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湖北宜昌埃迪卡拉系陡山沱组下部重晶石结核的形成过程和环境

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摘要 【目的】埃迪卡拉纪早期的海洋氧化还原状态一直是研究热点。通过分析陡山沱组下部重晶石结核的形成过程,旨在恢复埃迪卡拉纪早期的古海洋环境的氧化还原界面变化情况。【方法】通过沉积学、岩石矿物学分析,详细分析扬子板块北部金瓜墩剖面陡山沱组下部重晶石结核的形成过程,以此来推断其沉积环境。【结果】围岩层理围绕结核展布,显示结核形成于早期埋藏阶段。结核主要由重晶石、石英和黄铁矿组成,矿物分布具空间差异,核部以黄铁矿为主,核部外围则以重晶石为主。大部分重晶石结核核心部位发育自形/半自形黄铁矿聚合体和石英矿物;核心向外缘方向发育放射状交织生长的重晶石与石英矿物聚合体。研究认为重晶石结核矿物分布的不均一性反映了结核形成时环境条件的变化:结核核部的黄铁矿、石英形成于硫酸盐还原带;之后结核生长位置过渡到硫酸盐—甲烷过渡带,产甲烷带有机质分解过程释放的钡离子向上迁移,在硫酸盐—甲烷过渡带上部与硫酸根离子反应生成重晶石沉积。【结论】重晶石结核的形成具有阶段性。随着硫酸根浓度的升高,埃迪卡拉纪早期海洋中硫酸盐还原界面可能已经下降到水岩界面附近的沉积物中,部分甲烷在硫酸盐—甲烷过渡带被氧化,从而减少了它们向大气中的排放。

关键词 扬子板块;埃迪卡拉纪;陡山沱组;重晶石结核

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0 引言

新元古代埃迪卡拉纪是地球演化历史中的一个关键时期,发生了一系列重大生物演化事件,如后生多细胞动物的起源和复杂生物群落的出现等(Xiao and Narbonne, 2020)。同时在埃迪卡拉纪的地层中记录的无机碳同位素($\delta^{13}\text{C}_{\text{carb}}$)、碳酸盐晶格硫同位素($\delta^{34}\text{S}_{\text{CAS}}$)、黄铁矿硫同位素($\delta^{34}\text{S}_{\text{py}}$)和铁组分等地球化学指标发生了剧烈的波动,说明该时期地球表生环境也发生了重大变化(Xiao and Laflamme, 2009)。在

雪球地球结束之后,随着大陆风化作用加强,大量营养盐进入海洋,使海洋初级生产力得到了极大的提高,大量有机质被埋藏,同时促使海洋以及大气的氧含量逐渐升高,进而促进了生物快速演化(Planavsky *et al.*, 2010; Sahoo *et al.*, 2012; Lang *et al.*, 2018)。之后多细胞藻类的繁盛以及埃迪卡拉生物群甚至后生动物的出现,例如,华南埃迪卡拉纪的蓝田生物群(Yuan *et al.*, 2011)、庙河生物群(Xiao *et al.*, 2002)和石板滩生物群(Xiao *et al.*, 2021),说明地球环境变得更加宜居。生物与环境之间往往是相互关联与制

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约,因此探讨埃迪卡拉纪古海洋环境一直是学界的热点议题。

前人应用各种地球化学指标已经对埃迪卡拉纪的古海洋氧化还原条件进行了多次重建,取得了多种不同的认识。大多数模型显示出当时的海洋深水盆地是广泛缺氧的(Canfield *et al.*, 2007; Canfield *et al.*, 2008; Li *et al.*, 2010; Li *et al.*, 2015; Jin *et al.*, 2018; Wang *et al.*, 2018),相对还原的海洋状态可能一直持续到古生代早期(Dahl *et al.*, 2010; Sperling *et al.*, 2015; Jin *et al.*, 2016)。然而,埃迪卡拉纪海洋的氧化还原模式与同时期沉积地层中的化石记录有些许出入。例如,地球化学指标显示发育在约600 Ma的蓝田生物群、约550 Ma的庙河生物群的保存环境多为缺氧硫化环境(Wang *et al.*, 2014),而以宏体底栖生物为主的化石生物群的生存环境应为含氧水体(Xiao *et al.*, 2002; Yuan *et al.*, 2011)。目前,氧化还原敏感元素和钼同位素($\delta^{98/95}\text{Mo}$)等地球化学指标的研究表明,埃迪卡拉纪早期的深部海水在部分地区可能存在短期相对氧化的情况(Sahoo *et al.*, 2012; Chen *et al.*, 2015),可以为早期生物提供有利的生存环境。总之,前期关于古海洋环境的恢复研究多建立在地球化学分析基础上,缺乏相应的沉积学和矿物学证据。

矿物结核是一种重要的矿物聚合体,是一类在沉积岩中广泛存在,成分与围岩差异较大的沉积构造。结核的类型通常按其形成时期分为同生结核、成岩结核以及后生结核。同生结核是与围岩同时期形成的结核,结核内部与围岩通常可见由于成岩压实作用而变形的层理,在海洋中常见有铁锰结核(Cronan and Tooms, 1967; Hein and Koschinsky, 2014);成岩结核形成于成岩过程中沉积物质的再分配,结核多呈扁平状,内部层理平直不弯曲,部分切穿围岩层理,这类结核对沉积时期的古环境重建有着重要作用(Sellés-Martínez, 1996);后生结核则为在已成岩的地层中发生矿物质交换作用后形成的结核,由于其形成在成岩作用之后,所以结核内部的层理继承于围岩,与围岩层理平行相接(Sellés-Martínez, 1996)。其中,成岩结核和同生结核均可以反映沉积时期的古海水环境,但同生结核在早期地层中保存较少而成岩结核更为常见,因此成岩结核是古海洋研究领域的关注对象。成岩结核除最常见的碳酸盐结核和硅质结核外,重晶石结核也在地质

历史时期也广泛分布,是我们研究结核沉积时期水体环境的重要媒介(Wang and Arthur, 2020)。

湖北宜昌三峡地区是我国埃迪卡拉系层型剖面所在地,也是国内外学者开展埃迪卡拉纪古生物学、地层学和古环境研究重点关注的地区。湖北宜昌金瓜墩剖面埃迪卡拉系陡山沱组下部的钙质泥岩中发育大量的重晶石结核。本文以重晶石结核为研究对象,着重从重晶石结核的沉积学、岩石学和矿物学特征入手,探讨结核的类型、形成过程、物质来源等,并进一步讨论其古海洋环境指示意义。

1 地质背景

华南扬子板块埃迪卡拉系沉积于被动大陆边缘(Zhao and Cawood, 2012)。在埃迪卡拉纪,扬子板块西北部为浅水陆架,东南部为深水盆地,两者之间为狭窄的斜坡(Jiang *et al.*, 2011)(图1a)。在湖北宜昌三峡地区,埃迪卡拉系为浅水陆盆沉积,它上覆于成冰系南沱组冰碛岩之上,下伏于寒武系产出小壳化石的含燧石条带碳酸盐岩,由陡山沱组和灯影组组成(周传明等, 2021)。三峡地区的陡山沱组由下往上分为四个岩性段,Ⅰ段发育全球分布的盖帽白云岩,Ⅱ段主要为富有机质的细碎屑岩夹碳酸盐岩,常见毫米至厘米级燧石结核,产出类型丰富的带刺疑源类化石(Ouyang *et al.*, 2021)。Ⅲ段普遍发育中—厚层碳酸盐岩,其中燧石结核或薄层中也产出丰富的带刺疑源类化石(Ouyang *et al.*, 2017; Shang *et al.*, 2019)。Ⅳ段则为高水位沉积的黑色碳质页岩夹碳酸盐岩透镜体(Zhu *et al.*, 2007; 杨爱华等, 2015)。

金瓜墩剖面(30°45′21″ N, 110°58′14″ E)位于湖北省宜昌市秭归县庙沟北部约1 km,靠近金瓜墩村,构造单元上位于黄陵背斜南缘(图1b)。古地理位置位于扬子板块的北部(图1a)。金瓜墩剖面陡山沱组由上述四个岩性段组成,出露良好。本文研究的重晶石结核发育在金瓜墩剖面陡山沱组Ⅱ段下部的青灰色薄层—中层泥质白云岩和白云质泥岩中,产出层位距陡山沱组Ⅱ段底部约5 m,含重晶石结核地层厚约0.5 m(图1c)。

2 实验方法

研究涉及的初步岩石学观察在野外进行,其余全部矿物学观察及矿物成分分析均在中国科学院南

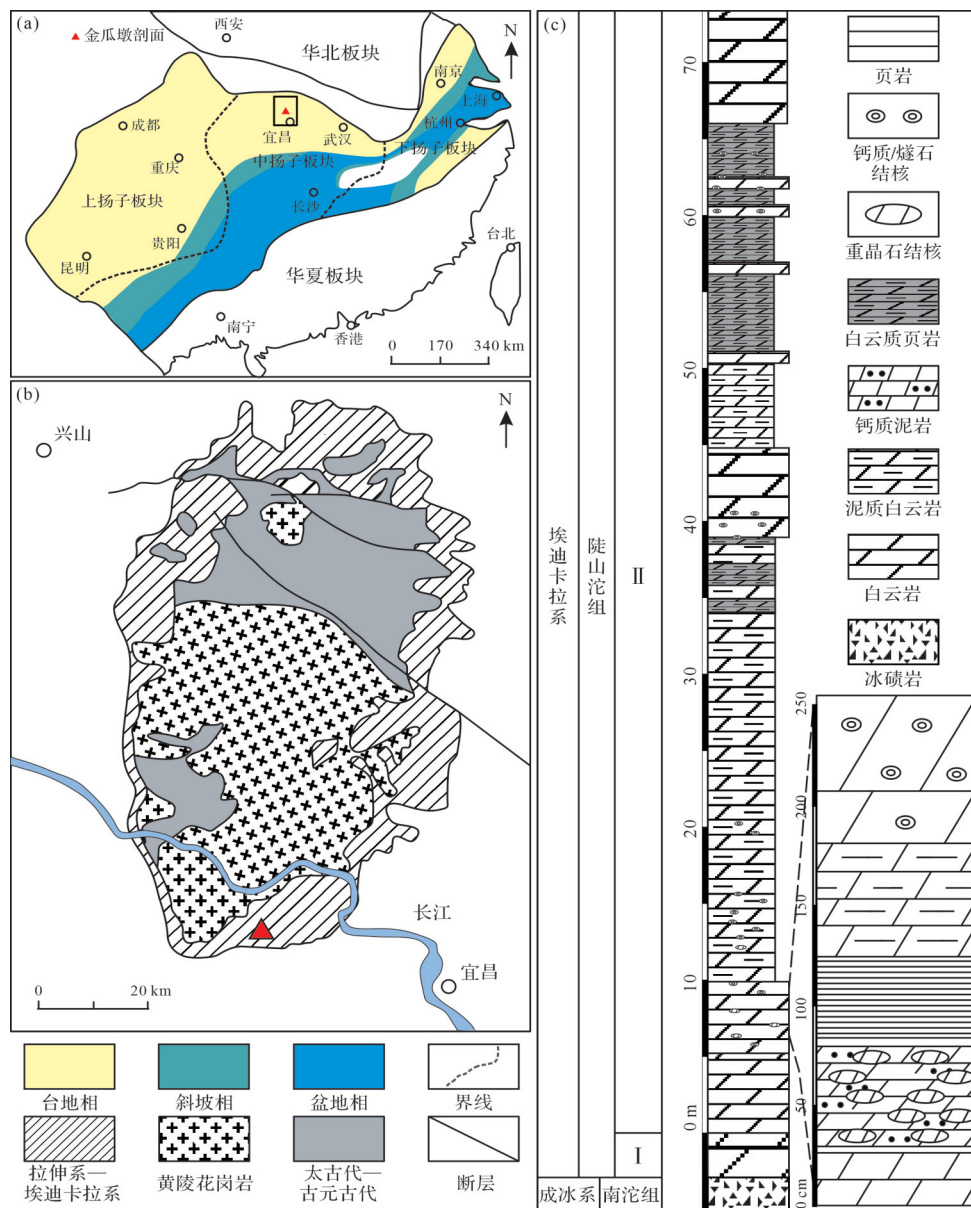


图1 (a) 华南埃迪卡拉纪古地理图(据 Wang *et al.*, 2020 修改); (b) 三峡地区简化地质图(据 Ouyang *et al.*, 2021 修改); (c) 金瓜墩剖面陡山沱组地层柱状图(据 Ouyang *et al.*, 2021 修改; 红色三角形为金瓜墩剖面位置)
Fig.1 (a) Ediacaran paleogeographic map of South China (modified from Wang *et al.*, 2020); (b) simplified geological map of the Yangtze Gorges area (modified from Ouyang *et al.*, 2021); (c) lithostratigraphic column of the Doushantuo Formation at the Jingquandun section(modified from Ouyang *et al.*, 2021; red triangle in B marks the location of the Jingquandun section)

京地质古生物研究所实验技术中心完成。首先将结核样品磨制岩石光面和薄片,薄片制作采用岩石化石薄片 75 mm×50 mm 标准进行制备,并使用金刚石悬浮液进行抛光处理。使用奥林巴斯偏光显微镜(BX51)进行岩石薄片的观察、描述和照相。根据光学显微镜观察结果,挑选岩石薄片重点位置使用拉曼场发射联用扫描电子显微镜(TESCAN MAIA 3 GMU)进行微米尺度的观察。利用背散射电子衍射

(EBSD)成像技术获取重晶石结核的内部矿物组成特征,即通过各矿物组成元素的平均原子序数的大小以灰度变化对目标矿物进行成像(平均原子序数大小与成像灰度呈负相关),成像条件为电压 20 kV、工作距离为 10.00 mm 的真空环境。用 532 nm 的 Ar 激光器获得 2 mW 功率的拉曼光谱来进行矿物测定。为了获得高信噪比的高质量单点谱,将激光束聚焦在平滑截面上,每次单点扫描测量 3 次,总积累时间

为48 s。使用WITec Project5软件对光谱进行数据平滑、归一化、拟合和叠加。标准拉曼光谱数据引用自开源数据库<https://rruff.info/>。

3 结果

3.1 岩石学特征

金瓜墩剖面的重晶石结核在陡山沱组二段下部厚约0.5 m的地层中分布较均匀,大部分为独立个体(图2a),少量由2至4个小结核聚集组成。重晶石结核的形状多种多样,包括椭球状、飞碟状、胶囊状和球状。根据结核部位位置是否发育明显的黄铁矿组成的“内核”将重晶石结核分为两大类。在此基础上,按照结核的形态以及黄铁矿“内核”的发育情况将重晶石结核进一步分为三小类(图2c):(1)球状、椭球状无黄铁矿的结核(图2c1,2);(2)椭球状具有致密黄铁矿圈层的结核(图2c3);(3)椭球及胶囊状具松散黄铁矿“内核”的结核(图2c4,5)。结核的大小变化较大,长轴、短轴和高度分别介于2~8 cm、2~7 cm和2~6 cm。结核的长轴一般与地层层面平行,在结核周围地层层理围绕结核弯曲(图2b)。对结核进行垂向切割,发现球状的结核内部没有明显的黄铁矿集合体(图2c1),而胶囊状和部分椭球状的结核内发育黄铁矿、石英集合体组成的“内核”(图2c3~5)。在这些结核中,没有黄铁矿“内核”的样品内多常见碳酸盐矿物(图3),而在具有高含量黄铁矿的结核样品内,接近结核内部“内核”或“圈层”的区域未见碳酸盐矿物(图3g),但在边缘区域同样可见碳酸盐矿物分布(图3i),同时,碳酸盐矿物总体呈层状且平行于围岩层理产出。

3.2 矿物学特征

重晶石结核的主要矿物为重晶石和石英,在偏光显微镜下观察粗略估计重晶石约占总矿物的30%~40%,石英约占40%~50%,其他的次要矿物包括黄铁矿、白云石、黏土矿物等。能谱测试结果显示,重晶石结核的主要成分为 SiO_2 、 BaO 、 SO_3 、 Fe_2O_3 、 CaO ,以及微量的 Al_2O_3 、 Na_2O 、 TiO_2 等。

结核内的重晶石矿物晶体肉眼可见呈放射状分布(图2c)。光学显微镜观察,单偏光下重晶石矿物无色透明,正交偏光下干涉色为I级灰白。重晶石颗粒多为大量光性一致的非规则晶形的颗粒集合体,晶体粒径差异大,最小为10 μm ,最大大于500 μm ,形态差异较大,边缘不规则。

石英矿物是结核内常见的矿物类型,此类矿物

在单偏光下与重晶石光性相近难以区分,扫描电镜背散射模式显示石英晶体颗粒形态不规则,在结核内与重晶石、黄铁矿矿物无序交织发育,但与两者的接触边界清晰,生长次序关系难以判别。

结核内分布的第三类主要矿物为黄铁矿,具有自形、半自形和他形矿物形态,以及呈草莓状聚集体产出。黄铁矿晶体粒径差异较大,部分聚合成密集的集合体,呈球形黄铁矿壳的形态包裹于结核内核外缘,成为内核的黄铁矿外壳。黄铁矿外壳内部区域发育弥散的自形半自形黄铁矿及石英颗粒(图3b, c, e, f),自形半自形黄铁矿的粒径较大,最大可达100 μm 。在重晶石结核的边缘则多为弥散的他形、半自形黄铁矿矿物颗粒(图3e~i),矿物颗粒粒径最大可达100 μm ,最小不足5 μm 。重晶石结核中也发育它形黄铁矿和草莓状黄铁矿,它们多出现在结核内核的外层,以弥散形式出现(图3j~l)。

其他矿物包括白云石、黏土矿物等。白云石在标本中呈白色,在单偏光下无色透明或白色,具闪突起,正交偏光下为高级白干涉色,矿物形态多不规则,单个颗粒粒径最大大于1 000 μm ,最小约100 μm 。光学显微镜与扫描电镜下观察与重晶石接触边界不清晰,且与重晶石和石英等交切,表明其形成应略早于两者。另外,结核内发育方解石,一般呈脉状产出且多沿裂隙侵入,初步判断方解石为后期热液等成因。黏土矿物在结核内多呈片状产出,光学显微镜下不可见,仅在扫描电镜下可观察到(图3d)。

4 讨论

4.1 海洋中的重晶石矿物

重晶石结核的主要组成矿物为重晶石,它是一种常见的钡的难溶矿物,其成分为硫酸钡(BaSO_4),硫酸钡在水中的溶度积常数极小(1.1×10^{-10}),20 $^{\circ}\text{C}$ 常温下在水中溶解度仅有2.4 mg/L(金晨阳等,2021)。重晶石矿物按成因过程可分为四种类型:(1)成岩重晶石,形成于成岩阶段的孔隙水中,大部分认为与硫酸盐—甲烷过渡带有关(Slack *et al.*, 2021; Zhou *et al.*, 2021);(2)远洋重晶石,一般广泛形成于广海上层水体中,多为有机质分解过程中释放的钡与海水中的硫酸根结合形成,由于部分有生物作用参与,所以也称为生物重晶石(biogenic barite)。在生产力较低的海洋中,这类重晶石的钡可以反映海洋生产力

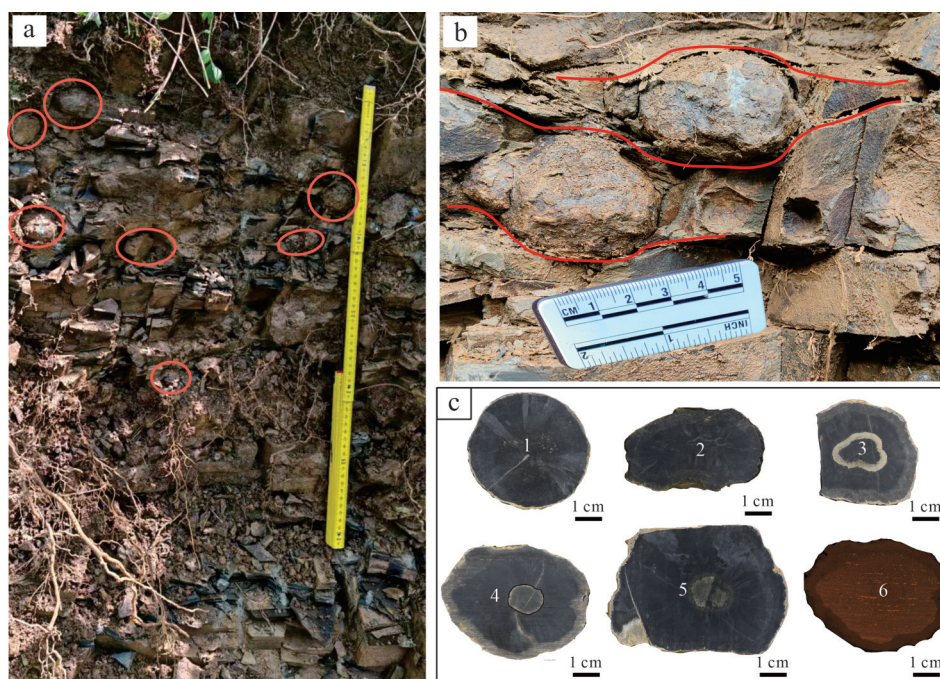


图2 金瓜墩剖面重晶石结核产出特征及结核光面的光学和能谱图像

(a) 金瓜墩剖面结核剖面分布情况, 红色圆圈内为重晶石结核, 照片中量尺长 60 cm; (b) 金瓜墩剖面重晶石结核产出状态及其与围岩的接触关系; (c) 1, 2. 球状、椭球状无黄铁矿的结核; 3. 具有致密黄铁矿层的结核; 4, 5. 具松散黄铁矿“内核”的结核; 6. 重晶石结核钙的能谱图像, 样品内部平行分布的含钙矿物

Fig.2 Occurrence of barite nodules at the Jinguadun section and their optical and Energy Dispersive Spectrometer (EDS) images

(a) occurrence of barite nodules at the Jinguadun section, with barite nodules marked by red circles, the photo shows a ruler with a measurement of 60 cm; (b) contact of barite nodules and surrounding rock; (c) 1, 2. spheroidal and elliptic nodules without pyrite; 3. nodules with dense pyrite layer; 4, 5. nodules of dispersed pyrite "core"; 6. energy spectrum image of calcium in barite nodules, parallel distribution of calcium-containing minerals inside the sample

的大小(Gingele *et al.*, 1999; Wei *et al.*, 2021), 但这类重晶石进入沉积物中后部分会在贫硫酸根的区域溶解, 成为成岩重晶石的一个重要物源; (3) 热液重晶石, 是海底热液活动的产物之一。热液具有元素富集的特征, 多利于形成各类重要的热液型矿床(林秋伶等, 2023); (4) 冷泉重晶石, 形成于海底富有机质的冷泉环境, 其钡的主要来源于陆源物质的分解(Aquilina *et al.*, 1997), 冷泉重晶石三氧同位素的异常可以识别早期硫酸盐还原驱动的甲烷厌氧氧化过程(SD-AOM)(Gong *et al.*, 2018)。

作为一种硫酸盐矿物, 重晶石沉淀后的化学性质极为稳定, 因此对其进行岩石矿物学和地球化学分析能够得到较为可靠的环境信息(Dymond *et al.*, 1992)。例如: Bao *et al.* (2008) 通过对马里诺冰期后盖帽白云岩中的重晶石进行三氧同位素分析, 提出雪球地球结束后大气存在极高的 CO_2 浓度; Shen *et al.* (2009) 则通过对古太古代地层中重晶石的多硫同位素分析, 识别出了 34 亿年前的硫酸盐还原细菌的信号; Peng *et al.* (2013) 发现在新元古代冰期形成的

杂砾岩中发育的重晶石记录了古冰川的氧同位素信号。埃迪卡拉纪的重晶石分布通常集中于埃迪卡拉纪早期和晚期, 主要发育在盖帽碳酸盐岩(Hoffman, 2011) 和“Shuram/EN3”碳同位素负漂移事件前后的沉积时期(Cui *et al.*, 2022)。

4.2 形成过程分析

结合岩石矿物学综合分析, 金瓜墩剖面发育的重晶石结核形成于成岩阶段早期的沉积物中, 属于成岩结核。主要依据有以下两点: 首先是围岩与结核的接触关系, 围岩层理绕结核边缘弯曲, 结核切穿围岩层理、围岩微层围绕结核发生改变; 其次结核内残留有平行于围岩层理的碳酸盐(主要为白云石)矿物(Goldberg *et al.*, 2006)。以上沉积学证据证明结核应形成于围岩沉积物压实之前, 为成岩阶段早期的沉积结构。

重晶石结核的生长从其内部开始。首先, 重晶石的生长应围绕一个核部开始, 该核部的原始物质应为有利于硫酸根还原反应发生的富有机质囊团。在具有较高孔隙度的浅表层沉积物中, 有机质囊团

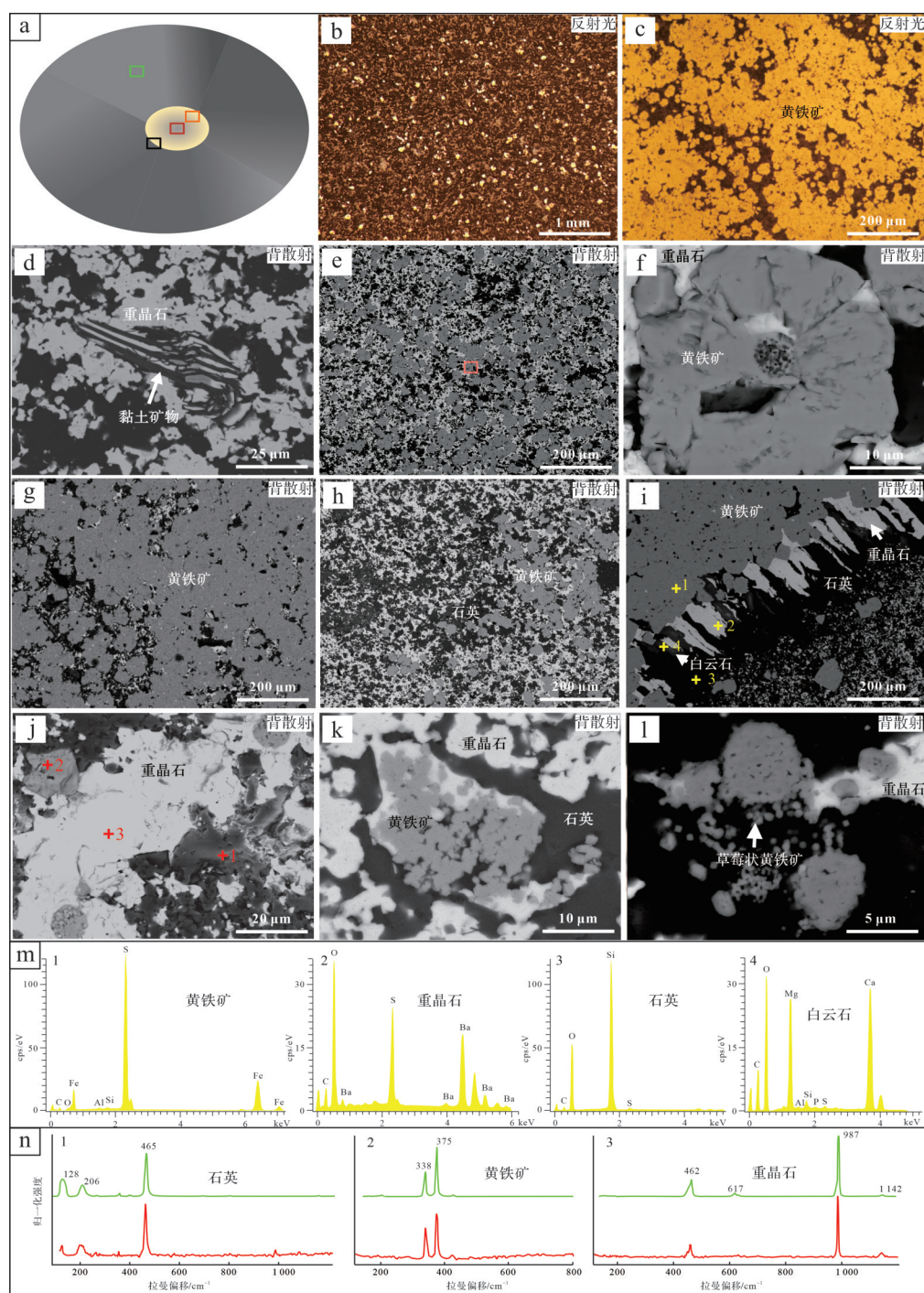


图3 重晶石结核光学显微镜和扫描电子显微镜图像及能谱点扫描、拉曼谱图

(a)结核纵向剖面示意图(b为a中红色框内区域,c,e,g为a中紫色框内区域,d,j,k,l为a中绿色框内区域);(b,c,e-h)具有弥散状黄铁矿内核的重晶石结核内层的光学照片(反射光)及背散射图像,f为e中橙色框内区域;(d)结核内的黏土矿物;(i)具有致密黄铁矿内核的结核的背散射图像;(j)生长在重晶石内部的草莓状黄铁矿;(k)他形黄铁矿集合体;(l)草莓状黄铁矿;(m)结核内矿物能谱扫描图(编号为i中的黄色点位);(n)结核内不同矿物的拉曼光谱谱图(编号为图j的红色点位)(绿色谱线为开源数据库的标准谱线)

Fig.3 Image of barite nodules under optical and scanning electron microscopes, energy spectrum scanning and Raman laser spectrum

(a) schematic lengthways section of nodules (b is the area in the red box in a; c, e, and g are the area in the purple box in a; h and i are the area in the black box in a; d, j, k, and l are the area in the green box in a); (b, c, e-h) optical photographs (reflected light) and EBSD images of the inner layer of barite concretion with a dispersed pyrite core, f is the area in the orange box in e; (d) the clay minerals in nodules; (i) EBSD images of nodules with dense pyrite cores; (j) pyrite framboids that inside barite; (k) anhedral pyrite aggregate; (l) pyrite framboids; (m) energy spectrum of minerals in nodules (The yellow sites in i are numbered); (n) Raman spectral spectra of different minerals in nodules (The red sites in figure j are numbered) (green spectral lines are standard spectral lines in open access database)

在细菌硫酸盐还原作用(Bacterial Sulfate Reduction, BSR)作用下降解,硫酸根在此过程中被还原生成硫氢根(公式(1)),后随着硫氢根的扩散与沉积物中游离的亚铁离子反应,生成黄铁矿沉积(图4,公式(2))。囊团内硫氢根向外扩散过程中会与周围微环境中的亚铁离子相遇而产生黄铁矿沉积的高峰区,从而导致围绕囊团致密黄铁矿外壳的生成(Raiswell and Canfield, 1998; Xiao *et al.*, 2010)(图2c3~5)。如图2所示,并不是所有的重晶石结核均有黄铁矿内核。总体来看,在形成过程中具一定压实的椭圆状或胶囊状结核多具黄铁矿内核,而形变程度较低的近球状结核则多无黄铁矿内核,这应与黄铁矿内核形成时所处的浅表沉积物中的埋藏深度有关。埋藏深度越深则硫氢根扩散速率越低,离子扩散区域受限,形成黄铁矿的高峰峰面越集中,越有利于黄铁矿内核的形成。与之相反,埋葬深度较浅,硫氢根在沉

积物中的扩散速率较快,则不利于黄铁矿沉淀高峰峰面的形成。随着埋藏深度的进一步增加,黄铁矿集合体形成后被逐渐压扁。此外,所有重晶石结核内残留的层状碳酸盐矿物均与围岩层理平行分布(图2c6),显示结核形成后并未受到显著的后期挤压。结核形成初期核部位置有机质含量高低也可能决定是否形成黄铁矿内核,但因所有结核内部残留的有机质均较低,有机质的原始含量无法估计,无法对以上假设进行验证。总之,黄铁矿内核形成于硫酸盐还原带,在此成岩作用带,发生有机质厌氧氧化驱动的硫酸盐还原作用,生成大量的硫氢根,后与环境中的亚铁离子结合形成黄铁矿沉淀。硫酸盐还原带主要的化学反应如下:

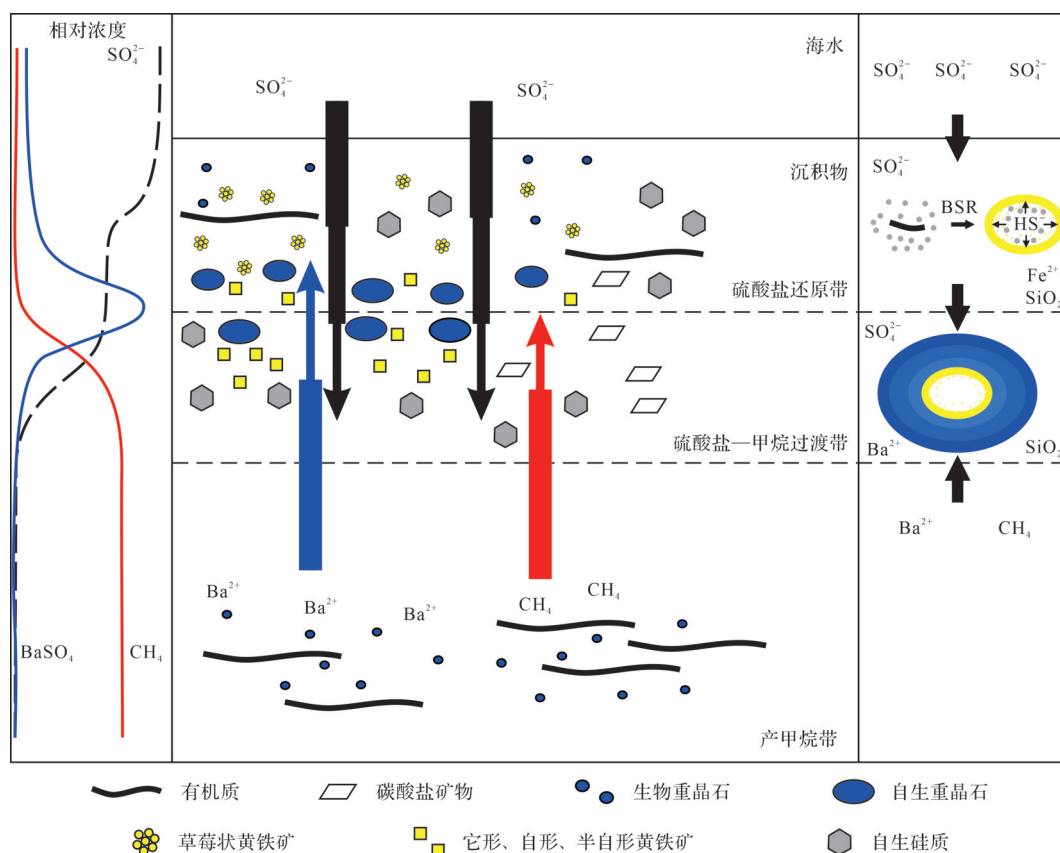
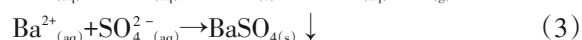
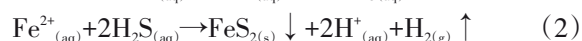
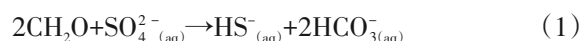


图4 陡山沱组下部重晶石结核的形成模式

左侧为沉积物孔隙水中各组分的相对浓度变化曲线,中间为沉积物中不同氧化还原带的生物地球化学过程及重晶石结核形成模式(据Zan *et al.*, 2022修改),右侧为结核的形成过程示意图(据Xiao *et al.*, 2010修改)

Fig.4 Conceptual model of dominant biogeochemical processes occurring in different redox zones within marine sediments and barite nodule formation

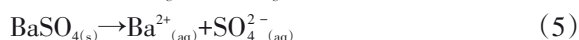
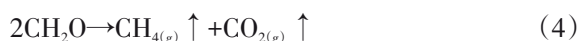
On the left are the relative concentration profiles of each component in the pore fluid, in the middle are the biogeochemical processes in different redox zones within sediments and proposed formation model for the Doushantuo barite nodules (modified from Zan *et al.*, 2022), and on the right are the diagram of the formation of nodules (modified from Xiao *et al.*, 2010)

根据环境中的氧化还原条件与硫酸根浓度,硫酸根还原带可以位于底层水体、水—沉积物界面或沉积物中。其中硫酸根主要来源于海水,硫酸根在硫酸盐还原带被还原为硫氢根(Canfield, 1991),在孔隙水中向下或向上扩散。孔隙水中的亚铁离子来源于该时期较广泛缺氧富铁的海水的渗透以及沉积物中含铁氧化物还原过程的再释放(Lohan and Bruland, 2008),在与硫氢根交汇处即硫酸根被还原的区域可形成大量的黄铁矿沉淀。

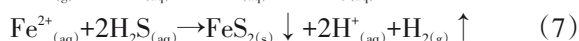
如上所述,在有机质含量较高的反应区会形成富含黄铁矿的球形区域(钟建华, 1994)。随着埋藏深度逐渐增加,椭球状黄铁矿聚合体可能在过程中逐渐变得更加致密,形成阻断内部空间与外环境的屏障。在这种相对封闭的空间中,硫氢根与亚铁离子的供应受到限制,导致该区域黄铁矿颗粒的分布密度逐渐降低。伴随着黄铁矿沉淀,氢离子析出,也促使黄铁矿壳内部相对封闭空间形成酸性微环境,这导致沉积物软泥中黏土矿物发生降解,释放出硅离子(巫锡勇等, 2014),最终导致稳定的自生石英矿物的沉积。岩石薄片观察(图3g)显示石英矿物与黄铁矿多为交织生长,矿物形成无明显的先后顺序,应为同期沉积生成。石英与黄铁矿的沉淀化学条件均为微酸性环境,也有利于两种矿物的同时生成(肖冬生和付强, 2011)。

重晶石的形成需要沉积水体中有过饱和的钡离子和硫酸根。硫酸钡的溶解度极低,而根据前人对陡山沱组的研究,埃迪卡拉纪早期的海洋有一个稳定且充足的硫酸根库(Wang *et al.*, 2021),因此,与硫酸根相比,重晶石的沉淀对水体中钡离子的浓度变化应有更加敏感的反应。正常情况下海水中游离的钡离子浓度较低,难以使硫酸钡过饱和沉淀,但海水中游离的钡离子浓度有以下几个快速增加的途径,如生物死亡腐烂分解后会在其体腔内短期释放出较多钡离子(Bemstein *et al.*, 1992),陆源含钡矿物(如一些碱金属、碱土金属铝硅酸盐矿物)的大量输入,以及富钡海底热液输入等。结核样品中的重晶石与前人报道的生物成因的重晶石、热液成因的重晶石在晶形及粒径大小方面有较大区别。例如,热液成因的重晶石通常呈花状晶形,而生物成因的重晶石则呈微米级颗粒(Bréhéret and Brumsack, 2000; Paytan *et al.*, 2002)。推测结核内重晶石矿物的形成可能与海底甲烷释放有关。在产甲烷带,随着有机

质的降解(公式(4)),有机质中生物成因硫酸钡可发生重新溶解释放出游离的钡离子(公式(5)),这部分钡离子应是重晶石结核中硫酸钡矿物形成的主要离子来源(Brumsack and Gieskes, 1983; Bréhéret and Brumsack, 2000)。产甲烷带发生的主要化学反应如下:



在硫酸盐—甲烷过渡带发生以下反应:



在BSR反应中生成了硫氢根和碳酸氢根(公式(6)),与海水中的铁、钙、镁阳离子反应(公式(7), (8)),促进黄铁矿和白云石、方解石等的沉积,但沉积物中过多的亚铁离子会在形成大量黄铁矿时形成酸性环境,不利于碳酸盐矿物的沉淀(王勇等, 2023),而酸性的水环境是硅质沉积的重要条件(钱一雄等, 2021)。在硫酸盐—甲烷过渡带与上覆的硫酸盐还原带交汇处,硫酸根与从沉积物内扩散至此的游离钡离子发生化学反应,从而在两种离子的接触锋面形成重晶石矿物沉淀的峰值区(公式(3))。重晶石与石英矿物沉淀的pH值相近,重晶石与石英可同时沉积相互交织生成(图3k)。石英与碳酸盐矿物沉积的化学条件差异较大,因此在适宜重晶石和石英沉淀的酸性条件下难以生成大量的白云石等碳酸盐矿物。

4.3 结核形成的阶段性分析

重晶石结核形成体现了水体环境氧化还原反应带的变化。结核形成过程经历了硫酸盐还原带,硫酸盐—甲烷过渡带,反应离子则大部分来源于产甲烷带。总的来说,重晶石结核从结核核心到结核边缘的形成过程具有阶段性。首先在沉积物内具有较多有机质的区域形成一些以松散的黄铁矿聚合体为主的外壳;其次随着在沉积物中埋藏深度的增加,重晶石开始围绕黄铁矿外壳进行沉积,同时部分黄铁矿含量较高的聚合体也逐渐致密,由于黄铁矿聚合体的隔离作用,使得聚合体内部的空间变得相对封闭,受物质来源控制的重晶石难以维持稳定的钡离子和硫酸根供给而较少在其内部沉积。在黄铁矿生成的反应过程中维持的微酸性环境有利于石英的稳

定沉积,因此在黄铁矿聚合体内部形成了石英为主的矿物组成,外部则发育重晶石和石英交织生长的放射状混合矿物。这些外部的重晶石和石英矿物多围绕黄铁矿内核发育。部分球状或近球状的重晶石结核内并未发现有黄铁矿内核发育,这种现象应与结核沉积初期埋藏深度较浅有关。在相对开放的反应环境中,硫酸根与有机质反应产生的硫化氢离子扩散速度较快,较快的扩散速度并不利于黄铁矿矿物的集中沉积。

4.4 环境指示意义

首先,根据上文分析,研究区的成岩重晶石结核的形成与从海水中渗入的硫酸根和沉积物中重晶石溶解产生的钡离子密切相关。重晶石的形成模式符合水—沉积物界面附近形成重晶石的模式,在该模型中含钡流体沿孔隙扩散至上层沉积物中,在富硫酸根的孔隙水环境中形成硫酸钡过饱和状态而发生沉淀(Torres *et al.*, 1996a, 1996b; Naehr *et al.*, 2000; Paytan *et al.*, 2002),与孔隙水中甲烷和硫酸根浓度变化紧密相关。根据沉积物中甲烷和硫酸盐浓度变化以及二者化学反应的主导情况,金瓜墩重晶石结核的形成过程与三个不同氧化还原带有关,不同的氧化还原带生成了不同的自生沉积矿物。因此,本研究中的重晶石结核很可能保留了沉积物中不同区域的信息。而沉积物中的硫酸盐—甲烷过渡带的存在也佐证了该时期海洋中较高浓度的硫酸根,足够让游离的硫酸根进入沉积物深部。

其次,华南地区埃迪卡拉系广泛发育重晶石沉积,但在多个地区报道的重晶石沉积的形成过程有很大差异。例如:湘黔天柱云洞地区的埃迪卡拉系—寒武系铅锌矿床以及郭素雄和杨进军(2022)在湘西地区陡山沱组报道的层状重晶石。这些报道中的重晶石与本研究中的重晶石结核存在明显的不同。在产出状态上,层状或脉状分布的重晶石与重晶石结核之间存在显著差异。部分学者认为该地区的大型硫化物矿床多为热液成矿(赵代珍, 1986; 陈建书等, 2011; 温汉捷等, 2017; 罗邦良等, 2021);而在三峡地区也有较多的重晶石沉积被发现(Jiang *et al.*, 2006; 柳永清等, 2009),这些重晶石具有扇状结构,尽管与金瓜墩剖面的重晶石结核有一些差异。然而,通过对围岩的构造以及极负的碳同位素($\delta^{13}\text{C}_{\text{carb}}$)、锶同位素($^{87}\text{Sr}/^{86}\text{Sr}$)的异常高值和重

晶石的三氧同位素($\Delta^{17}\text{O}$)等地球化学指标的分析,它们被认为与甲烷渗漏相关(Jiang *et al.*, 2006; 蒋干清等, 2006; Wang *et al.*, 2008; 王家生等, 2012; Slack *et al.*, 2021)。以上差异体现出埃迪卡拉纪海洋中由于甲烷释放形成的重晶石沉积具有一定的空间局限性。

另外,有研究认为富含有机质的缺氧上升流可带来深水区的大量游离钡离子(Hendy, 2010),这也可能是本研究中重晶石结核形成的重要物源。金瓜墩剖面位于扬子板块北部的秭归地区,该地区广泛发育碎屑岩沉积,前人的大量工作指示该地区可能存在广泛的上升流作用(Fan *et al.*, 2014; Cheng *et al.*, 2022)。上升流活动的区域极易形成缺氧水体环境,以及富有机质沉积、硅质沉积和磷酸盐沉积(张尚锋等, 2012),这些为重晶石结核提供了物质基础。尽管上升流会消耗海水中的硫酸根离子,促使硫酸盐还原界面变浅,从而导致扩散至沉积物孔隙水中硫酸根浓度降低,但由于硫酸钡在海水中的溶解度极低,大量游离钡离子的存在也可以导致在沉积物相对局部区域集中生成重晶石沉积矿物。总体来看,重晶石结核的形成更受控于游离钡离子的供应,而非硫酸根的浓度。金瓜墩剖面重晶石结核的发育也可能与扬子板块近陆边缘的上升流有关。上升流为表层水带来了丰富的营养物质,提高了初级生产力,促使了生物成因重晶石的聚集,以保证在后期的有机质降解中大量钡离子的释放。

5 结论

(1) 研究区重晶石结核的形成应在成岩过程的早期的软沉积物中,结核形成前期以黄铁矿、石英矿物形成为主,后期以重晶石和石英的沉积占主导。

(2) 重晶石结核中重晶石矿物的形成应与硫酸盐还原驱动的甲烷厌氧氧化过程(SD-AOM)有关,在沉积物孔隙水硫酸盐亏损区有机质降解过程中释放的钡离子为重晶石结核的形成提供了主要的钡元素。

(3) 金瓜墩剖面的重晶石结核内不同矿物的形成次序,可能记录了埃迪卡拉纪早期的硫酸盐还原带、硫酸盐—甲烷过渡带、产甲烷带的环境信息。硫酸盐—甲烷过渡带的存在也说明该时期的海洋中已经有了高含量的硫酸根,可以将硫酸盐还原带下降到水—岩界面附近的沉积物中。

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Petrological and Mineralogical Characteristics of Barite Nodules in the Lower Part of the Ediacaran Doushantuo Formation, Yichang, Hubei Province

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Abstract: [Objective] The redox states of the Early Ediacaran ocean have long been a research hotspot, particularly its material composition and distribution. The formation process of sedimentary barite nodules in the lower part of the Doushantuo Formation was studied to explore the redox variation of the Ediacaran ocean immediately after the Snowball Earth event using sedimentology and petrology. Additionally, a detailed analysis of the formation process of barite nodules in the lower part of the Doushantuo Formation in the northern part of the Yangtze Block, specifically at the Jinguadun profile, was conducted to infer its depositional environment. [Methods] Analysis on sedimentary environments of barite nodules from calcareous mudstone of the lower Doushantuo Formation in Jinguadun section were developed via sedimentologic and petromineralogical methods. [Results] Based on field observations, the surrounding rock layers were found to exhibit a distribution pattern around the nodules. Examining the contact relationships between the nodules and their internal bedding, in accordance with the summary by Sellés-Martínez in 1996, indicates that the barite nodules in this profile formed during the early burial stage. The barite, quartz, and pyrite are the three top authigenic sedimentary minerals in the nodules. The mineral distribution is stratified in the barite nodules. Specially, the inner layer contains dense pyrite aggregates dominated by euhedral-to-subhedral pyrite grains and quartz minerals that grow interwoven together. From the core to the outer edge, radial aggregates were developed in barite and quartz. This study preliminarily demonstrates that the formation of authigenic sedimentary minerals occurring in different parts of the barite nodules precipitate in different redox zones. First, in the sulfate reduction zone within the sediment, an area enriched in organic matter forms a loose outer shell primarily composed of pyrite aggregates. Subse-

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quently, as burial depth increases towards the sulfate-methane transition zone, barite begins to deposit around the pyrite outer shell, causing the high-content pyrite aggregates to gradually become denser. The isolating effect of the pyrite aggregates results in a relatively closed internal space, impacting the deposition of stable barium ions and sulfate radicals by barite. In a slightly acidic environment, the process of pyrite generation promotes the stable deposition of quartz, leading to an internal mineral composition predominantly consisting of quartz. Simultaneously, the external environment evolves into a radial mixture of interwoven barite and quartz. This process highlights the interaction between pyrite and barite under different geological conditions and their influence on the deposition of barium ions and sulfate radicals. The Ba^{2+} sources in the barite likely originate from the methanogenic zone, where dissolution of labile and biogenic barite associated with organic matter occurs. The upward spreading Ba^{2+} ions react with downward diffusing seawater sulfate radicals and deposit barium sulfate in the upper front of sulfate-methane transition zone. [Conclusions] In summary, the barite nodules form in the early diagenetic soft sediments, exhibiting a phased development. In the initial stages, they are primarily composed of pyrite and quartz; in the later stages, barite and quartz deposition becomes dominant. With the increase in sulfate concentration, it is suggested that in the Early Ediacaran oceans, the sulfate reduction interface may have descended into the sediments near the water-rock interface. As a result, methane in the sulfate-methane transition zone underwent oxidation, thereby reducing their emissions into the atmosphere.

Key words: Yangtze Block; Ediacaran; Doushantuo Formation; barite nodules