SIMS bias on isotope ratios in dolomite-ankerite: δ^{13}C & δ^{18}O matrix effects

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Abstract

This work [1,2] explores the effects of Fe^{2+} substitution on SIMS δ^{13}C and δ^{18}O bias (or instrumental mass fractionation) in the analysis of carbonate minerals with compositions that fall along the dolomite-ankerite solid solution [$CaMg(CO_3)_2$-$CaFe(CO_3)_2$]. Bias is the per mil (‰) difference between measured 'raw' and 'true' (i.e., VPDB or VSMOW) values of δ^{13}C or δ^{18}O. We document the development of a suite of SIMS calibration standards (13 each for C and O isotopes) spanning the chemical compositional range between Fe# = 0.004 and 0.789 [Fe# = molar Fe/(Mg+Fe)].

[Background and motivation] Accurate isotope ratio measurements from sample materials by SIMS require the use of matrix-matched standards to correct for mass fractionation (bias) that occurs: 1) during the production and acceleration of ions from the sample surface (sputtering), 2) during the transmission of secondary ions through the mass spectrometer, and 3) during detection.

For a given configuration of the ion microprobe at WiscSIMS (CAMECA IMS 1280), the influence of instrumental parameters to total bias during an analytical session can be held nearly constant; any instrumental drift that occurs can be monitored and corrected by regularly analyzing a running-standard. For minerals that exhibit solid-solution behavior, this leaves the component of total bias that is a function of variable chemical composition (i.e., the sample matrix effect) in need of calibration.

There is at present no comprehensive theoretical model for accurately predicting secondary ion yields and thoroughly accounting for the bias imparted to isotope ratios during sputtering. Accurate isotope ratio determinations are thus only possible if a sufficient number of well-characterized standards are employed to empirically characterize, on a session-by-session basis, the total instrumental bias as a function of variable chemical composition.

[Results] Under routine operating conditions, the magnitude of SIMS δ^{18}O bias *decreases* exponentially with increasing Fe# (by ~10.5‰; Fig. 1a, right-hand axis). That is, the bias is greatest for end-member dolomite (-13.5‰) and smallest for the most Fe-rich ankerite (-3‰ for Fe# = 0.789).

In contrast, the magnitude of SIMS δ^{13}C bias *increases* exponentially with increasing Fe# (by ~4.5‰; i.e., values become more negative and hence move further away from true VPDB values; Fig. 3a, right-hand axis). That is, the bias is smallest for end-member dolomite (~ ~47.5‰) and largest for the most Fe-rich ankerite (~ -52‰ for Fe# = 0.789).

Minor Mn substitution appears to contribute no secondary matrix effects to measurements of SIMS δ^{13}C and δ^{18}O bias from the suite of dolomite-ankerite calibration standards [at concentrations < 2.6% molar Mn/(Ca+Mg+Fe+Mn)].

In constructing working calibration curves (Figs. 1-3), measured values of SIMS δ^{13}C and δ^{18}O bias for the suite of calibration standards are normalized to a running standard for drift-monitoring purposes (commonly end-member dolomite standard UW6220; normalized values are thus expressed as 'bias*(STD-UW6220)').

[SIMS δ^{18}O bias calibration] The compositional dependence of SIMS δ^{18}O bias (i.e. the sample matrix effect) is expressed using the Hill equation, which has wide-ranging applicability in describing empirical relationships of the 'component concentration' vs. 'measured effect' type, especially for systems that behave nonlinearly and reach saturation. For calibrations employing either 10- or 3-μm-diameter spot-size measurements, this yields residual values ≤ 0.3-0.4‰ relative to the certified reference material NBS-19 for most standards in the suite (Figs. 1 and 2, left-hand axes).

Analytical precision for δ^{18}O is ± 0.3‰ (2SD, standard deviations) for 10-μm spots and ± 0.7‰ (2SD) for 3-μm spots, based on the spot-to-spot reproducibility of a running standard (n = 8) that 'brackets' each set of 10 sample measurements. The total analytical uncertainty for individual sample spot analyses of dolomite-ankerite is approximated by a combination of precision and calibration residuals (propagated in quadrature), suggesting accuracy of ± 0.5‰ (2SD) for 10-μm spots and ± 1‰ (2SD) for 3-μm spots.

[Results: SIMS δ^{13}C bias calibration] The compositional dependence of SIMS δ^{13}C bias (i.e. the sample matrix effect) is again expressed using the Hill equation, although the modeled effect for carbon is the opposite of that observed for oxygen (Fig. 3a; left-hand axis). For calibrations employing the commonly used 6-μm-diameter spot-size, this yields residual values ≤ 0.3‰ relative to NBS-19 for most standards in the suite. Analytical precision for δ^{13}C is ± 0.6-1.2‰ (2SD), based on the spot-to-spot reproducibility of a running standard (n = 8) that 'brackets' each set of 10 sample measurements. The total analytical uncertainty for individual sample spot analyses of dolomite-ankerite is approximated by combination of precision and the calibration residual (propagated in quadrature), suggesting accuracy of ± 1.0-1.5‰ (2SD).

[Concluding remarks] It is common for the magnitude of SIMS δ^{13}C and δ^{18}O bias measured from calibration standards to vary by several per mil from session-to-session. We find, however, that the overall distribution of standard data points in relation to one another in working calibration plots (i.e., bias*(STD-UW6220) vs. Fe# for either δ^{13}C or δ^{18}O; Figs. 1-3) remains remarkably consistent from session-to-session. The values of the Hill equation curve shape parameters 'n' (a sigmodicity factor) and 'k' (= Fe# at 1/2 bias max) remain unchanged, whereas the best-fit value of the 'bias*max' parameter behaves as an analytical session-specific scaling factor. Thus while the accuracy and precision of in situ stable isotope analyses by SIMS are improved using multiple calibration standards, the constant shape of the Hill function for δ^{13}C and δ^{18}O analyses at WiscSIMS shows that an approximate correction can be made for variable Fe# based on just two standards (dolomite and Fe-rich ankerite).

Analytical Method

SIMS (secondary ion mass spectrometry)

Briefly,
[1] Focused beam of Cs+ ions bombards sample (sputtering)
[2] Impact causes sample ionization (i.e., production of $^{18}O^-$ & $^{16}O^-$ ions, $^{13}C^-$ & $^{12}C^-$ ions)
[3] Ions of interest collected, counted and ratios of different isotopes calculated (e.g., $^{18}O/^{16}O$, $^{13}C/^{12}C$)
[4] Isotope ratios coverted to conventional 'δ-values' by comparison to international reference standards

Process

Samples of naturally-occurring dolomites and ankerites were aquired for testing.

Subsampling. The subsequent assessment of chemical and isotopic homogeneity will be considered valid only for this subsample volume of material. Likewise, the bulk δ^{18}O VSMOW and δ^{13}C VPDB values determined by conventional phosphoric acid digestion and gas-source mass spectrometry will pertain only to this subsample.

Rinds were abraded away to expose fresh crystal surfaces.

1/6 mm

Clean grain seperates were prepared (~500 micron size-fraction).

An example of a mount with 20 grains of each potential standard.

The extent of chemical homogeneity was assessed by EPMA; the degree of isotopic homogeneity (δ18O & δ13C) was assessed by SIMS.

~10% of tested materials were found to be suitable.

Powdered aliquots of those materials that were accepted for use as calibration standards were lastly analyzed in triplicate by conventional phosphoric acid digestion and gas-source mass spectrometry to calibrate the δ18O VSMOW and δ13C VPDB values of each standard

δ^{18}O Calibration

10-μm-diameter spot-size

$$bias^*(STD-UW6220) = \frac{(bias^*_{max})x^n}{k^n + x^n}$$

Best fit curve		
Adj. R2	0.996	
	Value	SE
bias max	11.5	0.4
k	0.10	0.01
n	1.2	0.1

Fig. 1. (a) Plot relating SIMS δ^{18}O bias (‰) to the cation composition of the dolomite-ankerite solid solution series [Fe# = Fe/(Mg+Fe)] for a typical calibration using a 10-μm-diameter spot-size. The sample matrix effect can be accurately estimated using the Hill equation, which is commonly employed to describe relations of 'concentration' vs. 'effect', especially in systems that behave nonlinearly and reach saturation. **(b)** Plot of the calibration residual. For most standards in the suite, the averaged measured value of δ^{18}O bias*(STD-UW6220) differs by less than 0.3‰ from the value predicted by the calibration (depicted by dashed lines).

3-μm-diameter spot-size

$$bias^*(STD-UW6220) = \frac{(bias^*_{max})x^n}{k^n + x^n}$$

Adj. R2	0.993	
	Value	SE
Bias max	11.1	0.2
k	0.10	-
n	1.2	-

Fig. 2. (a) Plot relating SIMS δ^{18}O bias (‰) to the cation composition of the dolomite-ankerite solid solution series [Fe# = Fe/(Mg+Fe)] for a typical calibration using a 3-μm-diameter spot-size. The sample matrix effect can be accurately estimated using the same model parameters as in the 10-μm-spot-size calibration. **(b)** Plot of the calibration residual. For most standards in the suite, the averaged measured value of δ^{18}O bias*(STD-UW6220) differs by less than 0.3‰ from the value predicted by the calibration (depicted by dashed lines).

δ^{13}C Calibration

6-μm-diameter spot-size

Best fit curve		
Adj. R2	0.989	
	Value	SE
Bias ma	5.1	0.4
k	0.10	0.02
n	1.0	0.1

$$bias^*(STD-UW6220) = (-1)\frac{(bias^*_{max})x^n}{k^n + x^n}$$

Fig. 3. (a) Plot relating SIMS δ^{13}C bias (‰) to the cation composition of the dolomite-ankerite solid solution series [Fe# = Fe/(Mg+Fe)] for a typical calibration using a 6-μm-diameter spot-size. **(b)** Plot of the calibration residual. For all standards in the suite, the averaged measured value of δ^{13}C bias*(STD-UW6220) differs by less than 0.3‰ from the value predicted by the calibration (depicted by dashed lines).

Towards understanding the landscape of SIMS matrix effects for Ca-Mg-Fe carbonates

δ^{18}O

SIMS δ^{18}O bias model for the Dolomite-Ankerite series integrated with extant work [3] on the Siderite-Magnesite and Calcite-Magnesite joins of the Ca-Mg-Fe carbonate ternary

Carbonate Ca-Mg-Fe ternary diagram showing the range of compositions of UW Dolomite-Ankerite SIMS δ18O calibration standards

δ^{13}C

Carbonate Ca-Mg-Fe ternary diagram showing the range of compositions of UW Dolomite-Ankerite SIMS δ13C calibration standards

[1] Śliwiński et al., (in review). SIMS bias on isotope ratios in dolomite-ankerite, Part I: δ18O matrix effects. Geostand. Geoanal. Res.   [2] Śliwiński et al., (in prep.). SIMS bias on isotope ratios in dolomite-ankerite, Part I: δ13C matrix effects. Geostand. Geoanal. Res.   [3] Valley and Kita, 2009. MAC, **41**