Secondary Ion Mass Spectrometry Bias on Isotope Ratios in Dolomite−Ankerite, Part II: δ^{13}C Matrix Effects

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This study is Part II of a series that documents the development of a suite of calibration reference materials for *in situ* SIMS analysis of stable isotope ratios in Ca-Mg-Fe carbonates. Part I explored the effects of Fe^{2+} substitution on SIMS δ^{18}O bias measured from the dolomite–ankerite solid solution series $[CaMg(CO_3)_2-CaFe(CO_3)_2]$, whereas this complementary work explores the compositional dependence of SIMS δ^{13}C bias (calibrated range: Fe# = 0.004–0.789, where Fe# = molar Fe/(Mg+Fe)). Under routine operating conditions for carbonate δ^{13}C analysis at WiscSIMS (CAMECA IMS 1280), the magnitude of instrumental bias increased exponentially by 2.5–5.5‰ (session-specific) with increasing Fe-content in the dolomite structure, but appeared insensitive to minor Mn substitution [< 2.6 mole % Mn/(Ca+Mg+Fe+Mn)]. The compositional dependence of bias (i.e., the matrix effect) was expressed using the Hill equation, yielding calibration residual values ≤ 0.3‰ relative to CRM NBS-19 for eleven carbonate reference materials (6-μm-diameter spot size measurements). Based on the spot-to-spot repeatability of a drift monitor material that 'bracketed' each set of ten sample-spot analyses, the analytical precision was ± 0.6–1.2‰ (2s, standard deviations). The analytical uncertainty for individual sample analyses was approximated by combining the precision and calibration residual values (propagated in quadrature), suggesting an uncertainty of ± 1.0–1.5‰ (2s).

Keywords: SIMS, carbon isotopes, dolomite, ankerite, matrix effects.

Cette étude est la deuxième partie d'une série qui documente le développement d'une suite de matériaux de référence destiné à la calibration pour l'analyse in situ, par la méthode SIMS, des rapports d'isotopes stables dans les carbonates de Ca-Mg-Fe. La partie I a exploré les effets de la substitution de Fe^{2+} sur le biais dans la mesure du δ^{18}O au SIMS à partir de la solution solide de la série dolomite-ankérite $[CaMg(CO_3)_2-CaFe(CO_3)_2]$, alors que ce travail complémentaire explore la dépendance à la composition du biais dans la mesure du δ^{13}C au SIMS (plage calibrée : Fe# = 0.004 à 0.789, avec Fe# = Fe/ (Mg+Fe) molaire). Dans des conditions de fonctionnement de routine pour l'analyse du δ^{13}C des carbonates avec le WiscSIMS (CAMECA IMS 1280), l'importance du biais instrumental a augmenté de façon exponentielle de 2,5–5,5‰ (spécifique à chaque session) avec l'accroissement du contenu en Fe dans la structure de la dolomite, mais a semblé insensible à la substitution mineure du Mn [< 2,6% molaire, Mn/ (Ca+Mg+Fe+Mn)]. La dépendance à la composition du biais (i.e., l'effet de matrice) a été exprimé en utilisant l'équation de Hill, donnant des valeurs résiduelles de calibration ≤ 0,3‰ par rapport au CRM NBS-19 pour douze matériaux carbonatés de référence (avec une taille de spot d'analyse de 6 μm de diamètre). Basé sur la répétabilité «spot à spot» d'un matériau de contrôle de la dérive analysé avant et après chaque ensemble de dix échantillons analysés, la précision analytique a été de ±0.6–1.2‰ (écarts-types de 2s). L'incertitude analytique pour les analyses d'échantillons individuels a été approchée en combinant la précision et les valeurs résiduelles de calibration (propagée en quadrature), ce qui suggère une incertitude de ±1.0–1.5‰ (2s).

Mots-clés : SIMS, isotopes du carbone, dolomite, ankérite, effets de matrice.

Accurate isotope ratio measurements from sample materials by secondary ion mass spectrometry (SIMS) require the use of matrix-matched reference materials (RMs) to correct for mass fractionation that occurs as follows: (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 (e.g., Hervig *et al.* 1992, Eiler *et al.* 1997, Fitzsimons *et al.* 2000, Valley and Kita 2009, Huberty *et al.* 2010). Collectively, these instrumental mass fractionation effects can be referred to as the measurement or instrumental 'bias', *sensu* the International Vocabulary of Metrology (VIM 2008). The term 'bias' denotes here an 'estimate of a systematic measurement error' (2.18, VIM 2008), the effects of which can be compensated for by a correction or calibration. A systematic measurement error, the causes of which can be known or unknown, is the 'component of measurement error that in replicate measurements remains constant or varies in a predictable manner' (2.17, VIM 2008).

For a given configuration of the ion microprobe, the influence of instrumental parameters on mass fractionation (or bias) during an analytical session can be held largely constant (any minor changes in the magnitude of bias are accounted for by appropriate drift-monitoring materials). For minerals that exhibit solid solution behaviour, this leaves the component of total bias that is a function of chemical composition in need of calibrating (i.e., the sample matrix effect). 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-characterised RMs are employed to empirically characterise, on a session-by-session basis, the bias as a function of chemical composition.

The focus of this study is an empirical characterisation of SIMS $\delta^{13}C$ bias for the dolomite–ankerite solid solution series [$CaMg(CO_3)_2$–$CaFe(CO_3)_2$]. A comprehensive suite of RMs was developed for the purpose of calibration SIMS analyses across the range Fe# = 0.004–0.789 [Fe# = molar Fe/(Mg+Fe)]. This work is complementary to a recent contribution (Śliwiński *et al.* 2015a), wherein we reported on the development of a suite of $\delta^{18}O$-calibration RMs and presented a SIMS $\delta^{18}O$ bias calibration for carbonates that fall along this compositional spectrum. The nature of SIMS $\delta^{13}C$ bias effects in the analysis of carbonate minerals has been investigated previously for various end-member compositions (e.g., Ca, Mg, CaMg (dolomite), Fe, Mn, Zn, Sr, Pb, Ba), but has been investigated only to a limited extent along the dolomite–ankerite and siderite–magnesite solid solutions (e.g., Riciputi *et al.* 1998).

Experimental procedures

Overview of the methodological approach

Samples of naturally occurring carbonate minerals with compositions along the dolomite–ankerite solid solution series were assessed to determine the extent to which each is homogenous in terms of $\delta^{13}C$ and cation composition (expressed here as the Fe#). Most aspects of the methodology are as described in the first part of this study (see Śliwiński *et al.* 2015a). This includes the following: 1) our approach to preparing clean grain separates of each assessed potential RM, 2) the preparation of grain mounts for SIMS analysis, 3) analysis of the cation chemistry and its variability by EPMA and 4) bulk analysis by conventional phosphoric acid digestion and gas-source mass spectrometry to determine the average (bulk) $\delta^{13}C$ (VPDB) value of each material that was accepted for use as a SIMS $\delta^{13}C$-calibration RM.

Potential reference materials with suitably homogenous cation chemistry were evaluated for carbon isotope homogeneity on the 6-μm scale by SIMS. There are many conceivable SIMS studies that would/do benefit from this admittedly smaller-than-routine spot size (~ 10–15 μm diameter) in the analysis of carbon isotopes in carbonate minerals. An example is the study of chemo-isotopically zoned carbonate cements in clastic rocks (e.g., Śliwiński *et al.* 2015b). It is not uncommon in such studies to observe chemical zoning on the sub-10 micrometre scale. It is then of interest, for example, for the interpretation of evolving conditions during sediment diagenesis, to establish whether changes in the chemistry of successive cement zones are associated with changes in the isotope ratios of carbon and of oxygen ($\delta^{18}O$, $\delta^{13}C$). We find that a 6-μm-diameter spot size allows for analysing smaller-than-routine sample domains, all the while providing a degree of analytical precision (± 1.0‰, *2s*, standard deviations) that allows for meaningful interpretations of any isotopic variability that is uncovered at such a scale.

During assessment, typically twenty grains of each potential RM were measured once each to determine the extent of carbon isotope homogeneity; a potential RM passed testing if the value of 2 standard deviations (*2s*) of this set of measurements fell below 1.0‰ (for RMs with slight heterogeneity, a *2s* value of up to ± 1.4‰ was acceptable). The instrumental configuration and analytical protocol employed at WiscSIMS for small-spot carbonate $\delta^{13}C$ analyses (6-μm-diameter spot size; see next sub-section) typically yields a variability within ± 1.0‰ (*2s*) for measurements of a nominally homogenous material; this is based on considerations of counting statistics, the sample-spot-to-spot repeatability of measured $\delta^{13}C$ values and the overall stability of the

instrument. The WiscSIMS calibration protocol for minerals that exhibit solid solution behaviour calls for measuring each RM four times (four different grains, once each) and using the average value to calculate the bias associated with each composition. A practical SIMS δ^{13}C-calibration RM for routine use is thus one for which the value of two standard deviations of $n = 4$ replicate analyses varies by less than $\pm$ 1.0‰. Analyses of carbon isotope ratios in carbonate minerals are inherently less precise than δ^{18}O determinations due to the lower concentration and less efficient ionisation of carbon under similar primary ion beam conditions.

Carbon isotope determinations by SIMS

Carbon isotope measurements were performed using a CAMECA IMS 1280 large radius multi-collector SIMS at the WiscSIMS Laboratory (Department of Geoscience, University of Wisconsin-Madison). The data set reported here was collected during multiple analytical sessions; the example calibration curve that will be presented and discussed was constructed using data from session S13.

Instrumental conditions: A 10 kV, 0.6 nA primary beam of ^{133}Cs$^+$ ions was focused to a ~ 6 μm diameter on the sample surface, resulting in a sputtering depth of ~ 1 μm. Sample surfaces were made conductive by applying a thin gold coat (ca. 60 nm), and charge neutralisation was aided by an electron flood gun. The secondary optics were configured as follows: transfer lens magnification of 200, contrast aperture diameter of 400 μm, field aperture 4000 μm × 4000 μm, entrance slit width of 122 μm, energy slit width of 40 eV and an exit slit width of 243 μm, which corresponds to a mass resolving power of ~ 5000 (sufficient to resolve hydride interferences on ^{13}C). Secondary ion signals were detected simultaneously using axial electron multipliers for ^{13}C$^-$ and ^{13}CH$^-$ (axial and H2, respectively), and a Faraday cup (L2) for ^{12}C$^-$. During routine sample analyses, the ^{13}CH$^-$ signal serves as a monitor of organic matter and other contaminants, which can affect values of δ^{13}C (especially in biocarbonates). A typical count rate for ^{12}C$^-$ ions was in the range of 6–13 × 10^6 cps and varied with the composition analysed (e.g. 7.5 × 10^6 cps for calcite, 6.9 × 10^6 cps for end-member dolomite and 12.7 × 10^6 cps for high-Fe ankerite (Fe# = 0.789); session S13 data). The baseline of the Faraday cup (10^{11} Ω resistor) was calibrated once daily, whereas the gain of the electron multipliers was systematically checked and the high voltage adjusted, if necessary, during each set of bracketing RM analyses (after the second of four RM measurements). The duration of a single measurement was ~ 4 min, which included an initial 20 s of pre-sputtering to remove the overlying gold coat, followed by an automated ~ 60 s

routine that centred the secondary ion beam in the field aperture and optimised its transmission into the mass spectrometer, and lastly a collection period of secondary ion signals of 160 s (twenty cycles of 8-s integrations).

Results and discussion

The suite of SIMS δ^{13}C-calibration RMs representing the dolomite–ankerite solid solution series consists of thirteen carbonate materials ranging in composition from end-member dolomite to ankerite with an Fe# of 0.789 (Figure 1, Table 1). The range of δ^{13}C values represented by the suite, calibrated by phosphoric acid digestion of mg-size samples and gas-source mass spectrometry, extends from -8.36 to 3.19‰ VPDB (Table 2, Appendix A). Analyses by SIMS using a 6-μm-diameter spot size have shown the δ^{13}C value of these RMs to be homogenous to within $\pm$ 1.2‰ (2s for $n = 20$, spot-to-spot repeatability; Table 2). This article is accompanied by online supporting information, which includes: (i) complete EPMA and SIMS data sets (Appendices S1 and S2), (ii) a description of how sample analyses are corrected for SIMS δ^{13}C bias and the associated propagation of errors (Appendix S3), (iii) additional examples of calibration curves (Appendix S4) and (iv) an assessment of the repeatability of our potential RM assessment process (Appendix S5).

Data presentation and a sample calibration

Instrumental mass fractionation (i.e., bias) associated with measurements of δ^{13}C-calibration RMs is expressed by the formulation:

$$\alpha^{13}C_{SIMS} = \frac{1 + (\delta^{13}C_{raw}/1000)}{1 + (\delta^{13}C_{VPDB}/1000)} \qquad (1)$$

(modified after Kita et al. 2009), where 'δ^{13}C$_{raw}$' represents the background and detector dead-time (when electron multipliers are used) corrected δ^{13}C value of a standard measured by SIMS; this value is expressed in conventional per mil notation (‰) and calculated relative to the ^{13}C/^{12}C ratio in Vienna Pee-Dee Belemnite (VPDB; i.e., normalised to ^{13}C/^{12}C$_{VPDB}$ = 0.0112372; Craig 1957, Allison et al. 1995), but it has not been corrected for bias and is therefore not accurate relative to VPDB. The 'δ^{13}C$_{VPDB}$' term represents the average δ^{13}C value of the same RM determined by conventional phosphoric acid digestion and gas-source mass spectrometry (McCrea 1950) and is expressed on the VPDB scale (Table 2, Appendix A). Because values of α^{13}C$_{SIMS}$ are often close to unity, they are consistently expressed throughout this article using δ-notation in per mil (‰) and referred to as 'bias':
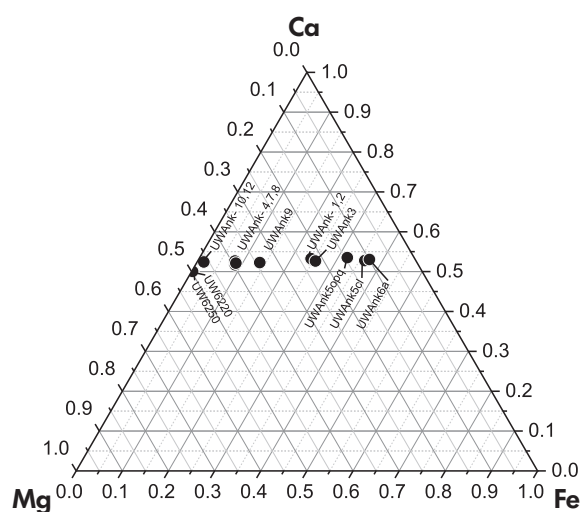
Figure 1. Carbonate Ca-Mg-Fe ternary diagram showing the range of compositions of UW dolomite–ankerite SIMS δ^{13}C-calibration RMs in this study (see Table 1).

$$\text{bias} = 1000 \cdot (\alpha^{13} C_{SIMS} \text{-1}) \qquad (2)$$

Please note that all equations presented here are formulated such that all mathematical operations involving multiplication or division are performed on α-terms (e.g., if two isotope ratio values that are expressed using δ-notation are to be multiplied or divided, they are firstly converted to α-values, then multiplied and/or divided, and subsequently converted back to values in δ-notation). We explicitly avoid the common approximation, where $\delta_A - \delta_B \cong 1000\ln(\alpha_{A-B})$

The values of bias for each of the δ^{13}C-calibration RMs, calculated by Equation (2), are tabulated in Table 3 for multiple analytical sessions spanning a 2-year period. Table 3 includes the averages of the measured δ^{13}C values. The entire SIMS data set is provided in Appendix S2.

A sample calibration relating the magnitude of SIMS δ^{13}C bias to variation in cation chemistry of the dolomite–ankerite solid solution series is shown in Figure 2a (data from session S13; Table 3). Note the two different vertical axes; the left-hand axis represents the *working calibration curve*, where the δ^{13}C bias of each RM is normalised to the bias of the drift-monitoring material that is systematically measured throughout the duration of an analytical session. During the analysis of samples with compositions that fall along the dolomite–ankerite series, the drift monitor is commonly the end-member dolomite RM (UW6220; Śliwiński *et al.* 2015a):

$$\delta^{13} C \, bias^* (RM - UW6220)$$
$$= 1000 \cdot \left[\frac{1 + (bias_{RM} / 1000)}{1 + (bias_{UW6220} / 1000)} \text{-1} \right] \qquad (3)$$

The right-hand axis of Figure 2a represents values of SIMS δ^{13}C bias (‰) that are corrected for instrumental drift but that *are not* normalised to the bias of the drift monitor material (i.e., values that represent the per mil difference between $\delta^{13}C_{raw}$ and $\delta^{13}C_{VPDB}$). The error propagation associated with Equation (3) is of the same general form as that described in appendix S5 of Śliwiński *et al.* (2015a). Each batch of ten sample measurements is systematically bracketed by eight analyses of the drift monitor material, several grains of which are embedded into each sample mount (four analyses of UW6220 before, and four more after, each group of ten sample measurements). Instrumental drift is thus systematically monitored throughout the duration of the analytical session; this allows for assigning to each sample-spot measurement a value of δ^{13}C bias (based on the Fe# of the analysed spot) that is appropriately scaled to the instrumental conditions during calibration (see Appendix S3).

The effect of Fe-substitution on SIMS δ^{13}C bias in dolomite–ankerite and a matrix bias correction

Under routine operating conditions for carbonate mineral δ^{13}C analysis at WiscSIMS, the magnitude of SIMS δ^{13}C bias increases exponentially with increasing Fe-content (i.e., Fe#) in the dolomite–ankerite solid solution. For the sample calibration shown in Figure 2a, the difference in bias between the end-members of the series amounts to -4‰ (session S13 data, Table 3); that is, the bias was smallest for end-member dolomite (-47.53‰) and largest for the most Fe-rich ankerite (-51.75‰ at Fe# = 0.789). All SIMS δ^{13}C bias values discussed in this article are negative (whether or not they are normalised to the bias of the drift monitor material); thus, to avoid confusion with regard to terminology, please note the following: as values become more negative, the absolute magnitude of SIMS δ^{13}C bias *increases*; that is, the per mil difference between the 'raw' δ^{13}C values measured by SIMS and 'true' $\delta^{13}C_{VPDB}$ values becomes larger (and *vice versa*).

Considering the calibration data shown in Figure 2a (session S13, Table 3), the magnitude of δ^{13}C bias* (RM-UW6220): (i) changes most rapidly (by ~ 2.5‰) in the narrow compositional range of 'nonferroan' dolomite, defined by Fe# between 0.0 and 0.1 (*sensu* Chang *et al.* 1996), (ii) changes more gradually (by another ~ 0.75‰ from 2.50 to 3.25‰) in the equally narrow compositional range of 'ferroan dolomite' (Fe# between 0.1 and 0.2) and

Table 1.
Average chemical composition of each SIMS $\delta^{18}O$ and/or $\delta^{13}C$-calibration RM in the dolomite–ankerite suite (analysed by EPMA)

RM	EPMA session i.d. and date	No. of grains	No. of EPMA analyses	Mg (mol %)	2s	Ca (mol %)	2s	Fe (mol %)	2s	Mn (mol %)	2s	Fe# [Fe/(Mg+Fe)]	2s	2SE	Fe % m/m	2s	2SE	RM for $\delta^{13}C$?	RM for $\delta^{18}O$?
UW6250	(S1) 2006 Sept.	15	15	49.80%	1.00%	50.10%	1.00%	0.20%	0.20%	–	–	0.004	0.005	0.001	0.05	0.15	0.04	Yes	Yes
UW6220	(S1) 2006 Sept.	15	15	49.66%	1.00%	50.23%	1.00%	0.20%	0.10%	–	–	0.004	0.004	0.001	0.06	0.11	0.03	Yes	Yes
UWAnk10	(S5a) 2014 Dec.	22	66	46.33%	0.67%	52.67%	0.69%	0.91%	0.19%	0.08%	0.03%	0.019	0.004	0.000	0.54	0.11	0.01	Yes	No[b]
UWAnk11	(S5a) 2014 Dec.	20	60	47.62%	1.98%	50.51%	2.06%	1.54%	0.38%	0.25%	0.46%	0.031	0.008	0.001	0.91	0.23	0.03	No	No
UWAnk12	(S5a) 2014 Dec.	21	63	46.06%	0.78%	52.31%	0.77%	1.45%	0.33%	0.17%	0.04%	0.031	0.007	0.001	0.86	0.19	0.02	Yes	Yes
UWAnk7	(S5b) 2014 Dec.	21	63	39.60%	0.60%	51.60%	0.60%	8.60%	0.50%	0.20%	0.10%	0.178	0.010	0.001	5.05	0.33	0.04	No[a]	Yes
UWAnk8	(S5b) 2014 Dec.	19	57	38.80%	1.90%	52.00%	0.90%	8.00%	0.70%	1.20%	0.60%	0.171	0.019	0.003	4.69	0.42	0.06	No	Yes
UWAnk4	(S3) 2014 Mar.	20	30	38.84%	2.90%	51.46%	2.90%	8.46%	1.00%	1.24%	0.50%	0.179	0.020	0.004	4.93	0.57	0.10	Yes	Yes
UWAnk9	(S5b) 2014 Dec.	19	57	33.90%	0.80%	52.00%	0.60%	13.60%	1.00%	0.50%	0.20%	0.286	0.018	0.002	7.89	0.60	0.08	Yes	Yes
UWAnk1	(S2) 2012 July	22	22	22.11%	1.70%	52.03%	2.00%	24.10%	2.00%	1.72%	1.00%	0.522	0.038	0.008	13.58	1.21	0.26	Yes	Yes
UWAnk2	(S2) 2012 July	22	22	22.11%	2.80%	52.40%	3.70%	23.90%	2.40%	1.60%	0.90%	0.519	0.065	0.014	13.39	2.26	0.48	Yes	Yes
UWAnk3	(S3) 2014 Mar.	18	54	21.50%	3.10%	51.90%	2.70%	25.20%	3.20%	1.40%	0.70%	0.540	0.056	0.008	14.05	1.57	0.21	Yes	No
UWAnk5opq	(S4) 2014 July	21	66	14.11%	3.74%	52.21%	4.62%	31.24%	2.80%	2.43%	0.64%	0.689	0.084	0.010	17.12	2.54	0.31	Yes	Yes
UWAnk5d	(S4) 2014 July	20	61	10.76%	1.70%	51.44%	2.00%	35.27%	1.50%	2.54%	0.60%	0.766	0.034	0.004	19.16	1.41	0.18	Yes	Yes
UWAnk6a	(S4) 2014 July	22	68	9.66%	1.90%	51.64%	2.60%	36.09%	2.00%	2.61%	0.60%	0.789	0.041	0.005	19.56	1.69	0.20	Yes	Yes

a This RM is not routinely used for $\delta^{13}C$ calibration (2SE > 0.60‰ for n = 4). It may be used, however, if analysed repeatedly a sufficient number of times to drive the value of 2SE below 0.60‰ (approx. n = 10).
b This RM is not routinely used for $\delta^{18}O$ calibration (2SE > 0.15‰ for n = 4). It may be used, however, if analysed repeatedly a sufficient number of times to drive the value of 2SE below 0.15‰ (approx. n = 10).

Table 2.
Measured extent of $\delta^{13}C$ homogeneity in the suite of dolomite–ankerite RMs (by SIMS; 6-µm spot size)

RM	Source locality	SIMS session i.d. and date	No. of grains	No. of SIMS analyses	True[a] average $\delta^{13}C$ (‰, VPDB)	2s	2SE
UW6250[b]	Thornwood, Westchester County, New York, USA	(SD1(2)) 2006 July	8	8	1.29	1.43	0.51
UW6220	Tuckahoe, Westchester County, New York, USA	(SD1(2)) 2006 July	8	8	0.84	0.53	0.19
UWAnk10	St. Johnsville, Montgomery County, New York, USA	(S13) 2014 Dec.	20	20	-1.52	0.71	0.16
UWAnk12	Unknown	(S13) 2014 Dec.	21	21	3.19	1.13	0.25
UWAnk7	near Selåsvann, Aust-Agder, Norway	(S13) 2014 Dec.	21	20	-8.36	0.63	0.14
UWAnk8[b]	Quincy/Salem Neck, Norfolk/Essex Counties, Massachusetts, USA	(S13) 2014 Dec.	19	20	-4.15	1.38	0.31
UWAnk9	near Llallagua, Potosi Dept., Bolivia	(S13) 2014 Dec.	19	20	-6.99	1.15	0.26
UWAnk1	Pulaski County, Arkansas, USA	(SD2(2)) 2012 July	22	21	-7.38	1.01	0.22
UWAnk2	Pulaski County, Arkansas, USA	(SD2(2)) 2012 July	22	22	-7.35	1.06	0.23
UWAnk3	Pulaski County, Arkansas, USA	(S5) 2014.Apr.	18	20	-7.34	1.20	0.27
UWAnk5opq	Erzberg Mine, near Eisenerz, Styria, Austria	(S10) 2014 Sept.	21	25	-4.59	0.89	0.18
UWAnk5cl	Erzberg Mine, near Eisenerz, Styria, Austria	(S10) 2014 Sept.	20	22	-4.57	0.74	0.16
UWAnk6a	Erzberg Mine, near Eisenerz, Styria, Austria	(S10) 2014 Sept.	22	24	-4.40	0.86	0.18

[a] $\delta^{13}C$ VPDB value determined by conventional phosphoric acid digestion and gas-source mass spectrometry (see Appendix A).
[b] This RM may be used for calibration only if analysed repeatedly a sufficient number of times to drive the standard error (at the 95% confidence level) below 0.60‰.

finally (iii) tapers off, changing by only an additional ~ 1‰ throughout the more extended compositional range of ankerite (Fe# $\geq$ 0.2). The near exponential change in $\delta^{13}C$ bias*(RM-UW6220) vs. Fe# for compositions near the dolomite end of the solid solution necessitates careful corrections in the analysis of unknown samples with an Fe-content that could otherwise be considered 'negligible'. As an example consider a sample of dolomite with a composition resembling that of RM UWAnk10, with a Fe# of 0.019 (equivalent to 0.54% m/m Fe); failure to correct for this arguably low concentration of Fe results in an accuracy error of 1‰ (Figure 2a, Table 3).

The relation between SIMS $\delta^{13}C$ bias*(RM-UW6220) and Fe# for the suite of $\delta^{13}C$-calibration RMs can be modelled using the Hill equation (Equation 4; e.g., see review of Goutelle et al. 2008) in much the same way as the relation between $\delta^{18}O$ bias*(RM-UW6220) and Fe# (see Śliwiński et al. 2015a):

$$\delta^{13}C\,bias^*(RM - UW6220) = \frac{(bias^*_{max})\,x^n}{k^n + x^n} \quad (4)$$

The parameters of Equation (4) are defined as follows: 'x' is the Fe# (based on EPMA data) is defined for values between 0 and 1 (i.e., it is constrained by the physical limits of solid solution), 'n' is a sigmoidicity factor, and 'k' is the value of 'x' (i.e., Fe#) at ½ bias*$_{max}$. For a hypothetical data set for which the Hill function saturates and reaches a plateau value as x approaches 1, the term 'bias*$_{max}$' would correspond to the largest (i.e., most negative) value of $\delta^{13}C$ bias*(RM-UW6220) observed during a particular analytical session for those RMs with the highest Fe numbers.

Model parameters and the uncertainty associated with the matrix bias correction: The $\delta^{13}C$-calibration RM data (Figure 2a, session S13, Table 3) was modelled using OriginPro (v.9.0) software, yielding the following best-fit values for the three parameters of the Hill equation (Equation 4): $n = 1.0 \pm 0.1$, $k = 0.10 \pm 0.02$, bias*$_{max} = -5.1 \pm 0.4$ (uncertainties are standard errors; adjusted $R^2 = 0.989$; Figure 2a). The function is asymptotic in nature; for this reason, the value of the 'bias*$_{max}$' parameter is slightly larger than the maximum observed value of $\delta^{13}C$ bias*(RM-UW6220) for those RMs with the highest Fe

Table 3.
SIMS $\delta^{13}C$ bias data for dolomite–ankerite calibration RMs measured during multiple analytical sessions

RM	Fe#[a]	$\delta^{13}C$ True[b] (‰, VPDB)	Session 13, 2014.Dec. (spot size = 6 μm)			Session 10, 2014.Sept. (spot size = 6 μm)			Session 5, 2014.Apr. (spot size = 6 μm)			Session SD2(2), 2012.July (spot size = 6 μm)			Session SD1(2), 2006.July (spot size = 6 μm)		
			$\delta^{13}C$ raw[c] (‰)	$\delta^{13}C$ bias[c,d] (‰)	$\delta^{13}C$ bias* (RM-UW6220)[e]	$\delta^{13}C$ raw[c] (‰)	$\delta^{13}C$ bias[c,d] (‰)	$\delta^{13}C$ bias* (RM-UW6220)[e]	$\delta^{13}C$ raw[c] (‰)	$\delta^{13}C$ bias[c,d] (‰)	$\delta^{13}C$ bias* (RM-UW6220)[e]	$\delta^{13}C$ raw[c] (‰)	$\delta^{13}C$ bias[c,d] (‰)	$\delta^{13}C$ bias* (RM-UW6220)[e]	$\delta^{13}C$ raw[c] (‰)	$\delta^{13}C$ bias[c,d] (‰)	$\delta^{13}C$ bias* (RM-UW6220)[e]
UW6250	0.004	1.29	-46.43	-47.78	-0.26	–	–		-45.39	-46.19	0				-36.05	-37.29	–
UW6220	0.004	0.84	-46.73	-47.53	0	-42.19	-42.99	0							-36.58	-37.39	–
UWAnk10	0.019	-1.52	-45.73	-48.61	-1.13	–	–		–	–		–	–		–	–	–
UWAnk12	0.031	3.19	-50.50	-48.61	-1.13	–	–		–	–		–	–		–	–	–
UWAnk7	0.178	-8.36	-59.17	-50.58	-3.20	–	–		–	–		–	–		–	–	–
UWAnk8	0.171	-4.15	-55.37	-50.65	-3.27	–	–		–	–		–	–		–	–	–
UWAnk9	0.286	-6.99	-57.99	-50.88	-3.51	-52.33	-45.29	-2.40	-58.64	-51.49	-5.56	–	–		–	–	–
UWAnk1	0.522	-7.38	-58.84	-51.61	-4.27	–	–		–	–		-55.16	-48.14		–	–	–
UWAnk2	0.519	-7.35	–	–		–	–		–	–		-55.31	-48.32		–	–	–
UWAnk3	0.540	-7.34	–	–		–	–		-58.57	-50.88	-4.92	–	–		–	–	–
UWAnk5opq	0.689	-4.59	-56.71	-51.90	-4.59	-54.86	-45.43	-2.55	–	–		–	–		–	–	–
UWAnk5cl	0.766	-4.57	-56.43	-51.64	-4.31	-54.57	-45.53	-2.65	–	–		–	–		–	–	–
UWAnk6a	0.789	-4.40	-56.27	-51.75	-4.42	-54.26	-45.40	-2.52	–	–		–	–		–	–	–

[a] Fe# = molar Fe/(Mg+Fe); the uncertainties that accompany this EPMA-derived parameter are tabulated in Table 1.

[b] $\delta^{13}C$ VPDB value determined by conventional phosphoric acid digestion and gas-source mass spectrometry (see Appendix A).

[c] Value corrected for instrumental drift relative to UWC-3 Reference Bracket (session-specific; see Appendix S2).

[d] Value calculated using Equations (1) and (2).
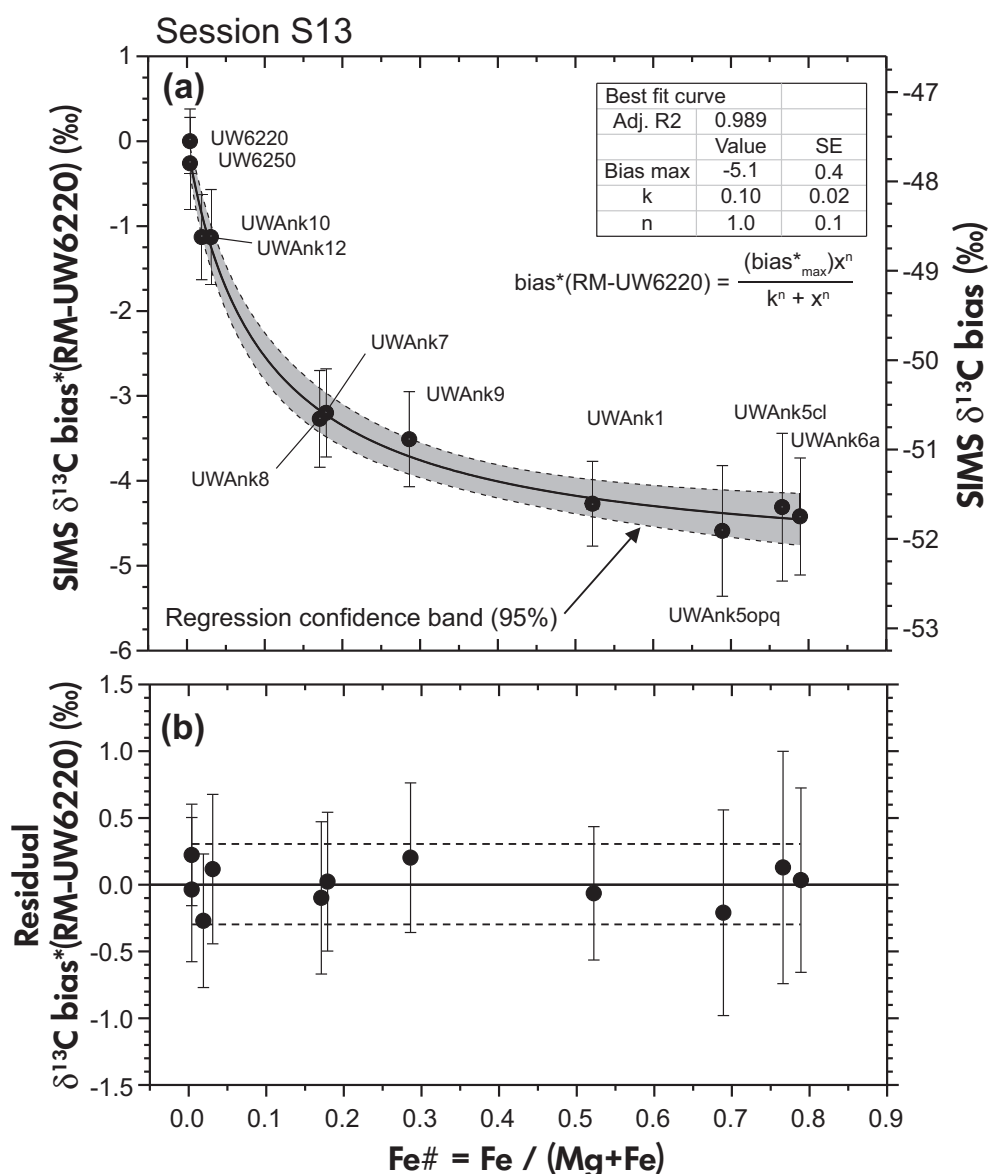
[e] Value calculated using Equation (3).

Figure 2. (a) Plot relating SIMS $\delta^{13}C$ bias (‰) to the cation composition of the dolomite–ankerite solid solution series [Fe# = Fe/(Mg+Fe), molar] for a typical calibration using a 6-μm-diameter spot size. The matrix effect can be accurately estimated using the Hill equation, which is commonly employed to describe relations of the 'concentration' vs. 'effect' type, especially in systems that behave non-linearly and reach saturation. Dark grey shading = 95% confidence band of best-fit trend. (b) Plot of the calibration residual. For all reference materials in the suite, the averaged measured value of $\delta^{13}C$ bias*(RM-UW6220) differs by less than 0.3‰ from the value predicted by the calibration (depicted by dashed lines).

numbers. For each RM in the suite, the measured average value of $\delta^{13}C$ bias*(RM-UW6220) differs by less than 0.3‰ from the value predicted by the model (Figure 2b); this is a measure of calibration accuracy relative to the CRM NBS-19 (Verkouteren and Klinedinst 2004).

Residual analysis: The residual of the Hill equation model (see section above) exhibits no significant correlation to minor variations (on the order of several mole %; Table 1) in the abundance of Ca ($R^2 = 0.21$, 95% CL) or Mn ($R^2 = 0.00$, 95% CL) in the suite of dolomite–ankerite calibration RMs. No secondary matrix corrections are thus necessary for the compositions of this study (Figure 1). It is interesting to note that despite the similar ionic radius, mass and charge of the Mn^{2+} and Fe^{2+} cations and their largely shared preference for the same

structural site in the dolomite crystal lattice (Reeder and Dollase 1989), the substitution of up to 2.61 mole % Mn in the suite of RMs (i.e., Mn/(Ca+Mg+Fe+Mn); Table 1) has no measureable effect on SIMS δ^{13}C bias*(RM-UW6220) in contrast to Fe^{2+} at similar concentrations. Treating Fe^{2+} and Mn^{2+} as a single species with regard to their apparent effect on SIMS δ^{13}C bias (i.e., (Fe+Mn)/(Fe+Mn+Mg)) neither significantly improves nor degrades the quality of the Hill model (compare Figure 2 and Appendix S4c and d). Work is currently in progress on the development of an end-member kutnohorite RM (CaMn(CO$_3$)$_2$ with the crystal structure of dolomite) to comprehensively assess the effect of Mn^{2+} substitution on both δ^{13}C and δ^{18}O bias in relation to end-member dolomite.

Constancy of the Hill fit throughout multiple sessions:
It is possible for the magnitude of SIMS bias measured from calibration RMs to vary by up to several per mil from session to session. In the first part of this study, we demonstrated that despite these session-specific differences in the magnitude of SIMS δ^{18}O bias, the overall distribution of δ^{18}O-calibration RM data points in relation to one another in plots of δ^{18}O bias*(RM-UW6220) vs. Fe# remains remarkably consistent (data from three analytical sessions, collected over a 2-year period); the values of the Hill equation shape parameters 'n' and 'k' remain unchanged, whereas the best-fit value of the 'bias*$_{max}$' parameter behaves as an analytical session-specific scaling factor (Śliwiński et al. 2015a). Based on data from three C-isotope sessions, a similar behaviour is observed for measurements of SIMS δ^{13}C bias. For example, the magnitude of δ^{13}C bias*(RM-UW6220) for RM UWAnk1 (Fe# = 0.522) varies from -2.5 to -5.5‰ (data from sessions S13, S10, S5; Table 3). Despite this, the 'best-fit' values of the Hill equation shape parameters 'n' and 'k' determined for the full suite of δ^{13}C-calibration RMs (from session S13 data; Figure 2a) can be used as constants to fit a trend to RM data points from a prior analytical session (developmental session S10, Appendix S4), allowing only the 'bias*$_{max}$' parameter to vary in response to session-specific nuances in tuning. In other words, the shape of the curve relating bias to Fe# does not change measurably, and thus corrections can be approximated if the curve is scaled according to the magnitude of bias, which in turn can be estimated with as few as two RMs (dolomite and ankerite with Fe# > 0.5). Accuracy and precision are improved with larger RM data sets.

The compositional dependence of SIMS δ^{13}C vs. δ^{18}O bias: similarity in matrix bias correction model parameters despite inverted trend behaviour as a function of increasing Fe#: In this subsection, we will discuss changes

in SIMS bias as a function of Fe# for both δ^{13}C and δ^{18}O in dolomite–ankerite in absolute terms; that is, we will discuss trends in values that are not normalised to the drift monitor material (UW6220). Normalisation is necessary for constructing working calibration curves (used for drift-monitoring purposes), but is a less direct means of visualising how the per mil difference between measured 'raw' and 'accurate' (i.e., calibrated to the CMRs VSMOW or VPDB) values of δ^{13}C and δ^{18}O evolves with increasing Fe-content in the solid solution.

In the first part of this study, we have shown that under routine operating conditions for carbonate mineral δ^{18}O analysis at WiscSIMS (IMS 1280), the magnitude of SIMS δ^{18}O bias *decreases* exponentially with increasing Fe-content in the dolomite–ankerite solid solution (magnitude of change: ~ 10‰; see Figure 2a in Śliwiński et al. 2015a (data from session S12)); that is, the bias is *greatest* for end-member dolomite (-13.63‰) and *smallest* for the most Fe-rich ankerite (-3.26‰ for Fe# of 0.789). The compositional dependence of SIMS δ^{18}O bias was modelled using a Hill equation, with the curve shape parameters 'n' and 'k' empirically constrained as follows: n = 1.2 ± 0.1, k = 0.10 ± 0.01 (uncertainties in both cases are 1 standard error). In contrast, the magnitude of SIMS δ^{13}C bias *increased* exponentially with increasing Fe-content (by -4‰; i.e., values became more negative and hence move further away from the 'true' VPDB values; see Figure 2a herein, session S13 data); that is, the bias is *smallest* for end-member dolomite (-47.53‰) and *largest* for the most Fe-rich ankerite (-51.75‰ for Fe# = 0.789). To state the results differently, what we observed is that with increasing Fe# in the dolomite–ankerite solid solution, the measured ^{18}O/^{16}O ratios increased and the ^{13}C/^{12}C ratios decreased relative to the ratios that would be measured in the absence of matrix effects. That is, the matrix effect fractionates O-isotopes and C-isotopes in opposite directions. Despite this, it is interesting to note that the curve shape parameters of the Hill equation used to model the compositional dependence of SIMS δ^{13}C bias (n = 1.0 ± 0.1, k = 0.10 ± 0.02) are within fitting error of those of the δ^{18}O bias model (Śliwiński et al. 2015b, Śliwiński et al. 2015a). We stress that at the present time, however, these are empirical observations for data from the IMS 1280 instrument and tuning protocols at the WiscSIMS laboratory.

Conclusions

In this two-part study, we have demonstrated the highly systematic, non-linear, nature of SIMS instrumental bias (or instrumental mass fractionation) on measurements of δ^{13}C and δ^{18}O from carbonate minerals of the dolomite–ankerite solid solution series. We focused specifically on the component of total bias that is a function of variable chemical

composition (i.e. the sample 'matrix effect'), as for a given configuration of the SIMS (ion microprobe) the contribution of instrumental parameters to the total bias observed in calibration RM measurements can be held largely constant (minor variations can be accounted for by drift-monitoring). A suite of calibration RMs was developed (thirteen each for $\delta^{13}C$ and $\delta^{18}O$), ranging in composition from end-member dolomite to ankerite with extensive Fe^{2+} substitution (Fe# = 0.789, where Fe# = Fe/(Mg+Fe), expressed on a molar basis).

With the routine configuration and tuning conditions of the CAMECA IMS 1280 for carbonate mineral analysis at WiscSIMS, the $\delta^{13}C$ bias increased exponentially by -2.5 to -5.5‰ (session-specific) with increasing Fe# in dolomite–ankerite. Bias was accurately modelled using the Hill equation, and a consideration of the calibration residual indicates that the uncertainty associated with the sample matrix bias correction (i.e., difference in Fe#) for the typical 6-μm-diameter spot size measurements is on the order of ± 0.3‰ (2s, standard deviations) in relation to the certified reference material NBS-19. The spot-to-spot repeatability (precision) assigned to individual sample analyses, based on replicate measurements (n = 8) of the drift monitor material that 'brackets' each set of ten sample measurements, was ± 0.6–1.2‰ (2s). Adding these terms in quadrature indicates that the accuracy of these analyses was ~ ± 1.0–1.5‰ (2s) relative to NBS-19 if there are no additional sources of error.

Acknowledgements

References

Allison C.E., Francey R.J. and Meijer H.A.J. (1995)
Reference and intercomparison materials for stable isotopes of light elements. IAEA-TECDOC, 825, 155–162.

Chang L.L.Y., Howie R.A. and Zussman J. (1996)
Rock forming minerals, Volume 5B: Non-silicates: Sulphates, carbonates, phosphates and halides. Longman (Harlow, Essex), 383pp.

Craig H. (1957)
Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide. Geochimica et Cosmochimica Acta, 12, 133–149.

Eiler J.M., Graham C. and Valley J.W. (1997)
SIMS analysis of oxygen isotopes: Matrix effects in complex minerals and glasses. Chemical Geology, 138, 221–244.

Fitzsimons I.C.W., Harte B. and Clark R.M. (2000)
SIMS stable isotope measurement: Counting statistics and analytical precision. Mineralogical Magazine, 64, 59–83.

Goutelle S., Maurin M., Rougier F., Barbaut X., Bourguignon L., Ducher M. and Maire P. (2008)
The Hill equation: A review of its capabilities in pharmacological modelling. Fundamental and Clinical Pharmacology, 22, 633–648.

Hervig R.L., Williams P., Thomas R.M., Schauer S.N. and Steele I.M. (1992)
Microanalysis of oxygen isotopes in insulators by secondary ion mass spectrometry. International Journal of Mass Spectrometry and Ion Process, 120, 45–63.

Huberty J.M., Kita N.T., Kozdon R., Heck P.R., Fournelle J.H., Spicuzza M.J., Xu H. and Valley J.W. (2010)
Crystal orientation effects on instrumental bias of $\delta^{18}O$ in magnetite by SIMS. Chemical Geology, 276, 269–283.

Kita N.T., Ushikubo T., Fu B. and Valley J.W. (2009)
High precision SIMS oxygen isotope analysis and the effect of sample topography. Chemical Geology, 264, 43–57.

McCrea J.M. (1950)
On the isotopic chemistry of carbonates and a paleotemperature scale. Journal of Chemical Physics, 18, 849–857.

Reeder R.J. and Dollase W.A. (1989)
Structural variation in the dolomite–ankerite solid-solution series: An X-ray, Mössbauer and TEM study. American Mineralogist, 74, 1159–1167.

Riciputi L.R., Paterson B.A. and Ripperdan R.L. (1998)
Measurement of light stable isotope ratios by SIMS: Matrix effects for oxygen, carbon and sulfur isotopes in minerals. International Journal of Mass Spectrometry, 178, 81–112.

Śliwiński M.G., Kitajima K., Kozdon R., Spicuzza M.J., Fournelle J.H., Denny A. and Valley J.W. (2015a)
Secondary ion mass spectrometry bias on isotope ratios in dolomite–ankerite, Part I: $\delta^{18}O$ matrix effects. Geostandards and Geoanalytical Research. doi:10.1111/j.1751-908X.2015.00364.x.

Śliwiński M.G., Kozdon R., Kitajima K., Denny A., Spicuzza M.J. and Valley J.W. (2015b)
In-situ, micron-scale $\delta^{13}C$ and $\delta^{18}O$ analyses (by SIMS) of chemo-isotopically zoned carbonate cements of diagenetic origin – a case study on the implications for the thermal and burial history of the Eau Claire Fm., Illinois Basin (USA). American Association of Petroleum Geologists Annual Convention and Exhibition, Denver, Colorado, 31 May–03 June.

references

Valley J.W. and Kita N.T. (2009)
In situ oxygen isotope geochemistry by ion microprobe. In: Fayek M. (ed.), Secondary ion mass spectrometry in the Earth sciences. Mineralogical Association of Canada Short Course, 41, 19–63.

Verkouteren R.M. and Klinedinst D.B. (2004)
Value assignment and uncertainty estimation of selected light stable isotope reference materials: RMs 8543-8545, RMs 8562-8564, and RM 8566. NIST Special Publication, 260–149, 1–56.

VIM (2008)
International vocabulary of metrology – Basic and general concepts and associated terms (VIM). Joint Committee for Guides in Metrology, Bureau International des Poids et Mesures (Sévres, France), 200:2008, 90pp.

Supporting information

The following supporting information may be found in the online version of this article:

Appendix S1. Supplementary electron probe microanalysis data table.

Appendix S2. Complete SIMS data table (6-μm spot-size sessions).

Appendix S3. Procedure for correcting a sample measurement for SIMS $\delta^{13}C$ bias and the associated propagation of errors.

Appendix S4. (a) Calibration plot relating SIMS $\delta^{13}C$ bias*(STD-UW6220) to increasing Fe-content along the dolomite–ankerite solid solution. (b) Plot of the calibration residual. (c) Calibration reference material data and (d) model residual for session S13 with the inclusion of Mn in the matrix model. (e) Explanatory captions for Appendices S4a–d.

Appendix S5. Reproducibility of the assessment process of potential reference materials.

This material is available as part of the online article from: http://onlinelibrary.wiley.com/doi/10.1111/j.1751-908X.2015.00380.x/abstract (This link will take you to the article abstract).

Appendix A.
Results of conventional phosphoric acid digestion and gas-source mass spectrometric analyses on the suite of UW dolomite−ankerite reference materials

WiscSIMS RM i.d.	Analysis i.d.	δ¹³C (‰) (VPDB)
UW6250	C4-246-10	1.29
	C4-246-11	1.30
	C4-246-14	1.28
	Avg. and 2s	**1.29 ± 0.02**
UW6220	C4-245-4	0.84
	C4-245-5	0.83
	C4-245-6	0.85
	C4-246-9	0.83
	C4-246-13	0.85
	Avg. and 2s	**0.84 ± 0.02**
UWAnk10	C4-245-21	-1.51
	C4-245-22	-1.52
	C4-245-23	-1.53
	Avg. and 2s	**-1.52 ± 0.02**
UWAnk12	C4-240-5	3.18
	C4-240-6	3.19
	C4-240-7	3.19
	Avg. and 2s	**3.19 ± 0.01**
UWAnk7	C4-245-2	-8.36
	C4-245-1	-8.36
	C4-245-19	-8.35
	Avg. and 2s	**-8.36 ± 0.01**
UWAnk8	C4-245-14	-4.13
	C4-246-1	-4.17
	C4-246-2	-4.16
	Avg. and 2s	**-4.15 ± 0.04**
UWAnk9	C4-245-9	-6.98
	C4-245-10	-6.99
	C4-245-11	-6.99
	Avg. and 2s	**-6.99 ± 0.01**
UWAnk1	C4-234-2	-7.37
	C4-234-9	-7.39
	C4-234-10	-7.37
	Avg. and 2s	**-7.38 ± 0.02**
UWAnk2	C4-234-6	-7.34
	C4-234-7	-7.34
	C4-234-11	-7.36
	Avg. and 2s	**-7.35 ± 0.02**
UWAnk3	C4-327-6	-7.34
	C4-237-7	-7.33
	C4-327-8	-7.35
	Avg. and 2s	**-7.34 ± 0.02**
UWAnk5opq	C4-240-12	-4.59
	C4-240-13	-4.59
	C4-240-14	-4.59
	Avg. and 2s	**-4.59 ± 0.00**
UWAnk5 cl	C4-240-9	-4.57
	C4-240-10	-4.56
	C4-240-11	-4.58
	Avg. and 2s	**-4.57 ± 0.02**
UWAnk6a	C4-240-5	-4.40
	C4-240-7	-4.40
	C4-246-3	-4.40
	Avg. and 2s	**-4.40 ± 0.00**