THE DELINEATION OF THE MIXING ZONE USING CLUMPED ISOTOPES

Peter K. Swart and Chaojin Lu

KEY FINDINGS

- The Δ_{47} values of carbonates, affected by freshwater and marine fluids, can be used in conjunction with the $\delta^{18}O$ values of the carbonates ($\delta^{18}O_{carb}$) to determine the $\delta^{18}O_{fluid}$ values of the diagenetic fluids.
- These data show that the zone of covariance between $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ values, previously interpreted as representing diagenesis within the zone of mixing between fresh and marine fluids, takes place largely within the freshwater phreatic zone. The purpose of this work is to refine the hypotheses previously suggested.

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. Allan and Matthews (1982) outlined a series of changes in $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ values expected to be visible within carbonates exposed to freshwater diagenesis and these trends have been used by numerous workers to interpret their isotopic records. Of relevance to this study is that a zone of strong covariance (ZOC) between the $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ values is suggested to represent diagenesis within the mixing zone. The goal of this study will be to test the principal assumption made in the model of freshwater diagenesis of Allan and Matthews (1982) that variations in the $\delta^{18}O_{carb}$ values within the ZOC reflects differences in the $\delta^{18}O$ values of the fluids ($\delta^{18}O_{fluid}$).

THE MIXING ZONE

The mixing zone is a region in the subsurface in which meteoric waters mix with marine fluids producing a gradient in salinity as well as in both the $\delta^{13}C$ values of the dissolved inorganic carbon (DIC) and the $\delta^{18}O$ values of the fluids ($\delta^{18}O_{fluid}$). As such, Allan and Matthews (1982) proposed that carbonate diagenesis taking place along this gradient would result in diagenetically altered materials with $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ values reflecting the gradients in the $\delta^{13}C_{DIC}$ and $\delta^{18}O_{fluid}$ values, producing a covarying trend between the $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ values. This mixing trend is found in all recently altered carbonates from coastal locations and is documented in numerous papers on both Quaternary and more ancient carbonates. The mixing-zone also found fame for the production of solutions which were undersaturated with respect to various carbonate minerals (Badiozamani, 1973), even though the original end member solutions would have been saturated with respect to these minerals.

Does the Zone of Covariance Really Represent the Mixing Zone?

For a number of years, it has been noted that the position of the zone in which the $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ values are strongly correlated (zone of covariance; ZOC) was inconsistent with the location of the mixing zone based on known sea-level history. For example, it is well established that global sea level was approximately 130 m lower than at present during the last glacial period. Assuming that the water table was 2-3 m higher than sea level (similar to the position of the water table in South Florida relative to sea level) this would have positioned the mixing-zone about 80-120 m lower, so at around 200 m below current sea level and well below the ZOC. The ZOC, therefore, cannot be a result of diagenesis in the mixing-zone. Instead Swart and Oehlert (2019) suggested that the covarying trends resulted from greater amounts of freshwater diagenesis in the upper portion of the ZOC when compared to the lower portion. Furthermore, it was suggested that the majority of the fresh water phreatic zone is rather geochemically inactive as it is already supersaturated with respect to carbonate minerals. Swart and Oehlert (2019) proposed that the carbonate sequence became cemented as the water table is dragged up and down by tidal variation and long-term sea-level changes.

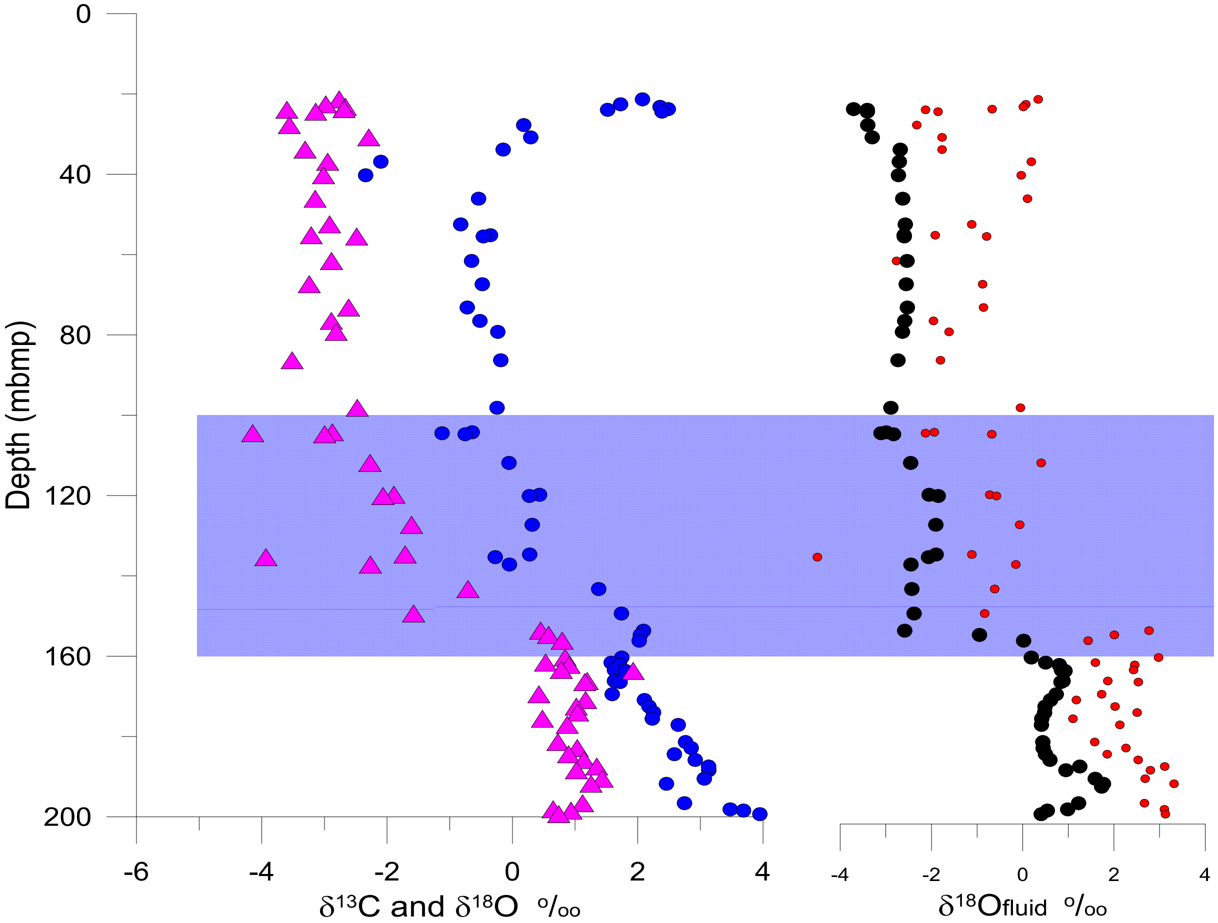

Figure 1: Comparison of the $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ values of carbonates compared to the calculated $\delta^{18}O_{fluid}$ values. The data shown in black circles, represent the end of a covarying trend between temperature and the $\delta^{18}O_{fluid}$ values calculated using a five point moving correlation, while the red points are simply the raw $\delta^{18}O_{fluid}$ values.

RESULTS AND INTERPRETATIONS

The Allan and Matthews (1982) model predicts a steady increase in the $\delta^{18}O_{fluid}$ values through the ZOC as a result of salinity gradients due to the mixture of freshwater and seawater in the mixing zone. The Swart and Oehlert (2019) model suggests that the ZOC does not represent the mixing zone, but rather alteration at the boundary between the vadose and phreatic zone (water table). It therefore predicts a binary response of the $\delta^{18}O_{fluid}$ values with the values through the majority of the ZOC, reflecting meteoric $\delta^{18}O_{fluid}$ values. The difference between these two models can be tested using a similar approach to that applied to the Inverted 'J'. Preliminary data from this approach are shown in Figure 1. The average $\delta^{18}O_{fluid}$ value (~ -2‰) is slightly more positive than rainfall in Miami, but consistent with rainwater expected during the last glacial when these rocks were altered. The $\delta^{18}O_{fluid}$ values in the ZOC are like those measured in the freshwater portion. Diagenesis in the marine zone produces $\delta^{18}O_{fluid}$ values of ~ +2 to +3‰, in agreement with values measured on Great Bahama Bank (Lowenstam and Epstein, 1957; Shinn et al., 1989; Swart et al., 2009). The data indicate a constant fluid composition throughout the ZOC, in support of the Swart and Oehlert (2019) model.

SIGNIFICANCE

This study shows how the clumped isotope values can be used in innovative ways to refine the interpretation of diagenetic alteration in carbonates.

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