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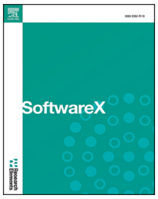

D4Xgui: A tool for baseline correction and standardization of carbonate clumped isotope raw data

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ABSTRACT

Accurate and precise mass spectrometric determination of ppm-ppb quantities of mass 47–49 *clumped* isotopologues of carbonate-derived CO_2, expressed as Δ_{47}–Δ_{49} values, requires advanced processing schemes. Here, we introduce D4Xgui, a user-friendly processing tool that allows correction of mass-spectrometric raw intensities for a pressure baseline artifact, before standardization is carried out using D47crunch. D4Xgui enables rapid processing of multi-session data under consideration of full error-propagation, interactive visualization of results including tools for data quality assurance, calculation of carbonate crystallization temperature from finally processed data, and rapid re-evaluation of datasets with revised processing parameters. Though the primary focus of D4Xgui is on carbonates it can also be applied to the correction of mass spectrometric raw data obtained on CO_2 from other sources.

Metadata

Code metadata.

Nr.	Code metadata description	Metadata
C1	Current code version	v1.0.0
C2	Permanent link to code/repository used for this code version	https://github.com/itsMig/D4Xgui/releases/tag/v1.0.0
C4	Legal Code License	MIT License
C5	Code versioning system used	git
C6	Software code languages, tools, and services used	Python, Streamlit
C7	Compilation requirements, operating environments & dependencies	Python 3.11 +, with D47crunch, D47calib, matplotlib, numpy, ogls, pandas, plotly, Streamlit
C8	If available Link to developer documentation/manual	https://github.com/itsMig/D4Xgui
C9	Support email for questions	bernecker@em.uni-frankfurt.de

1. Motivation and significance

Carbonate clumped isotope thermometry enables determination of carbonate formation temperatures [1] and allows identification of effects of isotopic disequilibrium [2] or secondary alteration [3,4], among others. Its application relies on thermodynamically driven fractionation of stable carbon and oxygen isotopes among different carbonate isotopologues, a phenomenon that favors increasing excess formation (relative to stochastically predicted isotope partitioning) of multiply heavy substituted isotopologues (*clumped isotopes*) with decreasing temperature [5]. Since excess abundances of multiply substituted isotopologues cannot be analysed directly within the carbonate directly, samples are quantitatively reacted with phosphoric acid and measurements are performed on the evolved CO_2. Precise analysis of excess abundances of multiply substituted isotopologues was initially restricted to CO_2 of

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mass 47 (mainly made up of $^{13}C^{18}O^{16}O$) and the corresponding metric defined as the Δ_{47} value. Recent improvements in instrumentation have also enabled highly precise quantification of excess abundances of mass 48 (mainly made up of $^{12}C^{18}O^{18}O$) and 49 (exclusively made up of $^{13}C^{18}O^{18}O$) isotopologues [6–8]. Analysis of Δ_{48} alongside Δ_{47} values makes it possible to identify rate-limiting processes involved in carbonate (bio-)mineralization and to correct Δ_{47} values for these non-thermal biases, finally achieving accurate reconstruction of carbonate crystallization temperature [7,9]. The addition of Δ_{48} and Δ_{49} to the Δ_{47} toolkit can also help to identify isobaric interferences that follow compound-specific vectors in Δ_{47}/Δ_{48}- and Δ_{48}/Δ_{49}-space [10].

Gas-source isotope ratio mass spectrometry represents a well-established technique for the analysis of relative abundances of CO_2 isotopologues of masses 44–49. Carbonate-derived CO_2 is repeatedly measured against a working gas of known oxygen (expressed as $\delta^{18}O$) and carbon (expressed as $\delta^{13}C$) isotope compositions, and the isotopic composition of unknown sample CO_2 is expressed as δ^{45}, δ^{46}, δ^{47}, δ^{48} and δ^{49} values relative to that of the working gas. Precise and accurate determination of Δ_{47}, Δ_{48} and Δ_{49} values requires enhanced counting statistics, achieved through multiple alternating replications of unknowns and standards. State-of-the-art processing schemes for the determination of $\delta^{13}C$, $\delta^{18}O$, and Δ_{47}-Δ_{49} values from mass spectrometric raw δ^i values generally consider corrections for (i) isobaric contributions from ^{17}O-bearing isotopologues [11–13], (ii) compositional non-linearity [14] and iii) scale compression [15]. Compositional non-linearity can arise from secondary electrons which affect measured m/z_{47}–m/z_{49} intensities. These drive the baseline below m/z_{47}–m/z_{49} to negative intensities, the extent of which depends on the pressure of CO_2 in the ion source [pressure baseline effect, PBL;16]. Compositional non-linearity is expressed by slopes $\neq$ zero in correlation plots of δ^i vs Δ_i values for CO_2 gases (or carbonates) of different bulk isotopic compositions, that were equilibrated at a given temperature. This bias is driven by a mismatch of bulk isotopic compositions, when comparing the sample analyte with that of the working gas. Since the negative PBL signal scales with the fixed-intensity m/z_{44} beam and –over a short term– the PBL signal doesn't change in magnitude, samples characterized by a lighter δ^i composition compared to that of the working gas will have a negative Δ_i bias, and vice versa. Recently developed software allows correction of mass spectrometric raw data for (i), (ii) and (iii) [e.g.,17,18], but lacks optimized scaling-factor-based correction of mass-spectrometric raw intensities utilizing a half-mass cup, which can introduce artificial bias on δ^i values, ultimately influencing final Δ_i values [6,19]. In addition, some processing schemes lack full error propagation [e.g., 18].

Here, we introduce a data processing tool that allows the most accurate determination of fully error-propagated Δ_i values of CO_2 extracted from carbonates. In the first step, a PBL correction algorithm, which fully corrects for the secondary electron-induced bias in mass spectrometric raw δ^i and Δ_i values, through optimized scaling factors is added to the data processing scheme of John and Bowen [18]. In the second step, PBL-corrected δ^{45}-δ^{49} values are standardized with D47crunch [17,20], which allows determination of final and fully error-propagated Δ_i values. Learning a programming language to apply state-of-the-art mathematical processing frameworks is a time-consuming task in itself. With our D4Xgui app, we make a user-friendly data processing scheme available for the carbonate clumped isotope community.

2. Software description

2.1. Software architecture

D4Xgui is developed in Python and built using the Streamlit framework for interactive web applications. The tool enables users to apply baseline correction to mass-spectrometric carbonate clumped isotope raw data. Moreover, it integrates the D47crunch library for clumped isotope standardization and full error propagation. The software components are modular for ease of maintenance and future extension. The core architecture separates data acquisition and input validation, PBL correction computations, standardization workflows, visualization modules, and export functionalities. Interactive plots utilize Plotly and Streamlit's native charting capabilities, enabling real-time feedback and rapid data inspection.

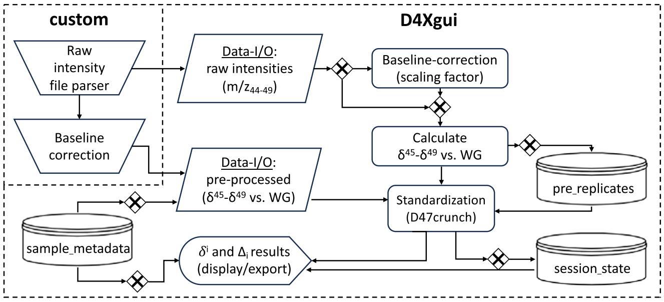


Fig. 1. Flowchart illustrating the internal data architecture of D4Xgui. It is possible to upload eithe raw m/z_{44-49} data or pre-processed δ^{45}-δ^{49} data directly into D4Xgui. The (optional) baseline-correction algorithm is utilizing a half-mass cup signal; if this signal is not available, the user can directly calculate δ^{45}-δ^{49} values from mass-spectrometric raw data. In order to simply use D47crunch, the user can directly upload pre-processed δ^{45}-δ^{49} data. Uploaded or calculated δ^{45}-δ^{49} data can (optionally) be stored in the `pre_replicates` table for later use. The session state may (optionally) be stored with an identifier in the `session_state` table, including uploaded data and processing results – dependend on a user's current session. The (optional) `sample_metadata` table is utilized to apply post- or pre-processing filters, based on sample metadata.

D4Xgui is equipped with multiple data input interfaces; a graphical overview can be found in Fig. 1. Input data (mass-spectrometric m/z_{44-49} data or pre-processed δ^{45}-δ^{49}) can be directly uploaded into D4Xgui using a file navigation context menu and via drag-and-drop functionality. Internally, D4Xgui is backed by a self-contained, disk-based local SQLite database containing a table for pre-processed δ^{45}-δ^{49} values (`pre_replicates` table). In addition to this, a metadata database (`sample_metadata` table) is used to store metadata such as sample name, session, and other sample-specific information, all of which can be used for pre- and post-processing filtering. These databases can be managed through a *Database Management* page. D4Xgui is designed to also allow processing without the use of any database functionality, provided that the necessary data is uploaded prior to processing. Another database (`session_states` table) is utilized for storing entire session caches in a *Save & Reload* page.

2.1.1. Internal data structure

No significant differences were obtained if data evaluation started from the cycle or replicate level; for this reason D4Xgui will always calculate mean replicate values before adding data into the internal database.

Database–pre_replicates table: The `pre_replicates` table is used to store pre-processed δ^{45}-δ^{49} values together with information on `UID`, `Sample`, `Session` and `Timetag`. These data can be derived from the upload, or from D4Xgui's internal calculations.

Database–metadata table: Sample metadata is internally managed through the `sample_metadata` table, and can be provided in *.xlsx* format to make advanced filtering accessible in both, the *Data-I/O* page for pre-processing and, moreover, in pages dedicated to the graphical representation of post-processing results. Metadata can additionally be modified and new entries added to it via the *Database Management* page, *Sample Metadata* tab. These filtering capabilities allow users to, for example, select a specific sample type, whereupon the app will provide all session data that includes archived samples of the chosen type, facilitating easy (re-)processing of multi-session datasets. Metadata filters are based on `Sample`, `Session`, `Project`, `Publication`, `Type`, `Mineralogy` and `in charge` in the actual build.

Database–D4Xgui session state: At any point, it is additionally possible to dump the entire session cache of D4Xgui into another self-contained database `session_states`. This functionality allows the user to store the session state at any point, and either continue processing at a later time, or archive the results for future inspection. To do so, the *Save & Reload* page can be utilized by saving the current session state of the app together with a custom identifier.

2.1.2. Upload options

Before uploading data directly to D4Xgui, it is necessary to format machine-generated raw data to ensure compatibility. While some vendors for analytical setups provide automated *.csv* outputs, others store raw data in undocumented proprietary formats or require human interaction to produce exports. Available tools for parsing raw data from binary files are e.g., isoreader [21] as a script-based option for R users, or Easotope [18] as a multi-platform GUI tool for **.did* files, produced by IsoDat (Thermo Scientific, MAT253 or 253 +).

Upload option A – Uploading raw intensity data: Raw intensity data can either be uploaded in cycle, acquisition or replicate hierarchy. In the current version, uploaded raw m/z intensities can only be corrected for a negative PBL (i.e., for the contribution of secondary electrons) if the gas-source mass spectrometer is equipped with an additional half-mass cup that continuously monitors the PBL intensity [e.g. at $m/z_{47.5}$, see 22]. If no half-mass cup is available, we advise employing a custom, baseline scan-based correction of raw intensities [e.g., 16,19,23]. Otherwise, data can also be processed without prior correction of raw intensities, ignoring potential bias in δ^i values, which ultimately increases uncertainty in final results [6]. The following features are required for each instance: `UID`, `Sample`, `Session`, `Timetag`, `Replicate`, `raw_r44`, `raw_r45`, `raw_r46`, `raw_r47`, `raw_r48`, `raw_r49`, `raw_r47.5`, `raw_s44`, `raw_s45`, `raw_s46`, `raw_s47`, `raw_s48`, `raw_s49`, `raw_s47.5`.

Upload option B–Uploading pre-processed δ^{45}-δ^{49} values: Replicate-level δ^{45}-δ^{49} values, whether PBL-corrected or not, can be uploaded. Given that the D47crunch module is invoked for standardization, its relevant features must be uploaded per instance: `UID`, `Sample`, `Session`, `Timetag`, `d45`, `d46`, `d47`, `d48`, `d49`.

2.2. Software functionalities

The main functionalities of D4Xgui include:

- Correction of raw isotopologue intensities for pressure baseline bias caused by secondary electron effects in isotope-ratio mass spectrometry.
- Least-squares regression for optimization of standardization parameters within the D47crunch framework.
- Comprehensive error propagation that includes analytical uncertainty, as well as contributions from standardization steps.
- Interactive visualization of raw, corrected, and standardized data, enabling quality control at every level.
- Metadata management to allow filtering of multi-session or multi-sample datasets.
- Export capabilities for processing outputs and figures.

2.2.1. Baseline correction and standardization

An overview of the processing pipeline for carbonate clumped isotope data is given in Fig. 2. Pressure baseline (PBL)-correction of mass spectrometric raw data has been shown to be essential for accurate determination of Δ_{47}-Δ_{49} values, as it is designed to eliminate non-linearity-derived biases both in δ^i and Δ_i values [6,19]. For D4Xgui, we implemented the methodology proposed by Fiebig et al. [7] and later refined by Bernecker et al. [6]. The PBL (i.e., the negative signal arising from secondary electrons) is continuously monitored at half-mass cup $m/z_{47.5}$, and subtracted from m/z_{47}, m/z_{48} and m/z_{49} intensities after scaling the $m/z_{47.5}$ intensity by cup-specific scaling factors utilizing an optimizer algorithm. Optimal scaling factors can be determined iteratively based on the prerequisite that PBL-corrected δ^i and Δ_i values (vs. reference gas) obtained for CO_2 gases or carbonates equilibrated at a given temperature should be characterized by slopes closest to zero if plotted against each other [6,7].

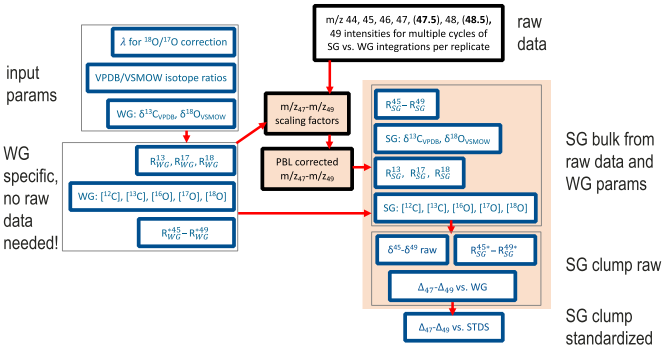


Fig. 2. Schematic overview of the processing steps involved in the process of calculating baseline-corrected, standardized and fully error-propagated clumped isotope values from mass spectrometric raw intensity data. The major difference between commonly used processing schemes [e.g.,18] is the optimized scaling factor determination for baseline correction – this part already requires calculating δ^i and Δ_i metrics by iteratively refining scaling factors (orange in the flowchart). Once the best-fit scaling factors are determined, m/z_{47-49} raw intensity data gets corrected and the processing scheme is conducted one last time with the final intensites. Abbreviations: WG = working gas, SG = sample gas. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Moreover, users can define custom sets of internal standards with precisely constrained long-term assigned Δ_i values. These standards are then used by the optimization algorithm, which adjusts the scaling factors to minimize the absolute differences between measured and assigned Δ_i values. For each mass (47–49), the scaling factor is obtained by minimizing the sum of squared deviations between all pairs of standards, comparing the differences in their measured and assigned values:

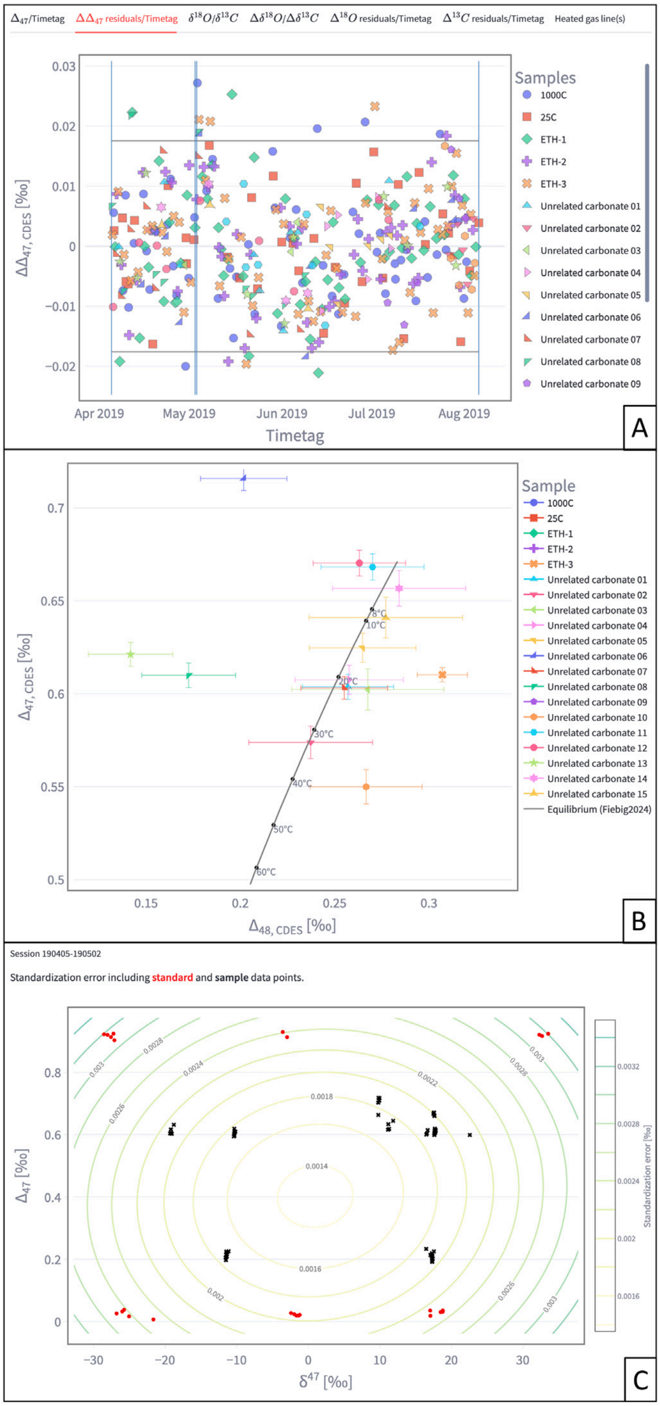
$$sf_{\mathrm{i,opt}} = \min\left(\sum_{k<l}\left[\left(\Delta_i^k(sf_{\mathrm{i}})_{\mathrm{meas.}} - \Delta_i^l(sf_{\mathrm{i}})_{\mathrm{meas.}}\right) - \left(\Delta^k_{i\,\mathrm{ass.}} - \Delta^l_{i\,\mathrm{ass.}}\right)\right]^2\right) \quad (1)$$

where k and l index individual standards, i is the cardinal mass (47–49), and sf is the corresponding scaling factor.

Baseline-corrected data can be stored in the `pre_replicates` table, where they will be accessible for future processing. Pre-processed carbonate clumped isotope data (δ^{45}-δ^{49}) are finally standardized relative to equilibrated gas- and/or carbonate anchors of well-defined Δ_i compositions [e.g., 10,24–26]. For this step, the optimized correction algorithm implemented for D47crunch is used, which is outlined in detail by Daëron [17]. This algorithm considers least-squares optimization on unknowns and anchors and reports final clumped isotope results with fully propagated errors, accounting for both autogenic and allogenic analytical uncertainties. Full propagation of analytical uncertainties arising from preparation and analysis of samples and standards is essential to i) determine realistic uncertainties of estimated carbonate formation temperatures, ii) distinguish between different rate-limiting processes involved in carbonate (bio)mineralization, and iii) test the inter-laboratory reproducibility of analyses. D4Xgui provides the option to report unknown sample values on the CDES [7,25] and the I-CDES [24]. Custom standardization sets can be defined prior to processing, allowing anchoring of unknown sample data relative to internal reference materials that were calibrated against equilibrated gases or internationally assigned carbonate anchors.

2.2.2. Formation temperature estimates

D4Xgui allows calculation of apparent formation temperatures from standardized Δ_{47} values considering empirical Δ_{47}-T calibrations of



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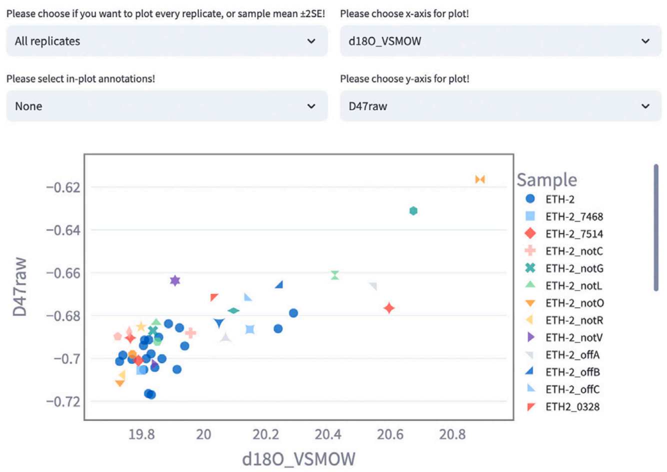
Standardization error including **standard** and **sample** data points.

Fig. 3. **A**: Demonstrative screenshot of the *Standardization Results* page, displaying $\Delta\Delta_{47}$ residuals over time. Repeatability (2SD) characteristic for the selected interval is automatically calculated and displayed as horizontal line. **B**: Demonstrative screenshot of the *Dual Clumped Space* page, displaying Δ_{47} and Δ_{48} data relative to the position of equilibrium [10]. **C**: Demonstrative screenshot of the *Standardization Error* page, displaying standardization-related uncertainties in δ_{47}/Δ_{47}-space [17].

Fiebig et al. [10], Swart et al. [8] and Anderson et al. [27]. Additional calibrations (i.e., Anderson et al. [27], Breitenbach et al. [28], Daëron et al. [29], Jautzy et al. [30], Huyghe et al. [31] and Peral et al. [32]), re-processed by Daëron & Vermeesch [33] using OGLS regression [34], as well as the composite OGLS23 calibration, are available from the D47calib module [35].


Please choose if you want to plot every replicate, or sample mean ±2SE!
All replicates

Please choose x-axis for plot!
d18O_VSMOW

Please select in-plot annotations!
None

Please choose y-axis for plot!
D47raw

Fig. 4. Demonstrative screenshot of the *Discover Results* page, displaying $\delta^{18}O$ data vs. $\Delta_{47,raw}$ data for individual replicates of carbonate standard ETH-2. CO_2-H_2O re-equilibration is indicated for replicates showing both elevated $\Delta_{47,raw}$ and $\delta^{18}O$ values. $\Delta_{47,CDES90}$ values of these samples plot outside the long-term repeatability interval characteristic of ETH-2 (0.2093 ± 0.0017 ‰) in the absence of significant analytical bias [36].

3. Illustrative examples

D4Xgui offers access to a wealth of graphical outputs.

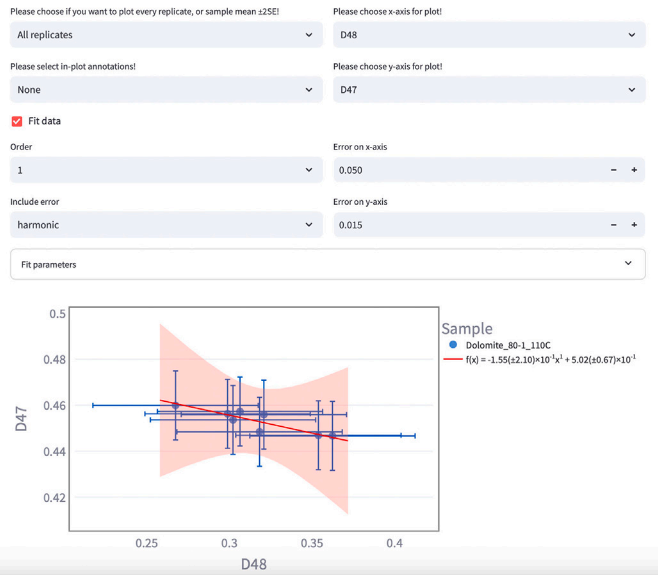
- Temporal evolution of replicate $\delta^{13}C$, $\delta^{18}O$, raw and final Δ_i values and corresponding residuals Fig. 3(A),
- Presentation of Δ_i data in dual clumped isotope space (sample mean values including fully propagated ±1SE or ±2SE uncertainties, or individual replicate values) relative to the equilibrium Δ_{47}/Δ_{48} and Δ_{47}/Δ_{49} relationships [6,10] Fig. 3(B),
- Standardization-derived contribution of analytical uncertainties in δ^i /Δ_i space [17] Fig. 3(C),
- Custom plots in which any two columns (e.g., sample name, acquisition time, isotopic composition, etc.) of any dataset can be plotted against each other, are accessible from the *Discover Results* page (Figs. 4 and 5). Optionally, linear or higher-order regression analysis can be performed on selected data.

3.1. Identifying H_2O-driven partial re-equilibration of analyte CO_2

When CO_2, either derived from acid digestion of carbonate samples or directly introduced through autofingers [22], partially re-equilibrates with water, its oxygen and clumped isotope compositions can be reset, leaving characteristic correlations between $\delta^{18}O$, Δ_{47} and Δ_{48} in CO_2 replicates from a given sample. We were able to identify this effect through data inspection at the replicate level (Fig. 4). Partial re-equilibration with H_2O can occur in an autosampler over carbonate samples with high surface area [36]. These correlations are especially pronounced for samples with extreme oxygen and clumped isotope compositions. Due to multiple factors influencing the final result, such as varying degrees of re-equilibration on a sample-to-sample basis or distinct oxygen isotope values of the analyte leading to differently pronounced mixing effects, this effect cannot be corrected for. It is therefore of utmost importance to identify re-equilibration bias [36].

3.2. Identifying isobaric interferences

Fiebig et al. [10] have recently shown that the presence of a few hundred ppb-quantities of NO_2 in the analyte CO_2 can introduce significant bias in measured Δ_{47} and Δ_{48} values determined by isotope-ratio mass spectrometry. Samples whose Δ_{47} and Δ_{48} values are significantly biased by variable amounts of NO_2 plot along a characteristic slope of −0.30 ±


Please choose if you want to plot every replicate, or sample mean ±2SE!
All replicates

Please choose x-axis for plot!
D48

Please select in-plot annotations!
None

Please choose y-axis for plot!
D47

☑ Fit data

Order
1

Error on x-axis
0.050

Include error
harmonic

Error on y-axis
0.015

Fit parameters

Fig. 5. Demonstrative screenshot of the *Discover Results* page, showing compromised sample Dolomite_80-1 [37,52], whose replicates show variable extents of NO_2 bias in their Δ_{47}, Δ_{48} values.

0.05 (Fig. 5). The visualization capabilities of D4Xgui make identification of NO_2 and other isobaric interferents in Δ_{47}/Δ_{48} and Δ_{48}/Δ_{49} space straightforward, as affected data follow predicted deviation slopes [10]. Compromised samples can, therefore, be reliably identified and mitigation strategies (that eliminate isobaric bias) can easily be tested for their efficacy.

4. Impact

D4Xgui was developed as an open-source Python module by Miguel Bernecker et al. (bernecker@em.uni-frankfurt.de), tested at Goethe University Frankfurt am Main, and has already been successfully utilized for peer-reviewed publications. These studies improved the methodology [6,10,36,37] and, moreover, investigated the Δ_{47}/Δ_{48} compositions of pedogenic carbonates [38–40], cold- and warm-water corals [41], coccolith chalk [42], molluscs [43–45], diagenetically reset carbonates [46,47], methane seep carbonates [48], brachiopods [49], diagenetically formed dolomites [50], and speleothems [51].

5. Conclusions

D4Xgui represents a state-of-the-art processing tool for carbonate clumped isotope data processing. This user-friendly, open-source tool provides a streamlined workflow for accurate correction and standardization of mass spectrometric raw data, while considering full error propagation. The extensive graphical outputs facilitate data visualization and real-time assessment of data quality, all through an accessible interface that doesn't require prior programming knowledge.

By providing a common platform for data processing and analysis, D4Xgui not only simplifies complex workflows but also promotes consistency and transparency in carbonate clumped isotope research. Developed using the flexible Streamlit framework, D4Xgui is designed to allow further community-driven customization. Its modular plug&play architecture enables easy integration of new features as the field of clumped isotope research steadily evolves. Planned future updates include the integration of an Application Programming Interface (API), which will enhance data management and enable script-based interaction with the database. Moreover, we are already working on the integration of Easotope databases, which will enable seamless incorporation of archived datasets. This addition will also ensure that data processed through D4Xgui adheres to the FAIR principles, promoting findability, accessibility, interoperability, and long-term data reuse across laboratories.

CRediT authorship contribution statement

Miguel Bernecker: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Mathieu Daëron:** Writing – original draft, Software, Methodology, Conceptualization. **Philip Tauxe Staudigel:** Writing – review & editing, Visualization. **Sven Hofmann:** Validation, Methodology, Conceptualization. **Jens Fiebig:** Writing – review & editing, Validation, Supervision, Software, Resources, Methodology, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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