TEMPERATURE AND VARIATIONS IN THE SALINITY OF FLUIDS REVEALED BY CLUMPED ISOTOPIC ANALYSES

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OBJECTIVES

- This work aims to establish and refine a new approach to unravel the temperature and $\delta^{18}O_{fluid}$ values of carbonates that have been overprinted numerous times by diagenetic events.
- In this method the Δ_{47} and $\delta^{18}O$ values are measured in the carbonates which allow the determination of the $\delta^{18}O$ of the diagenetic fluids ($\delta^{18}O_{fluid}$). Once the temperature and the $\delta^{18}O_{fluid}$ values are determined, the covariation of these parameters provides estimates of the fluid composition during changes in sea level.
- Preliminary data show that cores, previously interpreted as either being affected only by fresh or marine waters, have more complicated histories and supports evidence that regions of the cores previously thought to have been only affected by meteoric fluids, also have had significant cementation by calcite formed in the marine realm.

INTRODUCTION

The interpretation of changes in the $\delta^{13}C$ and $\delta^{18}O$ values of marine carbonates ($\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$) during early diagenesis is one of the most often used applications of stable C and O isotopes in carbonate rocks. Allan and Matthews (1982) outlined a series of changes in these values expected within carbonates exposed to freshwater diagenesis and these trends have been used by numerous workers to interpret their isotopic records. However, such samples are often a mixture of original unaltered materials and diagenetically altered/added carbonates, processes that occurred at different times and from fluids with varying salinities and $\delta^{18}O$ values. In order to unravel these patterns, we have developed a model using X-ray diffraction, clumped isotope, and conventional $\delta^{18}O$ and $\delta^{13}C$ values We have applied this to carbonate samples from the upper ~350 m of the Clino core, drilled in the Bahamas (Ginsburg, 2001) and present preliminary data.

THE MODEL

Assuming equilibrium and no solid-state reordering, clumped isotope values of carbonates provide the temperature of formation and/or diagenesis (Eiler et al., 2014). Using the $\delta^{18}O_{carb}$ value it is possible to determine the $\delta^{18}O_{fluid}$ value if the rocks are composed only of a single mineral. However if the mineralogy of the rock is known then the $\delta^{18}O_{carb}$ value can be corrected using estimates of the $\delta^{18}O_{carb}$ values of dolomite and aragonite based on previous studies (Swart and Melim, 2000; Swart et al., 2009). Once corrected the $\delta^{18}O_{fluid}$ values can be calculated using an equation linking the $\delta^{18}O_{carb}$ value and temperature (Kim and O'Neil, 1997). However, the $\delta^{18}O_{fluid}$ values and temperatures can still show a range of values, even

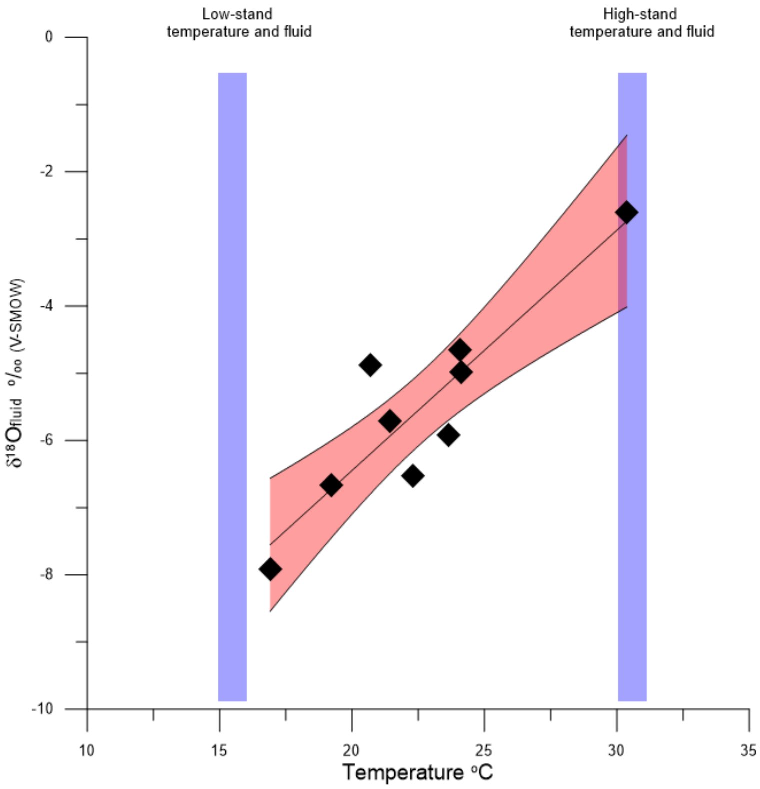

Fig. 1: Correlation between the $\delta^{18}O_{fluid}$ values and Δ_{47} derived temperatures for the upper 10 samples from Clino core (20 to 30 mbmp) showing a positive correlation and with end members representing diagenesis during periods of higher temperature with more positive $\delta^{18}O_{fluid}$ values and lower temperatures with more negative values.

over intervals of several meters that probably represent diagenesis at a range of temperatures and from different fluids.

Typically, if one examines a short interval (10 m) of the Clino core, the $\delta^{18}O_{fluid}$ values and Δ_{47} derived temperatures exhibit a positive correlation (Fig. 1). The simplest interpretation of this trend is that one end of the correlation, corresponding to the higher temperatures (25-30°C), represents alteration during sea level high stands. Conversely, the lower temperatures correspond to more negative $\delta^{18}O_{fluid}$ values, diagenesis by meteoric fluids during the low stands when temperatures were lower. The higher temperatures correspond to $\delta^{18}O_{fluid}$ values of -2 to -4‰ while the low temperatures to between values of -6 and -8 ‰. Using this approach it is possible to using a rolling window approach as applied during previous studies (Oehlert and Swart, 2019) to determine the slope and intercept of the correlation between temperature and $\delta^{18}O_{fluid}$. The goodness of the fit between temperature and the $\delta^{18}O_{fluid}$ values can be assessed by calculating the regression coefficient over an interval of 10 m. In a simple system that represents mixing between only two components, a low stand and a highstand, the regression coefficient would approach unity. In a system influenced by repeated sea level changes, the correlation coefficient would be lower as the system is overprinted by subsequent diagenetic events and there is mixing between multiple generations of calcite.

Work Completed

In order to test this approach, we sampled the Clino core at an interval of ~ 1 m between the start of recovery (~ 20 mbmp) to ~350 mbmp. At each interval we measured the mineralogy and Δ_{47} values of the carbonates (The $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ are measured as part of the determination of the Δ_{47} values). The $\delta^{18}O_{carb}$ values were corrected for amounts of aragonite and dolomite and the $\delta^{18}O_{fluid}$ values calculated from a moving window regression between the temperature and $\delta^{18}O_{fluid}$

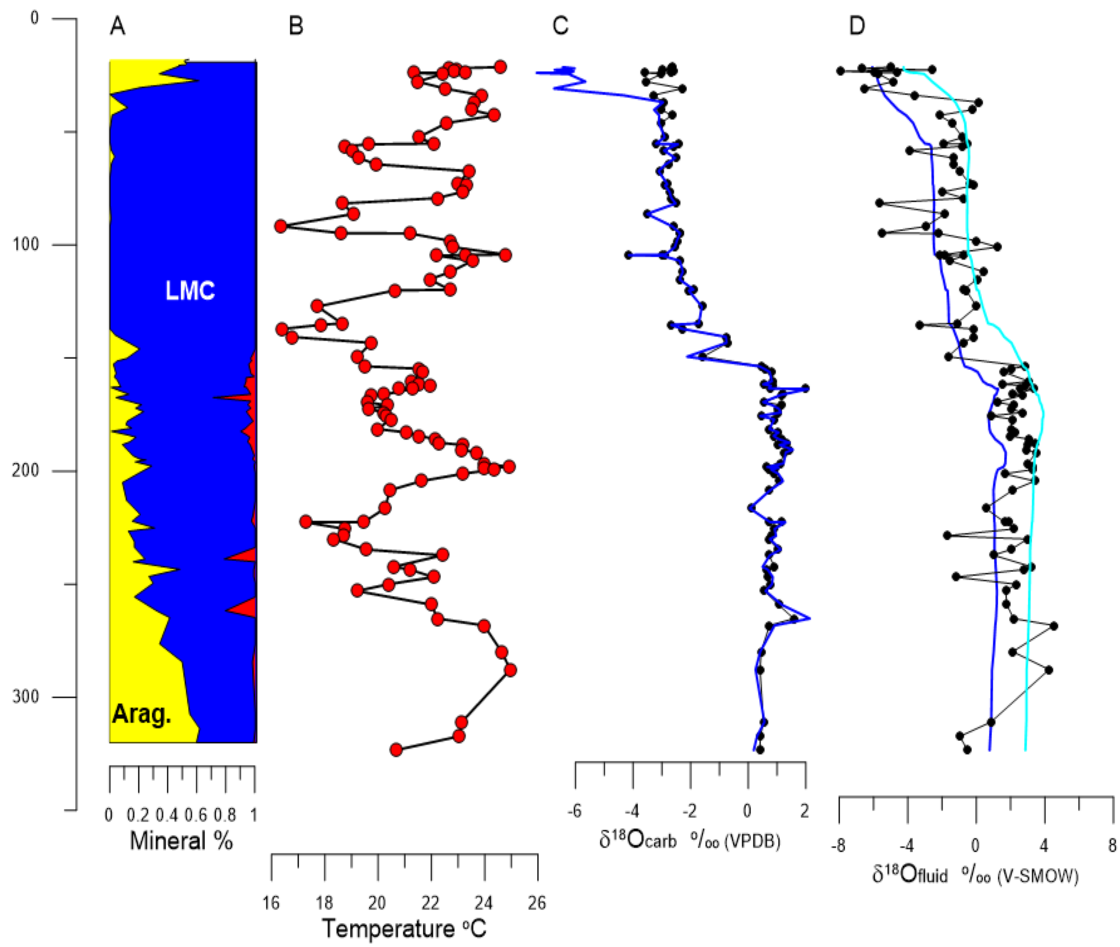

Fig.2: A) Mineralogy of interval in the Clino core between 20 and 350 mbmp, red= dolomite; B) Three point moving average of temperature calculated using Δ_{47} values; C) The $\delta^{18}O_{carb}$ values of bulk (black) and corrected for the presence of dolomite and aragonite (blue); D) Estimates of the $\delta^{18}O_{fluid}$ end members at 15°C (dark blue) and 25°C (light blue).

values. The mineralogy, calculated temperatures, corrected and uncorrected $\delta^{18}O_{carb}$ and $\delta^{18}O_{fluid}$ values are shown in Fig. 2. In Figure 2D the dark blue line represents calculated $\delta^{18}O_{fluid}$ values at 15°C and the light blue at 25°C. These data reveal that in the interval between 50 and 150 mbmp, previously only thought to have been affected by meteoric alteration, calcite components exist that were altered in fluid with $\delta^{18}O$ values more positive than 0 ‰ or in other words seawater. In the lower portion of the core (> 150 mbmp), the $\delta^{18}O_{fluid}$ values range between 0 and +3‰, perhaps indicative of saline surface brines and fluids originating affected by recrystallization deeper in the section.

Proposed Work

1) Replicate all of the already measured Δ_{47} values in order to reduce the errors on the temperature estimates which presently are ~+/- 3°C.
2) Measure the Δ_{48} values which will help constrain disequilibrium.
3) Add additional geochemical markers (Na and S) that may help constrain the salinity of the diagenetic fluids.

SIGNIFICANCE

There are several important findings from this study.

1) Based on the correlation between the temperatures and the δ^{18}Ofluid values, there appears to be low-Mg calcite forming from marine fluids within the zone previously thought to be solely affected by meteoric diagenesis. This LMC seems to be forming at temperatures between 25-30°C so probably during the high stands. During the low stands, meteoric calcite is forming at temperatures probably between 15-20°C.
2) Lower in the core (> 150 mbmp), LMC also seem to form over a range of temperatures (20-30°), with the fluid values falling between +1 and +3‰. Elevated values could reflect (i) evolved fluids arising from carbonate recrystallization at higher temperatures that migrated from deeper in the section, (ii) evaporated surface waters, or (iii) reflect disequilibrium arising from microbial sulfate reduction.
3) The δ^{18}Ofluid values in the upper portion of the core are more negative than current δ^{18}O values for rainfall in the Bahamas, indicating perhaps a wetter climate during the last interglacial, a finding supported by previous research.

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