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New SIMS U–Pb zircon age on the macroscopic multicellular eukaryotes from the early Mesoproterozoic Gaoyuzhuang Formation, North China

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Abstract

Decimetre-scale carbonaceous macrofossils from the Mesoproterozoic Gaoyuzhuang Formation in the Yanshan Range are known as the current oldest unambiguous evidence of macroscopic multicellular eukaryotes. Here, we reported a new SIMS zircon age of 1588.8 ± 6.5 Ma from a volcanic tuff in the Qianxi County of Hebei Province, about 11 m above the macrofossil's horizon. This new age provides a direct age constraint on the macroscopic eukaryotic fossils from the Gaoyuzhuang Formation. It indicates that macroscopic life with the moderate diversity and certain morphological complexity had already evolved at the beginning of the Mesoproterozoic, and implies a possibility of discovering macroscopic eukaryotes in earlier rocks. This study also calls for a stratigraphic framework to integrate biological and environmental studies in different regions for a better understanding of the evolution of multicellular organisms and environmental change during this important period.

1. Introduction

The emergence of multicellular organisms is a critical milestone in the evolution of life on Earth (Bonner, 1998; Niklas and Newman, 2020). The current oldest unambiguous evidence of macroscopic multicellular eukaryotes is the decimetre-scale carbonaceous macrofossils from the Mesoproterozoic Gaoyuzhuang Formation in the Yanshan Range, North China (Zhu *et al.* 2016; Chen *et al.* 2023). These macrofossils display multiple regular morphologies (cuneate, linear, oblanceolate and tongue-shaped) and large dimensions up to several centi- to decimetres, exhibiting resemblances to some living macroalgae (Zhu *et al.* 2016; Chen *et al.* 2023). Their age has been approximately constrained to 1560 Ma–1580 Ma by zircon U–Pb ages from two outcrops in Yanqing, Beijing (Li *et al.* 2010) and Jizhou, Tianjin (Tian *et al.* 2015, 2020) which are about one hundred kilometres apart (Fig. 1(a)).

The lack of direct age constraint on these macrofossils hinders our understanding of the timing of the origin and early evolution of macroscopic eukaryotes. Macrofossils with regularly repeated forms were mainly found in Qianxi County of Hebei Province (Zhu *et al.* 2016; Chen *et al.* 2023), but the host sections lack relevant geochemical and geochronological studies of Gaoyuzhuang Member 3. Considering the variational facies of the Gaoyuzhuang Formation in the Yanshan Range (Liang and Jones, 2021), direct age constraints for the macrofossil assemblages are necessary to understand the relationship between the origin of multicellular organisms and associated environmental conditions (Zhang *et al.* 2018).

Here, a new zircon age of a volcanic tuff several meters above the fossil horizon at the Qianxi section is reported. The precise SIMS U–Pb zircon age provides a direct age constraint for the important fossil assemblage.

2. Materials and methods

The Mesoproterozoic Gaoyuzhuang Formation is widely distributed in the Yanshan Range and is considered to be accumulated during a marine transgression (Tian and Zhai, 1996). Located between the sandstone of the Dahongyu Formation and the silty dolomite of the Yangzhuang Formation, the Gaoyuzhuang Formation is dominated by carbonate and is subdivided into four members (Tian and Zhai, 1996). Member 3 of the Gaoyuzhuang Formation constitutes a large portion of this rock unit, which is about 680 m thick in the type section at Northern Jizhou District, Tianjin Municipality, with the lower half dominated by medium to thick-bedded dolostones and the upper half dominated by dolomitic limestones. The dolomitic limestones

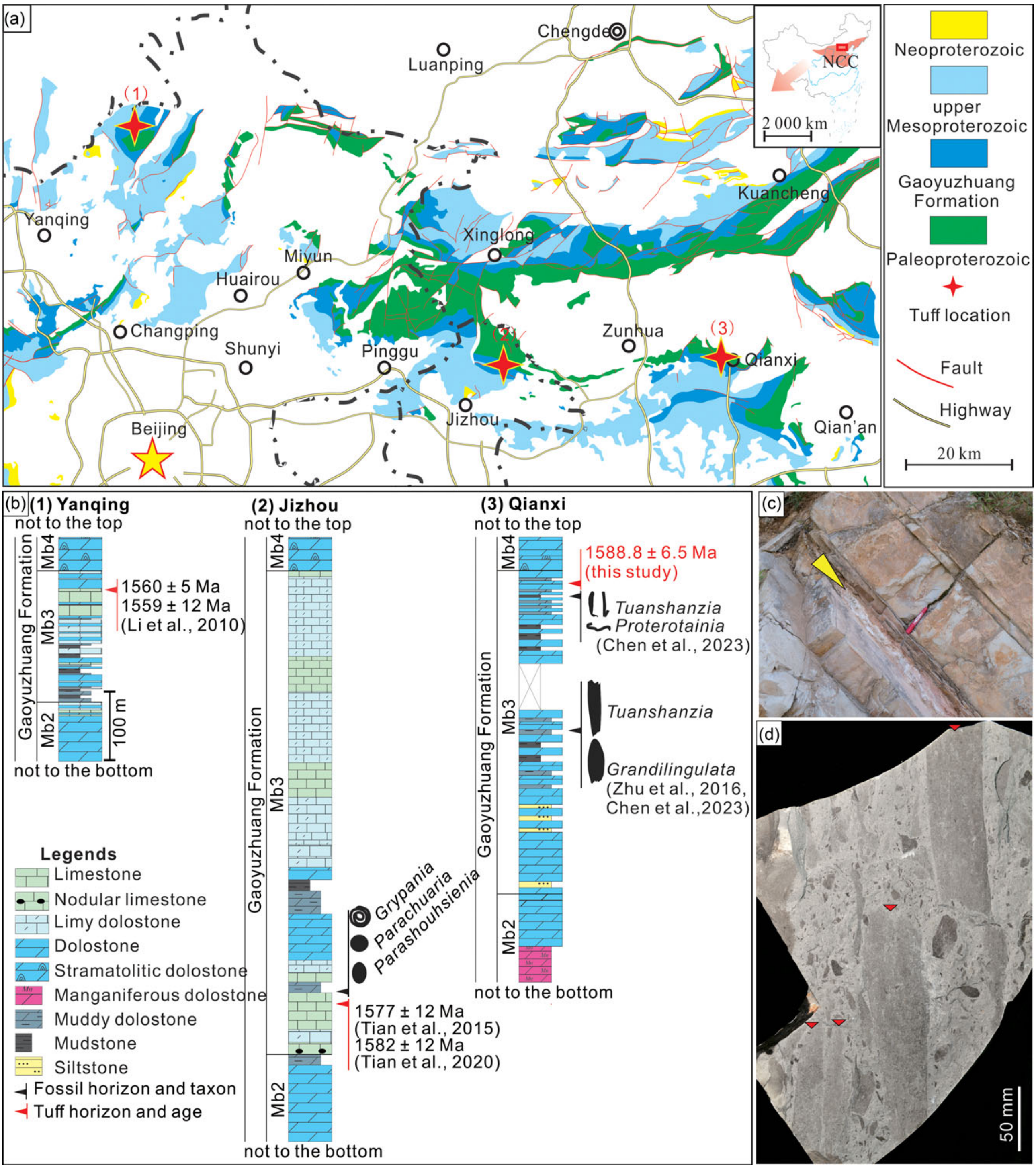

Figure 1. (Colour online) Geological setting of the sample. (a) Distribution of Proterozoic outcrops in the Yanshan Range showing the reported tuff locations. (b) Correlation of the horizons of reported zircon U–Pb ages and fossils at (1) Yanqing, (2) Jizhou and (3) Qianxi. (c) Outcrop photograph of the tuff bed (yellow arrow) in the section. (d) Macrofossils (red arrows) from Member 3 of the Gaoyuzhuang Formation in Qianxi, Hebei.

bear small fossiliferous siliceous concretions (Shi *et al.* 2017) and molar-tooth structures (Mei and Tucker, 2011).

In the section at Qianxi County of Hebei Province, Member 3 is about 470 m thick, dominated by medium to thick-bedded dolostone and argillaceous dolostone, with subordinate siltstone and mudstone. The blade-like macrofossils were reported in muddy dolostone about 225 m above the bottom of this member (Zhu *et al.* 2016; Chen *et al.* 2023). Many smaller macrofossils have recently been discovered in the dolomitic mudstone about 435 m above the bottom (Chen *et al.* 2023).

About 11 m above the upper macrofossil horizon (Fig. 1(b)), the sample QXHY-6 was obtained from a tuff bed at an outcrop ca. 800 m west of the urban district of Qianxi County (Fig. 1(a), 40° 07′ 50″ N, 118° 16′ 32″ E).

Zircon crystals were separated from ca. 5 kg sample (QXHY-6) by the conventional density and magnetic separation methods.

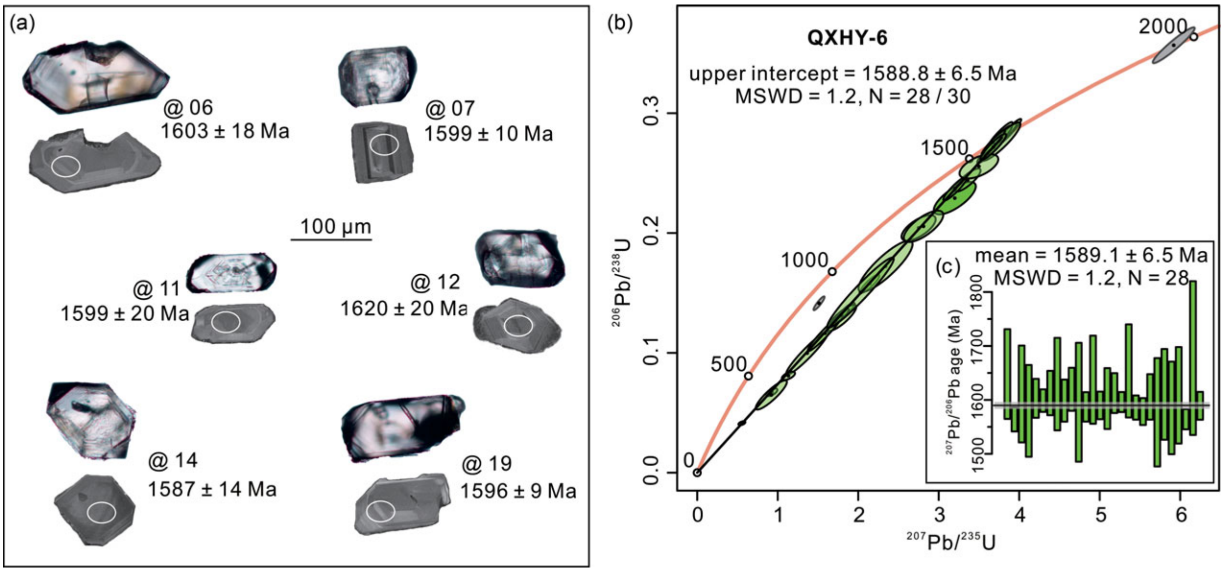

Figure 2. (Colour online) SIMS zircon U–Pb age for the tuffs sample QXHY-6. (a) Images of representative dated zircons (transmission light and CL) show the SIMS analysis dots (white ovals) and the $^{207}Pb/^{206}Pb$ ages. (b) Wetherill U–Pb concordia diagram. (c) Weighted average of the $^{207}Pb/^{206}Pb$ ages.

Mounted in an epoxy disk with the reference zircons of Plešovice and Qinghu, the grains were then polished to section the crystals in half for analysis. All zircon crystals were documented with transmitted and reflected light photomicrographs and cathodoluminescence (CL) images to reveal their external and internal structures.

U, Th and Pb isotopes were measured using a CAMECA IMS 1280-HR at the Beijing Research Institute of Uranium Geology, following conventional methods (Li *et al.* 2009). The O_2^- primary beam, accelerated at ~13 kV with an intensity of ca. 10 nA, was used to bombard the zircon surfaces, resulting in ellipsoidal analysis spots with sizes of about 20 μm × 30 μm, respectively. Analyses of the unknown grains were interspersed with those of the reference zircon at a ratio of 3:1.

The ratios of U–Th–Pb are determined relative to the reference zircon of Plešovice (337 Ma) (Sláma *et al.* 2008). The measured compositions were corrected for common Pb using non-radiogenic ^{204}Pb. Corrections were sufficiently small to be insensitive to the choice of common Pb composition and an average of present-day crustal composition was used for the common Pb assuming that the common Pb was largely surface contamination introduced during the sample preparation (Stacey and Kramers, 1975). Uncertainties on individual analyses are reported at 1 σ level. Weighted mean ages for pooled U/Pb (and Pb/Pb) analyses are quoted with a 95% confidence interval. The data reduction is done using the online program IsoplotR (Vermeesch, 2018).

Analyses of zircon reference Qinghu were interspersed with unknowns, and eight analyses yielded a weighted mean $^{206}Pb/^{238}U$ age of 160.6 ± 2.1 Ma (MSWD = 0.9), consistent, within error, of the reported value of 159.5 ± 0.2 (Li *et al.* 2013).

3. Results

Zircon crystals from the tuff sample QXHY-6 are mostly subhedral to euhedral, which are 75–180 μm in length and 35–80 μm in width, respectively (Fig. 2(a)). Oscillatory zones are distinct in the CL images (Fig. 2(a)), and the ratios of Th/U are mostly higher than 0.4 (Table S1), suggesting the zircons are of magmatic origin.

Excluding two obvious outliers, 28 of 30 analyses yielded a relatively consistent $^{207}Pb/^{206}Pb$ age ranging from 1564 Ma to 1678 Ma, respectively. They lie on a discordia line going through zero in the U–Pb concordia plot with an upper intercept of 1588.8 ± 6.5 Ma (Fig. 2(b)), indicating that they suffered recent Pb loss. The upper intercept age of 1588.8 ± 6.5 Ma is consistent with the weighted mean age of $^{207}Pb/^{206}Pb$ within error (1589.1 ± 6.5 Ma, Fig. 2(c)), representing the crystallization age of these zircons.

4. Discussion and conclusion

These macrofossils are important for our understanding of early eukaryote evolution and associated biological innovation. In this study, we present a new SIMS U–Pb zircon age from a volcanic tuff above the macrofossil-bearing horizon in the same section. A discordia line going through zero in the U–Pb concordia plot indicates these zircons suffered recent Pb loss. The $^{207}Pb/^{206}Pb$ system was maintained during the stoichiometric loss of total lead, contributing to the consistent $^{207}Pb/^{206}Pb$ ages of these zircons (Spencer *et al.* 2016). The upper intercept age of 1588.8 ± 6.5 Ma, which is consistent with the weighted mean $^{207}Pb/^{206}Pb$ age within error, is interpreted as the depositional age of this tuff, and a direct age constraint on the macrofossil horizon.

Zircons from tuff layers in the Gaoyuzhuang Formation in other sections were previously dated by laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) and sensitive high-resolution-ion microprobe (SHRIMP). Ages of 1582 ± 12 Ma (SHRIMP) and 1577 ± 12 Ma (LA-MC-ICPMS) were obtained from a volcanic tuff at the bottom of Member 3 of the Gaoyuzhuang Formation in the Jizhou section (Tian *et al.* 2015, 2020), and ages of 1560 ± 5 Ma (LA-MC-ICPMS) and 1559 ± 12 Ma (SHRIMP) were obtained from a tuff at the top of Member 3 in the Yanqing section (Li *et al.* 2010). These two sets of ages constrained Member 3 to ca. 1580–1560 Ma. Within the lithostratigraphic framework, the new dated horizon at the top of

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Member 3 at Qianxi section approximately corresponds to the ca. 1560 Ma volcanic ash layers in the Yanqing section.

At face value, the newly obtained date seems to be older than the previously published radio-isotopic date from the equivalent horizons in the Yanqing section. This apparent difference could be reconciled by the precision of 1–2% of these methods (Gehrels, 2014; Yang *et al.* 2017) or reflects the lithostratigraphic diachroneity. Within the wide distribution range of the Gaoyuzhuang Formation, the thickness of Member 3 varies greatly in the Yanshan Range (Fig. 1(b)). In Jizhou, Tianjin, the thickness is up to ca. 680 m (Shang *et al.* 2019), while it is ca. 470 m in Qianxi (Chen *et al.* 2023). Depending on the lithostratigraphic subdivision, the thickness of Member 3 was reported to be ca. 190 m (Shang *et al.* 2019) or ca. 300 m (Mei, 2007) in the Gan'gou section of Yanqing. The lithological characteristics of Member 3 also vary largely (Fig. 1(b)). Nodular limestones at the bottom are obvious at the Yanqing and Jizhou sections (Shang *et al.* 2019), but are missing at the Qianxi section (Chen *et al.* 2023). Limestone is also absent at the Qianxi section, but common in the Jizhou and Yanqing sections. With much wider distribution than the underlying Dahongyu Formation, the Gaoyuzhuang Formation is considered to have formed during a continued marine transgression (Huang, 2006). The erosion–deposition processes can lead to the spatial and temporal variations of the depositional sequences (Meng *et al.* 2011).

In most cases, lithostratigraphic boundaries are diachronous, and are not considered as precise markers for temporal correlation. The new SIMS U–Pb zircon age provides a direct age constraint on the macroscopic eukaryotic fossils, and; therefore, is critical for better understanding the evolution of multicellular organisms with environmental change (Yang *et al.* 2022).

At Jizhou section, evidence for a progressive oxygenation event was found in the lower part of Member 3, the approximate level of the macrofossil horizon at Qianxi section (Zhang *et al.* 2018). The evidence was verified by subsequent studies in other areas with different methods, which suggest an important link between the development of macroscopic life and oceanic oxygenation at this time (Shang *et al.* 2019; Tang *et al.* 2022; Xie *et al.* 2022; Ye *et al.* 2023; Xu *et al.* 2023). However, neither chronological nor geochemical work on Member 3 were carried out in the Qianxi area, where most of those macrofossils with regularly repeated forms were found. The new age calls for biological and environmental studies to be carried out on the same stratigraphic section. Furthermore, a stratigraphic correlation framework is urgently needed to integrate biological and environmental studies that are carried out in different areas of the Yanshan Range, to obtain a holistic perspective on the relationship between the evolution of life and the environment.

The early Mesoproterozoic was thought to be characterized by generally low environmental oxygen concentrations, which restricted the emergence and evolution of multicellular organisms (Holland, 2006; Lyons *et al.* 2014). The origin of eukaryotic multicellularity was thought to have a later occurrence after the oxygen levels increased. Molecular clocks estimate that multicellular eukaryotes originated at the transition between the Mesoproterozoic and Neoproterozoic (Sharpe *et al.* 2015). However, more and more fossil evidence indicates that multicellular eukaryotes made their appearances in the early Mesoproterozoic and may have appeared even earlier (Javaux and Lepot, 2018).

With the new direct age constraint reported herein, the macroscopic eukaryotic fossils from the Gaoyuzhuang Formation suggest that macroscopic life had already evolved in moderate diversity and certain morphological complexity at the beginning of the Mesoproterozoic. These new insights also emphasize the possibility of finding fossils of multicellular eukaryotes during this period and even earlier to the Paleoproterozoic.

Supplementary material. To view supplementary material for this article, please visit https://doi.org/10.1017/S0016756824000220

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Competing interests. The authors of the paper declare no conflict of interest.

References

Bonner JT (1998) The origins of multicellularity. *Integrative Biology: Issues, News, and Reviews* **1**, 27–36.

Chen K, Miao L, Zhao F and Zhu M (2023) Carbonaceous macrofossils from the early Mesoproterozoic Gaoyuzhuang Formation in the Yanshan Range, North China. *Precambrian Research* **392**, 107074.

Gehrels G (2014) Detrital zircon U-Pb geochronology applied to tectonics. *Annual Review of Earth and Planetary Sciences* **42**, 127–149.

Holland HD (2006) The oxygenation of the atmosphere and oceans. *Philosophical Transactions of the Royal Society B: Biological Sciences* **361**, 903–915.

Huang X (2006) Tectonic evolution of the Meso-Neoproterozoic sedimentary basin in Yanshan range. *Geological Survey and Research* **29**, 263–270.

Javaux EJ and Lepot K (2018) The Paleoproterozoic fossil record: implications for the evolution of the biosphere during Earth's middle-age. *Earth-Science Reviews* **176**, 68–86.

Li H, Zhu S, Xiang Z, Wenbo S, Songnian L, Hongying Z, Jianzhen G, Sheng L and Fengjie Y (2010) Zircon U-Pb dating on tuff bed from Gaoyuzhuang Formation in Yanqing, Beijing: further constraints on the new subdivision of the Mesoproterozoic stratigraphy in the northern North China Craton. *Acta Petrologica Sinica* **26**, 2131–2140.

Li X, Liu Y, Li Q, Guo C and Chamberlain K (2009) Precise determination of Phanerozoic zircon Pb/Pb age by multicollector SIMS without external standardization. *Geochemistry, Geophysics, Geosystems* **10**, Q04010.

Li X, Tang G, Gong B, Yang Y, Hou K, Hu Z, Li Q, Liu Y and Li W (2013) Qinghu zircon: a working reference for microbeam analysis of U-Pb age and Hf and O isotopes. *Chinese Science Bulletin* **58**, 4647–4654.

Liang T and Jones B (2021) Characteristics of primary rare earth elements and yttrium in carbonate rocks from the Mesoproterozoic Gaoyuzhuang Formation, North China: implications for the depositional system. *Sedimentary Geology* **415**, 105864.

Lyons TW, Reinhard CT and Planavsky NJ (2014) The rise of oxygen in Earth's early ocean and atmosphere. *Nature* **506**, 307–315.

Mei M (2007) Sedimentary features and their implication for the depositional succession of non-stromatolitic carbonates, Mesoproterozoic Gaoyuzhuang Formation in Yanshan area of North China. *Geoscience* **21**, 45–56.

Mei M and Tucker ME (2011) Molar tooth structure: a contribution from the Mesoproterozoic Gaoyuzhuang Formation, Tianjin City, North China. *Acta Geologica Sinica - English Edition* **85**, 1084–1099.

Meng Q, Wei H, Qu Y and Ma S (2011) Stratigraphic and sedimentary records of the rift to drift evolution of the northern North China craton at the Paleo- to Mesoproterozoic transition. *Gondwana Research* **20**, 205–218.

Niklas KJ and Newman SA (2020) The many roads to and from multicellularity. *Journal of Experimental Botany* **71**, 3247–3253.

Shang M, Tang D, Shi X, Zhou L, Zhou X, Song H and Jiang G (2019) A pulse of oxygen increase in the early Mesoproterozoic ocean at ca. 1.57–1.56 Ga. *Earth and Planetary Science Letters* **527**, 115797.

Sharpe SC, Eme L, Brown MW and Roger AJ (2015) Timing the origins of multicellular eukaryotes through phylogenomics and relaxed molecular clock analyses. In *Evolutionary Transitions to Multicellular Life: Principles and mechanisms* (eds I Ruiz-Trillo, AM Nedelcu), pp. 3–29. Dordrecht: Springer Netherlands.

Shi M, Feng Q, Khan MZ and Zhu S (2017) An eukaryote-bearing microbiota from the early mesoproterozoic Gaoyuzhuang Formation, Tianjin, China and its significance. *Precambrian Research* **303**, 709–726.

Sláma J, Košler J, Condon DJ, Crowley JL, Gerdes A, Hanchar JM, Horstwood MS, Morris GA, Nasdala L, Norberg N and Schaltegger U (2008) Plešovice zircon—a new natural reference material for U-Pb and Hf isotopic microanalysis. *Chemical Geology* **249**, 1–35.

Spencer CJ, Kirkland CL and Taylor RJM (2016) Strategies towards statistically robust interpretations of in situ U–Pb zircon geochronology. *Geoscience Frontiers* **7**, 581–589.

Stacey JS and Kramers JD, (1975) Approximation of terrestrial lead isotope evolution by a two-stage model. *Earth and Planetary Science Letters* **26**, 207–221.

Tang D, Fu X, Shi X, Zhou L, Zheng W, Li C, Xu D, Zhou X, Xie B, Zhu X and Jiang G (2022) Enhanced weathering triggered the transient oxygenation event at ~1.57 Ga. *Geophysical Research Letters* **49**, e2022GL099018.

Tian H, Zhang J, Li H, *et al.* (2015) Zircon LA-MC-ICPMS U-Pb dating of tuff from Mesoproterozoic Gaoyuzhuang Formation in Jizhou county of North China and its geological significance. *Acta Geosci Sin* **36**, 647–658.

Tian H, Li H, Zhang J, *et al.* (2020) SHRIMP U-Pb dating for zircons from the tuff bed of the Mesoproterozoic Gaoyuzhuang Formation in Jizhou Section, Tianjin, and its constraints on the Mesoproterozoic bio-environmental events. *Geological Survey and Research* **43**, 153–160.

Tian S, Zhai Z (1996) *Petrostratigraphy of Tianjin*. Wuhan: China University of Geosciences Press.

Vermeesch P (2018) IsoplotR: a free and open toolbox for geochronology. *Geoscience Frontiers* **9**, 1479–1493.

Xie B, Zhu J, Wang X, Xu D, Zhou L, Zhou X, Shi X and Tang D (2022) Mesoproterozoic oxygenation event: from shallow marine to atmosphere. *GSA Bulletin* **135**, 753–766.

Xu D, Qin Z, Wang X, Li J, Shi X, Tang D and Liu J (2023) Extensive sea-floor oxygenation during the early Mesoproterozoic. *Geochimica et Cosmochimica Acta* **354**, 186–196.

Yang C, Li X, Zhu M and Condon DJ (2017) SIMS U–Pb zircon geochronological constraints on upper Ediacaran stratigraphic correlations, South China. *Geological Magazine* **154**, 1202–1216.

Yang C, Li Y, Selby D, Wan B, Guan C, Zhou C and Li XH (2022) Implications for Ediacaran biological evolution from the ca. 602 Ma Lantian biota in China. *Geology* **50**, 562–566.

Ye Y, Wang H, Wang X, Li J, Wu C and Zhang S (2023) Regional and global proxies for varying ocean redox conditions at ~1.57 Ga: a causal connection with volcanism-induced weathering. *Geosystems and Geoenvironment* **2**, 100173.

Zhang K, Zhu X, Wood RA, Shi Y, Gao Z and Poulton SW (2018) Oxygenation of the Mesoproterozoic ocean and the evolution of complex eukaryotes. *Nature Geoscience* **11**, 345–350.

Zhu S, Zhu M, Knoll AH, Yin Z, Zhao F, Sun S, Qu Y, Shi M and Liu H (2016) Decimetre-scale multicellular eukaryotes from the 1.56-billion-year-old Gaoyuzhuang Formation in North China. *Nature Communications* **7**, 11500.