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1 A community effort to improve inter-laboratory 2 standardization of the carbonate clumped isotope 3 thermometer using carbonate anchors

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18 Key Points

- 19 • The exclusive use of carbonate reference materials is a robust method for the
20 standardization of Δ_{47} measurements yielding very good analytical reproducibility
21 between laboratories, with residual inter-laboratory discrepancies quantitatively
22 consistent with in-lab analytical uncertainties.
- 23 • Δ_{47} measurements using different acid temperatures, different designs of sample
24 preparation lines and different mass spectrometer models are statistically
25 indistinguishable.
- 26 • We propose updated guidelines to standardize and report Δ_{47} measurements in future
27 studies using exclusively carbonates.
- 28 • We propose new consensus Δ_{47} values for a set of 6 carbonate reference materials
29 including the four ETH standards and two IAEA standards.

30 Abstract

31 Increased adoption and improved methodology in carbonate clumped isotope thermometry
32 has greatly enhanced our ability to interrogate a suite of Earth-system processes. However,
33 inter-laboratory discrepancies in quantifying carbonate clumped isotope (Δ_{47}) measurements
34 persist, and their specific sources remains unclear. To address inter-laboratory differences as
35 a clumped isotope community, we first provide community consensus values for four
36 carbonate standards relative to heated and equilibrated gases with 1,447 individual
37 measurements from nine laboratories. Then we analyzed the four carbonate standards and an
38 additional three standards, spanning a broad range of δ^{47} and Δ_{47} compositions, a total of
39 5,202 times on 26 mass spectrometers representing 23 unique laboratories. We use three
40 standards to calculated values for the other four standards and find that the use of carbonate
41 reference materials is a robust method for standardization that yields inter-lab discrepancies
42 consistent with intra-lab analytical uncertainty. The use of carbonate reference materials,
43 along with measurement and data processing practices described herein, provides the
44 carbonate clumped isotope community with a robust way to achieve inter-laboratory
45 agreement as we continue to use and improve this powerful geochemical tool.

51 Plain Language Summary

52 1 Introduction

55 Carbonate clumped isotope (Δ_{47}) thermometry is the most developed branch of the rapidly
56 evolving field of clumped isotope geochemistry. Given the broad range of applications in
57 Earth Sciences (e.g. Affek & Eiler, 2006; Eagle et al., 2010; Ferry et al., 2011; Ghosh,
58 Adkins, et al., 2006; Ghosh, Garzione, et al., 2006; Grauel et al., 2013; Guo & Eiler, 2007;
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63 et al., 2013; Guo & Eiler, 2007; Huntington et al., 2011; Passey & Henkes, 2012) and the
64 improvement of analytical methods including automation (Bernasconi et al., 2013, 2018;
65 Defliese & Lohmann, 2015; Dennis et al., 2011; Fiebig et al., 2019; Ghosh, Adkins, et al.,
66 2006; He et al., 2012; Hu et al., 2014; Huntington et al., 2009; Meckler et al., 2014; Müller,
67 Fernandez, et al., 2017; Passey et al., 2010; Petersen et al., 2019; Petersen et al., 2016;

Schmid & Bernasconi, 2010), the last 5-10 years have seen an increasing number of laboratories implementing this technique. The great potential of this thermometric method can only be fully exploited if the precision and accuracy of the obtained data is sufficient to solve differences of a few degrees in formation temperatures. In addition, like for any other geochemical method, widely available reference materials that match the sample matrices are necessary so that data can be robustly compared across laboratories (Meier-Augenstein & Schimmelmann, 2019). Currently the situation in the field of clumped isotope geochemistry of carbonates, is far from satisfactory. Published values for the ETH reference materials, the only carbonates that have been recently measured in many different laboratories, show a range of values for the same sample of up to 0.053 ‰ (see Bernasconi et al. 2018, Thaler et al. 2020 for recent comparisons). This clearly calls for better standardization procedures to improve laboratory comparability.

The data normalization scheme used in clumped isotope geochemistry of carbonates in most laboratories is based on the comparison of the composition of the CO₂ liberated from carbonates by reaction with phosphoric acid with that of a set of CO₂ reference or standard gases with different bulk and clumped isotope compositions. These reference gases are prepared either by heating CO₂ at 1000°C (heated gases; HG) or CO₂ equilibration with water at low temperatures (equilibrated gases at *e.g.* 25°C, 50°C; EG). By comparison of the measured compositions with the theoretical predictions of the equilibrium thermodynamic abundance of multiply substituted isotopologues in heated and equilibrated gases (Wang et al. 2004 and updates in Petersen et al. 2019), the measurements are standardized to the scale that was named the “absolute reference frame” (ARF) by (Dennis et al., 2011). In more recent publications the ARF is often referred to as the “Carbon Dioxide Equilibration Scale” (CDES) which is the terminology we adopt here. This approach was designed to allow different laboratories to link their measurements to an internationally recognized scale firmly anchored to theory using relatively easy and established laboratory protocols to produce CO₂ reference gases of known composition. In spite of the introduction of the CDES, however, the method still has numerous open questions (see (Bernasconi et al., 2018; Petersen et al., 2019 for two recent discussions).

Two of the main problems still limiting the reliability of this method to yield accurate temperature reconstructions are the lack of internationally recognized reference materials for

a precise inter-laboratory calibration. Moreover, published Δ_{47} -temperature calibrations produced in different laboratories have differed in both temperature dependence (slope), and absolute values (intercept). Possible reasons for the differences in slope and intercepts of the Δ_{47} temperature dependence have been widely discussed in the literature (e.g. Bonifacie et al., 2017; Daëron et al., 2016b; Fernandez et al., 2017; Katz et al., 2017; Kelson et al., 2017; Petersen et al., 2019; Schauer et al., 2016). Discrepancies have been attributed to analytical artefacts such as CO₂-acid re-equilibration at different acid digestion temperatures (see Swart et al., (2019) for a recent discussion). Other main factors proposed to influence the calculated slope of the calibrations are the limitations of the datasets used in the individual studies, in particular in terms of number of samples and replicates and of the temperature range covered by the available samples ((Bonifacie et al., 2017; Fernandez et al., 2017). However, the discrepancies in the intercept of the calibrations, for example between (Kelson et al., 2017) and (Peral et al., 2018) and in laboratory comparability still remain a problem that can only be improved by using a more robust standardization method.

Petersen et al., (2019) in a recent effort to solve differences in calibrations, compiled raw data of a number of published temperature calibrations and recalculated them all in a consistent way using the revised “IUPAC” correction parameters to correct for the ¹⁷O abundance (Daëron et al., 2016a; Schauer et al., 2016). The goal was to test whether data processing differences and/or the use of consistent but incorrect ¹⁷O- correction parameters in the calculations were the root causes of inconsistencies. The result of this study was that differences among calibrations were reduced but not eliminated by the recalculation, implying that other factors must be responsible for the remaining discrepancies. These differences have pushed many laboratories to use laboratory-specific calibrations performed with the same analytical approach, as they take at least partially into consideration possible procedural differences (Petersen et al., 2019). However, if a laboratory changes analytical procedures or has not realized an in-house calibration, this approach is problematic. Good inter-laboratory reproducibility is a natural requirement for sufficiently mature analytical methods and striving to ensure that Δ_{47} measurements meet this goal is now key to its broad acceptance and quantitative usefulness.

While the definition of the CDES was a major milestone, a known problem with this approach is that while the CO₂ reference gases equilibrated at known temperature (HT or EG)

can be confidently used for correction of mass spectrometric fractionations/nonlinearities and for effects of the purification procedures, they cannot account for the effects of the phosphoric acid reaction on the composition of the produced CO₂. Among the factors responsible for discrepant calibrations and laboratory comparability two important ones cannot be tested with a gas-based standardization. These are (1) the absolute value and temperature dependence of the phosphoric acid fractionation factor (see Petersen et al., 2019 for a recent compilation) and (2) possible CO₂ equilibration effects during acid digestion of the sample. Swart et al. (2019) presented evidence that equilibration of CO₂ with water or hot metal surfaces during phosphoric acid reaction and transfer of the CO₂ to the mass spectrometer could be a factor leading to the alteration of the apparent temperature dependence of clumped isotopes in carbonates and on the absolute value of calculated Δ_{47} . As many laboratories use custom built extraction lines with very different designs and volumes of tubing and of acid vessels, these factors are impossible to precisely quantify for each laboratory.

We propose that these issues can be circumvented if carbonates, which undergo the same acid digestion as the samples, are used for normalization instead of gases, consistent with the principle of identical treatment of sample and standards (Carter & Fry, 2013; Werner & Brand, 2001a). In addition, normalizing results to some accepted values for the solids, as is commonly done with conventional oxygen isotopes in carbonates, makes it no longer necessary to precisely quantify acid fractionation factors at different temperatures (Bernasconi et al., 2018).

A carbonate standardization approach was introduced by (Schmid & Bernasconi, 2010) and improved by (Meckler et al., 2014), with the following benefits (1) the use of carbonates can more easily be fully automatized, eliminating time-consuming and possibly error-prone manual preparation of CO₂ reference gases (equilibrated at known temperature) by individual users on separate extraction lines and (2) in some automated system designed for small sample sizes, the gases had to be measured through a different capillary than the carbonates with potential biases that would go unrecognized and (3) in those systems the CO₂ reference gases are measured at constant beam intensity whereas the samples are measured with decreasing beams. These features argue in favor of carbonate standardization *a priori*, but it remains critical to assess *a posteriori* whether the results of this approach are as robust and accurate as expected, and whether they significantly improve the inter-laboratory

reproducibility of Δ_{47} measurements. Discussions at the Sixth International Clumped Isotope Workshop (Paris, 2017) led to the present inter-laboratory comparison exercise (InterCarb) to evaluate the benefits and drawbacks of a carbonate-based standardization approach as an alternative to the use of gas standards.

The primary goal of this study was to test whether the exclusive use of carbonate reference materials can solve inter-laboratory discrepancies and provide an alternative to the measurement of heated and equilibrated gases for the entire community. This is particularly important because of the increasing number of laboratories that using the commercial small-sample automated devices which cannot easily be standardized using the HG-EG approach. The InterCarb exercise also provides a natural opportunity to define the best community-derived absolute Δ_{47} values for the ETH standards of (Meckler et al., 2014): although these standards are already used in many laboratories, their current nominal Δ_{47} values are based on measurements from the ETH laboratory only. The InterCarb exercise can similarly establish community accepted values for other common carbonate reference materials, some of which have been in use for several years, in order to provide the community with a self-consistent set of carbonate reference materials with a broad range of bulk and clumped isotope compositions.

1.2. Nomenclature and data processing

Clumped isotope compositions are reported as an excess abundance of the CO_2 isotopologue of cardinal mass 47 (dominantly the isotopologues $^{13}\text{C}^{18}\text{O}^{16}\text{O}$) compared to a stochastic distribution according to the formula:

$$\Delta_{47}(\text{‰}) = \frac{R^{47}}{R^{47*}} - 1$$

where R^{47} is the abundance of the minor isotopologues 47 relative to the most abundant isotopologue with mass 44. The expected stochastic ratio R^{47*} is calculated using the measured abundance of ^{13}C and ^{18}O in the sample (Affek & Eiler, 2006). The measured abundance of isotopologues with m/z 47 in the sample with respect to the working gas (WG) in the mass spectrometer is reported in the traditional delta notation as:

$$\delta^{47}(\text{‰}) = \left[\left(\frac{R^{47}_{\text{sample}}}{R^{47}_{\text{working gas}}} \right) - 1 \right] \times 1000 .$$

201

202 The δ^{47} scale is a measure of the difference between the sample of interest and the WG of the
 203 specific instrument, therefore, it cannot be compared across laboratories. The same notation
 204 is used for 45, 46, 48 and 49 beams.

205

206 The CO₂ gas-based standardization scheme for clumped isotope thermometry in carbonates
 207 relies on a set of CO₂ reference gases with different bulk composition (δ^{47}), preferably chosen
 208 by the user to encompass the δ^{47} bulk composition of unknown samples, that have been
 209 heated at 1000°C to reach a near-stochastic distribution of all isotopologues and one set
 210 equilibrated with water at low temperatures to reach equilibrium enrichments in the mass-47
 211 isotopologues (Dennis et al., 2011). The heated gases having a stochastic distribution of all
 212 isotopologues define the zero point of the scale ($\Delta_{47} = 0.0266 \text{ ‰}$), the equilibrated gases a
 213 high point, e.g., at 25 °C $\Delta_{47} = 0.9196 \text{ ‰}$), with theoretical values linking measurements to
 214 theory calculated by Wang et al. (2004), and revised by Petersen et al., (2019). A wide range
 215 in δ^{47} compositions of gases used for normalization is generally chosen so that when plotted
 216 in a δ^{47} vs- Δ_{47} plot the broad range of compositions can be used to correct for an apparent
 217 dependence of Δ_{47} on δ^{47} which is caused by negative or sometimes positive signal
 218 backgrounds on the m/z 47 collector (Bernasconi et al., 2013; He et al., 2012). The large
 219 range in Δ_{47} (i.e. 25°C, 1000°C), on the other hand, is necessary to correct for scale
 220 compression caused by processes of scrambling and molecule recombination in the source of
 221 the mass spectrometer or elsewhere in the sample preparation/dual-inlet pipeline (Dennis et
 222 al., 2011). With properly chosen CO₂ reference gases with widely varying δ^{47} composition it
 223 is possible to cover the entire range of natural carbonate compositions, avoiding
 224 extrapolations in the (δ^{47} , Δ_{47}) compositional space (Fig. 1). Note that measurement errors
 225 (typically not better than 0.010‰) being relatively large compared to the natural
 226 compositional range (absolute value is less than 0.7‰), the large (>0.9 ‰) difference in Δ_{47}
 227 of the CO₂ reference gases minimizes analytical errors introduced by uncertainties resulting
 228 from the measurement of HG and EG.

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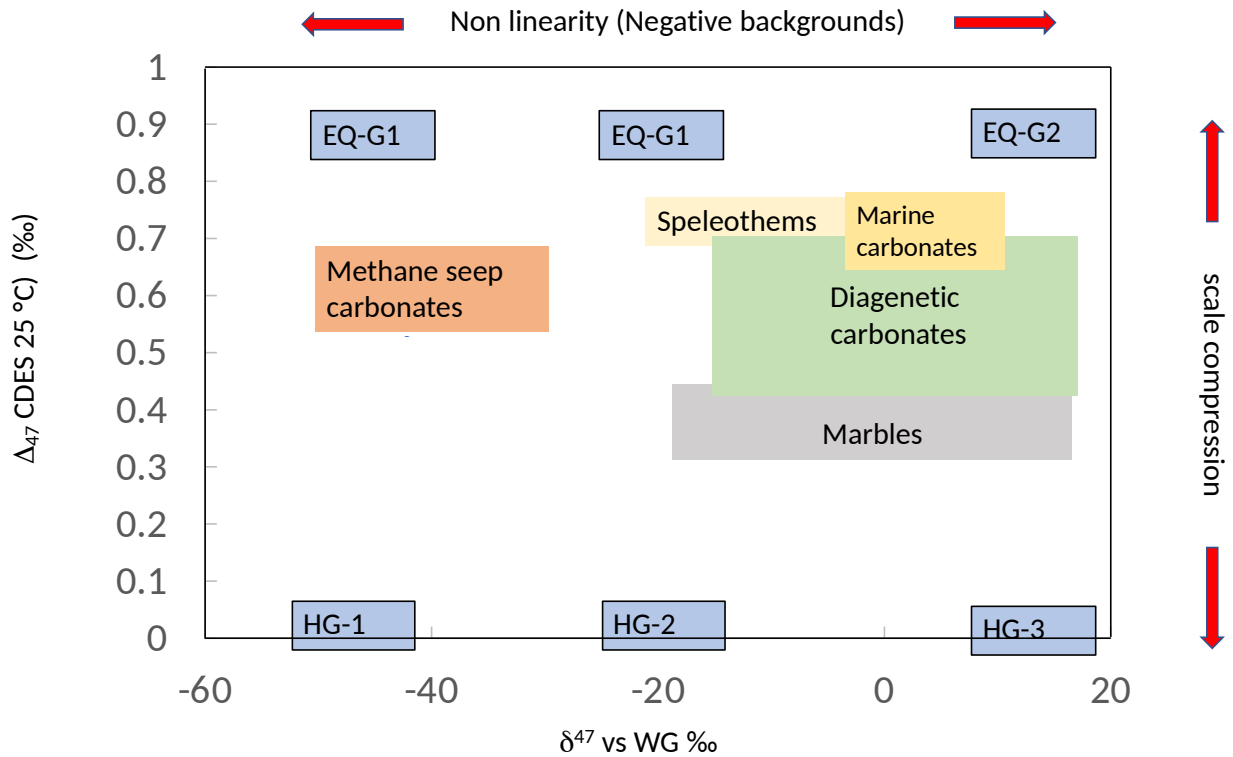


Fig 1 δ^{47} vs. Δ_{47} composition of heated and equilibrated gases in a range commonly used in many laboratories showing that the observed range in measured clumped isotope compositions in natural carbonates can be completely bracketed by heated and equilibrated CO₂ reference gases from which δ^{47} composition have been chosen by the user.

Meckler et al., (2014) attempted to achieve a similar framework as the CO₂ gas-based standardization but with carbonate standards. They described four carbonates that were developed at ETH Zürich to serve as replacements for HG-EGs and demonstrated that very good long- and short-term reproducibility can be achieved using only carbonates for data correction. Bernasconi et. al (2018) discussed in detail these standards and postulated, based on a limited inter-laboratory dataset, that carbonate standardization should improve inter-laboratory data comparability in most cases. This claim seems arguably strengthened by the results of Meinicke et al., (2020) Peral et al. (2018), Piasecki et al. (2019) and (Jautzy et al., 2021). The first three studies produced independent foraminifera-based and the fourth a synthetic carbonate-based Δ_{47} -temperature calibration anchored to the same set of carbonate standards, yielding statistically indistinguishable slopes and intercepts despite the use of independent sample sets and different analytical systems. The same conclusion was reached

by (Spooner et al., 2016)(Spooner et al., 2016) found that carbonate standardization removed data biases between the Caltech and the WHOI laboratories, which were present when not removed by normalization to the CDES by heated and equilibrated gases was used..

A possible limitation of carbonate standardization is that available carbonates have a smaller range in δ^{47} and, perhaps more importantly, a smaller range in Δ_{47} compositions than what is achievable with heated and equilibrated gases. In some cases, standardization procedures may require extrapolation to compositions that are not within the δ^{47} - Δ_{47} space created by carbonate standards (Fig. 2). In addition, the range of Δ_{47} compositions for carbonates is only on the order of 0.45 ‰ between 0 and 1000°C. The smaller range in Δ_{47} compared to HG-EG requires higher precision and thus high standard replication and a standard:sample ratio ≥ 1 to keep normalization errors small (see Daëron (this volume) for details).

1.2. InterCarb goals and design:

InterCarb was designed after the Paris' Clumped Isotope Workshop in 2017 to carefully evaluate the potential of carbonates to serve as a standardization scheme that improves inter-laboratory agreement for 'unknown' carbonates both inside and outside of the δ^{47} - Δ_{47} space defined by the anchor samples (Fig. 2). The main questions posed are:

1. Is it possible to produce consistent carbonate clumped isotope measurements across laboratories using exclusively carbonate reference materials? In other words, does the observed inter-laboratory scatter in Δ_{47} values match that expected from intra-laboratory analytical precision limits?
2. How well does the carbonate standardization approach perform when extrapolating beyond the δ^{47} - Δ_{47} compositional space sampled by a set of carbonate reference materials?
3. Do carbonate reference materials fully correct effects arising from different reaction temperatures, sample preparation protocols, and analytical equipment?
4. Can we define a self-consistent set of widely available reference materials with community-agreed on compositions accurately anchored to the CDES scale?

5. Does inter-laboratory reproducibility of carbonate clumped isotope analyses corrected using carbonate reference materials improve on the relatively large reported inter-laboratory differences using HG-EG standardization?

Approach:

It was decided to distribute and analyze a common set of 7 carbonate standards with a large range of δ^{47} and Δ_{47} compositions (Figure 2), treating three of them as “anchors” to the CDES and processing the remaining four as “unknowns”. Due to the relatively widespread use in different laboratories the three reference materials ETH-1, ETH-2 and ETH-3 (Meckler et al. 2014; Bernasconi et al. 2018) were chosen as anchors. They are still available today in relatively large quantities (>600 g), have been in use at ETH since 2013 and in many other laboratories for several years. Importantly, they have been thoroughly tested for homogeneity based on thousands of measurements in 80 to 150 μ g aliquot sizes in different laboratories.

The “unknown” InterCarb reference materials were chosen to cover a wide natural range in δ^{47} and Δ_{47} compositions. These samples had to be available in large quantities, inexpensive, and if possible distributed by an organization with a long-term perspective in order to ensure future data quality and availability for the increasing number of laboratories.

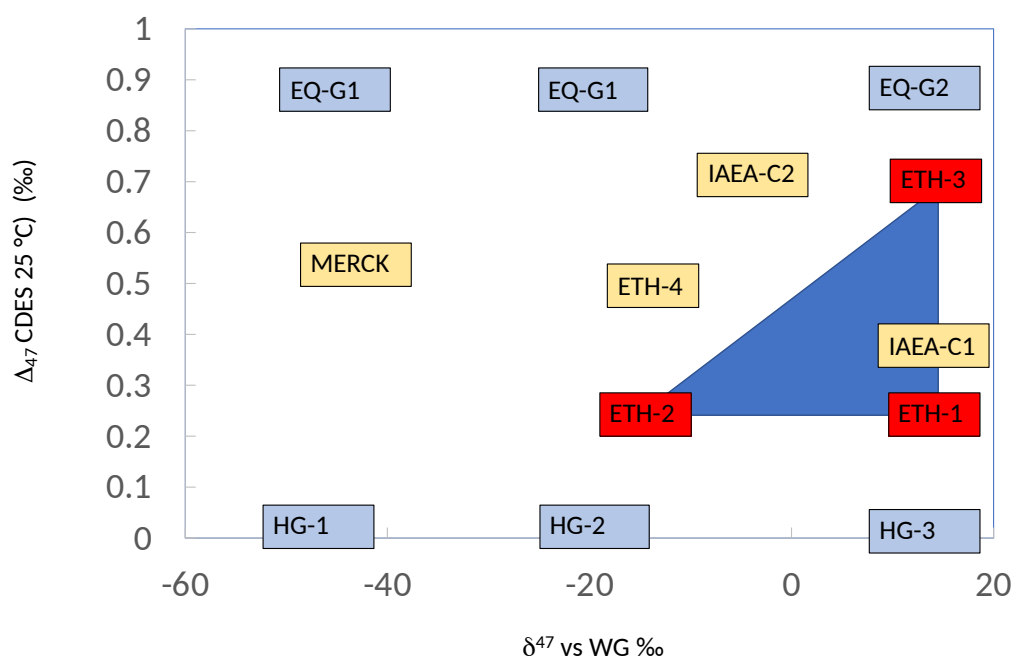


Fig 2. Approximate compositions of the anchor samples (red) and the unknowns (yellow) in δ^{47} - Δ_{47} space for a mass spectrometer with a working gas (WG) with a bulk isotope composition similar to that used in many laboratories (e.g. CO₂ provided by Oztech Trading corporation with $d18O$ close to X‰ and $d13C$ close to Y‰). Note the smaller achievable range compared to heated and equilibrated gases and the large extrapolation necessary for the determination of the composition for MERCK. Heated and equilibrated CO₂ reference gases have a larger Δ_{47} range allowing for more robust stretching calculations with identical numbers of standard:sample analyses.

2 Materials and Methods

2.1. Sample description

The anchor samples ETH-1 (Carrara marble heated at 600°C) ETH-2 (synthetic carbonate heated at 600°C) and ETH-3 (Upper cretaceous chalk) are described in detail in Bernasconi et al. (2018).

IAEA-C1 (marble from Carrara, Italy) is distributed by the International Atomic Energy Agency (IAEA) as a mechanically crushed and milled down to a dust-free fraction with grains ranging from 1.6 to 5 mm. All the provided 50g were milled and thoroughly homogenized in a ball mill at ETH Zürich to a grain size of less than 100 µm and filled in plastic vials of 0.5 g aliquots for distribution.

IAEA-C2 is a freshwater travertine from Bavaria distributed by IAEA as a powder which was homogenized further in a ball mill to a grain size of less than 100 µm at ETH Zürich, and filled in 0.5 g aliquots in plastic vials for distribution.

ETH-4 is synthetic carbonate with intermediate formation temperature and the same bulk isotope composition as ETH-2 (see Bernasconi 2018 for details).

MERCK (lot no. B1164559 515) is a ultra-pure commercially available synthetic calcite and was chosen for its very depleted $\delta^{13}C$ and $\delta^{18}O$, of approximately -41.7 ‰ and -15.5 ‰

(VPDB), respectively. This sample represents an extreme case of extrapolation from the δ^{47} - Δ_{47} space defined by the anchor materials (Fig. 2).

2.2 Instrumentation.

The reported data were produced with a variety of custom built (14 laboratories) and commercial (10 laboratories) preparation systems (ThermoFisher Scientific Kiel IV device and Nu instruments Nucarb). Reaction temperatures were generally 90 °C for “large-sample” custom preparation systems and 70°C for the Kiel and the NuCarb. Four mass spectrometer types were used: Thermo Fisher scientific MAT253 and 253Plus, Nu instruments Perspective and Elementar Isoprime 100. All participants contributed results they considered to be of a “publication-grade” quality.

2.3 Data processing, correction and error assessment.

It should be stressed that the InterCarb experiment, by design, is not intended to grade the analytical “performance” of individual laboratories. Each participating laboratory (or mass spectrometer, in the case of laboratories with several instruments) was thus randomly assigned an anonymous identifying number. Within each laboratory, analyses were grouped in different analytical sessions defined by the participants themselves. An analytical session is generally defined by a time where the behavior of the analytical system (preparation system, source tuning, backgrounds, isotope scrambling in the source) is considered to be similar. The database record of each analysis consists of a laboratory identifier; a session identifier; an analysis identifier; the name of the analyzed sample; the mass spectrometer model; the acid reaction temperature; the mass of reagent carbonate; and background-corrected δ^{45} , δ^{46} and δ^{47} values.

The only instrumental corrections to the raw data applied independently by each participating laboratory were background corrections (or “Pressure Baseline Correction”: PBL) to the ion currents/voltages (Bernasconi et al., 2013; He et al., 2012). The PBL is strongly dependent on instrument design and configuration, and varies temporally depending on many factors. This correction, therefore, can only be carried out by each participating laboratory according to its own established procedures and monitoring.

367

368 To avoid artefacts arising from different calculation/standardization procedures, rounding
 369 errors, and ^{17}O correction parameters, raw data from all laboratories were processed by a
 370 single Python script (SI file *intercarb-src.zip*) based on data reduction, standardization and
 371 error propagation methods described in detail in the companion paper (Daëron, this volume).
 372 Here we briefly summarize these calculations.

373

374 Session-averaged background-corrected δ^{45} and δ^{46} values for each of the three anchor
 375 samples were first used to calculate the bulk isotope composition of the working gas used in
 376 each session, based on (a) previously reported $\delta^{13}\text{C}_{\text{VPDB}}$ and $\delta^{18}\text{O}_{\text{VPDB}}$ values of ETH-1, ETH-
 377 2, and ETH-3 (Bernasconi et al., 2018), (b) the IUPAC oxygen-17 correction parameters of
 378 Brand et al. (2010) , and (c) a temperature-dependent oxygen-18 acid fractionation factor
 379 between CO_2 and calcite of (Kim et al., 2015). This recalculation of working gas bulk
 380 compositions avoids (small) discrepancies potentially introduced by inaccuracies in the
 381 nominal compositions of the working gases.

382 Raw Δ_{47} values were computed according to:

383

$$384 \quad \Delta_{47}^{\text{Raw}} = \left(\frac{R^{47}}{R^{47*}} - 1 \right)$$

385 Where R^{47} is the measured ratio and R^{47*} the calculated stochastic ratio of mass 47 over mass
 386 44 of CO_2 .

387 Δ_{47}^{Raw} values are then normalized to “absolute” Δ_{47} values using session-specific relationships
 388 of the form:

389

$$390 \quad \Delta_{47}^{\text{Raw}} = a \Delta_{47} + b \delta_{47} + c$$

391

392 For each session, the best-fit standardization parameters (a, b, c) are computed from an
 393 unweighted least-squares regression treating Δ_{47}^{Raw} as the response variable, only considering
 394 the three anchor samples ETH-1, ETH-2, and ETH-3. Absolute Δ_{47} values are then
 395 computed for all replicates within that session. Standardization parameters for all sessions are
 396 listed in (Table S1, supplementary information).

397

In the table and figures the uncertainty of the measurements is reported as 1SE of the mean either only considering uncertainties in the analyses of a given sample, or considering fully-propagated errors associated with the establishment of the reference frame. In both cases, the analytical error assigned to each individual raw Δ_{47} analysis is equal to the pooled “external” repeatability of raw Δ_{47} measurements for all samples (anchors and unknowns) within each session. This treatment of error is a new approach that more fully accounts for error in both the sample measurement and reference frame. A detailed description of these error estimates is presented in a companion paper (Daéron, this volume).

2.4 Clumped isotope composition of the ETH anchor materials.

The clumped isotope compositions of the four ETH reference materials relative to the CO₂ reference frame CDES were first reassessed based on new data provided by 9 laboratories that also provided HG and EG data measured during the same sessions as the ETH reference materials. Six of these laboratories reacted carbonates at 90 °C, two at 70 °C and only one at 25 °C. In keeping with tradition, we “project” the carbonate Δ_{47} values to an acid reaction temperature of 25 °C using the acid corrections of (Petersen et al., 2019), i.e. +0.66 ‰ and +0.088 ‰, respectively, for reactions at 70 °C and 90 °C.

3 Results and Discussion

3.1 Redetermination of nominal Δ_{47} values for the ETH standards relative to heated and equilibrated CO₂ gases

The weighted averages of the 4 standards projected to 25°C comprising 619 analyses of the carbonate standards and 828 heated and equilibrated gases from 9 different laboratories are reported in Table 1 and Fig 4. The large number of analyses and the appropriate consideration of the errors on the anchors (CO₂ gases references) is a first, and allows a robust redetermination of the accepted values of the ETH reference materials with 1SE uncertainties of 2 ppm or less.

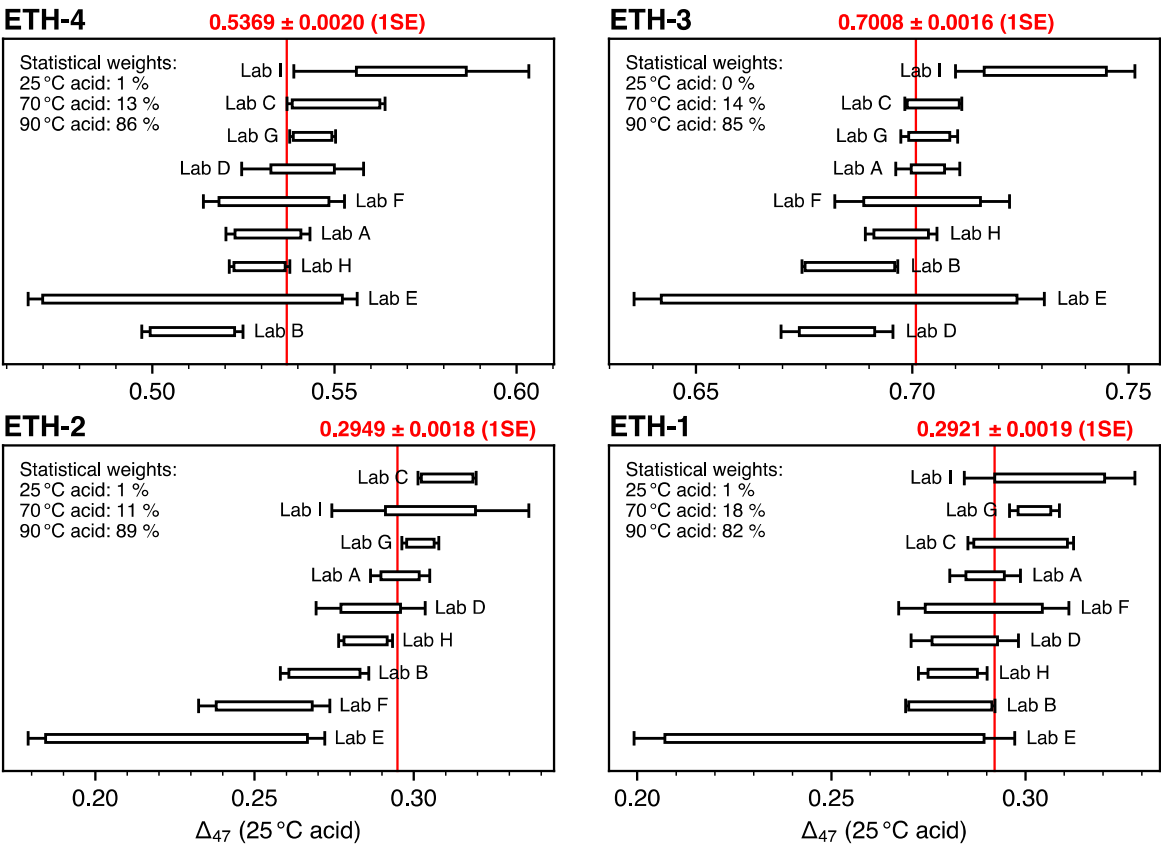
Table 1: Newly determined nominal Δ_{47} values of the ETH standards projected to 25°C reaction temperature using a correction factors of 0.088 ‰ and 0.066 ‰ for 90 °C and 70 °C reactions, respectively (Petersen et al. 2019). Reported error values are 1SE after

29

430 *propagating analytical uncertainties associated with carbonate unknowns and equilibrated*
431 *gas standards (Daëron, this volume)*
432

Sample	ETH-1	ETH-2	ETH-3	ETH-4
Δ_{47} (‰ CDES)	0.2920±0.0019	0.2949±0.0018	0.7008 ±0.0016	0.5369 ±0.0020

433
434 When compared with the published values in Bernasconi et al. (2018) the average Δ_{47} values
435 ETH-1 and ETH-2 are respectively 0.034 and 0.039 ‰ greater than the original values,
436 whereas ETH-3 increases by 0.010 and ETH-4 by 0.030 ‰. Such positive offset of D47
437 values reported in Bernasconi et al. (2018) versus other laboratories has also been observed in
438 Thaler et al. (2020).
439



440

441 *Figure 3. New determination of Δ_{47} values for the four ETH standards relative to the CDES*
 442 *using updated CO_2 equilibrium values and phosphoric acid fractionation factors from*
 443 *Petersen et al. (2019). Error bars correspond to the 95 % confidence limits taking into*
 444 *account fully propagated errors (ie. taking into account errors in both unknown and anchor*
 445 *analyses). The red numbers are the error-weighted average values. Note different horizontal*
 446 *scales for the different samples.*

447

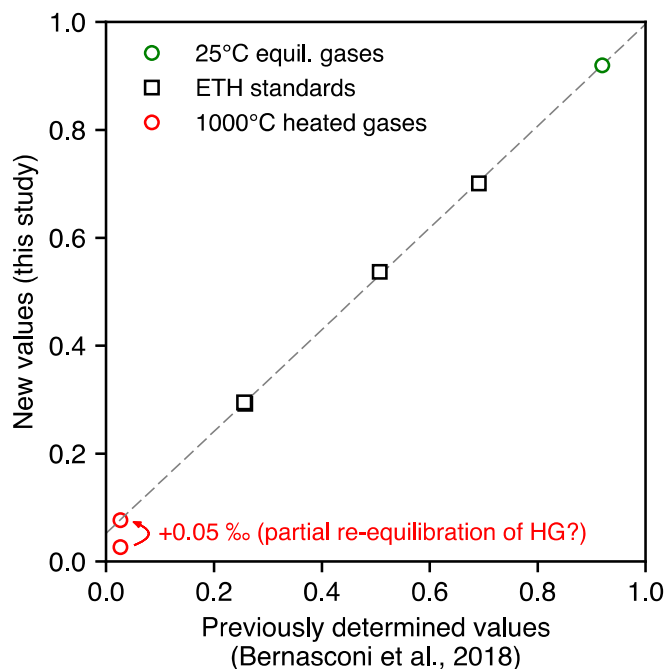
448

449 The observation that these changes in nominal values decrease as Δ_{47} increases suggests a
 450 simple hypothesis to explain this discrepancy: in the original study of Meckler et al. (2014),
 451 the carbonate samples and the heated/equilibrated CO_2 gases experienced different analytical
 452 procedures (i.e. measurements made for HGs passed through a unique set of capillaries and
 453 used the bellows-mode whereas carbonates were measured using the microvolume and gas-
 454 depletion). The potential effects of partial re-equilibration of the heated and 25 °C
 455 equilibrated gases at room temperature could be significant for the former yet remain
 456 minuscule for the latter, leading to an overestimation of Δ_{47} scale compression and thus
 457 applied stretching of the Δ_{47} scale towards theoretical values. The observed changes in
 458 apparent carbonate standard Δ_{47} values may therefore simply reflect partial re-equilibration of
 459 heated gases at least at the time of measurements at ETH (and reported in Meckler et al..
 460 2014), increasing their values in the original study by about 0.05 ‰ (Figure 4)

461

462 **Figure 4:** *New nominal Δ_{47} values for the ETH standards compared to previously reported*
 463 *ones. Apparent changes in these values scale linearly with the Δ_{47} difference between*
 464 *carbonate samples and 25 °C equilibrated CO_2 , suggesting that Δ_{47} values of heated gases*
 465 *in the original study may have been biased by $\sim +0.05$ ‰ through partial re-equilibration at*
 466 *room temperature at ETH at the time the measurements were performed.*

467



468

469

470 It has been suggested previously that ETH 1 and ETH 2 should be indistinguishable in Δ_{47}
 471 and close to stochastic distribution (Müller, Violay, et al., 2017), based on comparison with
 472 stochastic carbonates which showed that the Δ_{47} of ETH 1 and ETH 2 is very close (approx.
 473 0.006 ‰ higher) to the values of aliquots of the same carbonates heated at 1000°C. However,
 474 additional test measurements in multiple laboratories of samples heated at >1000°C are
 475 necessary to confirm this observation.

476

477 One laboratory (TT) observed a large difference in the value for ETH-1 and ETH-2, which is
 478 not what we should expect because both carbonates were heated under identical conditions.
 479 Their values of ETH-3 and 4 are very similar to other laboratories. The reason for these
 480 inconsistencies is probably due to the fact that ETH-1 was only measured four times with
 481 only limited number of HG/EG and ETH-2 and ETH-4 were not measured in the same
 482 session. In general, the labs with the smallest number of replicate measurements have
 483 uncertainties that are systematically larger. These results highlight the importance of
 484 correction procedures in clumped isotope analysis. Sufficient replication of both standards
 485 and samples is critical and offsets can arise when comparing results from different sessions.
 486 Due to these difficulties it is good practice to spread replicates of the same sample in different
 487 sessions over longer periods of time to obtain accurate results and follow a standard:sample
 488 ratio ≥ 1 .

489

Based on the results above, the difference between the average of ETH1/2 and ETH-3 is reduced by 0.0265 ‰ thus leading to a compression of the scale by about 6.1 % compared to the values reported by Bernasconi et al. (2018). As a consequence, the slopes of published temperature calibrations produced with carbonate standardization (Bernasconi et al., 2018; Jautzy et al., 2021; Meinicke et al., 2020; Peral et al., 2018; Piasecki et al., 2019) will become slightly shallower, with more positive y-intercepts. If results from previous publications are recalculated with the new standard values (see section 3.4), however, changes in calculated formation temperatures will be negligible. For this reason, when comparing data from publications using old accepted values of the ETH Standards for standardization (either those published by Meckler et al. (2013) or those recalculated with the IUPAC parameters by Bernasconi et al. (2018) to new ones, it is recommended to directly compare the reconstructed temperatures rather than recalculating the Δ_{47} . Full recalculation of old measurements require the availability of the entire dataset including standards and to use the same correction procedures such as the averaging method used in the original publications and is described in section 3.5. Based on the results above, the difference between the average of ETH1/2 and ETH-3 is reduced by 0.0265 ‰ thus leading to a compression of the scale by about 6.1 % compared to the values reported by Bernasconi et al. (2018). The slopes of published temperature calibrations produced with carbonate standardization (Bernasconi et al., 2018; Jautzy et al., 2021; Meinicke et al., 2020; Peral et al., 2018; Piasecki et al., 2019) will therefore become slightly shallower, with more positive y-intercepts. If results from previous publications and calibrations are recalculated with the new standard values (see below), changes in calculated formation temperatures will be negligible. For this reason, when comparing data from publications using old accepted values of the ETH Standards for standardization (either those published by Meckler et al. (2013) or those recalculated with the IUPAC parameters by Bernasconi et al. (2018) to new ones, it is recommended to directly compare the reconstructed temperatures rather than recalculating the Δ_{47} . Full recalculation of old measurements requires the availability of the entire dataset including standards used in the original publications.

Table 2. Results of CO₂ reference gases derived values of ETH reference carbonate materials, after acid temperature corrections based on Petersen et al. (2019). N is the number of replicate analyses of carbonate samples. Uncertainties reported here represent both reference frame errors and reproducibility errors.

Lab	N (ETH-1)	$\Delta 47$ (ETH-1)	$\pm 95\%$	N (ETH-2)	$\Delta 47$ (ETH-2)	$\pm 95\%$	N (ETH-3)	$\Delta 47$ (ETH-3)	$\pm 95\%$	N (ETH-4)	$\Delta 47$ (ETH-4)	$\pm 95\%$
Lab A	34	0.2896	0.0091	23	0.2957	0.0093	55	0.7036	0.0074	10	0.5318	0.0115
Lab B	14	0.2806	0.0115	13	0.2720	0.0139	15	0.6856	0.0111	12	0.5110	0.0139
Lab C	5	0.2988	0.0136	11	0.3105	0.0091	20	0.7049	0.0066	5	0.5504	0.0135
Lab D	16	0.2844	0.0138	13	0.2865	0.0171	15	0.6826	0.0129	15	0.5413	0.0167
Lab E	4	0.2482	0.0490	4	0.2255	0.0466	4	0.6831	0.0474	4	0.5111	0.0452
Lab F	4	0.2893	0.0219	4	0.2530	0.0206	5	0.7023	0.0202	4	0.5334	0.0194
Lab G	19	0.3023	0.0064	18	0.3021	0.0058	15	0.7039	0.0066	12	0.5440	0.0063
Lab H	58	0.2813	0.0088	51	0.2849	0.0085	59	0.6974	0.0083	47	0.5294	0.0083
Lab I	8	0.3062	0.0220	8	0.3052	0.0309	8	0.7307	0.0207	7	0.5711	0.0323

, it to reach a community consensus on how to report clumped isotope measurements, to reduce the confusion in the literature related to different scales used in this rapidly evolving field. Currently Δ_{47} are reported for different temperatures of phosphoric acid digestion, mostly projected to 25°C (CDES25) but also to 70 °C (CDES70) or 90 °C (CDES90) reaction. In the literature, phosphoric acid correction factors used by different research groups to convert results from 90 to 25°C reaction have varied between 0.069 ‰ (Wacker et al., 2014) to 0.092 ‰ e.g. (Bonifacie et al., 2017) thus representing a significant source of confusion and uncertainty. In contrast, carbonate-based standardization eliminates different phosphoric acid correction factors as a source of uncertainty and provides a consistent framework to report Δ_{47} without uncertainties related to the reaction temperature.

One possible option is to keep a projection to 25 °C acid reaction temperature, consistent with most clumped isotope publications to date. At first sight it could appear that maintaining the projection to a reaction temperature of 25 °C would make a comparison of new data to older publications easier. However, we emphasize that previously published Δ_{47} data, either normalized with heated and equilibrated gases or with carbonates, cannot be directly compared to the new ones. All previous carbonate-normalized data have to be recalculated in order to fully take into account the new standard values reported here. For HG/EG normalized data it is not possible to convert to the new scale, unless an adequate number of ETH standards had been measured during the same period of time. In this case, it

may be more reasonable to directly compare reconstructed temperatures with a laboratory specific calibration, rather than Δ_{47} values as suggested by Petersen et al. (2019).

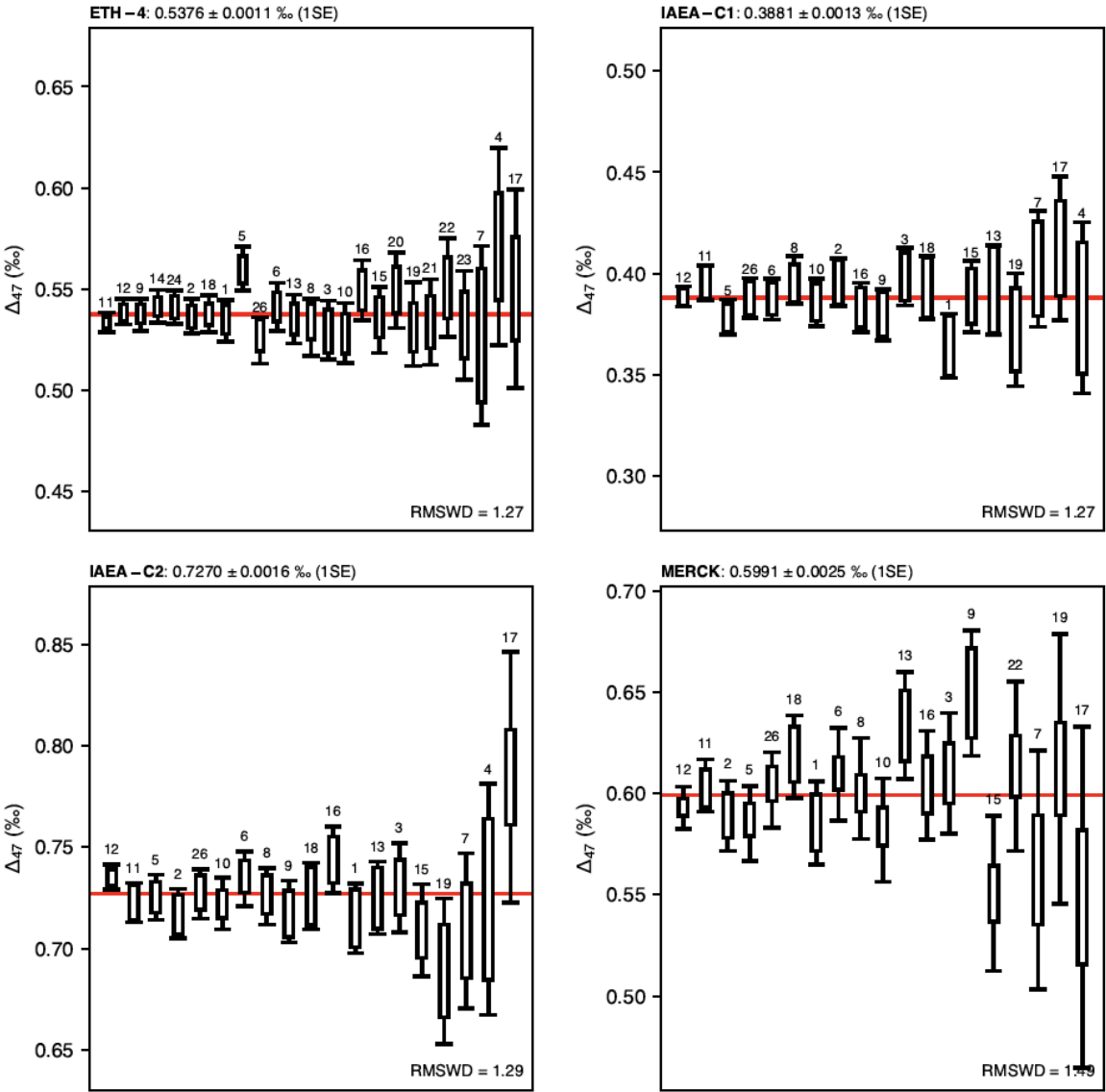
Maintaining a conversion to 25°C has the benefit that past reconstructed temperatures can be directly compared if samples and calibration data were treated equally. Reasons to change to projection to a different temperature, are that the values presented in this study were determined mostly with acid digestion at 90 °C and that the vast majority of laboratories currently active have moved to higher reaction temperatures of either 70 or 90 °C. Thus the conversion to 25°C reaction values could also be abandoned in favor of reporting data directly for acid reaction temperatures of 70 or 90 °C.

3.2 InterCarb results

We obtained data from 26 Mass spectrometers from 23 Laboratories. The Δ_{47} of the 4 unknown samples normalized to the new community-derived values of the ETH reference materials averaged per individual analytical session and mass spectrometer are listed in Table 3. Sample mean values obtained in each mass spectrometer are shown in Figure 5. The details of each analytical session, including the number of samples and standards measured, the composition of the working standard, the scaling parameters and the reproducibilities of the individual sessions are given in the supplementary information (Table S1). Some laboratories reported data for only a subset of the unknown samples, and both replication levels and analytical repeatabilities are very different from laboratory to laboratory (Table S1).

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573 *Figure 5. Final results by laboratory. Error bars correspond to fully propagated 95 %*
 574 *confidence limits, taking into account errors in both unknown and anchor analyses.*
 575 *Boxes correspond to 95 % confidence limits not accounting for normalization errors*
 576 *(i.e. only taking into account errors in unknown analyses). Results are sorted by*
 577 *increasing analytical errors and laboratories are identified by number. Overall*
 578 *error weighted average Δ_{47} values are displayed as solid red lines and reported in*
 579 *top left label. Root mean squared weighted deviation values (RMSWD, equivalent to*
 580 *reduced χ^2) are reported in bottom right labels. All plots have the same vertical*
 581 *scale.*

582

583 Laboratories with stronger analytical constraints (better in-lab repeatability of Δ_{47}
 584 measurements and/or greater number of analyses) generally converge towards the overall
 585 mean value for each unknown sample. This observation suggests that inter-laboratory
 586 variability observed here is largely due to random errors that can be alleviated by replication,
 587 even for laboratories with relatively large analytical errors on individual measurements. It is
 588 also notable that fully propagated analytical errors (i.e., taking into account uncertainties in
 589 the standardization procedure) can be substantially larger than the errors based only on the
 590 uncertainty associated with unknown sample analyses which is what is generally reported in
 591 the literature. The increase in error bar is also related to in-lab repeatability and the number
 592 of standards measured. In addition, this effect increases for unknown samples whose
 593 compositions lie outside the “anchor triangle” defined by ETH-1/2/3 (and are the highest for
 594 MERCK as it is farthest from the anchor triangle), consistent with the models of Daëron (this
 595 volume) and Kocken et al., (2019).

596

597 Table 3. Results of individual sessions by laboratory/mass spectrometer.

Lab	Session	ETH-4	IAEA-C1	IAEA-C2	MERCK	RMSWD
01	01	0.5367 ± 0.0160				
	02	0.4957 ± 0.0262				
	03	0.5360 ± 0.0057	0.3643 ± 0.0080	0.7149 ± 0.0088	0.5855 ± 0.0105	
	all	0.5345 ± 0.0052	0.3643 ± 0.0080	0.7149 ± 0.0088	0.5855 ± 0.0105	1.07
02	01	0.5355 ± 0.0047	0.3976 ± 0.0069	0.7187 ± 0.0070	0.5888 ± 0.0099	
	02	0.5432 ± 0.0115	0.3893 ± 0.0126	0.7120 ± 0.0130	0.5897 ± 0.0200	
	all	0.5367 ± 0.0044	0.3957 ± 0.0061	0.7172 ± 0.0061	0.5889 ± 0.0089	0.48
03	01	0.5382 ± 0.0120				
	02	0.5246 ± 0.0095	0.3985 ± 0.0073	0.7301 ± 0.0112	0.6099 ± 0.0152	
	all	0.5298 ± 0.0074	0.3985 ± 0.0073	0.7301 ± 0.0112	0.6099 ± 0.0152	0.89
04	01	0.5710 ± 0.0249	0.3830 ± 0.0215	0.7241 ± 0.0291		
05	01	0.5722 ± 0.0090	0.3727 ± 0.0064	0.7261 ± 0.0085	0.6159 ± 0.0148	
	02	0.5373 ± 0.0098	0.3915 ± 0.0081	0.7249 ± 0.0102	0.5455 ± 0.0168	
	03	0.5697 ± 0.0101	0.3737 ± 0.0094	0.7239 ± 0.0117	0.5848 ± 0.0180	
	all	0.5603 ± 0.0055	0.3786 ± 0.0044	0.7252 ± 0.0057	0.5852 ± 0.0094	1.65
06	01	0.5445 ± 0.0189	0.3873 ± 0.0140	0.7102 ± 0.0179	0.5975 ± 0.0313	
	02	0.5375 ± 0.0090				
	03	0.5444 ± 0.0091	0.3898 ± 0.0070	0.7456 ± 0.0095	0.6212 ± 0.0159	
	04		0.3835 ± 0.0091	0.7275 ± 0.0120	0.5951 ± 0.0204	
	all	0.5413 ± 0.0061	0.3874 ± 0.0052	0.7345 ± 0.0069	0.6094 ± 0.0117	0.82
07	01	0.5272 ± 0.0225	0.4023 ± 0.0146	0.7087 ± 0.0195	0.5621 ± 0.0301	
08	01	0.5299 ± 0.0205	0.4241 ± 0.0169	0.7199 ± 0.0203	0.5724 ± 0.0344	
	02	0.5540 ± 0.0241	0.3793 ± 0.0204	0.7453 ± 0.0227	0.6383 ± 0.0455	
	03	0.5154 ± 0.0257	0.3743 ± 0.0235	0.7167 ± 0.0227	0.5896 ± 0.0453	
	04	0.5937 ± 0.0344	0.3711 ± 0.0288	0.7036 ± 0.0320	0.5857 ± 0.0590	
	05	0.6080 ± 0.0361	0.3817 ± 0.0294	0.7587 ± 0.0349	0.7097 ± 0.0659	
	06	0.5475 ± 0.0277	0.3829 ± 0.0215	0.7132 ± 0.0243	0.6036 ± 0.0530	
	07	0.4676 ± 0.0341	0.3885 ± 0.0296	0.6781 ± 0.0340	0.4750 ± 0.0650	
	08	0.5855 ± 0.0348	0.4378 ± 0.0257	0.7537 ± 0.0316	0.6144 ± 0.0603	
	09	0.5549 ± 0.0348	0.4109 ± 0.0282	0.7494 ± 0.0376	0.6143 ± 0.0585	
	10	0.5651 ± 0.0305	0.3919 ± 0.0242	0.7247 ± 0.0365	0.6552 ± 0.0509	
	11	0.5024 ± 0.0359	0.3579 ± 0.0302	0.7312 ± 0.0389	0.6606 ± 0.0642	
	12	0.5021 ± 0.0467	0.4121 ± 0.0361	0.6896 ± 0.0424	0.6147 ± 0.0742	
	13	0.4732 ± 0.0261	0.3457 ± 0.0273	0.7392 ± 0.0310	0.6180 ± 0.0525	
	14	0.5300 ± 0.0198	0.4251 ± 0.0165	0.7419 ± 0.0218	0.6197 ± 0.0338	
	15	0.4682 ± 0.0268	0.4031 ± 0.0213	0.7096 ± 0.0262	0.5346 ± 0.0462	
	16	0.5550 ± 0.0380	0.3896 ± 0.0289	0.7219 ± 0.0386	0.5557 ± 0.0724	
	all	0.5310 ± 0.0072	0.3970 ± 0.0060	0.7257 ± 0.0071	0.6023 ± 0.0127	1.05
09	01	0.4809 ± 0.0202				
	02	0.5439 ± 0.0067				
	03	0.5579 ± 0.0090		0.7427 ± 0.0239		
	04	0.5259 ± 0.0066	0.3797 ± 0.0064	0.7153 ± 0.0083	0.6496 ± 0.0158	
	all	0.5373 ± 0.0041	0.3797 ± 0.0064	0.7182 ± 0.0078	0.6496 ± 0.0158	2.13

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599

600 As seen in Table S1, there are stark differences in the total number of replicate analyses and
601 the typical Δ_{47} reproducibility achieved in different laboratories. As a result, final
602 uncertainties in the average Δ_{47} values of unknown samples vary considerably (Figure 5). It is
603 thus not very useful to quantify inter-laboratory reproducibility in terms of a single, overall
604 scatter of Δ_{47} values. Inter-laboratory variability should be small among laboratories with
605 small analytical uncertainties, and larger among laboratories with few replicate analyses and/
606 or poor analytical repeatability. We may still, however, assess whether inter-lab discrepancies
607 are significantly larger than expected from in-lab analytical uncertainties, i.e., whether we can
608 detect the effects of hypothetical unrecognized sources of scatter beyond known analytical
609 errors.

610

611 In order to do so, we compute the “number-of-sigma” deviation obtained by each laboratory
612 for each unknown sample, relative to that sample’s overall weighted average value. For
613 example, the sigma-deviation for sample ETH-4 and Lab01 is equal to

23

(0.5345 – 0.5376) / 0.0052 = –0.60 and that for MERCK and Lab13 is equal to
 (0.6335 – 0.5991) / 0.0135 = +2.55. If the analytical errors reported in Table 4 are reasonably
 accurate, we expect the population of sigma-deviations among all labs to be distributed as the
 canonical Gaussian distribution ($\mu = 0$; $\sigma = 1$), and we can test this prediction using
 established statistical methods such as a Kolmogorov–Smirnov test of normality (Massey,
 1951). We carried out this test for the two cases: only considering the error of sample
 replication (Fig. 6, lower row) and secondly including the normalization error, (i.e. the fully
 propagated error (Fig. 6 upper row). If we neglect uncertainties arising from standardization
 (the “allogenic” errors of Daëron et al., this volume), the sigma-deviations are no longer
 normally distributed ($p = 0.003$, upper-left panel). As shown in the lower-left panel of Figure
 6, the distribution of sigma-deviations for all labs and all samples is statistically
 indistinguishable from the expected normal distribution ($p = 0.25$) when considering fully
 propagated analytical errors. Figure 6 also illustrates that neglecting standardization errors
 does not strongly affect the normality of sigma-deviations for ETH-4 and IAEA-C1, both of
 which have δ_{47} and Δ_{47} values within the range covered by the three anchor samples. By
 contrast, sigma-deviations for unknowns with “exotic” isotopic compositions (IAEA-C2 and
 especially MERCK) are only normally distributed if standardization uncertainties are
 correctly accounted for.

Based on these tests, we conclude that the inter-lab scatter observed in the InterCarb data set
 is neither smaller nor larger than expected from the analytical uncertainties computed within
 each laboratory, as long as standardization errors are taken into account. This important
 finding implies that, at least for the time being, we can rule out any systematic inter-
 laboratory discrepancies in carbonate-standardized Δ_{47} measurements, which arguably
 constitutes an important milestone in the progress of clumped-isotope techniques.

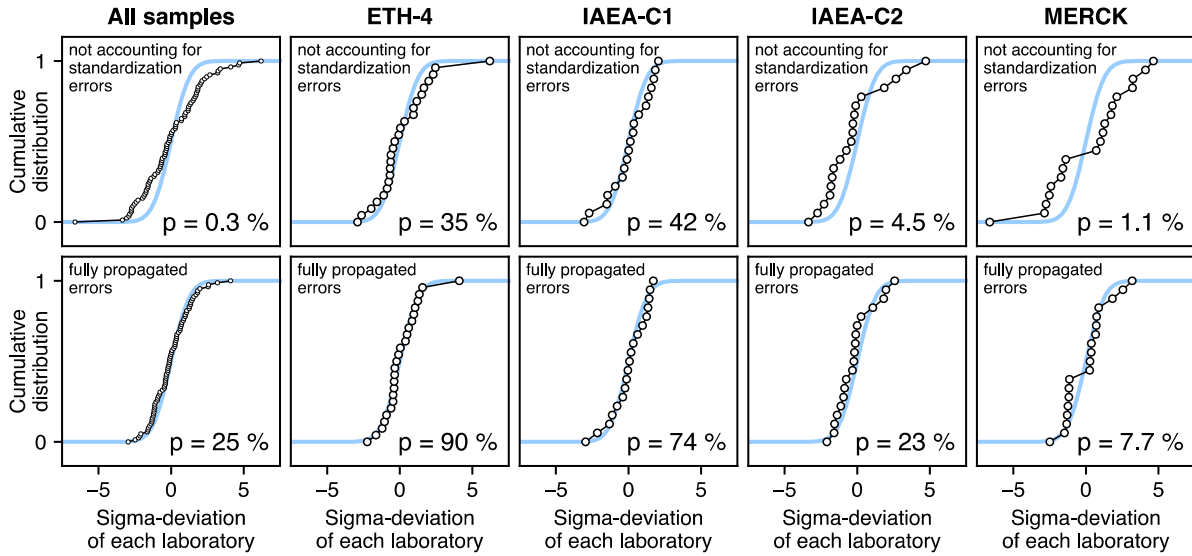


Figure 6: Kolmogorov–Smirnov tests of normality for the sigma-deviations obtained in each laboratory (circular markers), either neglecting standardization uncertainty (upper row) or considering fully propagated analytical errors (lower row). Lower-right corner Kolmogorov–Smirnov p-values correspond to the null hypothesis that the sigma-deviations are normally distributed with a mean of zero and a standard deviation of 1. Blue lines correspond to the canonical Gaussian distribution ($\mu = 0$; $\sigma = 1$).

3.3 Effects of acid reaction temperature and IRMS models

To test for the possible effect of acid temperature, a commonly discussed cause for different slopes in the published temperature calibration curves (Came et al., 2014; Fernandez et al., 2014; Swart et al., 2019), we plot the values of the laboratories reacting at 70 vs. those at 90°C (Fig. 7, Tab 7). Out of 26 mass spectrometers/extraction systems 11 react samples at 70 °C and 15 at 90 °C. Δ_{47} values averaged by acid temperature are statistically indistinguishable for all of the unknowns. Thus we can conclude that relative Δ_{47} differences between CO_2 evolved from different samples are independent of acid reaction temperature within the range of experimental conditions covered here, and for a very wide range of clumped isotope compositions spanning 0.392 (marbles) to 0.729 ‰ (carbonates formed at ambient temperatures).

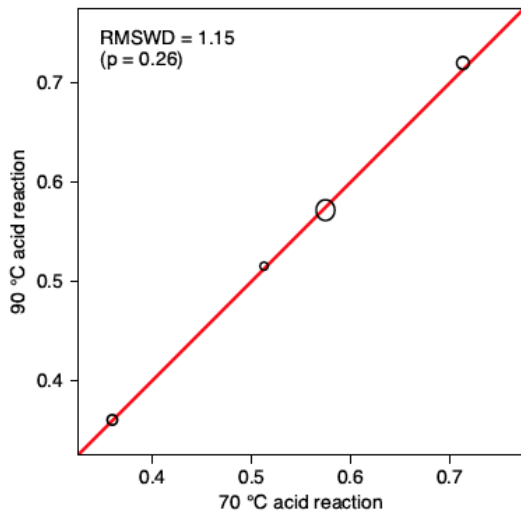


Figure 7. Results grouped by acid reaction temperature are statistically indistinguishable (see also Table 7).

	Δ_{47} (‰, $\pm 1SE$)		Difference
	70 °C	90 °C	
ETH-4	0.5380 ± 0.0016	0.5396 ± 0.0016	0.0016 ± 0.0023
IAEA-C1	0.3913 ± 0.0020	0.3921 ± 0.0019	0.0008 ± 0.0027
IAEA-C2	0.7264 ± 0.0024	0.7324 ± 0.0023	0.0060 ± 0.0033
MERCK	0.5985 ± 0.0036	0.5937 ± 0.0038	-0.0049 ± 0.0052
Avg (all samples)			0.0009 ± 0.0018

Table 7 Averages divided by acid temperature

The error weighted results separated by mass spectrometer type and design of associated preparation lines, another postulated source of differences for clumped isotope measurements (Swart et al., 2019), are shown in Figure 7 and Table 8. Out of the 25 participating laboratories, 8 groups are equipped with a Nu Perspective, 16 groups with different versions of a Thermo MAT253, and one laboratory uses an Isoprime 100. Most results are statistically indistinguishable across instruments. Only IAEA-C2 yielded a significantly (+.26 sigma) higher ($\Delta\Delta_{47}$ of +0.0111 and -0.012 vs Nu perspective and MAT253, respectively) mean Δ_{47}

value when analyzed with an Isoprime 100 versus other instrument models (but note that all of the Isoprime 100 data comes

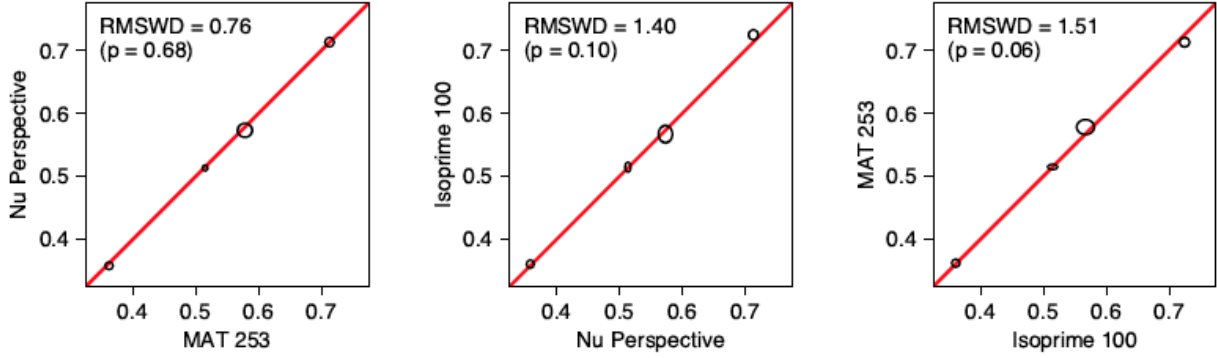


Figure 7. Effect of different mass spectrometer type and associated preparation lines for the 4 standards.

Table 8. Mass spectrometer effects, Errors-weighted by a factor of $1/\sigma^2$

	MAT 253 vs Nu Perspective	Nu Perspective Isoprime 100	Isoprime 100 vs MAT 253
ETH-4	-0.0002 ± 0.0024	-0.0013 ± 0.0036	0.0015 ± 0.0035
IAEA-C1	0.0034 ± 0.0032	-0.0025 ± 0.0035	-0.0009 ± 0.0033
IAEA-C2	-0.0002 ± 0.0038	-0.0110 ± 0.0043	0.0112 ± 0.0040
MERCK	0.0043 ± 0.0057	0.0056 ± 0.0068	-0.0099 ± 0.0066
Avg (all samples)	-0.0019 ± 0.0020	0.0023 ± 0.0024	-0.0004 ± 0.0023

from a single laboratory). Inter-instrument differences averaged over all four samples (bottom row of Table 8) remain, however, indistinguishable from zero. Thus, any potential biases introduced by the use of different mass spectrometer models and/or the design of the preparation line are

$$\Delta_{47}^{\text{old}} = u + v \delta_{47} + w^{\text{raw}} \Delta_{47}$$

$$\Delta_{47}^{\text{new}} = x + y \delta_{47} + z^{\text{raw}} \Delta_{47}$$

we can rearrange the above equations to express Δ_{47}^{new} as an affine function of $(\delta_{47}, \Delta_{47}^{\text{old}})$:

$$\Delta_{47}^{\text{new}} = a + b \delta_{47} + c \Delta_{47}^{\text{old}} \quad (\text{eq. X})$$

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699 with

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701
$$a = x - u/w$$

702
$$b = y - v/w$$

703
$$c = z/w$$

704

705 The above reasoning also applies if we choose to define δ_{47} relative to a fixed CO₂
 706 composition, e.g., relative to stochastic VPDB-CO₂ ($\delta^{13}\text{C}_{\text{VPDB}} = 0$; $\delta^{18}\text{O}_{\text{VSMOW}} \approx 41.5 \text{ ‰}$; $\Delta_{47} =$
 707 0 , $R_{47} = 4.834 \times 10^{-5}$). In that case, numerical values of the parameters (a, b, c) may be used to
 708 compute $^{\text{new}}\Delta_{47}$ for any unknown sample based only on its δ_{47} and $^{\text{old}}\Delta_{47}$ values (the former
 709 being defined relative to VPDB-CO₂ and computed assuming an acid $^{18}\text{O}/^{16}\text{O}$ fractionation
 710 factor of 1.01025).

711

712 Computing the numerical values of (a, b, c) requires knowing δ_{47} , $^{\text{old}}\Delta_{47}$, and $^{\text{new}}\Delta_{47}$ for three
 713 anchor samples. For instance, considering ETH-1, ETH-2, and ETH-3:

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715

716	Anchor	δ_{47}	$^{\text{old}}\Delta_{47}$	$^{\text{new}}\Delta_{47}$
717	ETH-1	0.010	0.258	0.2921
718	ETH-2	-28.375	0.256	0.2949
719	ETH-3	0.538	0.691	0.7008

720

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722 Writing equation X in matrix form yields:

723

$$724 \begin{pmatrix} 1 & \delta_{47}(\text{ETH } 1) & ^{\text{old}}\Delta_{47}(\text{ETH } 1) \\ 1 & \delta_{47}(\text{ETH } 2) & ^{\text{old}}\Delta_{47}(\text{ETH } 2) \\ 1 & \delta_{47}(\text{ETH } 3) & ^{\text{old}}\Delta_{47}(\text{ETH } 3) \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} ^{\text{new}}\Delta_{47}(\text{ETH } 1) \\ ^{\text{new}}\Delta_{47}(\text{ETH } 2) \\ ^{\text{new}}\Delta_{47}(\text{ETH } 3) \end{pmatrix}$$

725

726 thus:

727

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} 1 & \delta_{47}(\text{ETH } 1) & {}^{\text{old}}\Delta_{47}(\text{ETH } 1) \\ 1 & \delta_{47}(\text{ETH } 2) & {}^{\text{old}}\Delta_{47}(\text{ETH } 2) \\ 1 & \delta_{47}(\text{ETH } 3) & {}^{\text{old}}\Delta_{47}(\text{ETH } 3) \end{pmatrix}^{-1} \begin{pmatrix} {}^{\text{new}}\Delta_{47}(\text{ETH } 1) \\ {}^{\text{new}}\Delta_{47}(\text{ETH } 2) \\ {}^{\text{new}}\Delta_{47}(\text{ETH } 3) \end{pmatrix}$$

729

730

731 i.e.

732

$${}^{\text{new}}\Delta_{47} = 0.048529 - 0.000165 \times \delta_{47} + 0.944081 \times {}^{\text{old}}\Delta_{47} \quad (\text{eq. Y})$$

734

735 Equation (Y) is the unique affine function linking the ${}^{\text{old}}\Delta_{47}$ and ${}^{\text{new}}\Delta_{47}$ values of ETH-1/2/3. In
 736 this case, it is clear that the conversion from the old reference frame to the new one is not
 737 very sensitive to δ_{47} values: for unknown samples with δ_{47} values within ± 6 ‰ of ETH-1, the
 738 effect of the second term in eq. Y is less than 1 ppm, and less than 3 ppm for unknowns
 739 within ± 18 ‰ of ETH-1. In such cases, the conversion may be simplified as a simpler affine
 740 transformation of Δ_{47} , akin to a more traditional two-point normalization (e.g. VSMOW-
 741 VSLAP undetectable when using carbonate standardization. Sample sizes used for individual
 742 measurements ranged from 90-120 μg for Kiel IV preparation system, ~ 500 μg for NuCarb
 743 individual acid bath systems to a range of 3 to 12 mg for samples reacted in common acid
 744 bath custom-built extraction lines. As all small sample measurements are carried out at 70°C
 745 and large ones at 90°C, we can also conclude that there is no significant effect of sample sizes
 746 and variations in sample to acid ratios in the final results and likely a result of random
 747 uncertainty.

748

749 4. Guidelines for laboratory optimization and improving data quality in the future.

750

751 The results of this inter-laboratory exercise support the use of carbonate standardization for
 752 clumped isotope measurements. When considering all laboratories, the standard deviation of
 753 laboratory averages for the 4 unknowns range from 11 to 18 ppm for the samples requiring no
 754 to moderate extrapolation, to 25 ppm for MERCK, an extreme case of extrapolation. This
 755 spread across laboratories is still relatively large, and on the same magnitude to those
 756 obtained by HG-EG normalization if we consider what has been reported for 4 laboratories in
 757 (Dennis et al., 2011) and the scatter in the values reported by the 9 laboratories that provided
 758 data for the redetermination of the accepted values of ETH-1 to 3 in this study. However,

based on this study, we can clearly state that the large scatter is dominated by random errors, and there are strategies to improve the repeatability within each laboratory.

The scatter in the InterCarb data, (Fig. 5) is especially influenced by laboratories that show the largest errors in the individual sample reproducibility and have a significantly magnified normalization error induced by a small number of replicates of anchors. This observation underscores the necessity of increased replication and of the measurement of a sufficient number of standards to produce data of the quality that is required for meaningful interpretations. Special care needs to be taken when reconstructing small temperature changes, such as for the reconstruction of climate change and/or the study of high temperature processes where the small temperature sensitivity of clumped isotope thermometer requires high analytical precision.

We can, for example, define a target laboratory internal repeatability of 10 ppm at the 95% CI as a desirable goal with the currently available analytical systems. This arbitrary target number is within the shot-noise limits of modern IRMS instruments, and is necessary for applications in paleoclimate reconstructions, one of the main applications of clumped isotopes, as it corresponds to an uncertainty of approximately $\pm 3^{\circ}\text{C}$. If for each sample we select only the results from laboratories that have provided data with a combined error of less than 10 ppm (1SE), inter-laboratory standard deviation (1σ) becomes ≤ 10 ppm for ETH-4, IAEA-C1 and IAEA-C2 and ≤ 15 ppm for MERCK. It can be noted that this does not significantly change the average value of the reference materials.

Based on this example, it appears that with modern instrumentation from all manufacturers and with both custom built and commercially available systems used by the laboratories involved in this study, it is possible to reach this data quality and inter-laboratory consistency. The main factor to be taken into consideration is sufficient replication of both sample and standards (see Daëron, this volume, Bonifacie et al., 2017; Fernandez et al., 2017; Kocken et al., 2019). Based on this example, it appears that with modern instrumentation from all manufacturers and with both custom built and commercially available systems used by the laboratories involved in this study, it is possible to reach this data quality and inter-laboratory consistency. The main factor to be taken into consideration is sufficient replication of both sample and standards (see Daëron, this volume for a quantitative evaluation of this previously

792 suggested recommendation (Bonifacie et al., 2017; Fernandez et al., 2017; Kocken et al.,
793 2019).

794

795 With standardization with carbonates, the principle of identical treatment of samples and
796 standards (Werner & Brand, 2001b) is fulfilled, because in contrast to the use of HG-EG
797 standardization, the anchors are analytically treated exactly like the samples. With this
798 approach, we can exclude a number of factors possibly causing differences among
799 laboratories. Two important outcomes of this study are that acid reaction temperature and
800 instrument and preparation line design are not a cause for differences among laboratories
801 when standardization is based on carbonates, because we do not observe a difference between
802 reaction temperatures (at least between 70 and 90°C) and with a wide variety of custom built
803 and commercial preparation systems. Swart et al. (2019) proposed that preparation on
804 different lines can produce different slopes of a calibration curve although the samples,
805 normalized to heated and equilibrated gases, were measured on the same mass spectrometer.
806 They attributed the differences to partial equilibration of the produced CO₂ with the acid and/
807 or heated metal surfaces. The conclusion of that work was that the degree of re-equilibration
808 would depend on the design of the line, including the size of tubing, volume and quality of
809 acid, size and shape of the reaction vessel and the presence of hot metal surfaces. The lack of
810 resolvable differences observed in our dataset, however, indicates that while preparation line
811 differences may affect Δ_{47} measurements, standardization with carbonates eliminates any such
812 effects. We note that HG-EG standardization may fail to do so (Swart et al. 2019), although
813 we do not have evidence for this in the data reported here. Thus, when using carbonate
814 standardization, these factors can be ignored provided the carbonate standards cover a large
815 range in Δ_{47} . As the acid digestion conditions (e.g., reaction times), vary with the carbonate
816 mineralogy, possible effects on Δ_{47} might be mineral-specific. For this reason, it would be
817 highly desirable to produce reference materials for other minerals such as dolomite,
818 aragonite, magnesite and siderite. For dolomite, three samples were proposed by Müller et al.,
819 (2019) as possible reference materials for this common mineral and are available upon
820 request.

821

822 Standardization errors could be reduced by extending the range of bulk composition of the
823 anchor samples (e.g., as illustrated by Fig. 1 of *Daëron*, this volume), especially when
824 samples are measured that require significant extrapolation. A sample with an extreme bulk

composition like MERCK would be a useful addition as an anchor, regardless of its Δ_{47} value. While two heated standards for normalization are not strictly necessary, a “heated MERCK” anchor in combination with ETH-1 would allow verifying the PBL correction with greater confidence and with less replication than when using ETH-2 (keeping in mind that small quadratic components to PBL correction might introduce a significant bias over a δ^{47} range of 60 ‰, e.g., Fig. 7 from He et al., [2012]).

3.4 Reporting data normalized to carbonates: definition of the “InterCarb” Carbon Dioxide Equilibration scale (I-CDES)

An important consideration with this exercise, that there is a need for a community consensus on how to report clumped isotope measurements to reduce the confusion in the literature related to the different scales used in this rapidly evolving field. Currently Δ_{47} data are reported for different temperatures of phosphoric acid digestion, mostly projected to 25°C (CDES25) but also to 70 °C (CDES70) or 90 °C (CDES90) reaction. In the literature, phosphoric acid correction factors used by different research groups to convert results from 90 to 25°C reaction have varied between 0.069 ‰ (Wacker et al., 2014) to 0.092 ‰ e.g. (Bonifacie et al., 2017) thus representing a significant source of confusion and uncertainty. With the introduction of carbonate standardization, as long as standards and samples share the same mineralogy, direct standardization to accepted values of the solid phases removes the need for a phosphoric acid correction, independently of the temperature at which the samples were reacted. This eliminates different phosphoric acid correction factors as a source of uncertainty and provides a consistent framework to report Δ_{47} without uncertainties related to the reaction temperature.

For these reasons, we recommend that in the future carbonate clumped isotope data should be normalized to the three-carbonate reference materials ETH-1, ETH-2 and ETH-3 using their nominal values reported in table 1. These nominal values have been determined at 90°C and at 70 °C and were projected to 25°C using correction factors of 0.088 ‰ and 0.066 ‰ for 90 °C and 70 °C reactions, respectively (Petersen et al. 2019). To clearly distinguish these data normalization scheme from previous ones we propose the denomination I-CDES (InterCarb - Carbon Dioxide Equilibration Scale) to indicate that the data were normalized with the scheme based on the three carbonates described in this paper. This procedure is

analogous to the change from the PDB to the VPDB scale, which was accomplished by defining a consensus offset of +1.95 ‰ between the original PDB reference material and the NBS19 carbonate. This was subsequently improved by defining a second anchor point with the L-SVEC Lithium carbonate standard (Coplen et al., 2006). We note that because the carbonate values are firmly anchored to the CDES scale via HG/EG measurements in multiple laboratories, the two scales are equivalent. However, I-CDES has the advantage that it follows the principle of equal treatment of sample and standards and thus is preferred because it removes inter-laboratory uncertainties and is based on traceable solid standards.

In line with the tradition we keep a projection to 25 °C acid reaction temperature. However, we emphasize that previously published Δ_{47} data, either normalized with heated and equilibrated gases or with carbonates, cannot be directly compared to the new ones. All previous carbonate-normalized data have to be recalculated in order to fully take into account the new values of the ETH standards reported here. For HG/EG normalized data it may not be possible to establish the compatibility to the new scale, unless an adequate number of ETH standards had been measured during the same period of time in the same laboratory. In this case, as suggested by Petersen et al. (2019), it may be more reasonable to directly compare reconstructed temperatures with a laboratory-specific calibration, rather than Δ_{47} values, although the uncertainties are difficult to estimate for such comparisons.

3.5 Converting Δ_{47} values from the previous carbonate-based values to the I-CDES

Redefining the nominal Δ_{47} values for a set of three carbonate reference materials is equivalent to defining a new reference frame: there is a one-to-one relationship between the Δ_{47} values of unknown samples standardized using the old nominal values and the new ones. In this section we summarize how to directly convert Δ_{47} from an arbitrary “old” set of standard values (e.g., Bernasconi et al. 2018) ($^{\text{old}}\Delta_{47}$) to a “new” one ($^{\text{new}}\Delta_{47}$, e.g., expressed in the I-CDES) without fully reprocessing the original raw data, by computing this one-to-one relationship explicitly.

Considering that $^{\text{old}}\Delta_{47}$ and $^{\text{new}}\Delta_{47}$ are both derived from the same underlying raw data (δ_{47} , $^{\text{raw}}\Delta_{47}$) by way of affine functions of the form: standardization):

891

$$\Delta_{47}^{\text{new}} \approx 0.048529 + 0.944081 \times \Delta_{47}^{\text{old}} \quad (\text{eq. Z})$$

893

894 For instance, to convert the Δ_{47}^{old} value of ETH-4 reported by Bernasconi et al. (2018) to the
 895 I-CDES defined in this study, we only need to know that $\delta_{47}(\text{ETH-4}) = -28.8 \text{ ‰}$ and
 896 $\Delta_{47}^{\text{old}}(\text{ETH-4}) = 0.507 \pm 0.004 \text{ ‰}$. The Δ_{47}^{new} value predicted by eq. Y is then $0.5318 \pm$
 897 0.004 ‰ , to be compared with the independently constrained values reported here in Table 1
 898 ($0.5369 \pm 0.0020 \text{ ‰}$) and Fig. 5 ($0.5376 \pm 0.0011 \text{ ‰}$). This approximation can also be
 899 described as a simple two-point correction between old and new values, constrained by ETH-
 900 1 and ETH-3 (or, alternatively, by ETH-3 and the average of ETH-1 and ETH-2). This
 901 assumption is valid as long as the PBL correction has been done appropriately and has a very
 902 low residual slope.

903

904 5. Outlook for future improvements

905

906 InterCarb has shown that with carbonate standardization it is possible to reach an inter-
 907 laboratory reproducibility that is similar to what can be reached within a single laboratory.
 908 The use of carbonate standards allows for a better monitoring of the performance of the entire
 909 preparation system, including acid reaction and sample purification. Regular and systematic
 910 measurement of carbonate reference material distributed within a run or measurement
 911 interval is a prerequisite to correct for short- and long-term variations in the analytical
 912 systems. In this study, analyses were grouped in measurement intervals, and all data were
 913 processed assuming no short-term variation in the instrumentation. However, especially with
 914 "small sample approaches" relying on short (~30 min) measurements of many replicates, one
 915 can observe short-term variations (Bernasconi et al. 2018, Fig. 4). Thus a moving window
 916 correction with a variable window size may be desirable.

917

918 Replicate sample measurements should be spread in time as much as possible. With a moving
 919 window approach, this even allows the incorporation of standardization errors into observed
 920 reproducibility, if corrections of replicate measurements are based on independent standard
 921 measurements. The number and distribution of standards in a run are also important
 922 parameters that can improve reproducibility and reduce errors. This has been discussed in
 923 detail by (Kocken et al., 2019) who concluded that carbonate standards with bulk and

clumped-isotope compositions similar to those of unknowns should be analyzed with greater frequency than the other anchors, while preserving a minimal level of replication for each anchor.

For InterCarb all aliquots of IAEA C1, IAEA C2 and MERCK that were distributed stemmed from a single bottle. The results demonstrate that these carbonates were homogeneous at a 100 μg level within this aliquot, but we strongly recommend verifying that additional aliquots purchased from IAEA and MERCK are identical to the ones tested here. Finally, as there are postulated differences in phosphoric acid fractionation for different mineralogies, there should be a community effort to identify and characterize reference materials for other carbonates such as aragonite and siderite, similarly to the dolomite reference materials proposed by (Müller et al., 2019).

6. Conclusions

- This study has shown that carbonate-based standardization is robust in spite of the smaller range of isotopic composition, compared to heated/equilibrated gas compositions.
- The smaller range of clumped and bulk isotope compositions of anchor samples compared to HG-EG standardization scheme requires a sufficient number of replicate measurements of standards in order to minimize error, particularly when extrapolating to “exotic” compositions, in (δ^{47} , Δ_{47}) space.
- Standardization with ETH-1, ETH-2 and ETH-3 provides a robust framework for converting carbonate clumped isotope data to the CDES. Data standardized with this method should be reported as I-CDES.
- We propose new community accepted values for the 4 ETH standards, two samples distributed by the IAEA: C1 and C2 and for MERCK.
- We note that only the 4 ETH standards are fully tested for homogeneity over multiple batches. When a laboratory purchases samples of IAEA-C1, C2 and MERK we recommend checking the composition against the aliquots distributed through InterCarb.
- Laboratories can now carefully use the seven carbonate standards studied here to

move into the Carbon Dioxide Equilibration Scale (CDES), ensuring robust inter-lab comparability within a consistent reference frame, we term this approach the I-CDES.

- Carbonate standardization removes uncertainties due to poorly known acid fractionation factors and different preparation systems and thus reduces differences between laboratories.
- It is recommended to switch to carbonate standardization in order to follow the principle of equal treatment between samples and standards and improve inter-laboratory data comparability.
- IAEA C2 can be used as a substitute for ETH-3 to correct for scale compression, or as independent reference material to monitor the long-term reproducibility of an instrument and the correction procedures.
- The use of a reference material with an extreme bulk isotope composition such as MERCK is recommended, as the large range of compositions reduces standardization errors for samples with “exotic” bulk compositions (as previously suggested by some authors but precisely quantified in Daëron et al., this volume).
- Error should include both replication error and reference frame error in proper statistical data treatment and reporting of uncertainties.

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1166 Supplementary information

1167 Table S1 analytical session details for all mass spectrometers/Laboratories

Lab	Session	Number of analytes							Working gas		Scaling parameters			Reproducibility (ppm)			
		E1	E2	E3	E4	C1	C2	M	N _t	δ ¹³ C _{VYON}	δ ¹⁸ O _{KNOV}	a	b	c	δ ¹³ C _{VYON}	δ ¹⁸ O _{VYON}	Δ ₄₇
01	01	16	17	10	7	0	0	0	46	-3.58	25.38	0.91	(6.0 × 10 ⁻⁴)	-0.893	41	91	31.5
	02	6	5	3	1	0	0	0	11	-3.52	25.58	0.89	(-2.1 × 10 ⁻²)	-0.765	34	64	22.8
	03	150	146	65	72	19	21	22	488	-3.63	25.22	0.98	(-2.9 × 10 ⁻³)	-0.965	33	74	33.5
02	01	19	24	20	18	4	5	4	87	-36.89	8.76	0.99	(-5.6 × 10 ⁻⁴)	-0.955	17	92	13.0
	02	6	8	5	4	2	3	2	23	-36.88	8.83	0.98	(-5.5 × 10 ⁻⁴)	-0.931	25	77	16.1
03	01	37	24	17	9	0	0	0	83	-10.44	31.64	0.98	(-1.6 × 10 ⁻⁴)	-0.917	22	56	27.9
	02	29	32	12	14	17	13	11	121	-3.65	25.28	1.00	(-1.7 × 10 ⁻⁴)	-0.917	46	93	25.2
04	01	6	9	7	9	6	4	0	35	-6.57	27.18	0.97	5.0 × 10 ⁻³	-1.022	259	562	40.6
05	01	3	3	5	2	3	2	2	13	-10.43	31.31	0.95	1.7 × 10 ⁻³	-0.970	15	27	8.6
	02	13	13	13	12	10	11	8	73	-3.62	25.05	0.99	(3.8 × 10 ⁻⁴)	-0.968	15	24	20.9
	03	7	10	10	8	5	4	4	41	-3.63	25.06	0.90	1.1 × 10 ⁻³	-0.901	42	113	17.3
06	01	6	3	5	3	3	3	3	19	-2.95	25.52	0.83	(-3.8 × 10 ⁻⁴)	-0.920	22	25	21.0
	02	6	6	6	6	0	0	0	20	-2.98	24.93	0.92	(-9.9 × 10 ⁻⁴)	-0.920	14	71	13.3
	03	3	3	3	3	3	3	3	14	-3.01	24.90	0.88	(3.6 × 10 ⁻⁴)	-0.932	10	43	9.4
	04	6	6	6	6	0	6	6	30	-2.95	25.28	0.90	(-1.4 × 10 ⁻⁴)	-0.926	18	61	17.3
07	01	5	4	4	2	4	4	3	19	-11.64	35.75	0.87	3.5 × 10 ⁻³	-0.836	91	303	23.9
08	01	5	6	9	4	4	4	4	29	-2.68	25.86	0.94	(-9.2 × 10 ⁻⁴)	-0.686	13	25	28.4
	02	5	4	14	6	4	5	4	35	-2.64	25.96	0.94	(8.6 × 10 ⁻⁴)	-0.741	83	88	33.2
	03	4	4	13	4	3	5	6	32	-2.64	25.91	0.93	(-1.7 × 10 ⁻⁴)	-0.728	15	33	33.2
	04	4	5	9	5	4	4	4	28	-2.67	25.85	0.85	(1.3 × 10 ⁻⁴)	-0.629	17	51	44.5
	05	3	6	8	4	4	4	4	26	-2.70	25.79	0.87	(1.3 × 10 ⁻³)	-0.660	16	56	43.3
	06	4	4	16	6	6	6	4	39	-2.63	25.90	0.92	(3.9 × 10 ⁻⁴)	-0.693	85	54	37.8
	07	3	4	16	6	6	4	6	38	-2.66	25.90	0.96	(-1.9 × 10 ⁻³)	-0.709	19	52	48.8
	08	4	4	16	4	4	4	4	33	-2.66	25.89	1.03	(3.9 × 10 ⁻⁴)	-0.806	12	46	42.7
	09	6	6	8	4	4	4	4	27	-2.67	25.84	0.92	(1.6 × 10 ⁻⁴)	-0.722	19	25	46.7
	10	6	6	6	4	4	2	4	25	-2.63	25.91	0.97	(4.4 × 10 ⁻⁴)	-0.767	36	39	40.5
	11	6	5	8	4	4	3	4	27	-2.67	25.87	0.97	(2.5 × 10 ⁻⁴)	-0.760	11	31	49.5
	12	6	6	8	3	4	4	4	28	-2.66	25.86	1.02	(7.9 × 10 ⁻⁴)	-0.767	58	40	61.3
	13	4	6	8	6	4	4	6	31	-2.63	25.93	0.89	(1.3 × 10 ⁻³)	-0.685	19	38	41.0
	14	6	7	5	4	4	4	4	26	-2.59	25.90	0.90	(-3.6 × 10 ⁻⁴)	-0.665	76	104	27.4
	15	6	4	8	4	4	4	4	27	-2.68	25.79	0.95	(-2.0 × 10 ⁻³)	-0.685	21	52	36.0
	16	2	2	10	5	4	2	4	22	-2.63	25.89	0.96	(-5.4 × 10 ⁻⁴)	-0.765	40	39	38.8
09	01	4	4	5	6	0	0	0	15	-3.60	25.36	0.89	3.8 × 10 ⁻³	-0.856	22	74	28.3
	02	26	19	16	24	0	0	0	81	-3.36	19.94	0.90	5.2 × 10 ⁻³	-0.928	46	98	18.4
	03	21	17	13	19	0	1	0	66	-3.53	24.49	0.92	(-1.0 × 10 ⁻²)	-0.968	72	1667	22.4
	04	19	16	13	16	8	7	2	74	-3.60	25.27	0.98	(-9.6 × 10 ⁻³)	-0.994	44	56	16.0
10	01	7	7	8	2	0	11	0	30	-7.43	32.38	0.98	1.9 × 10 ⁻³	-1.077	24	38	35.1
	02	15	15	21	15	11	20	11	101	-7.41	32.42	0.93	(-2.0 × 10 ⁻⁴)	-0.877	25	44	23.0
	03	17	18	25	9	22	31	20	135	-7.43	32.37	0.96	(-2.8 × 10 ⁻⁴)	-0.900	31	92	30.0
11	01	24	24	28	28	0	0	0	100	-3.63	25.37	0.99	(-8.1 × 10 ⁻⁵)	-0.974	23	91	19.1
	02	20	18	15	15	0	0	0	64	-3.60	25.53	0.98	(3.5 × 10 ⁻⁴)	-0.996	35	270	28.9
	03	69	62	74	66	13	13	8	298	-3.02	24.99	0.91	(-2.2 × 10 ⁻⁴)	-1.065	34	89	25.0
	04	36	34	34	35	6	4	8	150	-3.01	25.06	1.00	(-3.1 × 10 ⁻⁴)	-1.068	76	210	33.7
	05	90	83	92	78	12	10	9	367	-2.76	25.78	0.98	(-5.0 × 10 ⁻⁵)	-1.088	97	317	19.3
12	01	7	7	9	5	5	6	5	37	-3.75	25.15	0.89	3.7 × 10 ⁻³	-0.904	7	41	10.2
	02	7	6	6	6	5	5	33	3	-3.74	25.18	0.87	4.6 × 10 ⁻³	-0.897	8	50	9.3
	03	8	7	12	5	5	5	40	3	-3.74	25.17	0.88	5.5 × 10 ⁻³	-0.909	9	51	9.7
	04	6	7	6	5	5	5	4	31	-3.74	25.17	0.88	5.3 × 10 ⁻³	-0.908	7	51	8.7
13	01	58	51	59	47	6	12	9	235	-10.29	33.18	0.98	(-3.7 × 10 ⁻⁴)	-0.993	176	239	26.8
14	01	4	7	10	10	0	0	0	27	-3.63	24.95	0.93	(1.3 × 10 ⁻⁴)	-0.972	42	159	19.3
	02	10	11	8	7	0	0	0	32	-3.61	25.04	0.97	(5.8 × 10 ⁻⁴)	-1.021	40	128	30.0
	03	6	4	4	3	0	0	0	13	-10.38	31.93	0.84	(-1.7 × 10 ⁻²)	-0.747	39	59	20.5
	04	2	2	2	2	0	0	0	4	-10.40	31.92	0.86	(-1.0 × 10 ⁻³)	-0.794	20	29	9.2
	05	4	4	3	4	0	0	0	11	-10.40	31.92	0.91	(-1.6 × 10 ⁻³)	-0.807	27	60	11.0
	06	5	6	6	7	0	0	0	20	-10.43	31.84	0.99	(1.3 × 10 ⁻⁴)	-0.908	39	53	22.4
	07	3	5	2	1	0	0	0	7	-10.41	31.85	0.97	(-1.7 × 10 ⁻⁴)	-0.877	51	43	12.8
	08	11	7	3	5	0	0	0	22	-10.47	31.66	0.94	(-7.8 × 10 ⁻⁴)	-0.920	61	84	23.4
	09	4	2	3	4	0	0	0	9	-10.43	31.82	0.95	(-4.8 × 10 ⁻⁴)	-0.907	55	83	12.0
	10	4	4	1	3	0	0	0	8	-10.49	31.73	0.99	(1.7 × 10 ⁻⁴)	-0.926	40	71	13.3
15	01	4	4	4	4	0	0	0	12	-32.89	36.92	0.96	(-2.5 × 10 ⁻³)	-0.887	87	70	14.6
	02	4	4	4	4	4	4	4	21	-3.72	24.98	1.02	4.6 × 10 ⁻³	-1.027	59	41	14.0
16	01	5	6	6	6	4	3	2	23	-10.49	31.56	0.99	(-4.1 × 10 ⁻³)	-0.979	47	109	10.1
17	01	3	5	2	5	6	6	3	23	-9.73	23.81	0.81	(6.3 × 10 ⁻⁴)	-0.940	65	204	29.3
18	01	168	147	172	169	20	20	25	714	-3.45	25.25	0.81	(1.5 × 10 ⁻⁴)	-0.722	65	110	37.7
	02	17	14	17	13	4	4	4	66	-3.41	25.42	0.83	(1.6 × 10 ⁻³)	-0.761	21	52	45.7
	03	11	12	13	14	2	4	2	51	-3.52	25.12	0.96	(6.0 × 10 ⁻⁴)	-0.835	23	45	40.5
19	01	4	4	5	7	5	4	4	26	-24.48	25.66	0.99	(2.0 × 10 ⁻⁴)	-0.970	69	193	23.4
	02	7	8	10	7	0	0	0	28	5.03	38.66	0.99	(2.0 × 10 ⁻⁴)	-0.962	164	416	22.5
20	01	9	6	6	6	0	0	0	23	-3.63	28.89	0.93	(-2.1 × 10 ⁻³)	-0.921	11	50	14.3
21	01	3	3	3	3	0	0	0	8	-3.62	25.20	0.90	1.0 × 10 ⁻³	-0.886	65	139	11.4
22	01	8	8	8	7	0	0	7	33	-3.54	25.37	0.98	9.9 × 10 ⁻³	-0.951	155	443	20.5
23	01	6	6	6	6	0	0	0	20	-10.77	31.02	1.00	4.4 × 10 ⁻³	-0.948	47	91	20.5
24	01	19	18	15	12	0	0	0	60	-4.40	25.32	0.98	(2.1 × 10 ⁻⁴)	-0.955	42	107	9.9
26	01	4	4	4	5	3	3	3	19	-40.04	5.51	0.89	(2.2 × 10 ⁻⁴)	-0.998	96	145	15.0
	02	6	7	6	3	3	3	3	24	-40.03	5.40	0.92	(-1.1 × 10 ⁻²)	-1.014	50	88	8.7

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