

Leveraging longer reference frames to characterize clumped isotope outliers and ^{17}O effects

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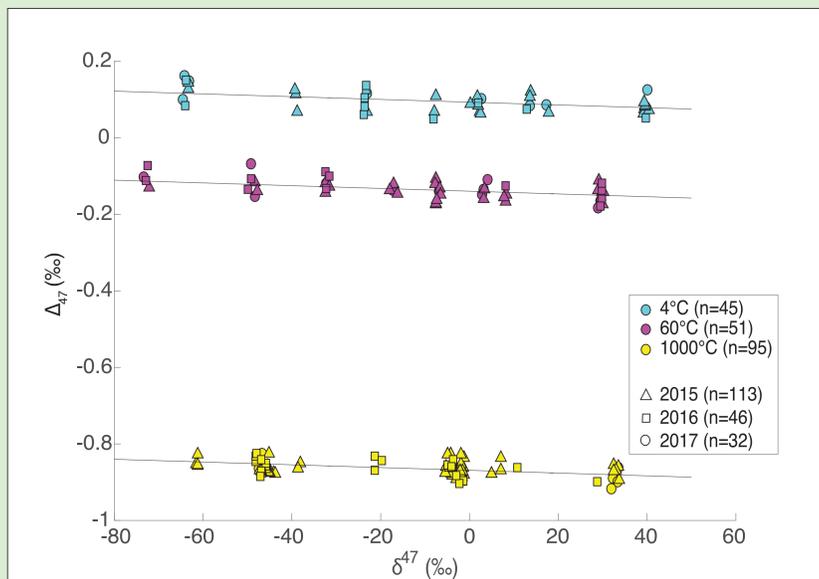
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Abstract

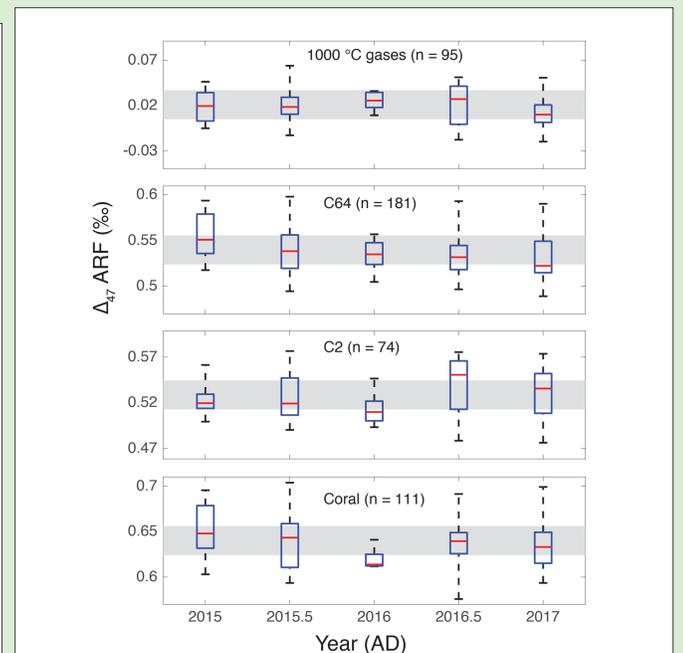
The stability of UW's reference frame minimizes it as an error source and allows unique questions to be addressed

- What controls the variance of carbonate and gas standards?
- Where do outliers come from and how do we account for them?
- What is the effect of ^{17}O on temperature calibrations?
- Heated gases (1000°C) and CO_2 equilibrated with water of varying isotopic composition at 4 and 60°C
- No discernable change over more than two years (January, 2015-July 2017)
- Allows other potential sources of Δ_{47} uncertainty to be characterized with less ambiguity

A stable reference frame across multiple years

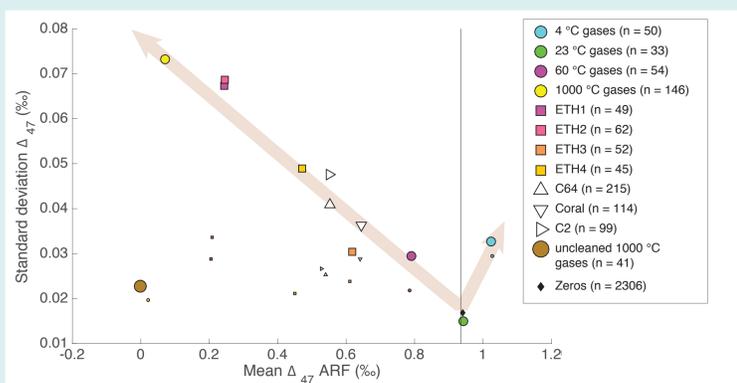


Reference frame gases from 2015 (triangle), 2016 (square) and 2017 (circle). Regressions are constructed from all data, but nearly identical lines would be generated from individual years and other subsets



Box and whisker plots of reference material in 6 month intervals. In all cases, the inner quartile (blue box) overlaps longterm mean of zero enrichment gases (n=2302) within 1 s.d.

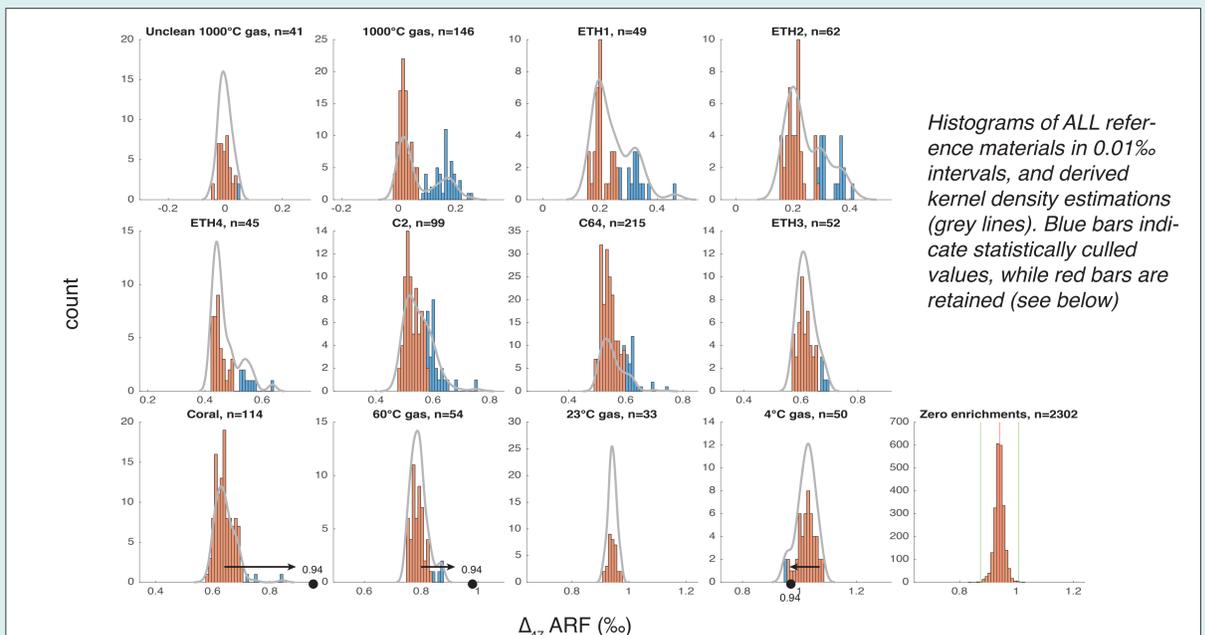
Outliers Explained! predictable resetting of carbonate and gas standards



Standard deviation vs. mean Δ_{47} for ALL gas and carbonate reference materials (large symbols) and for statistically culled samples (small symbols)

Motivation:

- When ALL carbonate and gas standards are considered - minimum variance at $\Delta_{47} \sim 0.94\text{‰}$ expected at 23°C
- Increasing variance toward higher and lower values, except in uncleaned heated gases
- Suggests a predictable mechanism for outliers likely related to the preparatory line



Histograms of ALL reference materials in 0.01‰ intervals, and derived kernel density estimations (grey lines). Blue bars indicate statistically culled values, while red bars are retained (see below)

- All are skewed toward $\Delta_{47} \sim 0.94\text{‰}$, except uncleaned 1000°C gases.
- When the 4σ standard deviation of zero gases (n=2302; bottom right, green vertical bars) is centered on the mode of all other populations, only intervals toward $\sim 0.94\text{‰}$ fall outside this range (blue bars).
- Two populations obvious in 1000°C cleaned, increasingly overlap at lower temperatures.

Implications and Open questions:

- Data further from room T (e.g. ETH1 and 2) may be noisier, even if they are homogenous. This is detectable only with the large sample sizes attainable with a long reference frame.
- **Have you pitched an outlier?** If yes, a similar process may affect your prep line. We would be interested in labs sharing ALL data in this project and other data compilations.
- What is the best way to cull outliers when measuring unknown samples fewer than dozens of times?
- What methods can further reduce water in preparatory systems to decrease the occurrence of outliers?

Negligible effect of fluid ^{17}O excess on Δ_{47} -T relationship in abiogenic calcites

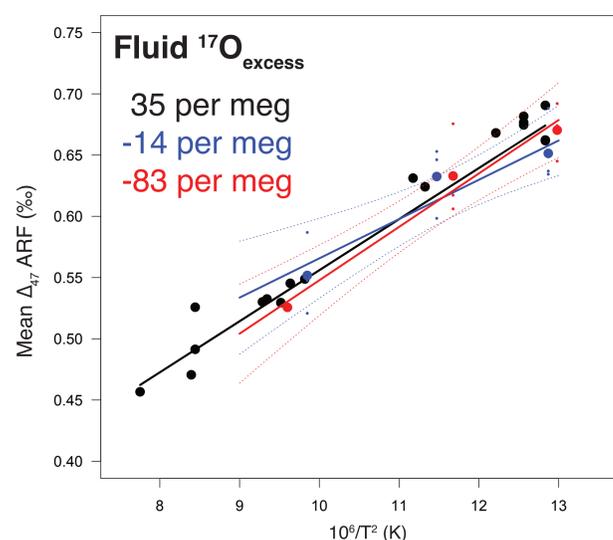
- Evaporation produces waters with ^{17}O excess of -14 and -83 per meg
- Precipitate calcite at $\sim 4, 22$ and 45°C by mixing NaHCO_3 and CaCl_2 solutions (with carbonic anhydrase) and passively degassing
- No significant difference from UW Kelson et al. (2017) calibration using local DI water with ^{17}O excess of 35 per meg.

Explanation and Implications:

- Assuming a uniform offset between fluid and carbonate ^{17}O excess, >100 per meg variations in solution values have small effect on K

1. $K = {}^{17}\text{R}_{\text{std}} ({}^{18}\text{R}_{\text{std}})^{-\lambda}$, where $\lambda = 0.528$
2. $^{17}\text{O excess} = \ln({}^{17}\text{R}/{}^{17}\text{R}_{\text{std}}) - 0.528 \cdot \ln({}^{18}\text{R}/{}^{18}\text{R}_{\text{std}})$
3. $K = \exp(^{17}\text{O excess}) \cdot {}^{17}\text{R}_{\text{std}} ({}^{18}\text{R}_{\text{std}})^{-\lambda}$

^{17}O excess (per meg)	K from eq 3	$\Delta\Delta_{47}$ Brand-varK (‰)
35	0.01022484	
0 (Brand)	0.01022461	
-14	0.01022434	-2.9×10^{-4}
-83	0.01022364	8.9×10^{-6}



Δ_{47} -T dependence for calcites precipitated from waters with variable ^{17}O excess (blue, red) compared with Kelson et al. (2017) (black)

Summary and Conclusions

- UW reference frame is stable on multiannual timescales
- Outliers skew toward Δ_{47} equivalent to room T, with implications for low Δ_{47} standards.
- Outliers can be culled, but what approach is best?
- Fluid ^{17}O excess does not detectably affect the Δ_{47} -T relationship over a range of >100 per meg

References

Kelson et al., 2017. Toward a universal carbonate clumped isotope calibration: Diverse synthesis and preparatory methods suggest a single temperature relationship. GCA 197, 104-131

Brand et al., 2010. Correction for the ^{17}O interference in d_{13}C measurements when analyzing CO_2 with stable isotope mass spectrometry. Pure Appl. Chem 82, 8, 1719-1733