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Full propagation of analytical uncertainties in Δ_{47} measurements

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Abstract

Clumped-isotope measurements in CO₂ and carbonates (Δ_{47}) present a number of technical challenges and require correcting for various sources of analytical non-linearity. For now we lack a formal description of the analytical errors associated with these correction steps, which are not accounted for in most data processing methods currently in use. Here we formulate a quantitative description of Δ_{47} error propagation, fully taking into account standardization errors and their properties. We describe various standardization strategies, along with the assumptions they rely on, in the context of this model, and propose a new, “pooled” standardization approach designed to yield more robust/accurate corrections. User-friendly online resources and an open-source Python library are also provided to facilitate the use of these error models. Among other uses, the mathematical framework described here may be helpful to improve standardization protocols (e.g., anchor/unknown ratios) and inform future efforts to define community reference materials.

1 Introduction

Clumped-isotope geochemistry is the study of statistical anomalies in the abundance of multiply substituted isotopologues in natural materials [Eiler & Schauble, 2004; Eiler, 2011]. Mass spectrometric measurements of Δ_{47} , quantifying the excess abundance of ¹³C – ¹⁸O bonds in CO₂ and, by extension, in carbonate minerals, constitute the most widely used branch of this relatively young but rapidly evolving field of research. The appeal of carbonate Δ_{47} measurements is largely based on the fact that the clumped-isotope compositions of natural carbonates directly or indirectly constrain their crystallization temperatures and/or thermal histories, with a broad range of Earth science applications. Establishing a robust calibration of the carbonate Δ_{47} thermometer, however, has long remained a vexing challenge, with inter-laboratory discrepancies equivalent to large uncertainties in reconstructed temperatures, sometimes exceeding 10 °C [e.g., Bonifacie *et al.*, 2017; Petersen *et al.*, 2019].

Despite keeping in mind that “true” calibration differences between certain types of carbonates are not to be excluded *a priori*, various potential causes for these discrepancies have been put forward, such as (a) inconsistent or inaccurate ^{17}O correction parameters [Daëron *et al.*, 2016; Schauer *et al.*, 2016; Olack & Colman, 2019], (b) systematic effects arising from different data processing methods, and (c) poorly-corrected analytical biases resulting from instrumental and/or methodological differences between laboratories. Petersen *et al.* [2019] tested the first two of these hypotheses and found that using unified methods for ^{17}O correction and subsequent data processing reduced inter-laboratory discrepancies without eliminating them. Testing the third hypothesis is one of the goals of the recently completed inter-laboratory comparison exercise “InterCarb”, whose results are reported in a companion study [Bernasconi *et al.*, 2021].

How to accurately estimate the analytical uncertainties affecting Δ_{47} measurements constitutes a distinct but related issue. Although Fernandez *et al.* [2017] pointed out that non-robust statistics based on small numbers of observations frequently yield underestimated uncertainties, there is no consensus today as to whether this is the primary cause of inter-laboratory discrepancies. Both Daëron & Blamart [2016] and Kocken *et al.* [2019] called attention to the uncertainties associated with Δ_{47} standardization (i.e. conversion of “raw Δ_{47} ” measurements to “absolute” values), but for now we lack an explicit, formal description of this source of analytical error, which most data processing methods do not currently account for. This issue is critical in the context of the InterCarb exercise, which aims to test whether different laboratories, when analyzing a common set of four unknown and three reference carbonate samples, obtain analytically consistent results, i.e. results displaying no more inter-laboratory scatter than expected based on intra-laboratory analytical errors. The present work aims to formulate a comprehensive model of analytical errors in Δ_{47} measurements, including those arising from standardization using carbonate and/or carbon dioxide standards; to describe various standardization strategies along with the assumptions they rely on; and to provide user-friendly data processing tools implementing these error models.

2 Methods

2.1 A brief summary of mass spectrometric measurements of Δ_{47} in carbonates

Clumped-isotope analyses of carbonates are typically performed using dual-inlet gas-source isotope-ratio mass spectrometry. In each analysis, a certain amount of carbonate mineral reacts with pure phosphoric acid at a fixed temperature (usually 25, 70 or 90 °C). Each such reaction typically produces between 1 and 100 μmol of CO_2 , which is collected in a series of cryogenic traps and carefully purified to eliminate isobaric contaminants (i.e. species with a molecular mass of 47 amu, or compounds liable to produce such species through fragmentation/recombination reactions). Although our primary focus is on measurements of Δ_{47} in carbonate minerals, most aspects of the present study apply just as well to Δ_{47} in CO_2 samples which were not produced by acid digestion of carbonates.

The purified CO_2 is then introduced to the “sample” side of a dual-inlet system and, from there, into a Nier-type ion source. In most systems currently in use, analyte CO_2 is compared with a “working gas” reference CO_2 through the frequent, regular toggling of a change-over valve. The bulk isotopic composition ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) and mass-47 to mass-44 abundance ratio of each analyte are deter-

mined by comparing ion currents for the analyte and the working gas, averaged over long integration times, typically tens of minutes or longer. These integration times are necessary because counting statistics are one of the primary factors limiting precision when observing rare isotopologues such as $^{16}\text{O}^{13}\text{C}^{18}\text{O}$, which makes up only 45 ppm of natural CO_2 [Huntington *et al.*, 2009].

For the past decade Δ_{47} measurements have been standardized by comparison with specially prepared CO_2 standards with known clumped-isotope compositions and variable bulk isotope compositions [Dennis *et al.*, 2011]. Carbonate reference materials have increasingly been also used for standardization, either in addition to or as a replacement for CO_2 standards [Meckler *et al.*, 2014; Bernasconi *et al.*, 2018]. Although here we primarily consider standardization using carbonate reference materials, the mathematical framework presented below generally applies as well to CO_2 standards.

2.2 Terminology

We define below, in the context of this work, a number of terms. A **sample** is an amount of presumably homogeneous carbonate material subjected to one or more **analyses** (otherwise known as replicate measurements/observations). Each analysis corresponds to a single acid reaction followed by purification of the evolved CO_2 and by a series of dual-inlet IRMS measurements, yielding **working-gas delta values** (δ_{45} to δ_{49}). These working-gas deltas are then converted to “raw” (non-standardized) values of $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and Δ_{47}^{raw} . The specifics of this conversion have been extensively covered elsewhere [e.g., Huntington *et al.*, 2009; Daëron *et al.*, 2016], and are not directly relevant to the topics discussed here. Analyses are generally grouped into **sessions**, each of them usually corresponding to a given time span over which analytical conditions are presumed to have remained stable. One key assumption is that the various analytical/instrumental non-linearities which affect Δ_{47}^{raw} observations remain constant over the duration of each session. These non-linearities include a **scrambling effect** likely reflecting recombination of isotopologues in the IRMS gas source or elsewhere in the sample preparation apparatus [Dennis *et al.*, 2011]; a **compositional slope** reflecting small biases in the electrical background of the ion beam measurements [He *et al.*, 2012; Bernasconi *et al.*, 2013]; and a **working gas offset** resulting from the (knowingly inaccurate) assumption that the dual-inlet working gas is stochastic. Within each session, the samples/analyses are divided into two groups: **anchors**, whose Δ_{47} values are assigned *a priori*, and **unknowns**, whose Δ_{47} values are to be determined. Here we define a **standardization model** as any mathematical procedure aiming to estimate these unknown Δ_{47} values by comparing the anchor and unknown analyses, explicitly or implicitly constraining analytical non-linearities within each session.

2.3 Objectives and strategy

Our aim is to model how random, zero-centered, presumably Gaussian measurement errors propagate into final, “absolute” Δ_{47} values averaged over a number of analyses/sessions. We do not attempt to account for non-random biases such as those potentially arising, for instance, from errors in the isotopic composition of the working gas, or from assigning inaccurate Δ_{47} values to one or more anchors. The models described here will hopefully provide a framework to report more accurate estimates of the uncertainty associated with clumped-isotope measurements, and inform the choices we make in the laboratory.

We start by describing a general formulation of the standardization function used to compute the “absolute” Δ_{47} value of each analysis. Quantifying the parameters defining this function within a given session is equivalent to constraining the analytical/instrumental non-linearities mentioned above, and may be treated as a classical least-squares minimization problem.

We follow up by estimating the analytical precision of “raw” measurements (before standardization) based, following oft-repeated recommendations, on the pooled external repeatability of a group of standards and/or unknown samples. The general formulation used here then makes it straightforward to propagate the raw measurement errors into the “autogenic” uncertainty of each analysis (that directly arising from the raw errors of this particular analysis) and an independent component of “allogenic” uncertainties arising from the least-squares model errors, i.e. from the standardization itself.

We finish by describing the general properties of these two components of error, and briefly discuss several practical standardization approaches applicable to real-world data sets.

2.4 Standardization to an “absolute” Δ_{47} reference frame within a single session

Computing “absolute” Δ_{47} values traditionally involves two chained affine transformations designed to correct for known instrumental non-linearities (eqs. 5-6 of *Dennis et al.* [2011], using the original notation):

$$\Delta_{47-[SGvsWG]0} = \Delta_{47-[SGvsWG]} - \delta_{[SGvsWG]}^{47} \times \text{Slope}_{EGL} \quad (1)$$

$$\Delta_{47-RF} = \Delta_{47-[SGvsWG]0} \times \text{Slope}_{ETF} + \text{Intercept}_{ETF} \quad (2)$$

This is mathematically equivalent to the following formulation:

$$\Delta_{47}^{raw} = a \Delta_{47} + b \delta_{47} + c \quad (3)$$

In this equation, the parameters (a , b , c) respectively account for scrambling effects, the compositional slope, and the working gas offset. To estimate these parameters, a natural approach is to use classical least-squares minimization methods, treating Δ_{47}^{raw} as the response/dependent variable and (Δ_{47} , δ_{47}) as explanatory variables. Despite uncertainties on δ_{47} usually being as large as those on Δ_{47}^{raw} , the former may safely be treated as an explanatory variable because b is typically small enough (10^{-2} or less) for errors on δ_{47} to have a negligible impact.

Without compelling reasons to do otherwise, we assign equal weights to all measurements belonging to the same session. The best-fit standardization parameters (a , b , c) for any given session are thus those minimizing the following χ^2 statistic, summed over all anchor analyses within that session (unknown analyses are not considered here because their Δ_{47} values are not known *a priori*):

$$\chi^2 = \sum (\Delta_{47}^{\text{raw}} - a \Delta_{47} - b \delta_{47} - c)^2 \quad (4)$$

This computation, whose mathematical details are summarized in appendix A, yields a triplet of best-fit values for (a , b , c), thus defining the standardization function of eq. (3) for this session. It also yields a covariance matrix V_0 for the best-fit values of (a , b , c). At this stage, the covariance matrix is unscaled, meaning that it only constrains the *relative* scaling between model standard errors and covariances in (a , b , c). The additional piece of information needed to scale these model errors is the uncertainty assigned to each observation, i.e. the analytical precision of individual Δ_{47}^{raw} measurements.

2.5 Estimating the analytical precision of raw measurements

The uncertainty assigned to individual Δ_{47}^{raw} measurements, noted σ_{47}^{raw} , may be quantified in various ways, but always keeping in mind that over-reliance on the statistics of small numbers is problematic [Fernandez *et al.*, 2017]. We propose that in most cases a robust estimate of σ_{47}^{raw} can be obtained by considering carbonate samples deemed free of contaminants and isotopically homogeneous, be them anchors, unknown samples, or carbonate standards treated as unknowns, and computing the pooled Δ_{47} repeatability of analyses within this group:

$$\sigma_{47}^2 = \frac{1}{N_a - N_s} \sum (\Delta_{47} - \overline{\Delta_{47}})^2 \quad (5)$$

where $\overline{\Delta_{47}}$ is the average Δ_{47} value for the sample considered, N_a the total number of analyses considered, and N_s the number of different samples considered. The Δ_{47}^{raw} repeatability of analyses is then:

$$(\sigma_{47}^{\text{raw}})^2 = (a \sigma_{47})^2 = \frac{1}{N_a - N_s} \sum (\Delta_{47}^{\text{raw}} - a \overline{\Delta_{47}} - b \delta_{47} - c)^2 \quad (6)$$

It bears noting that if the group of samples used to estimate σ_{47}^{raw} within a single session only comprises three anchors, then $(\sigma_{47}^{\text{raw}})^2$ is equal to the reduced chi-squared statistic $\chi^2/(N_a - 3)$ for that session. In such case, scaling the standardization errors by σ_{47}^{raw} is equivalent to the common practice of estimating least-square model errors based on the scatter/variance of residuals. Taking additional samples into account increases confidence in our estimate by virtue of increasing the statistical degrees of freedom ($N_f = N_a - N_s$), on the condition that the replicability of these additional samples is equal to (or indistinguishable from) that of carbonate standards. In our experience this condition is frequently met when samples are well-mixed, finely ground, relatively pure carbonate powders.

2.6 Propagation of standardization errors within a single session

Regardless of its estimation method, σ_{47}^{raw} may now be used to quantify the standard model errors ($\sigma_a, \sigma_b, \sigma_c$) on the best-fit standardization parameters and their covariances (c_{ab}, c_{bc}, c_{ac}):

$$\begin{bmatrix} \sigma_a^2 & c_{ab} & c_{ac} \\ c_{ab} & \sigma_b^2 & c_{bc} \\ c_{ac} & c_{bc} & \sigma_c^2 \end{bmatrix} = (\sigma_{47}^{\text{raw}})^2 V_0 \quad (7)$$

These model errors and covariances fully describe the standardization uncertainty associated with anchor measurement errors, and can now be propagated explicitly to the session average Δ_{47} value of a given unknown sample, noted $\overline{\Delta_{47}}$:

$$\overline{\Delta_{47}} = (\overline{\Delta_{47}^{\text{raw}}} - b \overline{\delta_{47}} - c)/a \quad \Rightarrow \quad \sigma(\overline{\Delta_{47}})^2 = J \times C \times J^T \quad (8)$$

with $\overline{\Delta_{47}^{\text{raw}}}$ and $\overline{\delta_{47}}$ being the session average values of Δ_{47}^{raw} and δ_{47} , respectively; J the Jacobian matrix of $\overline{\Delta_{47}}$; and C the covariance matrix of $(\overline{\Delta_{47}^{\text{raw}}}, a, b, c)$:

$$J = \left[\frac{\partial \overline{\Delta_{47}}}{\partial \overline{\Delta_{47}^{\text{raw}}}}, \frac{\partial \overline{\Delta_{47}}}{\partial a}, \frac{\partial \overline{\Delta_{47}}}{\partial b}, \frac{\partial \overline{\Delta_{47}}}{\partial c} \right] = \frac{1}{a} \left[1, -\overline{\Delta_{47}}, -\overline{\delta_{47}}, -1 \right] \quad (9)$$

$$C = \begin{bmatrix} \sigma(\overline{\Delta_{47}^{\text{raw}}})^2 & 0 & 0 & 0 \\ 0 & \sigma_a^2 & c_{ab} & c_{ac} \\ 0 & c_{ab} & \sigma_b^2 & c_{bc} \\ 0 & c_{ac} & c_{bc} & \sigma_c^2 \end{bmatrix} = \begin{bmatrix} (\sigma_{47}^{\text{raw}})^2/N_a & 0 & 0 & 0 \\ 0 & \sigma_a^2 & c_{ab} & c_{ac} \\ 0 & c_{ab} & \sigma_b^2 & c_{bc} \\ 0 & c_{ac} & c_{bc} & \sigma_c^2 \end{bmatrix} \quad (10)$$

The structure of the above covariance matrix makes it clear that $\sigma(\overline{\Delta_{47}})^2$ for an unknown sample is the sum of two statistically independent sources of error: an “autogenic” component σ_u reflecting uncertainties in Δ_{47}^{raw} measurements for that sample, and an “allogenic” component σ_s reflecting uncertainties in the standardization model:

$$\sigma(\overline{\Delta_{47}})^2 = \sigma_u^2 + \sigma_s^2 \quad (11)$$

$$\sigma_u^2 = \sigma_{47}^2/N_a \quad (12)$$

$$\sigma_s^2 = \frac{1}{a^2} \left(\overline{\Delta_{47}}^2 \sigma_a^2 + \overline{\delta_{47}}^2 \sigma_b^2 + \sigma_c^2 + 2(\overline{\Delta_{47}} \overline{\delta_{47}} c_{ab} + \overline{\Delta_{47}} c_{ac} + \overline{\delta_{47}} c_{bc}) \right) \quad (13)$$

2.7 Combining data from several independent sessions

As long as the standardization of each session only takes into accounts analyses from that session, the values of $\overline{\Delta_{47}}$ computed as above within each session are statistically independent from each other. The final Δ_{47} value for a given unknown sample may thus be simply computed as the weighted average of $\overline{\Delta_{47}}$ from different sessions. Using a weighted average for this last step is necessary to account for inter-session differences in the number of analyses of that sample, and also potentially in raw analytical repeatability (unless, for instance, a conscious choice is made to use a single estimate of σ_{47}^{raw} constrained by all sessions):

$$\Delta_{47}^{\text{final}} = \sum_i \omega_i \left(\overline{\Delta_{47}} \right)_i \quad \text{with sessions noted as } i \quad (14)$$

$$\omega_i = \sigma \left(\overline{\Delta_{47}} \right)_i^{-2} / \sum_i \sigma \left(\overline{\Delta_{47}} \right)_i^{-2} \quad (15)$$

$$\sigma \left(\Delta_{47}^{\text{final}} \right)^2 = \sum_i \omega_i^2 \sigma \left(\overline{\Delta_{47}} \right)_i^2 = 1 / \sum_i \sigma \left(\overline{\Delta_{47}} \right)_i^{-2} \quad (16)$$

3 Discussion

3.1 Properties of standardization errors

The standardization model of section 2.4 is mathematically equivalent to the least-squares fitting of a two-dimensional plane described by eq. (3) in a three-dimensional space (δ_{47} , Δ_{47}^{raw} , Δ_{47}). Most properties described below arise naturally from this geometry.

Standardization uncertainties depend greatly on the bulk (δ_{47}) and clumped-isotope (Δ_{47}) composition of the unknown samples to be standardized. It is thus useful to describe this uncertainty in terms of an “error field” which can be mapped in (δ_{47} , Δ_{47}) space, as shown in fig. 1. The minimum standardization error coincides, in (δ_{47} , Δ_{47}) space, with the barycenter of the anchor analyses, and its value is equal to $\sigma_{47}/N^{1/2}$, with N being the total number of anchor analyses.

Outside of a polygon defined by the anchor samples, standardization errors increase steeply. As illustrated in fig. 1, this increase is comparatively slower if analyses are evenly distributed between anchor samples, which tightens constraints on parameters a and b .

Fig. 1 also illustrates the benefits of using anchors with extreme isotopic compositions, which increases the area of the anchor polygon. One potential drawback of relying on isotopically extreme anchors, however, is that our “planar” model approximation might then break down. For instance, a small quadratic component to the compositional nonlinearity (term $b \delta_{47}$ in eq. 3), whose effect would be negligible over a δ_{47} range of 30 ‰, might introduce a significant bias over a range of 60 or 100 ‰ (e.g., fig. 7 from *He et al.* [2012]).

The properties outlined above are fully consistent with the Monte Carlo simulations of *Kocken et al.* [2019]. In particular, they explain all of the main patterns displayed in their fig. 5. The primary difference between our approach and that of *Kocken et al.*, beyond the difference in mathematical methods, is that their simulations focus on the empirical transfer function (eq. 2), which corresponds

to parameters a and c . Here we show that the uncertainty from compositional non-linearities (eq. 1) behaves in a similar way, and that all of these corrections can be propagated explicitly in a unified manner, side-stepping the need for Monte Carlo simulations.

3.2 Impact of standardization errors

Because the relative contributions of the autogenic and allogenic error components defined above (eqs. 11–13) are sensitive to the distribution of analyses among anchor and unknown samples and on the isotopic composition of unknowns relative to the anchor polygon, they are expected to vary greatly between laboratories and/or sessions. The InterCarb dataset, comprising over five thousand analyses from 22 different laboratories [Bernasconi *et al.*, 2021], offers an excellent opportunity to quantify these two components in a wide range of realistic settings.

A compilation of σ_s versus σ_u for the average Δ_{47} value of unknown samples obtained in each of the 77 InterCarb sessions is shown in figure 2. As expected, standardization errors for IAEA-C1, a marble sample which plots within the anchor polygon defined in $(\delta_{47}, \Delta_{47})$ space by ETH-1/2/3, are generally slightly smaller than autogenic errors, resulting in a modest increase of the total Δ_{47} error (σ_{47}) relative to the autogenic error. Samples IAEA-C2 (natural travertine) and ETH-4 (synthetic calcite), both of them located outside of the anchor polygon, display larger standardization errors, thereby increasing σ_{47} by an average factor of 1.5 and up to a factor of 2. Finally, in the case of the MERCK sample, a synthetic carbonate with extremely depleted $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, standardization errors generally dominate. As a result, propagating them into the total Δ_{47} error increases σ_{47} by an average factor of 2.5 and up to a factor of 4.

3.3 Correlations between samples

Compared to most other isotopic or elemental tracers, carbonate clumped isotopes stand out in that analytical uncertainties remain large relative to the range of Δ_{47} values typical of natural samples. Standardization errors contribute a sizable portion of these uncertainties, but it is notable that they do so in a way that is strongly correlated between samples, as illustrated by the joint 95 % confidence ellipses for the average Δ_{47} values of unknown samples shown in figure 3.

Appendix B provides full computational details for the covariance between the session-averaged Δ_{47} values of two unknowns samples (B.1); the uncertainties characterizing Δ_{47} differences between samples (B.2); and weighted mean Δ_{47} values averaged over several samples (B.3). The key point to keep in mind is that full analytical errors are not independent between samples of the same session, with the following consequences: (1) when averaging many Δ_{47} measurements within a single session, analytical errors will not tend to zero but to the standardization error for this sample; (2) the error on Δ_{47} differences between samples of similar compositions (as is often the case in paleoclimate records) is largely unaffected by standardization errors, but only if they are analyzed within the same session.

3.4 Gaussian approximation of standardization errors

The error propagation formulas presented in section 2.6 are first-order Taylor approximations. Because Δ_{47} is not a linear combination of $(\Delta_{47}^{\text{raw}}, \delta_{47}, a, b, c)$, propagated errors in Δ_{47} are not strictly Gaussian. However, after quantifying the non-Gaussian effects of these approximations using Monte Carlo simulations of the full InterCarb dataset (Appendix C), we find that these deviations from normality remain entirely negligible in practice.

As an extreme example, figure 4 shows the Monte Carlo distribution of standardization errors for the average Δ_{47} value of IAEA-C2 in one of the InterCarb sessions, chosen because it is the “least Gaussian” distribution of the whole dataset, i.e. the least likely to be Gaussian ($p = 2 \times 10^{-7}$) based on a Kolmogorov-Smirnov test. Even in this worst-case example, differences between the Monte Carlo cumulative distribution function (CDF) and the Gaussian CDF computed from eqs. (11–13) remain minuscule: the Monte Carlo average of Δ_{47} for this particular sample is 0.6659 ‰ (versus 0.6640 ‰ for the propagated value), and the width of the 95 % spread of values in the Monte Carlo dataset is ± 0.0494 ‰ (versus ± 0.0491 ‰ for the Gaussian approximation).

3.5 Statistical weighting options

For the sake of simplicity, the error model described above rests on simple assumptions, for example by assigning equal statistical weights to all analyses. In the following sections we briefly discuss various ways in which this error model could be modified to better reflect real-life analytical conditions.

3.5.1 Equal session weights

In the general case where all sessions are considered equal, we recommend that each session should first be standardized using eqs. (21) and (23). The *overall* Δ_{47}^{raw} repeatability should then be computed using a slightly modified version of eq. (6), with N_A being the number of anchor samples, N_U the number of unknown samples, and N the total number of analyses:

$$(\sigma_{47}^{\text{raw}})^2 = \frac{1}{N - N_A - N_U} \sum \left(\Delta_{47}^{\text{raw}} - a \overline{\Delta_{47}} - b \delta_{47} - c \right)^2 \quad (17)$$

This overall repeatability should then be used to scale the covariance matrix of each session according to eq. (7).

3.5.2 Different session weights

It may be justified in some cases to assign different statistical weights to analyses from different sessions. We would not generally recommend doing so based only on observed differences in σ_{47} (which will inevitably vary slightly between sessions), unless these differences are statistically significant with a high level of confidence. On the other hand, data produced under different analytical conditions may in some cases reasonably be expected to be more or less precise: for example, measurements obtained using greater ion currents should be more precise due to counting statistics alone.

In such cases, we may first divide sessions into groups expected to share similar analytical precision levels. Pooled Δ_{47}^{raw} repeatabilities for each group may then be computed according to eq. (17), and subsequently applied to covariance matrix scaling according to eq. (7).

3.6 Pooled standardization model taking unknown samples into account

3.6.1 Principle

By only considering anchor samples to constrain the standardization parameters (a , b , c) of each session, the models described so far neglect some useful information. As a matter of fact, even without prior knowledge of the Δ_{47} values of unknown samples, we expect the relative mapping of anchors and unknowns in $(\delta_{47}, \Delta_{47})$ space to be preserved between sessions. This approach is only useful when some of the sessions have unknown samples in common, but in that case it is likely to substantially increase the number of observations constraining the standardization model, making it more robust (less sensitive to outliers in the anchor analyses) and more precise (by virtue of increasing the model's degrees of freedom).

In practice, instead of treating each session as a separate least-squares problem, we now aim to minimize an “pooled” version of the χ^2 defined in eq. (4), this time summed over all analyses (including both anchors and unknowns) in all sessions considered:

$$\chi^2 = \sum (\Delta_{47}^{\text{raw}} - a_i \Delta_{47} - b_i \delta_{47} - c_i)^2 \quad (18)$$

where Δ_{47}^{raw} and δ_{47} are the observations from each analysis, (a_i, b_i, c_i) are the standardization parameters for session (i), and Δ_{47} is either a nominal value assigned *a priori* (for anchor analyses) or an additional, free model parameter equal to the Δ_{47} value of the relevant unknown sample. The pooled regression model now rests on a number of observations equal to the total number of analyses, with a number of model parameters equal to the number of unknown samples plus three times the number of sessions.

Because some of the χ^2 terms include the product of two model parameters, this is not a linear least-squares problem and the direct solution of Appendix A no longer applies. One may, however, call upon well-established numerical approaches designed to optimize non-linear problems. In our experience, the classical Levenberg-Marquardt method [Levenberg, 1944; Marquardt, 1963], as implemented by the [LMFIT](#) Python package [Newville *et al.*, 2014], is well suited to this task. Even for large datasets of several thousand analyses, it is able to quickly and reliably output a vector of best-fit values for all model parameters (including Δ_{47} values for all unknown samples) along with the corresponding covariance matrix, thus directly providing standard errors and covariances between unknown sample Δ_{47} values.

3.6.2 Benefits

The benefits of a pooled standardization model may not be immediately obvious, but this approach should yield systematic improvements in the robustness and accuracy of the standardization procedure. For instance, considering the samples shown in figure 1, it may be clear that forcing the Δ_{47} value of MERCK to remain consistent between sessions should greatly contribute to constrain variations in the compositional slope (b) between sessions, even without knowing MERCK's true composition. The same argument could be made if one were to analyze heated and equilibrated gases along with carbonate standards, treating them as entirely unknown samples: even without any knowledge of CO_2 equilibrium values nor of acid fractionation effects, the large spread of Δ_{47} between heated and equilibrated gases would strongly constrain variations of the scrambling effect (a) between sessions, thereby reducing standardization errors for all samples.

Figure 5 illustrates this reduction in standardization errors by showing $(\delta_{47}, \Delta_{47})$ plots for the four sessions from Lab #12 in the InterCarb dataset, comparing the error fields resulting either from the pooled standardization approach (one model with 153 degrees of freedom) or from the earlier approach ignoring unknown samples (four independent models with 20, 16, 24, and 16 degrees of freedom, respectively). Although the locations and values of the error field minima remain largely unaffected by the choice of standardization method, in this case the pooled model strongly reduces standardization errors for analyses plotting outside of the anchor polygon (from 10–11 ppm down to 6 ppm for MERCK), despite the fact that no assumption was made regarding the true Δ_{47} values of unknown samples.

3.6.3 Caveat

The pooled approach depends critically on our earlier assumption that samples are homogeneous, which we acknowledge to be generally but not universally true. It is however simple enough, in the presence of samples suspected to be heterogeneous (i.e. whose Δ_{47} repeatability is demonstrably worse than for carbonate standards with a statistically high level of confidence), to treat each of the corresponding analyses as belonging to separate samples.

3.7 ClumpyCrunch and D47crunch

The calculations discussed above may be tedious to implement from scratch. The simplest way to take advantage of these error models is to use the latest version of the open-source ClumpyCrunch web application (<https://clumpycrunch.pythonanywhere.com>), which implements both the independent-sessions method of section 2.6 and the pooled standardization approach of section 3.6. Those wishing to experiment at a deeper level may install the underlying, open-source D47crunch library for Python (<https://doi.org/10.5281/zenodo.4314550>), which also supports computing different repeatabilities for different groups of sessions (section 3.5.2); explicitly treating some samples as potentially inhomogeneous (section 3.6); modeling temporal drifts in parameters a , b , c (appendix A.2); computing standard errors for Δ_{47} differences and/or means accounting for analytical covariance between samples (appendix B.2-B.3); and assessing whether the Δ_{47} repeatabilities of two samples differ significantly. Both D47crunch and ClumpyCrunch also output robust 95 % confidence limits for final Δ_{47} values based on the number of degrees of freedom in the standardization models.

4 Conclusion

The framework presented here provides a quantitative/predictive description of Δ_{47} error propagation, fully taking into account standardization errors and their properties. It corroborates and extends earlier investigations based on Monte Carlo simulations [Kocken *et al.*, 2019]. This mathematical formulation is found not to introduce large deviations from normality: in other words, if Δ_{47}^{raw} errors are Gaussian, the fully propagated Δ_{47} errors may also be treated as Gaussian for all practical purposes. What's more, as reported by Bernasconi *et al.* [2021], using this framework yields a very reasonable ($p = 0.19$) prediction for the distribution of inter-laboratory scatter in Δ_{47} values within the InterCarb dataset.

Based on this framework, we describe a new, “pooled” standardization method designed to make full use of the constraints available from both anchor and unknown analyses. This approach is expected to yield substantially improved standardization models, both in terms of precision and robustness. We also provide new online resources and a Python library aiming to make the use of such error models as simple as possible. This library being open-source and fully documented, implementing the methods described here in existing software such as Easotope [John & Bowen, 2016] should be straightforward.

Most published clumped-isotope studies so far have lacked a rigorous propagation of standardization errors. This, of course, is not a problem in itself, but the InterCarb results unambiguously demonstrate that these standardization uncertainties are both necessary and sufficient to explain the inter-laboratory scatter observed in this large dataset ($N = 5329$). Going one step further, it could be argued that the ongoing persistence of inter-laboratory discrepancies in Δ_{47} calibrations [Petersen *et al.*, 2019] is due, at least in part, to largely ignored standardization errors. Whatever the case, it seems likely that future comparisons between results obtained in different laboratories would greatly benefit from more accurate error estimates.

Finally, although all statistical models are interpretative approximations, their ultimate value depends less on their exactness than on their practical usefulness. At the very least, the framework described here may help improve standardization protocols (e.g., anchor/unknown ratios, compositional distribution of anchors) and inform our collective effort to establish inter-laboratory reference materials.

Data and code

The complete raw data and all associated code used in this work are available under a Modified BSD License at <https://doi.org/10.5281/zenodo.4314593>.

Notations

a : scrambling factor, one of the standardization parameters, quantifying the amount of molecular recombination during the analytical procedure; its value should lie between 0 and 1.

b : compositional slope, one of the standardization parameters, quantifying small systematic errors in the electrical background of the ion collectors; it may be positive or negative and its absolute value should ideally remain small (10^{-2} or less).

c : working gas offset, one of the standardization parameters, accounting for the fact that the working gas is not necessarily stochastic; in settings where the working gas is equilibrated at room temperature, $c \approx -a$

N_a : Number of analyses.

N_f : Degrees of freedom in a regression model.

N_A : Number of anchor samples.

N_U : Number of unknown samples.

Δ_{47} : delta notation (in ‰) for the clumped-isotope anomaly associated with mass-47 CO_2 ; either denotes the “true” value for a given sample, or the “absolute” value computed from one or more IRMS measurements after standardization.

Δ_{47}^{raw} : “raw” Δ_{47} value from an IRMS measurement, before standardization.

δ_{47} : delta notation (in ‰) for the mass-47 to mass-44 abundance ratio of an analyte CO_2 , generally defined relative to a working reference gas.

σ_{47} : analytical error/uncertainty assigned to individual measurements of Δ_{47} (eq. 5).

σ_{47}^{raw} : analytical error/uncertainty assigned to individual measurements of Δ_{47}^{raw} (eq. 6).

σ_s : allogenic error, i.e. the analytical error/uncertainty on a Δ_{47} measurement arising from the standardization function (eq. 13).

σ_u : autogenic error, i.e. the analytical error/uncertainty on a Δ_{47} measurement arising from the analyses of the unknown sample itself (eq. 12).

Appendix A: Least squares regression

A.1 General linear case

Consider a linear model f defined as:

$$y = f(x, a_1, a_2 \dots a_p) = \sum_{i=1}^p a_i f_i(x) \quad (19)$$

where x is a scalar or vectorial explanatory variable; y the response variable; $(f_1 \dots f_p)$ a series of functions of x ; and $(a_1 \dots a_p)$ a series of scalar factors which are the model parameters to be estimated.

Given n observations $((x_1, y_1) \dots (x_n, y_n))$ to fit, we construct the following matrices:

$$A = \begin{bmatrix} f_1(x_1) & f_2(x_1) & \dots & f_p(x_1) \\ f_1(x_2) & f_2(x_2) & \dots & f_p(x_2) \\ \vdots & \vdots & & \vdots \\ f_1(x_n) & f_2(x_n) & \dots & f_p(x_n) \end{bmatrix} \quad Y = \begin{bmatrix} y_1 \\ y_2 \\ \vdots \\ y_n \end{bmatrix} \quad (20)$$

The best-fit parameters $(a_1 \dots a_n)$ and their unscaled variance-covariance matrix V_0 are then:

$$\begin{bmatrix} a_1 \\ a_2 \\ \vdots \\ a_p \end{bmatrix} = V_0 \times A^T \times Y \quad V_0 = (A^T \times A)^{-1} \quad (21)$$

A.2 Application to the standardization model

The standardization model of eq. (3) is equivalent to the above formulation if:

$$\begin{aligned} y &= \Delta_{47}^{\text{raw}} & f_1(x) &= \Delta_{47} \\ x &= (\delta_{47}, \Delta_{47}) & f_2(x) &= \delta_{47} \\ (a_1, a_2, a_3) &= (a, b, c) & f_3(x) &= 1 \end{aligned} \quad (22)$$

In this case:

$$A = \begin{bmatrix} \Delta_{47} & \delta_{47} & 1 \\ \Delta_{47} & \delta_{47} & 1 \\ \vdots & \vdots & \vdots \\ \Delta_{47} & \delta_{47} & 1 \end{bmatrix} \quad \begin{matrix} \leftarrow \text{analysis \#1} \rightarrow \\ \leftarrow \text{analysis \#2} \rightarrow \\ \leftarrow \text{analysis \#n} \rightarrow \end{matrix} \quad \begin{bmatrix} \Delta_{47}^{\text{raw}} \\ \Delta_{47}^{\text{raw}} \\ \vdots \\ \Delta_{47}^{\text{raw}} \end{bmatrix} = Y \quad (23)$$

To take into account an uncertainty, noted σ , assigned to the observations, A and Y should both be divided by σ , which will leave the best-fit parameters unchanged and scale the variance-covariance matrix V_0 by a factor of σ^2 (as in eq. 7).

Alternatively, to assign individual uncertainties, noted $(\sigma_1 \dots \sigma_n)$ to the n analyses, each line of A and each element of Y should be divided by the corresponding σ value:

$$A = \begin{bmatrix} \Delta_{47}/\sigma_1 & \delta_{47}/\sigma_1 & 1/\sigma_1 \\ \Delta_{47}/\sigma_2 & \delta_{47}/\sigma_2 & 1/\sigma_2 \\ \vdots & \vdots & \vdots \\ \Delta_{47}/\sigma_n & \delta_{47}/\sigma_n & 1/\sigma_n \end{bmatrix} \quad \begin{matrix} \leftarrow \text{analysis \#1} \rightarrow \\ \leftarrow \text{analysis \#2} \rightarrow \\ \leftarrow \text{analysis \#n} \rightarrow \end{matrix} \quad \begin{bmatrix} \Delta_{47}^{\text{raw}}/\sigma_1 \\ \Delta_{47}^{\text{raw}}/\sigma_2 \\ \vdots \\ \Delta_{47}^{\text{raw}}/\sigma_n \end{bmatrix} = Y \quad (24)$$

Extending this model with additional parameters should be rather straightforward. For instance, in order to account for a temporal drift in the compositional non-linearity, one could reformulate the model, with t denoting time and an additional standardization parameter d , as:

$$\Delta_{47}^{\text{raw}} = a \Delta_{47} + (b + td) \delta_{47} + c \quad (25)$$

Which would correspond to:

$$A = \begin{bmatrix} \Delta_{47} & \delta_{47} & 1 & t \delta_{47} \\ \Delta_{47} & \delta_{47} & 1 & t \delta_{47} \\ \vdots & \vdots & \vdots & \vdots \\ \Delta_{47} & \delta_{47} & 1 & t \delta_{47} \end{bmatrix} \quad \begin{matrix} \leftarrow \text{analysis \#1} \rightarrow \\ \leftarrow \text{analysis \#2} \rightarrow \\ \\ \leftarrow \text{analysis \#n} \rightarrow \end{matrix} \quad \begin{bmatrix} \Delta_{47}^{\text{raw}} \\ \Delta_{47}^{\text{raw}} \\ \vdots \\ \Delta_{47}^{\text{raw}} \end{bmatrix} = Y \quad (26)$$

Appendix B: Δ_{47} covariance

B.1 Covariance between unknown samples

Consider two unknown samples A and B, whose session-averages compositions ($\overline{\delta_{47}}$, $\overline{\Delta_{47}^{\text{raw}}}$, and $\overline{\Delta_{47}}$) are respectively noted δ_A , δ_B , Δ_A^{raw} , Δ_B^{raw} , Δ_A , and Δ_B . Defining X as the column vector $[\Delta_A, \Delta_B]$, we can express its Jacobian J_X relative to the system of variables $(\Delta_A^{\text{raw}}, \Delta_B^{\text{raw}}, a, b, c)$ and the covariance C of this quintuplet as:

$$J_X = \frac{1}{a} \begin{bmatrix} 1 & 0 & -\Delta_A & -\delta_A & -1 \\ 0 & 1 & -\Delta_B & -\delta_B & -1 \end{bmatrix} \quad C = \begin{bmatrix} (\sigma_{47}^{\text{raw}})^2/N_A & 0 & 0 & 0 & 0 \\ 0 & (\sigma_{47}^{\text{raw}})^2/N_B & 0 & 0 & 0 \\ 0 & 0 & \sigma_a^2 & c_{ab} & c_{ac} \\ 0 & 0 & c_{ab} & \sigma_b^2 & c_{bc} \\ 0 & 0 & c_{ac} & c_{bc} & \sigma_c^2 \end{bmatrix} \quad (27)$$

The covariance matrix of X is then:

$$C_X = J_X \times C \times J_X^T \quad (28)$$

Because of the structure of J and C , the non-zero terms of C_X are equal to:

$$\text{cov}(\Delta_A, \Delta_B) = \frac{1}{a^2} \begin{bmatrix} \Delta_A & \delta_A & 1 \end{bmatrix} \times \begin{bmatrix} \sigma_a^2 & c_{ab} & c_{ac} \\ c_{ab} & \sigma_b^2 & c_{bc} \\ c_{ac} & c_{bc} & \sigma_c^2 \end{bmatrix} \times \begin{bmatrix} \Delta_B \\ \delta_B \\ 1 \end{bmatrix} \quad (29)$$

$$\text{cov}(\Delta_A, \Delta_B) = \frac{1}{a^2} (\Delta_A \Delta_B \sigma_a^2 + \delta_A \delta_B \sigma_b^2 + \sigma_c^2 + (\Delta_A \delta_B + \delta_A \Delta_B) c_{ab} + (\Delta_A + \Delta_B) c_{ac} + (\delta_A + \delta_B) c_{bc}) \quad (30)$$

The covariance between mean Δ_{47} values of two samples averaged over several sessions is zero if the samples were never analyzed in the same session. Otherwise, with ω_{Ai} and ω_{Bi} weights defined as in (15):

$$\Delta_A^{\text{final}} = \sum_i \omega_{Ai} \Delta_{Ai} \quad \text{with } i \text{ denoting all sessions including A} \quad (31)$$

$$\Delta_B^{\text{final}} = \sum_j \omega_{Bj} \Delta_{Bj} \quad \text{with } j \text{ denoting all sessions including B} \quad (32)$$

$$\text{cov}(\Delta_A^{\text{final}}, \Delta_B^{\text{final}}) = \sum_k \omega_{Ak} \omega_{Bk} \text{cov}(\Delta_{Ak}, \Delta_{Bk}) \quad \text{with } k \text{ denoting all sessions including both A and B} \quad (33)$$

B.2 Standard errors on Δ_{47} differences between samples

Consider two unknown samples A and B, whose session-averages compositions ($\overline{\delta_{47}}$, $\overline{\Delta_{47}^{\text{raw}}}$, and $\overline{\Delta_{47}}$) are respectively noted δ_A , δ_B , Δ_A^{raw} , Δ_B^{raw} , Δ_A , and Δ_B . Defining x as the difference ($\Delta_A - \Delta_B$), we can express its Jacobian J_x relative to the system of variables (Δ_A^{raw} , Δ_B^{raw} , a , b , c) as:

$$J_x = \frac{1}{a} \begin{bmatrix} 1, & -1, & \Delta_B - \Delta_A, & \delta_B - \delta_A, & 0 \end{bmatrix} \quad (34)$$

and compute the variance of x using the same covariance matrix C as above:

$$\sigma_x^2 = J_x \times C \times J_x^T \quad (35)$$

$$\sigma_x^2 = \sigma_{47}^2 \left(\frac{1}{N_A} + \frac{1}{N_B} \right) + \frac{(\Delta_B - \Delta_A)^2 \sigma_a^2 + (\delta_B - \delta_A)^2 \sigma_b^2 + 2(\Delta_B - \Delta_A)(\delta_B - \delta_A)c_{ab}}{a^2} \quad (36)$$

B.3 Standard errors on mean Δ_{47} values averaged over several samples

As an example, we treat here the problem of a weighted average of three samples. Consider three unknown samples A, B, and C, whose session-averages compositions ($\overline{\delta_{47}}$, $\overline{\Delta_{47}^{\text{raw}}}$, and $\overline{\Delta_{47}}$) are respectively noted δ_A , δ_B , δ_C , Δ_A^{raw} , Δ_B^{raw} , Δ_C^{raw} , Δ_A , Δ_B , and Δ_C . Defining W as the weighted average ($x_A \Delta_A + x_B \Delta_B + x_C \Delta_C$) and w as the weighted average ($x_A \delta_A + x_B \delta_B + x_C \delta_C$), we can express the Jacobian of W relative to the system of variables (Δ_A^{raw} , Δ_B^{raw} , Δ_C^{raw} , a , b , c) as:

$$J_W = \frac{1}{a} \begin{bmatrix} x_A & x_B & x_C & -W & -w & -1 \end{bmatrix} \quad (37)$$

and compute the variance of W using the same method as above:

$$\sigma_W^2 = J_W \times \begin{bmatrix} (\sigma_{47}^{\text{raw}})^2 / N_A & 0 & 0 & 0 & 0 & 0 \\ 0 & (\sigma_{47}^{\text{raw}})^2 / N_B & 0 & 0 & 0 & 0 \\ 0 & 0 & (\sigma_{47}^{\text{raw}})^2 / N_C & 0 & 0 & 0 \\ 0 & 0 & 0 & \sigma_a^2 & c_{ab} & c_{ac} \\ 0 & 0 & 0 & c_{ab} & \sigma_b^2 & c_{bc} \\ 0 & 0 & 0 & c_{ac} & c_{bc} & \sigma_c^2 \end{bmatrix} \times J_W^T \quad (38)$$

$$\sigma_W^2 = \sigma_{47}^2 \left(\frac{x_A^2}{N_A} + \frac{x_B^2}{N_B} + \frac{x_C^2}{N_C} \right) + \frac{W^2 \sigma_a^2 + w^2 \sigma_b^2 + \sigma_c^2 + 2(wWc_{ab} + Wc_{ac} + wc_{bc})}{a^2} \quad (39)$$

Note that the second term above is equal to the value of the standardization error field at the weighted barycenter of the samples in (δ_{47} , Δ_{47}) space.

Appendix C: Monte Carlo assessment of the normality of Δ_{47} errors

Because Δ_{47} is not a linear function of $(\Delta_{47}^{\text{raw}}, \delta_{47}, a, b, c)$, the propagation of standardization errors described in section 2.6 is an approximation. Here we used a Monte Carlo simulation based on the full InterCarb dataset to investigate how much autogenic and allogenic errors deviate from a Gaussian approximation. In each step of the simulation, we offset the original Δ_{47}^{raw} values observed in each of the 5329 analyses by random, independent, zero-centered Gaussian errors with a standard deviation equal to the session's σ_{47}^{raw} value. We then standardize all sessions of the modified dataset and record the final, session-averaged Δ_{47} values of each unknown sample ($N = 226$) for a total of 10^4 iterations. Each of these session averages is submitted to a Kolmogorov-Smirnov (KS) test of normality [Massey, 1951], comparing the distribution of these 10^4 values to a normal distribution centered on the original session-averaged value and whose width depends of the original propagated errors. Each of the 226 KS tests yields a p-value corresponding to the null hypothesis that the two distributions are identical. By design, if the Gaussian approximation of the propagated errors holds true, these p-values should be evenly distributed in the [0–1] interval. We may quantify how well they do so by performing a new KS test comparing the distribution of p-values to the uniform distribution, yielding a new, final p-value for the hypothesis that the errors in the InterCarb dataset follow Gaussian distributions.

We run this simulation in three different configurations, considering only autogenic errors, only standardization errors, or both. Initially, the random errors introduced in each iteration are scaled according to the Δ_{47} repeatability of each session (fig. 6A). We then repeat the simulations twice, by scaling the random errors according to a constant Δ_{47} repeatability of 50 ppm and 5 ppm, respectively (figs. 6B, 6C).

Predictably, based on eqs. (12-13), we find that autogenic errors behave in a Gaussian manner ($p = 0.81$), but this is clearly not the case for standardization errors ($p = 1 \times 10^{-28}$). Because the error propagation formula of eq. (8) is equivalent to a first-order Taylor expansion, the non-normality of standardization errors is expected worsen as Δ_{47} repeatability increases, as is the case in fig. 6B, and to become negligible when Δ_{47} repeatability is small enough (fig. 6C).

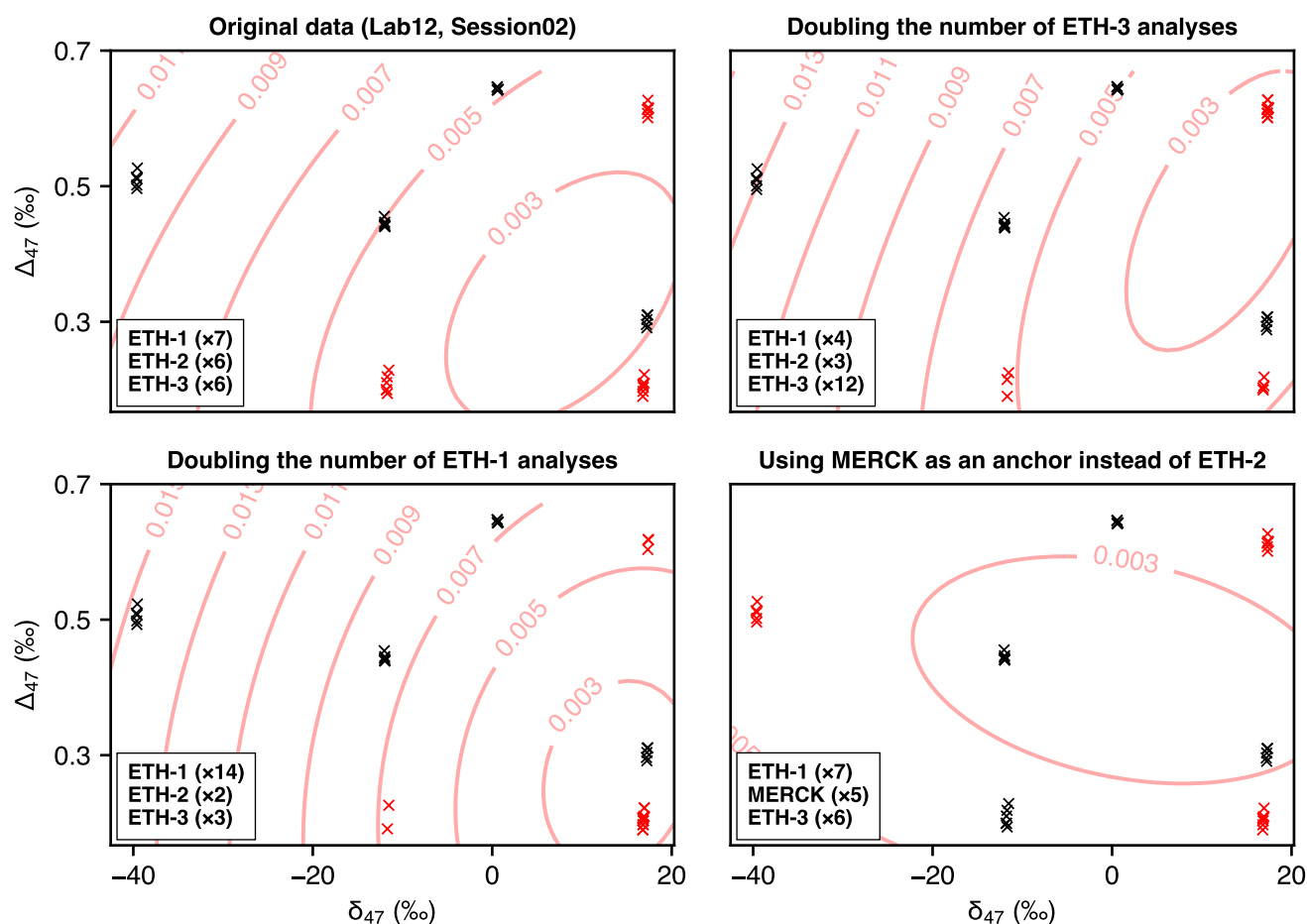


Figure 1: Properties of standardization errors. Upper left panel shows the unknown and anchor analyses (black and red crosses, respectively) and contours of the standardization error field (red lines) for Session #2 of Lab #12 in the InterCarb dataset. Upper right and lower left panels modify the original data by changing the distribution of anchor analyses between ETH-1, ETH-2, and ETH-3, keeping the total number of anchor analyses constant, illustrating that the error minimum coincides in $(\delta_{47}, \Delta_{47})$ space with the barycenter of anchor analyses. The lower right panel corresponds to the original data but treats ETH-2 as an unknown and MERCK as an anchor, highlighting the benefits of using isotopically extreme anchors.

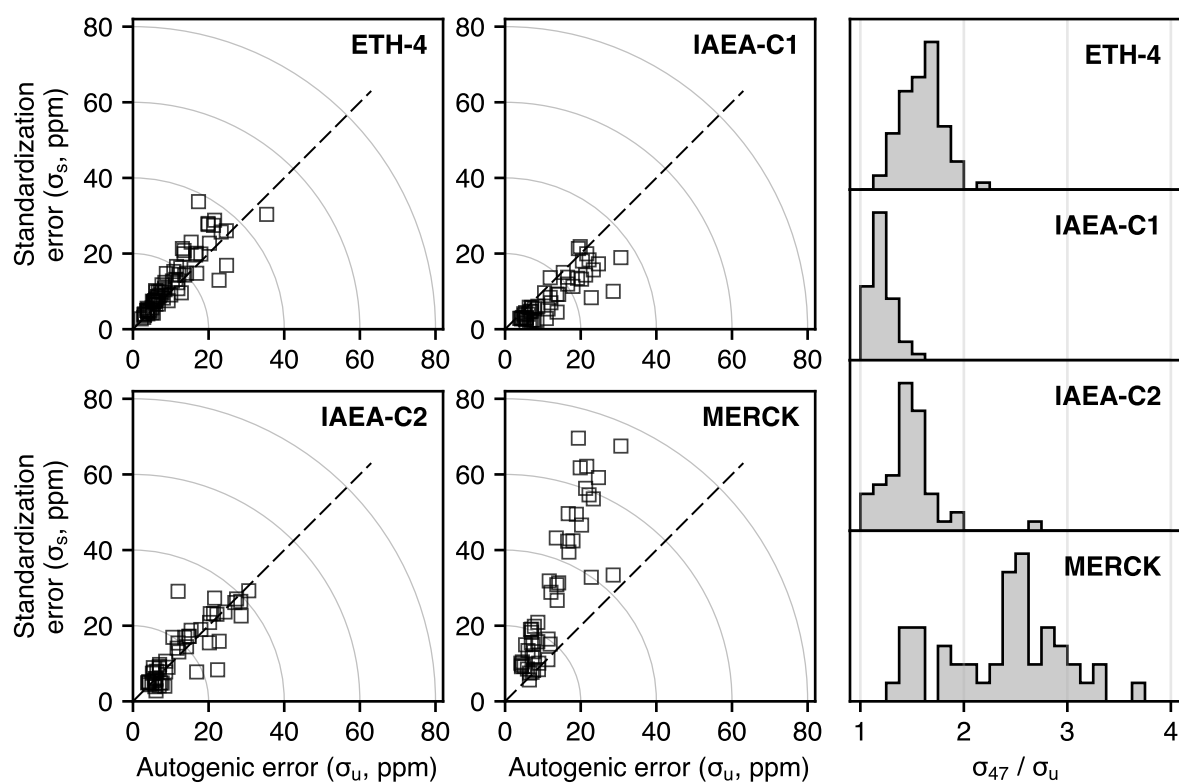


Figure 2: Autogenic versus standardization errors. Each square marker corresponds to the error components for the average Δ_{47} value of an unknown sample in each of the InterCarb sessions. Histograms characterize the ratios of total analytical error (σ_{47}) to autogenic errors (σ_u) for each of the unknown samples.

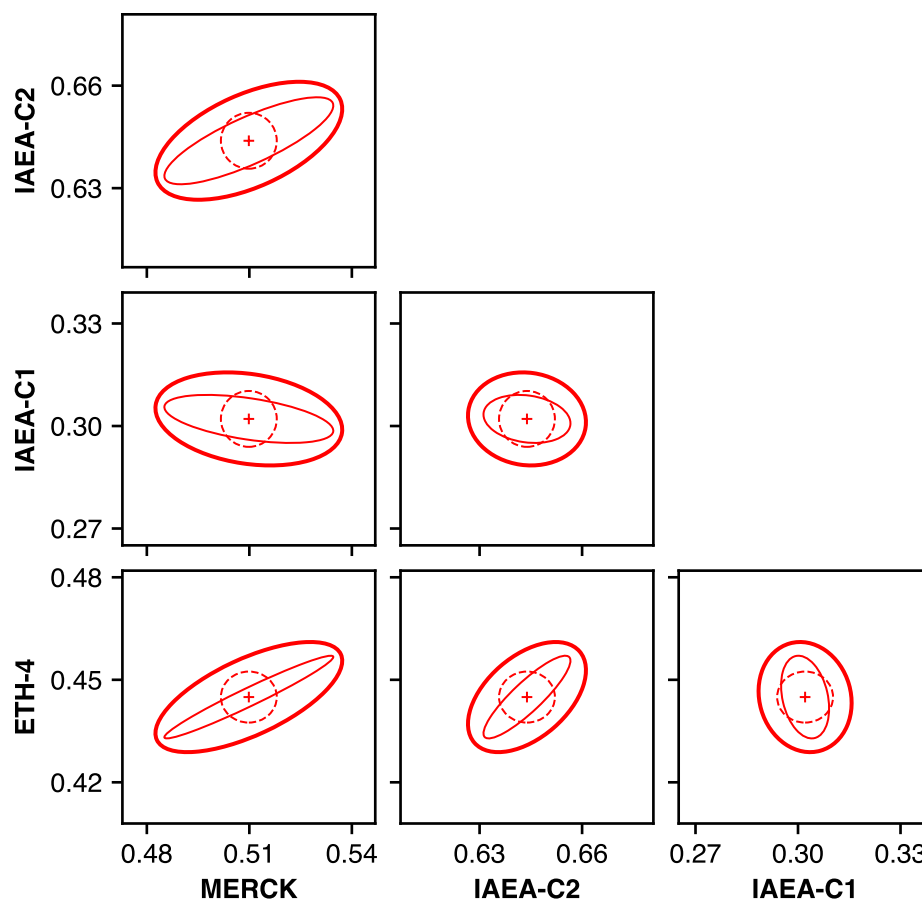


Figure 3: Covariance of errors in session-averaged Δ_{47} values for unknowns samples. Thick red lines correspond to joint 95 % confidence ellipses for the average Δ_{47} values of each unknown sample in Session02 of Lab12 (cf upper left panel of fig. 1). Thin red lines and dashed red lines correspond to joint 95 % confidence ellipses only taking into account standardization and autogenic errors, respectively.

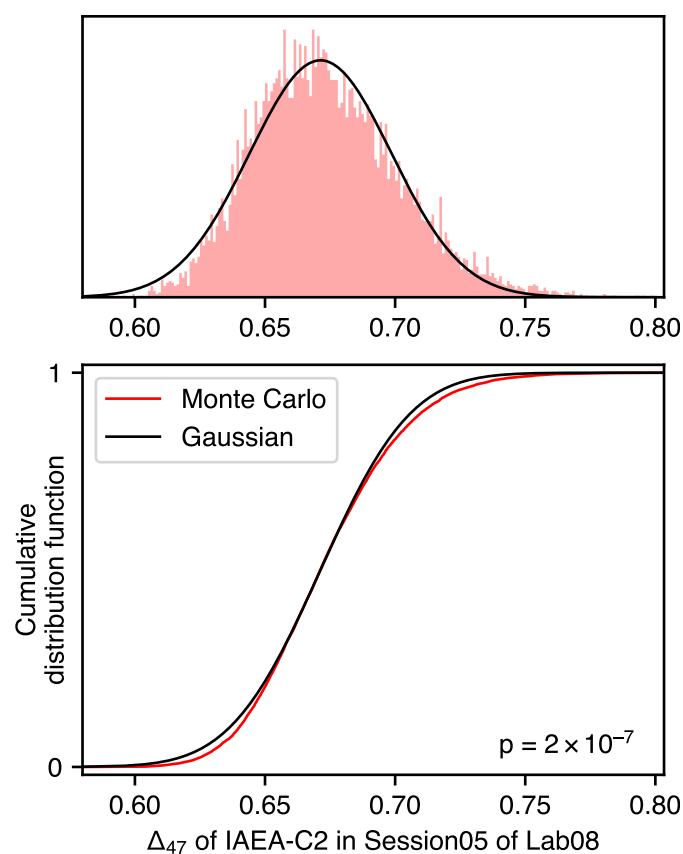


Figure 4: Error distribution for the “least Gaussian” average Δ_{47} value in the InterCarb dataset. Upper panel: red area corresponds to the Monte Carlo histogram of the average Δ_{47} value of IAEA-C2 in Session #7 of Lab #8, black line is the Gaussian probability distribution computed from eqs. (11–13). Lower panel: Monte Carlo (red line) and Gaussian (black line) cumulative distributions functions for this average Δ_{47} value. In the lower left corner, p is the Kolmogorov-Smirnov p -value for the null hypothesis that these two distributions are identical.

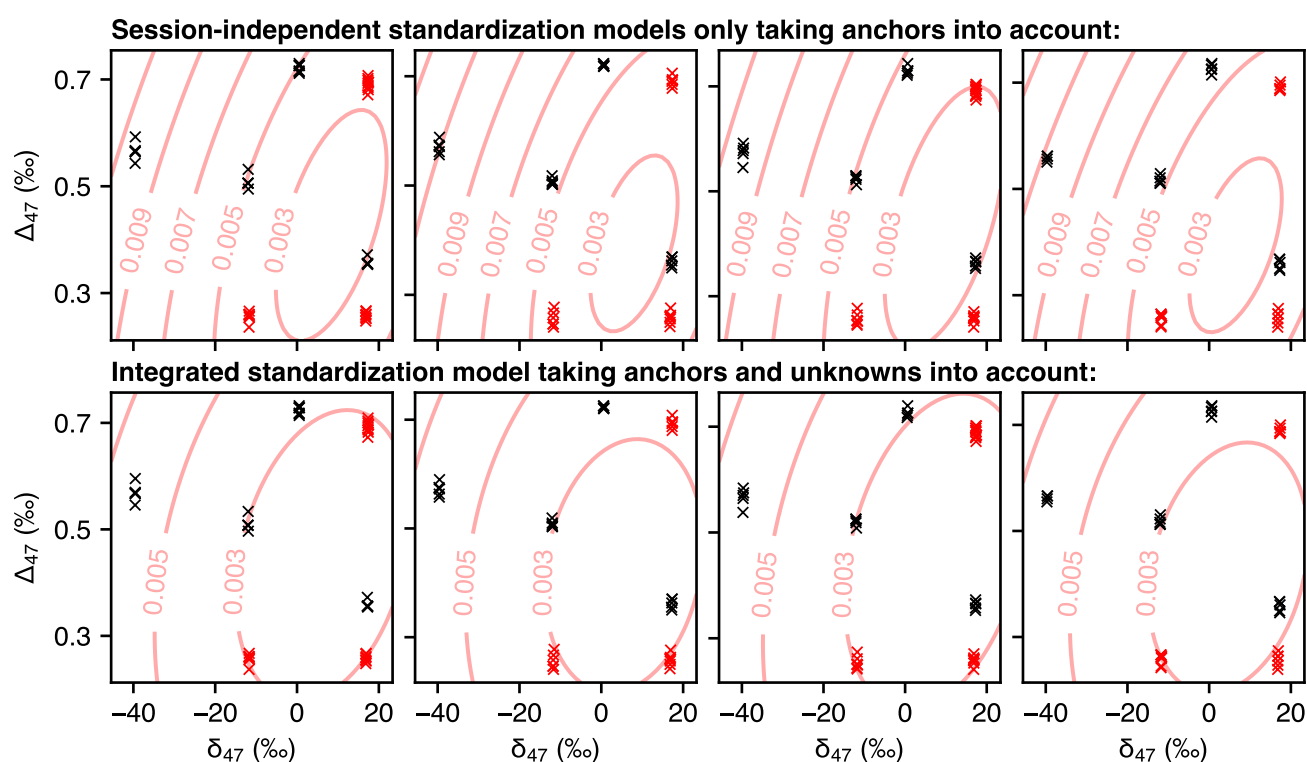


Figure 5: Benefits of a pooled standardization model. Unknown and anchor analyses (black and red crosses, respectively) and contours of the standardization error fields (red lines) for the four sessions of Lab #12 in the InterCarb dataset. Upper row: using four independent models only taking anchor analyses into account, with 20, 16, 24, and 16 degrees of freedom, respectively. Lower row: using a pooled standardization model with 153 degrees of freedom taking anchors and unknowns into account as described in section 3.6.

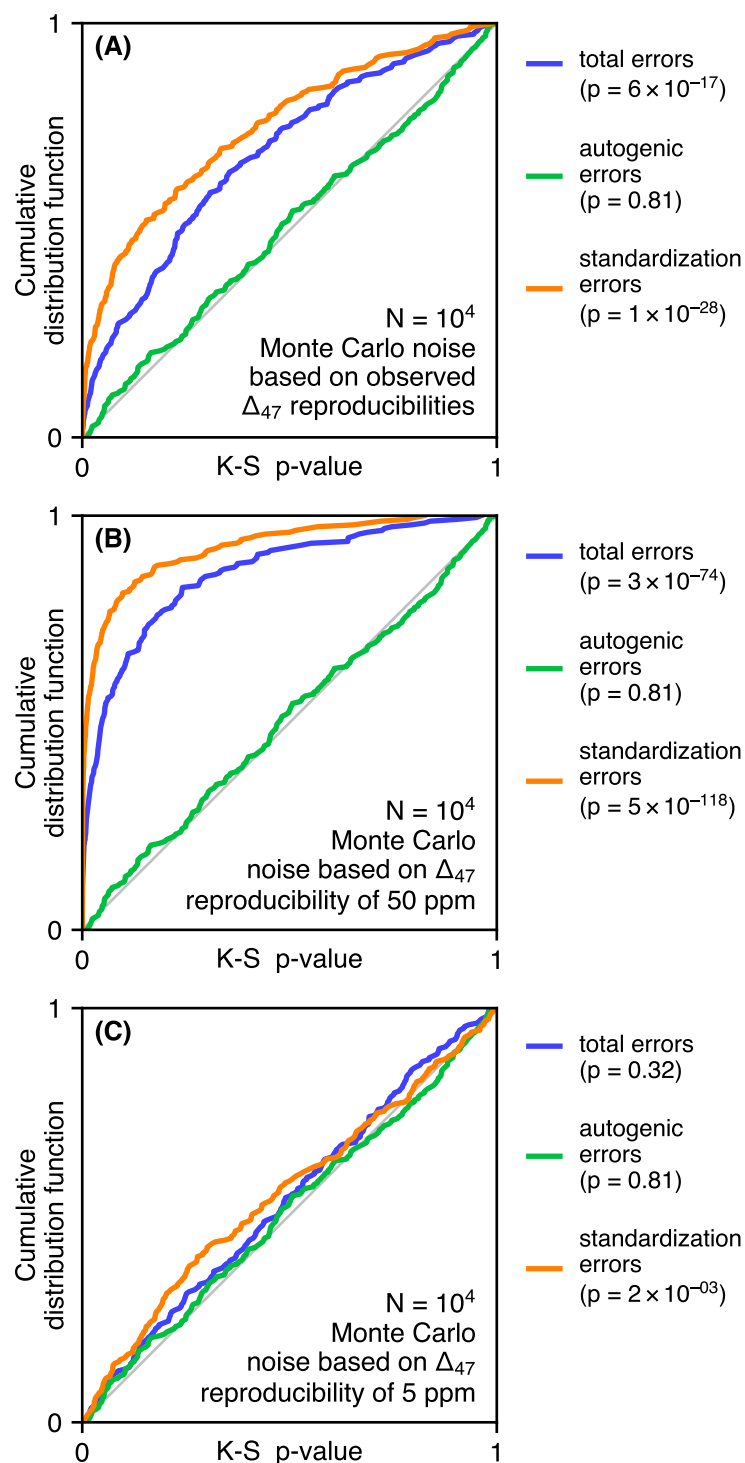


Figure 6: Monte Carlo simulation results All three panels display the cumulative distribution function of the p-values obtained from 10^4 Monte Carlo simulations of the full InterCarb dataset (see Appendix C for computational details). When the random offsets used by the simulation are scaled according to the original data (A), autogenic errors behave in a Gaussian manner, but the standardization (“allogenic”) errors do not, due to the limits of the first-order Taylor approximations used here for error propagation. As expected, greatly increasing (B) or decreasing (C) the random offsets used by the simulation results modulates the non-Gaussianity of standardization errors, while autogenic errors, despite being respectively increased or decreased (not shown here), remain Gaussian.

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