Dual Clumped Isotopes (Δ_{47} and Δ_{48}) of Modern Carbonate Sediments

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Project Objectives

- Measure the Δ_{47} and Δ_{48} values in modern biogenic and abiogenic sediments.
- Using the dual clumped proxy to ascertain the degree of equilibrium in Modern carbonates.
- Understanding the mechanisms of sediment formation (e.g. direct precipitation or breakdown from existing allochems).

Project Rationale

The application of clumped isotopes has caused a revolution in the Earth Sciences. By examining the difference between the measured and the theoretical 47/44 mass ratios, the calculated value (Δ_{47}) has been found to be directly related to the temperature of carbonate formation/alteration (Wang et al., 2004; Ghosh et al., 2006). However, some carbonates, such as corals (Thiagarajan et al., 2011; Saenger et al., 2012), cave calcites (Daeron et al., 2011; Affek et al., 2014) and microbial associated dolomites (Murray et al., 2021), show unrealistic Δ_{47} temperatures attributable to non-equilibrium processes during their formation. Recently, it has been possible to also measure the Δ_{48} value and when used together with the Δ_{47} value, these two clumped species are known as the dual clumped isotope proxy. This coupled proxy is able to discern the kinetic isotope effects (e.g. CO_2 absorption and degassing) present in corals (Bajnai et al., 2020), cave calcites (Fiebig et al., 2021), spring carbonates (Parvez et al., 2023), and microbial-induced dolomites (Lu and Swart, 2023) (Fig. 1). In this study we use the dual clumped proxy to better understand the formation of sediments on the Great Bahama Bank (GBB), the origin of which has long been controversial (Broecker and Takahashi, 1966; Shinn et al., 1989; Morse et al., 2003; Swart et al., 2014; Purkis et al., 2019; Purkis et al., 2023). The samples used in this study were collected by Swart et al (2008) and Reijmer et al. (2009) and represent a range of compositions from mudstone to grainstone.

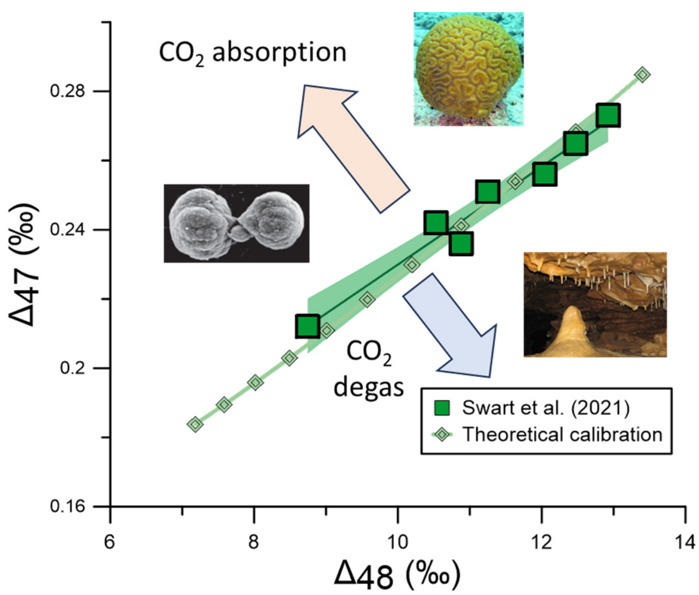

Figure 1: The crossplot of Δ_{47} and Δ_{48} values and differential kinetic behaviors in different carbonates.

PRELIMINARY DATA

The preliminary clumped isotope data shows that while there are no statistically significant differences in the Δ_{47} values between the different facies, the Δ_{48} values are significantly elevated in the mud dominated facies. (Fig. 2A and B). When comparing the Δ_{47} and Δ_{48} values to the calibration line of Swart et al. (2021), most of the muddy sediments (mudstone and wackestone) fall below the calibration line (Fig. 3C). In contrast, the grainy sediments (packstone and grainstone) appear to have a bimodal distribution, with values falling not only below the calibration, but also above (Fig. 3C). The possible reason for those variations of Δ_{47} and Δ_{48} values can be explained by multiple sources of sediments and the different disequilibrium formation processes by which these components were formed.

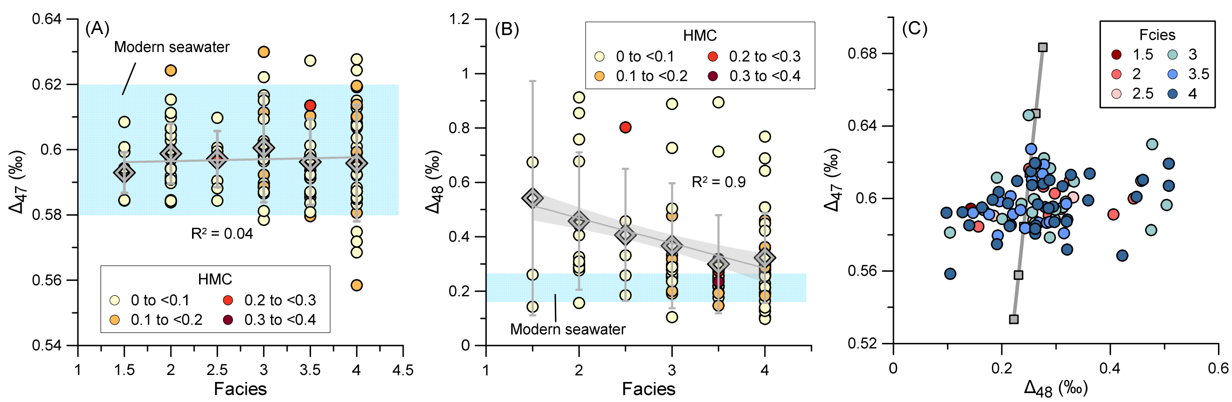

Figure 2: The crossplot of Δ_{47} and Δ_{48} values depending on facies in the GBB; a facies number of 1 corresponds to a mudstone, while a facies number of 5 is a grainstone; (A) The Δ_{47} values in different facies; (B) The Δ_{48} values in different facies; (C) The Δ_{47} and Δ_{48} values in different facies compare with the calibration line. From Facies 1.5 to 4, Modern sediments become grainier.

The spatial distribution of the Δ_{47} and Δ_{48} values show the heterogeneous Δ_{47} temperatures across the platform top. The Δ_{47} temperatures of the muds show lower Δ_{47} temperatures (<25°C) than those (>25°C) in the western margin (Fig. 3A). In addition, the area in which the whitings are found show a significant higher Δ_{48} values than the marginal area (Fig. 3B). This indicates that the intense precipitation associated with disequilibrium processes occurs in the intraplatform in which the mud accumulates.

PROPOSAL WORK

In order to further investigate the kinetic effects of dual clumped isotopes in modern sediments on GBB, we propose to; 1) Continue to measure Δ47 and Δ48 values of surface sediments of all the ~ 260 samples collected in triplicates; 2) Some preliminary measurements have been made on Δ47 and Δ48 values of red and green algae and these values appear to plot on the calibration line proposed by Swart et al. (2021). However, more species, replicates, and locations need to be measured and compared with the modern sediments; 3) Evaluate the influence of contamination of the Δ_{47} and Δ_{48} values. The Δ48 value had been previously used as a measure of contamination of the Δ_{47} value of a sample. It is important to make sure that, the Δ_{48} values that are measured, particularly values that are more positive than expected, are not artifacts.

Significance

This study will establish base line values for the Δ_{47} and Δ_{48} values of Modern sediments as well as casting light on the origin of some of the more controversial sediments, such as the muds in the GBB. Preliminary data suggest that all the surface samples on GBB have formed in disequilibrium with respect to the Δ_{47} and Δ_{48} values, a finding that has profound implications on the use of these proxies in the geological record.

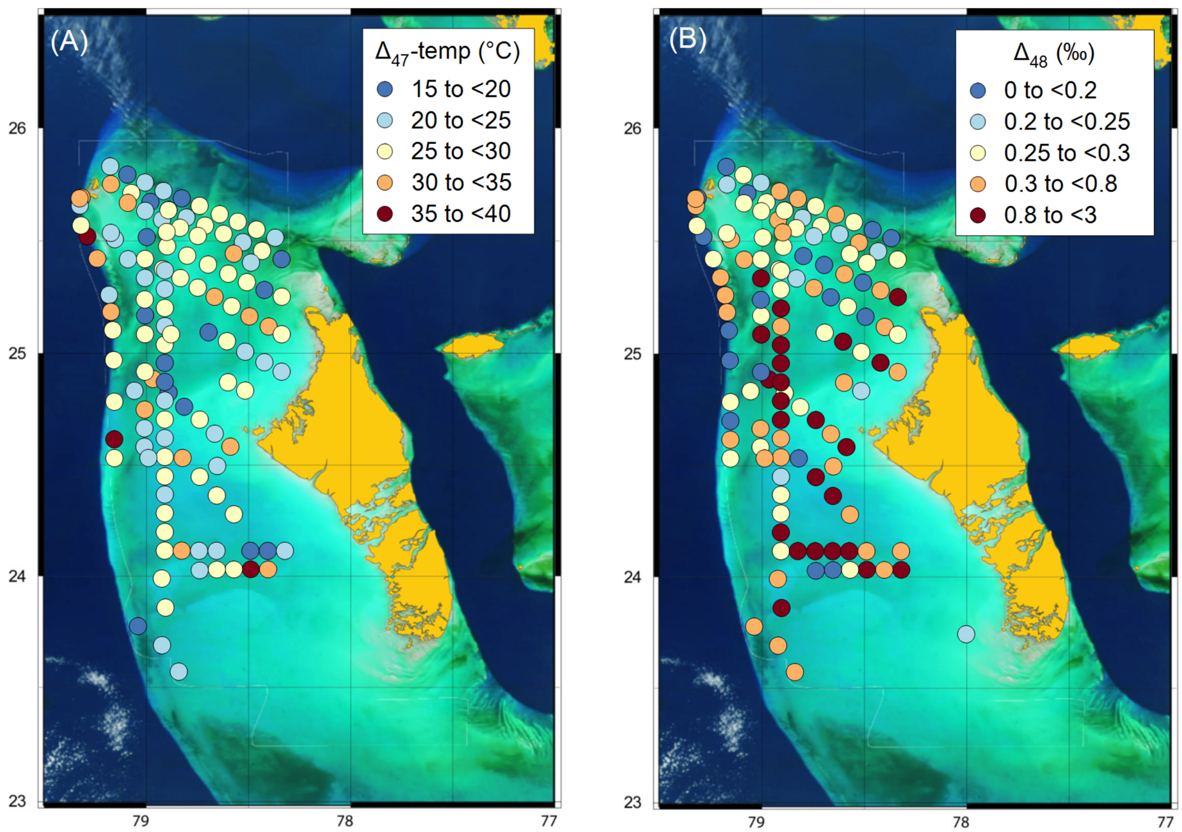

Figure 3: The distribution of Δ_{47} temperatures and Δ_{48} values in the GBB.

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