

THE INFLUENCE OF DIAGENESIS ON THE C, B, AND S ISOTOPIC COMPOSITION OF CARBONATE SEDIMENTS

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PROJECT OBJECTIVES

- To rigorously calibrate the stable isotopes of B, C, and S so that these chemical proxies can be used to study both the paleoenvironment and the diagenesis of carbonates in older time periods.
- To use compound specific C isotopic analysis to confirm interpretations made using bulk organic $\delta^{13}\text{C}$ values during freshwater diagenesis.
- To investigate the behavior of B and S stable isotopes during meteoric and marine diagenesis.

PROJECT RATIONALE

Chemical proxies such as C ($\delta^{13}\text{C}$), B ($\delta^{11}\text{B}$), and S ($\delta^{34}\text{S}$) isotopes measured within carbonate rocks and organic material have been widely used to understand changes in the Earth's environment through time. For example, changes in $\delta^{13}\text{C}$ values have been suggested to indicate changes in the burial of organic material (Hayes et al., 1999; Saltzman et al., 2004), changes in $\delta^{11}\text{B}$ values indicate variations in the pH of the oceans (Kasemann et al., 2010; Ohnemueller et al., 2014), and variations in $\delta^{34}\text{S}$ indicate changes in the anoxic state of the oceans and the concentration of O_2 in the atmosphere (Jenkyns, 2010; Lyons and Gill, 2010). However, recent work by various authors has cast some doubt on some of these interpretations.

Carbon: While carbonate sediments deposited in the deep marine environment are immune to meteoric diagenesis, they do not necessarily record changes in the $\delta^{13}\text{C}$ values of the dissolved inorganic carbon in the oceans. In particular, sediments deposited adjacent to carbonate platforms or in epeiric seas, the type of record preserved in the deep geological record, can be composed of different skeletal allochems all with varying $\delta^{13}\text{C}$ values (Swart and Eberli, 2005). Within the meteoric realm the $\delta^{13}\text{C}$ values of the carbonates are heavily affected by dissolution and precipitation reactions, yielding very negative $\delta^{13}\text{C}$ values (Melim et al., 2001). As meteoric diagenesis occurs on a global scale, similar negative signals can be seen in globally disparate settings, a phenomenon often cited as indicating original signals (Swart and Kennedy, 2012).

Boron: The $\delta^{11}\text{B}$ value of Modern marine carbonates has been widely used as a paleo-pH proxy (Honisch et al., 2004). Several studies have applied the method to important geological transitions, characterized by large $\delta^{13}\text{C}$ values such as the Permian-Triassic boundary and the Marinoan glacial event (Kasemann et al., 2010; Ohnemueller et al., 2014) and claimed pH drops associated with these boundaries. However, studies documenting the behavior of $\delta^{11}\text{B}$ are lacking although a recent study did show that large

changes in $\delta^{11}\text{B}$ values can be associated with freshwater diagenesis (Stewart et al., 2015).

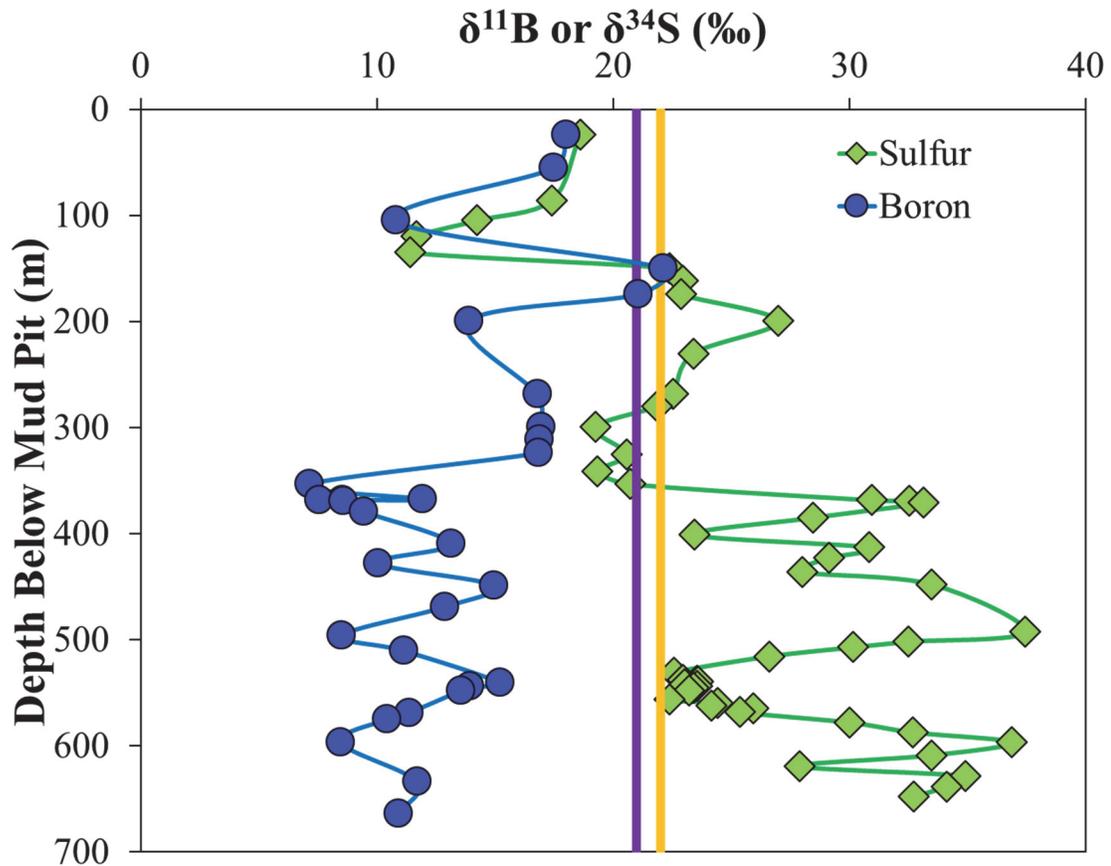


Figure 1: Variations in the B (34 samples) and S (63 samples) isotopes from the Clino core. The two vertical lines reflect the $\delta^{34}\text{S}$ values of the Modern (purple) and Pliocene (yellow) oceans.

Sulfur: Although it has been suggested that the $\delta^{34}\text{S}$ values of carbonate associated sulfate (CAS) are relatively immune to diagenesis (Gill et al., 2008), it is safe to assume that because of the predominance of bacterial sulfate reduction (BSR) and the large fractionation associated with this process, that the $\delta^{34}\text{S}$ values of pore fluids, and consequently any diagenetic calcite formed in association with BSR, will likely be different than the original carbonate value.

SCOPE OF WORK

Sulfur and Boron

Meteoric Diagenesis: We have started to investigate the changes in the $\delta^{11}\text{B}$ and $\delta^{34}\text{S}$ values from sections of the Clino core which have unequivocally been altered by meteoric fluids. The sampling for $\delta^{11}\text{B}$ values was designed not only to replicate the samples measured previously (Stewart et al., 2015), but also to encompass the entire core (Fig. 1). These values will also be measured on other cores from the Bahamas in our collection. Although our initial $\delta^{11}\text{B}$ values

within the zone of meteoric diagenesis are similar to those measured previously (Stewart et al., 2015), these data record a large drop in pH within the top portion of the freshwater phreatic lens as defined by Swart and Oehlert (2018).

Marine Diagenesis: Carbonate sediments are normally recrystallized/neo-morphosed as they are buried in the marine realm. During burial, the timing of BSR relative to recrystallization controls whether the original $\delta^{34}\text{S}$ values of the sediments are preserved. For example, if BSR reduces the concentration of sulfate in the pore fluids to zero before the initiation of sediment recrystallization, then the $\delta^{34}\text{S}$ values of the recrystallized sediment should be similar to the values in the original sediment. However, if BSR is not complete, then the residual sulfate will have a very positive $\delta^{34}\text{S}$ value and as recrystallization starts the new carbonate will incorporate S with more positive $\delta^{34}\text{S}$ values. The changes in the $\delta^{34}\text{S}$ value of the CAS from the Clino core reflect these scenarios (Fig. 1). The pH values of the pore waters in both of these previous scenarios will probably be lower than those prevailing during sediment deposition. In fact, in the section of the Clino core dominated by marine diagenesis, the $\delta^{11}\text{B}$ values are substantially lower, reflecting the low pH throughout. Although the sampling interval of B and S isotopes is different, the $\delta^{11}\text{B}$ values do not seem to correlate with the zones in which the $\delta^{34}\text{S}$ values are elevated, reflecting enhanced BSR.

Carbon Isotopes: The work of Oehlert and Swart (2014) clearly show that within the zone of meteoric diagenesis there is strong positive covariance between the $\delta^{13}\text{C}$ values of the carbonate and the $\delta^{13}\text{C}$ values of the organic material. In order to explain these data, it was proposed that during sub-aerial exposure terrestrial C-3 vegetation colonized the islands masking the original $\delta^{13}\text{C}$ values of the local marine organic material. In order to test this hypothesis, we will (i) measure the $\delta^{13}\text{C}$ values of the organic material in other cores from the Bahamas and Pacific, (ii) extract distinct organic compounds from the cores, which might reflect the original shallow marine biota, and measure their $\delta^{13}\text{C}$ values using compound specific isotopic techniques.

SIGNIFICANCE

The application of geochemical proxies towards understanding the ancient need to be rooted in rigorous calibration studies, in which the Recent is the key to the past. This is true not only for the stable isotopes of B, C, and S, but also for a myriad of other hopeful isotopic proxies. In this regard it is useful to quote from a recent paper (Swart, 2015) *'So that we do not 'Throw the Baby out with the Bath Water' (Marshall, 1992), such proxies should be cautiously applied to older materials. Only then can the potential of geochemical indices be made available to correctly study both the paleoenvironment and the diagenesis of carbonates in older time periods.'*

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