

Using Dual Clumped Isotope Proxies (Δ_{48} and Δ_{47} values) to identify microbial associated dolomite

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Traditionally the influence of microbial process on carbonate precipitation has been inferred by measuring the $\delta^{13}\text{C}$ values of the precipitates. However, in most carbonate diagenetic environments, where the system is rock buffered, this is either not possible or the changes in $\delta^{13}\text{C}$ values are barely evident. Here we present a new approach using the Δ_{48} values that show extreme disequilibrium in dolomites that have unequivocally formed under conditions of bacterial sulfate reduction. This contrast to the Δ_{48} values of dolomites forming under open marine conditions. The open system dolomite, previously interpreted as being formed in an environment of actively flowing seawater, exhibit conventional $\delta^{34}\text{S}$, $\delta^{11}\text{B}$, $\delta^{18}\text{O}$, $\delta^{34}\text{S}$, $\delta^{13}\text{C}$ values and Sr concentrations, shows Δ_{47} and Δ_{48} values close to equilibrium as defined by precipitation experiments [1]. In contrast, the bulk sediments containing up to 50% dolomite that has been interpreted to have formed under closed system conditions have $\delta^{34}\text{S}$ values as high as +30‰, low $\delta^{11}\text{B}$ values (+4 to +10 ‰), and elevated Sr concentrations. The chemically isolated dolomites from these bulk samples, possess Δ_{47} values close to equilibrium, but Δ_{48} values that are significantly more negative than expected. The Δ_{47} and Δ_{48} values of these dolomites are shown in figure 1 (purple = closed system, blue = open system) relative to calcite formed at known temperatures and the theoretical equilibrium line; data from Swart et al. [1]. Such negative Δ_{48} values might be predicted from pore waters with pH values close to 8.1 and slightly elevated concentrations of dissolved inorganic carbon [2]. The discovery of this anomaly using the dual clumped isotopic proxy offers important implications in the understanding of the formation of ancient dolomites.

1. Swart, P.K., et al., *A calibration equation between Δ_{48} values of carbonate and temperature*. Rapid Communications in Mass Spectrometry, 2021. **35**(17): p. e9147.
2. Guo, W.F., *Kinetic clumped isotope fractionation in the DIC-H₂O-CO₂ system: Patterns, controls, and implications*. Geochimica et Cosmochimica Acta, 2020.

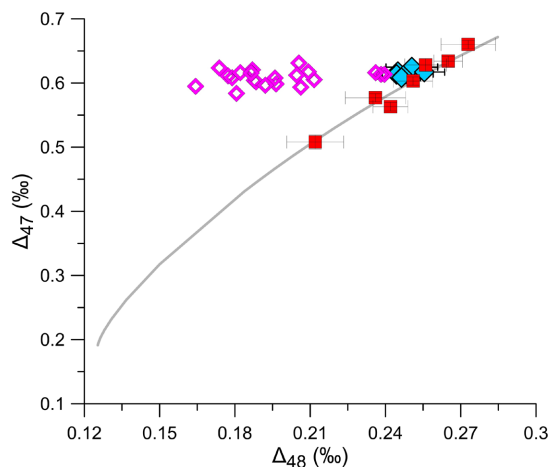


Figure 1