TOWARDS AN UNDERSTANDING OF THE USE OF CLUMPED ISOTOPES TO STUDY DIAGENESIS

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PROJECT OBJECTIVES

- To understand the behavior of the clumped isotope proxy (Δ_{47} values) during meteoric and early marine burial diagenesis.
- To examine the calibration between the Δ_{47} value of aragonite and temperature.

PROJECT RATIONALE

The clumped isotope proxy (Δ_{47} value) has enabled temperatures to be obtained directly from carbonates through a single analysis. The clumped isotope proxy has the potential to revolutionize the study of diagenesis, as it is now possible to obtain both the temperature and the $\delta^{18}O$ of the fluid without using other proxies such as fluid inclusions. However, like many geochemical tools there are many uncertainties which need to be resolved before the full potential of the technique can be realized. The work proposed here will address one of these issues and build on papers published by current and past PhD students and visiting scientists, Monica Arienzo, Sean Murray, Florian Smit, and Philip Staudigel (Murray, 2016; Murray et al., 2016, Staudigel and Swart, 2014; Staudigel and Swart, 2016).

SCOPE OF WORK

Deep Marine Sites: We have already extensively examined two sites from the Leg 166 Bahamas transect. In ODP Sites 1006 and 1003, the uppermost sediments record a general down core cooling trend at both sites, averaging ~14°C (Figs 1A & 1B). In addition to adding two more sites from Leg 166, Sites 1005 and 1007 (Fig. 1), we will examine sites from other DSDP/ODP/IODP expeditions as appropriate.

Shallow Cores: We propose to examine the clumped isotope behavior in a series of shallow-water cores drilled from sequences which have been exposed to well constrained meteoric diagenetic conditions. These cores include the Clino and Unda cores on Great Bahama Bank, as well as other cores from the Bahamas. We will make use of our new model (Swart and Oehlert, 2018), which reinterprets variations in the stable C and O isotopic composition of these cores.

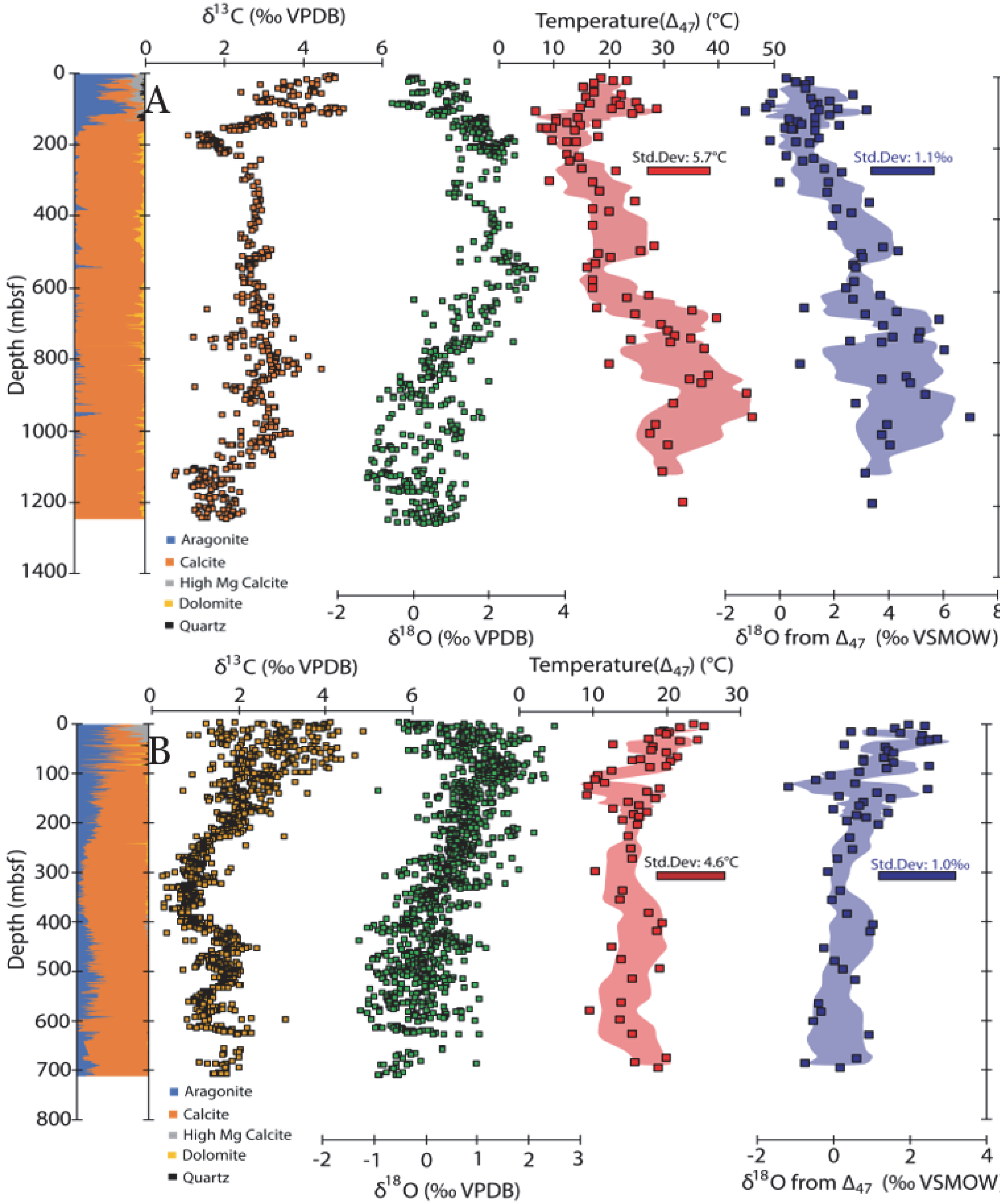

Figure 1: Mineralogy and isotopic composition of ODP Site 1003 (top) and 1006 (bottom).

<u>Ancient Samples</u>: As the first application of our studies to older materials we will examine the diagenesis of the European chalk using outcrop and core material. Some of this work was presented at the 2017 sponsors meeting, but we have already initiated new projects utilizing samples of macrofossils and bulk rocks from the chalk in the U.K. and the U.S. A second area of research will utilize samples from the Carboniferous, collected on the Isle of Man in the Irish Sea (Dickson and Coleman, 1980). These samples were some of the first in which individual generations of cements were

separated and analyzed for their $\delta^{13}C$ and $\delta^{18}O$ values. Utilizing the small sample capability of the Kiel device, we have cross-calibrated the University of Miami and Cambridge laboratories and started to analyze samples as small as 130 μg (compared to 8 mg in Miami).

Synthetic carbonate calibration: We have experimentally precipitated calcite and aragonite over a range of temperatures (5 to 75°C). These samples have resulted in a temperature calibration unique to the University of Miami (Staudigel et al., In Review) (Fig. 2). We propose to extend the range of this calibration to lower (-10°C) and higher temperatures (95°C) and investigate differences in the calibration when precipitating aragonite compared to calcite.

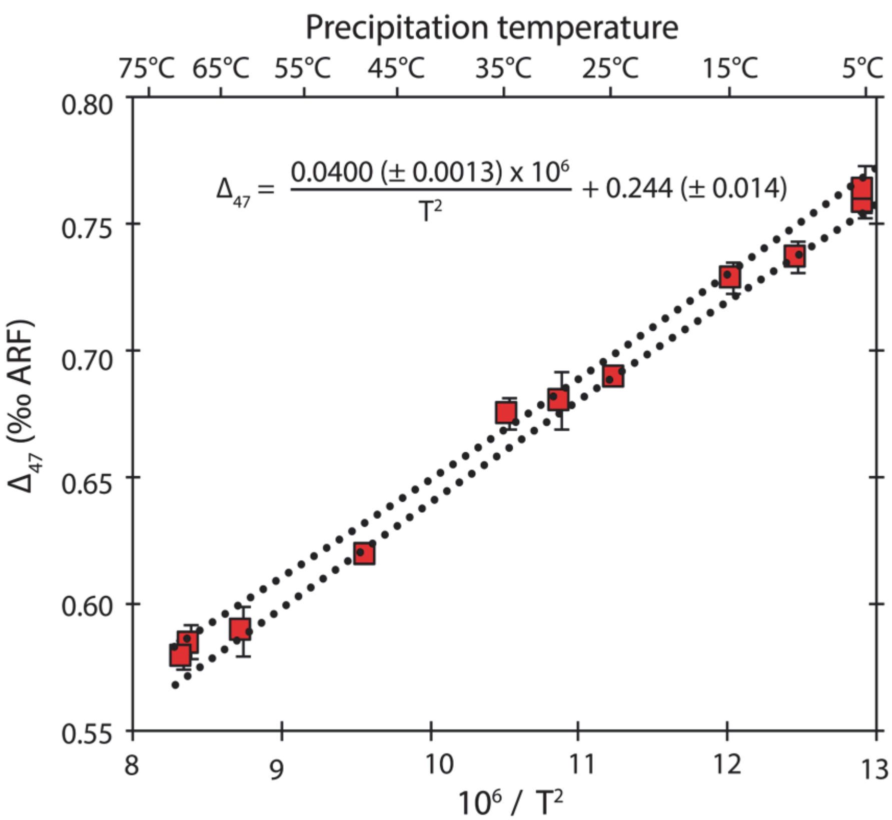

Figure 2: Relationship between Δ_{47} and temperature for samples precipitated in Miami.

SIGNIFICANCE

As the clumped isotopic proxy is applied to progressively older materials, it will become important to ascertain the extent of the influence of early diagenesis upon the eventual signature. At the present time, many such studies have skipped this fundamental step when interpreting their data. The work completed to date clearly illustrates the utility of clumped isotopes for studying early and late stages of diagenesis, enabling more nuanced interpretations of other isotope systems.

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