



RESEARCH ARTICLE

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Correction algorithm for online continuous flow $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ carbonate and cellulose stable isotope analysesM. N. Evans^{1,2}, K. J. Selmer^{1,3}, B. T. Breeden III^{1,4}, A. S. Lopatka¹, and R. E. Plummer¹

Key Points:

- Cellulose and carbonate CF-IRMS data contain systematic error
- Corrections must be validated by application to independent data
- The correction scheme may be used for data-intensive applications

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Abstract We describe an algorithm to correct for scale compression, runtime drift, and amplitude effects in carbonate and cellulose oxygen and carbon isotopic analyses made on two online continuous flow isotope ratio mass spectrometry (CF-IRMS) systems using gas chromatographic (GC) separation. We validate the algorithm by correcting measurements of samples of known isotopic composition which are not used to estimate the corrections. For carbonate $\delta^{13}\text{C}$ ($\delta^{18}\text{O}$) data, median precision of validation estimates for two reference materials and two calibrated working standards is 0.05‰ (0.07‰); median bias is 0.04‰ (0.02‰) over a range of 49.2‰ (24.3‰). For α -cellulose $\delta^{13}\text{C}$ ($\delta^{18}\text{O}$) data, median precision of validation estimates for one reference material and five working standards is 0.11‰ (0.27‰); median bias is 0.13‰ (−0.10‰) over a range of 16.1‰ (19.1‰). These results are within the 5th–95th percentile range of subsequent routine runtime validation exercises in which one working standard is used to calibrate the other. Analysis of the relative importance of correction steps suggests that drift and scale-compression corrections are most reliable and valuable. If validation precisions are not already small, routine cross-validated precision estimates are improved by up to 50% (80%). The results suggest that correction for systematic error may enable these particular CF-IRMS systems to produce $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ carbonate and cellulose isotopic analyses with higher validated precision, accuracy, and throughput than is typically reported for these systems. The correction scheme may be used in support of replication-intensive research projects in paleoclimatology and other data-intensive applications within the geosciences.

1. Introduction

Mean and variance-calibrated, high-throughput stable isotope analyses are increasingly required in paleoclimatology. They have application, for example, in the efficient replication of high-resolution time series analyses derived from reef coral aragonite, foraminiferal calcite, and wood-derived α -cellulose for the study of changes in paleoclimatic means and variances [e.g., Cobb *et al.*, 2003; McCarroll and Loader, 2004; Koutavas *et al.*, 2006; Linsley *et al.*, 2008; Anchukaitis and Evans, 2010; Cobb *et al.*, 2013; McGregor *et al.*, 2013]. Continuous flow isotope ratio mass spectrometry (CF-IRMS) is a rapid, economical, but relatively low-precision approach to high-throughput stable isotopic analyses of these materials [Brenna *et al.*, 1997; Werner *et al.*, 1996; Spötl and Vennemann, 2003; Spötl, 2011]. However, if much of the uncertainty in such CF-IRMS analyses arises from systematic rather than random error [Spötl and Vennemann, 2003; Leuenberger and Filot, 2007; Evans, 2008; Young *et al.*, 2011], then it may be possible to detect, model, and remove the systematic error component during the process of isotopic data correction and scaling [Coplen *et al.*, 2006].

For example, it has been observed that amplitude or integrated peak area biases in measured isotopic composition may arise in the analysis of carbonate isotopic composition by continuous flow mass spectrometry [Spötl and Vennemann, 2003]. Depending on analytical method, runtime isotopic drift in oxygen isotopic composition may arise in continuous flow preparation systems from systematic differences in the time between acidification and analysis of evolved CO_2 analyte gas [Spötl, 2011]; analyses of batch acid versus sequential acid injection and analyses (results not shown) suggest that differential reaction and equilibration times for the former procedure cause a systematic drift in the $\delta^{18}\text{O}$ measurements. Isotopic analyses should also be corrected for scale differences arising from using intermediate working standards to correct to international reference scales [Coplen *et al.*, 2006].

Similarly, dual C/O measurements on cellulose samples in a low-temperature pyrolysis system (1080°C) [Werner *et al.*, 1996] may be subject to scale compression and bias in both isotopes. This is because of the presence of catalytic glassy carbon and deposition of excess sample carbon in the pyrolysis reactor [Young *et al.*, 2011], and thermal conversion into both CO and CO₂ at this temperature [Leuenberger and Filot, 2007]. The use of carbon monoxide as analyte and associated potential dependence of isotopic composition on ion beam amplitude in an ion source optimized for CO₂ analysis [e.g., Thermo Electron Corporation, 2005; IsoPrime Ltd., 2009] may also create observed amplitude or integrated peak area biases in measured isotopic composition, especially for small samples and for preparation systems with evidence of memory effects [e.g., Santrock and Hayes, 1987; Evans, 2008]. Measurements are also commonly subject to runtime isotopic drift, arising from changes in the state of the thermal conversion reactor as consumables are used and elemental sample carbon is added to the system [e.g., Young *et al.*, 2011].

It is the purpose of this technical report to describe an algorithm for mean and amplitude correction of carbon ($\delta^{13}\text{C}$) and oxygen ($\delta^{18}\text{O}$) isotopic analyses made by CF-IRMS. The essential elements of the approach are correction of systematic error in the raw data with respect to signal amplitude [Spotl and Vennemann, 2003], sequential sample drift [e.g., Evans, 2008], and variance [Coplen *et al.*, 2006]. We validate the algorithm in two online CF-IRMS contexts—measurement on carbonate-derived analyte CO₂ and measurement on α -cellulose-derived analyte CO—by applying corrections to samples of known isotopic composition but which were not used to estimate the corrections themselves.

2. Methods

Scripted correction codes are useful for consistent treatment of data, real-time quality control, and spot analysis of instrument performance and emerging data streams. Because we use working standards of known isotopic composition and similar chemical composition as the basis for these corrections, and because these working standards are analyzed in batches together with the unknowns, *differential* (working standard versus unknown sample) biases are automatically removed, an approach known as the principle of Identical Treatment (IT principle) [Werner and Brand, 2001; Brand *et al.*, 2014]. However, biases associated with measurement conditions common to both working standards and unknown samples, if present, must be detected and removed. We do so as follows.

2.1. Data Correction Algorithm

“Raw” sample isotope data are generally reported by CF-IRMS data acquisition software with Craig corrections (as described in IsoPrime Ltd. [2009] and de Groot [2008]) as applicable, and linear correction for within-analysis isotopic drift, as detected by measurements on a monitoring gas. The following algorithm does not replace such raw data corrections. Using measurements of two international reference materials or working standards of known $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotopic composition made before, between, and after blocks of sample analyses, we propose a series of additional corrections for systematic uncertainties as follows.

1. A stiff smoothing spline (“spline correction”) is fit to each set of raw working standard data, resulting in runtime drift corrections for each working standard and isotope over the course of the batch data acquisition.
2. Following observations of Spotl and Vennemann [2003], an amplitude correction is fit as a logarithmic function of peak signal amplitude (“amplitude correction”) for each working standard and isotope. If the resulting regressions do not intersect the range of amplitudes observed for samples or are not statistically significant at the $P < 0.10$ level, the regressions are not applied.
3. Once drift and amplitude corrections have been made, we estimate the two-point slope and intercept of the working standards for each isotope using their known isotopic values. The two-point correction is then applied to correct for both mean and variance bias in the samples. Results from both sets of corrections (those derived from fit to working standard 1 and working standard 2 calibration data) are then averaged to produce the best estimate of the corrected data.

A set of MATLAB-compatible (Mathworks, Natick, MA, USA) functions has been developed to implement these corrections in a Windows OS/Excel (Microsoft, WA, USA) environment and is available upon request. It reads batch files of data produced by Ionvantage (IsoPrime Ltd., UK), detects working standards, sequentially performs the described corrections, reports analytical outliers, produces diagnostic plots of the results,

Table 1. Carbonate Validation Study^a

Material	δ_C (s.d.)	Bias	δ_O (s.d.)	Bias
IAEA-CO-1	2.48 (0.04)	0.01	-2.42 (0.10)	0.02
JTB1	1.68 (0.04)	0.10*	-8.65 (0.07)	-0.06*
LSVEC	-46.67 (0.13)	0.07	-26.73 (0.08)	0.03
MCC	-36.00 (0.05)	-0.10*	-21.92 (0.04)	0.12*
Median values	0.05	0.04	0.07	0.02

^aValues in parentheses are 1σ precisions after corrections. Bias columns are the difference between calibrated and validation means or reference values and validation means of the materials. Reference values used in corrections were δ_C : LSVEC = -46.6, IAEA-CO-1 = 2.492 and δ_O : LSVEC = -26.7, IAEA-CO-1 = -2.4. Reference values for estimating biases (differences) were δ_C : JTB1 = 1.78, MCC = -36.10; δ_O : JTB1 = -8.71, MCC = -21.80. Asterisk indicates the corrected validation mean is statistically different from the corresponding calibration sample (*t* test, *df* = 18) or reference value (*z*-test, *df* = 9) at the $P < 0.05$ level. *N* = 10 for all reported validation means. To minimize propagated round-off error, an extra significant digit is retained in reported mean values. Median values are for precisions and biases across all working standard validation analyses and are values reported in abstract.

and creates MATLAB workfiles and Excel spreadsheets for further quality control and data analysis. With minor adjustments, the function for reading input data should be adaptable for use with inputs from other data acquisition software, such as Isodat (Thermo Scientific, Waltham, MA, USA), and Callisto (Sercon Group, Cheshire, UK).

analyzer, were sealed in Exetainer vials (Labco Ltd., Lampeter, UK) and loaded into a custom 180-position Multiflow autosampler rack (Elementar Americas, Cherry Hill, NJ), which was kept at 65°C. Following standard analytical procedure [IsoPrime Ltd., 2009], sample vials were first flushed with 99.999% He. Samples were then batch acidified by manual injection with approximately 100 μ L of concentrated phosphoric acid (density = 1.92 g/mL), delivered by 1 mL slip tip syringe with an 18 $\frac{1}{2}$ gauge needle (Beckton Dickinson and Co, Washington, DC) from a reservoir kept at 90–95°C on a hotplate to maintain low acid viscosity for the transfer. Samples were reacted for 1 h prior to start of sequential isotopic data acquisition; note that in this procedure, reaction time is a function of batch position. Prior to mass analysis on an Isoprime (Isoprime House, Cheadle, UK) mass spectrometer via reference gas injector and continuous flow interface, the CO₂ sample stream was passed through a Nafion (Ion Power Inc., New Castle, DE) water trap. Carbon and oxygen stable isotope ratios were acquired relative to research grade (99.999% purity) carbon dioxide monitoring gas and reported with background, Craig and within-sample drift corrections by Ionvantage data acquisition software (Isoprime Ltd., Cheadle, UK) to produce the “raw” data for this study. Ionvantage software is not set to perform a background blank correction, but is set to detect sample peaks of absolute (from zero baseline) collector amplitude greater than 500 fA (>0.05 nA). Such peaks are not detected. No measurement blank correction has been applied, as routine analyses on empty, He-flushed and acidified sample vials give signals of 0.05–0.1 nA. As described in section 2 and Table 1, the raw data were then corrected and normalized to within-batch measurements made on samples of the international carbonate reference materials IAEA-CO-1 and LSVEC [Stichler, 1995] with reference $\delta^{13}C$ and $\delta^{18}O$ values as listed in Table 1.

3.2. Cellulose Analysis

Experimental batches were dried in a 60°C oven prior to storage in a desiccator. Prior to their analysis, batches were then placed overnight in a sealed autosampler through which 99.999% He was flowing at a few mL/min. Instrument linearity (dependence of $\delta^{18}O$ and $\delta^{13}C$ on signal amplitude at the collectors) was tested daily and confirmed to be <0.03‰/nA over the 1–10 nA range. 100 \pm 10 μ g, silver-encapsulated cellulose samples (no carbon added to samples inside capsules), producing approximately 4–6 nA signal at the collectors, were loaded in a 99-position zero-blank autosampler (Costech Analytical, Valencia, CA, USA) and converted to a mixture of carbon monoxide, carbon dioxide, water, and hydrogen gases [Leuenberger and Filot, 2007] over glassy carbon chips in a quartz tube at 1080°C [Werner et al., 1996], within a stream of 99.999% carrier Helium flowing at 110 mL/min. Carbon dioxide and water were removed using an inline ascarite/magnesium perchlorate trap, and carbon monoxide was separated from nitrogen in the sample using a 0.8 m long molecular sieve 5 A kept at 70°C (Costech Analytical, Valencia, CA, USA). Separation of CO and N₂ peaks (a small amount of N, with characteristically low 30/28 ratio, may be present in industrial or extracted α -cellulose [Anchukaitis et al., 2008]) was verified by analysis of the chromatogram. The sample stream was then introduced into an Isoprime stable isotope mass spectrometer via an open split continuous flow interface with no sample stream dilution. Carbon and oxygen stable isotope ratios were acquired

and creates MATLAB workfiles and Excel spreadsheets for further quality control and data analysis. With minor adjustments, the function for reading input data should be adaptable for use with inputs from other data acquisition software, such as Isodat (Thermo Scientific, Waltham, MA, USA), and Callisto (Sercon Group, Cheshire, UK).

3. Experiment

3.1. Carbonate Analysis

Prior to batch analysis, instrument linearity (dependence of $\delta^{18}O$ and $\delta^{13}C$ on signal at the collectors) was confirmed to be <0.03‰/nA over a range of approximately 2–14 nA. 100 \pm 10 μ g carbonate samples (74 \pm 7 μ g for the lithium carbonate standard LSVEC), producing approximately 8–12 nA of signal at the

analyzer, were sealed in Exetainer vials (Labco Ltd., Lampeter, UK) and loaded into a custom 180-position Multiflow autosampler rack (Elementar Americas, Cherry Hill, NJ), which was kept at 65°C. Following standard analytical procedure [IsoPrime Ltd., 2009], sample vials were first flushed with 99.999% He. Samples were then batch acidified by manual injection with approximately 100 μ L of concentrated phosphoric acid (density = 1.92 g/mL), delivered by 1 mL slip tip syringe with an 18 $\frac{1}{2}$ gauge needle (Beckton Dickinson and Co, Washington, DC) from a reservoir kept at 90–95°C on a hotplate to maintain low acid viscosity for the transfer. Samples were reacted for 1 h prior to start of sequential isotopic data acquisition; note that in this procedure, reaction time is a function of batch position. Prior to mass analysis on an Isoprime (Isoprime House, Cheadle, UK) mass spectrometer via reference gas injector and continuous flow interface, the CO₂ sample stream was passed through a Nafion (Ion Power Inc., New Castle, DE) water trap. Carbon and oxygen stable isotope ratios were acquired relative to research grade (99.999% purity) carbon dioxide monitoring gas and reported with background, Craig and within-sample drift corrections by Ionvantage data acquisition software (Isoprime Ltd., Cheadle, UK) to produce the “raw” data for this study. Ionvantage software is not set to perform a background blank correction, but is set to detect sample peaks of absolute (from zero baseline) collector amplitude greater than 500 fA (>0.05 nA). Such peaks are not detected. No measurement blank correction has been applied, as routine analyses on empty, He-flushed and acidified sample vials give signals of 0.05–0.1 nA. As described in section 2 and Table 1, the raw data were then corrected and normalized to within-batch measurements made on samples of the international carbonate reference materials IAEA-CO-1 and LSVEC [Stichler, 1995] with reference $\delta^{13}C$ and $\delta^{18}O$ values as listed in Table 1.

3.2. Cellulose Analysis

Experimental batches were dried in a 60°C oven prior to storage in a desiccator. Prior to their analysis, batches were then placed overnight in a sealed autosampler through which 99.999% He was flowing at a few mL/min. Instrument linearity (dependence of $\delta^{18}O$ and $\delta^{13}C$ on signal amplitude at the collectors) was tested daily and confirmed to be <0.03‰/nA over the 1–10 nA range. 100 \pm 10 μ g, silver-encapsulated cellulose samples (no carbon added to samples inside capsules), producing approximately 4–6 nA signal at the collectors, were loaded in a 99-position zero-blank autosampler (Costech Analytical, Valencia, CA, USA) and converted to a mixture of carbon monoxide, carbon dioxide, water, and hydrogen gases [Leuenberger and Filot, 2007] over glassy carbon chips in a quartz tube at 1080°C [Werner et al., 1996], within a stream of 99.999% carrier Helium flowing at 110 mL/min. Carbon dioxide and water were removed using an inline ascarite/magnesium perchlorate trap, and carbon monoxide was separated from nitrogen in the sample using a 0.8 m long molecular sieve 5 A kept at 70°C (Costech Analytical, Valencia, CA, USA). Separation of CO and N₂ peaks (a small amount of N, with characteristically low 30/28 ratio, may be present in industrial or extracted α -cellulose [Anchukaitis et al., 2008]) was verified by analysis of the chromatogram. The sample stream was then introduced into an Isoprime stable isotope mass spectrometer via an open split continuous flow interface with no sample stream dilution. Carbon and oxygen stable isotope ratios were acquired

Table 2. α -Cellulose Validation Study^a

Material	δ_C (s.d.)	Bias	δ_O (s.d.)	Bias
AKC	-13.80 (0.10)	0.09	23.61 (0.24)	-0.11
AWS	-22.22 (0.07)	-0.08*	21.42 (0.22)	-0.12
H1	-29.91 (0.26)	0.17*	20.13 (0.27)	-0.23*
L6	-29.23 (0.28)	-0.07	39.24 (0.75)	0.56*
Switsur	-24.31 (0.09)	0.19*	27.38 (0.32)	0.08
IAEA-CH3	-24.96 (0.13)	0.24*	32.61 (0.27)	-0.09
Median values	0.11	0.13	0.27	-0.10

^aValues in parentheses are 1σ precisions after corrections. Bias columns are the difference between calibrated and validation means, or reference values and validation means of the materials. Reference values used in corrections were δ_C : AKC = -13.71, SAC = -25.3; δ_O : AKC = 23.5, SAC = 31.0. Reference values for estimating biases (differences) were δ_C : AKC = -13.8, AWS = -22.3, H1 = -29.7, L6 = -29.3, Switsur = -24.12, and IAEA-CH3 = -24.72; δ_O : AKC = 23.5, AWS = 21.3, H1 = 19.9, L6 = 39.8, Switsur = 27.3, and IAEA-CH3 = 32.52. An asterisk indicates the corrected validation mean is statistically different from the corresponding calibration sample (*t* test, *df* = 18) or reference value (*z*-test, *df* = 9) at the *P* < 0.05 level. *N* = 10 for all reported validation means. To minimize propagated round-off error, an extra significant digit is retained in reported mean values. Median values are for precisions and biases across all working standard validation analyses and are values reported in abstract.

relative to a 99.997% purity carbon monoxide monitoring gas and reported with background, Craig and within-sample drift corrections by Ionvantage data acquisition software (Ionvantage Ltd., Cheadle, UK). Ionvantage software is not set to perform a background blank correction, but is set to detect sample peaks of absolute (from zero baseline) collector amplitude greater than 200,000 fA (>0.2 nA). Such peaks are not detected. No measurement blank correction has been applied, as routine analyses on empty silver sample capsules give signals of less than 0.1 nA. As described in section 2, these “raw” data were then corrected and normalized to the V-PDB ($\delta^{13}C$) and V-SMOW ($\delta^{18}O$) international reference materials via within-batch analysis of calibrated working standard α -celluloses designated “SAC” and “AKC,” and with

known $\delta^{13}C$ and $\delta^{18}O$ values for SAC and AKC with respect to the V-PDB and V-SMOW reference standards previously determined and as listed in Table 2.

3.3. Data Analysis

For both CF-IRMS systems, we used working standards and the IT principle to develop and apply corrections to sample measurements. We term the working standards thus used “calibration” data. By construction, the means of the final corrected calibration data are the known isotopic values of the working standards on the international reference scales. In each experiment, the “samples” were of materials of a priori known isotopic composition, but the “sample” data were *not* used to develop the corrections; in other words, these are “out-of-sample” tests of the validity of the corrections. We report these sample data as “validation” analyses.

In principle, if the corrections are valid, then the corrected values for validation materials should be within analytical precision of the known values. The precision on validation data should be approximately equal to the precision of the corrected calibration data. For each experiment, then, we report the validation precision and bias for each sample material with respect to known values, and perform statistical tests to assess the probability that the corrected validation means for the sample materials are no different from the known values (Tables 1 and 2).

As a secondary test, we can estimate the bias and precision arising from use of either standard as basis for amplitude and drift correction. This is because for each of two correcting standards, we obtain drift, amplitude, and two-point corrections. In other words, we can use working standard 1 to correct working standard 2, then compare working standard 2 corrections to the known value of working standard 2. Conversely, we can use working standard 2 data to calibrate and correct working standard 1 data, then compare the results

to the known value of working standard 1. We term these exercises “routine runtime” cross-validation exercises and use the results of 15 (12) batches of carbonate (cellulose) analyses to evaluate how well the validation experiments (Tables 1 and 2) represent routine results (Figures 2 and 3).

In a third test, we examine the precisions of validation samples, cross-validation estimates, and routine cross-validation estimates as a function of the

Table 3. Sequential Correction Precisions: Carbonate Validation Study^a

Correction	Validation ^b		Cross-Validation ^c		Routine C-V ^d	
	$\sigma_{\delta C}$	$\sigma_{\delta O}$	$\sigma_{\delta C}$	$\sigma_{\delta O}$	$\sigma_{\delta C}$	$\sigma_{\delta O}$
Raw	0.13	0.12	0.19	0.15	0.22	0.16
Spline	0.05	0.09	0.11	0.13	0.11	0.18
Amplitude	0.05	0.09	0.11	0.13	n/a	n/a
Two-point	0.05	0.09	0.11	0.13	0.10	0.17

^aSequential “Raw,” “spline-corrected,” “amplitude,” and “two-point” corrections are as described in section 2.

^bResults from validation study (Table 1).

^cResult from cross-validation analysis of validation study (Table 1).

^dResults from cross-validation analysis of routine sample batches (Figure 2).

Table 4. Sequential Correction Precisions: α -Cellulose Validation Study^a

Correction	Validation ^b		Cross-Validation ^c		Routine C-V ^d	
	$\sigma_{\delta_{13}C}$	$\sigma_{\delta_{18}O}$	$\sigma_{\delta_{13}C}$	$\sigma_{\delta_{18}O}$	$\sigma_{\delta_{13}C}$	$\sigma_{\delta_{18}O}$
Raw	0.17	0.35	0.31	0.49	0.23	1.03
Spline	0.15	0.33	0.28	0.49	0.19	0.50
Amplitude	0.15	0.33	0.29	0.52	n/a	n/a
Two-point	0.14	0.30	0.26	0.47	0.12	0.35

^aSequential "Raw," "spline-corrected," "amplitude," and "two-point" corrections are as described in section 2.

^bResults from validation study (Table 2).

^cResult from cross-validation analysis of validation study (Table 2).

^dResults from cross-validation analysis of routine sample batches (Figure 3).

correction (spline, amplitude, and two-point) step across all materials and cross-validation exercises (Tables 3 and 4). These results suggest the extent to which each of the corrections is valuable.

4. Results

Precision and accuracy estimates for validation analyses of CO₂ derived from carbonate materials are in Table 1; for analyses of CO derived from α -cellulose,

results are in Table 2. Note that because materials of known and substantially different isotopic composition are few, the algorithm is applied in validation to samples of *materials* that were also used to correct the reported data (i.e., IAEA-CO-1, LSVEC, and AKC). Although these materials were used for both calibration and validation, only corrected validation data are reported in Tables 1 and 2. Results of the routine runtime validation experiments are in Figures 2 and 3. We illustrate these results using histograms of the validation data for C and O isotopic data from each working standard and report the 5th, 50th, and 95th percentile values for precision and bias over all *n* validation data from the batch data sets analyzed. Tables 3 and 4 give validation, cross validation, and routine runtime cross-validation results by correction step for the validation studies (first four columns), and the cross-validation results for routine sample analyses (section 2).

5. Discussion

In principle, if systematic errors in isotopic analyses can be detected, we can model and correct for them, resulting in more precise and accurate results. However, the more complex the suite of corrections, the more important that their efficacy is evaluated using validation tests, because of the potential for artificial skill from overfitting of the calibration data. Analysis of samples of known isotopic composition which were *not* themselves used to estimate the corrections is required for assessment of the results.

For the carbonate materials we analyzed, we found that the median validation precisions across the carbonates analyzed are 0.05 and 0.07‰ for δ_C and δ_O , respectively (Table 1). For the LSVEC reference material, the precision achieved is better than reported in *Stichler* [1995], which was 0.15 and 0.25‰ for δ_C and δ_O , respectively. Because precisions are small, the biases in some of the validation data sets (JTB1, EACARB) are statistically different from zero. However, the median biases (0.04 and 0.02‰ for δ_C and δ_O , respectively; Table 1) are small relative to the known range across in δ_C and δ_O across working standards (49.2 and 24.3‰, respectively; Table 1 and Figures 1a and 1b). Median biases are also small relative to the distribution of routine runtime cross-validation precisions (Figure 2), and hence may be negligibly small in practical measurement and application.

For the α -cellulose materials we analyzed, we found that the median validation precisions across five α -cellulose working standards and one reference material are 0.11 and 0.27‰ for δ_C and δ_O , respectively (Table 2). These precisions are comparable to those achieved routinely in high-temperature pyrolysis systems with near-quantitative conversion of α -cellulose into analyte CO above 1400°C [*Leuenerger and Flot*, 2007]. Median bias (0.13 and -0.10‰ for δ_C and δ_O , respectively; Table 2) include 5 of 12 comparisons that are statistically distinguishable from zero bias, but these biases are again small relative to the calibrated ranges in δ_C and δ_O across all materials analyzed (16.1 and 19.1‰, respectively; Table 2 and Figures 1c and 1d) and may be negligible in practical measurement and application; results are similar to those achieved by *Young et al.* [2011].

Validation study precisions and biases for both carbonate and cellulose experiments (Tables 1 and 2) fall within the 5th–95th percentile ranges of the routine runtime precision and bias estimates (Figures 2 and 3). This result suggests that the validation experiment results shown in Tables 1 and 2 are likely to be

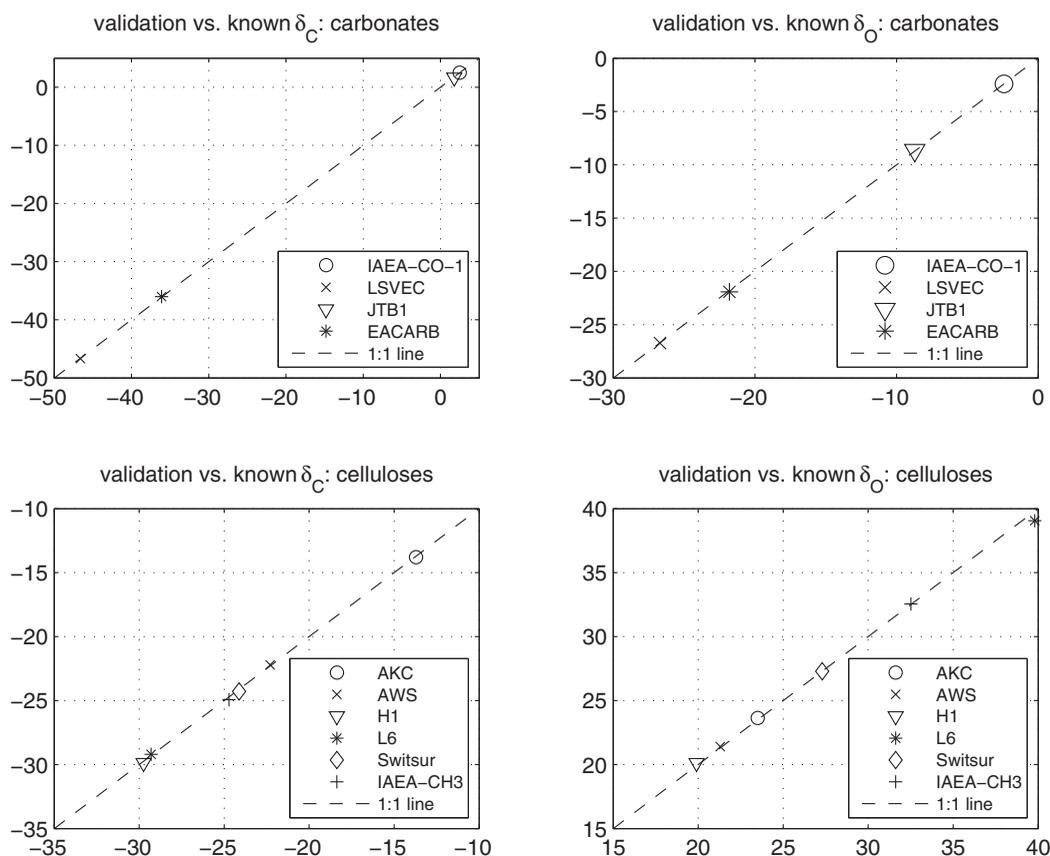


Figure 1. Validation versus known isotopic values for various standards (validation estimates and known values are given in Tables 1 and 2).

representative of the true random error and systematic bias for unknown samples and that the long-term systematic bias in corrected data is not significantly different from zero.

Results as a function of correction step (Tables 3 and 4) suggest that the spline and two-point corrections are most valuable when raw precisions are poor (Tables 3 and 4, last two columns). In the results of the single validation studies presented (Tables 1 and 2), some spline and amplitude corrected validation precisions are higher than raw precisions, suggesting that there might be artificial skill in these corrections if raw precision is already low (first four columns of Tables 3 and 4). In practice over additional routine tests (last two columns of Tables 3 and 4), the amplitude correction is rarely significant at $P < 0.10$ for both correction standards.

Uncertainty in the correction scheme presented here arises from both empirical and structural uncertainties. Empirical sources of uncertainty include the statistical estimation of the spline, amplitude, and two-point corrections. A multipoint correction for mean and variance might be preferable to a two-point correction, especially for less widely separated correcting standard values, and certainly for application to samples whose isotopic compositions fall well outside the correcting standard ranges. Our routine cross-validation results suggest that it is unusual to find amplitude corrections in both correcting standards (Tables 3 and 4), and there may be some artificial skill in cases in which raw precision is already small but amplitude corrections are identified. This may not be the case when amplitude corrections are defined by many data over much wider amplitude ranges than tested in this study (section 3), and for experiments in which amplitude effects may be substantial [e.g., *Spotl and Vennemann, 2003*]. Two-point precision is approximately that achieved after the drift and amplitude correction in the validation study and in routine cross-validation of many batch runs. This reflects the small effect of amplitude scaling by scaling factors routinely determined to be within 10% of unity in both systems studied here.

As examples of structural uncertainty, the drift correction might be formulated as piecewise linear rather than a spline; the amplitude correction might not be log linear in statistical modeling. The chosen ordering of the

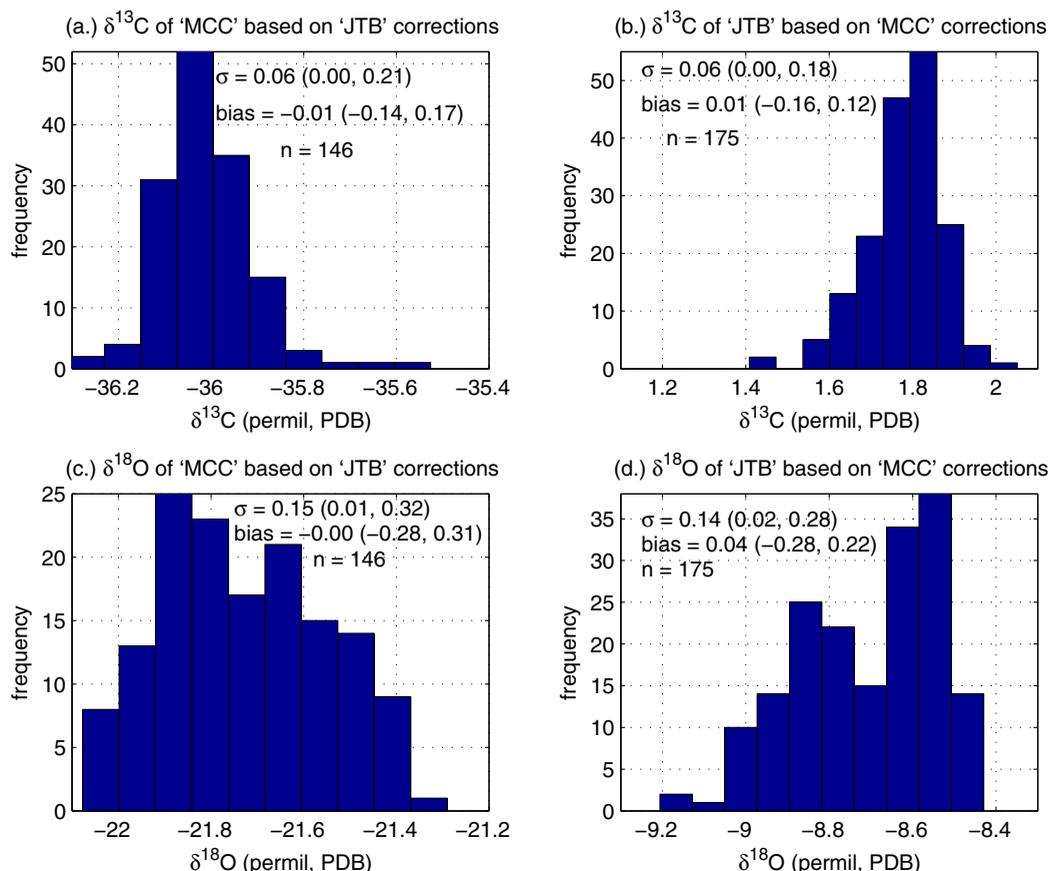


Figure 2. Routine carbonate $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ precision and bias with respect to known isotopic value for one working standard, based on drift, amplitude, and two-point corrections derived from the other. (a) $\delta^{13}\text{C}$ of the MCC working standard based on JTB-derived runtime corrections. MCC is isotopically similar to the predecessor EACARB working standard, with calibrated known $\delta^{13}\text{C} = -36.01 \pm 0.06\text{‰}$ and $\delta^{18}\text{O} = -21.73 \pm 0.12\text{‰}$ with respect to the LSVEC/IAEA-CO-1 scale. Results listed on figures are median (5th and 95th) percentile estimates for n corrections. (b) As in Figure 2a, except for $\delta^{13}\text{C}$ of JTB based on MCC runtime corrections. (c) As in Figure 2a, except for $\delta^{18}\text{O}$. (d) As in Figure 2b, except for $\delta^{18}\text{O}$. Validation estimates and known values are given in Table 1.

correction steps may also affect results. For instance, for cellulose analyses, we sequentially implement the drift, amplitude and two-point corrections using a suite of 24 correcting standards measured within a 99 position batch. (For carbonate analyses, we typically use a suite of 20 correcting standards in an 80 position batch.) However, there is no structural reason why the amplitude correction might not be performed prior to the drift correction. Reversing the order of drift and amplitude corrections for both the carbonate and cellulose validation experiments gives similar validation precision and bias estimates reported in the abstract and as shown in Tables 1 and 2. Although the amplitude correction is only rarely used in our experience (Tables (1–4) and Figures 2 and 3), the data suggest that results are not sensitive to order of operations.

Although the algorithm described here detects and corrects for three potential sources of systematic uncertainty in CF-IRMS data streams, it merely contributes to the comprehensive set of quality controls and standard operating protocols that produce long-term stability, precision, accuracy, and traceability of corrected data. As others have shown, those procedures may also include examination of chromatography [e.g., *Spotl and Vennemann, 2003*] and similar quality checks of complementary data, adherence to the IT principle [Werner and Brand, 2001] (for instance, controlling for possible carbonate matrix effects by use of working standards with similar chemical purity to that of the unknown samples; controlling for effects of mass interferences associated with N in celluloses by use of working standards with N composition spanning that of the unknown samples), blind laboratory intercomparison tests [e.g., *Coplen et al., 2006; Boettger et al., 2007*], reporting of reference values to which data sets were corrected [e.g., *Coplen et al., 2006*], calibration by multiple working standards over a wide range of isotopic values [e.g., *Evans, 2008*], and estimation of the external reproducibility using not only repeat analyses of working standards but also repeat analyses of samples

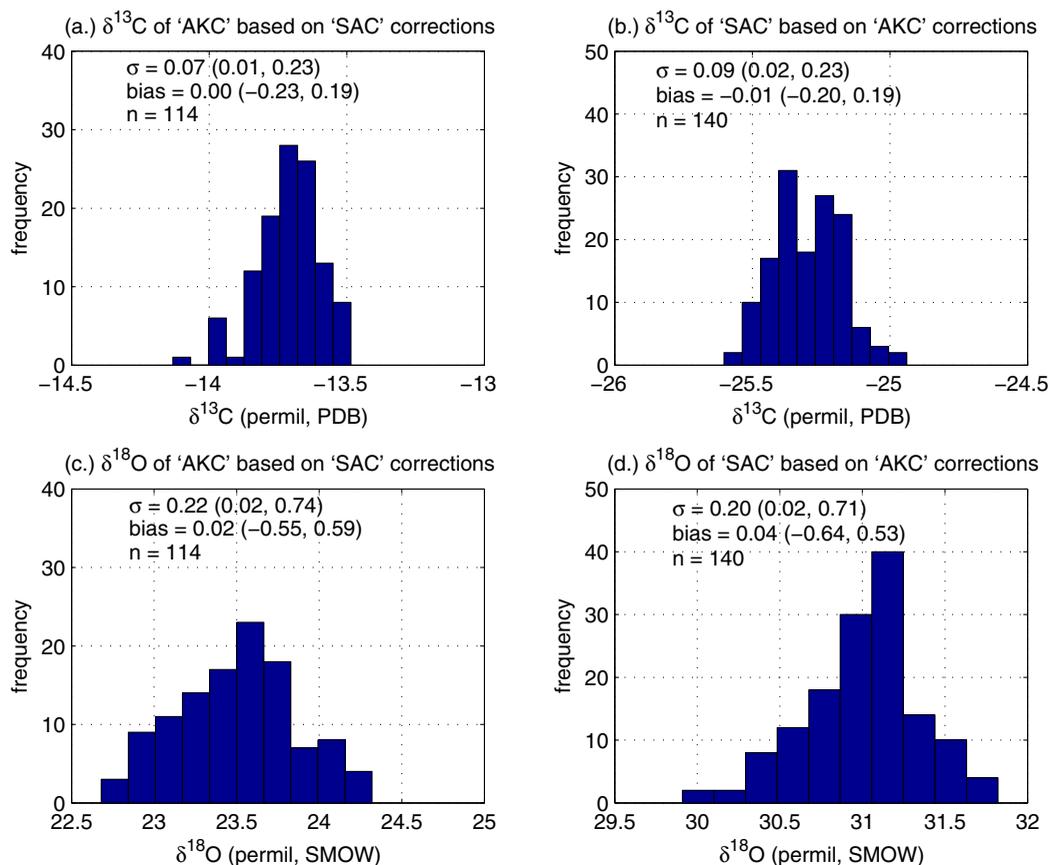


Figure 3. Routine cellulose $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ precision and bias with respect to known isotopic value for one working standard, based on drift, amplitude, and two-point corrections derived from the other. (a) $\delta^{13}\text{C}$ of the AKC working standard based on SAC-derived runtime corrections, based on the calibrated known values of and scale estimated from SAC and AKC cellulose working standards with values as noted in Table 2. Results listed are median (5th and 95th) percentile estimates for n corrections. (b) As in Figure 3a, except for $\delta^{13}\text{C}$ of SAC based on AKC runtime corrections. (c) As in Figure 3a, except for $\delta^{18}\text{O}$. (d) As in Figure 3b, except for $\delta^{18}\text{O}$. Validation estimates and known values are given in Table 2.

[e.g., Linsley et al., 2006; Koutavas et al., 2006]. Large, reproducible and validated corrections reported by this algorithm may indicate systematic problems in measurement protocols that may be identified and for which improved analytical procedures may be developed and be used to resolve.

6. Conclusion

CF-IRMS analyses using GC separation may be subject to runtime drift, signal amplitude and scale compression biases arising from changes in preparation system and mass analyzer conditions. Detection and correction of these biases may be used to produce corrected data sets with improved and validated precision and accuracy. Together with objective and automated data correction algorithms such as those presented here, high-throughput CF-IRMS systems enable rapid development of validated, precise, and accurate data streams in support of a wide range of data-intensive geoscientific applications.

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