

THE USE OF Δ_{47} AND Δ_{48} DISEQUILIBRIUM IN UNDERSTANDING DOLOMITE FORMATION

Chaojin Lu and Peter K. Swart

PROJECT OBJECTIVES

- To investigate the utility of dual clumped isotope thermometry (Δ_{47} and Δ_{48}) to understand the processes of dolomitization.
- To use Δ_{47} and Δ_{48} values to decipher the kinetic isotopic effects during microbial induced dolomitization.

PROJECT RATIONALE

Dual clumped isotope thermometry can not only be used to reconstruct the temperature of the reactive fluid, but also allows us to decipher kinetic effects present during the formation of carbonate minerals (Swart et al., 2021a). While recent studies have examined the disequilibrium in the behavior of Δ_{47} and Δ_{48} values during the formation of biogenic and inorganic carbonates such as corals and speleothems, the kinetic behavior of Δ_{47} and Δ_{48} values in dolomite has not been well explored.

In this investigation, we have applied the dual clumped approach to Cenozoic dolomites from the Bahamas (Clino and San Salvador cores) (Fig. 1) and other dolomites standards. The San Salvador dolomites formed within a seawater-buffered open system, which is reflected in the invariable $\delta^{34}\text{S}$ values and Sr concentrations. In contrast, Clino dolomites formed in a semi-closed environment and have elevated $\delta^{34}\text{S}$ values, suggestive of bacterial sulfate reduction (BSR), and high Sr concentrations indicating closed system recrystallization (Fig. 1).

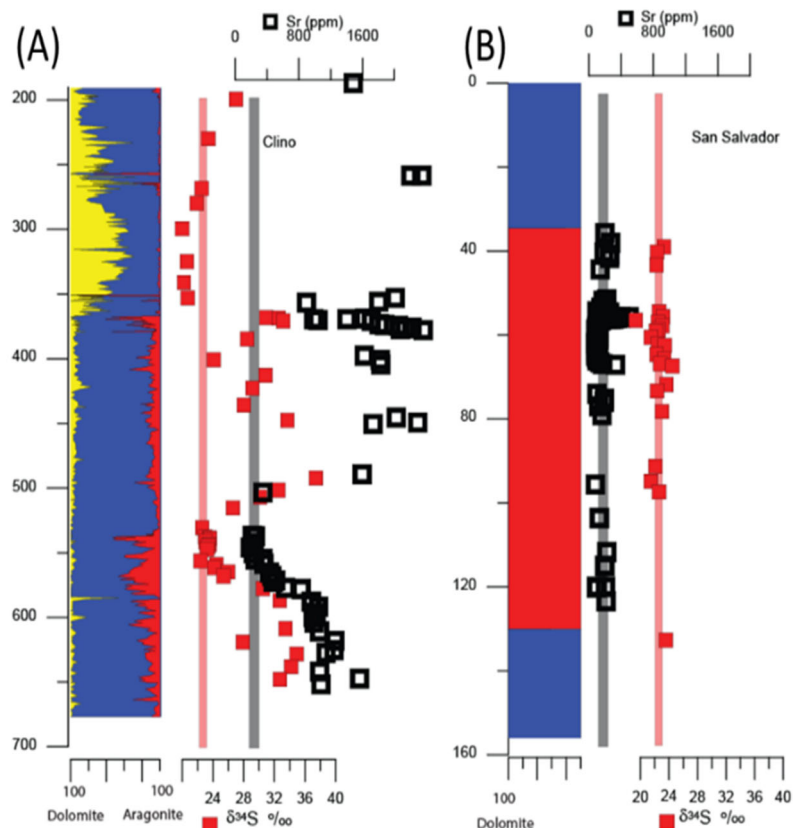


Figure 1: The profiles of sulfur isotopes and Sr concentrations in Clino and San Salvador cores (Murray et al., 2021). (A) Sulfur isotopes and Sr concentrations in Clino dolomites. (B) Sulfur isotopes and Sr concentrations in San Salvador dolomites.

APPROACH

The ISoDIC model has been developed by Guo (2020) in order to investigate changes in the Δ_{47} and Δ_{48} values of dissolved inorganic carbonate (DIC) during such processes as DIC-H₂O exchange, CO₂ degassing, and absorption (Fig. 2). During the formation of dolomite, the change of bicarbonate concentrations (HCO₃⁻) via CO₂ hydration in the dolomitizing fluid is a critical factor in breaking the hydration of Mg ions with water and overcoming the kinetic barrier. Therefore, it is believed that this model is applicable to offer the quantitative constraints on the Δ_{47} and Δ_{48} values depending on the changes of pH and DIC concentrations (Fig. 2). We will apply this model to recent dolomites formed by various different mechanisms, including normal marine fluids (San Salvador), closed system marine fluids under the influence of BSR (Clino), and hypersaline reflux (Qatar), possibly affected by microbial processes. A second phase of this project will apply the model to ancient dolomites throughout the Proterozoic and Phanerozoic.

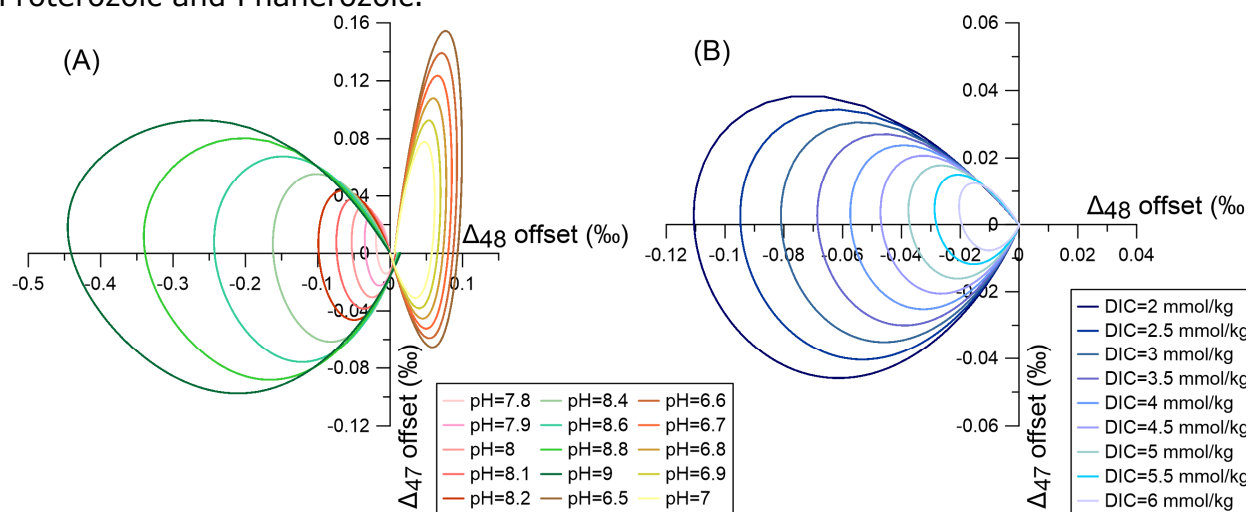


Figure 2: Comparison between measured and modeled offsets of Δ_{47} and Δ_{48} between the measured and expected values (Guo, 2020). (A) The modeled patterns of the Δ_{47} and Δ_{48} offsets in a range of pH values compared with the measured data. (B) The modeled patterns of the Δ_{47} and Δ_{48} offsets in a range of DIC concentrations compared with the measured data.

SIGNIFICANCE

This study will show for the first time the potential of the dual clumped isotope technique as an aid to understanding the formation of dolomite.

REFERENCES

- Guo, W., 2020. Kinetic clumped isotope fractionation in the DIC-H₂O-CO₂ system: patterns, controls, and implications. *Geochimica et Cosmochimica Acta*, 268, 230-257.
- Murray, S.T., Higgins, J.A., Holmden, C., Lu, C. and Swart, P.K., 2021. Geochemical fingerprints of dolomitization in Bahamian carbonates: Evidence from sulphur, calcium, magnesium and clumped isotopes. *Sedimentology*, 68, 1-29.
- Swart, P. K., Lu, C., Moore, E., Smith, M., Murray, S. and Staudigel, P., 2021. A Calibration Equation Between Δ_{48} Values of Carbonate and Temperature. *Rapid Communications in Mass Spectrometry*, 35(17), e9147.