Long-term Reproducibility of Carbonate Standard Δ_{47} values: An Intra-laboratory Comparison

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1. INTRODUCTION

"Clumped" isotope geochemistry is based on the abundances of multiple rare isotope substitutions in molecules (e.g., $^{13}C^{18}O^{16}O$, $^{13}C^{18}O^{16}O$, and $^{15}N_2$), which provide information on thermodynamic and kinetic controls on their formation. For carbonate clumped isotope geochemistry, acid digestion of carbonate minerals is used to produce CO_2, which is then analyzed on a high-precision isotope ratio gas source mass spectrometer. Applications to paleoclimate of carbonate clumped isotope thermometry require measurements that are accurate and reproducible. Since the development of this technique over a decade ago, new digestion systems and mass spectrometers have been developed, with individual laboratory and community practices for measurement and data analysis evolving. To date, no standard operating procedure exists, with individual laboratory and community practices continuing to vary. Here we implement a recent proposal for carbonate-based standardization and assess the impact on the long-term accuracy and precision of measurements over multiple years on two instruments with four configurations.

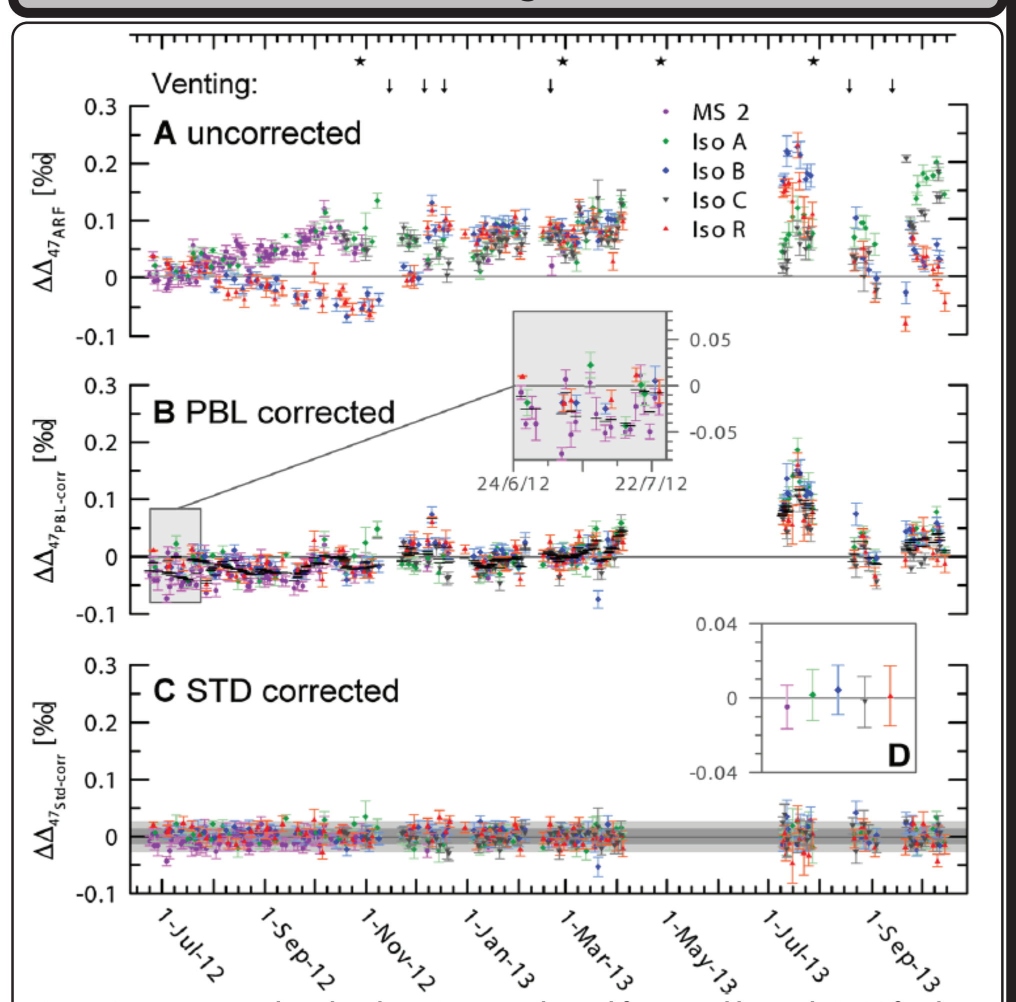
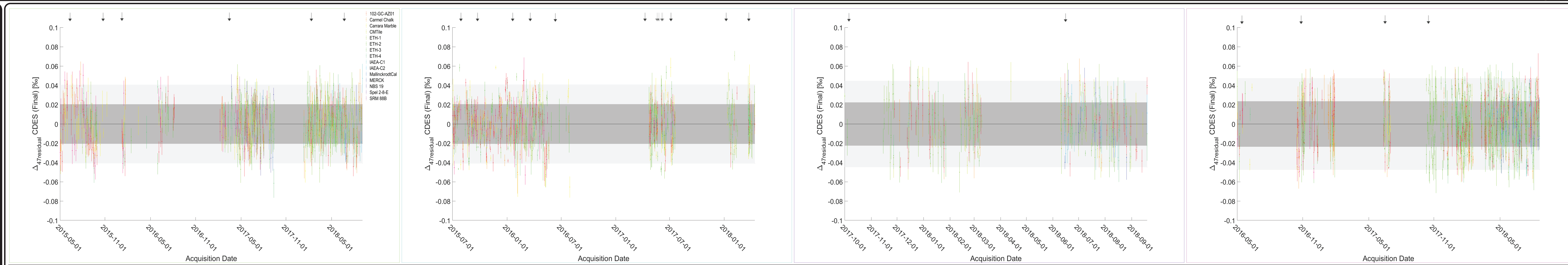


Figure 1. Figure reproduced and caption paraphrased from Meckler et al., 2014 for data from ETH-Zurich. Standard offsets from accepted values (Δ_{47}) before and after the correction steps. This study excluded standards with residuals of more than 0.06 per mil. (A) Uncorrected Δ_{47} values set in the absolute hreference frame. (B) Δ_{47} after the pressure baseline correction. Black bars indicate average offsets using an 11-point window. (C) Residual Δ_{47} values after correction for standard offsets and variations in scale compression. Gray shaded bands represent divergence of 1 and 2 standard deviations from the accepted values (Δ_{47} of zero). (D) Observed average offsets and standard deviations for the five standards.



Chewbacca | R2-D2 (Sarlacc) | R2-D2 (NuCarb) | BB8

Figure 2. Carbonate standard Δ_{47} CDES residual values compared to long-term averages for Pass B2 on all machines. Arrows indicate the beginning of a new correction interval. Gray shaded bands represent divergence of 1 and 2 standard deviations from the accepted values.

2. METHODS

Instrumentation and calculations:

- Measurements were made on a Thermo MAT 253 and a Nu Perspective IS gas source mass spectrometer, yielding four instrument configurations
- Two different digestion systems were used:
  - Common acid bath system with reaction temperatures of 90°C and an automated digestion system, with the capacity to measure gas standards in breakseals
  - Individual sample reaction vessel at 70°C with an automated digestion system

Types of standards:

- We utilize four gas standards on the common acid bath system
- We utilize sixteen carbonate standards (including internationally measured ETH and IAEA standards) and applied as working and/or consistency standards

Mass spectrometric corrections:

- Non-linearity correction: Equilibrated gases and/or working carbonate standards with a stochastic distribution can be used for constraining this mass spectrometric correction. For the common acid bath system, we use both gas and carbonate standards for the non-linearity correction, while the individual reaction vessels use only carbonate standards for the non-linearity correction
- Empirical transfer function (ETF): Equilibrated gases and/or working carbonate standards can be used for constraining scale compression. We only use working carbonate standards for the ETF

3. Pass B2

Standard	Chewbacca			R2D2 (Sarlacc)			R2D2 (NuCarb)			BB8		
	N	D47 (CDES) ‰	S.E.	N	D47 (CDES) ‰	S.E.	N	D47 (CDES) ‰	S.E.	N	D47 (CDES) ‰	S.E.
Carmel Chalk	86	0.662	0.002	95	0.665	0.002	33	0.658	0.004	129	0.664	0.002
Carrara Marble	63	0.353	0.002	91	0.371	0.003	1	0.363	--	27	0.368	0.005
CMTile	45	0.374	0.003	12	0.368	0.006	62	0.375	0.003	89	0.377	0.002
ETH-1	78	0.262	0.002	76	0.262	0.002	66	0.264	0.003	174	0.263	0.002
ETH-2	63	0.256	0.002	75	0.263	0.002	56	0.257	0.003	170	0.259	0.002
ETH-3	52	0.691	0.003	69	0.693	0.003	29	0.692	0.004	78	0.688	0.003
ETH-4	69	0.499	0.002	69	0.518	0.002	23	0.513	0.005	82	0.516	0.002
IAEA-C1	8	0.357	0.008	--	--	--	*17*	0.366	0.005	19	0.359	*0.005*
IAEA-C2	8	0.705	0.006	--	--	--	13	0.721	0.005	21	0.724	0.004
MallinckrodtCal	6	0.499	0.009	--	--	--	--	--	--	--	--	--
MERCK	2	0.608	0.017	--	--	--	11	0.605	0.008	22	0.591	0.005
NBS 19	7	0.388	0.012	--	--	--	--	--	--	--	--	--
SRM 88B	20	0.592	0.004	10	0.577	0.002	--	--	--	--	--	--
TV03	35	0.687	0.004	52	0.700	0.003	--	--	--	15	0.770	0.008
Veinstrom	80	0.711	0.002	93	0.713	0.002	47	0.705	0.003	125	0.715	0.002

4. Pass B3

Standard	Chewbacca			R2D2 (Sarlacc)			R2D2 (NuCarb)			BB8		
	N	D47 (CDES) ‰	S.E.	N	D47 (CDES) ‰	S.E.	N	D47 (CDES) ‰	S.E.	N	D47 (CDES) ‰	S.E.
102-GC-AZ01	15	0.682	0.006	--	--	--	--	--	--	--	--	--
Carmel Chalk	374	0.668	0.001	97	0.666	0.002	48	0.666	0.004	216	0.664	0.002
Carrara Marble	382	0.369	0.001	102	0.369	0.003	9	0.368	0.000	91	0.374	0.004
CMTile	73	0.374	0.002	12	0.366	0.006	94	0.378	0.003	173	0.376	0.002
ETH-1	158	0.264	0.002	81	0.264	0.003	70	0.259	0.003	236	0.262	0.002
ETH-2	139	0.260	0.002	74	0.265	0.002	62	0.260	0.003	216	0.263	0.002
ETH-3	123	0.693	0.002	70	0.694	0.003	36	0.691	0.005	98	0.688	0.003
ETH-4	128	0.510	0.002	66	0.519	0.002	36	0.518	0.004	131	0.510	0.002
IAEA-C1	17	0.347	0.006	--	--	--	*17*	0.365	0.005	34	0.362	*0.005*
IAEA-C2	11	0.711	0.004	--	--	--	13	0.715	0.005	30	0.720	0.005
MallinckrodtCal	13	0.526	0.011	--	--	--	--	--	--	--	--	--
MERCK	6	0.590	0.011	--	--	--	13	0.589	0.008	35	0.588	0.005
NBS 19	7	0.378	0.009	--	--	--	--	--	--	--	--	--
Spel 2-8-E	10	0.689	0.010	--	--	--	--	--	--	--	--	--
SRM 88B	8	0.595	0.009	10	0.573	0.002	--	--	--	--	--	--
TV01	5	0.679	0.007	--	--	--	--	--	--	--	--	--
TV03	115	0.699	0.002	53	0.699	0.003	--	--	--	21	0.711	0.007
Veinstrom	234	0.708	0.001	95	0.712	0.002	65	0.711	0.003	246	0.713	0.002

Table 1. Mean Δ_{47} values, n, and errors for carbonate standards for Passes B2 (above, top two sections of data) and B3 (above, bottom three sections of data).

2. METHODS (cont.)

Calculations:

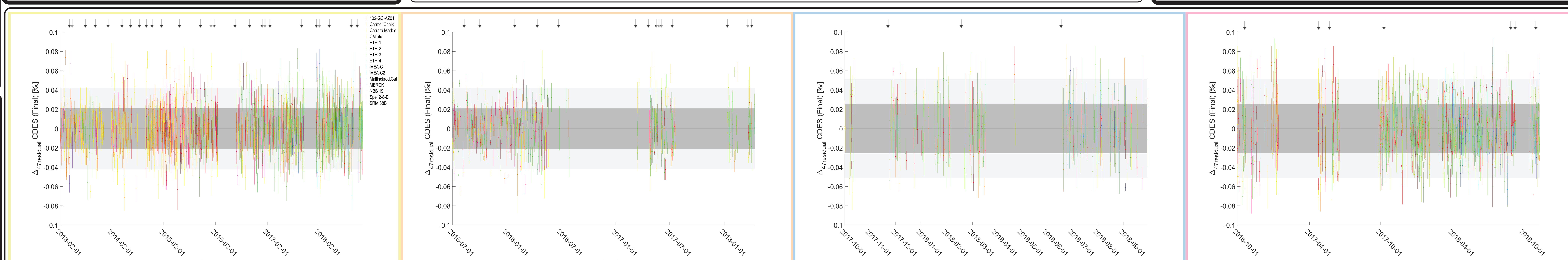
- Data from six years of analyses were entered into Easotope[4] over a two year period
- Initial calculations were done utilizing the Gonfiantini parameter set
- Here, data are reported using the Brand parameter set[2] on the absolute reference frame (ARF)
- Different subsets of standards were used for drift corrections, nonlinearity corrections, and the ARF
- Acid digestion corrections are from a publication[3]

Instrument drift and outlier treatment:

- Drift correction: Instrument drift is characterized using a 10-standard moving-average
- Any standard values that are more than 3 sigma from the mean are excluded

Working standards:

- Here we report results for two different sets of working standards (Pass B2 and Pass B3)
- For Pass B2, scale compression is constrained using reported values[1] for ETH-1, ETH-2, ETH-3. Values for the remaining standards are calculated using these values
- For Pass B3, scale compression is constrained using reported values[1] for ETH-1, ETH-2, ETH-3 and bootstrapped values from Pass B2 for five internal standards (Carrara Marble, CMTile (homogenized Carrara Marble tile), Veinstrom, TV03, and Carmel Chalk)



Chewbacca | R2-D2 (Sarlacc) | R2-D2 (NuCarb) | BB8

Figure 3. Same as Figure 2, for Pass B3.

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