The Impact of Early Freshwater and Marine Diagenesis upon the $\delta^{34}S$ values of Carbonate Associated Sulfate

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The $\delta^{34}S$ values of carbonate associated sulfate (CAS) has been widely used as a stratigraphic tool as well as a mechanism for determining changes in the global sulfur cycle relating to ocean anoxia. Although early work established that CAS $\delta^{34}S$ values remained unaltered during certain types of freshwater diagenesis, the basic premise, that the $\delta^{34}S$ values of the CAS reflect the value of seawater at the time of carbonate formation, has remained largely unchallenged. To investigate this we analyzed the $\delta^{34}S$ values of CAS in a core from the Bahamas which has experienced a number of well-constrained diagenetic events including subaerial exposure, freshwater diagenesis, and alteration within the mixing zone, and marine conditions. These data shows that within the vadose and freshwater phreatic zones the $\delta^{34}S$ values vary between seawater and slightly more negative values, interpreted to be a result of the incorporation of S derived from the oxidation of H_2S. Within the freshwater phreatic zone the $\delta^{34}S$ values increase reflecting close system diagenesis and the influence bacterial sulfate reduction (BSR). Transitioning through the mixing-zone the $\delta^{34}S$ values return to marine values indicating mixing with relatively unaltered marine material. Within the zone of marine diagenesis, the $\delta^{34}S$ values vary between marine values close to non-depositional surfaces, and relatively positive values in portions affected by closed system diagenesis and BSR. This pattern produces positive covariance between $\delta^{34}S$ and $\delta^{13}C$ values.