Application of Clumped Isotope Palaeothermometry to reconstruct thermal evolution of recrystallised calcite in fine-grained micrites

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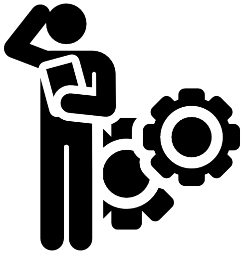
Contents

What are we trying to achieve?

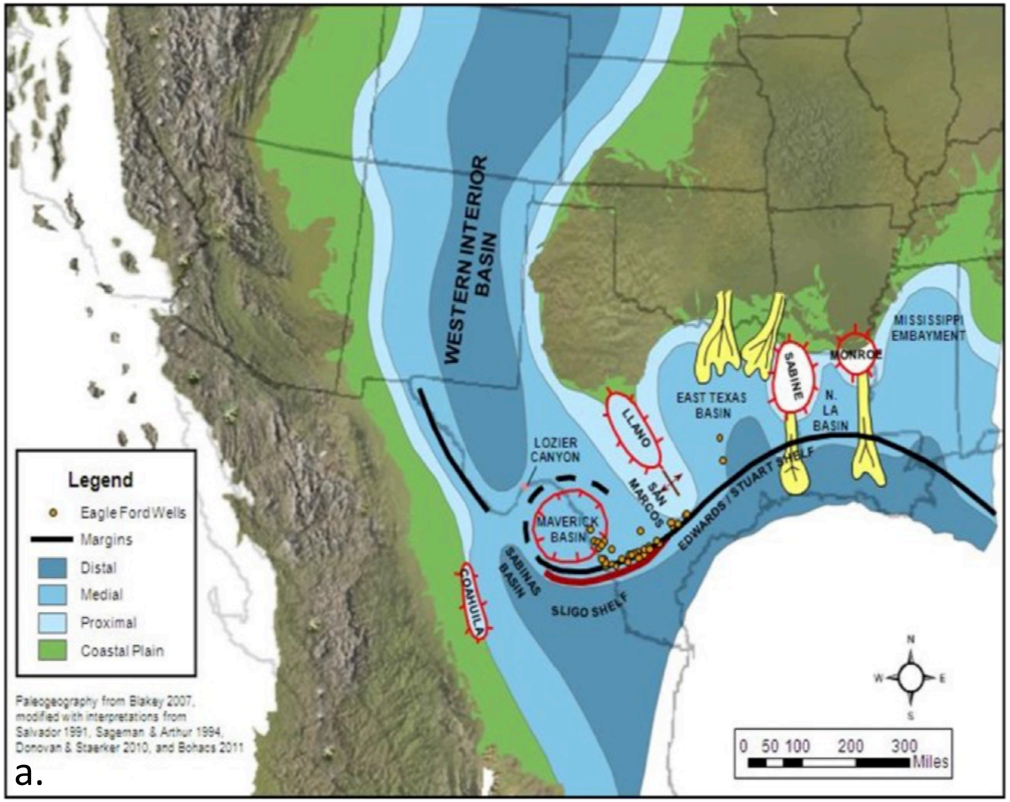


Problem: Understanding the thermal evolution of carbonates in fine-grained micrites.

Aim: To investigate the evolution of carbonate content in micritic sediments through the analysis of carbonate clumped isotopes.

Hypothesis: The temperatures recorded by clumped isotopes will represent minimum estimates of the maximum burial temperatures because of dissolution and reprecipitation during burial

Case Study: Eagle Ford Shale Texas



Dataset:

- 18 outcrop samples
- Location of samples is from the Lozier Canyon and San Antonio Canyon
- Samples are mixed carbonate silliclastic
- Outcrop samples have been interpreted to be immature

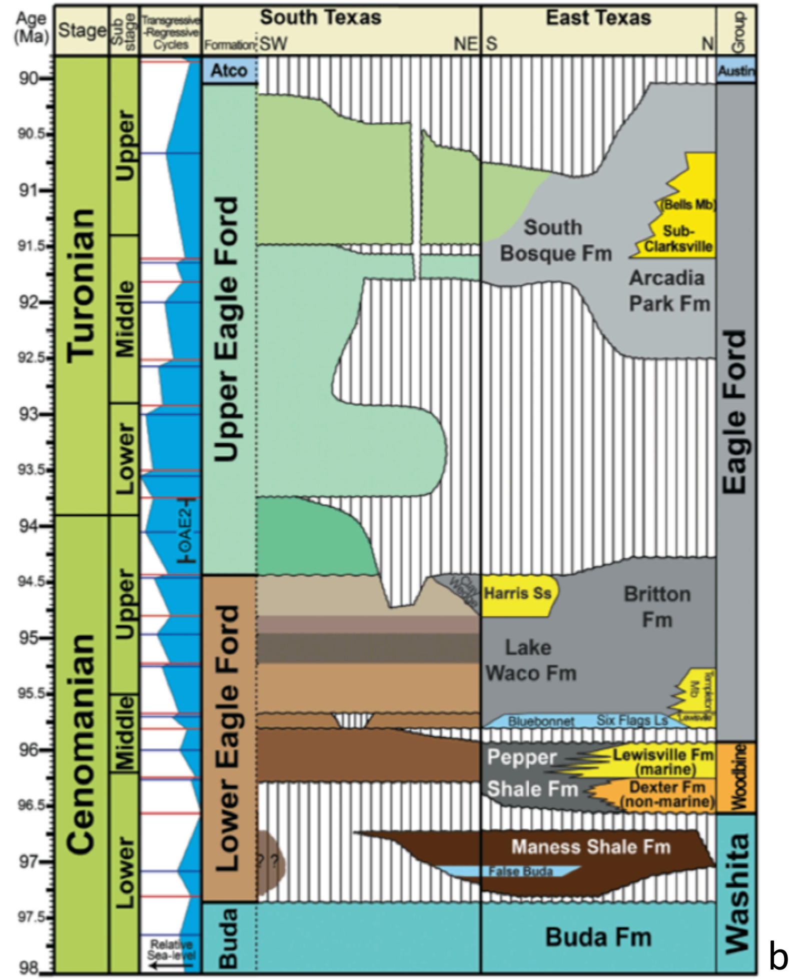


Figure a – Stratigraphic column of the Cenomanian to Turonian modified by Patterson (2018). Original from Denne & Breyer (2016).
Figure b - Paleogeographic map during the Cretaceous, superimposed with present day states taken from Donovan & Staerk (2010).

Methodology

Step One

Sample Preparation

Powdering using a pestle and mortar to a homogeneous grain size.

Step Two

Sample Characterisation

- Scanning Electron Microscopy – identify textures
- Fourier Transform Infrared – compositional analysis

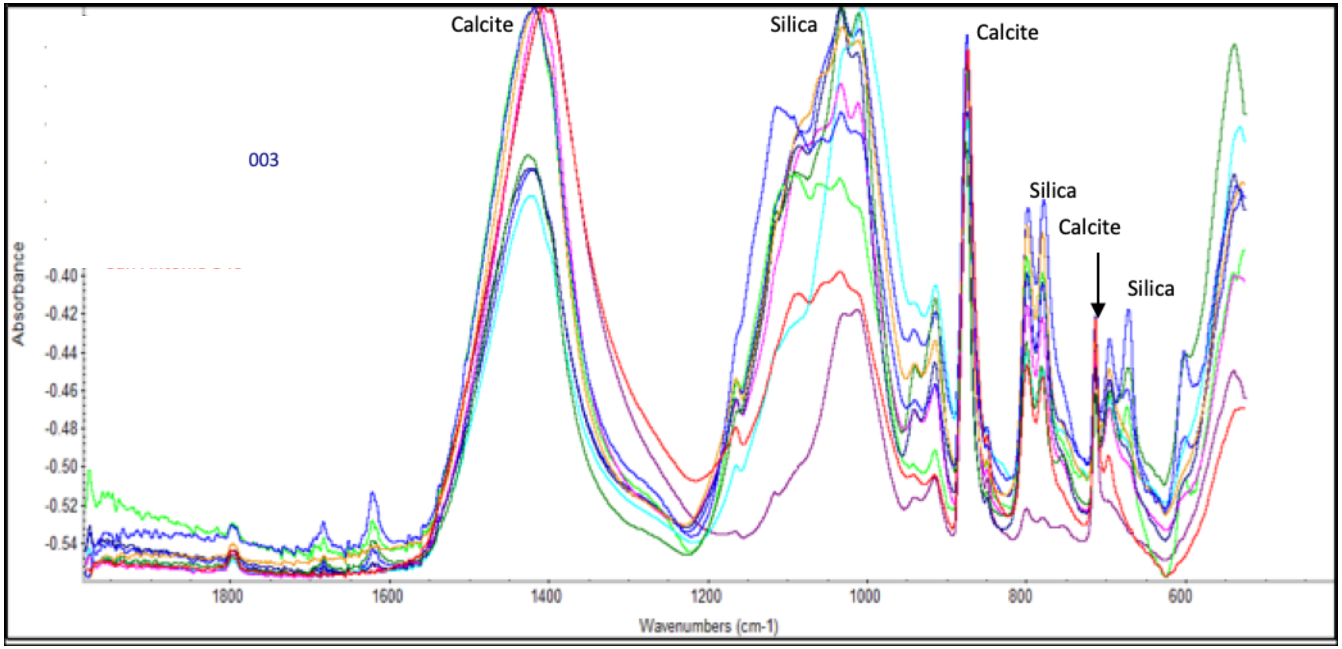
Step Three

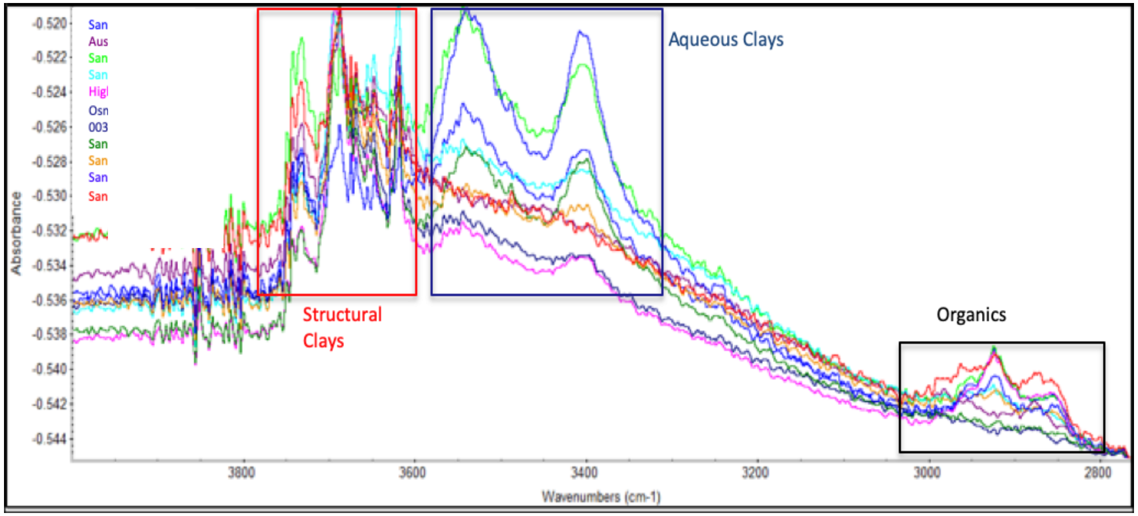
Stable Isotope Analysis

- Clumped isotope measurements
- Bulk isotope measurements

Results – Sample Characterisation

Composition

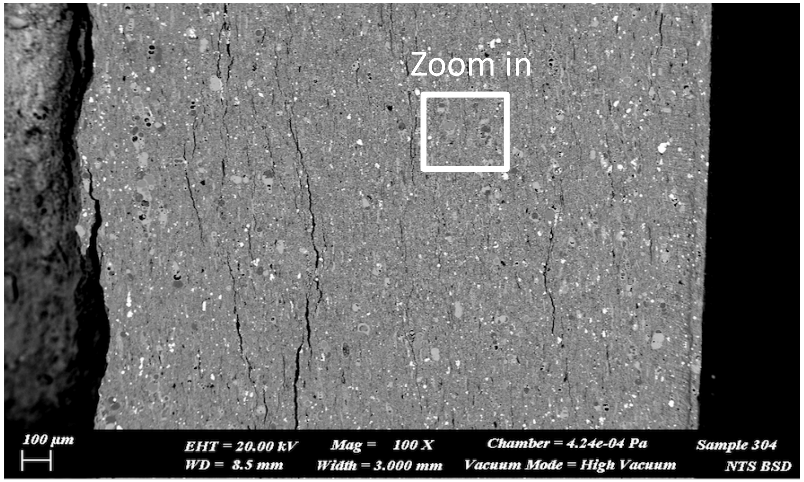




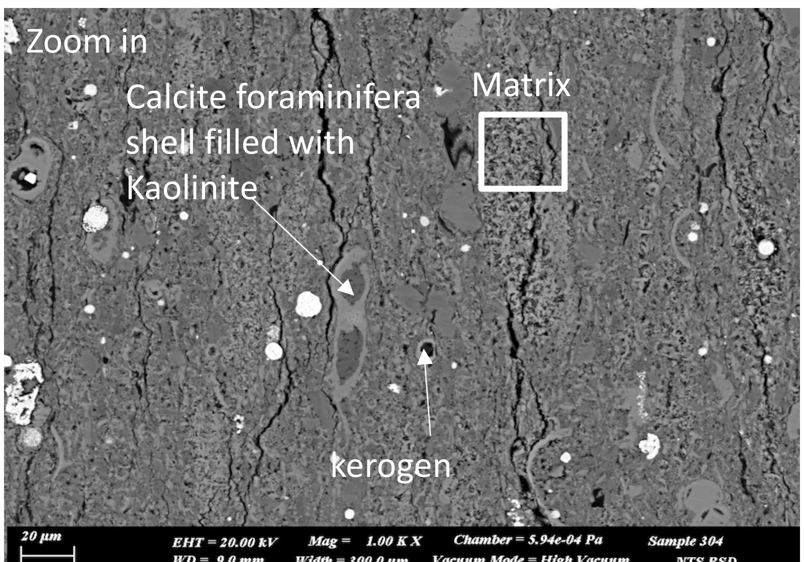
- One species of carbonate – Calcite
- Calcite mixed with silicates – samples show approximately 50:50 of calcite to silicate
- Organics can also be detected

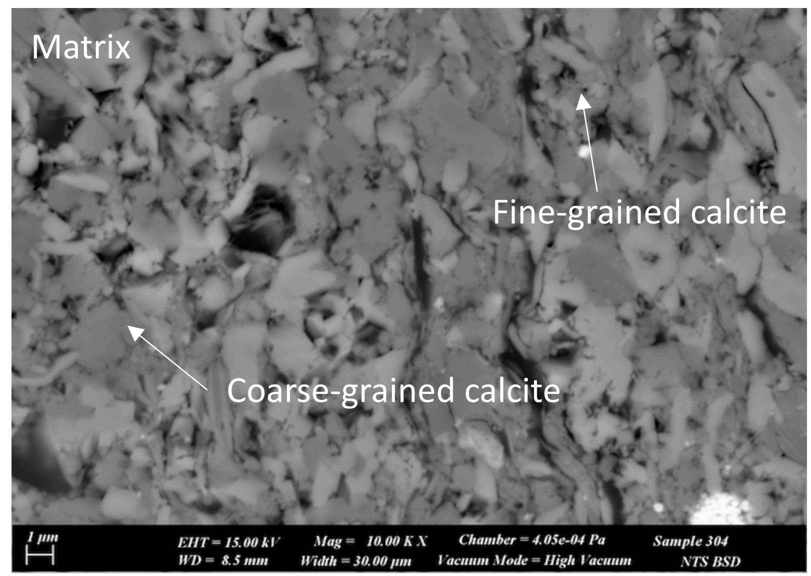
Results – Sample characterisation

Textures



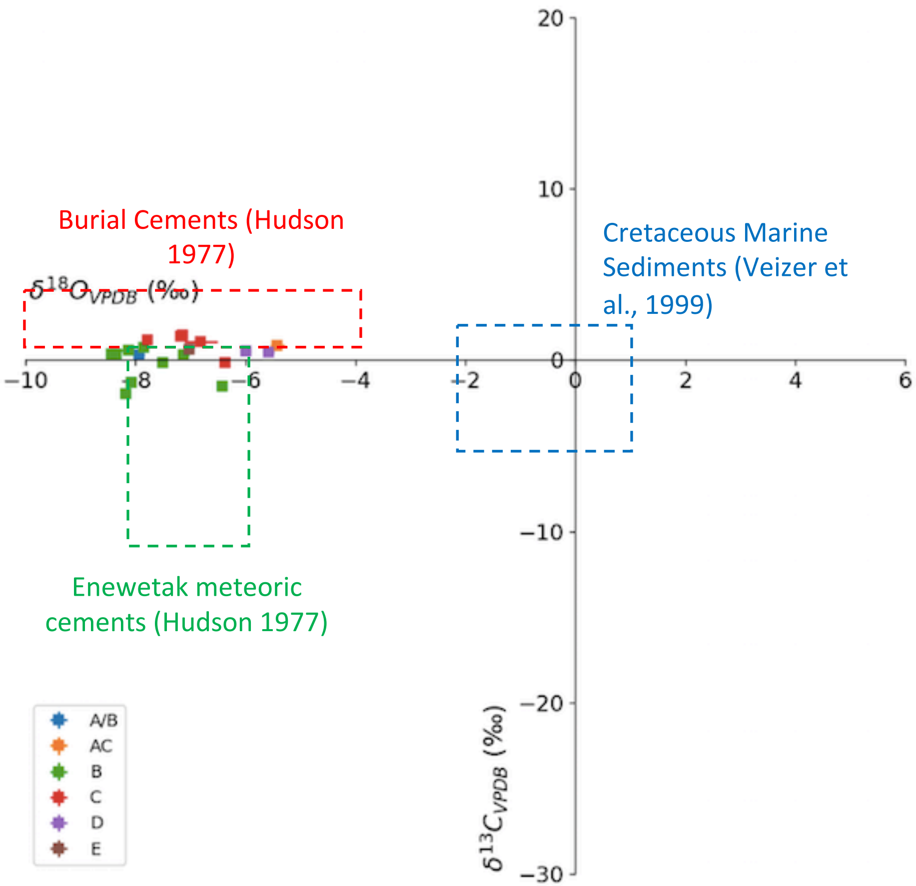
- Heterogenous samples
  - Foraminifera
  - Matrix – crystal size variation
  - Kerogen
  - Micro-fracturing
- Matrix – two dominant grain sizes of calcite – fine and coarse



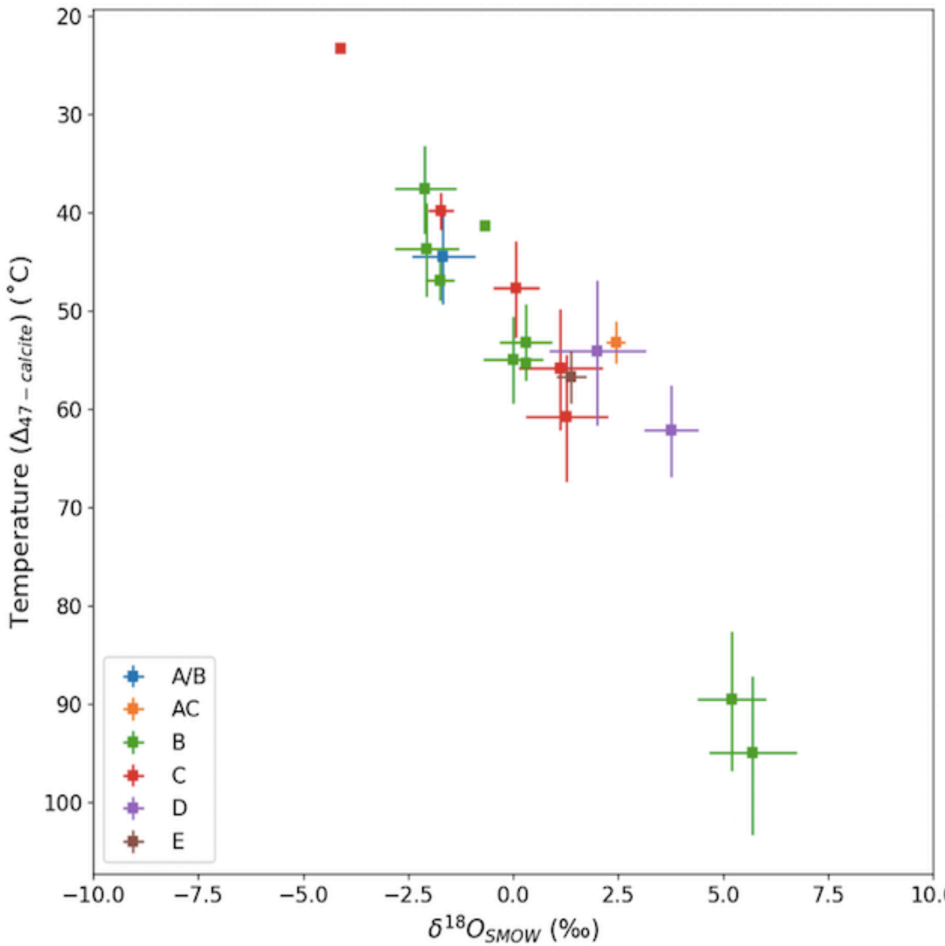


Results - Stable Isotopes

Bulk Isotopes



Clumped Isotopes



- Variation of 3 ‰ $\delta^{18}O_{calcite}$ and 5 ‰ $\delta^{13}C_{calcite}$
- Falls within burial cements and meteoric cements, but does not represent Cretaceous marine sediments

- Positive linear correlation
- Temperature range from 25 to 105°C with data that is relatively continuous

Discussion – Solid State Mixing

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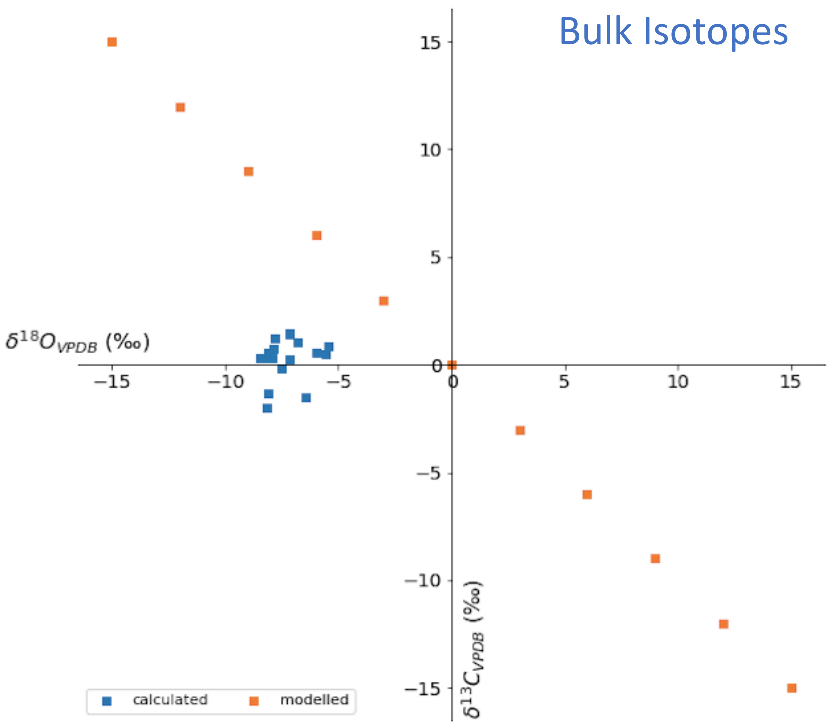
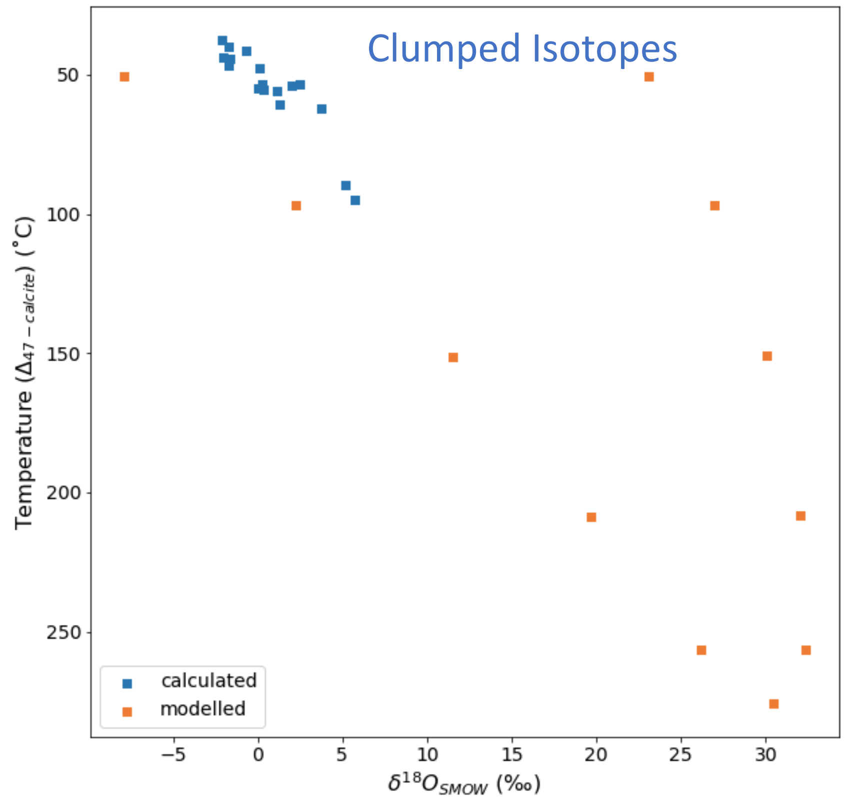
- Solid-state mixing = mixing of two end members causing deviation in measured isotopic values. (Defliese & Lohmann, 2015).
  - Dependent on end member compositions in $\delta^{18}O_{calcite}$ and $\delta^{13}C_{calcite}$. and independent of end member Δ_{47} values
  - Overestimations and underestimations of Δ_{47} are possible from solid state mixing
- 22 scenarios were run using Defliese and Lohmann (2015)'s numerical mixing model
  - Model 11 showed the highest Pearson Coefficient Correlation for both bulk and clumped isotope
- Is this model feasible?
  - Bulk isotope values are extreme – hydrothermal fluids produce these bulk isotopes
  - If we had mixing from these end members it would likely show more spread across the modelled data
  - Calculated data shows a cluster
- Conclude – mixing is possible but unlikely





Discussion – Carbonate Recrystallisation

Past Research:

- Dissolution and reprecipitation can occur during burial with minimal/ no effect on the calcite composition, however the Δ_{47} values can be reset and no longer represent depositional temperatures and now represent the minimum estimate of the maximum burial temperatures (John, 2015).
- In fine-grained dolomite recrystallisation has the potential to affect $T(\Delta_{47})$ at relatively shallow depths (<1 Km) and low temperatures (12 to 35°C) (Veillard et al., 2019).

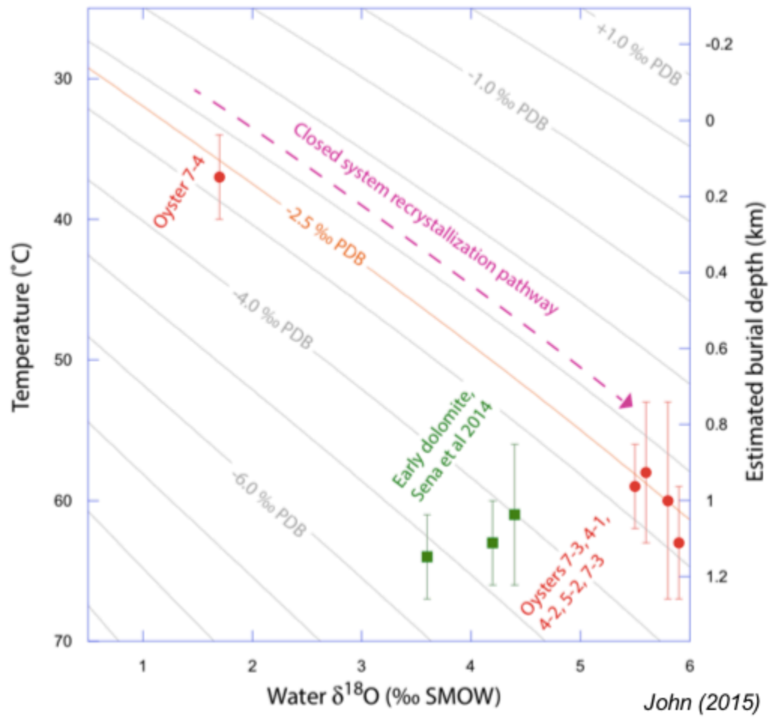
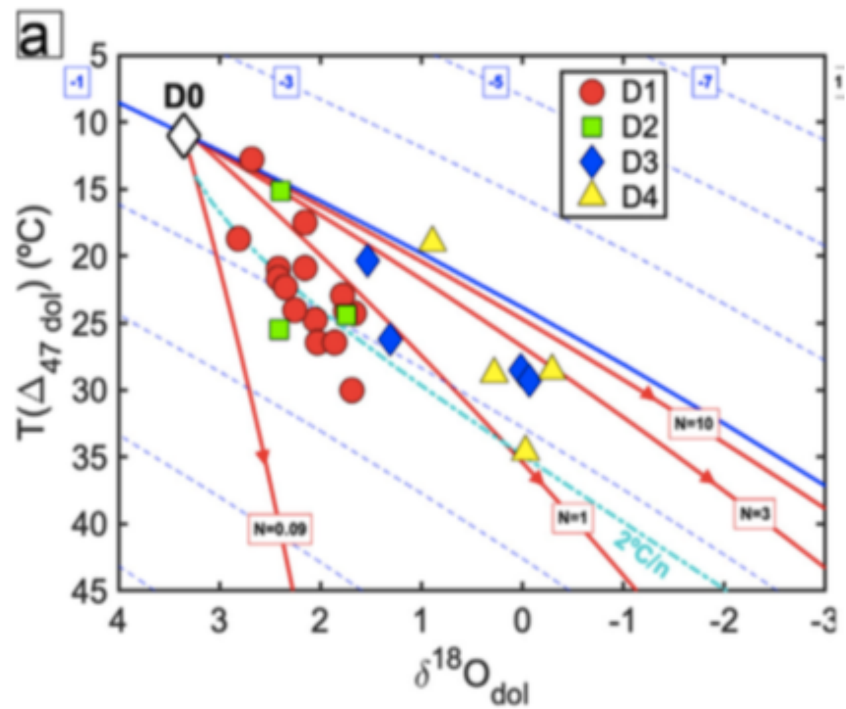


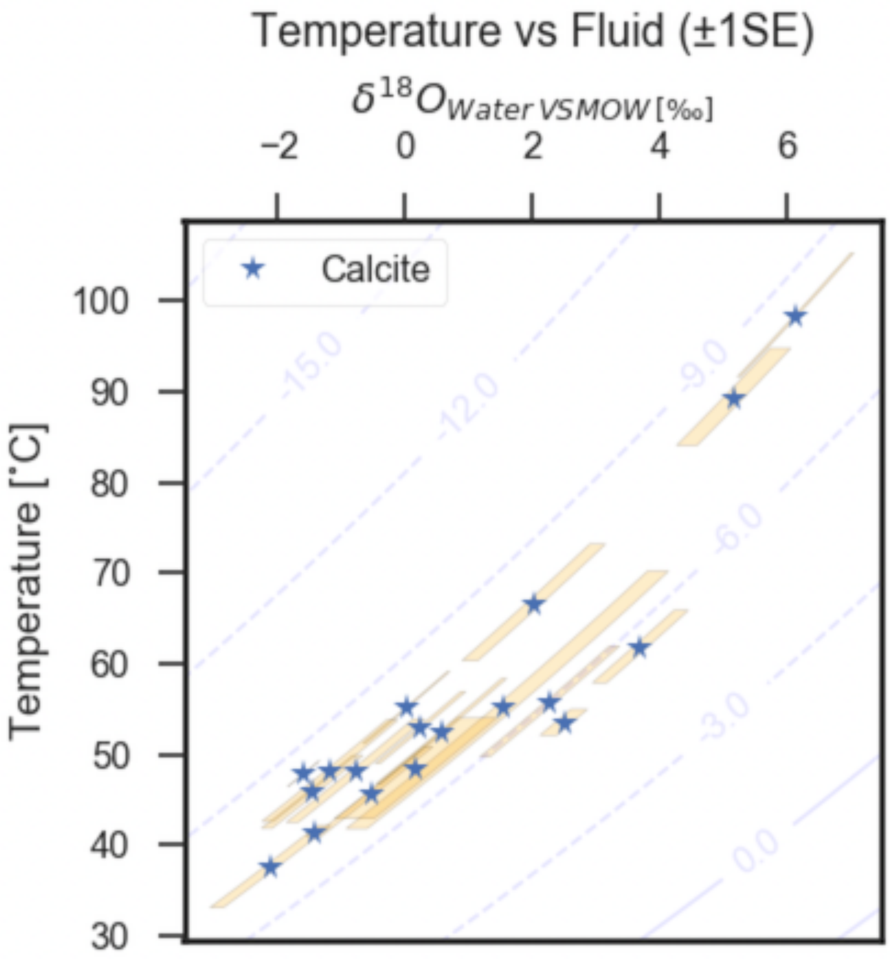
Figure shows a positive correlation between temperature and fluid composition. Oysters follow the 'closed system' recrystallisation path.

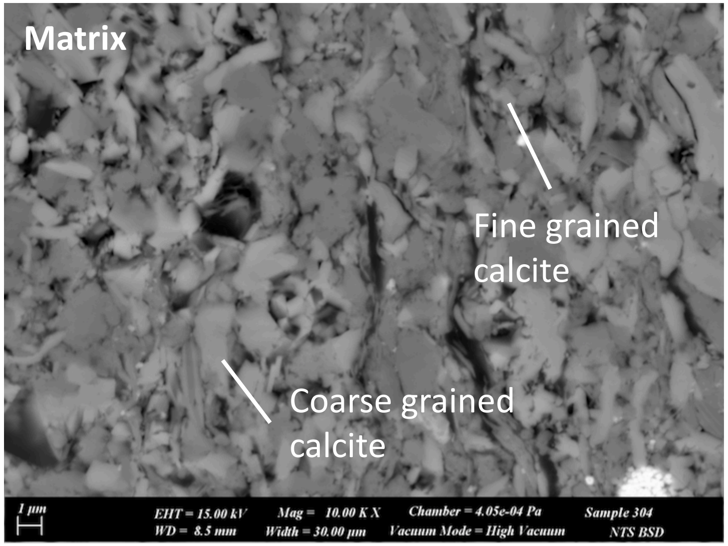


Red lines represent models with varying rock water rations. Data represents four phases of recrystallisation all following a linear correlation. Temperature increase shows and increase in fluid composition. Veillard et al., (2019).

Discussion – Carbonate Recrystallisation

This study:

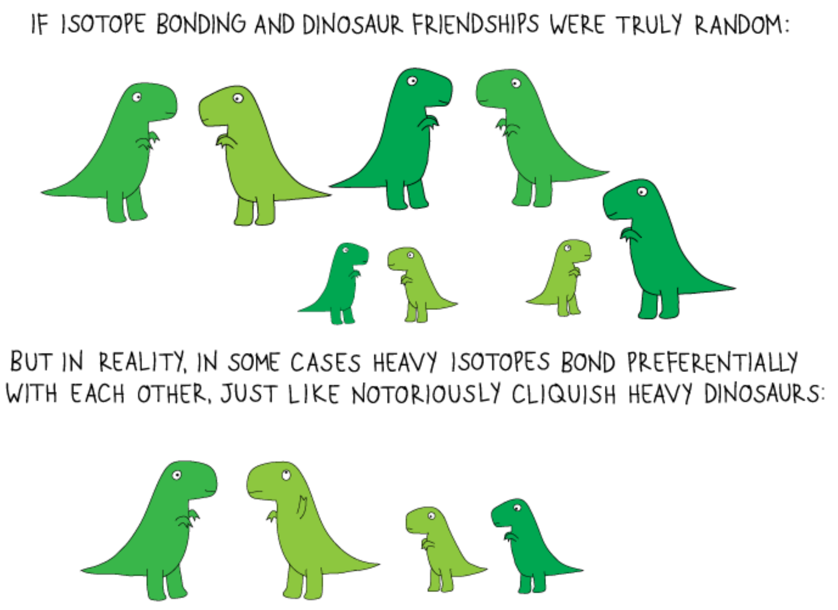




- Small variation in calcite composition
- Positive correlation between fluid composition and temperature
- Matrix SEM images supports multiple phases of calcite
- Samples show temperatures higher than modern day temperatures and Cretaceous temperatures.
- Linear range in temperatures not clustering at one particular temperature

Conclusions

- $T(\Delta_{47})$ show temperatures ranging from 25 to 105°C.
- Temperatures do not represent modern day seawater temperatures or Cretaceous Marine sediments
- Bulk isotopes do not represent Cretaceous marine sediments, but represent burial cements or meteoric cements.
    - Meteoric cements are unlikely as temperatures are very high
    - More likely to be linked to burial
- What do the temperatures represent?
    - Recrystallisation during burial causing resetting of Δ_{47}
    - Temperatures represent a minimum estimate of the maximum burial temperature
    - Agree with the hypothesis
- Were the temperatures what was expected?
    - Temperature >70˚C were not expected due to regional burial proxies indicating lower temperatures



Further work

To investigate why clumped isotope temperatures have higher recorded temperatures than expected from previous studies burial proxies.

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