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Dual clumped isotopes reveal an out-of-equilibrium state in shallow-water carbonate sediments on Great Bahama Bank

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While non-skeletal carbonate grains and muds precipitated on shallow-water platforms have been widely used to reconstruct past ocean temperatures and chemistry, the question remains as to what degree the geochemical signatures of carbonate sediments are in equilibrium with their original environments. In order to evaluate the extent of equilibrium, we have applied the dual clumped isotope proxy (Δ_{47} and Δ_{48}) to surface sediments (aragonite > 90%, n = 150) ranging from mudstones (< 63 µm) to non-skeletal grainstones in Great Bahama Bank. While there is no statistical difference in the mean Δ_{47} values of the various facies, there are very large ranges of Δ_{47} values within each facies (~ 0.1 ‰) equivalent to a temperature uncertainty of 25°C. Our Δ_{48} data reveals an out-of-equilibrium state where the muddy sediments have more positive values than the equilibrium, while the grainy facies are more negative. The positive Δ_{48} disequilibrium in the muds is proposed to be a result of the photosynthetic removal of CO_2 caused by the activity of cyanobacteria which in turns promotes the precipitation of calcium carbonate in the water column (whitings area). In contrast, the grainstones, that are mainly composed of ooids and peloids, show a negative Δ_{48} disequilibrium which is greatly contributed from the CO_2 absorption induced by microbial sulfate reduction. Our findings highlight the importance of kinetic processes in defining the geochemistry of non-skeletal grains and muds as well as microbialites in Precambrian carbonates which were suggested to be a product of kinetic interactions in an alkaline ocean.