A Diagenetic Origin for δ¹⁸O Variability on the Margins of the Great Bahama Bank, Insights from Clumped Isotopes*

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Abstract

The sediments deposited at ODP Site 1003 on the margin of Great Bahama Bank (GBB) exhibit a range of chemical and isotopic compositions. The mineralogy at this site consists predominantly of low-Mg calcite (LMC) and in the upper portion (< 200 mbsf) High Magnesium Calcite (HMC) and Aragonite. The aragonite and HMC are derived predominantly from the Bank itself, while the LMC is derived from pelagic sources and that produced by neomorphism of aragonite and HMC and recrystallization of biogenic LMC. The variability of the carbonate δ¹⁸O presents an interesting challenge. Modern sediments at Site 1003 have a composition between -0.5‰ and 0‰, which over the upper 200m increases to +2.0‰. This corresponds to a decrease in aragonite abundance and a consequent increase in (LMC). Below 200 mbsf there is a trend back towards negative δ¹⁸O values, not accompanied with any mineralogical change. Here we investigate these two trends using clumped isotopes (Δ47) to determine if these are primary “mixing model” effects or a result of carbonate diagenesis. Porewater chemistry is extremely sensitive to the alteration of carbonates, changes too small to detect via chemical or isotopic measurement of the sediments can make significant changes to the pore fluid. Here we present porewater data, which provide evidence for diagenesis at this site. Strontium ion concentration gradients provide a minimum estimate for diagenetic rate, as they reach the saturation state of Celestite (SrSO₄) in the upper 200m of sediment. Additionally we present porewater δ¹⁸O and Sr⁸⁷/Sr⁸⁶ of pore fluids; these two measurements provide evidence for deeper diagenesis at this site. The chemical processes present in the subsurface at ODP Site 1003 demonstrate that the co-evolution of sediments and porewaters occurs over a range of temperatures due to geothermal heating, necessitating independent verification of temperature. The precision of this method is constantly improving and as more facilities are able to measure clumped isotopes of carbonates, it could become an invaluable tool for understanding systems such as these.
What are clumped isotopes?  

Because of the many stable isotopes of Carbon (12, 13 AMU) and Oxygen (16, 17, 18 AMU), there are many \( n = 18 \) different isotopic configurations for the molecule \( \text{CO}_2 \) between 44-49 AMU. There is a preference for heavier isotopes to bond to one another “clump”, which is more common at lower temperatures (Wang et al. 2004). This can, in carbonate minerals, be used as a proxy for the temperature of formation (Shauble et al., Ghosh et al., 2006). Because this process is not dependent on the isotopic composition of the fluid from which the mineral formed, this technique has great utility in thermally constraining complex systems, like those present during sediment diagenesis.

Equilibrated Gas Standards
A universal inter-laboratory reference frame (Dennis et al., 2011)

Measuring Pressure Baseline
Correcting for instrument drift and error (He et al., 2012)

Calculating Temperature
Figure from Eller et al., 2011

Calculating water \( \delta^{18}O \)
For any measured \( \delta^{18}O_{\text{carbonate}} \), there exists a range of temperature and \( \delta^{18}O_{\text{water}} \). Clumped isotopes thermally constrain this system.

References Cited


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### Problem and Goals

Oxygen isotope variations can be quantified in carbonates by (1) physical examination of the sediments, and (2) by examining the geochemistry. Geochemical techniques include:

- Rises of trace elements such as Fe from the pore fluids
- δ¹⁸O isotopes of the solids and pore fluids
- Stable oxygen isotopes of the solids and gases

### Study Location

Samples are taken from the Site 1003 from Leg 166 of the ODP. These sites are originally composed of anagpore derived from the Bahamas platform and LAM from seafloor sources. Prominent sources were squeezed from the sediments during Leg 166 and all trace elements analyzed as well as δ¹⁸O (See isotopes; right hand panel). Modeling using these values suggests isotopic exchange between sediments and pore water is prevalent at depth, which could be facilitated by the neomorphism of sediments. With increasing depth not only is argonite converted to LAM, but the input of LAM diminishes. The goal is to understand how these changes are retained in the geohistory as an analogue for ancient sediments.

### The Bahamas Transect

A series of cores were collected on the margin and platform top of the GBB. The three highlighted, which constitute the three most distal sites, display a great deal of isotopic variability from one another; as seen below. This variability could be the result of differences in sediment input. Here we investigate a the δ¹⁸O variability of a diagenetic origin for this using clumped isotopes.

### Significant

- Clumped isotope signatures record a record of original depositional and diagenetic temperatures.
- The best way to use the fluid in which neomorphism and recrystallization occurred.
- Using this method, we have found that sediments deposited adjacent to carbonate platforms as GBB in which the majority of the sediments are argonite, undergo rapid metamorphism to LAM.
- Similar high rates of diagenesis would restrict to periods in which the oceans experienced high Mg/Ca ratios (Argonite Sea).

**Reference Cited:**


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**Upper 200 mbsf: diagenesis or sediment mixing?**

The upper 200 mbsf show strong evidence of mixing because derived from pelagic and platform sources. Highly significant (n = 26, p < 0.001) correlations between mineralogy, conventional isotopes, and clumped isotopes suggest variability in oxygen isotopes could be the result of recrystallization at 20 ± 0.7°C (stated by Elderfield). Measured isotopic temperatures at 1003 are slightly lower 15°C. These sediments record a change in water δ¹⁸O over this interval, suggesting that these reactions occurred in a sediment-buffered system.

**End-member mixing for 25°C - 35°C**

- Water δ¹⁸O calculated using measured δ¹⁸O, mineralogy, temperature from clumped isotopes and weighed mean of carbonates 1 n (1986) and 0.05 n (2010) (Leshkevich et al., 2010).

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**Pore Fluid Oxygen and Strontium Chemistry**

### 1. Oxygen Isotopes: the smoking gun for recrystallization

Co-evolving porewater and sediment

\[ \phi \times \delta^{18}O_{\text{water}} + (1 - \phi) \times \delta^{18}O_{\text{carbonate}} = \text{constant (closed system)} \]

\[ \delta^{18}O_{\text{water-carbonate}} = \frac{1000 + \delta^{18}O_{\text{carbonate}}}{1000 + \delta^{18}O_{\text{water}}} \]

\[ 1000 \ln \delta^{18}O_{\text{water-carbonate}} = 18.03 \times 10^{3}/T - 32.42 \]

As sediments recrystallize, pore fluids become more enriched in O\(^{18}\). This behavior is observed at periplatform sites on the ODP 166 Transect, suggesting extensive diagenesis is occurring at depth.

### 2. Reaction-diffusion model for Strontium Isotopes

As aragonite dissolves, strontium accumulates in pore fluids. This process can be an early step in the diagenesis of platform-derived sediments.

**Reference Cited**


*Highest Sr\(^{2+}\) abundance ever measured in porewaters by ODP: 4380μM (500x seawater) Data from Kramer et al., (2000)