Characteristics of the carbon cycle in Late Mesoproterozoic: Evidence from carbon isotope composition of paired carbonate and organic matter of the Shennongjia Group in South China

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Abstract

The late Mesoproterozoic Era (1300–1000 Ma) was a critical period that witnessed the origin and early evolution of multicellular eukaryotes. Multiple studies have reported observations that the carbon isotope composition of carbonate (δ¹³C_{carb}) underwent a substantial increase after ca. 1250 Ma. The high δ¹³C_{carb} values suggest that the fraction of organic carbon burial (f_{org}) had increased, which, consequently, might have promoted the oxidation of surface environments and the diversification of multicellular eukaryotes. However, details of the carbon cycle during this critical time interval remain elusive, which is pivotal to testing this hypothesis. In this study, we analyzed the stable carbon isotope composition of paired organic matter (δ¹³C_{org}) and carbonate, as well as the thermal characteristics of the organic matter, from the Shennongjia Group in South China, which has been constrained to an age of ~1340–1150 Ma. A gradual increase in δ¹³C_{carb}, from ~−2‰ to >+4‰, is observed in the interval from the middle...
Shennongjia Group. Above which, the $\delta^{13}C_{\text{carb}}$ declines to $\sim$2‰ in the uppermost. The paired $\delta^{13}C_{\text{org}}$ values show an extensive range of compositions, from $\sim$22 to $\sim$32‰. Raman spectral data revealed that the organic matter in the Shennongjia Group experienced a wide range of thermal history, which might be ascribed to the involvement of detrital organic matter. We reconstructed the $\Delta^{13}C_{\text{carb-org}}$ and $f_{\text{org}}$ values in two different scenarios: one included all the $\delta^{13}C_{\text{org}}$ data, while the other screened the $\delta^{13}C_{\text{org}}$ data to minimize the possible effects of detrital organic matter. The results of these two reconstructions show similar temporal trends. Intriguingly, the $\Delta^{13}C_{\text{carb-org}}$ are generally larger than the modern counterpart, which can be attributed to higher $pCO_2$. The calculated $f_{\text{org}}$ of the Shennongjia Group is generally lower than the modern value, 20%. However, the $f_{\text{org}}$ experienced a substantial increase between $ca.$ 1250 and 1190 Ma, suggesting enhanced oxidation of surface environments, which might have paved the way for the diversification of multicellular eukaryotes.

**Keywords**: Late Mesoproterozoic, Shennongjia Group, Carbon cycle, Organic matter, Carbon isotopes, Raman spectroscopy

1. **Introduction**

    Following the Great Oxidation Event in the early Paleoproterozoic, the interval from $ca.$ 1.8 to 0.8 billion years ago (Ga) is generally recognized as the ‘boring billion’ or Earth’s middle age, during which the Earth’s surface environments were relatively stable, and the evolution of life was in stasis (Buick et al., 1995; Brasier and Lindsay, 1998; Knoll et al., 2006; Cawood and Hawkworth, 2014). However, many recent reports have revealed that multicellular eukaryotes diversified in the late Mesoproterozoic (Butterfield, 2001; Tang et al., 2020, 2021; Strother and Wellman, 2021; Maloney et al., 2021). For example, multiple types of fossils have been observed during this time interval, including the crown groups of Rhodophyta and Chlorophyta, respectively represented by the fossils *Bangiomorpha pubescens* and *Proterocladus antiquus*, as well as possible fungal fossils *Opisthokonta giraldae* (Butterfield, 2001; Loron et al., 2019; Tang
et al., 2020). Meanwhile, phylogenetic data also suggest that the diversification of photosynthetic eukaryotes occurred during the late Mesoproterozoic (Yoon et al., 2004, 2010; Parfrey et al., 2011; Yang et al., 2016; Sanchez-Baracaldo et al., 2017; Evanovich and Guerreiro, 2020; Strassert et al., 2021). These emerging scenarios are substantially different from the biological evolutionary stasis hypothesized for the boring billion (Buick et al., 1995; Brasier and Lindsay, 1998; Butterfield and Smith, 2015). Unfortunately, the mechanisms triggering these biological innovations remain largely unknown, which impedes an understanding of the co-evolution of life and environment during this critical time interval.

The atmospheric oxygen content ($p_{O_2}$) may represent a critical limiting factor for the evolution of eukaryotes in Precambrian environments (Planavsky et al., 2014). Multiple lines of evidence, e.g., the unfractionated Cr isotopes in black shale and ironstones, and the absence of negative Ce anomaly in carbonate, suggest that a very low $p_{O_2}$ characterized the late Mesoproterozoic, potentially around 1% of the present atmospheric level (PAL) (Planavsky et al., 2014; Cole et al., 2016; Bellefroid et al., 2018; Liu et al., 2021). By contrast, new $\delta^{53}$Cr values measured in the Taizi black shale (~1.25 Ga, lower part of the upper Shennongjia subgroup) and late Mesoproterozoic carbonate (~1.1 Ga), suggest that the $p_{O_2}$ in the late Mesoproterozoic may have been higher than 1% PAL (Gilleaudeau et al., 2016; Canfield et al., 2018; Zhang et al., 2021).

Recently, Canfield et al. (2021) investigated the Raman characteristics of different types of organic matter and found no detrital graphitic carbon in the interval from 1.7 to 0.7 Ga, and their model reveals that the $p_{O_2}$ could have been as high as 24% PAL. Thus, it remains uncertain regarding the oxygenation state of the late Mesoproterozoic, and more proxies and investigations of other sedimentary sequences are required to better evaluate these different interpretations.

Accumulation of oxygen in the Earth’s surface environments is generally accompanied by the burial of organic matter in sediments sourced from oxygenic photosynthesis in the water column. Therefore, a proxy recording the amount of organic matter buried would be a valuable tool for unraveling the evolutionary history of $p_{O_2}$ (e.g., Karhu and Holland, 1996; Berner, 2006; Krissansen-Totton et al., 2021). As light carbon isotopes are preferentially used during carbon fixation, an increase in the burial of organic matter would typically induce a positive shift of the
carbon isotope composition of carbonate ($\delta^{13}C_{\text{carb}}$) and organic carbon ($\delta^{13}C_{\text{org}}$) (e.g., Hayes et al., 1999; Kump and Arthur, 1999). Thus, the $\delta^{13}C_{\text{carb}}$ and $\delta^{13}C_{\text{org}}$ are widely used as indicators for the fraction of organic carbon burial [$f_{\text{org}} = F_{\text{bo}}/(F_{\text{bo}} + F_{\text{bc}})$, where $F_{\text{bo}}$ is the flux of organic carbon burial, and $F_{\text{bc}}$ represents the flux of carbonate burial], which is then used to infer the oxidation state of the Earth’s surface environments (Hayes et al., 1999; Bartley and Kah, 2004). It has been observed that the $\delta^{13}C_{\text{carb}}$ values increase substantially from $\sim$0‰ in the early Mesoproterozoic to $\sim$+4‰ in the late Mesoproterozoic (Kah et al., 1999; Bartley and Kah, 2004; Kah et al., 2012; Silva-Tamayo et al., 2018; Lathrop, 2018; George et al., 2019; Paula-Santos et al., 2021). These moderately positive $\delta^{13}C_{\text{carb}}$ values are generally attributed to elevated rates of organic carbon burial. However, it has to be noted that other factors, in addition to the $f_{\text{org}}$, may contribute to the high $\delta^{13}C_{\text{carb}}$ values observed in the late Mesoproterozoic. Thus, it is urgent to understand the full carbon cycle in this critical time interval.

Based on a simple box model, at steady state, the $f_{\text{org}}$ can be calculated by the following equations:

$$f_{\text{org}} = (\delta^{13}C_{\text{carb}} - \delta^{13}C_{\text{in}}) / (\delta^{13}C_{\text{carb}} - \delta^{13}C_{\text{org}})$$

The $\delta^{13}C_{\text{in}}$ is the average $\delta^{13}C$ value of the carbon entering the oceans, which is generally assumed to be $\sim$5‰ in Phanerozoic (Kump and Arthur, 1999). For convenience, the term ($\delta^{13}C_{\text{carb}} - \delta^{13}C_{\text{org}}$) is identified as the $\Delta^{13}C_{\text{carb-org}}$, which is approximately the carbon isotope fractionation during carbon fixation (Hayes et al., 1999). Thus, both $\delta^{13}C_{\text{carb}}$ and $\delta^{13}C_{\text{org}}$ data are required in order to correctly reconstruct variations in $f_{\text{org}}$. However, compared with relatively well-characterized $\delta^{13}C_{\text{carb}}$ values during the late Mesoproterozoic, much less is known about the contemporary record of $\delta^{13}C_{\text{org}}$ values.

The measurement of $\delta^{13}C_{\text{org}}$ is usually based on bulk organic matter, which may contain two sources, authigenic organic matter synthesized by primary producers in the ocean and detrital organic carbon sourced from continental weathering (Jiang et al., 2012; Johnston et al., 2012). Since the detrital organic matter commonly has different carbon isotopic compositions from the authigenic component, the $\delta^{13}C_{\text{org}}$ of the bulk organic carbon may not faithfully record the characteristics of the carbon cycle during the deposition, as well as the $f_{\text{org}}$ (Johnston et al., 2012).
This case would be evident when total organic carbon (TOC) contents are low (Johnston et al., 2012), like most samples investigated here. Thus, it is critical to evaluate the characteristics of the organic matter before applying the $\delta^{13}$C$_{org}$ to reconstruct the carbon cycle in deep time.

In this study, we aim to unravel the details of the carbon cycle through the late Mesoproterozoic and reconstruct the history of $f_{org}$ in this time interval. Specifically, we analyzed paired $\delta^{13}$C$_{carb}$ and $\delta^{13}$C$_{org}$ of the samples collected from the Shennongjia Group in South China, which has been constrained to the age of the late Mesoproterozoic from ~1.4 to 1.1 Ga (Li and Leng, 1991; Li et al., 2013; Du et al., 2016). Meanwhile, we investigated the distribution and degree of structural order of organic matter in the rocks with micro-Raman spectroscopy. Finally, we reconstructed the $f_{org}$ of this time interval with the bulk $\delta^{13}$C$_{org}$ values and the filtered $\delta^{13}$C$_{org}$ data according to the TOC and Raman spectral data, respectively. Our study provides insights into the mechanisms that triggered the diversification of multicellular eukaryotes in the late Mesoproterozoic ocean.

2. Geological setting

The study area is located in the Shennongjia Forestry District in the northwestern part of Hubei Province, which might be an independent micro-block close to the northern margin of the Yangtze block (Fig. 1A-B, Qiu et al., 2015). The regional geology and stratigraphy are adapted from Li and Leng (1991). The Shennongjia Group, the oldest strata in this area, is >10 km thick. The base of the Shennongjia Group is not exposed, whereas the top is unconformably overlain by Neoproterozoic strata. In ascending order, the Shennongjia Group is divided into eleven formations: including the Yingwodong, Dayanping, Luanshigou, Dawokeng, Kuangshishan, Taizi, Yemahe, Wenshuihe, Shicaohe, Songziyuan, and Wagangxi formations. An unconformity between the Kuangshishan and Taizi formations divides the whole sequence into lower and upper Shennongjia subgroups. The contacts between all the other formations are conformable.

The chronological framework of the Shennongjia Group has been well-constrained. The youngest zircon U-Pb age of the detrital zircons recovered from the Dayanping Formation, the lowermost exposed formation, is $1398 \pm 20$ Ma, which sets the maximum depositional age of the
exposed Shennongjia Group (Li et al., 2013). Meanwhile, U-Pb dating of zircons collected from bentonites from the lower Yemahe and Shicaohe formations provides the depositional ages of 1215.8 ± 2.4 Ma and 1180 ± 15 Ma, respectively (Li et al., 2013; Du et al., 2016). Furthermore, baddeleyite grains from a mafic dike intruding into the Shicaohe Formation were dated to 1083.2 ± 4.6 Ma and 1115 ± 9 Ma (Li et al., 2013), constraining the minimum age for the Shennongjia Group to ca. 1100 Ma. Therefore, the Shennongjia Group provides an extensive record of the late Mesoproterozoic.

**Fig. 1** (A) A simplified geological map showing the distribution of the Shennongjia Group and the location of the study sections. (B) Plate tectonic framework of China. The study area is located on the northern margin of the Yangtze Block. (C) Generalized stratigraphic column of the Mesoproterozoic Shennongjia Group, including inferred relative sea levels and the three sections investigated in this study. The regional geology and stratigraphy are adapted from Li and Leng (1991). See the main text for the details of the dating.
The interval studied here spans the middle Luanshigou Formation to the uppermost Shicaohe Formation; limited outcrop and unsuitable lithology prohibited sampling of the lowermost, i.e., the Dayanping and Yingwodong formations, and uppermost, i.e., the Songziyuan and Wagangxi formations, parts of the Shennongjia Group. The investigated interval crops out in three sections, i.e., the Zhufeng, Tiechanghe, and Guanmenshan sections (Fig. 1C). The Zhufeng section (GPS: 31°27′3″ N, 110°15′50″E) includes, in ascending order, the middle to the upper part of the Luanshigou Formation, and the Dawokeng and Kuangshishan formations, as well as the lower part of the Taizi Formation. The Tiechanghe section (GPS: 31°36′6″N, 110°24′52″E) consists of the upper part of the Taizi Formation and the Yemahe and Wenshuihe formations. The Guanmenshan section (GPS: 31°25′58″N, 110°21′56″E) is composed of the uppermost part of the Wenshuihe Formation, Shicaohe Formation, and the lower part of the Songziyuan Formation.

The middle Luanshigou Formation mainly comprises median- to thick-bedded silicified dolostone with limited stromatolite occurrences. In the upper Luanshigou Formation, the lithology switches to thin- to median-bedded grey dolostone interbedded with red argillaceous dolostone with abundant centimeter-size columnar and non-branching stromatolites (Fig. 2A-B). Halite pseudomorphs have been observed in the uppermost red dolostone (Li et al., 2013; Zou et al., 2019). The top of the Luanshigou Formation is characterized by a ~1 m thick bed of conglomerate consisting of quartz clasts. The overlying Dawokeng Formation mainly consists of intermediate to thickly bedded crystalline dolostone, micrite, and sandy dolostone (Fig. 2C); while abundant conical stromatolites characterize the upper part with diameters from centimeter to decimeter scale and heights between a decimeter to meters (Fig. 2D). The base of the Kuangshishan Formations is characterized by a layer of ~8 m thick black shale and a layer of ~2.5 m thick ironstone. Upward, the Kuangshishan Formation switches to thick-bedded dolostone with abundant large domal and columnar stromatolites (Fig. 2E-F). Occurrences of the conical stromatolites in the upper Dawokeng and lower Kuangshishan formations suggest that this interval was mainly deposited in the subtidal zone (Kah et al., 2009), which is supported by the deposition of black shale at the base of the Kuangshishan Formation. The other intervals were deposited in the intertidal zone.
Fig. 2 Photos of the outcrop sections showing particular sedimentary characteristics of each lithological formation of the Shennongjia Group investigated in this study. A-B: Luanshigou Formation, A: Centimeter-size columnar non-branching stromatolites; B: Red argillaceous dolostone. C-D: Dawokeng Formation, C: Laminar dolomitic microbial mats in the lower part; D: Decimeter-size conical stromatolites in the uppermost part. E-F: Kuangshishan Formation, E: Meter-size conical stromatolites; F: Domal stromatolites. G: Taizi Formation, interbedded thin carbonate and mudstone in the uppermost Taizi Formation. H: Bentonite (arrowed) in the low part of the Yemahe Formation. I: Densely packed domal to irregular centimeter-size stromatolites from the middle Wenshuihe Formation. J-L: Shicaohe Formation. J: Thick-beded gray siliceous dolostone with fine wrinkly to undulated microbialite laminations of the Shicaohe Formation. K: Red colored oblique centimeter-size columnar stromatolites of the upper Shicaohe Formation. L: Thin-beded red argillaceous dolostone of the upper Shicaohe Formation.
Fig. 3 Photomicrographs of selected samples from the Shennongjia Group. A-B: Micrite dolomites in the Dawokeng (A) and the Shicaohe (B) formations; C: Micritic limestone in the Taizi Fm.; D-E: Microcrystalline limestone in the Taizi (D) and Wenshuihe (E) formations; F: Fine crystalline dolostone in the Yemahe Fm.; G-H: Laminated microbial dolostones in the Luanshigou Fm.; I: Well preserved clotted structure in microcrystalline dolostone in the Shicaohe Fm.; J: Peloidal micritic intraclasts in the Luanshigou Fm.; K: Sparry intraclasts in the Yemahe Fm., L: Oolites in the Shicaohe Fm.. Scale bars are 200 μm in A-L.

The base of the lower Taizi Formation consists of a ~0.2 m thick weathering crust and a bed of sandstone, which changes to ~35 m stromatolitic dolostone and ~4 m thick nodular limestone in the lower part. Upward, the main part of the lower Taizi Formation in the Zhufeng section is
characterized by interbedded sandstone and mudstone in the middle and black shales in the upper part. The upper Taizi Formation in the Tiechanghe section is generally divided into three parts: the lower part of black shale and sandstone, the middle part of medium to thick-bedded carbonate, and the upper part of interbedded thin carbonate and shales (Fig. 2G). The Yemahe Formation is characterized by thick-bedded dark dolostone, red-colored stromatolitic dolostone in the lower part, and gray medium-to-thick-bedded dolostone in the upper part. A bentonite layer also occurs in the lower Yemahe Formation (Fig. 2H, Li et al., 2013). The Wenshuihe Formation is subdivided into three parts: thick-bedded gray dolostone in the lower part, thin-to-medium bedded gray micritic limestone, dolomitic limestone, and stromatolitic limestone in the middle part (Fig. 2I), and thin-bedded fine siltstone, shale, and gray-green dolostone in the upper part. Compared with the lower Shennongjia subgroup, domal stromatolites are widespread in the Yemahe and Wenshuihe formations, which point to a stable shallow-water depositional environment. The Shicaobe Formation mainly comprises thin-bedded red argillaceous dolostone and thick-bedded gray siliceous dolostone with abundant microbialites and centimeter size columnar stromatolites (Fig. 2J-L). In summary, the Shennongjia sequence was mainly deposited in the shallow-marine environments of a peritidal carbonate platform and carbonate platform margin (Li and Leng, 1991; Kuang et al., 2018).

3. Materials and methods

3.1. Sample preparation

A total of 432 samples were collected for investigations on carbonate carbon and oxygen and organic carbon isotope composition, of which 175 samples were from the Zhufeng section (~1350 m thick), 177 samples from the Tiechanghe section (~3900 m thick), and 80 samples from the Guannmenshan section (~1700 m thick). Large hand specimens as fresh as possible were collected from field outcrops. Before sample processing, the petrofacies of each sample were evaluated in thin sections. Only samples with micritic, microcrystalline, and fine crystalline texture were chosen in this study (Fig. 3). In the laboratory, these samples were first cut into small chips, during which any weathered surface and veins, if present, were cut away. The rock chips,
~50–100 g of each sample, were cleaned in Milli-Q (MQ) water three times and dried overnight in an oven at 50 ºC. After drying, the samples were ground into homogenized powders (~200 meshes) with a shatter box. The puck mill between samples was cleaned by grinding baked quartz sand, MQ water and ethanol.

3.2. Carbonate $\delta^{13}C$ and $\delta^{18}O$ analysis

The carbonate carbon ($\delta^{13}C_{\text{carb}}$) and oxygen ($\delta^{18}O_{\text{carb}}$) isotope compositions were analyzed online by a Kiel IV carbonate device coupled to a ThermoFisher MAT 253 isotope ratio mass spectrometer (IRMS) in the State Key Laboratory of Geological Processes and Mineral Resources (GPMR) at China University of Geosciences (CUG-Wuhan). Approximately 50–300 μg of homogenized rock powders were reacted with 100% H$_3$PO$_4$ under vacuum at 70 ºC for 250–450 s. The produced CO$_2$ was transferred to the IRMS for isotopes analysis. All $\delta^{13}C_{\text{carb}}$ and $\delta^{18}O_{\text{carb}}$ values are reported in ‰ relative to the Vienna Pee Dee belemnite (V-PDB) with an accuracy better than ±0.1‰ (1σ, n = 30) based on multiple analyses of laboratory standards (GBW04416, $\delta^{13}C_{\text{carb}} = +1.61$‰, $\delta^{18}O_{\text{carb}} = -11.59$‰; GBW04417, $\delta^{13}C_{\text{carb}} = -6.06$‰, $\delta^{18}O_{\text{carb}} = -24.12$‰; and internal standard, ISTB-1, $\delta^{13}C_{\text{carb}} = -10.63$‰, $\delta^{18}O_{\text{carb}} = -8.63$‰) (Supplementary Data Table S1).

3.3. Organic $\delta^{13}C$ analysis

Approximately 5–50 g homogeneous rock powders were decarbonated with 10% HCl at room temperature for 24 h with episodic agitation. Before washing the HCl residues, the pH of the supernatant was measured. If the pH was close to 7, additional acid was added to assure complete carbonate dissolution. After carbonate was completely dissolved, insoluble residues were washed with DI water until neutral and dried in an oven at 60 ºC. The carbonate content of the samples was calculated using the weights of the rock powders prior to and after acid treatment. The TOC content and organic carbon isotope compositions ($\delta^{13}C_{\text{org}}$) were determined online by an elemental analyzer (Flash EA2000) coupled to a ThermoFisher MAT 253 IRMS at the State Key Laboratory GPMR at CUG-Wuhan. The temperature of the flash combustion was set at 1050 ºC, while the reduction furnace was fixed at 680 ºC. Standards GBW04407 ($\delta^{13}C_{\text{org}} =$
−22.4‰) and GBW04408 (δ13Corg = −36.9‰) were used to calibrate the carbon isotope analyses. The analytical accuracy was better than ±0.1‰ (1σ) based on multiple standards and duplicate sample analyses. The TOC content was calculated based on the volume of CO2 produced during combustion, with a reproducibility better than ±10 wt.‰.

3.4. Elemental analyses

Aliquots of ~100 mg homogeneous rock powders were dissolved in 5% v/v trace metal grade acetic acid. After dissolution, the liquid was collected through centrifugation, while the residue was cleaned with DI water for three times, and all the supernate was added to the collected liquid. The trace elements analyses were measured using inductively coupled plasma mass spectrometry (Agilent 7700e ICP-MS) at the Wuhan Sample Solution Analytical Technology Co., Ltd. The accuracy of the analyses was determined by repeated analyses of internal standards and was typically better than 10% (2σ).

3.5. Micro-Raman spectroscopy analysis

Micro-Raman spectroscopy was performed on thin sections (n = 11) and decarbonated residues (n = 11). The cleaned and dried acid-insoluble residues were transferred to clean glass slides. The organic particles in the thin sections and glass slides were analyzed. A total of 162 single-point Raman spectra of 22 samples, including in situ organic matter in thin section (n = 86) and organic matter in acid-treated residues (n = 76), were analyzed using Raman spectroscopy. In addition, in order to further improve the image visualization of the micron-scale minerals and organic matter, we selected several thin sections for mapping. Raman spectra were obtained on a WITec α-300R confocal Raman imaging system with a 532 nm laser source at BGEQ, CUG-Wuhan (Ouyang et al., 2020). The laser beam diameter was focused with a 50X or 100X objective lens to collect inelastically scattered photons. The laser power at the sample was ~1–5 mW. Single-point Raman spectra were acquired as averages of 3 spectra of 15 s duration for each sample varies and between three and twenty spectra per sample were acquired (Supplementary Data Table S2).

The Raman spectra were analyzed with the software “WITec Project 5.0”. The measured Raman spectral range was set between 0 and 3200 cm⁻¹, but only the range of 1000–1800 cm⁻¹
was used for organic matter spectral baseline correction and deconvolution using the Lorenz function. The deconvolution method was according to Kouketsu et al. (2014), which is briefly summarized here. After a linear baseline correction to remove background fluorescence, Raman spectra were decomposed into five (D1, D2, D3, D4 and G bands, respectively set at 1340-1350 cm\(^{-1}\), 1600-1620 cm\(^{-1}\), 1510 cm\(^{-1}\), 1245 cm\(^{-1}\), and 1593 cm\(^{-1}\)) The calculated Lorentz functions were then added as linear combinations to obtain modeled Raman spectra, which fits the original Raman spectra with a coefficient higher than 0.99. After deconvolution, the Raman parameters, including peak center position (\(\omega\)), full width at half maxima (FWHM) and peak intensity (I) were extracted for each peak (Table S2).

4. Results

4.1. Geochemical compositions of Shennongjia carbonate

The carbonate in the Shennongjia Group is dominated by dolostone, with minor limestone occurring in the Taizi and Wenshuihe formations. The Mn contents range from 3.7 to 2028.9 ppm, with an average of 223.9 ± 317.7 ppm (\(n = 92\)), while the Sr contents vary from 15.8 to 1695.2 ppm, with an average of 162.2 ± 347.0 ppm (\(n = 92\)) (Fig. 4). Generally, the dolostone is more enriched in Mn but depleted in Sr concentrations relative to the limestone. For example, the Sr concentrations of the limestone in the uppermost Taizi Formation reached as high as ~1700 ppm (Fig. 4). With limited exception, the Mn/Sr ratios of most of the samples are lower than 10 (Fig. 4, Table S1).

The \(\delta^{13}C_{\text{carb}}\) values of the Shennongjia Group range from –2.6 to +4.7‰, with an average of +0.5 ± 1.6‰ (\(n = 403\)). In the Zhufeng section, a gradual positive shift in \(\delta^{13}C_{\text{carb}}\), from −1.5 to +1.0‰, is observed in the interval from the middle Luanshigou to the top Kuangshishan Formation, which is followed by a slight negative shift to −1‰ in the lowermost part of the Taizi Formation (Fig. 4). The limited carbonate occurrences in the middle Taizi Formation suggest that the \(\delta^{13}C_{\text{carb}}\) values might vary around 0‰. In the uppermost Taizi Formation from the Tiechanghe section, a gradual positive shift from 0 to +3.2‰ is observed (Fig. 4). Upward, the lower Yemahe Formation has relatively constant values of +2.2‰, followed by a gradual
negative shift to $\sim +1\%$ in the upper Yemahe and lower Wenshuihe formations. The middle Wenshuihe Formation is characterized by an episode of substantially high $\delta^{13}C_{\text{carb}}$ values to $> +4\%$ (Fig. 4). The high $\delta^{13}C_{\text{carb}}$ values, through two episodes of a negative shift occurring in the uppermost Wenshuihe and middle Shicaohe formations, respectively, declined to $-1\%$ in the uppermost Shicaohe Formation cropping out in the Guanmenshan section (Fig. 4).

The corresponding $\delta^{18}O_{\text{carb}}$ values vary from $-12.3$ to $+0.1\%$ with a mean value of $-6.1\%$ ($n = 403$). Generally, the $\delta^{18}O_{\text{carb}}$ values are more positive than $-8\%$. In the interval from Luanshigou to the upper Dawokeng formations, the $\delta^{18}O_{\text{carb}}$ values fluctuate around $-5\%$. Two episodes of a negative shift are recorded in the upper Dawokeng and lowermost Taizi, during which the $\delta^{18}O_{\text{carb}}$ declines to $-8\%$ and $-12\%$, respectively. In the intervening Kuangshishan Formation, the $\delta^{18}O_{\text{carb}}$ values vary around $-8\%$ (Fig. 4). In the interval from the Yemahe to the Shicaohe formations, the $\delta^{18}O_{\text{carb}}$ values are generally around $-5\%$ without stratigraphic variation (Fig. 4).

4.2. Carbon isotope composition of organic matter

The $\delta^{13}C_{\text{org}}$ values of the Shennongjia Group range from $-22$ to $-32\%$. A gentle negative shift is present in the lower Shennongjia Subgroup from the middle Luanshigou to the uppermost Kuangshishan Formation, in which the $\delta^{13}C_{\text{org}}$ declines from $-26$ to $-27\%$ (Fig. 4). Distinctly low $\delta^{13}C_{\text{org}}$ values, $<-30\%$, occur in the lowermost part of the Kuangshishan Formation. Variations of $\delta^{13}C_{\text{org}}$ in the interval from the upper Taizi to the top Wenshuihe Formation are similar to that of the $\delta^{13}C_{\text{carb}}$: two episodes of positive shifts occur in the uppermost Taizi and upper Wenshuihe formations, respectively, along with a gradual negative shift in the Yemahe and lower Wenshuihe formations and a sharp negative shift in the uppermost Wenshuihe Formation (Fig. 4). The $\delta^{13}C_{\text{org}}$ increases distinctly from $-28$ to $>-24\%$ in the lowermost Shicaohe Formation, which coincides with a slight positive shift in $\delta^{13}C_{\text{carb}}$. Upwards, the $\delta^{13}C_{\text{org}}$ declines again to $-27\%$ in the lower to middle Shicaohe Formation and stays constant in the middle. In the upper Shicaohe Formation, the $\delta^{13}C_{\text{org}}$ increases again to $-25\%$ (Fig. 4).
Fig. 4 Litho- and Chemostratigraphy (Mn and Sr contents, Mn/Sr ratio, δ¹³C_carb, δ¹⁸O_carb, δ¹³C_org, Δ¹³C_carb-org) of the three sections. The solid black lines denote the LOWESS regression (span = 20%), while the light grey shaded shows a regression with 2σ bootstrapped errors. A: Zhufeng section; B: Tiechanghe section; C: Guanmenshan section.
Fig. 5 Cross-plots between geochemical parameters of the samples collected from the Shennongjia Group. A: $\delta^{13}$C$_{org}$ vs $\Delta^{13}$C$_{carb-org}$; B: $\delta^{13}$C$_{carb}$ vs $\Delta^{13}$C$_{carb-org}$; C: $\delta^{13}$C$_{carb}$ vs $\delta^{18}$O$_{carb}$; D: Mn/Sr and Mn contents vs $\delta^{13}$C$_{carb}$, respectively; E: TOC vs $\delta^{13}$C$_{org}$; F: $\delta^{13}$C$_{carb}$ vs $\delta^{13}$C$_{org}$. LSG: Luanshigou Fm.; DWK: Dawokeng Fm.; KSS: Kuanshishan Fm.; TZ: Taizi Fm.; YMH: Yemahe Fm.; WSH: Wenshuihe Fm.; SCH: Shicaohe Fm.

4.3. Carbon isotope fractionation

The carbon isotope fractionation during carbon fixation is often estimated from the difference between the $\delta^{13}$C of carbonate and paired organic matter. In the Shennongjia Group the $\Delta^{13}$C$_{carb-org}$ typically ranges from 22‰ to 32‰. Stratigraphically, the $\Delta^{13}$C$_{carb-org}$ increases gradually from ~24 to ~28‰ in the lower Shennongjia subgroup (Fig. 4). In the upper
Shennongjia subgroup, the $\Delta^{13}C_{\text{carb-org}}$ values vary around 30‰ in the uppermost Taizi Formation, gradually decline to 28‰ in the upper Wenshuihe Formation (Fig. 4), and further to 24‰ in the lowermost Shicaohe Formation. Higher in the section, the $\Delta^{13}C_{\text{carb-org}}$ values average 26‰ (Fig. 4). A distinct negative correlation is observed between the $\Delta^{13}C_{\text{carb-org}}$ and $\delta^{13}C_{\text{org}}$, whereas a weaker positive correlation is present between the $\Delta^{13}C_{\text{carb-org}}$ and $\delta^{13}C_{\text{carb}}$ (Fig. 5A-B).

4.4. Raman spectroscopy of organic matter

Raman images clearly distinguish minerals and organic matter distribution in the samples (Fig. 6). In the samples with high TOC content (>0.1%), organic matter is easily observed and present as distinct laminae (Fig. 6A-A'), massive organic grains likely originated from chips of microbial mats (Fig. 6A') and clumps of organic located between or embracing matrice minerals (Fig. 6B'-C'). By contrast, in the samples with low TOC content (<0.1%), less organic matter is observed and is distributed distinctly different from the organic matter observed in the samples with TOC >0.1% (Fig. 6D'-E'). For example, in sample LSG-17, the organic particles are small in size and distribute irregularly (Fig. 6D'), while in sample LSG-63, almost no organic matter was observed (Fig. 6E'). In addition, the samples with low TOC content generally contain multiple non-carbonate minerals, such as quartz, hematite, rutile, and apatite (Fig. 6D'-E'), which might be mainly sourced from terrestrial erosion.

All the Raman spectra of the single-point analysis show two broad bands at around 1350 cm$^{-1}$ (D1 band) and 1600 cm$^{-1}$ (G+D2 band) (Fig. 7A), suggesting that disordered organic matter is the main component. The intensity ratio of these two bands $I_{1350}/I_{1600}$ ranges from 0.7 to 1.7, with an average of 1.13 ± 0.27 ($n = 162$, Fig. 7, Table S2). Meanwhile, the FWHM values of the D1, D2 and G bands vary from 58.3 cm$^{-1}$ to 109.6 cm$^{-1}$, 4.8 cm$^{-1}$ to 51.5 cm$^{-1}$ and from 28.6 cm$^{-1}$ to 78.5 cm$^{-1}$, respectively. Therefore, the FWHM of the D1-band (~78.7 cm$^{-1}$) is about 1.7 times that of the G-band (45.4 cm$^{-1}$) and 2.7 times as large as that of the D2-band (29.1 cm$^{-1}$) (Table S2). The FWHM-D1 is generally used to evaluate the peak metamorphic temperatures of carbonaceous material that experienced low- to medium-grade metamorphism (Lahfid et al., 2010; Kouketsu et al., 2014; Delarue et al., 2016). Using the empirical formula by Kouketsu et al. (2014), the burial temperature of the samples analyzed here ranges from 242 to 353°C, averaging 309 ±
26 °C (n = 162). Generally, the metamorphic temperature of the morphological organic matter, such as the chips of possible microbial mats, fossils grains and organic layers, is around 280 °C (Fig. 7), which is lower than the average value of the bulk organic matter.

**Fig. 6** Optical photomicrographs from thin sections (A-E) and the corresponding micro-Raman mapping (A’-E’) of samples with different TOC contents from the Shennongjia Group. F: Raman spectra of the primary minerals observed in the Shennongjia Group. White arrow: organic grains from possible microbial mats; Red arrow: laminar organic matter.
Fig. 7 A: Raman spectra of selected organic matter observed in the Shennongjia Group and the calculated metamorphic temperatures and $I_{-1350}/I_{-1600}$ ratios (I values). B: Box-and-Whisker plots of the peak intensity ratio $I_{-1350}/I_{-1600}$ from the micro-Raman spectra and the corresponding $\delta^{13}C_{org}$ values.

5. Discussion

5.1. Evaluation of primary geochemical signatures

The samples analyzed here are petrographically well preserved, consisting of micritic to micro-crystalline and limited fine-grained carbonates that generally preserve original sedimentary
structures, e.g., oolite, intraclasts, stromatolites, or microbial structures (Fig. 3). Most of these samples are enriched in carbonate, >80 wt.%. In general, δ13C_carb of carbonate-rich samples such as the micritic dolomite can be well-preserved and remain unaltered by diagenetic processes due to the relatively small quantity of carbon dissolved in secondary meteoric fluids (Scholle and Arthur, 1980; Marshall, 1992). The limited variation of δ13C_carb values is also supported by multiple proxies indicating late meteoric diagenesis (Fig. 5C-D). First, the δ18O_carb values of most samples are higher than −8‰, and no correlation is observed between δ13C_carb and δ18O_carb values (e.g., Banner and Hanson, 1990; Algeo et al., 1992, Fig. 5C). Secondly, with limited exception, the Mn/Sr ratios of these samples are lower than 10, and no correlation is present between the δ13C_carb and Mn/Sr ratios (Fig. 5D). Due to the lower-oxygen contents in Precambrian relative to Phanerozoic oceans, it is likely that the Precambrian seawater Mn content might be higher than the Phanerozoic seawater. The criterion of the Mn/Sr value evaluating secondary alterations of carbonate would be higher in Precambrian. Therefore, the Mn/Sr values presented here support the argument that limited alteration occurred (Derry et al., 1992; Kaufman and Knoll, 1995). This is supported by the absence of correlation between the δ13C_carb and Mn contents (Fig. 5D). Lastly, since the samples analyzed in this study are not organic-rich (generally <0.1 wt.%), the influence of reoxidized 12C-enriched organic matter on δ13C_carb during diagenesis is expected to be limited. Therefore, these suggest that primary δ13C_carb values are preserved in the studied rock samples.

Different from the δ13C_carb, which is mainly influenced by meteoric diagenesis, variations of δ13C_org values are customarily attributed to the degradation of organic matter in early diagenesis, e.g., in the water column or sediments, and the thermal cracking of kerogen during deep burial (Van Os et al., 1995). Except for the upper Taizi Formation, all sampled carbonates were deposited in shallow marine sedimentary environments characterized by abundant stromatolitic microbialites. We infer that the organic matter in these samples might experience similar degradation history. We consider that the absolute values might have been altered by about ±2.5‰ (e.g., Freudenthal et al., 2001; Galimov, 2004; Yamaguchi et al., 2010), whereas the stratigraphic trends should be preserved. Secondly, the Shennongjia Group only experienced low-grade burial metamorphism, below the greenschist facies, as shown by Raman spectra of laminated organic matter that indicate
peak metamorphic temperature around 280 °C (see more below). Therefore, thermal diagenesis and metamorphism should have a limited influence on the $\delta^{13}$C$_{org}$ (Hayes et al., 1983; Des Marais et al., 2001). This inference is also supported by the co-variations between the $\delta^{13}$C$_{org}$ and $\delta^{13}$C$_{carb}$ values observed in some stratigraphic intervals, e.g., the interval from the upper Taizi to the lower Shicaohé formations (Fig. 4B).

![Fig. 8 Integrated Litho- and Chemostratigraphy of the Shennongjia Group in the study area.](image)

Light gray shaded areas correspond to 2σ bootstrapped errors on the LOWESS regression (solid black line) with spans of 6.5%, 6.5% and 15% for $\delta^{18}$O$_{carb}$, $\delta^{13}$C$_{carb}$ and $\delta^{13}$C$_{org}$ data, respectively.

5.2. Integrated $\delta^{13}$C$_{carb}$ chemostratigraphy of the Mesoproterozoic

Since the residence time of oceanic dissolved inorganic carbon (DIC) is much longer than the period of seawater circulation, $10^5$ vs. $10^3$ years (Hayes et al., 1999), $\delta^{13}$C$_{carb}$ can be a valuable chemostratigraphic tool for global correlations, particularly for Precambrian strata that
generally lack available index fossils. It is well known that the $\delta^{13}\text{C}_{\text{carb}}$ values are near zero after the highly positive carbonate carbon isotope excursion during the early Paleoproterozoic (~2.22 to 2.06 Ga, also named as the Lomagundi-Jatuli Event) (Karhu and Holland, 1996). These relatively constant and near-zero $\delta^{13}\text{C}_{\text{carb}}$ values appear to extend through the early Mesoproterozoic (e.g., Buick et al., 1995; Frank et al., 1997; Xiao et al., 1997; Brasier and Lindsay, 1998; Lindsay and Brasier, 2000; Guo et al., 2013; Luo et al., 2014). It has been noted that the $\delta^{13}\text{C}_{\text{carb}}$ values in the late Mesoproterozoic are different from the early Mesoproterozoic, which changed to more positive values sometime after 1.3 Ga (estimated to be post ~1.25 Ga) (e.g., Whelan et al., 1990; Knoll et al., 1995; Kah et al., 1999, 2012; Bartley and Kah, 2004; Bartley et al., 2007; Maheshwari et al., 2009; Gilleaudeau and Kah 2013; Lathrop, 2018; Paula-Santos et al., 2021).

The chronologic framework provided here indicates that the Shennongjia Group covers the transition from the early- to late-Mesoproterozoic from ~1400 to 1100 Ma (Li and Leng, 1991; Li et al., 2013; Qiu et al., 2015; Du et al., 2016), which may provide insights into the $\delta^{13}\text{C}_{\text{carb}}$ chemostratigraphy of the Mesoproterozoic. The $\delta^{13}\text{C}_{\text{carb}}$ values of the Shennongjia Group have been analyzed by three independent research groups (Supplementary Data Table S3), and they are all compiled in Fig. 8 (Tian et al., 2018; Zou et al., 2019; this study). In ascending order, the $\delta^{13}\text{C}_{\text{carb}}$ chemostratigraphy of the Shennongjia Group can be divided into three periods.

The earliest period is the lower Shennongjia subgroup, generally characterized by low $\delta^{13}\text{C}_{\text{carb}}$ values ranging from –2 to +2‰ (Fig. 8). This is consistent with the global phenomenon reported for the early Mesoproterozoic (e.g., Buick et al., 1995; Frank et al., 1997; Lindsay and Brasier, 2000; Guo et al., 2013). However, it should be noted that high $\delta^{13}\text{C}_{\text{carb}}$ values > +2‰ have been observed in the Yingwodong and Dayanping formations (Fig. 8, Tian et al., 2018; Zou et al., 2019). These high $\delta^{13}\text{C}_{\text{carb}}$ values are distinctly different from those in the early Mesoproterozoic. One possible reason is that these were local phenomena deposited in restricted sedimentary basins influenced by high primary productivity. Therefore, these values may not represent a global phenomenon. The second potential reason, although unlikely, is the wrong placement of these two formations in the Shennongjia sequence. First, the section containing
these two formations is located a long distance (~30 km) away from the three sections investigated here, and the correlation is not well established. Thirdly, the chronological constraint on these two formations is the youngest detrital zircon from the Dayanping Formation, ca. 1398 ± 20 Ma (Li et al., 2013). Thus, the actual age may be much younger than this. In order to differentiate these two possibilities, it is necessary to refine the chronological age and sedimentary environment of these two formations.

The middle period includes the lower part of the upper Shennongjia subgroup from the uppermost Taizi to the upper Wenshuihe formations, which contains the most distinctive $\delta^{13}C_{\text{carb}}$ chemostratigraphy of the Shennongjia Group. In this period, the $\delta^{13}C_{\text{carb}}$ experienced a gradual positive shift from $+2$ to $+5\%_o$ (Fig. 8). This positive shift is constrained to ca. 1200 Ma based on the zircon U-Pb age of bentonite deposits cropping out in the lower Yemahe Formation (Li et al., 2013). The highest $\delta^{13}C_{\text{carb}}$ values observed in the middle Wenshuihe Formation, around $+5\%_o$, are similar to that reported in the contemporaneous strata (~1200 Ma), e.g., the Bass Formation in the Grand Canyon Supergroup, USA (Lathrop, 2018), the Raipur Group in the Chattisgarh basin (Patranabis-Deb et al., 2016) and the Lakheri limestone in the Vindhyan basin, India (Gilleaudeau et al., 2018).

The youngest period covers the uppermost Wenshuihe and the Shicaohe formations, in which the high $\delta^{13}C_{\text{carb}}$ values observed in the Wenshuihe Formation decline back to $–1\%_o$ (Fig. 8). The negative shift is constrained to ca. 1150 Ma (Li et al., 2013; Wang et al., 2013; Du et al., 2015). A similar negative shift has been observed in other locations, although the magnitude is larger than the one observed here (see below for details, Azmy et al., 2001; Bartley et al., 2007; Lathrop, 2018).

In order to refine the $\delta^{13}C_{\text{carb}}$ chemostratigraphy characteristics of the transition from early to late Mesoproterozoic, in addition to the new data presented in this study, we compiled all the published $\delta^{13}C_{\text{carb}}$ data from twenty worldwide sedimentary sequences, covering most of the Mesoproterozoic continental blocks (Fig. 9, see Supplementary materials for the sections and $\delta^{13}C_{\text{carb}}$ Data; Table S3). Meanwhile, these data were grouped into 12 time slices from 1600 to 1000 Ma, each of which covered 50 million years.
Fig. 9 Integrated $\delta^{13}$C$_{\text{carb}}$ chemostratigraphy of the Mesoproterozoic. (A) The Box-and-Whisker plot of the Mesoproterozoic $\delta^{13}$C$_{\text{carb}}$ in 12 time slices; and (B-C) Histogram distributions of the $\delta^{13}$C$_{\text{carb}}$ in each time slice. B: late Mesoproterozoic, C: early Mesoproterozoic; (D) Temporal variation characteristics of the $\delta^{13}$C$_{\text{carb}}$ in the Mesoproterozoic. See the supplementary information for data sources. Light gray shaded areas correspond to $2\sigma$ bootstrapped error on the LOWESS regression (solid black line) with spans of 9.5%.

The binary division of the Mesoproterozoic $\delta^{13}$C$_{\text{carb}}$ is apparent (Fig. 9). Before 1300 Ma, with limited exception, all the $\delta^{13}$C$_{\text{carb}}$ values are located in the range from $-2$ to $+2\permil$ with an average of $+0.01 \pm 1.18\permil$ ($n = 1829$), providing vital support to previous observations (Buick et al., 2001).
The limited lower δ\textsuperscript{13}C\text{carb} values <–2‰, e.g., the Bangemall Group in northwestern Australia, could be caused by the oxidation and remineralization of organic matter during late and patchy dolomitization or also possibly by isotopic re-equilibration during metamorphism (Buick et al., 1995; Chu et al., 2007; Guo et al., 2013). Meanwhile, the limited higher δ\textsuperscript{13}C\text{carb} values >+2‰ were likely attributed to local conditions, for instances such as those high δ\textsuperscript{13}C\text{carb} values observed in the Yingwodong and Dayanping formations, which could be attributed to a restricted sedimentary basin with high primary productivity or evaporation (Buick et al., 1995). The statistical analysis of the δ\textsuperscript{13}C\text{carb} in binned age suggests that the average values of δ\textsuperscript{13}C\text{carb} are lower than 0‰ in the intervals from 1600 to 1500 Ma and from 1350 to 1300 Ma, which slightly increased to ~+0.5‰ in the interval from 1500 to 1350 Ma (Fig. 9A).

Between 1300 and 1000 Ma, the δ\textsuperscript{13}C\text{carb} values are >0‰, and they have an average of +1.11 ± 1.76‰ (n = 2651). These significantly deviate from the stable δ\textsuperscript{13}C values in the early Mesoproterozoic (Fig. 9B-C). The most intriguing trend is the gradual positive excursion in the interval from 1300 to 1200 Ma, in which the mean δ\textsuperscript{13}C\text{carb} values increase from –1 to +2‰ and the peak δ\textsuperscript{13}C\text{carb} reached as high as +6‰ around ~1200 Ma (Fig. 9D). This positive shift has been observed in India (Maheshwari et al., 2009; Patranabis-Deb et al., 2016), Siberia (Bartley et al., 2007), and Laurentia (Beeunas and Knauth, 1985; Moon, 2015; Lathrop, 2018). Therefore, such 13C-enriched carbonates also occur in the Yemahe and Wenshuihe formations of the Shennongjia Group (this work; Tian et al., 2018; Zou et al., 2019), thereby suggesting a possibly global phenomenon. In addition, some studies have proposed that the sharply δ\textsuperscript{13}C\text{carb} positive excursion up to +5‰ around 1200 Ma can be served as a marker for global stratigraphic correlation (Frank et al., 2003; Bartley et al., 2007; Lathrop, 2018; Silva-Tamayo et al., 2018; Paula-Santos et al., 2021) and consequently, these new observations from South China raise questions about the term ‘boring billion’ adopted for the Mesoproterozoic.

Following the peak values around 1200 Ma, the δ\textsuperscript{13}C\text{carb} experienced another negative shift (Fig. 9). In the interval from 1200 to 1000 Ma, the δ\textsuperscript{13}C\text{carb} values frequently vary from −2 to +4‰, along with higher mean values than in the early Mesoproterozoic. This negative shift
supports the assignment that the uppermost Shennongjia Group was deposited around ~1150 Ma. It is also interesting to note that substantially lower $\delta^{13}\text{C}_{\text{carb}}$ values $<-2\%_o$ are observed during the interval from ~1100 to 1050 Ma, in several worldwide localities such as in the Turukhansk Group in Siberia (Knoll et al., 1995; Bartley et al., 2001), Vazante Group in Brazil (Azmy et al., 2001; Misi et al., 2011), Bylot Supergroup in the Nunavut of Canada (Kah et al., 1999, 2001), and Atar/El Mreîti Group in West Africa (Kah et al., 2012; Gilleaudeau and Kah, 2013; Silva-Tamayo et al., 2018). The lowest values close to $-6\%_o$ are generally present in deep-water sedimentary environments and ascribed to the diagenetic oxidation and anaerobic remineralization of organic carbon (Gilleaudeau and Kah, 2013). Considering the higher $\delta^{13}\text{C}_{\text{carb}}$ values of coeval samples from shallow marine environments, varying from +2 to +4$\%_o$, it seems there was a large water-depth dependent $\delta^{13}\text{C}$ gradient in the late Mesoproterozoic. This is substantially different from the early Mesoproterozoic and Paleoproterozoic (Hotinski et al., 2004; Luo et al., 2014).

The temporal profile of the Mesoproterozoic $\delta^{13}\text{C}_{\text{carb}}$ shows that the magnitude of the variations was much more significant in the late Mesoproterozoic relative to the early Mesoproterozoic (Fig. 9). The limited variation magnitude of early Mesoproterozoic $\delta^{13}\text{C}_{\text{carb}}$ would be attributed to the large DIC reservoir size indicated by the high $p\text{CO}_2$ values, which buffered the fluctuations in $\delta^{13}\text{C}_{\text{carb}}$ (Kah et al., 2001; Kaufman and Xiao, 2003; Bartley and Kah, 2004). The increased magnitude of variation of $\delta^{13}\text{C}_{\text{carb}}$ in the late Mesoproterozoic would be related to the decrease in $p\text{CO}_2$ revealed by multiple proxies, e.g., calcified cyanobacteria fossils observed in some late Mesoproterozoic formations (Sheldon, 2006; Kah and Riding, 2007; Sheldon et al., 2021). This is also supported by the larger water-depth dependent $\delta^{13}\text{C}_{\text{carb}}$ gradient in the late Mesoproterozoic relative to the late Paleoproterozoic and early Mesoproterozoic (Hotinski et al., 2004; Luo et al., 2014).

5.3. Types of organic matter

Organic matter in marine sedimentary rocks comprises the autochthonous organic matter sourced from organisms living in the seawater and the heterochnhonous organic matter input from continents by rivers, glaciers, and wind. The latter mainly consists of biospheric organic
matter from terrestrial biomes since the colonization of the continents and detrital organic matter
(this study will use) or petrogenic organic matter released during the continental weathering (e.g.,
Jiang et al., 2012; Johnston et al., 2012, Galy et al., 2015 and references therein). For example, it
has been a well-known phenomenon that detrital organic matter including both kerogen and
graphitic carbon, can be redeposited in marine sediments through erosion and riverine
transportation (Sackett et al., 1974; Dickens et al., 2004; Sparkes et al., 2020). Based on the
survey of 70 globally distributed rivers, it has been estimated that the flux of riverine detrital
organic carbon to the oceans would be $43 \times 10^6$ tons/y (Galy et al., 2015). If no marine sediments
and organic matter are involved during deposition, this flux will yield a marine sediment TOC of
0.22 wt.% in consideration of the total sediment discharge of $19,000 \times 10^6$ tons/y (Milliman and
Farnsworth, 2013). This is much higher than the amounts of detrital carbon recycled, which was
estimated to be 0.01 to 0.1 wt.% (Canfield et al., 2021). The fraction of detrital organic matter in
the Precambrian might be higher than today’s as the $pO_2$ was much lower than the present
(Canfield, 2021; Krissansen-Totton et al., 2021).

It is challenging to identify the detrital organic matter in deep time sedimentary rocks,
except for particular organic matter types such as graphite and charcoal. Raman spectral
parameters, i.e., widths and intensities of peaks and the intensity ratio of $I_{-1350}/I_{-1600}$, would be
a valuable tool to differentiate the types of organic matter in Proterozoic samples (Qu et al., 2017;
Canfield et al., 2021; Cañadas et al., 2022). In the Shennongjia Group, both the widths and
intensities of the peaks have a significant variation range. Specifically, the FWHM-D1 ranges
from 58 cm$^{-1}$ to 110 cm$^{-1}$, and the $I_{-1350}/I_{-1600}$ values change from 0.71 to 1.71 (Table S2).
Since a close positive relationship is observed between the $I_{-1350}/I_{-1600}$ and the FWHM-D1
values ($r = 0.76, n = 162$), the following discussion will focus on the $I_{-1350}/I_{-1600}$.

Intriguingly, a close relationship is observed between the $I_{-1350}/I_{-1600}$ and the TOC
contents (Fig. 7B, 10A). Generally, the $I_{-1350}/I_{-1600}$ values of the TOC-lean samples (<0.1%)
are higher and have a more extensive variation range than those of high TOC samples (>0.1%).
For example, for the 16 samples with TOC <0.1 wt.%, the $I_{-1350}/I_{-1600}$ ratio ranges from 0.7 to
1.7 with an average of $1.2 \pm 0.2$ ($n = 112$), whereas for the 6 samples having TOC >0.1 wt.% it is
typically lower than 1.0 and center on 0.82 ± 0.1 (n = 50, Fig. 7B). In addition, a significant positive relationship is present between the \( I\text{-1350}/I\text{-1600} \) and the \( \delta^{13}\text{C}_{\text{org}} \) values (Fig. 7B, 10B). Meanwhile, the samples with higher \( I\text{-1350}/I\text{-1600} \) values generally also have a larger variation range in \( \delta^{13}\text{C}_{\text{org}} \) (Fig. 7B).

Since the variations in \( I\text{-1350}/I\text{-1600} \) values are not depth-dependent, it is unlikely that the distinct differences were caused by different burial depths of the Shennongjia Group. Although we still have a lot to learn about the factors affecting the Raman signatures, the close relationships between the TOC and \( I\text{-1350}/I\text{-1600} \) values suggest that the factor has much more impact on TOC-lean samples. A reasonable interpretation for these Raman spectral parameters is the involvement of detrital organic matter. The detrital organic matter sourced from erosion from orogens could experience higher metamorphic temperature compared with the autochthonous organic matter. In other words, the detrital organic matter is generally aged and thermodynamic stable. It has a higher degree of structural order and higher \( I\text{-1350}/I\text{-1600} \) values than the autochthonous organic matter. The fraction of detrital organic matter in low TOC samples would be much higher than in high TOC samples. Thus, the low TOC samples could have a higher mean \( I\text{-1350}/I\text{-1600} \) value and a more extensive variation range as they are more susceptible to detrital organic matter relative to the high TOC samples (Fig. 10). Meanwhile, this can also interpret the more extensive variation range observed in TOC-lean samples compared with the high TOC samples, as the fraction of detrital organic matter in the former would be higher and more variable than that of the latter. Therefore, the Raman spectral characteristics suggest that a fraction of the organic matter in the Shennongjia samples might be detrital.

The presence of detrital organic carbon in marine sediments may be attributed to the low \( \rho O_2 \) during that time. The oxygen dependence of organic weathering suggests that the oxidative weathering flux of organic matters would be small in the Mesoproterozoic (Krissansen-Totton et al., 2021), which is consistent with the inferred high \( \delta^{13}\text{C}_{\text{in}} \) value, i.e., −1.8‰, in the Mesoproterozoic based on a simple box model (Luo et al., 2014). Therefore, it is likely that detrital organic matter is present in Precambrian marine sedimentary rock. By contrast, the absence of graphitic carbon would be ascribed to its low concentration as multiple studies have
demonstrated that the graphitic carbon only accounts for a small fraction of the detrital organic carbon, 0.01 to 0.1 wt.% vs. 0.22 wt.%. Thus, attention should be paid when applying the weathering model of organic matter to reconstruct the \( pO_2 \) in deep time (Canfield et al., 2021).

### 5.4. Factors affecting the \( \delta^{13}C_{org} \)

The carbon isotope composition of dissolved inorganic carbon (DIC, \( \delta^{13}C_{DIC} \)) is a principal factor affecting the \( \delta^{13}C_{org} \) value. As sourced from the same DIC pool, the \( \delta^{13}C_{org} \) theoretically should have similar variation trends in \( \delta^{13}C_{carb} \) with an offset determined by the carbon isotope fractionation occurring during the carbon fixation (Hayes et al., 1999). Although co-variation has been observed in some stratigraphic intervals, e.g., the Yemahe and Wenshuihe formations (Fig. 4), the positive correlation between the \( \delta^{13}C_{org} \) and \( \delta^{13}C_{carb} \) is not a primary characteristic for the Shennongjia Group investigated here (Fig. 5F). Generally, the \( \delta^{13}C_{org} \) has a larger variation range relative to the \( \delta^{13}C_{carb} \), particularly for the samples with low TOC contents in the Shennongjia Group. For example, the \( \delta^{13}C_{carb} \) values center on \(-1.2 \pm 0.4\%\) (\( n = 68 \)) in the Luanshigou Formation, whereas the paired \( \delta^{13}C_{org} \) values range from \(-23.4 \) to \(-29.1\%\) with an average of \(-26.3 \pm 1.4\%\) (\( n = 62 \)) (Fig. 4A). These suggest that some other factors might influence the \( \delta^{13}C_{org} \) values of the samples in the Shennongjia Group.

It is well known that, in addition to the \( \delta^{13}C_{DIC} \), many other factors also have substantial impacts on the \( \delta^{13}C_{org} \) value, such as the microbial composition and growth rate of primary productivity (e.g., Hayes et al., 1999). For example, cyanobacteria, which were the main primary producers in Precambrian oceans, generally have a larger carbon isotope fractionation value compared with green sulfur bacteria (e.g., Summons and Powell, 1986). The \( \delta^{13}C_{org} \) of the organic matter in the ecosystem dominated by cyanobacteria would be much lower than that of the ecosystem dominated by green sulfur bacteria if the \( \delta^{13}C_{DIC} \) values were the same. The samples analyzed here are dominated by stromatolitic microbialite, which is a complex ecosystem characterized by versatile biogeochemical cycles (Houghton et al., 2014). Due to the low temporal resolution of the samples analyzed here, discrete biogeochemical processes could not be differentiated. It is very likely that cyanobacteria would be the predominant autotrophs and the primary source of organic matter, although anoxygenic photoautotrophic microbes might
be present in the lower part of the microbial mat. As all the cyanobacteria have similar carbon isotope fractionation, it requires further investigation whether the changes in cyanobacteria compositions, as well as the geological and geochemical evidence for these changes, could induce the frequent variations in \( \delta^{13}\text{C}_{\text{org}} \) observed in this study.

The growth rate of microbial mats could be another factor affecting the \( \delta^{13}\text{C}_{\text{org}} \) value (Popp et al., 1989). During high growth rates, dissolved CO\(_2\) might be a limiting factor, which could dramatically decrease the carbon isotope fractionation and, consequently, elevate the \( \delta^{13}\text{C}_{\text{org}} \) value. This case has been widely observed in microbial mats, particularly those developed in hypersaline environments (see Schouten et al., 2001 and references therein). In contrast, this factor could be insignificant during low growth rates. The relatively constant \( \delta^{13}\text{C}_{\text{carb}} \) values suggest that this factor cannot reliably be used to infer the frequent variation in \( \delta^{13}\text{C}_{\text{org}} \) observed across short stratigraphic intervals of the Shennongjia Group.

The other possibility accounting for the extensive variation range of \( \delta^{13}\text{C}_{\text{org}} \) would be the inclusion of detrital organic matter. As discussed above, the Raman spectral characteristics observed in the Shennongjia Group suggest that part of the organic matter might be detrital (see part 5.3). As the carbon isotope composition of the detrital organic matter usually is different from that of the authigenic organic matter, the involvement of the detrital organic carbon could significantly impact the \( \delta^{13}\text{C}_{\text{org}} \) values of bulk organic carbon. This impact would be more distinct for organic-lean samples since the fraction of detrital organic carbon could be higher and more variable compared with the high TOC samples. This is consistent with the observation in the Shennongjia Group that the large variation range of \( \delta^{13}\text{C}_{\text{org}} \) is mainly observed in low TOC samples, such as the Luanshigou Formation (Fig. 4). For example, for the samples with TOC contents <0.1 wt.%, the \( \delta^{13}\text{C}_{\text{org}} \) values range from −24 to −30‰ with an average of −27‰, whereas those with TOC >0.1%, the \( \delta^{13}\text{C}_{\text{org}} \) values are generally lower than −29‰.

Intriguingly, a positive correlation is observed between the \( \delta^{13}\text{C}_{\text{org}} \) and \( I\text{-1350}/I\text{-1600} \), as well as between the \( \delta^{13}\text{C}_{\text{org}} \) and FWHM-D1 (Fig. 10). This suggests that the detrital organic matter has higher \( \delta^{13}\text{C} \) values compared with authigenic organic matter. This may reflect higher \( \delta^{13}\text{C}_{\text{org}} \) values generally observed in TOC-low samples as they typically contain a higher fraction
of detrital organic matter compared with the TOC-high samples (Fig. 7B). It is reasonable as the detrital organic matter is generally aged and thermodynamically more stable (Des Marais, 2001; Johnston et al., 2012).

Fig. 10 Cross plots between the I-1350/I-1600 and TOC contents (A) and δ\textsuperscript{13}C\textsubscript{org} values (B), and between the metamorphic temperatures reconstructed from FWHM-D1 and TOC contents (C) and δ\textsuperscript{13}C\textsubscript{org} values (D), respectively.

5.5. Characteristics of the carbon cycle in the late Mesoproterozoic

The acquisition of the paired δ\textsuperscript{13}C\textsubscript{carb} and δ\textsuperscript{13}C\textsubscript{org} data allows unraveling some essential characteristics of the carbon cycle in the late Mesoproterozoic. As the δ\textsuperscript{13}C\textsubscript{org} values might be affected by detrital organic matter, we reconstructed the parameters of the carbon cycle, i.e., the Δ\textsuperscript{13}C\textsubscript{carb-org} and f\textsubscript{org}, for two different scenarios. Scenario 1 considers that all the organic matter is authigenic and included all the δ\textsuperscript{13}C\textsubscript{org} data in the reconstruction, whereas Scenario 2 considers the possible effects of the detrital organic matter and screened the δ\textsuperscript{13}C\textsubscript{org} data (see below for details). The results of the two scenarios are displayed in Fig. 11. Generally, the reconstructed two parameters have very similar temporal variation trends. Specifically, the Δ\textsuperscript{13}C\textsubscript{carb-org} values of
Scenario 1 are about 2‰ lower than those of Scenario 2, while the $f_{org}$ values of Scenario 1 are generally higher than those of Scenario 2. It is worth noting that the $f_{org}$ of Scenario 1 reached as high as 35% in the upper Wenshuihe Formation, about 1200 Ma, which coincided with the highest $\delta^{13}$C$_{\text{carb}}$ values. It has to be pointed out that the reconstruction of the $f_{org}$ assumes the $\delta^{13}$C$_{\text{in}}$ was −5‰. If the $p$O$_2$-dependent weathering dynamic of organic matter is considered, the $\delta^{13}$C$_{\text{in}}$ could be higher than −5‰ in late Mesoproterozoic, and the $f_{org}$ could be lower than that reconstructed here (Krissansen-Totton et al., 2021). Below we mainly discuss the primary characteristics of these two parameters of Scenario 2.

For statistical analysis, the study Shennongjia Group is divided into intervals according to the resolution of the carbon isotope data. Generally, each interval in the lower Shennongjia subgroup and Taizi Formation is ~50 m, whereas the upper Shennongjia subgroup is ~200 m. For the $\delta^{13}$C$_{\text{carb}}$, the average value of each interval is used. For the $\delta^{13}$C$_{\text{org}}$, we first screened the data with a protocol similar to that used in Liu et al. (2021). As discussed above, it is likely that the $\delta^{13}$C$_{\text{org}}$ of the detrital organic matter was higher than that of the authigenic organic matter. We chose the lowermost 10% of each strata interval as the best approximation of the $\delta^{13}$C$_{\text{org}}$ of authigenic organic carbon. Then, the average of the screened $\delta^{13}$C$_{\text{org}}$ was used to reconstruct the carbon cycle.

The filtered $\delta^{13}$C$_{\text{org}}$ values are generally located in the range from −27 to −31‰ with limited exceptions down to −32‰ in the uppermost Taizi Formation (Fig. 11B). Temporally, the $\delta^{13}$C$_{\text{org}}$ decreases gradually from −28‰ in the Luanshi Formation to −30‰ in the uppermost Taizi Formation, which then increases back to −28‰ in the Shicaohe Formation. The corresponding $\Delta^{13}$C$_{\text{carb-org}}$ values are generally located from 26 to 31‰ with an average of 28.6 ± 1.9‰ ($n = 49$), which are much larger than that based on original bulk $\delta^{13}$C$_{\text{org}}$ data (Fig. 11C). Specifically, the $\Delta^{13}$C$_{\text{carb-org}}$ experienced a gradual increase from the middle Luanshi Formation to the uppermost Taizi Formation, in which the $\Delta^{13}$C$_{\text{carb-org}}$ increased from 26 to 31‰ (Fig. 11C). Upwards, the $\Delta^{13}$C$_{\text{carb-org}}$ varies around 30‰ in the Yemahe and Wenshuihe formations, whereas the $\Delta^{13}$C$_{\text{carb-org}}$ values of the Shicaohe Formation are generally <29‰. It is clear that the $\Delta^{13}$C$_{\text{carb-org}}$ values of the late Mesoproterozoic are greater than that in typical modern marine
environments, which is about 25‰ (Bidigare et al., 1997; Pagani et al., 1999; Kump and Arthur, 1999). This would be ascribed to higher $p$CO$_2$ in the late Mesoproterozoic indicated by the calcified cyanobacterial fossils and paleosol records (Sheldon, 2006; Kah and Riding, 2007).

Combining the filtered $\delta^{13}$C$_{org}$ data and a simple box model of the carbon cycle, we reconstructed the temporal variations of the $f_{org}$ in the interval from ca. 1340 to 1150 Ma (Fig. 11D). Generally, the $f_{org}$ can be divided into three periods: the lower Shennongjia subgroup (ca. 1340 to 1250 Ma), the Wenshuihe and Yemahe formations (ca. 1250 to 1190 Ma), and the Shicaohe Formation (ca. 1190 to 1150 Ma).

The $f_{org}$ values are typically lower than 20% in the first and third periods, which is the modern value of the fraction of organic carbon burial. In the first period, the $f_{org}$ displays a gradual increase from 13% to 17% with some brief increases to >20% in the Kuangshishan Formation, whereas in the third period, the $f_{org}$ experienced a gradual decline (Fig. 11D). The low $f_{org}$ values in these two periods are very similar to that in the early Mesoproterozoic (Guo et al., 2013; Luo et al., 2014; Krissansen-Totton et al., 2015; Canfield et al., 2020), which could be attributed to low primary productivity (Brasier and Lindsay, 1998; Anbar and Knoll, 2002; Reinhard et al., 2013; Crockford et al., 2018). For example, based on the triple oxygen isotope composition of sedimentary sulfate, the primary productivity of the early Mesoproterozoic was estimated to be 6 to 41% of pre-anthropogenic levels (Crockford et al., 2018). The other factor for the low $f_{org}$ would be the low preservation efficiency of organic matter (Logan et al., 1995).

The primary producers of early Mesoproterozoic and older oceans were likely dominated by bacteria, such as cyanobacteria (Brocks et al., 2005, 2017; Flannery and George, 2014; Luo et al., 2015; Isson et al., 2018; Gueneli et al., 2018). This is supported by the occurrence of abundant and morphologically diverse microbial mats and stromatolites observed in the Shennongjia Group, e.g., the Kuangshishan and Dawokeng formations. Relative to eukaryotes, bacterial organisms are much smaller in size, however. Therefore, the residence time of this organic matter is much longer than that of eukaryotic organic matter, and much of it would be remineralized in the water column, inducing low $f_{org}$ (e.g., Butterfield, 2009; Lenton et al., 2014).
Fig. 11 Characteristics of the carbon cycle in the late Mesoproterozoic reconstructed from δ¹³C_carb and δ¹³C_org. A: Integrated δ¹³C_carb chemostratigraphy of the Shennongjia Group. B: Bulk δ¹³C_org data (grey circles) and statistically processed δ¹³C_org data. C-D: Calculated Δ¹³C_carb-org and
$f_{org}$ values according to the bulk (grey) and averaged (squares) $\delta^{13}C_{\text{carb}}$ and $\delta^{13}C_{\text{org}}$. Red squares: averaged values of the specified intervals (50 m for each interval for the lower Shennongjia subgroup and Taizi Formation; whereas 200 m for each interval of the upper Shennongjia subgroup). Light blue square: averaged $\delta^{13}C_{org}$ values of screened $\delta^{13}C_{org}$ data in each specified interval according to the protocol described in the text. (E) Molecular-clock estimated range of early photosynthetic eukaryotes (Evanovich and Guerreiro, 2020) and organic-walled microfossils records of the late Mesoproterozoic. The distribution of microfossil assemblages was collected from the ~1350 Ma Xiamaling Formation (Miao et al., 2021), ~1350–1150 Ma Sarda and Avadh formations (Prasad and Asher, 2001), >1250 Ma Kamo Group (Nagovitsin, 2009), ~1300–1200 Ma Thule Supergroup (Samuelsson et al., 1999) and ~1100 Ma Atar/El Mreîti Group (Beghin et al., 2017). The lines denote the LOWESS regression with spans of 25%.

In contrast, the second period is characterized by higher $f_{org}$ values relative to the other two periods (Fig. 11D). Overall, the $f_{org}$ values of this period are clearly larger than the modern value and that of the early Mesoproterozoic (Hayes et al., 1999; Canfield et al., 2020). Specifically, the $f_{org}$ increased sharply from 17% to 25% in the uppermost Taizi Formation, followed by a slight decrease to ~20% in the middle and another increase back to ~25% at the end of this period. The high $f_{org}$ value in this period was likely attributed to enhanced primary productivity since evidence suggests that the microbial composition was still dominated by bacterial organisms (Blumenberg et al., 2012; Gueneli et al., 2018). The increased primary productivity would be caused by enhanced continental weathering related to the early amalgamation of the Rodinia supercontinent (Zhao et al., 2002, 2004; Roberts, 2013). Although the details require further investigation, this is supported by the unconformity surface observed at the base of the Taizi Formation. Enhanced continental weathering would elevate the P fluxing into the ocean, which has been supposed as a primary factor delaying the innovation and evolution of life in the early Mesoproterozoic ocean (Reinhard et al., 2017, 2020; Ozaki et al., 2019; Guilbaud et al., 2020; Chen et al., 2022).
The variation trends of \( f_{\text{org}} \) reconstructed here for the late Mesoproterozoic are consistent with the lower-temporal-resolution ones based on compiled \( \delta^{13}\text{C}_{\text{carb}} \) and \( \delta^{13}\text{C}_{\text{org}} \) data (Krissansen-Totton et al., 2015; Canfield et al., 2020). However, it has to be noted that the \( f_{\text{org}} \) values reconstructed of Scenario 2 are generally lower than that reported in Canfield et al. (2020, their Table 5 and Figure 8). This is mainly attributed to the \( \delta^{13}\text{C}_{\text{org}} \) data used in the previous calculation taken as the average of all samples without considering the impact of petrogenic organic matter, which would overestimate the \( f_{\text{org}} \).

5.6. Implications for coevolution of Earth-surface environment and biotic evolution in late Mesoproterozoic

The burial of organic carbon is closely related to the flux of \( \text{O}_2 \) released into the Earth’s surface environments. If we assume that the total \( \text{CO}_2 \) entering the Earth’s surface did not change substantially in the Mesoproterozoic (Hayes and Waldbauer, 2006), the variations in \( f_{\text{org}} \) can provide insights into the reconstruction of \( p\text{O}_2 \) in the late Mesoproterozoic. The low \( f_{\text{org}} \) values in the lower sequence of the Shennongjia Group suggest that flux \( \text{O}_2 \) released into the atmosphere was limited, which would be a typical phenomenon of the early Mesoproterozoic (Canfield et al., 2020). This is consistent with multiple lines of evidence indicating low oxygen contents in this period, e.g., non-fractionated Cr isotopes of black shales and ironstones (Planavsky et al., 2014; Cole et al., 2016), absence of Ce anomaly of carbonates (Tang et al., 2016; Liu et al., 2021), deficiency of redox-sensitive elements (Partin et al., 2013), the generally low \( I/(\text{Ca} + \text{Mg}) \) ratios of carbonate (Hardisty et al., 2017; Lu et al., 2018) and low oceanic sulfate concentration (Kah et al., 2004; Luo et al., 2015).

Intriguingly, the \( f_{\text{org}} \) increased significantly between \( ca. \) 1250 to 1190 Ma to \( f_{\text{org}} \) values much larger than the modern value. This suggests that the oxygen flux into the atmosphere would be, if not higher, similar to the modern case, which would consequently promote an increase in the \( p\text{O}_2 \). In the Shennongjia Group, for example, high \( \delta^{53}\text{Cr} \) values up to +1‰ and high \( \delta^{98}\text{Mo} \) values have been observed in the Taizi and Wenshuihe formation, respectively (Canfield et al., 2018; Ye et al., 2021), and significant negative Ce anomalies have been found in the Taizi and Wenshuihe formations (Canfield et al., 2018; Zou et al., 2019; Li et al., unpublished data). In addition,
widespread occurrence of laminated gypsum evaporite (up to 150 cm thick) has been observed in the Bylot Supergroup in Society Cliffs platform, as well as in the Atar Group in Mauritania, suggesting that marine sulfate concentrations substantially increased from <1 mM in the early Mesoproterozoic to >2.5 mM in the late Mesoproterozoic (Kah et al., 2001; Manning-Berg, 2014). This is supported by the variation rate of the sulfur isotope composition of carbonate-associated sulfate, which suggests that seawater sulfate concentration was as high as 4.5 mM at ca. 1200 Ma (Kah et al., 2004).

The substantial increase in $pO_2$ in the early part of the late Mesoproterozoic might have promoted the evolution of eukaryotes. It has been proposed that the early development of eukaryotes was slow (Knoll et al., 2006; Huntley et al., 2006; Cohen and Macdonald, 2015; Riedman and Sadler, 2018). For example, the origin of eukaryotes occurred at least in the latest Paleoproterozoic ca. 1.65 Ga (Yin et al., 2005; Knoll et al., 2006; Lamb et al., 2009; Peng et al., 2009; Agić et al., 2015, 2017; Javaux and Lepot, 2018; Miao et al., 2019), and possibly earlier. However, convincing multicellular eukaryotes appeared in the late Mesoproterozoic, about 600 million years later (Butterfield, 2001; Tang et al., 2020; Strother and Wellman, 2021). The slow evolution of eukaryotes was mainly attributed to low $pO_2$ (Anbar and Knoll, 2002; Planavsky et al., 2014; Lyons et al., 2014; Lenton et al., 2014; Cole et al., 2016; Tang et al., 2016). Therefore, the increase in $pO_2$ in the early of the late Mesoproterozoic could have triggered a diversification of eukaryotic life, which is supported by recent discoveries. First, phylogenetic investigations estimate that the emergence of Rhodophyta and Chlorophyta occurred between 1242–1061 Ma and between 1203 to 984 Ma, respectively (Fig. 11E, Yoon et al., 2004, 2010; Parfrey et al., 2011; Yang et al., 2016; Sanchez-Baracaldo et al., 2017; Evanovitch and Guerreiro, 2020; Strassert et al., 2021). Second, different types of multicellular eukaryotic fossils have been discovered in the latest Mesoproterozoic, including the Bangiomorpha pubescens at ca. 1050 Ma, which is supposed to be the crown group of red algae (Gibson et al., 2017), the Proterocladus antiquus at ca. 1000 Ma which represents the earliest green algae (Tang et al., 2020), and the possible fungi fossil at ca. 1010-890 Ma (Loron et al., 2019). These fossils records suggest that their origin would be much earlier, which might be related to the oxygenation events, at least
episodic, that occurred in the late Mesoproterozoic. However, it has to be noted that the marine ecosystem was still dominated by prokaryotes, whereas the abundance of eukaryotes was very limited (Brocks et al., 2017; Gueneli et al., 2018). This indicates that other factors might also substantially impact the evolution of marine eukaryotes, e.g., concentrations of enzyme-related trace metals (Anbar and Knoll, 2002).

6. Conclusions

Carbon isotope compositions of paired carbonate and organic matter ($\delta^{13}C_{\text{carb}}$ and $\delta^{13}C_{\text{org}}$) of the Shennongjia Group (~1340–1150 Ma) in South China were systematically analyzed. Based on these data, we reconstructed the $\delta^{13}C_{\text{carb}}$ chemostratigraphy of the Mesoproterozoic, investigated the characteristics of the carbon cycle and Earth’s surface environment in the late Mesoproterozoic. Similar to the early Mesoproterozoic, the early period of late Mesoproterozoic (>1250 Ma) is characterized by low and stable $\delta^{13}C_{\text{carb}}$ values ranging from ~−1‰ to +2‰. A substantial increase in $\delta^{13}C_{\text{carb}}$ is observed in the interval from ca. 1250 to 1190 Ma, with the largest value to >+5‰ at ca. 1200 Ma. In the late Mesoproterozoic, the $\delta^{13}C_{\text{carb}}$ declined to ~−2‰. The paired $\delta^{13}C_{\text{org}}$ values show much more scatter, from ~−22 to ~−32‰, in the Shennongjia Group.

Raman spectral data demonstrated that the organic matter in the Shennongjia Group has a wide range of thermal maturity, recorded by the $I_{-1350}/I_{-1600}$ and FWHM-D1. Generally, the fossil organic matter and the organic matter sourced from possible microbial mats have lower thermal maturity than the average value. Meanwhile, close relationships are observed between the Raman parameters, $I_{-1350}/I_{-1600}$ and FWHM-D1, and TOC contents and $\delta^{13}C_{\text{org}}$. These characteristics suggest that detrital organic matter might be present in the samples of the Shennongjia Group, and its carbon isotope composition could be higher than the authigenic organic matter. The involvement of the detrital organic matter might have a substantial impact on the $\delta^{13}C_{\text{org}}$ of TOC-low samples.

The reconstructed $\Delta^{13}C_{\text{carb-org}}$ and $f_{\text{org}}$ values of the two different scenarios show similar temporal trends. The $\Delta^{13}C_{\text{carb-org}}$ values are generally larger than the modern counterpart, which
could be attributed to higher $p$CO$_2$. Based on a simple box model, with a limited exception in upmost Taizi, Yemahe, and Wenshuihe formations, the calculated $f_{\text{org}}$ of the Shennongjia Group is generally lower than 20%. However, it is worth noting that the $f_{\text{org}}$ experienced a substantial increase in ca. 1250 to 1190 Ma, suggesting enhanced oxidation of surface environments, which might have paved the way for the origin and early evolution of multicellular eukaryotes.

**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.

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**Reference**


cycle informs interpretations of Mesoproterozoic Era phosphorus dynamics. Earth-Science Reviews 208, 103267.


Krissansen-Totton, J., Kipp, M.A., Catling, D.C., 2021. Carbon cycle inverse modeling suggests large changes in fractional organic burial are consistent with the carbon isotope record and may have contributed to the rise of oxygen. Geobiology 19(4), 342–363.


Geology Review 51(5), 456–472.
Paleoproterozoic Hutuo Supergroup, North China Craton. Precambrian Research 337, 105549.


