked and analyzed using a Thermo-Scientific MAT 253 gas mass spectrometer, and ran against internationally recognized standard NBS-19.

A high resolution oxygen isotope paleoclimate record were created using individual benthic foraminifera species *Uvigerina bradyana*. *Uvigerina* reside in the sediment pore water, continuously recording stable bottom water conditions. This species were used to observe paleoclimatic trends and conditions in the Late Pleistocene.

Planktonic foraminifera reside on the sea surface (0-20m water depth) and capture $\delta^{18}O$ values of the seawater that get incorporated into their calcium carbonate tests. Individual *Globigerinoides ruber* and *Globigerinoides sacculifer* have lifespans of 2-4 weeks (Sperro, 1998) acting as a recorder for sea surface conditions at a near monthly rate. Therefore, we can deduce changes in the hydrology and sea surface conditions (El Niño teleconnections) by changes in the isotopic variance with any divergence in the population statistics (Koutavas et al., 2006). Subsequently, the overall distribution of $\delta^{18}O$ in a specific sediment interval can give a measure of Zambezi discharge frequency and intensity (ENSO teleconnections) within the specified interval of deposition. For our study site, sediment intervals cut at 2cm, create a sense of interrannual variability within a 10 to 20-year period assuming a quasi-steady sedimentation rate of 1m/kyr (or 1cm/10yrs). This individual foraminifera approach has been used previously to infer changes in the ENSO variance from eastern Pacific deep sea sediments (Koutavas et al.,2006), but the characteristics of this sequence are ideal for this method because bioturbation mixing does not influence the population statistics in any given sample.

Planktonic foraminifera (*G. sacculifer* and *G. ruber*) were sonicated in deionized water to remove the iron-aluminum coating and exterior clastic material contamination from the cohesive sediment in which they were deposited. Each specimen was then air dried and mounted on carbon tape. The laser spot size used was 50μm and had a repetition frequency of 3.5 J/cm^2. Three different standards (NIST-610, NIST-612, and GOR-132G) were ran twice (at the beginning and end) of analysis to calculate and correct machine drift. These standards and methodology were implemented following published methods in Evans et al., 2015.

To ensure that the exterior iron-aluminum coating and other elevated trace elements were not contaminating the signal, elemental values were recorded after the initial exterior (micrometers) of the foraminifera was ablated. In addition, forams with an elevated signal of aluminum (>100ppm aluminum) were discarded as evidence of contamination (Evans et al., 2015).

Specific climatic events were identified by splicing carbon dates (courtesy of Masako Yamane) from the U1477A core to get absolute dating with regards to the stratigraphy of the spliced core set. Antarctic ice core EPICA Dome C deuterium data was then used to confirm climate event identification and analysis by matching distinct oxygen isotope curves to convert depth (m) to age (kyr). In conjunction, these were used to locate and identify well dated HS events and observe their expression at the study location.

Chapter 3

Results

Here we present a high resolution benthic $\delta^{18}O$ record at depth. In this record, one can clearly observe global stadial transitions at depth recorded in differing marine isotope stage (MIS) progressions. Stadial events are sustained periods with cooler global temperatures, increased land glaciers and lower sea levels. Alternatively, interstadial events are sustained periods of warmer global temperatures, minimal land glaciers and higher sea levels. Stadial events are depicted by even numbered MIS stages (ex. 2,4 and 6) and interstadial events are odd numbered (1,3 and 5), with the current Holocene interstadial period defined as MIS 1.

The record can be interpreted as a measure of sea level in the last 100ky with lower $\delta^{18}O$ values related to higher sea level and warmer global temperatures and heavier or higher $\delta^{18}O$ values related to lower sea level and cooler global climates. At the top of the core, the modern day interglacial period MIS 1 spans from 0-5m depth, characterized by warmer global temperatures and higher sea level. As one moves down to $\sim$13m in depth, one can see the effect of HS1 with a drastic negative spike in $\delta^{18}O$ indicating warmer and sustained temperatures of about +3°C following the established relationship of 0.22°C/‰. From 15-20m depth, one can observe the transition to MIS 2, the LGM where sea level was $\sim$120m lower than present day (Stanford et al., 2011). As we move farther down the core we see the transition to MIS 3 from 30-50m depth with various negative $\delta^{18}O$ spikes related to specific paleoclimatic phenomena (HS events) in the Pleistocene. Around 60m is the MIS 4 transition. At ~68m and ~73m depth are negative $\delta^{18}O$ spikes related to prominent Dansgaard-Oschegger (DO) events 18 and 20 respectively. At ~80m is the transition to MIS 5a the end of the last prominent interglacial period.

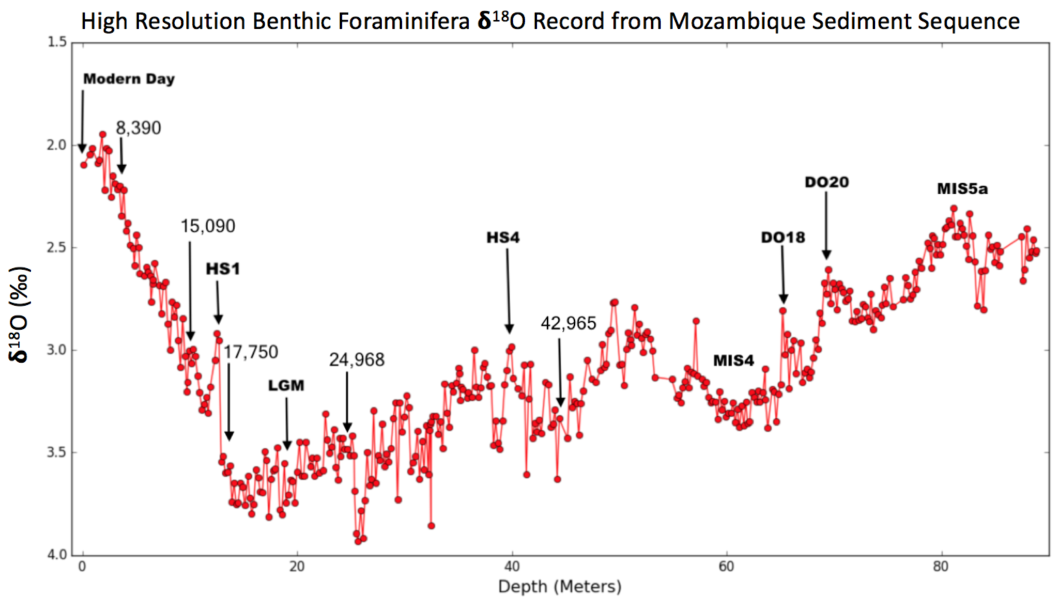

Figure 3.1: Paleoclimate event identification labeled in bold with carbon dates at depth courtesy of Masako Yamane. One can clearly see the transition from modern day to the Last Glacial Maximum with an abrupt warming event recorded in Heinrich Stadial 1. As one moves down the core, Heinrich Stadial 4 is denoted by the sustained rise to lower $\delta^{18}O$ values near 40m depth and constrained by the carbon date ~43m. Deeper in the core one can see transition from MIS 4 to MIS 5a.

3.1 Conversion of Depth to Age

To convert composite depth to age we must assign specific spikes and drops observed in the $\delta^{18}O$ record to similar observed peaks in the well dated high resolution EPICA Dome C Antarctic ice core record. By matching observed trends in the ice core data (deuterium ^2H) and that found in the benthic $\delta^{18}O$ record we can tie these curves together and convert depth to age. After 25 trend points were assigned, a linear fill between points was applied assuming a quasi-steady sedimentation rate between specific points. To further instill confidence in the conversion of depth to age, carbon-14 dates were added and spliced into the sequence.

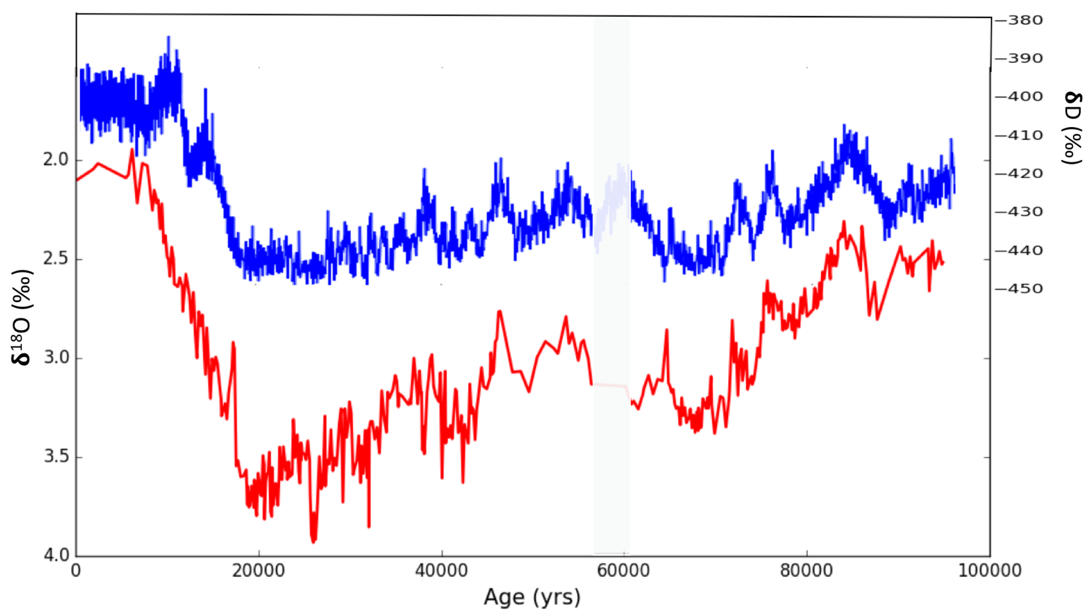

Figure 3.2: EPICA Dome C ice core deuterium data (blue line) plotted on top of benthic foraminifera record. Grey bar denotes slicing gap in sedimentary sequence. We know by lining up $\delta^{18}O$ measurements from the various cores that a sediment section on the order of 5m was not recovered. The $\delta^{18}O$ benthic record allows a high-resolution comparison to Antarctic ice cores through time. Comparing the records, one can see the effect of ice cap/ocean volumetric changes and their relationship and response with various meltwater pulses over the last 100ky. A paleo-ocean proxy of this stature helps deduce the land ice-ocean volume interplay and one can deduce changes in eustastic sea level in the Late Pliestocene.

HS events are northern hemispherically derived events and have an antiphase relationship with regards to the differing hemispheres in terms of temperature and the $\delta^{18}O$ response. These events have a cooling effect in the northern hemisphere and a warming effect in the southern hemisphere. Subsequently, the expression of HS events in this southern hemisphere benthic $\delta^{18}O$ record is characterized by a sharp decrease in $\delta^{18}O$ over the course of the event.

If one plots the $\delta^{18}O$ record at depth on top of the seismic section, one can see the interplay and response of HS events with respect to various reflectors that line up with specific HS and DO events. These events are characterized by southward shifts in the ITCZ with elevated and sustained discharge from the Zambezi. These reflectors are due to the response of changes in sediment density from increased riverine sediment output, suspension, and deposition onto the continental slope ∼120km from the river mouth.

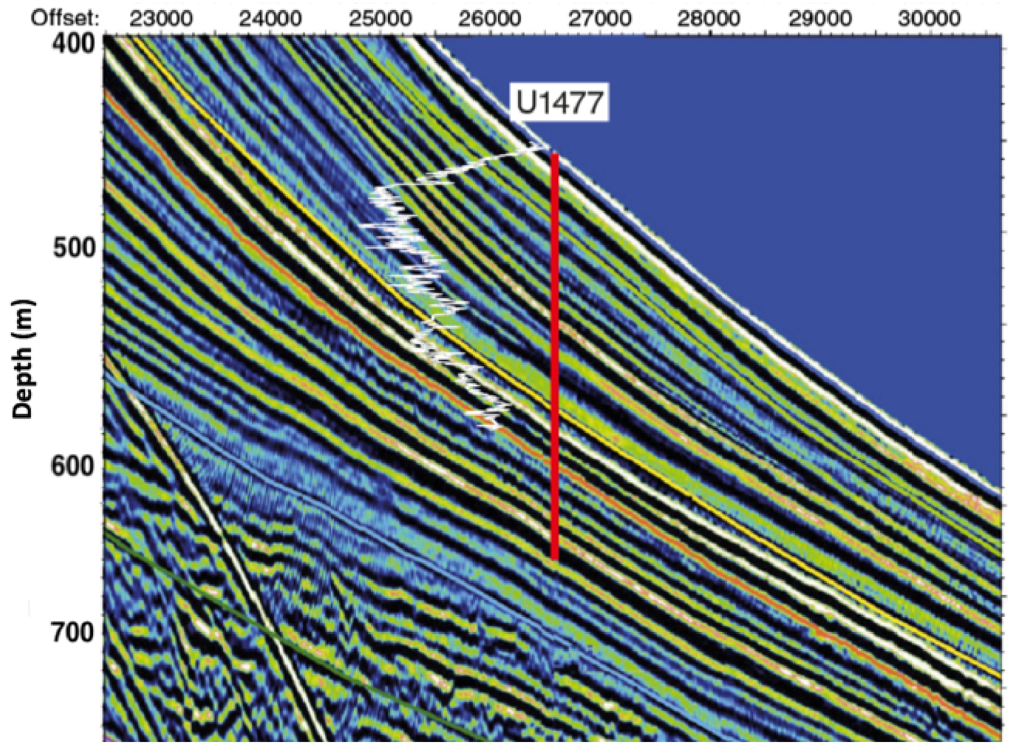

Figure 3.3: Plotted $\delta^{18}O$ record plotted on seismic section at depth. Elucidates sea level, sediment interplay. Reflectors are associated with changes in density due to elevated levels of terrigenous material being deposited on the continental slope. Large flood events on the Zambezi River Delta are characterized by fine grained clay rich deposits on the slope. One can observe six prominent reflectors during times with minimal sea level change. This can be attributed to large increases in discharge intensity accompanied by changes in sediment density.

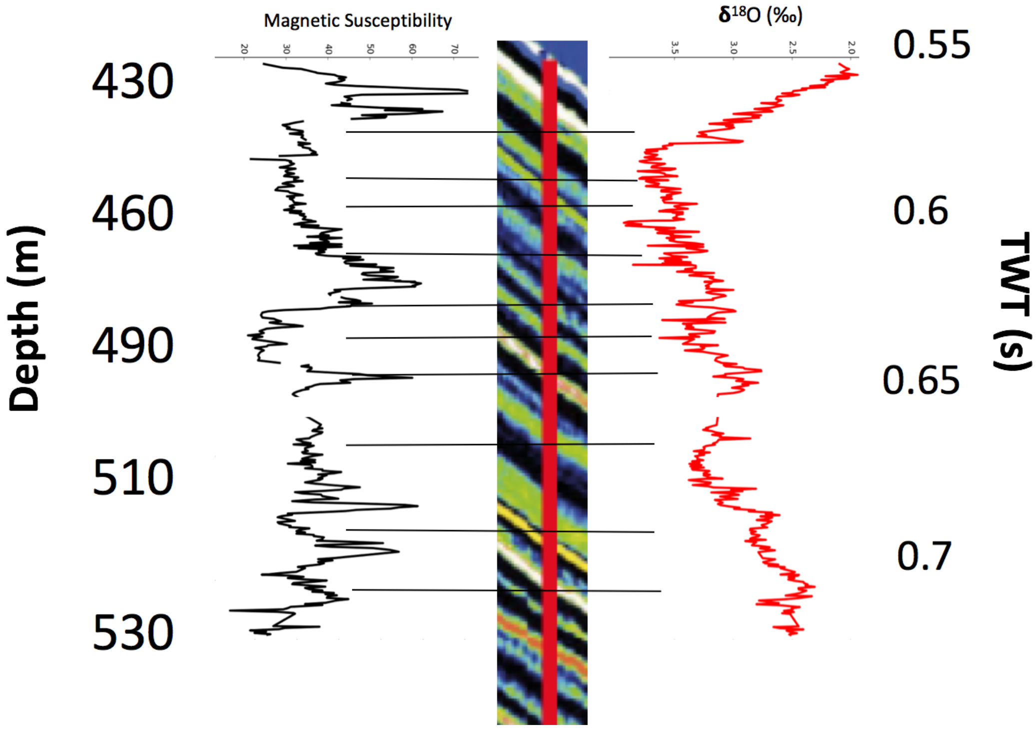

Figure 3.4: Plotted $\delta^{18}O$ record and magnetic susceptibility (MS) at depth on seismic section. Reflectors match up with paleoclimate events that are associated with elevated precipitation events and subsequent discharge/flood events from the Zambezi Delta. Reflectors are associated with changes in density due to elevated levels of terrigenous material being deposited on the continental slope. Note that many Heinrich events match up with prominent reflectors and DansgaardOeschger (D-O) events 18,19, and 20 are present as well, with the largest reflector being the MIS 4 to 5a transition. Note a potential correlation of higher sea level with higher MS.

3.2 Magnetic Susceptibility Variations at Depth

Magnetic susceptibility (MS) anomalies in a high deposition sedimentary sequence can be related to the interplay of sea level change and the tapping, resuspension and deposition of various sediment supplies with differing magnetic signatures. The magnetic susceptibility of specific sedimentary sequences are related by the concentrations of detrital-dominated paramagnetic and ferromagnetic mineral concentrations. The percentage of the mineral magnetite is the dominant signal with regards to changes in MS, which is dictated by terrigenous input via the Zambezi River. At the study site, there is an inner mud belt and an outer mud belt distributed toward and along the Mozambique shelf (Wiles et al., 2017). These two mud belts and the influx of riverine sediment comprise the downslope deposition at the coring location. Changes in the magnetic susceptibility of the sediment can potentially elucidate changes in sea level. If one plots the benthic $\delta^{18}O$ record against the MS at depth one can see a positive correlation. There appears to be a correlation with higher sea level stands and higher magnetic susceptibility as evident in the last deglaciation with peaks in MS during times of sea level rise. One would expect lower MS values with smaller grain size (De Jong et al., 2000). During proposed large discharge events associated with HS events one would expect increasing amounts of fine-clay dominated material deposited on the continental slope and consequently drops outs in MS during these events. If one looks at the most recent and prominent HS1 event, this relationship is evident (fig. 3.5).

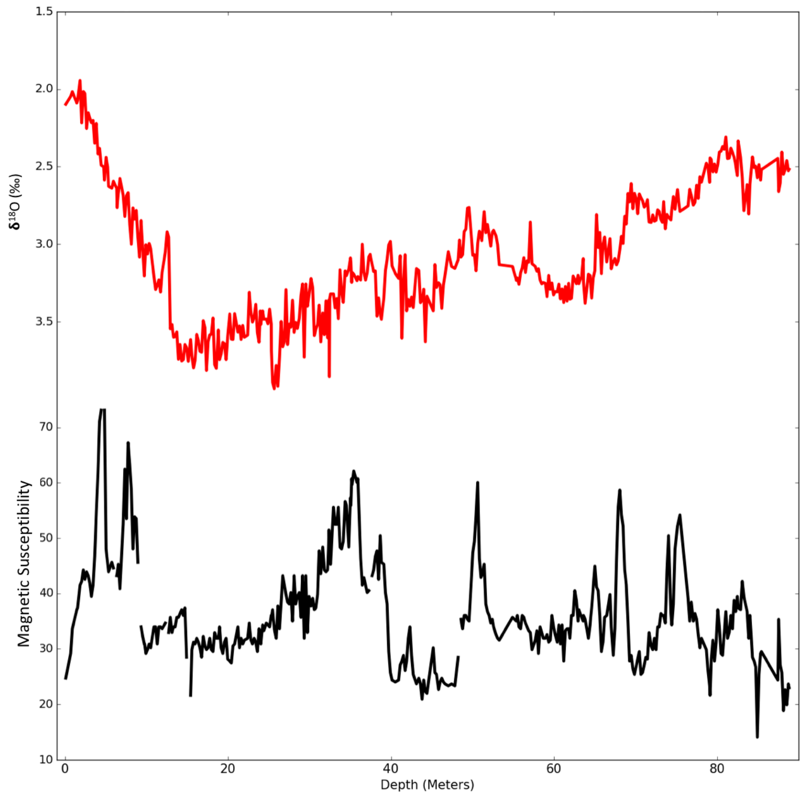

Figure 3.5: Magnetic susceptibility (MS) (black) plotted against $\delta^{18}O$ (red) of benthic foraminifera. This figure elucidates the sea-level sediment source and deposition interplay. The relationship of sea level change and large discharge events at the mouth of a major river system have an effect on the tapping, resuspension and deposition of various sediment supplies. We can tease out potential large discharge events by drop outs in MS by means of fine grained clay rich deposits on the continental slope. It is assumed that the percent of magnetite in clay-dominated sediments is low, or alternately the magnetic signature would be minimal due to decreases in grain size (De Jong et al., 2000).

3.3 Surface Ocean Signal

To get a proper sense of the climatic annual and interannual variability at the study location, Simple Ocean Data Assimilation (SODA) was used to recreate various data sets on sea surface temperature (SST) and sea surface salinity (SSS) in the last 140 years (Carton et al., 2002). These data can be combined to form a predicted $\delta^{18}O$ pseudoproxy using the paleotemperature equation for $\delta^{18}O$ and a $\delta^{18}O$sw-salinity slope of 0.3‰/1 psu. This method emphasizes the seasonality at the study location and will provide a baseline for expectation in the planktonic foraminifera as a bimodal distribution of $\delta^{18}O$ values by the winter to summer seasonal transition. If this bimodal behavior is observed in a specified sediment interval, then this instills confidence that we are truly sampling sea surface conditions throughout the entire year. Subsequently, statements about the interannual hydroclimate variability can be made with confidence by observing changes in the extremes (tails) of the histogram as extreme flood or drought events (ENSO teleconnections). Using the paleotemperature equation to convert the observed temperature and salinity in the Mozambique Channel to a predicted $\delta^{18}O$ of calcite, and then applying a Monte Carlo sampling technique to randomly sample 1000 months from the complete monthly SODA time series, we can get a representation of what the planktonic foram population should show, assuming that there were no seasonal biases in production.

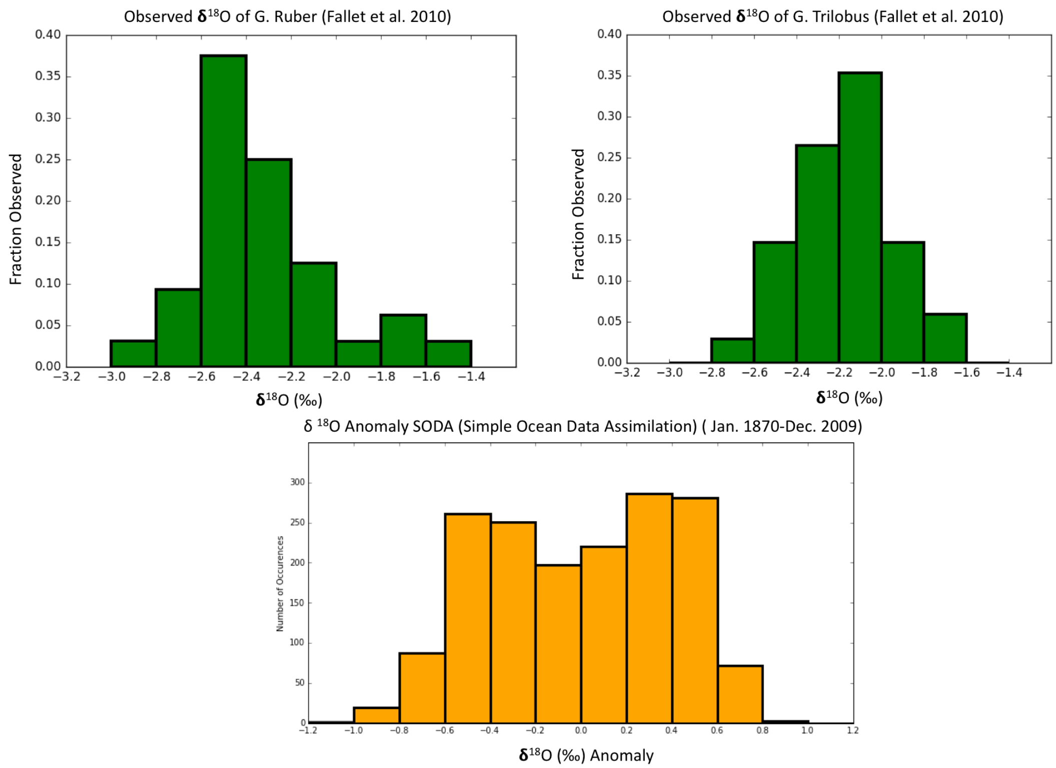

Figure 3.6: Normalized values of *G. trilobus* (left) and *G. ruber* (right) observed in sediment traps collected continuously in three week intervals in the Mozambique Channel from November 2003 to November 2005 published by Fallet et. al in 2010. One of the conclusions of the paper was a strong seasonality with respect to the two different species analyzed. SODA SST/SSS anomalies converted into estimated ^{18}O anomaly for the specified study location over a 140 year interval using 1000 randomly sampled data points and one point per month. This creates a baseline expectation of what we should see in the modern foraminiferal (proxy) observations. Note the bimodal behavior of all the histograms coinciding with seasonality of the Mozambique Channel. 1000 data points randomly sampled 1000 times, Monte Carlo approach (bottom). SODA anomaly data courtesy of Sara Sanchez.

3.4 Individual $\delta^{18}O$ measurements of planktonic foraminifera

Here, we present a series of individual $\delta^{18}O$ measurements of planktonic foraminifera *G. sacculifer* and *G. ruber* at targeted paleoclimate events. Both species calcify year-round with a stronger seasonality observed in *G. sacculifer* than *G. ruber*. The distribution of these values gives rise to sea surface conditions in sub-decadal resolution. First we present data from the core top, then LGM, and finally HS4.

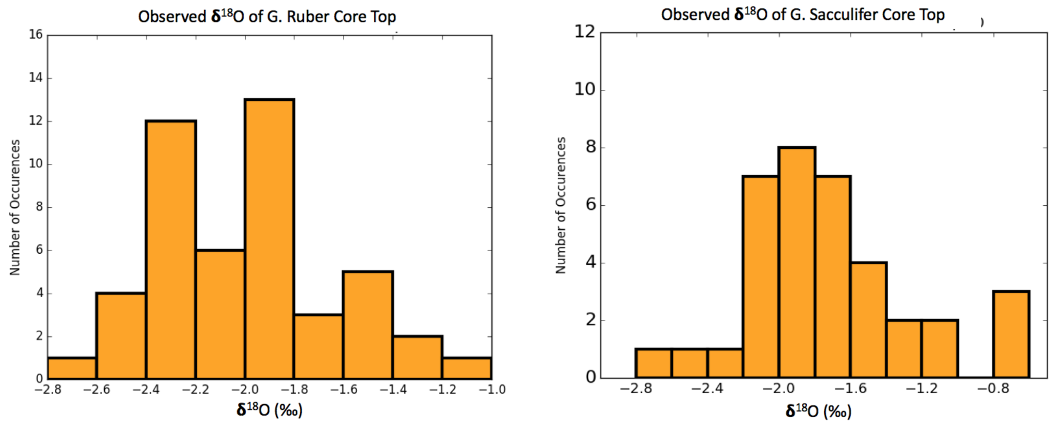

Figure 3.7: $\delta^{18}O$ measurements of (right) at the top of the core. The core top is the upper 4cm and is representative of 20th and 19th century sea surface conditions. One should note the bimodality of the *G. ruber* data which instills confidence we are indeed sampling year-round sea surface conditions. The histogram tails of both species indicate more arid conditions observed in the past century which is consistent with other published data (Gaughan and Waylen, 2012).

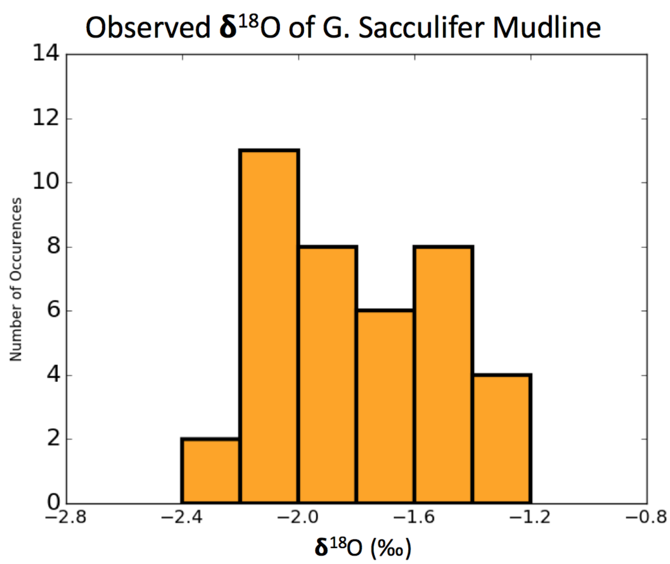

Figure 3.8: Oxygen isotopic variability from the mudline: upper most portion of core (representative of the last $\sim$50 yrs.), measured from individual specimens of the planktonic foraminifera *Globigerinoides sacculifer*, largely capture the features of annual and interannual variability observed in the instrumental data. Standard deviation: 0.3308. 39 samples analyzed. Range: 1.281

Here, we present planktonic foraminfiera $\delta^{18}O$ data from the LGM, the most recent glacial period which took place 20-24kya. During the LGM, sea level was 120m lower than present (Stanford et al.,2011) leading to a potential greater influence of freshwater (Zambezi discharge). The *G. ruber* data show a reduced seasonality and an increase in more negative $\delta^{18}O$ values indicating a potential increase in flood events during LGM or alternatively a more direct route of freshwater discharge from Zambezi during the LGM sea level low-stand. The *G. sacculifer* data show the similar seasonal trend observed in core top measurements. The negative behavior of the tails should be noted as they are consistent with *G. ruber* data showing elevated freshwater discharge events in the LGM consistent with flooding of the Mozambique Margin.

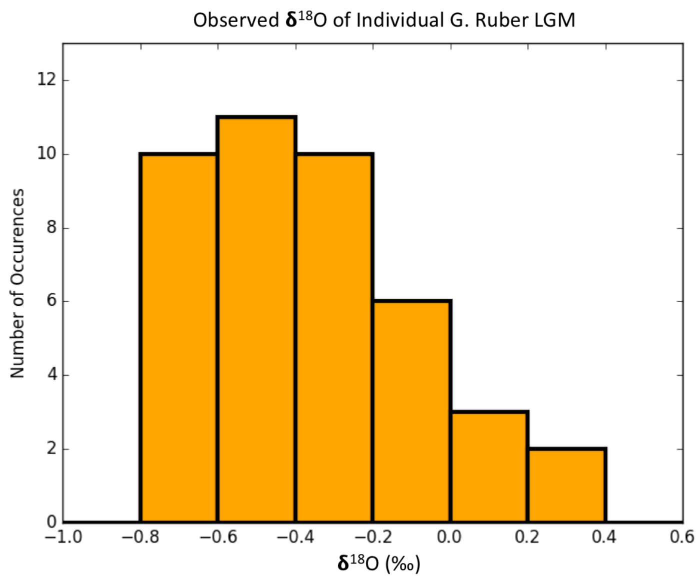

Figure 3.9: $\delta^{18}O$ measurements of individual planktonic foraminifera *G. ruber* during the LGM. 42 samples analyzed. Average $\delta^{18}O$: -0.35243

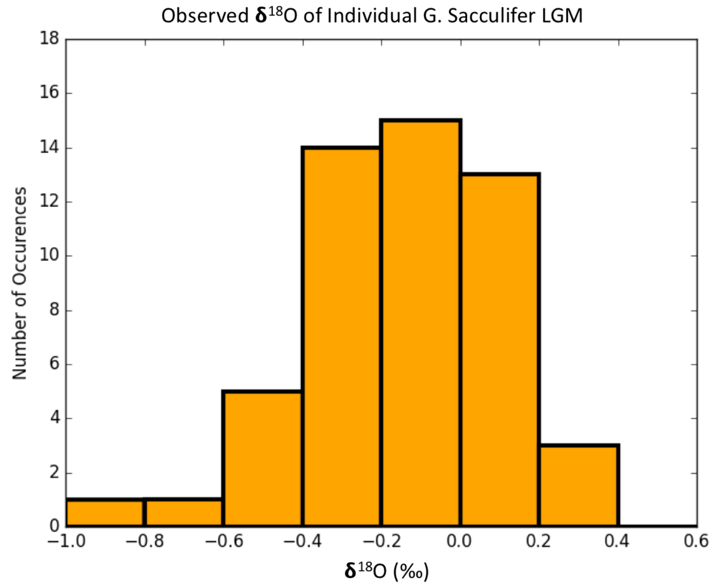

Figure 3.10: $\delta^{18}O$ measurements of individual planktonic foraminifera *G. sacculifer* during the LGM. 53 samples analyzed. Average $\delta^{18}O$ value: -0.14623.

Here we present planktonic foraminfiera $\delta^{18}O$ data from HS4. This specific HS event was targeted due to its strength and the fact that it took place during a period with minimal sea level change. In the *G. ruber* data one can see a negative shift in mean $\delta^{18}O$ values during HS4 indicative of warmer temperatures and increased freshwater discharge events. Note the bimodality present in both histograms instilling confidence in year-round sampling. During HS4 the sea surface conditions are more variable indicated by the wider range of $\delta^{18}O$ values.

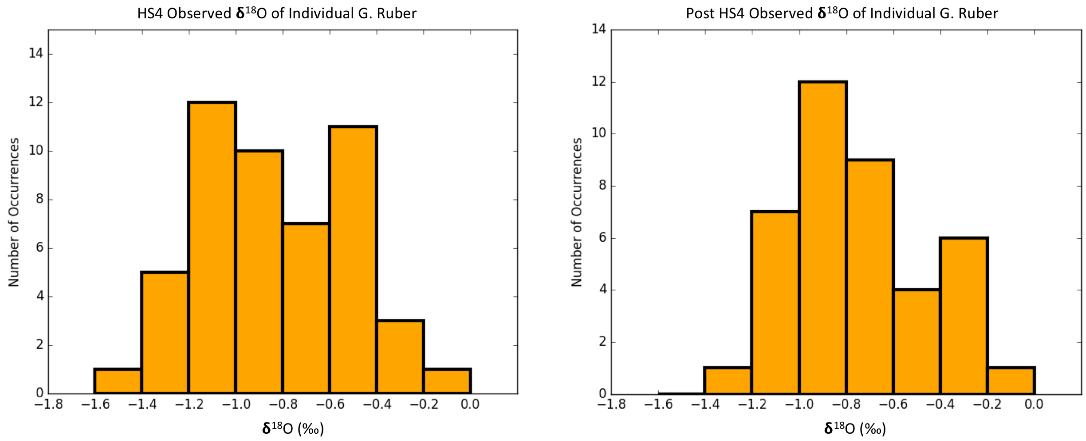

Figure 3.11: $\delta^{18}O$ measurements of individual planktonic foraminifera *G. ruber* during (left) and after (right) HS4. One can see a negative shift in mean $\delta^{18}O$ values during HS4 indicative of warmer temperatures and increased freshwater discharge events. During HS4 the sea surface conditions are more variable indicated by the wider range of $\delta^{18}O$ values.

3.5 Laser Ablation Induced Mass Coupled Plasma of Individual Planktonic Foraminifera

Ratios of 'X'/Ca were calculated where 'X' are large incompatible elements (Ba, U, La, Nd, Y, Sr, Mn). Large-ion lithophile elements (LILE) have been shown to be enriched in the continental crust due to their large ionic radius and low charge behavior. These specific elements were measured to elucidate changes in the surface seawater chemistry recorded in these planktonic foraminifera. One would expect to see an elevated signal in seawater with regards to these LILE elements (Ba, Sr, U) as well as other incompatible elements in large discharge events or periods of sustained flood intensity in the Mozambique Channel. These methods are ideal for the study site because the Zambezi River Basin drains 5 different sub-basins with differing geology (crystalline basement, extrusive igneous rocks, metamorphic facies, and extensive sedimentary packages) making it representative of a diverse continental crust with varying levels of large incompatible elements.

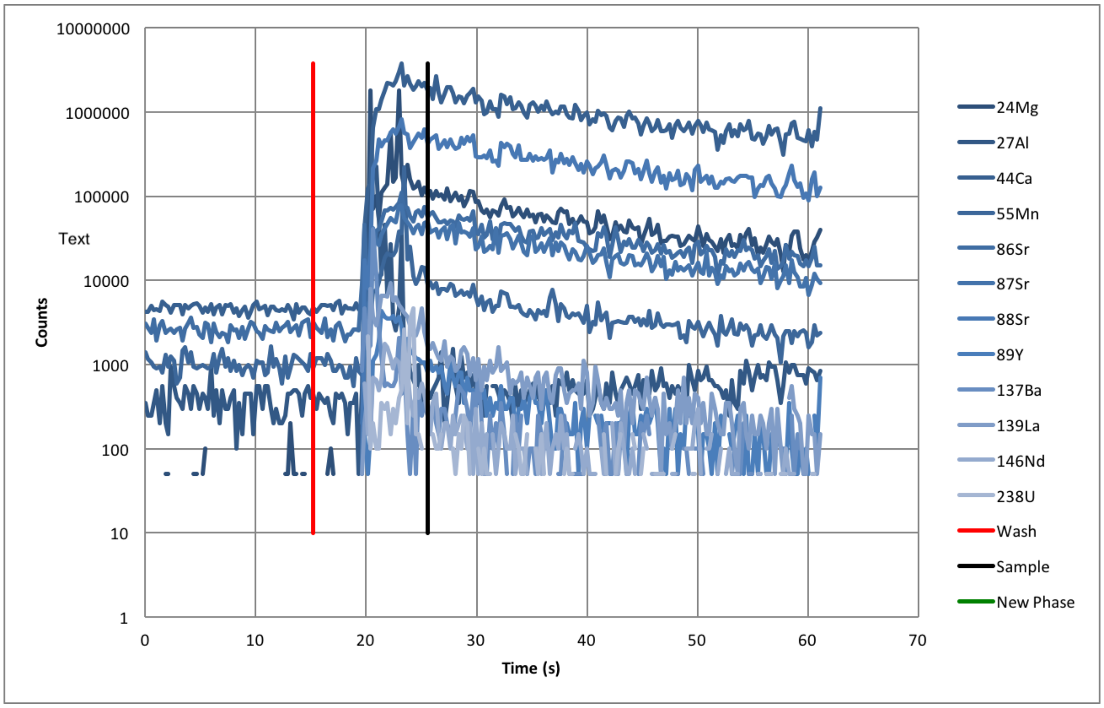

Figure 3.12: Typical output of laser ablation data counts (ppm) from *G. sacculifer* . Laser ablation of carbonate test begins at 20 seconds with increasing time (seconds) related to ablating deeper into the chamber wall. Note the small period fluctuations in elemental signal can be attributed to the diurnal calcification of foraminifera (day versus night) (Spero et al., 2015).

3.6 Barium Ratios in Planktonic Foraminifera recorded by LA-ICMPS

Here we present Ba/Ca data over specific climatic events. Barium is the most representative, predominantly elevated, and reliable signal for discharge events in foraminifera due to its similar ionic radius and charge to calcium. Foraminifera cannot easily distinguish Ba from Ca ions while creating their calcite ($CaCO_3$) test (Lea and Spero, 1992). In the barium data one can see a consolidated ratio and level in the modern foraminifera with a slightly elevated level during the the Last Glacial Maximum. As one transitions to the HS4 intervals, one can see much more variable Ba/Ca values which is attributed to more variable and intense discharge events over the course of this global climate event with the highest value of 7.5676 μmol/mol during HS4.

To tease out the effect of sea level change and its potential influence on barium concentrations in the Mozambique Channel, one can use the LGM as a proxy as sea level was the lowest during this time and volumetric mixing was likely the highest.

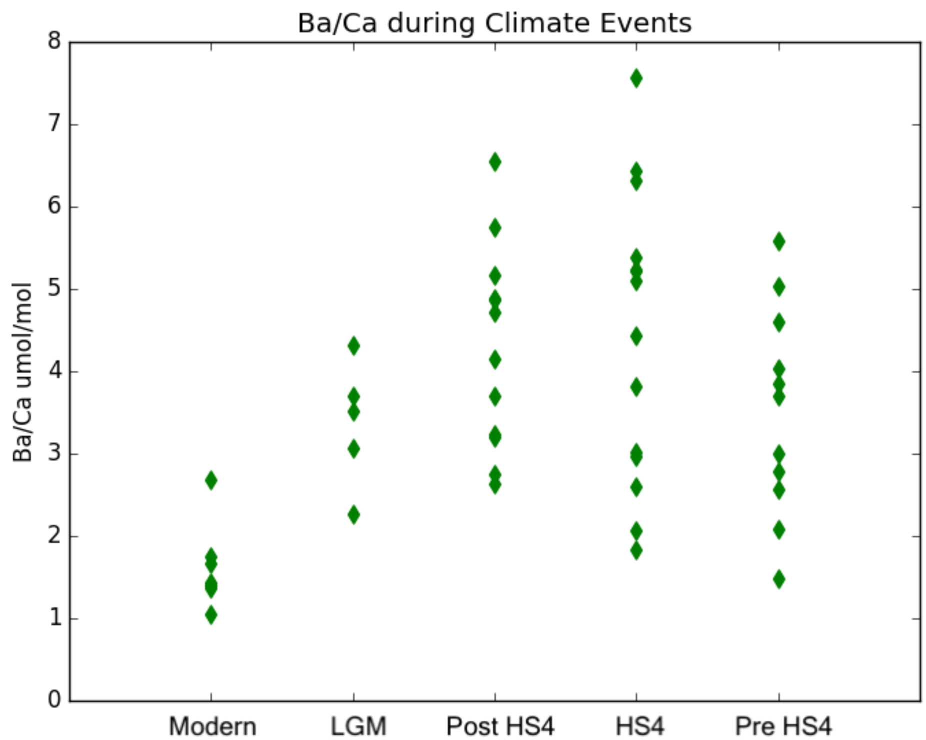

Figure 3.13: Plotted are ratios of Ba/Ca of individual planktonic foraminifera in micromol/mol over various climate events.

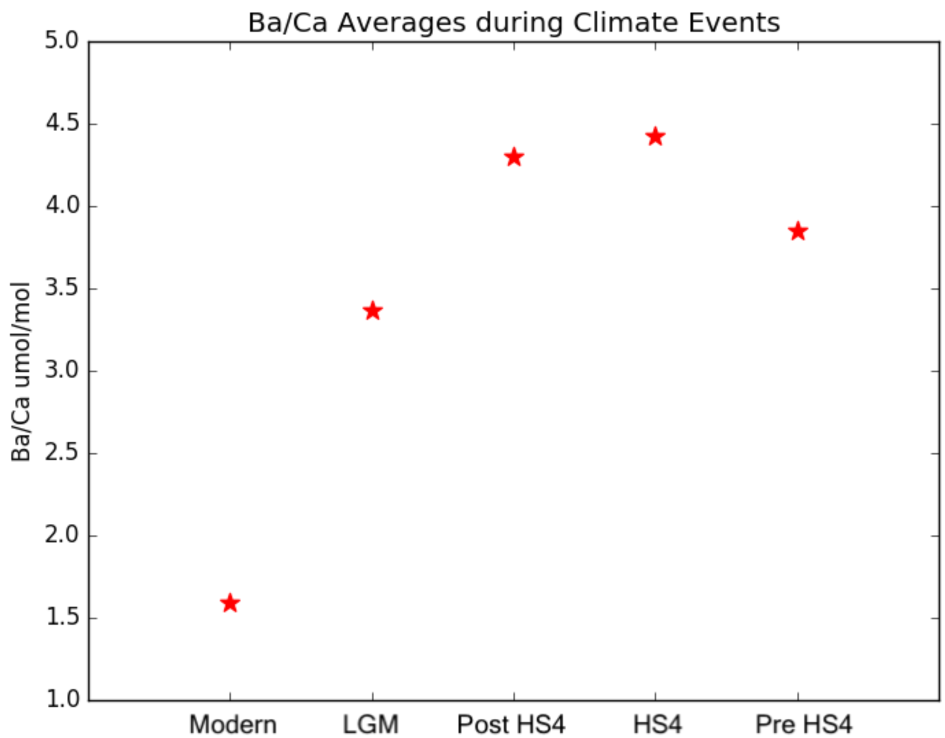

Figure 3.14: Plotted are averages of all values observed per climate event interval. This is useful as one can see the average values change from Pre Heinrich Stadial 4 (HS4) to HS4. There is also a clear transition from modern to the Last Glacial Maximum (LGM) to HS4 intervals indicating changes in seawater chemistry and elucidates changes in hydrology of S. Central Africa.

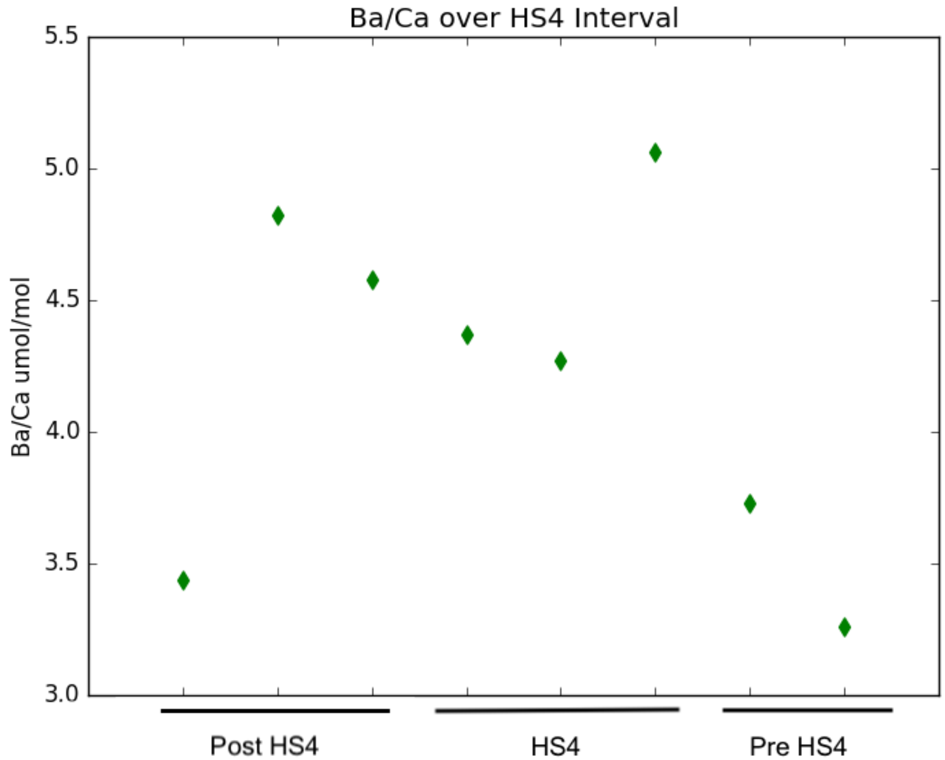

Figure 3.15: Averages ratios of Ba/Ca of planktonic foraminifera sampled at 2cm intervals spanning the duration of the Heinrich Stadial 4 (HS4). Results show a more variable seawater chemistry indicative of variable and extreme discharge events into the Mozambique Channel. Note an elevation of Ba/Ca values during and after HS4 with a return to similar ratios before and after HS4.

3.7 Magnesium Ratios in Planktonic Foraminifera recorded by LA-ICMPS

Here we present magnesium/calcium ratios of individual planktonic foraminifera at targeted climate events. Magnesium ratios in foraminifera have been shown to be temperature dependant, with higher Mg/Ca ratios relating to higher temperatures (Lea et al., 2000). Data show varying average sea surface temperatures all within range of observed modern temperature range in the Mozambique Channel. The average value of each climate event is ∼3.5mmol/mol indicating there is no evidence for systematic SST changes at the study site over the course of these events. This instills confidence in Mg/Ca data as a proxy for SST.

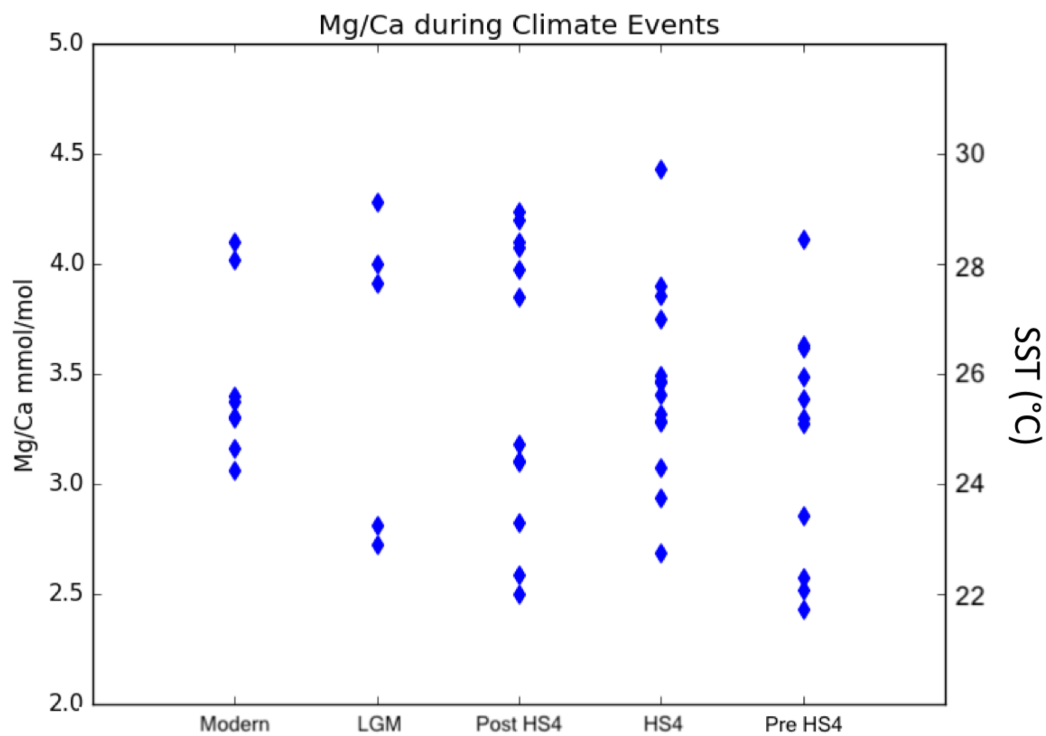

Figure 3.16: Plotted are ratios of Mg/Ca of individual planktonic foraminifera in mmol/mol over various climate events. One can see a bimodal cluster of data points in each climate event indicative of the seasonality in the Mozambique Channel. Estimation of SST from Mg/Ca ratios comes from (Sadekov et al., 2009)

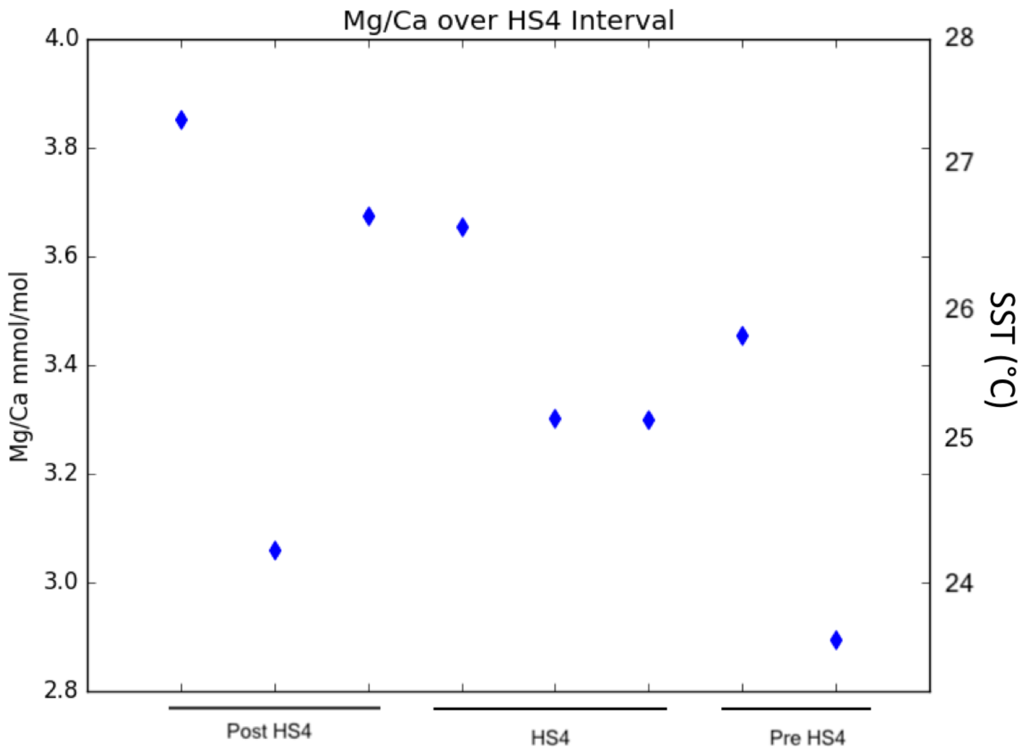

Figure 3.17: Average ratios of Mg/Ca of planktonic foraminifera sampled at 2cm intervals spanning the duration of the Heinrich Stadial 4.

Chapter 4

Discussion and Conclusion

4.1 Discussion

The bimodality of the histograms in the planktonic foraminifera (*G. ruber*) data indicate and instill confidence that we are sampling specimens that are calcifying year-round and any large deviation from these seasonal peaks can be attributed to extreme sea surface conditions. With regards to analysis of the histogram data, one must look at the behavior of the tails of the histogram to elucidate the hydroclimate variability extremes of the region. The tails emphasize deviations from the standard, with more negative oxygen isotope values (or left-skewing) relating to increased freshwater input (flooding events) and more positive values (or right-skewing) corresponding to increased drought events.

Using Mg/Ca ratios of planktonic foraminifera (fig. 3.16, 3.17) over specific climate events we observe no evidence for SST changes in the Mozambique Channel outside the present seasonal range. All Mg/Ca values retrieved by LA-ICMPS are within range of observed modern yearly range of ~24-29°C (fig. 1.3). This allows us to investigate $\delta^{18}O$ in planktonic foraminifera to deduce salinity changes (increased freshwater discharge from Zambezi flood events) in the Mozambique Channel by eliminating the possibility of temperature's effect on the oxygen isotope fractionation at the study site.

To tease out the effect of sea level change on barium ratios, we can look at the LGM, a time where sea level was near the lowest during the last 100ky and volumetric mixing of Zambezi River water was likely highest. During the LGM we observe an elevation of barium values compared to modern day (fig.3.14) and a positive correlation in the $\delta^{18}O$ of planktonic foraminifera with a higher influence of the Zambezi freshwater discharge (fig 3.9,3.10). Alternatively, during HS4, we see a return to the bimodal $\delta^{18}O$ planktonic foraminifera distribution (fig. 3.11) observed in modern day (fig. 3.7) but a significant elevation in average barium values from $\sim$1.5μmol/mol to $\sim$4.5μmol/mol.

4.1.1 Last Glacial Maximum

During the LGM there was a reduction in $\delta^{18}O$ variance in *G. ruber* at the study location with an emphasis in negative $\delta^{18}O$ values and a reduction in positive $\delta^{18}O$ values (fig. 3.9). This could be explained by a potential dampened seasonality accompanied by a reduction in SSS/SST variations during this ice age event. The change in distribution of surface water conditions could alternatively be explained by a stronger influence of the Zambezi discharge at the LGM sea level low-stand where sea level was 120m lower than present (Stanford et al., 2011). This could have allowed for a more direct route of Zambezi discharge flowing directly through a paleochannel into the location of coring or simply a greater influence of this freshwater input (fig. 1.2) into the Mozambique Channel. This freshwater will interact and incorporate $H_2{}^{16}O$ into the foraminifera changing the mass composition.

Comparing the *G. ruber* (fig. 3.9) and *G. sacculifer* (fig. 3.10) data we see a similar shift in the mean by $\sim$0.2‰which also observed in the core top (modern day) and attributed to seasonality recorded in the *G. sacculifer* . If one looks at the negative tails of *G. sacculifer* histogram they are consistent with other observations of increased freshwater discharge in the Mozambique via Zambezi flooding and discharge events. The *G. ruber*, *G. sacculifer* , and the

LA-ICMPS data all agree and show similar trends suggesting that the LGM was characterized by large freshwater discharge events.

Other studies (McGee et al., 2013) have indicated that during the LGM there was a southward shift in the ITCZ of 1-5° due to higher temperatures observed in the Southern Hemisphere. During the LGM there was dissimilar polar ice coverage by volume and spatial amount with respect to the two polar regions. There was increased ice coverage in the Northern Hemisphere and subsequently increased albedo, there was an increase in backscatter radiation and cooler temperatures in the north. This differential atmosphere-heat balance caused a potential shift in the ITCZ southward and subsequently caused increased precipitation and discharge events in of in the Southern Hemisphere recorded at the study location. This is supported by the LA-ICMPS measurements of the planktonic foraminifera as there is a consistently elevated signal of Ba/Ca ratios (fig. 3.13,3.14) with an average value of 3.3695 μmol/mol. Compare this signal to modern values of 1.5917 μmol/mol. Alternatively, this elevated signal could be attributed to the effect of lower sea level and the greater influence of the Zambezi River discharge into the Mozambique Channel and subsequently higher mixing rates. Otherwise, this could be the effect of the Zambezi flowing through an incised valley with a more direct route to our study site.

Heinrich Stadial 1

Heirich Stadial 1 was the most intense and recent event in the last 100ky. Due to this we have used it as a proxy for comparison to the observed and expected response of other HS events. As mentioned in Section 1.2.1, south of the coring location, wind-driven convergence and wintertime cooling of surface water in the northern subantarctic pumps water into the sub-thermocline depths. During HS events, this wind system shifted southward, and there was greater backlogging of oceanic heat in the Southern Hemisphere (Hessler et al., 2011). This change would alter the characteristics of the ocean water sinking from the surface in the northern subantarctic and consequentially the expression of these events in the benthic $\delta^{18}O$ record.During

HS events, there was a reduction or partial shutdown in AMOC resulting in elevated and sustained accumulation of heat in the southern oceans (Hessler et al., 2011). This led to a warming of these surface waters which can be observed in the benthic record as a negative excursion in $\delta^{18}O$ throughout the course of an HS event. It is assumed that once an HS event has concluded, the bottom waters characteristics will return to its normal state at the study location, where cold dense water will sink just south of the subtropical convergence zone.

During this event, there is evidence for major changes in AMOC 18kya (McGee et al., 2013). The spike in oxygen isotopes (fig. 3.1) can literally be interpreted as a $\sim$3°C rise in temperature or a change of sea level on an order of $\sim$60 meters. There is evidence for some steady sea level rise during HS1, so this could conceivably be a mix of sea level rise coupled with a drastic and sustained spike in southern hemisphere surface ocean temperature over the course of this event. As increased ice debris entered the North Atlantic, it likely altered deep ocean circulation pathways by the flood of fresh water into the North Atlantic which disrupted the typical behavior of the Gulf Stream (Hessler et al., 2011) where northward transported waters cool, condense and sink in the high latitudes. These ocean pathways have a dictating effect on the distribution of global thermodynamics as these pathways cool and regulate global temperatures. The increase in northward cross-equatorial heat transport during HS1 had a partial or total shutdown of the northward meridional overturning circulation during HS1 (McGee et al., 2013). During HS1, there is evidence of changes in precipitation patterns and climatic variations that are spatially heterogeneous (McGee et al., 2013). Shifting sea surface conditions coupled by the atmospheric-ocean heat transport pathways interpolated with changes in the ITCZ zone location subsequently create the generation of Hadley cells which causes changes in latitudinal precipitation/drought locations/events (McGee et al., 2013). This event had a variety of effects on global ocean and atmospheric temperature and caused abnormal hydroclimatological changes to varying locations throughout the globe which are ultimately dictated by changes in major ocean circulation pathways.

4.1.2 Heinrich Stadial 4

Prevailing evidence suggests that there was an increase in discharge events from the Zambezi River, flooding the Mozambique Margin and subsequently altering sea water chemistry in the channel. From this narrative, we would expect that the Mozambique hydroclimate experienced more variable and intense hydrological changes over the course of HS4. Over the course of this global climatic event, North Atlantic Deep Water (NADW) formation was disrupted and subsequently the Atlantic Meridional Overturning Circulation (AMOC) was dampened or potentially shut down (Goldstein et al., 2014). This led to an uneven distribution of thermodynamic energy and global temperatures with cooler temperatures in the northern hemisphere. This led to a southward shift of the ITCZ and this was accompanied by stronger evaporation south of the equator and subsequently elevated precipitation at higher southern latitudes due to shifts in latitudinal circulation cells. The planktonic foraminifera $\delta^{18}O$ values observe a negative shift in mean value from during and after HS4 (fig. 3.11). The $\delta^{18}O$ *G. ruber* data (fig. 3.11) show a much more variable SST/SSS conditions with a wider range of $\delta^{18}O$ values which could be attributed to more discharge events and more drastic shifts in SSS and SST over the course of HS4.

The LA-ICMPS data show more elevated and variable Ba/Ca values associated with more intense flood and discharge events during HS4 (fig. 3.13). If one looks at (fig. 3.15) where values were averaged at 20mm intervals (or 10-20 year periods) we can see an initial average value $<3.45\mu$mol/mol then, average values are elevated with varying intensity during and after HS4 ranging from 3.7 to 4.7μmol then concluding back to pre-HS4 values $<3.45\mu$mol/mol. If one looks at Ba/Ca ratios from individual planktonic foraminifera during HS4 the highest value is 7.5676 μmol/mol. Ba/Ca ratios in foraminifera are directly proportional to barium concentration in seawater (Lea and Spero, 1992). The large drainage area and diverse geologic environment that the Zambezi catchment covers is representative of LILE elements and one would expect to see elevated levels of these elements in the Mozambique Channel during large river discharge events.

4.1.3 Mudline vs. Core Top

The mudline-core top comparison documents the fact that histograms of individual $\delta^{18}O$ are capable of resolving decadal-century shifts, since we know from modern measurements of SST that there was an approximately 1°C warming of the region across the 20th century. Measurements from the mudline (fig. 3.8), the uppermost portion of the core, are representative of the last ~50-75 years shows a shift in mean $\delta^{18}O$ value in *G. sacculifer* by +0.2‰from the core top (fig. 3.7) which is the top 4cm which is representative of ~100-150 years. This shift is consistent with observed 1°C warming observed in global oceans in the last century. Mudline average *G. sacculifer* $\delta^{18}O$ value is -1.7595‰whereas the average *G. sacculifer* $\delta^{18}O$ value for the core top is -1.682‰. The average value of $\delta^{18}O$ in *G. sacculifer* recorded by sediment traps in the Mozambique Channel from 2003-2006 is -2.1764‰(Fallet et al., 2014). This shift of 0.181‰from mudline to the 21st century shows a 0.9°C shift in temperature in the past century. This warming is consistent with that observed in multiple ocean atlas measurements that compile measurements taken since the start of the industrial revolution.

This shift in mean $\delta^{18}O$ value of -0.4169 from mudline to modern sampling in Mozambique translates to a shift of mean surface temperature in the Mozambique Channel by 1.9°C in the late Holocene. It should be noted that this change in surface temperature could be exacerbated by the Pacific Decadal Oscillation (PDO) during foraminifera/sediment trap sampling in 2003-05. This sampling period fell during the El Niño or warm phase of the ENSO system.

4.2 Conclusion

Over the course of global paleoclimate events, one can see a response in ocean conditions from surface to bottom waters recorded in planktonic and benthic foraminifera recovered from an ultra-high deposition marine sedimentary sequence. During HS4, there were elevated Ba/Ca ratios in sea surface residing foraminifera associated with an increase in discharge intensity from the Zambezi consistent with theoretical arguments of a southward shifting ITCZ. This data was complemented with planktonic $\delta^{18}O$ measurements that displayed a negative shift in mean value and a wider range of values indicating increased freshwater discharge and more variable sea surface conditions during HS4. The agreement among the data sets leads to the conclusion that during HS4 there was more intense precipitation and subsequent flood events into the Mozambique Channel. We can attribute these changes by a southward shift in the ITCZ in response to the high latitude northern hemispheric disruptions via elevated iceberg discharge into the North Atlantic and subsequent changes in AMOC affecting global ocean circulation and climate. During the LGM, when sea level was 120m lower, the influence of the Zambezi in the Mozambique Channel was much more prevalent, with large negative $\delta^{18}O$ shifts in planktonic forams and elevated barium levels compared to modern day. This could be attributed to increased discharge due to changing precipitation bands over the course of the LGM. Alternatively, there was a smaller volume of seawater in the Mozambique Channel during the LGM, which subsequently led to higher mixing and dilution rates and changes in seawater chemistry from Zambezi discharge.

The $\delta^{18}O$ benthic record contributes a high-resolution comparison to Antarctic ice cores and the effect of ice cap/ocean volumetric changes and their relationship and response with various land glacier and ice cap growth and melt events over the last 100ky. A paleo-ocean proxy of this stature can assist in deducing the land ice-ocean volume interplay and the effect of evolving atmospheric conditions as a driver for changes in global surface temperature conditions and sea level. Unlike the ice core data, the benthic $\delta^{18}O$ record documents Southern Hemisphere ocean conditions in high resolution and the response to Northern Hemisphere derived climate events. The antiphase relationship observed from Northern to Southern Hemisphere $\delta^{18}O$ signals over the course of these events draws on the relationship of global ocean circulation changes and contrary ocean responses across the equator.

The work in this thesis is currently being prepared for submission for publication of the material.

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