https://doi.org/10.3799/dqkx.2023.202

磷循环及磷组分在古海洋环境重建中的应用

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摘　要: 磷作为地球生命DNA和RNA的核心组成部分,是地质历史时期海洋表层初级生产力的主要限制性营养元素,对全球大气-海洋氧化还原状态及气候变化具有重要调节作用.总结了海洋中磷的源及汇,阐述了磷组分的构成及其在研究磷的埋藏、转化与循环中的应用,分析了古老地层中磷的沉积特征与生物-环境演化的关系,明确了不同地质时期磷循环特征、机制及其与大气-海洋-生态之间的反馈作用,这对于认识生命与地球环境的关系具有深远意义.

关键词: 磷储库;磷块岩;初级生产力;碳埋藏;氧化还原环境;生物演化;地球化学.

中图分类号: P595　　**文章编号:** 1000－2383(2025)01－246－23　　**收稿日期:** 2023－09－15

Phosphorus Cycling and Phosphorus Speciation Application in Reconstruction of Paleo-Marine Environment

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Abstract: Phosphorus (P), as a central component of DNA and RNA of life on earth, is the major limiting nutrient for marine productivity on geological time scales, and plays an important role in regulating the global atmosphere-ocean redox state and Earth's climate. This paper summarizes the source and sink of P in the ocean, and expounds the composition of P speciation and its application in the study of P burial, diagenetic transformations and marine P cycle, and analyzes the sedimentary P characteristics in the ancient strata and their links with life-environment evolution, which helps clarify features and mechanism of P cycling in different geological periods and its feedback on atmosphere-ocean-ecology system. This is of far-reaching significance for understanding the relationship between life and Earth's environment.

Key words: phosphorous reservoir; phosphorite; primary productivity; organic carbon burial; redox conditions; biological evolution; geochemistry.

磷是地球上生命所需的关键营养元素(Föllmi, 1996;Tyrrell, 1999;Kraal *et al*., 2017),是DNA(Deoxyribonucleic Acid,脱氧核糖核酸)和RNA(Ribonucleic Acid,核糖核酸)的核心构成部分,在通过ATP(Adenosine Triphosphate,三磷酸腺苷)参与能量传递以促进细胞新陈代谢方面起着至关重要的作用

基金项目:中国石油天然气股份有限公司科学研究与技术开发项目(No. 2021DJ05);国家自然科学基金项目(No. 42230812).

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引用格式:李婷婷,朱光有,张义杰,陈志勇,2025.磷循环及磷组分在古海洋环境重建中的应用.地球科学,50(1):246－268.

Citation: Li Tingting, Zhu Guangyou, Zhang Yijie, Chen Zhiyong, 2025. Phosphorus Cycling and Phosphorus Speciation Application in Reconstruction of Paleo-Marine Environment. *Earth Science*, 50(1): 246－268.

(Tyrrell, 1999; Allen and Gillooly, 2009; Laakso and Schrag, 2018; Thompson *et al.*, 2019).全球海洋中磷的源–汇平衡控制了地质历史时期初级生产力水平(Froelich *et al.*, 1982; Krom *et al.*, 1991; Tyrrell, 1999; Elser *et al.*, 2007; Mather *et al.*, 2008),是海洋中决定性限制营养元素(Tyrrell, 1999),直接控制了光合作用产生O_2的速率,并通过影响有机碳埋藏(Ingall *et al.*, 1993)以及大气O_2与CO_2的分压(Berner and Canfield, 1989; Van Cappellen and Ingall, 1996; Lenton and Watson, 2000; Boyle *et al.*, 2014; Papadomanolaki *et al.*, 2022),从而间接影响了碳与氧循环、大气–海洋氧化还原状态(Van Cappellen and Ingall, 1996; Lenton and Watson 2000; Bjerrum and Canfield, 2002; Holland, 2006; Algeo and Ingall, 2007; Konhauser *et al.*, 2007; Planavsky *et al.*, 2010; Rego *et al.*, 2023)、古气候(Filippelli and Delaney, 1992; Shen *et al.*, 2018)以及生物进化的速度(Elser *et al.*, 1996; Karl, 2000; Shi *et al.*, 2021).海洋中的磷通过与有机质和(或)铁(氢)氧化物结合的方式被移除水体并在沉积物中发生埋藏,随后在沉积物中经过磷汇转换转化为含磷矿物如碳氟磷灰石(CFA),并最终形成含磷沉积岩如磷块岩(P_2O_5>15 wt%, wt%表示质量百分数)(Froelich *et al.*, 1982; Föllmi, 1996).作为重要的矿产资源,这类沉积在现代工业中通常被用作农用化学肥料中最主要的磷来源(Glenn *et al.*, 1994; Amundson *et al.*, 2015),其全球需求量仍在持续增加(Cordell *et al.*, 2009; Filippelli, 2011).另外含磷沉积岩中保存下来的特殊化石如硬体(Lamboy, 1993; Thomas *et al.*, 2000; Porter, 2004; Muscente *et al.*, 2023)及软体生物化石(Allison, 1988; Xiao and Knoll, 1999; Xiao, 2004; Schopf and Kudryavtsev, 2010; Zhang *et al.*, 2015)提供了认识生物演化历史的直接窗口(Xiao and Knoll, 2000; Butterfield, 2003; Ye *et al.*, 2023).

因此,追踪沉积岩中磷在地质历史时期的变化对于解释地质历史过程中生物生产力的变化(Mort *et al.*, 2007; Diaz *et al.*, 2008; Shen *et al.*, 2015; Müller *et al.*, 2022),认识磷、碳、氧循环及其之间的耦合关系(Ingall *et al.*, 1993; Cox *et al.*, 2018; Hermans *et al.*, 2019; Ozaki *et al.*, 2019; Rico and Sheldon, 2019; Guilbaud *et al.*, 2020; Alcott *et al.*, 2022; Kipp, 2022; Ge *et al.*, 2023),重建气候、环境与生态之间的长期反馈机制(Filippelli and Delaney, 1992; Föllmi, 1996; Bjerrum and Canfield, 2002; Planavsky *et al.*, 2010; Reinhard *et al.*, 2017; 殷鸿福等, 2018; Li *et al.*, 2020; Longman *et al.*, 2021; Mills *et al.*, 2021; Song *et al.*, 2023)具有重要作用.近年来,随着顺序提取法(Sequential extraction method, SEDEX)的提出(Ruttenberg, 1992)与改进(Thompson *et al.*, 2019),使得对沉积岩中不同磷组分构成进行识别和定量成为可能.目前,该方法已被广泛用于研究现代沉积物及古代沉积岩,以约束地层记录中磷的分布,认识沉积物中磷的埋藏特征与成岩转化过程以及重建海洋磷循环作用(Slomp *et al.*, 2004; Mort *et al.*, 2007; Kraal *et al.*, 2010; Creveling *et al.*, 2014; Egger *et al.*, 2015; Dijkstra *et al.*, 2018; Thompson *et al.*, 2019; Bowyer *et al.*, 2020; Hao *et al.*, 2020; Schobben *et al.*, 2020; Müller *et al.*, 2022; Qiu *et al.*, 2022; Bowyer *et al.*, 2023; Ge *et al.*, 2023).本文系统总结了海洋中磷的生物地球化学循环过程及其在沉积物中的埋藏与转化,概括了磷组分的构成及其在古海洋环境中的应用,阐述了磷及磷循环对海洋初级生产力的控制作用及其与碳、氧循环之间的耦合关系,明确了地质历史时期磷的分布特征及其与环境–生态之间的反馈作用,以实现对磷循环特征、机制及其作用的深入认识.

1 磷的海洋生物地球化学循环

海洋磷储库中磷的来源有陆源输入、热液活动、火山作用及被沉积物释放回到水体中的磷(再循环的磷)(图1).其中,由含磷沉积岩及火成岩的大陆风化作用产生的陆源输入磷是海洋磷储库最为重要的磷来源(Föllmi, 1996; Hao *et al.*, 2020).有研究表明,在埃迪卡拉纪早期,有大量磷被注入到海洋中,这些磷被认为是来自剧烈的冰川风化及大火成岩省的风化作用(Konhauser *et al.*, 2007; Planavsky *et al.*, 2010; Horton, 2015; Reinhard *et al.*, 2017).再循环的磷也是海洋磷储库较为重要的磷来源(Hao *et al.*, 2020).这部分磷是沉积物中埋藏的磷首先被释放到孔隙水中,再经扩散作用进入上覆海洋磷储库中,主要通过以下两种释放方式产生:一种是沉积物中与铁(氢)氧化物结合的磷(P_{Fe})经过还原溶解作用被释放到孔隙水中(Lucotte *et al.*, 1994; März *et al.*, 2008);另一种是被光合作用生物利用与有机质结合在一起沉降到沉积

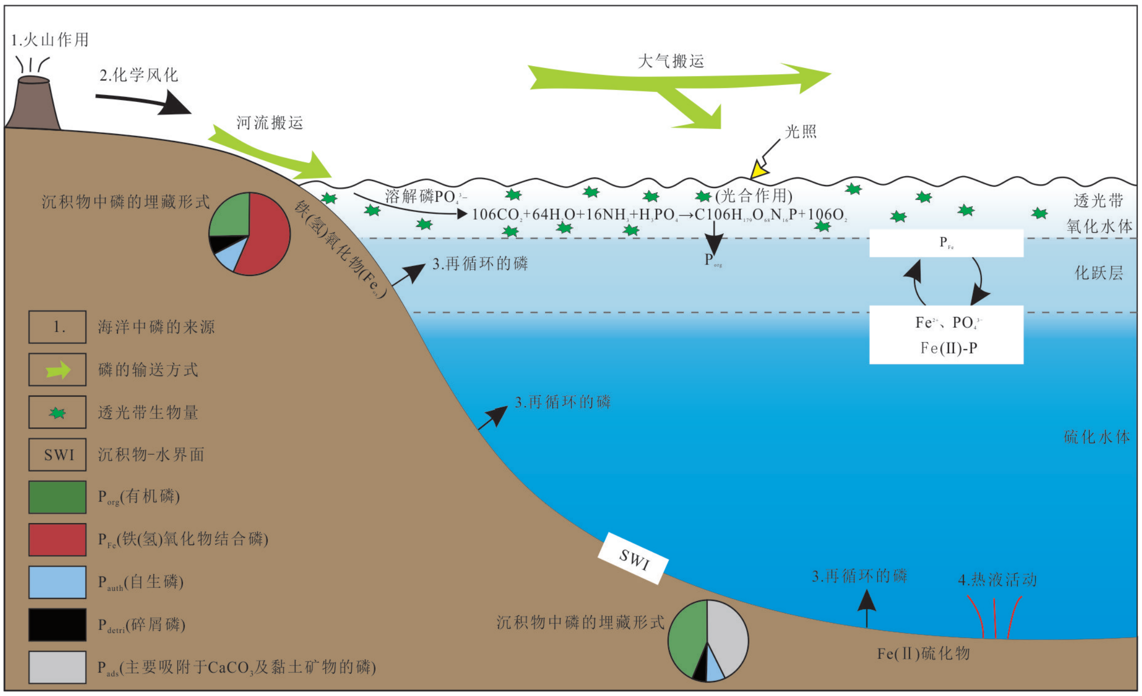

图1　磷的海洋生物地球化学循环简图(据Kraal *et al*.(2017)修改)

Fig.1　Schematic diagram of biogeochemical cycle of P (modified after Kraal *et al.* (2017))

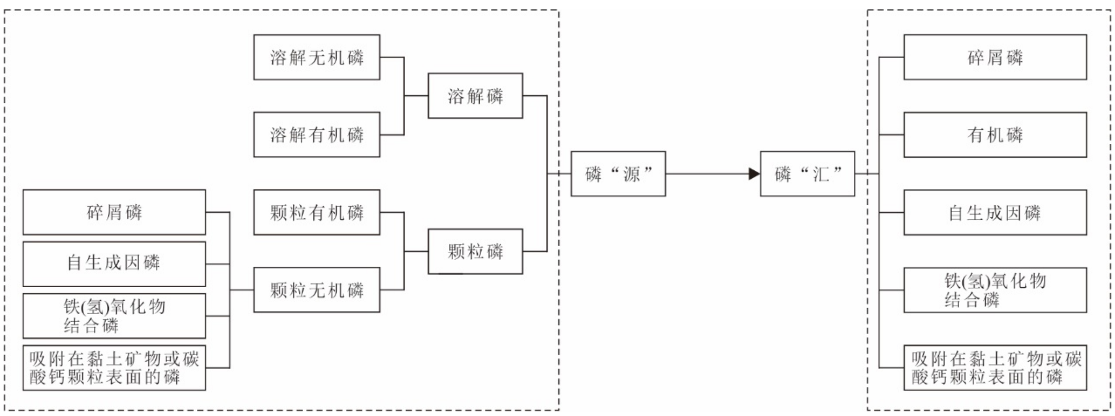

图2　河流输送的磷"源"与埋藏于沉积物的磷"汇"的组分构成

Fig.2　Phosphorus speciation of phosphorus sources carried by rivers and sinks buried in sediments

物中的有机磷(P_{org})伴随有机质发生矿化作用,被释放到孔隙水中(Föllmi,1996;März *et al*.,2008).火山作用及热液活动也可以向海洋磷储库供给磷,但是在整个地质历史时期,相比前两种磷来源,这两种方式的贡献可能是微不足道的(Föllmi,1996).

如图1,进入海洋中的大多数磷是由河流搬运而来,一小部分通过大气搬运(Mahowald *et al*.,2008;Okin *et al*.,2011).由河流输送的磷包含溶解磷和颗粒磷两种形式(Canfield *et al*.,2020)(图2),其中颗粒磷约占95%(Föllmi,1996).溶解磷由溶解无机磷和溶解有机磷组成(Meybeck,1982).颗粒磷由颗粒有机磷(约占40%)和颗粒无机磷组成,后者又包含碎屑磷(P_{detri})、自生成因磷(P_{auth},如CFA)、铁(氢)氧化物结合磷(P_{Fe})以及吸附在黏土矿物或碳酸钙颗粒表面的磷(P_{ads})(Froelich,1988).碎屑磷(P_{detri})主要赋存于火成岩成因或变质岩成因的磷灰石中,它是不能被海洋生物利用的(Rasmussen,1996).由河流输送的磷在进入海洋时会转化为溶解磷(Canfield *et al*.,2020),在表层水体中被生物体利用,并促进海洋初级生产力的提高.

海洋磷储库中非碎屑磷的移除方式主要有

两种：一种是通过与铁(氢)氧化物结合(P_{Fe})，沉降进入沉积物中；一种是在表层水体中被生物利用形成有机磷(P_{org})并沉降进入沉积物中(Föllmi, 1996)．第一种情况在氧化环境中比较常见，还有部分发生于有热液活动的区域，这是因为热液活动过程释放的 Fe^{2+} 经氧化作用会形成铁氧化物颗粒(Froelich *et al.*, 1982；Wheat *et al.*, 1996；Feely *et al.*, 1998；Baturin, 2007)．

2　海洋沉积物中磷的埋藏及转化

海洋磷储库中的磷一般通过碎屑磷、有机质及含铁矿物三种载体的搬运，穿过水柱进入沉积物中(图 3)．海洋沉积物中磷的埋藏及其从沉积物回到水柱中发生再循环的程度高度依赖于水柱及沉积物孔隙水的氧化还原状态(Poulton, 2017)．如图 3a，在氧化底水条件下，沉积物中埋藏的大部分有机质(高达 90%)可能被矿化并释放出溶解磷进入孔隙水中(Krom and Berner, 1981；Ruttenberg and Berner, 1993；Ingall and Jahnke, 1994, 1997；Van Cappellen and Ingall, 1994；Anderson *et al.*, 2001)．由于氧化还原过渡带位于沉积物中，沉积物上部氧化带一方面阻止了铁(氢)氧化物的还原溶解及其伴生磷的释放，另一方面位于其中的铁(氢)氧化物可以对缺氧带孔隙水中扩散出来的磷进行吸附并保留在该处沉积物中(Slomp *et al.*, 1996；Algeo and Ingall, 2007)．如图 3b，在缺氧铁化底水条件下，沉积物中埋藏的磷会在厌氧成岩过程中，通过有机质降解和含铁矿物的还原溶解，被释放回孔隙水及上覆水柱中(Lovley and Phillips, 1988；Ruttenberg and Berner, 1993；Guilbaud *et al.*, 2020)．如图 3c，在缺氧硫化底水条件下，沉积物中埋藏的有机质在硫酸盐还原反应过程中会将磷释放进入孔隙水并向上覆水体扩散．在水体中存在硫化氢的情况下，铁(氢)氧化物结合的磷也会因快速还原反应被释放出来回到水柱中(Canfield *et al.*, 1992)，而产生的 Fe^{2+} 会在沉积物中以铁硫化物形式沉淀(Kraal *et al.*, 2017)．在以上所有氧化还原状况下，被释放进入孔隙水中的磷可能会形成自生成因磷(主要为碳氟磷灰石(CFA))在沉积物较深部位发生沉淀(Van Cappellen and Berner, 1988；Ruttenberg and Berner, 1993；Anderson *et al.*, 2001；Hsu *et al.*, 2014)；也有部分在铁化底水条件下由于 Fe^{2+} 和 HPO_4^{2-} 的富集以含铁矿物如蓝铁矿($Fe_3(PO_4)_2 \cdot 8H_2O$)的形式沉淀(Egger *et al.*, 2015；Dijkstra *et al.*, 2016；Xiong *et al.*, 2019)，这显著提高了磷的埋藏效率；还可能会被铁(氢)氧化物重新吸附(Slomp *et al.*, 1996)，取决于具体的环境条件．

3　磷组分的组成及其在古海洋环境中的应用

沉积物中埋藏的磷(即总磷，P_{total})由铁(氢)氧化物结合的磷(P_{Fe})、有机磷(P_{org})、黏土矿物或

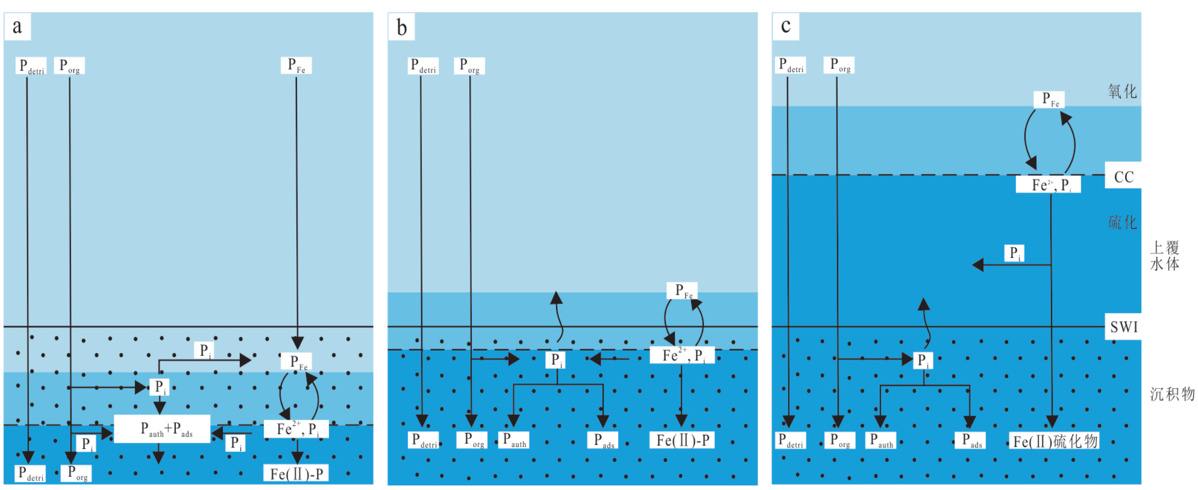

图 3　不同氧化还原底水条件下沉积物中磷的埋藏及成岩转化

Fig.3　P burial and diagenetic processes in the sediment under different bottom water redox conditions

P_i. 被释放的磷；P_{detri}. 碎屑磷；P_{org}. 有机磷；P_{auth}. 自生成因磷；P_{Fe}. 铁(氢)氧化物结合磷；P_{ads}. 主要吸附于 $CaCO_3$ 及黏土矿物的磷；Fe(Ⅱ)-P. 含铁矿物(如蓝铁矿)结合磷；CC. 化跃层；SWI. 沉积物-水界面

碳酸钙颗粒表面吸附的磷(P_{ads})、自生成因磷(P_{auth},主要为碳氟磷灰石(CFA))及不能被海洋生物利用的碎屑磷(P_{detri},主要为火成岩或变质岩成因的碎屑磷灰石)组成(Ruttenberg,1992).P_{Fe}、P_{org}及P_{auth}之和构成了活性磷(P_{react})(Ruttenberg,1992;Föllmi,1996;Mort *et al.*,2007;Guilbaud *et al.*,2020).这些磷组分能够得以量化归功于SEDEX的建立.该方法最早是由Ruttenberg(1992)提出的,其优势在于可以对光学及X射线衍射方法无法检测出来的细粒的、磷含量低的海洋沉积物中的不同磷组分进行分离和测量,并且可以将火成岩或变质岩成因的碎屑磷灰石与自生成因的磷灰石区分开.然而,对于古代沉积岩中通常发育的结晶程度较高的矿物如赤铁矿和磁铁矿,该方法可能因无法对这些矿物充分溶解而不能进行量化,因此Thompson *et al.*(2019)对其进行了改进以便将与这些矿物伴生的磷提取出来.目前,SEDEX及在其基础上有所改进的方法已被广泛应用于现代海洋沉积物(Ruttenberg and Berner,1993;Lucotte *et al.*,1994;Eijsink *et al.*,2000;Schenau and De Lange,2001;Slomp *et al.*,2004;Egger *et al.*,2015;Kraal *et al.*,2015;Dijkstra *et al.*,2018)及古代沉积岩(Ruttenberg and Berner,1993;Lucotte *et al.*,1994;Eijsink *et al.*,2000;Schenau and De Lange,2001;Slomp *et al.*,2004;Egger *et al.*,2015;Kraal *et al.*,2015;Dijkstra *et al.*,2018)中磷组分的定量研究.

对海洋沉积物中不同形式的磷进行识别和量化,对于认识沉积物中磷的埋藏特征及成岩转化过程、探究海洋磷循环作用及其对大气-海洋生物地球化学循环的影响具有重要意义(Ruttenberg and Berner,1993;Lucotte et al.,1994;Eijsink *et al.*,2000;Schenau and De Lange,2001;Slomp *et al.*,2004;Egger *et al.*,2015;Kraal *et al.*,2015;Dijkstra *et al.*,2018).沉积物中磷组分(P_{Fe}、P_{org}、P_{auth}、P_{detri})的含量及各组分之间的关系,如P_{total}与P_{total}/Al,以及C_{org}/P_{org}与C_{org}/P_{react}(表1)被广泛用于约束磷的埋藏、转化及磷的再循环作用(Krom and Berner,1981;Ingall *et al.*,1993;Ruttenberg and Berner,1993;Anderson *et al.*,2001;März *et al.*,2008;Kraal *et al.*,2010;Creveling *et al.*,2014;Bowyer *et al.*,2020;Guilbaud *et al.*,2020;Schobben *et al.*,2020;Qiu *et al.*,2022).沉积物中的P_{org}与P_{Fe}在埋藏成岩作用过程中被释放的程度及通过磷汇转换形成P_{auth}被最终固定在沉积物或再循环回到上覆水柱的程度,取决于孔隙水及水柱的氧化还原条件(Ruttenberg and Berner,1993).缺氧铁化底水条件下,P_{org}及P_{Fe}相对于P_{auth}减少可能揭示沉积物中发生了大量的磷汇转换作用(Guilbaud *et al.*,2020).P_{total}与P_{total}/Al的变化与海洋中磷的可得性或者沉积物中磷是否发生再循环有关(Bowyer *et al.*,2020;Guilbaud *et al.*,2020).比如,华北淮南盆地新元古代早期沉积的缺氧铁化沉积物的P_{total}含量低被认为反映了该时期海洋磷储库小,并因此限制了初级生产力的提高,而中元古代沉积的缺氧硫化沉积物的P_{total}含量低被认为是在广泛硫化环境下沉积物中的磷发生了强烈的再循环回到上覆水柱中,并促进了初级生产力的提高及碳埋藏(Guilbaud *et al.*,2020).P_{total}/Al高于海相页岩平均值(0.009),指示了海洋水体中磷含量降低(Turekian and Wedepohl,1961;Schobben *et al.*,2020).通过C_{org}/P_{org}和C_{org}/P_{react}相对于Redfield比的情况(Xiong *et al.*,2019),可以判断沉积物中被释放的磷发生再循环回到水柱中的程度以及磷循环的控制因素(Ruttenberg and Berner,1993).海洋浮游植物的C_{org}/P_{org}摩尔比值(即Redfield比)约为106∶1(Redfield,1958).由于有机质降解过程中,磷的再生速度要比碳的快,导致磷会被优先释放,从而使得沉积物中的C_{org}/P_{org}高于Redfield比(Krom and Berner,1981;Ingall and Van Cappellan,1990;Ingall *et al.*,1993;Ingall and Jahnke,1997;Anderson *et al.*,2001;Algeo and Ingall,2007;Kraal *et al.*,2012).海洋贫营养条件下或沉积物中有机质矿化不完全时,沉积物中C_{org}/P_{org}会显著升高(Ingall *et al.*,1993;Van Cappellen and Ingall,1994;Ingall and Jahnke,1997;Slomp *et al.*,2004;Reinhard *et al.*,2017).然而,对于P_{org}含量极低的沉积物(如中白垩统沉积物),很可能是在漫长的成岩过程中P_{org}向更加稳定的矿物相如P_{auth}发生了磷汇转换,这种情况下的C_{org}/P_{org}不能用于指示有机质中磷相对于碳的优先释放(Ruttenberg and Berner,1993;Anderson *et al.*,2001;Algeo and Ingall,2007).在C_{org}/P_{org}高于Redfield比基础上,若C_{org}/P_{react}高于Redfield比则被认为是沉积物中P_{org}和

P_{Fe}释放的溶解磷发生了再循环回到水柱中(Ingall *et al.*, 1993; Dale *et al.*, 2016; Xiong *et al.*, 2019),而C_{org}/P_{react}低于C_{org}/P_{org}可能是被释放的磷有部分通过磷汇转换作用形成了P_{auth}被固定在沉积物中(Qiu *et al.*, 2022).前一种情况通常发生于缺氧水体环境中特别是硫化水体中,在该环境下成岩过程中释放出来的磷更有可能逃离沉积物而不太可能以P_{react}形式沉淀,从而有利于沉积物中的磷发生再循环回到上覆水体中并对促进海洋初级生产力提高起到正反馈作用(Ingall *et al.*, 1993; Ingall and Jahnke, 1994; Van Cappellen and Ingall, 1996; Anderson *et al.*, 2001; Schenau and De Lange, 2001; Algeo and Ingall, 2007; Kraal *et al.*, 2017).Algeo and Ingall(2007)对显生宙形成于缺氧环境中的富有机质沉积岩的C_{org}/P_{total}数据进行了梳理,发现古生代(541~252 Ma, Ma表示10^6 a)沉积的地层中的C_{org}/P_{total}均值远高于Redfield比,因此C_{org}/P_{react}也始终高于Redfield比,表明该时期的磷循环可能在调节O_2含量中发挥了重要控制作用.考虑到古代沉积岩中的P_{auth}在成岩作用或变质作用过程中,可能会向结晶程度更高的磷灰石形式转化,使测得的P_{auth}偏低而P_{detri}偏高,从而导致P_{react}偏低(Kraal *et al.*, 2010; Creveling *et al.*, 2014; Thompson *et al.*, 2019; Guilbaud *et al.*, 2020).因此,在使用C_{org}/P_{react}比值前,需要判断P_{auth}是否在沉积后向P_{detri}转化.比如,有研究通过建立碎屑来源为主的Al含量与P_{react}及P_{detri}的相关关系,结合测试样品与现代大陆边缘沉积物及现代贫营养环境的P_{detri}含量对比结果来判断P_{auth}是否向P_{detri}发生转化(Bowyer *et al.*, 2020; Guilbaud *et al.*, 2020).

表1　不同时代沉积物中C_{org}/P_{org}及C_{org}/P_{react}比值分布

Table 1　C_{org}/P_{org} and C_{org}/P_{react} ratios of sediments from different periods

时代	地区	底水氧化还原状态	C_{org}/P_{org}	C_{org}/P_{react}	资料来源
现代	Black Sea	缺氧(硫化)	1 370/1	288/1	Kraal *et al.* (2017)
现代	Black Sea(shelf)	氧化	85/1~170/1	50/1~100/1	Kraal *et al.* (2017)
现代	Peru Margin(OMZ)	缺氧		150/1~200/1	Böning *et al.* (2004); Lomnitz *et al.* (2016)
现代	Northern Arabian Sea (OMZ)	缺氧	600/1	140/1	Kraal *et al.* (2012)
现代	Baltic Sea	缺氧(硫化)	150/1~350/1	95/1~260/1	Mort *et al.* (2010)
		缺氧(铁化)	185/1~340/1	150/1~255/1	
		氧化	100/1~180/1	70/1~120/1	
现代	大陆边缘沉积环境	氧化	-	均值42/1~80/1	Baturin (2007)
现代	Saanich Inlet	缺氧(硫化)	-	152/1	Calvert *et al.* (2001)
现代	Cariaco Basin	缺氧(硫化)	-	195/1	Canfield *et al.* (2020)
		氧化	-	108/1	
白垩纪(OAE2)	Morocco (Tarfaya shelf)	缺氧(硫化)	-	最高达1 500/1	Poulton *et al.* (2015)
		缺氧(铁化)	-	最高达800/1	
白垩纪(OAE3)	French Guiana	缺氧(铁化)	>1 000/1	<50/1	März *et al.* (2008)
二叠纪-三叠纪之交	华南	缺氧	20/1~5 780/1	最高达318/1	Müller *et al.* (2022)
二叠纪-三叠纪之交	Svalbard	缺氧(硫化)	1 600/1~3 060/1	85/1~233/1	Schobben *et al.* (2020)
		缺氧(铁化)	2 380/1~3 930/1	60/1~235/1	

续表1

时代	地区	底水氧化还原状态	C_{org}/P_{org}	C_{org}/P_{react}	资料来源
		氧化	210/1～3 190/1	≤50/1	
泥盆纪	America (Illinois basin)	缺氧	-	3 900/1	Ingall *et al*. (1993)
		氧化	-	150/1	
奥陶纪-志留纪之交	华南	缺氧	-	均值>535	Wang *et al*. (2022)
		氧化	-	均值>43	
奥陶纪-志留纪之交	华南	缺氧(硫化)	最高达36 500/1	最高达4 860/1	Qiu *et al*. (2022)
		缺氧(铁化)	最高达25500/1	最高达2 520/1	
		氧化	最高达8 500/1	最高达1 600/1	
寒武纪	Australia (Georgina Basin)	缺氧(铁化)	79/1～17 000/1	<20/1	Creveling *et al*. (2014)
新元古代(1.0～0.9 Ga)	华北(淮南盆地)	缺氧(铁化)	135/1	24/1	Guilbaud *et al*. (2020)
新元古代(～0.66～0.65 Ga)	华南	缺氧(硫化)	最高达11 293	最高达771	Bowyer *et al*. (2023)
		氧化	-	<106/1	
	Australia	缺氧(硫化)	最高达1 397	>106/1(最高达315)	
中元古代(下马岭组)	华北	缺氧(硫化)	-	80/1	Wang *et al*. (2017); Canfield *et al*. (2018, 2020)
		缺氧(铁化)	-	均值61/1	
		氧化	-	均值85/1	
～2.65～2.43 Ga	South Africa	缺氧	最高达～8 000/1	-	Alcott *et al*. (2022)

注:Ga表示10^9 a.

虽然SEDEX及在其基础上有所改进的方法提供了更多关于磷循环的信息,但是这些方法在提取流程及效率方面也存在一些不足.比如,Ruttenberg(1992)建立的SEDEX方法大体分为5个提取步骤,耗时约48 h,而Thompson *et al*.(2019)为了解决该方案对结晶程度更高的含铁矿物提取效率低的问题,增加了针对磁铁矿与赤铁矿的提取步骤,从而使提取时间增加了约12 h.尽管如此,这一提取方法在分离铁(氢)氧化物结合磷与其他含铁矿物(如蓝铁矿)结合磷上仍存在困难,导致这些矿物对铁结合磷的贡献还不太清楚(Egger *et al*.,2015).另外,在埋藏成岩过程中,由于重结晶作用的影响,P_{auth}(如碳氟磷灰石)在提取过程中可能不太容易被醋酸钠溶解,这部分P_{auth}可能会被当作P_{detri}的一部分被提取出来(Creveling *et al*.,2014).由此看来,单纯依靠磷组分方法研究磷的埋藏、转化与循环还是不够的,而将磷组分分析与微观岩石学观察及成岩研究相结合的跨学科方法将会改善对沉积环境中磷的不同存在形式的判别,从而提高对磷的生物地球化学循环的认识.

4 磷及磷循环对生物-环境演化的重要作用

如前所述,磷及磷循环在控制全球海洋初级生产力,碳、氧循环,大气-海洋氧化还原状态,古气候以及生物进化方面发挥了重要作用.气候、海洋与沉积物氧化还原条件等因素的变化反过来又会强烈地影响磷的供应及磷循环(März *et al*.,2008),因此这些因素之间形成了正/负反馈作用(图4).

4.1 磷对海洋初级生产力的控制作用

在地质历史时期,磷通常被认为是海洋初级生产力的主要限制营养元素(Redfield,1958;Krom *et al*.,1991; Van Cappellen and Ingall,1996; Tyrrell,1999; Bjerrum and Canfield,2002; Mather *et al*.,2008;Horton,2015;Reinhard *et al*.,2017).同样地,

氮也是限制海洋光合作用生物量的主要营养元素(Canfield *et al.*,2020).然而,二者的供给方式不同,决定了磷在调节海洋初级生产力中发挥了决定性控制作用(Redfield,1958;Ingall *et al.*,1993;Van Cappellen and Ingall,1996;Tyrrell,1999).海洋中生物可利用氮的主要来源为海洋生物对大气N_2的固氮作用(Tyrrell,1999),而磷的主要来源为陆源输入(Föllmi,1996;Hao *et al.*,2020).由于光合作用生物体通常会将氮和磷按一定的比例利用起来(Redfield,1958;Tyrrell,1999),若海洋中磷含量发生了变化,海洋中的氮含量会通过固氮作用及以反硝化与厌氧氨氧化为主的氮的移除作用之间的平衡来调整,以满足生物体的需求(Tyrrell,1999;Fennel *et al.*,2005).因此,一旦海洋中磷元素缺乏,海洋初级生产力将受到限制.

4.2　磷对大气–海洋体系中碳、氧循环的影响

磷不仅对海洋初级生产力起着关键控制作用,而且可以进一步影响有机碳的生成与埋藏,从而影响大气CO_2及大气与海洋中O_2含量,最终会对大气–海洋氧化还原状态及气候的变化起到重要调节作用(图 4)(Berner and Canfield,1989;Föllmi,1996;Van Cappellen and Ingall,1996;Colman *et al.*,1997;Tyrrell,1999;Berner *et al.*,2003;Bergman *et al.*,2004;Algeo and Ingall,2007;Reinhard *et al.*,2017).前人的研究(Van Cappellen and Ingall,1996;Lenton and Watson,2000;Wallmann,2003;Mort *et al.*,2007)表明,在相对较短的地质时间内($<10^3$ a),缺氧环境有利于增强沉积物向上覆水柱中磷的再循环,从而促进了海洋初级生产力的提高.基于此,有机质的沉降通量增大,进而增加了水柱中呼吸作用对O_2的需求量(Van Cappellen and Ingall,1996),因此有利于缺氧水体环境的保持与扩张,这形成了一个正反馈作用(图 4,循环 1).例如,二叠纪–三叠纪之交全球海洋广泛缺氧被认为是由于海洋磷储库变化驱动了对海洋中O_2的消耗(Hotinski *et al.*,2001;Meyer *et al.*,2008).现代 Baltic Sea 及许多近岸海域水体中的O_2浓度下降,贫氧程度及范围的增加被认为是海洋中磷的注入量增加引起的,并因此对底栖生物的生存造成了不利影响(Carstensen *et al.*,2014).然而,在较长的地质时间内($>10^6$ a),由生物可利用磷驱动的初级生产力的提高,会使有机碳埋藏通量增加,一方面极大地降低了水柱中O_2被用于呼吸作用的机会,最终导致大气O_2浓度的增加,从而形成了一个负反馈作用(图 4,循环 2).在这种情况下,一旦大气O_2浓度达到一个临界阈值,就会驱动海洋进入氧化状态(Handoh and Lenton,2003),比如新元古代大氧化事件(NOE)的发生(Planavsky *et al.*,2010;Och and Shields‑Zhou,2012)及白垩纪中期海洋缺氧事件(OAEs)的结束(Handoh and Lenton,2003;Tsandev and Slomp,2009)被认为与海洋中磷可得性的增加有关.另一方面,沉积物中有机碳的富集会造成大气pCO_2及全球温度显著下降(Arthur *et al.*,1988;Kuypers *et al.*,1999;Barclay *et al.*,2010;Longman *et al.*,

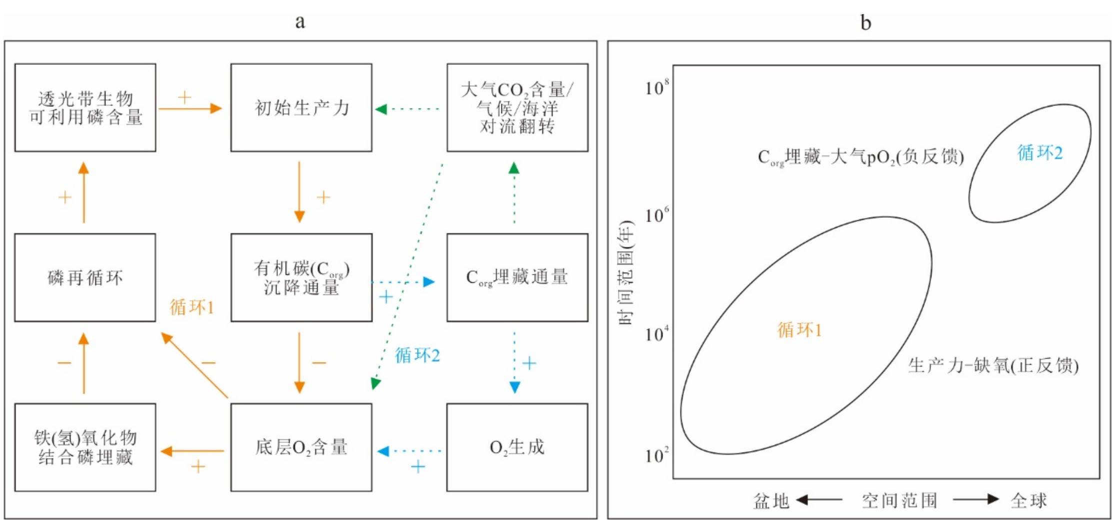

图 4　海洋中磷循环与初级生产力及碳、氧循环的关系(据 Algeo and Ingall (2007)修改)

Fig.4　Marine P cycling and its relationships with primary production, and carbon and oxygen cycles (modified after Algeo and Ingall (2007))

2021).Qiu *et al*.(2022)对华南地区上奥陶统-下志留统岩石样品的生物地球化学模型分析结果表明,伴随着磷循环速率增加,全球有机碳埋藏速率增加一倍以上,大气 CO_2 浓度从 900 ppm (ppm 表示 10^{-6})降至约 500 ppm,这导致赫南特期相比凯迪期主冰期,全球温度下降了 4 ℃.

4.3　太古宙-寒武纪地层中磷的沉积特征及其与生物-环境演化的关系

对地球历史上海洋沉积物中的磷含量进行估算,对于了解生物圈增长及主要的生物地球化学循环的演变至关重要(Kipp and Stüeken,2017).如图 5,现有的数据显示,显生宙及新元古代地层沉积中的总磷含量明显要比中元古代、古元古代及太古宙地层沉积中的总磷含量高.在新元古代之前的地质时间里特别是中元古代及太古宙,富磷地层沉积比较有限,但在之后的地质时间里富磷地层沉积十分常见,这与早期报道的磷块岩大量产出的地质时期如显生宙新近纪、晚白垩世-始新世、侏罗纪、二叠纪、中奥陶世、寒武纪以及新元古代成冰纪(720～635 Ma)与埃迪卡拉纪(635～541 Ma)相一致(Cook and Shergold,1984;Filippelli and Delaney, 1992; Holland, 2005; Fan *et al*., 2016;Reinhard *et al*.,2017).这些含磷沉积岩通常与富有机质岩相如黑色页岩(Cook and Shergold,1984;Föllmi,1996)及碳酸盐岩如以叠层石为主的微生物岩相伴生(陈孟莪等,1999;Crevelling *et al*.,2014).尽管古元古代也有一些磷块岩沉积(Sisodia, 2009),但是其沉积规模要比新元古代之后沉积的小得多,因此其作为矿产资源的经济可行性可能比较低(Papineau *et al*.,2009).

4.3.1　太古宙　目前没有研究报道过太古宙地层中发育磷块岩沉积(Holland,2005).已开展的研究表明,该时期沉积的铁层及页岩中的磷含量较低(Bjerrum and Canfield,2002;Planavsky *et al*.,2010;Reinhard *et al*.,2017),这可能与该时期大气与水体的氧化还原状态有关.在地球历史的大部分时间里,缺氧铁化的海洋环境占据主导地位(Planavsky *et al*.,2011;Poulton and Canfield,2011;Sperling *et al*.,2015),在这种条件下从水柱中沉降的磷多数与含铁矿物及有机质结合(Bjerrum and Canfield,2002;Zegeye *et al*.,2012;Derry,2015;Jones *et al*.,2015; Kipp and Stüeken, 2017; Reinhard *et al*.,2017).然而,由于大气 O_2 含量极低,向水柱中输送的氧化剂(如 O_2、SO_4^{2-} 等)有限(Fennel *et al*.,2005;Laakso and Schrag,2018),制约了再矿化作用的发生及结合磷的释放与再循环(Kipp and Stüeken, 2017).据 Rego *et al*.(2023)对太古代(～2.74 Ga)海水磷浓度的最新估算结果,该时期海水溶解磷平均浓度为 0.063±0.05 μM(μM 表示微摩尔),远低于现代海水平均值(～2.3 μM),指示了地球历史早期海水磷浓度普遍低,这与模拟实验得出的大陆风化带来的磷源供应量低、有机质再矿化造成的磷再循环少及含铁矿物吸附作用引起大量磷发生埋藏的结果一致(Bjerrum and Canfield,2002;Kipp and Stüeken,2017;Hao *et al*.,2020).例如,Hao *et al*.(2020)认为大陆风化作用可能是太古宙海洋中磷的主要来源,但是受该时期地表山区抬升有限(Flament *et al*., 2008, 2013)、植被缺乏(Drever,1994;Hao *et al*.,2020)、早期形成的火成岩中磷含量低(Cox *et al*.,2018)以及大气 pCO_2 降低(Hao *et al*.,2020)的影响,很大程度上制约了磷向海洋的供应,从而限制了生产力的提高并延迟了大气 O_2 含量的增加(Kipp and Stüeken,2017).据 Reinhard *et al*.(2009)和 Poulton(2017),在晚太古代(约 2.7 Ga)之后,大陆边缘缺氧海洋中的富硫化氢水体增加,其分布于铁化的深部水体之上,可能增加了沉积物中磷向水柱中的再循环.在缺氧环境下,特别是有溶解硫化物的情况下,磷的再循环增强,这造成铁(氢)氧化物矿物发生还原溶解并释放出固持的磷,并且细菌硫酸盐还原过程中有机质中的磷优先被释放(Ingall *et al*., 1993).太古宙地层中磷含量低可能解释了发生于～3.0 Ga 的最早的有氧光合作用及 GOE(大氧化事件,2.4～2.0 Ga)期间大气 O_2 富集之间的时间延迟(Bekker *et al*., 2004;Lyons *et al*., 2014;Planavsky *et al*., 2014;Fournier *et al*., 2021).

4.3.2　古元古代　有研究推测古元古代磷块岩的沉积可能与地球表层 O_2 水平的短暂上升有关(Holland,2005;Partin *et al*.,2013).很多氧化还原敏感元素及非传统金属同位素的研究结果表明,在 GOE 发生前的古元古代初期就已经存在氧化风化作用及有氧光合作用(Anbar *et al*.,2007;Bosak *et al*., 2013; Planavsky *et al*., 2014; Koehler *et al*.,2018;Ostrander *et al*.,2019).随着地表氧化作用的开始,向海洋环境中输送的硫酸盐增多,这为形成

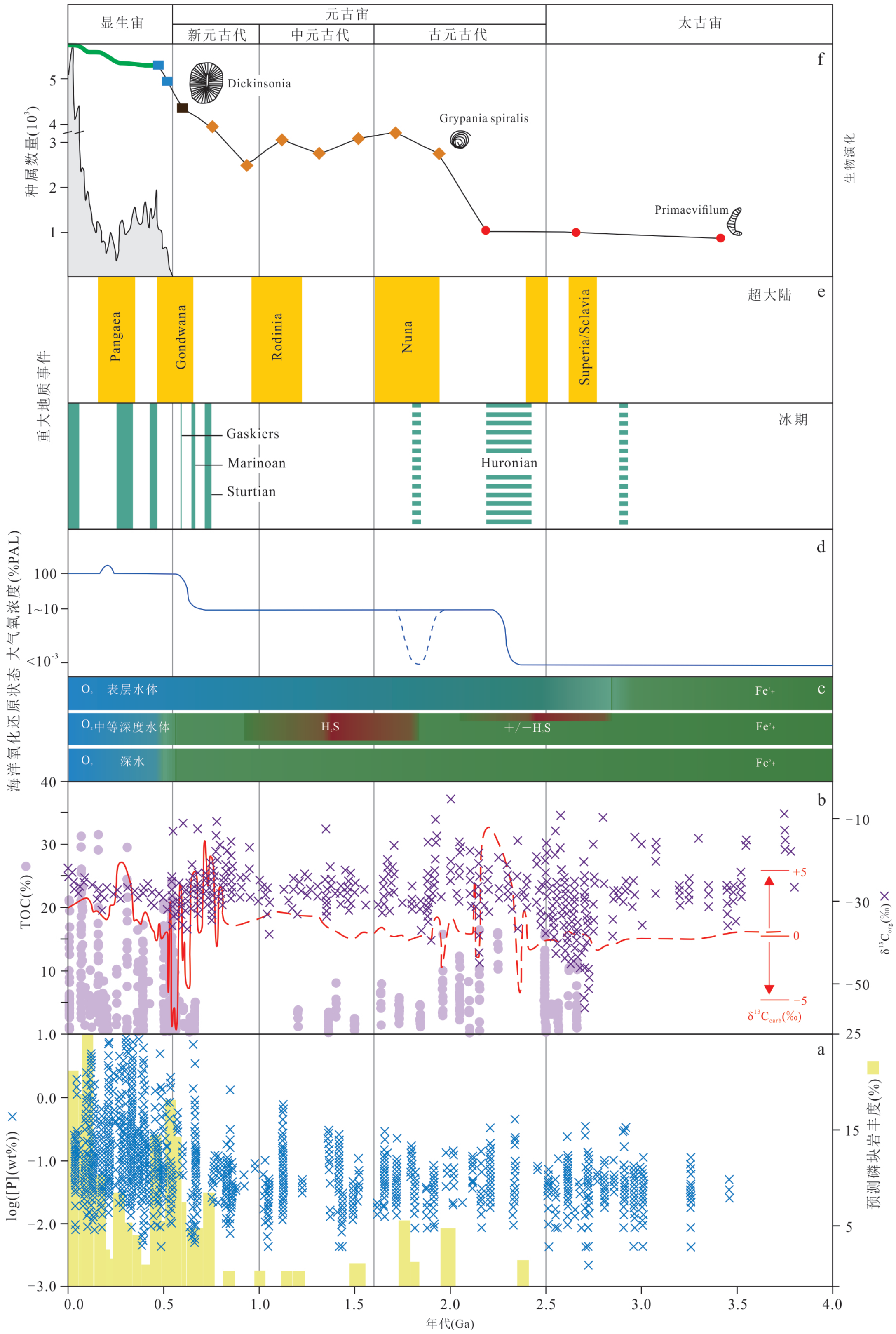

图 5　不同时期地层中磷的沉积特征及其与生物-环境演化的关系

Fig.5　Sedimentary characteristics of P and its link with life-environment evolution on geological times

a. 磷含量及预测磷块岩产出丰度(Planavsky *et al.*, 2014; Reinhard *et al.*, 2017); b. TOC(Och and Shields-Zhou, 2012)及 $\delta^{13}C_{carb}$(Kipp and Stüeken, 2017)与 $\delta^{13}C_{org}$(Brasier and Lindsay, 1998; Bergman *et al.*, 2004; Halverson *et al.*, 2005; Och and Shields-Zhou, 2012)分布; c. 海洋氧化还原状态(Poulton, 2017); d. 大气氧含量(Sahoo *et al.*, 2012); e. 超大陆及冰期(Och and Shields-Zhou, 2012); f. 生物演化(Och and Shields-Zhou, 2012)

溶解态硫化物创造了条件，并进一步推动海洋和沉积物氧化还原状态发生改变. 这一转变会使早期被含铁矿物吸附的磷发生释放，导致水柱或孔隙水中生物可利用磷增加(Canfield *et al.*, 1992)，像太古宙那种磷受限的状态结束(Stüeken *et al.*, 2012; Poulton, 2017)，由此提高了海洋表层初级生产力及碳埋藏，最终造成产氧量增加(Van Cappellen and Ingall, 1994)，并在GOE达到高峰(Kipp and Stüeken, 2017). GOE是古元古代记录的地球历史上发生的第一次大气O_2的显著增加和富集(Kirschvink *et al.*, 2000; Barley *et al.*, 2005; Holland, 2006). Canfield(1998)提出在GOE之后，海洋深部仍然是缺氧的，并且随着海水中硫酸盐浓度升高，硫化水体扩张，形成了广泛的氧化还原分层(Planavsky *et al.*, 2011; Poulton and Canfield, 2011; Lyons *et al.*, 2014)，同时条带状铁层(BIFs)沉积时期结束(~1.8 Ga)(Och and Shields-Zhou, 2012). 在这种水体环境下，由含铁矿物还原及有机质硫酸盐还原反应释放的溶解磷的再循环作用增强(Ingall *et al.*, 1993; Poulton, 2017)，返回水柱中的生物可利用磷逐渐增加(Poulton, 2017)，从而对该时期初级生产力产生正反馈作用(Guilbaud *et al.*, 2020)，并可能导致沉积物中C_{org}/P_{org}比值升高. Alcott *et al.*(2022)就在对来自南非2.65~2.43 Ga的钻孔岩石样品的研究中发现，形成于硫化环境条件下的样品的C/P比值高于Redfield比值，认为是由于氧化风化增加了溶解硫酸盐的输入、溶解态硫化物的生成以及沉积磷组分的再循环，从而形成了对初级生产力的正反馈作用，并通过生物地球化学模拟揭示了该时期磷循环的演化可能是驱动地球大气发生氧化的关键一步.

4.3.3 中元古代 与整个地质历史时期其他时代相比，中元古代(1.6~1.0 Ga)最显著的特征就是环境相对稳定(如图5)：(1)大气O_2含量始终处于较低水平(<0.1%~10% PAL, present atmospheric level)，尽管具体多低仍存在争论(Lyons *et al.*, 2014; Planavsky *et al.*, 2014; Cole *et al.*, 2016; Zhang *et al.*, 2016; Hardisty *et al.*, 2017; Planavsky *et al.*, 2018; Hodgskiss *et al.*, 2019)；(2)海洋深部处于普遍缺氧状态(Canfield, 1998; Kendall *et al.*, 2011; Planavsky *et al.*, 2011; Poulton and Canfield, 2011; Partin *et al.*, 2013; Reinhard *et al.*, 2013; Lyons *et al.*, 2014; Sperling *et al.*, 2015; Gilleaudeau *et al.*, 2019)，局部发育硫化条件如在高产的陆棚区及陆表海环境(Kump *et al.*, 2005; Gilleaudeau *et al.*, 2019; Guilbaud *et al.*, 2020)；(3)生物生产力水平低(Derry, 2015)，如黑色页岩匮乏及有机碳含量普遍低(Och and Shields-Zhou, 2012)所示；(4)地球碳循环相对稳定，如有机碳及无机碳同位素数据无显著变化(Buick *et al.*, 1995; Brasier and Lindsay, 1998; Bartley and Kah, 2004)所示；(5)相对温暖稳定的气候条件(Condie *et al.*, 2001; Holland, 2006; Kasting and Ono, 2006)；(6)生物演化处于近乎停滞的状态(Brasier and Lindsay, 1998; Anbar and Knoll, 2002; Tang *et al.*, 2021). Ozaki *et al.*(2019)基于地质记录建立了中元古代C-N-P-O-S的生物地球化学模型，结果显示生物产氧速率约为现今值的25%，这可能很大程度上与该时期海洋磷匮乏有关. 中元古代地层中磷含量低且磷块岩产出有限，这被认为是由于注入海洋的磷通量低引起的(Canfield *et al.*, 2020; 黄天正等, 2022)，可能与该时期构造运动不活跃有关(Brasier and Lindsay, 1998; Guilbaud *et al.*, 2020; Tang *et al.*, 2021; 黄天正等, 2022). Song *et al.*(2023)近期对华北克拉通中元古界下马岭组(~1.4 Ga)的研究表明，下马岭组沉积时期轨道尺度气候变化对中元古代海洋氧化还原时空异质性具有影响，并进一步讨论了由其引起的氧化还原状态变化与磷循环的关系. 除此之外，中元古代铁化为主的普遍缺氧的海洋环境导致沉积物与水柱之间的磷循环效率较低(Reinhard *et al.*, 2017; Laakso and Schrag, 2018; Ozaki *et al.*, 2019)，进一步限制了海洋中生物可利用磷的供应，从而制约了海洋初级生产力的提高. 由此引起的沉积物中有机碳埋藏量低可能是造成中元古代大气O_2始终处于较低水平的重要原因(Derry, 2015; Canfield *et al.*, 2020; 张水昌等, 2022).

4.3.4 新元古代–寒武纪 新元古代–寒武纪是地质历史上第一次重要的成磷时期(Cook and Shergold, 1984; Papineau, 2010)，全球范围内沉积了大量磷块岩及富磷的碳酸盐岩及页岩(Cook and Shergold, 1984; Shimura *et al.*, 2014; Reinhard *et al.*, 2017)，如中国华南(She *et al.*, 2013; Fan *et al.*, 2016; 李凯月和佘振兵, 2017)及塔里木盆地周缘(黄剑云等, 2007)、哈萨克斯坦(Cook and Shergold,

1984；黄剑云等，2007）、澳大利亚（Cook and Shergold，1984；Cook，1992）、蒙古（Cook and Shergold，1984；黄剑云等，2007）、伊朗及西伯利亚（Cook，1992；Kamaye and Romanovitch，2005）等．如图5a～5f，在 850 Ma 之后，浅海相页岩中磷含量及磷块岩丰度发生了显著变化，磷循环的这一根本性转变大致与之前推断的大气-海洋氧化还原状态的转变（Shields-Zhou and Och，2011）、地球气候系统的严重扰动（Hoffman and Schrag，2002）以及动物的出现（Xiao *et al.*，2000；Love *et al.*，2009；Erwin *et al.*，2011）相吻合．在此期间，沉积物碳同位素呈现极端性波动，这被认为是对大气-海洋氧化还原状态、气候、构造及生物发生重大变化的响应（Derry *et al.*，1992；Des Marais *et al.*，1992；Kaufman and Knoll，1995；Shields and Veizer，2002；Halverson *et al.*，2005；Melezhik *et al.*，2009；李杨凡和李飞，2022；黄少英等，2023）．随着新元古代冰期（～720 Ma 和 ～650 Ma）（Hoffman and Schrag，2002；Macdonald *et al.*，2010）的结束，气候转暖条件下硅酸盐风化作用增强（Planavsky *et al.*，2010；Horton，2015），向海洋输送的营养供应增加，如有研究表明在埃迪卡拉纪早期，有大量磷注入到海洋中（Konhauser *et al.*，2007；Planavsky *et al.*，2010；Reinhard *et al.*，2017），这会促进初级生产力的提高，从而增加有机碳埋藏（Froelich *et al.*，1982；Kirschvink *et al.*，2000），正如该时期有机碳含量持续较高所证实（图 5b）．这些作用最终推动大气和海洋向更加氧化的方向转变，即新元古代大氧化事件（NOE），这是地球历史上发生的第二次重要的氧化事件（Berner *et al.*，2003；Planavsky *et al.*，2010；Shields-Zhou and Och，2011；Och and Shields-Zhou，2012；Lyons *et al.*，2014），为埃迪卡拉纪后生动物的出现及多样化和寒武纪生命大爆发创造了重要条件（赵相宽等，2018）．与这些动物相关的生物扰动加上微生物磷合成作用，会进一步增强沉积物中磷的埋藏（Boyle *et al.*，2014；Dale *et al.*，2016）．

4.4　磷循环在寒武纪以来生物-环境演化研究中的应用

除了以上地质时期，磷循环在研究地质历史上重大事件如奥陶纪-志留纪之交、晚泥盆世弗拉阶-法门阶之交及二叠纪-三叠纪之交生物大灭绝、白垩纪海洋缺氧事件（OAEs）的发生机制方面也有广泛应用．Shen *et al.*（2018）研究认为大陆风化作用增强诱发的海洋磷储库扩大引起的真核藻类产量增加可能引起了碳循环发生变化，从而促进了晚奥陶世冰川事件和生物灭绝的发生．Longman *et al.*（2021）通过建立生物可利用磷供应量及全球生物地球化学模型，重建了晚奥陶世磷输送对海洋系统的影响，进一步揭示了晚奥陶世全球变冷、冰川作用和严重的生物大灭绝可能是由于磷向海洋输送增加及与之相关的海洋生产力的增加所驱动的．Qiu *et al.*（2022）的研究表明磷的再循环将使有机碳的长期埋藏率增加一倍，导致全球降温～4 ℃，由其引起的海洋缺氧水体扩张和全球变冷是造成晚奥陶世生命灾难性损失的关键因素．

Rimmer *et al.*（2004）通过高碳磷比揭示了晚泥盆世生产力-缺氧反馈机制．Goddéris and Joachimski（2004）利用气候和全球生物地球化学循环模式确定弗拉阶-法门阶之交碳同位素偏移的机制，认为海平面控制下的陆地植物分布面积及磷供应量变化是影响有机碳埋藏、CO_2 分压及全球气候的主要因素．Percival *et al.*（2020）认为来自陆地和/或深水上涌的营养物质流入及沉积物中磷的再循环对造成晚泥盆世海洋缺氧做出了重大贡献，是弗拉阶-法门阶之交生物大灭绝的原因．

Shen *et al.*（2015）评估了二叠纪-三叠纪之交海洋初级生产力的水平，认为化学风化作用和物理风化作用加剧分别使得营养物质和颗粒沉积物输入通量增加．Zhang *et al.*（2020）通过建立碳、磷、铀循环的全球模型，证实了二叠纪-三叠纪之交海洋缺氧水体扩张．Schobben *et al.*（2020）研究了该时期海洋大面积进入缺氧状态的机制，认为大灭绝之前火山作用导致的风化作用增强增加了磷的流入，从而提高了近陆架环境中海洋初级生产力和氧气的消耗，同时陆地生态系统的崩溃改变了铁和硫酸盐的相对风化流入量，导致磷的再循环作用增强，从而使得缺氧水体在大陆架的大部分区域扩张．Li *et al.*（2020）的碳磷循环模型和 Hülse *et al.*（2021）的研究分别强调了大火成岩省（LIP，Large Igneous Province）和碳循环变化之间的关系，以及二叠纪末气候极端变暖引发的微生物代谢活动的变化、海洋氧化还原状态和碳循环之间的关系．Ge *et al.*（2023）对二叠纪-三叠纪之交的铁、硫、磷、氮相关数据进行了综合评价，发现二叠

纪末大灭绝期间全球多个地区的浅海均经历了缺氧，认为氧化还原状态的转变与海洋硫、氮、磷循环的空间梯度变化密切相关.

Bjerrum *et al*.(2006)量化了白垩纪海平面上升幅度对磷循环和有机碳埋藏的影响.Kraal *et al*.(2010)研究了白垩纪塞诺曼阶-土伦阶之交OAE2期间海洋磷埋藏情况.Ruvalcaba Baroni *et al*.(2014)的研究表明来自原北大西洋磷供应增加在驱动OAE2的发生上发挥了关键作用.Mort *et al*.(2007)、März *et al*.(2008)和Poulton *et al*.(2015)研究了康尼亚克阶-圣通阶OAE3期间铁、硫、磷循环与氧化还原变化的关系.

5 总结

海洋中的磷主要来源于大陆风化作用为主的陆源供给及沉积物中埋藏的磷向上覆水柱的再循环，并通常以P_{org}及P_{Fe}的形式从水体中移除进入沉积物，最终是否能保留在沉积物中取决于底水-沉积物氧化还原状态.保留下来的磷大部分会向CFA为主的P_{auth}转化，成为海洋中磷最主要的汇.

磷组分是约束磷的埋藏与转化、磷的再循环作用的重要指标.P_{total}与P_{total}/Al的变化被用于判断海洋中磷的可得性或者沉积物中磷是否发生再循环.C_{org}/P_{org}摩尔比值高于Redfield比值(～106)指示沉积物中的磷相对于碳发生了优先释放.在此基础上C_{org}/P_{react}若大于Redfield比则认为沉积物中由P_{org}和P_{Fe}释放的溶解磷发生再循环回到水柱中.

海洋中磷的源-汇关系决定了生物可利用磷储库的大小，控制了表层初级生产力水平，从而影响着有机碳的生成与埋藏，最终对全球大气-海洋氧化还原状态及气候的变化起到重要调节作用.太古宇、元古界及寒武系含磷沉积岩及寒武纪以来重大关键期磷的相关研究提供了了解不同地质时期磷循环特征、机制及其与大气-海洋-生态之间的反馈作用的实例，这对于认识生命与地球环境的关系具有深远意义.

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