Oldest-known Neoproterozoic carbon isotope excursion: Earlier onset of Neoproterozoic carbon cycle volatility

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Abstract

The Neoproterozoic Era (1000–541 Ma) is characterized by the largest negative carbon isotope excursions in Earth history. Younger Neoproterozoic excursions are well-documented on multiple continental margins and associated with major events including snowball Earth glaciations, ocean-atmosphere oxygenation, and the evolution of animal multicellularity. However, due to a large gap in carbon isotopes before 900 Ma, the onset of early Neoproterozoic carbon cycle volatility has heretofore been obscure. Here, we present a mid-amplitude, negative carbon isotope excursion with δ13C values reaching a nadir of −6‰ from the Majiatun Formation in the Dalian Basin of the North China Craton dated between 950 and 920 Ma. The whole-rock 87Sr/86Sr ratios of limestone and dolostone are as low as ~0.7055, which is compatible with the Tonian age of the global carbonate curve. Identification of the Majiatun anomaly thus fills the critical gap in carbon isotopes and implies the onset of Neoproterozoic carbon cycle volatility ~130 m.y. earlier than previously thought. Now 5 negative carbon isotope excursions occur with increasing amplitude throughout Neoproterozoic time, implying deeper roots for the biogeochemical processes that may have causally led to late Neoproterozoic snowball glaciation, oxygenation, and biological innovation.

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1. Introduction

The Neoproterozoic Era (1000–541 Ma) is one of the most dynamic intervals of global change in Earth history, with large and episodic perturbations to the carbon cycle (Cox et al., 2016), severe snowball Earth glaciations (Hoffman et al., 2017), and the rise of atmospheric oxygen and large Metazoa (Lyons et al., 2014). The Neoproterozoic carbon isotope excursions are the most negative anomalies recorded in Earth history (Grotzinger et al., 2011; Rose et al., 2012) and are intimately linked with the notable events occurring in the cryosphere, ocean-atmosphere, and biosphere at this time. Practically, the isotopic anomalies diagnostic of the era are also one of the chief ways that Neoproterozoic stratigraphic sequences in basins of different continental margins are correlated (Cox et al., 2016). Establishing a complete Neoproterozoic carbon isotope record would thus benefit stratigraphic correlations as well as efforts to better understand the roots of the late Neoproterozoic dramatic environmental changes. Defining exactly when in early Neoproterozoic time the start of carbon isotope fluctuations began is thus critical in order to establish the temporal origins of early Neoproterozoic biogeochemical processes that preceded the profound late Neoproterozoic environmental changes.

Here we focus on the carbon isotope chemostratigraphy of earliest Neoproterozoic time (the Tonian Period, 1000–720 Ma). An accurate understanding of marine carbon biogeochemical cycles and global correlations of Tonian strata is difficult due to both generally limited stratigraphic preservation and age constraints. In the Tonian δ13C compilation, there are few records between 1000 and 900 Ma (Cox et al., 2016). Thus, except for the well-constrained ca. 811 Ma Bitter Springs anomaly (Maloof et al., 2006) and the ca. 735 Ma Islay anomaly (Macdonald et al., 2010) during the later Tonian, any indication of putative δ13C excursions with reliable early Tonian age constraints is lacking.
Our study of the Dalian Basin of North China spanning ca. 1000–920 Ma (Yang et al., 2012; Zhang et al., 2016; Zhao et al., 2019) therefore fills a critical gap in the Tonian δ13C record and constrains the initiation of Neoproterozoic carbon cycle volatility.

2. Geological setting and studied sections

2.1. Paleogeographic setting

The North China Craton (NCC) was formed by the amalgamation of two blocks between ca. 1.95–1.8 Ga, followed by a long history of deposition from ca. 1.8 Ga to ca. 250 Ma (Zhai and Santosh, 2011; Zhao et al., 2005). Throughout Proterozoic time, the sedimentary depocenter migrated from the southern margin of NCC (the Xiong'er rift system ca. 1.8–1.6 Ga (Cui et al., 2011; Zhao et al., 2002)) to the northern margin of NCC (the Yan-Liao rift system ca. 1.7–1.3 Ga (Gao et al., 2007; Zhang et al., 2015)), and then shifted again to the southeastern NCC margin (the Xuhuai rift system ca. 1.1–0.9 Ga (Peng et al., 2011a; Yang et al., 2012; Zhang et al., 2016)). On the southeastern margin of North China Craton, the ca. 1.1–0.9 Ga Xuhuai rift system covers an area of about 0.1 million km² with a maximum extent of about 1000 km and includes the Dalian Basin in the Liaodong Peninsula, the Pyongnam Basin in the central Korean Peninsula, the Xuhuai Basin in the Xuzhou-Huaibei (Xuhuai) area of the Jiangsu and Anhui Provinces, and possibly other basins along the southern margin of NCC (Peng et al., 2011a; Peng et al., 2011b) (Fig. 1). Within each of these basins, there is a Neoproterozoic sequence comprised of clastic sediments at the base and carbonates interlayered with clastic sedimentary rocks at the top.

The Dalian Basin is situated in the southern Liaoning Province (Liaodong Peninsula) of eastern NCC. Before offset of the Tan-Lu (Tanlu) fault took place in the Mesozoic with ~550 km of sinistral displacement (e.g., Xu et al. (1987)), the Dalian Basin was located in the southeastern part of NCC (Fig. 1). The basement of the basin consists of the Archean (ca. 3.8–3.2 Ga) Anshan Complex (e.g., Liu et al., 1992; Wu et al., 2008) and the Paleoproterozoic (ca. 2.2–1.9 Ga) Liaohe Group that were metamorphosed ca. 1.9–1.8 Ga (Li and Zhao, 2007; Zhao et al., 2005). The basement was overlain by the Neoproterozoic and Paleozoic–Cenozoic sedimentary and volcanic rocks (BGMRL, 1989). The Triassic Sulu continent-continent collision resulted in deformation and large scale folding in the region (Yang et al., 2011).

Fig. 1. (A) Geological map of China and Korea Peninsula highlighting North China Craton (NCC, blue). (B) Archean–Paleoproterozoic basement and Mesoproterozoic–Neoproterozoic cover of NCC (modified from Peng et al. (2011a)). (C) Simplified geological map of the early Neoproterozoic sedimentary rocks in the Liaodong Peninsula (Dalian and adjacent region, modified from BGMRL (1989)). Sampled sections are indicated (stars). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
Table 1
Sources of previously published data in Figs. 2 and 7.

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2.2. Study sections

The Neoproterozoic strata in the Dalian Basin are composed of three groups (in stratigraphic order): the Xihe, Wuxingshan, and Jinxian groups (BGMRL, 1989) (Fig. 2). The Xihe Group consists of sandstone, shale, and quartzite with some limestone interlayers of the Diaoyu, Nanfen, and Qiaotou formations. The Wuxingshan Group includes (in stratigraphic order) the siliciclastic Changlingzi Formation, the limestone-predominant Nanguanling Formation, and the dolostone-predominant Ganjingzi Formation. The Jinxian Group includes five formations (in stratigraphic order): the carbonate-dominated Yingchengzi, Shisanlitai, and Majiatun formations, the siliciclastic-dominated Cuijiatun Formation, and the dolostone-predominant Zhaotundatun Formation. The Xihe-Wuxingshan-Jinxian groups unconformably overlie the Yongning Formation, and are unconformably overlain by the poorly-dated Getun Formation and Dalinzi Formation, which both contain uncorroborated ichnofossils and small shelly fossils (Hong et al., 1991).

Our studied samples were collected from six sections in the Dalian and Jinzhou regions of the Dalian Basin of China (Fig. 1). The Yuanjiaogou section (39°29‘41.29″N, 121°36‘42.85″E) includes the Nanguanling and Ganjingzi formations. The Zhaotundatun section (39°24‘06.93″N, 121°31‘59.74″E) consists of the Ganjingzi, Yingchengzi (incomplete exposure), and Shisanlitai formations. The Zhaokanzi section (39°23‘09.04″N, 121°30‘20.67″E) includes the Yingchengzi, Shisanlitai, Majiatun, and Dalinzi formations. The Luhai section (39°17‘05.46″N, 121°41‘58.64″E) includes the Shisanlitai, Majiatun, Cuijiatun, and Xingmincun formations. The Luhai section (39°07‘01.65″N, 121°42‘18.21″E) includes the Cuijiatun and Xingmincun formations. The Xingmincun section (39°07‘35.69″N, 121°42‘36.78″E) is composed of the Xingmincun, Getun, and Dalinzi formations. The chem stratigraphy of six sections were spliced together to create a composite δ13C record using stratigraphic marker beds, lithology, and formational boundaries. Details of the general lithostratigraphic are shown in Fig. 2.

In the Wuxingshan Group, The Nanguanling Formation consists of thin-to-thick-bedded dark gray limestone in the lower part and thick-bedded limestone with interbedded molar tooth structures and stromatolites in the upper part (Fig. 3 A). The succeeding Ganjingzi Formation is up to 300 m in thickness and subdivided into three parts: thick-bedded gray stromatolitic dolostone with calcite dolostone in the lower part, thin-bedded dark gray dolostone in the middle part, and thick-bedded gray dolostone with stromatolitic dolostone in the upper part (Fig. 3 B).

In the Jinxian Group, The Yingchengzi Formation is separated from the underlying Ganjingzi Formation by micritic limestone. The ~110-m-thick Yingchengzi Formation consists of thick-bedded gray micritic and stromatolitic limestone in the lower part and silty limestone in the upper part (Fig. 3 D). The Shisanlitai Formation is ~100 m thick and marked by a red-colored sequence that consists of stromatolitic limestone interbedded with salt and gypsum pseudomorphs in the upper part of the Shisanlitai Formation (Fig. 3 E). The lower part of the Shisanlitai

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Fig. 2. Simplified stratigraphic column of the Neoproterozoic successions in the Dalian Basin (modified from BGMRL (1989)) with six studied sections shown in Fig. 1. U-Pb geochronologic and biological data are indicated next to the stratigraphic columns. The biology and sedimentary structure information are from: Hong et al. (1991); Kuang et al. (2011); Meng et al. (2006). See Table 1 for sources of previously published lithostratigraphic and geochronological data. (Detrital zircon in blue; diabase sill in red). By-badoleyte; DZ-detrital zircon; Zr-magnetic zircon. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
2.3. Age controls

U-Pb geochronology constrains the Xihe-Wuxingshan-Jinxian Groups of the Dalian Basin to have been deposited ca. 1050–924 Ma: the minimum depositional age of the sequence is constrained by the age of mafic sills (ca. 900 Ma; U-Pb on baddeleyite) (Zhang et al., 2016) intruding the uppermost formation; the maximum depositional age of the uppermost carbonate strata is constrained by the youngest detrital zircon (ca. 924 ± 25 Ma) (Yang et al., 2012); and the maximum depositional age of the sequence is constrained by the youngest detrital...
zircon (ca. 1056 ± 22 Ma) from the underlying Diaoyutai Formation (Yang et al., 2012) (Fig. 2). The Xihe-Wuxingshan-Jinxian Groups thus fill a critical gap in the Tonian δ13C record.

3. Samples and methods

In total, 162 samples from carbonate rocks were collected for stable isotope study from the six sections (Fig. 2). Samples of fresh carbonate were selected, i.e., those without late-stage cements, significant recrystallization, or vein intrusions. Petrographic images of the Majiatun Formation and surrounding units depict compositions of homogenous micritic limestone (>70% carbonate content) with little to no post-depositional alteration (Fig. 3 P–Q). For the element and isotope analyses, 10–20 g of sample fragments were rinsed 3 times with Milli-Q (MQ) water to remove clay minerals and any soluble salts. After drying, the samples were powdered into homogenized powders (~200 meshes) with either a microdrill or an agate mortar.

3.1. Carbon and oxygen stable isotopes

Carbon and oxygen isotope analyses of bulk carbonate samples were performed using a mass spectrometer (MAT 253 (Thermo Fisher Scientific)) with GasBench II system at Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS). Approximately 300 μg of

![Fig. 4. Measured 87Sr/86Sr values for samples of the Wuxingshan and Jinxian groups (left) and a cross-plot of 87Sr/86Sr and Mn/Sr (right).](image)

![Fig. 5. Cross-plots of geochemical measurements for the Wuxingshan and Jinxian groups. Cross-plots of δ13C (% VPDB) and δ18O (% VPDB) against elemental ratios (Mn/Sr, Fe/Sr, Mg/Ca) are used to evaluate diagenetic alteration and the lithologic dependence of isotopic values. Correlation coefficients of linear regressions (r² values) are indicated.](image)
sample powder was reacted with 100% phosphoric acid at 70°C within a 12 mL vial tube filled with He, and generated CO₂ gas was introduced into the mass spectrometer for measurement of isotopic composition. Precision and accuracy are monitored by running the NBS-19 standard. Isotopic data are expressed in units per mil (‰) relative to Vienna Pee Dee Belemnite (VPDB), and δ¹³C and δ¹⁸O were acquired simultaneously. All samples are measured relative to an internal gas standard, and then converted to the VPDB scale using the known composition of NBS-19 (δ¹³C = 1.95‰; δ¹⁸O = −2.20‰) following the correction method of Paul et al. (2007). The reproducibility of the measurements of the standard (n = 27) was 0.1‰ (1σ) for δ¹³C, and 0.2‰ (1σ) for δ¹⁸O.

3.2. Strontium isotopes

For Sr isotopic analysis, two simple principles were applied for elemental screening: low Mn/Sr mass ratio (in most cases ≤0.8) and high Sr concentration (in most cases, ≥300 μg/g for limestone and ≥80 μg/g for dolostone). The dissolution method for strontium isotope is according to Li et al. (2020). Firstly, approximately 100 mg of carbonate rock materials were first pre-leached with 4 mL of 1% acetic acid and ultra-pure water in order to remove the absorbed Sr contamination on mineral surfaces and from ion-exchange sites and clay minerals (Li et al., 2020). Then removing the supernatant, the remained samples were then dissolved in 3.0 mL of 1% acetic acid, and the leachate was dried and re-dissolved in 1.1 mL 2.5 M HCl and finally purified by a resin column filled with 2 mL of AG50W × 12 (200–400 mesh). The Sr isotopic measurements were performed on a Triton Plus TIMS at IGGCAS using a double Re filament. The whole procedure blank was lower than 200 pg for Sr. The mass fractionation of Sr was corrected using an exponential law with ⁸⁶Sr/⁸⁸Sr = 0.72469 + 0.000011 × 10⁻⁶n. The international standard sample NBS-987 was employed to evaluate instrument stability during the period of data collection. Repeated measurement of NBS987 yielded ⁸⁷Sr/⁸⁶Sr = 0.710254 ± 0.000011 (2σ), showing good agreement with the reported values (Li et al., 2015; Li et al., 2016).

3.3. Element concentrations

For major element analysis, ~50 mg rinsed dry powders were weighed and dissolved with 0.2 M HCl and then diluted before analysis. The element ratios of Mg/Ca, Mn/Sr, and Fe/Sr were analyzed using an IRIS Advantage Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) at IGGCAS. A certified reference material was measured after every 10 samples and analytical precision was <3% for analyzed elements.

4. Results

4.1. Carbon and oxygen isotopes

The composite δ¹³C record of the six sections is presented in Fig. 7 and the carbon isotope results are provided in Supplementary Table. Consistent δ¹³C values and patterns are observed between similar lithologic units from different sections. In the composite isotope stratigraphy, most of the stratigraphy yields slightly positive δ¹³C values, but in the Majiatun Formation δ¹³C values plunge sharply negative to at far as −5.7‰. This negative excursion in the Majiatun Formation is reproduced in two stratigraphic sections (Luhai and Zhaokanzi). The δ¹⁸O values are variable from −15‰ to 0‰. Generally, tendencies through the stratigraphy have δ¹⁸O increasing to its maximum value (~0‰) in the Ganjingzi Formation, reaching its lowest value (~−15‰) in the Cuijiatun Formation, and then returning back to typical values (~−6‰ to ~−10‰) in the Xingmuncin Formation.

4.2. Strontium isotopes and element concentrations

Strontium isotope compositions and element ratios are shown in Fig. 4 and Supplementary Table. Mn/Sr and Fe/Sr ratios vary from 0.05 to 13.10 and from 0.2 to 256.7, respectively. Mn/Sr ratios are generally below 8.0, with only one exception (13.1). Except two limestone samples in shale layers from the Cuijiatun Formation (106.5 and 114.7), one dolomitic limestone sample from the Nanguanling Formation (256.7), and one sample from the ShisanliTai Formation (52.7), Fe/Sr ratios are between 0.2 and 38.4. Samples display ⁸⁷Sr/⁸⁶Sr ratios between 0.7055 and 0.7288. The lowest bulk sample ⁸⁷Sr/⁸⁶Sr ratios from the best-preserved samples, based on the screening methods described above, define ranges of 0.7057–0.7058 in the Nanguanling Formation, 0.7061–0.7064 for dolostone in the Ganjingzi Formation, 0.7055–0.7060 in the Yingchengzi-ShisanliTai formations, and 0.7066–0.7067 in the Majiatun-Xingmuncin formations, with Mn/Sr ratios of 0–2.0.

5. Discussion

5.1. Diagenetic alteration

Carbon isotopic composition can be potentially altered by later geological processes (metamorphic materials, silicilastic grains, authigenic components, burial diagenesis, and/or meteoric diagenesis), especially in Precambrian strata with long and complicated geological histories (Derry, 2010; Kaufman and Knoll, 1995; Knauth and Kennedy, 2009; Schrag et al., 2013). The empirical element concentrations and isotope ratios can be used to identify the magnitude of diagenesis effects, e.g., Mn/Sr, Mg/Ca, Fe/Sr, and δ¹⁸O/δ¹³C (Banner, 1995; Brand and Veizer, 1980; Kaufman and Knoll, 1995). Enrichment in Fe and Mn and depletion in Sr for sedimentary carbonates are usually considered to be altered by post-depositional diagenesis (Brand and Veizer, 1980; Derry et al., 1992; Narbonne et al., 1994). Meteoric diagenesis can result in lowering δ¹³C or δ¹⁸O values, increasing the Mn/Sr (or Fe/Sr) ratio(s).

![Fig. 6. Cross-plots of δ¹⁸O (‰ VPDB) against δ¹³C (‰ VPDB) data for carbonates of the Wuxingshan-Jinxian groups. These m values mean slopes. Linear regression of all data shown yields weakly positive correlations in the Xingmuncin (r² value = 0.39) and ShisanliTai (r² value = 0.44) formations, and weakly negative correlations in the Cuijiatun (r² value = 0.01), Majiatun (r² value = 0.45), Yingchengzi (r² value = 0), Ganjingzi, (r² value = 0.23) and Nanguanling (r² value = 0.02), arguing against alteration as an explanation of isotopic variations. Inset shows an enlarged view of the Majiatun excursion, and their correlations are both weak and negative in the Luhai section (r² value = −0.41) and Zhaokanzi section (r² value = −0.11).]
and a strong linear correlation between these element and isotope values (Kaufman and Knoll, 1995). Samples with a Mn/Sr ratio < 10 and a Fe/Sr ratio < 40 generally indicate minimal diagenetic alteration of $\delta^{13}C$ signatures (Kaufman and Knoll, 1995; Veizer, 1983). In the Dalin Basin, most samples are characterized by Mn/Sr < 8 and Fe/Sr < 38 (Fig. 5). Cross-correlations between element ratios (Mn/Sr or Fe/Sr) and isotopic ratios ($\delta^{13}C$ or $\delta^{18}O$) are statistically weak ($r^2$ values << 0.6; Fig. 5). Only one plot ($\delta^{18}O$ vs. Mg/Ca) yields a significant $r^2$ value (0.63), as the $\delta^{18}O$ values of dolomite are obviously greater than those of calcite (Fig. 5), which show good agreement with isotopic fractionation between these two minerals (Zheng, 2011). Such element ratios and weak cross-correlations indicate our samples only experienced a minor degree of diagenetic alteration and can thus be taken to represent the composition of contemporaneous seawater.

Cross-plotting of $\delta^{13}C$ and $\delta^{18}O$ is also a useful test of diagenesis. Oxygen isotope compositions are sensitive to diagenesis owing to the high concentration of oxygen in diagenetic fluids, whereas carbon isotopic abundances commonly have relatively little influence by meteoric or hydrothermal fluids (Banner and Hanson, 1990; Kaufman and Knoll, 1995). In the studied samples, except for several samples in the Cuijiatun and Xingmincun formations dropping below even −11.5‰, most obtained $\delta^{18}O$ values range from 0‰ to −11.5‰ (Supplementary Table). Meteoric fluids containing dissolved inorganic carbon from oxidized organic matter can lead to decreases in $\delta^{13}C_{\text{org}}$, as well as $\delta^{18}O_{\text{org}}$, yielding a corresponding positive covariation between the two values (Kauth and Kennedy, 2009). A lack of $\delta^{13}C$ and $\delta^{18}O$ covariance in studied successions ($r^2$ values <0.6) further indicates reliable carbon isotopic compositions of depositional seawater in the Wuxingshan and Jinjiang groups (Fig. 6). It is also noteworthy that the C-O correlations in the Majiutan excursion are both weak and negative in the Luhai ($r^2$ value = 0.41) and Zhaokanzi ($r^2$ value = 0.11) sections (Fig. 6). The $\delta^{13}C$ excursion in the Majiutan Formation and data from other formations can exclude the possibility of diagenetic alteration and be interpreted as a primary oceanographic signal. We refer to this carbon isotope excursion, for the purposes of this paper, as the Majiutan anomaly, which is reproduced in two stratigraphic sections (Luhai and Zhaokanzi) (Fig. 7) and is consistent with limited previous data from the Majiutan Formation (Hua and Cao, 2004; Qiao et al., 1996).

5.2. Carbon isotope correlation across North China Craton and age calibration of the Majiutan anomaly

Previously published carbon isotope data from the Pyongnam Basin (North Korea) and the Xuhuai Basin (Jiangsu-Anhui Provinces), also from the North China Craton, can similarly be correlated and compared using sequence stratigraphy, paleontology, and intruding sills (Cao, 2000; Hong et al., 1991; Hong and Yang, 1992; Liu et al., 2005; Niu and Zhu, 2002; Peng et al., 2011a; Peng et al., 2011b; Tang et al., 2005; Yin et al., 2015; Zhang et al., 2010). This mid-amplitude excursion (~9‰) to values as negative as −6‰ has also been noticed in preliminary $\delta^{13}C$ profiles from these correlative strata across the North China Craton (Fig. 7). In the Xuhuai Basin, $\delta^{13}C$ variations shift from muted

Fig. 7. Composite early Tonian carbon isotope record of the North China Craton (right) and simplified stratigraphic sections through the Dalian-Xuhuai-Pyongnam basins (right) that are correlated on the basis of lithostratigraphy. Carbon isotope profiles are from the Wuxingshan-Jinxian Groups of Dalian Basin (from this study, Qiao et al. (1996), Hua and Cao (2004), and Kuang et al. (2011)) and inferred correlation between the Huaibei Group (Xuhuai Basin, Xiao et al. (2014)) and Sangwon Supergroup (Pyongnam Basin, Park et al. (2016)). See Supplementary Table for isotopic data and Table 1 for sources of previously published lithostratigraphic and geochronological data. In the correlation of these basins into a composite $\delta^{13}C$ record for North China Craton, original stratigraphic height data of the Xuhuai basin were modified by a stretching factor of 0.29 and a shift of +62 m for the Wangshan Formation and by a stretching factor of 0.29 and a shift of −85 m for the Shijia to Zhaowei formations based on Xiao et al. (2014). See more lithologic information of the Dalian basin sequence from Fig. 2.
positive values (±0% to +5.3‰) in the Zhaowei-Weiji formations to negative values (−1% to −3‰) in the Shijia Formation, and return back to positive values in the Wangshan Formation (0% to +5‰) (Xiao et al., 2014). In the Pyongnam Basin, the Sangwon Supergroup exhibits moderately positive δ13C values between −0.6‰ and +5.3‰, until reaching a nadir of −6‰ in the Okhyonri Formation of the Mukchon Group (Park et al., 2016). Identification of the Majiatun anomaly across the craton supports the correlation of these basins as well as the fidelity of the anomaly itself (Fig. 7). δ13C/δ18O ratios we studied from −0.7055 to −0.7067 are closer to the original Sr isotopic composition than ratios from Zheng et al. (2004) between −0.7074 and −0.7080, and our new Sr data are also compatible with an early Tonian age by correlation with Xuhuai basin (Kuang et al., 2011; Zhou et al., 2020). The Xihe-Wuxingshan-Jinxian groups thus fill a critical gap in the Tonian δ13C record. Furthermore, correlation across North China allows tighter age constraints for the ca. 940 Ma Majiatun anomaly: <950 Ma (Xuhuai Basin) and >924 ± 5 Ma (Dalian Basin) (He et al., 2017; Zhang et al., 2016) (Fig. 7). The relatively well-dated Majiatun anomaly starts developing the picture of the early Tonian carbon cycle (Fig. 8).

5.3. Possible origins of the Majiatun anomaly and Neoproterozoic carbon cycle perturbations

As of yet, the Majiatun anomaly has only been observed in North China and thus it may not be a global oceanographic phenomenon. Local explanations are possibly sufficient. For example, mafic sills intruding both the Qiaotou Formation in the Dalian basin and Niyuan Formation in the Xuhuai basin are 945 Ma (Zhao et al., 2019), potentially coeval with the Majiatun anomaly. The δ13C values of −6‰ observed are indeed similar to the values for volcanic emissions (−6‰ to −7‰). Furthermore, the Permian/Triassic extinction and associated −5‰ carbon excursion has been suggested to be caused by eruption of the coeval Siberian Traps (Renne et al., 1995). However, numerical modeling of the carbon cycle argues that even the extensive Siberian Traps was volumetrically too small and its associated CO2 emissions were insufficient to cause the magnitude of the negative carbon excursion (Berner, 2002; Payne and Kump, 2007). Therefore, the possibility that the relatively average-sized mafic sills intruding North China at this time could explain the magnitude of the Majiatun anomaly is deemed unlikely. Another possible source of light carbon could be the oxidation of organic matter and/or petroleum leaks, but the Wuxingshan-Jinxian Groups are poor in organic contents (total organic carbon <0.1% Supplementary Table). Until the Majiatun anomaly is both (i) identified on another continent and (ii) proven to be synchronous, it is difficult to discern whether it is a local or a global oceanographic phenomenon. Nonetheless, being able to rule out the most likely local explanations, we therefore consider more regional-scale explanations for the carbon isotope excursion.

With the identification of the ca. 940 Ma Majiatun anomaly, a more complete picture of δ13C variation in earliest Neoproterozoic time emerges and establishes the onset of Neoproterozoic carbon cycle variability (Fig. 8). Prior to our work, the oldest known negative δ13C anomaly was the ca. 810 Ma Bitter Springs anomaly (Swanson-Hysell et al., 2015). The Majiatun anomaly is as large as the later Bitter Springs anomaly, but significantly pre-dates it by ~130 Myr. In terms of their senses and magnitudes, the negative shifts of ~9‰ of the Bitter Springs and the Majiatun anomalies are identical. Combined isotopic, paleo-magnetic, and stratigraphic data suggest that the Bitter Springs anomaly was associated with rapid shifts in paleolatitude of the continents, where temporarily relocating carbon depositories out of the tropical weathering belt resulted in reduced organic carbon burial and the observed negative excursion (Maloff et al., 2006; Swanson-Hysell et al., 2012). Face-value interpretation of paleomagnetic data from the Bitter Springs Formation itself is consistent with hypothesized rapid shifts in paleolatitude, however the interpretation of the Australian data is ambiguous (Swanson-Hysell et al., 2012). Nonetheless, paleolatitude shifts during the Bitter Springs anomaly have been documented on multiple continents with high-quality paleomagnetic data (Jing et al., 2020; Maloff et al., 2006; Niu et al., 2016), confirming the link between continental motions and carbon cycle reorganizations (Maloff et al., 2006).

Similar to those observed during the Bitter Springs anomaly, large shifts in the paleolatitude of North China and contiguous continents (Laurentia and Baltica) argues for paleogeographic changes during the Majiatun anomaly (Fairchild et al., 2017; Cong et al., 2018) (Fig. 9). These three continents transited both evaporitic and tropical belts during this time, which would have caused significant changes in weathering and depositional patterns. Motion in/out of the tropics can increase/reduce, respectively, the fraction of organic carbon burial (Maloff et al., 2006). Since these continents were likely part of the larger Rodinia supercontinent at this time (Cawood and Pisarevsky, 2006; Evans, 2009; Li et al., 2008), the changes in continental paleolatitude depicted may be expected globally and therefore of even greater climatic significance. The stratigraphic record of the Dalian Basin is consistent with the departure of the NCC from the tropics during the Majiatun anomaly as stromatolites are abundant and diverse in carbonates both below and above the Majiatun Formation, but absent within it (Hua and Cao, 2004) (Figs. 3 and 7). This observation is consistent with an explanation that a fast shift of paleolatitude may affect the
An earliest Neoproterozoic carbon isotope anomaly has been documented in the ca. 940 Ma Majiatun Formation of North China. Pre-dating the Bitter Springs anomaly by ~130 Myr, the so-called "Majiatun anomaly" is the first of 5 increasingly negative carbon isotope excursions to occur throughout the era.

**Author contributions**

Zhiyue Zhang: Investigation; Methodology; Data curation; Visualization; Writing—original draft; Writing—review & editing. Peng Peng: Conceptualization; Funding acquisition; Project administration; Supervision; Investigation; Methodology; Data curation; Validation; Writing—original draft; Writing—review & editing. Lianjun Feng: Funding acquisition; Project administration; Methodology; Data curation; Validation; Writing—original draft; Writing—review & editing. Youlian Li: Methodology; Data curation; Writing—original draft.

**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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Appendix A. Supplementary data

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References


