

THE ROLE OF DIAGENESIS IN THE CONTROL OF B, S, AND CLUMPED ISOTOPES: THE ROLE OF EARLY DIAGENESIS

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PROJECT OBJECTIVES

- To constrain the behavior of the stable isotopes of boron (^{11}B and ^{10}B), sulfur (^{32}S and ^{34}S), and clumped isotopes during marine and meteoric diagenesis.

PROJECT RATIONALE

In this project we will investigate the behavior of three isotopic systems (clumped isotopes of CO_2 (Δ_{47}), boron isotopes, and sulfur isotopes) during early meteoric and marine diagenesis. Despite the fact that the fundamental behavior of these systems has not been studied under well-constrained diagenetic conditions, these geochemical systems have already been widely applied to ancient geological problems. The ratio of $^{11}\text{B}/^{10}\text{B}$ ($\delta^{11}\text{B}$) has been used as a proxy of pH during well-known global carbon isotope events such as the P-T boundary and the Marinoan glaciation (Clarkson et al., 2015; Ohnemueller et al., 2014). Sulfur isotopes ($\delta^{34}\text{S}$) of carbonate associated sulfate (CAS) have been widely used in conjunction with carbon isotopes as indicators of anoxia (Lyons and Gill, 2010) and clumped isotopes have been used to ascertain the temperature of the Precambrian oceans (Bergmann et al., 2018).

SIGNIFICANCE

The application of all three of these proxy systems has the potential to dramatically change the interpretation of significant events which have occurred during Earth's history. For example, one interpretation of the dramatic change in carbon isotopes which has been widely documented at the P-T boundary, was that massive amounts of isotopically negative carbon was released from the oxidation of clathrates which in turn lowered the pH of the oceans. Hence, the interpretation of changes in the $\delta^{11}\text{B}$ values of carbonates at the P-T boundary apparently supported this hypothesis (Clarkson et al., 2015). However, later work has shown changes in the $\delta^{11}\text{B}$ values of equal magnitude associated with meteoric alteration (Stewart et al., 2015). These changes take place as a result of the degradation of organic material at the interface between the vadose and fresh-water phreatic zone and the concomitant reduction in pH. Of similar importance is whether changes in the $\delta^{34}\text{S}$ values of carbonate associated sulfate are related to anoxia or simply a product of bacterial sulfate reduction (BSR) associated with carbonate recrystallization (Swart, 2015). During burial BSR usually takes place. Under closed system conditions, the concentration of sulfate is drawn down. As a result of the large fractionation of S during this process, the $\delta^{34}\text{S}$ values of the pore fluids are elevated. If carbonates are recrystallized at the same time, the

newly formed carbonate will incorporate the more positive signal. Failure to recognize this process will result in a misinterpretation of geochemical signals. Finally, the recognition that the clumped isotope signal present at mass 47 can give an indication of temperature has radically improved the interpretation of the formation of carbonates. However, the question remains whether changes in Δ_{47} reflect original temperatures or are a product of diagenesis (Staudigel, 2018).

PROPOSED WORK

We propose to study the behavior of these three isotope systems in well-studied marine and meteoric diagenetic regimes.

Meteoric: As an example of meteoric systems we will use core material from the Bahamas and the Dominican Republic. Both of these archives have well established diagenetic histories and we will examine the behavior of diagenetic systems associated with exposure surfaces, the vadose zone, the freshwater phreatic zone and the mixing zone.

Marine: Marine diagenesis will be studied using both the marine portions of cores from the Bahamas as well as material from various ODP and IODP drilled expeditions. These will include Leg 166 and Expedition 359.

SIGNIFICANCE

Many of the geochemical signatures which are now being taken as evidence of changes in the original environment may in fact be artifacts of diagenesis. If true, while these geochemical proxies may not be able to provide information on the original environment of deposition, understanding the diagenetic signal may allow use of these proxies to better understand carbonate diagenesis and the development of carbonate reservoirs.

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