

PS A Diagenetic Origin for $\delta^{18}\text{O}$ Variability on the Margins of the Great Bahama Bank, Insights from Clumped Isotopes*

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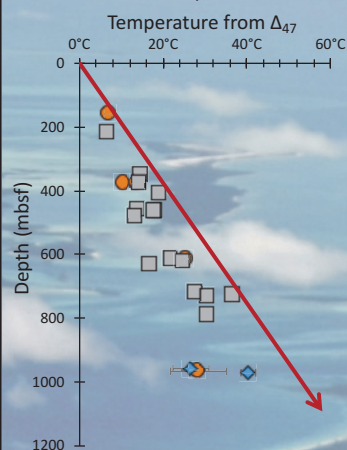
Abstract

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 $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ values, not accompanied with any mineralogical change. Here we investigate these two trends using clumped isotopes ($\Delta 47$) 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 (SrSO_4) in the upper 200m of sediment. Additionally we present porewater $\delta^{18}\text{O}$ and $\text{Sr}^{87}/\text{Sr}^{86}$ 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.

Measuring clumped isotopes at the

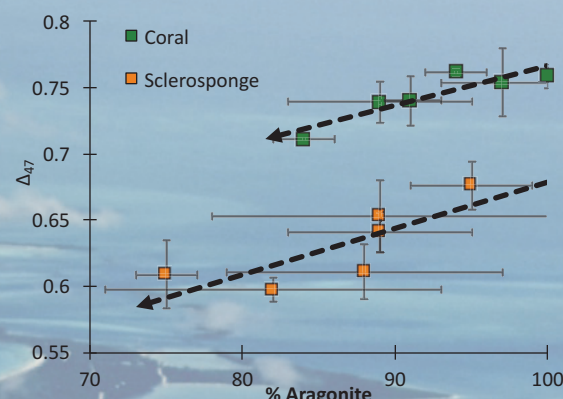


Cementation temperatures in Antarctic Core, AND-2A



Other exiting work!

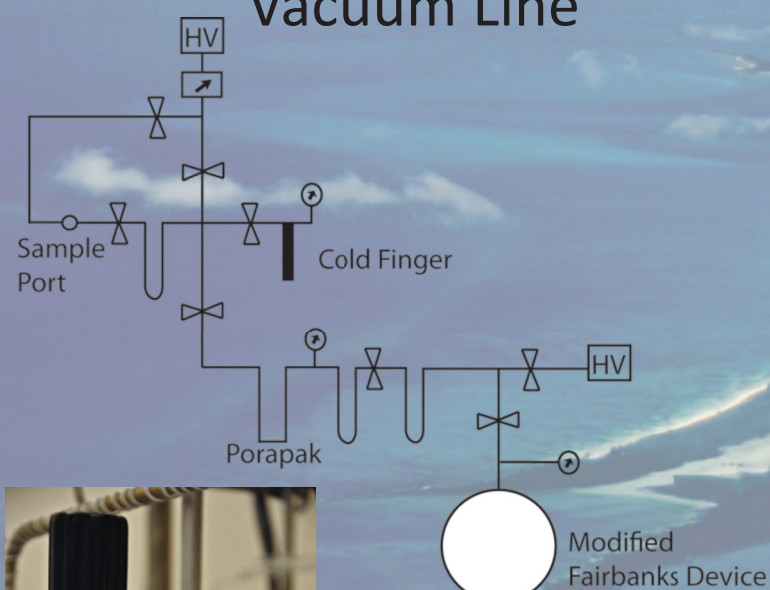
Biases in Δ_{47} from sampling technique



What are clumped isotopes? 3

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 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 (Schauble 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.

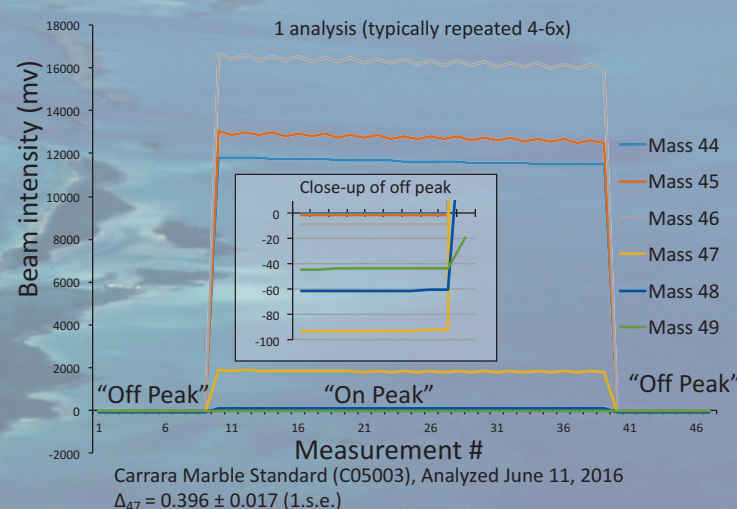
Vacuum Line



Top: Schematic of the SIL Vacuum Line. Vacuum is maintained using two Turbo Pumps (labeled as HV). Bottom Left: Sample vessel for transfer to MS. Bottom Right: Sample being digested in H_3PO_4 in reaction vessel.

Measuring Pressure Baseline

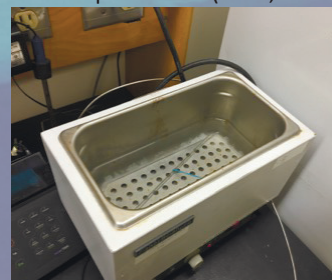
Correcting for instrument drift and error (He et al., 2012)



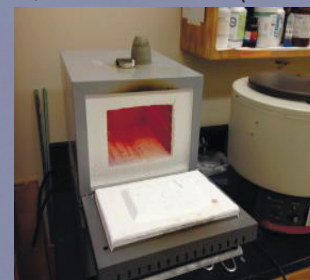
Equilibrated Gas Standards

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

Water equilibrated (25°C, 50°C)

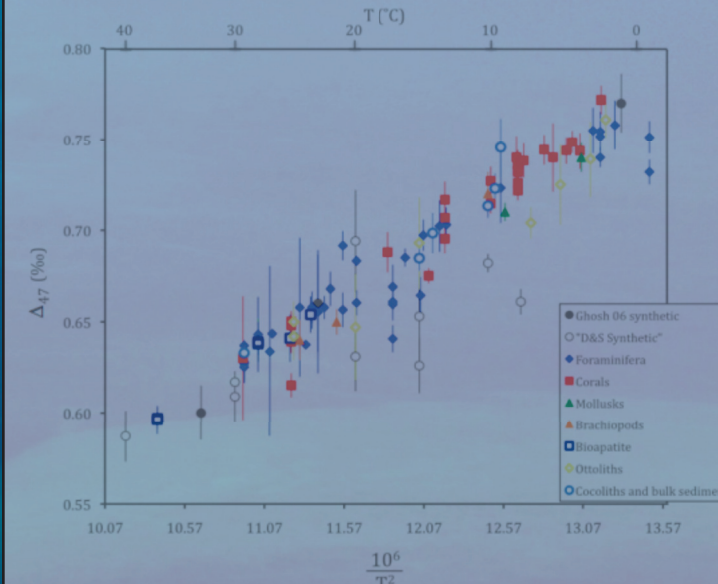


Quartz-tube heated (1000°C)



Calculating Temperature

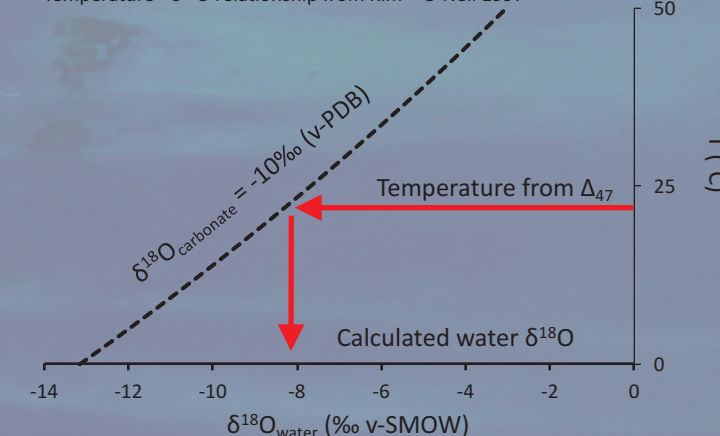
Figure from Eiler et al., 2011



Calculating water $\delta^{18}\text{O}$

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

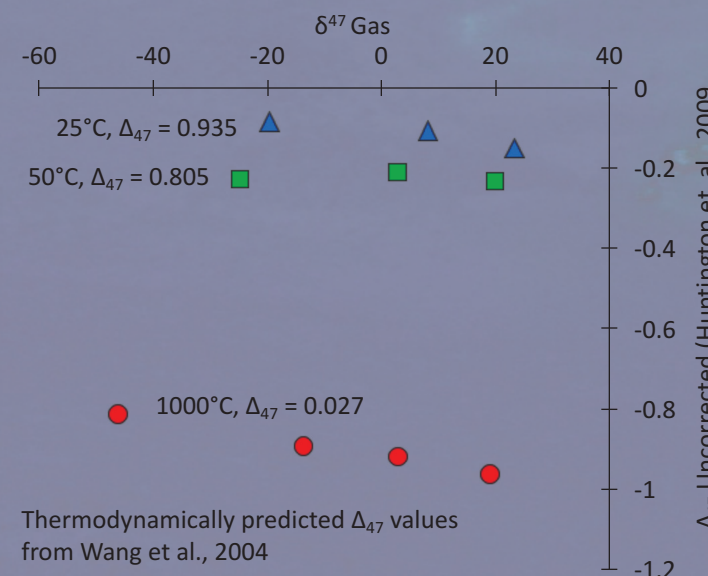
Temperature - $\delta^{18}\text{O}$ relationship from Kim + O'Neil 1997



MAT-253 Mass Spectrometer



Built to measure CO_2 between masses 44-49



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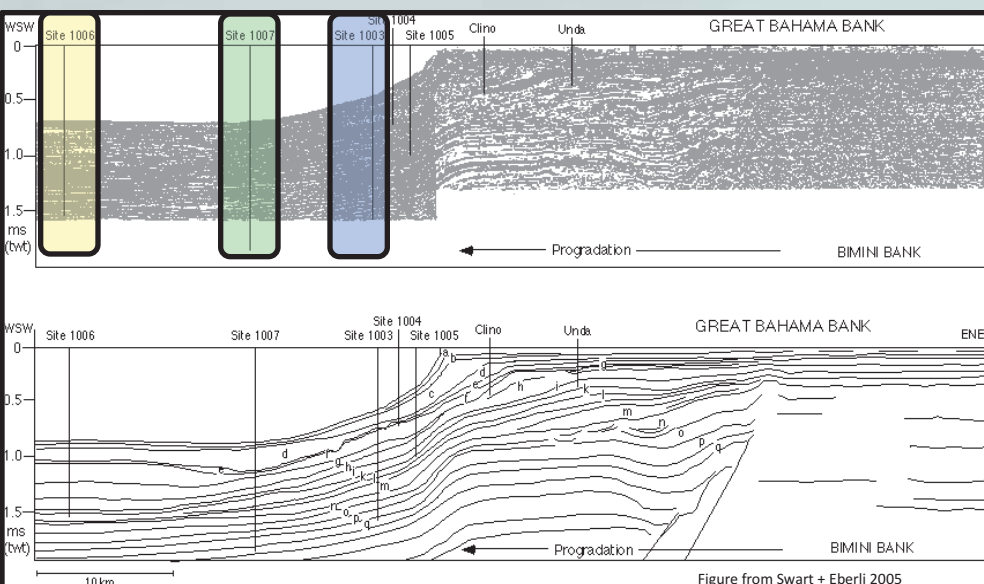
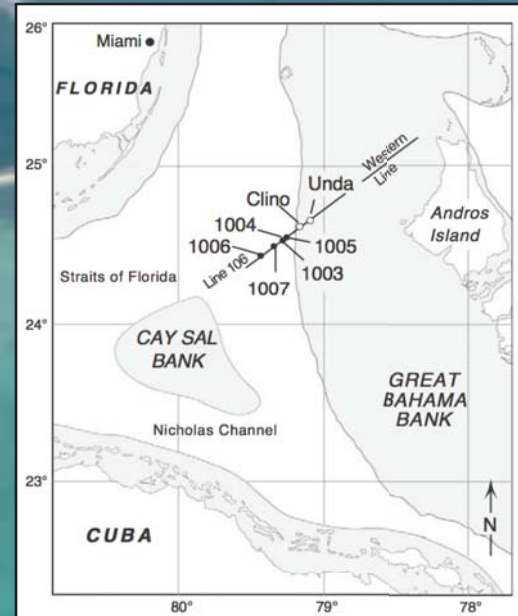
Problem and Goals

Rates of neomorphism and recrystallization can be quantified in carbonates by (i) physical examination of the sediments, and (ii) by examining the geochemistry. Geochemical techniques include

- Fluxes of trace elements such as Sr from the pore fluids
- Sr-isotopes in the solids and pore fluids **2**
- Stable oxygen isotopes of the solids and pore fluids **1**
- Calcium isotopes $\delta^{44/40}\text{Ca}$
- Clumped Isotopes Δ_{47} **3**

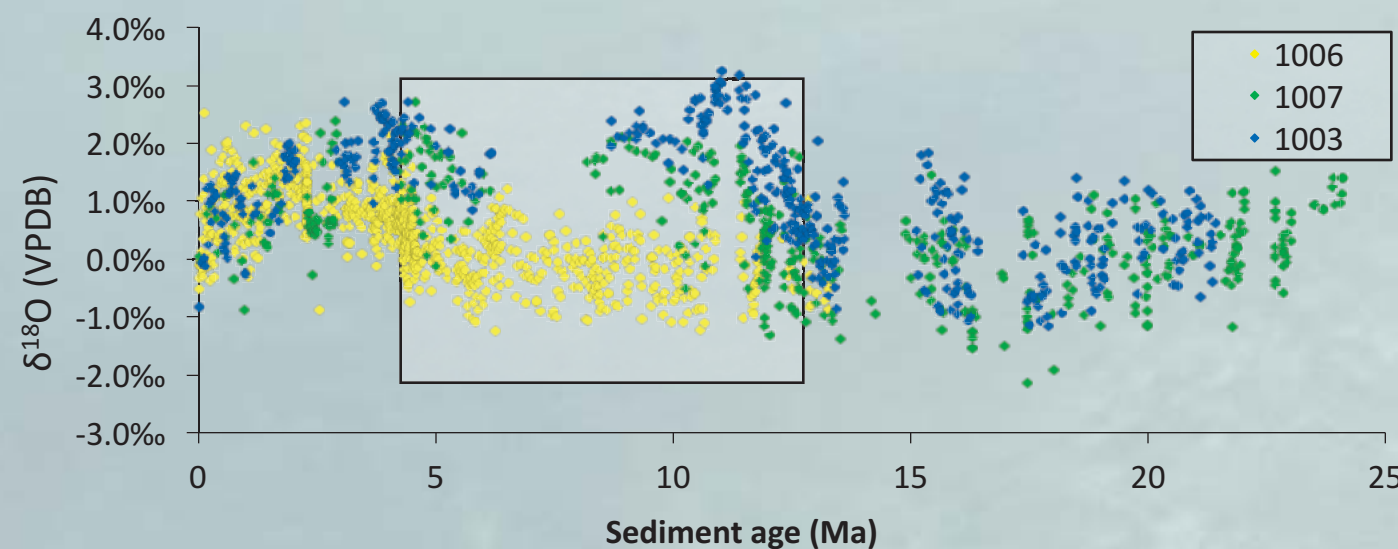
Study Location

Samples are taken from the Site 1003 from Leg 166 of the ODP. These sites are originally composed of aragonite derived from the Bahama platform and LMC from pelagic sources. Porewater samples were squeezed from the sediments during Leg 166 and all trace elements were analyzed as well as O **1** and Sr isotopes **2** (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 aragonite converted to LMC, but the input of LMC diminishes. The goal is to understand how these signals are retained in the geochemistry as an analogue for ancient sediments.

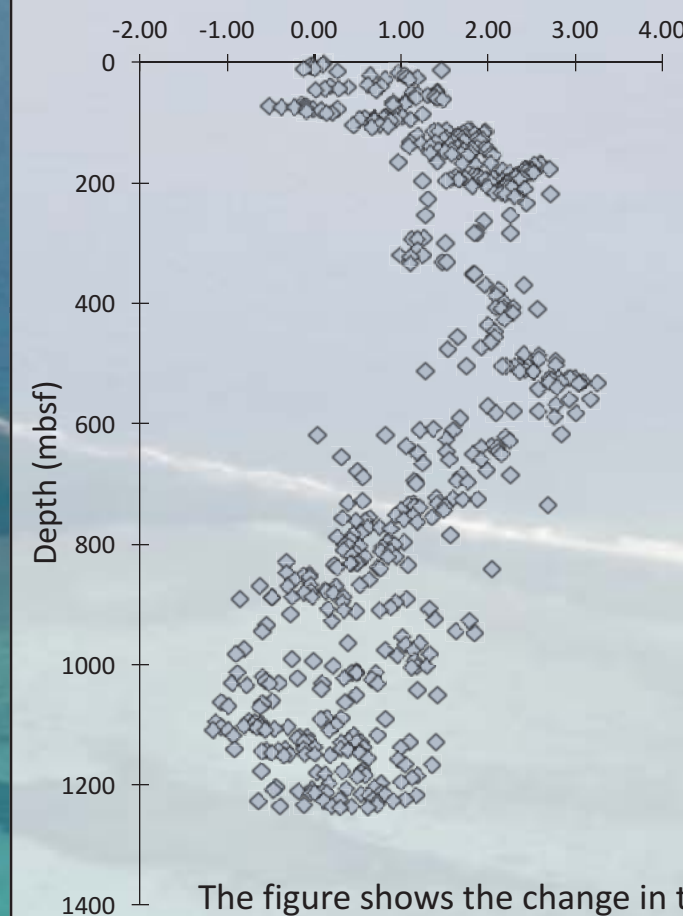


The Bahamas Transect

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 possibility of a diagenetic origin for this using clumped isotopes.



Sediment Composition



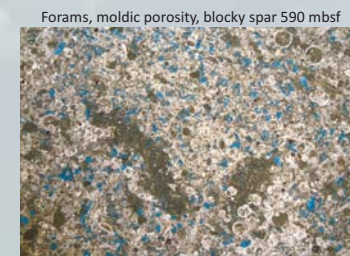
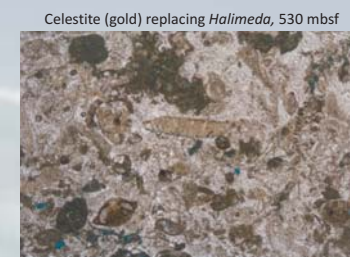
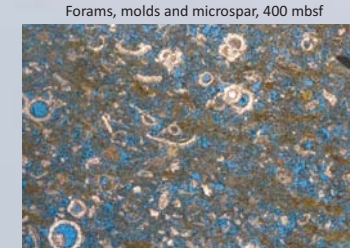
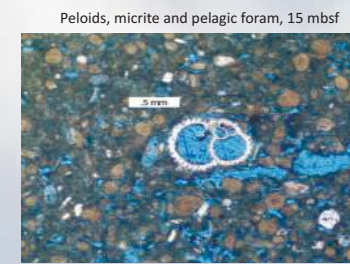
0-200 mbsf
Trend towards more positive $\delta^{18}\text{O}$ values, highly variable. Most variance correlates with changes in %Aragonite **1**, $\delta^{13}\text{C}$ **2** and Δ_{47} **3**. Indicative of an overall cooling (downward) trend. This trend, which is accompanied by a change in water $\delta^{18}\text{O}$ values suggest a substantial portion (70%) of this is a result of neomorphism near the seafloor.

200-520 mbsf
Abrupt loss of peloidal material in sediment, nearly complete loss of aragonitic material. Some variability which appears to correlate with changes in Δ_{47} **3**, although further sampling would be necessary to confirm this behavior. Sharp decreases in $\delta^{18}\text{O}$ correlate with a hiatus in deposition.

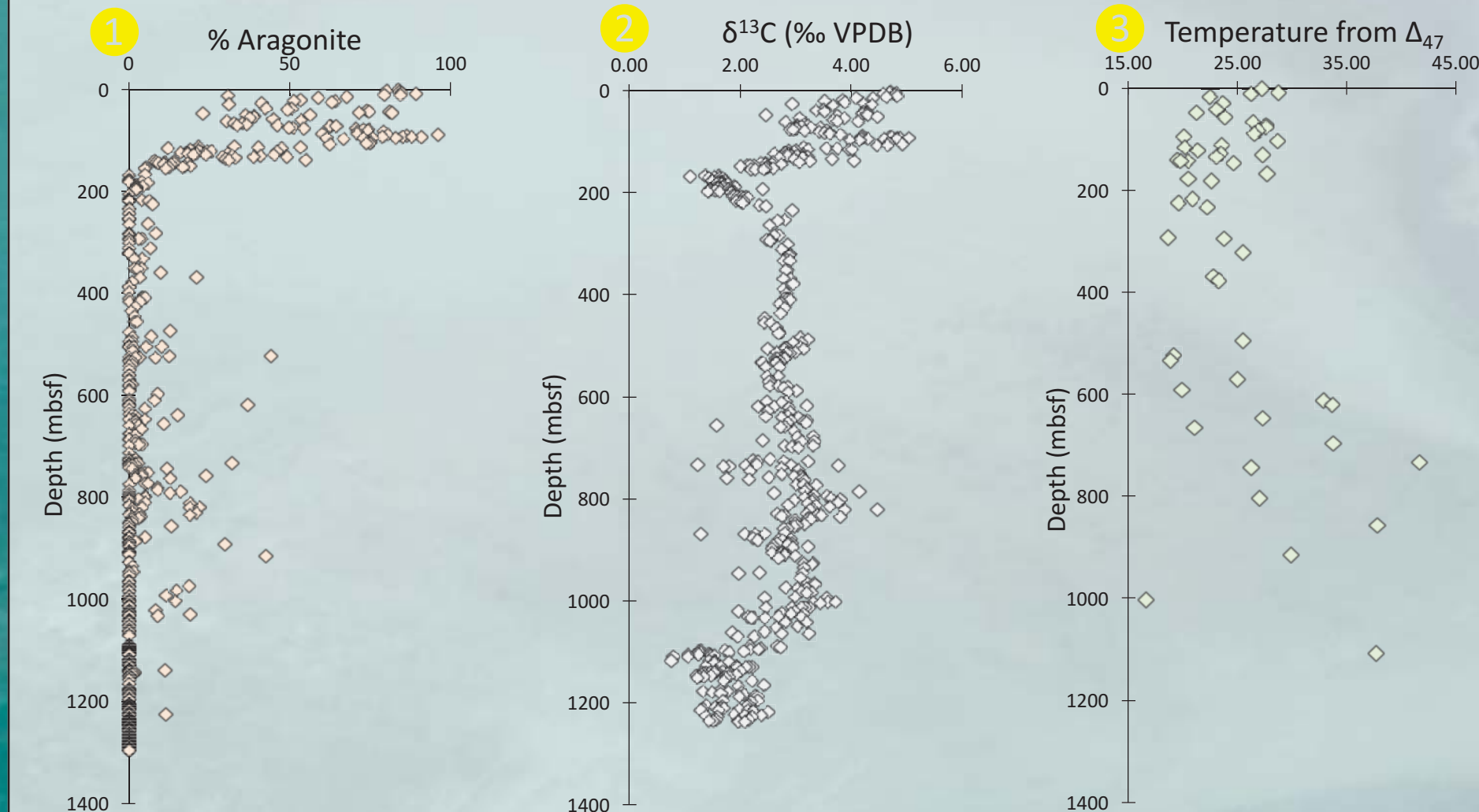
520-900 mbsf
Trend towards more negative $\delta^{18}\text{O}$ values (downcore), associated with higher temperatures from clumped isotopes. Suggesting recrystallization at depth in a more $\delta^{18}\text{O}$ enriched pore water at higher temperatures. See Pore fluids panel for more detail. Some aragonite and dolomite present.

900 mbsf
High variability in $\delta^{18}\text{O}$, trend towards more negative $\delta^{13}\text{C}$ **2** values. No overall trend in $\delta^{18}\text{O}$ or clumped isotopes

Petrography

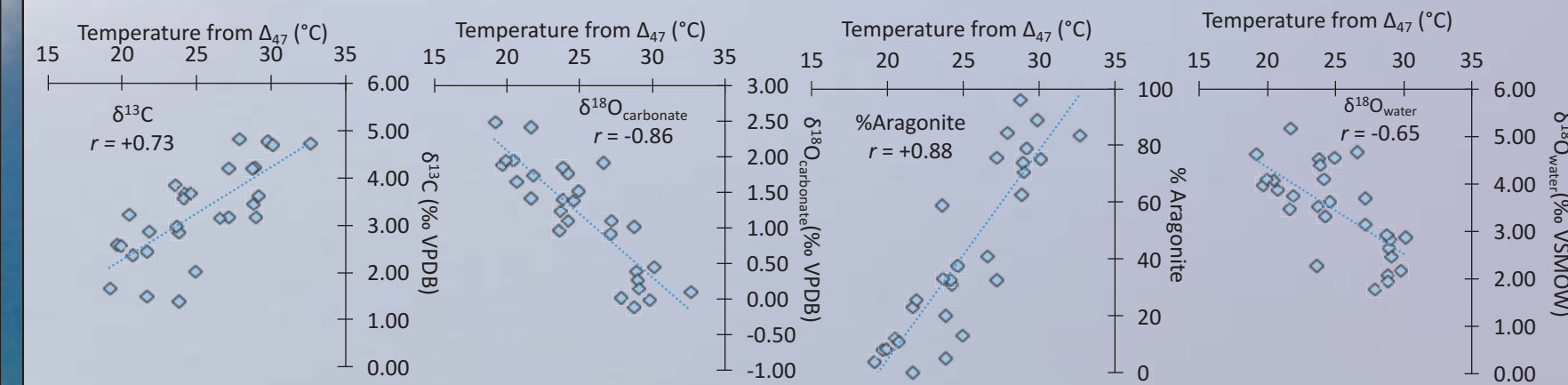


The figure shows the change in the $\delta^{18}\text{O}$ in the bulk sediments with increasing depth.



Upper 200 mbsf: diagenesis or sediment mixing?

The upper 200 mbsf shows strong evidence of mixing between material derived from pelagic and platform sources. Highly significant ($n = 28$, $p < 0.001$) correlations between mineralogy, conventional isotopes, and clumped isotopes suggest variability in oxygen isotopes could be the result of recrystallization at $20 \pm 0.5^\circ\text{C}$. Measured benthic temperatures at 1003 are slightly lower 16°C . These sediments record a change in water $\delta^{18}\text{O}$ over this interval, suggesting that these reactions occurred in a sediment-buffered system.



End-member mixing linear statistics:
Calcite / Aragonite end-members

	Calcite	Aragonite
$\delta^{13}\text{C}$ (VPDB)	1.98‰	5.09 ± .07‰
$\delta^{18}\text{O}$ (VPDB)	2.00‰	-0.07 ± 0.07‰
Temperature	20.6°C	31.2 ± 0.57°C
Water $\delta^{18}\text{O}$ (SMOW)	4.3‰	2.8 ± .8‰

Water $\delta^{18}\text{O}$ calculated using measured $\delta^{18}\text{O}$, mineralogy, temperature from clumped isotopes and weighted mean of Grossman + Ku (1986) and Kim + O'Neil (1997)

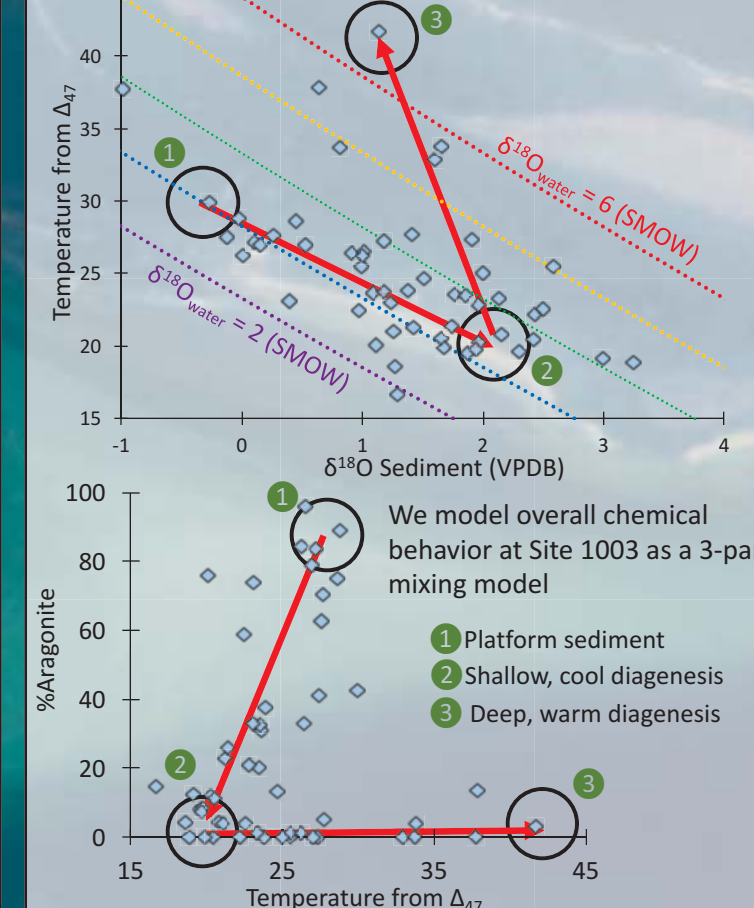
$$\% \text{Recrystallization} = \frac{T(\Delta_{47}^{\text{original}}) - T(\Delta_{47}^{\text{measured}})}{T(\Delta_{47}^{\text{original}}) - T(\text{benthic})}$$

$$(31.2^\circ\text{C} - 20.6^\circ\text{C}) / (31.2^\circ\text{C} - 16.0^\circ\text{C}) = 70\%$$

Age at 200 mbsf: 2.7 myr \rightarrow 25% / myr

These estimates suggest the deeper sediment consists of roughly 30% original calcite, which is less reactive than the aragonite material. This confirms a previous interpretation that some of this trend is a result of changes in sediment source. The high temperatures recorded in sediments deeper than 200mbsf suggest that this neomorphosed material may react further with porewaters, however this interpretation is difficult to confirm.

Overall Chemical Behavior



Significance

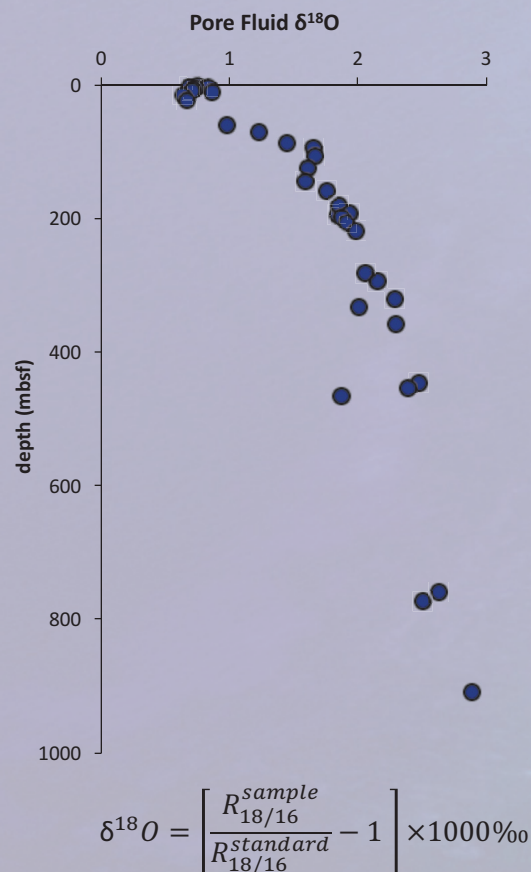
- Clumped Isotopic signatures record a record of original depositional and diagenetic temperatures.
- These can be used to constrain the fluid in which neomorphism and recrystallization occurred.
- Using this method, we have shown that sediments deposited adjacent to carbonate platforms such as GBB in which the majority of the sediments are aragonite, undergo rapid transformation to LMC.
- Similar high rates of diagenesis would restricted to periods in which the oceans experienced high Mg/Ca ratios (Aragonite Seas).

Reference Cited:

- Grossman, E. L., and Ku, T.-L., 1986, Oxygen and carbon isotope fractionation in bogenic aragonite: temperature effects: Chemical Geology, v. 59, p. 59-74.
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Pore Fluid Oxygen and Strontium Chemistry

1 Oxygen Isotopes: the smoking gun for recrystallization



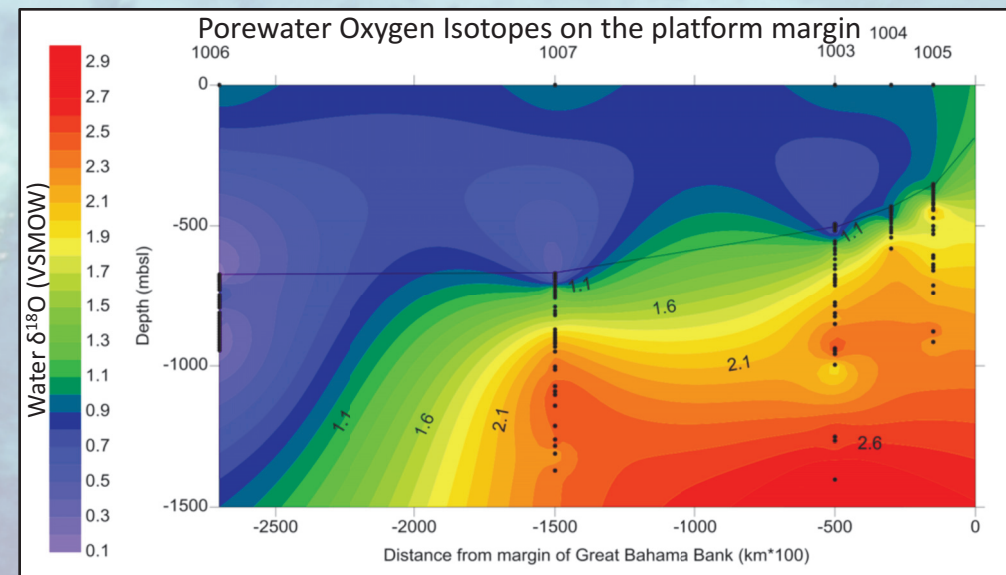
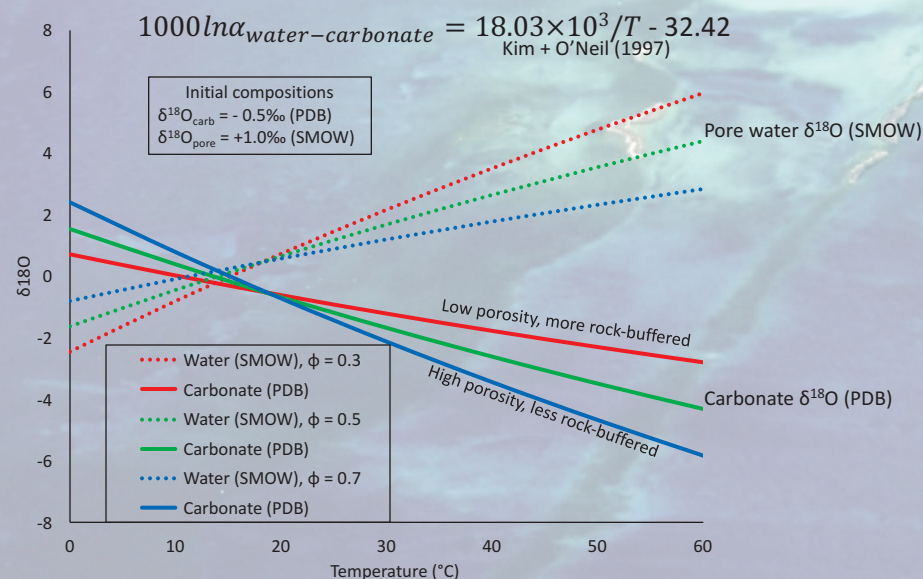
Co-evolving porewater and sediment

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

$$\alpha_{water-carbonate} = \frac{1000 + \delta^{18}O_{carbonate}}{1000 + \delta^{18}O_{water}}$$

$$1000 \ln \alpha_{water-carbonate} = 18.03 \times 10^3 / T - 32.42$$

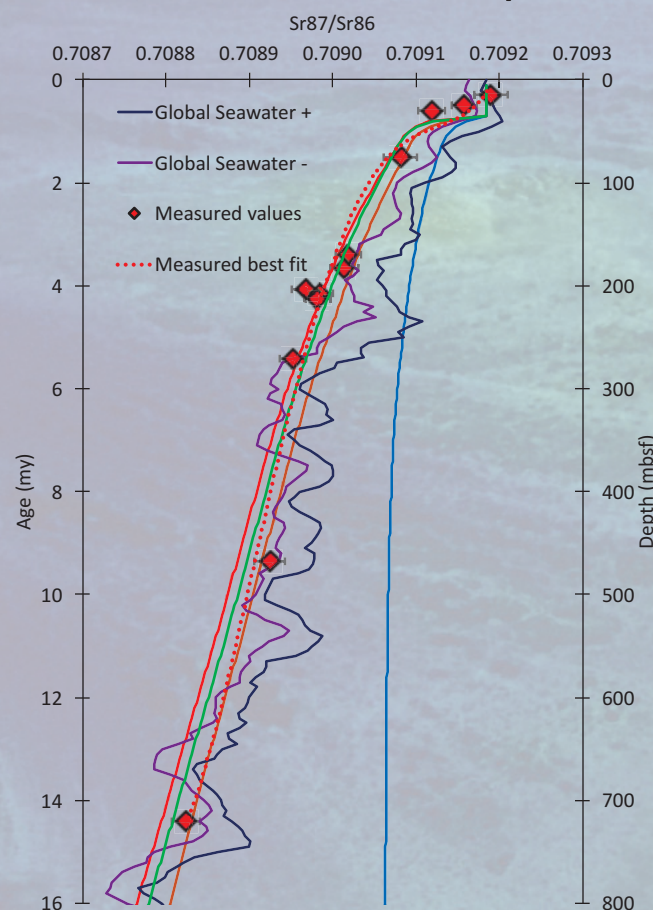
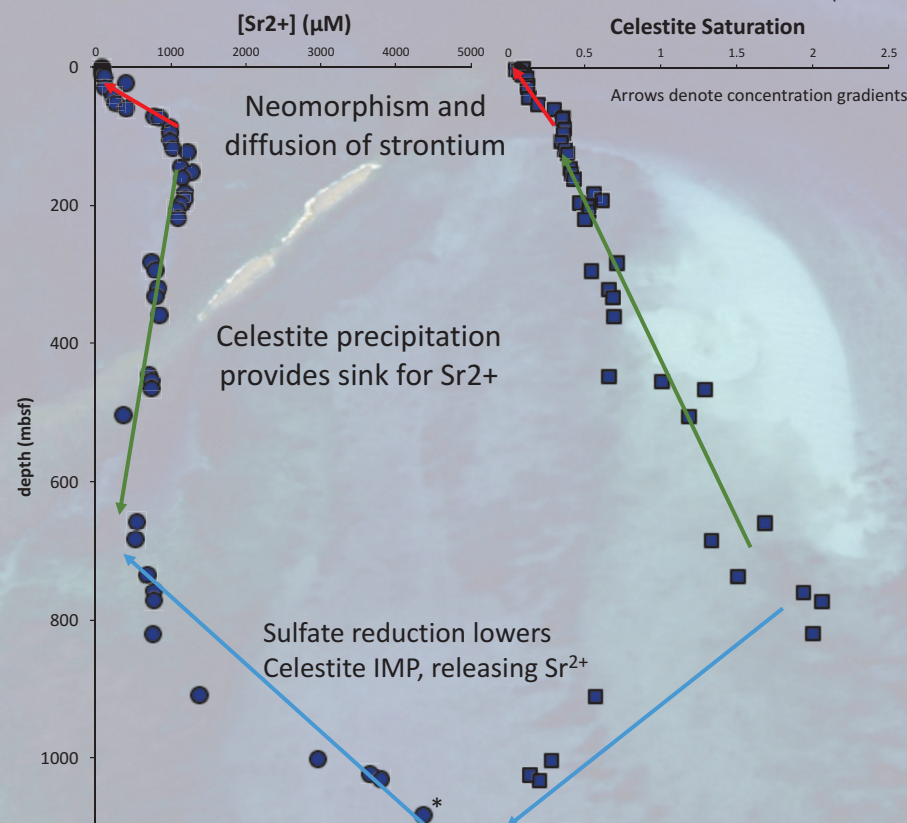
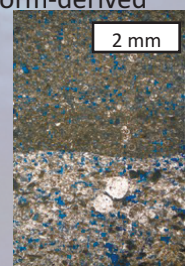
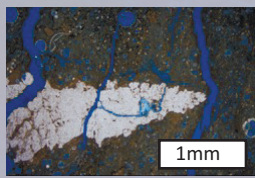
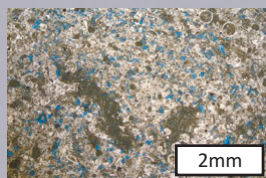
Kim + O'Neil (1997)



As sediments recrystallize, pore fluids become more enriched in O^{18} . This behavior is observed at all 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.



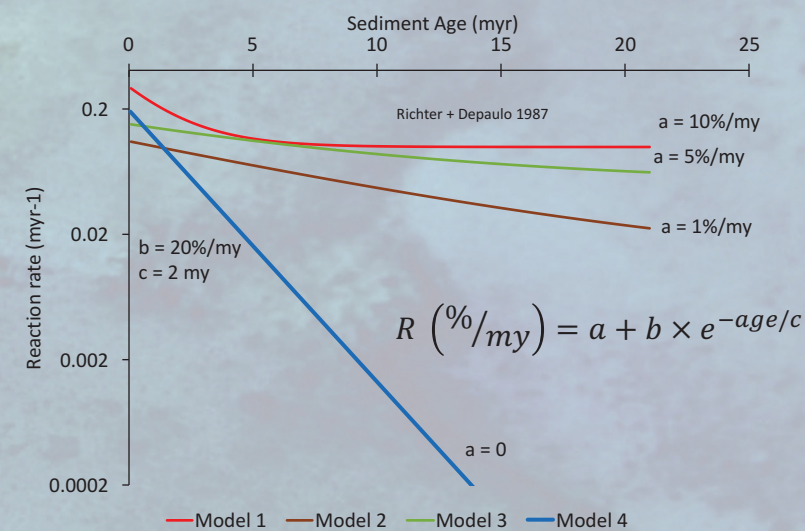
Strontium isotopes show significant upward transport of Strontium. Reaction-diffusion models estimate recrystallization rates between 1-10%/my at depth.

$$\frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial z^2} D + \frac{\partial C}{\partial z} V + RM(C_s - KC_f)$$

Mathur and Fantle 2015

D = diffusion coefficient
C = concentration
Cx = Concentration in (S) Solids, (F) Fluids
K = equilibrium distribution coefficient
M = solid/fluid mass ratio

V = advective velocity
R = reaction rate



Sediments tend to become less reactive with time, plotted are several hypothetical diagenetic behaviors

Reference Cited

- Kim, S.-T., and O'Neil, J. R., 1997, Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates: *Geochimica et Cosmochimica Acta*, v. 16, p. 3461-3475.
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*Highest Sr^{2+} abundance ever measured in porewaters by ODP: $4380 \mu M$ (500x seawater)
Data from Kramer et al., (2000)

