Evaluating Formation Fluid Models and Calibrations Using Clumped Isotope Paleothermometry on Bahamian Dolomites

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Abstract

The use of stable oxygen isotopes to understand the mechanisms of dolomite formation has been hampered by the inability to precipitate well-ordered dolomite under normal Earth surface conditions. Several studies have attempted to address this problem, either by precipitating high temperatures ordered dolomites and extrapolating the data to low temperatures or by using more disordered very-high Mg-calcites as a proxy for low temperature dolomites. The result is eight equations that disagree significantly from each other (by as much as ~3.6‰ in the $\delta^{18}\text{O}$ value of the precipitating fluid at 25°C), and produce differences which can greatly affect the interpretation of the formation mechanisms for low temperature dolomites. However, by combining the recently developed clumped-isotope paleothermometer, an independent isotopic measurement (Δ_{47}) that directly relates to the temperature of formation, to Late Miocene to Pleistocene aged dolomites from the Bahamas with a well-constrained thermal and fluid history, we have attempted to narrow down the viable equations used to interpret the $\delta^{18}\text{O}$ values of dolomites.

The clumped-isotope temperatures measured on the Bahamian dolomites (16-37°C) agrees with the range of temperatures expected in the Bahamas. Pairing these temperatures with geological and mineralogical arguments, we favor the equation suggested by Matthews and Katz (1977), as it is the only one that produces realistic $\delta^{18}\text{O}$ fluid values across the range of clumped-isotope temperatures. Both the clumped-isotope temperatures and $\delta^{18}\text{O}$ values of the precipitating fluid show a strong positive covariance that we have interpreted as reflecting the mixing of surface brines that have undergone varying amounts of evaporation and normal seawater. The different mechanisms driving these fluids included formation by normal marine seawater driven by the compensatory flow of the mixing zone, bank wide Kohout convection, and evaporative brine reflux.

Introduction

It is well known that massive dolomites commonly replace shallow-water carbonate sediments formed at Earth surface temperatures (Land, 1980, 1998), yet the failure of laboratory studies to reproduce ordered stoichiometric dolomite under similar conditions has limited our ability to understand their formation. Modern seawater for example is significantly over saturated with respect to dolomite (Arvidson and Mackenzie, 1999), yet the mineral does not readily precipitate from marine waters and most attempts to precipitate dolomite in the laboratory at reasonable sedimentary temperatures have met with failure; the exception being studies in which very high Mg-calcites, sometimes referred to as protodolomites, which lack evidence of cation ordering (Gregg et al., 2015), were formed at temperatures between 25 and 100 °C (Fritz and Smith, 1970; Vasconcelos and McKenzie, 1997).

Although the $\delta^{18}\text{O}$ value of dolomite ($\delta^{18}\text{O}_{\text{dolomite}}$) has been frequently employed to understand dolomite formation, the estimates of equilibrium $\delta^{18}\text{O}$ values for dolomites have varied widely (Land, 1980). Several approaches have been employed to establish the fractionation factor (α) between the $\delta^{18}\text{O}_{\text{dolomite}}$ and the $\delta^{18}\text{O}$ of the precipitating fluid ($\delta^{18}\text{O}_{\text{fluid}}$) (equation 1). The fractionation factor varies as a function of temperature and usually has the form as defined in equation 2. In equation 2, variables A and B vary according to the mineral under consideration and T is temperature in degrees Kelvin (K).

$$\alpha_{DF} = \frac{\delta^{18}\text{O}_{\text{Dolomite}} + 1000}{\delta^{18}\text{O}_{\text{Fluid}} + 1000} \quad (1)$$

$$1000 \ln \alpha_{\text{Dolomite-Fluid}} = A(10^6 T^{-2}) + B \quad (2)$$

New equations defining α are still being proposed with little agreement as to which relationship is correct (Land, 1980, 1983; Horita, 2014). Some of the earliest attempts to determine the α value for dolomites involved examining co-occurring calcites and dolomites (Friedman and Hall, 1963; Degens and Epstein, 1964; Sheppard and Schwarcz, 1970) and were based on the premise that the dolomite and calcite formed at the same time and from the same fluid in isotopic equilibrium. Working under the assumption that the equilibrium relationship between calcite and its parent fluid has been fairly well constrained (Friedman and O'Neil, 1977; Kim and O'Neil, 1997), any oxygen isotopic difference between co-evolved calcite and the dolomite could then be attributed to the equilibrium fractionation value of the dolomite and the

parent fluid (Land, 1980, 1983; Budd, 1997). While many studies did show a consistent enrichment of the ^{18}O of dolomites compared to calcite by 3 to 6‰, this method was hindered by the difficulty in establishing that the calcites and dolomites being studied were cogenetic and the wide range of differences in $\delta^{18}\text{O}$ observed.

Later studies approached the problem by examining the equilibrium isotopic fractionation of well-ordered dolomites precipitated at elevated temperatures (Northrop and Clayton, 1966; O'Neil and Epstein, 1966; Matthews and Katz, 1977; Horita, 2014) and extrapolating these results to lower temperatures. This method proved to be unsatisfactory as the extrapolation to sedimentary temperatures resulted in significant error. Other studies precipitated very-high Mg-calcites or protodolomites at lower temperatures (Fritz and Smith, 1970; Vasconcelos et al., 2005). However, as it is known that $\delta^{18}\text{O}_{\text{dolomite}}$ values are sensitive to both ordering and stoichiometry (Vahrenkamp and Swart, 1994), there is some doubt whether these equations are applicable to well-ordered, more stoichiometric forms of the mineral (Gregg et al., 2015). A final method used a theoretical approach (Zheng, 1999) based on a modified increment method, but it is uncertain if this equation is applicable to naturally occurring dolomite as well (Horita and Clayton, 2007). If all of these various calibrations are considered together, the result is a range in the $\delta^{18}\text{O}_{\text{dolomite}} - \delta^{18}\text{O}_{\text{fluid}}$ fractionation (α) of $\sim 1.0315 - 1.0351$ for a dolomite precipitated at 25°C . Assuming the temperature of formation is known, this range is large enough ($\sim 3.6\text{‰}$ at 25°C) to render the $\delta^{18}\text{O}_{\text{fluid}}$ value of little use in distinguishing between the different types of fluids that are reasonable for dolomite formation (Figure 1).

Clumped Isotopes

The clumped isotope paleothermometer (Ghosh et al., 2006; Huntington et al., 2009) is dependent upon the systematic change in the abundance of carbonate molecules that have multiple substitutions of rare, heavy isotopes in their structure (e.g. $^{13}\text{C}^{18}\text{O}^{16}\text{O}_2$). A number of studies (Ghosh et al., 2006; Ghosh et al., 2007; Dennis and Schrag, 2010; Eagle et al., 2010; Tripathi et al., 2010; Daëron et al., 2011; Thiagarajan et al., 2011; Passey and Henkes, 2012; Saenger et al., 2012; Eagle et al., 2013; Grauel et al., 2013; Henkes et al., 2013; Zaarur et al., 2013; Came et al., 2014; Fernandez et al., 2014; Tang et al., 2014; Wacker et al., 2014; Defliese et al., 2015; Kele et al., 2015; Kluge et al., 2015; Tripathi et al., 2015; Bonifacie et al., 2016; Kelson et al., 2016; Winkelstern et al., 2016) have shown a measurable difference in the abundance of these multiply substituted “clumped” isotopologues with changes in temperature

within a variety of organic and inorganic carbonates that have formed at known temperatures. This technique has enabled a new approach to the problems of studying dolomites as the change in abundance of clumped isotopes is strictly controlled by the temperature of the system and is therefore completely independent of the composition of the parent fluid.

The measurement of clumped isotopes is based on the mass 47 of CO₂, primarily focused on the most abundant multiply substituted species ¹³C¹⁸O¹⁶O, derived from the acid digestion of carbonates. The variable Δ₄₇ (Wang et al., 2004) is used to describe the deviation of mass 47 CO₂ isotopologues in carbonate samples (R₄₇) relative to the same bulk isotopic composition except that it has been stochastically redistributed (R*₄₇), .

$$\Delta_{47} = \left(\frac{R_{47}}{R_{47}^*} - 1 \right) \times 1000 \quad (3)$$

Changes in the Δ₄₇ value are then directly related to temperature through calibrations, with decreasing Δ₄₇ values associated with increasing formation temperatures.

The work described in this paper applies clumped-isotope paleothermometry to dolomites that have formed on secluded Cenozoic aged islands in the Bahamas. While dolomite is commonplace in the ancient, the context of its formation is often difficult to establish as increasing age often positively correlates with increased burial depth, diagenesis, metamorphism, and exposure to variable environmental settings that all could overprint the original dolomite composition. By examining dolomites that have formed in the more recent past, the variables which have contributed to a dolomites formation can be better constrained.

Interpreting δ¹⁸O_{fluid} values

In this study, the calculated clumped-isotope temperatures have been utilized to better constrain how each of the different δ¹⁸O_{dolomite}-δ¹⁸O_{fluid}-temperature calibrations would impact the interpretation of the conditions and formation mechanisms of the Bahamian dolomites. The interpretations are based on a generalized range of δ¹⁸O_{fluid} values that could possibly have existed in the Bahamas relative to the modern day environment. The various models of formation have then been evaluated based on the geologic context of the samples and the ability of the different isotopic calibrations to accurately describe the formation of low temperature dolomites.

The Bahamas (Figure 2) are composed of series of isolated carbonate platforms that currently receive no fluvial siliciclastic input and have no known interactions with high temperature hydrothermal or tectonically induced fluids either in the modern or in ancient times

extending back to the late Miocene. The modern day sea-surface temperatures range from ~ 22 to 30°C in the open waters with $\delta^{18}\text{O}_{\text{fluid}}$ compositions ranging from +0‰ to +2.5‰, averaging around $+1.5 \pm 0.3\text{‰}$ (Swart et al., 2009). With the exception of glacio-eustatic changes in sea level, there is no geologic evidence to suggest that the environment in the Bahamas has changed significantly since the Miocene.

Based on these constraints, three different interpretations of the possible $\delta^{18}\text{O}_{\text{fluid}}$ values of the dolomites have been proposed. The first is over the range of +0.0 to +2.5‰, where the $\delta^{18}\text{O}_{\text{fluid}}$ values are indicative of formation from normal marine seawaters. Dolomites formed from these fluids are thought to have most likely have formed through the flushing process of Kohout convection (Kohout, 1967), in which flow is driven by the inward movement of cold dense fluids surrounding the platform to displace the warmer pore fluids of the platform interior, as it is capable of supplying the large amounts of seawater to the sight of dolomitization over an extended period of time (Figure 3) and has already been attributed to the formation of some dolomites in this study (Caspard et al., 2004). Other models of fluid flows that could have contributed to dolomitization by normal seawater are well discussed in Budd (1997). The second interpretation is for when the calculated $\delta^{18}\text{O}_{\text{fluid}}$ values fall below the range for normal seawater (<0‰), where it is assumed that the parent fluid would have a significant incorporation of fresh water, which typically has a $\delta^{18}\text{O}_{\text{fluid}}$ value less than 0‰, and would therefore be described as a mixed fluid most likely formed in the mixing zone, a chemical layer where seawater and fresh water intermix. Associated with the mixing zone is a compensatory fluid flow of normal seawater that has also been suggested to be a driver behind dolomitization associated with the mixing zone (Vahrenkamp and Swart, 1994; Budd, 1997), however dolomites formed from this flow would have a $\delta^{18}\text{O}_{\text{fluid}}$ value similar to normal seawater (+0 to +2.5‰) while dolomites formed within the chemical mixing zone or within the freshwater lens would have lower $\delta^{18}\text{O}_{\text{fluid}}$ values indicative of a mixture between normal seawater and freshwater. There are, however, significant arguments which will be discussed later to suggest that dolomite cannot form within the chemical mixing zone or from fresh water. In cases where the $\delta^{18}\text{O}_{\text{fluid}}$ values are greater than ~+2.5‰, these fluids are interpreted to have been produced by the process of evaporation of normal marine seawater and are therefore described as evaporative fluids.

Samples

Several studies have identified extensive dolomitization throughout the Bahamian platform from the Cretaceous to the Modern in the form of both well-ordered stoichiometric dolomites and less ordered calcian dolomites (Goodell and Garman, 1969; Supko, 1977; Beach and Ginsburg, 1980; Kaldi and Gidman, 1982; Pierson, 1983; Williams, 1985; Dawans and Swart, 1988; Vahrenkamp, 1988; Vahrenkamp and Swart, 1994; Swart and Melim, 2000; Winkelstern and Lohmann, 2016). The samples in this study have been taken from cores collected on San Salvador, Little Bahama Bank (LBB), and Great Bahama Bank (GBB) (Figure 4).

San Salvador

The ~168 m core was drilled in the late 1960's and has been the focus of multiple studies (Supko, 1970, 1977; Swart et al., 1987; Dawans and Swart, 1988; McNeill et al., 1988; Vahrenkamp et al., 1991). The core penetrated Pleistocene to Miocene aged carbonates as determined through biostratigraphy (Supko, 1970, 1977), Sr-isotopes (Swart et al., 1987) and magnetostratigraphy (McNeill et al., 1988). A series of dolomitization events, identified using Sr-isotopes and the uranium disequilibrium series dating (Swart et al., 1987; Vahrenkamp et al., 1991), suggested the low-Mg calcite (LMC) was diagenetically altered to dolomite during two to five different dolomitization periods between the early Miocene and the Modern (to as recently as <150 ka BP). Six exposure surfaces have been identified within the Pliocene aged interval, each capped with a hard crystalline mimetic, calcian dolomite which displays dolomite ordering but has more Ca than a stoichiometric dolomite (Dawans and Swart, 1988). The crystalline mimetic dolomite gradually transitions into a more friable microsucrosic, fabric destructive, dolomite which is stoichiometric and well-ordered in a series of alternations (Dawans and Swart, 1988). These crystalline mimetic dolomites replace coarse grained, shallow water sediments while the microsucrosic dolomites replace wackestones and mudstones. These cycles may have formed in response to small amplitude (a few meters) Pliocene sea-level cycles (Dawans and Swart, 1988). Between these two textural end members, there is often a transitional texture, termed crystalline microsucrosic, which is comprised of features characteristic of both crystalline mimetic and microsucrosic textures. Also present in the Miocene section of the core is a dolomite termed crystalline non-mimetic that is completely fabric destructive due to the formation of large anhedral to euhedral dolomite crystals. In total, 37 dolomite samples between

185 37 m and 134 m depth were collected for this study along with a single LMC sample from 158.5
186 m depth (Figure 4).

187 Little Bahama Bank

188 Two cores were studied from LBB, Walkers Cay (WC1) and Grand Bahama Island
189 (GB2) (Williams, 1985) (Figure 2). The cores are of Middle Miocene to Pleistocene age
190 (McNeill, 1989), with three distinct periods of dolomitization indicated by Sr isotopes in the Late
191 Miocene, Late Pliocene, and Early Pleistocene (Vahrenkamp, 1988; Vahrenkamp et al., 1991).
192 The carbon and oxygen isotopes in the upper portion of both cores show a distinct shift from
193 positive to negative values over ~5m (Vahrenkamp and Swart, 1994) (Figure 5). This shift
194 corresponds to a sharp boundary between sediment compositions of pure LMC to pure dolomite
195 at ~52m. Despite fluctuations in sea level across the Bahamas during the Pleistocene (Hearty and
196 Kindler, 1995), there is no carbon or oxygen isotopic evidence in these cores to suggest that the
197 transition from LMC to dolomite occurred due to falling sea level exposing the sediments to
198 meteoric fluids. Similar to San Salvador, the dolomites in these cores transition from crystalline
199 mimetic to microsucrosic textures associated with sea-level cycles indicated by the presence of
200 non-depositional surfaces.

201 Twelve samples were analyzed from WC1 between 52.1 and 92 m depth. All of these
202 were 100% dolomite except for the sample at 52.1 m which was pure LMC and samples at 59.1
203 m, 61.0 m, and 64.6 m which were between 76% and 90% dolomite, with the remnant portion
204 being LMC. Eleven samples were collected from GB2 between 48.2 m and 89.9 m depth, all of
205 which were 100% dolomite.

206 Great Bahama Bank

207 The Unda core was drilled on the GBB (Figure 2). The sediments in Unda are composed
208 mostly of reefal deposits and platform derived sediments with some deeper marginal deposits
209 towards the bottom of the core (Swart and Melim, 2000; Kenter et al., 2001). While dolomite is
210 found in minor quantities above 108 m, from 292-360 m, just below the Miocene-Pliocene
211 boundary, platform to middle-reef sediments are nearly fully dolomitized. The reef in this section
212 has been interpreted based on faunal assemblages (Budd and Manfrino, 2001) to have formed in
213 relatively deep water (20 to 40 m), implying that formation temperatures should be lower than
214 those in the other cores. The reef section is capped by a subaerial exposure horizon which is also
215 a phosphatic marine hardground (Melim et al., 2001). The dolomites in this reefal section

predominately have a crystalline mimetic texture with some intercalated microsucrosic dolomite. In total, 12 samples were taken from the completely dolomitized reefal section of Unda between 292 and 332 m depth. Each sample was analyzed for composition using X-ray diffraction and the majority contained 100% dolomite, with less than 1% LMC present in samples collected at the depth of 301.75 m and 311.45 m and 3% aragonite found in the sample from depth 302.79 m.

Age of Dolomitization from Sr-isotopes

The timing of dolomitization in these cores has been constrained using $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Swart et al., 1987; Vahrenkamp, 1988; Vahrenkamp and Swart, 1990; Vahrenkamp et al., 1991; Swart et al., 2001). Throughout the Neogene, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of seawater has been steadily increasing (Burke et al., 1982; DePaolo, 1986). If it is assumed that the only sources of strontium contributing to the dolomites has been derived from the (i) seawater at the time of dolomitization and (ii) the precursor carbonate, it is possible to compare the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio measured in the dolomite samples with the marine Sr-isotope curve of DePaolo (1986). The age from this curve would reflect the oldest possible age of dolomite formation as well as the youngest possible age of the original sediments (Saller, 1984; Swart et al., 1987; Vahrenkamp et al., 1991). This method works under the assumption that the Sr isotope value of the dolomite is reflective of the last set of fluids the dolomite came into equilibrium with and that the precipitating fluid had the same Sr-isotope composition of seawater at that time. The Bahamas, being an isolated carbonate platform, is sheltered from the common contaminants of strontium, including underlying basalts, aluminosilicates, and the comingling of dramatically different aged sediments making the location ideal for the use of this technique.

San Salvador: The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio throughout the core showed an increasing trend from 0.70851 at the bottom of the core to 0.70912 at the Plio-Pleistocene boundary. The $^{87}\text{Sr}/^{86}\text{Sr}$ values generally agree with the corresponding value of seawater at the time of deposition (Swart et al., 1987). Some deviation from the increasing trend is found between 53 m and 79 m, which stratigraphically were dated to have formed at some point during the Pliocene, but are as radiogenic as modern seawater, ~ 0.70923 (DePaolo, 1986). These values suggest dolomitization in this interval occurred less than 500,000 ka BP. The timing of dolomitization was further constrained using $^{234}\text{U}/^{230}\text{Th}$ ratios to less than 150,000 ka BP. Assuming that dolomitization could not have taken place when the sediments were exposed to meteoric fluids due to the lack of supplied Mg and an undersaturation with respect to dolomite, this age places the timing of

dolomite formation to periods when sea level was as high as it is in the Modern, such as during marine isotope stage 5e, or during other sea level changes associated with the current high stand. *Little Bahama Bank*: Dolomitization on LBB was proposed to have taken place in three distinct phases (Vahrenkamp et al., 1991). The first phase was shown to have occurred between 11.5 and 8.3 Ma (0.70893 to 0.70894) to sediments originally deposited in the Middle to Late Miocene. This was followed by a second major phase of dolomitization at the end of the Pliocene, between 2.8 and 2.2 Ma (0.70899 to 0.70809). A third minor phase was shown to have occurred shortly after the second phase, separated by a non-diagenetically altered limestone layer on top of the phase II dolomites. This unit is dated between the Latest Pliocene and Early Pleistocene (0.70912).

Unda: The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of bulk samples in Unda suggest ages that are similar to the chronostratigraphic ages determined by magnetostratigraphy and biostratigraphy (McNeill et al., 2001) which extend from the late Miocene through the Pleistocene. This agreement suggests that diagenesis occurred shortly after deposition. Dolomites that have been isolated from the core have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that are slightly more radiogenic than the carbonates believed that are believed to be original suggesting dolomitization occurred shortly after deposition (Swart et al., 2001).

Methods

Whole rock samples were powdered using a Spex SamplePrep Mixer/Mill 8000 or mortar and pestle. Each sample consisted of 8.0 ± 0.2 mg of powder weighed into two K1250A 3.71 mm diameter gas checks plain copper-boats in 4.0 ± 0.1 mg amounts. Sample digestion methods followed the routine established in Murray et al. (2016) for 90 °C reactions in a common acid bath (CAB). Copper boats were loaded into a vacuum chamber carousel resting above a CAB with the temperature controlled by a circulating water bath. The CAB was loaded with 3.5 mL of 105% phosphoric acid (H_3PO_4) and attached to the carousel and the entire system was pumped down from atmosphere to a pressure similar to the vapor pressure of phosphoric acid (2×10^{-6} mbars). At most four 2-boat samples are run on a single aliquot of acid before the acid was replaced. One run typically consisted of one carbonate standard (Carrara marble) followed by three samples.

Once dropped in the acid, the sample boats were stirred by a PyrexTM coated stirrer bar, and were typically reacted between 45 and 60 minutes, as determined by the complete cessation of bubbles visible in the phosphoric acid. The produced CO₂ gas was removed and isolated using a series of U-traps with liquid nitrogen and -90°C methanol. The gas was then passed through a PorapakTM Type Q 50-80 mesh U-trap maintained at a temperature of -20 to -30 °C using a methanol slush. Cleaned samples were removed from the processing line using a 25 ml pear-shaped glass vessel with an Ace Glass valve and transferred to a dual-inlet Thermo MAT 253 mass spectrometer. Samples were analyzed at a signal intensity of 12 V on mass-44 against an in house working gas (WG) that has been cryogenically purified. Analysis took place over multiple intervals between 2012 and 2015. The procedures varied over this time period, being modified to take advantage of advances in the field. Prior to August, 2014, samples were measured over ten acquisitions of 6 on-peak sample-standard measurements (click-clacks). After August 2014, the pressure-baseline (PBL) correction, as described in He et al. (2012), was implemented to manually account for the negative voltages present on the peaks on masses 47 to 49 when high amounts of CO₂ were being analyzed. Using the PBL, samples were measured over six acquisitions of 15 on-peak click-clacks which were preceded and succeeded by 5 off-peak click-clacks measuring the PBL. Masses 44 to 49 were then corrected for the PBL by retroactively adding the measured amount back onto peak voltages during post processing.

Although no statistically significant differences (Mann-Whitney, 2-tail, $p = 0.77$) were found between the Δ_{47} values calculated using the methods prior or post to August, 2014 (Murray et al., 2016), the main benefit of the PBL correction was improved precision. In addition, many samples run prior to August 2014 were measured subsequently using the PBL and the two sets of results are in agreement.

The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values were simultaneously generated during the measurement of clumped isotopes by measuring masses 45/44 and 46/44 and correcting for the typical isobaric interferences using methods based on Craig (1957) and modified for a multi-collector mass spectrometer as described in Gonfiantini et al. (1993). The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the samples were calculated relative to NBS-19 and data reported against V-PDB. To account for the differential fractionation of CO₂ produced from dolomite relative to calcite during dissolution in phosphoric acid at 90°C, a constant correction of -0.8‰ was applied to the $\delta^{18}\text{O}$ values of dolomite samples (Sharma and Clayton, 1965; Land, 1980; Vahrenkamp and Swart, 1994). The

$\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values average standard deviation from replicated samples is 0.03‰ and 0.1‰ respectively.

In February of 2015, the working gas on the mass spectrometer was changed (from WG1 to WG2). The working gases had different $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values as determined by measurement against NBS-19 and reported relative to Vienna Pee Dee Belemnite (V-PDB) (WG1: $\delta^{13}\text{C} = -2.7\text{‰}$ $\delta^{18}\text{O} = -6.4\text{‰}$, WG2: $\delta^{13}\text{C} = -9.8\text{‰}$ $\delta^{18}\text{O} = -7.4\text{‰}$).

Data reduction and normalization for the calculation of the raw Δ_{47} value ($\Delta_{47\text{-raw}}$), which is the Δ_{47} of the sample relative to the working gas, followed the methods of Huntington et al. (2009), except for the ^{17}O correction which was based on Craig (1957) and followed the recommendations made in Gonfiantini et al. (1993). Final Δ_{47} values ($\Delta_{47\text{-processed}}$) were calculated from the $\Delta_{47\text{-raw}}$ values using the procedures and standardization methods described Dennis et al. (2011) to place the $\Delta_{47\text{-raw}}$ values into the carbon dioxide equilibrium scale. This is done by using a collection of standardized CO_2 gases that have been either driven to a stochastic distribution by heating to 1000°C for several hours in a muffle furnace (heated gases) or by equilibration with one of our internal laboratory water samples in a temperature controlled water bath at either 25°C or 50°C over a period of days. The methods by which these gases are produced and measured can be found in Murray et al. (2016). These standardized CO_2 gases are then used to produce a reference framework which accounts for scrambling, compositional nonlinearity, and the non-stochastic nature of the WG by relating the measured Δ_{47} of the standard gases to their modeled expected values as determined in Wang et al. (2004). All measured data for heated and water-equilibrated standard gases used to calculate Δ_{47} values in this study can be found in the supplementary materials.

An acid digestion temperature fractionation factor was applied to the $\Delta_{47\text{-processed}}$ value for all samples relative to their bulk mineralogy as determined by X-ray diffraction performed on a Panalytical X-pert Pro and standardized against mixed sediments with a known bulk composition. The Δ_{47} fractionation factor applied for dolomite was 0.153‰ (Murray et al., 2016) and 0.092‰ for calcite (Henkes et al., 2013) with any samples composed of a mixed composition being corrected based on a linear interpolation between the two end member fractionations. This method could underestimate the true value based on the non-linearity of Δ_{47} values with respect to end-member mixing of CO_2 gases (Defliese and Lohmann, 2015),

however the difference in isotopic values ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) between the end members is small enough to make this effect negligible.

Recent work has found that the methods used to correct for the abundance of ^{17}O present in CO_2 molecules at masses 45 and 46 can have a significant impact (up to 0.1‰) on the Δ_{47} -processed value of samples if their $\delta^{13}\text{C}$ value is substantially different than the $\delta^{13}\text{C}$ value of the WG (Daëron et al., 2016; Schauer et al., 2016). Both Daëron et al. (2016) and Schauer et al. (2016) compared the impacts of the ^{17}O corrections described in Santrock et al. (1985) relative to the more recent Brand et al. (2010) correction, and both recommended that the correction scheme of Brand et al. (2010) be used in laboratories moving forward. Our laboratory previously used an alternative ^{17}O correction scheme based on the work of Craig (1957) and described by Gonfiantini et al. (1993)

All of the data from cores San Salvador, GB2, WC1, and Unda presented in this work have been reevaluated using the recommended Brand et al. (2010) correction. The effect of this change on the $\Delta_{47\text{-raw}}$ value is minimal, typically in the third decimal place and similar or less than the analytical error on the measurement. Looking at the processed Δ_{47} value ($\Delta_{47\text{-processed}}$), an average difference in the $\Delta_{47\text{-processed}}$ value calculated using the Brand et al. (2010) correction and those calculated using the Craig (1957) correction, is $0.021 \pm 0.008\text{‰}$. This difference is slightly larger than the average reported error on $\Delta_{47\text{-processed}}$ values for individual samples measured in this study ($\sim 0.013\text{‰}$), and can be translated to an average decrease on reported temperatures of ~ 3 to 5°C . The reason the difference is larger in the $\Delta_{47\text{-processed}}$ value relative to the $\Delta_{47\text{-raw}}$ value is the compounding influence of the small changes calculated in $\Delta_{47\text{-raw}}$ values for heated and water equilibrated gases used to produce the $\Delta_{47\text{-processed}}$ value by placing the $\Delta_{47\text{-raw}}$ value into the Dennis et al. (2011) reference frame. Further interpretation of the effects of this change on the data presented in this study can be found in the supplementary material, but it is currently considered that the differences attributed to the different ^{17}O corrections are inconsequential to the conclusions presented in the rest of this work. We also reanalyzed some of the dolomite acid digestion temperature fractionation work presented in Murray et al. (2016) and found that the differing ^{17}O corrections have no impact on the reported fractionation measured in that study. These data and further discussion are presented in the supplementary material; however, the rest of this work is presented in its original form using the modified Craig (1957) correction.

Temperatures were calculated for both dolomite and calcite using the calibration of Ghosh et al. (2006) in the absolute reference frame of Dennis et al. (2011). Recently published dolomite specific calibrations (Bonifacie et al., 2016; Winkelstern et al., 2016) produce similar temperatures to those calculated using the Ghosh et al. (2006) within the temperature range of the samples being reported, but we continue using the Ghosh calibration as it is most similar to our own internally measured calibration on manually precipitated calcites using the Brand et al. (2010) correction ($\delta^{13}\text{C}$: -9.96 to +0.30 ; $\delta^{18}\text{O}$: -13.66 to +1.50) over a larger range of temperatures and no significant difference has been found between calcite and dolomite calibrations. In order to check for contamination, samples were scrutinized based on their offset of δ^{48} and Δ_{48} from that of standardized gases (Huntington et al., 2009) and to replicates of itself. Any sample that exceeded one standard deviation of the average values was removed from further analysis, but the data is still presented in the supplementary materials.

In order to check for long term stability in measurements, a Carrara marble sample was measured daily producing an average processed Δ_{47} value ($\pm 1\sigma$ standard deviation) during the time frame of running these samples was $0.392 \pm 0.029\text{‰}$ ($n = 443$) which is comparable to the reported average value from four different laboratories of $0.395 \pm 0.008\text{‰}$ (Dennis et al., 2011) despite being a different samples of Carrara marble. Since 2014, four other standards (ETH 1 to 4), distributed to clumped-isotope laboratories by Eidgenössische Technische Hochschule (ETH), Zürich, have also been measured. The average measured values ($\pm 1\sigma$) were $0.278 \pm 0.017\text{‰}$ ($n = 7$), $0.295 \pm 0.017\text{‰}$ ($n = 5$), $0.698 \pm 0.016\text{‰}$ ($n = 5$), and $0.565 \pm 0.014\text{‰}$ ($n = 7$) for standards ETH 1, 2, 3, and 4 respectively. Our values for ETH 1 and 3 are within one standard deviation of the reported values in Meckler et al. (2014), but 2 and 4 exceed their value by $\sim 0.035\text{‰}$. However, that study does not report standard deviations of their accepted Δ_{47} values for the ETH standards making it difficult to compare.

The parent fluid values for dolomites were calculated using the published calibrations of O'Neil and Epstein (1966), Northrop and Clayton (1966), Fritz and Smith (1970), Sheppard and Schwarcz (1970), Matthews and Katz (1977), Vasconcelos et al. (2005), and Horita (2014). The calibrations used in this study for O'Neil and Epstein (1966), Northrop and Clayton (1966), Fritz and Smith (1970), and Sheppard and Schwarcz (1970) were originally published in Land (1983), based on the measured data from the respective studies and the formulas calculated assuming a

fluid composition of 0‰. The composition of the parent fluid for calcite samples was calculated from the calibration of Kim and O'Neil (1997).

Results

A summary of the stable and clumped-isotope results are presented in Table 1. All Δ_{47} values presented in the rest of this work are the Δ_{47} -processed values in the carbon dioxide equilibrium scale. Errors on both temperatures and Δ_{47} values are $\pm 1\sigma$ of the replicates.

San Salvador

The $\delta^{18}\text{O}_{\text{dolomite}}$ values range from +1.2 to +2.9‰, with a general trend of lower values in the upper 10 m and bottom 70 m of the dolomitized section. The $\delta^{13}\text{C}_{\text{dolomite}}$ values have a slightly decreasing trend up core with values ranging from +2.9 to +1.5‰. The calcite sample from the bottom of the core has isotopic values of -1.3 and -2.1‰ for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ respectively. The Δ_{47} values of the dolomites varied between $0.657 \pm 0.007\text{‰}$ and $0.738 \pm 0.003\text{‰}$. The calcite sample had an average Δ_{47} value of $0.689 \pm 0.003\text{‰}$. This would suggest a range of formation temperatures for the dolomites between 19 ± 1 to 37 ± 2 °C, and 29 ± 1 °C for the calcite.

Little Bahama Bank

The LBB dolomites have more positive $\delta^{18}\text{O}$ values than those from San Salvador ranging from +2.8 to +3.9‰. The $\delta^{13}\text{C}$ values (+1.3 to +2.8‰) are similar to those in San Salvador. The pure calcite from the top of WC1 has $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of -2.1‰ and -0.3‰, respectively. The mixed carbonate samples from the upper part of WC1 have more negative $\delta^{18}\text{O}$ values than the pure dolomites in the core, most likely due to the presence of small amounts of calcite. The Δ_{47} values of the GB2 dolomites ranged from 0.720‰ to 0.762‰. This range produced an average calculated temperature of 20 ± 3 °C. The WC1 core had Δ_{47} values between 0.712‰ and 0.752‰, equating to an average temperature of 20 ± 3 °C. The LMC sample produced an average temperature of 32 ± 3 °C and the three mixed dolomite/LMC samples had temperatures ranging from 16 to 26 °C using linear interpolation between the calcite and dolomite acid fractionation factors.

Great Bahama Bank

The dolomitized section of the Unda core shows minimal changes in $\delta^{18}\text{O}_{\text{dolomite}}$ values, varying from +2.2 to +3.2‰, with a slight increasing trend, while the $\delta^{13}\text{C}$ values only range by 0.4‰ from +2.6 to +3.0‰. The Unda dolomites yielded Δ_{47} values ranging between 0.740 and 0.758‰. This is equivalent to a temperature range of 16 to 19 °C.

Discussion

The dolomites found in Cenozoic aged Bahamian sediments offer an opportunity to understand the process of dolomitization because they are young in age, have never been buried to significant depths, or subjected to elevated temperatures. Despite the fact that the dolomitizing fluids are likely to be derivatives of normal seawater (see below), there are still a number of possible fluid compositions and mechanisms that must be considered. These include dolomitization from mixing-zone derived fluids, normal seawater, and evaporated fluids. Hence, knowledge of the temperature of formation, as derived from the clumped-isotope data, enables the values of the $\delta^{18}\text{O}_{\text{fluid}}$ to be determined and consequently help constrain the mechanisms and solutions involved.

Isotopic Composition of the Fluids

Each of the eight equations proposed to link temperature to the fractionation between the $\delta^{18}\text{O}_{\text{dolomite}}$ and $\delta^{18}\text{O}_{\text{fluid}}$ values (Northrop and Clayton, 1966; O'Neil and Epstein, 1966; Fritz and Smith, 1970; Sheppard and Schwarcz, 1970; Matthews and Katz, 1977; Zheng, 1999; Vasconcelos et al., 2005; Horita, 2014) can be used to generate $\delta^{18}\text{O}_{\text{fluid}}$ values using the $\delta^{18}\text{O}_{\text{dolomite}}$ and temperatures calculated from clumped isotopes (Figure 6). All of these equations produce a similar co-varying trend between temperature and $\delta^{18}\text{O}_{\text{fluid}}$ values. There are no clear trends between the $\delta^{18}\text{O}_{\text{dolomite}}$ and $\delta^{18}\text{O}_{\text{fluid}}$ values or between the $\delta^{18}\text{O}_{\text{dolomite}}$ values and temperature. There may be a slight trend of decreasing $\delta^{18}\text{O}_{\text{dolomite}}$ values and increasing temperature visible in San Salvador, WC1, and GB2, but core Unda has little variation in the $\delta^{18}\text{O}_{\text{dolomite}}$ value and that trend is not apparent (Figure 7). This would suggest that the composition of the fluid covaries with its temperature and that these two variables are balanced in such a way as to have little impact on the $\delta^{18}\text{O}_{\text{dolomite}}$ value. However, the errors on clumped isotope temperatures (average error of $3 \pm 2^\circ\text{C}$), as well as the $\delta^{18}\text{O}_{\text{fluid}}$ values calculated using

those temperatures (average error of $0.8 \pm 0.5\%$, though this reported error does not take into account the error on temperature measurements), are large enough that they could be masking trends with the $\delta^{18}\text{O}_{\text{dolomite}}$ and what is seen is simply an artifact. If the trend is real, then in the three-part system of the variables $\delta^{18}\text{O}_{\text{dolomite}}$, $\delta^{18}\text{O}_{\text{fluid}}$, and temperature, the mechanism most likely to control the $\delta^{18}\text{O}_{\text{fluid}}$ value during periods of increased temperature is evaporation. Based on the large range of fluid compositions calculated for the Bahamian dolomites, there would have to have been multiple fluids that have undergone different amounts of evaporation that have contributed to the bulk dolomitization of the Bahamas.

When comparing the mean $\delta^{18}\text{O}_{\text{fluid}}$ value ($\pm 1\sigma$) for all the samples determined using each equation, the most negative average $\delta^{18}\text{O}_{\text{fluid}}$ values are calculated using the equations of Northrop and Clayton (1966) ($-1.53 \pm 1.09\%$) and O'Neil and Epstein (1966) ($-1.26 \pm 1.10\%$) and the most positive average $\delta^{18}\text{O}_{\text{fluid}}$ values are calculated using the equations of Matthews and Katz (1977) ($+1.73 \pm 0.90\%$) and Vasconcelos et al. (2005) ($+1.99 \pm 0.80\%$) relationships. The $\sim 3.6\%$ range in $\delta^{18}\text{O}_{\text{fluid}}$ values predicted from a single $\delta^{18}\text{O}_{\text{dolomite}}$ value at a specific temperature from these eight different equations can therefore suggest formation of these dolomites by fluids comprised anywhere from fresh water mixed with normal seawater ($\delta^{18}\text{O}_{\text{fluid}} < 0\%$) to evaporative brines ($\delta^{18}\text{O}_{\text{fluid}} > 2.5\%$). In order to determine which relationship is the most applicable to the Bahamas, it is necessary to critically evaluate all of the equations and ascertain which produces $\delta^{18}\text{O}_{\text{fluid}}$ values that are consistent with the various models of dolomitization proposed for the Bahamas.

The various equations have been separated into three groups based on the $\delta^{18}\text{O}_{\text{fluid}}$ values calculated using the samples analyzed in this study. First, there are the equations which produce predominantly negative $\delta^{18}\text{O}_{\text{fluid}}$ values (range of $\delta^{18}\text{O}_{\text{fluid}}$ values from -3.0 to $+2.0\%$) (Northrop and Clayton, 1966; O'Neil and Epstein, 1966; Sheppard and Schwarcz, 1970) Second, are the equations that produce mostly positive values (range of $\delta^{18}\text{O}_{\text{fluid}}$ values from -1.0 to $+3.5\%$) (Zheng, 1999; Horita, 2014). Finally, there are the equations that produce values which are exclusively positive (range of $\delta^{18}\text{O}_{\text{fluid}}$ values from 0.0 to $+4\%$) (Fritz and Smith, 1970; Matthews and Katz, 1977; Vasconcelos et al., 2005) (Figure 6).

Evaluation of Dolomitization Mechanisms

Assuming that the first group of equations which produce predominately negative $\delta^{18}\text{O}_{\text{fluid}}$ values (Northrop and Clayton, 1966; O'Neil and Epstein, 1966; Sheppard and Schwarz, 1970) are valid, then the model of dolomitization would most likely have to involve a mixture of meteoric and marine waters (mixing-zone dolomitization). Dolomitization within the mixing zone has been suggested by numerous authors (Badiozamani, 1973; Land, 1973; Ward and Halley, 1985; Humphrey, 1988; Stoessell et al., 1989; Cander, 1994; Humphrey, 2000), the driving force relying on the non-linear behavior of the activity of Ca^{2+} and CO_3^{2-} causing the resultant mixtures of seawater and freshwater to be under saturated (saturation index < 0) with respect to calcite (Figure 8) even if the original end members were at saturation or even over saturated (Badiozamani, 1973; Plummer, 1975). At the same time, dolomite remains oversaturated (saturation index > 0) through most of this interval, thereby favoring the dissolution of calcite and aragonite and the formation of dolomite through the reaction shown in equation 4:

While the chemical composition of the meteoric endmember varies depending upon the location and the nature of the local limestone, if it is assumed that the ground waters are saturated with respect to LMC and contain 0.01 mM Mg^{2+} , then a mixture of groundwater with normal seawater would be saturated with respect to ordered dolomite ($\text{pK} = 18.06$) (Carpenter, 1980) at compositions greater than 1% seawater. The fluids would therefore be oversaturated with respect to dolomite and undersaturated with respect to LMC between 1 and 21% seawater, and undersaturated with respect to aragonite between 1 and 34% (Figure 8). If instead the fluid precipitated a 'partially' ordered dolomite ($\text{pK} = 17$) (Carpenter, 1980), the viable range for undersaturation with respect to aragonite while oversaturated with respect to dolomite is reduced to a mixture of only 15% to 34% seawater. This can be reduced even further to 15% to 25% if considering LMC. Using these ranges and assuming a value of -4‰ for meteoric water in the Bahamas, similar the average value measured for rainfall on San Salvador (Baldini et al., 2007), and a value of +1‰ for seawater, then the range of expected $\delta^{18}\text{O}_{\text{fluid}}$ values would lie between -

2.25 and -3.25%. Outside of these ranges of fresh and seawater mixtures, the precipitation of dolomite is no longer advantaged.

One of the major problems of the mixing-zone model is that in most studies on Modern mixing-zones, no dolomite has ever been identified (Steinen and Matthews, 1973; Plummer et al., 1976; Halley and Harris, 1979; Hardie, 1987; Stoessell et al., 1989). This suggests that despite the chemical benefits of the mixing zone, the kinetic barriers to dolomite formation are most likely still preventing formation in the Modern. Gaines (1980) even noted that the rate of dolomitization would actually decrease in the presence of increasingly mixed fluids.

It has also been suggested that the mixing-zone model could not produce large volumes of dolomite and is instead more a source for localized dolomitization (Budd, 1997), unless there is constant migration of the mixing zone throughout the dolomitized body (Humphrey and Quinn, 1989). This has led to multiple reviews (Plummer et al., 1976; Machel and Mountjoy, 1986; Hardie, 1987; Purser et al., 1994; Budd, 1997) suggesting that despite being chemically favorable, mixing-zone fluids do not address the other major inhibitors to dolomite formations, in particularly kinetic inhibitors, and instead is strictly an optimal thermodynamic point for dolomite formation.

From the perspective of the data presented in this work, we suggest it is unlikely that fluids from the mixing zone could have contributed to the positive trend between $\delta^{18}\text{O}_{\text{fluid}}$ and temperature found in our samples. If some of our samples were to have formed from mixing-zone fluids, then it would be expected that no trend would exist between the clumped-isotope temperatures and $\delta^{18}\text{O}_{\text{fluid}}$ values as the $\delta^{18}\text{O}_{\text{fluid}}$ value would be primarily controlled by the amount of mixing that is occurring between seawater and the freshwater lens.

The primary role of mixing-zone fluids in the Bahamas could have been the extensive dissolution of calcium carbonate due to the fluids being undersaturated with respect to calcite. The increasing porosity caused by the dissolution would thus increase fluid flow through the islands and the platform making it easier for seawater to supply Mg to the site of dolomitization (Plummer, 1975; Hardie, 1987; Beach, 1995). In addition, freshwater discharge through the base of the mixing zone causes the movement of a similar volume of seawater through the sediments, providing a mechanism for driving normal seawater through the platform. This would produce a model for the formation of the Bahamian dolomites that involved normal seawater as the dolomitizing fluid with the driving force for the fluids being a result of the discharge of

freshwater through the mixing zone causing a concomitant flow of seawater (Land, 1991; Vahrenkamp et al., 1991; Vahrenkamp and Swart, 1994), or through the process of Kohout convection (Simms, 1984; Whitaker and Smart, 1990; Whitaker and Smart, 1993; Frank and Bernet, 2000; Caspard et al., 2004).

If dolomitization takes place in normal seawater rather than in the mixing zone, the three equations which produced the more negative $\delta^{18}\text{O}_{\text{fluid}}$ values can be excluded from consideration (Northrop and Clayton, 1966; O'Neil and Epstein, 1966; Sheppard and Schwarcz, 1970). The equations of Zheng (1999) and Horita (2014), both of which yield some negative $\delta^{18}\text{O}_{\text{fluid}}$ values, can similarly be disregarded. While current evidence does not support dolomitization by mixing zone fluids, if future evidence suggests that dolomitization in the mixing zone is a more viable option, these formulas should be reevaluated as possibilities. At the moment, we take the position that dolomitization from mixed fluids is not a viable option for any dolomite body and instead the mixing zone acts primarily as a mechanism to propel marine waters through the platform top.

Of the remaining three equations, we have excluded those of Fritz and Smith (1970) and Vasconcelos et al. (2005) as they included precipitated Ca-Mg carbonates that did not exhibit the high degree of ordering found in true dolomites (Gregg et al., 2015). However, with respect to clumped isotopes, no study has found a significant difference in the relationship between carbonate mineralogy and the relationship between Δ_{47} and precipitation temperature (Defliese et al., 2015; Bonifacie et al., 2016). In Murray et al. (2016), it was also shown that the stoichiometry of a dolomite had no impact on its Δ_{47} acid digestion fractionation. Therefore, although the clumped-isotope temperatures are likely not influenced by the stoichiometry and order of a dolomite relative to a very high Mg-calcite, there is evidence suggesting these factors influence the $\delta^{18}\text{O}$ value of the carbonate (Vahrenkamp and Swart, 1994) thus eliminating the equations of Fritz and Smith (1970) and Vasconcelos et al. (2005) from consideration for the ordered dolomites used this study and with respect to their use in future studies. This leaves only the calibration of Matthews and Katz (1977), which yielded $\delta^{18}\text{O}_{\text{fluid}}$ values for all of the Bahamian dolomites from +0.5 to +3.5‰, a range which we consider to be realistic considering the various constraints on the fluids already discussed. This range of values is similar to those calculated from clumped-isotope temperatures measured on Andros Island, Bahamas (~+2‰) from dolomites collected in the shallow sections of a core (Winkelstern and Lohmann, 2016).

However, in that work, the authors opted to use the calibration of Horita (2014) to calculate their fluid values. Re-calculating their $\delta^{18}\text{O}_{\text{fluid}}$ values with Matthews and Katz (1977), the $\delta^{18}\text{O}_{\text{fluid}}$ values would increase by $\sim 1\text{‰}$ which is still within range of normal Bahamian fluids. It is therefore concluded that over the range of temperatures the Bahamian dolomites formed under (~ 15 to 35°C), the equation of Matthews and Katz (1977) produces the most realistic $\delta^{18}\text{O}_{\text{fluid}}$ values.

Whereas the lower range of the fluid values calculated using Matthews and Katz (1977) is consistent with Bahamian seawater, a single fluid source is unable to explain the $\sim 3\text{‰}$ range or the strong covariation with temperature, thus suggesting that the Bahamian dolomites formed from an array of derivatives of normal seawater that have undergone varying amounts of evaporation.

Constraints of the Formation Mechanisms

Using the ranges of both the precipitation temperature and the $\delta^{18}\text{O}_{\text{fluid}}$ values (Table 2), the following section explores the implications that these values have on the refinement of dolomitization models that have been proposed in the Bahamas.

Little Bahama Bank

The dolomites sampled from both GB2 and WC1 have similar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values as well as clumped-isotope temperatures. The $\delta^{18}\text{O}_{\text{dolomite}}$ value in both cores is $\sim +3\text{‰}$ with the WC1 samples containing small amounts of calcite having a lower bulk $\delta^{18}\text{O}$ value. Such a $\delta^{18}\text{O}_{\text{dolomite}}$ value would be typical for formation by normal marine seawater corresponding to $\delta^{18}\text{O}_{\text{calcite}}$ values of 0‰ . The $\delta^{13}\text{C}_{\text{dolomite}}$ value is stable in both cores at $+2\text{‰}$ before decreasing to -3‰ in the upper 10 m. This has been attributed to a mixed diagenetic signal and a greater incorporation of LMC in the bulk sediment (Vahrenkamp and Swart, 1994). The clumped-isotope temperatures lay within a narrow range in both cores (18 to 25°C), with a few outliers present (Figure 9), and is similar to temperatures of normal Modern seawater in the Bahamas (Slowey and Curry, 1995). The relative consistency of the $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, and clumped-isotope values between the two cores suggests a common dolomitizing fluid, in agreement with previous studies on these cores (Williams, 1985; Vahrenkamp, 1988; Vahrenkamp et al., 1991; Vahrenkamp and Swart, 1994).

The calculated $\delta^{18}\text{O}_{\text{fluid}}$ value suggests fluids with compositions between +0.7 and +2.5‰ in both cores. The average $\delta^{18}\text{O}_{\text{fluid}}$ values are $+1.4 \pm 0.5\text{‰}$ and $+1.6 \pm 0.6\text{‰}$ for the GB2 and WC1 cores respectively. Such values are typical for normal seawaters found in the Bahamas (Epstein and Mayeda, 1953; Shinn et al., 1989; Swart, 2000; Swart et al., 2009). The presence of calcite in some of the WC1 samples has skewed the calculated $\delta^{18}\text{O}_{\text{fluid}}$ values for these samples to outside this range, although that is most likely an effect of trying to compensate for the presence of calcite in the calculation by using a linear mixing model between the dolomite and calcite fluid calibrations. There is an increasing trend in $\delta^{18}\text{O}_{\text{fluid}}$ values with depth in the GB2 core that is not evident in the WC1 core. This could be a result of under sampling in GB2 or the samples with mixed calcite and dolomite at the top of the WC1 core confusing the trend. Considering the small size of LBB relative to GBB and the parallel isotopic signals between the two cores, the requisite model of dolomitization is likely to be similar at both locations or include a bank encompassing fluid flow. Based on the relatively low clumped-isotope temperatures ($< 20^\circ\text{C}$) of some of the samples relative to Bahamas surface fluids, the influx of bottom waters by Kohout convection could account for a bank wide dolomitization and also explain colder fluid temperatures calculated by clumped isotopes. The range of fluid compositions of WC1 and GB2, are larger than in Unda but not as large as San Salvador (Table 2) and suggests a greater contribution from evaporative fluids for these dolomites than those in which Unda formed. This would imply some contribution from sea-surface fluids, most likely contributed through density reflux of evaporative pools or restricted water from LBB. The partially dolomitized section of WC1 could be attributed to periods of freshwater discharge driving seawater influx as it is active for a shorter period of time and would not be expected to dolomitize large portions of the bank.

Unda

The $\delta^{13}\text{C}$ values in Unda decrease up section from +3.2 to +2.2‰. This same trend is not visible in the larger data set from the same core shown in Melim et al. (2001), thus suggesting that this trend is most likely a result of sampling bias in this study. The $\delta^{18}\text{O}_{\text{dolomite}}$ values are fairly constant throughout the sampled section, ranging from +2.6 to +3.0‰. The clumped-isotope temperatures are lower than both San Salvador and Little Bahama Bank, ranging from 16 to 19°C with an average of $18 \pm 1^\circ\text{C}$, in good agreement with earlier interpretations that the Unda core formed in deeper, cooler, waters than both the San Salvador and the LBB cores.

The calculated $\delta^{18}\text{O}_{\text{fluid}}$ values suggest the dolomitizing fluids ranged in composition from +0.5 to +1.7‰, with an average value of $+1.2 \pm 0.3\text{‰}$. This is within range of formation by normal marine fluids. These results require a fluid flow mechanism not only active at depth, but also probably limited spatially, otherwise it would be expected that a larger portion of the core would have been dolomitized instead of just the reefal section. An active mixing zone could have driven sea-water influx with the restriction coming from the depth of the fresh water lens. This is appealing due to the presence of a sub-aerial exposure surface capping the majority of the fully dolomitized section suggesting that after deposition the mixing zone would have passed through these sediments. The principle argument against this is that colder clumped-isotope temperatures would have not been produced from the surface fluids drawn in by fluids associated with the mixing zone. However, the depth of the mixing zone can vary depending on the size of the fresh water lens, so it is possible that colder fluids occurred deeper in the section. Sub-aerial exposure is also indicative of glacio-eustatic sea level change which, as a fluid driver, was modeled to have formed a gravity-driven flow of pore waters beneath the formation of a freshwater lens (Simms, 1984). A secondary control would be the rate of sea level rise after the sub aerial exposure surface as an initially slower rate would have allowed for an extended period of influx that would have diminished if the rate increased. Fluctuating rates of sea level change could have allowed more time for dolomitization in specific sections of the core and less in others explaining the partial dolomitization of portions of the core. The other alternative for preferential dolomitization is increased porosity and permeability associated with the reefal sediments that compose the fully dolomitized section. These could have acted as a conduit for increased fluid flow relative to the rest of the core therefore preferentially dolomitizing this section.

San Salvador

The dolomitized portion of San Salvador suggests formation from fluids ranging between normal marine seawater (+0.3‰) and evaporative saline fluids (+3.9‰). These are the most positive $\delta^{18}\text{O}_{\text{fluid}}$ values of any of the Bahamian samples, perhaps suggesting a slightly different mechanism of dolomitization compared to GBB and LBB.

Within a single deepening then shallowing sea-level cycle (between 54.2 and 66.9 m depth), capped at the top and bottom by exposure surfaces, Figure 10 shows that there are slightly elevated temperatures and $\delta^{18}\text{O}_{\text{fluid}}$ values at the tail-ends of the cycle. This suggests interaction with warm-evaporative fluid input during low-stands. Towards the middle of the

cycle, both the temperature and the $\delta^{18}\text{O}_{\text{fluid}}$ values decrease suggesting a greater input from normal marine seawater. Such trends imply a downward flux of saline fluids during periods of low sea level, possibly originating from shallow saline ponds found on many of the modern islands in the Bahamas, including San Salvador.

Insight into the process can be obtained by examining the shallow pools of Modern San Salvador island which are fed by the surrounding ocean and have elevated temperatures (Pinckney et al., 1995; Dalman, 2009) and $\delta^{18}\text{O}_{\text{fluid}}$ values. While direct measurements of the fluids on San Salvador have not been performed, analyses from similar evaporative pools in the Bahamas such as Little Darby Island, Lee Stocking Island, and Eleuthera have measured $\delta^{18}\text{O}$ values between +1.3 and +4.9‰ (Figure 11). In the case of Little Darby, dolomite has been found immediately beneath the ponds surface (Piggot, 2014). The reflux mechanism has been shown to exist on GBB (Whitaker and Smart, 1990; Whitaker and Smart, 1993) and has been suggested to be a viable fluid driver with increases in salinity of as little as 37 to 42‰ (Simms, 1984). Measurements of salinity in Salt Pond, one of the many evaporative pools on San Salvador, showed salinity variations in the pool from 20 to 356‰ (Shamberger and Foos, 2004) with the vast majority of measurements suggesting the fluid in the pond would be capable of reflux flow.

Based on the clumped-isotope temperatures and calculated fluid composition, a reflux type model involving these evaporative pools is the favored mechanism of dolomitization for the majority of the core compared to other proposed fluid models including dolomitization in the mixing zone (Supko, 1977) and Kohout convection (Dawans and Swart, 1988). However, the data from the 54.2 to 66.9 m section does suggest a period of time when dolomitization was dominantly associated with a more normal seawater type fluid. This could have been accomplished during periods of elevated sea level when the ponds on the island would be unrestricted and the amount of reflux would have been reduced. During such a time, other fluid flow models, such as Kohout convection, would dominate the circulation of fluid within the island. This model is supported by the Sr-isotope data of Swart et al. (1987) and Vahrenkamp et al. (1991) where it was shown that the portion of the core between 54.2 to 66.9 m was considerably younger than other portions of the core. The age date of less than 150 ka for the 54.2 to 66.9 m section opens up the possibility of formation during marine isotope stage 5E.

Conclusions

In this study, it is suggested that the use of geologically well constrained dolomites favors the dolomite-fluid equation proposed by Matthews and Katz (1977). Excluding calibrations based on very-high Mg-calcite samples (Fritz and Smith, 1970; Vasconcelos et al., 2005), this was the only one of the eight equations tested that produced $\delta^{18}\text{O}_{\text{fluid}}$ values greater than 0‰ for all pure dolomite samples from these cores. However, this study only covers a temperature range of ~15 to 35°C in dolomite formation temperatures, and while the Matthews and Katz (1977) equation appears to best represent these low temperature dolomites from the Bahamas, it is not necessarily the best equation for higher temperature dolomites.

With knowledge of the fluid composition of the Bahamian dolomites, we have reevaluated the mechanism of dolomitization of these sediments. The fluids involved in the dolomite formation on LBB were probably derived from normal marine seawaters driven by a combination of bank-wide Kohout convection, or the more restricted flows of seawater influx associated with the mixing zone in conjunction with hypersaline reflux. The Unda dolomite also formed from normal seawater, but at a slightly greater depth and from more consistently colder fluids when compared to LBB. Dolomitization probably occurred by seawater driven by the mixing zone during a period of low-stand sea level taking advantage of the porosity and permeability of the reefal sediments. On San Salvador, the bulk of dolomitization can be attributed to reflux-migrating fluids derived from the evaporative pools with $\delta^{18}\text{O}_{\text{fluid}}$ between +2.5 and +3.9‰ and temperatures exceeding 30°C on the surface of the island. A section of the core between 54.2 to 66.9 m depth below sea surface has a different signal with $\delta^{18}\text{O}_{\text{fluid}}$ and temperatures more closely resembling normal marine seawater. This section was dolomitized significantly later age than the rest of the core, probably during marine isotope stage 5.

The data presented here suggests that there may have been several mechanisms of dolomite formation operating simultaneously and/or synchronously to dolomitize the Bahamas from the late Miocene to the Modern. No single model can directly explain the range of $\delta^{18}\text{O}_{\text{fluid}}$ values or the correlation between increasing clumped-isotope temperatures and $\delta^{18}\text{O}_{\text{fluid}}$ values.

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735

Figure Captions

Figure 1 – The eight different formulas proposed for relating $\delta^{18}\text{O}_{\text{dolomite}}$ values to temperature and the composition of the fluid plotted as temperature of formation against $1000 \cdot \ln(\alpha)$. Note the large range ($\sim 3.6\%$) of values for $1000 \cdot \ln(\alpha)$ for any individual temperature that can be produced. This range is large enough that the interpretation of dolomite formation becomes contingent upon which formula is chosen.

Figure 2 – Map of the Bahamas identifying the various core locations used in this study for clumped isotope analysis. Both WC1 and GB2 are located on Little Bahama Bank, Unda is located on the Western edge of Great Bahama Bank, and San Salvador is on the Eastern edge of the Bahamas. Little Darby and Eleuthera are locations where evaporative pond waters have been analyzed for $\delta^{18}\text{O}_{\text{fluid}}$.

Figure 3 – Illustrations of three likely mechanisms that contributed to the formation of dolomites in the Bahamas. A) Kohout convection, B) coastal mixing of fresh surface waters and a compensatory flow of marine water, C) evaporative brine reflux.

Figure 4 - Petrographic and dolomite textural description of the four Bahamian cores used in this study. Descriptions are based on previous studies of these cores: San Salvador (Dawans and Swart, 1988); WC1 and GB2 (Vahrenkamp and Swart, 1994); Unda (Swart and Melim, 2000).

Figure 5 - Carbon and oxygen isotopes for the cores from Little Bahama Bank. Error bars represent $\pm 1\sigma$ although they are typically smaller than the symbol size. Data not indicated as being from this study are taken from the work of Vahrenkamp and Swart (1994). Oxygen isotopes have been corrected for the difference in acid digestion fractionation between LMC and dolomite of -0.8% based on the bulk % dolomite present in the sample determined by X-ray diffraction. The sudden change in isotopic composition is associated with a change in mineralogy from calcite to dolomite.

Figure 6 – Eight plots of the $\delta^{18}\text{O}_{\text{dolomite}}$ against temperature of formation from clumped isotopes for all four Bahamian cores. The contours represent different values of $\delta^{18}\text{O}_{\text{fluid}}$ (‰, VSMOW) as calculated using the eight different $\delta^{18}\text{O}_{\text{dolomite-fluid}}$ calibrations, including A) Northrop and Clayton (1966), B) O’Neil and Epstein (1966), C) Sheppard and Schwarz (1970), D) Fritz and Smith (1970), E) Matthews and Katz (1977), F) Zheng (1999), G) Vasconcelos et al. (2005), and H) Horita (2014). Based on a geological context, any calibration that had a significant portion of the $\delta^{18}\text{O}_{\text{fluid}}$ values falling below the 0‰ line (red) was considered invalid due to the implied interpretation of dolomitization by fresh water. Error bars represent $\pm 1\sigma$ of replicates.

Figure 7 – Individual plots of $\delta^{18}\text{O}_{\text{dolomite}}$ values against the calculated $\delta^{18}\text{O}_{\text{fluid}}$ values using Matthews and Katz (1977) for each of the four Bahamian cores used in this study. Average clumped-isotope temperatures are represented by changing color with blue being the coldest temperatures measured in that core and red being the warmest. To better show trends, the temperature scales are independent for each core and error bars have been excluded (errors for each measurement can be found in the supplementary material), however, and average error of all the samples from each individual core is presented. Note how in each core there is a limited

range of $\delta^{18}\text{O}_{\text{dolomite}}$ values over a range of $\delta^{18}\text{O}_{\text{fluids}}$ values with no recognizable trend between the two variables, but there is a strong trend of increasing temperature with increasing $\delta^{18}\text{O}_{\text{fluids}}$ values.

Figure 8 – Theoretical saturation relationships for both ordered ($\text{pK}=18.06$) and disordered ($\text{pK}=17.00$) dolomite (Carpenter, 1980) as well as low-Mg calcite ($\text{pK} = 8.48$) and aragonite ($\text{pK} = 8.34$) (Plummer and Busenberg, 1982) assuming a groundwater with 0.01 mM Mg^{2+} . Notice how the mixed fluid is rapidly saturated with respect to dolomite with little seawater input. Only with greater amounts of mixing does it eventually become saturated with respect to calcite and then aragonite.

Figure 9 – Calculated clumped-isotope temperatures ($\pm 1\sigma$) relative to depth for the cores in this study. The gray rectangles represent the typical yearly range of seawater temperature in the Bahamas.

Figure 10 – Zoomed in section of the San Salvador core between two subaerial exposure horizons (yellow squiggles) interpreted to be a deepening upwards sea-level cycle. The clumped-isotope temperatures and $\delta^{18}\text{O}_{\text{fluid}} (\pm 1\sigma)$ both show a trend of elevated values during the shallow ends of the cycle and reduced values when sea level was high.

Figure 11 – Plot of the calculated clumped-isotope temperatures and $\delta^{18}\text{O}_{\text{fluid}}$ values using the Matthews and Katz (1977) calibration. This plot shows the large range of fluids that formed the Bahamian dolomites in this study. The blue square represents normal marine seawaters in the Bahamas, drawn based on the surface seawater temperature range in the Bahamas and average $\delta^{18}\text{O}_{\text{fluid}}$ values ($\pm 1\sigma$) measured off Great Bahama Bank (Swart et al., 2009). The red square is indicative of the evaporative pools found on Bahamian islands with the range of temperatures from Pickney et al. (1997) and Dalman (2009) and the $\delta^{18}\text{O}_{\text{fluid}}$ range based on the average measured values ($\pm 1\sigma$) from evaporative ponds on Eleuthera and Little Darby in the Bahamas. Error bars have been omitted for clarity.

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Table 1 - Summary of Bahamian core clumped isotope analysis

Depth (m)	(n)	$\delta^{13}\text{C}_{\text{carbonate}}$ (‰), VPDB	$\delta^{18}\text{O}_{\text{carbonate}}$ (‰), VPDB	Δ_{47} (‰)	Temp. (°C)	$\delta^{18}\text{O}_{\text{fluid}}$ (‰)
<i>WCI</i>						
52.12	2	-0.34±0.01	-2.09±0.01	0.668±0.004	34±1	2.2±0.2
54.56	2	1.29±0.00	3.15±0.10	0.742±0.021	19±4	0.9±0.9
57.91	2	2.88±0.06	2.31±0.12	0.759±0.002	15±1	-0.4±0.2
60.96	2	2.76±0.02	1.90±0.01	0.713±0.011	25±2	2.0±0.5
64.62	1	2.6	1.7	0.749	22	1.2
68.58	2	1.82±0.01	3.40±0.03	0.714±0.002	24±1	2.5±0.1
71.93	2	2.30±0.01	3.39±0.06	0.730±0.010	21±2	1.7±0.4
76.20	2	2.55±0.02	3.89±0.03	0.733±0.007	20±1	2.1±0.3
79.25	2	2.52±0.01	3.73±0.02	0.741±0.009	19±2	1.5±0.5
82.30	2	2.72±0.03	3.72±0.12	0.750±0.027	17±5	1.1±1.1
87.48	2	2.24±0.01	2.81±0.06	0.720±0.003	23±1	1.6±0.2
92.05	2	2.53±0.04	3.24±0.06	0.733±0.003	20±6	1.1±0.1
<i>GBII</i>						
48.16	3	1.35±0.01	3.33±0.08	0.747±0.013	17±2	0.8±0.6
49.07	2	1.99±0.08	3.31±0.13	0.745±0.002	18±1	0.9±0.0
54.25	3	2.19±0.04	3.01±0.14	0.738±0.009	19±2	0.9±0.5
57.30	3	1.96±0.08	3.53±0.18	0.720±0.022	23±4	2.3±0.9
59.13	2	1.99±0.09	3.37±0.01	0.743±0.021	19±4	1.1±1.0
65.84	3	2.84±0.04	2.94±0.06	0.742±0.021	19±2	0.7±0.5
68.88	3	2.46±0.13	3.27±0.35	0.741±0.012	19±2	1.1±0.5
74.13	3	1.95±0.03	3.34±0.10	0.725±0.009	22±2	1.9±0.4
80.16	3	2.00±0.02	3.21±0.07	0.718±0.012	23±3	2.1±0.6
84.12	3	2.27±0.07	3.27±0.15	0.730±0.008	21±2	1.6±0.5
89.92	3	2.59±0.03	3.07±0.03	0.711±0.019	25±4	2.3±0.9
<i>Unda</i>						
292.33	3	2.23±0.03	2.85±0.09	0.746±0.015	18±3	1.2±0.8
296.90	3	2.80±0.05	2.76±0.10	0.756±0.021	16±4	0.6±1.0
301.75	3	2.66±0.07	2.81±0.18	0.742±0.021	19±4	1.4±1.2
302.79	3	2.82±0.06	2.85±0.13	0.744±0.016	18±3	1.3±0.9
304.90	3	2.62±0.01	2.95±0.08	0.754±0.010	16±2	0.9±0.5
306.40	4	2.44±0.13	2.74±0.33	0.757±0.014	16±3	0.5±0.7
309.37	4	2.52±0.04	3.01±0.07	0.751±0.017	17±3	1.5±0.5
311.45	4	2.44±0.13	2.90±0.13	0.740±0.016	19±3	1.7±0.8
313.94	2	2.80±0.03	2.79±0.17	0.744±0.001	18±1	1.3±0.2
321.87	3	2.77±0.03	2.87±0.05	0.740±0.016	19±3	1.6±1.0
326.59	3	2.92±0.02	2.79±0.08	0.758±0.021	16±4	1.1±0.1

Table 2 - Core Summary of Pure Dolomites

Core	$\delta^{18}\text{O}_{\text{dolomite}}$ (‰), VPDB	$\delta^{13}\text{C}_{\text{dolomite}}$ (‰), VPDB	Temperature (°C)*	$\delta^{18}\text{O}_{\text{fluid}}$ (‰)!
WC1	2.8 - 3.9	1.3 - 2.7	17 -24	0.9 - 2.5
GB2	2.9 - 3.5	1.4 - 2.8	18 - 25	0.7 - 2.3
San Salvador	1.2 - 2.9	1.5 - 2.9	19 - 37	0.3 - 3.9
Unda	2.6 - 3.0	2.2 - 3.2	16 -19	0.5 - 1.7

*: Temperature is calculated from clumped isotopes using the calibration of Ghosh et al. (2006) in the

!: The $\delta^{18}\text{O}_{\text{fluid}}$ was calculate using the equation of Matthews and Katz (1977) using temperatures calc