

文章编号: 1009-3850(2012)01-0076-13

# 古海洋生产力与氧化还原指标——元素地球化学综述

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**摘要:** 海洋表层初级生产力大小以及水体氧化还原条件是古海洋和古气候研究的重要内容, 而元素地球化学是研究初级生产力以及氧化还原条件最常用的手段。主量元素 Fe 和 Si 是限制生物的营养元素, 痕量金属元素 Cu、Ni 和 Zn 是微营养元素, 而营养条件是沉积生产力的限制因素, 因此这些元素的含量能反映初级生产力大小。Ba 和 Mo 是随有机质一起沉淀下来的, 与水体的有机碳通量有关, 也是古生产力大小的指标。对氧化还原敏感的痕量金属元素含量(如 Cr、V 和 U) 以及元素比值(如  $V/(V+Ni)$ 、 $V/Cr$ 、 $Ni/Co$ 、 $U/Th$  和  $V/Sc$ ) 常用来重构水体的氧化还原条件。

**关键词:** 初级生产力; 氧化还原; 元素地球化学; 古海洋

中图分类号: P595

文献标识码: A

大量有机质的富集与埋藏不仅能控制化石能源的分布, 还能通过影响全球碳循环来调节全球气候变化<sup>[1]</sup>。而有机质的富集主要受到海洋初级生产力和保存条件的控制<sup>[2]</sup>。海洋初级生产力是指浮游生物(主要是浮游植物)在单位时间单位体积内通过光合作用生产有机碳的数量, 也即固定能量的速率<sup>[3]</sup>。而保存条件主要包括沉积水体的氧化还原条件以及沉积速率。现代海洋环境中初级生产力和水体含氧量可以直接测量, 而古海洋的初级生产力大小和氧化还原条件需要通过地球化学(如元素、同位素以及生物标志物等)或物理形态(如草莓状黄铁矿粒径大小等)来间接的研究。在这些指标中, 本文仅对元素地球化学指标进行综述。

## 1 古生产力指标

沉积物中有机质的富集与海洋表层初级生产力大小、水体的氧化还原条件以及早期的埋藏环境密切相关。海洋表层生物生产力大小取决于表层水体的营养物质丰富程度<sup>[4]</sup>, 营养物质越丰富, 生物越繁盛, 光合作用造碳能力就越强, 生产力就越大。另一个能表征水体表层初级生产力的途径是通过水体的有机碳通量: 高的生产力会造成高密度

的有机碳“雨”, 增强水体的有机碳通量, 有机碳通过与痕量金属元素的络合作用或者通过有机质的分解形成局部的硫酸盐还原微环境造成某种痕量金属元素的沉淀, 水体有机碳通量越大, 某些痕量金属元素埋藏量就越大。能反映水体营养水平的元素有 C、N、P、Fe、Si、Cu、Ni 和 Zn。然而 C、N 和 P 受到在循环以及后期成岩作用影响较大, 会造成元素的迁移, 很难代表当时表层水体的 C、N 和 P 含量, 用它们作为古生产力标志并不十分可靠<sup>[5-6]</sup>。通过与水体有机碳通量的关系来反演水体表层生物生产力的痕量金属元素有 Ba 和 Mo。下文将分别介绍这些生产力指标的研究进展。

### 1.1 Fe 和 Si

#### 1.1.1 Fe

Fe 是研究最多的海洋微量元素, 之所以受到学者们广泛的关注是因为铁控制着海洋初级生产力的大小, 影响海洋碳埋藏, 从而调节地质历史时期大气二氧化碳的浓度<sup>[7]</sup>。在过去的二十年里, 现代广海富铁实验已经表明铁能够刺激高硝酸盐低叶绿素水体(1/4 现代海洋均为此类水体)中浮游植物的生长<sup>[8-11]</sup>。而且, 根据模拟研究和野外调查, 在低纬度低营养海域, 铁的供应有助于调节固氮生物

收稿日期: 2011-09-09; 改回日期: 2011-12-04

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固氮作用<sup>[12~13]</sup>。这两种海域的总和占现代海洋的一半,说明铁对海洋生物生产力的贡献之大。地质历史冰川时期海洋的富铁是造成 1/4 大气二氧化碳浓度减少的原因<sup>[14]</sup>。令人疑惑的是,铁是第四个最丰富的地壳元素,在海洋中浓度却很低。这就涉及到铁的海洋生物地球化学循环过程。这个过程具有金属元素海洋生物地球化学循环的某些共同点,是理解元素古生产力指标的基础。

铁的循环包括铁的输出以及铁的输出。海水中溶解铁的浓度取决于铁的来源、生物对铁的需求与藻类的生理特征、海洋循环周期、铁的滞留时间、能与铁结合的生物配合基以及微粒铁的存在时间。相对于 1000 年的海洋循环周期来说,铁在海水中的残留时间较短(100~200 年),这使得铁在海洋的输出较快。在海水中主要存在两种铁的生物地球化学作用:铁的净化(scavenging)与铁的重新矿化(remobilization)。从海岸河流、海岸和浅海沉积物的重新悬浮、季节性海冰的消融、尘土、火山以及海底热液来的铁,在海洋表层水体中刺激生物特别是浮游植物的生长,生物的摄食将水体中溶解的铁浓度降低到铁的氢氧化物不能沉淀的水平<sup>[15]</sup>,在这种条件下,借助光化学还原过程<sup>[16]</sup>,配位体将从岩石颗粒中释放出来的铁络合,形成胶体(0.02~0.4 μm)。溶解的有机质(小于 0.2 μm 的颗粒)促使这些胶体物质聚合形成凝胶体,最终形成有机颗粒,也即图 1 中的微粒铁。这些颗粒将铁从溶解相移除,变为固体相沉淀下来,这个过程称为铁的净化。在海洋表层混合层(风浪引起的水体混合,层薄)以下的水体中,下沉的颗粒被生物分解和转化,释放出铁和有机配位体<sup>[17]</sup>,形成溶解和胶体状态的铁,这种过程称为铁的重新矿化。配位体络合从颗粒分解中释放出来的铁,从而增加水体的溶解铁的含量<sup>[18]</sup>。而铁的净化则降低水体中溶解铁的浓度,这些净化铁的颗粒和胶体通过聚合最终沉淀到海底。

现代海洋研究认为<sup>[19]</sup>,在赤道海域 0~250m 的水体中,铁的净化远大于铁的重新矿化(图 1),海水溶解性铁的浓度降低,溶解铁的浓度一般小于 0.1 nmol/L。下沉的含铁颗粒通量在紧靠海水混合带的下部(约 50m 深)达到最大,往下则由于铁的重新矿化,含铁颗粒通量开始降低<sup>[20~21]</sup>。在表层水体透光带内叶绿素含量达到最大的深度(DCM, deep chlorophyll maximum, 约 120m 深<sup>[22]</sup>),生物摄食消耗大量的铁,水体中溶解铁的浓度达到最低值(图 1)。

在 250~1000m 深的水体,微粒铁被异养菌等生物的重新矿化明显多于铁的净化<sup>[18]</sup>,大量的铁以溶解铁和胶体铁的形式释放到水体中,重新参与循环,并致使水体溶解铁的浓度得到显著的提高(图 1)。在铁的再生过程中,细菌和食草动物(grazers)起到重要作用<sup>[23~24]</sup>,它们摄食铁,并释放到水体中<sup>[25]</sup>。生物对铁的摄食作用由不同的机制驱使,大致分为原核生物和真核生物,这两类生物分别代表不同的摄食机制。原核生物中的异养和自养细菌通过以含铁细胞为基础的铁传输系统来获取铁<sup>[26~27]</sup>。含铁细胞能绑定铁,并能将铁从各种颗粒和矿物中溶解出来<sup>[28]</sup>。相反,真核生物如硅藻属不能形成含铁细胞,它们曾经被认为是直接从溶液中获取无机的三价铁<sup>[29]</sup>。后来人们发现溶解的三价铁在被获取之前必须被还原成低价态的铁<sup>[30]</sup>,而位于原核生物细胞膜之中的铁还原酶可以对铁进行还原。这两种铁的摄取机制将铁从颗粒中释放出来,重新参与循环,使该层海水富含溶解的铁,铁浓度曲线几乎呈直线的上升(图 1)。

在 1000m 以下的水体中,铁的净化又大于铁的重新矿化<sup>[18]</sup>,导致海水中溶解铁的浓度产生一个小幅度的明显的降低(图 1)。

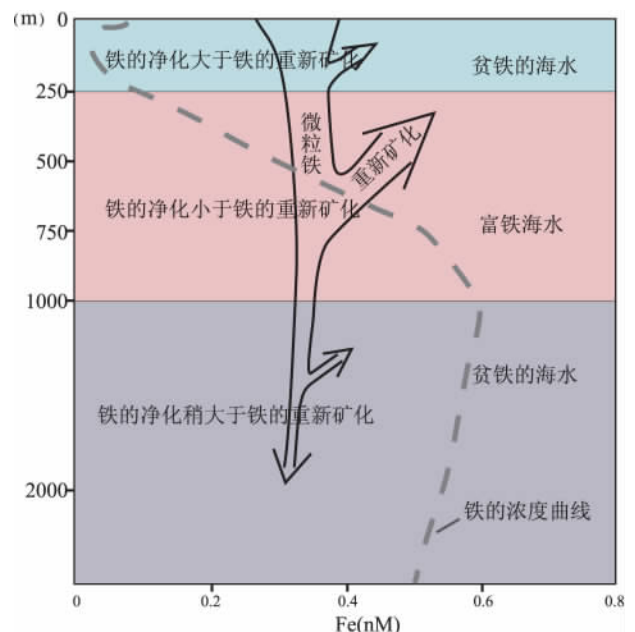


图 1 现代海洋铁的生物地球化学循环<sup>[19]</sup>(有修改)

Fig. 1 The biogeochemical cycle of iron in the ocean(modified from P W Boyd et al., 2010)

如上文所述,海洋浮游植物的生长需要铁元素<sup>[25]</sup>,铁的供应控制大部分海域的初级生产力<sup>[12]</sup>,海洋表层水铁的富集能引起浮游植物的大量繁

殖<sup>[31]</sup>。铁的生物地球化学循环过程中,决定海洋表层浮游植物生产力是上层水体的铁浓度,目前利用铁来研究海洋生物生产力主要有两种形态的铁:总铁<sup>[32]</sup>和碳酸盐铁<sup>[33]</sup>。

从以上铁的生物地球化学循环可知,上层水体铁浓度高的有可能造成沉积物中高的总铁含量,也有可能形成低的总铁含量。反过来,而沉积物中高的总铁含量一般指示沉积表层水体较高的铁含量,沉积物中低的总铁含量可能反映表层水体高的铁含量也可能反映低的铁含量。

胡超涌等<sup>[33]</sup>研究认为古海水中铁的浓度可以利用海相碳酸盐来恢复。在热力学平衡条件下,进入碳酸盐中的铁离子与海水中的可溶性铁成正比,其分配系数  $D_{\text{Fe}/\text{Ca}}$  约为 4<sup>[34]</sup>。与其它生产力指标容易受后期改造作用的影响不同,碳酸盐中的铁离子被束缚在方解石晶格中,除非发生溶解和重结晶,碳酸盐中的铁不容易损失,故生产力信息可以长期保存。相比总铁,碳酸盐铁作为古生产力指标更为可靠,其含量越高,水体营养越丰富,古生产力就越高。

## 2. Si

生物硅也称为蛋白石,是海洋沉积物的主要成分之一。生物硅起源于海洋透光带中硅藻属、放射虫和硅质海绵的细胞膜(骨架),超过 40% 的海洋生物生产力与硅藻属有关<sup>[35]</sup>。生物硅在海底的富集一般与上覆水体的初级生产力有关<sup>[36]</sup>,而且生物硅的全球埋藏效率约为 3%<sup>[37]</sup>,高于有机碳埋藏效率<sup>[38]</sup>一个数量级。表层水长期的生物硅记录比有机碳更为有效。因此生物硅常被作为重构海洋古生产力的参数<sup>[39~41]</sup>。从另一角度,海洋表层生物生产力调节着海洋与大气之间的二氧化碳的输入<sup>[42~44]</sup>,生物硅在碳的生物泵中扮演着重要的角色<sup>[35,46~47]</sup>,与碳循环密切关联,是气候变化的一个响应过程。生物硅能作为古生产力参数的一个前提是生物硅大部分由硅藻属形成,而硅藻属最早出现于侏罗纪,直到晚白垩世才是硅藻属的繁盛期。因此,对于白垩纪之前的地层,生物硅不太适合用于古海洋生产力研究。

### 1.2 Cu、Ni 和 Zn

海洋痕量金属元素的分布受控于参与的生物地球化学循环过程<sup>[48~51]</sup>,生物颗粒的形成、沉淀以及分解过程主导痕量元素的在海水中的浓度变化<sup>[52~55]</sup>。这些正在下沉的颗粒通过微生物的分解、解吸附或者不稳定组分的溶解作用将固定的那些

元素重新释放到水体中。同样,这些生物颗粒也可以吸附溶解相的痕量元素,与它们一起沉入海底埋藏下来。有机组织及其伴随的 C、N 和 P 被表层水的浮游植物固定,随后在温跃层通过氧化过程将其释放重新参与循环再生。别的生物颗粒比如碳酸钙和蛋白石在更深的水体重新参与循环再生。活性痕量金属元素参与这些循环有不同的方式:要么以微营养和骨架成分主动参与循环,要么通过被吸收到颗粒表面或与各种固体一起沉淀的形式被动参与循环。

金属元素可以与浮游有机质一起沉淀下来的,还能通过影响水体/沉积物的氧化还原状态来间接控制金属元素的分布<sup>[56~57]</sup>。现代海洋研究认为<sup>[58~59]</sup>,Cu、Ni 和 Zn 与有机碳呈线性正相关关系。Cu 作为微营养元素在水体中被生物摄食<sup>[60]</sup>,在沉入海底以后,还可以从沉积物中的有机载体中释放出来<sup>[61~62]</sup>。表层水体的有机体固定溶解的锌,控制着深度为 200m 以上水体中 Zn 的浓度<sup>[63]</sup>。尽管还存在某些争议<sup>[64]</sup>,海水中溶解 Zn 浓度的降低抑制浮游植物的生长<sup>[65~69]</sup>。Zn 之所以对有机体生长重要是因为它是几乎 300 种酶辅助因素,这些酶包括酒精脱氢酶、碳脱水酶以及羧基酶,它们参与新陈代谢几乎所有的方面<sup>[65]</sup>。总而言之,Cu、Ni 和 Zn 作为营养元素与有机质结合<sup>[70~72]</sup>或形成有机质络合物<sup>[73~74]</sup>沉淀埋藏下来,高的 Cu、Ni 和 Zn 含量指示高的有机碳输入<sup>[75]</sup>,反映较高的古生物生产力。从其生物地球化学循环来看,Cu、Ni 和 Zn 在水体和沉积物中存在释放和再循环过程,低的 Cu、Ni 和 Zn 含量不一定是低的有机碳输入和低的生物生产力。

### 1.3 生源 Ba

沉积物中的元素 Ba 多数以硫酸钡形式存在于沉积物和水体中<sup>[76~78]</sup>。对于这些硫酸钡晶体的成因,大多数学者认为,在硅藻细胞膜或其它颗粒的还原微环境中,伴随着有机质的分解,硫酸钡晶体发生沉淀<sup>[76,79~80]</sup>。这些微还原环境是有机质分解造成的,硫酸钡晶体沉淀的数量越多,说明有机质输入就越大。因此富有机质沉积物中 Ba 的升高与生物生产力的提高有关<sup>[81~84]</sup>,微量元素生源 Ba 常用来估算海洋初级生产力的变化<sup>[82~83,85,87~91]</sup>。

Ba 的来源包括:(1) 生源钡;(2) 陆源铝硅酸盐的钡;(3) 海底热液钡的沉淀;(4) 某种底栖有机生物体的分泌物<sup>[82]</sup>。除了热液活动区域,其它环境沉积物中 Ba 的来源主要有生源和陆源。只有生源贡

献的那部分 Ba 才能反映初级生产力。计算生源 Ba 常用的公式为<sup>[82, 92~93]</sup>:

$$Ba_{bio} = Ba_{total} - (Al \times Ba/Al_{aluminum}) \quad (1)$$

这个公式假设沉积物中所有的铝都是来自铝硅酸盐,  $Ba/Al_{aluminum}$  比值用于估计陆壳 Ba 的丰度<sup>[94-95]</sup>。采用  $Ba/Al_{aluminum} = 0.0075$  来计算生源钡的含量<sup>[86]</sup>。

生源 Ba 虽然可以作为古海洋生产力指标,但在缺氧环境中应用生源 Ba 来研究古生产力要谨慎。因为在缺氧环境中,沉积物表面和(或)底部水体普遍发生硫酸盐还原反应,硫酸钡是硫酸盐的潜在来源,当硫酸盐供应不足时,硫酸钡会发生部分溶解,从而造成钡含量的较少,导致估算的生产力偏低。

#### 1.4 生源 Mo

Mo 富集的化学机制并没有完全解决,曾经认为其机制是海水或孔隙水中的钼酸盐  $MoO_4^{2-}$  被还原为难溶的辉钼矿  $MoS_2$ <sup>[96]</sup>。最近研究认为,Mo 以 Fe-Mo-S 串联结构的形式沉淀的过程得到了同行普遍的认可。在水体或孔隙水中出现 HS<sup>-</sup>时,一个 S 代替  $MoO_4^{2-}$  中的一个氧,形成的硫代钼酸盐 ( $MoO_nS_{4-n}^{2-}$ ) 更容易与铁的硫化物结合从而沉淀下来<sup>[97~100]</sup>。Zheng 等<sup>[101]</sup> 发现 Mo 只有在水体或沉积物孔隙水中的硫化氢浓度达到  $100\mu M$  的时候,才会转化成活性元素被固定沉淀下来。这个机制强调 Mo 的还原是 Mo 在还原条件下沉淀下来的第一步。实验表明,早在形成铁的单硫化物时,Mo 就可以被结合沉淀下来<sup>[102]</sup>。铁的硫化物是 Mo 沉淀的重要载体<sup>[103~106]</sup>。Tribovillard 等<sup>[107]</sup> 发现,黑色页岩中的 Mo 往往与富硫的无定形有机质结合在一起。用碱性溶液或酒精可以将沉积物中的 Mo 从有机质中分离出来<sup>[108~110]</sup>。另一方面,部分 Mo 能从有机质中利用物理的方法分离出来,这些含 Mo 的成分明显的作为独立的相与有机质纠缠在一起,而不是与化学键的形式结合在一起<sup>[110]</sup>。根据这些现象, Muramoto 等<sup>[111]</sup> 认为 Mo 与有机质的这种联系是由于铁的硫化物与有机质相结合,使得水体中的有机絮状物变得更重从而沉积下来,否则这些有机质将会浮在水体中。因此 Mo 与有机质之间存在间接的关系,两者不是以化学键的形式结合。值得一提的是,由于多接收杯-电感耦合等离子体质谱(MC-ICP-MS, Multi-Collector Inductively Coupled Plasma Mass Spectrometer) 测试技术的应用而发展起来的 Mo 元素的同位素分馏有时候就是被认为是被硫化了的沉

积物中钼酸盐转化为硫代钼酸盐的过程中形成的<sup>[112~114]</sup>。

尽管在生物地球化学循环过程中需要 Mo 被生物摄食和利用<sup>[115~118]</sup>,但是生物的摄食在 Mo 的沉淀中似乎是可以忽略的<sup>[119]</sup>。相对于 Mo 沉积埋藏的数量,生物摄食的那部分的量明显较少。因此, Mo 元素的富集主要在于水体或孔隙水中的 HS<sup>-</sup> 的浓度以及铁的硫化物的形成。高的海洋生物生产力造成大量的有机碳输入,产生高强度的硫酸盐还原,形成大量的硫化氢,与钼酸盐反应生成硫代钼酸盐,从而与铁的硫化物和有机质一起埋藏下来。有机碳的输入越多,沉淀埋藏下来的 Mo 就越多。Mo 作为有机碳输入的参数有一个优势就是 Mo 受后期的变化影响较少,因为铁的硫化物与 Mo 的结合是不可逆的<sup>[120]</sup>。多数研究表明,在黑色页岩和缺氧海相盆地沉积物中有机质含量与 Mo 浓度存在正相关关系<sup>[73, 121~129]</sup>。有机质在 Mo 的净化沉淀过程中扮演着重要的角色。富有机质沉积物中的 Mo 含量可以作为海洋表层生物初级生产力参数,间接的反映生产力的大小。与 Ba 一样,只有生源 Mo 才与有机质相关,生源 Mo 的计算与生源钡公式相同。

## 2 氧化还原参数指标

氧化还原条件包括两个端元:氧化或还原。本文氧化还原状态遵循的 Typson 和 Pearson<sup>[130]</sup> 的划分:氧化(oxic) — 贫氧(suboxic) — 缺氧(anoxic) — 硫化静海(euoxic)。氧化环境中底水的氧气浓度大于  $2ml O_2/L H_2O$ ; 贫氧环境中底水氧气浓度为  $0.2 \sim 2 ml O_2/L H_2O$ ; 缺氧环境中底水的氧气浓度为  $0 \sim 0.2 ml O_2/L H_2O$  水体中不含游离的硫化氢; 硫化静海环境中底水的氧气浓度为  $0 ml O_2/L H_2O$ , 水体中充满了游离的硫化氢。颜佳新等(2007) 根据 Typson 和 Pearson<sup>[130]</sup> 的划分方案,将其翻译成中文为常氧(oxic, 底水氧气浓度大于  $2 ml/L$ ) — 贫氧(Dysoxic, 底水氧气浓度为  $0.2 \sim 2ml/L$ ) — 准厌氧(Suboxic, 底水氧气浓度为  $0 \sim 0.2 ml/L$ ) — 厌氧(Anoxic, 底水氧气浓度为  $0 ml/L$ )。将 Typson 和 Pearson 划分的缺氧细分为准厌氧和厌氧。作者在本文中采用 Typson 和 Pearson 原始的划分。

痕量元素在海水中往往以溶解相或以吸附到颗粒表面的形式存在。这些溶解的痕量元素从水体中沉淀埋藏下来一般受生物或非生物过程的控制。生物过程包括浮游生物(主要为浮游植物)对这些微营养痕量元素的摄食。非生物过程一般相

对局限在氧化环境中,但在贫氧环境中,溶解在水体中的痕量元素通过从水体向沉积物-水界面的扩散或者沿着沉积物中氧化还原梯度发生迁移的方式形成部分富集。在还原环境中非生物过程特别有效,包括金属离子在有机质或矿物质表面的吸附、有机金属络合物的形成以及与硫化物/铁的硫化物及(或)不容氢氧化物的沉积。理论上,这些过程的变化将会导致痕量元素的富集,而元素的富集又能映射出当时的沉积条件和早期成岩环境。因此沉积物中痕量元素的丰度和比值可以重构古沉积条件,特别是氧化还原条件<sup>[131-142]</sup>。

## 2.1 元素含量

### 1. Cr

Cr 在氧化海水中多数以六价态的铬酸盐阴离子  $\text{CrO}_4^{2-}$  形式存在,少部分以三价态淡绿色的  $\text{Cr}(\text{H}_2\text{O})_4(\text{OH})_2^+$  形式存在<sup>[74]</sup>,是一个保守的溶解性离子<sup>[52]</sup>。在还原环境中铬酸盐  $\text{CrO}_4^{2-}$  被还原为三价的  $\text{Cr}^{3+}$  离子和氢氧根离子 ( $\text{Cr}(\text{OH})_2^+$ ,  $\text{Cr}(\text{OH})_3$ ,  $(\text{Cr}, \text{Fe})(\text{OH})_3$ )。后者与腐殖酸/富里酸形成复杂的化合物,或者吸附到铁的氢氧化物和锰的氢氧化物上沉淀下来<sup>[137, 143]</sup>。因此,高的 Cr 含量一般反映还原的环境。值得注意的是,由于与黄铁矿的结构和电子的不相容性,三价的铬很少被自生的铁的硫化物捕捉<sup>[144-145]</sup>。此外铬能否形成不溶的硫化物尚未清楚<sup>[145]</sup>。因此,在有机质的细菌硫酸盐还原矿化过程中, Cr 并没有以硫化物的形式聚集在沉积物中,且在随后的沉积物压实过程中,通过扩散和水平方向的迁移重新释放到上覆水体中。而且, Cr 可以随陆源碎屑组分(比如铬铁矿、粘土矿物以及可被 Cr 代替 Mg 的铁镁矿物,<sup>[146-148]</sup>)一起沉淀输入沉积物中。Cr 的输入与富集的复杂性限制了它作为古环境参数的应用。

### 2. V

在氧化水体中 V 以五价态的  $\text{HVO}_4^{2-}$  和  $\text{H}_2\text{VO}_4^-$  的保守形式存在<sup>[52]</sup>。在远洋和半远洋沉积物中, V 与 Mn 的氧化还原循环有着紧密的联系<sup>[149]</sup>。V 可以吸附到 Mn 和 Fe 的氢氧化物<sup>[150-151]</sup>以及高岭石上<sup>[143]</sup>。Breit 和 Wanty<sup>[143]</sup> 报道,只要氧化条件出现, V 很少与有机质颗粒结合,且有机质分解时其上少量的 V 元素也会很快的释放出来。在轻度还原的条件下,五价态的 V 被还原为四价态的 V,形成  $\text{VO}^{2+}$  离子,促进带羟基的  $\text{VO}(\text{OH})_3^-$  与不溶的氢氧化物  $\text{VO}(\text{OH})_2$  的联系。在腐殖酸和富里酸出现时更有利于这个过程的发生。V 与硫化氢不能形成稳

定的硫化物,然而当孔隙水中硫化氢出现时, V 被有机质颗粒的吸附性能就大大的增强<sup>[152-153]</sup>,因为在这种条件下五价的 V 被还原为四价态 V 离子,这种离子与有机颗粒或有机包粒具有强的吸附性。Morford 和 Emerson<sup>[154]</sup> 也认为海洋环境中 V 在沉积物的聚集是通过表面吸附过程或形成有机金属配合体(organometallic ligands)来实现的。在强还原如硫化的条件下,游离态的  $\text{H}_2\text{S}$  将 V 进一步还原为三价态的 V,后者被地质卟啉捕获或者以固态氧化物  $\text{V}_2\text{O}_3$  或氢氧化物  $\text{V}(\text{OH})_3$  的形式沉淀下来<sup>[143, 155]</sup>。V 在还原条件下被还原为四价态和三价态分别对应着非硫化和硫化的还原状态。V 或许不被铁的硫化物结合<sup>[137]</sup>,并在铁、锰的氢氧化物还原带之下的孔隙水中沉淀埋藏下来<sup>[149, 154]</sup>。因此, V 能作为水体氧化还原的参数, V 越富集表明水体越还原。

### 3. U

U 在氧化海水中以六价态的离子形式存在<sup>[152]</sup>,双氧铀根与碳酸盐结合形成溶解相  $\text{UO}_2(\text{CO}_3)_3^{4-}$ <sup>[153, 156]</sup>,不被任何颗粒捕获沉淀<sup>[157]</sup>,是一个保守的离子<sup>[52]</sup>。在还原条件下,六价态的 U 被还原为四价态的 U,其氧化价态向还原价态的转变条件与三价铁向二价铁的转变类似<sup>[153, 158-162]</sup>,四价态 U 离子易于被有机质颗粒吸附<sup>[157, 163-164]</sup>,与有机质一起沉淀下来。自生 U 的富集主要发生在沉积物中而不是在水体中,因为 U 从六价态被还原为四价态,与游离  $\text{H}_2\text{S}$  的数量是一个反耦合关系,且这种还原反应不被水体中的铁和锰的氧化还原循环直接影响<sup>[137, 162]</sup>,尽管 Zheng 等<sup>[165-166]</sup> 假设自生 U 可以被铁和硫酸盐还原速率调节。Emerson 和 Huested<sup>[152]</sup> 也认为 U 和硫化氢不能形成稳定的硫化物。因此,在沉积物中 U 富集的过程是:  $\text{UO}_2(\text{CO}_3)_3^{4-}$  从水体中扩散进入沉积物,发生还原反应,随后通过吸附或作为  $\text{UO}_2$  (常见的沥青铀矿)、 $\text{U}_3\text{O}_7$  或  $\text{U}_3\text{O}_8$  的形式沉淀下来<sup>[153, 158-162]</sup>。既然 U 的富集主要发生在沉积物中,那么控制 U 的富集就主要有氧的渗透深度以及沉积速率这两个因素。当氧渗透到自生 U 富集的深度时会造成 U 的迁移<sup>[160, 162, 165-166]</sup>。底水氧含量的增加或者(和)有机质输入的减少或者生物扰动深度的变化都会引起氧渗透深度的加深。换句话说,沉积物孔隙水越还原,氧的渗透深度越浅,越有利于 U 的富集。沉积速率越慢,就有更多的时间让双氧铀离子扩散到沉积物中,造成 U 的富集<sup>[167]</sup>。因此, U 的含量可以反映水体的氧化还原条件,含量越高水体越还原。

## 2.2 元素比值

由于微量元素会受到陆源组分的影响,简单的利用微量元素绝对含量来判断水体的氧化还原条件并不准确。因此,微量元素比值也经常用来作为氧化还原环境的示踪。元素比值中作为分子的元素的化学行为特征与氧化还原条件强烈相关,而作为分母的元素一般与氧化还原条件关系比前者弱或与氧化还原条件相关性差。因此这些元素的比值能反映水体的氧化还原条件。

### 1. $V/(V+Ni)$

Hatch 和 Leventhal<sup>[168]</sup>通过研究美国堪萨斯地区宾夕法尼亚上统海相黑色页岩地球化学特征发现,DOP(黄铁矿矿化度)与 $V/(V+Ni)$ 存在正相关关系,并通过DOP值反映的氧化还原条件来分析 $V/(V+Ni)$ 对氧化还原状态的响应,认为 $V/(V+Ni) \geq 0.84$ 时反映硫化静海的环境, $V/(V+Ni)$ 处于 $0.54 \sim 0.72$ 时反映非硫化缺氧的环境, $V/(V+Ni)$ 处于 $0.46 \sim 0.60$ 时反映贫氧的水体环境。Lewan 和 Maynard<sup>[169]</sup>以及 Lewan<sup>[170]</sup>也认为油气烃源岩中的 $V/(V+Ni)$ 比值主要受氧化还原条件控制。需要指出的是, $V/(V+Ni)$ 比值估算的氧化还原条件往往会偏向还原<sup>[135]</sup>。

### 2. $V/Cr$

Cr一般与沉积物中陆源碎屑相结合,可以替换粘土矿物中的Al<sup>[171-172]</sup>。相反,V一般以四价态的形式与有机质结合,并聚集在还原条件下的沉积物中<sup>[152,173]</sup>。因此, $V/Cr$ 比值常用来作为古氧化还原参数<sup>[171,174-178]</sup>。Ernst<sup>[174]</sup>认为, $V/Cr$ 比值为2时代表缺氧的沉积条件, $H_2S$ 开始出现在上覆水体中; $V/Cr < 2$ 说明沉积水体更为氧化,当 $V/Cr = 1$ 时 $O_2-H_2S$ 界面出现在沉积物中。Graf(1975)也认为 $V/Cr = 2$ 反映缺氧的沉积条件。Jones 和 Manning<sup>[178]</sup>将 $V/Cr$ 与DOP值对比分析发现, $V/Cr = 2$ 时对应DOP=0.42的值, $V/Cr < 2$ 的数据点,其DOP值均小于0.42,也即 $V/Cr < 2$ 反映氧化的水体环境; $V/Cr = 4.25$ 时对应这贫氧向缺氧的过渡位置;建议将 $V/Cr < 2$ 划分为氧化条件, $V/Cr$ 为 $2 \sim 4.25$ 时为贫氧条件, $V/Cr > 4.25$ 时为缺氧条件。仔细分析Jones 和 Manning<sup>[178]</sup>赖以划分 $V/Cr$ 值的 $V/Cr$ 与DOP的交汇图(其文献中的图4)发现, $V/Cr = 4.25$ 最为贫氧向缺氧的过渡并不明显,指示缺氧的区域仍然有部分 $V/Cr$ 值小于4.25;而 $V/Cr = 2$ 作为判断氧化与贫氧的界限最为明显。因此用 $V/Cr = 4.25$ 作为贫氧与缺氧的界限并不是太可靠,

而 $V/Cr = 2$ 作为氧化与贫氧的界限最为可靠。而且当 $V/Cr < 1.2$ 时绝大部分对应的数据点DOP值均小于0.42,也就是说 $V/Cr < 1.2$ 时,反映的是氧化的水体环境,大于1.2时为贫氧至缺氧的环境。值得注意的是, $V/Cr$ 值会受到碳酸盐含量的影响,碳酸盐含量高则Cr会变低,从而 $V/Cr$ 值变大<sup>[174]</sup>。

### 3. $Ni/Co$

在沉积物中Ni和Co都出现在黄铁矿中<sup>[172,179]</sup>并且成岩黄铁矿中的 $Ni/Co > 1$ 。Jones 和 Manning<sup>[178]</sup>将 $Ni/Co$ 值与DOP值对比分析发现, $Ni/Co$ 小于5时,DOP值均小于0.42,也即指示氧化环境; $Ni/Co$ 比值大于7时,DOP值一般大于0.75,也即指示缺氧环境。因此他们建议 $Ni/Co < 5$ 为氧化环境, $Ni/Co$ 为 $5 \sim 7$ 时为贫氧环境, $Ni/Co > 7$ 时为缺氧环境。然而从他们的 $Ni/Co$ 与DOP的交汇图中(其文献中的图4),贫氧与缺氧的界限 $Ni/Co = 7$ 并不明显, $Ni/Co$ 为 $7 \sim 10$ 时,仍然有一部分数据点的DOP值为 $0.47 \sim 0.80$ 之间,也就是说 $Ni/Co$ 为 $Ni/Co > 7$ 时也可以反映贫氧的条件。因此, $Ni/Co$ 比值常用作氧化还原指标<sup>[176,180]</sup>,值越高说明沉积环境越还原。

### 4. $U/Th$

Th在低温地表环境中是个不易发生迁移的元素,富集在抗风化物中。在细粒沉积物中Th是重矿物或粘土的成分。U在还原环境中容易以四价态的形式沉淀下来。因此 $U/Th$ 比值可以反映沉积水体的氧化还原条件,是沉积环境的氧化还原条件常用的测量参数<sup>[178,181-185]</sup>,还原环境中 $U/Th$ 比值一般较高。Jones 和 Manning<sup>[178]</sup>将 $U/Th$ 比值与DOP对比分析认为, $U/Th < 0.75$ 时反映氧化水体环境, $U/Th$ 比值在 $0.75 \sim 1.25$ 时反映贫氧水体环境, $U/Th > 1.25$ 时反映缺氧的水体环境。值得一提的是,陆源碎屑物质的 $U/Th$ 比值为 $0.26 \pm 0.13$ <sup>[178]</sup>。

### 5. $V/Sc$

V也是一个氧化还原敏感元素,一般聚集在缺氧或近缺氧的水体之下的沉积物中<sup>[152,184]</sup>。由于V和Sc都是难溶元素,且V与Sc成比例性变化,所以如果利用 $V/Sc$ 比值来研究V的变化将会更有效<sup>[186]</sup>。地质历史时期大陆地壳的 $V/Sc$ 比值为 $4.7 \sim 9.1$ <sup>[187]</sup>。Kimura 和 Watanabe<sup>[186]</sup>通过研究前寒武—寒武界线的缺氧事件发现,海洋的缺氧会导致 $V/Sc$ 比值的升高, $V/Sc < 9.1$ 一般指示氧化的环境。

### 3 结语

海洋有机质的生产是全球碳循环的重要环节,海洋表层初级生产力水平控制着大气二氧化碳含量的变化。古海洋的初级生产力是研究古气候、古地理和古生态的重要指标。海洋水体氧化还原状态涉及到大洋缺氧、海水的循环、生命爆发和生物灭绝等地质现象。充分的挖掘古海洋生产力和氧化还原条件的信息,有助于推动古海洋学的发展。

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## Productivity and redox proxies of palaeo-oceans: An overview of elementary geochemistry

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**Abstract:** It is important for the study of palaeo-oceanography and palaeoclimatology to estimate the primary productivity in surface water and redox conditions in water columns. The study of primary productivity and redox conditions is usually carried out with the aid of elementary geochemistry. Since the availability of nutrients is the main limiting factor to planktonic productivity, the contents of bio-limiting nutrient elements( such as Fe and Si) and micro-nutrient elements( such as Cu, Ni and Zn) reflect the level of primary productivity. Ba and Mo which accumulate with the falling of organic matter setting are related to the organic-carbon flux. Therefore, Ba and Mo can also be used as primary productivity proxies. As for the redox-sensitive trace metal elements( such as Cr, V and U), their contents and elementary ratios( such as  $V/(V + Ni)$ ,  $V/Cr$ ,  $U/Th$  and  $V/Sc$ ) can be usually used to reconstruct the redox conditions in water columns.

**Key words:** primary productivity; redox; elementary geochemistry; palaeo-ocean