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

Sarah Robinson\textsuperscript{1}
Cédric. M John\textsuperscript{1}
Annabel Dale\textsuperscript{2}
Mark Osborne\textsuperscript{2}

\textsuperscript{1}Imperial College London
\textsuperscript{2}bp HQ Sunbury on Thames
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).
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

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

Textures

Zoom in

- Calcite foraminifera shell filled with kaolinite
- Kerogen
- Matrix

Matrix

- Fine-grained calcite
- Coarse-grained calcite

04/05/2020
Variation of $\delta^{18}O_{\text{calcite}}$ and $\delta^{13}C_{\text{calcite}}$

- 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

- Solid-state mixing = mixing of two end members causing deviation in measured isotopic values. (Defliese & Lohmann, 2015).
  - Dependent on end member compositions in $\delta^{18}O_{\text{calcite}}$ and $\delta^{13}C_{\text{calcite}}$. and independent of end member $\Delta_{47}$ values
  - Overestimations and underestimations of $\Delta_{47}$ 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
Past Research:

- Dissolution and reprecipitation can occur during burial with minimal/no effect on the calcite composition, however the $\Delta_{47}$ 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.](image)

![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).](image)
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 $\Delta_{47}$
  • 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

© dinotopes. All rights reserved
Further work

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


• PATTERTSON, S. A., 2018, ‘The Maness Shale: a comparison of the geomechanical and mineralogical properties within the Lower Eagle Ford Formation, South Texas’. BSc (Hons) Thesis, Texas Christian University, Texas