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1 **InterCarb: A community effort to improve inter-laboratory**
 2 **standardization of the carbonate clumped isotope**
 3 **thermometer using carbonate standards**

4
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61

62 **Key Points:**

- 63 • The exclusive use of carbonate reference materials is a robust method for the
 64 standardization of clumped isotope measurements
- 65 • Measurements using different acid temperatures, designs of preparation lines, and
 66 mass spectrometers are statistically indistinguishable
- 67 • We propose new consensus values for a set of 7 carbonate reference materials and
 68 updated guidelines to report clumped isotope measurements

69

70 **Abstract**

71 Increased use and improved methodology of carbonate clumped isotope thermometry has greatly
72 enhanced our ability to interrogate a suite of Earth-system processes. However, inter-laboratory
73 discrepancies in quantifying carbonate clumped isotope (Δ_{47}) measurements persist, and their
74 specific sources remain unclear. To address inter-laboratory differences, we first provide
75 consensus values from the clumped isotope community for four carbonate standards relative to
76 heated and equilibrated gases with 1,819 individual analyses from 10 laboratories. Then we
77 analyzed the four carbonate standards along with three additional standards, spanning a broad
78 range of δ^{47} and Δ_{47} compositions, for a total of 5,329 analyses on 25 individual mass
79 spectrometers from 22 different laboratories. Treating three of the materials as known standards
80 and the other four as unknowns, we find that the use of carbonate reference materials is a robust
81 method for standardization that yields inter-laboratory discrepancies entirely consistent with in-
82 laboratory analytical uncertainties. Carbonate reference materials, along with measurement and
83 data processing practices described herein, provide the carbonate clumped isotope community
84 with a robust approach to achieve inter-laboratory agreement as we continue to use and improve
85 this powerful geochemical tool. We propose that carbonate clumped isotope data normalized to
86 the carbonate reference materials described in this publication should be reported as Δ_{47} (I-
87 CDES) for Intercarb-Carbon Dioxide Equilibrium Scale.

88

89 1 Introduction

90 Carbonate clumped isotope (Δ_{47}) thermometry is the most developed branch of the
91 rapidly evolving field of clumped isotope geochemistry. Given the broad range of applications in
92 Earth Sciences (e.g. Affek & Eiler, 2006; Eagle et al., 2010; Ferry et al., 2011; Ghosh, Adkins, et
93 al., 2006; Ghosh, Garzzone, et al., 2006; Grauel et al., 2013; Guo & Eiler, 2007; Huntington et
94 al., 2011; Passey & Henkes, 2012, Dale et al, 2014, Mangenot et al., 2018, Veillard et al, 2019)
95 and the improvement of analytical methods including automation (Bernasconi et al., 2013, 2018;
96 Defliese & Lohmann, 2015; Dennis et al., 2011; Fiebig et al., 2019; Ghosh, Adkins, et al., 2006;
97 He et al., 2012; Hu et al., 2014; Huntington et al., 2009; Meckler et al., 2014; Müller, Fernandez,
98 et al., 2017; Passey et al., 2010; Petersen et al., 2019; Petersen et al., 2016; Schmid &
99 Bernasconi, 2010, Adlan et al, 2020), the last 5-10 years have seen an increasing number of
100 laboratories implementing this technique. The great potential of this thermometric method can
101 only be fully exploited if the precision and accuracy of the data is sufficient to resolve
102 differences of a few degrees in formation temperatures. In addition, like for any other
103 geochemical method, widely available reference materials that match the sample matrices are
104 necessary so that data can be robustly compared across laboratories (Meier-Augenstein &
105 Schimmelmann, 2019). Currently the situation in the field of carbonate clumped isotope
106 geochemistry is far from satisfactory. Published values for the ETH reference materials, the only
107 carbonates that have been recently measured in many different laboratories worldwide, show a
108 range of values for the same sample of up to 0.053 ‰ (see Bernasconi et al. 2018, Thaler et al.
109 2020 for recent comparisons). This clearly calls for better standardization procedures to improve
110 laboratory comparability.

111
112 The data normalization scheme currently used in clumped isotope geochemistry of carbonates in
113 most laboratories is based on the comparison of the composition of the CO_2 liberated from
114 carbonates by reaction with phosphoric acid with that of a set of CO_2 gases with different bulk
115 and clumped isotope compositions (Dennis et al., 2011). These gases are prepared either by
116 heating CO_2 at 1000 °C (heated gases; HG) or by CO_2 equilibration with water at low
117 temperatures (equilibrated gases; EG, at e.g. 25 °C, 50 °C). By comparing the measured
118 compositions with the theoretical predictions of the equilibrium thermodynamic abundance of
119 multiply substituted isotopologues in heated and equilibrated gases (Wang et al. 2004 and

120 updates in Petersen et al. 2019), the measurements are standardized to the scale that was named
121 the “absolute reference frame” (ARF) by Dennis et al., (2011). In more recent publications the
122 ARF is often referred to as the “Carbon Dioxide Equilibration Scale” (CDES), a terminology
123 introduced by Passey and Henkes (2012). This approach was designed to allow different
124 laboratories to link their measurements to an internationally recognized scale firmly anchored to
125 theory using relatively easy and established laboratory protocols to produce CO₂ standard gases
126 of known composition. Early comparisons of Δ_{47} CDES values for carbonates run in different
127 laboratories and normalized with HG/EG normalization were promising (Dennis et al., 2011).
128 While Bonifacie et al. (2017) reported similar Δ_{47} CDES values for nine dolomite samples covering
129 a range of almost 0.4‰ measured at both at Caltech and IPGP laboratories with HG/EG
130 normalization, Spooner et al. (2016) found that carbonate standardization improved agreement
131 between data they obtained on samples ran both at Caltech and WHOI laboratories, compared to
132 when they were using HG/EG normalization. Such recurrent cases of poor inter-laboratory
133 reproducibility (see also Bernasconi et al., 2018 and Thaler et al., 2020) suggest that there is still
134 unexplained differences in the results among laboratories (see Petersen et al. (2019) for a recent
135 review).

136
137 Apart from preservation problems such as diagenesis and solid-state reordering, two known
138 issues still limiting the reliability of this method to yield accurate temperature reconstructions
139 are: [1] the lack of internationally recognized carbonate reference materials for a precise inter-
140 laboratory calibration, and [2] that published Δ_{47} -temperature calibrations produced in different
141 laboratories have differed in both temperature dependence (slope), and absolute values
142 (intercept). Possible reasons for the differences in slope and intercepts of the Δ_{47} temperature
143 dependence have been widely discussed in the literature (e.g. Kluge et al, 2015; Bonifacie et al.,
144 2017; Daëron et al., 2016; Fernandez et al., 2017; Katz et al., 2017; Kelson et al., 2017; Petersen
145 et al., 2019; Schauer et al., 2016). Discrepancies have been attributed to analytical artefacts such
146 as CO₂-acid re-equilibration at different acid digestion temperatures (see Wacker et al. 2013;
147 Swart et al., 2019, for a recent discussion). Other factors proposed to influence the calculated
148 slope of the calibrations are the limitations of the datasets used in the individual studies, in
149 particular in terms of the number of samples and replicates and of the temperature range covered
150 by the available samples (Bonifacie et al., 2017; Fernandez et al., 2017). However, the

151 discrepancies in the intercept of the calibrations, for example between Kelson et al. (2017) and
152 Peral et al. (2018), and a generally poor laboratory comparability remain problems that should be
153 mitigated by using a more robust standardization method.

154
155 Petersen et al. (2019), in a recent effort to resolve differences in calibrations, compiled raw data
156 of a number of published temperature calibrations and recalculated them all in a consistent way
157 using the revised “IUPAC” correction parameters to correct for the ^{17}O abundance (Daëron et al.,
158 2016; Schauer et al., 2016). The goal was to test whether data processing differences and/or the
159 use of consistent but incorrect ^{17}O - correction parameters in the calculations were the root causes
160 of inconsistencies. The result of this study was that differences among calibrations were reduced
161 but not eliminated by the recalculation, implying that other factors must be responsible for the
162 remaining discrepancies. These differences have pushed many laboratories to use laboratory-
163 specific calibrations performed with the same analytical approach, as they at least partially take
164 into consideration possible procedural differences (Petersen et al., 2019). However, if a
165 laboratory changes analytical procedures or has not generated a robust in-house calibration, this
166 approach is problematic. Achieving an inter-laboratory reproducibility at the level of accuracy
167 necessary for meaningful interpretations of the observed variations is a requirement for Δ_{47}
168 thermometry to reach its potential as a mature analytical method with broad acceptance and
169 quantitative usefulness.

170
171 While the definition of the CDES was a major milestone (Dennis et al., 2011), a known problem
172 with this approach is that while the CO_2 standard gases equilibrated at known temperature (HG
173 or EG) can be confidently used for correction of mass spectrometric fractionations/nonlinearities
174 and for effects of the purification procedures, they cannot account for the effects of the
175 phosphoric acid reaction on the composition of the produced CO_2 . Among the factors responsible
176 for discrepant calibrations and laboratory comparability, two important ones cannot be tested
177 with a gas-based standardization: (1) the absolute value and temperature dependence of the
178 phosphoric acid fractionation factor (see Petersen et al., 2019 for a recent compilation) and (2)
179 possible CO_2 equilibration effects during acid digestion of the sample. Swart et al. (2019)
180 presented evidence that equilibration of CO_2 with water or hot metal surfaces during phosphoric
181 acid reaction and transfer of the CO_2 to the mass spectrometer could be a factor leading to the

182 alteration of the apparent temperature dependence of clumped isotopes in carbonates and on the
183 absolute value of calculated Δ_{47} . As many laboratories use custom built extraction lines with
184 different designs and volumes of tubing and of acid vessels, these factors are impossible to
185 precisely quantify for each laboratory and may further contribute to inter-laboratory
186 discrepancies.

187
188 We propose that these issues can be circumvented if carbonates, which undergo the same acid
189 digestion as the samples, are used for normalization instead of or in addition to gases, consistent
190 with the principle of identical treatment of sample and standards (Carter & Fry, 2013; Werner &
191 Brand, 2001a). In addition, normalizing results to accepted carbonate reference material values,
192 as is commonly done with conventional carbon and oxygen isotope analysis in carbonates,
193 removes the requirement to precisely quantify acid fractionation factors at different temperatures
194 (Bernasconi et al., 2018).

195 A carbonate standardization approach was introduced by Schmid & Bernasconi (2010) and
196 improved by Meckler et al. (2014), with the following benefits: (1) the use of carbonates can
197 more easily be fully automated, eliminating time-consuming and possibly error-prone manual
198 preparation of CO₂ standard gases (equilibrated at known temperature) by individual users on
199 separate extraction lines; (2) in some automated systems designed for small sample sizes, the
200 gases had to be measured through a different capillary than the carbonates with potential biases
201 that would go unrecognized; and (3) in those systems the equilibrated and heated gases are
202 measured at constant beam intensity, whereas the samples are measured with decreasing beams.
203 These features argue in favor of carbonate standardization *a priori*, but it remains critical to
204 assess *a posteriori* whether the results of this approach are as robust and accurate as expected,
205 and whether they significantly improve the inter-laboratory reproducibility of Δ_{47} measurements.
206 Discussions at the Sixth International Clumped Isotope Workshop (Paris, 2017) led to the present
207 inter-laboratory comparison exercise (InterCarb) to evaluate the benefits and drawbacks of a
208 carbonate-based standardization approach as an alternative to the use of gas standards.

209
210 The primary goal of this study was to test whether the exclusive use of carbonate reference
211 materials can minimize inter-laboratory discrepancies and provide an alternative to the
212 measurement of heated and equilibrated gases for the entire community. This is particularly

213 important because of the increasing number of laboratories using commercial small-sample
 214 automated devices which cannot easily be standardized using the HG-EG approach. The
 215 InterCarb exercise also provides an opportunity to define the best community-derived absolute
 216 Δ_{47} values for the ETH standards of Meckler et al. (2014). Although these standards are already
 217 used in many laboratories, their current nominal Δ_{47} values are based on measurements from the
 218 ETH laboratory only. The InterCarb exercise can similarly establish community accepted values
 219 for other common carbonate reference materials, some of which have been in use for several
 220 years, in order to provide the community with a self-consistent set of carbonate reference
 221 materials with a broad range of bulk and clumped isotope compositions.

222

223 **1.1. Nomenclature and data processing**

224

225 Clumped isotope compositions are reported as an excess abundance of the CO₂ isotopologue of
 226 cardinal mass 47 (dominantly the isotopologues ¹³C¹⁸O¹⁶O) compared to a stochastic distribution
 227 according to the formula:

228

$$R_{47} = R^{47} / R^{47*} - 1$$

229

230 where R^{47} is the abundance of the minor isotopologue with mass 47 relative to the most abundant
 231 isotopologue with mass 44. The stochastic ratio R^{47*} is calculated using the measured abundance
 232 of ¹³C and ¹⁸O in the sample (Affek & Eiler, 2006). According to the IUPAC guidelines the
 233 formula does not include the factor 1000 (Coplen, 2011). Also we omit here the classically
 234 included terms involving R_{45*} and R_{46*} , which are assumed to be zero by definition when
 235 computing $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, and in practice never exceed ± 0.00002 ‰ in our calculations (Daeron
 236 et al. 2016). The measured abundance of isotopologues with m/z 47 in the sample with respect to
 237 the working gas (WG) in the mass spectrometer is reported in the traditional delta notation as:

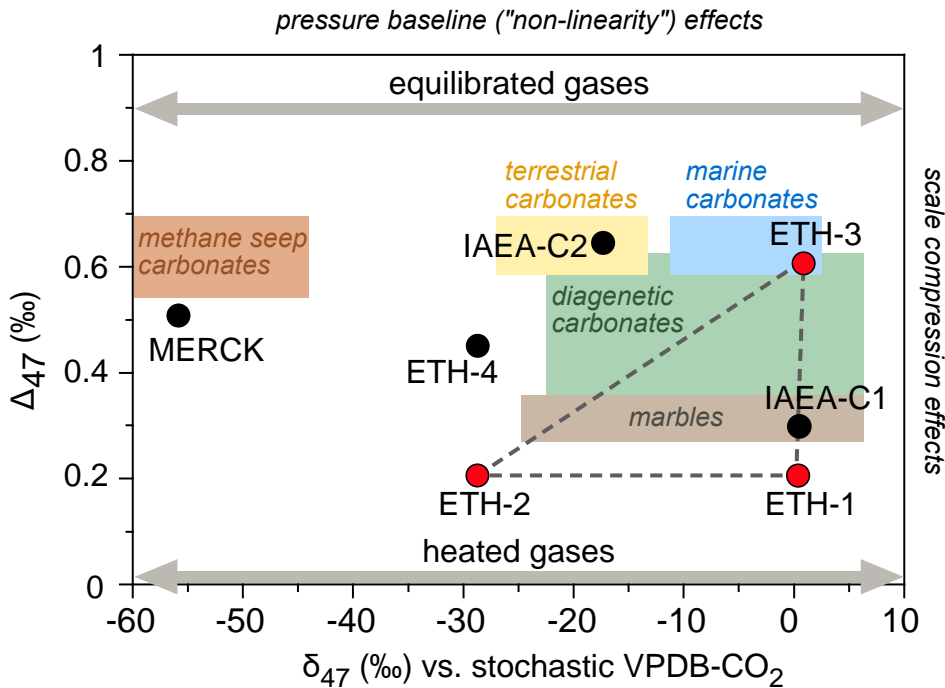
238

$$\delta^{47} = R^{47} / R_{\text{WG}}^{47} - 1$$

239

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

243
244 The CO₂ gas-based standardization scheme for clumped isotope thermometry in carbonates relies
245 on a set of CO₂ standard gases with different bulk compositions (δ^{47}), preferably chosen by the
246 user to encompass the δ^{47} values of unknown samples, that have been (1) heated at 1000°C to
247 reach a near-stochastic distribution of all isotopologues, and (2) equilibrated with water at low
248 temperatures to reach equilibrium enrichments in the mass-47 isotopologues (Dennis et al.,
249 2011). The heated gases, having a stochastic distribution of the heavy isotopes among all
250 isotopologues, define the zero point of the CDES scale ($\Delta_{47} = 0.0266$ ‰) and the equilibrated
251 gases define a high point (e.g., at 25 °C $\Delta_{47} = 0.9196$ ‰). The theoretical values linking
252 measurements to theory were calculated by Wang et al. (2004), and revised by Petersen et al.
253 (2019). A wide range in δ^{47} values of gases used for normalization is generally chosen to allow
254 for accurate correction for an apparent dependence of Δ_{47} on δ^{47} which is caused by inaccurate
255 pressure-dependent background corrections on the m/z 47 collector observed on many
256 instruments (Bernasconi et al., 2013; He et al., 2012). The large range in Δ_{47} (i.e., 25 °C, 1000
257 °C), on the other hand, is necessary to correct for scale compression caused by processes of
258 scrambling and molecule recombination in the source of the mass spectrometer or elsewhere in
259 the sample preparation, transfer lines and/or the capillaries (Dennis et al., 2011, Swart et al.
260 2019). With properly chosen CO₂ standard gases with widely varying δ^{47} values it is possible to
261 cover the entire range of natural carbonate compositions, avoiding extrapolations in the δ^{47} vs.
262 Δ_{47} compositional space (Fig. 1). Note that with measurement errors (typically not better than
263 0.010 ‰) being relatively large compared to the natural compositional range (less than 0.5 ‰;
264 Fig. 1), the large (0.9 ‰) difference in Δ_{47} of the CO₂ standard gases minimizes errors introduced
265 by uncertainties resulting from the measurement of HG and EG.
266



267

268

269 **Figure 1.** δ^{47} vs. Δ_{47} values of carbonate standards (Δ_{47} on the I-CDES scale proposed here) and heated
 270 and equilibrated gases in comparison to the compositional ranges of typical natural carbonates. The
 271 observed range in measured clumped isotope compositions in natural carbonates can be completely
 272 bracketed by heated and equilibrated CO_2 standard gases from which δ^{47} values have been chosen by the
 273 user. δ^{47} values for the anchor samples used in InterCarb (red) and the unknowns (black) are reported for
 274 a theoretical working gas with stochastic isotope distribution, derived from VPDB. Actual δ^{47} values will
 275 vary by laboratory depending on the composition of the working gas. Note the smaller achievable range
 276 in both δ^{47} and Δ_{47} values when using carbonate standards compared to heated and equilibrated gases, and
 277 the large extrapolation necessary for the determination of the composition for MERCK. Heated and
 278 equilibrated CO_2 standard gases have a larger Δ_{47} range, allowing for more robust stretching calculations
 279 with identical numbers of standard:sample analyses.

280

281 Meckler et al. (2014) attempted to achieve a similar framework as the CO_2 gas-based
 282 standardization but with carbonate standards. They described four carbonates that were
 283 developed at ETH Zürich to serve as replacements for HG-EGs and demonstrated that good
 284 long- and short-term reproducibility can be achieved using only carbonates for data correction.
 285 Bernasconi et. al (2018) discussed in detail these standards and postulated, based on a limited
 286 inter-laboratory dataset, that carbonate standardization should generally improve inter-laboratory

287 data comparability. This claim seems arguably strengthened by the results of Meinicke et al.
 288 (2020), Peral et al. (2018), Piasecki et al. (2019), Kele et al. (2015) as recalculated by Bernasconi
 289 et al. 2018), and Jautzy et al., (2020). The first three studies produced independent foraminifera-
 290 based the fourth a travertine and the fifth a synthetic carbonate-based Δ_{47} -temperature calibration
 291 anchored to the same set of carbonate standards, yielding statistically indistinguishable slopes
 292 and intercepts despite the use of independent sample sets and in the case of Peral et al. (2018), a
 293 different analytical system. In addition, a reanalysis of samples from five previous calibrations
 294 by Anderson et al. (2020) using carbonate standardization revealed no significant differences in
 295 temperature dependence of Δ_{47} between the different sample sets.

296
 297 A possible limitation of carbonate standardization is that available carbonates have a smaller
 298 range in δ^{47} and, perhaps more importantly, a smaller range in Δ_{47} values than what is achievable
 299 with heated and equilibrated gases. In some specific cases, standardization procedures may
 300 require extrapolation to compositions that are not within the δ^{47} - Δ_{47} space created by carbonate
 301 standards (Fig. 1). In addition, the range of Δ_{47} values for carbonates is only on the order of 0.5
 302 ‰ between 0 and 1000 °C. The smaller range in Δ_{47} compared to HG-EG requires higher
 303 precision and thus high standard replication and a ~50:50 standard to sample replicate ratio to
 304 keep normalization errors small (see Daëron (this volume) and Kocken et al., 2019 for details).

305

306 **1.2. InterCarb goals and design:**

307
 308 InterCarb was designed with the aim to carefully evaluate the potential of carbonates to serve as
 309 a standardization scheme that improves inter-laboratory agreement for ‘unknown’ carbonates
 310 both inside and outside of the δ^{47} - Δ_{47} space defined by the anchor samples (Fig. 2). The main
 311 questions posed are:

- 312
- 313 1. Is it possible to produce consistent carbonate clumped isotope measurements across
 314 laboratories using carbonate reference materials exclusively? In other words, does the
 315 observed inter-laboratory scatter in Δ_{47} values match that expected from intra-laboratory
 316 analytical precision?

- 317 2. How well does the carbonate standardization approach perform when extrapolating
318 beyond the δ^{47} - Δ_{47} compositional space sampled by a set of carbonate reference
319 materials?
- 320 3. Do carbonate reference materials fully correct effects arising from different reaction
321 temperatures, sample preparation protocols, and analytical equipment?
- 322 4. Can we define a self-consistent set of widely available reference materials with
323 community-agreed compositions accurately anchored to the CDES scale?
- 324 5. Does the use of carbonate reference materials for standardization improve the inter-
325 laboratory reproducibility compared to HG-EG standardization?

326

327 **1.3 Approach:**

328

329 Seven carbonate standards with a large range of δ^{47} and Δ_{47} values (Fig. 1) were distributed
330 among participating laboratories and analyzed, treating three carbonates as “anchors” (whose
331 Δ_{47} values are assigned *a priori*) and the remaining four as “unknowns” (whose Δ_{47} values are
332 unknown, to be determined by comparison with the anchors). Due to their relatively widespread
333 use in different laboratories, the three reference materials ETH-1, ETH-2 and ETH-3 (Meckler et
334 al. 2014; Bernasconi et al. 2018) were chosen as anchors. They are still available today in
335 relatively large quantities (>600 g), have been in use at ETH since 2013 and in many other
336 laboratories for several years. Importantly, they have been thoroughly tested for homogeneity
337 based on thousands of measurements in 80 to 150 μ g aliquot sizes in different laboratories and no
338 changes in composition have been noticed at ETH in the 7 years they have been in use.

339

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

344

345 **2 Materials and Methods**

346 **2.1. Sample description**

347

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

351

352 IAEA-C1 (marble from Carrara, Italy) is distributed by the International Atomic Energy Agency
353 (IAEA) as a mechanically crushed and milled product with grains ranging from 1.6 to 5 mm. All
354 50 g provided were ground and thoroughly homogenized in a ball mill at ETH Zürich to a grain
355 size of less than 100 µm and transferred in 0.5 g aliquots to plastic vials for distribution.

356

357 IAEA-C2 is a freshwater travertine from Bavaria distributed by IAEA as a powder which was
358 treated identically to IAEA-C1.

359

360 ETH-4 is a commercially available synthetic calcite (Riedel-De Haën; calcium carbonate Puriss.
361 p.a.; Lot No. 30800) with intermediate formation temperature and the same bulk isotope
362 composition as ETH-2 (see Bernasconi 2018 for details).

363

364 MERCK (Catalog No. 1.02059.0050; lot no. B1164559 515) is an ultra-pure, commercially
365 available synthetic calcite and was chosen for its very low $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, of
366 approximately -41.7 ‰ and -15.5 ‰ (VPDB), respectively. This sample represents an extreme
367 case of extrapolation from the $\delta^{47}\text{-}\Delta_{47}$ space defined by the anchor materials (Fig. 2).

368

369 **2.2 Instrumentation:**

370

371 The reported data were produced with a variety of preparation systems including custom built
372 (13 laboratories) and commercial systems (11 laboratories; Protium MS IBEX, ThermoFisher
373 Scientific Kiel IV device and Nu Instruments Nucarb). Reaction temperatures were generally 90

374 °C for “large-sample” custom preparation systems and 70 °C for the Kiel and the NuCarb. Four
375 mass spectrometer types were used: Thermo Fisher Scientific MAT253 and 253Plus, Nu
376 Instruments Perspective, and Elementar Isoprime 100. All participants contributed results they
377 considered to be of a “publication-grade” quality, based on their existing quality-control
378 procedures.

379 **2.3 Clumped isotope compositions of the ETH anchor materials.**

380
381 The clumped isotope compositions of the four ETH reference materials relative to the CO₂
382 reference frame CDES were first reassessed based on new data provided by 9 laboratories that
383 also provided HG and EG data measured during the same sessions as the ETH reference
384 materials. Data processing was performed with the same Python script that was used to process
385 the carbonate data in order to avoid any differences in data processing (see section 2.4).

386
387 Although, strictly speaking, ¹³C-¹⁸O clumping in carbonate represents a mass-63 anomaly, the
388 clumped isotope composition of carbonate minerals is reported as Δ_{47} i.e. as the mass-47 excess
389 in the CO₂ produced by acid digestion of these minerals, including the respective temperature-
390 dependent isotopic fractionation. As initially all reactions were carried out at 25°C (Ghosh et al.
391 2006), the Δ_{47} values have traditionally been reported for a 25°C acid temperature. With the
392 advent of automated extraction lines, reaction temperatures have been raised to 70 or 90°C. To
393 account for the temperature dependence of the acid fractionation factor (Guo et al., 2009,
394 Petersen et al. 2019) and to project these results back to the original 25°C acid reaction, various
395 acid temperature correction values have been reported over time, based on experimental
396 observations and/or theoretical predictions. Given that here seven out of ten laboratories reacted
397 carbonates at 90 °C, two at 70 °C, and only one at 25 °C, our redetermination of the Δ_{47} values
398 of ETH-1/2/3/4 relative to the CDES projected to 25°C would substantially rely on the accuracy
399 of these acid temperature corrections (which typically range between 60–90 ppm). Here we
400 report instead the Δ_{47} values of CO₂ produced by reacting ETH-1/2/3/4 at 90 °C. With this
401 choice the numerical effect of poorly known acid corrections is minimized, because the data
402 from 70 °C and 25 °C reactions have relatively little influence on the final, error-weighted
403 average Δ_{47} values (cf statistical weights in Fig. 2). We thus propose to break with tradition and

404 define the nominal Δ_{47} values of the anchor standards as those of CO₂ produced at 90 °C,
405 providing the most robust relationship to the CDES.

406 **2.4 Data processing, correction and error assessment.**

407
408 It should be stressed that the InterCarb experiment, by design, is not intended to grade the
409 analytical “performance” of individual laboratories. Each participating laboratory (or mass
410 spectrometer, in the case of laboratories with several instruments) was thus randomly assigned an
411 anonymous identifying number. Within each laboratory, analyses were grouped in different
412 analytical sessions defined by the participants themselves. An analytical session is generally
413 defined by a time in which the behavior of the analytical system (preparation system, source
414 tuning, backgrounds, isotope scrambling in the source) is considered to be similar. The database
415 record of each analysis consists of a laboratory identifier; a session identifier; an analysis
416 identifier; the name of the analyzed sample; the mass spectrometer model; the acid reaction
417 temperature; the mass of reagent carbonate; and background-corrected δ^{45} , δ^{46} and δ^{47} values.

418
419 The only instrumental corrections to the raw data applied independently by each participating
420 laboratory were background corrections (“Pressure Baseline Correction” or PBL) to the ion
421 currents/voltages (Bernasconi et al., 2013; He et al., 2012). The PBL is strongly dependent on
422 instrument design (it is not observed in some instruments) and configuration, and varies
423 temporally depending on many factors. This correction, therefore, can only be carried out by
424 each participating laboratory according to its own established procedures and monitoring.

425
426 To avoid artefacts arising from different calculation/standardization procedures, rounding errors,
427 and ¹⁷O correction parameters, raw data from all laboratories were processed by a single Python
428 script (<http://doi.org/10.5281/zenodo.4314449>) based on data reduction, standardization and
429 error propagation methods described in detail in the companion paper (Daëron, this volume).
430 Here we briefly summarize these calculations.

431
432

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

440

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

442

$$R_{47}^{\text{abs}} = R^{47} / R^{47*} - 1$$

443

444 Where R^{47} is the measured ratio and R^{47*} the calculated stochastic ratio of mass 47 over mass 44
 445 of CO_2 , assuming perfectly linear IRMS measurements and a stochastic working gas. Values are
 446 then normalized to “absolute” Δ_{47} values (noted R_{47}^{abs} in the equation below, and simply Δ_{47}
 447 thereafter) using session-specific relationships of the form:

448

$$R_{47}^{\text{raw}} = a R_{47}^{\text{abs}} + b \delta^{47} + c$$

449

450 For each session, the best-fit standardization parameters (a, b, c) are computed from an
 451 unweighted least-squares regression, treating R_{47}^{raw} as the response variable, only considering the
 452 three anchor samples ETH-1, ETH-2, and ETH-3. Note the advantage of this form over that in
 453 Dennis et al. 2011 is the ability to have three standards with distinct Δ_{47} values whilst being able
 454 to solve for b (compositional nonlinearity) (Daëron et al. 2016). Absolute Δ_{47} values are then
 455 computed for all replicates within that session. Standardization parameters for all sessions are
 456 listed in Table S1 (supplementary information).

457

458 In figure labels and in tables, measurement uncertainties are reported as 1SE of the mean,
 459 considering fully-propagated errors taking into account reference frame corrections. In Figures 2
 460 and 4, different types of error bars reflect either these full analytical errors, or those only
 461 considering uncertainties in the analyses of a given sample. In both cases, the analytical error
 462 assigned to each individual raw Δ_{47} analysis is equal to the pooled “external” repeatability of raw

463 Δ_{47} measurements for all samples (anchors and unknowns) within each session. This treatment of
464 error is a new approach that more fully accounts for error in both the sample measurement and
465 reference frame.

466 **3 Results and Discussion**

467 **3.1 Redetermination of nominal Δ_{47} values for the ETH standards relative to heated and** 468 **equilibrated CO₂ gases**

469 The weighted averages of the 4 standards (projected to 90 °C for the reactions at 25 and 70°C
470 using the acid temperature correction suggested by Petersen et al. 2019), comprising 619
471 analyses of the carbonate standards and 828 heated and equilibrated gases from 9 different
472 laboratories, are reported in Table 1 and Fig 4. The large number of analyses and the appropriate
473 consideration of the errors on the anchors (CO₂ gas analyses) distinguishes this effort from
474 previous work, and allows a robust redetermination of the accepted values of the ETH reference
475 materials with 1SE uncertainties of 2 ppm or less.

476

477

Laboratory	all	A	B	C	D	E	F	G	H	I	J	
N of sessions	34	4	4	11	7	1	2	1	1	1	2	
N of H/E CO2	946	44	193	257	85	47	21	38	192	13	56	
ETH-1	N of analyses	232	34	14	5	54	4	4	19	58	8	32
	Δ_{47} (90 °C acid)	0.2052	0.2016	0.1926	0.2108	0.1940	0.1601	0.2013	0.2143	0.1932	0.2183	0.2152
	\pm 1SE	0.0016	0.0046	0.0058	0.0069	0.0042	0.0245	0.0107	0.0032	0.0045	0.0109	0.0036
	Statistical weight		0.118	0.074	0.053	0.146	0.004	0.022	0.241	0.124	0.021	0.197
ETH-2	N of analyses	215	23	13	11	51	4	4	18	51	8	32
	Δ_{47} (90 °C acid)	0.2085	0.2077	0.1840	0.2225	0.1978	0.1374	0.1650	0.2141	0.1968	0.2172	0.2170
	\pm 1SE	0.0015	0.0047	0.0070	0.0046	0.0050	0.0233	0.0101	0.0029	0.0043	0.0154	0.0033
	Statistical weight		0.105	0.047	0.108	0.092	0.004	0.023	0.272	0.125	0.010	0.213
ETH-3	N of analyses	264	55	15	20	54	4	5	15	59	8	29
	Δ_{47} (90 °C acid)	0.6132	0.6156	0.5975	0.6169	0.6102	0.5950	0.6143	0.6159	0.6094	0.6428	0.6124
	\pm 1SE	0.0014	0.0037	0.0056	0.0033	0.0038	0.0237	0.0099	0.0033	0.0042	0.0103	0.0035
	Statistical weight		0.140	0.062	0.175	0.134	0.003	0.020	0.179	0.110	0.018	0.158
ETH-4	N of analyses	162	10	12	5	55	4	4	12	47	7	6
	Δ_{47} (90 °C acid)	0.4505	0.4438	0.4230	0.4624	0.4506	0.4230	0.4454	0.4560	0.4414	0.4831	0.4646
	\pm 1SE	0.0018	0.0058	0.0071	0.0068	0.0049	0.0226	0.0095	0.0032	0.0042	0.0161	0.0057
	Statistical weight		0.093	0.064	0.068	0.133	0.006	0.035	0.314	0.177	0.012	0.097

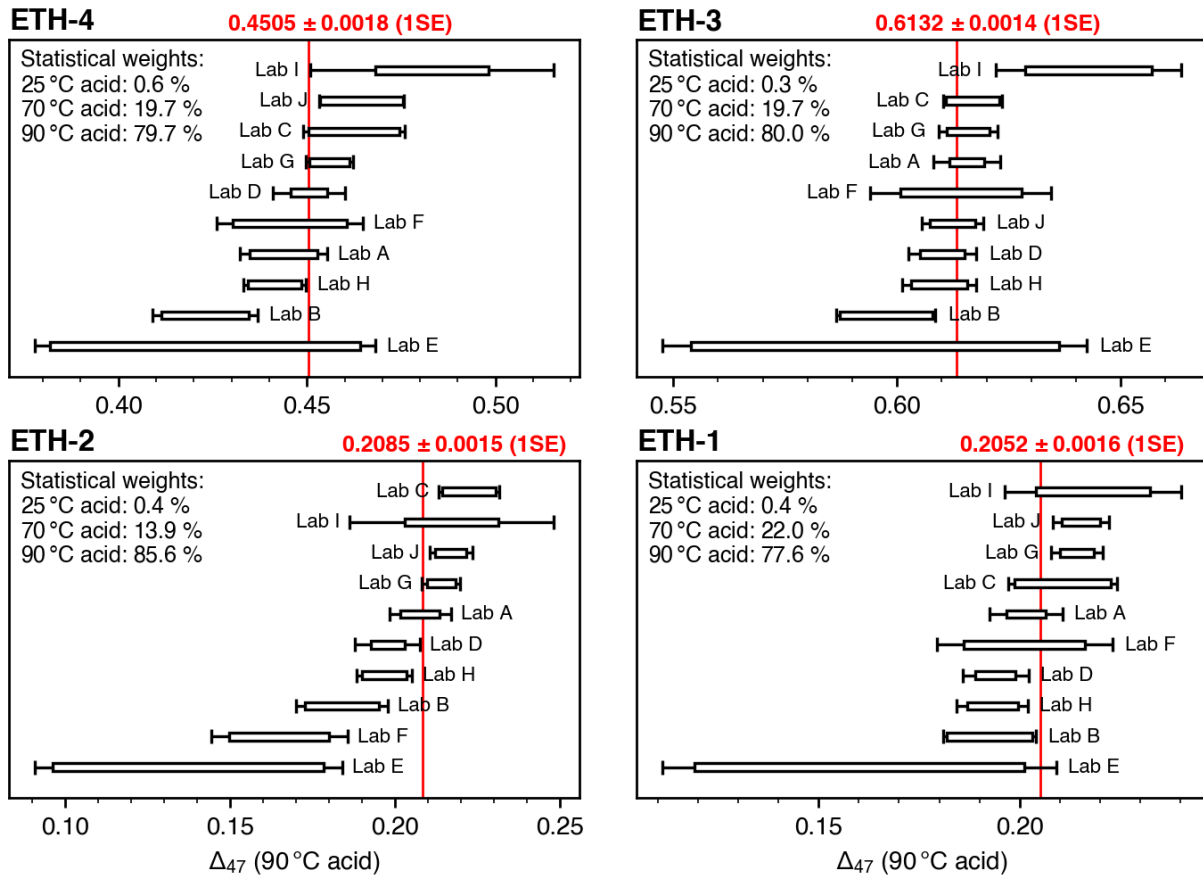
478

479 **Table 1.** Newly determined nominal Δ_{47} values of the ETH standards projected to 90 °C acid reaction
 480 using acid correction factors of -0.088 ‰ and -0.022 ‰ for 25 °C and 70 °C reactions, respectively
 481 (Petersen et al. 2019). Reported standard errors represent analytical uncertainties associated both with
 482 reference frame errors (HG/EG) and carbonate sample reproducibility (Daëron, this volume).

483

484 When compared with the published values in Bernasconi et al. (2018) the average Δ_{47} values
 485 ETH-1 and ETH-2, projected back to 25 °C (+0.088 ‰), are respectively 0.035 and 0.040 ‰
 486 greater than the original values, whereas ETH-3 increases by 0.010 and ETH-4 by 0.031 ‰.
 487 Such positive offset of Δ_{47} values reported in Bernasconi et al. (2018) versus other laboratories
 488 has also been reported in Fiebig et al. (2019) and Thaler et al. (2020).

489



490

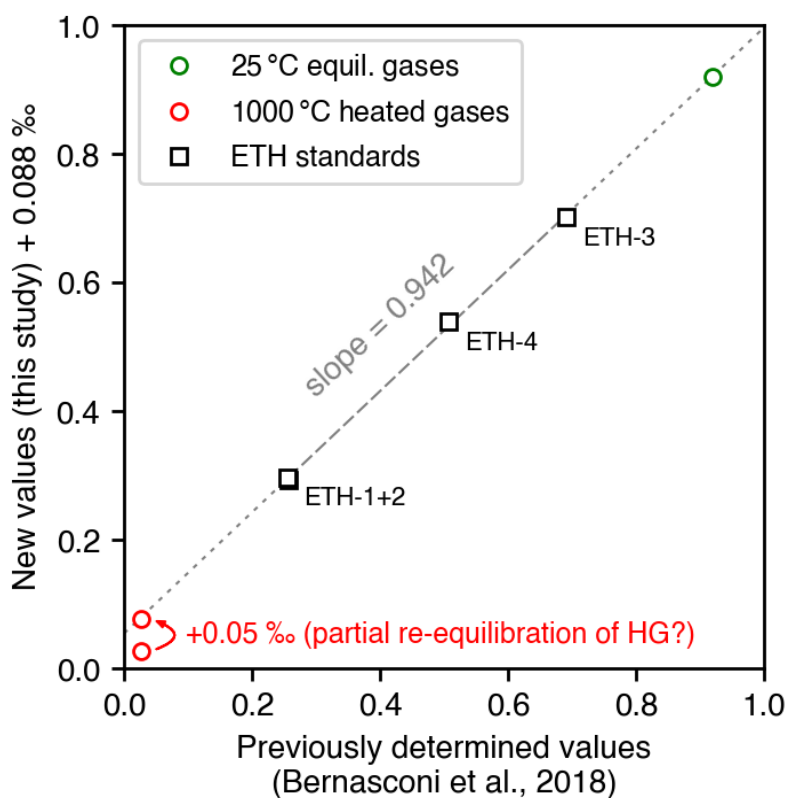
491 **Figure 2.** New determination of Δ_{47} values for the four ETH standards relative to the CDES using updated
 492 CO_2 equilibrium values. These measurements, using acid reaction temperatures of 90 °C, 70 °C or 25 °C,
 493 are projected to 90 °C using acid corrections of -0.088 ‰ and -0.022 ‰ for 25 °C and 70 °C reactions,
 494 respectively (Petersen et al. 2019). Error bars correspond to 95 % confidence limits taking into account
 495 fully propagated errors (i.e. taking into account errors in both unknown and anchor analyses). Boxes
 496 correspond to 95 % confidence limits not accounting for normalization errors (i.e. only taking into
 497 account errors in unknown analyses). Red numbers are the error-weighted average values (with statistical
 498 weights summarized in upper-left corners). Note different horizontal scales for the different samples.

499

500

501 The observation that these changes in nominal values decrease as Δ_{47} increases suggests a simple
 502 hypothesis to explain this discrepancy: in the original study of Meckler et al. (2014), the
 503 carbonate samples and the heated/equilibrated CO_2 gases experienced different analytical
 504 procedures. The HGs were measured as large samples at constant beam intensity through a

505 different capillary than the carbonates, which were measured using the microvolume and a
 506 decreasing beam). The potential effects of partial re-equilibration for the heated gases in the gas
 507 preparation line or in the capillaries of the mass spectrometer could be significant whereas it
 508 would be minuscule for the gases equilibrated at 25°, leading to an overestimation of Δ_{47} scale
 509 compression and thus of the stretching applied to the Δ_{47} scale towards theoretical values. The
 510 observed changes in apparent ETH-1 and ETH-2 Δ_{47} values may therefore simply reflect partial
 511 re-equilibration of heated gases at the time of measurements at ETH (and reported in Meckler et
 512 al., 2014), increasing their values in the original study by about 0.05 ‰ (Fig. 3).
 513



514
 515 **Figure 3.** New nominal Δ_{47} values for the ETH standards compared to previously reported ones. The
 516 dashed gray line is a linear regression through the new versus old values of ETH-1/2/3/4, whose
 517 extrapolation coincides with 25 °C equilibrated CO_2 but not with heated gases. Apparent changes in the
 518 ETH-1/2/3/4 values thus scale linearly with the Δ_{47} difference between carbonate samples and 25 °C
 519 equilibrated CO_2 , suggesting that Δ_{47} values of heated gases in the original study may have been biased by
 520 $\sim +0.05$ ‰ through partial re-equilibration at room temperature between the quenching of heated CO_2 and
 521 its ionization in the IRMS source.
 522

523 It has been suggested previously that ETH-1 and ETH-2 should be indistinguishable in Δ_{47} and
524 close to stochastic distribution (Müller, Violay, et al., 2017). This is because Δ_{47} values of ETH-
525 1 and ETH-2, originally heated to 600 °C, were found to be higher by only around 0.006 ‰ from
526 the same carbonates heated at 1000 °C to achieve stochastic distribution of the isotopes.
527 However, additional test measurements in multiple laboratories of samples heated at >1000 °C
528 are necessary to confirm this observation.

529
530 One laboratory (Lab F) did however observe a large difference in the value for ETH-1 and ETH-
531 2, although their values of ETH-3 and ETH-4 are similar to other laboratories. The reason for
532 these inconsistencies is probably due to the fact that ETH-1 was only measured four times with a
533 limited number of HG/EG, and ETH-2 and ETH-4 were not measured in the same session. In
534 addition, the labs with the smallest number of replicate measurements have uncertainties that are
535 systematically larger (Table 1). These results highlight the importance of correction procedures
536 in clumped isotope analysis. Sufficient replication of both standards and samples is critical and,
537 if insufficient, offsets can arise when comparing results from different sessions. Due to these
538 difficulties it is good practice to spread replicates of the same sample in different sessions over
539 longer periods of time to obtain accurate results and follow a ~50:50 standard to sample replicate
540 ratio.

541
542 Based on the results above, the difference between the average of ETH1/2 and ETH-3 is reduced
543 by 0.028 ‰, thus leading to a compression of the scale by about 5.6 % compared to the values
544 reported by Bernasconi et al. (2018). As a consequence, the slopes of published temperature
545 calibrations produced with carbonate standardization (Kele et al, 2015; Bernasconi et al., 2018;
546 Jautzy et al., 2021; Meinicke et al., 2020; Peral et al., 2018; Piasecki et al., 2019) will become
547 slightly shallower, with more positive y-intercepts. If Δ_{47} results from previous publications are
548 also recalculated with the new standard values (see section 3.4), however, changes in calculated
549 formation temperatures will be negligible. For this reason, when comparing data from
550 publications using old accepted values of the ETH standards for standardization (either those
551 published by Meckler et al. (2014) or those recalculated with the IUPAC parameters by
552 Bernasconi et al. (2018)) to newer data, it is recommended to directly compare the reconstructed
553 temperatures rather than recalculating Δ_{47} . Full recalculation of old measurements requires the

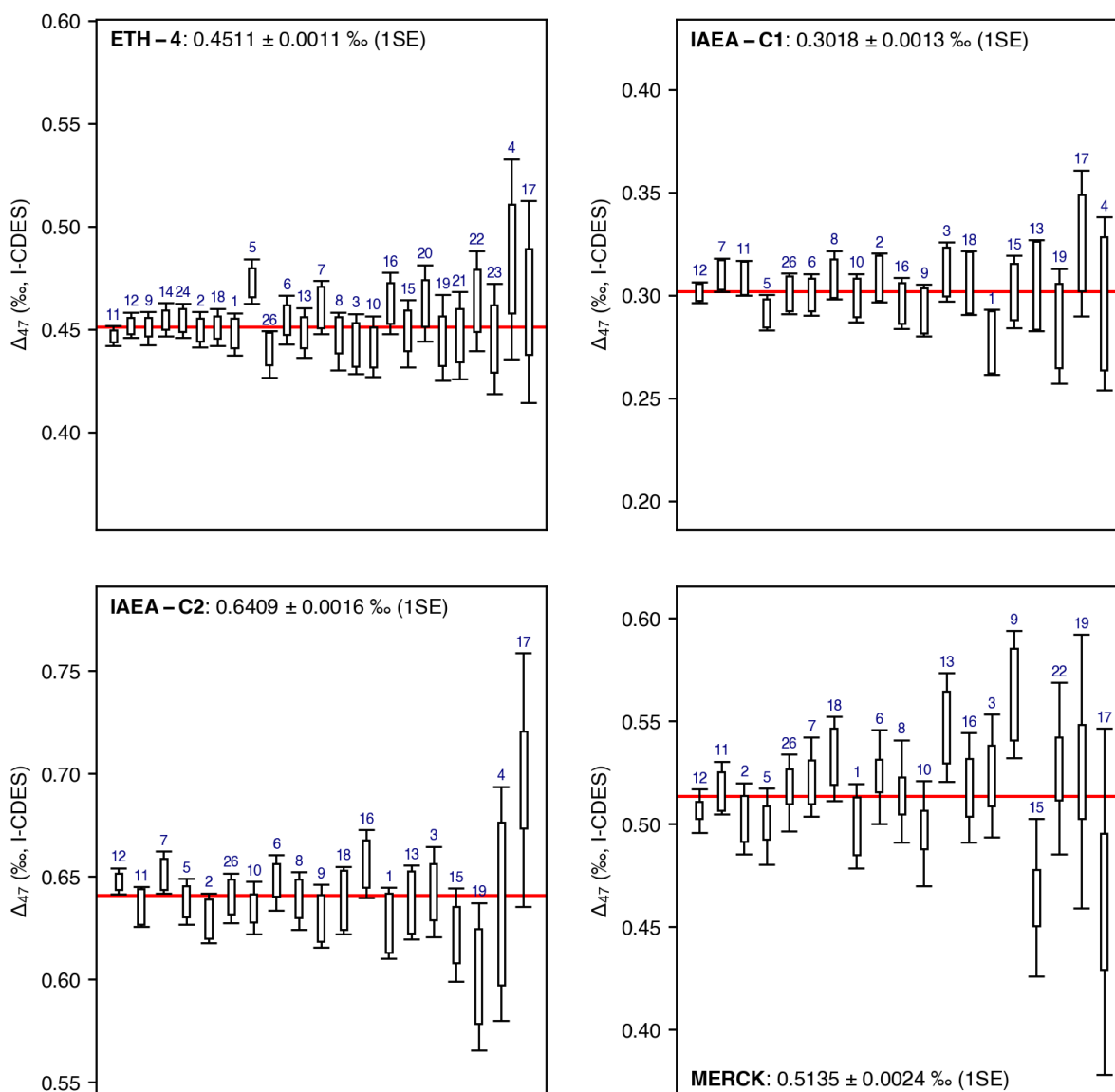
554 availability of the entire dataset including standards and the same correction procedures (e.g.,
555 averaging method) used in the original publications, and is described in Appendix 1.

556

557 **3.2 InterCarb results**

558 Results for the unknown carbonate samples were obtained from 26 mass spectrometers in 22
559 laboratories. Δ_{47} values of the 4 unknown samples were normalized to the new community-
560 derived values of ETH-1, ETH-2, and ETH-3 (Table 1), averaged per individual analytical
561 session and mass spectrometer (Tables 2 and S1). Sample mean values obtained in each mass
562 spectrometer are shown in Figure 4. The details of each analytical session, including the number
563 of samples and standards measured, the composition of the working standard, the scaling
564 parameters and the reproducibilities of the individual sessions are given in the supplementary
565 information (Table S1). Some laboratories reported data for only a subset of the unknown
566 samples, and both replication level and analytical reproducibility vary from laboratory to
567 laboratory (Table S1).

568 To clearly distinguish Δ_{47} values normalized to the carbon dioxide reference scale (CDES) using
569 carbonates rather than heated and equilibrated gases, we propose the new acronym (I-CDES),
570 short for InterCarb-CDES, to reflect the use of the proposed InterCarb reference materials for
571 data standardization (see section 3.5 for more details).



572
 573 **Figure 4.** Final InterCarb results by laboratory. Error bars correspond to fully propagated 95 %
 574 confidence limits, taking into account errors in both unknown and anchor analyses. Boxes correspond to
 575 95 % confidence limits not accounting for normalization errors (i.e., only taking into account errors in
 576 unknown analyses). Results are sorted by increasing analytical errors, and laboratories are identified by
 577 number. Overall error weighted average Δ_{47} values are displayed as solid red lines and reported in each
 578 panel. All plots have the same vertical scale.
 579
 580 Laboratories with stronger analytical constraints (i.e. better in-lab repeatability of Δ_{47}
 581 measurements and/or greater number of analyses) generally converge towards the overall mean

582 value for each unknown sample. This observation suggests that the observed inter-laboratory
583 variability is largely due to random errors that can be alleviated by replication, even for
584 laboratories with relatively large analytical errors on individual measurements. It is also notable
585 that fully propagated analytical errors (i.e., taking into account uncertainties in the
586 standardization procedure) can be substantially larger than the errors based only on the
587 uncertainty associated with unknown sample analyses, which is what is generally reported in the
588 literature. The increase in error is also related to in-lab repeatability and the number of standards
589 measured. In addition, error increases for unknown samples whose compositions lie outside the
590 “anchor triangle” defined by ETH-1/2/3. This is illustrated by the increased scatter and errors
591 associated with MERCK, the carbonate material farthest from the “anchor triangle”, consistent
592 with the models of Daëron (this volume, see also Kocken et al., 2019).

593
594 As seen in Table S1, there are stark differences in the total number of replicate analyses and the
595 typical Δ_{47} reproducibility achieved in different laboratories. As a result, final uncertainties in the
596 average Δ_{47} values of unknown samples vary considerably (Fig. 4). It is thus not very useful to
597 quantify inter-laboratory reproducibility in terms of a single, overall scatter of Δ_{47} values: inter-
598 laboratory variability should be small among laboratories with small analytical uncertainties, and
599 larger among laboratories with few replicate analyses and/or poor analytical repeatability. We
600 may still, however, assess whether inter-lab discrepancies are significantly larger than expected
601 from in-lab analytical uncertainties, i.e., whether we can detect the effects of hypothetical
602 unrecognized sources of scatter beyond known analytical errors.

603

604

605

606

607

Lab	ETH-4		IAEA-C1		IAEA-C2		MERCK	
	$\Delta_{47(I-CDES)} (\% \pm 1SE)$	N	$\Delta_{47(I-CDES)} (\% \pm 1SE)$	N	$\Delta_{47(I-CDES)} (\% \pm 1SE)$	N	$\Delta_{47(I-CDES)} (\% \pm 1SE)$	N
1	0.4477 ± 0.0052	80	0.2773 ± 0.0080	19	0.6275 ± 0.0088	21	0.4991 ± 0.0105	22
2	0.4499 ± 0.0044	22	0.3086 ± 0.0060	6	0.6299 ± 0.0061	8	0.5025 ± 0.0089	6
3	0.4430 ± 0.0074	23	0.3114 ± 0.0073	17	0.6427 ± 0.0112	13	0.5235 ± 0.0152	11
4	0.4841 ± 0.0248	9	0.2959 ± 0.0215	6	0.6368 ± 0.0291	4		
5	0.4734 ± 0.0055	22	0.2916 ± 0.0044	18	0.6378 ± 0.0057	17	0.4987 ± 0.0094	14
6	0.4545 ± 0.0060	12	0.3004 ± 0.0051	12	0.6471 ± 0.0069	12	0.5229 ± 0.0116	12
7	0.4607 ± 0.0066	8	0.3099 ± 0.0042	16	0.6520 ± 0.0052	15	0.5231 ± 0.0098	8
8	0.4442 ± 0.0072	73	0.3099 ± 0.0060	67	0.6383 ± 0.0071	62	0.5159 ± 0.0127	70
9	0.4505 ± 0.0041	65	0.2926 ± 0.0064	8	0.6309 ± 0.0078	8	0.5630 ± 0.0158	2
10	0.4416 ± 0.0075	26	0.2987 ± 0.0060	33	0.6348 ± 0.0065	62	0.4954 ± 0.0130	31
11	0.4468 ± 0.0025	222	0.3085 ± 0.0043	31	0.6354 ± 0.0050	27	0.5175 ± 0.0066	25
12	0.4521 ± 0.0032	21	0.3015 ± 0.0026	20	0.6479 ± 0.0032	21	0.5064 ± 0.0054	19
13	0.4484 ± 0.0062	47	0.3048 ± 0.0113	6	0.6376 ± 0.0091	12	0.5470 ± 0.0135	9
14	0.4548 ± 0.0041	46						
15	0.4480 ± 0.0083	8	0.3016 ± 0.0090	4	0.6217 ± 0.0116	4	0.4642 ± 0.0195	4
16	0.4627 ± 0.0076	4	0.2962 ± 0.0063	4	0.6563 ± 0.0084	3	0.5176 ± 0.0136	2
17	0.4634 ± 0.0250	5	0.3254 ± 0.0181	6	0.6971 ± 0.0314	6	0.4623 ± 0.0429	3
18	0.4510 ± 0.0046	196	0.3060 ± 0.0079	26	0.6386 ± 0.0084	28	0.5317 ± 0.0104	31
19	0.4460 ± 0.0106	14	0.2851 ± 0.0142	5	0.6015 ± 0.0183	4	0.5256 ± 0.0339	4
20	0.4627 ± 0.0095	6						
21	0.4470 ± 0.0108	3						
22	0.4639 ± 0.0124	7					0.5269 ± 0.0213	7
23	0.4453 ± 0.0137	6						
24	0.4544 ± 0.0042	12						
26	0.4378 ± 0.0058	8	0.3008 ± 0.0051	6	0.6396 ± 0.0062	6	0.5152 ± 0.0095	6
w. avg	0.4511 ± 0.0011	945	0.3018 ± 0.0013	310	0.6409 ± 0.0016	333	0.5135 ± 0.0024	286

608

609 **Table 2.** Average Δ_{47} values ($\pm 1SE$, fully propagated uncertainties) obtained by each participating
 610 laboratory. A full table of average Δ_{47} values for all analytical sessions is included in supplementary
 611 materials (Table S3).

612

613

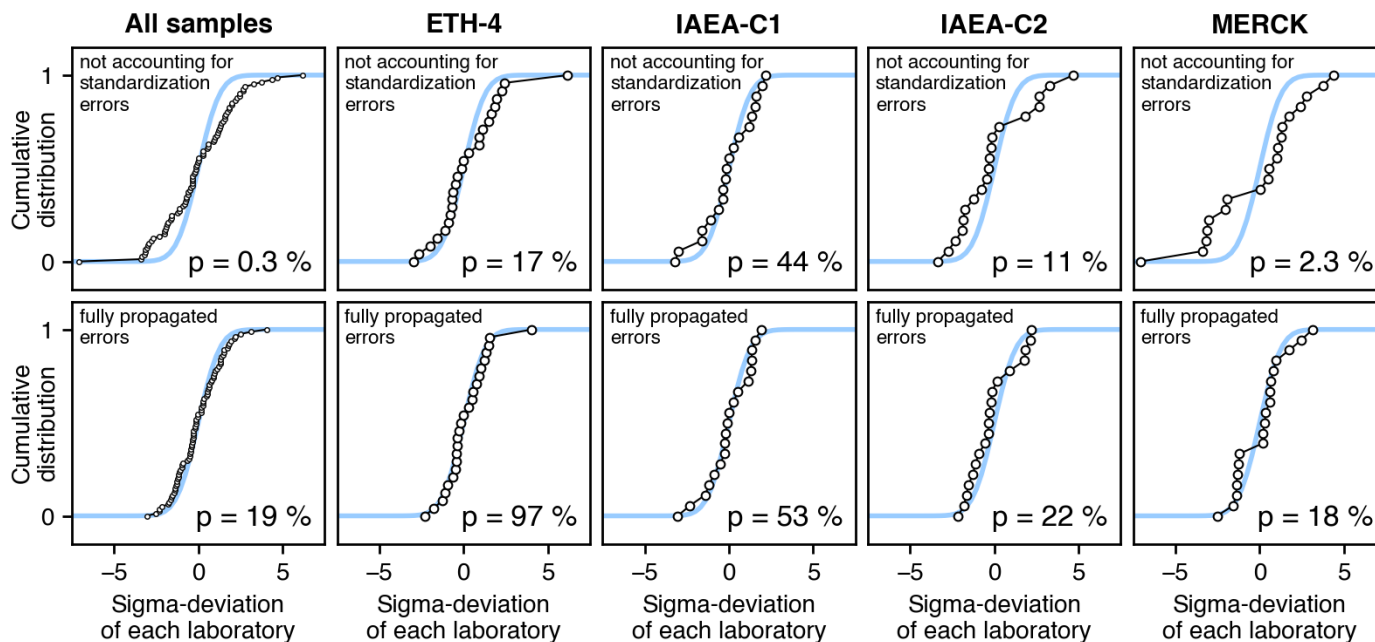
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615 In order to do so, we compute the “number-of-sigma” deviation obtained by each laboratory for
616 each unknown sample, relative to that sample’s overall weighted average value. For example, the
617 sigma-deviation for sample ETH-4 and Lab01 is equal to $(0.4477 - 0.4511) / 0.0052 = -0.66$ and
618 that for MERCK and Lab13 is equal to $(0.5470 - 0.5135) / 0.0135 = +2.48$. If the analytical
619 errors reported in Table 2 are reasonably accurate, we expect the population of sigma-deviations
620 among all labs to be distributed as the canonical Gaussian distribution ($\mu = 0$; $\sigma = 1$), and we can
621 test this prediction using established statistical methods such as a Kolmogorov–Smirnov test of
622 normality (Massey, 1951). We carried out this test for two cases: only considering the error of
623 sample replication (Fig. 5, upper row) and secondly including the normalization error, (i.e. the
624 fully propagated error (Fig. 5, lower row). If we neglect uncertainties arising from
625 standardization (the “allogenic” errors of Daëron, this volume), the sigma-deviations are no
626 longer normally distributed ($p = 0.003$, upper-left panel). As shown in the lower-left panel of
627 Figure 6, the distribution of sigma-deviations for all labs and all samples is statistically
628 indistinguishable from the expected normal distribution ($p = 0.19$) when considering fully
629 propagated analytical errors. Figure 6 also illustrates that neglecting standardization errors does
630 not strongly affect the normality of sigma-deviations for ETH-4 and IAEA-C1, both of which
631 have δ^{47} and Δ_{47} values within the range covered by the three anchor samples. By contrast,
632 sigma-deviations for unknowns with “exotic” isotopic compositions (IAEA-C2 and especially
633 MERCK) are only normally distributed if standardization uncertainties are correctly accounted
634 for.

635

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

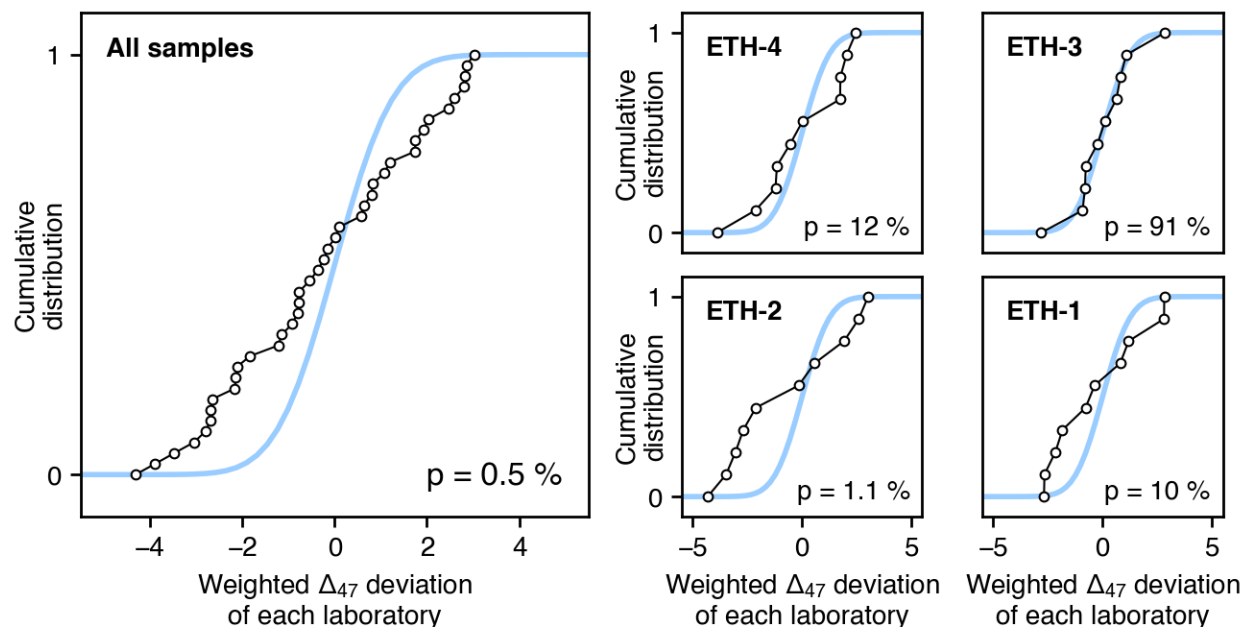
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644
 645 **Figure 5.** Kolmogorov–Smirnov tests of normality for the sigma-deviations obtained in each laboratory
 646 participating in the Intercarb effort (circular markers), either neglecting standardization uncertainty (upper
 647 row) or considering fully propagated analytical errors (lower row). Lower-right corner Kolmogorov–
 648 Smirnov p-values correspond to the null hypothesis that the sigma-deviations are normally distributed
 649 with a mean of zero and a standard deviation of 1. Blue lines correspond to the canonical Gaussian
 650 distribution ($\mu = 0$; $\sigma = 1$).

651
 652 On demonstrating that we can fully account for inter-laboratory error using carbonate
 653 standardization, we revisit the results obtained for ETH1-4 using HG and EG (Fig. 2). Applying
 654 the same Kolmogorov–Smirnov test of normality yields unambiguous evidence that the inter-
 655 laboratory scatter observed here, using HG/EG standardization, is significantly greater than
 656 predicted from known analytical errors alone ($p = 0.005$, Fig. 6), contrary to the opposite finding
 657 for the InterCarb results, using carbonate-based standardization ($p = 0.19$, Fig. 5).

658



659

660

661 **Figure 6.** Kolmogorov–Smirnov tests of normality for the sigma-deviations, considering fully propagated
 662 analytical errors (accounting for uncertainties associated with conversion to the CDES reference frame),
 663 obtained in each laboratory participating in the ETH-1/2/3/4 determination using HG and EG (circular
 664 markers). Lower-right corner Kolmogorov–Smirnov p-values correspond to the null hypothesis that the
 665 sigma-deviations are normally distributed with a mean of zero and a standard deviation of 1. Blue lines
 666 correspond to the canonical Gaussian distribution ($\mu = 0$; $\sigma = 1$).

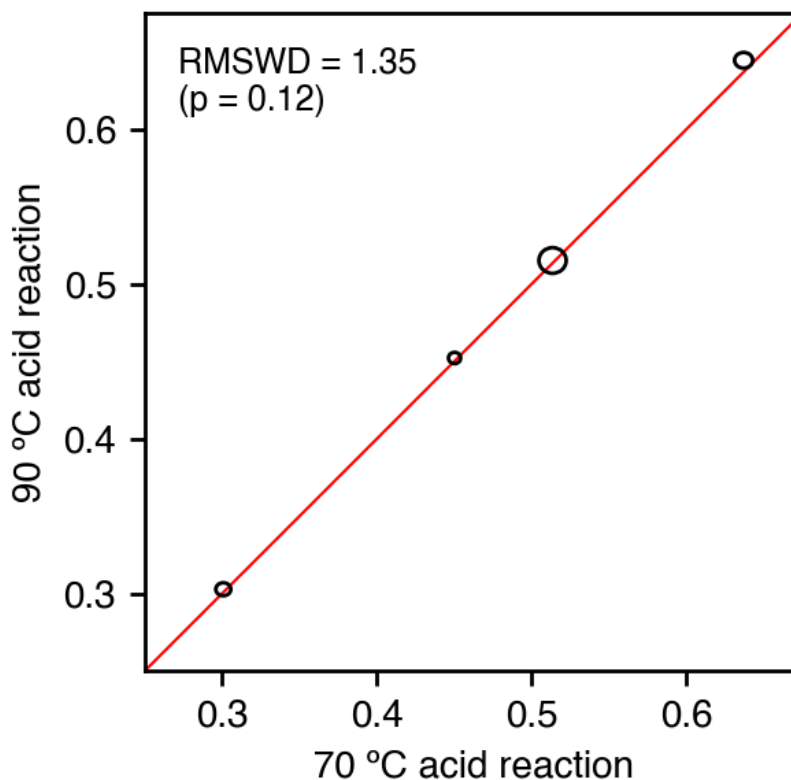
667

668 3.3 Effects of acid reaction temperature and IRMS models

669

670 Out of 25 sample preparation systems, 10 convert samples to CO₂ by acid reactions at 70 °C and
 671 14 at 90 °C. To test for the possible effect of acid temperature, a commonly discussed cause for
 672 different slopes in the published temperature calibration curves (Came et al., 2014; Fernandez et
 673 al., 2014; Swart et al., 2019), we plot the Δ_{47} values of unknowns obtained by laboratories
 674 reacting at 70 °C vs. those obtained at 90 °C (Fig. 8, Table 3). Because acid fractionation effects
 675 equally affect anchors and unknowns, carbonate-standardized results can be compared directly
 676 without acid temperature correction. Δ_{47} values averaged by acid temperature are statistically
 677 indistinguishable for all of the unknowns. This implies that relative Δ_{47} differences between CO₂

678 evolved from different samples are independent of acid reaction temperature within the range of
 679 experimental conditions covered here, and for a very wide range of $\Delta_{47(I-CDES)}$ values spanning
 680 0.302 ‰ (marbles) to 0.641 ‰ (carbonates formed at ambient temperatures).
 681



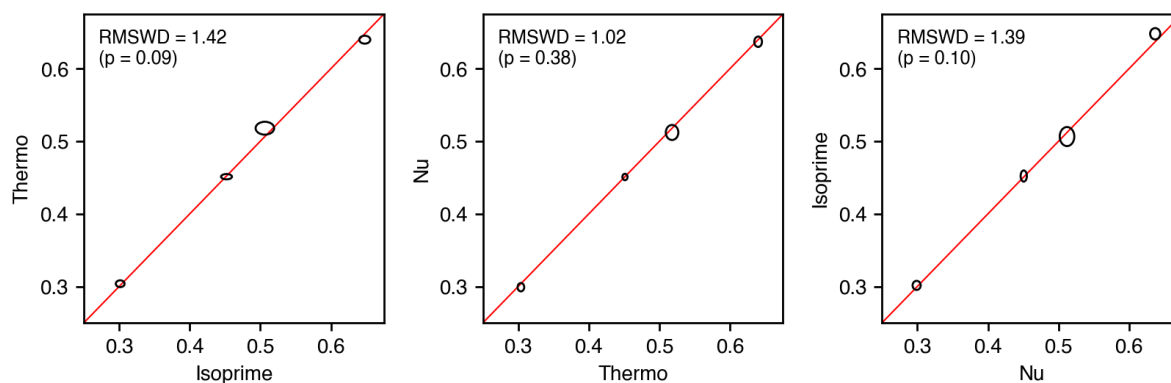
682
 683
 684 **Figure 7.** Error-weighted average $\Delta_{47(I-CDES)}$ values of unknowns obtained from acid reactions at
 685 90 °C vs 70 °C. Solid black ellipses correspond to 95 % confidence limits. (see also Table 3).
 686

	70 °C acid	90 °C acid	Difference ($\pm 1SE$)
ETH-4	0.4501 \pm 0.0016	0.4521 \pm 0.0015	0.0020 \pm 0.0022
IAEA-C1	0.3006 \pm 0.0020	0.3026 \pm 0.0017	0.0020 \pm 0.0026
IAEA-C2	0.6369 \pm 0.0024	0.6445 \pm 0.0021	0.0076 \pm 0.0032
MERCK	0.5134 \pm 0.0036	0.5151 \pm 0.0034	0.0017 \pm 0.0049
average (all samples)			0.0033 \pm 0.0017

687
 688 **Table 3.** Error-weighted average $\Delta_{47(I-CDES)}$ values ($\pm 1SE$) for each unknown as a function of acid reaction
 689 temperature (see also Fig. 7).

690
 691 The error-weighted results separated by mass spectrometer type and design of associated
 692 preparation lines, another postulated source of inter-lab disagreement (Swart et al., 2019), are
 693 shown in Figure 8 and Table 4. Out of the 22 participating laboratories, 8 use the Nu Perspective,
 694 16 use versions of the Thermo MAT253, and one uses an Isoprime 100. Most results are
 695 statistically indistinguishable across instruments. Only IAEA-C2 yielded a significantly ($>2\sigma$)
 696 higher mean Δ_{47} value ($\Delta\Delta_{47}$ of +0.0110 and +0.0081 ‰ vs Nu perspective and MAT253,
 697 respectively) when analyzed with an Isoprime 100 versus other instrument models (but note that
 698 all of the Isoprime 100 data comes from a single laboratory). Inter-instrument differences
 699 averaged over all four samples (bottom row of Table 4) remain, however, indistinguishable from
 700 zero. Thus, any potential biases introduced by the use of different mass spectrometer models
 701 and/or the design of the preparation line which could cause partial equilibration of the produced
 702 CO₂ with the acid and/or heated metal surfaces (Swart et al.2019) are undetectable when using
 703 carbonate standardization. Sample sizes used for individual measurements ranged from 90-120
 704 μg for the Kiel IV to $\sim 500 \mu\text{g}$ for the NuCarb individual acid vial preparation systems, and to 3-
 705 12 mg for samples reacted in common acid bath custom-built extraction lines. The fact that small
 706 sample measurements are carried out at 70 °C and large ones at 90 °C, also suggests that there is
 707 no significant effect of sample sizes and variations in sample to acid ratios in these results.

708
 709



710
 711 **Figure 8.** Error-weighted average $\Delta_{47(I-CDES)}$ values of unknowns obtained using different mass
 712 spectrometer types. Solid black ellipses correspond to 95 % confidence limits.

713

	MAT 253 vs Isoprime 100	Nu Perspective vs MAT 253	Isoprime 100 vs Nu Perspective
ETH-4	-0.0009 ± 0.0035	-0.0004 ± 0.0024	0.0013 ± 0.0036
IAEA-C1	0.0023 ± 0.0032	-0.0048 ± 0.0030	0.0025 ± 0.0035
IAEA-C2	-0.0081 ± 0.0039	-0.0029 ± 0.0037	0.0110 ± 0.0043
MERCK	0.0115 ± 0.0065	-0.0059 ± 0.0056	-0.0056 ± 0.0068
average (all samples)	0.0012 ± 0.0022	-0.0035 ± 0.0019	0.0023 ± 0.0024

714

715 **Table 4.** Error-weighted average $\Delta_{47(i-CDES)}$ values ($\pm 1SE$) for each unknown as a function of mass
716 spectrometer types.

717 **3.4. Guidelines for improving data quality in the future.**

718

719 The results of this inter-laboratory exercise support the use of carbonate standardization for
720 clumped isotope measurements. When considering all laboratories, the standard deviation of
721 laboratory averages for the 4 unknowns range from 0.011 ‰ to 0.018 ‰ for the samples
722 requiring no to moderate extrapolation, to 0.025 ‰ for MERCK, an extreme case of
723 extrapolation. The spread across laboratories is still relatively large, and of the same magnitude
724 as those obtained by HG-EG normalization if we consider either (1) what has been reported on 4
725 carbonate standards for 4 laboratories in Dennis et al. (2011) or (2) the scatter in the values
726 reported by the 10 laboratories that provided data for the re-determination of the accepted values
727 of ETH-1 to ETH-3 in this study. However, based on this study, we can clearly state that the
728 large scatter is dominated by random errors, and there are strategies to improve the repeatability
729 within each laboratory.

730

731 The scatter in the InterCarb data (Fig. 4) is especially influenced by laboratories that show the
732 largest errors in the individual sample reproducibility and have a significantly magnified
733 normalization error induced by a small number of replicates of anchors. This observation
734 underscores the necessity of increased replication, ideally in separate sessions, and of the
735 measurement of a sufficient number of standards to produce data of the quality that is required
736 for meaningful interpretations. Special care needs to be taken when reconstructing small
737 temperature changes, such as for the reconstruction of climate change and/or the study of high

738 temperature processes where the small temperature sensitivity of the clumped isotope
739 thermometer requires highest analytical precision.

740

741 We can, for example, define a target laboratory internal repeatability of 0.010 ‰ (1SE) as a
742 desirable goal with the currently available analytical systems. This arbitrary target number is
743 within the shot-noise limits of modern IRMS instruments, and is necessary for applications in
744 paleoclimate reconstructions, one of the main applications of clumped isotopes, as it corresponds
745 to an uncertainty of approximately ± 3 °C. If for each sample we select only the results from the
746 laboratories that have provided data with a combined error of less than 0.010 ‰ (1SE; Table 2),
747 inter-laboratory standard deviation (1SD) becomes ≤ 10 ppm for ETH-4 (N=22), IAEA-
748 C1(N=15) and IAEA-C2 (N=13) and ≤ 0.015 ‰ for MERCK (N=11; with SE < 0.0135). It can
749 be noted that this does not significantly change the average value of the reference materials.

750

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

756

757 With standardization using carbonates, the principle of identical treatment of samples and
758 standards (Werner & Brand, 2001b) is fulfilled, in contrast to the use of HG/EG standardization.
759 Two important outcomes of this study are that acid reaction temperature and instrument and
760 preparation line design are not a cause for differences among laboratories when standardization
761 is based on carbonates. The lack of resolvable differences observed in our dataset, indicates that
762 if preparation line differences affect Δ_{47} measurements, standardization with carbonates corrects
763 any such effects whereas HG-EG standardization may fail to do so (Swart et al. 2019). Thus,
764 when using carbonate standardization, these factors can be ignored provided the carbonate
765 standards cover a large range in Δ_{47} .

766 As the acid digestion conditions (e.g., reaction times, temperatures) vary with the carbonate
767 mineralogy, possible effects on Δ_{47} might be mineral-specific. For this reason, it would be highly
768 desirable to produce reference materials for other minerals such as dolomite, aragonite,

769 magnesite and siderite. For dolomite, three samples were proposed by Müller et al. (2019) as
770 possible reference materials and are available upon request.

771
772 Standardization errors could be reduced to some extent by extending the range of bulk
773 composition of the anchor samples (e.g., as illustrated by Fig. 1 of *Daëron*, this volume),
774 especially when samples are measured that require significant extrapolation. A sample with an
775 extreme bulk composition like MERCK would be a useful addition as an anchor, regardless of its
776 Δ_{47} value. While with a three-anchor system, two heated standards for normalization are not
777 strictly necessary, a “heated MERCK” anchor in combination with ETH-1 would furthermore
778 allow verifying the PBL correction with greater confidence and with less replication than with
779 ETH-2 (keeping in mind that small quadratic components to PBL correction might introduce a
780 significant bias over a δ^{47} range of 60 ‰, e.g., Fig. 7 from He et al., [2012]).

781
782 3.5 Reporting data normalized to carbonates: definition of the “InterCarb” Carbon
783 Dioxide Equilibrium Scale (I-CDES)

784
785 There is a need for a community consensus on how to report clumped isotope measurements,
786 both to promote data comparability and to reduce confusion stemming from the different scales
787 used in the literature. Currently Δ_{47} data are reported for different temperatures of phosphoric
788 acid digestion, mostly projected to 25 °C but also to 70 °C or 90 °C reactions, and generally
789 labeled respectively as $\Delta_{47\text{CDES}25}$, $\Delta_{47\text{CDES}70}$ and $\Delta_{47\text{CDES}90}$, a terminology introduced in Bonifacie
790 et al. (2017). In the literature, phosphoric acid correction factors used by different research
791 groups to convert results from 90 to 25 °C reaction temperatures have varied between 0.069 ‰
792 (Wacker et al., 2014) to 0.092 ‰ (e.g., Bonifacie et al., 2017), thus representing a significant
793 source of uncertainty and confusion.

794
795 The direct standardization to accepted values of solid phases, on the other hand, removes the
796 need for a phosphoric acid correction, yielding results which are independent of the temperature
797 at which the samples were reacted. In InterCarb this has only been tested for calcites, the

798 mineralogy of all standards used here. Further studies are necessary in particular for dolomite
799 and siderite, as these minerals require longer reaction times and there are contrasting findings in
800 the literature on whether they require different phosphoric acid fractionations (Bonifacie et al.,
801 2017; Müller et al. 2019, van Dijk et al., 2019; Petersen et al. 2019), possibly affecting the
802 absolute values of samples with such mineralogies. Nevertheless, the use of the InterCarb
803 reference carbonates, allows for a consistent correction of instrumental effects and normalization
804 to the I-CDES, independent of the mineralogy. Possible effects related to the longer reaction time
805 remain to be tested, and require intercomparison samples of different mineralogy. In any case for
806 all calcites carbonate standardization eliminates different phosphoric acid correction factors as a
807 source of uncertainty and provides a consistent framework to report Δ_{47} without uncertainties
808 related to the reaction temperature.

809
810 For these reasons, we recommend that in the future, carbonate clumped isotope values should be
811 reported relative to a carbonate reference frame uniquely defined by the absolute Δ_{47} values
812 reported in Table 1 for ETH-1, ETH-2, and ETH-3. Unknown samples may be anchored to this
813 reference frame either (a) directly by comparison to ETH-1/2/3, (b) indirectly by comparison
814 with several of the four other carbonate standards used here (Figure 4), or (c) by comparison
815 with a set of in-house laboratory standards whose composition is well-constrained relative to the
816 materials reported here. To clearly distinguish this data normalization scheme from previous
817 ones the denomination I-CDES (InterCarb - Carbon Dioxide Equilibration Scale) should be used,
818 and, where applicable, the notation $\Delta_{47(I-CDES)}$. This approach is analogous to the change from
819 the PDB to the VPDB scale, which was accomplished by assigning a consensus offset of +1.95
820 ‰ between the original PDB reference material and the NBS19 carbonate. This was
821 subsequently, albeit temporarily, improved by defining a second anchor point with the L-SVEC
822 Lithium carbonate standard (Coplen et al., 2006). We note that because the carbonate Δ_{47} values
823 in Table 1 are firmly anchored to the CDES scale via HG/EG measurements in multiple
824 laboratories, the two scales are in principle equivalent. However, I-CDES has three major
825 advantages (1) it follows the principle of equal treatment of sample and standards (2) it removes
826 uncertainties related to fractionation effects due to different acid reaction temperatures and
827 designs of the preparation lines and (3) it is based on traceable, stable materials (calcium
828 carbonates) that are widely available to interested laboratories. . What is more, the results

829 summarized in Fig. 5 imply that I-CDES standardization yields consistent Δ_{47} values
830 independent of laboratory and/or analytical protocols, so that inter-laboratory scatter is
831 accurately predicted by the fully-propagated analytical uncertainties computed within each
832 laboratory. By contrast, this does not always seem to be the case for gas-based standardization to
833 the CDES reference frame (Fig. 6), suggesting the existence of poorly understood sources of
834 inter-lab discrepancies in that approach. The broad availability of carbonate reference materials
835 with widely varying bulk and clumped isotope compositions is an important step to help
836 establish a worldwide equivalence among laboratories, and to help new laboratories establish and
837 verify their analytical procedures. .

838
839 The decision that $\Delta_{47(I-CDES)}$ values are reported for an acid reaction temperature of 90 °C implies
840 that the I-CDES value of any given sample will be almost 0.1 ‰ lower than $\Delta_{47CDES25}$ values
841 which is currently the most common, but not the sole, convention used to report clumped
842 isotopes. At first sight it may seem a disadvantage to lose the ability to intuitively compare new
843 results to those obtained through different standardization approaches in the published literature.
844 However, it will make it immediately obvious that I-CDES-normalized values cannot directly be
845 compared to data standardized to the ETH-1/2/3/4 values reported by Bernasconi et al. (2018).
846 To directly compare previous carbonate-normalized Δ_{47} values and the already published
847 calibration equations produced with ETH standard normalisation ((Kele et al, 2015; Bernasconi
848 et al., 2018; Jautzy et al., 2020; Meinicke et al., 2020; Peral et al., 2018; Piasecki et al., 2019) to
849 future data reported on the I-CDES scale, previous data have to be recalculated as described in
850 detail in the Appendix. We emphasize again, however, that the previously reported temperatures
851 calculated from the original calibrations using the original ETH standard values are directly
852 comparable to temperatures calculated for samples normalized and calibrations recalculated to
853 the I-CDES. This is because only the nominal values of the standards have changed, and thus the
854 data normalization is internally consistent and traceable to the same solid standards.

855
856 In principle, I-CDES data are directly comparable to data produced by phosphoric acid reaction
857 at 90°C using the HG/EG approach. With InterCarb, the nominal values of the ETH standards
858 are robustly linked to the CDES, as they are now based on the average results of 10 laboratories,
859 and are not only based on the values determined at ETH in 2013. Some laboratories may still

860 want to continue measuring HG and EG to keep established laboratory procedures and/or to
861 cover ranges in bulk compositions that require large extrapolations. However, the results of
862 InterCarb, and the discussions in the literature (e.g. Petersen et al. 2019) show that with the
863 HG/EG approach there are still poorly understood interlaboratory discrepancies (as suggested by
864 Fig. 6) which are absent in the carbonate-based normalization (see Fig 5). For this reason, it is of
865 paramount importance that several of the InterCarb reference carbonates are incorporated in the
866 laboratory procedures to ensure interlaboratory data compatibility. The use of matrix-matched
867 reference materials is necessary so that delta values can be unambiguously compared on a like-
868 for-like basis (see Meier-Augenstein and Schimmelmann, 2019 for a recent discussion).

869 For laboratories using large sample common-acid bath methodologies and preferring gas-based
870 data correction, we recommend that in addition to HG/EG a minimum of two of the InterCarb
871 reference materials (or in-house standards with values calibrated to ETH standards) should be
872 measured within the same analytical sessions as the samples and used in the data correction
873 scheme. We recommend choosing two standards with a large difference in Δ_{47} , for example
874 ETH-1 and ETH-3 or ETH-2 and IAEA-C2, depending on the bulk composition of the unknown
875 samples (see Fig. 1). In the case of samples very low δ^{47} we additionally recommend the use of
876 MERCK. The comparison of I-CDES data to older HG/EG normalized data, is in principle
877 possible, with the caveat that in absence of measurements of widely available carbonates, a direct
878 comparison remains uncertain. A community effort to robustly anchor the composition of legacy
879 standards measured in the first laboratories, may alleviate this problem in the near future.

880 For laboratories with commercially available single acid vial, small sample preparation systems
881 we discourage the use of HG/EG, as the gases would most probably be measured under different
882 conditions than the samples, an approach which is prone to error. In addition, InterCarb shows
883 that carbonate-based standardization can provide robust and accurate data without the use of
884 gases.

885

886 **3.6. Outlook for future improvements**

887

888 InterCarb has shown that with carbonate standardization it is possible to reach an inter-laboratory
889 reproducibility that is as good as what can be reached within a single laboratory. The use of

890 carbonate standards allows for a better monitoring of the performance of the entire preparation
891 system, including acid reaction and sample purification. Regular and systematic measurement of
892 carbonate reference material distributed within a run or measurement interval is a prerequisite to
893 correct for short- and long-term variations in the analytical systems. In this study, analyses were
894 grouped in measurement intervals, and all data were processed assuming no short-term variation
895 in the instrumentation. However, especially with "small sample approaches" relying on short
896 (~30-45 min) measurements of many replicates, one can observe short-term variations
897 (Bernasconi et al. 2018, Fig. 4). Thus a moving window correction with variable window size
898 may be desirable in these cases.

899
900 Replicate sample measurements should be spread in time as much as possible. The number and
901 distribution of standards in a run are also important parameters that can improve reproducibility
902 and reduce errors. This has been discussed in detail by Kocken et al. (2019) who concluded that
903 carbonate standards with bulk and clumped-isotope compositions similar to those of unknowns
904 should be analyzed with greater frequency than the other anchors, while preserving a minimal
905 level of replication for each anchor.

906
907 For InterCarb, all distributed aliquots of IAEA-C1, IAEA-C2 and MERCK originated from
908 single bottles. The results suggest that after milling, these carbonates were homogeneous within
909 these bottles, but we strongly recommend verifying that additional bottles purchased from IAEA
910 and MERCK are identical to the ones tested here. Finally, as there is currently no consensus in
911 the literature on whether different carbonate mineralogies exhibit the same phosphoric acid
912 fractionation effects (e.g. Müller et al. 2017; van Dijk et al. 2019; Bonifacie et al. 2017, Petersen
913 et al. 2019) and on possible differences in the temperature-dependence of the phosphoric acid
914 fractionation for dolomite (Defliese et al. 2015; Murray et al. 2016), there should be a
915 community effort to identify and characterize reference materials for other carbonates such as
916 aragonite and siderite, similar to the dolomite reference materials proposed by Müller et al.
917 (2019).

918 **4 Conclusions**

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- This study demonstrates that carbonate-based standardization of clumped isotope measurements solves many open questions so far limiting the application of carbonate clumped isotope thermometry as a mature and reliable tool in Earth sciences.
 - Carbonate-based standardization is robust in spite of the smaller range of isotopic compositions compared to the heated/equilibrated gas approach, even when extrapolation is necessary..
 - Inter-laboratory discrepancies observed in this study among 22 laboratories are not greater than those predicted from intra-laboratory analytical uncertainties.
 - We propose a set of 7 widely available calcite reference materials for normalization of carbonate clumped isotope measurements with new community-accepted values: the 4 ETH standards, two samples distributed by the IAEA (C1 and C2), and a synthetic carbonate produced by MERCK.
 - Standardization with ETH-1, ETH-2 and ETH-3 provides a robust framework for converting carbonate clumped isotope data to the CDES using reference materials matching the sample matrix and, thus, following the principle of equal treatment of samples and standards.
 - Data standardized with this method should be reported as I-CDES to explicitly signify that the data were normalized using these reference materials or a combination of HG/EG and at least two of the reference carbonates.
 - Carbonate standardization removes the need to apply an acid digestion fractionation factor, eliminating uncertainties due to poorly known acid fractionation factors and different preparation systems and thus reduces differences between laboratories.
 - 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, this volume).
 - Data expressed in the I-CDES are directly comparable to samples reacted at a temperature of 90°C normalized to the CDES with HG/EG. However, we emphasize that carbonate standardisation is preferred to pure HG/EG

951 normalization because it is based on traceable carbonate samples that can be
 952 measured in every laboratory. Reporting the measured compositions of carbonate
 953 reference materials together with the samples is the only way to ensure inter-
 954 laboratory consistency.

- 955 ● Robust standardization of clumped isotope measurements requires the analysis of
 956 a sufficient number of replicates of both samples and standard materials (either
 957 gases or carbonates) alongside unknowns to minimize error and obtain accurate
 958 measurements within a single laboratory.
- 959 ● Replicate analyses should be distributed in time and ideally span different
 960 correction intervals
- 961 ● When reporting data, error should include both replication error and reference
 962 frame error in proper statistical data treatment and reporting of uncertainties

963 **Appendix:**

964 **A. Converting older, carbonate-anchored Δ_{47} values to the I-CDES**

965
 966 This section describes the steps necessary to convert existing Δ_{47} measurements to the I-CDES,
 967 provided that they were either standardized using carbonate anchors or analyzed simultaneously
 968 with several carbonate anchors. This mathematically exact approach is a simpler alternative to
 969 fully reprocessing the original raw data (with the caveat that this conversion will not provide, by
 970 itself, any error estimates).

971
 972 By way of example, let us consider measurements originally standardized using ETH-1/2/3 with
 973 the nominal Δ_{47} values reported by Bernasconi et al. (2018). The “old” Δ_{47} values of these
 974 measurements are noted $^{\text{old}}\Delta_{47}$, and we wish to compute the “new” Δ_{47} values, noted $^{\text{new}}\Delta_{47}$, that
 975 would be obtained if the same data were standardized to the I-CDES.

976
 977 Both old and new Δ_{47} values are derived from the same set of raw measurements using affine
 978 relationships of the form:

979

$$\Delta_{47}^{\text{old}} = x_1 + y_1 \delta^{47} + z_1 \Delta_{47}^{\text{raw}}$$

980 (A.1)

981

982 (A.2) $\Delta_{47}^{new} = x_2 + y_2\delta^{47} + z_2\Delta_{47}^{raw}$

983

984 We can rearrange the above equations to express Δ_{47}^{new} as

985 a function of δ^{47} and Δ_{47}^{old} :

986 (A.3) $\Delta_{47}^{new} = a + b\delta^{47} + c\Delta_{47}^{old}$

987

988

989 Computing the numerical values of (a,b,c) is thus all that is required to compute Δ_{47}^{new} for any

990 sample whose (δ^{47} , Δ_{47}^{old}) values are known. This computation only requires knowing (δ^{47} , Δ_{47}^{old}

991 , Δ_{47}^{new}) for three different anchors, for instance ETH-1/2/3. In matrix form, eq. (A.3) then

becomes:

993

994 (A.4) Thus:
$$\begin{pmatrix} 1 & \delta_{(ETH1)}^{47} & \Delta_{47(ETH1)}^{old} \\ 1 & \delta_{(ETH2)}^{47} & \Delta_{47(ETH2)}^{old} \\ 1 & \delta_{(ETH3)}^{47} & \Delta_{47(ETH3)}^{old} \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} \Delta_{47(ETH1)}^{new} \\ \Delta_{47(ETH2)}^{new} \\ \Delta_{47(ETH3)}^{new} \end{pmatrix}$$

996

997 (A.5)
$$\begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} 1 & \delta_{(ETH1)}^{47} & \Delta_{47(ETH1)}^{old} \\ 1 & \delta_{(ETH2)}^{47} & \Delta_{47(ETH2)}^{old} \\ 1 & \delta_{(ETH3)}^{47} & \Delta_{47(ETH3)}^{old} \end{pmatrix}^{-1} \begin{pmatrix} \Delta_{47(ETH1)}^{new} \\ \Delta_{47(ETH2)}^{new} \\ \Delta_{47(ETH3)}^{new} \end{pmatrix}$$

998

1000

1001 In this example, the Δ_{47}^{old} and Δ_{47}^{new} values are the old and new nominal values of ETH-1/2/3. If

1002 the δ^{47} values are defined as usual by reference to a working gas, (a,b,c) will vary when different

1003 working gases are used. However, the above equations remain valid if δ^{47} is defined instead by

1004 reference to a fixed, hypothetical CO₂ composition, e.g., stochastic VPDB-CO₂ ($\delta^{13}C_{VPDB} = 0 \text{ ‰}$;

1005 $\delta^{18}O_{VSMOW} \approx 41.5 \text{ ‰}$; $\Delta_{47} = 0 \text{ ‰}$, $R^{47} = 4.834 \times 10^{-5}$). In that case, numerical values of the

1006 parameters (a,b,c) can be determined once and then used to compute Δ_{47}^{new} for any unknown

1007 sample based only on its Δ_{47}^{old} and δ^{47} values (the latter being defined relative to VPDB-CO₂ and

1008 computed by applying an acid ¹⁸O/¹⁶O fractionation factor of 1.01025 to said sample).

1009 Importantly, this particular transformation applies to all data sets originally standardized in the
1010 reference frame defined by the “old” nominal values of ETH-1/2/3.

1011

1012 For instance, the relationship linking the ETH-1/2/3 reference frame of Bernasconi et al. (2018)
1013 to the I-CDES is defined by:

1014

1015

1016 (A.6)

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} 1 & 0.010 & 0.258 \\ 1 & -28.375 & 0.258 \\ 1 & 0.538 & 0.691 \end{pmatrix}^{-1} \begin{pmatrix} 0.2052 \\ 0.2085 \\ 0.6132 \end{pmatrix} = \begin{pmatrix} -0.037997 \\ -0.000182 \\ 0.942590 \end{pmatrix}$$

1017

1018

1019 Thus:

1020

$$1021 \quad (A.7) \quad \Delta_{47}^{\text{new}} = -0.037997 - 0.000182 \delta^{47} + 0.942590 \Delta_{47}^{\text{old}}$$

1022

1023

1024

1025

1026 In this case, it is clear that the conversion from the old reference frame to the new one is not very
 1027 sensitive to δ^{47} values: for unknown samples with δ^{47} values within ± 6 ‰ of ETH-1 (or
 1028 stochastic VPDB-CO₂), the effect of the second term in Eq. (A.7) is less than 1 ppm, and less
 1029 than 3 ppm for unknowns within ± 18 ‰ of ETH-1. In such cases, the conversion may be
 1030 simplified as a simpler affine transformation, akin to a more traditional two-point normalization
 1031 (e.g., VSMOW-VSLAP standardization):

1032

$$1033 \quad (A.8) \quad \Delta_{47}^{\text{new}} = 0.942590 \Delta_{47}^{\text{old}} - 0.037997$$

1034

1035 For instance, to convert the Δ_{47}^{old} value of ETH-4 reported by Bernasconi et al. (2018) to the I-
 1036 CDES, we only need to know that $\delta^{47}_{(\text{ETH4})} = -28.8$ ‰ and $\Delta_{47}^{\text{old}} = 0.507 \pm 0.004$ ‰. The Δ_{47}^{new}
 1037 value predicted by eq. (A.7) is then 0.445 ± 0.004 ‰, to be compared with the independently
 1038 constrained values reported here in Table 1 (0.450 ± 0.002 ‰) and Table 2 (0.451 ± 0.001 ‰).

1039

1040 The above computation could also be performed using any arbitrary set of three carbonate
 1041 materials whose $(\delta^{47}, \Delta_{47}^{\text{old}}, \Delta_{47}^{\text{new}})$ values are known, provided that they span a wide enough
 1042 range in δ^{47} and Δ_{47} . This is true even if the carbonates in question were not originally used to
 1043 standardize the raw data, as would be the case for CO₂-standardized measurements. In the case
 1044 where only two suitable carbonate standards X and Y are available, an acceptable approach

1045 would be to neglect effects (equivalent to setting the value of b to zero in eq. (A.3)) by solving
 1046 the following equation:

1047

1048 (A.9)
$$\begin{pmatrix} a \\ c \end{pmatrix} = \begin{pmatrix} 1 & \Delta_{47(X)}^{\text{old}} \\ 1 & \Delta_{47(Y)}^{\text{old}} \end{pmatrix}^{-1} \begin{pmatrix} \Delta_{47(X)}^{\text{new}} \\ \Delta_{47(Y)}^{\text{new}} \end{pmatrix}$$

1049

1050

1051

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1082 **Data**

1083 All data analyzed as part of this study, along with all code used to process them, are available at
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1085

1086 **Author contributions**

1087 The community designed the study at the Paris 2017 International Clumped Isotope Workshop.
1088 S.M.B. prepared materials, gathered results and wrote the first draft of the manuscript. M.D.
1089 created all code and conducted all analysis of the results. S.M.B., M.D., K.D.B., N.M., and M.B.
1090 organized the effort and contributed to early drafts. All authors contributed to the analyses and
1091 curation of data shared in this study. All authors contributed to the final version of the
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1094 **References**

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