Using SIMS to decode noisy stratigraphic δ$^{13}$C variations in Ediacaran carbonates

Shuhai Xiao$^{a,⁎}$, Huan Cui$^{b,c,d,e}$, Junyao Kang$^{a}$, Kathleen A. McFadden$^{f}$, Alan J. Kaufman$^{g}$, Kouki Kitajima$^{d,e}$, John H. Fournelle$^{e}$, Maxwel Schwida, Morrison Nolan$^{a}$, Jean-Marc Baele$^{h}$, John W. Valley$^{d,e}$

$^a$ Department of Geosciences, Virginia Tech, Blacksburg, VA 24061, USA
$^b$ Research Group of Analytical, Environmental and Geo-Chemistry, Division of Earth System Science, Vrije Universiteit Brussel, Brussels, Belgium
$^c$ ET-HOME (Evolution and Tracers of the Habitability of Mars and Earth) Astrobiology Research Consortium, Belgium
$^d$ NASA Astrobiology Institute, University of Wisconsin, Madison, WI 53706, USA
$^e$ Department of Geoscience, University of Wisconsin, Madison, WI 53706, USA
$^f$ ConocoPhillips, Houston, TX 77079, USA
$^g$ Department of Geology and Earth System Science Interdisciplinary Center, University of Maryland, College Park, MD 20742, USA
$^h$ Department of Geology, Faculty of Engineering, University of Mons, Mons, Belgium

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ABSTRACT

Carbonate carbon isotope (δ$^{13}$C$_{carb}$) chemostratigraphy is a valuable tool in Precambrian stratigraphic correlation. The effectiveness of this tool rests on the assumption that δ$^{13}$C$_{carb}$ data record global seawater signals. However, in some cases δ$^{13}$C$_{carb}$ data exhibit rapid and noisy stratigraphic variations that may have been influenced by authigenic or diagenetic carbonate minerals. To assess the contribution of non-primary minerals towards bulk carbonate carbon isotope values, we acquired SIMS (secondary ion mass spectrometry) δ$^{13}$C$_{carb}$ data, electron microscopic data, and CL (cathodoluminescence) microscopic data from two Ediacaran successions—the lower Member II of the Doushantuo Formation in South China and the Mooifontein Member of the Zaris Formation in southern Namibia. The Doushantuo samples came from a stratigraphic interval with noisy meter-scale δ$^{13}$C$_{carb}$ variations of up to 10‰, whereas the Mooifontein Member is characterized by consistent δ$^{13}$C$_{carb}$ values with limited meter-scale variations of less than ~4‰. Our data show that the meter-scale stratigraphic variations in δ$^{13}$C$_{carb}$ are also mirrored in the SIMS data at μm-mm scales in both Doushantuo and Mooifontein samples. The Doushantuo samples, SIMS δ$^{13}$C$_{carb}$ values of authigenic calcite vary by up to 10‰ over μm-mm scales and can be either higher or lower than those of the co-existing dolomite matrix, which also appears to be affected by authigentic carbonate on the basis of petrographic observation. Bulk-sample δ$^{13}$C$_{carb}$ values measured on powders microdrilled from the same SIMS specimens are within the range of SIMS δ$^{13}$C$_{carb}$ values. Thus, we infer that bulk-sample δ$^{13}$C$_{carb}$ Values of Doushantuo samples represent mixtures of different carbonate components. The Doushantuo and Mooifontein SIMS δ$^{13}$C$_{carb}$ data validate the traditional method of using chemostratigraphic consistency to evaluate authigenic/diagenetic alteration, but given that secondary phases may be $^{13}$C-enriched relative to matrix carbonate, caution is warranted when taking maximum values to approximate primary chemostratigraphic trends.

1. Introduction

Carbonate carbon isotopes (δ$^{13}$C$_{carb}$) have been applied widely in paleoclimatology, paleoceanography, and chemostratigraphic correlation. This is particularly true in the study of Precambrian stratigraphic correlation (Kaufman and Knoll, 1995), because few Precambrian fossils can be considered as robust index fossils for biostratigraphic correlation. In the past four decades, available Precambrian δ$^{13}$C$_{carb}$ data have grown enormously and are often the basis of Ediacaran stratigraphic correlation and subdivision (Xiao et al., 2016). These data also revealed two unusual and enigmatic features of Ediacaran δ$^{13}$C$_{carb}$ chemostratigraphy. First, exceptionally large δ$^{13}$C$_{carb}$ excursions, such as the Shuram negative excursion reaching −12‰ VPDB (Grotzinger et al., 2011) and the Hüttenberg positive excursion reaching +12‰
VPDB (Cui et al., 2018), have been reported from Ediacaran carbonate successions. These large excursions are difficult to explain using simple steady-state models, which limit $\delta^{13}$C$_{carb}$ variations between ca. $-5\%$ (when carbon burial is 100% carbonate) and ca. 20% (when carbon burial is 100% organic carbon). As a result, various non-steady-state models have been proposed to explain these exceptionally high-magnitude excursions (Rothman et al., 2003; Shields et al., 2019). Second, irregular point-to-point variations in $\delta^{13}$C$_{carb}$, sometimes with values between $\sim 40\%$ and 6% at decimeter–meter scales, are observed in some Ediacaran successions such as the lower Doushantu Formation (Jiang et al., 2003; McFadden et al., 2008; Wang et al., 2008; Zhou et al., 2016). These variations are also difficult to explain using traditional carbon cycle models, and localized anaerobic oxidation of methane during early or late diagenesis has been invoked as a major driver of such irregular and noisy stratigraphic variations in $\delta^{13}$C$_{carb}$ values (Jiang et al., 2003; Wang et al., 2008; Zhou et al., 2016; Cui et al., 2017; Wang et al., 2017; Cui et al., 2019). These interpretations echo hypotheses stating that extremely anomalous $\delta^{13}$C$_{carb}$ values and noisy stratigraphic variations may be related to the precipitation of authigenic carbonate minerals (Schrag et al., 2013; Sun and Turchyn, 2014), meteoric and burial diagenesis (Knauth and Kennedy, 2009; Derry, 2010), mixing of sediments derived from different environments with different isotopic signatures (Swart, 2008), and rock-fluid interactions (Higgins et al., 2018; Hoffman and Lamothe, 2019). Such secondary or authigenic/diagenetic processes presents a challenge in $\delta^{13}$C$_{carb}$ chemostratigraphy, which assumes that bulk $\delta^{13}$C$_{carb}$ records primary dissolved inorganic carbonate isotopic signatures of the global ocean. Addressing this challenge requires in-situ, micrometer-scale $\delta^{13}$C data coupled with diligent petrographic analysis in order to tease apart $\delta^{13}$C signatures between sedimentary and diagenetic components. Secondary ion mass spectrometry (SIMS) offers a powerful tool to address this issue because it can achieve the necessary spatial resolution and has recently been calibrated and tested for $\delta^{13}$C and $\delta^{18}$O analysis of carbonate minerals (Valley and Kita, 2009; Śliwiński et al., 2016b; Denny et al., 2020; Turnier et al., 2020).

In this study, we used SIMS to analyze $\delta^{13}$C$_{carb}$ of four Ediacaran samples, three from the lower Doushantu Formation in South China and one from the Mooifontein Member in southern Namibia. The Doushantu samples were chosen because they came from a stratigraphic interval with noisy $\delta^{13}$C$_{carb}$ variations and they contain authigenic carbonate components that can be independently identified via petrography and cathodoluminescence (CL) microscopy. The Mooifontein sample, on the other hand, came from a stratigraphic interval with more consistent $\delta^{13}$C$_{carb}$ values and a limited range of variations, thus offering a comparison with the Doushantu samples. The main goals of this study are to test (1) whether the meter-scale stratigraphic variations in $\delta^{13}$C$_{carb}$ which are up to 10% in the lower Doushantu Formation and $\approx$4% in the Mooifontein Member, are also captured in the SIMS data at µm–mm scale; (2) whether $\delta^{13}$C$_{carb}$ values of authigenic/diagenetic carbonate are distinct from, higher than, or lower than bulk-sample $\delta^{13}$C$_{carb}$ values measured from microdrilled powders; and (3) whether $\delta^{13}$C$_{carb}$ analysis of microdrilled powders represent a mixture of sedimentary and authigenic signatures. By answering these questions, we hope to demonstrate that SIMS is a useful tool to evaluate the influence of authigenic/diagenetic carbonate minerals on $\delta^{13}$C$_{carb}$ values of microdrilled powders.

2. Geological and stratigraphic background

The three Doushantu samples were collected from lower Member II of the Doushantu Formation at the well-studied Jiulongwan section in the Yangtze Gorges area of South China. At Jiulongwan, the Doushantu Formation is about 154 m thick and can be divided into four members (Fig. 1; see published and new $\delta^{13}$C$_{carb}$ data in Supplementary Data 1). Member I is ca. 4 m thick and represents the cap dolostone directly overlying terminal Cryogenian glaciogenic diamictite of the Nantuo Formation. It is characterized by negative $\delta^{13}$C$_{carb}$ values around $\sim 3.5\%$, representing the negative excursion labeled “EN1” in Fig. 1. However, localized occurrences of extremely negative $\delta^{13}$C$_{carb}$ values as low as $\sim 48\%$ have been reported from void-filling calcite cement (Jiang et al., 2003; Wang et al., 2008; Zhou et al., 2010; Bristow et al., 2011; Zhou et al., 2016; Wang et al., 2017; Cui et al., 2019). The origin of these extremely negative $\delta^{13}$C$_{carb}$ signatures is a matter of debate, with interpretations ranging from early diagenetic or authigenic calcite cement related to methane gas hydrate release that led to the termination of the terminal Ediacaran snowball Earth glaciation (Jiang et al., 2003; Wang et al., 2008), to late diagenetic calcite cement related to the oxidation of thermogenic methane (Bristow et al., 2011; Cui et al., 2019). Member II is ca. 71 m thick (meterage ca. 4–75 m in Fig. 1) and consists of argillaceous dolostone interbedded with mudstone. Microdrilled powders (hereafter bulk samples) generally have positive $\delta^{13}$C$_{carb}$ values, representing the positive excursion labeled “EP1” in Fig. 1, although the lower part of Member II is characterized by noisy stratigraphic variations between $\sim 5\%$ and 7%. Fossiliferous chert nodules, as well as calcite nodules, are present in this member and they preserve a diverse assemblage of acanthomorphic acritarchs (Zhang et al., 1998; Xiao, 2004; McFadden et al., 2009; Liu and Moczydłowska, 2019). These chert nodules typically consist of a silica core surrounded by a pyrite and calcite rim. Petrographic and SIMS $\delta^{13}$S$_{pyrite}$ data indicate that these chert nodules were lithified during early diagenesis (Xiao et al., 2010). Member III is ca. 65 m thick (meterage ca. 75–141 in Fig. 1), with thick-bedded dolostone in the lower interval and ribbon rocks (i.e., thin-bedded limestone with thin argillaceous dolostone intercalations) in the upper interval. Acanthomorphic acritarchs and other microfossils have been reported from chert nodules and bands in Member III (Zhang et al., 1998; Liu et al., 2014; Liu and Moczydłowska, 2019). Bulk-sample $\delta^{13}$C$_{carb}$ values register a negative excursion (labeled “EN2” in Fig. 1) at the Member II–III transition, followed by a positive excursion (“EP2” in Fig. 1) in the lower Member III and then a pronounced negative excursion ($\sim 10\%$; “EN3” in Fig. 1) in the upper portion of Member III. The negative excursion EN3 continues into Member IV (meterage 141–154.1 m in Fig. 1), where negative $\delta^{13}$C$_{carb}$ values are measured from dolomite concretions hosted in black shales. The negative excursion EN3 is thought to be equivalent to the Shuram negative excursion recorded in Oman and globally (Grotzinger et al., 2011; Zhou et al., 2017a).

The three Doushantu samples analyzed in this study—JLW15.1, JLW23.5, JLW35.2—were collected from lower Member II, at stratigraphic horizons 15.1 m, 23.5 m, and 35.2 m, respectively, above the base of the Doushantu Formation (Fig. 1). Radiometric dates from ash beds in the Doushantu Formation in the Yangtze Gorges area constrain the depositional age of these three samples between 632.5 ± 0.5 Ma and 551.1 ± 0.7 Ma (Condon et al., 2005). We note that 551.1 ± 0.7 Ma age came from an ash bed at the uppermost Miaohe Member at a nearby section in the Yangtze Gorges area and the correlation between the Miaohe Member and Member IV has yet to be confirmed (An et al., 2015; Xiao et al., 2017; Zhou et al., 2017a). Regardless of whether the Miaohe Member is partially equivalent to or younger than Member IV, the 551.1 ± 0.7 Ma age remains a minimum constraint on the depositional age of the three analyzed samples. Via lithostratigraphic correlation, additional radiometric dates from the Doushantu Formation at the Jiulongwan section in the Yangtze Gorges area (Condon et al., 2005) and in the Zhanguiping area to the north of the Yangtze Gorges (Liu et al., 2009; Zhou et al., 2017b) indicate that JLW15.1 and JLW23.5 are likely between 632.5 ± 0.5 Ma and 614.0 ± 7.6 Ma, and JLW35.2 between 614.0 ± 7.6 Ma and 609 ± 5 Ma (Fig. 1). These age constraints are consistent with an astronomical time scale for the lower Doushantu Formation, which places the first 22 m of the Doushantu Formation between 636.8 ± 0.7 Ma and 625.6 ± 0.7 Ma (Sui et al., 2018).

The Mooifontein sample, 16AarFarm, was collected from the...
Mooifontein Member, Zaris Formation, Kuibis Subgroup, Nama Group at an outcrop (26.75036°S, 16.49832°E) about 4.5 km southeast of Farm Aar in the Witpus sub-basin of southern Namibia (Vickers-Rich et al., 2016). The Mooifontein Member near Farm Aar is more than 40 m thick (Fig. 2; see published and new δ¹³C values in Supplementary Data 2), with its upper boundary truncated by modern erosion. It was deposited in oxic to manganous suboxic environments on a carbonate ramp in the terminal Ediacaran Period (Saylor et al., 1998; Wood et al., 2015; Tostevin et al., 2016). It consists of thin- to medium-bedded limestone and contains abundant calcareous tubular fossils of Cloudina riemkeae (Fig. 3d–f) (Grant, 1990). Bulk-sample δ¹³C values of the Mooifontein Member are mostly in the range of 0–4‰ (Sayloret al., 1998; Wood et al., 2015; Vickers-Rich et al., 2016), much narrower than the ~10‰ range documented in the lower Doushantuo Formation at Jiulongwan. The depositional age of the Mooifontein Member is constrained by a radiometric date of 548.8 ± 1 Ma (Grotzinger et al., 1995), subsequently recalculated as 547.32 ± 0.31 Ma (Schmitz, 2012), from the equivalent Zaris Formation in the Zaris sub-basin of southern Namibia.

3. Methods

3.1. Sample preparation

Three Doushantuo samples (JLW15.1, JLW23.5, JLW35.2) that contain chert nodules and one Mooifontein sample (16AarFarm) that contains internal molds of Cloudina riemkeae were chosen for this study. The handsamples were trimmed to remove weathered surfaces and cut in half to prepare mirrored thin and thick sections for petrographic and SIMS analyses, respectively. Thin sections were examined on a standard transmitted light petrographic microscope. For SIMS sample preparation, a one-inch diameter billet was extracted from the thick section. Five one-millimeter drill holes were made on the one-inch round thick section, and anthracite, quartz, dolomite, calcite, and pyrite standards were used as standards. The one-inch round thick section was cut in half to prepare mirrored thin and thick sections for petrographic and SIMS analyses, respectively.
were placed in these drill holes and secured with epoxy. Only the calcite standard UWC-3 and the dolomite standard UW6220 were used in this study, and the other standards will be used in future SIMS analyses of organic C, silica O, and pyrite S isotopic compositions. The round thick section with the standards was then polished to microprobe grade for analyses using reflected light microscopy, SEM (scanning electron microscopy), SIMS, EPMA (electron probe microanalysis), and cathodoluminescence (CL) microscopy.

3.2. Pre-SIMS light microscopic and SEM imaging

Reflected light microscopic and SEM images of polished thick sections were produced to guide the selection of SIMS analytical spots. SEM (scanning electron microscopy) was performed in the Ray and Mary Wilcox Scanning Electron Microscopy Laboratory, Department of Geoscience, University of Wisconsin–Madison. BSE (back scattered electron) SEM images were acquired with a Hitachi S3400 VP SEM with EDS (energy dispersive spectrometry) using a Thermo Fisher thin window detector. SEM images were acquired using an accelerating voltage of 15 keV. Areas (domains) selected for SIMS analysis were imaged at various magnifications and these images were used to help navigate during SIMS sessions.

3.3. SIMS

SIMS analyses were conducted on a CAMECA IMS 1280 at the WiscSIMS (Wisconsin Secondary Ion Mass Spectrometry) Lab, Department of Geoscience, University of Wisconsin–Madison. The analyses include three SIMS sessions. During the sessions (Mar. 15–17, 2017), carbon two–isotopes (12C, 13C) were measured with a 7-μm-diameter beam size. Measurements of δ13C were made using one Faraday cup and two electron multiplier detectors measuring 12C−, 13C−, and 13C1H−, respectively. The UWC-3 calcite standard and the UW6220 dolomite standard were used to calibrate analyses of carbon isotopes (Valley and Kita, 2009; Śliwiński et al., 2016b). Carbon isotope ratios are reported in standard per mil (‰) notation relative to VPDB, calculated as δ13Cunknown = [(13C/12C)unknown / (13C/12C)VPDB – 1] × 1000. Measured ratios of 13C/12C were calculated as “raw” δ–values (δ13Craw) before converting to the VPDB scale (see below) based on eight analyses of a running standard (UWC-3) that bracket each group of 10–15 sample analyses. The entire dataset can be found in Supplementary Data 3–4.

Measurements of 13C/12C were made using a 133Cs+ primary ion beam with an intensity of ~ 600 pA. The secondary ion intensity of 12C was ~7 × 106 cps. 13CH was analyzed to evaluate the effect of hydrogen, which might be in the form of organic matter or water, on the SIMS results. An electron flood gun in combination with a gold coating (~40 nm) was used for charge compensation. The total analytical time per spot was about 4 min including pre-sputtering (20 s), automatic centering of the secondary ion beam in the field aperture (60 s), and analysis (160 s). Applied high-voltage on EM for 13C was automatically adjusted after every analysis. The baseline noise level of the Faraday cup was measured at the beginning of each analysis day.

The raw isotope ratios obtained by SIMS are biased by an instrumental mass fractionation (IMF or bias) that can vary in magnitude depending on instrumental conditions, mineralogy, and sample composition (Śliwiński et al., 2016b). To address the effect of Fe/Mg on IMF, a suite of standards along the dolomite-ankerite series were analyzed at the beginning of the session and used to generate a calibration curve relative to the running standard UW6220 (Valley and Kita, 2009; Śliwiński et al., 2016b; Śliwiński et al., 2016a; Denny et al., 2020). After SIMS analysis, this calibration curve was used to determine the composition-specific IMF based on the Fe concentration (Fe# = molar Fe/(Fe + Mg)): determined using an electron microprobe, see EPMA procedures below) of each SIMS pit. We also applied matrix correction regarding Mg, Fe and Mn in calcite. Details can be found in Turner...
et al. (2020). The spot-to-spot precision of $\delta^{13}C$ values based on all bracketing analyses on standard UWC-3 is $\pm 0.6\%$ (2SD; see Supplementary Data 3).

3.4. Post-SIMS SEM, EPMA, and CL microscopic analyses

After SIMS analysis, the gold coating was removed before further SEM, EPMA, and CL microscopic analyses. SEM imaging was performed in the Ray and Mary Wilcox Scanning Electron Microscopy Laboratory, Department of Geoscience, University of Wisconsin–Madison. BSE images of carbon-coated samples were acquired with a Hitachi S3400 VP SEM with EDS using a Thermo Fisher thin window detector. Each SIMS pit was examined by SEM for possible irregularities. SEM images were acquired using an accelerating voltage of 15 keV or 20 keV at a working distance of 10 mm. All the SIMS pits were imaged by SEM and are shown with corresponding $\delta^{13}C$ values in Supplementary Data 4.

Electron probe microanalysis (EPMA) was conducted in the Eugene Cameron Electron Microbeam Lab, Department of Geoscience, University of Wisconsin–Madison. EPMA was performed with the Cameca SXFive field emission electron probe, operated at 20 kV and 50 nA, and either a focused beam or a 3–4 µm defocused beam, using wavelength dispersive crystal spectrometers (Supplementary Data 3). Counting times were 10 s on peak and 10 s on background, for all elements except those noted in the following listing: Al Kα (20 s) and Si Kα (20 s) were acquired on a large TAP crystal; As Kα (20 s) and Se Kα (20 s) on LIF; S Kα and Ca Kα (27 s) on large PET; Fe Kα, Mn Kα and Co Kα on LIF; and Ni Kα, Cu Kα and Zn Kα on large LIF. Standards used were Balmat pyrite (Fe, S), NBS glass K412 (Si, Al, Ca), arsenopyrite (As), and freshly polished metals for the balance. PHA modes used were integral, except for Al and Si which were differential mode. Software used was Probe for EPMA (Donovan et al., 2018). Off peak backgrounds were acquired, and matrix correction was conducted using the Armstrong/Leve Scott algorithm (Armstrong, 1988). EPMA data are presented in Supplementary Data 3.

Cathodoluminescence (CL) microscopy was carried out at University of Mons, Belgium. Cathodoluminescence excitation was achieved with a cold cathode CITL CL system (Cambridge Image Technology – model Mk5, UK). The unit was operated at 15 kV and 500 µA acceleration voltage and beam current, respectively. With these settings, the unfocused beam had a current density of about 8 µA/mm². Cathodoluminescence microscopic images were captured with a Peltier-cooled digital color camera (Lumenera model Infinity 4, Canada), set from 0.1 s to a few seconds exposure time depending on CL intensity and microscope magnification. Multiple frame averaging was used to reduce noise. Color calibration of the camera (white balance) was performed using the blue-filtered, tungsten-halogen light source of
Fig. 4. SIMS $\delta^{13}$C data of JLW15.1A, a subsample of JLW15.1. (a) Reflected light photomicrograph montage of the sample, with labeled rectangles denoting areas or domains for SIMS and EPMA analyses. Calcite (Cal), dolomite (Dol), pyrite (Py), quartz (Qz), and anthracite (An) standards were mounted on the sample and polished for SIMS and EPMA analyses. (b–d) Backscattered electron microscopic images of domains 1–3, respectively, which are marked in (a). Major minerals (dolomite, calcite, pyrite, and silica), SIMS spots, and corresponding $\delta^{13}$C measurements (yellow: calcite measurements) are marked on the figure. The spot-to-spot precision of $\delta^{13}$C values based on all bracketing analyses on standard UWC-3 is ±0.6‰ (2SD; see Supplementary Data 3). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 5. SIMS $\delta^{13}$C data of JLW15.1A mapped on cathodoluminescence (CL) images. (a–c) CL images corresponding to Fig. 4b–d. (d) Magnified view of central part of (c).
Fig. 6. SIMS $\delta^{13}C$ data of sample JLW15.1B, a subsample of JLW15.1. (a) Reflected light photomicrograph montage of the sample, with labeled rectangles denoting areas or domains for SIMS and EPMA analyses. Calcite (Cal), dolomite (Dol), pyrite (Py), quartz (Qz), and anthracite (An) standards were mounted on the sample and polished for SIMS and EPMA analyses. (b–d) Backscattered electron microscopic images of domains 1–3, respectively, which are marked in (a). Major minerals (dolomite, calcite, pyrite, and silica), SIMS spots, and corresponding $\delta^{13}C$ measurements (yellow: calcite measurements) are marked on the figure. The spot-to-spot precision of $\delta^{13}C$ values based on all bracketing analyses on standard UWC-3 is $\pm 0.6\%$ (2SD; see Supplementary Data 3). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 7. SIMS $\delta^{13}C$ data of JLW15.1B mapped on cathodoluminescence (CL) images. (a), (b–c), and (d) are CL images corresponding to Fig. 6b–d, respectively.
the microscope, which may result in CL colors that are slightly different from other equipment (especially around the yellow band, which is narrow) but ensures more or less standardized observation conditions.

4. Results

4.1. Petrographic observations

Petrographic observations were made using petrographic microscopy (Fig. 3), backscattered SEM (Figs. 4, 6, 8, 10, and 12), secondary electron SEM (Supplementary Data 4), and CL microscopy (Figs. 5, 7, 9, 11, and 13), to independently identify different carbonate phases, including authigenic or early diagenetic carbonate; the term authigenesis is used here as a synonym of early diagenesis or pre-compaction diagenesis. Key petrographic observations support that the chert nodules in JLW15.1, JLW23.5, and JLW35.2 were silicified during early diagenesis. These observations include: (1) sedimentary microlaminae in the dolostone matrix warp around the chert nodules (Fig. 3b–c), indicating that the chert nodules were lithified before compaction; (2) sedimentary microlaminae are also preserved within the chert nodules, but they are more widely spaced than those outside the chert nodules (Fig. 3b–c), consistent with the pre-compaction lithification of the chert nodules; and (3) some chert nodules contain exceptionally preserved microfossils (Xiao et al., 2004; Xiao et al., 2010), often in three dimensions, again suggesting silicification occurred prior to compaction.

The chert nodules typically consist of a silica core surrounded by a pyrite rim and a calcite rim (Figs. 3a–c, 4a, 6a, 8a). The relative portions of the silica core, pyrite rim, and calcite rim can vary. For example, some chert nodules in JLW35.2 are dominated by a proportionally large calcite rim, with a reduced silica core and sometimes lacking a well-defined pyrite rim. In any case, most chert nodules are sharply defined by a pyrite/calcite rim that is petrographically distinct from the dolomite matrix (Fig. 3a–c). Thus, like the silica core, the pyrite and calcite rims are also likely early diagenetic in origin, although the calcite rim may post-date the silica core (Xiao et al., 2010). McFadden et al. (2008) and Xiao et al. (2010) analyzed two of the three Doushantuo samples for bulk-sample δ34S_pyrite using the chromium reduction method and δ34S_pyrite of individual pyrite crystals in the matrix and in the pyrite rims using SIMS: JLW23.5 (bulk-sample matrix pyrite δ34S = 16.4‰ VCDT; SIMS rim pyrite δ34S = 15.2–20.3‰ VCDT, average ± 1 s.d. = 18.1 ± 1.2‰ VCDT, n = 28; SIMS matrix pyrite δ34S = 24.4–39.8‰ VCDT, average ± 1 s.d. = 30.6 ± 4.7‰ VCDT, n = 8) and JLW15.1 (bulk-sample matrix pyrite δ34S = 7.9‰ VCDT; SIMS rim pyrite δ34S = 19.2–27.3‰ VCDT, average ± 1 s.d. = 24.6 ± 1.6‰ VCDT, n = 34). The positive and highly variable δ34S_pyrite values indicate continuous sulfate reduction and pyrite precipitation in pore waters with limited supply of seawater sulfate, suggesting that localized
microbial processes (e.g., microbial sulfate reduction) may have played a critical role in the formation of the pyrite rim during early diagenesis (Xiao et al., 2010).

In addition to the calcite rim surrounding chert nodules, there are other carbonate phases in the Doushantu samples that can be targeted for SIMS δ¹³C analysis. Some Doushantu nodules have a relatively small silica core surrounded by a thick calcite rim (e.g., Fig. 10a) and thus would be more appropriately called calcite nodules, which can easily be analyzed using SIMS. In addition, there are small patches of calcite cements in the nodule interior and within the dolomite matrix.

Fig. 9. SIMS δ¹³C data of JLW23.5 mapped on cathodoluminescence (CL) images. (a) CL image corresponding to Fig. 8b (upper), (b) to Fig. 8c (lower right), (c) to Fig. 8c (central left), (d) to Fig. 8d, (f) to Fig. 8e (left), (g) to Fig. 8e (right, and (h) to Fig. 8f. (e) is magnified view of lower right of (d), showing calcite cement (central right) in dolomitic matrix. Note the presence of multiple CL colors in dolomitic matrix, indicating the presence of multiple phases of carbonate minerals including authigenic carbonate.
These patches are sometimes elongate in shape and conform to bedding (e.g., Fig. 8b upper right; 8d lower right; 8e). They do not seem to be post-compaction dissolution vugs that were subsequently filled with cements. Instead, they are interpreted as authigenic calcite cement that formed prior to sediment compaction, because porosity needed for the precipitation of such cement patches would have been greatly reduced after compaction. In a sense, these patches of cement can be regarded as smaller versions of calcite nodules shown in Fig. 10a. Thus, there are multiple phases of calcite cements, possibly representing one or more generations of cementation, that can be targeted for SIMS analysis. Finally, the dolomite matrix can also be targeted for SIMS analysis, as long as the effect of diffuse organic matter in the matrix is carefully evaluated by monitoring the $^{13}$CH peak.

The Mooifontein sample (16AarFarm) consists of homogeneous, coarsely recrystallized limestone. The tubular fossil *Cloudina riemkeae* is abundant. Most *Cloudina* specimens are preserved as internal molds, with the test lost and the interior of the tube filled with coarse recrystallized calcite (Fig. 3d). Bulk-sample $^{13}$C$_{carb}$ values of the Mooifontein Member are consistently in the range of 1–4‰, as measured in multiple sections in the Witpust sub-basin (Saylor et al., 1998; Wood et al., 2015; Vickers-Rich et al., 2016). Because of the homogeneous nature of this sample, SIMS analysis is targeted on the calcite crystals in a mold of *Cloudina* (i.e., within *Cloudina* tube; Fig. 12a) and in the matrix (i.e., outside *Cloudina* tube; Fig. 12b).

### 4.2. SIMS $^{13}$C$_{carb}$, bulk-sample $^{13}$C$_{carb}$, and EPMA data

SIMS $^{13}$C$_{carb}$ and EPMA elemental measurements are provided in Supplementary Data 3. All SIMS $^{13}$C$_{carb}$ data are mapped on post-SIMS secondary electron SEM images showing SIMS pits (Supplementary Data 4). SIMS $^{13}$C$_{carb}$ values are also mapped on back-scattered electron SEM images and CL images of analytical domains (Figs. 4–13). SIMS $^{13}$C$_{carb}$ are summarized in Fig. 14. The relationships between SIMS $^{13}$C$_{carb}$, carbonate components, and elemental concentrations are shown in Fig. 15.

In the three Doushantuo samples, SIMS $^{13}$C$_{carb}$ shows large spatial variations at μm-mm scales within the calcite rim, generally over 5‰ and in some cases greater than 10‰ (e.g., Figs. 6d, 10b). In contrast,
the Mooifontein sample shows much lower-magnitude spatial variability, with an overall range of 4.4‰ but typically < 1‰ at the μm-scale. The difference in variability between the Doushantuo and Mooifontein samples is illustrated in Fig. 14, with the former showing much greater ranges and standard deviation values than the latter.

Spatial variations in SIMS $\delta^{13}$C$_{\text{carb}}$ at μm-mm scales (histograms and box-and-whisker plots in Fig. 14) roughly match the stratigraphic $\delta^{13}$C$_{\text{carb}}$ variations at meter scales measured by acidification and gas source mass spectrometry (red double-arrowed lines in Fig. 14). For the Doushantuo samples, the stratigraphic variations shown in Fig. 14 represent the range of bulk-sample $\delta^{13}$C$_{\text{carb}}$ values in strata one meter above and below the SIMS sample, which approximately represent variations over ~1 Myr according to an astronomically tuned time scale for the lower Doushantuo Formation at the Jiulongwan section (Sui

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**Fig. 11.** SIMS $\delta^{13}$C data of JLW35.2 mapped on cathodoluminescence (CL) images. (a) CL image corresponding to Fig. 10b, (b) to Fig. 10c, (d) to Fig. 10d, (e) to Fig. 10e, and (f) to Fig. 10f–g. (c) is magnified view of lower right of (b), showing calcite cement (central) in dolomitic matrix. (g) CL image of dolomitic matrix near area shown in (c). Note the presence of multiple CL colors in calcite/chert nodule (a, d, f), calcite cement (c, central), and dolomitic matrix (c, peripheral; g), indicating the presence of multiple phases of authigenic carbonate minerals.
et al., 2018). For the Mooifontein samples, the stratigraphic variation shown in Fig. 14 represents the range of bulk-sample δ¹³C values in the 40 m strata of the Mooifontein Member (Wood et al., 2015; Vickers-Rich et al., 2016).

Bulk-sample δ¹³C values measured on powders drilled from the matrix of the same samples used for SIMS analysis are denoted by green arrows in Fig. 14. In all cases, the bulk-sample δ¹³C values are within the ranges of SIMS δ¹³C values and for the Doushantuo samples, the bulk-sample measurements are in the central 50% percentile of SIMS measurements (Figs. 14 and 15a).

In Fig. 15b, SIMS δ¹³C data are categorized according to different carbonate phases. Not only do the various authigenic calcite components (e.g., calcite rims, calcite nodules, and calcite cements) show spatial variability in δ¹³C, the dolomite matrix is also characterized by
variable $\delta^{13}C$ data (symbols filled in gray in Fig. 15b, c; data only available for JLW23.5). The variation in matrix $\delta^{13}C$ is probably caused by the occurrence of authigenic carbonate in the matrix, as evidence from the CL images revealing carbonate minerals with multiple CL colors (e.g., Figs. 9e, 11c, g). It is important to note that individual $\delta^{13}C$ measurements of authigenic calcite can be either higher or lower than those of dolomite matrix.

When SIMS $\delta^{13}C_{\text{Carb}}$ data are plotted against Mg, Mn, and Fe contents as determined by EPMA, no systematic correlations are observed (Fig. 15c–f). Thus, it is unlikely that these excursions in $\delta^{13}C$ are related to the calibration of SIMS data, which uses the elemental concentration of Mg, Mn, and Fe (Śliwiński et al., 2016b; Śliwiński et al., 2016a; Denny et al., 2020; Turnier et al., 2020).

5. Discussion

The noisy $\delta^{13}C$ profile in the lower Doushantuo Formation is an enigmatic feature that complicates chemostratigraphic correlation. Some authors considered such noisy variations chemostratigraphically significant and attempted to identify regionally correlatable negative $\delta^{13}C$ excursions in the lower Member II of the Doushantuo Formation (Tahata et al., 2013; Zhu et al., 2013; Gao et al., 2018). For example, the negative $\delta^{13}C$ excursion WANCE from the lower Member II has been proposed as a chemostratigraphic marker in South China (Zhu et al., 2013). However, the chemostratigraphic value of such excursions has been questioned because they occur in a stratigraphic interval with highly variable $\delta^{13}C$ values and are not regionally consistent (Zhou and Xiao, 2007; Xiao et al., 2012). The SIMS data presented here help us to understand the potential origin of these regionally inconsistent excursions and to dissect the noisy chemostratigraphic trend in the lower Member II of the Doushantuo Formation.

Given the spatial variation in SIMS $\delta^{13}C$ data at μm-mm scales, we propose that the noisy $\delta^{13}C$ profiles in the lower Member II likely represent variable mixing of different carbonate phases, including sedimentary dolomite, authigenic calcite cement, and even late diagenetic carbonate components. Because the dolomite matrix can also contain authigenic carbonate minerals (e.g., Figs. 9e, 11c, g) with highly variable $\delta^{13}C$ at μm-mm scales, as shown in sample JLW23.5 (Figs. 8 and 9), sampling via microdrilling in an attempt to avoid calcite cements and veins is unlikely to mitigate this problem. Thus, we caution against the use of noisy $\delta^{13}C$ excursions in the lower Member II for regional or global chemostratigraphic correlation.

The origin of μm-mm scale $\delta^{13}C$ variations in the lower Member II remains uncertain. However, given that this stratigraphic unit in South China is widely influenced by methanogenesis and methane oxidation (Jiang et al., 2003; Wang et al., 2008; Zhou et al., 2016), it is possible that the μm-mm scale $\delta^{13}C$ variations may be related to pore-water microbial and diagenetic processes that control methane oxidation.

Fig. 14. Histograms and box-and-whisker diagrams of SIMS $\delta^{13}C$ measurements of the four analyzed samples. Each box-and-whisker plot shows the median, 1st and 3rd quartiles, range, and outliers (±3rd quartile + 1.5 * interquartile range, or ± 1st quartile − 1.5 * interquartile range; denoted by circular dots). For comparison, bulk-sample $\delta^{13}C$ values of the same samples are denoted by green arrows, with values marked above; note that duplicate measurements were attempted for JLW15.1 and JLW23.5, and the green arrows point to the average of the duplicates. Additionally, stratigraphic variations in $\delta^{13}C$ at meter scales are marked by red double-arrowed lines, with ranges of $\delta^{13}C$ values annotated above. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
Together, methanogenesis, methanotrophy, and methane oxidation can result in highly variable δ¹³C signatures in authigenic carbonate (Meister et al., 2018), depending on whether methane is oxidized in situ or escapes from sediments, and whether it is oxidized aerobically or anaerobically.

This study has several broader implications for δ¹³C chemostratigraphy. First, integrated SIMS and petrographic analyses offer a powerful tool to individually interrogate different generations of carbonate cement (Denny et al., 2020), to evaluate the influence of authigenic/diagenetic carbonate minerals on δ¹³C chemostratigraphy, and to dissect the origin of noisy chemostratigraphic trends. The data presented here show that chemostratigraphic variations at meter scales can be captured at the μm-mm scales, the latter reflecting the influence of authigenic/diagenetic carbonate minerals. Thus, our study verifies the traditional view that noisy chemostratigraphic trends are suggestive of diagenetic alteration, and indicates that chemostratigraphic consistency is a useful tool to evaluate diagenetic alteration. In our case study, for example, the lower Member II of the Doushantuo Formation was probably influenced by authigenic/diagenetic alteration to a greater degree than the Mooifontein Member.

Our study also casts doubt on the traditional practice of taking the maximum δ¹³C values to approximate primary chemostratigraphic trends. As shown in the Doushantuo samples, δ¹³C values of authigenic calcite can be greater or lower than those of the dolomitic matrix, making it difficult to infer primary chemostratigraphic trends from noisy data using either the maximum values or moving averages. In such cases, coupled SIMS and petrographic analysis is an indispensable tool to disentangle the paragenetic sequence and isotopic signals from noisy data.

6. Conclusions

By contrasting the Doushantuo and Mooifontein data, we show that meter-scale chemostratigraphic variations in δ¹³C_carb (up to 10‰ in the lower Member II of the Doushantuo Formation and ~4‰ in the Mooifontein Member) are also captured in SIMS δ¹³C_carb variations at μm-mm scale. In the Doushantuo samples, petrographically identified authigenic calcite—which may have been influenced by localized porewater processes such as methanogenesis and methane oxidation—has a wider range of SIMS δ¹³C_carb values and can be isotopically heavier or lighter than co-existing dolomite matrix. In both the Doushantuo and Mooifontein samples, the range of SIMS δ¹³C_carb values encompasses bulk-sample δ¹³C_carb values measured on micro-drilled powders, suggesting that, in some cases, even micro-sampling may incorporate a quantitatively significant proportion of authigenic/diagenetic components, such as cements, which may be isotopically distinct from sedimentary signatures. With its capability to obtain accurate μm-mm scale δ¹³C_carb data and when integrated with detailed petrographic and
microscopic data, SIMS is a powerful technique to understand the origin of noisy petrographic patterns. The data presented here confirm that, not surprisingly, only stratigraphically consistent δ13C_carb data are useful in chronostratigraphic correlation, and indicate that the traditional practice of taking the maximum δ13C_carb values to approximate primary chronostratigraphic trends should be treated with caution, particularly when there are rapid and irregular variations paired with petrographic evidence for authigenic or diagenetic carbonate.

Declaration of Competing Interest

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

Acknowledgements

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.precamres.2020.105686.

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