TWIN CLUMPED PROXIES AND BEYOND: A NEW CLUMPED ISOTOPE PROXY, Δ_{48}

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PROJECT OBJECTIVES

- To determine the rates of change in the Δ_{48} value in carbonate minerals relative to changes in the Δ_{48} value during heating and cooling for the purposes of geospeedometry. This allows the determination of the burial history of carbonate containing rocks.
- Improve the calibration between temperature and Δ_{48} values.

PROJECT RATIONALE

The clumped isotope proxy has caused a revolution in the application of stable oxygen isotopes to carbonate rocks. By examining the difference between the measured and the theoretical 47/44 ratio, the Δ_{47} value can be determined. Calculation of this value eliminates variations in the original C and O isotopic variability of the system and has been shown to be related to temperature in a number of geological systems, both theoretically and experimentally (Ghosh et al., 2006). Since the paper of Ghosh et al. (2006) there have been literally 100s of papers which have not only revised the calibration (Bonifacie et al., 2017; Kelson et al., 2017), but also applied this proxy towards the determination of temperature of carbonate formation (Henkes et al., 2013), the study of diagenesis (Ritter et al., 2015; Staudigel et al., 2018), burial history (Shenton et al., 2015), paleoclimate (Breitenbach et al., 2018),

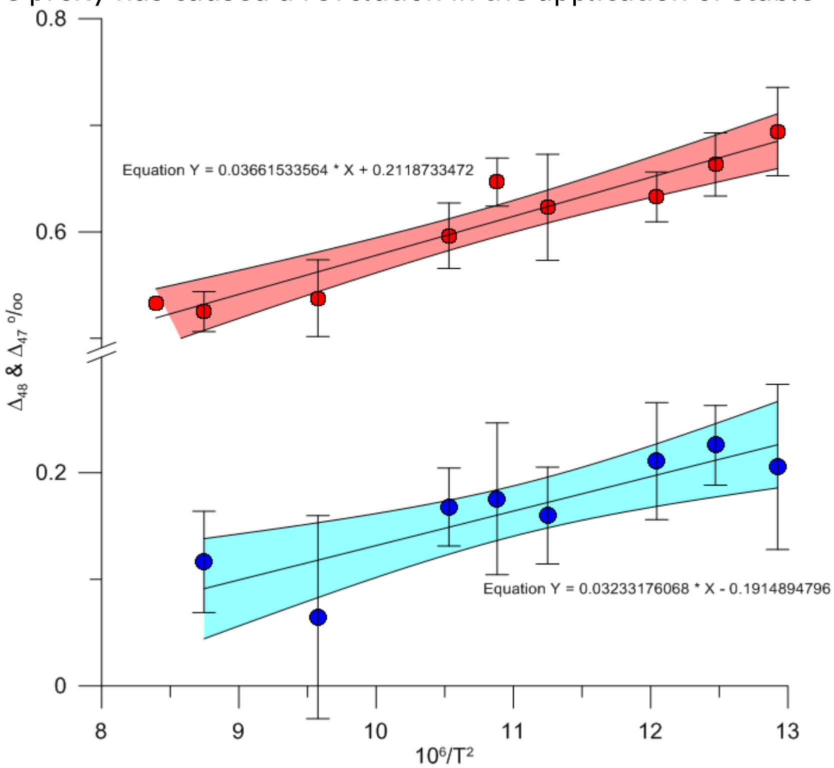

Fig. 1: Comparison of calibration lines for Δ_{47} (red) and Δ_{48} values (blue) using the 253-plus with 95% confidence limits. The equation from the 253-plus is statistically identical to that measured on the 253 (Staudigel et al., 2018).

orogenic uplift (Hough et al., 2014), extraterrestrial geology (Halevy et al., 2011), archaeology (Müller et al., 2017), evolution and physiology of dinosaurs (Eagle et al., 2011) and many other applications.

While studies to date have concentrated on mass 47, there are also clumped isotope species at masses 48 and 49. In the work described here we will continue an attempt to make meaningful clumped isotope measurements on CO_2 at mass 48 ($^{12}C^{18}O^{18}O$ and $^{13}C^{17}O^{18}O$) thus enabling calculation of a Δ_{48} value. The combination of Δ_{47} and Δ_{48} measurements (the 'twin' clumped proxy) have the potential to add a powerful new tool useful in the understanding of equilibrium and non-equilibrium processes, not only during carbonate formation, but also during solid-state reordering. In a first effort we presented a calibration between Δ_{48} values and temperature (Fig. 1) at the 2019 sponsors meeting.

SCOPE OF WORK

Our work will concentrate on two studies.

1. Improve the calibration between Δ_{48} values and temperature, a preliminary version of which is shown in Figure 1.
2. Determine the rates of change of Δ_{48} values (relative to Δ_{47}) which take place during the heating of carbonate minerals.

The Δ_{47} values of carbonates change by solid-state processes when they are heated. The rates of such change have been investigated in low-Mg calcite (LMC), aragonite, and dolomite (Lloyd et al., 2018; Passey and Henkes, 2012; Staudigel and Swart, 2016). Upon cooling the carbonates reequilbrate, but stop doing so once a temperature characteristic of the mineral is attained. This is the so-called blocking temperature. While the different rates of cooling have not been studied, the eventual measured Δ_{47} value may be different than this temperature (usually higher) depending upon the cooling (and heating) history. The blocking temperature for different carbonate mineralogies follows the expected pattern so that dolomite> calcite> aragonite. There have been as yet no studies on high-Mg calcite (HMC) or dolomites with varying stoichiometry, although it might be expected that calcium-rich dolomites would fall between LMC and dolomite and HMC between LMC and aragonite. Our preliminary work, presented at the 2019 sponsors meeting, is summarized in Figure 2. These data suggest that the Δ_{48} proxy changes at faster rates than Δ_{47}. We will verify this by conducting a range of heating experiments on different carbonate minerals at different temperatures.

SIGNIFICANCE

Understanding the history of the Earth's ocean and climate has largely relied on the use of the stable isotopes of C and O in carbonates. The carbon isotopic composition has been widely used to make interpretations about the global carbon cycle while the oxygen isotope composition has been used to ascertain temperature and ice volume. In older sediments it is clear that while the

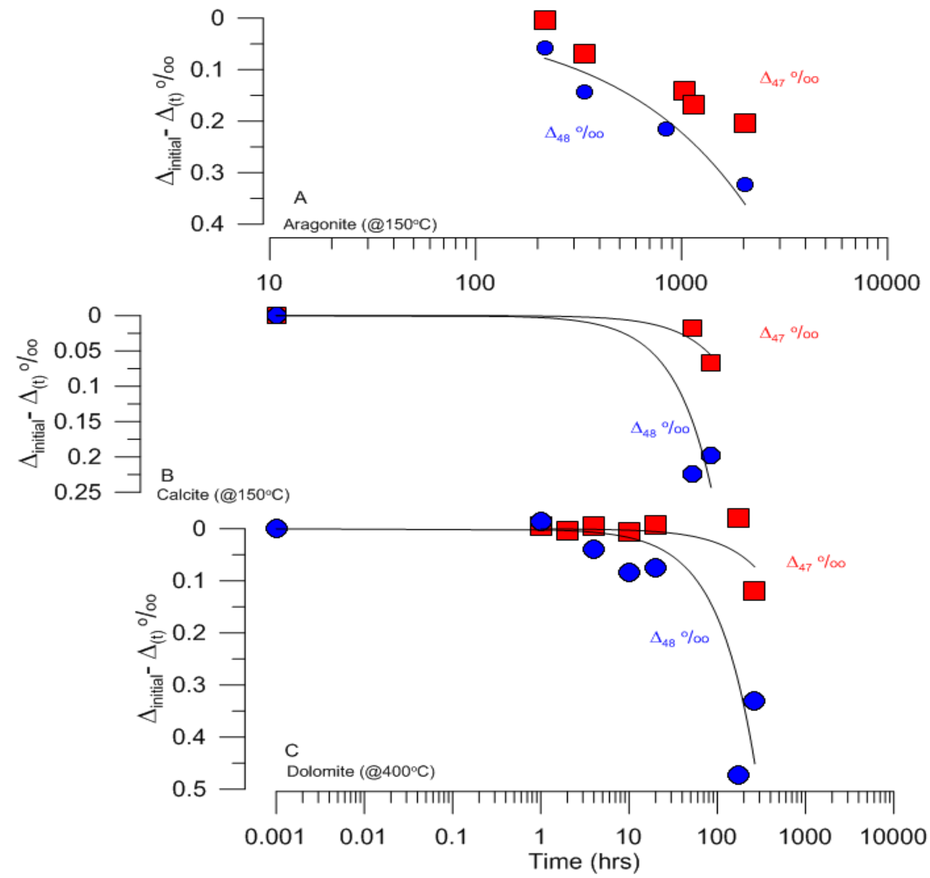

Fig. 2: Preliminary data for changes in aragonite and dolomites for Δ_{47} and Δ_{48} values as a result of heating. Fig. 2A shows changes in values for aragonite as a function of time for samples held at 150°C. Fig 2B: Similar data for LMC at 150°C. Fig. 2C: Similar data for dolomite for sample held at 40O°C. In all cases rate of change of Δ_{48} are faster than Δ_{47}. Overall changes in Δ_{47} values of dolomite are similar to that observed by Lloyd et al. (2018) (at 407°C) even though their experiments were in sealed tubes.

oxygen has been affected by diagenesis, the carbon isotopic composition is retained as alteration takes place in a closed system and unlike oxygen, it is unaffected by temperature. The Δ_{48} value, in combination with the Δ_{47} value, is able to provide additional constraints upon the history of such rocks as the two systems have different blocking temperatures within a single mineral. In situations where there are mixed calcite and dolomite assemblages sophisticated reconstructions of geothermal histories are possible, particularly where there are evolved paragenetic sequences with multiple generations of minerals that can be chemically and physically separated.

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