## Reconstructing sea surface temperatures in the Caribbean during the early-mid Holocene from a reef exposure in Cañada Honda, Enriquillo Valley, Dominican Republic

by:

Jose A. Morales Collazo

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Félix R. Román Velázquez, Ph.D. Member of the Graduate Committee

Amos Winter, Ph.D. Member of the Graduate Committee

Hernán Santos Mercado, Ph.D. Member of the Graduate Committee

Wilson R. Ramírez Martínez, Ph.D. President of the Graduate Committee

Julio M. Morell Rodríguez, M.S. Representative of Graduate Studies

Lizzette A. Rodríguez Iglesias, Ph.D. Chairperson of the Department of Geology Date

Date

Date

Date

Date

Date

### Abstract

Temperatures during the Holocene are driven by seasonal changes in insolation; however, a better understanding of insolation mechanisms and how it affects tropical climate is still necessary. This study presents annual growth rates seasonally resolved oxygen and carbon isotopic and Sr/Ca trace elemental variations from five fossils Montastraea sp. corals from Cañada Honda Enriquillo Valley, Dominican Republic. U/Th dates obtained from fossil corals in M1 facies indicate earlymid Holocene dates ranging from 8.0-8.9 ka B.P. The aragonite skeleton composition was confirmed by X-ray diffraction. Growth rates in Montastraea sp. corals, with a record of 30-80 years, collected at this site, range from  $2.07 \pm 0.14$  to  $3.55 \pm 0.37$  mm/yr (n=5). High sedimentation rates in the reef were estimated to range from  $1.53 \pm 0.18$  to  $2.48 \pm 0.45$  mm/yr (n=8).  $\delta^{18}$ O measurements range from -0.69 to -2.41 (n=430) values that are heavier relative to modern corals from the tropics by ~2‰. Sr/Ca measurements range from 9.07 to 9.70 mmol/mol (n=430), values higher than modern corals from the tropics. Both proxies suggest colder environments during this time period. Calculated SST for each variable suggest temperature variations of 6°-7°C values never reported by any proxy from the Early Holocene, but may be explained by periods of freshwater influx. A low correlation index (R) estimated (0.26-0.85) suggests that both paleothermomethers are reacting to different variables.

## Resúmen

Las temperaturas durante el Holocene son impulsadas por cambios estacionales en insolación, sin embargo, un mejor entendimiento de los mecanismos de insolación y como estos afectan el clima en los trópicos es aun necesario. Este estudio presenta tasas de crecimientos anual resuelto estacionalmente por variaciones isotópicas de oxígeno y carbono, y elementos traza Sr/Ca en cinco corales fósiles de la especie Montastraea sp. en Cañada Honda, Valle Enriquillo, Republica Dominicana. Dataciones de U/Th obtenidas de corales fósiles en facies M-1 indican edades del Holoceno temprano-tardío que oscilan entre 8.0-8.9 kya A.P. La composición del esqueleto aragonítico fueron confirmados en un análisis de XRD. La tasa de crecimiento en corales Monstrastraea sp., en un récord de 30-80 años, colectados en esta zona, varían entre  $2.07 \pm 0.14$ to  $3.55 \pm 0.37$  mm/yr (n=5). Las altas tasas de sedimentación en el arrecife fueron estimadas y varian entre  $1.53 \pm 0.18$  to  $2.48 \pm 0.45$  mm/yr (n=8). Medidas de  $\delta^{18}$ O varian entre -0.69 to -2.41 (n=430), valores pesados relativo a corales modernos en el trópico por ~2‰. Medidas de Sr/Ca varían entre 9.07 to 9.62 mmol/mol (n=430), valores más altos, que corales modernos en el trópico. Las TSM calculadas para cada variable sugieren variaciones en temperatura de 6°-7°C. Valores como estos no han sido reportados por ningún proxy durante el Holoceno temprano. El bajo índice de correlación (R) estimado (0.02-0.85) sugiere que ambos paleotermometros estan reaccionando a diferentes variables.

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## 1. Introduction

During the last few decades several initiatives have raised awareness of drastic changes in climate suggesting that anthropogenic forcing was superimposed on climate variability at centennial scales (Saenger et al., 2008). Since 1980's anthropogenic impact has been reported to become more severe with time (Hughes, 1994). The role of human activity on climate variability is barely understood and is one of the most important questions facing scientists today (Pandolfi, 2002).

A direct and reasonable way to obtain adequate information to answer this question is to study seasonal records of temperature using fossil corals as proxies. Fossil corals are means to study past climate (Grottoli, 2001) at seasonal resolution, however, studies using corals as a proxy for paleoclimate reconstruction and climate variability in the Caribbean region have shown significant discrepancies (Saenger et al., 2008). One of the problems is that fossil coral skeletons are commonly altered early in their diagenetic history by recrystallization, micritization and neomorphism among others processes. These processes alter the original character, texture, and geochemistry of the corals and can produce chronological errors in radiocarbon and U/Th dating and isotopic and trace elemental changes in the coral skeletons (Sayani et al., 2011; Saenger et al., 2008). Due to the unstable nature of the aragonite mineral, it is quite difficult to find adequate fossil corals that provide accurate geochemical information during the early-mid Holocene. The Holocene fossil corals present at the gully called Cañada Honda in the Enriquillo Valley, Dominican Republic, have been very well preserved retaining their geochemical nature and provide a unique opportunity to study paleoclimate as well as coral reef changes since the early Holocene (Cuevas et al. 2005; Greer and Swart, 2006).

#### 1.1 Objective statement

Banded corals can serve as a paleoclimatic archives to reconstruct past climate in the preindustrial periods (Felis and Pätzold, 2004). The geochemical composition of the coral skeleton can be used as proxy record for climate variations, because within the chronology of the coral growth, information about the environment when they were calcified in is stored (Greer and Swart, 2006).  $\delta^{18}$ O isotopic values and trace element ratios (Sr/Ca) can reflect specific marine environment characteristics of the coral as it precipitated its skeleton (Felis and Pätzold, 2004; Greer and Swart, 2006).

This study attempts to reconstruct sea surface temperature (SST) variations using Sr/Ca ratios and  $\delta^{18}$ O isotopic values from coral skeletons. The SST records obtained from the coral skeletons were used to assess climate change and explore seasonality during the early Holocene. A decadal to multi-decadal SST record (approximately from 8.0-8.4ka B.P.) from corals present at a reef exposure in Enriquillo, Dominican Republic is reported here.

The length of the records obtained are in the same timeframe as climate cycles such as El Niño Southern Oscillation (ENSO) or North Atlantic Oscillation (NAO) (Giannini et al., 2001a; Greer et al., 2006), and solar sunspot cycles that have been found to have constant 11-year cyclicity (Haigh, 2011). The results obtained will provide information to develop climate interpretations of natural climate variability during the early Holocene in the northern Caribbean and the interaction between natural vs. anthropogenic factors producing climate change.

#### 1.2 Background

#### *1.2.1 The Holocene climate*

The Holocene epoch (11,700yr – present) (Walker et al., 2009) is an interglacial period that has experienced substantial changes in climate variability. A study by Wanner et al. (2008) used selected proxy reconstructions of different climate variables from models such as General Circulation Models (GCMs) and Earth Models of Intermediate Complexity (EMIC) to study global climate change since the Mid-Holocene. Other studies looked at the microfauna, pollen and vegetation distribution during this epoch. These studies provide evidence of the impact of orbital variations in climate and explored events of rapid climate change (Mayewski et al., 2004; Wanner et al. 2008). These studies have shown millennial-scale climate variations of polar cooling, tropical acidity and major atmospheric oscillations and have attributed them to super-imposed changes in insolation and solar variability (Mayewski et al., 2004; Greer and Swart, 2006).

The early Holocene, defined as 11,700-8.200yr (Walker et al., 2012) is a stage of continued deglaciation in the Northern Hemisphere as a consequence of the lagged response of the ice sheet and insolation forcing before the Holocene (Mayewski et al., 2004). From the Pleistocene, the early Holocene resulted in a global change from dry and cool to warmer and more humid climate conditions that still persists (Greer and Swart, 2006). Climate during the early Holocene is characterized by an amplification of 30Wm<sup>-2</sup> in insolation during boreal summer in phase with precessional insolation leading to warmer summers and colder winters (Luan et al., 2012). Concentrations of CO<sub>2</sub> have increased from 270ppm at 11ka (Indermuhle et al, 1999) to over 400ppm today (Tans and Keeling, 2015) and it is still debatable what is causing this major increase (Ruddiman et al., 2011). A predominant anomaly has been identified during the early Holocene at the interval of 9-8ka before present called the Glacial Aftermath by Mayewski et al. (2004). It was a unique event that occurred in the Northern Hemisphere when large ice sheets form the Pleistocene was still present. There is evidence at this time of a cool Northern Hemisphere in which a lot of ice rafting and stronger atmospheric circulation took place (Mayewski et al., 2004).

#### 1.2.2 The 8.2kya event

Within the early Holocene, there is a brief abrupt near-global cooling event ~8.2ka named the "8.2ka event" in which climate became much dryer and windy, for about 150 years (Kobashi et al., 2007; Wiersma, 2008) than the Glacial Aftermath itself. The exact timing of this event remains ambiguous, but precise characterization of methane and nitrogen isotopes from air bubbles trapped in Greenland ice cores suggests the event started approximately at  $8175 \pm 30$  years ago with temperatures that dropped by  $3.3-7.4^{\circ}$  (Kobashi et al., 2007). The most accepted hypothesis for this phenomenon establishes that this event took place due to the massive flow of freshwater running from proglacial lakes Agassiz and Ojibway due to the ongoing deglaciation (Kobashi et al., 2007; Wiersma, 2008; Morril et al., 2013). Consequently, the Atlantic Meridional Overturning Circulation (AMOC) slowed drastically due to a decrease in the sea surface salinity enabling a dryer and cooler near-global environment as shown by anomalies in proxies such as ice cores and speleothems (Morril et al., 2013). Other hypothesis suggest that this happened as a consequence of a repeating pattern of long-term anomalies as manifestation of solar output influences due to atmospheric circulation (Rohling and Pälike, 2005) or that a solar minimum triggered the cooling (Kobashi et al., 2007).

The 8.2ka event has been characterized in-near the Caribbean region using speleothems (Lachniet et al., 2004; Cheng et al., 2009; Winter et al., 2013) and sediment stratigraphy (Sallun et al., 2012). Cheng et al. (2009) and Sallun et al. (2012) determined that the South American Monsoon intensified during this time period and that it correlates to climate variations of North Atlantic climate events. Winter et al. (2013) interpreted that this event was associated with increased precipitation in the Eastern Caribbean and that stalagmite growth rates were much faster than any other growth period except for modern. So far, records in the Caribbean that address this event using proxies in the marine setting are scarce. Some of the reasons are the lack of time resolution from proxies such as foraminifera, or the poor preservation of skeletal organisms such as scleractinean corals in the geologic record. The coral samples used for this project have been dated to be 8.0 to 8.9 ka B.P. and are pristinely preserved. These corals existed during this interval providing the opportunity to study the 8.2kya event anomalies.

#### 1.2.3 Climate change and the Caribbean.

As means to study the past to predict the future, scientists have developed procedures to study past climate using proxies. Paleoclimate is the study of climate through time across Earth's history by looking at changes in weather conditions known as climate change (Dinse, 2009). The idea of climate change in the past was brought up when evidence of glacial deposits was found in places were no a glacier are present today (Riebeek, 2005). These findings motivated the study of ice cores, speleothems, scleractinian corals and other proxies providing valuable information of climate variability (Felis and Pätzold, 2004; Riebeek, 2005). Climate reconstruction methods can be done by measuring the concentration of oxygen isotopes archived in these proxies. Other means of understanding climate change, is to document changes in sea surface temperatures (SST) through time using trace elemental concentrations such as Sr/Ca and Mg/Ca present in calcareous marine organisms (Swart et al., 2002; Rosenthal and Linsley., 2006).

El Niño Southern Oscillation (ENSO) and the North Atlantic Oscillation (NAO) are the major components of climate variability such as SST at an interannual timescale (Giannini et al., 2001a). SST is partially responsible of both precipitation and temperature changes that have a major impact in ecosystem dynamics and therefore human development (Giannini et al., 2001a; Cobb et al., 2013. Coral records from Bonaire indicate that southern Caribbean Sea was dominated by cooler conditions during the Holocene compared to today (Giry et al., 2012).

ENSO is a phenomenon that occurs in the equatorial Pacific (Donders, 2005). El Niño, or the oceanic component, is seen as the irregular warming in SST while Southern Oscillation, or the atmospheric component, is the variation in surface air pressure from Central Pacific to the South American coasts (Donders, 2005; Birgmark, 2014). It is known that the effects of this climate variability extends globally via the atmospheric bridge including the Caribbean (Alexander et al., 2002), but its strength is yet to be understood. Sediments record from a lake in Equador showed that ENSO frequencies were larger (~15 years) during the early Holocene, suggesting a weaker ENSO during this time period (Rodbell et al., 1999). In addition, NAO is known to be a major climate variability pattern in the North Atlantic. It is widely affected by the strength of the Icelandic Low and the Azores High pressure systems during winter climate variability (Charlery et al., 2006, Birgmark, 2014). NAO has positive and negative oscillation depending on the atmospheric pressure generated. When the pressure gradient between the Azores and Iceland is lower than normal then it is a negative phase and positive when they are higher. These variations will have

different climatic effects in the mid and high-latitutes by controlling the strength of the subpolar winds from the west (Felis et al., 2004). The relationship between NAO and SST has been studied and it influences with amount of ice in the Polar Regions (Birgmark, 2014).

Several studies have looked over the effects of ENSO and NAO in the Caribbean and have found that their combined forcing is one of the factors responsible for climate variability in the region. After a winter season of positive NAO, sea level pressure (SLP) is responsible for dry weather in the subtropical regions and is augments the dryness associated with a warm ENSO during the summer. Otherwise, after a winter season of negative NAO, a wet climate following a warm ENSO increases due to the wetness associated with the warmer SST in the tropical North Atlantic during spring (Giannini et al., 2001a). ENSO also seems to be a primary driver in the development of hurricane activity in the Caribbean because it alters the vertical wind shear (Klotzbach, 2011). Overall, ENSO effects in the Caribbean are augmented by the NAO, which is negatively correlated to the amount of rainfall in the region (Birgmark, 2014) and it has been found to have increased with time (Giannini et al., 2001b; Giry et al., 2012). Foraminiferal and phytoplankton Mg/Ca SST reconstructions in the Caribbean during the Holocene, suggests that warming of the western Atlantic and Caribbean region is due to a trend in the NAO mean state from a positive phase in the early Holocene towards a negative phase in the late Holocene due to insolation (Giry et al., 2012). Both ENSO and NAO seem to have an impact in the strength of the trade winds in the Caribbean which influences the SST because of cooling due to evaporation. However, the strength of these two patterns is hard to assess as they are affected by locally driven phenomena such as upwelling and advection and also the seasonal changes (Birgmark, 2014).

During the last few decades, air climate in the Caribbean has become warmer at an average rate of  $0.27^{\circ}$ C/decade (Chollett et al., 2012) with temperature seasonality of  $2.8 \pm 0.2^{\circ}$ C within periods of 3-6 years (Giry et al., 2012). This warming rate is drastic compared to the preindustrial period as it took approximately 2000 years to raise the temperature  $0.6^{\circ}$ C during the early Holocene (Marcott et al., 2013). Seasonality has decreased since the mid-late Holocene and periodicity is associated with ENSO-NAO cycles at present. It has been predicted that by 2100, temperatures will exceed the Holocene temperature mean by 3°C of global warming similar to the rise in temperature since the last ice age (Hagelaars, 2013).

#### 1.2.4 Corals as proxies

The geochemical composition of coral skeletons is one of the most accurate ways to recover past records of timescale variations in tropical climate because the environmental information in which these organism grew is stored within their skeleton chronologically. (Grottoli, 2001; Greer and Swart, 2006). Corals are aimals from the phylum *Cnidaria* that are mostly allocated roughly at 23-24° latitude where mean annual temperatures are not under 24°C or 18°C during the winter minimum and salinities range from 32-40 PSU (Felis and Pätzold, 2004). It is known, that ocean circulation can transport tropical warm waters that lead to coral colonies at higher latitutes (Felis and Pätzold, 2004). Scleractinean corals live in colonies most commonly in surface waters (can live down to 4km deep) with skeletal growth rates usually ranging from 5-25mm/yr (Grottoli, 2001; Felis and Pätzold, 2004). Basically, their body consists of a polyp overlaying a skeleton built of aragonite (CaCO<sub>3</sub>) that lives in symbiosis with a unicellular photosynthetic phytoplankton known as zooxantellae.

Typically, scleractinian corals deposit a high density (HD) band and a low density (LD) band within the interval of one year. Understanding the causes of short- and long-term changes of coral populations in reefs provide valuable climate information and scleractinian corals growth bands are high-resolution archives of past climates and coral reef environments (Felis and Patzold, 2004; Brachert et al., 2006). In an optimal temperature environment, corals precipitate skeleton at a faster rate, while the opposite occurs in sub-optimal temperature conditions (Grottoli, 2001). Density bands can be measured by luminance and by coupling a LD and a HD band, a sclerochronology can be estimated. Climate information can be obtained by analyzing trace elements and isotope geochemistry which can be related to time.

Mid-late Holocene centennial paleoclimate records with sub-annual resolution have been obtained from single coral skeletons using geochemistry and Sclerochronology (Winter et al., 2003). Holocene millennial records of continuous paleoclimate data with sub-annual resolution from coral skeletons have been more difficult to obtain because of the lack of unaltered individual coral colonies. To develop Holocene millennial records of continuous paleoclimate data with sub-annual resolution from coral skeletons a pristine coral reef with aragonitic corals, oriented in growth position and located at the proper stratigraphic framework would be needed. The probability of finding such a place is extremely low not only because most Holocene reefs are

submerged but also because Holocene reefs records are fragmentary with most of the corals broken and out of place (Hubbard, 1997).

The Sr/Ca ratio obtained from the coral skeleton is one of the trace element analysis used for climate reconstruction, the others being Mg/Ca and U/Ca. Calcium ion (Ca<sup>+2</sup>) is substituted within the crystal structure by many divalent trace ions such as strontium  $(Sr^{+2})$  and magnesium  $(Mg^{+2})$ dissolved in water (Faure, 1998), which keeps the chemical identity of the environment preserved in the skeleton. This is because corals do not incorporate rubidium (Rb) in their skeleton meaning that Sr does not come from radiogenic decay but the waters the coral skeleton is precipitated. Beck et al., 1992 found an inverse relationship between the amount of Sr and SST in corals from southwest Pacific Ocean with a precision better than 0.1%, allowing precise documentation of paleotemperatures by measuring Sr/Ca ratios in the coral skeleton. Sr/Ca ratio as a paleothermometer, requires to be calibrated with modern sea water, because calculated SST-Sr/Ca are highly dependent on the location (Saenger et al. 2008). Swart et al. (2002) calibrated the relationship of Sr/Ca and temperature in the scleractinean coral Montastraea annularis producing a high correlation ( $R^2 = 0.83$ ; Sr/Ca (mmol/mol) between the two variables. Other paleothermometers have already been tested such as Mg/Ca and U/Ca ratios. However, these ratios have shown to be affected by other variables other than temperature, leaving Sr/Ca as the most reliable proxy (Beck et al., 1997; Swart and Grottoli, 2003; Felis and Pätzold, 2004).

Oxygen isotopes (<sup>18</sup>O/1<sup>6</sup>O) are also incorporated as part of the skeleton and are directly influenced by the marine environment (Grottoli, 2001). This isotopic tool has proven to be very successful in reconstructing past climate and even pointing out climate variability and patterns (Felis et al., 2004, Cobb et al., 2013). Even though  $\delta^{18}$ O shows a high correlation with temperature, it is also sensitive to salinity variations (Smith, 2006) in contrast with Sr/Ca ratio, which seems to be affected only by temperature (Swart and Grottoli, 2003) and have better temperature resolution (Swart et al., 2002). Greer and Swart (2006) conducted a study in Enriquillo using  $\delta^{18}$ O and  $\delta^{13}$ C isotopic compositions from coral skeletons directed to study decadal ciclicity patterns. Their data suggested the primary driver for the decadal oscillations in  $\delta^{18}$ O and  $\delta^{13}$ C was salinity. This study concluded that the isotopic variability was affected by local precipitation and that fresh water flooding influenced the  $\delta^{18}$ O and  $\delta^{13}$ C variations more significantly than the temperature fluctuations. This study reported decadal and multidecadal variations in  $\delta^{18}$ O and  $\delta^{13}$ C in the coral

skeletons and suggested Sr/Ca as a better proxy to determine possible temperature variations, since Sr/Ca is not affected by salinity.

Proxy records require an accurate timescale based on absolute ages. Many studies have relied on radiocarbon dating for sclerochronology, however radiocarbon is significantly affected by ocean reservoir effects and variations of radiocarbon in the atmosphere. The uranium-thorium (U/Th) radiogenic dating method is more accurate because is considered to provide absolute ages compared to radiocarbon, therefore, it has better resolution (Felis and Pätzold, 2004). U/Th dating has been used in coral samples as young as a few years (Cheng et al., 2013) and as old as the last interglacial period (Felis et al., 2004). The reliability of this method is based in the fact that corals do not incorporate non-radiogenic <sup>230</sup>Th (at least its concentration is fairly negligible) and that carbonates are uranium rich. This means that the only source of <sup>230</sup>Th is radiogenic and produced from the decay of <sup>238</sup>U in-situ and in the coral skeleton (Cobb et al., 2003). The absolute age provided by the U/Th dating method is combined with the internal chronology present in the coral to provide a reliable timescale.

#### 1.3 Study Area

### 1.3.1 Geologic history

Cenozoic plate tectonic history establishes that during the Late Eocene, under-thrusting and accretion took place against the Hispaniola (Fig. 1). The formation of the Peralta Belt exposed deep-water sediments that now are deposited in the Southern Hispaniola. Then in the Early Miocene, oblique movement of the oceanic plate caused a transpressional uplift and thrusting of the Peralta Belt and the converging plate sediments. Geologic structures in the region explicitly show evidence of the tectonic events during this period that led to the geomorphic features present in Southern Hispaniola.

The southernmost part of the island is dominated by very young anticlinal mountains and synclinal valleys. This geomorphology results from the active reverse and oblique-slip faulting during the Late Miocene's transpression of the North America-Caribbean boundary characterizing this region by its low topography and fault bounded Neogene basins like Enriquillo Valley (Mann and Lawrence, 1991; Mann et al., 2008). Later during the Pliocene, undergoing ramping and thrusting started in the area (Mann, 1999) surrounding the basins with The Sierra de Neiba and Sierra de Bahoruco (Fig. 2) steep mountain ranges mainly composed of faulted Paleocene-Miocene carbonates and oceanic basalts from the Late Cretaceous (Mann, 1999) that will serve as the main source of modern deposits within the basins. Sea level rise during the Holocene, after the last interglacial period, flooded the basin forming a gulf known at the time as Enriquillo Bay (Mann et al., 1999). Fringing and patch reefs developed along the marine gulf with an average elevation of the surface of the reef crest at approximately 5m below sea level (Mann et al., 1984). At this time, active tectonism has not significantly affected the basin, as uplift/subduction during the Holocene appears to be minimal (< 1m) (Mann et al., 1995).

# Geologic Map of La Hispaniola



Figure 1: Geologic map of La Hispaniola. Red square indicates the location of Enriquillo Lake in southwestern, Dominican Republic (Modified from Escuder Viruete et al., 2002)

#### 1.3.2 Location

Enriquillo Valley, located in the south-westernmost part of Southern Hispaniola (Fig. 2), is an east-west trending feature from the Caribbean Sea to the Baie de Port-au-Prince in Haiti (Greer and Swart, 2006), settled in a tropical climate with little seasonal temperature variations (25<sup>°</sup>C) but affected by significant variability in precipitation produced by seasonal changes (Teneva, 2006). The valley is a Neogene marine sedimentary basin with an ideal setting for biofacies and lithofacie studies (McLaughlin and Van Den Bold., 1991). It contains fossiliferous rich reefal carbonates and thick evaporite deposits and clastic rocks, all very well preserved due to the semi-arid environment present (McLaughlin and Van Den Bold, 1991; Pierce, 2014). The valley formed as result of north-south compression subsidence (Mann et al., 1984) and contains very well preserved subaerial exposures of shallow-water reef environments dating approximately  $5297 \pm 41$  to  $7203 \pm 77$  years before present according to U/Th dating (Greer and Swart, 2006) at different locations in Enriquillo and 6.9-8.9ka using radiocarbon dates in Cañada Honda (Hubbard et al., 2004). During the early Holocene rapid sea level rise flooded the valley resulting on transgressive deposits that eventually formed shallowing upward sequences (Cuevas et al., 2005). Quaternary deposits from local rivers isolated the open bay separating the Caribbean Sea and forming the hypersaline Lago Enriquillo around 5ka (Cuevas et al., 2005). Drastic evaporation dominated in the lake as fluvial influxes in the region created erosional gullies, exposing the Holocene coral reefs in an arid environment. Constant sediment influx of calcareous composition (Cuevas et al., 2005) covered much of the reef creating a very well preserved exposure. The constant influx could have been responsible for low growth rates ranging from 1.3-4.5 mm/yr (Cuevas et al., 2005) in *Montastraea sp.* compared to low sedimentation growth rates that vary from 5 and 7.5 mm/yr (Dokken et al., 2003) to 8.5-10 mm/yr (Gischler and Oschmann, 2005). The chemistry of the water have also been widely influenced by seeping spring waters, some of them considered to be a source of sulfur (Buck et al., 2005). This study takes place in Cañada Honda, one of the erosional gullies that is initially described in Taylor (1985) and later described in detail by Hubbard et al. (2004) and Cuevas et al. (2005).

The Enriquillo Valley, unlike few places, has the conditions that allow the preservation of the reef structure and corals skeletons (Hubbard et al. 2004). The valley used to be a bay filled with marine water in a restricted environment with limited wave action, which resulted in the absence of *Acropora palmata* (Hubbard et al., 2004). High sediment influx from the mountains

that bound the lake on the north and south affected the growth of the corals into forming columnar assemblages of platy corals as means of adapting to the environment (Hubbard et al., 2008). As a consequence these corals grew under stress conditions (Cuevas et al., 2005; Hubbard et al., 2008) and corals under stress, may be subject to alterations in Sr/Ca ratio. Even though Sr in the aragonite skeleton is mostly dependent on the water concentrations rather than inhibitors (such as KCN) or the amount of light, Ca is highly affected by the latter, generally inhibiting calcification (Marshall and Mculloch, 2002). This will result in higher Sr/Ca ratios to those crystals that precipitate.

The Holocene fringing reef exposure, generally, is highly abundant by corals in growth position of the species Montastraea sp. and Siderastrea sp. with the absence of Acropora palmata and Diploria sp. which marks a difference compared to other reefs in the Caribbean (Taylor et al., 1985; Cuevas et al., 2005; Greer and Swart, 2006; Hubbard et al., 2008). Still the coral species' diversity varies as the reef accreted suggesting changes in the ecology of the reef with time. Two major coral morphologies were surveyed: cone shaped and pancake shaped (Fig. 3), which are formed depending on the sediment influx rate of the area (Hubbard et al., 2008). Cone shaped corals are mostly formed when the coral outgrows the sediment input and pankace shaped corals when corals keep up with the sediment input (Hubbard et al., 2008). The climate and temperature conditions of the area have made possible the preservation of these rocks and most of its ecology and zonation of the fossilized reef (Greer and Swart, 2006). Stratigraphy shows little degree of faulting and erosion due to being uplifted during the Pliocene (~4Mya), prior to the reef development (Cooke 1989; Mann et al, 1999). Enriquillo reef exposures, with some exceptions, resembles modern reefs throughout the Caribbean, however, evidence from  $\delta^{234}$ U suggests that this reef does not seem to have evolved in a closed system with normal seawater and that it is highly probable that these corals grew highly influenced by freshwater (Edwards, 1988).



Figure 2: Map of Lago Enriquillo, Dominican Republic. Red star indicates the approximate location of Cañada Honda where this study takes place (Modified from Gonzalez et al., 2013)



Figure 3: Pancake morphology from a coral piece in Cañada Honda. Not that each layer presented may be interpreted as a sedimentation event (Hubbard et al., 2004).

## 2. Methodology

Five procedures were used to complete this research: 1) sampling of corals in growth position along specific stratigraphic intervals; 2) skeletal assessment to determine the degree of preservation and mineralogy of the samples; 3) measurement of changes in density (i.e. luminosity in x-rays) to determine growth rates in corals; 4) coral dating using U/Th radiogenic method; and 5) isotopic  $({}^{18}O/{}^{16}O)$  and trace elemental (Sr/Ca) geochemical analysis to determine paleotemperatures related to SST. Montastraea sp. corals were used since many previous works have studied the skeletization in these species and have develop correlations (and equations) that establish the relationship between the isotopic and trace elemental concentrations to the temperatures, making possible to use their skeletons as paleothermometers (Greer and Swart, 2006). In this way the geochemistry in the skeleton, specifically Sr/Ca and  $\delta^{18}$ O values were measured and used as proxy records of SST. Growth rates and SST variations obtained are compared with growth rates and SST variations of modern and ancient corals available in the literature (Felis et al., 2004; Greer and Swart, 2006; Smith, 2006; Giry et al., 2012; Cobb et al., 2013, Winter et al., 2003 and others) and from undergoing research in La Parguera, Puerto Rico. Measurement of the coral bands combined with radiometric dates provides timelines along the coral skeletons to study climate change including and making emphasis in rates of change and variability.

### 2.1 Sampling procedures

This research focuses on analyzing *Montastraea sp.* coral samples from the Massive Zone 1 (M1) shown in the Cañada Honda facies map (Fig. 4). The study area was surveyed prior to sampling, to identify major features already described on previous surveys done by Hubbard et al. (2004) and Cuevas et al. (2005) (Fig. 5). Possible samples were surveyed by looking at the taphonomy (external preservation and bioerosion) their geometry (growth position) and morphology. These characteristics are pertinent as this study relies in that the geochemistry and growth position of the corals needs to remain intact data to assess if the corals grew in situ and to obtain accurate paleoclimate data. As most corals of interest were grouped and assembled in columns, each of the columns were assigned a number seaward to landward (except M1-2 which is more seaward than M1-1 due to mislabeling) and each of the pieces an uppercase letter from bottom to top. Each column and individual coral were photographed as means to document their exact position prior to sampling for future references.

Twenty four specimens were sampled and documented based on the facies map and stratigraphy; four of them were discarded due to not being the correct coral species or major diagenetic alteration leaving only 20 samples for further analysis (Fig. 6). Their position was measured both laterally and vertically using a measuring tape, using previous markings and facies boundaries described by Hubbard et al. (2004). M1-1 was the column of greater interest, because they cover the whole M1 facies from bottom to top, being a possible tool to study a continuous growth assemblage (Fig. 7). Some samples were cut in half in the field along the growth axis, using a portable Nakita Doc 7301 cutting machine for easier transportation and to reassure the degree of preservation of the coral. These samples were carefully cleaned to remove the external sediment and dust from the cutting machine, packed and sent to the Geology Department of the University of Puerto Rico, Mayagüez Campus.



Figure 4: Facies map of Cañada Honda erosional gully. The focus of this study was to analyze coral samples within Massive Zone 1, shown in pink. (Modified from Hubbard et al., 2004; Cuevas et al., 2005).



Figure 5: A portion of Cañada Honda fossil reef stratigraphy. Vertical trancects are shown in columns with the distance relative to the southern end of the outcrop on the bottom. Elevation in meters is shown on the vertical scale of each column. Location where samples were collected in this study is circled in red (Modified from Cuevas et al., 2005).



Figure 6: Samples collected from M1 facies assembled relative to their vertical position. Relative elevations were estimated based on the measurements taken from the visible layers. Horizontal position relative to the southern end of the outcrop is given for each column. Dashed lines indicate that the corresponding layer was not visible at that point.



Figure 7: Photo of M1-1 and M1-2 columns with the Mad layer and Shell layer boundaries marked.

#### 2.2 Sample preparation

The geometry of the samples was studied, to estimate the growth axis, as this is the area of interest for microsampling. Samples were cut in longitudinal slabs of 5mm thick using a SMI Fulker DiMet C/149B masonry and concrete saw. This thickness is required to be able to obtain clear x-ray images for the measurement of coral growth rates. A slab that is too thick will block the light form the x-ray machine, thus obscuring the growth bands. Each of the 24 samples was radiographed in the San Antonio Hospital at Mayagüez radiography facilities and both digital and physical copies of the radiographies were obtained.

Four samples (M1-1D<sub>c</sub>, M1-1E<sub>e</sub>, M1-2B<sub>a</sub> and M1-2E) from the 24 samples collected were selected for micro-sampling based on the position, preservation and growth patterns shown in the radiography. Corals from the column 1 (M1-1) are important, because they comprise the whole M1 facies (Fig. 6 and 7). M1-1D<sub>c</sub>, M1-1E<sub>e</sub> were selected as they showed clear banding and the best preservation in both hand sample and radiography. Samples from column 2 (M1-2) M1-2B<sub>a</sub> and M1-2E were chosen because they stratigraphically overlap those already chosen from column 1 as means to understand the lateral variations of the reef. One sample (M1-1G<sub>b</sub>) identified as diagetic altered was chosen to obtain measurements of altered materials for comparisons and also because its position was at the top of the M1 facie. M1-1G<sub>b</sub> showed bioerosion and observed variations in coloration that led to possible diagenetic alteration. This sample is associated with beds that have been interpreted as storm deposits that separate facies M1 from M2. These deposits were described in Hubbard et al. (2004) and Cuevas et al. (2005) as the *Madrasis* "Mad" layer, based on the abundant broken pieces of the *Madrasis sp.* coral (Fig. 7)

#### 2.3 Assessment of coral skeleton integrity

Pristine coral skeleton preservation and original aragonitic composition is a major requirement for the samples used in this study. To test the integrity of the coral skeleton, samples were analyzed using a Siemens X-Ray Difractometer (XRD) D500 from the UPRM Geology Department. A section of the coral was sampled and pulverized using a mortar and pestle until a very fine powder was produced. The samples were analyzed using a step of 0.02, a time of 1 sec and range from 15-65° 2-Theta scale. Results obtained were compared to the aragonite XRD analysis done by Downs (2006) to reassure the aragonitic composition and discard any sediment contamination of the samples. Peaks for aragonite are expected to be present at 26.2° (I<sub>1</sub>=100%), 45.86° (I<sub>2</sub>=65%) and 27.2° (I<sub>3</sub>=52%). From this analysis, the presence of calcite and its dominance over aragonite can be studied by looking at possible peaks at 29.4° (I<sub>1</sub>=100%), 43.1° (I<sub>2-3</sub>=18%) and 39.4° (I<sub>2-3</sub>=18%). Since peaks at 43.1° and 39.4° for calcite have the same intensity percent (I), it can't be distinguished between I<sub>2</sub> or I<sub>3</sub>.

#### 2.4 Montastraea sp. Growth rate estimates

Extension rates were obtained by measuring the lineal distance of the high density (HD) and low density (LD) bands in digital images obtained from X-rays using Coral X-radiograph densitometry system (Coral-XDS) software. The software was calibrated using the radiography image scale, obtained from the digital image, both for the x and y axis. The accuracy of this scaling method was tested by measuring the dimensions of  $M1-1E_e$  and comparing it to the scale produced digitally. For each sample, a transect (Fig. 8) was drown following the growth direction using the oblique setting trying to avoid any dark spots or possible luminance errors in the image as those will give inaccurate densitometry results. The densitometry analysis was done at steps of 0.1cm following the intended microsampling intervals (see section 2.7) at an automatic scale based on the previous calibration. The software automatically builds a graph of luminance as a function of extension (Fig. 8) where maximum or LD and minimum or HD luminance points are detected. However, some of the maximums and minimums are not detected and had to be entered manually using the add maximum or add minimum feature. Once the plot was completed, it was obtained from the software through a screenshot and the data extracted as a .DAT file for further study. Using the data obtained from the software, since each couplet of LD-HD bands represents a year of skeletal growth, the chronology of the years present in the coral skeleton is developed by counting the number of couplets present in the sample (Winter et al., 2000). With this information, growth rates were calculated using equation 1 for samples M1-1D<sub>c</sub>, M1-1E<sub>e</sub>, M1-2B<sub>a</sub>, M1-2E and test sample M1-1G<sub>b</sub>

$$Growth \, rate = \frac{Coral \, growth \, extension \, (mm)}{number \, of \, couplets \, (yr)} \tag{1}$$



Figure 8: Example of the densitometry analysis done on  $M1-1E_e$ . Sample radiography with a drawn transect (red square) on the left and the output plot obtained from Coral XDS for that sample on the right.

### 2.5 Sedimentation rate estimates

Sedimentation rates were estimated using equation 2 by looking at the pancake morphology developed by some corals in this fossil reef. Each pancake of the coral is associated with a sedimentation event (Hubbard et al., 2008), meaning, that by measuring the extension of a pancake along the growth axis with relation to the growth bands, sedimentation rates can be estimated. Sample M1-2B<sub>a</sub> is an example of pancake morphology where eight events, labeled from M1-2B<sub>a</sub>-S1 to M1-2B<sub>a</sub>-S8 from bottom to top, of sedimentation can be observed (Fig. 9). Each of the events was analyzed using the method described for growth rates (see section 2.4),





Figure 9: Pancake morphology of sample M1-2B<sub>a</sub>. Sample radiography marked with the observed boundaries of the pancake morphology (dashed red lines) and a drawn transect (dashed green line) on the left and a sketch of the sedimentation events on the right.

#### 2.6 Radiogenic dating

The four coral samples analyzed for isotopes and trace elements (M1-1D<sub>c</sub>, M1-1E<sub>e</sub>, M1-2B<sub>a</sub> and M1-2E) were also dated using uranium thorium radiogenic dating (U/Th). In addition, sample M1-1A<sub>a</sub> located at the base and M1-4A<sub>e</sub> at the top of the M1 facies (Strat figure), although not analyzed for isotopes and trace elements, were dated since they are expected to be the oldest and youngest coral samples respectively. Fragments of the coral skeleton of approximately 1g were obtained from each coral skeleton sample. The sampling location along coralline structure was documented in detail and was deliberately taken close to the location that was micro-sampled for geochemical analyses (see section 2.7). The powdered samples were analyzed in a multi-collector inductive coupled plasma mass spectrometer (MC-ICP-MS) at the University of Minnesota. Decay constants were obtained and used for U as  $\lambda_{238} = 1.55125 \times 10^{-10}$  (Jaffey et al., 1971) and  $\lambda_{234} =$ 2.82206x10<sup>-6</sup> (Cheng et al., 2013) and for Th as  $\lambda_{230} = 9.1705 \times 10^{-6}$  (Cheng et al., 2013). Radiogenic  $\delta^{234}$ U isotope was calculated using equation 3 and  $\delta^{234}$ U<sub>initial</sub> was calculated based on 230Th age (t) using equation 4. Corrected <sup>230</sup>Th assumes an initial <sup>230</sup>Th/<sup>232</sup>Th ratio of  $4.4 \pm 2.2 \times 10^{-6}$  a value known for secular equilibrium with the bulk earth <sup>232</sup>Th/<sup>238</sup>U value of 3.8. Errors for this analysis are arbitrarily assumed to be 50% and present day is established as 1950 A.D. More details on the method used are described by Cobb et al., (2003) and Cheng et al. (2013).  $\delta^{234}$ U obtained during U/Th dating, is studied to try and understand the nature of the waters where this corals formed as this is a tool frequently used to test diagenesis and open system behavior in marine environments (Robinson et al., 2003). Regular seawater mean  $\delta^{234}$ U values for the Atlantic is  $144 \pm 3\%$  ranging from 140 to 150‰ (Edwards et al., 1985; Edwards et al., 1987). Input of freshwater into the system is known to decrease the  $\delta^{234}$ U values in the coral skeleton (Robinson et al., 2004; Mey et al., 2005).

$$\delta^{234} U = ([^{234}U/^{238}U]_{activity} - 1) * 1000$$
(3)  
$$\delta^{234} U_{initial} = \delta^{234} U_{measured} * e^{\lambda_{234}t}$$
(4)

#### 2.7 Microsampling

From the four coral samples selected for isotopes and trace elements analysis (M1-1D<sub>c</sub>, M1-1E<sub>e</sub>, M1-2B<sub>a</sub> and M1-2E), 500 samples (~100-130 per coral) were micro-sampled each millimeter (1mm or 0.1cm) using a X0 Micromill with a 1mm drill bit (Fig. 10). The sampling was also performed in test sample M1-1G<sub>b</sub>, however, only 20 micro-samples were collected as this is a test sample to asses values of altered materials (see section 2.3). The procedure was performed by following the growth axis along the thecal wall of a corallite using the naked eye and the radiography. Micro-samples were obtained at increments of 1mm approximately and each sample address a sub-monthly resolution time-series given growth rates of approximately 10mm/yr (Nurhati et al., 2009). Powders were carefully collected and weighted using a Mettler UMT2 Micro-balance consecutively for both stable isotope (80-100µg) and trace element analysis (150-200µg). Excess of powders were carefully placed in a glass vial and stored for future references. Both the micro-sampling and the geochemical analyses were done at Cobb's Lab in Georgia Intitute of Technology.



Figure 10: X-Ray radiographs and fossil *Montastraea sp.* coral samples analyzed in this study. Black bars are at a scale of 10cm both vertically and horizontally. Test sample  $M1-1G_b$  is labeled in red. Red lines indicate microsampling transects at increments of 1mm along the thecal wall, blue brackets indicate the position where the dating sample was obtained and black arrow indicate growth direction.
#### 2.8 Stable isotope analysis

<sup>18</sup>O/<sup>16</sup>O and <sup>13</sup>C/<sup>12</sup>C isotopic ratios were analyzed using a GV Isoprime Mass Spectrometer equipped with a Multiprep device with an analytical precision of ±0.05‰ (1 $\sigma$ ). A *Porites* aragonite standard (PDA) converted to Pee Dee Belemnite (PDB) values was used as a standard. Weighted powders (80-100µg), including the standards, were quantitatively transferred to an acid-cleaned glass tube and documented for analysis. A quality control assessment provided by the laboratory technician (Table 1) was done to discard samples that were damaged before or during the analysis. For each analytical run, standard deviation was calculated using the standard (PDA) results obtained from the analysis. Isotopic values were corrected by adding the correction factor (Standard <sup>18</sup>O/<sup>16</sup>O – PDA Mean <sup>18</sup>O/<sup>16</sup>O) to the raw values of <sup>18</sup>O/<sup>16</sup>O. Results obtained are compared to results obtained from similar coral samples in Enriquillo by Greer and Swart (2006) for reproducibility. Values of  $\delta^{18}$ O obtained are converted to temperature using a calibration done by Leder et al. (1996) shown in equation 5, keeping the oxygen isotope values of the water constant ( $\delta^{18}$ O<sub>w</sub> = 0). With this assumption, variations in  $\delta^{18}$ O will be solely attributed to changes in temperature due to fractionation of the isotopes and not to variations in <sup>18</sup>O/<sup>16</sup>O in the water (Greer and Swart, 2006).

Table 1: Quality control for the stable isotope analyses. Samples who did not meet these requirements were discarded and not taken into consideration for interpretations.

| Parameter   | <b>Expected values</b> |
|---|------------------------|
| Standard Deviation <sup>18</sup> O/ <sup>16</sup> O | < 0.07                 |
| Standard PDA <sup>18</sup> O/ <sup>16</sup> O       | ~ -5.32                |
| Standard PDA <sup>13</sup> C/ <sup>12</sup> C       | ~ -1.32                |
| Leak Rate   | < 1000                 |
| Pno Acid  | < 100                  |
| Total CO <sub>2</sub>                               | ~ 1000                 |
| Exp   | 0                      |

$$SST = 5.33 - 4.519 (\pm 19) * (\delta^{18}O_c - \delta^{18}O_w)$$
(5)

#### 2.9 Trace metal analysis

Sr/Ca ratios were measured using a Horiba JY Ultima-C Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) with analytical precision of  $\pm 0.08-0.24\%$  (1 $\sigma$ ) using the Schrag (1999) nearest-neighbor correction method. Weighted samples (150-200µg) were quantitatively transferred into acid-washed polypropylene tubes and diluted with 2% nitric acid (HNO<sub>3</sub>). Each sampled was centrifuged using a S1-0236 Vortex-Genie Mixer, 120V to ensure a well-mixed solution. A calibration curve was constructed using previously prepared standards with calcium concentration of 20, 30, 40 and 50 ppm as means to discard contaminated samples.

To obtain Sr/Ca-derived SST, a Sr/Ca calibration using modern corals from a reef in the region under the same marine conditions would be ideal. However, this is impossible as this reef was formed in a semi closed bay environment that no longer exists. Still, calibrations made by Swart et al. (2002) in Ball Buoy Reef, Southern Florida (Eq. 6), Felis et al. (2004) in the Gulf of Aqaba, Red Sea (Eq. 7), Flannery et al. (2013) in Dry Tortugas, Florida (Eq. 8), Giry et al (2012) in Bonaire, Southern Caribbean (Eq. 9) and Smith (2006) in Dry Tortugas, Florida (Eq. 10) were tested to obtaine possible SST estimates. The environment present in the Red Sea and Bonaire are probably the most consistent to Enriquillo. The Red Sea is a semi-closed environment similar to what Enriquillo was before the closure of the bay and a model of SST seasonality anomaly done by Giry et al. (2012) suggest that there were similar conditions in SST about 6kya between Bonaire and Southern Hispaniola.

| Sr/Ca = 10.781 - 0.0597 * SST ( | 7) |
|---------------------------------|----|
| bi/eu 10.701 0.0577 bb1         | '  |

- Sr/Ca = 10.205 0.0392 \* SST (8)
- Sr/Ca = 10.6 0.050 \* SST (9)
- Sr/Ca = 9.962 0.0282 \* SST (10)

## 3. Results

### 3.1 Densitometry analysis

Densitometry analysis for samples M1-1D<sub>c</sub>, M1-1E<sub>e</sub>, M1-2B<sub>a</sub>, M1-2E and M1-1G<sub>b</sub> are plotted in (Fig. 11) and interpreted in (Fig. 12) with luminance intensity in the Y axis and extension in the X axis (See appendix 1-5 for individual plots). Interpretation of luminance variation in sample M1-1D<sub>c</sub> (15.03cm) shows constant values with 1 cm intervals of thinner growth at 7cm and 12 cm. Sample M1-2E (8.36cm) shows a decreasing trend in luminance values from 0-6cm then increases from that point with variations of growth thickness approximately every 1-2cm. Sample M1-1E<sub>e</sub> (10.24cm) shows increasing trend in luminance values with thickness variations of 3.5cm during two intervals and 1cm the following two intervals. Sample M1-2B<sub>a</sub> (10.61cm) shows decreasing trend in luminance values from 1-6.5cm and then increases from that point. Growth thickness variations in this sample are less drastic during the first 5.5 cm (2-3cm) and then vary more rapidly (0.5-1cm) towards the end. Densitometry plots for each section of M1-2B M1-2Ba are presented in (Fig. 13). Base-M1-2Ba extends for 2.50cm followed by mid-M1-2Ba which extends for 3.54cm and then by top-M1-2B<sub>a</sub> for the last 3.35cm. Sample M1-1G<sub>b</sub> (17.47cm) shows variable luminance values trends within the coral. There is a decreasing trend during the first 3.8cm followed by a decrease-increase trend from 4.3-9cm. At 9.2 cm there is an increasing trend in luminance values later followed by a decrease-increase trend from 11.2-15.4 cm from where it decreases until the end of the plot. Thickness variations in this coral are not as remarkable, yet lengthy. Thinner growth occurs during the first 6.5 cm, then at 8.4-9.1cm and later at 13-15cm.



Figure 11: Densitometry analysis of samples of  $M1-1D_c$ , M1-2E,  $M1-1E_e$ ,  $M1-2B_a$ , M1-2E and  $M1-1G_b$  produced by Coral-XDS. Figures include estimated growth rate and transect at the bottom of the figure for each sample. Refer to appendix 1-5 for drawn transects.



Figure 12: Interpreted densitometry analysis of samples  $M1-1D_c$ , M1-2E,  $M1-1E_e$ ,  $M1-2B_a$  and  $M1-1G_b$  produced by Coral-XDS. Blue arrows indicate visual trends of luminance intensity; red arrows indicate intervals of relatively thicker extension and green arrows intervals of relatively thinner extensions. Refer to appendix 1-5 for drawn transects.



Figure 13: Densitometry analysis of the eight sedimentation events (S1-S8) interpreted from sample M1-2B<sub>a</sub> produced by Coral-XDS. Figures include estimated growth rate and coral transect at the bottom of the figure for each section. Refer to Fig. 9 for drawn transects.

## 3.2 Skeletal composition

The output produced by the XRD analysis shows a graph with intensity counts in the Y axis and the 2theta in the X axis (Fig. 14, see appendix fig 6-10 for individual plots). All four samples (M1-1D<sub>c</sub>, M1-1E<sub>e</sub>, M1-2B<sub>a</sub>, M1-2E) and the test sample sample (M1-1G<sub>b</sub>) only show aragonite peaks. The spectrum shows two prominent peaks at approximately 26° (1800-2100 counts) and 27° (1000-1100 counts) matching the aragonitic peaks I<sub>1</sub> and I<sub>3</sub> respectively. There is also a separate peak at approximately 46° (1300-1600 counts) which corresponds to the I<sub>2</sub> peak for aragonite. The distinctive calcite peak I<sub>1</sub> expected at 29° is not present in any of the samples, including test sample M1-1G<sub>b</sub>.



Figure 14: XRD results for samples  $M1-1D_c$ , M1-2E,  $M1-2B_a$  and  $M1-1G_b$ . Peaks for aragonite (red) are marked for each sample. Note the absence of the calcite peak (green arrow) in each sample. Refer to appendix 6-10 for individual plots.

### 3.3 Growth rates estimates

Calculated growth rates for each studied samples (M1-1D<sub>c</sub>, M1-2E, M1-1E<sub>e</sub>, M1-2B<sub>a</sub> and M1-1G<sub>b</sub>) are summarized in (Table 2). The extensions based on the variations in luminosity from this table may differ from those given in the densitometry analysis because a single band at the end of the transect might have not been analyzed by the Coral XDS software. Average growth rates in stratigraphy position along the reef range from  $2.07 \pm 0.14$  to  $3.55 \pm 0.37$  mm/yr with an average value of  $2.77 \pm 0.56$  mm/yr (n=5) in a time lapse of 30-80 years. Growth rates measured decrease as we move up stratigraphically in both M1-1 and M1-2. Growth rates measured increase laterally as we move landward (north) (Fig. 15).

Table 2: Summary of the densitometry analysis, growth rate and sedimentation rate estimates.

| Sample ID          | Years (n) | Extension (mm) | Growth Rate (mm/yr) |
|--------------------|-----------|----------------|---------------------|
| M1-1Dc             | 42        | 149.31         | $3.55 \pm 0.37$     |
| M1-1Ee             | 33        | 101.04         | $3.06\pm0.45$       |
| M1-2Ba             | 40        | 105.13         | $2.62\pm0.48$       |
| M1-2E              | 32        | 82.66          | $2.58\pm0.20$       |
| M1-1G <sub>b</sub> | 83        | 171.97         | $2.07\pm0.14$       |

| Section ID             | Years (n) | Extension (mm) | Sedimentation rate (mm/yr) |
|------------------------|-----------|----------------|----------------------------|
| M1-2B <sub>a</sub> -S1 | 8         | 15.04          | $1.88 \pm 0.33$            |
| M1-2Ba-S2              | 3         | 6.32           | $2.10 \pm 0.30$            |
| M1-2Ba-S3              | 5         | 11.57          | $2.31 \pm 0.43$            |
| M1-2Ba-S4              | 7         | 17.40          | $2.48 \pm 0.45$            |
| M1-2Ba-S5              | 2         | 3.84           | $1.92 \pm 0.07$            |
| M1-2Ba-S6              | 6         | 11.78          | $1.96 \pm 0.15$            |
| M1-2Ba-S7              | 3         | 6.49           | $2.16 \pm 0.57$            |
| M1-2Ba-S8              | 6         | 9.21           | $1.53 \pm 0.18$            |



Figure 15: Growth rates of M1 facies' columns M1-1 and M1-2. Samples used for densitometry analysis are circled in red.

#### 3.4 Sedimentation rate estimates

Estimated sedimentation rates for each section in sample M1-2B<sub>a</sub> (S1 to S8) are summarized in (Table 2). Sedimentation rates range from  $1.53 \pm 0.18$  to  $2.48 \pm 0.45$  mm/yr with an average value of  $2.06 \pm 0.30$  mm/yr (n=8) in time intervals of 2-8 years. The events started at a rate of 1.88mm/yr then became more rapid until the fourth sedimentation event (S4) with a maximum rate of 2.48mm/yr. Sedimentation slowed down to 1.92mm/yr then increased until the seventh sedimentation event (S7) at 2.16mm/yr where rated slowed to 1.53mm/yr (Fig. 16).



Figure 16: Sedimentation rates of each section in M1-2Ba (S1-S8). Sedimentation rate boundaries are marked with red dashed lines.

#### 3.5 U/Th Radiogenic dating

Each of the four samples (M1-1D<sub>c</sub>, M1-1E<sub>e</sub>, M1-2B<sub>a</sub>, M1-2E) under study, including the sample at the base of the facies (M1-1A<sub>b</sub>) and another at the top of the facies (M1-4A<sub>e</sub>), have U/Th dates that range from  $8036 \pm 26$  to  $8910 \pm 28$  yr B.P. (Fig. 17). As expected, Sample M1-1A<sub>b</sub> is the oldest coral of M1-1 and corals get younger following the vertical growth of the column. Samples in M1-2 get younger following the vertical growth of the columns, however, overlapping samples on M1-2 are much older than those in M1-1. Sample M1-4Ae was the exception to this, as it dated since is older than samples from M1-1.  $\delta^{234}$ U was measured as part of the dating process, and it ranges from  $87.9 \pm 1.4$  to  $113.3 \pm 1.3\%$  with an average value of  $104.7 \pm 1.4\%$ .



Figure 17: U/Th radiometric dates of M1 facies' columns M1-1, M1-2 and M1-4. Samples used for radiogenic dating analysis are circled in red. **3.6 Stable Isotopes analysis** 

The  $\delta^{18}$ O and  $\delta^{13}$ C values from the samples under study (M1-1D<sub>c</sub>, M1-1E<sub>e</sub>, M1-2B<sub>a</sub>, and M1-2E) and test sample (M1-1G<sub>b</sub>) are plotted with depth in Fig. 18 and isotopic ranges and variation are summarized in Table 3.  $\delta^{18}$ O and  $\delta^{13}$ C values are very similar in all samples.  $\delta^{18}$ O variations are not large and most values are around (average) -1.56‰ with the exception of sample M1-2B<sub>a</sub> with an average of 1.18‰.  $\delta^{13}$ C variations is not large either and most samples under study average -2.06‰ with the exception of sample M1-1D<sub>c</sub> with an average of 2.45‰. Sample M1-1G<sub>b</sub>  $\delta^{18}$ O values (-1.41 to -2.25‰) fall within the values obtained for the samples under study with a variation of 0.84‰. However,  $\delta^{13}$ C values were lower (2.43 to -4.04‰) with a variation of 1.61‰.

#### 3.7 Trace elemental analysis

Sr/Ca ratio for the samples under study (M1-1D<sub>c</sub>, M1-1E<sub>e</sub>, M1-2B<sub>a</sub>, and M1-2E) and sample (M1-1G<sub>b</sub>) are plotted along with  $\delta^{18}$ O and  $\delta^{13}$ C in Fig. 18 and results are summarized in Table 3. Samples M1-1D<sub>c</sub>, M1-1E<sub>e</sub>, M1-2B<sub>a</sub>, and M1-2E, Sr/Ca results vary from 9.07-9.70 mmol/mol with variations that relatively similar among them. Sample M1-1G<sub>b</sub> have lower values (8.84-9.31 mmol/mol) than the other samples. In the majority of the cases, Sr/Ca follows the expected inverse trend in variation relative to  $\delta^{18}$ O. Sample M1-1D<sub>c</sub> and M1-2E have correlation indexes (R) of 0.85 and 0.72 however; calculated correlation index for samples M1-1E<sub>e</sub> (0.02) and M1-2B<sub>a</sub> (0.20) are considerably lower.

Table 3: Stable isotope composition range of values and variability for samples  $M1-1D_c$ ,  $M1-1E_e$ ,  $M1-2B_a$ , M1-2E. Sample  $M1-1G_b$  is shown in italics as this was a test sample.

| Sample<br>ID       | δ <sup>18</sup> Ο<br>range<br>(‰) | δ <sup>18</sup> O<br>variation<br>(‰) | δ <sup>13</sup> C<br>range<br>(‰) | δ <sup>13</sup> C<br>variation<br>(‰) | Sr/Ca<br>range<br>(mmol/mol) | Sr/Ca<br>Variation<br>(mmol/mol) |
|--------------------|-----------------------------------|---------------------------------------|-----------------------------------|---------------------------------------|------------------------------|----------------------------------|
| M1-1D <sub>c</sub> | -0.69 to -2.23                    | 1.54                                  | -3.51 to -5.96                    | 2.45                                  | 9.30-9.66                    | 0.36                             |
| M1-1E <sub>e</sub> | -0.84 to -2.41                    | 1.57                                  | -3.37 to -5.47                    | 2.10                                  | 9.07-9.62                    | 0.55                             |
| M1-2B <sub>a</sub> | -0.77 to -1.95                    | 1.18                                  | -3.23 to -5.28                    | 2.05                                  | 9.30-9.70                    | 0.40                             |
| M1-2E              | -0.81 to -2.38                    | 1.57                                  | -3.17 to -5.21                    | 2.04                                  | 9.24-9.67                    | 0.43                             |
| $M1-1G_b$          | -1.41 to -2.25                    | 0.84                                  | -2.43 to -4.04                    | 1.61                                  | 8.84-9.31                    | 0.47                             |



Figure 18: Geochemical  $\delta^{18}$ O, Sr/Ca and  $\delta^{13}$ C records for samples M1-1D<sub>c</sub>, M1-1E<sub>e</sub>, M1-2B<sub>a</sub>, M1-2E plotted with depth. Plots are ordered from older to youngest samples from left to right.

# 4. Discussion

#### 4.1 Coral mineralogy composition

XRD analysis for the samples studied (M1-1D<sub>c</sub>, M1-1E<sub>e</sub>, M1-2B<sub>a</sub>, and M1-2E) are similar and consistent to the spectral analysis done by Downs (2006) using a pure aragonite standard. The analysis indicates the samples studied are 100% aragonite in composition. The possibility of secondary aragonite was not tested in this study, however, secondary aragonite is expected to yield both high  $\delta^{18}$ O and Sr/Ca (Sayani et al., 2011) and this was not the case for the latter. Additionally Greer and Swart (2006) already concluded the presence of secondary aragonite is negligible based on Fluorescence and SEM analyses done in coral samples from the same reef in Enriquillo Valley. The test sample (M1-1G<sub>b</sub>) also shows 100% aragonitic composition suggesting this sample was not recrystallized but affected in other ways. The anomaly coloration may have been caused by sediments deposited in the interstices of the coral skeleton during storm events or simply by the stress the coral was subjected to.

#### 4.2 Montastraea sp. Growth rates

The estimated average growth rates for each samples  $(M1-1D_c, M1-1E_e, M1-2B_a, and M1-$ 2E), located at depths between 16.5-18.0 meters below the paleo sea level at 8.5kya, are much lower than values reported form modern corals of the species Montastraea sp. 6.5 mm/yr in Looe Key (Smith, 2006) and Bonaire 6.6-10.0mm/yr (Giry et al, 2011) at unknown depths. The possible difference in depth and zonation, which plays a major role in Montastraea sp. growth rates (Hubbard and Scaturo, 1985; Morelock et al., 2000; Hubbard et al., 2008), can account to differences in growth rate estimates between studies. At least, in this study, the effect of the depth component affecting the growth of these corals is present. It seems that at the base of the reef, growth rates were much faster and as the coral column grew up, its rates slowed. The average growth rate results obtained in this study are very similar and consistent with another study done in the same coral species (Montastraea sp.) of the same reef (Cañada Honda) at the same facies (M1) by Cuevas et al (2005). Cuevas et al (2005) reported average growth rates values of 2.6-3.2mm/yr while this project measured average growth rates of  $2.07 \pm 0.14$  to  $3.55 \pm 0.37$  mm/yr. They are also similar to a modern and fossil sample analyzed in Dry Tortugas by Smith (2006) (3.0 mm/yr) at approximately 13 m deep. The causes for these slow rates are not further explained. Sample M1-1Gb show the lowest average growth rate of the study (2.07mm/yr). Located just above sample M1-1G<sub>b</sub> are the mud and rubble deposits named as the Mad Layer (Fig. 7). The low growth rates in the sample may be the result of massive inputs of sedimentation represented by the Mad Layer.

Another component affecting growth rates of these corals can be due the effects of high turbid waters as consequence of high sediment influx. At some point, light reaching the corals and the symbiotic photosynthetic organism *Zooxanthellae sp.* may be limited thus inhibiting photosynthesis and calcification rate respectively (Hubbard and Scaturo, 1985).

#### 4.3 Sedimentation rate estimates

Sedimentation rates estimated from the eight sections (S1-S8) of sample M1-2B<sub>a</sub> vary between average values of  $2.06 \pm 0.30$  mm/yr. The results in this study agree with sedimentation rates of  $1.67 \pm 0.05$  mm/yr estimated from *Montastraea sp.* corals in M2 done by Hubbard et al., (2004). To compare these sediment rates to modern sedimentation rates from other studies (Rogers, 1990), a conversion of these values to mg cm<sup>-2</sup> d<sup>-1</sup> can be done using equation 11, by making simple conversions and assuming all of the incoming sediments of Enriquillo are of carbonate provenance. Cuevas et al. (2005), estimated that non-carbonate material in the reef in Cañada Honda are very low (<10%), implying that the rest of it is of carbonate provenance from the surrounding mountain ranges, making this assumption not far from accurate. Converted values yield sedimentation rates of  $1.53 \pm 0.22$  mg cm<sup>-2</sup> d<sup>-1</sup> which are higher than modern sedimentation rates estimated in reefs from Discovery Bay, Jamaica (0.5-1.1 mg cm<sup>-2</sup> d<sup>-1</sup>) and lower than modern sedimentation rates in Puerto Rico (2.5-2.6 mg cm<sup>-2</sup> d<sup>-1</sup>) by Rogers (1990).

Sediment rates are equal or almost equal to growth rates estimated in this study, suggesting that corals were keeping up with the upcoming sediment influx. These sedimentation events occur in episodes of 3-8 years consistent with ENSO/NAO. The consequent rainfall caused by this climate phenomena, could be responsible for the high sediment influx that led to developing the pancake morphology.

Sedimentation rate 
$$\left(\frac{mg}{cm^2*d}\right) =$$
 Sedimentation rate  $\left(\frac{cm}{d}\right)$  \* sediment density  $\left(\frac{mg}{cm^3}\right)$  (11)

### 4.4 Radiogenic dating and $\delta^{234}U$

U/Th dates obtained from the samples (M1-1D<sub>c</sub>, M1-1E<sub>e</sub>, M1-2B<sub>a</sub>, M1-2E, M1-1A<sub>b</sub>, M1-4A<sub>e</sub>) show that these skeletons were precipitated early in the Holocene Epoch (8036 ± 26 to 8910 ± 28 yr B.P.). These dates are consistent to those reported by Hubbard et al. (2004) ranging from 8.400-8.900 yr B.P. (See appendix 11). As expected, pieces cut from the same colony have younger dates following the vertical growth of the columnar assemblage. Also, as expected, the ages of corals located at stratigraphic similar levels but different lateral positions have different ages and coral samples from M1-2 (southward from M1-1) are considerably older than M1-1. M1-4A<sub>e</sub> was expected to be the youngest coral, due to its stratigraphic position (Fig. 17) but this was not the case. M1-4A<sub>e</sub> is older than samples M1-1D<sub>c</sub> and M1-1E<sub>e</sub> but younger than M1-2B<sub>a</sub>, M1-2E.

 $\delta^{234}$ U values of the studied corals are lower than those expected from open seawater (Fig. 19). Similar  $\delta^{234}$ U values were also obtained by Edwards (1988) in coral samples from Cañada Honda and other corals from the Enriquillo Valley. Edwards (1988) interpreted a trend in which values seems to be getting closer to seawater (saltier) composition as they become younger, similar to the samples in this study. The decrease in  $\delta^{234}$ U from the samples in this study to the samples from Edwards (1988) may indicate events of freshwater influx which may be due to storm events as evident from the Mad Layer deposits.



Figure 19: Plot of  $\delta^{234}$ U concentration relative to time. The Enriquillo Valley fossil corals in this study (M1-1D<sub>c</sub>, M1-1E<sub>e</sub>, M1-2B<sub>a</sub>, M1-2E, M1-1A<sub>b</sub>, M1-4A<sub>e</sub>) and a study from Edwards (1988) show lower  $\delta^{234}$ U concentrations relative to open ocean corals from Bonaire (Giry et al.,2012). In both studies the  $\delta^{234}$ U concentration in the corals follow a trend in which values seems to be getting closer to seawater composition as they become younger. In the studied samples the values show a similar trend but the data is more scattered. Range of seawater values (dashed lines) and trends (blue lines) are marked (Modified from Edwards, 1988).

#### 4.5 Stable Isotopes

 $\delta^{18}$ O and  $\delta^{13}$ C values from *Monstrastraea sp.* obtained in this study are compared to values from modern marine corals (Tucker and Wright, 1990; Smith, 2006) and Enriquillo Valley fossil corals from other studies (Greer and Swart, 2006), (Fig. 20),  $\delta^{18}$ O values obtained from the corals in this study (-0.69 to -2.41‰) are considerably heavier relative to values for modern corals ranging approximately from -3.0 to -6.0 (Tucker and Wright, 1990; Smith, 2006) and -1.94 to -4.94 from other studies in the Enriquillo Valley of (Greer and Swart, 2006). These results support the idea by Greer and Swart (2006) that the enrichment in  $\delta^{18}$ O of the Enriquillo Holocene corals relative to modern values is probably due to the corals being exposed to a high salinity environment. However, samples from Greer and Swart (2006) were younger (5.3-7.2kya B.P) and at shallower depths (13.44 - 15.57 feet below sea level). Then it is possible that samples in this study (8.0-8.9kya B.P) at depths of 31.5-33.0 feet below sea level, suffered from a more severe saline conditions.  $\delta^{18}$ O and  $\delta^{13}$ C patterns suggest interannual variability in a decadal and multi-decadal oscillations for samples under study in records of approximately 30-40 years. The magnitude of the variations obtained for  $\delta^{18}$ O (1.18-1.57‰) are compared to other studies in Fig. 21. The values in this study are relatively lower compared to those obtained by Greer and Swart (2006) (1.51-3.00‰), Smith (2006) (~2.5‰) and Eemian sample from Winter et al. (2003). However, they are similar (~1.0-1.5‰) to fossil corals (2.9kya B.P.) studied by Felis et al. (2004) and modern corals from Cobb et al., (2013) and Winter et al., (2000). The opposite was expected, as it is known that the seasonality in the past was higher that the seasonality today (Winter et al., 2003; Giry et al., 2012).



Figure 20:  $\delta^{18}$ O vs.  $\delta^{13}$ C values obtained for samples M1-1D<sub>c</sub>, M1-1E<sub>e</sub>, M1-2B<sub>a</sub>, M1-2E, M1-1A<sub>b</sub> and sample M1-1G<sub>b</sub>. Expected  $\delta^{18}$ O vs.  $\delta^{13}$ C values of modern marine corals are shown in beige (Tucker and Wright, 1990). Maximum and minimum  $\delta^{18}$ O vs.  $\delta^{13}$ C values from fossil corals in Dry Tortugas (4.2-5.1kya B.P.) (Smith, 2006) are shown in yellow and from Enriquillo Valley (5.3-7.2kya B.P.) (Greer, 2001; Greer and Swart, 2006) are plotted in brown.



Figure 21:  $\delta^{18}$ O vs. age in corals from this study and other studies in the Caribbean. Negative ages indicate age B.P..  $\delta^{18}$ O variations are given for each sample and sample M1-1G<sub>b</sub> is plotted as a hollowed icon because its age is extrapolated to have been precipitated 8000 yr B.P. Blue line represents a trend, interpreted to be the Holocene Sea Level Curve. Holocene sub-divisions were added as proposed by Walker et al. (2012).

#### 4.6 Trace Elemental Concentrations

Analyzed Sr/Ca ratios in this study are compared to Caribbean Diploria sp. samples (6.2kya B.P. to modern) in Bonaire (Giry et al., 2012), Monstrastraea sp. samples (5.1kya B.P. to modern) in Dry Tortugas (Smith, 2006) and modern Monstrastraea sp. samples in Parguera, Puerto Rico (Winter et al., 2003) as seen in Fig. 22. It is understood that comparing geochemical data with corals from other genus is not optimal, however, Sr/Ca ratio records in the Caribbean on fossil corals that grew in waters that have close to similar SST (Giry et al., 2011) are very scarce. Mean Sr/Ca results in this study are relatively higher (9.40-9.50 mmol/mol) than modern samples (8.90-9.20 mmol/mol), mid Holocene samples (9.18-9.28 mmol/mol) and Eemian sample (9.35 mmol/mol) from the locations mentioned above. Although, secondary aragonite alteration causes high Sr/Ca ratios (Enmar et al., 2006; Hendy et al., 2007; Sayani et al., 2011), this is not a likely scenario for the studied corals (see section 4.1). It is possible that the high Sr/Ca ratio relative to modern corals have been produced by input of strontium from groundwater and/or high sediment influx. Discharge of sulfurous spring water associated with residual Pliocene volcanism towards the southern part of the lake (La Zurza, Borbollones and others) may have been a source of strontium (Mann and Lawrence, 1991; Buck et al, 2005). Other possibilities for higher Sr/Ca ratios are slower calcification rates estimated in these samples (Smith 2006, Inoue et al., 2007), sampling an off axis (non-corallite) section of the coral (Rosenthal and Linsley, 2006) or simple contamination during sample collection and/or processing.

Variations in Sr/Ca ratios range from 0.36 to 0.55 mmol/mol and are relatively higher than Bonaire Sr/Ca ratio variations (0.15-0.30 mmol/mol) in corals from the last 4.2kya B.P but close to mid Holocene corals from 6.2kya B.P., all reported by Giry et al. (2012). Sr/Ca variations in the studied corals are also higher than variations (0.19 mmol/mol) in modern samples from Parguera, but similar to Eemian corals (0.40 mmol/mol) of Mona Island, all reported by Winter et al. (2003). These result are consistent to seasonality variations since the Eemian (Winter et al.,2003; Felis et al., 2004).



Figure 21: Sr/Ca vs. age in corals from this study and other studies in the Caribbean. Negative ages indicate age B.P..  $\delta^{18}$ O variations are given for each sample and sample M1-1G<sub>b</sub> is plotted as a hollowed icon because its age is extrapolated to have been precipitated 8000 yr B.P. Blue line represents a trend, interpreted to be the Holocene Sea Level Curve. Holocene sub-divisions were added as proposed by Walker et al. (2012).

## 4.7 SST from $\delta^{18}O$

SST- $\delta^{18}$ O derived temperatures calculated for studied samples using the equation derived by Leder et al., (1996) are plotted in (Fig. 23). These temperatures range from 8-15°C which can be considered too cold relative to scleractinean corals in the Caribbean where temperatures vary, in general, from 18-30°C (Felis and Pätzold, 2004). Modern *Monstrastraea sp.* SST- $\delta^{18}$ O derived temperature from Dry Tortugas (Smith, 2006) show temperatures that range from 22.9-30°C and from La Parguera, Puerto Rico (Winter et al., 2000; Winter et al., 2003) temperatures that range from 26-30°C. Fossil *Monstrastrea sp.* temperatures from Dry Tortugas indicate changes in temperatures from -1.9 to +1.5 at 5.1kya B.P. relative to modern samples in the same location. Accounting for these temperature changes, Dry Tortugas show SST no colder than 21°C. Temperatures obtained from coral samples in Enriquillo Valley produced by Greer and Swart (2006) is reported to be ~12.7°C. These values fall within the range obtained in this study and agree that this is inconsistent with temperature changes in the region (Greer and Swart, 2006). Winter et al (2003) sample from the last interglacial period showed temperatures from 22.5-32.0°C, which are temperatures warmer than the ones obtained, this also show increased seasonality relative to modern corals and samples in this study.

According to Leder et al (1996), a change in 1‰ of  $\delta^{18}$ O represents a change in temperature of approximately 4°C. That means that variations of  $\delta^{18}$ O in this study (-0.69 to -2.41‰) show temperature changes of roughly 7°C in an interval of 8.0-8.4kya. Such a drastic change in temperature has not been recorded during this period (Fensterer et al., 2013), not even during the major 8.2kya cooling event (2-3°C) (Thomas et al., 2007; Wiersma, 2008). This means, that salinity variations have a more prominent impact in  $\delta^{18}$ O from these samples than temperature variation in the water (Greet and Swart, 2006). This also implies that salinities in Enriquillo Bay during this period were almost double the amount compared to modern seawater.

#### 4.8 SST from Sr/Ca

With slightly higher Sr/Ca ratios in this study, it is expected that temperatures will be slightly colder (Rosenthal and Linsley, 2006). SST-Sr/Ca derived temperatures were calculated using Sr/Ca calibration equations 6-10 but only SST calculated from calibration equations 7 and 9 were plotted in (Fig. 23). It is understood that temperatures calculated from SST-Sr/Ca are highly dependent on the location (Saenger et al. 2008) and that a calibration from Enriquillo, where this corals formed, is required, however such place no longer exists. Because of this, possible analogues such as the Red Sea (Felis et al., 2004) that may have a similar environment to Enriquillo Bay and Bonaire (Giry et al., 2011) that shared similar SST are compared to other Sr/Ca in open marine waters (Fig. 24). Calculated SST using calibration produced by Swart et al. (2002), Flannery et al. (2013) and Smith (2006) from open marine waters yield colder and more variable temperatures (12-26°C respectively) than those from Giry et al. (2011) (20.0-26.0°C) and Felis et al. 2004 (20.3-27.6°C). Both Bonaire and Red Sea calibration show temperatures appropriate for coral skeletons (18-30°) (Felis and Pätzold, 2004). According to the variation in Sr/Ca, a change of approximately 6-7°C took place and such a change as not been recorded during this time period (8.0-8.4kya B.P.) (Fensterer et al., 2013). This big change could be due to influence of fresh water in this system which has already been stablished by  $\delta^{234}$ U (see section 4.4). Decadal to multidecadal pulses of freshwater from storm precipitation (Greer and Swart, 2006) combined with spring water seepage into these waters (Buck et al., 2005), could be responsible for the high variability in Sr/Ca ratio and therefore wide range in temperature.



Figure 23: Stacked SST record estimated from  $\delta^{18}$ O using Leder et al. (1996) and Sr/Ca using Giry et al. (2011) and Felis et al. (2004) respectively for samples M1-1D<sub>c</sub>, M1-1E<sub>e</sub>, M1-2B<sub>a</sub> and M1-2E with time. U/Th radiogenic dates are given for each sample. Refer to appendix 12-14 for individual plots.



Figure 24: Sr/Ca ratios vs. SST calculated from calibration equations 6-10 in sample M1-2B<sub>a</sub> M1-1D<sub>c</sub>, M1-1E<sub>e</sub>, M1-2B<sub>a</sub> and M1-2E. This graphs shows maximum and minimum temperatures obtained from each curve. Hollowed circles have been identified as outlier values and not considered for interpretations.

## 4.9 SST correlation between different proxies ( $\delta^{18}O$ and Sr/Ca)

Correlation indexes (R) between SST-derived from  $\delta^{18}$ O and Sr/Ca for the samples under study vary between (0.02-0.85). The lowest values of 0.02 (M1-1E<sub>e</sub>) and 0.20 (M1-2B<sub>a</sub>) can be attributed to each variable reacting to a different parameter. A possibility is that specific events of salinity variations (Fig temp) might have drastically altered the chemistry of the  $\delta^{18}$ O but not strongly affecting the chemistry of Sr/Ca (Greer and Swart, 2006). Higher correlations of 0.85 (M1-1D<sub>c</sub>) and 0.72 (M1-2E) are higher than modern *Monstrastraea sp.* samples in Dry Tortugas (0.56-0.67) by Smith (2006). Smith (2006) attributed the correlation between the variables to a reaction of each to a different forcing other than temperature, which seems to be the case in this samples in this study. Still, it is considered that Sr/Ca is reacting to temperature, even though; variations are influenced by changes in the water chemistry from seawater.

## 5. Conclusion

The reef developed in Enriquillo Bay during the early to middle Holocene have unique qualities rarely seen in other reef ecosystems. Arid climate combined with high carbonate sediment influx, preserved the pristine composition of the coral skeleton and adapted their morphology for survivability. Corals in the Massive Zone 1 dated from 8.9-8.0 kya B.P. in this study consistent with radiocarbon dates obtained by Hubbard et al. (2004) in the same zone. From the four samples analyzed, two were dated near 8.3kya while the other two dated near 8.0kya which represents a 300yr gap. The samples under study integrity of the coral skeleton of the analyzed samples remains intact as 100% aragonite indicating that these samples suffered little or no alteration therefore discarding diagenesis as an influencing variable in the results obtained.

Calculated growth rates in this were lower compared to open marine settings corroborating Greer and Swart (2006) theory, that high sediment conditions were present at the times these corals were forming and that Cañada Honda fossil reef reflects severe stress conditions due to high sediment influx. Between the 300 year gap, there is a slight increase in growth rate that shows more suitable conditions for aragonite precipitation, possibly to warmer temperatures since the 8.2kya cooling event. The pancake morphology and higher sedimentation rates compared to open marine settings indicate severe stress conditions during reef development. The similarities between sedimentation rates and growth rates may indicate that corals were able to keep up with the sediment influx; however, the veracity of this hypothesis must be tested by calculating sedimentation rates in more than one sample.

Isotopic  $\delta^{18}$ O enrichment and high variability of these values related to expected variations for this period, in this bay seems to respond to high salinity environments as pointed by Greer and Swart, (2006). The magnitude of  $\delta^{18}$ O variations in this study shows similarities to variations of younger corals from the late Holocene and modern times. It is possible that salinity caused variations in  $\delta^{18}$ O combined with temperature caused variations in  $\delta^{18}$ O, produced seasonalities that are not compatible with the variations expected to be produced by known seasonality records. The temperature variations of 5-7°C suggested by the isotopic data are most likely due to massive events of freshwater influx coming into the small lake from the prominent Sierra the Neiba and Sierra the Bahoruco. Uranium isotopes ( $\delta^{234}$ U) corroborates that these samples were subject to freshwater influx backed up by evidence of storm deposits such as the Mad Layer. Measurements of Sr/Ca ratio are enriched relative to all fossil corals from the Eemian and mid-Holocene and also to modern samples. As SST and Sr/Ca ratios are inversely related (Swart et al., 2002), this implies that temperature values relative to the previously mentioned periods are colder, even colder than the sample from the Last Interglacial Period studied by Winter et al (2003). There are various possibilities to the Sr/Ca enrichment: 1) Corals grew in colder waters as expected from the early Holocene therefore incorporating more Sr into their skeleton; 2) Strontium rich sulfurous groundwater from springs associated with Pliocene volcanisms; 3) Slow growth rates due to limitations of photosynthesis and calcification of the coral skeleton; 4) Methodical errors such as sampling an off axis section of the coral and contamination during the sample processing could lead to higher Sr/Ca ratios.

Greer and Swart (2006) made a fair suggestion saying that SST calculations could be resolved using Sr/Ca ratios. However, it is clear that estimated absolute SSTs are not necessarily accurate. While  $\delta^{18}$ O is primarily affected by changes in salinity rather than temperature, the temperature driven Sr/Ca shows to be strongly influenced by changes in the water chemistry caused by freshwater inflow. Another problem is that in order to obtain accurate temperatures, a calibration done with modern samples growing in the same environment is required, but since such place does not exist anymore, this is impossible to achieve. Consequently, the only way is to rely on analogue calibrations or calibrate using a coral sample from Barahona Bay southeast of Enriquillo. However trends in temperature variation are consistent with climate variations during the time period. Both proxies follow a trend similar to the Holocene sea level curve when compared from records obtained in other studies, suggesting that they responded to increased temperatures during this time period.

Both  $\delta^{18}$ O values and Sr/Ca measurements variations in both suggest temperature variations of approximately 5-7°C. This variation is inconsistent with any record produced during this period (Greer and Swart, 2006), not even during the drastic 8.2kya cooling event (2-3°C) (Thomas et al., 2007; Wiersma, 2008). Yet, these variations are not necessarily unexpected since surface waters combined with ground waters stored in the massive mountain chains surrounding the relative small lake will account for such drastic temperature records. The anomalous variations show the sensitivity to other variables (salinity and freshwater inflow), yet, low correlation index (R) in some samples show that  $\delta^{18}$ O values and Sr/Ca are reacting to different mechanisms in some

cases. This study was unable to address any cyclicity patterns and a more continuous and longer record of  $\delta^{18}$ O values and Sr/Ca is necessary.

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## Appendix



Appendix 1: Drawn transect and densitometry analysis of sample M1-1D<sub>c</sub>.





Appendix 2: Drawn transect and densitometry analysis of sample M1-1Ee.





Appendix 3: Drawn transect and densitometry analysis of sample M1-2E.





Appendix 4: drawn transect and densitometry analysis of sample M1-2B<sub>a</sub>.



Appendix 5: Densitometry analysis of test sample M1-1Gb.



Appendix 5: Drawn transect and densitometry analysis of test sample M1-1Gb.



Appendix 6: XRD analysis of sample M1-1Dc.



Appendix 7: XRD analysis of sample M1-1Ee.



Sample: M1-2E - File: José Morales-2014-8-12-M1-2E.RAW - Type: 2Th/Th locked - Start: 15.000 ° - End: 65.000 ° - Step: 0.020 ° - Step time: 1. s - Temp.: 25 °C (Room) - Time Started: 16 s - 2-Theta: 1
Operations: Background 1.000,1.000 | Background 1.000,1.000 | Smooth 0.150 | Import

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Appendix 8: XRD analysis of sample M1-2E.



Appendix 9: XRD analysis of sample M1-2Ba.



Appendix 10: XRD analysis of sample M1-1G<sub>b</sub>.





Appendix 11: Cañada Honda facies map from Hubbard et al., 2004 at the top and radiocarbon dating from Taylor et al. (1984) and Hubbard et al., 2004. at the bottom.



Appendix 12: Sea surface temperature plot for sample M1-2Ba.



Appendix 13: Sea surface temperature plot for sample M1-2E.



Appendix 14: Sea surface temperature plot for sample M1-1Dc.



Appendix 15: Sea surface temperature plot for sample M1-1E<sub>e</sub>.

|       | Sample M1-2Ba  |          |       |         |          |       |            |        |        |          |         |  |  |  |
|-------|----------------|----------|-------|---------|----------|-------|------------|--------|--------|----------|---------|--|--|--|
| Denth | Internal       |          |       | SST     |          |       | Sr/Ca      |        |        | SST      | SST     |  |  |  |
| (mm)  | Chronology(vr) | δ18Ο     | STDEV | (Leder) | δ13C     | STDEV | (Shrag)    | RSD    | STDEV  | (Giry)   | (Felis) |  |  |  |
|       |                |          |       | (°C)    |          |       | (mmol/mol) |        |        | (°C)     | (°C)    |  |  |  |
| 0     | 0.33           | -1.457   | 0.039 | 11.9142 | -4.08286 | 0.004 | 9.45609    | 0.0667 | 0.0063 | 22.8782  | 22.193  |  |  |  |
| 1     | 0.66           | -1.053   | 0.017 | 10.0885 | -4.27986 | 0.009 | 9.558533   | 0.0667 | 0.0064 | 20.82934 | 20.477  |  |  |  |
| 2     | 1              | -1.433   | 0.032 | 11.8057 | -4.61586 | 0.011 | 9.55192    | 0.0667 | 0.0064 | 20.96161 | 20.588  |  |  |  |
| 3     | 1.25           | -1.922   | 0.016 | 14.0155 | -5.20186 | 0.01  | 9.422586   | 0.0667 | 0.0063 | 23.54828 | 22.754  |  |  |  |
| 4     | 1.5            | -1.658   | 0.015 | 12.8225 | -4.31086 | 0.006 | 9.431997   | 0.0667 | 0.0063 | 23.36007 | 22.596  |  |  |  |
| 5     | 1.75           | -1.518   | 0.023 | 12.1898 | -4.82086 | 0.011 | 9.365639   | 0.0667 | 0.0062 | 24.68722 | 23.708  |  |  |  |
| 6     | 2              | -1.633   | 0.02  | 12.7095 | -4.61086 | 0.009 | 9.497335   | 0.0667 | 0.0063 | 22.0533  | 21.502  |  |  |  |
| 7     | 2.33           |          |       |         |          |       | 9.411952   | 0.0667 | 0.0063 | 23.76097 | 22.932  |  |  |  |
| 8     | 2.66           | -1.279   | 0.007 | 11.1098 | -4.69286 | 0.007 | 9.389955   | 0.0667 | 0.0063 | 24.20089 | 23.301  |  |  |  |
| 9     | 3              | -1.442   | 0.028 | 11.8464 | -4.52586 | 0.015 | 9.410635   | 0.0667 | 0.0063 | 23.78731 | 22.954  |  |  |  |
| 10    | 3.5            | -0.87    | 0.023 | 9.26153 | -4.18186 | 0.004 | 9.414237   | 0.0667 | 0.0063 | 23.71527 | 22.894  |  |  |  |
| 11    | 4              | -1.086   | 0.024 | 10.2376 | -5.07186 | 0.005 | 9.527974   | 0.0667 | 0.0064 | 21.44052 | 20.989  |  |  |  |
| 12    | 4.5            | -1.176   | 0.017 | 10.6443 | -4.28086 | 0.01  | 9.502464   | 0.0667 | 0.0063 | 21.95071 | 21.416  |  |  |  |
| 13    | 5              | -0.771   | 0.007 | 8.81415 | -4.41786 | 0.011 | 9.473099   | 0.0667 | 0.0063 | 22.53802 | 21.908  |  |  |  |
| 14    | 5.5            | -1.18    | 0.024 | 10.6624 | -4.58786 | 0.011 | 9.560766   | 0.0667 | 0.0064 | 20.78468 | 20.439  |  |  |  |
| 15    | 6              | -0.792   | 0.017 | 8.90905 | -4.04886 | 0.002 | 9.482728   | 0.0667 | 0.0063 | 22.34544 | 21.747  |  |  |  |
| 16    | 6.33           | -0.864   | 0.021 | 9.23442 | -4.45586 | 0.011 | 9.398491   | 0.0667 | 0.0063 | 24.03018 | 23.158  |  |  |  |
| 17    | 6.66           | -1.21    | 0.053 | 10.798  | -4.41686 | 0.007 | 9.435808   | 0.0667 | 0.0063 | 23.28383 | 22.533  |  |  |  |
| 18    | 7              | -0.931   | 0.025 | 9.53719 | -4.03686 | 0.002 | 9.481433   | 0.0667 | 0.0063 | 22.37135 | 21.768  |  |  |  |
| 19    | 8              | -1.09    | 0.044 | 10.2557 | -4.30686 | 0.004 | 9.429914   | 0.0667 | 0.0063 | 23.40172 | 22.631  |  |  |  |
| 20    | 8.33           | -1.251   | 0.036 | 10.9833 | -4.50286 | 0.007 | 9.498821   | 0.0667 | 0.0063 | 22.02358 | 21.477  |  |  |  |
| 21    | 8.66           | -0.969   | 0.035 | 9.70891 | -4.64686 | 0.011 | 9.552496   | 0.0667 | 0.0064 | 20.95009 | 20.578  |  |  |  |
| 22    | 9              | -1.186   | 0.034 | 10.6895 | -4.98586 | 0.008 | 9.510167   | 0.0667 | 0.0063 | 21.79667 | 21.287  |  |  |  |
| 23    | 9.5            | -0.98729 | 0.011 | 9.79154 | -4.13429 | 0.008 | 9.548018   | 0.0667 | 0.0064 | 21.03964 | 20.653  |  |  |  |
| 24    | 10             | -1.09129 | 0.01  | 10.2615 | -4.96229 | 0.008 | 9.494901   | 0.0667 | 0.0063 | 22.10199 | 21.543  |  |  |  |
| 25    | 11             | -1.31529 | 0.02  | 11.2738 | -4.54929 | 0.012 | 9.529276   | 0.0667 | 0.0064 | 21.41447 | 20.967  |  |  |  |

Appendix 18: Geochemical analysis and calculated SST from simple M1-Ba

| 26 | 11.25 | -1.02129 | 0.007 | 9.94519 | -4.40429 | 0.006 | 9.575517 | 0.0667 | 0.0064 | 20.48965 | 20.192 |
|----|-------|----------|-------|---------|----------|-------|----------|--------|--------|----------|--------|
| 27 | 11.5  | -1.11629 | 0.016 | 10.3745 | -4.63529 | 0.008 | 9.444261 | 0.0667 | 0.0063 | 23.11479 | 22.391 |
| 28 | 11.75 | -1.41529 | 0.012 | 11.7257 | -4.25929 | 0.007 | 9.410054 | 0.0667 | 0.0063 | 23.79893 | 22.964 |
| 29 | 12    |          |       |         |          |       | 9.460241 | 0.0667 | 0.0063 | 22.79518 | 22.123 |
| 30 | 12.5  | -1.34029 | 0.029 | 11.3868 | -4.61529 | 0.009 | 9.418169 | 0.2585 | 0.0243 | 23.63663 | 22.828 |
| 31 | 13    | -1.63729 | 0.028 | 12.7289 | -5.08029 | 0.005 | 9.473476 | 0.2585 | 0.0245 | 22.53048 | 21.902 |
| 32 | 13.33 | -1.26929 | 0.014 | 11.0659 | -4.69529 | 0.005 | 9.406341 | 0.2585 | 0.0243 | 23.87317 | 23.026 |
| 33 | 13.66 | -1.52729 | 0.011 | 12.2318 | -4.17529 | 0.012 | 9.359198 | 0.2585 | 0.0242 | 24.81604 | 23.816 |
| 34 | 14    | -1.51029 | 0.027 | 12.155  | -4.46629 | 0.01  | 9.300716 | 0.2585 | 0.024  | 25.98567 | 24.795 |
| 35 | 14.25 | -1.33029 | 0.011 | 11.3416 | -4.26329 | 0.008 | 9.360864 | 0.2585 | 0.0242 | 24.78273 | 23.788 |
| 36 | 14.5  | -1.81329 | 0.022 | 13.5242 | -4.61829 | 0.009 | 9.382903 | 0.2585 | 0.0243 | 24.34193 | 23.419 |
| 37 | 14.75 | -1.66429 | 0.024 | 12.8509 | -3.90429 | 0.01  | 9.421861 | 0.2585 | 0.0244 | 23.56279 | 22.766 |
| 38 | 15    | -1.45729 | 0.017 | 11.9155 | -3.98229 | 0.006 | 9.562834 | 0.2585 | 0.0247 | 20.74332 | 20.405 |
| 39 | 15.33 | -1.66829 | 0.015 | 12.869  | -5.11529 | 0.009 | 9.544518 | 0.2585 | 0.0247 | 21.10965 | 20.712 |
| 40 | 15.66 | -1.71929 | 0.006 | 13.0995 | -4.17929 | 0.005 | 9.424081 | 0.2585 | 0.0244 | 23.51837 | 22.729 |
| 41 | 16    | -1.34829 | 0.027 | 11.4229 | -3.42929 | 0.008 | 9.429296 | 0.2585 | 0.0244 | 23.41407 | 22.642 |
| 42 | 17    | -1.19029 | 0.01  | 10.7089 | -3.75929 | 0.011 | 9.474687 | 0.2585 | 0.0245 | 22.50627 | 21.881 |
| 43 | 17.5  | -0.99229 | 0.017 | 9.81414 | -3.94429 | 0.006 | 9.459477 | 0.2585 | 0.0245 | 22.81046 | 22.136 |
| 44 | 18    | -1.35529 | 0.017 | 11.4545 | -3.94529 | 0.009 | 9.568549 | 0.2585 | 0.0247 | 20.62902 | 20.309 |
| 45 | 18.2  | -1.26029 | 0.009 | 11.0252 | -4.32629 | 0.015 | 9.683468 | 0.2585 | 0.025  | 18.33064 | 18.384 |
| 46 | 18.4  | -1.43329 | 0.015 | 11.807  | -3.91329 | 0.011 | 9.529673 | 0.2585 | 0.0246 | 21.40655 | 20.96  |
| 47 | 18.6  | -1.65529 | 0.028 | 12.8102 | -3.22629 | 0.007 | 9.523771 | 0.2585 | 0.0246 | 21.52458 | 21.059 |
| 48 | 18.8  | -1.16529 | 0.017 | 10.5959 | -3.56229 | 0.008 | 9.671619 | 0.2585 | 0.025  | 18.56761 | 18.583 |
| 49 | 19    | -1.40029 | 0.014 | 11.6579 | -4.22729 | 0.007 | 9.604468 | 0.2585 | 0.0248 | 19.91064 | 19.707 |
| 50 | 19.25 | -1.31529 | 0.028 | 11.2738 | -4.27129 | 0.006 | 9.557247 | 0.2585 | 0.0247 | 20.85506 | 20.498 |
| 51 | 19.5  | -1.52129 | 0.015 | 12.2047 | -3.65429 | 0.006 | 9.556352 | 0.2585 | 0.0247 | 20.87296 | 20.513 |
| 52 | 19.75 | -1.20229 | 0.02  | 10.7631 | -3.99529 | 0.006 | 9.624397 | 0.2585 | 0.0249 | 19.51206 | 19.374 |
| 53 | 20    | -1.39529 | 0.011 | 11.6353 | -4.52729 | 0.008 | 9.498664 | 0.2585 | 0.0246 | 22.02672 | 21.48  |
| 54 | 20.5  | -1.51829 | 0.02  | 12.1911 | -3.71129 | 0.013 | 9.520409 | 0.2585 | 0.0246 | 21.59183 | 21.115 |
| 55 | 21    | -1.24429 | 0.017 | 10.9529 | -3.96229 | 0.006 | 9.640962 | 0.2585 | 0.0249 | 19.18075 | 19.096 |
| 56 | 21.33 | -1.808   | 0.058 | 13.5004 | -4.874   | 0.013 | 9.524973 | 0.2585 | 0.0246 | 21.50055 | 21.039 |

| 57 | 21.66 | -1.514   | 0.031 | 12.1718 | -4.907 | 0.024 |          |        |        |          |        |
|----|-------|----------|-------|---------|--------|-------|----------|--------|--------|----------|--------|
| 58 | 22    | -1.62    | 0.034 | 12.6508 | -4.367 | 0.018 | 9.502335 | 0.2585 | 0.0246 | 21.95331 | 21.418 |
| 59 | 22.33 | -1.757   | 0.044 | 13.2699 | -3.998 | 0.013 | 9.604014 | 0.2585 | 0.0248 | 19.91972 | 19.715 |
| 60 | 22.66 | -1.122   | 0.048 | 10.4003 | -3.925 | 0.023 | 9.602657 | 0.2585 | 0.0248 | 19.94686 | 19.738 |
| 61 | 23    | -1.474   | 0.047 | 11.991  | -5.172 | 0.011 | 9.592931 | 0.2585 | 0.0248 | 20.14138 | 19.901 |
| 62 | 23.5  | -1.115   | 0.021 | 10.3687 | -4.358 | 0.021 | 9.608543 | 0.2585 | 0.0248 | 19.82913 | 19.639 |
| 63 | 24    | -1.945   | 0.045 | 14.1195 | -4.669 | 0.031 | 9.521144 | 0.2585 | 0.0246 | 21.57711 | 21.103 |
| 64 | 24.33 | -1.744   | 0.032 | 13.2111 | -3.986 | 0.014 | 9.568614 | 0.2585 | 0.0247 | 20.62773 | 20.308 |
| 65 | 24.66 | -1.771   | 0.052 | 13.3331 | -4.041 | 0.015 | 9.57612  | 0.2585 | 0.0248 | 20.47759 | 20.182 |
| 66 | 25    | -1.73    | 0.038 | 13.1479 | -4.136 | 0.031 | 9.562615 | 0.2585 | 0.0247 | 20.74769 | 20.408 |
| 67 | 26    | -1.642   | 0.041 | 12.7502 | -3.963 | 0.025 | 9.433875 | 0.2585 | 0.0244 | 23.3225  | 22.565 |
| 68 | 27    | -1.075   | 0.045 | 10.1879 | -4.131 | 0.023 | 9.448744 | 0.2585 | 0.0244 | 23.02512 | 22.316 |
| 69 | 27.5  | -1.472   | 0.048 | 11.982  | -4.555 | 0.021 | 9.55946  | 0.2585 | 0.0247 | 20.8108  | 20.461 |
| 70 | 28    | -1.537   | 0.064 | 12.2757 | -4.354 | 0.028 | 9.618938 | 0.2585 | 0.0249 | 19.62124 | 19.465 |
| 71 | 28.16 | -1.311   | 0.046 | 11.2544 | -4.095 | 0.01  | 9.612426 | 0.2585 | 0.0248 | 19.75148 | 19.574 |
| 72 | 28.33 | -1.205   | 0.033 | 10.7754 | -4.679 | 0.028 | 9.614642 | 0.2585 | 0.0249 | 19.70716 | 19.537 |
| 73 | 28.5  | -1.488   | 0.077 | 12.0543 | -4.072 | 0.02  | 9.5101   | 0.2585 | 0.0246 | 21.79799 | 21.288 |
| 74 | 28.66 | -1.56    | 0.054 | 12.3796 | -4.631 | 0.012 | 9.60274  | 0.2585 | 0.0248 | 19.9452  | 19.736 |
| 75 | 28.83 | -1.283   | 0.038 | 11.1279 | -4.27  | 0.019 | 9.463175 | 0.2585 | 0.0245 | 22.73649 | 22.074 |
| 76 | 29    | -1.59967 | 0.051 | 12.5589 | -4.271 | 0.018 | 9.524981 | 0.2585 | 0.0246 | 21.50038 | 21.039 |
| 77 | 29.5  | -1.25667 | 0.035 | 11.0089 | -4.652 | 0.017 | 9.544732 | 0.2585 | 0.0247 | 21.10536 | 20.708 |
| 78 | 30    | -1.49767 | 0.03  | 12.098  | -5.289 | 0.017 | 9.526269 | 0.2585 | 0.0246 | 21.47462 | 21.017 |
| 79 | 30.33 | -1.33367 | 0.048 | 11.3569 | -4.248 | 0.01  | 9.532412 | 0.2585 | 0.0246 | 21.35176 | 20.914 |
| 80 | 30.66 | -1.01167 | 0.052 | 9.90174 | -3.875 | 0.015 | 9.613676 | 0.2585 | 0.0249 | 19.72647 | 19.553 |
| 81 | 31    | -0.99867 | 0.06  | 9.84299 | -4.672 | 0.02  | 9.628163 | 0.2585 | 0.0249 | 19.43674 | 19.311 |
| 82 | 32    | -1.16767 | 0.019 | 10.6067 | -3.737 | 0.022 | 9.58699  | 0.2585 | 0.0248 | 20.2602  | 20.000 |
| 83 | 32.5  | -1.23767 | 0.027 | 10.923  | -4.459 | 0.02  | 9.632149 | 0.2585 | 0.0249 | 19.35703 | 19.244 |
| 84 | 33    | -1.55967 | 0.051 | 12.3781 | -5.173 | 0.038 | 9.450583 | 0.2585 | 0.0244 | 22.98834 | 22.285 |
| 85 | 33.5  | -1.45967 | 0.046 | 11.9262 | -4.437 | 0.02  | 9.542021 | 0.2585 | 0.0247 | 21.15958 | 20.753 |
| 86 | 34    | -1.50567 | 0.048 | 12.1341 | -4.762 | 0.013 | 9.56549  | 0.2585 | 0.0247 | 20.6902  | 20.36  |
| 87 | 34.5  | -1.43367 | 0.061 | 11.8088 | -3.868 | 0.018 | 9.4613   | 0.2585 | 0.0245 | 22.774   | 22.106 |

| 88 | 35    | -1.23167 | 0.059 | 10.8959 | -3.891 | 0.013 | 9.549549 | 0.2585 | 0.0247 | 21.00901 | 20.627 |
|----|-------|----------|-------|---------|--------|-------|----------|--------|--------|----------|--------|
| 89 | 35.33 | -1.29167 | 0.031 | 11.1671 | -4.156 | 0.016 | 9.5723   | 0.2585 | 0.0247 | 20.554   | 20.246 |
| 90 | 35.66 | -1.28367 | 0.042 | 11.1309 | -4.744 | 0.014 | 9.691229 | 0.2726 | 0.0264 | 18.17542 | 18.254 |
| 91 | 36    | -1.55467 | 0.055 | 12.3556 | -5.246 | 0.019 | 9.707466 | 0.2726 | 0.0265 | 17.85067 | 17.982 |
| 92 | 36.5  | -1.93267 | 0.068 | 14.0637 | -4.953 | 0.018 | 9.604266 | 0.2726 | 0.0262 | 19.91469 | 19.711 |

| Sample M1-2E |                |          |       |         |          |       |            |        |        |          |         |
|--------------|----------------|----------|-------|---------|----------|-------|------------|--------|--------|----------|---------|
| Depth        | Internal       |          |       | SST     |          |       | Sr/Ca      |        |        | SST      | SST     |
| (mm)         | Chronology(yr) | δ18Ο     | STDEV | (Leder) | d13C     | STDEV | (Shrag)    | RSD    | STDEV  | (Giry)   | (Felis) |
|              | 0/(1/          |          |       | (°C)    |          |       | (mmol/mol) |        |        | (°C)     | (°C)    |
| 1            | 0.33           | -1.23594 | 0.05  | 10.9152 | -4.00658 | 0.18  |            |        |        |          |         |
| 2            | 0.66           | -1.37744 | 0.06  | 11.5547 | -4.31448 | 0.19  |            |        |        |          |         |
| 3            | 1              | -1.1236  | 0.05  | 10.4075 | -4.16369 | 0.19  | 9.555074   | 0.0845 | 0.0081 | 20.89851 | 20.535  |
| 4            | 1.5            | -1.32172 | 0.06  | 11.3029 | -4.25911 | 0.19  | 9.510047   | 0.0845 | 0.008  | 21.79906 | 21.289  |
| 5            | 2              | -0.98305 | 0.04  | 9.77242 | -3.84986 | 0.17  | 9.583893   | 0.0845 | 0.0081 | 20.32213 | 20.052  |
| 6            | 2.5            | -1.21072 | 0.11  | 10.8013 | -4.04648 | -0.09 | 9.53168    | 0.0845 | 0.0081 | 21.3664  | 20.927  |
| 7            | 3              | -1.3683  | 0.05  | 11.5134 | -4.55921 | 0.18  | 9.45631    | 0.0845 | 0.008  | 22.87379 | 22.189  |
| 8            | 3.5            | -1.0794  | 0.06  | 10.2078 | -3.62178 | 0.2   | 9.432754   | 0.0845 | 0.008  | 23.34491 | 22.584  |
| 9            | 4              | -1.77791 | 0.04  | 13.3644 | -4.37508 | 0.16  | 9.35068    | 0.0845 | 0.0079 | 24.98641 | 23.958  |
| 10           | 4.16           | -1.88967 | 0.08  | 13.8694 | -4.77591 | 0.2   | 9.30163    | 0.0845 | 0.0079 | 25.9674  | 24.78   |
| 11           | 4.33           | -1.62086 | 0.08  | 12.6546 | -3.79006 | 0.21  | 9.314765   | 0.1484 | 0.0138 | 25.7047  | 24.56   |
| 12           | 4.5            | -1.77089 | 0.07  | 13.3326 | -3.98566 | 0.17  | 9.346658   | 0.1484 | 0.0139 | 25.06684 | 24.026  |
| 13           | 4.66           | -1.75755 | 0.08  | 13.2724 | -4.12359 | 0.18  | 9.297687   | 0.1484 | 0.0138 | 26.04625 | 24.846  |
| 14           | 4.83           | -1.82701 | 0.08  | 13.5863 | -3.84297 | 0.18  | 9.308689   | 0.1484 | 0.0138 | 25.82622 | 24.662  |
| 15           | 5              | -2.21061 | 0.08  | 15.3197 | -4.41331 | 0.17  | 9.341285   | 0.1484 | 0.0139 | 25.17429 | 24.116  |
| 16           | 5.33           | -2.11869 | 0.1   | 14.9044 | -4.35586 | 0.2   | 9.266196   | 0.1484 | 0.0137 | 26.67608 | 25.374  |
| 17           | 5.66           |          |       |         |          |       | 9.247604   | 0.1484 | 0.0137 | 27.04791 | 25.685  |
| 18           | 6              | -2.38413 | 0.11  | 16.1039 | -4.29841 | 0.19  | 9.266766   | 0.1484 | 0.0137 | 26.66467 | 25.364  |
| 19           | 6.33           | -2.2686  | 0.11  | 15.5818 | -4.62265 | 0.19  | 9.245633   | 0.1484 | 0.0137 | 27.08735 | 25.718  |
| 20           | 6.66           | -2.18119 | 0.1   | 15.1868 | -4.52258 | 0.21  | 9.272966   | 0.1484 | 0.0138 | 26.54068 | 25.26   |
| 21           | 7              | -1.91732 | 0.1   | 13.9944 | -4.43659 | 0.2   | 9.369748   | 0.1484 | 0.0139 | 24.60505 | 23.639  |
| 22           | 7.33           | -1.96813 | 0.09  | 14.224  | -3.98705 | 0.2   | 9.327097   | 0.1484 | 0.0138 | 25.45806 | 24.353  |
| 23           | 7.66           | -1.67417 | 0.09  | 12.8956 | -3.92638 | 0.18  | 9.25674    | 0.1484 | 0.0137 | 26.86519 | 25.532  |
| 24           | 8              | -1.41947 | 0.08  | 11.7446 | -4.53504 | 0.17  | 9.34131    | 0.1484 | 0.0139 | 25.17379 | 24.115  |
| 25           | 8.5            | -1.75546 | 0.07  | 13.2629 | -4.17555 | 0.2   | 9.430323   | 0.1484 | 0.014  | 23.39355 | 22.624  |

Appendix 18: Geochemical analysis and calculated SST from simple M1-2E

| 26 | 9     |          |      |         |          |      | 9.358604 | 0.1484 | 0.0139 | 24.82793 | 23.826 |
|----|-------|----------|------|---------|----------|------|----------|--------|--------|----------|--------|
| 27 | 9.33  | -1.40753 | 0.07 | 11.6906 | -4.64032 | 0.21 | 9.408801 | 0.1484 | 0.014  | 23.82398 | 22.985 |
| 28 | 9.66  | -1.79354 | 0.08 | 13.435  | -4.26553 | 0.19 | 9.479771 | 0.1484 | 0.0141 | 22.40457 | 21.796 |
| 29 | 10    | -1.28554 | 0.06 | 11.1393 | -4.94072 | 0.22 | 9.398085 | 0.1484 | 0.0139 | 24.03829 | 23.164 |
| 30 | 10.5  | -1.90723 | 0.09 | 13.9488 | -4.8974  | 0.22 | 9.4701   | 0.1484 | 0.014  | 22.598   | 21.958 |
| 31 | 11    | -1.53227 | 0.07 | 12.2543 | -4.03885 | 0.18 | 9.380242 | 0.1484 | 0.0139 | 24.39517 | 23.463 |
| 32 | 11.33 | -1.25811 | 0.06 | 11.0154 | -4.60592 | 0.2  | 9.433387 | 0.1484 | 0.014  | 23.33227 | 22.573 |
| 33 | 11.66 | -1.59577 | 0.08 | 12.5413 | -4.52064 | 0.2  | 9.526043 | 0.1484 | 0.0141 | 21.47914 | 21.021 |
| 34 | 12    | -1.227   | 0.06 | 10.8748 | -4.579   | 0.2  | 9.411808 | 0.1484 | 0.014  | 23.76383 | 22.935 |
| 35 | 13    | -1.13217 | 0.05 | 10.4463 | -4.73578 | 0.21 | 9.501541 | 0.1484 | 0.0141 | 21.96918 | 21.431 |
| 36 | 13.33 | -1.5899  | 0.08 | 12.5148 | -5.21483 | 0.23 | 9.537162 | 0.1484 | 0.0141 | 21.25676 | 20.835 |
| 37 | 13.66 | -1.50614 | 0.07 | 12.1362 | -4.62971 | 0.2  | 9.439213 | 0.1484 | 0.014  | 23.21574 | 22.475 |
| 38 | 14    | -1.55479 | 0.07 | 12.3561 | -4.07806 | 0.18 | 9.413372 | 0.1484 | 0.014  | 23.73256 | 22.908 |
| 39 | 14.5  | -0.80589 | 0.04 | 8.97183 | -3.82143 | 0.17 | 9.368827 | 0.1484 | 0.0139 | 24.62347 | 23.654 |
| 40 | 15    | -1.10736 | 0.05 | 10.3342 | -4.41627 | 0.2  | 9.505422 | 0.1484 | 0.0141 | 21.89155 | 21.366 |
| 41 | 15.33 | -1.5023  | 0.07 | 12.1189 | -3.99009 | 0.18 | 9.561072 | 0.1484 | 0.0142 | 20.77856 | 20.434 |
| 42 | 15.66 | -1.03386 | 0.05 | 10.002  | -4.01841 | 0.18 | 9.448507 | 0.1484 | 0.014  | 23.02985 | 22.32  |
| 43 | 16    | -0.81521 | 0.04 | 9.01395 | -4.13893 | 0.18 | 9.444032 | 0.1484 | 0.014  | 23.11935 | 22.395 |
| 44 | 17    | -1.48296 | 0.07 | 12.0315 | -4.18236 | 0.19 | 9.52448  | 0.1484 | 0.0141 | 21.51039 | 21.047 |
| 45 | 17.25 | -0.96539 | 0.05 | 9.69258 | -3.20361 | 0.14 | 9.452608 | 0.1484 | 0.014  | 22.94783 | 22.251 |
| 46 | 17.5  | -0.86306 | 0.04 | 9.23016 | -3.99291 | 0.18 | 9.41974  | 0.1484 | 0.014  | 23.6052  | 22.802 |
| 47 | 17.75 | -1.23101 | 0.06 | 10.893  | -4.4429  | 0.2  | 9.586188 | 0.1484 | 0.0142 | 20.27624 | 20.014 |
| 48 | 18    | -1.09713 | 0.05 | 10.2879 | -3.49873 | 0.16 | 9.518729 | 0.1484 | 0.0141 | 21.62542 | 21.144 |
| 49 | 18.25 | -0.87008 | 0.04 | 9.26191 | -3.99387 | 0.18 |          |        |        |          |        |
| 50 | 18.5  | -1.17295 | 0.06 | 10.6305 | -4.28707 | 0.19 |          |        |        |          |        |
| 51 | 18.75 | -1.54009 | 0.08 | 12.2897 | -3.76038 | 0.17 | 9.441903 | 0.1484 | 0.014  | 23.16193 | 22.43  |
| 52 | 19    | -0.83334 | 0.04 | 9.09585 | -3.40991 | 0.15 | 9.420898 | 0.1484 | 0.014  | 23.58205 | 22.782 |
| 53 | 19.33 | -1.59886 | 0.08 | 12.5552 | -4.02346 | 0.18 | 9.500294 | 0.1484 | 0.0141 | 21.99413 | 21.452 |
| 54 | 19.66 | -0.976   | 0.05 | 9.74057 | -3.173   | 0.14 | 9.452503 | 0.1484 | 0.014  | 22.94994 | 22.253 |
| 55 | 20    | -1.21932 | 0.06 | 10.8401 | -4.01398 | 0.18 | 9.456903 | 0.1484 | 0.014  | 22.86194 | 22.179 |
| 56 | 20.33 | -1.48303 | 0.07 | 12.0318 | -3.62116 | 0.16 | 9.426959 | 0.1077 | 0.0102 | 23.46081 | 22.681 |

| 57 | 20.66 | -1.18315 | 0.06 | 10.6767 | -3.83996 | 0.17 | 9.307252 | 0.1077 | 0.01   | 25.85496 | 24.686 |
|----|-------|----------|------|---------|----------|------|----------|--------|--------|----------|--------|
| 58 | 21    | -1.64868 | 0.08 | 12.7804 | -4.2601  | 0.19 | 9.318546 | 0.1077 | 0.01   | 25.62908 | 24.497 |
| 59 | 21.33 | -1.63772 | 0.08 | 12.7309 | -3.58769 | 0.16 | 9.239863 | 0.1077 | 0.01   | 27.20275 | 25.815 |
| 60 | 21.66 | -1.35641 | 0.07 | 11.4596 | -3.766   | 0.17 | 9.228448 | 0.1077 | 0.0099 | 27.43103 | 26.006 |
| 61 | 22    | -1.35066 | 0.07 | 11.4336 | -4.37902 | 0.19 | 9.672757 | 0.1077 | 0.0104 | 18.54485 | 18.564 |
| 62 | 22.5  | -1.60487 | 0.08 | 12.5824 | -3.78996 | 0.17 | 9.40287  | 0.1077 | 0.0101 | 23.9426  | 23.084 |
| 63 | 23    | -1.94245 | 0.09 | 14.1079 | -4.65951 | 0.21 | 9.314325 | 0.1077 | 0.01   | 25.71349 | 24.567 |
| 64 | 23.5  | -2.26594 | 0.11 | 15.5698 | -4.96204 | 0.22 | 9.36526  | 0.1077 | 0.0101 | 24.6948  | 23.714 |
| 65 | 24    | -2.18709 | 0.1  | 15.2135 | -4.29768 | 0.19 | 9.268054 | 0.1077 | 0.01   | 26.63891 | 25.342 |
| 66 | 24.5  | -1.76615 | 0.08 | 13.3112 | -3.66711 | 0.16 | 9.314936 | 0.1077 | 0.01   | 25.70127 | 24.557 |
| 67 | 25    | -1.77477 | 0.08 | 13.3502 | -4.21469 | 0.19 | 9.326523 | 0.1077 | 0.01   | 25.46954 | 24.363 |
| 68 | 25.5  | -1.88919 | 0.09 | 13.8672 | -4.04677 | 0.18 | 9.447042 | 0.1077 | 0.0102 | 23.05916 | 22.344 |
| 69 | 26    | -1.69255 | 0.08 | 12.9787 | -3.50934 | 0.15 | 9.351585 | 0.1077 | 0.0101 | 24.9683  | 23.943 |
| 70 | 26.5  | -1.46271 | 0.07 | 11.94   | -4.41269 | 0.19 | 9.362399 | 0.1077 | 0.0101 | 24.75201 | 23.762 |
| 71 | 27    | -1.74513 | 0.08 | 13.2162 | -4.29191 | 0.19 | 9.377846 | 0.1077 | 0.0101 | 24.44307 | 23.503 |
| 72 | 27.2  | -2.11647 | 0.1  | 14.8943 | -4.39551 | 0.19 | 9.339976 | 0.1077 | 0.0101 | 25.20048 | 24.138 |
| 73 | 27.4  | -1.84508 | 0.09 | 13.6679 | -3.52423 | 0.16 | 9.321742 | 0.1077 | 0.01   | 25.56516 | 24.443 |
| 74 | 27.6  | -1.41349 | 0.07 | 11.7175 | -3.79085 | 0.17 | 9.368665 | 0.1077 | 0.0101 | 24.6267  | 23.657 |
| 75 | 27.8  | -1.68146 | 0.08 | 12.9285 | -4.53186 | 0.2  | 9.418582 | 0.1077 | 0.0101 | 23.62836 | 22.821 |
| 76 | 28    | -1.92806 | 0.09 | 14.0429 | -4.58666 | 0.2  |          |        |        |          |        |
| 77 | 29    | -1.65832 | 0.08 | 12.824  | -3.84831 | 0.17 | 9.217343 | 0.1077 | 0.0099 | 27.65313 | 26.192 |
| 78 | 29.33 | -1.7025  | 0.08 | 13.0236 | -4.68356 | 0.21 | 9.221539 | 0.1077 | 0.0099 | 27.56921 | 26.122 |

|       | Sample M1-1Dc SST SST SST SST |          |       |                 |        |       |                       |                       |        |                |                 |  |  |  |
|-------|-------------------------------|----------|-------|-----------------|--------|-------|-----------------------|-----------------------|--------|----------------|-----------------|--|--|--|
| Depth | Internal                      | 5400     |       | SST             | 1420   |       | Sr/Ca                 | <b>D</b> ( <b>D</b> ) |        | SST            | SST             |  |  |  |
| (mm)  | Chronology(yr)                | 0180     | SIDEV | (Leder)<br>(°C) | 013C   | SIDEV | (Snrag)<br>(mmol/mol) | KSD                   | SIDEV  | (Giry)<br>(°C) | (Fells)<br>(°C) |  |  |  |
| 0     | 0.2                           | -1.34367 | 0.04  | 11.40204        | -4.355 | 0.022 | 9.495557              | 0.2764                | 0.0262 | 22.08885       | 21.532          |  |  |  |
| 1     | 0.4                           | -1.53267 | 0.02  | 12.25614        | -4.972 | 0.023 | 9.501903              | 0.2764                | 0.0263 | 21.96193       | 21.425          |  |  |  |
| 2     | 0.6                           | -1.95367 | 0.053 | 14.15863        | -4.969 | 0.019 | 9.485964              | 0.2764                | 0.0262 | 22.28071       | 21.692          |  |  |  |
| 3     | 0.8                           | -1.47167 | 0.046 | 11.98048        | -4.345 | 0.01  | 9.593488              | 0.2764                | 0.0265 | 20.13024       | 19.891          |  |  |  |
| 4     | 1                             | -1.07867 | 0.051 | 10.20451        | -4.098 | 0.02  | 9.630799              | 0.2764                | 0.0266 | 19.38402       | 19.266          |  |  |  |
| 5     | 1.14                          | -1.44767 | 0.048 | 11.87202        | -4.758 | 0.025 | 9.573221              | 0.2764                | 0.0265 | 20.53558       | 20.231          |  |  |  |
| 6     | 1.28                          | -1.98967 | 0.034 | 14.32132        | -4.867 | 0.014 | 9.344835              | 0.2764                | 0.0258 | 25.10331       | 24.056          |  |  |  |
| 7     | 1.42                          | -1.23067 | 0.027 | 10.8914         | -4.094 | 0.026 | 9.518597              | 0.2764                | 0.0263 | 21.62807       | 21.146          |  |  |  |
| 8     | 1.57                          | -1.09167 | 0.052 | 10.26326        | -4.56  | 0.015 | 9.536254              | 0.2764                | 0.0264 | 21.27491       | 20.85           |  |  |  |
| 9     | 1.71                          | -1.80267 | 0.037 | 13.47627        | -5.141 | 0.024 | 9.498005              | 0.2764                | 0.0262 | 22.0399        | 21.491          |  |  |  |
| 10    | 1.85                          | -1.71067 | 0.053 | 13.06052        | -4.422 | 0.011 | 9.516025              | 0.2764                | 0.0263 | 21.67951       | 21.189          |  |  |  |
| 11    | 2                             | -1.35467 | 0.045 | 11.45175        | -3.912 | 0.019 | 9.5608                | 0.2764                | 0.0264 | 20.78399       | 20.439          |  |  |  |
| 12    | 2.33                          | -1.17967 | 0.041 | 10.66093        | -4.42  | 0.03  | 9.627502              | 0.2764                | 0.0266 | 19.44996       | 19.322          |  |  |  |
| 13    | 2.66                          | -1.58967 | 0.047 | 12.51372        | -4.675 | 0.031 | 9.511936              | 0.2764                | 0.0263 | 21.76128       | 21.257          |  |  |  |
| 14    | 3                             | -2.09067 | 0.068 | 14.77774        | -5.1   | 0.027 | 9.462401              | 0.2764                | 0.0262 | 22.75198       | 22.087          |  |  |  |
| 15    | 3.5                           | -1.53067 | 0.066 | 12.2471         | -4.036 | 0.018 | 9.526234              | 0.2764                | 0.0263 | 21.47532       | 21.018          |  |  |  |
| 16    | 4                             | -1.28167 | 0.054 | 11.12187        | -4.005 | 0.029 | 9.562877              | 0.2764                | 0.0264 | 20.74245       | 20.404          |  |  |  |
| 17    | 4.16                          | -1.41267 | 0.058 | 11.71386        | -4.836 | 0.024 | 9.554793              | 0.2764                | 0.0264 | 20.90413       | 20.539          |  |  |  |
| 18    | 4.33                          | -1.42667 | 0.058 | 11.77712        | -4.509 | 0.022 | 9.496886              | 0.2764                | 0.0262 | 22.06227       | 21.509          |  |  |  |
| 19    | 4.5                           | -1.107   | 0.057 | 10.33253        | -3.919 | 0.013 | 9.527756              | 0.2764                | 0.0263 | 21.44487       | 20.992          |  |  |  |
| 20    | 4.66                          | -1.031   | 0.038 | 9.989089        | -3.724 | 0.01  | 9.541438              | 0.2764                | 0.0264 | 21.17124       | 20.763          |  |  |  |
| 21    | 4.83                          | -1.478   | 0.049 | 12.00908        | -5.175 | 0.026 | 9.468948              | 0.2764                | 0.0262 | 22.62103       | 21.977          |  |  |  |
| 22    | 5                             | -1.578   | 0.054 | 12.46098        | -4.651 | 0.026 | 9.404058              | 0.2764                | 0.026  | 23.91885       | 23.064          |  |  |  |
| 23    | 5.33                          | -1.617   | 0.029 | 12.63722        | -4.885 | 0.021 | 9.432497              | 0.2764                | 0.0261 | 23.35005       | 22.588          |  |  |  |

Appendix 19: Geochemical analysis and calculated SST from simple M1-1Dc

| 24 | 5.66  | -1.203 | 0.052 | 10.76636 | -4.706 | 0.015 | 9.482158 | 0.2764 | 0.0262 | 22.35685 | 21.756 |
|----|-------|--------|-------|----------|--------|-------|----------|--------|--------|----------|--------|
| 25 | 6     | -1.75  | 0.029 | 13.23825 | -5.362 | 0.009 | 9.423298 | 0.2764 | 0.026  | 23.53404 | 22.742 |
| 26 | 6.33  | -1.654 | 0.038 | 12.80443 | -5.485 | 0.019 | 9.427632 | 0.2764 | 0.0261 | 23.44737 | 22.669 |
| 27 | 6.66  | -1.671 | 0.055 | 12.88125 | -4.816 | 0.025 | 9.41948  | 0.2764 | 0.026  | 23.6104  | 22.806 |
| 28 | 7     | -1.333 | 0.031 | 11.35383 | -4.272 | 0.034 | 9.65883  | 0.2764 | 0.0267 | 18.8234  | 18.797 |
| 29 | 7.33  | -1.46  | 0.04  | 11.92774 | -4.295 | 0.016 | 9.544969 | 0.2764 | 0.0264 | 21.10062 | 20.704 |
| 30 | 7.66  | -1.639 | 0.045 | 12.73664 | -5.455 | 0.033 | 9.517378 | 0.2764 | 0.0263 | 21.65244 | 21.166 |
| 31 | 8     | -1.662 | 0.034 | 12.84058 | -4.702 | 0.023 | 9.504574 | 0.2764 | 0.0263 | 21.90853 | 21.381 |
| 32 | 8.2   | -1.308 | 0.051 | 11.24085 | -4.487 | 0.01  | 9.325286 | 0.2764 | 0.0258 | 25.49428 | 24.384 |
| 33 | 8.4   | -1.431 | 0.051 | 11.79669 | -5.243 | 0.022 | 9.455332 | 0.2764 | 0.0261 | 22.89337 | 22.205 |
| 34 | 8.6   | -1.495 | 0.049 | 12.08591 | -5.354 | 0.029 | 9.437977 | 0.2764 | 0.0261 | 23.24046 | 22.496 |
| 35 | 8.8   |        |       |          |        |       | 9.390732 | 0.2764 | 0.026  | 24.18536 | 23.288 |
| 36 | 9     | -1.523 | 0.049 | 12.21244 | -4.44  | 0.035 | 9.425086 | 0.2764 | 0.026  | 23.49828 | 22.712 |
| 37 | 9.16  | -1.303 | 0.023 | 11.21826 | -4.497 | 0.034 | 9.4869   | 0.2764 | 0.0262 | 22.262   | 21.677 |
| 38 | 9.33  | -1.664 | 0.033 | 12.84962 | -5.518 | 0.03  | 9.480045 | 0.2764 | 0.0262 | 22.3991  | 21.792 |
| 39 | 9.5   | -1.414 | 0.061 | 11.71987 | -4.818 | 0.028 | 9.457693 | 0.2764 | 0.0261 | 22.84615 | 22.166 |
| 40 | 9.66  | -1.432 | 0.048 | 11.80121 | -4.744 | 0.019 | 9.537693 | 0.2764 | 0.0264 | 21.24615 | 20.826 |
| 41 | 9.83  | -1.387 | 0.03  | 11.59785 | -5.571 | 0.018 | 9.584788 | 0.2764 | 0.0265 | 20.30423 | 20.037 |
| 42 | 10    | -1.801 | 0.059 | 13.46872 | -5.163 | 0.031 | 9.411887 | 0.2764 | 0.026  | 23.76226 | 22.933 |
| 43 | 10.5  | -2.042 | 0.04  | 14.5578  | -5.051 | 0.023 | 9.333233 | 0.2764 | 0.0258 | 25.33535 | 24.251 |
| 44 | 11    | -1.356 | 0.047 | 11.45776 | -4.465 | 0.022 | 9.455605 | 0.2764 | 0.0261 | 22.88789 | 22.201 |
| 45 | 11.5  | -1.452 | 0.046 | 11.89159 | -4.918 | 0.03  | 9.48676  | 0.2764 | 0.0262 | 22.2648  | 21.679 |
| 46 | 12    | -1.981 | 0.043 | 14.28214 | -5.628 | 0.016 | 9.446357 | 0.2764 | 0.0261 | 23.07287 | 22.356 |
| 47 | 12.25 | -1.431 | 0.036 | 11.79669 | -4.184 | 0.021 | 9.462292 | 0.2764 | 0.0262 | 22.75416 | 22.089 |
| 48 | 12.5  | -1.65  | 0.021 | 12.78635 | -4.484 | 0.018 | 9.531435 | 0.2764 | 0.0263 | 21.3713  | 20.931 |
| 49 | 12.75 | -1.14  | 0.042 | 10.48166 | -4.876 | 0.018 | 9.617246 | 0.2764 | 0.0266 | 19.65508 | 19.493 |
| 50 | 13    | -1.436 | 0.072 | 11.81928 | -5.388 | 0.025 | 9.510122 | 0.2764 | 0.0263 | 21.79756 | 21.288 |
| 51 | 13.25 | -1.978 | 0.049 | 14.26858 | -5.961 | 0.031 | 9.351512 | 0.2764 | 0.0258 | 24.96977 | 23.945 |
| 52 | 13.5  | -1.651 | 0.051 | 12.79087 | -4.498 | 0.017 | 9.500388 | 0.2764 | 0.0263 | 21.99224 | 21.451 |
| 53 | 13.75 | -1.958 | 0.04  | 14.1782  | -5.355 | 0.036 | 9.571722 | 0.2764 | 0.0265 | 20.56555 | 20.256 |
| 54 | 14    | -2.071 | 0.038 | 14.68885 | -5.187 | 0.027 | 9.447484 | 0.2764 | 0.0261 | 23.05031 | 22.337 |

| 55 | 14.2  | -1.91822 | 0.033 | 13.99845 | -4.51244 | 0.025 | 9.446504 | 0.2764 | 0.0261 | 23.06992 | 22.353 |
|----|-------|----------|-------|----------|----------|-------|----------|--------|--------|----------|--------|
| 56 | 14.4  | -1.43022 | 0.036 | 11.79317 | -4.21544 | 0.018 | 9.543273 | 0.2764 | 0.0264 | 21.13453 | 20.732 |
| 57 | 14.6  | -1.26622 | 0.046 | 11.05206 | -4.45644 | 0.02  | 9.482288 | 0.0564 | 0.0053 | 22.35424 | 21.754 |
| 58 | 14.8  | -1.49622 | 0.022 | 12.09143 | -4.96844 | 0.034 |          |        |        |          |        |
| 59 | 15    | -2.07522 | 0.046 | 14.70793 | -5.49344 | 0.014 | 9.353492 | 0.0564 | 0.0053 | 24.93017 | 23.911 |
| 60 | 15.25 | -1.99822 | 0.06  | 14.35997 | -4.62944 | 0.032 | 9.391195 | 0.0564 | 0.0053 | 24.17609 | 23.28  |
| 61 | 15.5  | -1.78722 | 0.028 | 13.40646 | -3.83944 | 0.019 | 9.396211 | 0.0564 | 0.0053 | 24.07579 | 23.196 |
| 62 | 15.75 | -1.39122 | 0.032 | 11.61693 | -4.76544 | 0.011 | 9.381607 | 0.0564 | 0.0053 | 24.36787 | 23.44  |
| 63 | 16    | -1.84422 | 0.038 | 13.66404 | -5.12844 | 0.016 | 9.388219 | 0.0564 | 0.0053 | 24.23562 | 23.33  |
| 64 | 16.16 | -2.23322 | 0.031 | 15.42193 | -5.34844 | 0.024 | 9.380481 | 0.0564 | 0.0053 | 24.39039 | 23.459 |
| 65 | 16.33 | -2.20622 | 0.039 | 15.29992 | -4.55244 | 0.022 |          |        |        |          |        |
| 66 | 16.5  | -1.89222 | 0.023 | 13.88095 | -5.14644 | 0.007 | 9.479102 | 0.0564 | 0.0053 | 22.41797 | 21.807 |
| 67 | 16.66 | -1.72722 | 0.051 | 13.13532 | -5.25144 | 0.009 | 9.386445 | 0.0564 | 0.0053 | 24.27111 | 23.359 |
| 68 | 16.83 | -2.19322 | 0.027 | 15.24117 | -5.33644 | 0.036 | 9.37708  | 0.0564 | 0.0053 | 24.45841 | 23.516 |
| 69 | 17    | -2.07322 | 0.053 | 14.69889 | -5.08444 | 0.035 | 9.430496 | 0.0564 | 0.0053 | 23.39009 | 22.622 |
| 70 | 17.5  | -1.56422 | 0.058 | 12.39872 | -5.00144 | 0.028 | 9.475324 | 0.0564 | 0.0053 | 22.49353 | 21.871 |
| 71 | 18    | -1.69422 | 0.065 | 12.98619 | -5.01644 | 0.007 | 9.421902 | 0.0564 | 0.0053 | 23.56197 | 22.765 |
| 72 | 18.33 | -2.14122 | 0.072 | 15.00618 | -5.02244 | 0.021 |          |        |        |          |        |
| 73 | 18.66 | -1.56222 | 0.049 | 12.38968 | -4.27044 | 0.031 | 9.437965 | 0.0564 | 0.0053 | 23.24071 | 22.496 |
| 74 | 19    | -1.25822 | 0.062 | 11.01591 | -4.30344 | 0.031 | 9.473491 | 0.0564 | 0.0053 | 22.53019 | 21.901 |
| 75 | 20    | -1.17622 | 0.047 | 10.64535 | -4.39644 | 0.022 | 9.491055 | 0.0564 | 0.0054 | 22.17889 | 21.607 |
| 76 | 20.33 | -1.27622 | 0.055 | 11.09725 | -4.48644 | 0.011 | 9.474971 | 0.0564 | 0.0053 | 22.50057 | 21.877 |
| 77 | 20.66 | -1.90522 | 0.038 | 13.9397  | -5.65844 | 0.011 | 9.545142 | 0.0564 | 0.0054 | 21.09715 | 20.701 |
| 78 | 21    | -1.30322 | 0.055 | 11.21926 | -4.26744 | 0.027 | 9.442936 | 0.0564 | 0.0053 | 23.14128 | 22.413 |
| 79 | 21.5  | -1.61422 | 0.051 | 12.62467 | -5.15844 | 0.01  | 9.473962 | 0.0564 | 0.0053 | 22.52077 | 21.893 |
| 80 | 22    | -1.67922 | 0.054 | 12.91841 | -5.18844 | 0.021 | 9.453889 | 0.0564 | 0.0053 | 22.92223 | 22.23  |
| 81 | 22.25 | -1.61422 | 0.047 | 12.62467 | -5.23044 | 0.016 | 9.378695 | 0.0564 | 0.0053 | 24.42609 | 23.489 |
| 82 | 22.5  | -1.62622 | 0.043 | 12.6789  | -4.29044 | 0.015 | 9.474281 | 0.0564 | 0.0053 | 22.51437 | 21.888 |
| 83 | 22.75 | -1.03622 | 0.054 | 10.01269 | -4.28144 | 0.008 | 9.492715 | 0.0564 | 0.0054 | 22.14571 | 21.579 |
| 84 | 23    | -1.43022 | 0.056 | 11.79317 | -4.95444 | 0.032 | 9.514961 | 0.0564 | 0.0054 | 21.70079 | 21.207 |
| 85 | 23.2  | -1.79989 | 0.037 | 13.4637  | -4.759   | 0.02  | 9.458587 | 0.0564 | 0.0053 | 22.82825 | 22.151 |

| 86  | 23.4  | -1.15189 | 0.045 | 10.53539 | -3.888 | 0.012 | 9.412984 | 0.0564 | 0.0053 | 23.74031 | 22.915 |
|-----|-------|----------|-------|----------|--------|-------|----------|--------|--------|----------|--------|
| 87  | 23.6  | -1.06689 | 0.041 | 10.15128 | -4.392 | 0.022 | 9.490968 | 0.0564 | 0.0054 | 22.18065 | 21.609 |
| 88  | 23.8  | -1.26489 | 0.042 | 11.04604 | -5.075 | 0.015 | 9.554728 | 0.0564 | 0.0054 | 20.90544 | 20.541 |
| 89  | 24    | -1.41189 | 0.021 | 11.71033 | -4.733 | 0.02  | 9.466609 | 0.0564 | 0.0053 | 22.66782 | 22.017 |
| 90  | 24.2  | -1.69889 | 0.019 | 13.00728 | -4.338 | 0.012 | 9.439924 | 0.0564 | 0.0053 | 23.20152 | 22.464 |
| 91  | 24.4  |          |       |          |        |       |          |        |        |          |        |
| 92  | 24.6  | -1.09289 | 0.052 | 10.26877 | -5.044 | 0.016 | 9.478972 | 0.0564 | 0.0053 | 22.42056 | 21.81  |
| 93  | 24.8  | -1.38489 | 0.038 | 11.58832 | -5.191 | 0.016 | 9.474965 | 0.0564 | 0.0053 | 22.50071 | 21.877 |
| 94  | 25    | -1.21189 | 0.051 | 10.80653 | -4.194 | 0.027 | 9.428441 | 0.0564 | 0.0053 | 23.43119 | 22.656 |
| 95  | 25.33 | -0.92689 | 0.06  | 9.518616 | -3.528 | 0.019 | 9.417184 | 0.0564 | 0.0053 | 23.65631 | 22.844 |
| 96  | 25.66 | -1.04989 | 0.068 | 10.07445 | -4.541 | 0.021 | 9.488628 | 0.0564 | 0.0053 | 22.22744 | 21.648 |
| 97  | 26    | -1.35389 | 0.028 | 11.44823 | -4.905 | 0.012 | 9.457377 | 0.0564 | 0.0053 | 22.85246 | 22.171 |
| 98  | 26.25 | -1.62189 | 0.06  | 12.65932 | -4.496 | 0.018 | 9.396394 | 0.0564 | 0.0053 | 24.07212 | 23.193 |
| 99  | 26.5  | -1.27889 | 0.027 | 11.1093  | -3.79  | 0.025 | 9.411081 | 0.0564 | 0.0053 | 23.77839 | 22.947 |
| 100 | 26.75 | -1.16789 | 0.015 | 10.60769 | -4.462 | 0.012 | 9.45649  | 0.0564 | 0.0053 | 22.87021 | 22.186 |
| 101 | 27    | -1.67289 | 0.045 | 12.88979 | -5.352 | 0.017 | 9.46648  | 0.0564 | 0.0053 | 22.67039 | 22.019 |
| 102 | 27.25 | -1.72489 | 0.043 | 13.12478 | -4.278 | 0.026 | 9.367336 | 0.0564 | 0.0053 | 24.65327 | 23.679 |
| 103 | 27.5  | -1.50289 | 0.03  | 12.12156 | -4.085 | 0.017 | 9.455578 | 0.0564 | 0.0053 | 22.88845 | 22.201 |
| 104 | 27.75 | -1.33689 | 0.046 | 11.37141 | -4.233 | 0.009 | 9.478325 | 0.0564 | 0.0053 | 22.4335  | 21.82  |
| 105 | 28    | -1.72489 | 0.045 | 13.12478 | -4.872 | 0.037 | 9.419203 | 0.0564 | 0.0053 | 23.61594 | 22.811 |
| 106 | 28.25 | -1.89789 | 0.033 | 13.90656 | -4.932 | 0.024 | 9.332587 | 0.0564 | 0.0053 | 25.34826 | 24.262 |
| 107 | 28.5  | -1.55989 | 0.028 | 12.37914 | -3.948 | 0.023 | 9.461861 | 0.0564 | 0.0053 | 22.76278 | 22.096 |
| 108 | 28.75 | -1.40789 | 0.03  | 11.69225 | -4.486 | 0.012 | 9.403861 | 0.0564 | 0.0053 | 23.92278 | 23.068 |
| 109 | 29    | -1.29089 | 0.062 | 11.16353 | -4.932 | 0.023 | 9.413125 | 0.0564 | 0.0053 | 23.73751 | 22.912 |
| 110 | 29.5  | -1.29789 | 0.027 | 11.19516 | -5.164 | 0.028 | 9.340513 | 0.0564 | 0.0053 | 25.18974 | 24.129 |
| 111 | 30    | -1.68789 | 0.052 | 12.95757 | -5.22  | 0.035 | 9.311947 | 0.0564 | 0.0052 | 25.76107 | 24.607 |
| 112 | 30.16 | -1.42989 | 0.044 | 11.79167 | -4.234 | 0.027 | 9.389747 | 0.0564 | 0.0053 | 24.20507 | 23.304 |
| 113 | 30.33 | -1.16389 | 0.056 | 10.58962 | -4.215 | 0.016 | 9.470958 | 0.0564 | 0.0053 | 22.58083 | 21.944 |
| 114 | 30.5  | -0.82989 | 0.035 | 9.080273 | -4.522 | 0.018 | 9.536849 | 0.0564 | 0.0054 | 21.26303 | 20.84  |
| 115 | 30.66 | -1.69589 | 0.044 | 12.99373 | -4.768 | 0.019 | 9.350446 | 0.0564 | 0.0053 | 24.99108 | 23.962 |
| 116 | 30.83 | -1.12889 | 0.037 | 10.43145 | -4.094 | 0.024 | 9.363392 | 0.0564 | 0.0053 | 24.73215 | 23.746 |

| 117 | 31    | -0.83289 | 0.03  | 9.09383  | -4.534 | 0.029 | 9.540848 | 0.0594 | 0.0057 | 21.18305 | 20.773 |
|-----|-------|----------|-------|----------|--------|-------|----------|--------|--------|----------|--------|
| 118 | 31.33 | -0.79889 | 0.044 | 8.940184 | -4.338 | 0.019 | 9.630146 | 0.0594 | 0.0057 | 19.39707 | 19.277 |
| 119 | 31.66 |          |       |          |        |       | 9.296091 | 0.0594 | 0.0055 | 26.07817 | 24.873 |
| 120 | 32    | -0.95489 | 0.04  | 9.645148 | -4.269 | 0.012 | 9.526578 | 0.0594 | 0.0057 | 21.46844 | 21.012 |
| 121 | 32.5  |          |       |          |        |       | 9.463225 | 0.0594 | 0.0056 | 22.73551 | 22.073 |
| 122 | 33    | -1.59489 | 0.059 | 12.53731 | -4.892 | 0.019 | 9.356072 | 0.0594 | 0.0056 | 24.87855 | 23.868 |
| 123 | 33.33 |          |       |          |        |       | 9.445131 | 0.0594 | 0.0056 | 23.09739 | 22.376 |
| 124 | 33.66 | -1.07889 | 0.042 | 10.2055  | -4.665 | 0.016 | 9.457323 | 0.0594 | 0.0056 | 22.85354 | 22.172 |
| 125 | 34    | -1.82789 | 0.008 | 13.59023 | -5.454 | 0.01  | 9.367034 | 0.0594 | 0.0056 | 24.65931 | 23.685 |
| 126 | 34.5  | -1.70589 | 0.033 | 13.03892 | -4.734 | 0.017 | 9.365284 | 0.0594 | 0.0056 | 24.69433 | 23.714 |
| 127 | 35    | -1.30389 | 0.035 | 11.22228 | -4.53  | 0.031 | 9.327599 | 0.0594 | 0.0055 | 25.44803 | 24.345 |
| 128 | 36    | -1.26189 | 0.049 | 11.03248 | -4.863 | 0.028 | 9.3845   | 0.0594 | 0.0056 | 24.31001 | 23.392 |
| 129 | 36.5  | -1.82689 | 0.031 | 13.58572 | -5.483 | 0.02  | 9.399437 | 0.0594 | 0.0056 | 24.01125 | 23.142 |
| 130 | 37    | -1.83889 | 0.039 | 13.63994 | -5.04  | 0.015 | 9.399426 | 0.0594 | 0.0056 | 24.01148 | 23.142 |
| 131 | 37.25 | -1.64189 | 0.057 | 12.7497  | -4.437 | 0.012 |          |        |        |          |        |
| 132 | 37.5  | -1.10689 | 0.046 | 10.33204 | -4.22  | 0.038 | 9.557093 | 0.0594 | 0.0057 | 20.85815 | 20.501 |
| 133 | 37.75 | -1.31289 | 0.022 | 11.26295 | -4.979 | 0.013 | 9.587652 | 0.0594 | 0.0057 | 20.24696 | 19.989 |
| 134 | 38    | -1.11189 | 0.048 | 10.35463 | -3.508 | 0.021 | 9.454294 | 0.0594 | 0.0056 | 22.91412 | 22.223 |
| 135 | 38.25 | -1.18089 | 0.027 | 10.66644 | -4.537 | 0.014 | 9.562492 | 0.0594 | 0.0057 | 20.75017 | 20.411 |
| 136 | 38.5  | -1.32189 | 0.037 | 11.30362 | -4.951 | 0.018 | 9.525447 | 0.0594 | 0.0057 | 21.49105 | 21.031 |
| 137 | 38.75 | -1.66689 | 0.03  | 12.86268 | -5.243 | 0.012 | 9.468563 | 0.0594 | 0.0056 | 22.62874 | 21.984 |
| 138 | 39    | -1.58189 | 0.048 | 12.47856 | -4.464 | 0.015 | 9.478787 | 0.0594 | 0.0056 | 22.42426 | 21.813 |
| 139 | 39.2  | -1.27989 | 0.021 | 11.11382 | -4.244 | 0.022 | 9.473033 | 0.0594 | 0.0056 | 22.53934 | 21.909 |
| 140 | 39.4  |          |       |          |        |       | 9.535943 | 0.0594 | 0.0057 | 21.28114 | 20.855 |
| 141 | 39.6  | -1.03489 | 0.03  | 10.00667 | -4.358 | 0.026 | 9.585103 | 0.0594 | 0.0057 | 20.29794 | 20.032 |
| 142 | 39.8  |          |       |          |        |       | 9.464611 | 0.0594 | 0.0056 | 22.70779 | 22.05  |
| 143 | 40    | -1.97489 | 0.04  | 14.25453 | -5.264 | 0.022 | 9.419121 | 0.0594 | 0.0056 | 23.61759 | 22.812 |
| 144 | 40.33 |          |       |          |        |       | 9.461189 | 0.0594 | 0.0056 | 22.77621 | 22.107 |
| 145 | 40.66 |          |       |          |        |       | 9.450299 | 0.0594 | 0.0056 | 22.99402 | 22.29  |
| 146 | 41    | -0.82689 | 0.022 | 9.066716 | -4.286 | 0.039 | 9.548957 | 0.0594 | 0.0057 | 21.02086 | 20.637 |
| 147 | 41.33 |          |       |          |        |       | 9.605307 | 0.0594 | 0.0057 | 19.89385 | 19.693 |

| 148 | 41.66 |          |       |          |        |       | 9.433322 | 0.0594 | 0.0056 | 23.33356 | 22.574 |
|-----|-------|----------|-------|----------|--------|-------|----------|--------|--------|----------|--------|
| 149 | 42    | -1.21089 | 0.018 | 10.80201 | -4.393 | 0.022 | 9.437965 | 0.0594 | 0.0056 | 23.24069 | 22.496 |
| 150 | 42.25 | -0.99589 | 0.031 | 9.830427 | -4.069 | 0.012 | 9.500053 | 0.0594 | 0.0056 | 21.99893 | 21.456 |
| 151 | 42.5  | -0.69289 | 0.033 | 8.46117  | -4.168 | 0.022 | 9.544752 | 0.0594 | 0.0057 | 21.10496 | 20.708 |
| 152 | 42.75 | -0.76189 | 0.055 | 8.772981 | -4.421 | 0.014 | 9.520159 | 0.0594 | 0.0057 | 21.59683 | 21.12  |
|     |       |          |       |          |        |       |          |        |        |          |        |

| Sample M1-1Ee |                |          |       |         |          |       |            |        |        |          |         |
|---------------|----------------|----------|-------|---------|----------|-------|------------|--------|--------|----------|---------|
| Donth         | Internal       |          |       | SST     |          |       | Sr/Ca      |        |        | SST      | SST     |
| (mm)          | Chronology(yr) | δ18Ο     | STDEV | (Leder) | d13C     | STDEV | (Shrag)    | RSD    | STDEV  | (Giry)   | (Felis) |
|               | 0/11/          |          |       | (°C)    |          |       | (mmol/mol) |        |        | (°C)     | (°C)    |
| 0             | 0.16           |          |       |         |          |       | 9.085231   | 0.0594 | 0.0054 | 30.29538 | 28.405  |
| 1             | 0.33           | -1.55289 | 0.046 |         | -3.813   | 0.023 | 9.158833   | 0.0594 | 0.0054 | 28.82335 | 27.172  |
| 2             | 0.5            | -1.20989 | 0.035 |         | -3.779   | 0.016 | 9.298074   | 0.0594 | 0.0055 | 26.03851 | 24.84   |
| 3             | 0.66           | -1.64089 | 0.052 |         | -4.661   | 0.015 | 9.077548   | 0.0594 | 0.0054 | 30.44904 | 28.534  |
| 4             | 0.83           | -0.83589 | 0.036 |         | -4.125   | 0.023 | 9.353861   | 0.0594 | 0.0056 | 24.92278 | 23.905  |
| 5             | 1              | -1.81689 | 0.046 |         | -3.973   | 0.03  | 9.373672   | 0.0594 | 0.0056 | 24.52655 | 23.573  |
| 6             | 2              | -1.92989 | 0.049 |         | -3.846   | 0.011 | 9.456994   | 0.0594 | 0.0056 | 22.86012 | 22.178  |
| 7             | 2.5            | -1.60789 | 0.019 |         | -3.67    | 0.012 | 9.438997   | 0.0594 | 0.0056 | 23.22005 | 22.479  |
| 8             | 3              | -1.74689 | 0.013 |         | -4.897   | 0.014 | 9.456725   | 0.0594 | 0.0056 | 22.86549 | 22.182  |
| 9             | 3.5            | -1.73889 | 0.052 |         | -4.453   | 0.024 | 9.227437   | 0.0594 | 0.0055 | 27.45126 | 26.023  |
| 10            | 4              | -1.37789 | 0.015 |         | -3.901   | 0.015 |            |        |        |          |         |
| 11            | 1              | -1.30089 | 0.043 |         | -3.966   | 0.028 | 9.506289   | 0.0594 | 0.0056 | 21.87422 | 21.352  |
| 12            | 2              | -1.92389 | 0.054 |         | -4.273   | 0.014 |            |        |        |          |         |
| 13            | 2.33           | -1.45389 | 0.019 |         | -4.105   | 0.031 | 9.491293   | 0.0594 | 0.0056 | 22.17414 | 21.603  |
| 14            | 2.66           | -1.80189 | 0.04  |         | -4.59    | 0.013 | 9.436793   | 0.0594 | 0.0056 | 23.26415 | 22.516  |
| 15            | 3              | -1.52489 | 0.032 |         | -3.372   | 0.007 | 9.431723   | 0.0594 | 0.0056 | 23.36554 | 22.601  |
| 16            | 3.33           | -2.07789 | 0.043 |         | -4.456   | 0.021 | 9.48169    | 0.0594 | 0.0056 | 22.3662  | 21.764  |
| 17            | 3.66           | -1.75389 | 0.047 |         | -3.692   | 0.022 | 9.498721   | 0.0594 | 0.0056 | 22.02558 | 21.479  |
| 18            | 4              | -2.08389 | 0.048 |         | -5.033   | 0.018 | 9.46634    | 0.0594 | 0.0056 | 22.67319 | 22.021  |
| 19            | 4.5            | -2.21289 | 0.033 |         | -4.089   | 0.019 | 9.441558   | 0.0594 | 0.0056 | 23.16885 | 22.436  |
| 20            | 5              | -1.90789 | 0.044 |         | -4.228   | 0.013 | 9.561078   | 0.0594 | 0.0057 | 20.77844 | 20.434  |
| 21            | 5.33           | -2.06789 | 0.036 |         | -4.66    | 0.021 | 9.533989   | 0.0594 | 0.0057 | 21.32022 | 20.888  |
| 22            | 5.66           | -1.743   | 0.057 |         | -4.62133 | 0.026 |            | 0.0594 | 0      |          |         |

Appendix 20: Geochemical analysis and calculated SST from simple M1-1Ee

| 23 | 6     | -2.252 | 0.04  | -4.52133 | 0.027 | 9.400232 | 0.0594 | 0.0056 | 23.99536 | 23.128 |
|----|-------|--------|-------|----------|-------|----------|--------|--------|----------|--------|
| 24 | 7     | -1.772 | 0.042 | -4.03633 | 0.026 | 9.475446 | 0.1008 | 0.0096 | 22.49108 | 21.869 |
| 25 | 7.5   | -2.089 | 0.033 | -5.08133 | 0.014 | 9.473869 | 0.1008 | 0.0096 | 22.52261 | 21.895 |
| 26 | 8     | -2.084 | 0.057 | -4.19533 | 0.014 | 9.369925 | 0.1008 | 0.0094 | 24.6015  | 23.636 |
| 27 | 8.5   | -2.021 | 0.026 | -3.99433 | 0.021 | 9.529771 | 0.1008 | 0.0096 | 21.40457 | 20.959 |
| 28 | 9     |        |       |          |       | 9.506393 | 0.1008 | 0.0096 | 21.87213 | 21.35  |
| 29 | 9.5   | -2.127 | 0.058 | -4.35633 | 0.012 | 9.420033 | 0.1008 | 0.0095 | 23.59934 | 22.797 |
| 30 | 10    | -1.63  | 0.027 | -4.19733 | 0.019 | 9.493332 | 0.1008 | 0.0096 | 22.13336 | 21.569 |
| 31 | 11    | -1.912 | 0.035 | -4.74233 | 0.022 | 9.439454 | 0.1008 | 0.0095 | 23.21093 | 22.471 |
| 32 | 11.33 | -2.03  | 0.037 | -4.16533 | 0.027 | 9.439631 | 0.1008 | 0.0095 | 23.20738 | 22.468 |
| 33 | 11.66 | -1.672 | 0.036 | -4.48533 | 0.03  | 9.533522 | 0.1008 | 0.0096 | 21.32956 | 20.896 |
| 34 | 12    | -1.839 | 0.031 | -4.27633 | 0.01  | 9.485142 | 0.1008 | 0.0096 | 22.29716 | 21.706 |
| 35 | 12.2  | -1.699 | 0.037 | -3.71733 | 0.03  | 9.412418 | 0.1008 | 0.0095 | 23.75163 | 22.924 |
| 36 | 12.4  | -1.786 | 0.034 | -5.31633 | 0.031 | 9.405481 | 0.1008 | 0.0095 | 23.89039 | 23.041 |
| 37 | 12.6  | -1.738 | 0.034 | -4.54433 | 0.016 | 9.580939 | 0.1008 | 0.0097 | 20.38121 | 20.102 |
| 38 | 12.8  | -2.286 | 0.029 | -4.46433 | 0.018 | 9.390676 | 0.1008 | 0.0095 | 24.18648 | 23.289 |
| 39 | 13    | -1.961 | 0.054 | -4.06933 | 0.022 | 9.375868 | 0.1008 | 0.0095 | 24.48264 | 23.537 |
| 40 | 13.5  | -1.836 | 0.04  | -3.90333 | 0.012 | 9.413626 | 0.1008 | 0.0095 | 23.72748 | 22.904 |
| 41 | 14    | -1.942 | 0.066 | -4.56033 | 0.027 | 9.360227 | 0.1008 | 0.0094 | 24.79545 | 23.799 |
| 42 | 14.2  | -1.922 | 0.034 | -3.44433 | 0.029 | 9.379265 | 0.1008 | 0.0095 | 24.4147  | 23.48  |
| 43 | 14.4  | -1.707 | 0.043 | -3.60533 | 0.027 | 9.394003 | 0.1008 | 0.0095 | 24.11994 | 23.233 |
| 44 | 14.6  | -2.089 | 0.029 | -4.44033 | 0.031 | 9.441934 | 0.1008 | 0.0095 | 23.16132 | 22.43  |
| 45 | 14.8  | -1.71  | 0.057 | -4.03933 | 0.023 | 9.413689 | 0.1008 | 0.0095 | 23.72622 | 22.903 |
| 46 | 15    | -1.654 | 0.065 | -3.61133 | 0.038 | 9.387916 | 0.1008 | 0.0095 | 24.24169 | 23.335 |
| 47 | 15.14 | -2.205 | 0.046 | -4.57333 | 0.032 | 9.411185 | 0.1008 | 0.0095 | 23.77629 | 22.945 |
| 48 | 15.28 | -1.839 | 0.042 | -4.05833 | 0.028 | 9.343944 | 0.1008 | 0.0094 | 25.12113 | 24.071 |
| 49 | 15.42 | -2.101 | 0.041 | -4.17633 | 0.036 | 9.38403  | 0.1008 | 0.0095 | 24.31941 | 23.4   |
| 50 | 15.57 | -1.645 | 0.057 | -3.68433 | 0.012 | 9.449358 | 0.1008 | 0.0095 | 23.01284 | 22.306 |
| 51 | 15.71 | -2.412 | 0.064 | -4.62733 | 0.009 | 9.394811 | 0.1008 | 0.0095 | 24.10377 | 23.219 |
| 52 | 15.85 | -1.664 | 0.035 | -3.708   | 0.021 | 9.483604 | 0.1008 | 0.0096 | 22.32792 | 21.732 |
| 53 | 16    | -2.087 | 0.055 | -4.102   | 0.026 | 9.481896 | 0.1008 | 0.0096 | 22.36207 | 21.761 |

| 54 | 16.33 | -1.767   | 0.069 | -4.467  | 0.023 | 9.402891 | 0.1008 | 0.0095 | 23.94219 | 23.084 |
|----|-------|----------|-------|---------|-------|----------|--------|--------|----------|--------|
| 55 | 16.66 | -1.44    | 0.03  | -3.678  | 0.019 | 9.410085 | 0.1008 | 0.0095 | 23.7983  | 22.963 |
| 56 | 17    | -2.07    | 0.063 | -4.615  | 0.011 | 9.4949   | 0.1008 | 0.0096 | 22.10199 | 21.543 |
| 57 | 17.14 | -1.894   | 0.034 | -3.962  | 0.035 | 9.465072 | 0.1008 | 0.0095 | 22.69856 | 22.042 |
| 58 | 17.28 | -1.471   | 0.034 | -4.264  | 0.021 | 9.483055 | 0.1008 | 0.0096 | 22.33889 | 21.741 |
| 59 | 17.42 | -2.022   | 0.052 | -5.471  | 0.018 | 9.460763 | 0.1008 | 0.0095 | 22.78475 | 22.115 |
| 60 | 17.57 | -2.265   | 0.05  | -4.659  | 0.024 | 9.366473 | 0.1008 | 0.0094 | 24.67055 | 23.694 |
| 61 | 17.71 | -1.888   | 0.028 | -3.827  | 0.022 | 9.467658 | 0.1008 | 0.0095 | 22.64683 | 21.999 |
| 62 | 17.85 | -1.875   | 0.031 | -4.729  | 0.017 | 9.492994 | 0.1008 | 0.0096 | 22.14011 | 21.575 |
| 63 | 18    | -1.74    | 0.064 | -3.887  | 0.017 | 9.45474  | 0.1008 | 0.0095 | 22.9052  | 22.215 |
| 64 | 18.33 | -1.871   | 0.042 | -3.773  | 0.021 | 9.480103 | 0.1008 | 0.0096 | 22.39794 | 21.791 |
| 65 | 18.66 | -1.74    | 0.063 | -3.776  | 0.031 | 9.5207   | 0.1008 | 0.0096 | 21.58599 | 21.111 |
| 66 | 19    | -2.006   | 0.062 | -5.313  | 0.012 | 9.467053 | 0.1008 | 0.0095 | 22.65893 | 22.009 |
| 67 | 19.25 | -1.613   | 0.056 | -3.378  | 0.022 | 9.531917 | 0.1008 | 0.0096 | 21.36166 | 20.923 |
| 68 | 19.5  | -1.884   | 0.053 | -4.857  | 0.021 | 9.579433 | 0.1008 | 0.0097 | 20.41135 | 20.127 |
| 69 | 19.75 | -1.556   | 0.048 | -3.866  | 0.017 | 9.5097   | 0.0845 | 0.008  | 21.80601 | 21.295 |
| 70 | 20    |          |       |         |       | 9.474099 | 0.0845 | 0.008  | 22.51801 | 21.891 |
| 71 | 20.5  | -1.507   | 0.05  | -4.396  | 0.016 | 9.566529 | 0.0845 | 0.0081 | 20.66941 | 20.343 |
| 72 | 21    | -1.855   | 0.043 | -3.528  | 0.029 | 9.494636 | 0.0845 | 0.008  | 22.10728 | 21.547 |
| 73 | 22    | -1.592   | 0.031 | -3.438  | 0.023 | 9.517595 | 0.0845 | 0.008  | 21.6481  | 21.163 |
| 74 | 22.33 | -1.634   | 0.039 | -4.147  | 0.017 | 9.552614 | 0.0845 | 0.0081 | 20.94771 | 20.576 |
| 75 | 22.66 | -1.76    | 0.022 | -4.069  | 0.014 | 9.56618  | 0.0845 | 0.0081 | 20.67639 | 20.349 |
| 76 | 23    | -1.925   | 0.023 | -3.995  | 0.033 | 9.458794 | 0.0845 | 0.008  | 22.82411 | 22.147 |
| 77 | 23.33 | -1.501   | 0.034 | -4.179  | 0.029 | 9.519763 | 0.0845 | 0.008  | 21.60474 | 21.126 |
| 78 | 23.66 | -1.898   | 0.047 | -5.022  | 0.015 | 9.521672 | 0.0845 | 0.008  | 21.56656 | 21.094 |
| 79 | 24    | -2.032   | 0.044 | -4.284  | 0.019 | 9.42593  | 0.0845 | 0.008  | 23.4814  | 22.698 |
| 80 | 24.5  | -1.612   | 0.029 | -3.971  | 0.021 | 9.427423 | 0.0845 | 0.008  | 23.45154 | 22.673 |
| 81 | 25    | -1.694   | 0.045 | -3.874  | 0.013 | 9.507741 | 0.0845 | 0.008  | 21.84517 | 21.328 |
| 82 | 25.5  | -1.67675 | 0.074 | -4.468  | 0.021 | 9.482214 | 0.0845 | 0.008  | 22.35573 | 21.755 |
| 83 | 26    | -1.648   | 0.038 | -4.0353 | 0.031 | 9.422469 | 0.0845 | 0.008  | 23.55062 | 22.756 |
| 84 | 26.25 | -1.977   | 0.054 | -4.2643 | 0.03  | 9.463847 | 0.0845 | 0.008  | 22.72305 | 22.063 |

| 85  | 26.5  | -1.186 | 0.026 | -4.3563 | 0.007 | 9.471208 | 0.0845 | 0.008  | 22.57585 | 21.94  |
|-----|-------|--------|-------|---------|-------|----------|--------|--------|----------|--------|
| 86  | 26.75 | -2.061 | 0.052 | -4.9693 | 0.018 | 9.369313 | 0.0845 | 0.0079 | 24.61373 | 23.646 |
| 87  | 27    | -2.047 | 0.043 | -4.6723 | 0.018 | 9.359622 | 0.0845 | 0.0079 | 24.80756 | 23.809 |
| 88  | 27.33 | -1.505 | 0.049 | -3.8473 | 0.019 | 9.382464 | 0.0845 | 0.0079 | 24.35072 | 23.426 |
| 89  | 27.66 | -1.18  | 0.037 | -4.0513 | 0.023 | 9.451442 | 0.0845 | 0.008  | 22.97116 | 22.271 |
| 90  | 28    | -1.749 | 0.045 | -4.8613 | 0.018 | 9.434472 | 0.0845 | 0.008  | 23.31057 | 22.555 |
| 91  | 28.14 | -1.921 | 0.047 | -3.7363 | 0.02  | 9.423422 | 0.0845 | 0.008  | 23.53156 | 22.74  |
| 92  | 28.28 | -2.019 | 0.036 | -4.6523 | 0.026 | 9.556279 | 0.0845 | 0.0081 | 20.87442 | 20.515 |
| 93  | 28.42 | -1.693 | 0.037 | -4.4673 | 0.019 | 9.589625 | 0.0845 | 0.0081 | 20.2075  | 19.956 |
| 94  | 28.57 | -2.088 | 0.016 | -4.355  | 0.02  | 9.620777 | 0.0845 | 0.0081 | 19.58447 | 19.434 |
| 95  | 28.71 | -1.489 | 0.044 | -4.3913 | 0.029 | 9.584924 | 0.0845 | 0.0081 | 20.30153 | 20.035 |
| 96  | 28.85 | -1.659 | 0.017 | -4.163  | 0.02  | 9.499307 | 0.0845 | 0.008  | 22.01387 | 21.469 |
| 97  | 29    | -1.371 | 0.033 | -4.25   | 0.02  | 9.569098 | 0.0845 | 0.0081 | 20.61804 | 20.3   |
| 98  | 29.25 | -1.786 | 0.054 | -5.002  | 0.016 | 9.531993 | 0.0845 | 0.0081 | 21.36014 | 20.921 |
| 99  | 29.5  | -1.981 | 0.048 | -3.971  | 0.009 | 9.528643 | 0.0845 | 0.0081 | 21.42714 | 20.978 |
| 100 | 29.75 | -1.465 | 0.057 | -3.55   | 0.011 | 9.485591 | 0.0845 | 0.008  | 22.28818 | 21.699 |
| 101 | 30    | -1.519 | 0.039 | -4.457  | 0.02  | 9.505846 | 0.0845 | 0.008  | 21.88308 | 21.359 |
| 102 | 30.33 |        | 0.05  |         | 0.027 | 9.540379 | 0.0845 | 0.0081 | 21.19243 | 20.781 |
| 103 | 30.66 | -1.075 | 0.041 | -3.901  | 0.014 |          |        |        |          |        |
|     |       |        |       |         |       |          |        |        |          |        |