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新元古代氧化事件促发“雪球地球”冰期气候？

崔一鑫¹, 李东东², 沈冰², 高晓鹏¹

1. 中国石化石油勘探开发研究院, 北京 102206

2. 北京大学地球与空间科学学院, 北京 100871

摘要: 新元古代氧化事件的启动时间、持续时长及氧气含量的上升幅度存在争议, 其与“雪球地球”发生的先后序列和因果联系也有待厘清. 系统梳理和分析了拉伸纪古生物化石演化、地球化学数据和模型, 对上述问题提出假说: 新元古代氧化事件可能早于“雪球地球”, “雪球地球”结束进一步促进了氧气含量的增加. 具体而言, 真核藻类在拉伸纪已广泛存在, 具备较高生产力的物质基础; 罗迪尼亚超大陆裂解引发了强烈的大陆风化, 导致磷等营养元素大量输入海水, 增强了有机质的生成与埋藏并促进氧气大量释放. O_2 含量上升和强烈大陆风化限制了 CH_4 、 CO_2 等温室气体, 使气温降低并引发“雪球地球”. “雪球地球”间冰期或冰后期, 冰川消融引起强烈的物理风化, 增强营养元素的供应, 提高有机碳埋藏效率和 O_2 水平, 进一步加强新元古代氧化. 然而, 拉伸纪地层划分与对比存在较大争议, 许多化石的生物学属性尚不明确, 多种地球化学数据难以耦合. 因此, 为厘清新元古代氧化事件与“雪球地球”的相互作用机制, 需要加强年代学、古生物学和地球化学等方面的综合研究.

关键词: 新元古代; 氧化事件; 雪球地球; 协同演化; 罗迪尼亚超大陆; 地球化学.

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Did the Neoproterozoic Oxygenation Event Trigger the Snowball Earth?

Cui Yixin¹, Li Dongdong², Shen Bing², Gao Xiaopeng¹

1. SINOPEC Petroleum Exploration and Production Research Institute, Beijing 102206, China

2. School of Earth and Space Sciences, Peking University, Beijing 100871, China

Abstract: The initiation time, the duration and the magnitude of oxygen increase of the Neoproterozoic Oxygenation Event (NOE) are controversial. The sequence and causal relationship between the NOE and the Snowball Earth also need to be clarified. This review analyzes previous studies of fossils, geochemical data and models in the Tonian, suggesting a hypothesis of possible linkages between the NOE and the Snowball Earth. The NOE may have occurred earlier than the Snowball Earth, and the end of Snowball Earth further promoted an increase of oxygen content. Specifically, eukaryotic algae were widely present during the Tonian and constructed a basis for high productivity. Rifting of the Rodinia supercontinent triggered intense continental weathering, leading to a large amount of nutrients such as phosphorus into seawater. Consequently, enhanced primary production elevated the burial of organic matter, and sufficient oxygen was released to the ocean and atmosphere, indicating the onset of the oxygenation event. On the other hand, abundant O_2 and intense continental weathering consumed greenhouse gases such as CH_4 and CO_2 , causing a decrease of temperature and driving the Snowball Earth. During the interglacial and postglacial periods of the Snowball Earth, glacier melting caused strong physical weathering

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作者简介: 崔一鑫 (1992—), 男, 博士, 助理研究员, 主要从事沉积地球化学和油气勘探研究. ORCID: 0009-0005-8448-523X. E-mail: cuiyixin.syky@sinopec.com

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and enhanced nutrient supply, improving organic carbon burial and O₂ level. To clarify the interactions between the NOE and the Snowball Earth, it is necessary to further study chronology, paleontology and geochemistry of the Tonian in the future.

Key words: Neoproterozoic; Oxygenation Event; Snowball Earth; co-evolution; Rodinia supercontinent; geochemistry.

0 引言

新元古代晚期大气和海水中的氧气含量发生第二次显著上升,即新元古代氧化事件(图 1)(Neoproterozoic Oxygenation Event, NOE)(Fike *et al.*, 2006; Och and Shields-Zhou, 2012; Lyons *et al.*, 2014; Lyons *et al.*, 2021).真核生物在新元古代发生快速演化,表现为种类显著增加、宏体化石多样化、后生动物出现和生物矿化作用发生(Erwin *et al.*, 2011; Lenton *et al.*, 2014; Javaux and Knoll, 2017; Riedman and Sadler, 2018; Xiao and Tang, 2018; 刘伟和张兴亮, 2021; 张兴亮, 2021; 袁训来等, 2023).基于生命-环境协同演化假说,新元古代复杂生物发展与氧化事件之间可能存在内在联系(Canfield *et al.*, 2007; Sperling *et al.*, 2013a; Pla-

navsky *et al.*, 2014a; Zhang *et al.*, 2016; Zhang *et al.*, 2018).此外,新元古代构造、气候条件和生物地球化学循环等均出现较大波动(图 1).例如,罗迪尼亚超大陆发生裂解(850~580 Ma)(Li *et al.*, 2008, 2013; Cawood *et al.*, 2016);全球经历两次极端冰室气候(Sturtian 和 Marinoan 冰期)(720~635 Ma),形成“雪球地球”(Hoffman *et al.*, 1998, 2017; 储雪蕾, 2004; Huang *et al.*, 2016; Lang *et al.*, 2018a, 2018b; 旷红伟等, 2019; 郎咸国等, 2023);埃迪卡拉纪晚期(580 Ma)发生地质历史上最大的 $\delta^{13}\text{C}_{\text{carb}}$ 负偏移事件(Shuram Excursion),指示全球碳循环剧烈扰动(Fike *et al.*, 2006; Derry, 2010; Grotzinger *et al.*, 2011; Cui *et al.*, 2017; Zhou *et al.*, 2017; 周传明等, 2019; Gong and Li, 2020).总体上,新元古代氧化事件和“雪球地球”等环境要素在促进生物进

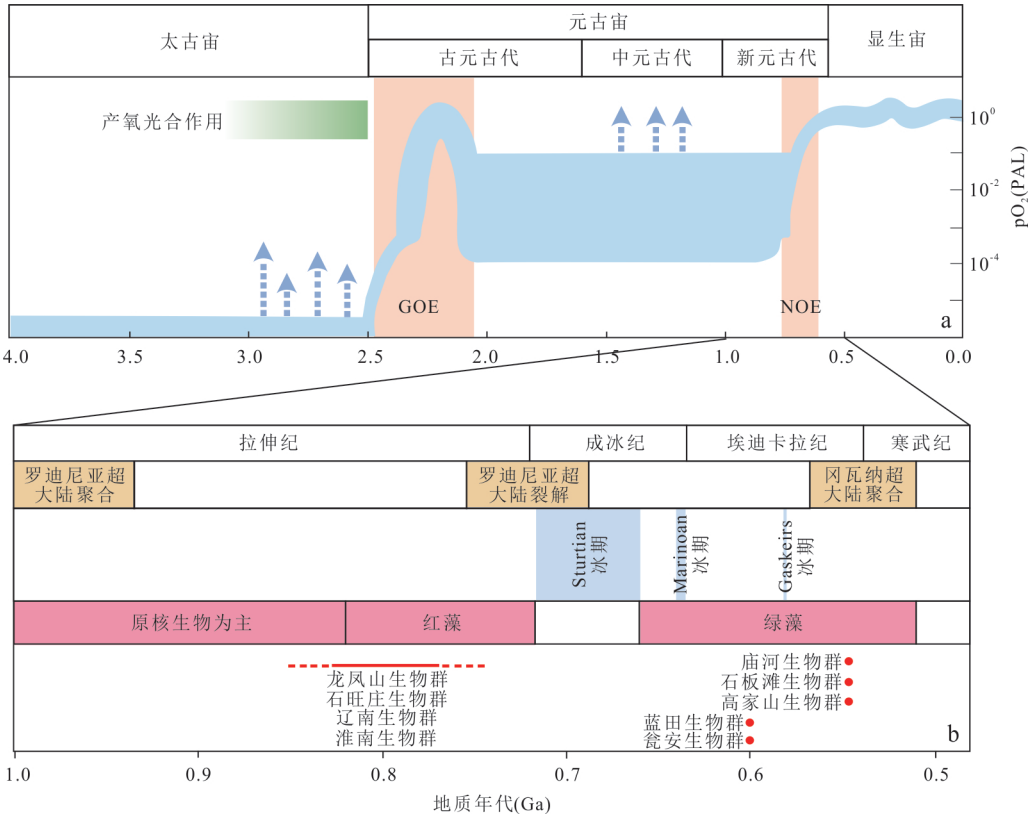


图 1 (a)地球大气氧气含量演化模式(修改自 Lyons *et al.*, 2014);(b)新元古代地球环境-生命协同演化(修改自刘伟和张兴亮, 2021)

Fig.1 (a) Evolution of atmospheric O₂ content on the Earth (modified from Lyons *et al.*, 2014); (b) co-evolution of environment and life in the Neoproterozoic (modified from Liu and Zhang, 2021)

化方面发挥了直接或关键的作用,但是确切的内在联系没有定论.新元古代氧化事件的触发机制尚不明确,其启动时间、持续时长及氧气含量的上升幅度也存在争议.新元古代氧化事件与“雪球地球”发生的先后序列和二者潜在的因果关系也亟待厘清.

本文针对上述问题提出假说,即新元古代氧化事件可能在拉伸纪启动,早于成冰纪“雪球地球”.从生命演化角度看,多细胞真核生物在中元古代已经出现,并在拉伸纪之前具有高度的多样化(Butterfield, 2000; Zhou *et al.*, 2017; Tang *et al.*, 2020; Li *et al.*, 2023).产氧真核生物可以有效促进有机碳埋藏和氧气累积.新元古代早期(约8.9 Ga)疑似海绵结构可能是最早的动物化石(Turner, 2021),也表明氧气含量可能足以支持动物生存.拉伸纪(约810 Ma)大量硫酸盐蒸发岩广泛沉积,表明较高 SO_4^{2-} 含量,指示强烈的有氧风化作用(Turner and Bekker, 2016).同时,C-S-Fe及氧化还原敏感金属元素等地球化学研究也证明拉伸纪存在氧化倾向.可见,在拉伸纪极可能发生了大氧化事件,生物圈开始变得复杂.但是,支持该假说的证据还需要进一步夯实和完善.因此,本文系统回顾和分析了新元古代氧化事件同期的古生物化石、地球化学证据和主流解释模型,以期对新元古代氧化事件与“雪球地球”之间的内在联系带来新的认识与启示.

1 新元古代氧化事件时期的生命演化

一般认为,氧气含量升高与生物演化互为因果.一方面,生物产氧作用是 O_2 的基本来源(Sánchez-Baracaldo *et al.*, 2017; Gibson *et al.*, 2018; Xiao and Tang, 2018).特别是随着海洋中初级生产者由原核蓝细菌转变为真核藻类,更大的有机质和更高的埋藏效率促进了 O_2 累积(Butterfield, 2009; Brocks *et al.*, 2017).另一方面,后生动物等复杂生命的演化需要充足的氧气(Lenton *et al.*, 2014; Lyons *et al.*, 2014; Planavsky *et al.*, 2014b).据估计,满足后生动物生理需求的 O_2 阈值为1%~10% PAL(Berkner and Marshall, 1965; Cloud, 1976; Runnegar, 1991; Mills *et al.*, 2014; Reinhard *et al.*, 2016; Sperling *et al.*, 2013a; Xiao, 2014; Mills *et al.*, 2024).大型动物及其捕食和掘穴等行为,以及生物矿化作用,需要更高的氧气水平来支持(Reinhard *et al.*, 2016).因此,真核藻类等初级生产

者的繁盛以及后生动物的出现,均被视为氧化事件的佐证.为了确定新元古代氧化事件的时间及 O_2 增幅,有必要回顾多细胞真核生物的出现和多样化,特别是早期后生动物化石记录(图2).然而,还有一种观点认为后生动物基础代谢所需的 O_2 含量很低($<0.5\%$ PAL)(Sperling *et al.*, 2013b; Reinhard *et al.*, 2016);线粒体活动的耗氧量甚至更低(0.02% PAL)(Richmond *et al.*, 1997; Gnaiger and Kuznetsov, 2002).可见,支持后生动物演化的 O_2 阈值无法确定,早期动物出现是否与NOE关联存在争议.

1.1 古元古代和中元古代真核生物的出现与多样化

实体化石、分子化石和生物分子钟研究表明,元古宙生物圈整体上经历了由原核生物向真核生物的转变.大量确切的真核生物化石在古元古代晚期和中元古代早期出现(Javaux *et al.*, 2004; Lamb *et al.*, 2009; Pang *et al.*, 2015; Javaux and Lepot, 2018; Miao *et al.*, 2019, 2024a, 2024b; Riedman *et al.*, 2023).例如,华北板块北缘长城群底部常州沟组和串岭沟组、南缘汝阳群白草坪组和北大尖组,以及澳大利亚Limbunya群发现的精美的疑源类化石,均具有较大的个体直径(200~500 μm)、复杂的表面纹饰和突起特征.一些多细胞真核生物也在中元古代早期出现,如~1.65 Ga串岭沟组多细胞化石*Qingshania magnifica*(Miao *et al.*, 2024a)、宏体藻类化石(Liu *et al.*, 2023)、~1.56 Ga高于庄组厘米级别的碳质压膜化石(Zhou *et al.*, 2017),以及 <1.4 Ga的串珠状化石*Horodyskia*(Li *et al.*, 2023).尽管存在这些比较复杂的化石记录,但是整个中元古代多细胞化石较少,以单细胞真核生物为主.直到中元古代晚期-新元古代早期,多细胞真核生物才开始在世界范围内广泛出现,如~1.05 Ga红藻化石(Butterfield, 2000; Gibson *et al.*, 2018)、~1.0 Ga绿藻化石(Tang *et al.*, 2020),以及大量生物属性未知的宏观藻类化石如*Chuarina*、*Tawuia*等,它们主要以碳质印模形式保存下来(Knoll *et al.*, 2006; Xiao and Dong, 2006; Tang *et al.*, 2017b; Li *et al.*, 2020).

因此,古元古代晚期和中元古代是真核生物出现以及早期演化阶段,表明生物圈在所谓“无聊的十亿年”(“Boring Billion”)并不平静(Buick *et al.*, 1995; Brasier and Lindsay, 1998).但是,这些真核生物的丰度和多样化速率显著低于新元古代和显生宙(Knoll, 2014).

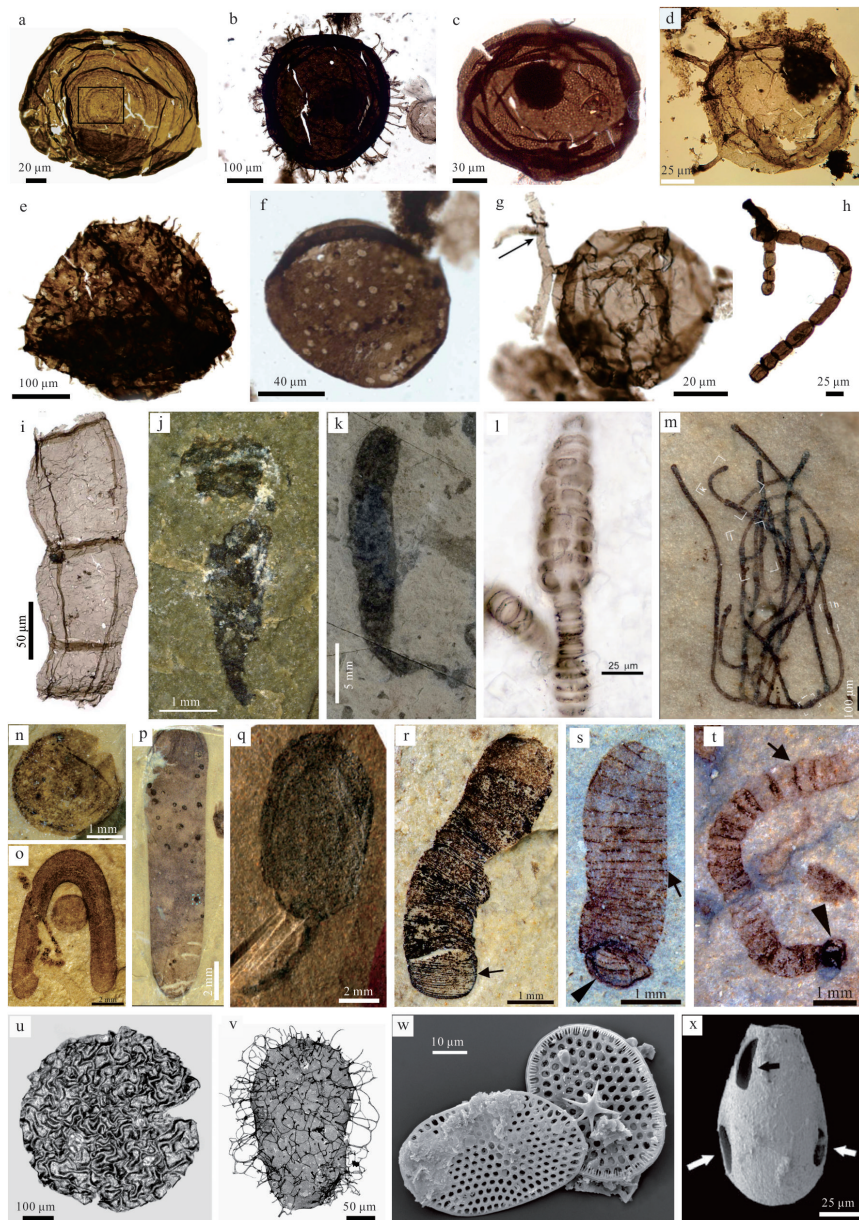


图2 新元古代“雪球地球”之前的早期真核生物化石

Fig.2 Early eukaryotic fossils before the Neoproterozoic Snowball Earth

a. *Valeria lophostriata*, ~1 650 Ma, 北大尖组化石, 最早的真核生物化石之一 (Pang *et al.*, 2015); b. *Shuiyousphaeridium macroreticulatum*, ~1 650 Ma, 北大尖组化石, 最早的真核生物化石之一 (Javaux and Lepot, 2018); c. *Dictyosphaera macroreticulata*, 北大尖组化石, 最早的真核生物化石之一 (Agić *et al.*, 2017); d. *Tappania plana*, ~1 450 Ma, 澳大利亚 Roper 群, 最早的真核生物化石之一 (Javaux *et al.*, 2001); e. *Trachyhystrichosphaera aimika*, 中元古代晚期-新元古代早期代表性化石 (Tang *et al.*, 2017a); f. Unnamed taxon, 1 150~900 Ma (Loron *et al.*, 2018); g. *Owasphaera giraldae*, ~950 Ma, 最早的真菌化石 (Loron *et al.*, 2019); h. *Arctacellularia tetragonalia*, ~1 000 Ma, 多细胞真核生物, 具有产氧光合能力 (Sfoma *et al.*, 2022); i. *Qingshania magnifica*, ~1 635 Ma, 串岭沟组多细胞真核生物化石, 最早的多细胞化石之一 (Miao *et al.*, 2024b); j. *Tuanshanzia* sp., ~1 635 Ma, 串岭沟组宏体碳质化石 (Liu *et al.*, 2023); k. ~1 560 Ma, 高于庄组, 早期多细胞真核生物化石 (Zhou *et al.*, 2017); l. *Bangiomorpha pubescens*, ~1 050 Ma, 最早的红藻化石之一 (Butterfield, 2000); m. *Proterocladus antiquus*, ~1.0 Ga 华北南芬组, 最早的绿藻化石之一 (Tang *et al.*, 2020); n. *Chuaria*, ~900 Ma, 刘老碑组化石, 多细胞产氧光合藻类之一 (Tang *et al.*, 2017b); o. *Tawuia*, ~900 Ma, 石旺庄组化石, 多细胞产氧光合藻类之一 (Li *et al.*, 2020); p. *Tawuia*, ~900 Ma, 刘老碑组化石 (Tang *et al.*, 2021); q. *Longfenghsania stipitata*, 长龙山组化石, 生物属性未知的藻类 (刘傲然等, 2018); r. *Sinosabellidites huainanensis*, 石旺庄组化石, 生物属性未知的藻类 (Li *et al.*, 2020); s. *Pararenicola gejiashuangensis*, 石旺庄组化石, 生物属性未知的藻类 (Li *et al.*, 2020); t. *Protoarenicola shijiacunensis*, 石旺庄组化石, 生物属性未知的藻类 (Li *et al.*, 2020); u. *Cerebrosphaera buicki*, 820~720 Ma, 一种真核生物化石 (Butterfield, 2015b); v. *Tappania* sp., ~800 Ma, 可能的真菌 (Butterfield, 2005); w. *Characodictyon skolepium*, ~750 Ma, 磷酸盐化微体化石 (Butterfield, 2015a); x. *Cycliocyrrillium torquata*, 780~740 Ma, VSM (Porter, 2016)

1.2 多细胞真核生物的多样化和疑似动物的出现

新元古代拉伸纪是衔接中元古代与成冰纪“雪球地球”冰期的一个关键过渡时期.拉伸纪化石以个体更大和形态更复杂的真核生物为主(Xiao and Tang, 2018; Pang *et al.*, 2020).统计数据表明,拉伸纪疑源类和宏体生物化石的多样性及形态复杂程度相较于中元古代显著增加(Vidal and Moczydlowska-Vidal, 1997; Huntley *et al.*, 2006; Xiao and Dong, 2006),但是在拉伸纪后期(800~720 Ma)呈现降低趋势(Riedman and Sadler, 2018).多细胞真核绿藻和红藻在拉伸纪广泛存在,如我国的胶辽徐淮地区发现了大量生物学属性未知的宏体藻类化石,表明产氧光合作用的增强(Butterfield *et al.*, 1994; Li *et al.*, 2020).一些疑源类也可能具有产氧光合作用,如*Navifusa*、*Arctacellulariatetragonala* (Sforna *et al.*, 2022; Demoulin *et al.*, 2024),这些疑源类在中元古代晚期至拉伸纪大量存在.拉伸纪蓝细菌具有厚壁孢子和异形胞,也被认为与氧气含量升高有关(Pang *et al.*, 2018).生物分子钟证据支持后生动物的祖先在拉伸纪已经出现并发生分化(Erwin *et al.*, 2011; dos Reis *et al.*, 2015).在8.9亿年前的微生物礁中发现了疑似海绵动物化石(Turner, 2021).一些疑源类或者瓶状化石表面出现圆形或半圆形的孔洞,表明拉伸纪存在真核生物的捕食行为(Porter *et al.*, 2003; Porter, 2016; Cohen *et al.*, 2017).

综上所述,真核生物在拉伸纪演化迅速,繁盛的真核藻类通过光合作用释放大量氧气可能激发了新元古代氧化事件的开始.疑似后动植物的出现可能指示拉伸纪的氧气含量达到了较高水平.然而,考虑到拉伸纪真核生物化石,特别是动物化石的鉴定和解释尚不明确,相关古生物学工作亟待推进.

1.3 新元古代氧化作用可能早于成冰纪“雪球地球”

真核生物在拉伸纪之前已经发生高度分化,其多样性及形态样式在拉伸纪进一步增加.特别是绿藻和红藻等光合真核生物的出现,使大量 O_2 释放到表生系统(Butterfield, 2009; Brocks *et al.*, 2017).据此推测,新元古代氧化事件在成冰纪之前即已启动.然而,关于真核藻类何时替代原核生

物成为主要的初级生产者仍无明确的时间限定.生物标志物表明直到成冰纪和埃迪卡拉纪真核藻类才占据主导(Brocks *et al.*, 2017),在中元古代及中-新元古代之交仍然以原核生物为主(Luo *et al.*, 2015; Li *et al.*, 2020).即使最近在中元古代的地层中检测到少量甌类(Zhang *et al.*, 2021)或原甌类(Brocks *et al.*, 2023),但是其丰度仍然很低.拉伸纪真核藻类丰度及氧气增幅需要进一步厘定.

一般认为后生动物的出现及分化需要足够的氧气支持.拉伸纪生物标志物数据及8.9亿年前疑似海绵化石表明,当时的 O_2 含量可能达到较高水平(Brocks *et al.*, 2016; Lyons *et al.*, 2021; Turner, 2021).但是,拉伸纪动物化石鉴定存疑且数量有限,无法确定最早的动物在该时期演化出现.后动物所需的 O_2 阈值也存在争议.另一方面,有观点认为 O_2 水平上升是动物行为诱发的,而不是动物出现的原因(Butterfield, 2009),意味着动物在相对低氧条件下可以进化出来.

新元古代氧化事件的启动可能早于成冰纪“雪球地球”,而基于古生物学证据较难衡量 O_2 上升的确切时间和幅度.生物地球化学研究为理解拉伸纪生命-环境协同演化提供了另一种视角.

2 新元古代氧化事件时期的生物地球化学循环

多种地球化学方法,如碳(C)、硫(S)、磷(P)、铁(Fe)、锌(Zn)和氧化还原敏感金属元素(Cr、Mo、U),已被广泛用于重建新元古代早期海洋氧化状态和大气 O_2 含量(Xiao *et al.*, 2014; Thomson *et al.*, 2015; Isson *et al.*, 2018).

2.1 拉伸系碳酸盐岩碳同位素组成波动

碳酸盐岩碳同位素组成($\delta^{13}C_{carb}$)被视为记录全球海洋碳循环的可靠指标(Kump, 1991; Kump and Arthur, 1999).自中元古代至拉伸纪早期(1000~811 Ma), $\delta^{13}C_{carb}$ 呈显著上升趋势(图3)(Xiao *et al.*, 1997; Kah *et al.*, 1999; Chu *et al.*, 2007; 高林志等, 2010; Halverson *et al.*, 2010; 旷红伟等, 2011; Kah *et al.*, 2012; Xiao *et al.*, 2014; Lyons *et al.*, 2021; Li *et al.*, 2022).较高 $\delta^{13}C_{carb}$ 主要源于有机碳埋藏量增加, ^{12}C 被优先利用,导致更多 ^{13}C 进入碳酸盐岩端元(Kump and Arthur, 1999).有机质的高效埋藏使大量 O_2 释放到表生系统中,指示拉

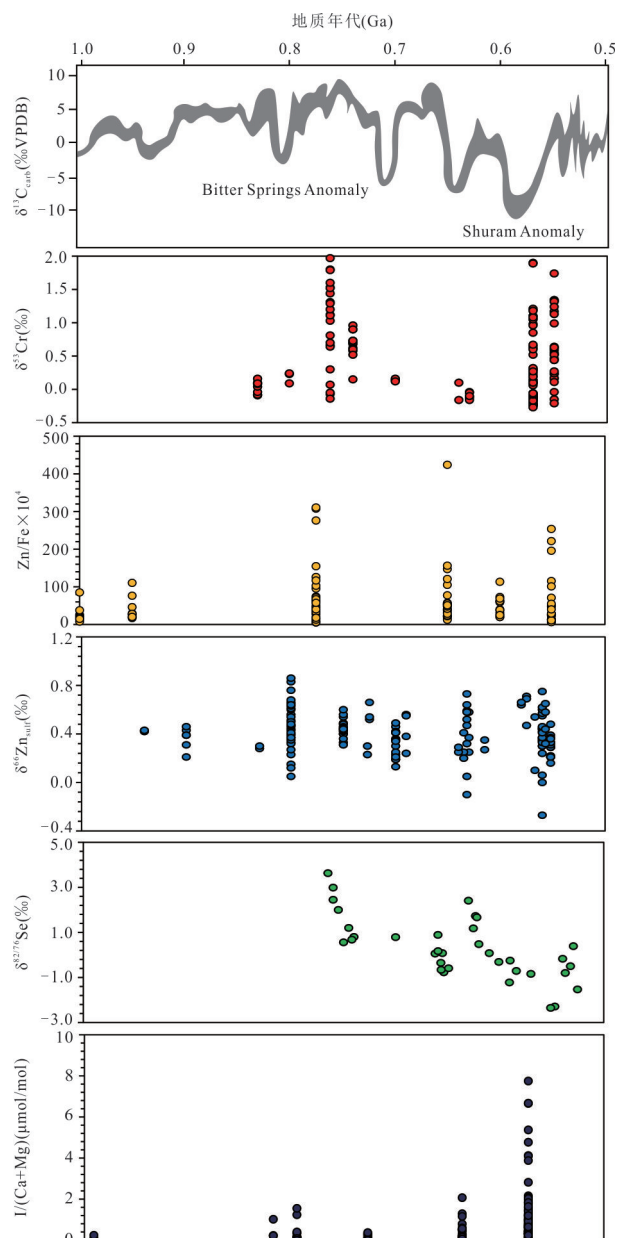


图3 新元古代地球化学演化特征

Fig.3 Various geochemical patterns in the Neoproterozoic. $\delta^{13}\text{C}_{\text{carb}}$ 数据参考 Lyons *et al.* (2021), $\delta^{53}\text{Cr}$ 数据参考 Cole *et al.* (2016), Zn/Fe 参考 Liu *et al.* (2016), $\delta^{66}\text{Zn}$ 数据参考 Isson *et al.* (2018), $\delta^{82/76}\text{Se}$ 数据参考 Pogge von Strandmann *et al.* (2015), I/(Ca+Mg) 数据参考 Hardisty *et al.* (2017)

伸纪早期可能已逐渐发生氧化事件.此外,拉伸纪早期较高的 $\delta^{13}\text{C}_{\text{carb}}$ 值可能是由贫 ^{13}C 自生碳酸盐沉积、碳酸盐强烈风化或大规模的真极移造成的 (Schrage *et al.*, 2013; Shields and Mills, 2017). 随后,在大约 811 Ma, $\delta^{13}\text{C}_{\text{carb}}$ 发生急剧负偏移,幅度超过 5‰,持续数百万年,即“Bitter Springs”漂移 (Halverson *et al.*, 2005, 2007; MacDonald *et al.*, 2010; Rooney *et al.*, 2014; Xiao *et al.*, 2014;

Wörndle *et al.*, 2019). 这次 $\delta^{13}\text{C}_{\text{carb}}$ 负漂移事件在全球范围内分布,被视为拉伸系横向对比的标志. $\delta^{13}\text{C}_{\text{carb}}$ 负漂移通常意味着有机碳埋藏量减少,一方面归因于富氧水体扩展,制约 Mo、N 等生物必需元素被利用,进而极大地限制了初级生产力 (Wörndle *et al.*, 2019); 另一方面,可能由于海平面波动或海洋环流的重新配置,以及大规模的真极移事件和 Rodinia 超大陆裂解,使有机碳大量氧化 (Maloof *et al.*, 2006; Wörndle *et al.*, 2019).

总体上,拉伸纪较高的 $\delta^{13}\text{C}_{\text{carb}}$ 值表明,此时有机质埋藏效率显著增强, O_2 向海洋和大气释放,表明新元古代氧化事件已经启动.持续较高的 $\delta^{13}\text{C}_{\text{carb}}$ 之间偶有较强波动发生,如“Bitter Springs”漂移,可能是由活跃的构造运动引发的.然而,深时 $\delta^{13}\text{C}_{\text{carb}}$ 是否记录了当时海水的真实 $\delta^{13}\text{C}$ 组成值得思考.最新的研究表明, $\delta^{13}\text{C}_{\text{carb}}$ 主要取决于水岩界面的地球化学组成,受沉积速率、表层沉积物异化锰/铁/硫酸盐还原强度等因素的影响 (Wang *et al.*, 2019; Cui *et al.*, 2021; Ding *et al.*, 2021), 不能简单认为其指示全球海洋碳循环.因此,将拉伸纪整体较高的 $\delta^{13}\text{C}_{\text{carb}}$ 和幕式 $\delta^{13}\text{C}_{\text{carb}}$ 负偏移解释为全球有机碳从大量埋藏转变为有限埋藏是不精细的,传统解释模型有待修正.

2.2 蒸发岩和岩盐包裹体记录的拉伸纪海水化学条件

海水硫酸盐是表层系统最大的氧化剂储库之一.海水硫酸盐通常来源于氧化风化作用,最终以蒸发岩、碳酸盐晶格硫 (CAS) 和黄铁矿的形式埋藏保存下来.蒸发岩硫同位素 ($\delta^{34}\text{S}_{\text{ev}}$)、碳酸盐岩硫酸根硫同位素 ($\delta^{34}\text{S}_{\text{CAS}}$) 和黄铁矿硫同位素 ($\delta^{34}\text{S}_{\text{py}}$) 可用于重建海洋硫循环 (Fike *et al.*, 2006; Lang *et al.*, 2018b).

硫酸盐蒸发岩中富存的 SO_4^{2-} 被认为是大陆硫化物在充足 O_2 条件下发生强烈氧化风化形成的 (Kah *et al.*, 2001; Horita *et al.*, 2002; Melezhik *et al.*, 2005; Bao *et al.*, 2008; Blättler *et al.*, 2018; Prince *et al.*, 2019). 大约 12 亿年前沉积的层状蒸发岩 (CaSO_4) 反映了中元古代晚期脉冲式氧化事件 (Kah *et al.*, 2001; 张水昌等, 2022). 然而,最古老的块状蒸发岩直到拉伸纪 (约 830 Ma) 才出现,以石膏和硬石膏为主,厚度达 500 m (Lindsay,

1987; Spear *et al.*, 2014). 这套块状蒸发岩沉积后不久便发生了“Bitter Springs”碳同位素漂移事件(约 811 Ma)(Thomson *et al.*, 2015; Turner and Bekker, 2016). 拉伸纪厚层蒸发岩在加拿大、澳大利亚和中非广泛分布(Behr *et al.*, 1983; Lindsay, 1987; Jackson *et al.*, 2003; Prince *et al.*, 2019). 8.3 亿年前蒸发岩的大量沉积表明, 拉伸纪强烈的有氧风化使大量 SO_4^{2-} 注入海洋, 使海水具有较高的 SO_4^{2-} 浓度. 加拿大 Minto Inlet 组(850 Ma)块状蒸发岩的 $\delta^{34}\text{S}_{\text{ev}}$ 和 $\Delta^{34}\text{S}$ (硫酸盐和黄铁矿之间的硫同位素分馏)保持稳定, 表明较高的 SO_4^{2-} 含量和较低的黄铁矿埋藏效率($< 30\%$), 指示了较高的 O_2 水平(Prince *et al.*, 2019). Minto Inlet 组的上覆地层 Wynniatt 组具有持续较低的 $\delta^{34}\text{S}_{\text{py}}$ 组成, 同样指示了丰富的海水硫酸盐储库, 以及拉伸纪较高的大气 O_2 含量(Thomson *et al.*, 2015).

包裹体可以直接记录地质历史时期水体和大气组成. 澳大利亚西南部 8.15 亿年前的蒸发岩气体包裹体分析显示, 当时 O_2 含量为 10.9% PAL(Blamey *et al.*, 2016). 可见, 拉伸纪大气 O_2 含量已经达到较高水平. 然而, 另一项针对拉伸纪(约 830 Ma)岩盐流体包裹体的研究表明, 该时期海相硫酸根浓度远低于现代水平, 直至新元古代晚期才出现大幅增加(Spear *et al.*, 2014).

因此, 基于蒸发岩和岩盐包裹体分析, 拉伸纪 O_2 水平提升, 标志新元古代氧化事件在此时已经开始. SO_4^{2-} 作为高效氧化剂, 与有机质发生氧化还原反应, 生成大量 H_2S 和 ^{12}C 并释放到海水中, 造成“Bitter Springs” $\delta^{13}\text{C}_{\text{carb}}$ 负漂移事件. 然而, 拉伸纪大规模蒸发岩沉积主要发生在温暖干旱的局限盆地(Lindsay, 1987; Turner and Bekker, 2016), 是否具有全球性有待进一步验证. 由于缺少拉伸纪早期 $\delta^{34}\text{S}_{\text{CAS}}$ 数据, $\delta^{34}\text{S}_{\text{CAS}}$ 化学地层学是拉伸系今后工作的一个方向. 此外, 应建立新的数值模型, 以更准确地估计拉伸纪海水 SO_4^{2-} 浓度和大气 O_2 水平.

2.3 重建拉伸纪海水氧化还原条件的其他地球化学证据

一般认为动物的出现与多样化受到氧气含量制约, 也会受到有害气体 H_2S 的影响. 基于上述讨论, 动物演化的 O_2 含量壁垒可能在拉伸纪被打破. 但是, 元古宙海水通常被认为具有化学分层模式, 包括表层氧化海水、深部铁化(以 Fe^{2+} 为

主)海水, 以及沿大陆边缘的硫化(以 H_2S 为主)海水(Canfield *et al.*, 2008; Li *et al.*, 2010; Planavsky *et al.*, 2011; Lyons *et al.*, 2014). 因此, 缺氧或硫化海水是制约动物演化的关键要素.

铬(Cr)是一种氧化还原敏感元素, 主要包括 Cr(VI)和 Cr(III)两种价态. Cr(VI)较 Cr(III)具有更强的可溶性和流动性, 较重的 ^{53}Cr 优先进入 Cr(VI)储库. 中国、美国、澳大利亚和加拿大等地元古宙铁矿和海相黑色页岩的 $\delta^{53}\text{Cr}$ 值表明, 在 800 Ma 之前铬的氧化作用有限, $\delta^{53}\text{Cr}$ 接近地壳平均值, 之后 $\delta^{53}\text{Cr}$ 发生显著分馏, 可达 2.0‰, 指示 O_2 水平明显提升(图 3)(Planavsky *et al.*, 2014a; Cole *et al.*, 2016; Canfield *et al.*, 2018). 锌(Zn)是真核生物必需的营养元素, Zn^{2+} 具有与 Fe^{2+} 相似的行为, 例如在缺氧条件下可以进入碳酸盐晶格, 或者以硫化物形式沉淀(Robbins *et al.*, 2013; Scott *et al.*, 2013). 当 Fe^{2+} 被氧化时, Zn^{2+} 可以稳定存在, 因此利用浅海碳酸盐岩中的 Zn/Fe 比值来示踪地球 O_2 演化. Zn/Fe 从中元古代到新元古代呈上升趋势(图 3), 表明 O_2 水平在拉伸纪升高(Liu *et al.*, 2016). 此外, 真核生物相对于原核生物更容易摄取锌, 并优先利用较轻的锌同位素. 富有机质黑色页岩中硫化物的锌同位素组成($\delta^{66}\text{Zn}$)在 800 Ma 之前与地壳值(约 0.30‰)或海水值(约 0.50‰)接近, 在 800 Ma 显著升高(约 0.90‰), 表明有机质埋藏量增大, 指示真核生物此时可能已占据生态优势(图 3)(Isson *et al.*, 2018). 海相页岩中的硒同位素组成($\delta^{82/76}\text{Se}$)可以作为一种新的氧化还原指标来示踪 O_2 演化. 在含氧量较高的海水中, 页岩 $\delta^{82/76}\text{Se}$ 值较低(Williams *et al.*, 2019). 拉伸纪(约 770 Ma)黑色页岩 $\delta^{82/76}\text{Se}$ 呈下降趋势(图 3), 标志着 O_2 水平在 Sturtian 冰期之前已经开始上升(Pogge von Strandmann *et al.*, 2015). 碘(I)是局部氧化还原敏感元素, 主要以氧化态 IO_3^- 和还原态 I^- 形式存在. IO_3^- 能够进入碳酸盐矿物并取代 CO_3^{2-} (Lu *et al.*, 2010; Podder *et al.*, 2017). 碳酸盐岩 I/(Ca+Mg)组成反映了海水碘浓度, 该比值在“Bitter Springs”碳同位素异常(约 810 Ma)期间明显升高(图 3), 表明存在局部氧化环境(Hardisty *et al.*, 2017; Lu *et al.*, 2017, 2018). I/(Ca+Mg)主要指示了浅层水体的氧化还原条件, 其是否指示拉伸纪全球性氧化事件需要进一步探究.

另一种观点认为, 拉伸纪主要发生了硫化水体

的扩张而不是消退.例如,美国 Chuar 群(750 Ma)的铁组分、Mo 浓度和 $\delta^{95}\text{Mo}$ 表明当时主要为硫化海水,占据了海底 1%~4%(Dahl *et al.*, 2011).拉伸纪 Mo、U 和 V 等氧化还原敏感金属元素含量总体较低,证明了缺氧海水特别是硫化水体的普遍存在(Scott *et al.*, 2008; Thomson *et al.*, 2015),可能抑制了生命演化.我国华北胶辽徐怀地区的 ^{238}U 同位素也支持拉伸纪早期海洋缺氧扩张(Zhang *et al.*, 2022).此外,海相碳酸盐岩的 Ce/Ce^* 负异常也表明拉伸纪早期的大气氧含量非常低,约 < 1% PAL(Ward *et al.*, 2019).拉伸纪(约 750 Ma)还出现了一种特殊的沉积构造,形态上是折叠的、被微晶方解石充填的裂缝,称为碳酸盐岩臼齿构造(Molar Tooth Structures, MTS).臼齿构造的 $\delta^{26}\text{Mg}$ 、 $\delta^{34}\text{S}_{\text{CAS}}$ 和 $\delta^{13}\text{C}$ 值表明,微晶方解石沉淀早于基质白云岩化过程,且异化硫酸盐还原和甲烷生成反应强烈, CH_4 强烈释放(Shen *et al.*, 2016).大量还原性气体 CH_4 的累积维持了元古宙(>750 Ma)大气和海洋较低的氧气水平.

综合看来,在恢复拉伸纪氧化还原状态时,利用不同的地球化学方法可能得出不同的结论.每一种地球化学指标的指示意义,以及是否具有全球代表性,都需要重新思考.总体上,各种地球化学指标反映了拉伸纪表生系统具有较强的非均质性,即氧化、硫化和铁化海水同时存在.因此,可以预期在拉伸纪存在氧气绿洲等局部宜居环境.

2.4 拉伸纪海底氧气绿洲

在现代委内瑞拉高盐泻湖中,蓝细菌微生物席营造了富含 O_2 的微环境,移动和穴居动物的出现与蓝细菌藻席密切相关(Gingras *et al.*, 2011).将今论古,拉伸纪微生物和宏体藻席通过光合作用产生大量氧气,可能营造适宜的海底氧气绿洲,在动物演化中发挥了关键作用(Rishworth *et al.*, 2016).例如,华北地区拉伸纪页岩中铁组分、微量金属元素(Cu、Zn、Ni、Mo、V)和碳-硫地球化学数据表明,当时氧化和铁化海水共存,验证了“海底氧气绿洲”模型(Wang *et al.*, 2021).然而,氧气“绿洲”是否广泛存在,以及该微型“避难所”附近的氧气水平有待进一步确定.

3 新元古代氧化事件驱动机制

3.1 生命演化推动新元古代氧化事件

根据化石记录和生物分子钟证据,真核藻类

在拉伸纪之前出现,并在拉伸纪(约 800 Ma)占据生态优势,或者至少有区域生态优势.由于真核生物生成的有机质具有较高的埋藏效率,大量 O_2 释放到海洋和大气中,意味着新元古代氧化事件在拉伸纪可能已经启动.此外,多种地球化学指标表明拉伸纪海水氧化的趋势.

拉伸纪氧化水体支持动物的出现和生存,同时动物的滤食或捕食行为可以提高海水氧气水平.例如,海绵作为滤食性动物,可以吸收海水中大量悬浮有机物,成为重要的有机碳汇,有利于维持海水高氧.浮游动物捕食行为及大颗粒粪便同样增强了有机碳埋藏(Butterfield, 2009),使氧气释放.陆生真菌和地衣在 800~600 Ma 出现,通过呼吸作用消耗上层土壤中的氧气(Heckman *et al.*, 2001; Retallack *et al.*, 2013).因此,大量 O_2 被释放到大气中,而不是被输送到上层土壤以下的风化带,这被认为是新元古代氧化事件的一种驱动机制(Kump, 2014).新元古代氧化事件时间和幅度的厘定需要更可靠的化石证据.

3.2 板块构造运动引发新元古代氧化事件

活跃的构造运动被认为从根本上引发了地表的剧烈改变和生物圈的扰动.罗迪尼亚超大陆的拼合与裂解与新元古代生命-环境协同演化密切相关.罗迪尼亚超大陆在 12 亿年前开始拼合,之后在拉伸纪晚期裂解离散(Li *et al.*, 2008).

由于罗迪尼亚超大陆裂解,裂谷盆地广泛发育,为沉积物提供了充足的沉积空间,大量有机碳沿大陆边缘埋藏.罗迪尼亚超大陆裂解还伴随着幕式大规模岩浆活动及随之形成的大火成岩省(Large Igneous Province, LIP),如 Franklin 大火成岩省(约 720 Ma)(Lu *et al.*, 2022).强烈的玄武岩风化作用为海洋提供了丰富的营养元素磷,促进了海洋初级生产力.有机碳埋藏效率提高,大量氧气被释放到海水和大气中.可见,罗迪尼亚超大陆裂解拓展了大陆边缘的分布,导致强烈的玄武岩风化,最终刺激拉伸纪氧气含量上升.例如,海水 $^{87}\text{Sr}/^{86}\text{Sr}$ 同位素在 ~800 Ma 显著增加,表明大陆风化增强(Cox *et al.*, 2016; Chen *et al.*, 2022).

另一方面,构造运动将地球内部大量 CO_2 和 H_2S 气体带入表生体系,导致碳和硫储库增加.生物地球化学模拟结果表明,埃迪卡拉纪时期碳和硫储库的增加促进了有机碳和黄铁矿的埋藏,使当时大气 O_2

水平上升了50%(Williams *et al.*, 2019).同理,在拉伸纪罗迪尼亚超大陆裂解期间,大量 CO_2 和 H_2S 喷发,广阔的大陆边缘积累了巨大的碳和硫储库. Lee *et al.*(2016)也提出强烈的变质作用和岩浆作用释放大量的碳,主要以 CO_2 的形式保存于大陆边缘. 显著升高的大气 CO_2 浓度促进了初级生产力水平,最终汇入有机碳库,进一步触发了新元古代氧化事件.

因此,新元古代氧化事件与罗迪尼亚超大陆裂解之间存在因果联系. 新元古代氧化事件可能开始于拉伸纪晚期,与罗迪尼亚超大陆裂解时间耦合. 但是,与罗迪尼亚超大陆裂解相伴生的玄武岩风化强度、磷浓度和 O_2 水平需要更精确的模拟.

4 新元古代氧化事件与“雪球地球”的内在联系探讨

4.1 氧化事件与气候冰室之间的相互作用

新元古代氧化事件早于成冰纪“雪球地球”,二者之间可能存在一定的因果联系(图4).一方面,新元古代氧化事件可能是全球冰室的起因. CH_4 是早期地球大气和海洋的重要组成部分,也是一种还原性气体和有效的温室气体(Pavlov *et al.*, 2003; 罗根明和胡清扬, 2022). O_2 和 SO_4^{2-} 等氧化剂在成冰纪之前逐渐累积,降低了 CH_4 的“源”,提高了 CH_4 的“汇”,进而抑制了 CH_4 的积累. 因此,拉伸纪气温整体呈降低趋势(Pavlov *et al.*, 2003; Lyons *et al.*, 2021; Lu *et al.*, 2022). 当达到低温阈值时,成冰纪“雪球地球”将急速启动. 二氧化碳是另一种不可忽视的温室气体,二氧化碳浓度降低同样会使气温降低. 伴随罗迪尼亚超大陆裂解,大火成岩省显著发育,如Franklin大火成岩省(720~717 Ma)(Ernst *et al.*, 2021). 随后,大火成岩省强烈的玄武岩风化消耗了大量二氧化碳,导致温度急剧下降,引发了全球性冰川(Cox *et al.*, 2016; Lu *et al.*, 2022). 除甲烷崩溃和玄武岩风化假说外,大火成岩省侵入硫酸盐蒸发岩会产生大量硫酸盐气溶胶,进而提高行星反照率,产生气候冷却效应,最终导致成冰纪“雪球地球”(MacDonald and Wordsworth, 2017; Lu *et al.*, 2022).

另一方面,氧气水平上升可能是“雪球地球”的结果. 通常地,冰川融化将剥蚀大陆,向海水输送大量磷等营养物质. 因此,“雪球地球”间冰期和冰期后剧烈的物理风化作用会显著提高海洋磷含量,

进而提高初级生产力,使有机碳大量埋藏,大量 O_2 被释放到海水和大气中,促进新元古代氧化过程(Planavsky *et al.*, 2010; Hoffman *et al.*, 2017).

综上所述,新元古代氧化事件与“雪球地球”密切相关、相互作用. 但是需要注意到,构造运动从根本上控制了氧化事件与“雪球地球”之间的相互作用. 具体而言,罗迪尼亚超大陆裂解扩展了大陆边缘面积,引发了强烈的大陆风化. 磷等营养元素被大量输送到海水中,增强了有机碳的生成与埋藏,进而使氧气大量释放,标志着新元古代氧化事件的开始. O_2 含量上升限制了温室气体甲烷的释放,使气温降低,引发“雪球地球”发生. 强烈的大陆风化大量消耗了另一种温室气体 CO_2 ,也促进了“雪球地球”形成. “雪球地球”间冰期和冰期之后,冰川消融作用增强物理风化作用,提高了磷等营养元素的供应,进而提高了有机碳埋藏效率和 O_2 水平.

4.2 拉伸纪逐步氧化事件和幕式冰室气候

罗迪尼亚超大陆的裂解从根本上控制了新元古代氧化事件和冰室气候的相互作用. 考虑到罗迪尼亚超大陆的裂解主要发生在3个阶段(分别为825 Ma、780 Ma和720 Ma)(Li *et al.*, 2008, 2013),新元古代氧化事件和冰室气候应该也是逐步发生的.

在拉伸纪早期(1 000~820 Ma),多个大陆板块通过构造运动拼合在一起,形成罗迪尼亚超大陆. 此时真核藻类已经出现并呈现多样化,真核藻类生成的有机碳埋藏效率显著提升,使大量 O_2 释

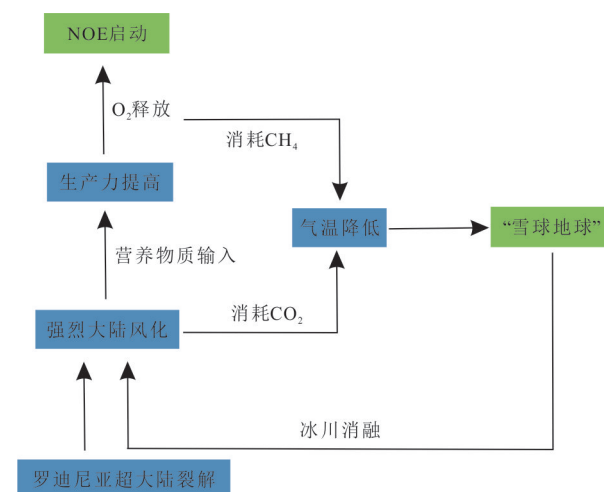


图4 新元古代氧化事件与“雪球地球”启动时期的大气与海洋环境变化

Fig.4 Atmospheric and oceanic changes in the Neoproterozoic Oxygenation Event and onset of Snowball Earth

放到地球表层,发生氧化事件.同时,有机碳埋藏量增多使大量 ^{12}C 进入有机碳库,导致无机碳库具有较高的碳同位素组成,即出现 $\delta^{13}\text{C}_{\text{carb}}$ 高原.在825 Ma出现了罗迪尼亚超大陆的第一次裂解高峰期,以活跃的地幔柱活动和强烈的化学风化为特征(郑永飞,2003;Li *et al.*, 2008).大量营养元素被输入海水,极大地刺激了初级生产力和有机碳埋藏.同时,大量硫酸盐蒸发岩的出现表明当时海水中 SO_4^{2-} 浓度较高,也指示了重要的氧化脉冲事件.此外,氧化脉冲事件使 CH_4 和 CO_2 等温室气体分别被大量氧化和强烈的化学风化消耗,进而导致气温下降,出现第一次幕式冰室气候.由于 SO_4^{2-} 和 Fe^{3+} 等氧化剂被大量输入海水,与有机质剧烈反应,引发“Bitter Springs” $\delta^{13}\text{C}_{\text{carb}}$ 负偏移事件.另一方面,古生物学证据表明全球物种多样性在拉伸纪后半期下降(Riedman and Sadler, 2018).真核和原核初级生产者可能经历绝灭,初级生产力降低,有机碳埋藏效率下降,使大量 ^{12}C 进入无机碳库, $\delta^{13}\text{C}_{\text{carb}}$ 值出现10‰左右的负偏移,即“Bitter Springs”碳同位素异常事件(约811 Ma).此时,微弱的初级生产者光合作用可能导致新元古代氧化趋势停滞, O_2 含量回落到低水平.“Bitter Springs”碳同位素异常事件之后 $\delta^{13}\text{C}_{\text{carb}}$ 快速回升,表明初级生产者再次增殖繁盛,产氧光合作用强度增强,表生地球再次经历氧化过程.

之后,罗迪尼亚超大陆又发生了两次大规模裂解(约780 Ma和约720 Ma).与825 Ma时第一次裂解相似,大陆边缘显著扩展,化学风化作用加剧,导致有机碳埋藏效率和氧气水平升高.可见,罗迪尼亚超大陆阶段式裂解与脉冲式氧化事件耦合. O_2 水平上升限制了 CH_4 和 CO_2 等温室气体,导致气候变冷.在720 Ma左右,构造活动与化学风化强度达到最高水平.气候变冷超过阈值,又或是数次冷却期的累积效应,最终形成极端“雪球地球”.在地球化学循环方面,Kaigas冰期(约780 Ma)之后, $\delta^{13}\text{C}_{\text{carb}}$ 同样发生了幅度约为10‰的负偏移,可与“Bitter Springs”碳同位素异常类比.

基于罗迪尼亚超大陆经历过三次裂解高峰期,拉伸纪可能发生过三次脉冲式氧化和间歇性气候变冷.构造运动和初级生产者转变从根本上控制了氧气水平和气候条件.氧气上升与全球性冰川相互作用、相互促进.然而,上述关于构造运动、氧气演化和气候变化的相互作用主要是基于推论,依

然缺少确凿的沉积学、地球化学和古生物学证据.例如,尚未在全球范围内发现825 Ma和780 Ma的冰川沉积物;要准确重建 O_2 演化曲线,需要更加深刻地理解地球化学参数的指示意义,依托更加科学的数值模型,以及如何解释“Bitter Springs”等碳同位素异常事件仍存在争议;虽然在拉伸纪后半期生物多样性总体呈下降趋势,但无法确定在825 Ma、780 Ma和720 Ma存在生物绝灭事件.因此,拉伸纪氧化事件和极端冰室气候等之间的相互联系需要进一步研究.

5 问题与展望

5.1 拉伸纪地层年代的精准厘定

地层年代是正确识别划分地层的最直接标准.然而,由于缺乏可靠的年代学数据,拉伸纪地层划分、对比存在不确定性.例如,华北地台青白口系长期以来被认为属于新元古代,而青白口系底部下马岭组放射性U-Pb定年约为1370 Ma,归属中元古代(Gao *et al.*, 2007; 高林志等, 2007; Gao *et al.*, 2008a, 2008b; 苏文博, 2016; 旷红伟等, 2023).因此,需要进一步细化沉积学和地层学工作,特别是夯实年代学证据,以推进拉伸纪研究发展.

5.2 拉伸纪化石的广泛发现和精准鉴定

除年代地层学外,生物地层学通常也是地层划分对比的重要依据.尽管*Chuaria*和*Tawuia*等多细胞生物在拉伸纪广泛分布(Xiao and Dong, 2006; Tang *et al.*, 2017b),但是拉伸纪地层缺乏标准化石,无法依据古生物学证据对拉伸纪地层进行识别、划分和对比.最近的一些研究发现一些疑源类化石,如*Trachyhystriosphera aimika*(Pang *et al.*, 2020)、*Cerebrosphaera*(Cornet *et al.*, 2019)可能对于拉伸纪的地层划分与对比具有潜力,但需要进一步的研究.

另一方面,无法确定动物的出现和多样化受控于大气和海水的氧气水平.目前已知拉伸纪间歇式氧化事件与8.9亿年前疑似的海绵化石在时间上吻合.此外,分子钟和生物标志物证据均表明真核生物特别是动物在拉伸纪之前或期间已经分化.然而,对这些微观和宏观化石的解释仍然存在争议,需要进一步敲定拉伸纪化石鉴定,并确定是否有足够的氧气支持动物的生存.

动物生存需要的氧气阈值是另一个关键要素.传统观点认为动物代谢的氧气阈值分布

在1%~10% PAL之间,但也有假说提出动物在低氧条件下可以生存,表明O₂不再是动物演化的限制因素.因此,对于氧气供应与动物生存的关系,以及早期动物化石的发现是否预示着较高的氧气水平,都需要进一步考虑.

5.3 地球化学数据的高分辨率分析和科学解释

拉伸系记录的“Bitter Springs”碳同位素负漂移事件被认为是进行地层划分对比的另一个标志.然而,拉伸纪大部分地层缺乏地球化学研究,相关数据较少,无法进行地球化学约束.因此,需要对拉伸系进行高分辨率地球化学测定,特别是建立起全球地球化学等时框架.此外,海相碳酸盐岩地球化学指标是否反映全球海水原始组成需要进一步评估和修正.例如, $\delta^{13}\text{C}_{\text{carb}}$ 表示水岩界面(Water-Sediment Interface, WSI)附近的碳循环过程,受到两个端元的控制,即海水溶解无机碳(DIC)和随孔隙水扩散上涌DIC.孔隙水扩散上涌的强度取决于多种因素,包括沉积速率、氧逸度和异化锰/铁还原反应强度等.另外,应明确Cr、Mo、V等非传统金属元素的地球化学循环过程和行为规律.只有进行高分辨率地球化学测试分析并进一步合理解释,才能建立更加科学、准确的数值模型,进而模拟恢复新元古代氧化事件和“雪球地球”的起止时间、持续时长、氧气和温度的变化幅度等.

通过对拉伸纪生命面貌系统回顾和对地球化学证据的全面梳理,可以推断新元古代氧化事件在成冰纪“雪球地球”之前已经启动.新元古代氧化事件的触发机制主要是伴随罗迪尼亚超大陆裂解,发生了强烈的大陆风化,大量营养元素输入海水,增强了有机质的生成与埋藏,使氧气含量大幅度提升.O₂含量上升和强烈大陆风化剧烈消耗CH₄、CO₂等温室气体,使气温骤降,引发“雪球地球”.但是,要敲定新元古代氧化事件与“雪球地球”之间的内在联系,仍然缺乏可靠的年代学、古生物学和地球化学证据.因此,需要进一步对拉伸纪地层年龄精准测定、对化石正确鉴定、对地球化学参数高分辨率分析和精确数值模拟.

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