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川南威远地区早寒武世氮循环及古环境意义

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摘要【目的】寒武纪早期是地质历史时期海洋环境演化的重要时期,深入探究该时期海洋氧化还原及氮循环演化有助于厘清同期有机质富集的主控因素。【方法】以川南威远地区筇竹寺组为研究对象,系统开展铁组分、氮同位素、硫同位素分析。【结果】威远地区在寒武纪早期,海洋环境响应同期海平面波动,氧化还原条件经历了多次转变。在寒武纪第二期,深部缺氧硫化水体扩张至浅水陆架环境,强烈的反硝化作用导致海水中的NO₃⁻持续被消耗,最终导致威远地区海洋氮循环以生物固氮为主。同时,较低的δ¹⁵N值暗示寒武纪第二期相对较低的初级生产力水平。在寒武纪第三期,显著升高的δ¹⁵N值表明海洋NO₃⁻库逐渐扩大,表层氧化海水逐步扩张。【结论】沉积环境的氧化还原条件是威远地区筇竹寺组有机质富集的主要控制因素。由海侵引起的强烈缺氧条件导致筇竹寺组产生三次显著的有机质富集。海平面的变化最终影响着寒武纪早期华南内陆架地区的氧化还原、氮循环演化及有机质富集。

关键词 筇竹寺组;氮同位素;铁组分;氧化还原;有机质

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0 引言

寒武纪早期(542~510 Ma)是地球生命演化的关键时期。继埃迪卡拉软体动物群的繁盛与灭绝之后,两侧对称及具矿物骨骼生物在此期间开始繁盛,并在寒武纪第三阶(Stage 3)达到顶峰,建立了与现今相类似的复杂生态系统,这一重大的生物演化事件被称为“寒武纪生命大爆发”^[1-5]。生物的生存和演化与环境之间的关系较为密切,一方面生物的生存需要适宜的环境(氧气含量、养分的可用性、海洋化学条件等)来维持其进行正常的生命活动^[6-8],另一方面生物的活动也会在一定程度上导致其生存环境发生改变(大气—海洋氧含量的波动、海洋硫酸盐含量的变化等)^[9-12]。因此,探究海洋的化学状态是理解生物演化事件的重要基础,而氧化还原环境的重建则是其中重要的一环。

在过去的研究中,氧化还原敏感元素(如U、V、

Mo)及铁组分已被广泛应用于指示区域底层水体的氧化还原条件,同时表明了一个非均质的寒武纪早期海洋,即表层氧化的海水,深部缺氧的海水及中间动态变化的硫化水体^[13-18]。然而,氧化还原敏感元素及铁组分在指示氧化还原环境时存在一定局限性,其指示广海的氧化还原演化的能力较为薄弱^[19-20]。氮元素作为生物的限制性营养元素,在不同的氧化还原环境下,氮的生物地球化学循环模式和氮同位素的分馏显著不同,保存在海洋沉积物中的氮同位素组成($\delta^{15}\text{N}$)具有表征广海氧化还原条件和评估古生产力水平的潜在能力^[21-23]。目前,华南地区利用氮同位素来表征寒武纪早期海洋氧化还原演化进行了一些工作,但是多数研究集中在相对深水的斜坡—盆地地区(如贵州道坨、贵州印江、湖南袁家等)^[24-28]。这些研究表明由寒武纪幸运阶—第三阶逐渐下降的 $\delta^{15}\text{N}$ 值,其中幸运阶较高的 $\delta^{15}\text{N}$ 值被解释为强烈的不

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完全反硝化作用或厌氧氨氧化作用^[28-30], 第二阶—第三阶较低的 $\delta^{15}\text{N}$ 值被解释为生物固氮作用或部分氨同化吸收^[24,31-32]。氮同位素对海洋表层溶解氧含量具有较高的敏感性^[33-34], 而且浅水陆架地区海洋化学状态的变化能够很好地响应海平面的升降以及氧化还原界面的变化, 因此针对陆架地区开展氮同位素研究, 能够有效地帮助人们认识海洋氧化还原演变过程; 同时, 综合利用氮同位素和铁组分指标能够更好地约束海洋表层至底层水体的氧化还原状态。因此, 为了更加深入地了解华南寒武纪早期海洋化学状态演化, 研究采集了上扬子威远地区筇竹寺组样品, 利用多指标的方法(铁组分、氮同位素、硫同位素

等), 重建寒武纪早期威远地区氧化还原演化过程及氮循环模式, 并结合前人的研究结果进一步探讨筇竹寺泥岩有机质的富集机制。

1 地质概况

华南克拉通在寒武纪早期位于古纬度30° N附近(图1a), 主要由扬子板块和华夏板块两部分构成(图1b)。扬子板块北以秦岭—大别造山带为界, 南以红河断裂带为界, 西以鲜水河断裂带为界, 华夏板块则以南东方向沿着江山—绍兴断裂带分布^[37-38]。随着新元古代裂谷事件的发生, 扬子板块在埃迪卡

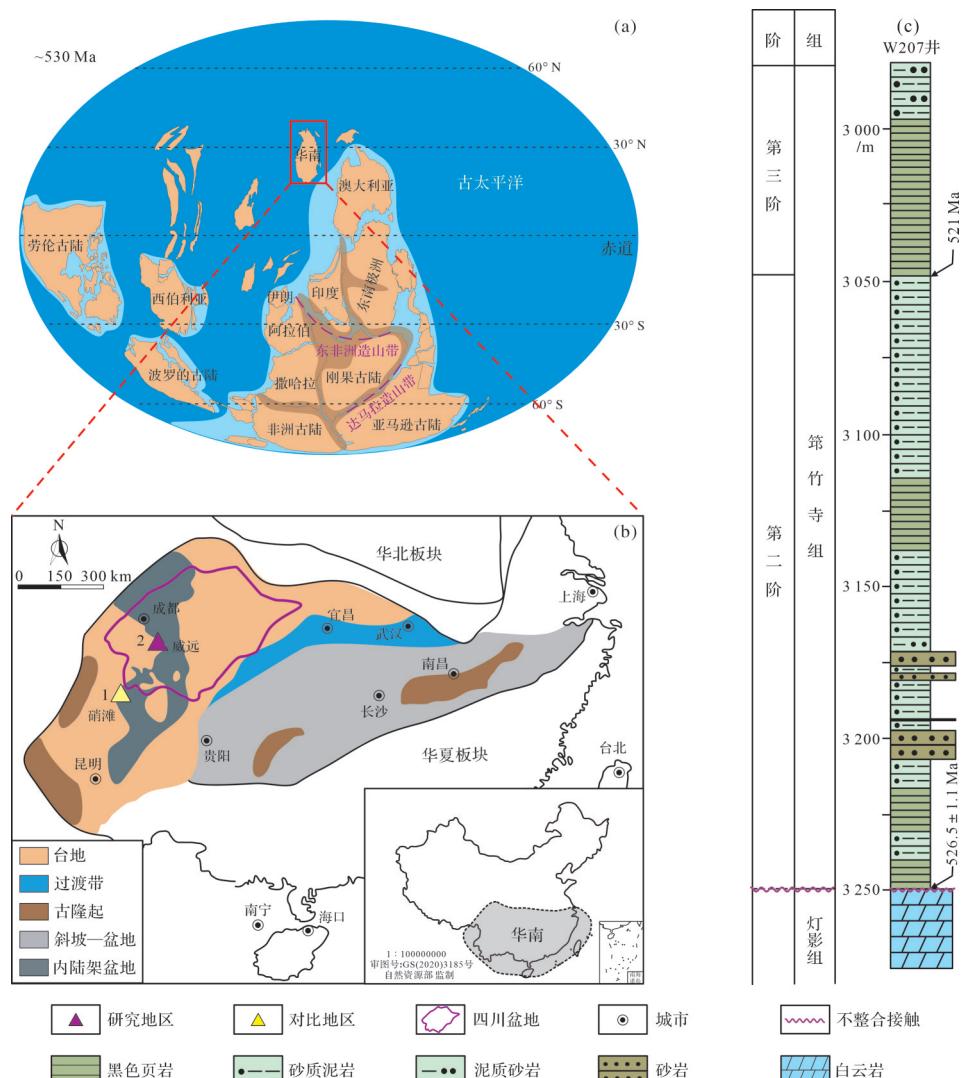


图1 (a)寒武纪早期的全球古地理图(据文献[35]修改);(b)寒武纪早期扬子台地古地理图(据文献[16,36]修改);黄色三角形代表研究区位置, 紫色圆形代表用于对比的硝滩剖面;(c)筇竹寺组地层序列;测年数据引自文献[46]

Fig.1 (a) Early Cambrian global paleogeography (modified from reference [35]); (b) paleogeographic map of the Yangtze Platform during the early Cambrian (modified from references [16,36]); The yellow triangle represents the studied location and the purple circle represents the Xiaotan section; (c) stratigraphic sequences of the Qiongzhusi Formation; The age data are from reference [46]

拉纪—寒武纪过渡时期从单一的裂谷盆地逐渐演化为由北西向南东展布的被动大陆边缘盆地^[24]。进而形成了三种不同的沉积格局,分别为浅水台地相、过渡带、斜坡—盆地相^[13,39-40](图1b)。此外,由于埃迪卡拉纪晚期至寒武纪早期发生的兴凯断裂作用,浅水陆架内部形成了一系列内陆架盆地(如绵阳—长宁拉张槽)^[37,41]。从沉积序列上看,在埃迪卡拉过渡时期,浅水陆架以碳酸盐岩沉积为主(如灯影组和朱家菁组),中—深水的斜坡和盆地相地区,以硅质岩沉积为主(如留茶坡组和老堡组)^[2,42-44]。在寒武纪第二期—第三期,伴随着全球性的海侵事件,整个扬子台地广泛沉积了一系列富有机质泥岩或页岩^[17-18,41,45]。

研究地区为四川盆地威远地区,其位于上扬子内陆架盆地西缘上斜坡(图1b)。样品采集该地区的W207钻井岩心,钻井岩心自下而上岩石地层单元为灯影组、筇竹寺组,二者不整合接触。其中灯影组主要由白云岩组成,筇竹寺组主要由黑色页岩、粉砂质泥岩以及泥质粉砂岩组成(图1c)。通过与具备完整地层演化框架及年代学约束的硝滩剖面进行对比,

基于样品高分辨的TOC演化曲线与硝滩剖面高度的一致性,研究确定W207钻井筇竹寺组底部起始沉积时间约为526.5 Ma,以及筇竹寺组上部寒武纪第三阶的时间界限(图2)。

2 样品与分析方法

研究共采集203个岩心样品,所有样品进行总有机碳(TOC)含量测试,以便进行地层对比^[13]。挑选44个样品进行铁组分、氮同位素、硫同位素测试。在进行地球化学分析前,所有样品利用去离子水清洗去除表面杂质后,粉碎至200目以下,以备地球化学分析。样品TOC含量、去碳酸盐部分总氮(TN_{decarb})、总碳(TC_{decarb})含量均在中国科学院广州地球化学研究所有机地球化学国家重点实验室完成。氮同位素测试在自然资源部第三海洋研究所海洋生物与生态实验室分析完成。铁组分及硫同位素在中国地质大学(武汉)生物地质与环境地质国家重点实验室分析完成。

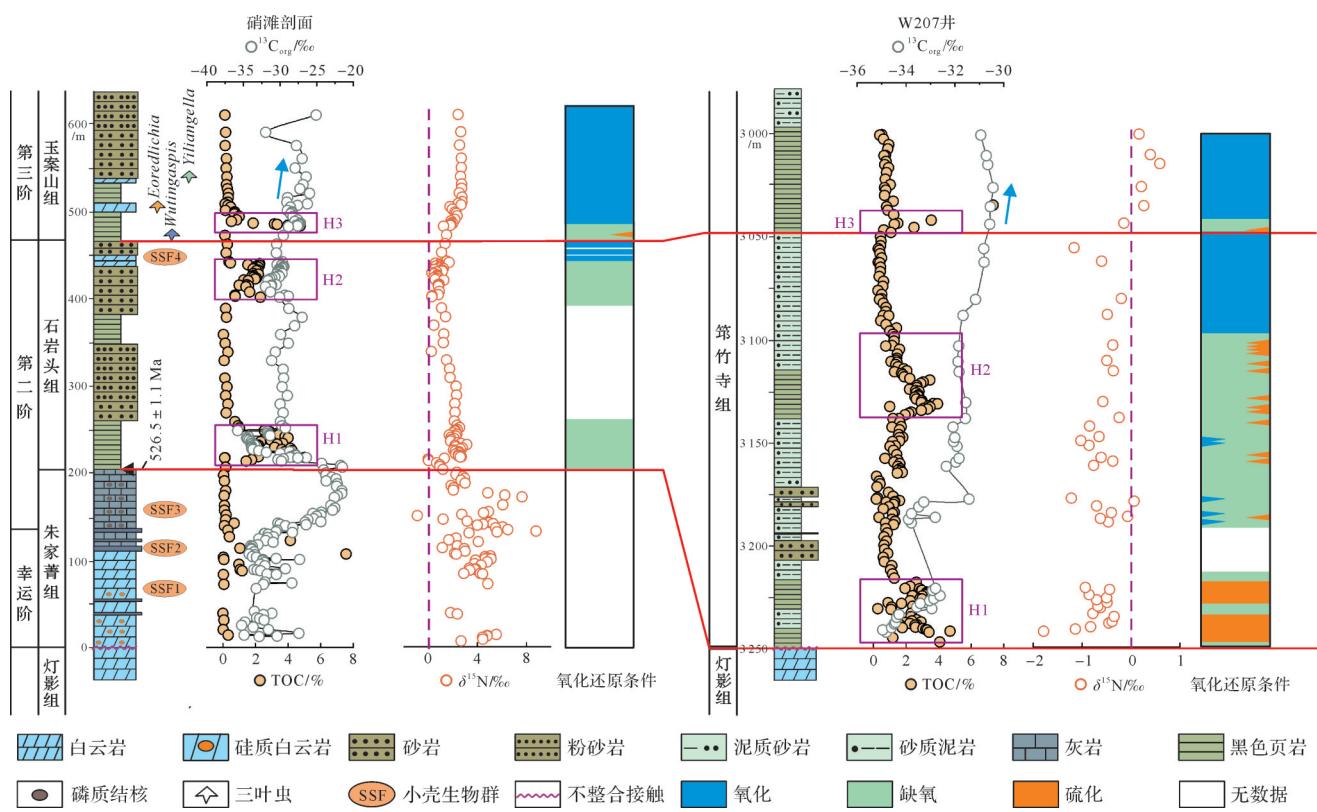


图2 硝滩剖面与W207井地层对比图

硝滩剖面TOC、 $\delta^{13}\text{C}_{\text{org}}$ 、 $\delta^{15}\text{N}$ 数据引自文献[30];测年数据引自文献[37,47];W207井筇竹寺组 $\delta^{13}\text{C}_{\text{org}}$ 数据引自文献[48];紫色矩形代表3个高TOC层位:H1、H2、H3

Fig.2 Stratigraphic correlation between Xiaotan section and well W207

The TOC, $\delta^{13}\text{C}_{\text{org}}$, and $\delta^{15}\text{N}$ data of the Xiaotan section are from reference [30]; the age data are from references [37,47]; and the $\delta^{13}\text{C}_{\text{org}}$ data of well W207 in the Qiongzhusi Formation are from reference [48]; The purple rectangles represent the three high-TOC layers: H1, H2, and H3

2.1 TOC含量

将约0.1 g样品粉末置于陶瓷坩埚中,加入1:1盐酸(HCl)去除碳酸盐组分,随后用去离子水清洗至中性,并在60 °C下烘干。TOC含量利用LECO CS-344碳硫分析仪进行分析。使用实验室内部标准B4016(TC=2.24%)进行数据监测,分析精度优于0.1%。

2.2 铁组分和硫同位素

Fe组分测试主要针对总铁(Fe_{T})和高活性铁(Fe_{HR})开展,其中 Fe_{HR} 主要包括黄铁矿铁(Fe_{py})、碳酸盐铁(Fe_{carb})、磁铁矿铁(Fe_{mag})和氧化物或氢氧化物铁(Fe_{ox})。 Fe_{py} 是利用 Ag_2S 沉淀中硫的质量百分比计算得到,其中 Ag_2S 沉淀通过铬还原法制取^[49]。 Fe_{carb} 、 Fe_{mag} 、 Fe_{ox} 含量通过程序萃取得到^[50]。硫同位素($\delta^{34}\text{S}_{\text{py}}$)测试通过将 Ag_2S 沉淀与过量的 V_2O_5 混合,进行灼烧得到。测试仪器为Thermo Fisher Scientific Delta V Plus同位素比质谱仪。使用三个IAEA国际标准(S1=-0.3‰; S2=22.65‰; S3=-32.5‰)进行数据监测,分析精度优于0.2‰。

2.3 TN_{decarb}含量、TC_{decarb}含量、氮同位素

称取约0.1 g样品粉末放入离心管中,加入1:1盐酸去除碳酸盐。称取约15 mg已除去碳酸盐的样品,进行TN_{decarb}含量、TC_{decarb}含量测试。测试仪器为

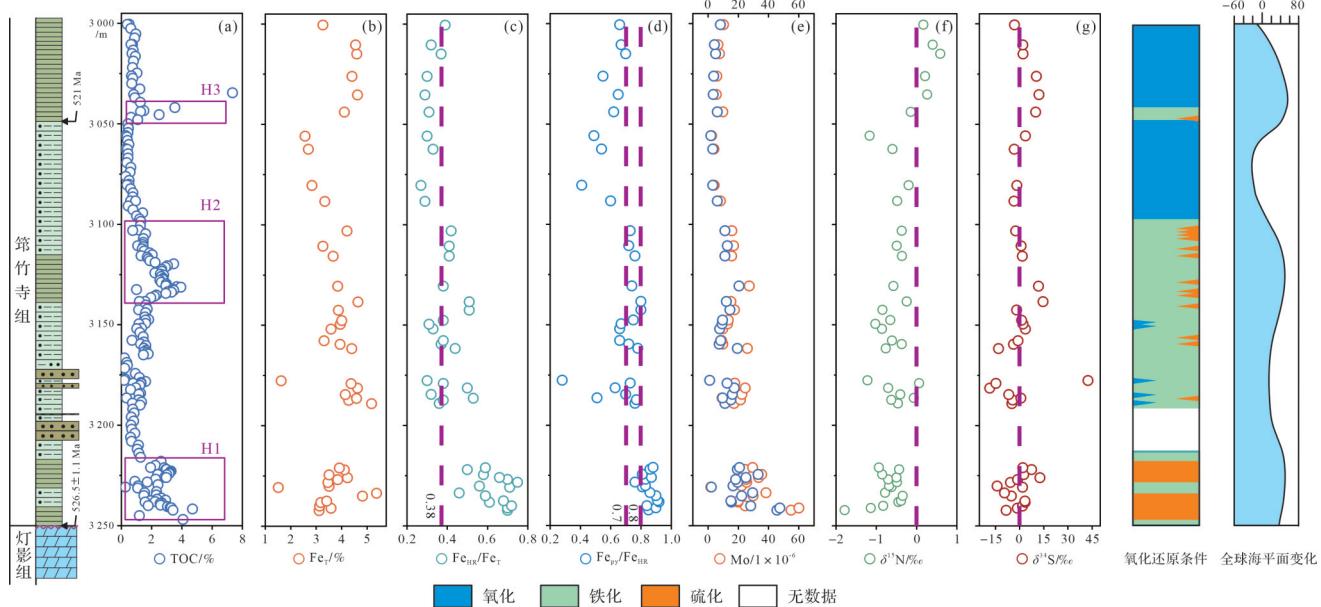


图3 W207井筇竹寺组地球化学参数

Mo含量引自文献[48];全球海平面变化曲线修改自文献[51];紫色矩形代表3个高TOC层位:H1、H2、H3

Fig.3 The geochemical data of well W207 in the Qiongzhusi Formation

The Mo contents are from reference [48] and the global sea-level change curve are modified from reference [51]; The purple rectangles represent the three high-TOC layers: H1, H2, and H3

VARIO EL cube元素分析仪,使用实验室内部标样IVA3380(TC=1.86%, TN=0.122%)进行数据监测,分析精度优于0.3%。

根据TN_{decarb}含量称取10~15 mg去碳酸盐样品,进行N同位素分析。测试仪器为Thermo Fisher Delta V Plus气体同位素比质谱仪,使用标样ACET($\delta^{15}\text{N}=-4.21\text{\textperthousand}$)进行数据监测,分析精度优于0.3‰。

3 结果

所有的地球化学结果见附表1,其中关键的地球化学指标见图3。TOC含量介于0.20%~7.35%(平均值为1.68%);Fe_T含量介于1.52%~5.37%(平均值为3.80%);Fe_{HR}/Fe_T介于0.27~0.25(平均值为0.46);Fe_{py}/Fe_{HR}介于0.28~0.92(平均值为0.72); $\delta^{15}\text{N}$ 介于-1.79‰~0.59‰(平均值为-0.51‰); $\delta^{34}\text{S}_{\text{py}}$ 介于-18.49‰~42.53‰(平均值为0.61‰)。

4 讨论

4.1 威远地区寒武纪早期古海洋氧化还原环境

Fe组分指标目前已广泛用于指示古海洋的氧化还原条件^[13-14, 20, 52-53]。为了保证指标的有效性,Fe组分指标建议使用在总铁含量大于0.5%的样品中^[54]。本

次研究样品总铁含量介于 1.52%~5.37% (平均值为 3.80%) (图 3b), 表明 Fe 组分数据是可靠的, 可用于判断古海洋氧化还原条件。 Fe_{HR}/Fe_T 小于 0.38 和大于 0.38 分别指示氧化条件, 缺氧条件^[20]。在缺氧条件下, Fe_{py}/Fe_{HR} 可进一步区分水体的硫化和铁化状态, Fe_{py}/Fe_{HR} 小于 0.7, 指示缺氧铁化的条件, Fe_{py}/Fe_{HR} 大于 0.7, 指示缺氧硫化的条件^[20,55]。

Zhao et al.^[48]利用筇竹寺组氧化还原敏感元素 Mo 对威远地区进行了氧化还原重建, 发现威远地区在筇竹寺组沉积时期经历了多期的氧化还原波动。这一认识整体上与本次研究 Fe 组分所指示的结果相一致。筇竹寺组底段(3 200~3 250 m)较高的 Fe_{HR}/Fe_T (0.46~0.75, 平均值为 0.63), Fe_{py}/Fe_{HR} (0.76~0.92, 平均值为 0.85) (图 3c,d), 指示强烈缺氧硫化的沉积环境, 这与同期强烈的 Mo 富集相一致。筇竹寺组中段(3 100~3 200 m)高度动态的变化的 Fe_{HR}/Fe_T (0.30~0.53, 平均值为 0.40), Fe_{py}/Fe_{HR} (0.28~0.80, 平均值为 0.63), 表明以间歇性硫化为主的水体化学条件, 且同时存在间歇性氧化(图 3c,d)。但是, 同期 Mo 元素并没有产生明显富集(图 3e)。这一现象可能是同期陆架地区或整个华南盆地较小的 Mo 储库所致^[15,45]。考虑到研究区位于相对浅水的陆架地区, 而且靠近内陆架盆地, 一个更加局限的环境可能导致局部海水中 Mo 元素的匮乏^[36]。筇竹寺上段(3 000~3 100 m)所有样品均表现出较低的 Fe_{HR}/Fe_T (0.27~0.39, 平均值为 0.32), Fe_{py}/Fe_{HR} (0.41~0.70, 平均值为 0.59), 反映持续的氧化条件, 这与同期较低的 Mo 含量相一致(图 3c~e)。基于铁组分重建的沉积环境整体由缺氧向氧化转变的过程, 同样得到样品 $\delta^{13}C_{org}$ 的支持。样品 $\delta^{13}C_{org}$ 曲线在筇竹寺组整段表现出明显的正偏, 而且这一 $\delta^{13}C_{org}$ 正偏现象同样出现在硝滩剖面(图 2), 表明海洋氧化还原状态逐渐向氧化过渡。有机质在耗氧降解过程中, 通常优先损失较轻的 ¹²C, 从而导致沉积物中富含较重的 ¹³C^[56]。值得注意的是, 寒武纪第三阶早期 Ni-Mo 多金属富集层(ca. 521 Ma)暗示整个扬子台地发生过一次短暂的缺氧事件^[36-37,57-58]。然而这次显著的缺氧事件并没有记录在本次样品的 Fe 组分数据中, 这可能受限于样品较低的分辨率。但是, 高分辨的 TOC 曲线在寒武纪第三阶早期显示出一次显著的升高(图 3a), 而且这一现象同时出现在扬子台地其他地区^[16,30,36,42], 可能间接地反映了此次短暂的缺氧事件。同时此次缺氧事件恰好对应着全球海平

面升高, 由此推断这一缺氧事件的出现可能源于同期的海侵(图 3)。此外, 结合威远地区氧化还原环境整体演化以及全球海平面变化特征, 发现氧化还原环境的转变与海平面的升降具有良好的对应关系(图 3)。因此, 海平面的变化可能对威远地区底层水体氧化还原条件起着重要的控制作用。

4.2 W207 井氮同位素信号有效性评估

陆源输入、早期成岩过程微生物的降解、晚成岩过程中热演化作用可能造成沉积物中的氮的损失, 进而改变其同位素信号^[33,59]。因此, 在使用氮同位素重建古海洋环境时, 首先要对沉积物的 $\delta^{15}N$ 值进行有效性评估。

陆源有机质输入可能造成海相沉积物内氮同位素值发生改变^[60-61]。然而, 陆生植物在泥盆纪后才发生大规模繁盛, 因此陆源有机质的输入对本次样品氮同位素信号的影响可以忽略^[24,62]。同时, $TN_{decarb}-TC_{decarb}$ 较高的相关性在很大程度上表明沉积物中的氮来自海洋而非陆源^[25]。

本次研究结果显示, 样品 TN_{decarb} 和 TC_{decarb} 之间具有较强的线性关系(图 4a), 表明沉积物中的氮主要来自有机质^[61]。其中与 Y 轴的正截距可能代表与黏土矿物结合的氮组分^[24,28]。这一部分氮主要源于早期成岩过程中有机质被微生物降解所释放的氮组分, 随后被黏土矿物吸附而保存下来^[63-64]。考虑到这一过程发生在一个相对封闭体系内, 氮组分并未发生损失, 因此该过程对氮同位素值的影响较小^[18,31,64]。

有机质热演化会造成氮的损失以及 $\delta^{15}N$ 值的升高^[23,33,59-60]。与现代海洋 C/N 比值(~6.6)相比, 本次样品表现出较高的 C/N 值(8.7~41.5, 平均值为 20.2), 可能指示氮含量在早期成岩或后期热演化过程中发生了损失。然而, 样品 $\delta^{15}N$ 值与 C/N_{decarb} , TN_{decarb} 含量、 TC_{decarb} 含量之间均不存在明显的线性相关性(图 4b~d), 说明氮同位素值并没有受到后期埋藏热演化作用的改造。因此, 氮同位素可以用于水体氧化还原环境的重建以及解释氮的生物地球化学循环。

4.3 W207 井氮同位素对古海洋沉积环境的指示

氮元素不仅是氨基酸、核酸、色素等生物分子的重要成分, 同时也是生物的限制性营养元素。在不同的氧化还原环境下, 氮的生物地球化学循环模式以及氮同位素组成具有明显不同^[33-34]。因此, 保存在沉积物中的氮同位素组成同时具有示踪氧化还原环境和重建古生产力水平的潜在能力^[23,33,65]。

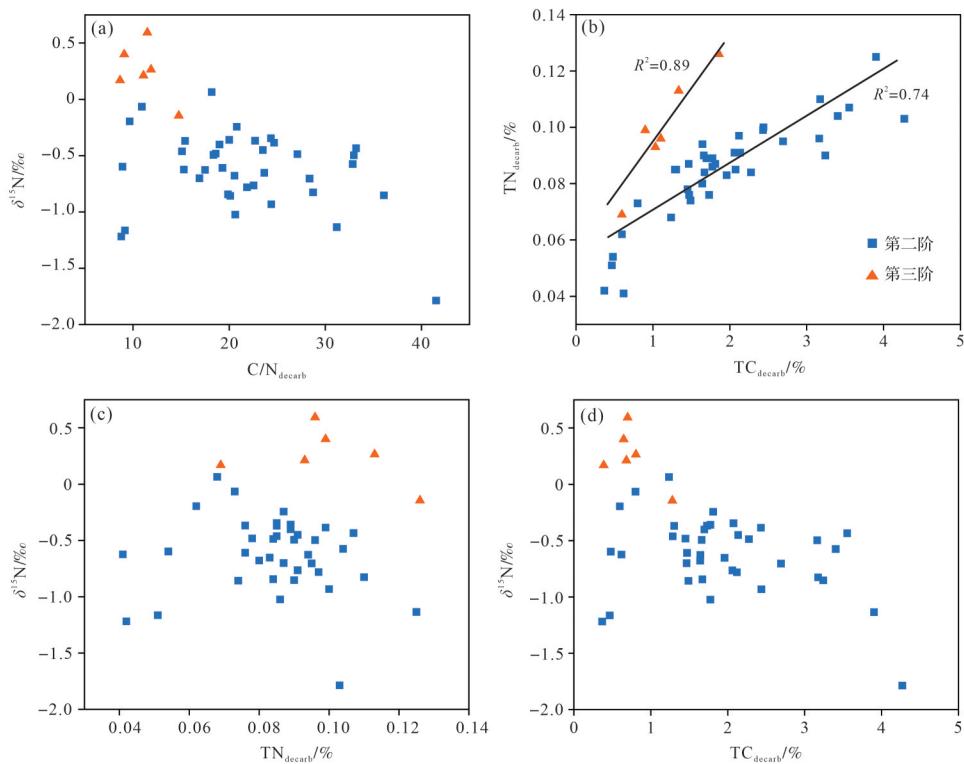


图4 W207井氮同位素信号有效性评估
 (a) $\delta^{15}\text{N}$ 、C/N_{decarb} 协变关系; (b) TN_{decarb}、TC_{decarb} 协变关系; (c) $\delta^{15}\text{N}$ 、TN_{decarb} 协变关系; (d) $\delta^{15}\text{N}$ 、TC_{decarb} 协变关系
 Fig.4 Evaluation of the availability of the nitrogen isotope signal in well W207
 (a) $\delta^{15}\text{N}$ vs. C/N_{decarb}; (b) TN_{decarb} vs. TC_{decarb}; (c) $\delta^{15}\text{N}$ vs. TN_{decarb}; (d) $\delta^{15}\text{N}$ vs. TC_{decarb}

本次研究结果显示,寒武纪第二阶所有样品具有较低的 $\delta^{15}\text{N}$ 值($-1.79\text{\textperthousand}$ $\sim 0.06\text{\textperthousand}$,平均值为 $-0.63\text{\textperthousand}$) (图3f),表明研究区海洋中氮循环以生物固氮作用为主,同时也反映海洋中较小的NO₃⁻储库^[25,63,66](图5a),而且这一现象同样出现在位于内陆架地区的硝滩剖面。结合硝滩剖面氮同位素记录(图2),幸运阶具有较高的 $\delta^{15}\text{N}$ 值(高达 9\textperthousand),这可能表明浅水陆架甚至是整个扬子海同期存在较大的NO₃⁻储库,强烈的不完全反硝化作用或厌氧氨氧化作用导致海水剩余NO₃⁻库中富集¹⁵N,进而被生物利用并保存在沉积物中^[24,30](图5b)。对于幸运阶—第二阶NO₃⁻储库明显的减小,一个可能的解释是,底层缺氧水体在随海侵逐渐扩张的过程中,持续的反硝化作用导致海水表层透光层中的NO₃⁻不断被消耗,从而导致研究区NO₃⁻库的缺乏,最终导致生物主要向大气摄取氮^[18,67]。此外,寒武纪第二阶较低的 $\delta^{15}\text{N}$ 值同时也暗示一个相对缺氧的海洋环境^[30],这与同期Fe组分数据所指示的结果一致(图3)。筇竹寺组底段较高的Fe_{HR}/Fe_T(0.46~0.75,平均值为0.63,图3c),表明底层缺氧水体在寒武纪第二阶已经扩展至浅水台地,同时表明

化学变化层的升高(图5a)。同期较高的Fe_{py}/Fe_{HR}(0.76~0.92,平均值0.85)以及较低的 $\delta^{34}\text{S}_{\text{py}}$ (低至 $-13.91\text{\textperthousand}$)(图3d,g),反映水柱中发生了强烈的细菌硫酸盐还原作用,促使大量的H₂S被释放至水柱中,进而导致广泛的硫化环境^[63]。此外,来自硝滩剖面大海段(ca. 530~528 Ma)碳酸盐岩样品显著的U同位素负偏表明寒武纪第二阶早期华南盆地甚至全球海洋底层缺氧水体存在扩张趋势^[68]。随后,在硝滩剖面石岩头组底部(ca. 526 Ma), $\delta^{13}\text{C}_{\text{carb}}$ 和 $\delta^{13}\text{C}_{\text{org}}$ 发生解耦^[30],且伴随着明显的 $\delta^{13}\text{C}_{\text{org}}$ 负偏(图2)。这种 $\delta^{13}\text{C}_{\text{org}}$ 负偏同样表现在本次研究筇竹寺组样品中(图2),其被解释为化学自养微生物或甲烷厌氧古菌富含¹²C生物量对总有机质的输入^[41,69]。以上证据均表明一个相对缺氧的沉积环境,这与样品筇竹寺组底部离散较负的 $\delta^{15}\text{N}$ 值(小于 $-1\text{\textperthousand}$)相一致^[18,25,28](图3f)。

寒武纪第三阶,筇竹寺组样品和硝滩剖面样品均出现明显的氮同位素正偏(图2),表明威远地区甚至整个内陆架地区NO₃⁻库逐渐扩大,生物可利用氮源主要来自NO₃⁻(图5c)。同时样品较低的Fe_{HR}/Fe_T以及明显的 $\delta^{34}\text{S}_{\text{py}}$ 正偏(图3c,g),表明沉积环境逐渐向

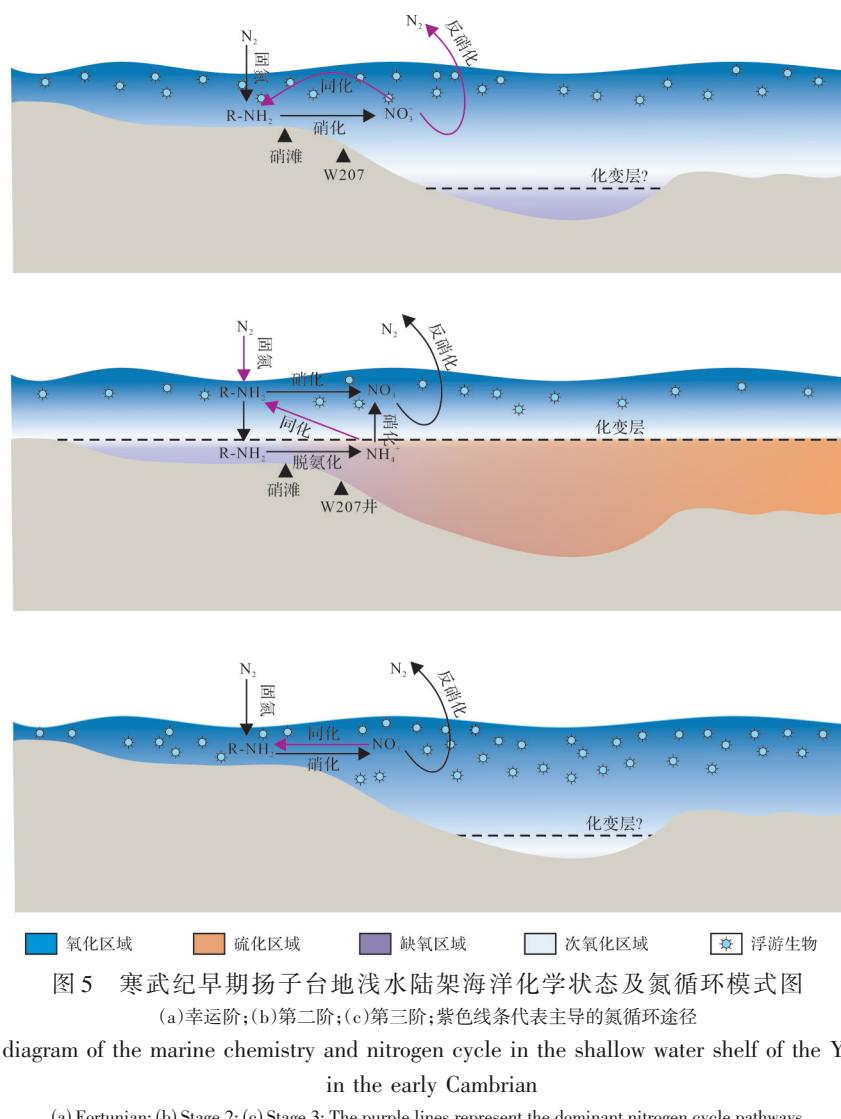


图5 寒武纪早期扬子台地浅水陆架海洋化学状态及氮循环模式图

(a)幸运阶;(b)第二阶;(c)第三阶;紫色线条代表主导的氮循环途径

Fig.5 Model diagram of the marine chemistry and nitrogen cycle in the shallow water shelf of the Yangtze Platform in the early Cambrian
 (a) Fortunian; (b) Stage 2; (c) Stage 3; The purple lines represent the dominant nitrogen cycle pathways

氧化过渡,这一现象同样得到硝滩剖面氧化还原重建的支持(图2)。此外,扬子台地一致的有机碳同位素正偏^[41]以及来自西伯利亚碳酸盐岩地层显著的U同位素正偏以及耦合变化的C、S同位素均支持全球表层海水的逐步氧化^[6,10,70]。

4.4 筏竹寺组泥岩有机质富集的控制因素

沉积物中有机质的富集主要受控于沉积环境的氧化还原条件、初级生产力^[71-72]。较高的生产力可以提供丰富的有机质来源,缺氧的沉积环境可为有机质提供良好的保存条件^[73]。基于筇竹寺组样品高分辨的TOC曲线(图3a),可以识别出三个显著的高TOC层位(H1、H2、H3),同时这三个层位整体上对应着强烈的缺氧甚至是硫化的沉积条件,而且这一特征同样出现在硝滩剖面。生物标志化合物表明,埃迪卡拉纪—早寒武纪时期,海水透光层中的初级生

产者主要为真核藻类^[26]。由于真核生物缺少固氮能力,并且优先同化周围环境中的NO₃⁻,因此海水中NO₃⁻含量对真核生物的繁盛具有至关重要的作用^[24,32,74]。威远地区在寒武纪第二阶较小的NO₃⁻储库,可能在一定程度上暗示同期相对较低的生产力水平。寒武纪第三阶较大且稳定的NO₃⁻储库以及更加氧化的水体环境,可能促进了同期后生动物的繁盛及生产力的提高^[4,16,75]。然而,由筇竹寺组微量元素(Cu、Zn、Ni)所指示的生产力结果却与之相反。寒武纪第二阶较高的微量元素富集系数被解释为相对较高的生产力水平,而寒武纪第三阶微量元素的亏损则被解释为低的生产力水平^[48]。对此,本次研究认为寒武纪第二阶较高的微量元素含量可能源于同期显著的缺氧条件导致的局部富集,不一定真实地代表生产力水平。

综上所述,高TOC层位H1、H2有机质的大量富集主要归因于强烈的缺氧甚至是硫化条件,而并非是较高的生产力水平。虽然氮同位素表明寒武纪第三阶具有较高的生产力水平,但是一个相对氧化的沉积环境可能导致有机质无法大量保存。基于TOC含量变化与氧化还原环境演化较高的一致性,本次研究认为威远地区筇竹寺组有机质的富集主要受控于沉积环境的氧化还原条件,由海平面上升所导致的三次强烈缺氧环境导致了有机质的大量富集。

5 结论

(1) 寒武纪第二阶—第三阶,威远地区发生了三次明显的缺氧事件,且与同期的海平面升高相一致。寒武纪第二阶,威远地区海洋氮循环以固氮作用为主,具有较小的 NO_3^- 储库以及相对较低的生产力水平;寒武纪第三阶,海洋表层 NO_3^- 储库逐渐扩张,沉积条件逐渐过渡到稳定的氧化环境。

(2) 威远地区筇竹寺组有机质富集主要受控于沉积环境的氧化还原条件,由海侵所导致的强烈缺氧条件促使了筇竹寺组三次显著的有机质富集。

(3) 威远地区和硝滩地区一致的TOC、氧化还原、氮同位素演化特征,显示上扬子内陆架地区具有类似的环境演化和有机质富集模式,海平面是影响上述变化的最重要因素。

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Nitrogen Cycle and Paleoenvironmental Implications in the Weiyuan Area, Southern Sichuan During the Early Cambrian

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Abstract: [Objective] The early Cambrian was a pivotal period of oceanic environmental evolution in Earth history. To gain the insight into evolutions of oceanic redox condition and nitrogen cycle, which can favor to ascertain the dominant control on coeval organic matter enrichment. [Methods] The present study conducted the iron speciation, nitrogen and sulfur isotopes analyses for the Qiongzhusi Formation in the Weiyuan area. [Results] The oceanic redox condition experienced several transitions in response to coeval sea-level fluctuations during the early Cambrian. In the Cambrian Age 2, the deep euxinic watermasses expanded to the shallow-water shelf environment, and intense denitrification resulted in the persistent consumption of NO_3^- in seawater, which eventually caused the nitrogen cycle dominated by biological nitrogen fixation. Synchronously, the low $\delta^{15}\text{N}$ values imply the relatively low primary productivity level in the Cambrian Age 2. The obviously increased $\delta^{15}\text{N}$ values in the Cambrian Age 3 suggest the stepwise expansion of NO_3^- reservoir and extension of surface oxygenated seawater. [Conclusions] The organic matter enrichment of the Qiongzhusi Formation in the Weiyuan area was dominantly controlled by redox conditions in the sedimentary environment, where the severe anoxia caused by transgression resulted in three significant organic matter enrichments. The redox conditions, nitrogen cycle, and enrichment of organic matter in inner shelf environments of South China were influenced by sea-level eustacy during the early Cambrian.

Key words: Qiongzhusi Formation; nitrogen isotope; iron speciation; redox; organic matter