Choice of ^{17}O Abundance Correction Affects Δ_{47} and Thus Calibrations for Paleothermometry

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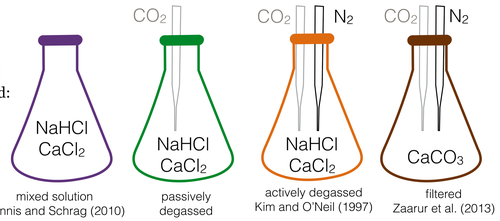
1. Abstract

- The clumped isotope composition of CO2 derived from carbonate (Δ_{47}) varies with temperature, making it a valuable geothermometer with broad applications. However, its accuracy is limited by inter-laboratory discrepancies of carbonate reference materials and Δ_{47}-temperature calibrations.
- Our primary goal was to produce a suite of carbonate samples grown at known temperatures to calibrate the Δ_{47} thermometer. We vary precipitation methods to test the hypothesis that different methods used by previous workers caused calibration discrepancies.
- We observe a dependency of Δ_{47} on $\delta^{13}C$, which should not exist according to clumped isotope theory. We observe this dependency in both carbonate calibration samples and in equilibrated and heated gases produced for the reference frame.
- We find that the correction for the abundance of ^{17}O affects calculated Δ_{47} and explains this dependency. The discrepancies are effectively removed when the fractionation between ^{17}O and ^{18}O of 0.528, as in global meteoric waters, is used.
- The method used to correct for ^{17}O abundance likely contributes to observed calibration discrepancies. Adopting λ=0.528 may reduce the uncertainty in Δ_{47} temperature reconstructions.

2. Initial goal: improve Δ_{47} calibrations

- Clumped isotope community has been hampered by discrepant calibrations.
- These calibrations likely diverged due to 1) differences in the methods used to precipitate carbonate samples or 2) differences in the analytical methods used to analyze the carbonates.
- **Here, we set out to replicate previous calcite precipitation methods under a constant analytical setting** (option 1). We grow 58 carbonates at known temperatures using several precipitation methods.

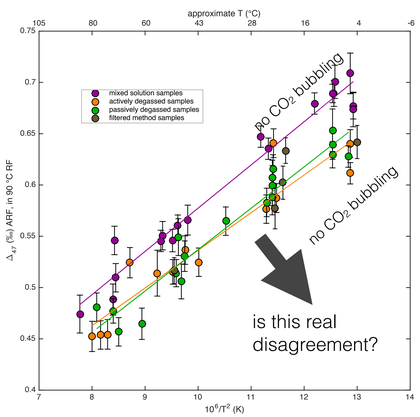
Precipitation methods used:



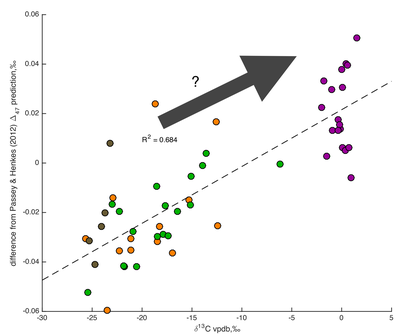
note: CO_2 gas bubbled into these experiments has $\delta^{13}C$ of -36 ‰ vpdb, which imparts a depleted $\delta^{13}C$ value to the resulting samples

3. Initial results: Δ47 depends on 13C (but it should not)

- Samples that are depleted in 13C are also depleted in Δ47. We suspect this is an analytical artifact.



Δ_{47} of UW synthetic carbonate samples plotted against growth temperature. Initially, we observed that samples were systemically depleted in Δ_{47}. These samples were depleted in ^{13}C as a result of the CO_2 that was bubbled through solution ($\delta^{13}C$ = -36 ‰ vpdb).



Difference between Δ_{47} of UW synthetic carbonate samples and the Δ_{47} values predicted by the theoretical calibration of Passey and Henkes (2012), plotted against $\delta^{13}C$ of the carbonates. We observe a correlation between $\delta^{13}C$ and Δ_{47}. Clumped isotope theory (e.g., Schauble et al., 2006) says that Δ_{47} should not depend on bulk isotopic composition of the mineral.

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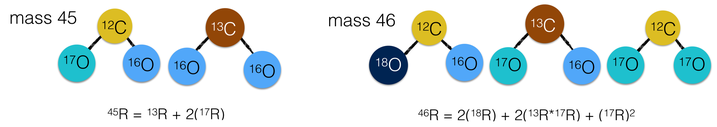
Schauer, A. J., Kelson, J., Saenger, C., & Huntington, K. W. (2016). Choice of 17O correction affects clumped isotope (Δ47) values of CO2 measured with mass spectrometry. Rapid Communications in Mass Spectrometry, 30(24), 2607-2616.

Zaarur, S., Affek, H. P., & Brandon, M. T. (2013). A revised calibration of the clumped isotope thermometer. Earth and Planetary Science Letters, 382, 47-57.

4. Basic Assumptions: 17O correction parameters

- To calculate Δ_{47}, we need ^{13}R, ^{18}R, and ^{17}R. To get those, we measure the molecules with masses 45 and 46.



$^{45}R = {}^{13}R + 2(^{17}R)$

$^{46}R = 2(^{18}R) + 2(^{13}R{*}^{17}R) + (^{17}R)^2$

- This is two equations but three unknowns! In order to solve the equations, you need to assume something else, like:

$$^{17}R = K{*}^{18}R^{\lambda}$$

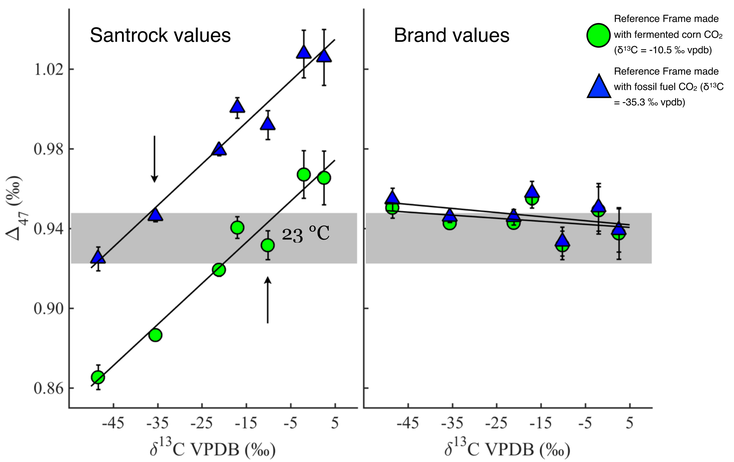
Most commonly, Santrock et al. (1985) is assumed, where K = 0.00922118 and λ = 0.5164

We think that Brand et al. (2010) is more appropriate, where K = 0.01022451 and λ = 0.528. Evidence below.

Acknowledgement: Colman and Olack (U Chicago) first thought of considering ^{17}O correction parameters. Go see their poster too (V43B-3158)!

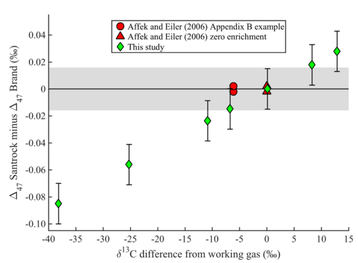
5. Using the Brand parameters removes Δ_{47} dependency on ^{13}C

- To show this, we use CO_2 gas with that has been equilibrated with water at 23 °C. We use a variety of $\delta^{13}C$ and $\delta^{18}O$ compositions. According to equilibrium calculations, all CO_2 equilibrated at 23°C should all have a Δ_{47} value of 0.935 ‰ (Wang et al., 2004) (gray band).
- When Santrock et al. (1985) values are used, we observe a dependence of Δ_{47} on d13C. This dependence is removed when Brand et al. (2010) values are used (Schauer et al., 2016).



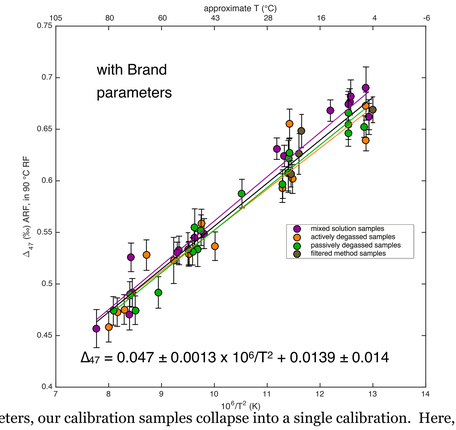
The amount of change observed with the choice ^{17}O parameters may not be straightforward or intuitive to predict.

Here, we show that the difference in Δ_{47} observed depends on the difference between the $\delta^{13}C$ of the sample and of the mass spectrometer working gas.



Acknowledgement: Daëron et al. (LSCE) came to a similar conclusion with numerical models (Daëron et al., 2016).
Go see their poster too (V43B-3152)!

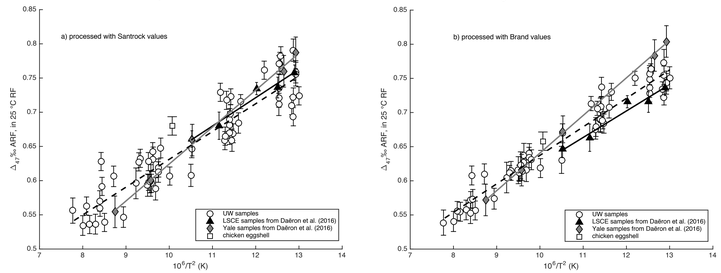
6. Back to the original goal: an improved Δ_{47} calibration?



Using the Brand parameters, our calibration samples collapse into a single calibration. Here, carbonate precipitation methods do not change our measured Δ_{47} value within error. Differences among previous calibrations were likely not due to carbonate precipitation method.

This is a robust calibration with 58 samples that can be applied to natural carbonates (Kelson et al., 2017).

7. Future work: 17O corrections and a community calibration



- Daeron et al. (2016) recalculated their carbonate calibration data and the Yale data using Brand et al. (2010) parameters.
- Choice of ^{17}O parameters does not change the Δ_{47}-temperature slope of any of the three sample suites.
- Choice of ^{17}O parameters can change intercepts in different ways .
- Could this be a small sample size problem?:
  - If we resample our larger sample population 10,000 times, 11% of the time we get a slope within error of Yale, 54% of time we get a slope within error of LSCE
- Future work should recalculate other previous calibrations (let's share data!)

7. Conclusions

- We observe systematic errors in calculated Δ_{47} of CO_2 gases and synthetic carbonate materials that are eliminated by choosing the ^{17}O correction parameters of Brand et al. (2010).
- The choice of ^{17}O correction parameters may be partially responsible for inter laboratory disagreements, including calibration discrepancies
- Once calculated with Brand parameters, our calibrations samples agree within measurement error, regardless of precipitation method. This suggests that methods used by previous workers that we replicated do not inherently cause disequilibrium compositions in the carbonate.
- These samples can be used to create a calibration that is robust to outliers (n = 56 samples).
- We advocate for reevaluating previous calibration data with appropriate ^{17}O correction parameters