

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

S.M. Bernasconi¹, M. Daëron², K.D. Bergmann³, M. Bonifacie⁴, A.N. Meckler⁵, H.P. Affek⁶, N. Anderson³, D. Bajnai⁷, E. Barkan⁶, E. Beverly^{8†}, D. Blamart², L. Burgener⁹, D. Calmels^{4†}, C. Chaduteau⁴, M. Clog¹⁰, B. Davidheiser-Kroll¹¹, A. Davies^{12††}, F. Dux^{13†}, J. Eiler¹⁴, B. Elliott¹⁵, A. C. Fetrow¹¹, J. Fiebig⁷, S. Goldberg³, M. Hermoso^{4,23}, K.W. Huntington¹⁶, E. Hyland⁹, M. Ingalls^{14†}, M. Jaggi¹, C.M. John¹², A. B. Jost³, S. Katz⁸, J. Kelson⁸, T. Kluge^{12†}, I.J. Kocken¹⁷, A. Laskar¹⁸, T.J. Leutert^{5†}, D. Liang¹⁸, J. Lucarelli¹⁵, T. J. Mackey^{3†}, X. Manganot^{4,14}, N. Meinicke⁵, S.E. Modestou⁵, I.A. Müller¹⁷, S. Murray¹⁹, A. Neary⁸, N. Packard⁸, B.H. Passey⁸, E. Pelletier⁸, S. Petersen⁸, A. Piasecki^{5††}, A. Schauer¹⁶, K.E. Snell¹¹, P.K. Swart²⁰, A. Tripathi¹⁵, D. Upadhyay¹⁵, T. Vennemann²¹, I. Winkelstern^{8††}, D. Yarian⁸, N. Yoshida^{22,24}, N. Zhang²², M. Ziegler¹⁷

¹Geological Institute, ETH Zürich, Sonneggstrasse 5, 8092 Zürich, Switzerland

²Laboratoire des Sciences du Climat et de l'Environnement, LSCE/IPSL, CEA-CNRS-UVSQ, Université Paris-Saclay, Orme des Merisiers, F-91191 Gif-sur-Yvette, France

³Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

^{3†}now at Earth and Planetary Sciences, University of New Mexico, Albuquerque, New Mexico, USA

⁴Université de Paris, Institut de Physique du Globe de Paris, CNRS, F-75005 Paris, France

^{4†}now at Geosciences Paris Sud (GEOPS), Université Paris-Saclay, CNRS, 91405 Orsay, France

⁵Bjerknes Centre for Climate Research and Department of Earth Science, University of Bergen, Bergen, Norway

^{5†}now at Max Planck Institute for Chemistry, Mainz, Germany; thomas.leutert@mpic.de

^{5††}now at Department of Earth Sciences, Dartmouth College, Hanover, NH, USA

⁶Institute of Earth Sciences, Hebrew University of Jerusalem, Jerusalem, Israel

⁷Institute of Geosciences, Goethe University Frankfurt, Frankfurt am Main, Germany

⁸Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, Michigan, USA

^{8†}now at Department of Earth and Atmospheric Sciences, University of Houston, Houston, Texas, USA

^{8††}now at Geology Department, Grand Valley State University, Allendale, Michigan, USA

⁹Marine, Earth and Atmospheric Sciences, North Carolina State University, Raleigh, USA

¹⁰Scottish Universities Environmental Research Centre (SUERC), Glasgow, Scotland

¹¹University of Colorado Boulder, Boulder, Colorado, USA

This is the author manuscript accepted for publication and has undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the [Version of Record](#). Please cite this article as [doi: 10.1029/2020GC009588](https://doi.org/10.1029/2020GC009588).

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37 ¹²Imperial College, London, UK

38 ^{12†}now at Karlsruher Institut für Technologie KIT

39 ^{12††}now at Stockholm University

40 ¹³School of Geography, University of Melbourne, Australia

41 ^{13†}now at School of Earth and Life Sciences, University of Wollongong, Australia

42 ¹⁴Geological and Planetary Sciences, California Institute of Technology, Pasadena, California,
43 USA

44 ^{14†}now at Department of Geosciences, The Pennsylvania State University, University Park, PA,
45 USA

46 ¹⁵Department of Earth, Planetary, and Space Sciences, University of California Los Angeles, Los
47 Angeles, CA, USA

48 ¹⁶University of Washington, Seattle, Washington, USA

49 ¹⁷Department of Earth Sciences, University of Utrecht, Utrecht, Netherlands

50 ¹⁸Institute of Earth Sciences, Academia Sinica, Taipei, Taiwan

51 ¹⁹Macquarie University, Australia

52 ²⁰ Department of Marine Geosciences, Rostiel School of Marine and Atmospheric Sciences,
53 University of Miami, Miami, FL, USA

54 ²¹Institute of Earth Surface Dynamics, University of Lausanne, Lausanne, Switzerland

55 ²²Earth-Life Science Institute, Tokyo Institute of Technology, Tokyo, Japan

56 ²³Univ. Littoral Côte d'Opale, Univ. Lille, CNRS, Laboratoire d'Océanologie et de Géosciences
57 (UMR 8187 LOG), 62930 Wimereux, France.

58 ²⁴National Institute of Information and Communications Technology, Tokyo, Japan

59

60 Corresponding authors: Stefano M. Bernasconi (stefano.bernasconi@erdw.ethz.ch) Mathieu
61 Daëron (daeron@lsce.ipsl.fr)

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63 Key Points:

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

70

71

72 Abstract

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

90 1 Introduction

91 Carbonate clumped isotope (Δ_{47}) thermometry is the most developed branch of the rapidly
92 evolving field of clumped isotope geochemistry. Given the broad range of applications in Earth
93 Sciences (e.g. Affek & Eiler, 2006; Eagle et al., 2010; Ferry et al., 2011; Ghosh, Adkins, et al.,
94 2006; Ghosh, Garzzone, et al., 2006; Grauel et al., 2013; Guo & Eiler, 2007; Huntington et al.,
95 2011; Passey & Henkes, 2012, Dale et al, 2014, Manganot et al., 2018, Veillard et al, 2019) and
96 the improvement of analytical methods including automation (Bernasconi et al., 2013, 2018;
97 Defliese & Lohmann, 2015; Dennis et al., 2011; Fiebig et al., 2019; Ghosh, Adkins, et al., 2006;
98 He et al., 2012; Hu et al., 2014; Huntington et al., 2009; Meckler et al., 2014; Müller, Fernandez,
99 et al., 2017; Passey et al., 2010; Petersen et al., 2019; Petersen et al., 2016; Schmid &
100 Bernasconi, 2010, Adlan et al, 2020), the last 5-10 years have seen an increasing number of
101 laboratories implementing this technique. The great potential of this thermometer can only be
102 fully exploited if precision and accuracy are sufficient to resolve differences of a few degrees in
103 formation temperatures. In addition, widely available reference materials that match the sample
104 matrices are necessary so that data can be robustly compared across laboratories (Meier-
105 Augenstein & Schimmelmann, 2019). Currently the situation in the field of carbonate clumped
106 isotope geochemistry is far from satisfactory. Published values for the ETH reference materials,
107 the only carbonates that have been recently measured in many different laboratories worldwide,
108 differ by up to 0.053 ‰ (see Bernasconi et al. 2018, Thaler et al. 2020 for recent comparisons).
109 For paleoclimate applications, however, a repeatability across laboratories of 0.01 ‰ or better is
110 a necessary goal for meaningful data comparison. This clearly calls for better standardization
111 procedures to improve laboratory comparability.

112 The data normalization scheme currently used in clumped isotope geochemistry of
113 carbonates in many laboratories is based on the comparison of the composition of the CO_2
114 liberated from carbonates by reaction with phosphoric acid with that of a set of CO_2 gases with
115 different bulk and clumped isotope compositions (Dennis et al., 2011). These gases are prepared

116 either by heating CO₂ at 1000 °C (heated gases; HG) or by CO₂ equilibration with water at low
117 temperatures (equilibrated gases at *e.g.* 25 °C, 50 °C; EG). 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 isotopic composition. Early comparisons of Δ_{47} CDES values for carbonates analyzed in
127 different laboratories and corrected with HG/EG normalization were promising (Dennis et al.,
128 2011). While Bonifacie et al. (2017) reported similar Δ_{47} CDES values for nine dolomite samples
129 covering a range of almost 0.4 ‰ measured 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 analyzed both at Caltech and WHOI laboratories,
132 compared to when they were using HG/EG normalization. Such recurrent cases of poor inter-
133 laboratory reproducibility (see also Bernasconi et al., 2018 and Thaler et al., 2020) suggest that
134 there are still unexplained differences in the results among laboratories (see Petersen et al. (2019)
135 for a recent review).

136 Apart from preservation problems, two known issues still limiting the reliability of this
137 method to yield accurate temperature reconstructions are: [1] the lack of internationally
138 recognized carbonate reference materials for a precise inter-laboratory calibration, and [2] that
139 published Δ_{47} -temperature calibrations produced in different laboratories have differed in both
140 temperature dependence (slope) and absolute value (intercept). Possible reasons for the
141 differences in slopes and intercepts of the Δ_{47} temperature dependence have been widely
142 discussed in the literature (*e.g.* Kluge et al, 2015; Bonifacie et al., 2017; Daëron et al., 2016;
143 Fernandez et al., 2017; Katz et al., 2017; Kelson et al., 2017; Petersen et al., 2019; Schauer et al.,
144 2016). Discrepancies have been attributed to analytical artefacts such as CO₂-acid re-
145 equilibration at different acid digestion temperatures (see Wacker et al. 2013; Swart et al., 2019,
146 for a recent discussion) and to slight pressure imbalances between sample and reference gas
147 (Fiebig et al., 2016). Other factors proposed to influence the calculated slopes of the calibrations
148 are the limitations of the datasets used in the individual studies, in particular in terms of the
149 number of samples and replicates and of the temperature range covered by the available samples
150 (Bonifacie et al., 2017; Fernandez et al., 2017). However, the discrepancies in the intercepts of
151 the calibrations, for example between Kelson et al. (2017) and Peral et al. (2018), and a generally
152 poor laboratory comparability remain problems that could be mitigated by using a more robust
153 standardization method.

154 Petersen et al. (2019), in a recent effort to resolve differences in calibrations, compiled
155 raw data of a number of published temperature calibrations and recalculated them all in a
156 consistent way using the revised IUPAC correction parameters to correct for the ¹⁷O abundance
157 (Daëron et al., 2016; Schauer et al., 2016). The goal was to test whether data processing
158 differences and/or the use of consistent but incorrect ¹⁷O- correction parameters in the
159 calculations were the root causes of inconsistencies. The result of this study was that differences
160 among calibrations were reduced but not eliminated by the recalculation, implying that other
161 factors must be responsible for the remaining discrepancies. These differences have pushed

162 many laboratories to use laboratory-specific calibrations performed with the same analytical
163 approach, as they at least partially take into consideration possible procedural differences
164 (Petersen et al., 2019). However, if a laboratory changes analytical procedures or has not
165 generated a robust in-house calibration, this approach is problematic. Achieving an inter-
166 laboratory reproducibility at the level of accuracy necessary for meaningful interpretations of the
167 observed variations is a requirement for Δ_{47} thermometry to reach its potential as a mature
168 analytical method with broad acceptance and quantitative usefulness.

169 While the definition of the CDES was a major milestone (Dennis et al., 2011), a known
170 problem with this approach is that while the CO₂ standard gases equilibrated at known
171 temperature (HG or EG) can be confidently used for correction of mass spectrometric
172 fractionations/nonlinearities and for effects of the purification procedures, they cannot account
173 for the effects of the phosphoric acid reaction on the composition of the produced CO₂. Among
174 the factors responsible for discrepant calibrations and laboratory comparability, two important
175 ones cannot be tested with a gas-based standardization: (1) the absolute value and temperature
176 dependence of the phosphoric acid fractionation factor (see Petersen et al., 2019 for a recent
177 compilation) and (2) possible CO₂ equilibration effects during acid digestion of the sample.
178 Swart et al. (2019) presented evidence that equilibration of CO₂ with water or hot metal surfaces
179 during phosphoric acid reaction and transfer of the CO₂ to the mass spectrometer could be a
180 factor leading to the alteration of the apparent temperature dependence of clumped isotopes in
181 carbonates and on the absolute value of calculated Δ_{47} . As many laboratories use custom built
182 extraction lines with different designs and volumes of tubing and of acid vessels, these factors
183 are impossible to precisely quantify for each laboratory and may further contribute to inter-
184 laboratory discrepancies.

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

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

206 comparison exercise (InterCarb) to evaluate the benefits and drawbacks of a carbonate-based
 207 standardization approach as an alternative to the use of gas standards.

208
 209 The primary goal of this study was to test whether the exclusive use of carbonate
 210 reference materials as a substitute for heated and equilibrated gases can minimize inter-
 211 laboratory discrepancies and provide an alternative to the measurement of heated and
 212 equilibrated gases for the entire community. This is particularly important because of the
 213 increasing number of laboratories using commercial small-sample automated devices which
 214 cannot easily be standardized using the HG-EG approach. The InterCarb exercise also provides
 215 an opportunity to define the best community-derived consensus Δ_{47} values for the ETH standards
 216 of Meckler et al. (2014). Although these standards are already used in many laboratories, their
 217 current nominal Δ_{47} values are based on measurements from the ETH laboratory only. The
 218 InterCarb exercise can similarly establish community accepted values for other common
 219 carbonate reference materials, some of which have been in use for several years, in order to
 220 provide the community with a self-consistent set of carbonate reference materials with a broad
 221 range of bulk and clumped isotope compositions.

222 1.1. Nomenclature and data processing

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

$$226 \Delta_{47} = R^{47} / R^{47*} - 1$$

227
 228 where R₄₇ is the ratio of the abundances of the set of minor isotopologues with mass 47
 229 (mostly ¹³C¹⁸O¹⁶O and trace amounts of ¹²C¹⁷O¹⁸O and ¹³C¹⁷O₂) divided by the abundance of the
 230 most abundant isotopologue with mass 44 (¹²C¹⁶O₂). The stochastic ratio R_{47*} is calculated
 231 using the measured abundance of ¹³C and ¹⁸O and measured or calculated abundance of ¹⁷O in
 232 the sample (Affek & Eiler, 2006). According to the IUPAC guidelines the formula does not
 233 include the factor 1000 (Coplen, 2011; though Δ_{47} is commonly reported in units of per mil,
 234 which implies multiplication by a factor of 1000). Also, we omit here the classically included
 235 terms involving R^{45*} and R^{46*}, which are assumed to be zero by definition when computing $\delta^{13}\text{C}$
 236 and $\delta^{18}\text{O}$, and in practice never exceed ± 0.00002 ‰ in our calculations (Daeron et al. 2016). The
 237 measured abundance of isotopologues with m/z 47 in the sample with respect to the working gas
 238 (WG) in the mass spectrometer is reported in the traditional delta notation as:

$$239 \delta^{47} = R^{47} / R_{WG}^{47} - 1$$

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

244

245 The CO₂ gas-based standardization scheme for clumped isotope thermometry in
246 carbonates relies on a set of CO₂ standard gases with different bulk compositions ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$,
247 leading to different δ^{47}), preferably chosen by the user to encompass the δ^{47} values of unknown
248 samples that have been (1) heated at 1000 °C to reach a near-stochastic distribution of all
249 isotopologues, or (2) equilibrated with water at low temperature to reach equilibrium
250 enrichments in the mass-47 isotopologues (Dennis et al., 2011). The heated gases, having a near-
251 stochastic distribution of the heavy isotopes among all isotopologues, define the zero point of the
252 CDES scale, through the assumption that at 1000 °C these gases achieve a $\Delta_{47} = 0.0266$ ‰, and
253 the water-equilibrated gases define a second, generally higher point on this scale (e.g., at 25 °C
254 $\Delta_{47} = 0.9196$ ‰). The theoretical values linking measurements to theory were calculated by
255 Wang et al. (2004) and revised by Petersen et al. (2019). A wide range in δ^{47} values of gases
256 used for normalization is generally chosen to allow for accurate correction for an apparent
257 dependence of Δ_{47} on δ^{47} , which is caused by inaccurate pressure-dependent background
258 corrections on the m/z 47 collector observed on many instruments (Bernasconi et al., 2013; He et
259 al., 2012). The large range in Δ_{47} (i.e., 25 °C, 1000 °C), on the other hand, is necessary to correct
260 for scale compression caused by processes of scrambling and molecule recombination in the
261 source of the mass spectrometer or elsewhere in the sample preparation, transfer lines and/or the
262 capillaries (Dennis et al., 2011, Swart et al., 2019). With properly chosen CO₂ standard gases
263 with widely varying δ^{47} values it is possible to cover the entire range of natural carbonate
264 compositions, avoiding extrapolations in the δ^{47} vs. Δ_{47} compositional space (Fig. 1). Note that
265 with measurement errors (typically no better than 0.010 ‰) being relatively large compared to
266 the natural compositional range (less than 0.5 ‰; Fig. 1), the large (0.9 ‰) difference in Δ_{47} of
267 the CO₂ standard gases minimizes errors introduced by uncertainties resulting from the
268 measurement of HG and EG.

269 Meckler et al. (2014) attempted to achieve a similar framework as the CO₂ gas-based
270 standardization but with carbonate standards. They described four carbonates that were
271 developed at ETH Zürich to serve as replacements for HG's and EG's and demonstrated that
272 good long- and short-term reproducibility can be achieved using only carbonates for data
273 correction. Bernasconi et al. (2018) discussed in detail these standards and postulated, based on a
274 limited inter-laboratory dataset, that carbonate standardization should generally improve inter-
275 laboratory data comparability. This claim seems arguably strengthened by the results of
276 Meinicke et al. (2020), Peral et al. (2018), Piasecki et al. (2019), Kele et al. (2015) as
277 recalculated by Bernasconi et al. (2018), and Jautzy et al., (2020). The first three studies produced
278 independent foraminifera-based the fourth a travertine and the fifth a synthetic carbonate-based
279 Δ_{47} -temperature calibration anchored to the same set of carbonate standards. These studies
280 yielded statistically indistinguishable slopes and intercepts despite the use of independent sample
281 sets and in the case of Peral et al. (2018), a different analytical system. In addition, a reanalysis
282 of samples from five previous calibrations by Anderson et al. (2021) using carbonate
283 standardization revealed no significant differences in temperature dependence of Δ_{47} between the
284 different sample sets. This, solved a long standing debate about variations in slope among
285 calibrations

286

287 A possible limitation of carbonate standardization is that available carbonates have a
288 smaller range in δ^{47} and, perhaps more importantly, a smaller range in Δ_{47} values than what is

289 achievable with heated and equilibrated gases. In some specific cases, standardization procedures
290 require extrapolation to compositions that are not within the δ^{47} - Δ_{47} space created by carbonate
291 standards (Fig. 1). In addition, the range of Δ_{47} values for carbonates is only on the order of 0.5
292 ‰ between 0 and 1000 °C. The smaller range in Δ_{47} compared to HG's and EG's requires higher
293 precision and also a larger number of replicates of both standards and samples. Daëron (2021)
294 and Kocken et al., 2019 suggest ~50:50 ratio of standard to sample replicates to keep
295 standardization errors small.

296 **1.2. InterCarb goals and design**

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

- 301
- 302 1. Is it possible to produce consistent carbonate clumped isotope measurements across
303 laboratories using carbonate reference materials exclusively? In other words, does the
304 observed inter-laboratory scatter in Δ_{47} values match that expected from intra-laboratory
305 analytical precision?
- 306 2. How well does the carbonate standardization approach perform when extrapolating
307 beyond the δ^{47} - Δ_{47} compositional space sampled by a set of carbonate reference
308 materials?
- 309 3. Do carbonate reference materials fully correct effects arising from different reaction
310 temperatures, sample preparation protocols, and analytical equipment?
- 311 4. Can we define a self-consistent set of widely available reference materials with
312 community-agreed compositions accurately anchored to the CDES scale?
- 313 5. Does the use of carbonate reference materials for standardization improve the inter-
314 laboratory reproducibility compared to using HG's and EG's?
- 315

316

317 **1.3 Approach**

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

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

333

334 2 Materials and Methods

335 2.1. Sample description

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

339 IAEA-C1 (marble from Carrara, Italy) is distributed by the International Atomic Energy Agency
340 (IAEA) as a mechanically crushed and milled product with grains ranging from 1.6 to 5 mm. All
341 50 g provided were ground and thoroughly homogenized in a ball mill at ETH Zürich to a grain
342 size of less than 100 μm and transferred in 0.5 g aliquots to plastic vials for distribution. Nishida
343 and Ishimura (2017) found that IAEA 603, which was produced from the same coarse marble as
344 IAEA C-1, was isotopically inhomogeneous. Whitish grains (1–2 per 100 grains; grain weight,
345 8–63 μg) were significantly depleted in ^{18}O and ^{13}C compared to translucent grains. In this study
346 we found no evidence of inhomogeneity in Δ_{47} for sample aliquots of 80–110 μg after the original
347 material was ground in the ball mill.

348

349 IAEA-C2 is a freshwater travertine from Bavaria distributed by IAEA as a powder which was
350 treated identically to IAEA-C1. XRD analysis shows it to be calcite (supplementary Fig. S1).

351

352 ETH-4 is a commercially available synthetic calcium carbonate (Riedel-De Haën; calcium
353 carbonate Puriss. p.a.; Lot No. 30800) determined to be calcite by XRD (supplementary Fig. S2
354 with intermediate formation temperature and the same bulk isotope composition as ETH-2 (see
355 Bernasconi 2018 for details).

356

357 MERCK (Catalog No. 1.02059.0050; lot no. B1164559 515) is an ultra-pure, commercially
358 available synthetic calcium carbonate determined to be calcite by XRD (Müller et al., 2019) and
359 was chosen for its very low $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of approximately -42.2 ‰ and -15.5 ‰
360 (VPDB), respectively. This sample represents an extreme case of extrapolation from the δ^{47} - Δ_{47}
361 space defined by the anchor materials (Fig. 2). The same product was recently used to prepare
362 the carbon isotope reference material USGS44 by Qi et al. (2020) which, after careful
363 determination of its Δ_{47} could be used as a substitute for the aliquots of MERCK distributed for
364 this study.

365 2.1. Instrumentation

366

367 The reported data were produced with a variety of preparation systems including custom
368 built (13 laboratories) and commercial systems (11 laboratories; Protium MS IBEX,
369 ThermoFisher Scientific Kiel IV device and Nu Instruments Nucarb). Reaction temperatures
370 were generally 90 °C for “large-sample” custom preparation systems and 70 °C for the Kiel and
371 the NuCarb. Four mass spectrometer types were used: Thermo Fisher Scientific MAT253 and
372 253Plus, Nu Instruments Perspective, and Elementar Isoprime 100. All participants contributed
373 results they considered to be of “publication-grade” quality, based on their existing quality-
374 control procedures.

375

376 **2.3 Clumped isotope compositions of the ETH anchor materials**

377 The clumped isotope compositions of the four ETH reference materials relative to the
378 CO₂ reference frame CDES were first reassessed based on new data provided by 10 laboratories
379 that also provided HG and EG data measured during the same sessions as the ETH reference
380 materials. The data were processed with the same Python script used for the carbonate data in
381 order to avoid any differences in data processing (see section 2.4).

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

401 **2.4 Data processing, correction and error assessment**

402 It should be stressed that the InterCarb experiment, by design, is not intended to grade the
403 analytical performance of individual laboratories. Each participating laboratory (or mass
404 spectrometer, in the case of laboratories with several instruments) was thus randomly assigned an
405 anonymous identifying number. Within each laboratory, analyses were grouped in different
406 analytical sessions defined by the participants themselves. An analytical session is generally
407 defined by a time in which the behavior of the analytical system (preparation system, source
408 tuning, backgrounds, isotope scrambling in the source) is considered to be similar. The database
409 record of each analysis consists of a laboratory identifier, a session identifier, an analysis

410 identifier, the name of the analyzed sample, the mass spectrometer model, the acid reaction
 411 temperature, the mass of the reacted carbonate, and background-corrected δ^{45} , δ^{46} and δ^{47} values.

412
 413 The only instrumental corrections to the raw data applied independently by each
 414 participating laboratory were background corrections (“Pressure Baseline Correction” or PBL) to
 415 the ion currents/voltages (Bernasconi et al., 2013; He et al., 2012, Fiebig et al., 2016; Fiebig et
 416 al., 2019). The PBL is strongly dependent on instrument design (it is not observed in some
 417 instruments) and configuration, and varies temporally depending on many factors. This
 418 correction, therefore, can only be carried out by each participating laboratory according to its
 419 own established procedures and monitoring.

420
 421 To avoid artefacts arising from different calculation/standardization procedures, rounding
 422 errors, and ^{17}O correction parameters, raw data from all laboratories were processed by a single
 423 Python script (<http://doi.org/10.5281/zenodo.4314448>) based on data reduction,
 424 standardization and error propagation methods described in detail in the companion paper
 425 (Daëron, 2021). Here we briefly summarize these calculations.

426
 427 Session-averaged, background-corrected δ^{45} and δ^{46} values for each of the three anchor
 428 samples were first used to calculate the bulk isotope composition of the working gas used in each
 429 session, 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
 430 ETH-3 (Bernasconi et al., 2018), (b) the IUPAC ^{17}O correction parameters of Brand et al. (2010),
 431 and (c) a temperature-dependent oxygen-18 acid fractionation factor between CO_2 and calcite of
 432 Kim et al. (2015). This recalculation of working gas bulk compositions avoids (small)
 433 discrepancies potentially introduced by inaccuracies in the nominal compositions of the working
 434 gases.

435
 436 Raw Δ_{47} values were computed according to:

$$\Delta_{47}^{\text{raw}} = R^{47} / R^{47*} - 1$$

437
 438
 439 Where R^{47} is the measured ratio and R^{47*} the calculated stochastic ratio of mass 47 over
 440 mass 44 of CO_2 , assuming perfectly linear IRMS measurements and a stochastic working gas.
 441 Values are then normalized to “absolute” Δ_{47} values (noted Δ_{47}^{abs} in the equation below, and
 442 simply Δ_{47} thereafter) using session-specific relationships of the form:

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

443
 444
 445 For each session, the best-fit standardization parameters (a, b, c) are computed from an
 446 unweighted least-squares regression, treating Δ_{47}^{raw} as the response variable, only considering the
 447 three anchor samples ETH-1, ETH-2, and ETH-3. Note the advantage of this form over that in
 448 Dennis et al. 2011 is the ability to have three standards with distinct Δ_{47} values whilst being able

449 to solve for b (compositional nonlinearity) (Daëron et al. 2016). Absolute Δ_{47} values are then
450 computed for all replicates within that session. Standardization parameters for all sessions are
451 listed in Table 2.

452

453 Throughout this study, the analytical error assigned to each individual raw Δ_{47} analysis is
454 equal to the pooled “external” repeatability of raw Δ_{47} measurements of anchors and unknowns
455 within each session. In the figures and tables, final measurement uncertainties are reported as
456 standard errors and/or 95 % confidence limits, considering fully-propagated errors taking into
457 account reference frame corrections. In Figures 2 and 4, different types of error bars are used to
458 represent analytical errors only considering uncertainties in the analyses of a given sample or the
459 full uncertainty considering standardization uncertainties (the “autogenic” errors of Daëron,
460 2021). In both cases, the analytical error assigned to each individual raw Δ_{47} analysis is equal to
461 the pooled “external” repeatability of raw Δ_{47} measurements for all samples (anchors and
462 unknowns) within each session. This treatment of error is a new approach that more fully
463 accounts for error in both the sample measurement and reference frame.

464

465 **3 Results and Discussion**

466 **3.1 Redetermination of nominal Δ_{47} values for the ETH standards relative to heated 467 and equilibrated CO₂ gases**

468 The weighted averages of the 4 standards (projected to 90 °C for the reactions at 25 and
469 70°C using the acid temperature correction suggested by Petersen et al. 2019), comprising 873
470 analyses of the carbonate standards and 946 heated and equilibrated gases from 10 different
471 laboratories, are reported in Table 1 and Fig 4. The large number of analyses and the appropriate
472 consideration of the errors on the anchors (CO₂ gas analyses) distinguishes this effort from
473 previous work and allow a robust redetermination of the accepted values of the ETH reference
474 materials with 1SE uncertainties of 2 ppm or less.

475 When compared with Bernasconi et al. (2018), the average Δ_{47} values ETH-1 and ETH-2,
476 projected back to 25 °C (+0.088 ‰), are respectively 0.035 and 0.040 ‰ more positive than the
477 original values, whereas ETH-3 increases by 0.010 and ETH-4 by 0.031 ‰. A similar positive
478 offset of Δ_{47} compared to the values reported in Bernasconi et al. (2018) has also been reported
479 in Fiebig et al. (2019), Bajnai et al. (2020) and Thaler et al. (2020).

480 The observation that these changes in nominal values decrease as Δ_{47} increases suggests a
481 simple hypothesis to explain this discrepancy: in the original study of Meckler et al. (2014), the
482 carbonate samples and the heated/equilibrated CO₂ gases experienced different analytical
483 procedures. The HGs were measured as large samples at constant beam intensity through a
484 different capillary than the carbonates, which were measured using the microvolume and a
485 decreasing beam. The potential effects of partial re-equilibration for the heated gases in the gas
486 preparation line or in the capillaries of the mass spectrometer could be significant whereas it
487 would be minuscule for the gases equilibrated at 25°, leading to an overestimation of Δ_{47} scale
488 compression and thus of the stretching applied to the Δ_{47} scale towards theoretical values. The
489 observed changes in apparent ETH-1 and ETH-2 Δ_{47} values may therefore simply reflect partial

490 re-equilibration of heated gases at the time of measurements at ETH (and reported in Meckler et
491 al., 2014), increasing their values in the original study by about 0.05 ‰ (Fig. 3).

492 It has been suggested previously that ETH-1 and ETH-2 should be indistinguishable in
493 Δ_{47} and close to stochastic distribution (Müller, Violay, et al., 2017). This is because Δ_{47} values
494 of ETH-1 and ETH-2, originally heated to 600 °C, were found to be higher by only around 0.006
495 ‰ from the same carbonates heated at 1000 °C to achieve stochastic distribution of the isotopes.
496 However, additional test measurements in multiple laboratories of samples heated at >1000 °C
497 are necessary to confirm this observation.

498
499 One laboratory (Laboratory F) did however observe a large difference in the value for
500 ETH-1 and ETH-2, although their values of ETH-3 and ETH-4 are similar to other laboratories.
501 The reason for these inconsistencies is probably due to the fact that ETH-1 was only measured
502 four times with a limited number of HG/EG, and ETH-2 and ETH-4 were not measured in the
503 same session. In addition, the laboratories with the smallest number of replicate measurements
504 have uncertainties that are systematically larger (Table 1). These results highlight the importance
505 of strict correction procedures in clumped isotope analysis. Sufficient replication of both
506 standards and samples is critical and, if insufficient, offsets can arise when comparing results
507 from different sessions. Due to these difficulties it is good practice to spread replicates of the
508 same sample in different sessions over longer periods of time to obtain accurate results and
509 follow a ~50:50 standard to sample replicate ratio.

510 Based on the results above, the difference between the average of ETH1/2 and ETH-3 is
511 reduced by 0.028 ‰, thus leading to a compression of the scale by about 5.8 % compared to the
512 values reported by Bernasconi et al. (2018). As a consequence, the slopes of published
513 temperature calibrations produced with carbonate standardization (Kele et al, 2015; Bernasconi
514 et al., 2018; Jautzy et al., 2021; Meinicke et al., 2020; Peral et al., 2018; Piasecki et al., 2019)
515 will become slightly shallower, with more positive y-intercepts. If Δ_{47} results from previous
516 publications are also recalculated with the new standard values (see section 3.4), however,
517 changes in calculated formation temperatures will be negligible. For this reason, when
518 comparing data from publications using old accepted values of the ETH standards for
519 standardization (either those published by Meckler et al. (2014) or those recalculated with the
520 IUPAC parameters by Bernasconi et al. (2018) to newer data, it is recommended to directly
521 compare the reconstructed temperatures rather than recalculating Δ_{47} . Full recalculation of old
522 measurements usually requires the availability of the entire dataset including standards and the
523 same correction procedures (e.g., averaging methods) used in the original publications (but see
524 Appendix A for an alternative calculation method).

525 **3.2 InterCarb results**

526 Results for the unknown carbonate samples were obtained from 25 mass spectrometers in
527 22 laboratories. The Δ_{47} values of the 4 unknown samples were normalized to the new
528 community-derived values of ETH-1, ETH-2, and ETH-3 of Table 1, then averaged per
529 individual analytical session and mass spectrometer (Tables 2 and 3). Mean Δ_{47} values obtained
530 for each sample in each mass spectrometer are shown in Figure 4. The details of each analytical
531 session, including the number of samples and standards measured, the isotopic composition of
532 the working standard, the scaling parameters and the internal reproducibilities (as 1SD) of the

533 individual sessions are listed in Table 2. Some laboratories reported data for only a subset of the
534 unknown samples, and both replication level and analytical reproducibility vary greatly from
535 laboratory to laboratory (Table 2).

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

540 The laboratory averages for the four unknowns show standard deviations of 0.011 ‰ for
541 ETH-4 and IAEA-C1, 0.018 ‰ for IAEA-C2 and 0.024 ‰ for MERCK, the most extreme case
542 of extrapolation (Table 3). Qualitatively, laboratories with stronger analytical constraints (i.e.
543 better intra-laboratory repeatability of Δ_{47} measurements and/or greater number of analyses)
544 generally converge towards the overall mean value for each sample (Fig. 4). This suggests that
545 the observed inter-laboratory variability is largely due to random errors that can be alleviated by
546 replication, even for laboratories with relatively large analytical errors on individual
547 measurements. It is also notable that fully propagated analytical errors that take into account
548 uncertainties in the standardization procedure can be substantially larger than the errors based on
549 the uncertainty associated with sample analyses alone, which is what is generally reported in the
550 literature. The increase in error is also related to intra-laboratory repeatability and the number of
551 standards measured. In addition, the error increases for unknown samples whose compositions
552 lie outside the “anchor triangle” defined by ETH-1/2/3. This is illustrated by the increased scatter
553 and errors associated with MERCK, the carbonate farthest from the “anchor triangle”, consistent
554 with the models of Daëron (2021, see also Kocken et al., 2019).

555 As seen in Table 2, there are stark differences in the total number of replicate analyses
556 and the typical Δ_{47} reproducibility achieved in different laboratories. As a result, final
557 uncertainties in the average Δ_{47} values of unknown samples vary considerably (Fig. 4). Inter-
558 laboratory variability is smaller among laboratories with small analytical uncertainties, and larger
559 among laboratories with few replicate analyses and/or poor analytical repeatability. If we chose
560 only laboratories that have provided data with average standard errors below 0.01 ‰ (Table 3),
561 which is within the shot-noise limits of modern IRMS instruments, inter-laboratory standard
562 deviation (1SD) becomes ≤ 9 ppm for ETH-4 (N=22), IAEA-C1(N=15) and IAEA-C2 (N=13)
563 and ≤ 0.015 ‰ for MERCK (N=11; with SE<0.0135). We note that this does not significantly
564 change the average value of the unknowns, and highlights the importance of sufficient sample
565 replication to obtain accurate results.

566 Next we may assess whether inter-laboratory discrepancies are significantly larger than
567 expected from intra-laboratory analytical uncertainties, i.e., whether we can detect the effects of
568 hypothetical unrecognized sources of scatter beyond known analytical errors.

569 In order to do so, we compute the “number-of-sigma” deviation obtained by each
570 laboratory for each unknown sample, relative to that sample’s overall weighted average value.
571 For example, the sigma-deviation for sample ETH-4 and Lab01 is equal to $(0.4477 - 0.4511) /$
572 $0.0052 = -0.66$ and that for MERCK and Lab13 is equal to $(0.5470 - 0.5135) / 0.0135 = +2.48$.
573 If the analytical errors reported in Table 3 are reasonably accurate, we expect the population of
574 sigma-deviations among all laboratories to be distributed as the canonical Gaussian distribution
575 ($\mu = 0$; $\sigma = 1$), and we can test this prediction using established statistical methods such as a
576 Kolmogorov–Smirnov test of normality (Massey, 1951). We carried out this test for two cases:

577 only considering the error of sample replication (Fig. 5, upper row) and secondly including the
 578 normalization error, (i.e. the fully propagated error (Fig. 5, lower row). If we neglect
 579 uncertainties arising from standardization (the “allogenic” errors of Daëron, 2021), the sigma-
 580 deviations are no longer normally distributed ($p = 0.003$, Fig. 5 upper-left panel). When
 581 considering fully propagated analytical errors, as shown in the lower-left panel of Figure 5, the
 582 distribution of sigma-deviations for all laboratories and all samples is statistically
 583 indistinguishable from the expected normal distribution ($p = 0.19$). Figure 5 also illustrates that
 584 neglecting standardization errors does not strongly affect the normality of sigma-deviations for
 585 IAEA-C1, which has δ^{47} and Δ_{47} values within the range covered by the three anchor samples.
 586 By contrast, sigma-deviations for unknowns with “exotic” isotopic compositions (ETH-4 and
 587 IAEA-C2 but especially MERCK) are only normally distributed if standardization uncertainties
 588 are correctly accounted for.

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

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

601 **3.3 Effects of acid reaction temperature and IRMS models**

602 Out of 25 sample preparation systems, 10 convert samples to CO_2 by acid reactions at 70
 603 °C and 14 at 90 °C. To test for the possible effect of acid temperature, a commonly discussed
 604 cause for different slopes in the published temperature calibration curves (Came et al., 2014;
 605 Fernandez et al., 2014; Swart et al., 2019), we plot the Δ_{47} values of unknowns obtained by
 606 laboratories reacting at 70 °C vs. those obtained at 90 °C (Fig. 7, Table 4). Because acid
 607 fractionation effects equally affect anchors and unknowns, carbonate-standardized results can be
 608 compared directly without acid temperature correction. Δ_{47} values averaged by acid temperature
 609 are statistically indistinguishable for all of the unknowns. This implies that relative Δ_{47}
 610 differences between CO_2 evolved from different samples are independent of acid reaction
 611 temperature within the range of experimental conditions covered here, and for a very wide range
 612 of $\Delta_{47(\text{I-CDES})}$ values spanning 0.302 ‰ (marbles) to 0.641 ‰ (carbonates formed at ambient
 613 temperatures).

614 The error-weighted results separated by mass spectrometer type and design of associated
 615 preparation lines, another postulated source of inter-laboratory disagreement (Swart et al., 2019),
 616 are shown in Figure 8 and Table 5. Out of the 22 participating laboratories, 8 use the Nu
 617 Perspective, 16 use versions of the Thermo MAT253, and one uses an Isoprime 100. Most results
 618 are statistically indistinguishable across instruments. Only IAEA-C2 yielded a significantly
 619 ($>2\sigma$) higher mean Δ_{47} value when measured on the Isoprime 100 ($\Delta\Delta_{47}$ of +0.0110 and
 620 +0.0081 ‰ vs Nu perspective and MAT253, respectively); but note that all of the Isoprime 100

621 data comes from a single laboratory. Inter-instrument differences averaged over all four samples
622 (bottom row of Table 4) remain, however, indistinguishable from zero. Thus, any potential
623 biases introduced by the use of different mass spectrometer models and/or the design of the
624 preparation line which could cause partial equilibration of the produced CO₂ with the acid and/or
625 heated metal surfaces (Swart et al., 2019) are undetectable when using carbonate
626 standardization. Sample sizes used for individual measurements ranged from 90-120 µg for the
627 Kiel IV to ~500 µg for the NuCarb individual acid vial preparation systems, and to 3-12 mg for
628 samples reacted in common acid bath custom-built extraction lines. The fact that small sample
629 measurements are carried out at 70 °C and large ones at 90 °C, also suggests that there is no
630 significant effect of sample sizes and variations in sample to acid ratios in these results.

631 **3.4. Guidelines for minimizing uncertainties in clumped isotope analyses**

632 The results of InterCarb strongly support the use of carbonate standardization for
633 clumped isotope measurements and show that it is possible to reach excellent data quality and
634 inter-laboratory consistency with instrumentation from all manufacturers and with both custom
635 built and commercially available sample preparation systems.

636 When considering all laboratories, the standard deviation of the averages for the four
637 unknowns range from 0.011 ‰ for ETH-4 to 0.024 ‰ for MERCK. The spread is still relatively
638 large, and not significantly better than that obtained by HG-EG normalization if we consider
639 either what has been reported on 4 carbonate standards for 4 laboratories in Dennis et al. (2011)
640 or the scatter in the values reported by the 10 laboratories that provided data for the re-
641 determination of the accepted values of ETH-1 to ETH-3 in this study. However, we can clearly
642 state that the large scatter is dominated by random errors and is especially influenced by the
643 laboratories with the largest errors in the individual sample reproducibility and a significantly
644 magnified normalization error induced by a small number of replicates of anchors (Fig. 4).
645 Based on these observations we present strategies to improve the repeatability within each
646 laboratory.

647 If we consider only laboratories with reported errors < 0.010 ‰ (1SE) which is a
648 desirable goal for the application of clumped isotopes in paleoclimate reconstructions, the
649 standard deviation of the result is ≤ 0.009 ‰ for the samples with no or moderate extrapolation
650 from the compositional triangle defined by the anchors. This correspond to uncertainties across
651 laboratories of approximately 3 °C at ambient temperatures. The laboratories with the smallest
652 errors are those that generally analyzed a large number of samples and standards, as seen by the
653 smaller 95 % CL errors and the small increase of the error when the normalisation error is
654 included (Fig. 4). This observation underscores the necessity of sufficient replication to produce
655 data of the quality that is required for meaningful interpretations. The number of necessary
656 replicates to reach a target temperature uncertainty can be reduced by improving the external
657 reproducibility of the measurements (see also Daëron, 2021; Bonifacie et al., 2017; Fernandez et
658 al., 2017; Kocken et al., 2019).

659 Spreading replicate sample measurements in time and over multiple analytical sessions
660 should help avoid analytical biases. The number and distribution of standards in a measuring
661 interval are also important parameters to improve reproducibility and reduce errors. This has
662 been discussed in detail by Kocken et al. (2019) and Daëron (2021) who both concluded that
663 carbonate standards with bulk and clumped-isotope compositions similar to those of unknowns
664 should be analyzed with greater frequency than the other anchors, while preserving a minimal

665 level of replication for each anchor. In this study, analyses were grouped in measurement
666 intervals, and all data were processed assuming no short-term variation in the instrumentation.
667 However, especially with "small sample approaches" (e.g. the Kiel device) relying on short (~30-
668 45 min) measurements of many replicates, one can observe short-term variations (e.g.
669 Bernasconi et al. 2018, Fig. 4). Thus a moving window correction with variable window size
670 may be desirable in these cases, likely calling for specific error propagation procedures which
671 remain yet to be defined.

672 Two important outcomes of this study are that acid reaction temperature and instrument
673 and preparation line design are not a cause for differences among laboratories when
674 standardization is based on carbonates. The lack of resolvable differences observed in our dataset
675 indicates that if preparation line differences affect Δ_{47} measurements, standardization with
676 carbonates corrects any such effects whereas HG-EG standardization may fail to do so (Swart et
677 al. 2019). Thus, when using carbonate standardization, these factors can be ignored provided the
678 carbonate standards cover a large range in Δ_{47} . Thus, following the principle of identical
679 treatment of samples and standards (Werner & Brand, 2001b) clearly reduces uncertainties
680 compared to the use of HG/EG standardization. We have to consider, however, that acid
681 digestion conditions (e.g., reaction times, temperatures) and the temperature dependence of
682 phosphoric acid fractionation (Defliese et al. 2015; Murray et al. 2016 ; van Dijk et al. 2019)
683 may differ with carbonate mineralogy, therefore possible effects on Δ_{47} could be mineral-
684 specific. For this reason, it would be highly desirable to produce reference materials for
685 dolomite, aragonite, magnesite and siderite. For dolomite, three samples were proposed by
686 Müller et al. (2019) as possible reference materials and are available upon request. Ideally it
687 would also be desirable to anchor the measurements in a carbonate absolute reference frame by
688 creating some carbonates with independently known clumped isotope compositions.

689 For InterCarb, all distributed aliquots of IAEA-C1, IAEA-C2 and MERCK originated
690 from single bottles. The IntrCarb results suggest that after milling, these carbonates were
691 homogeneous within these bottles, but we strongly recommend verifying that additional bottles
692 purchased from IAEA and MERCK are identical to the ones tested here. Nishida and Ishimura
693 (2017) found that IAEA 603, which was produced from the same coarse marble as IAEA-C1,
694 contained a minor amount of grains with different isotopic composition, thus it is recommended to
695 thoroughly mill and homogenize IAEA-C1 before use, especially for use in small-sample
696 preparation systems. Merk and ETH-4 are both very fine grained synthetic calcium carbonates,
697 and it has been suggested that the oxygen isotope composition of such fine-grained carbonates
698 could change with time due to exchange with atmospheric CO₂ (Qi et al. 2020). At the ETH
699 laboratory different aliquots of ETH-4 have been in use since 2013 and no alterations of its
700 oxygen or clumped isotope composition were observed. However we strongly recommend that
701 all standards are stored in a desiccator to reduce the chance of alteration.

702

703 Standardization errors could be reduced to some extent by increasing the range of bulk
704 composition of the anchor samples (e.g., as illustrated by Fig. 1 of *Daëron, 2021*), especially
705 when samples are measured that require significant extrapolation. A sample with an extreme
706 bulk composition like MERCK would be a useful addition as an anchor, regardless of its Δ_{47}
707 value. While with a three-anchor system, two heated standards for normalization are not strictly
708 necessary, a "heated MERCK" anchor in combination with ETH-1 would furthermore allow
709 verifying the PBL correction with greater confidence and with less replication than with ETH-2

710 (keeping in mind that small quadratic components to PBL correction might introduce a
711 significant bias over a δ^{47} range of 60 ‰, e.g., Fig. 7 from He et al., [2012]).

712
713 With InterCarb, the nominal values of the ETH standards are robustly linked to the
714 CDES, as they are now based on the average results of 10 laboratories, and are not only based on
715 the values determined at ETH in 2013. Some laboratories may still want to continue measuring
716 HG and EG to keep established laboratory procedures and/or to cover ranges in bulk
717 compositions that require large extrapolations. However, the results of InterCarb, and the
718 discussions in the literature (e.g. Petersen et al. 2019) show that with the HG/EG approach there
719 are still poorly understood interlaboratory discrepancies (as suggested by Fig. 6) which are
720 absent in the carbonate-based normalization (see Fig 5). For this reason, it is of paramount
721 importance that several of the InterCarb reference carbonates are incorporated in the laboratory
722 procedures to ensure interlaboratory data compatibility. The use of matrix-matched reference
723 materials is necessary so that delta values can be unambiguously compared on a like-for-like
724 basis (see Meier-Augenstein and Schimmelmann, 2019 for a recent discussion).

725 For laboratories using large sample common-acid bath methodologies and preferring gas-
726 based data correction, we recommend that in addition to HG/EG a minimum of two of the
727 InterCarb reference materials (or in-house standards with values calibrated to ETH standards)
728 should be measured within the same analytical sessions as the samples and used in the data
729 correction scheme. We recommend choosing two standards with a large difference in Δ_{47} , for
730 example ETH-1 and ETH-3 or ETH-2 and IAEA-C2, depending on the bulk composition of the
731 unknown samples (see Fig. 1). In the case of samples with very low δ_{47} values we additionally
732 recommend the use of MERCK.

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

738 Achieving the best possible reproducibility and accuracy is especially important when
739 reconstructing small temperature changes for the reconstruction of climate change and/or the
740 study of high temperature processes where the sensitivity of the clumped isotope thermometer is
741 low. We emphasize that the improvements in interlaboratory comparability that can be achieved
742 with carbonate standardisation, coupled with the reductions in the uncertainties of the
743 temperature calibrations (e.g., Anderson et al. 2021), is decreasing the uncertainties in
744 temperature reconstructions to levels comparable or better than other temperature proxies.

745

746 **3.5 Reporting data normalized to carbonates: definition of the “InterCarb”** 747 **Carbon Dioxide Equilibrium Scale (I-CDES)**

748 There is a need for a community consensus on how to report clumped isotope
749 measurements, both to promote data comparability and to reduce confusion stemming from the
750 different scales used in the literature. Currently Δ_{47} data are reported for different temperatures of
751 phosphoric acid digestion, mostly projected to 25 °C but also to 70 °C or 90 °C reactions, and

752 generally labeled respectively as $\Delta_{47\text{CDES}25}$, $\Delta_{47\text{CDES}70}$ and $\Delta_{47\text{CDES}90}$, a terminology introduced in
753 Bonifacie et al. (2017). In the literature, phosphoric acid correction factors used by different
754 research groups to convert results from 90 to 25 °C reaction temperatures have varied between
755 0.069 ‰ (Wacker et al., 2014) to 0.092 ‰ (e.g., Bonifacie et al., 2017), thus representing a
756 significant source of uncertainty and confusion.

757
758 The direct standardization to accepted values of solid phases, on the other hand, removes
759 the need for a phosphoric acid correction, yielding results which are independent of the
760 temperature at which the samples were reacted. In InterCarb this has only been tested for
761 calcites, the mineralogy of all standards used here. Further studies are necessary in particular for
762 dolomite and siderite, as these minerals require longer reaction times and there are contrasting
763 findings in the literature on whether they require different phosphoric acid fractionations
764 (Bonifacie et al., 2017; Müller et al. 2019, van Dijk et al., 2019; Petersen et al. 2019), possibly
765 affecting the absolute values of samples with such mineralogies. Aragonite may also have a
766 different phosphoric acid fractionation factor than calcite (Müller, Violay etl al. 2017).
767 Nevertheless, the use of the InterCarb reference carbonates, allows for a consistent correction of
768 instrumental effects and normalization to the I-CDES, independent of the mineralogy. Possible
769 effects related to the longer reaction time remain to be tested, and require intercomparison
770 samples of different mineralogy. In any case, for all calcites, carbonate standardization
771 eliminates different phosphoric acid correction factors as a source of uncertainty and provides a
772 consistent framework to report Δ_{47} without uncertainties related to the reaction temperature.

773
774 For these reasons, we recommend that in the future, carbonate clumped isotope values
775 should be reported relative to a carbonate reference frame uniquely defined by the absolute Δ_{47}
776 values reported in Table 1 for ETH-1, ETH-2, and ETH-3. Unknown samples may be anchored
777 to this reference frame either (a) directly by comparison to ETH-1/2/3, (b) indirectly by
778 comparison with several of the four other carbonate standards used here (Figure 4), or (c) by
779 comparison with a set of in-house laboratory standards whose composition is well-constrained
780 relative to the materials reported here. To clearly distinguish this data normalization scheme
781 from previous ones the denomination I-CDES (InterCarb - Carbon Dioxide Equilibration Scale)
782 should be use, with the notation $\Delta_{47(\text{I-CDES})}$. This approach is analogous to the change from the
783 PDB to the VPDB scale, which was accomplished by assigning a consensus offset of +1.95 ‰
784 between the original PDB reference material and the NBS19 carbonate. This was subsequently,
785 albeit temporarily, improved by defining a second anchor point with the L-SVEC lithium
786 carbonate standard (Coplen et al., 2006). We note that because the carbonate Δ_{47} values in
787 Table 1 are firmly anchored to the CDES scale via HG/EG measurements in multiple
788 laboratories, the two scales are in principle equivalent. However, I-CDES has three major
789 advantages: (1) it follows the principle of equal treatment of sample and standards, (2) it removes
790 uncertainties related to fractionation effects due to different acid reaction temperatures and
791 designs of the preparation lines and (3) it is based on traceable, stable materials (calcium
792 carbonates) that are widely available to interested laboratories. Furthermore, the results
793 summarized in Fig. 5 imply that I-CDES standardization yields consistent Δ_{47} values independent
794 of laboratory and/or analytical protocols, so that inter-laboratory scatter is accurately predicted
795 by the fully-propagated analytical uncertainties computed within each laboratory. By contrast,
796 this does not always seem to be the case for gas-based standardization to the CDES reference

797 frame (Fig. 6), suggesting the existence of poorly understood sources of inter-lab discrepancies
798 in that approach. The broad availability of carbonate reference materials with widely varying
799 bulk and clumped isotope compositions is an important step to help establish a worldwide
800 equivalence among laboratories and help new laboratories establish and verify their analytical
801 procedures.

802

803 **3.6 Comparability with previously published data**

804 The decision that $\Delta_{47(I-CDES)}$ values are reported for an acid reaction temperature of 90 °C
805 implies that the I-CDES value of any given sample will be almost 0.1 ‰ lower than its $\Delta_{47CDES25}$
806 values which is currently the most common convention used to report clumped isotopes. At first
807 sight it may seem a disadvantage to lose the ability to intuitively compare new results to those
808 obtained through different standardization approaches in the published literature. However, it
809 will make it immediately obvious that I-CDES-normalized values cannot directly be compared to
810 data standardized to the ETH-1/2/3/4 values reported by Bernasconi et al. (2018).

811 To directly compare previous carbonate-normalized Δ_{47} values and the already published
812 calibration equations produced with ETH standard normalisation (Kele et al, 2015; Bernasconi et
813 al., 2018; Jautzy et al., 2020; Meinicke et al., 2020; Peral et al., 2018; Piasecki et al., 2019) to
814 data reported on the I-CDES scale, previous data have to be recalculated as described in detail in
815 the Appendix. We emphasize again, however, that the temperatures calculated from the original
816 calibrations using the original ETH standard values are directly comparable to temperatures
817 calculated for samples normalized and calibrations recalculated to the I-CDES. This is because
818 only the nominal values of the standards have changed, and thus the data normalization is
819 internally consistent and traceable to the same solid standards.

820 In principle, I-CDES data are directly comparable to data produced by phosphoric acid
821 reaction at 90 °C using the HG/EG approach, with the important caveat that in absence of
822 measurements of widely available carbonates, a direct comparison remains uncertain, especially
823 for older data. A community effort to robustly anchor the composition of legacy standards
824 measured in the original laboratories, may alleviate this problem in the near future.

825 **4 Conclusions**

- 826 • This study demonstrates that carbonate-based standardization of clumped isotope
827 measurements solves many open questions that so far limited the application of
828 carbonate clumped isotope thermometry as a mature and reliable tool in Earth
829 sciences.
- 830 • Inter-laboratory discrepancies among 22 laboratories observed in this study are
831 not greater than those predicted from intra-laboratory analytical uncertainties.
- 832 • We propose a set of 2 high-purity carbonate reagents and 5 widely available
833 calcite reference materials for normalization of carbonate clumped isotope
834 measurements with new community-accepted values: the 4 ETH standards, two
835 samples distributed by the IAEA (C1 and C2), and a synthetic carbonate produced
836 by MERCK. The ETH standards are available upon request from S.M.
837 Bernasconi.

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- 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.
 - In principle data expressed in the I-CDES are directly comparable to samples reacted at a temperature of 90°C normalized to the classical CDES with HG/EG. However, we emphasize that carbonate standardisation is preferred to pure HG/EG normalization because it is based on traceable carbonate samples that can be measured in every laboratory. Reporting the measured compositions of carbonate reference materials together with the samples is the only way to ensure inter-laboratory consistency.
 - Robust standardization of clumped isotope measurements requires the analysis of a sufficient number of replicates of both samples and standard materials (either gases or carbonates) alongside unknowns to minimize error and obtain accurate measurements within a single laboratory.

854 **Appendix:**

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

856

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

862

863 By way of example, let us consider measurements originally standardized using ETH-
 864 1/2/3 with the nominal Δ_{47} values reported by Bernasconi et al. (2018). The “old” Δ_{47} values of
 865 these measurements are noted Δ_{47}^{old} , and we wish to compute the “new” Δ_{47} values, noted Δ_{47}^{new} ,
 866 that would be obtained if the same data were standardized to the I-CDES.

867

868 Both old and new Δ_{47} values are derived from the same set of raw measurements using
 869 “linear” (more accurately: affine) transformations of the form:

870

871 (A.1)
$$\Delta_{47}^{\text{old}} = x_1 + y_1 \delta^{47} + z_1 \Delta_{47}^{\text{raw}}$$

872

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

874

875 We can rearrange the above equations to express Δ_{47}^{new} as a function of δ^{47} and Δ_{47}^{old} :

876
877 (A.3)
878
$$\Delta_{47}^{\text{new}} = a + b\delta^{47} + c\Delta_{47}^{\text{old}}$$

879
880 Computing the numerical values of (a,b,c) is thus all that is required to compute Δ_{47}^{new} for
881 any sample whose (δ^{47} , Δ_{47}^{old}) values are known. This computation only requires knowing (δ^{47} ,
882 Δ_{47}^{old} , Δ_{47}^{new}) for three different anchors, for instance ETH-1/2/3. In matrix form, eq. (A.3) then
883 becomes:

884
885 (A.4)
886 Thus:
$$\begin{pmatrix} 1 & \delta_{(\text{ETH1})}^{47} & \Delta_{47(\text{ETH1})}^{\text{old}} \\ 1 & \delta_{(\text{ETH2})}^{47} & \Delta_{47(\text{ETH2})}^{\text{old}} \\ 1 & \delta_{(\text{ETH3})}^{47} & \Delta_{47(\text{ETH3})}^{\text{old}} \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} \Delta_{47(\text{ETH1})}^{\text{new}} \\ \Delta_{47(\text{ETH2})}^{\text{new}} \\ \Delta_{47(\text{ETH3})}^{\text{new}} \end{pmatrix}$$

887
888 (A.5)
$$\begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} 1 & \delta_{(\text{ETH1})}^{47} & \Delta_{47(\text{ETH1})}^{\text{old}} \\ 1 & \delta_{(\text{ETH2})}^{47} & \Delta_{47(\text{ETH2})}^{\text{old}} \\ 1 & \delta_{(\text{ETH3})}^{47} & \Delta_{47(\text{ETH3})}^{\text{old}} \end{pmatrix}^{-1} \begin{pmatrix} \Delta_{47(\text{ETH1})}^{\text{new}} \\ \Delta_{47(\text{ETH2})}^{\text{new}} \\ \Delta_{47(\text{ETH3})}^{\text{new}} \end{pmatrix}$$

889
890
891

892
893 In this example, the Δ_{47}^{old} and Δ_{47}^{new} values are the old and new nominal values of ETH-
894 1/2/3. If the δ^{47} values are defined as usual by reference to a working gas, (a,b,c) will vary when
895 different working gases are used. However, the above equations remain valid if δ^{47} is defined
896 instead by reference to a fixed, hypothetical CO₂ composition, e.g., stochastic VPDB-CO₂
897 ($\delta^{13}\text{C}_{\text{VPDB}} = 0$; $\delta^{18}\text{O}_{\text{VSMOW}} \approx 41.5 \text{‰}$; $\Delta_{47} = 0$, $R^{47} = 4.834 \times 10^{-5}$). In that case, numerical values of
898 the parameters (a,b,c) can be determined once and then used to compute Δ_{47}^{new} for any unknown
899 sample based only on its Δ_{47}^{old} and δ^{47} values (the latter being defined relative to VPDB-CO₂ and
900 computed by applying an acid ¹⁸O/¹⁶O fractionation factor of 1.01025 to said sample).
901 Importantly, this particular transformation applies to all data sets originally standardized in the
902 reference frame defined by the “old” nominal values of ETH-1/2/3.

903
904 For instance, the relationship linking the ETH-1/2/3 reference frame of Bernasconi et al.
905 (2018) to the I-CDES is defined by:

906
907
908 (A.6)
909
$$\begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} 1 & 0.010 & 0.258 \\ 1 & -28.375 & 0.258 \\ 1 & 0.538 & 0.691 \end{pmatrix}^{-1} \begin{pmatrix} 0.2052 \\ 0.2085 \\ 0.6132 \end{pmatrix} = \begin{pmatrix} -0.037997 \\ -0.000182 \\ 0.942590 \end{pmatrix}$$

910

911 Thus:

912

$$913 \quad (\text{A.7}) \quad \Delta_{47}^{\text{new}} = -0.038039 - 0.000183 \delta^{47} + 0.942603 \Delta_{47}^{\text{ol}}$$

914

915

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

922

$$923 \quad (\text{A.8}) \quad \Delta_{47}^{\text{new}} = 0.942603 \Delta_{47}^{\text{old}} - 0.038039$$

924

925 For instance, to convert the Δ_{47}^{old} value of ETH-4 reported by Bernasconi et al. (2018) to
 926 the I-CDES, we only need to know that $\delta^{47}_{(\text{ETH4})} = -28.8$ ‰ and $\Delta_{47}^{\text{old}} = 0.507 \pm 0.004$ ‰. The
 927 Δ_{47}^{new} value predicted by eq. (A.7) is then 0.445 ± 0.004 ‰, to be compared with the
 928 independently constrained values reported here in Table 1 (0.450 ± 0.002 ‰) and Table 3 (0.451
 929 ± 0.001 ‰).

930

931 The above computation could also be performed using any arbitrary set of three
 932 carbonate materials whose (δ^{47} , Δ_{47}^{old} , Δ_{47}^{new}) values are known, provided that they span a wide
 933 enough range in δ^{47} and Δ_{47} . This is true even if the carbonates in question were not originally
 934 used to standardize the raw data, as would be the case for CO₂-standardized measurements. In
 935 the case where only two suitable carbonate standards X and Y are available, an acceptable
 936 approach would be to neglect δ^{47} effects (equivalent to setting the value of b to zero in eq. (A.3))
 937 by solving the following equation:

938

$$939 \quad (\text{A.9}) \quad \begin{pmatrix} a \\ c \end{pmatrix} = \begin{pmatrix} 1 & \Delta_{47}^{\text{old}}(\text{X}) \\ 1 & \Delta_{47}^{\text{old}}(\text{Y}) \end{pmatrix}^{-1} \begin{pmatrix} \Delta_{47}^{\text{new}}(\text{X}) \\ \Delta_{47}^{\text{new}}(\text{Y}) \end{pmatrix}$$

941

942

943 Acknowledgments, Samples, and Data

944 SMB acknowledges instrumentation funding from ETH Zürich and support from Swiss
 945 National Science Foundation grants 200021_143485, 200020_160046. MD acknowledges the

946 clumped-isotope facility at LSCE is part of PANOPLY (Plateforme Analytique Géosciences
947 Paris-Saclay) and was supported by the following institutions: Région Ile-de-France; Direction
948 des Sciences de la Matière du Commissariat à l’Energie Atomique; Institut National des Sciences
949 de l’Univers, Centre National de la Recherche Scientifique; Université de Versailles/Saint-
950 Quentin-en-Yvelines. KDB and the MIT carbonate clumped isotope facility acknowledge
951 support from the Packard Foundation, the Agouron Foundation and NASA Exobiology Grant
952 80NSSC19K0464. MB acknowledges the program Emergences Ville de Paris for early funding
953 that allowed building her clumped isotope laboratory at Institut de Physique du Globe de Paris.
954 MB also thanks IPGP and Université de Paris for support for the organization of the VIth
955 Clumped Isotope Workshop in Paris in 2017. Funding was provided to CJ and the Imperial
956 College Clumped Isotope Laboratory by Qatar Petroleum, Shell, and the Qatar Science and
957 Technology Panel. Funding was provided to KH at University of Washington from NSF EAR
958 grants 1933130, 1713275, and 1156134. TV acknowledges the support of the Swiss National
959 Science Foundation grant 206021-164032. ANM acknowledges funding from the Trond Mohn
960 Foundation and the European Research Council (ERC) under the European Union’s Horizon
961 2020 research and innovation programme (grant agreement no. 638467). Funding was provided
962 to the Tripathi Laboratory at UCLA for these analyses from DOE BES grant DE-FG02-
963 13ER16402. Funding was provided to the Hyland Laboratory at NCSU for these analyses from
964 NSF EAR-FRES grant 1925973. Funding was provided to the Yoshida Laboratory at Tokyo
965 Tech. for these analyses from JSPS grant JP17H06105. Funding was provided to the CLIMB
966 Lab at the University of Bergen for these analyses by the European Research Council (ERC)
967 under the European Union’s Horizon 2020 research and innovation programme (grant agreement
968 No 638467) and by the Trond Mohn Foundation. Funding was provided to the UU Clumped
969 Laboratory at Utrecht University by the Netherlands Research Organization (NWO) through
970 VIDI grant 016.161.365. Funding was provided to the CUBES-SIL at CU Boulder by startup
971 funds from the University of Colorado Boulder and NSF EAR grant 1524785. The UM SCIPP
972 Laboratory was supported by startup funds from the University of Michigan. JR Kelson was
973 supported by NSF PRF grant 1854873. HPA acknowledges support by ERC (Grant no.724097)
974 and ISF (Grant no. 171/16 and 1000/16). Funding was provided to the Eiler lab at Caltech from
975 the DOE BES program, award number DE-SC0016561.

976 **Data**

977 All data analyzed as part of this study, along with all code used to process them, are
978 available at <https://github.com/mdaeron/InterCarb> and
979 <http://doi.org/10.5281/zenodo.4314448>.

980

981 **Author contributions**

982 The community designed the study at the Paris 2017 International Clumped Isotope
983 Workshop. S.M.B. prepared materials, gathered results and wrote the first draft of the
984 manuscript. M.D. created all code and conducted all analysis of the results. S.M.B., M.D.,
985 K.D.B., N.M., and M.B. organized the effort and contributed to early drafts. All authors
986 contributed to the analyses and curation of data shared in this study. All authors contributed to
987 the final version of the manuscript.

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1240 **Figure Captions**

1241 **Figure 1.** The δ^{47} vs. Δ^{47} values of carbonate standards (Δ^{47} on the I-CDES scale proposed
 1242 here) and heated and equilibrated gases in comparison to the compositional ranges of typical
 1243 natural carbonates. The observed range in measured clumped isotope compositions in natural
 1244 carbonates can be completely bracketed by heated and equilibrated CO₂ standard gases from
 1245 which δ^{47} values have been chosen by the user. The δ^{47} values for the anchor samples used in
 1246 InterCarb (red) and the unknowns (black) are reported for a theoretical working gas with
 1247 stochastic isotope distribution, derived from VPDB. Actual δ^{47} values will vary by laboratory
 1248 depending on the composition of the working gas. Note the smaller achievable range in both δ^{47}
 1249 and Δ^{47} values when using carbonate standards compared to heated and equilibrated gases and
 1250 the large extrapolation necessary for the determination of the composition for MERCK. Heated
 1251 and equilibrated CO₂ standard gases have a larger Δ^{47} range, allowing for more robust
 1252 stretching calculations with identical numbers of standard:sample analyses.

1253

1254 **Figure 2.** New determination of Δ^{47} values for the four ETH standards relative to the CDES
 1255 using updated CO₂ equilibrium values. These measurements, using acid reaction temperatures of
 1256 90 °C, 70 °C or 25 °C, are projected to 90 °C using acid corrections of -0.088 ‰ and -0.022 ‰
 1257 for 25 °C and 70 °C reactions, respectively (Petersen et al. 2019). Error bars correspond to 95 %
 1258 confidence limits taking into account fully propagated errors (i.e. taking into account errors in
 1259 both unknown and anchor analyses). Boxes correspond to 95 % confidence limits not accounting
 1260 for normalization errors (i.e. only taking into account errors in unknown analyses). Red numbers
 1261 are the error-weighted average values (with statistical weights summarized in upper-left corners).
 1262 All plots have the same horizontal scales for the different samples.

1263

1264 **Figure 3.** New nominal Δ^{47} values for the ETH standards compared to previously reported ones.
 1265 The dashed gray line is a linear regression through the new versus old values of ETH-1/2/3/4,
 1266 whose extrapolation coincides with 25 °C equilibrated CO₂ but not with heated gases. Apparent
 1267 changes in the ETH-1/2/3/4 values thus scale linearly with the Δ^{47} difference between carbonate
 1268 samples and 25 °C equilibrated CO₂, suggesting that Δ^{47} values of heated gases in the original
 1269 study may have been biased by $\sim +0.05$ ‰ through partial re-equilibration at room temperature
 1270 between the quenching of heated CO₂ and its ionization in the isotope-ratio mass spectrometer
 1271 source.

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1274 **Figure 4.** Final InterCarb results by laboratory. Error bars correspond to fully propagated 95 %
 1275 confidence limits, taking into account errors in both unknown and anchor analyses. Boxes
 1276 correspond to 95 % confidence limits not accounting for normalization errors (i.e., only taking
 1277 into account errors in unknown analyses). Results are sorted by increasing analytical errors, and
 1278 laboratories are identified by number. Overall error weighted average Δ^{47} values are displayed
 1279 as solid red lines and reported in each panel. All plots have the same vertical scale.

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1281 **Figure 5.** Kolmogorov–Smirnov tests of normality for the sigma-deviations obtained in each
1282 laboratory participating in the Intercarb effort (circular markers), either neglecting
1283 standardization uncertainty (upper row) or considering fully propagated analytical errors (lower
1284 row). Lower-right corner Kolmogorov–Smirnov p-values correspond to the null hypothesis that
1285 the sigma-deviations are normally distributed with a mean of zero and a standard deviation of 1.
1286 Blue lines correspond to the canonical Gaussian distribution ($\mu = 0$; $\sigma = 1$).

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1288 **Figure 6.** Kolmogorov–Smirnov tests of normality for the sigma-deviations, considering fully
1289 propagated analytical errors (accounting for uncertainties associated with conversion to the
1290 CDES reference frame), obtained in each laboratory participating in the ETH-1/2/3/4
1291 determination using HG and EG (circular markers). Lower-right corner Kolmogorov–Smirnov p-
1292 values correspond to the null hypothesis that the sigma-deviations are normally distributed with a
1293 mean of zero and a standard deviation of 1. Blue lines correspond to the canonical Gaussian
1294 distribution ($\mu = 0$; $\sigma = 1$).

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1297 **Figure 7.** Error-weighted average $\Delta 47(\text{I-CDES})$ values of unknowns obtained from acid
1298 reactions at 90 °C vs 70 °C. Solid black ellipses correspond to 95 % confidence limits. (see also
1299 Table 4).

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1301 **Figure 8.** Error-weighted average $\Delta 47(\text{I-CDES})$ values of unknowns obtained using different
1302 mass spectrometer types. Solid black ellipses correspond to 95 % confidence limits.

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1306 **Tables**

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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

1308

1309 **Table 1.** Newly determined nominal Δ_{47} values of the ETH standards projected to 90 °C acid
 1310 reaction using acid correction factors of -0.088 ‰ and -0.022 ‰ for 25 °C and 70 °C reactions,
 1311 respectively (Petersen et al. 2019). Reported standard errors represent analytical uncertainties
 1312 associated both with reference frame errors (HG/EG) and carbonate sample reproducibility
 1313 (Daëron, 2021).

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Lab	Session	Number of analyses								Working gas		Standardization parameters			Reproducibility (ppm)		
		E1	E2	E3	E4	Cl	CZ	M	Nf	$\delta^{13}\text{C}_{\text{VPDB}}$	$\delta^{18}\text{O}_{\text{VSMOW}}$	a	b	c	$\delta^{13}\text{C}_{\text{VPDB}}$	$\delta^{18}\text{O}_{\text{VSM}}$ ow	Δ_{47}
01	01	16	17	10	7	0	0	0	46	-3.58	25.38	0.91	(6.0 x10 ⁻⁴)	-0.893	41	91	31.5
	02	6	5	3	1	0	0	0	11	-3.52	25.58	0.89	(-2.1x10 ⁻³)	-0.765	34	64	22.8
	03	150	146	65	72	19	21	22	488	-3.63	25.22	0.98	(-2.9x10 ⁻⁵)	-0.965	33	74	33.5
02	01	19	24	20	18	4	5	4	87	-36.89	8.76	0.99	(-5.6x10 ⁻⁴)	-0.955	17	92	13.0
	02	6	8	5	4	2	3	2	23	-36.88	8.83	0.98	(-5.5 x10 ⁻⁴)	-0.931	25	77	16.1
03	01	37	24	17	9	0	0	0	83	-10.44	31.64	0.98	(-1.6x10 ⁻⁴)	-0.917	22	56	27.9
	02	29	32	12	14	17	13	11	121	-3.65	25.28	1.00	(-1.7 x10 ⁻⁴)	-0.917	46	93	25.2
04	01	6	9		9	6	4		35	-6.57	27.18	0.97	5.0 x10 ⁻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 x10 ⁻³	-0.970	15	27	8.6
	02	13	13	13	12	10	11	8	73	-3.62	25.05	0.99	(3.8x10 ⁻⁴)	-0.968	15	24	20.9
	03	7	10	10	8	5	4	4	41	-3.63	25.06	0.90	1.1 x10 ⁻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 x10 ⁻⁴)	-0.920	22	25	21.0
	02	6	6	6	6	0	0	0	20	-2.98	24.93	0.92	(-9.9 x10 ⁻⁵)	-0.920	14	71	13.3
	03	3	3	3	3	3	3	3	14	-3.01	24.90	0.88	(3.6 x10 ⁻⁴)	-0.932	10	43	9.4
	04	6	6	6	0	6	6	6	30	-2.95	25.28	0.90	(-1.4 x10 ⁻⁴)	-0.926	18	61	17.3
07	01	4	4	4	4	4	4	4	19	-11.64	35.75	0.87	3.5 x10 ⁻³	-0.836	91	303	23.9
08	01	5	6	9	4	4	4	4	29	-2.68	25.86	0.94	(-9.2x10 ⁻⁴)	-0.686	13	25	28.4
	02	5	4	14	6	4	5	4	35	-2.64	25.96	0.94	(8.6x10 ⁻⁴)	-0.741	83	88	33.2
	03	4	4	13	4	3	5	6	32	-2.64	25.91	0.93	(-1.7x10 ⁻⁴)	-0.728	15	33	33.2
	04	4	5	9	5	4	4	4	28	-2.67	25.85	0.85	(1.3x10 ⁻⁴)	-0.629	17	51	44.5
	05	3	6	8	4	4	4	4	26	-2.70	25.79	0.87	(1.3x10 ⁻⁴)	-0.660	16	56	43.3
	06	4	4	16	6	6	6	4	39	-2.63	25.90	0.92	(3.9x10 ⁻⁴)	-0.693	85	54	37.8
	07	3	4	16	6	6	4	6	38	-2.66	25.90	0.96	(-1.9x10 ⁻⁴)	-0.709	19	52	48.8
	08	4	4	16	4	4	4	4	33	-2.66	25.89	1.03	(3.9x10 ⁻³)	-0.806	12	46	42.7
	09	5	6	8	4	4	3	4	27	-2.67	25.84	0.92	(1.6x10 ⁻⁴)	-0.722	19	25	46.7
	10	6	6	6	4	4	2	4	25	-2.63	25.91	0.97	(4.4x10 ⁻⁴)	-0.767	36	39	40.5
	11	6	5	8	4	4	3	4	27	-2.67	25.87	0.97	(2.5x10 ⁻⁴)	-0.760	11	31	49.5
	12	6	6	8	3	4	4	4	28	-2.66	25.86	1.02	(7.9 x10 ⁻⁴)	-0.767	58	40	61.3
	13	4	6	8	6	4	4	6	31	-2.63	25.93	0.89	(1.3x10 ⁻⁵)	-0.685	19	38	41.0
	14	5	7	5	4	4	4	4	26	-2.59	25.90	0.90	(-3.6x10 ⁻⁴)	-0.665	76	104	27.4
	15	6	4	8	4	4	4	4	27	-2.68	25.79	0.95	(-2.0x10 ⁻³)	-0.685	21	52	36.0
	16	2	2	10	5	4	2	4	22	-2.63	25.89	0.96	(-5.4x10 ⁻⁴)	-0.765	40	39	38.8
09	01	4	4	5	6	0	0	0	15	-3.60	25.36	0.89	3.8x10 ⁻³	-0.856	22	74	28.3
	02	26	19	16	24	0	0	0	81	-3.36	19.94	0.90	5.2x10 ⁻³	-0.928	46	98	18.4
	03	21	17	13	19	0	1	0	66	-3.53	24.49	0.92	-1.0x10 ⁻²	-0.968	72	1667	22.4
	04	19	16	13	16	8	7	2	74	-3.60	25.27	0.98	-9.6x10 ⁻³	-0.994	44	56	16.0
10	01	7	7	8	2	0	11	0	30	-7.43	32.38	0.98	1.9x10 ⁻³	-1.077	24	38	35.1
	02	15	15	21	15	11	20	11	101	-7.41	32.42	0.93	(-2.0x10 ⁻⁴)	-0.877	25	44	23.0
	03	17	18	25	9	22	31	20	135	-7.43	32.37	0.96	(-2.8x10 ⁻⁴)	-0.900	31	92	30.0
11	01	24	24	28	28	0	0	0	100	-3.63	25.37	0.99	(-8.1x10 ⁻⁵)	-0.974	23	91	19.1
	02	20	18	15	15	0	0	0	64	-3.60	25.53	0.98	(3.5x10 ⁻⁴)	-0.996	35	270	28.9
	03	69	62	74	66	13	13	8	298	-3.02	24.99	0.91	(-2.2x10 ⁻⁴)	-1.065	34	89	25.0
	04	36	34	34	35	6	4	8	150	-3.01	25.08	1.00	(-3.1x10 ⁻⁴)	-1.088	87	210	33.7
	05	90	83	92	78	12	10	9	367	-2.76	25.78	0.98	(-5.0x10 ⁻⁴)	-1.088	97	317	19.3
12	01	7	7	9	5	5	6	5	37	-3.75	25.15	0.89	3.7x10 ⁻³	-0.904	7	41	10.2
	02	7	6	6	6	5	5	5	33	-3.74	25.18	0.87	4.6x10 ⁻³	-0.897	8	so	9.3
	03	8	7	12	5	5	5	5	40	-3.74	25.17	0.88	5.5x10 ⁻³	-0.909	9	51	9.7
	04	6	7	6	5	5	5	4	31	-3.74	25.17	0.88	5.3x10 ⁻³	-0.908	7	51	8.7
13	01	58	51	59	47	6	12	9	235	-10.29	33.18	0.98	-3.7x10 ⁻⁴	-0.993	176	239	26.8
14	01	4	7	10	10	0	0	0	27	-3.63	24.95	0.93	(1.3x10 ⁻⁴)	-0.972	42	159	19.3
	02	10	11	8	7	0	0	0	32	-3.61	25.04	0.97	(5.8x10 ⁻⁴)	-1.021	40	128	30.0
	03	6	4	4	3	0	0	0	13	-10.38	31.93	0.84	-1.7x10 ⁻³	-0.747	39	59	20.5
	04	2	2	2	2	0	0	0	4	-10.40	31.92	0.86	-1.0x10 ⁻³	-0.794	20	29	9.2
	05	4	4	3	4	0	0	0	11	-10.40	31.92	0.91	-1.6x10 ⁻³	-0.807	27	60	11.0
	06	5	6	6	7	0	0	0	20	-10.43	31.84	0.99	(1.3x10 ⁻⁴)	-0.908	39	53	22.4
	07	3	5	2	1	0	0	0	7	-10.41	31.85	0.97	(-1.7x10 ⁻⁴)	-0.877	51	43	12.8
	08	11	7	3	5	0	0	0	22	-10.47	31.66	0.94	-7.8x10 ⁻⁴	-0.920	61	84	23.4
	09	4	2	3	4	0	0	0	9	-10.43	31.82	0.95	(-4.8x10 ⁻⁴)	-0.907	55	83	12.0
	10	4	4	1	3	0	0	0	8	-10.49	31.73	0.99	(1.7x10 ⁻⁴)	-0.926	40	71	13.3
15	01	4	4	4	4	0	0	0	12	-32.89	36.92	0.96	-2.5x10 ⁻³	-0.887	87	70	14.6
	02	4	4	4	4	4	4	4	21	-3.72	24.98	1.02	4.6x10 ⁻³	-1.027	59	41	14.0
16	01		6	6	4	4			23	-10.49	31.56	0.99	-4.1x10 ⁻³	-0.979	47	109	10.1
17	01		5			6	6		23	-9.73	23.81	0.81	(6.3x10 ⁻⁴)	-0.940	65	204	29.3
18	01	168	147	172	169	20	20	25	714	-3.45	25.25	0.81	(1.5x10 ⁻⁴)	-0.722	65	110	37.7
	02	17	14	17	13	4	4	4	66	-3.41	25.42	0.83	(1.6x10 ⁻⁵)	-0.761	21	52	45.7
	03	11	12	13	14	2	4	2	51	-3.52	25.12	0.96	(6.0x10 ⁻⁴)	-0.835	23	45	40.5
19	01	4	4	5	7	5	4	4	26	-24.48	25.66	0.99	(2.0x10 ⁻⁴)	-0.970	69	193	23.4
	02	7	8	10	7	0	0	0	28	5.03	38.66	0.99	(2.0x10 ⁻⁴)	-0.962	164	416	22.5
20	01	9	6	6	6	0	0	0	23	-3.63	28.89	0.93	-2.1x10 ⁻³	-0.921	11	so	14.3
21	01					0	0	0	8	-3.62	25.20	0.90	1.0x10 ⁻³	-0.886	65	139	11.4
22	01	8	8	8		0	0		33	-3.54	25.37	0.98	9.9x10 ⁻³	-0.951	155	443	20.5
23	01	6	6	6	6	0	0		20	-10.77	31.02	1.00	4.4x10 ⁻³	-0.948	47	91	20.5
24	01	19	18	15	12	0	0	0	60	-4.40	25.32	0.98	(2.1x10 ⁻⁴)	-0.955	42	107	9.9
26	01	4	4	4		3			19	-40.04	5.51	0.89	(2.2x10 ⁻⁴)	-0.998	96	14.5	15.0
	02	6	7	6		3			24	-40.03	5.40	0.92	(-1.1 x10 ⁻⁴)	-1.014	50	88	8.7

1326 Table 2. Summary of all InterCarb analyses. N_f is the number of degrees of freedom when
1327 estimating pooled analytical repeatabilities and standardization model uncertainties.
1328 Standardization parameters a , b and c refer to the scrambling factor in the source, the
1329 compositional slope due to positive or negative backgrounds in the collectors and the working
1330 gas offset, respectively (see section 2.4 and Daëron, 2021). Values of standardization parameter
1331 b which are statistically indistinguishable from zero at 95 % confidence level are reported in
1332 parenthesis. Reproducibility is reported as 1 SD
1333

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MS	ETH-4		IAEA-C1		IAEA-C2		MERCK	
	$\Delta_{47}(\text{LCDES})$ ($\% \pm 1\text{SE}$)	N	$\Delta_{47}(\text{LCDES})$ ($\% \pm 1\text{SE}$)	N	$\Delta_{47}(\text{LCDES})$ ($\% \pm 1\text{SE}$)	N	$\Delta_{47}(\text{LCDES})$ ($\% \pm 1\text{SE}$)	N
1	0.4477 \pm 0.0052	80	0.2773 \pm 0.0080	19	0.6275 \pm 0.0088	21	0.4991 \pm 0.0105	22
2	0.4499 \pm 0.0044	22	0.3086 \pm 0.0060	6	0.6299 \pm 0.0061	8	0.5025 \pm 0.0089	6
3	0.4430 \pm 0.0074	23	0.3114 \pm 0.0073	17	0.6427 \pm 0.0112	13	0.5235 \pm 0.0152	11
4	0.4841 \pm 0.0248	9	0.2959 \pm 0.0215	6	0.6368 \pm 0.0291	4		
5	0.4734 \pm 0.0055	22	0.2916 \pm 0.0044	18	0.6378 \pm 0.0057	17	0.4987 \pm 0.0094	14
6	0.4545 \pm 0.0060	12	0.3004 \pm 0.0051	12	0.6471 \pm 0.0069	12	0.5229 \pm 0.0116	12
7	0.4607 \pm 0.0066	8	0.3099 \pm 0.0042	16	0.6520 \pm 0.0052	15	0.5231 \pm 0.0098	8
8	0.4442 \pm 0.0072	73	0.3099 \pm 0.0060	67	0.6383 \pm 0.0071	62	0.5159 \pm 0.0127	70
9	0.4505 \pm 0.0041	65	0.2926 \pm 0.0064	8	0.6309 \pm 0.0078	8	0.5630 \pm 0.0158	2
10	0.4416 \pm 0.0075	26	0.2987 \pm 0.0060	33	0.6348 \pm 0.0065	62	0.4954 \pm 0.0130	31
11	0.4468 \pm 0.0025	222	0.3085 \pm 0.0043	31	0.6354 \pm 0.0050	27	0.5175 \pm 0.0066	25
12	0.4521 \pm 0.0032	21	0.3015 \pm 0.0026	20	0.6479 \pm 0.0032	21	0.5064 \pm 0.0054	19
13	0.4484 \pm 0.0062	47	0.3048 \pm 0.0113	6	0.6376 \pm 0.0091	12	0.5470 \pm 0.0135	9
14	0.4548 \pm 0.0041	46						
15	0.4480 \pm 0.0083	8	0.3016 \pm 0.0090	4	0.6217 \pm 0.0116	4	0.4642 \pm 0.0195	4
16	0.4627 \pm 0.0076	4	0.2962 \pm 0.0063	4	0.6563 \pm 0.0084	3	0.5176 \pm 0.0136	2
17	0.4634 \pm 0.0250	5	0.3254 \pm 0.0181	6	0.6971 \pm 0.0314	6	0.4623 \pm 0.0429	3
18	0.4510 \pm 0.0046	196	0.3060 \pm 0.0079	26	0.6386 \pm 0.0084	28	0.5317 \pm 0.0104	31
19	0.4460 \pm 0.0106	14	0.2851 \pm 0.0142	5	0.6015 \pm 0.0183	4	0.5256 \pm 0.0339	4
20	0.4627 \pm 0.0095	6						
21	0.4470 \pm 0.0108	3						
22	0.4639 \pm 0.0124	7					0.5269 \pm 0.0213	7
23	0.4453 \pm 0.0137	6						
24	0.4544 \pm 0.0042	12						
26	0.4378 \pm 0.0058	8	0.3008 \pm 0.0051	6	0.6396 \pm 0.0062	6	0.5152 \pm 0.0095	6
w. avg	0.4511 \pm 0.0011	945	0.3018 \pm 0.0013	310	0.6409 \pm 0.0016	333	0.5135 \pm 0.0024	286
SD	0.011		0.011		0.018		0.024	

1334 **Table 3.** Average Δ_{47} values ($\pm 1\text{SE}$, fully propagated uncertainties) obtained by each mass
1335 spectrometer from the 22 laboratories. Note the larger standard deviation for the samples further
1336 from the calibration triangle defined by the anchors. The average Δ_{47} values for individual
1337 analytical sessions are reported in table 2.

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	$\Delta_{47(\text{I-CDES})}$ (70 °C reaction)	$\Delta_{47(\text{I-CDES})}$ (90 °C reaction)	Difference ($\pm 1\text{SE}$)
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

1341

1342 **Table 4.** Error-weighted average $\Delta_{47(\text{I-CDES})}$ values ($\%$; $\pm 1\text{SE}$) for each unknown as a
 1343 function of acid reaction temperature (see also Fig. 7).

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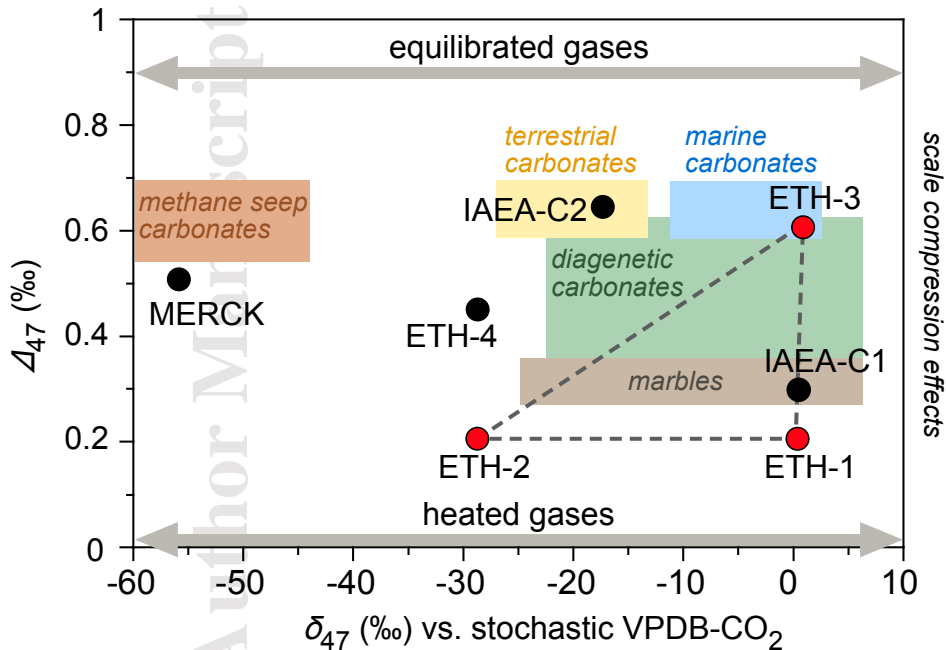
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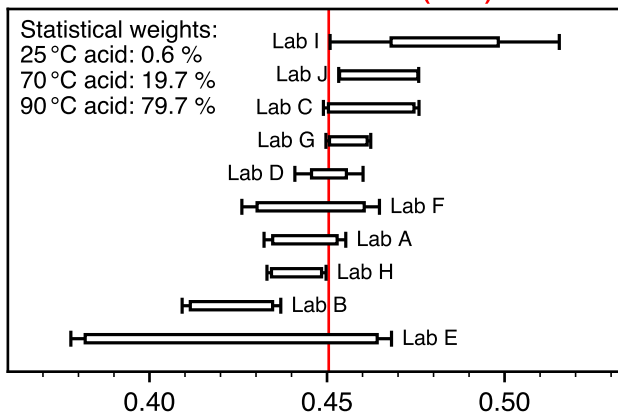
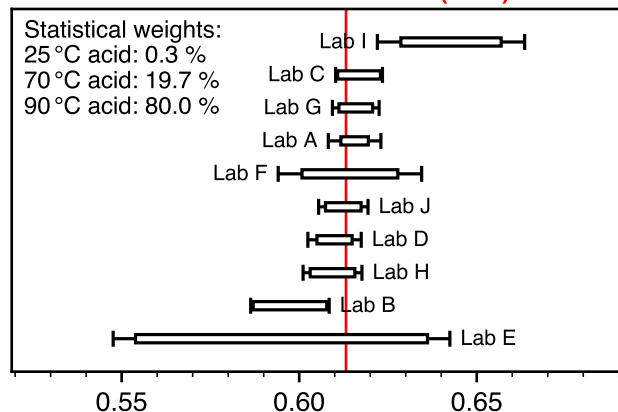
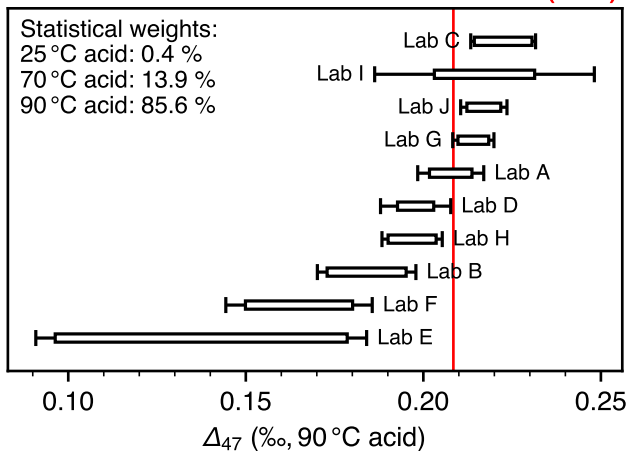
	MAT 253 vs Isoprime 100	Nu Perspective vs MAT 253	Isoprime 100 vs Nu Perspective
ETH-4	-0.0009 ± 0.0035	-0.0004 ± 0.0024	0.0013 ± 0.0036
IAEA-C1	0.0023 ± 0.0032	-0.0048 ± 0.0030	0.0025 ± 0.0035
IAEA-C2	-0.0081 ± 0.0039	-0.0029 ± 0.0037	0.0110 ± 0.0043
MERCK	0.0115 ± 0.0065	-0.0059 ± 0.0056	-0.0056 ±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

1349 **Table 5.** Error-weighted average $\Delta_{47(i\text{-CDES})}$ differences ($\pm 1\text{SE}$) for each unknown as a function of
1350 mass spectrometer type.

1351
1352

pressure baseline ("non-linearity") effects



ETH-4**0.4505 ± 0.0035 (95 %)****ETH-3****0.6132 ± 0.0027 (95 %)****ETH-2****0.2085 ± 0.0030 (95 %)****ETH-1****0.2052 ± 0.0031 (95 %)**