

# NEW APPROACHES TO CONSTRAINING THE TEMPERATURE VS. CLUMPED ISOTOPE CALIBRATION FOR DOLOMITE

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## PROJECT OBJECTIVES

- Measure the difference between the  $\Delta_{47}$  produced at 25 and 90°C for dolomites with different initial  $\Delta_{47}$  values
- Use this information to constrain the clumped isotope equation for dolomite

## PROJECT RATIONALE

The recognition that clumped isotopes of CO<sub>2</sub> are solely dependent upon temperature and not on the isotopic composition of the fluid from which they are formed has opened significant possibilities in unraveling the temperature and water signal as applied to diagenetic carbonates. At the University of Miami

we have two working clumped isotope mass spectrometers and are investigating a range of problems involving both the calibration of the method as well as its application to geological problems. For example in the study of Staudigel et al. (2018) we precipitate calcite samples at 10 different temperatures and developed our own calibration line (Fig. 1). In a second study we have been measuring exchange rates between the CO<sub>2</sub> and the phosphoric acid in an effort to understand error and artifacts

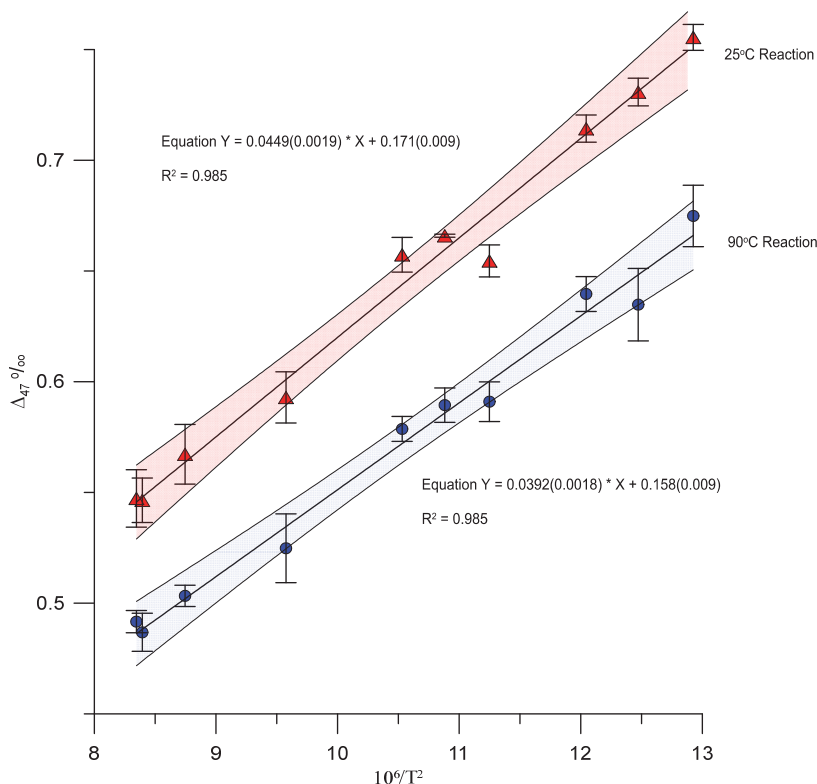


Figure 1: Comparison of the calibration lines between  $\Delta_{47}$  and temperature for calcites precipitated in the laboratory and reacted at 25 and 90°C. Notice the difference in slopes between the two lines.

arising from the extraction method (Swart et al., 2019). In addition to method development we have applied the clumped isotope method to a range of geological problems (Müller et al., 2017; Murray, 2016; Murray et al., 2016; Staudigel et al., 2018; Swart et al., 2016; Vahrenkamp et al., 2014). In one of these studies (Murray et al., 2016) we noticed that the difference between the  $\Delta_{47}$  of dolomite reacted at 25 and 90°C is not the same as for calcite (Swart et al., 2019) (Fig. 2). This is important because it has recently been proposed that the calibration between temperature and  $\Delta_{47}$  for dolomite is the same as that for calcite (Bonifacie et al., 2017). However, if our observation is correct then this suggests that the calibration lines for dolomite and calcite are probably not the same.

## SCOPE OF WORK

For over 50 years researchers have struggled to derive an equation linking the  $\delta^{18}\text{O}$  value of dolomite to temperature which is realistic at sedimentary temperatures (Clayton et al., 1968; Land, 1980). The problems with the nine equations which have been published so far is that they were either theoretical, derived at high temperature and extrapolated to low temperature, or derived on materials which were in fact not actually dolomite, but rather calcian or proto dolomite (Murray and Swart, 2017). As far as the  $\Delta_{47}$  values of dolomite are concerned, the one equation which exists at the present time suggests that there is no difference between dolomite and calcite (Bonifacie et al., 2017).

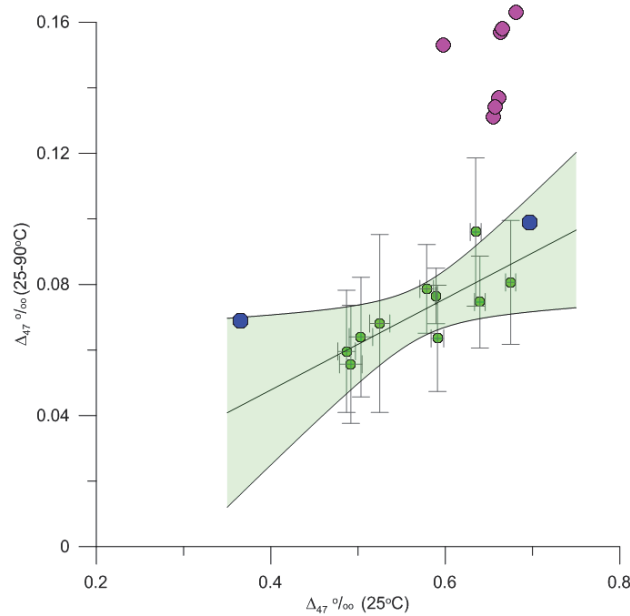


Fig. 2: Differences between 25 and 90°C reactions as shown in Fig 1 as a function of the 25°C clumped isotope value. Also shown are data from Murray et al. (2016) which show large acid fractionation for dolomite (purple dots) as well as acid fractionation for two natural calcites (blue dots).

However, not only are there a number equations for calcite, which if applied to a specific sample would yield quite a wide range of temperatures, but the dolomite equation suffers from the same problem as the previous equations involving the  $\delta^{18}\text{O}$  value of dolomite in that the low temperature end is mainly constrained by extrapolation from high temperature. We present a new approach which is based on two observations made during our study of the temperature dependence of the  $\Delta_{47}$  value in calcite. First, the slope between temperature and  $\Delta_{47}$  for calcite depends upon the temperature at which the samples were reacted. Samples reacted at 25°C have a steeper relationship with respect to formation temperature than those samples reacted at 90°C. Hence, with increasing formation

temperature the calibration lines converge. The explanation for this trend is that at high formation temperature the  $\Delta_{47}$  values are further away from theoretical equilibrium with the phosphoric acid at 90°C (Swart et al., 2019). During the reaction the CO<sub>2</sub> equilibrates with the acid at a rate which is proportional to the difference between its initial value and the equilibrium value. Hence, samples formed at high temperature tend to exchange with the acid more. The second observation is that the difference between dolomite and calcite reacted at 25 and 90°C is different than that for calcite (Fig. 2). These two observations are incompatible with the notion that the calibration line for dolomite is the same as that for calcite. In order to confirm this

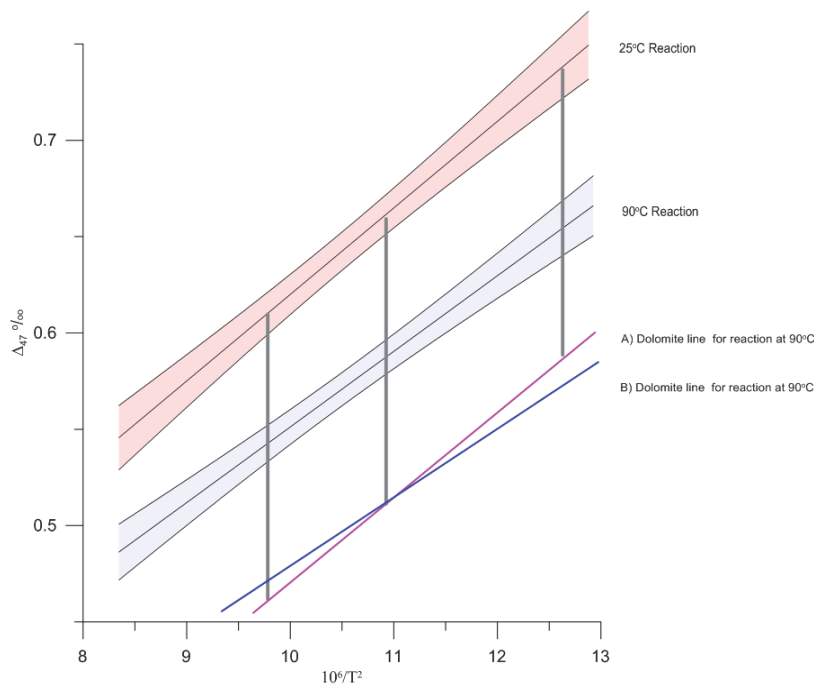


Fig. 3: Proposed position of the calibration line for dolomite based on the measured acid fractionation of 0.12‰. The proposed line is either parallel to the 25°C reaction line or the 90°C reaction line.

observation we are remeasuring the difference between dolomite and calcite using the NIST-88b as measured by Murray et al. (2016). We also intend to repeat these experiments using dolomites with much lower  $\Delta_{47}$  values. We propose two models, one in which there is a constant difference between calcite and dolomite irrespective of the initial  $\Delta_{47}$  of the sample, and one in which the difference becomes smaller as the  $\Delta_{47}$  of the sample become

more stochastic (Fig. 3).

## SIGNIFICANCE

The clumped isotope proxy has already shown that it is a powerful tool in reconstructing depositional temperatures, temperatures of diagenesis, and burial histories. In conjunction with the conventional  $\delta^{18}\text{O}$  value it is also able to provide information on the  $\delta^{18}\text{O}$  values of the fluids involved in deposition and/or diagenesis. While initial work has suggested that the  $\Delta_{47}$ -temperature equation is similar for dolomite and calcite, there are discrepancies in the behavior of dolomite and calcite which suggest that there may be some differences in the equation linking temperature to the  $\Delta_{47}$  value. The identification of such differences is crucial to enable the equation to be successfully used for dolomites and to provide information on dolomitization.

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