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Article

# New Standards and Online Matrix Effect Calibration Method for SIMS Dolomite Carbon-isotope Analysis

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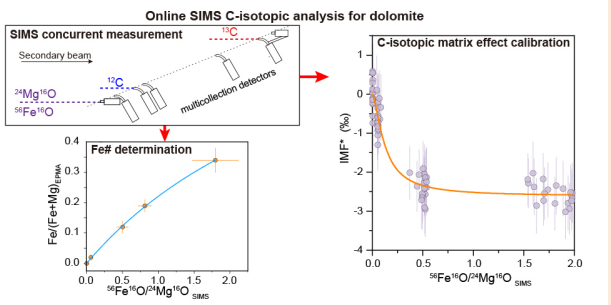
**ABSTRACT:** Dolomite [$CaMg(CO_3)_2$] is a major carbonate mineral playing a critical role in various geological processes. Its carbon isotopic composition ($\delta^{13}C$) serves as an irreplaceable tracer for understanding Earth's history and the deep-time global carbon cycle. Secondary ion mass spectrometry (SIMS) is one of the most dominant techniques for dolomite C- isotopic analysis. However, the widespread application is hindered by a shortage of high-quality dolomite standards. Furthermore, the classical off-line procedure, which is both inaccurate and inefficient due to its need for extra electron probe microanalyzer (EPMA) chemical compositions to calibrate the instrumental mass fractionation (IMF), poses a practical limitation. This study reports three new dolomite C-isotopic microanalysis standards (1001, 1026 and 1055) with Fe# values [molar Fe/(Mg + Fe)] varying from 0.02 to 0.35. By the concurrent SIMS measurement of $^{13}C^{-12}C^{-56}Fe^{16}O^{-24}Mg^{16}O$, an accurate and rapid online matrix effect calibration method for dolomite C-isotope analysis was developed. The overall uncertainty for individual sample analyses was estimated to be ±0.9‰ (2SD), derived by propagating the measurement precision and the calibration residuals in quadrature. The new method concurrently determines $\delta^{13}C$ and the $^{56}Fe^{16}O/^{24}Mg^{16}O$ ratio (a proxy for Fe#) in a single SIMS analysis, enabling accurate matrix-effect calibration that eliminates biases caused by spatial mismatch between separate EPMA and SIMS analytical domains. The advancement in accuracy and efficiency, as demonstrated by SIMS carbon isotope analysis of dolomite, has the potential to significantly enhance the fidelity of reconstructing ancient environments, establish more robust boundaries for carbon cycling, and refine the interpretation of geological records.




## INTRODUCTION

Dolomite, a carbonate composed of calcium magnesium carbonate, plays a critical role in various geological processes and has significant implications for understanding Earth's history and the global carbon cycle. Studying the carbon isotopic compositions of dolomite can provide valuable insights into paleoenvironmental conditions,[1] diagenetic processes,[2] and the deposit formation.[3] Carbon isotopes are widely used in geochemistry to trace the sources and pathways of carbon cycling in the Earth's surface and subsurface environments.[4] Secondary ion mass spectrometry (SIMS) is a powerful in situ analytical technique, offering remarkable spatial resolution at the micrometer scale and high precision at the sub-per mil level (δ-notation, ‰). However, biases in the measured isotope ratios introduced by the instrumental mass fractionation (IMF) are a major limitation of SIMS isotopic microanalysis.[5] Matrix-matched standard is indispensable for calibrating the IMF. For minerals with variable compositions, such as olivine,[6] garnet,[7] monazite,[8] and dolomite,[9] a series of standards covering different chemical compositions are

needed to characterize how the IMF varies with chemistry. Similarly, achieving accurate SIMS $\delta^{13}C$ measurements in dolomite requires the use of a sufficient number of standards to calibrate the IMF. Dolomite commonly forms solid-solution series between dolomite [$CaMg(CO_3)_2$] and ankerite [$CaFe(CO_3)_2$] end-members, via substitution of magnesium by iron. Sliwinski et al. developed a suite of standards and studied calibration methods for SIMS carbon isotope analysis of the dolomite–ankerite solid-solution series. Their work demonstrated that the IMF varies by up to 5.5‰ with changes in Fe# [molar Fe# = Fe/(Fe+Mg)].[9] Therefore, obtaining accurate SIMS $\delta^{13}C$ measurements of dolomite requires the use of matrix-matched standards to calibrate this composition-dependent IMF. A series of standards spanning a range of Fe# values is necessary to establish a reliable calibration curve. While previous studies have established standards for dolomite carbon isotopes, the available set of well-characterized, homogeneous standards covering a broad Fe# range remains limited. This study aims to develop new dolomite C-isotope standards, thereby complementing and expanding the existing reference materials.

The conventional matrix effect calibration method is an "off-line" procedure, which involves performing separate measurements of chemical compositions using an electron probe microanalyzer (EPMA) and carbon isotopic compositions using SIMS. This off-line method is time-consuming and inherently inaccurate due to the mismatch between EPMA and SIMS analytical domains. This spatial mismatch can lead to significant errors, particularly for compositionally zoned or heterogeneous minerals where the chemical composition varies at the micrometer scale. Consequently, the off-line method is inadequately suited for isotopic analysis of compositionally heterogeneous minerals. An ideal solution is to acquire both isotopic and compositional information from the exact same micro-volume during a single analysis.

Acquiring isotopic and matrix-relevant chemical compositions concurrently is an effective strategy to address the current challenges. Recently, based on new developed dolomite O-isotopic standards (dolomite 1001, 1006, 1026, 1055, and CTD-4), we established an accurate and efficient SIMS oxygen isotope online matrix effect calibration method for dolomite, which allows the accurate and paired determination of dolomite oxygen isotopes and Fe# values using SIMS.[10] Building upon our development of an online matrix-effect calibration method for SIMS oxygen isotope analysis in dolomite,[10] this study aims to extend this strategy to carbon isotopes. Carbon isotope microanalysis by SIMS presents distinct technical challenges, including lower secondary ion yields compared to oxygen and different potential isobaric interferences. Therefore, the objectives of this study are to develop and characterize new dolomite carbon isotope standards covering a range of Fe# values, and establish and validate an online calibration protocol specifically optimized for SIMS carbon isotope analysis. By concurrent measurement of $^{13}C^{-}$–$^{12}C^{-}$–$^{56}Fe^{16}O^{-}$–$^{24}Mg^{16}O^{-}$ from the same spot using SIMS, we can apply online matrix effect calibration for the carbon isotope analysis of dolomite, thereby overcoming the fundamental limitation of the offline procedure. This approach enables obtaining accurate and paired SIMS Fe# and $\delta^{13}C$ values in dolomite. The improved accuracy by avoiding biases caused by spatial mismatches in chemical composition and isotope analysis regions，and efficiency by using a single instrument enhance the capabilities of carbon isotope geochemistry and push its practical applications forward.

## EXPERIMENTAL

**Sample preparation.** Five dolomite O-isotopic standards (1001, 1006, 1026, 1055 and CTD-4) developed in our previous study,[10] as well as one dolomite C-isotopic standard DOL-8 loan from the State Key Laboratory of Geological Processes and Mineral Resources (GPMR), China University of Geosciences in Wuhan,[11] were further used to SIMS C-isotopic analysis. The 1001, 1026, 1006, 1055, and DOL-8 dolomites had average Fe# values of 0.02, 0.12, 0.19, 0.34, and 0, respectively.[10,11] These grains were placed within an epoxy mount with a diameter of 25 mm and positioned at a distance of 15 mm from the mount's central point to minimize the potential sample location effect.[12] In order to monitor analytical precision and instrumental drift, grains of the Oka calcite[13] and UWC-3 calcite,[14] standards were placed in close proximity to the center of each mount.

**SIMS Analysis.** Carbon isotopic homogeneity tests and concurrent $^{13}C^{-}$–$^{12}C^{-}$–$^{56}Fe^{16}O^{-}$–$^{24}Mg^{16}O^{-}$ measurements were conducted at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS) using a CAMECA IMS-1280 SIMS (CAMECA, Gennevilliers, France). A ~2 nA primary $Cs^{+}$ beam with a total impact energy of 20 keV was used to bombard the sample grains. The primary beam was focused in Gaussian mode with spot size of ~20 μm (10 μm beam size and 10 μm raster). To compensate for sample charging effects, an electron gun was employed during the analysis. The drift monitor materials were analysed every five sample spots. A high mass resolving power (MRP > 5000) was used, which far exceeds the ~2900 required to resolve the $^{12}C^{1}H^{+}$ interference from $^{13}C^{+}$. At this setting, the $^{56}Fe^{16}O^{+}$ peak (mass 55.9349) is fully resolved from nearby species like $^{40}Ca^{16}O^{+}$ (mass 55.9573), and $^{24}Mg^{16}O^{+}$ (mass 39.9795) from the potential $^{24}C_2{}^{16}O^{+}$ interference (mass ~39.995, requiring MRP ~2700) is also resolved.

The $\delta^{13}C$ homogeneity test of potential dolomite standards involved the utilization of a 7 × 7 mm field aperture, an entrance slit of approximately 61μm, and an energy slit set at 45 eV. Each analysis comprised 40 cycles with a counting time of 4 s per cycle.

The Faraday cup (L1, $10^{12}$ Ω) was used to detect the $^{12}C$ signals and electron multipliers (EM, H2) used for $^{13}C$ signals because of the low signal intensity. The intensity of the $^{12}C$ signal ranged from $1.4 \times 10^7$ to $1.8 \times 10^7$ counts per second (cps), while the $^{13}C$ signal exhibited an intensity ranging from $1.7 \times 10^5$ cps to $2.1 \times 10^5$ cps.

For the concurrent measurement of $^{13}C$–$^{12}C$–$^{56}Fe^{16}O$–$^{24}Mg^{16}O$, a field aperture 5 × 5 mm was utilized, along with an entrance slit approximately 61 μm and an energy slit of 45 eV. Each analysis comprised eight cycles. The determination of $^{12}C$ and $^{13}C$ carried out simultaneously using a Faraday cup (FC, L1, $10^{12}$Ω) and an electron multiplier (EM, H2), respectively, with a waiting time of 6 s and a counting time of 40 s in the multi-collector mode (Fig. 1). Subsequently, the determination of $^{24}Mg^{16}O$ and $^{56}Fe^{16}O$ was performed in sequence using a Faraday cup (FC, L'2, $10^{10}$ Ω) in the peak jumping mode, with a waiting time of 2 s and a counting time of 1 s. The intensity of the $^{13}C$ signal ranged from approximately $1.4 \times 10^5$ to $1.8 \times 10^5$ cps. For the $^{24}Mg^{16}O$ and $^{56}Fe^{16}O$ signals, the intensities ranged from $1.7 \times 10^7$ to $2.8 \times 10^7$ cps and $9.0 \times 10^4$ to $3.5 \times 10^7$ cps, respectively. The $^{56}Fe^{16}O/^{24}Mg^{16}O$ ratio varied between 0.00 and 1.98, with an internal precision of 0.04–1.31% (2× relative standard error, 2RSE) for a single-spot analysis.

The measured $^{13}C/^{12}C$ ratios were normalized to Vienna Pee-Dee Belemnite (VPDB) compositions ($^{13}C/^{12}C_{VPDB} = 0.0112372$) [15] in $\delta^{13}C$ per mil notation, and then calculated for the IMF as follows:

$$\delta^{13}C_m\ (‰) = 1000 \times \left(\frac{(^{13}C/^{12}C)_m}{0.0112372} - 1\right) \quad (1)$$

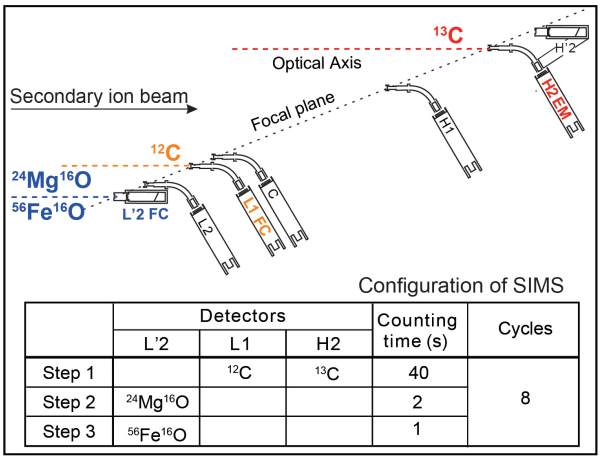
$$IMF\ (‰) = 1000 \times \left(\frac{1+(\delta^{13}C_m/1000)}{1+(\delta^{13}C_{IRMS}/1000)} - 1\right) \quad (2)$$

where $\delta^{13}C_m$ represents the SIMS-measured value, and $\delta^{13}C_{IRMS}$ represents the value determined by IRMS.

The IMF of each standard was then normalized to that of the end-member standard DOL-8 to obtain a relative instrumental mass fractionation, denoted as $IMF^*_{(standard\text{-}DOL\text{-}8)}$ as follows:

$$IMF^*_{(standard-DOL-8)}(‰) = 1000 \times \left(\frac{1+(IMF_{standard}/1000)}{1+(IMF_{DOL-8}/1000)} - 1\right) \quad (3)$$

**IRMS analysis.** The dolomite samples were subjected to bulk carbon isotope analysis at the Laboratory for Stable Isotope Geochemistry, IGGCAS. The analysis was conducted using a ThermoFisher 253 (Thermo Fisher Scientific Inc., Waltham, Massachusetts, U.S.) mass spectrometer equipped with a GasBench II system. Approximately 300 μg of the sample powder was reacted with 100% $H_3PO_4$ at a temperature of 70 °C within a 12 mL vial filled with helium. The resulting $CO_2$ gas was then introduced into the mass spectrometer for measurement of the isotopic composition. The reproducibility of the measurements, as determined by analyzing the national carbonate certified reference material GBW04405 (National Institute of Metrology, China), was ±0.15‰ (2 × standard deviation, 2SD, n = 19) for $\delta^{13}C$.




| | Detectors | | | Counting time (s) | Cycles |
|---|---|---|---|---|---|
| | L'2 | L1 | H2 | | |
| Step 1 | | $^{12}C$ | $^{13}C$ | 40 | 8 |
| Step 2 | $^{24}Mg^{16}O$ | | | 2 | |
| Step 3 | $^{56}Fe^{16}O$ | | | 1 | |

**Fig. 1** Schematic figure summarizing the SIMS instrumental settings during concurrent $^{13}C$–$^{12}C$–$^{56}Fe^{16}O$–$^{24}Mg^{16}O$ analysis (modified from Liu *et al.*, 2015).[17]

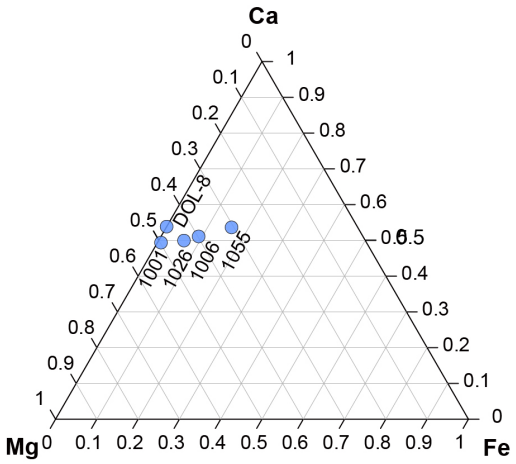



**Fig. 2** Ca–Mg–Fe diagram of the dolomite standards compositions.

The comprehensive SIMS and IRMS data for these samples can be found in the Supporting Information (Table S1-S3). Summarized information is provided in Tables 1 and 2.

## RESULTS AND DISCUSSION

**New dolomite C-isotope reference material.** Three dolomite samples (1001, 1026, and 1055) were identified as suitable candidates for use as SIMS dolomite C-isotope standards. These newly developed dolomite carbon isotope standards are available

**Table 1.** Summary of carbon isotope homogeneity in dolomite samples

| Sample number | Locality | EPMA[a] | | SIMS | | IRMS | | |
|---|---|---|---|---|---|---|---|---|
| | | Fe#= Fe/(Fe+Mg) | 2SD | 2SD of $\delta^{13}C$ homogeneity | N of analyses | Average $\delta^{13}C_{VPDB}$ (‰) | 2SD | N |
| **1001** | Cantera Azkarate, Azkarate quarry, Eugui, Esteríbar, Navarre, Spain | 0.02 | 0.01 | 0.98 | 68 | 2.66 | 0.06 | 6 |
| **1026** | Grigorievskiy quarry, Middle Urals, Russia | 0.12 | 0.02 | 0.71 | 66 | −5.74 | 0.03 | 6 |
| **1006** | Burguillos del Cerro, Badajoz, Spain | 0.19 | 0.02 | 1.40 | 65 | −8.26 | 0.04 | 6 |
| **J1055** | Stolzembourg, Putscheid commune, Vianden, Diekirch District, Luxembourg | 0.34 | 0.04 | 0.52 | 68 | −8.54 | 0.07 | 5 |

[a] EPMA data was reported in Xu *et al.* (2022) [10]

**Table 2.** Summarized information of analyzed dolomites

| Sample ID | Fe# (online) | 2SD | Average $\delta^{13}C_m$ (SIMS, ‰) | n | 2SD ‰ | Average IMF*(standard-DOL-8) | Average $\delta^{13}C_{calibrated}$ (online, ‰) | 2SD ‰ |
|---|---|---|---|---|---|---|---|---|
| **DOL-8** | 0.00 | 0.00 | 15.63 | 19 | 0.71 | 0.00 | −1.08 | 0.69 |
| **1001** | 0.02 | 0.00 | 18.82 | 19 | 0.71 | −0.61 | 2.63 | 0.76 |
| **1026** | 0.12 | 0.02 | 8.50 | 20 | 0.60 | −2.38 | −5.78 | 0.58 |
| **1055** | 0.34 | 0.04 | 5.48 | 20 | 0.54 | −2.55 | −8.51 | 0.53 |

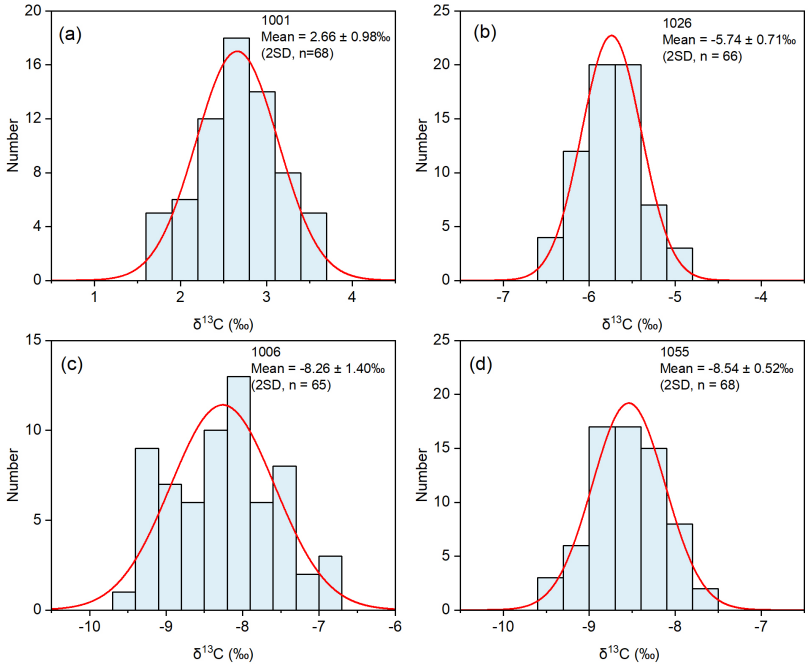



**Fig. 3** Histograms of the average measured $\delta^{13}C$ value normalized to the IRMS value for 1001 (a), 1026 (b), 1006 (c), and 1055 (d) dolomites.

to share with request. The chemical composition of these samples ranged from almost pure dolomite end-member $CaMg(CO_3)_2$ towards ankerite $Ca(Fe^{2+},Mg)(CO_3)_2$ (Fig. 2), with average Fe# values of 0.02±0.01 (dolomite 1001), 0.12±0.02 (dolomite 1026) and 0.34±0.04 (dolomite 1055), respectively (Table 1). All the SIMS-measured $\delta^{13}C$ results for the three samples exhibited a well-distributed Gaussian pattern, with 2SD values of 0.98‰ (n = 68; 1001), 0.71‰ (n = 66; 1026), and 0.52‰ (n = 68; 1055) (Fig. 3), confirming their suitability as dolomite C-isotope standards. Sample 1006 exhibits relatively large variability in its measured $\delta^{13}C$ values (2SD = 1.40%, n=65), indicating slight heterogeneity. The relatively large variation in $\delta^{18}O$ values is also observed in dolomite 1006 after online calibration.[10] The recommended $\delta^{13}C_{VPDB}$ values determined by IRMS are 2.66±0.16‰ (n =6, 2SD incorporate the 2SD of running standard GBW04405; 1001), −5.74±0.15‰ (n = 6, 2SD; 1026), −8.54±0.15‰ (n = 5; 1055), and −8.26±0.16‰ (n = 6, 2SD; 1006) (Table 2).

**Fe# value determination.** In this study, a good correlation was observed between the $^{56}Fe^{16}O/^{24}Mg^{16}O$ ratios acquired through SIMS and the EPMA Fe# values (Fig. 4). This relationship could be empirically fitted using either an exponential regression line

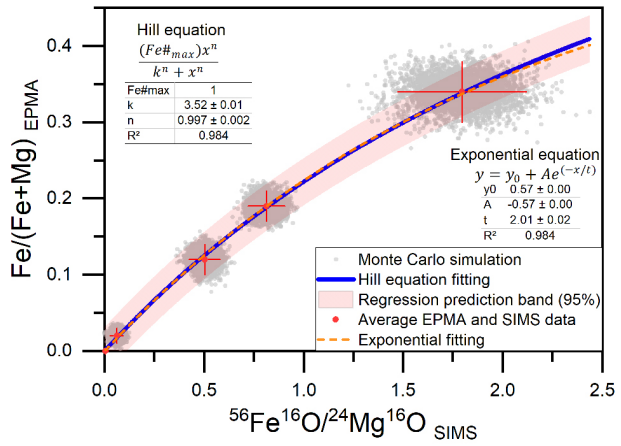



**Fig. 4** Correlation between average Fe# values determined by EPMA and average $^{56}Fe^{16}O/^{24}Mg^{16}O$ ratios of the new dolomite standards determined by SIMS, based on Monte Carlo simulation.

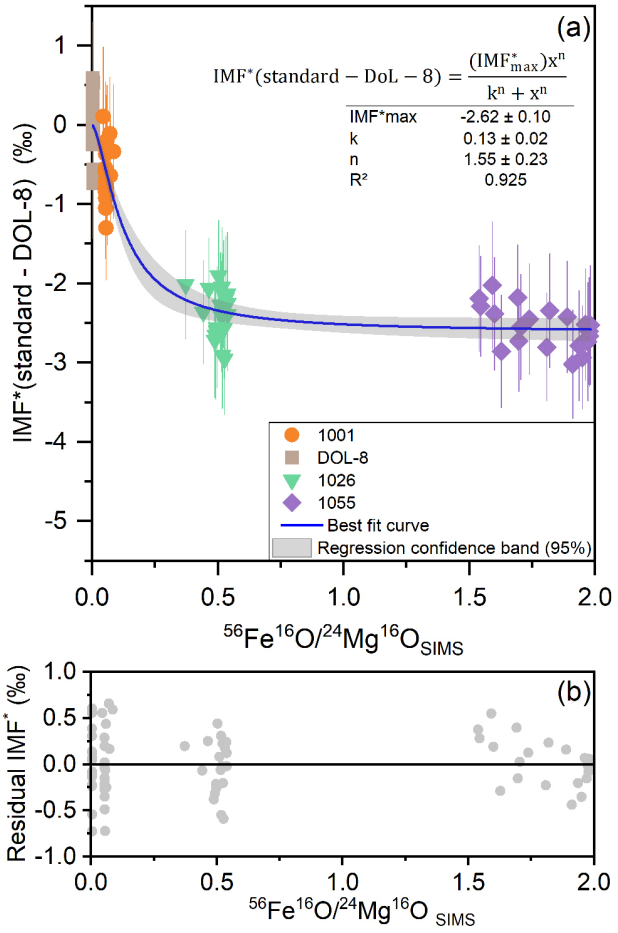



**Fig. 5** (a) Correlation between IMF*(standard to DOL-8) (‰) and $^{56}Fe^{16}O/^{24}Mg^{16}O$ determined by SIMS with the best-fit curve using a Hill equations and data of dolomite DOL-8, 1001, 1026 and 1055. (b) Plot of the residual of IMF* for the Hill equation fittings. Error bars are $2\sigma = \sqrt{2SE^2 + 2SD_{Oka}{}^2}$, 2SE is 2 × standard error of single spot analysis, $2SD_{Oka}$ is 2 × standard deviation of drift monitor material Oka.

described by the equation $y = -0.63e^{(-x/2.30)} + 0.63$ ($R^2 = 0.984$) (where 'y' denotes the Fe# value obtained via EPMA, and 'x' represents the $^{56}Fe^{16}O/^{24}Mg^{16}O$ ratio determined by SIMS) or Hill equation:

$$y = \frac{(Fe\#_{max})x^n}{k^n + x^n} \quad (4)$$

where 'x' is the $^{56}Fe^{16}O/^{24}Mg^{16}O$ ratios obtained by SIMS. '$Fe\#_{max}$', 'k' and 'n' are three parameters of this Hill equation. The $Fe\#_{EPMA}$–$^{56}Fe^{16}O/^{24}Mg^{16}O_{SIMS}$ data of new standards were fitted to the Hill equation (Fig. 4), yielding the parameters n = 1.00 ± 0.002, k = 3.52 ± 0.01 (standard errors; adjusted $R^2 = 0.984$). $Fe\#_{max}$ is fixed to 1 considering the physical limits of solid solutions. Hence, the Fe# value of individual analytical spot can be determined by utilizing this equation and the SIMS $^{56}Fe^{16}O/^{24}Mg^{16}O$ ratio.

Monte Carlo simulation was employed to fit the function considering both errors of the $^{56}Fe^{16}O/^{24}Mg^{16}O$ ratios acquired through SIMS and the EPMA Fe# values. In this simulation, randomly paired x and y (usually N = 3,000) of each sample were chosen from normal distribution. For five standards (Fig. 4), a total of 15,000 random numerical points are generated and modeled. Related fitting functions, parameters, as well as errors are shown in Fig. 4. Similar fitting results between an exponential and Hill equations within the low Fe# range are observed (Fig. 4). Although the empirical relationships between component concentration and measurement effect has been extensively descripted by the Hill equation,[16] we stress that calibration curves obtained in the low Fe# range should not be used in the high Fe# range. More standards with higher Fe# values must be developed to obtain more accurate calibration curves.

**Online matrix effect calibration.** Conventional off-line matrix effect calibration method for SIMS dolomite C-isotope analysis is based on the relationship between the IMF* and EPMA Fe# values.[9] In our current dolomite SIMS concurrent $^{13}C$–$^{12}C$–$^{56}Fe^{16}O$–$^{24}Mg^{16}O$ measurements, the good correlation between EPMA Fe# value and SIMS $^{56}Fe^{16}O/^{24}Mg^{16}O$ ratio suggests that the latter can substitute the EPMA Fe# for matrix effect calibration. This is further supported by the good non-linear correlation between the IMF* and $^{56}Fe^{16}O/^{24}Mg^{16}O$ ratios, as shown in Fig. 5, which can be fitted by Hill equation:

$$IMF^*_{(standard-DOL-8)}(‰) = \frac{(IMF^*_{max})x^n}{k^n + x^n} \quad (5)$$

With $R^2 = 0.925$, where 'x' represents the $^{56}Fe^{16}O/^{24}Mg^{16}O$ ratio determined by SIMS with concurrently carbon isotope analysis. '$IMF^*_{max}$', 'k' and 'n' are three parameters of this Hill equation. The IMF*–$^{56}Fe^{16}O/^{24}Mg^{16}O$ data of dolomite DOL-8, 1001, 1026 and 1055 were fitted to the Hill equation (Fig. 5) using OriginPro (2018) software, yielding the parameters n = 1.55 ± 0.23, k = 0.31 ± 0.02, $IMF^*_{max}$ = -0.26 ± 0.10 (standard errors; adjusted $R^2$ =

0.925). Table 2 presents the average $\delta^{13}C$ and Fe# values acquired through the SIMS online method. Sliwinski *et al.* also applied the Hill equation to describe the variation of IMF with Fe# in the dolomite–ankerite solid-solution series.[9] This equation is widely applicable for characterizing empirical relationships of the "component concentration versus measured effect" type, particularly in systems that exhibit nonlinear behavior and approach saturation.

A remarkable variation in IMF* was observed at the lower Fe# values (<0.2) in dolomite, whereas the variation became relatively modest when Fe# values exceeded 0.2 (Fig. 5). The dolomite standards investigated in this study cover an Fe# range from 0.01 to 0.35, thereby encompassing the region where IMF* shows significant variability. The present calibration is applicable to dolomite–ankerite solid solutions with Fe# ≤0.35 analyzed under identical instrumental conditions. We stress that calibration curves derived from the low Fe# range should not be extrapolated to the high Fe# range. Compared to oxygen isotopes (variation up to ~5.5‰),[10] the matrix effect for carbon isotopes in dolomite is less pronounced, varying by less than ~3‰ (Fig. 5).

The online method exhibited a single-spot analytical precision of ±0.61‰ (2SD) for $\delta^{13}C$ measurements, as determined by the spot-to-spot repeatability of a drift monitor material (Oka). Taking into account the maximum calibration residual, the estimated uncertainty arising from the calibration was approximately ±0.66‰ (2SD). The overall analytical uncertainty ±0.9‰ (2SD) was estimated by combining the internal precision from Oka repeatability (±0.61‰, 2SD) and the calibration residual uncertainty from the residuals of the Hill equation fit (±0.66‰, 2SD) in quadrature. Further online calibration experiments will provide practical support for investigating the matrix effect, as similar nonlinear relationships between chemical composition and instrumental bias have been observed in minerals exhibiting solid-solution behavior, such as olivine,[6] garnet[7] and monazite.[8]

**Merits, limitations and implications.** The conventional off-line procedure might introduce discrepancies between the EPMA and SIMS analytical domains, including differences in spot size, shape, and analysis depth. These discrepancies could result in noncoincidence in Fe# values between the two methods and consequently lead to a bias in the calibration of the matrix effect. The principal advantage of the online method is its ability to acquire both $\delta^{13}C$ and Fe# in situ and concurrently from the identical sputtered volume. This ensures perfect spatial coincidence for the data used in calibration, effectively eliminating a major source of bias in the analysis of compositionally variable minerals, bypassing any potential noncoincidence between the SIMS and EPMA analytical domains. Although EPMA remains an essential tool for initial mineral identification and to confirm that a sample's composition falls within the range of the calibration standards, the online method eliminates the need for additional EPMA mineral compositions for calibration. As a result, the online method proves to be a time- and cost-effective experimental approach. Collectively, an online method can greatly enhance the accuracy and efficiency of the analysis.

This study did not explore the effects of different beam sizes on the determinations of Fe# and $\delta^{13}C_{VPDB}$ values by SIMS. Smaller spot sizes may decrease the precision of the measurements. It would be necessary to verify the impact of different spot sizes in future research. We emphasize that the equations for calibrating the Fe# values and C-isotopic matrix effects are empirically obtained by analyzing the standards in our current instrumental conditions and that the equations obtained under different instrumental conditions (different sessions, different labs) may be different (*e.g.*, Xu *et al.* 2022).[10] Each analysis of an unknown sample needs to be calibrated with the equations fitted to the standards analyzed under the same conditions and should not be calibrated with extrapolated lines. Most natural dolomites exhibit low Fe# values, such as most sedimentary dolomites, while hydrothermal and diagenetic dolomites can reach higher Fe# values. The new standards developed in this study (Fe# varying from 0 to 0.34) cover the most common compositional range of natural dolomites. For extremely Fe-rich dolomite and ankerite, additional standards are needed. The relatively small standard dataset results in higher uncertainties for the fitted parameters of the calibration curves. Improving accuracy and precision requires larger standard data sets.

Building upon the development of an online calibration method involving concurrent measurements of $^{18}O–^{16}O–^{56}Fe^{16}O–^{24}Mg^{16}O$ [10] and $^{13}C–^{12}C–^{56}Fe^{16}O–^{24}Mg^{16}O$, we aim to continue exploring the utilization of this online calibration approach for simultaneous analysis of carbon and oxygen isotopes carbonates of dolomite-ankerite and even magnesite-siderite solid solutions through concurrent $^{18}O–^{16}O–^{13}C–^{12}C–^{56}Fe^{16}O–^{24}Mg^{16}O$ measurements. The goal is to obtain accurate and paired C-O isotopes and their corresponding Fe#. Furthermore, the online calibration strategy demonstrated that concurrently measuring the isotope of interest and matrix-sensitive ions has broader implications. It could be readily adapted to improve the accuracy of SIMS analysis for other stable isotope systems (e.g., silicon, sulfur) in a wide range of compositionally variable minerals. For instance, minerals common in igneous and metamorphic rocks such as olivine [$(Mg, Fe)_2SiO_4$], pyroxene [$(Ca, Mg, Fe)_2Si_2O_6$], and feldspar [solid solutions of $NaAlSi_3O_8$–$CaAl_2Si_2O_8$–$KAlSi_3O_8$] all exhibit significant matrix effects during SIMS analysis. Applying a similar online calibration strategy to these minerals could significantly advance in situ microanalysis in petrology and cosmochemistry. Additionally, we anticipate that this online calibration technique can be effectively applied in NanoSIMS due to its substantial mass dispersion (~22 times), which enables simultaneous detection of $^{18}O–^{16}O–^{13}C–^{12}C–^{56}Fe^{16}O–^{24}Mg^{16}O$ signals. By comparison, the mass dispersion of IMS-1280 is

approximately 17%, allowing the simultaneous measurement of $^{12}C$ and $^{13}C$ (or $^{16}O$ and $^{18}O$), but requiring peak jumping to $^{24}Mg^{16}O$, then to $^{56}Fe^{16}O$.

## CONCLUSION

New standards (dolomite 1001, 1026 and 1055) and matrix-effect online calibration method for SIMS dolomite C-isotopic analysis has been developed in this work. The matrix-effect online calibration method utilizes concurrent SIMS measurements of $^{13}C$–$^{12}C$–$^{56}Fe^{16}O$–$^{24}Mg^{16}O$, without the need for Fe# values obtained by EPMA. By performing online SIMS carbon analysis on newly developed dolomite C-isotopic standards, the novel online method demonstrates enhanced accuracy and efficiency. The applications of online method to dolomite O- and C-isotope analysis validate that this approach is an accurate and efficient stable isotope analytical method for composition-variable minerals. Furthermore, online method holds promise for the analysis of other stable isotopes in composition-variable minerals that exhibit evident matrix effects during SIMS analysis. Further investigations are necessary to validate this application.

## ASSOCIATED CONTENT

The supporting information (Tables S1−S3) is available at https://www.at-spectrosc.com.

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**Notes**

The authors declare no competing financial interest.

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## REFERENCES

1 J. Yuan, C. Huang, F. Zhao and X. Pan, *J. Pet. Sci. Eng.*, 2015, **135**, 596–607. https://doi.org/10.1016/j.petrol.2015.10.024

2 A. v. S. Hood, N. J. Planavsky, M. W. Wallace and X. Wang, *Geochim. Cosmochim. Acta*, 2018, **232**, 265–287. https://doi.org/10.1016/j.gca.2018.04.022

3 C. W. Wei, M. Deng, C. Xu, A. R. Chakhmouradian, M. P. Smith, J. Kynicky, W. L. Song, W. Chen and B. Fu, *Econ. Geol.*, 2022, **117**, 1327–1338. https://doi.org/10.5382/ECONGEO.4926

4 A. Giuliani, R. N. Drysdale, J. D. Woodhead, N. J. Planavsky, D. Phillips, J. Hergt, W. L. Griffin, S. Oesch, H. Dalton and G. R. Davies, *Sci. Adv.*, 2022, **8**, eabj1325. https://doi.org/10.1126/sciadv.abj1325

5 J. Y. Xu, G. Q. Tang, Y. Liu, J. C. Melgarejo and Q. L. Li, *At. Spectrosc.*, 2025, **46**, 17–23. https://doi.org/10.46770/AS.2024.281

6 J. Isa, I. E. Kohl, M.-C. Liu, J. T. Wasson, E. D. Young and K. D. McKeegan, *Chem. Geol.*, 2017, **458**, 14–21. https://doi.org/10.1016/j.chemgeo.2017.03.020

7 R. B. Ickert and R. A. Stern, *Geostand. Geoanal. Res.*, 2013, **37**, 429–448. https://doi.org/10.1111/j.1751-908X.2013.00222.x

8 L.-G. Wu, Q.-L. Li, Y. Liu, G.-Q. Tang, K. Lu, X.-X. Ling and X.-H. Li, *J. Anal. At. Spectrom.*, 2020, **35**, 1607–1613. https://doi.org/10.1039/D0JA00069H

9 M. G. Śliwiński, K. Kitajima, R. Kozdon, M. J. Spicuzza, J. H. Fournelle, A. Denny and J. W. Valley, *Geostand. Geoanalytical Res.*, 2016, **40**, 173–184. https://doi.org/10.1111/j.1751-908X.2015.00380.x

10 J.-Y. Xu, Q.-L. Li, G.-Q. Tang, K. Lu, Y. Liu, L.-J. Feng and J. Melgarejo, *Anal. Chem.*, 2022, **94**, 7944–7951. https://doi.org/10.1021/acs.analchem.2c00759

11 J. Lu, W. Chen, W. Zhang, H. Liu, A. Simonetti, Z. Hu, Y. Liu, K. Zhao and S. Jiang, *J. Anal. At. Spectrom.*, 2022, **37**, 278–288. https://doi.org/10.1039/D1JA00356A

12 N. T. Kita, T. Ushikubo, B. Fu and J. W. Valley, *Chem. Geol.*, 2009, **264**, 43–57. https://doi.org/10.1016/j.chemgeo.2009.02.012

13 G. Tang, X. Li, Q. Li, Y. Liu and X. Ling, *Surf. Interface Anal.*, 2020, **52**, 190–196. https://doi.org/10.1002/sia.6712

14 R. Kozdon, T. Ushikubo, N. T. Kita, M. Spicuzza and J. W. Valley, *Chem. Geol.*, 2009, **258**, 327–337. https://doi.org/10.1016/j.chemgeo.2008.10.032

15 H. Craig, *Geochim. Cosmochim. Acta*, 1957, **12**, 133–149. https://doi.org/10.1016/0016-7037(57)90024-8

16 S. Goutelle, M. Maurin, F. Rougier, X. Barbaut, L. Bourguignon, M. Ducher and P. Maire, *Fundam. Clin. Pharmacol.*, 2008, **22**, 633–648. https://doi.org/10.1111/j.1472-8206.2008.00633.x

17 Y. Liu, Q.-L. Li, G.-Q. Tang, X.-H. Li and Q.-Z. Yin, *J. Anal. At. Spectrom.*, 2015, **30**, 979–985. https://doi.org/10.1039/C4JA00459K