

地球早期碳循环与大氧化事件

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摘要: 碳是影响地球宜居性的重要元素, 地表系统和地球深部之间的碳循环作用对于全球气候的变化具有非常重要的影响。现今地球主要通过俯冲作用和火山作用调节全球碳循环过程, 然而地球早期的碳循环过程和现今地球存在显著的差异。本文结合前人的相关研究成果, 综合探讨了地球原始碳的来源、地球早期碳循环过程及其与大氧化事件的联系等问题。地球是从太阳星云中通过星子吸积增生演化形成的, 地球上的碳有一部分来自于地球的初始组成物质, 还有一部分是通过大碰撞事件以及后期增生过程获得的。在地球形成之初的岩浆海时期, 地核和地幔之间的分异作用使地核富集碳而地幔极度亏损碳, 岩浆海和地球早期大气之间的相互作用可以把大气中的碳带入地幔中, 原始地球和具有高 C/N 及 C/S 值的星胚碰撞可以提高地球的碳含量。此外, 富集挥发分的球粒陨石后期增生作用也可以为地球带来额外的碳。在早期板块构造阶段, 板块俯冲的地热梯度要比现在高 100℃ 左右, 俯冲的蚀变洋壳和洋底沉积物在很浅部会通过脱碳反应或者熔融作用发生完全的脱碳作用, 只有少量的碳可以通过碳酸盐化橄榄岩带入地球深部, 由此造成的温室效应可以抵消早期太阳光度不足对地表气候的影响。地球早期碳循环过程和大氧化事件具有紧密的联系, 大气中 CO₂ 含量的升高、有机物的埋藏、无机碳酸盐和有机碳俯冲循环效率的差异等都是形成大氧化事件的关键因素。

关键词: 碳循环; 大氧化事件; 俯冲带; 地球演化; 星子论

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Carbon cycle in the early Earth and the great oxidation event

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Abstract: Carbon is an important element affecting the habitability of the Earth. The carbon cycle between the surface and the deep of the Earth has a very important impact on the global climate change. Nowadays, the Earth regulates the global carbon cycle mainly through subduction and volcanism. However, there are significant differences of carbon cycle between the early Earth and the present Earth. Based on the previous research results, this paper comprehensively discusses the source of the Earth's original carbon, the process of the Earth's early carbon cycle and its relationship with the great oxidation event. The Earth evolved from the solar nebula through the accretion of planetesimals. Part of the carbon on the Earth comes from the initial composition of the Earth, and part is obtained through giant impacts and late veneer. During the magma ocean period at the beginning of the Earth's formation, the differentiation between the Earth's core and mantle made the Earth's core enriched carbon and the mantle extremely

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depleted carbon; the interaction between the magma ocean and the Earth's early atmosphere can bring atmospheric carbon into the mantle. The collision between the proto-Earth and the planetary embryo with high C/N and C/S values can increase the carbon content of the Earth. In addition, the late veneer of chondrites enriched in volatiles can also bring additional carbon to the Earth. In the early stage of plate tectonics, the geothermal gradient of ancient subduction is about 100°C higher than the modern subduction zone. The subducted altered ocean crust and ocean floor sediments will completely decarburize through decarburization reaction or melting at very shallow depth, and only a small amount of carbon can be brought into the deep mantle by carbonated peridotite. The resulting greenhouse effect can offset the impact of early solar luminosity deficiency on surface climate. The early carbon cycle process of the Earth is closely related to the great oxidation event. The increase of CO₂ content in the atmosphere, the burial of organic matter, and the difference of subduction efficiency between inorganic carbonate and organic carbon are the key factors to form the great oxidation event.

Key words: carbon cycle; great oxidation event; subduction zone; Earth evolution; planetesimal theory

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地球是目前已知的唯一孕育有生命和高度文明的行星,碳在地球文明的演化中扮演着关键的角色。碳作为太阳系中的第6位主要组成元素,具有从-4到+4价变化的氧化还原价态,可以和其它80多种元素结合形成各类具有不同特性的有机或无机化合物。作为生物分子的基础组成元素,碳对地球早期生命起源和演化都具有重要的意义(Hazen and Schiffries, 2013)。碳在地球不同圈层中的含量存在巨大的差异,其中地球深部碳占整个地球碳含量的90%以上(Dasgupta and Hirschmann, 2010; Dasgupta, 2013; Hazen and Schiffries, 2013; Marty *et al.*, 2013)。地表系统和地球深部系统之间的碳循环作用对于地表环境的演化具有非常重要的影响,是维持全球气候稳定和地球宜居性的重要因素(Berner, 1999, 2003)。一方面,地球深部的碳可以通过火山作用或其它去气作用返回地表,为生物光合作用提供碳源,产生温室效应并影响全球气候变化;另一方面,大气中的CO₂可以通过光合作用和风化作用分别形成有机物及碳酸盐矿物沉积到地表,再通过俯冲作用进入地球深部(Berner, 2003; Dasgupta, 2013; Kelemen and Manning, 2015; 张立飞等, 2017; 刘勇胜等, 2019; Plank and Manning, 2019)。大量研究表明现今地球每年通过俯冲作用进入地球深部的碳通量和释放回地表的碳通量基本相等,因此大气中的CO₂含量基本保持在一个稳定的区间,维持着全球气候的稳定(Berner, 2003; Dasgupta, 2013; Kelemen and Manning, 2015; Plank and Manning, 2019; 朱建江等, 2021)。

然而,地球碳循环能否一直保持现今这种相对稳定的状态?地球早期碳循环也是这样的吗?如果不是,现今地球不同圈层中碳的分布规律是如何演化过来的?地球早期碳是如何循环演化的?地球的碳是如何获得的?地表环境从地球形成之初到现在经历了怎样的变化?要回答这些问题就需要探讨地球的组成物质来源、地球的形成过程、地球早期构造活动及碳循环等系列问题。本文将从地球原始碳的来源、地球早期碳循环和大氧化事件的成因等几个方面来论述地球碳循环过程及对全球气候的影响。

1 地球原始碳的来源

要弄清地球原始碳的来源,首先需要了解太阳系行星的形成演化过程。星子论(planesimal theory)认为太阳系行星是由初始太阳系星云逐渐冷凝吸积形成的(Chambers, 2004; Obrien *et al.*, 2006; Papaloizou and Terquem, 2006; Wyatt, 2008; Albarède, 2009; Marty, 2012; Morbidelli *et al.*, 2012; Marty *et al.*, 2013)。按照星子论,行星的形成需要经历3个阶段。

第1阶段为星云尘埃到星子演化阶段。在星系演化的初始阶段,分子云由于自身重力坍塌在中心形成恒星,在太阳系中即形成太阳。根据角动量守恒,其它残余星云尘埃会逐渐沉积到一个厚层平面,形成绕太阳运行的星盘(Obrien *et al.*, 2006; Wyatt, 2008; Morbidelli *et al.*, 2012)。随着星云温度的降低,星云中不同元素逐渐聚合形成微小的矿

物颗粒。热力学计算表明大多数元素的冷凝聚合温度变化范围(ΔT)很窄, $\Delta T = RT_{50}^2 / \Delta H_{\text{at}}^{\circ}$, 其中 R 为气体常数, T_{50} 为气态元素有一半冷凝聚合成固态时的温度, $\Delta H_{\text{at}}^{\circ}$ 为原子化焓(Larimer, 1967; Grossman, 1972; Lodders, 2003)。除了碱金属元素、Eu 和 Yb 的冷凝聚合温度范围较大($\Delta T = 150 \sim 200$ K)外, 其它元素的聚合温度都只有几十摄氏度的变化范围(Albarede, 2009)。图 1a 表示不同元素在 $\Delta H_{\text{at}}^{\circ} - T_{50}$ 图解中的位置, 其中高难熔的铂族元素、铜系元素、Al、Ti、Zr、W 和大多数稀土元素冷凝聚合温度高于 1 600 K; 其次为难熔的亲石元素(Si、P、碱土元素和过渡族元素), 这些元素的冷凝聚合温度在 1 300 K 左右。当温度降至 850~1 150 K 时, 高温亲铜元素(As、Ga、Ge、Cu 和 Ag)、碱金属元素(Li、Na、K、Rb 和 Cs)和 Cl 开始冷凝聚合; 在更低温度(530~750 K), 低温亲铜元素(Pb、Bi、Sn、Zn、Cd、S 和 Te)以及除氯之外的其它卤族元素开始聚合成固态; 最后发生聚合的是 3 种最具挥发性元素(N、C 和 H)以及 Hg(Ganapathy and Anders, 1974; Davis and

Richter, 2007; Albarede, 2009)。这些元素在冷凝聚合的过程中会相互作用形成对应的矿物, 如氧化物、橄榄石、辉石、长石、金属或者由这些元素组成的单质(图 1b, Lodders, 2003; Albarede, 2009)。如图 1b 所示, 随着温度的降低, 在大量难熔性矿物(斜长石和单斜辉石)形成之后, 大部分组成地核的金属矿物和地幔硅酸盐矿物(橄榄石和斜方辉石)快速从星云中聚合沉淀出来(图 1b 中紫色部分); 随后是碱金属元素和高温亲铜元素聚合沉淀(图 1b 中绿色部分); 接着是低温亲铜元素、硫化物和卤族元素聚合沉淀(图 1b 中红色部分); 最后是挥发性元素 N、C、H 等聚合沉淀。这些从星云中冷凝聚合沉淀出来的颗粒汇聚到一定的规模, 由于引力坍塌作用会吸积形成更大体积的星子(Chiang and Youdin, 2010)。有些研究者认为星子的直径可达数百甚至上千千米(Johansen and Youdin, 2007; Cuzzi *et al.*, 2008, 2010; Morbidelli *et al.*, 2009; Chambers, 2010), 也有学者认为星子的直径可能小于 1 km(Weidenschilling, 2011)。

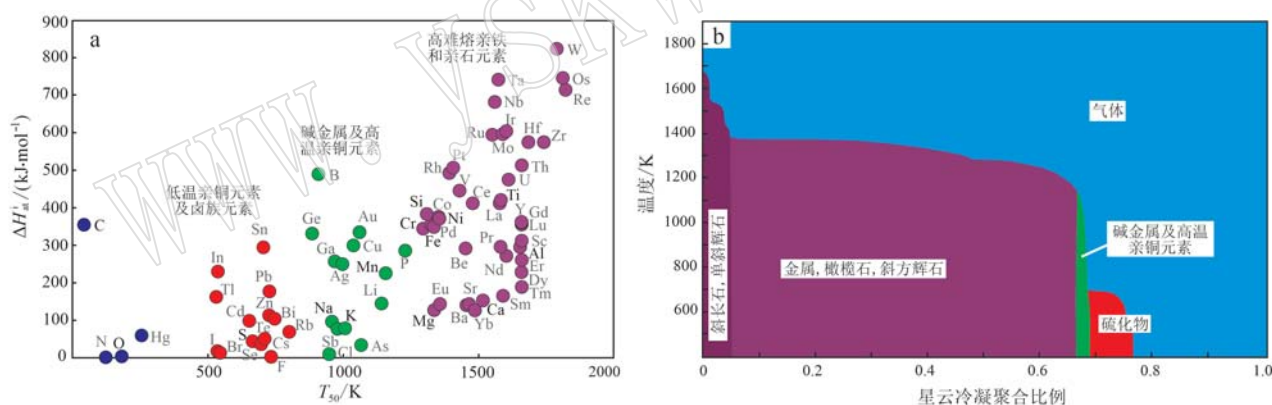


图 1 星云冷却过程中元素(a)及对应矿物(b)的逐步冷凝聚合图解[据 Albarede(2009)修改]

Fig. 1 Stepwise accretion of the elements (a) and minerals (b) on cooling of the solar nebula (modified after Albarede, 2009)

第 2 阶段为星子到星胚生长阶段。在星胚生长的初始阶段(逃逸增生阶段), 当一个星子长得比周围的星子大时, 由于几何横截面和引力场的增加使其可以快速地吸积吞并周围小的星子, 从而生长为大的星胚(Safronov and Zvjagina, 1969; Greenberg *et al.*, 1978; Wetherill and Stewart, 1993; Chambers, 2004; Morbidelli *et al.*, 2012)。然而, 当星胚生长到一定大小之后, 由于引力扰动作用会使其周围的星子相对运动速度发生变化, 这一过程会减缓大质量星胚进一步吸积星子的速率, 促使其其它小的星胚快速长大, 这一阶段称为“寡头生长阶段”。这一阶

段的最终结果是形成一个大小和间隔大致相当的行星胚胎系统, 这些行星胚胎嵌在一群总质量大致与星胚质量相当的星子中(Ida and Makino, 1992; Kokubo and Ida, 1998; O'Brien *et al.*, 2006; Morbidelli *et al.*, 2012)。

第 3 阶段为行星生长阶段。最初, 星胚彼此独立存在于一群星子中, 并通过引力作用和动力摩擦作用维持着星胚系统的平衡(Kokubo and Ida, 1998), 随着星云气体的减少, 或者其它巨行星的引力扰动, 有些星胚逐渐偏离其运行轨道, 平衡被打破, 星胚开始相互碰撞, 在这一阶段通过星胚之间

的相互碰撞以及吸积剩余的星子而形成行星 (Kenyon and Bromley, 2006; Morbidelli *et al.*, 2012)。

根据星子论, 地球是由一系列位于地球运转轨道上的星子吸积增生演化而来, 地球的组成物质则受控于这些聚合成地球的初始星子, 太阳系星盘中星子的成分与其处于太阳系星盘的位置有关 (Stevenson and Lunine, 1988; Ciesla and Cuzzi, 2006; Wyatt, 2008)。图 2 为太阳星盘的热结构图, 其中横坐标为行星到太阳中心的距离 (AU, 1 个天文单位, 即地球和太阳之间的平均距离), 纵坐标为温度, 红色实线和虚线为两条模拟的从太阳中心向外的温度梯度演化曲线 (Albarede, 2009), 不同颜色区域对应图 1a 中 4 组具有不同 T_{50} 的元素, “雪线” (snow line) 处于小行星带的位置, 在“雪线”的右侧气态水可以冷凝积聚成冰, 而其左侧则不能。太阳高能辐射作用会将星云气体往外驱散, 并在远离太阳的低温区域冷凝积聚, 而此时类地行星区域温度仍处于碱金属冷凝积聚阶段 (800~1 000 K) (Ganapathy and Anders, 1974; Wanke, 1981; Ebel and Grossman, 2000)。因此, 类地行星通常亏损挥发性元素, 而“雪线”附近以及“雪线”之外的行星则富集水和其它挥发性组分。为了研究碳在太阳系中的空间分布, 有学者提出了“灰线” (soot line) 概念 (Kress *et al.*, 2010)。“灰线”是人为定义的一条关于碳存在形式的边界线, 是多环芳烃发生不可逆裂解反应的边界线, 主要受温度控制 ($T \approx 500$ K, Li *et al.*, 2021)。

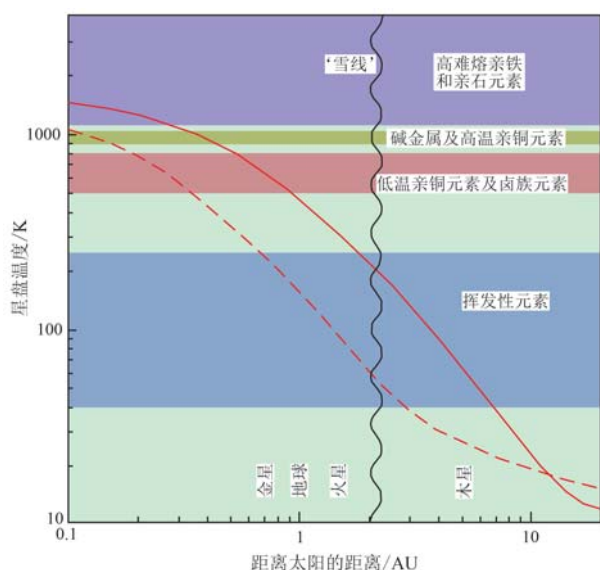


图 2 太阳星盘的热结构图 [据 Albarede (2009) 修改]

Fig. 2 The thermal structure of the planetary solar nebula (modified after Albarede, 2009)

太阳系中的碳在“灰线”左侧高温区域主要以气态的 CO 、 CO_2 和 CH_4 形式存在, 在“灰线”右侧低温区域可以形成难熔的有机分子及富碳颗粒; 在更低温区域 CO 、 CO_2 和 CH_4 可以冰的形式存在 (Kress *et al.*, 2010)。

关于地球原始碳的来源仍存在争议。有学者认为地球上的原始碳及其它挥发组分来自于地球的初始组成物质, 通过星子吸积增生演化形成 (Wood *et al.*, 2010, 2013; Boujibar *et al.*, 2014; Rubie *et al.*, 2015; Li *et al.*, 2016)。然而, 动力学模拟表明形成地球的星子、星胚在同一轨道演化, 它们位于太阳星盘的内圈, 演化初期具有很高的温度而使挥发组分难以保留 (Raymond *et al.*, 2006; Muralidharan *et al.*, 2008)。Li 等 (2021) 模拟表明在太阳星云演化的初期 (<1 Ma), “灰线”位于距离太阳几十个 AU 的位置, 之后随着太阳系热结构的转变, “灰线”逐渐向内移动到现今小于 1 AU 的位置。这也进一步表明地球在形成演化早期是缺乏碳元素的, 形成地球的初始物质不足以提供现今地球的碳含量 (Albarede, 2009; Mikhail and Füri, 2019; Hirschmann *et al.*, 2021; Li *et al.*, 2021)。

有研究者认为地球早期大碰撞作用是地球获得碳的一个重要途径 (Tsuno *et al.*, 2018; Grewal *et al.*, 2019)。星子吸积增生模型表明, 原始地球前 50% 质量增长是连续的, 并且在太阳系形成的前几百万年就完成了, 在之后的大约 100 Ma 内经历了几次星胚大碰撞事件, 使地球质量突然增加 (Canup and Asphaug, 2001; Kleine *et al.*, 2009; Ćuk and Stewart, 2012; Rubie *et al.*, 2015; Grewal *et al.*, 2019)。该模型认为原始地球和经过分异的星胚发生碰撞时, 碰撞星胚的核部会直接和原始地球核部融合, 不会和原始地球硅酸盐岩浆发生平衡分馏作用, 星胚的幔部则会直接和原始地球的幔部融合, 不发生核-幔分异作用而使获得的碳又重新汇聚到地核中 (图 3; Deguen *et al.*, 2011, 2014; Grewal *et al.*, 2019)。最近有实验研究表明, 行星星胚核部铁合金如果富集 S 和 Si, 则可以形成具有高 C/N 和 C/S 值的幔部 (Li *et al.*, 2016; Tsuno *et al.*, 2018; Grewal *et al.*, 2019)。星胚幔部富集碳, 具有高 C/N 和 C/S 值, 和地球碰撞后可以使地球地幔获得挥发性元素 C、S、N, 因此, 当具有高 C/N 和 C/S 值的星胚幔部和原始地球幔部融合时, 可以提高地球的碳含量 (图 3)。Grewal 等 (2019) 进一步通过模拟计

算证实具有 E 型球粒陨石成分的火星大小的星胚 (约为 0.1 个地球质量) 和原始地球碰撞可以形成具有现今地幔碳含量的全硅酸盐类地球 (BSE), 还认为这次大碰撞事件除了给地球带来了挥发性物质外, 还形成了月球, 使得月球具有和 BSE 相似的地球化学特征。

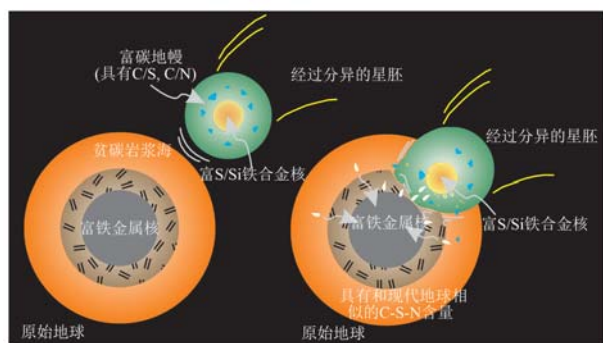


图 3 原始地球和星胚的碰撞融合模型[据 Grewal 等 (2019) 修改]

Fig. 3 A schematic depiction of the giant impact of proto-Earth and planetary embryos (modified after Grewal *et al.*, 2019)

另一个比较流行的观点认为地球上的原始碳主要来自富挥发分的球粒陨石后期增生 (late veneer) 作用 (Albarede, 2009; Rose-Weston *et al.*, 2009; Walker, 2009; Mann *et al.*, 2012; Wang and Becker, 2013)。后期增生模式认为在地球核-幔分异结束之后, 位于“雪线”之外富集挥发分的球粒陨石由于受到巨行星生长运动的影响, 轨道发生变化而向太阳系内部运动, 有些被地球捕获, 从而将挥发分带入地球 (Albarede, 2009; Rose-Weston *et al.*, 2009; Walsh *et al.*, 2011; Wang and Becker, 2013; Raymond and Izidoro, 2017)。这一模式最直接的证据来自于硅酸盐地幔具有和球粒陨石高度相似的亲铁元素 (HSEs: Re、Os、Ir、Ru、Pt、Rh、Pd 和 Au) 含量 (Becker *et al.*, 2006; Walker, 2009; Fischer-Gödde *et al.*, 2011; Fischer-Gödde and Becker, 2012)。在地球核-幔分异过程中, HSEs 大部分会进入地核, 使硅酸盐地幔亏损 HSEs 元素, 因此现今地球地幔高的 HSEs 含量需要外来物质的加入 (Albarede, 2009; Wang and Becker, 2013; Dasgupta and Grewal, 2019; Mikhail and Füri, 2019)。此外, 地幔具有和碳质球粒陨石相似的 S/Se 和 Se/Te 值也进一步表明后期增生在地球早期演化历史过程中扮演了非常

重要的角色 (Rose-Weston *et al.*, 2009; Wang and Becker, 2013)。然而, Dasgupta 和 Grewal (2019) 在总结地球和不同类型球粒陨石碳含量及不同挥发性元素之间的比值 (表 1) 时发现, 单独依靠后期增生作用也不能很好解释地球现今的碳含量和其它挥发性元素 (H、N、S) 比值之间的关系, 因此还需要考虑地球早期碳循环过程对现今地球碳含量的影响。

表 1 不同地球储库及球粒陨石 C 含量、C/S、C/N 和 C/H 比值

Table 1 C content and C/S, C/N, and C/H ratios of major terrestrial reservoirs and chondrite

储库类型	$w(C) / \%$	$w(C) / w(S)$	$w(C) / w(N)$	$W(C) / w(H)$
地球储库				
BSE	0.011 ± 0.002	0.49 ± 0.14	40.00 ± 8.00	1.13 ± 0.20
地幔	0.008 ± 0.002	0.36 ± 0.10	72.73 ± 37.72	2.00 ± 0.70
地壳-海洋-大气	0.002 ± 0.000	8.89 ± 2.22	12.50 ± 3.22	0.51 ± 0.04
地核	$0.50 (?)$	$0.32 (?)$	$85.00 (?)$	$8.40 (?)$
碳质球粒陨石				
CO	0.63 ± 0.24	0.32 ± 0.12	21.74 ± 19.16	10.40 ± 0.00
CV	0.92 ± 0.43	0.42 ± 0.20	23.96 ± 24.16	10.20 ± 0.00
CM	1.89 ± 0.48	0.58 ± 0.15	21.01 ± 8.35	3.20 ± 0.00
CI	4.24 ± 0.77	0.72 ± 0.13	19.66 ± 11.69	4.80 ± 0.00
顽火辉石球粒陨石				
EH	0.36 ± 0.13	0.06 ± 0.02	13.73 ± 7.26	11.00 ± 0.00
EL	0.48 ± 0.16	0.15 ± 0.05	24.43 ± 9.40	11.00 ± 0.00
普通球粒陨石				
H	0.11	0.06	>104.00	2.50 ± 0.70
L	0.09	0.04	46.10 ± 1.00	3.00 ± 1.0
LL	0.09	0.05	51.22 ± 1.20	2.60 ± 0.50

表中数据引自 Dasgupta 和 Grewal (2019); BSE 代表全硅酸盐地球; CO、CV、CM、CI 为碳质球粒陨石的几个亚类; EH、EL 为顽火辉石球粒陨石的几个亚类; H、L、LL 为普通球粒陨石的几个亚类。

2 地球早期碳循环过程

地球早期碳循环演化过程主要包括地球核-幔分异 (岩浆海时期) 以及地球大陆壳形成之后 (岩浆海固结之后, 前板块构造及早期板块构造阶段) 的碳循环过程。现代板块构造碳循环过程可详见张立飞等 (2017)、刘勇胜等 (2019)、朱建江等 (2021), 本文不再展开论述。

2.1 地球核-幔分异时 (岩浆海时期) 的碳循环过程

在原地球星子、星胚吸积增生形成地球的初期, 由于动力能和放射性热能的释放, 地球发生全部熔融形成岩浆海, 岩浆海演化过程会发生金属和硅酸盐组分的分异, 逐渐形成地核和地幔。地核主要由铁镍等金属元素组成, 地幔主要为硅酸盐矿物, 在

地核形成过程中金属核与硅酸盐地幔之间的元素(如亲铁元素)分馏,在很大程度上决定了早期地球不同储层中元素的分布,为后期地壳和地幔地球化学演化奠定了基础,同样的分馏过程也影响了早期地球挥发物的总体分布,特别是碳的总体分布(Dasgupta, 2013; Dasgupta and Grewal, 2019)。过去的几十年里,有许多研究者对碳在岩浆海中的分异作用进行了研究(Kuramoto and Matsui, 1996; Kuramoto, 1997; Dasgupta and Walker, 2008; Hirschmann and Dasgupta, 2009; Dasgupta and Hirschmann, 2010; Hirschmann, 2012; Dasgupta, 2013; Dasgupta *et al.*, 2013; Chi *et al.*, 2014; Li *et al.*, 2015, 2016; Dalou *et al.*, 2017; Tsuno *et al.*, 2018; Grewal *et al.*, 2019),其中最关键的是要确定碳在不同储层,也即地核、地幔和原始大气之间的分异过程。

通过确定碳在金属和硅酸盐之间的平衡分馏系数可以限定碳在地核和地幔之间的分布情况(Kuramoto and Matsui, 1996; Kuramoto, 1997; Dasgupta and Walker, 2008; Dasgupta *et al.*, 2013; Dasgupta and Grewal, 2019)。假设岩浆海时期,全地球碳都参与了金属-硅酸盐的分馏过程,如果 $D_C^{\text{metal/silicate}}$ (碳在金属和硅酸盐之间的分馏系数) < 1 , 那么碳主要富集于外部的硅酸盐层;如果 $D_C^{\text{metal/silicate}} \gg 1$, 则地球大部分碳将进入地核。Dasgupta 等(2013)的实验表明,在 1~5 GPa、1 500~2 100℃、氧逸度 $f_{O_2} = \text{IW}-1.5 \sim \text{IW}-2$ 条件下,碳表现出明显的亲铁性($D_C^{\text{metal/silicate}} = 150 \sim 5\,500$),并且碳的亲铁性随着压力升高而升高,随着温度升高而降低。图4所示为地球经历核-幔分异后碳在地核和全硅酸盐地球(BSE)之间的分布特征,计算结果表明碳会优先进入金属地核,其计算公式如下: $C_C^{\text{core}} = (C_C^0 - 0.677 C_C^{\text{mantle}}) / 0.323$, $C_C^{\text{mantle}} = C_C^0 / (0.323 D_C^{\text{metal/silicate}} + 0.677)$ 。计算的前提是假设地核(质量等于现今地球质量的 32.3%)和整个硅酸盐地幔达到平衡,其中 C_C^{core} 、 C_C^{mantle} 分别表示碳在地核和地幔中的含量, C_C^0 为全地球碳含量, $D_C^{\text{metal/silicate}}$ 为碳在金属和硅酸盐之间的分馏系数,模拟过程取 $D_C^{\text{metal/silicate}} = 500, 1\,000, 2\,500, 5\,500$ 。图4的模拟结果表明,如果初始地球碳含量大于等于 0.4%~3.5%,通过地核-地幔平衡分馏,早期地幔可以演化得到现今亏损地幔的碳含量;而要使早期地幔达到现今富集地幔的碳含量($50 \times 10^{-6} \sim 1\,000 \times 10^{-6}$),则需要地球的初始碳含量

大于 3.5%。然而,许多研究表明地球初始碳含量小于 $1\,000 \times 10^{-6}$ (McDonough, 2003; Marty, 2012),如果初始地球的碳含量大约只有 730×10^{-6} (McDonough, 2003),经过核-幔分异作用,地幔中将只剩下 $0.4 \times 10^{-6} \sim 4.5 \times 10^{-6}$ C,占现今地幔的 0.3%~3.8%,初始地球的碳大部分将进入金属地核。即使初始地球具有 3.5%的碳含量,通过核-幔分异也不能使 BSE 具有 $(765 \pm 300) \times 10^{-6}$ C (Marty, 2012)。此外,星子论表明地球演化初期具有很高的温度,使得组成地球的初始物质很难保留挥发组分,初始地球的碳含量可能更低,因此还需要其它的过程来解释现今地球 BSE 碳丰度。

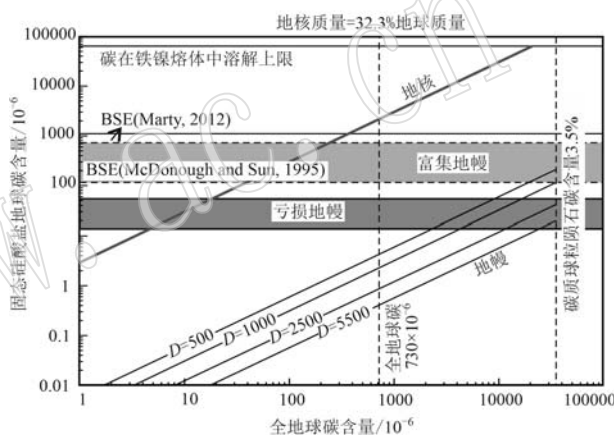


图4 岩浆海中金属和硅酸盐熔体中碳的平衡分配对地幔和地核碳储量的影响[据 Dasgupta 等(2013)修改]

Fig. 4 The effect of equilibrium partitioning of carbon between metallic and silicate melt in a magma ocean on the inventory of mantle and core carbon (modified after Dasgupta *et al.*, 2013)

在地核形成之后,地幔获得碳的一个可能机制是岩浆海和地球早期大气之间的相互作用(Hirschmann, 2012; Dasgupta *et al.*, 2013)。在石墨饱和条件下,硅酸盐岩浆中碳(CO_2 或者 CH_4)溶解度和压力成反比(Holloway *et al.*, 1992; Hirschmann and Withers, 2008; Dasgupta *et al.*, 2013),因此当地幔岩浆和早期富碳的大气相互作用时,有一部分大气中的碳可以溶解进入岩浆,当溶解碳的岩浆对流进入地球深部时,由于碳溶解度降低,岩浆中的碳又会以金刚石或铁碳化物的形式沉淀下来。通过这一循环过程,岩浆可以逐渐将大气中的碳带入地幔中,使地幔中碳含量升高(Dasgupta *et al.*, 2013)。此外,还有学者认为金属熔体不完全成核也可以导

致地幔亲铁元素和碳含量的升高 (Jones and Drake, 1986; Newsom and Sims, 1991; Dasgupta *et al.*, 2013)。该模型认为在地核形成过程中, 有一部分金属熔体会残留在地幔中, 这些金属熔体可以为地幔提供额外的碳源及难熔性亲铁元素 (Dasgupta *et al.*, 2013)。

2.2 地球大陆壳形成之后(岩浆海固结后)的碳循环过程

随着地球演化和不断散热, 岩浆海发生冷凝结晶, 逐渐演化出早期大陆地壳, 并进一步产生板块构造运动。关于地球早期大陆地壳演化和板块俯冲起始问题, 前人已经做了大量的研究, 具体可参见文献(刘树文等, 2015; 李三忠等, 2015a, 2015b; 孙卫东等, 2021)。板块构造体制是何时和怎样产生的, 目前仍具有很大的争议。大部分学者认为板块构造开始于太古宙或古元古代 (Condie and Kroner, 2008; Shirey and Richardson, 2011; Dhuime *et al.*, 2012, 2015; Tang *et al.*, 2016; Greber *et al.*, 2017; Bindeman *et al.*, 2018; Cawood *et al.*, 2018; Brown and Johnson, 2019; Holder *et al.*, 2019), 少部分学者认为板块构造开始于新元古代 (Stern, 2005; Stern *et al.*, 2016)。孙卫东等 (2021) 认为事实上这两种争议主要是由于不同学者对板块构造的定义不一致导致的。

Cawood (2020) 将板块构造分为前板块构造阶段、中-新太古代过渡阶段、古-中元古代早期板块构造阶段和现代板块构造阶段。

在前板块构造阶段(古太古代), 上地幔温度可能比现今高出 250℃ 左右 (Herzberg *et al.*, 2010; Korenaga, 2013), 这种高温地幔条件使得岩石圈的刚性和强度大幅度降低, 阻碍了板块俯冲作用的发生 (van Hunen and van den Berg, 2008; Sizova *et al.*, 2010), 此时地幔中的碳主要通过深源地幔柱或浅部软流圈地幔的上涌而释放到地表 (Dasgupta, 2013)。

中-新太古代过渡阶段, 地球构造体制兼具滞留盖型构造和间歇性的板块俯冲作用, 难以形成持续性的板块俯冲作用 (Liu *et al.*, 2020; 孙卫东等, 2021)。

古-中元古代早期板块构造阶段, 板块俯冲的地热梯度可能要比现今的高 87~100℃ (Dasgupta, 2013)。图 5 为早期板块俯冲 p - T 轨迹图, 其中的俯冲热力学条件主要依据地球动力学模拟以及岩石学实验数据得出 (Dasgupta and Hirschmann, 2010; Tsuno and Dasgupta, 2011; Dasgupta, 2013)。这一时期

俯冲的含碳岩石类型和成分都缺乏岩石学的限定, 因此假设俯冲板块的岩石类型和现今板块相似, 从上到下依次为洋底沉积物、碳酸盐化玄武岩和碳酸盐化橄榄岩 (这里只讨论碳酸盐矿物的脱碳作用)。图 5a 显示, 在任何压力条件下, 碳酸盐化泥质沉积物具有最低的脱碳及熔融温度, 因此俯冲作用过程中最容易发生脱碳作用。如果早期板块的俯冲地热梯度比现今最热的板块俯冲地热梯度 (Cascadia) 高约 100℃, 那么俯冲板块沉积物中的碳在 100~150 km 会通过脱碳反应或熔融作用全部脱出去。然而, 如果这一时期岩石记录的变质条件代表了板块俯冲的温压路径, 那么沉积物在 80~100 km 就会发生完全的脱碳作用。碳酸盐化玄武岩 (或碳酸盐化榴辉岩) 具有中等温度的脱碳及熔融温度 (图 5b), 如果早期板块沿着比 Cascadia 高 100℃ 的地热梯度俯冲, 碳酸盐化玄武岩在 125~170 km 将发生完全的脱碳作用 (Dasgupta *et al.*, 2004, 2005; Gerbode and Dasgupta, 2010); 如果早期板块沿着对应时期的变质岩石记录的温度压力轨迹俯冲, 那么碳酸盐化玄武岩会在更浅部 (80~120 km) 发生完全的脱碳反应 (Yaxley and Green, 1994; Dasgupta *et al.*, 2004; Yaxley and Brey, 2004; Dasgupta *et al.*, 2005; Gerbode and Dasgupta, 2010; Kiseeva *et al.*, 2012)。碳酸盐化橄榄岩位于俯冲板块的底部, 受上覆地幔楔热传导影响较小, 相比上层的碳酸盐化玄武岩及沉积岩地热梯度更低 (图 5c), 因此, 即使板块沿着比 Cascadia 高 100℃ 的地热梯度俯冲, 对应的地热梯度线也不会穿过碳酸盐化橄榄岩的熔融线, 因此在早期板块构造阶段, 碳酸盐化橄榄岩可以将地表的碳带入地球深部地幔。

通过以上讨论可以得出, 在早期板块构造阶段, 由于俯冲地热梯度的升高, 俯冲的蚀变洋壳 (碳酸盐化玄武岩) 和洋底沉积碳酸盐岩在很浅部就会通过脱碳反应或者熔融作用发生完全的脱碳作用, 因此在早期板块构造阶段, 有大量的 CO_2 可以通过岛弧火山释放到地表, 而只有少量的碳可以通过碳酸盐化橄榄岩带入地球深部。

3 地球早期碳循环和大氧化事件之间的成因联系

地表环境变化除了受地球碳循环控制外, 还受到太阳光度的影响 (Tajika, 2003; Feulner, 2012; Dasgupta,

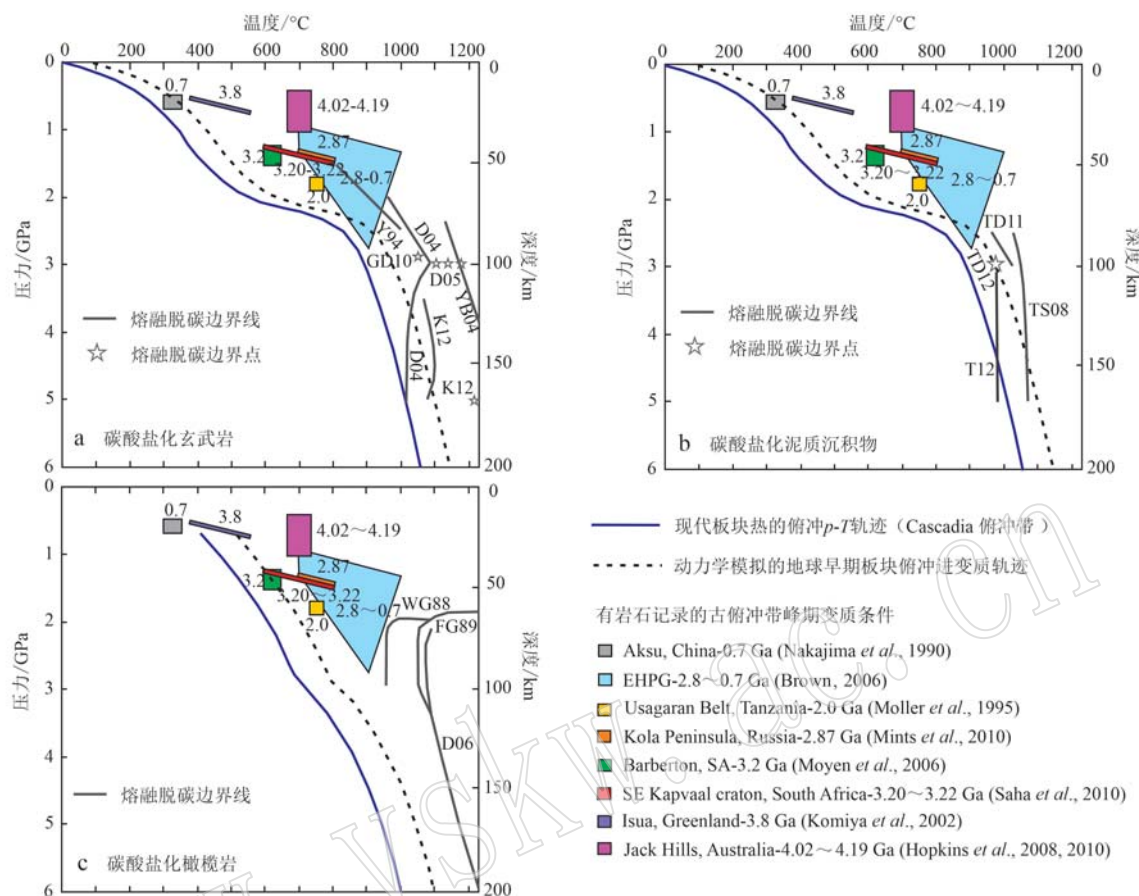


图5 早期板块俯冲 p - T 轨迹图[据 Dasgupta(2013)修改]

Fig. 5 The p - T trajectory of ancient subduction(modified after Dasgupta, 2013)

a—碳酸盐化玄武岩, 数据来源: Y94(Yaxley and Green, 1994), D04、D05(Dasgupta *et al.*, 2004, 2005), YB04(Yaxley and Brey, 2004), GD10(Gerbode and Dasgupta, 2010), K12(Kiseeva *et al.*, 2012); b—碳酸盐化泥质沉积物, 数据来源: TS08(Thomsen and Schmidt, 2008), TD11、TD12(Tsuno and Dasgupta, 2011, 2012), T12(Tsuno *et al.*, 2012); c—碳酸盐化橄榄岩, 数据来源: WG88(Wallace and Green, 1988), FG89(Falloon and Green, 1989), D06(Dasgupta and Hirschmann, 2006)

a—carbonated basalt, data source: Y94(Yaxley and Green, 1994), D04 and D05(Dasgupta *et al.*, 2004, 2005), YB04(Yaxley and Brey, 2004), GD10(Gerbode and Dasgupta, 2010), K12(Kiseeva *et al.*, 2012); b—carbonated pelitic sediments, data source: TS08(Thomsen and Schmidt, 2008), TD11 and TD12(Tsuno and Dasgupta, 2011, 2012), T12(Tsuno *et al.*, 2012); c—carbonated (lithospheric) mantle peridotite, data source: WG88(Wallace and Green, 1988), FG89(Falloon and Green, 1989), D06(Dasgupta and Hirschmann, 2006)

2013; Catling and Zahnle, 2020)。20 世纪 50 年代以来, 天体物理学家对恒星的结构和演化规律做了大量的研究, 通过计算发现在地球演化的前 20 亿年, 年轻的太阳光度只有现今的 70%~80%(Schwarzschild, 1958; Sagan and Mullen, 1972; Newman and Rood, 1977; Gough, 1981; Feulner, 2012)。假如早期地球(冥古宙至太古宙时期)大气成分和现今一致, 那么地表温度会低于零摄氏度, 早期地球表面不会存在液态水(Budyko, 1969; Kasting and Catling, 2003; Zahnle, 2006; Zahnle *et al.*, 2007)。然而, 有许多证据表明早期地球已经存在液态水, 例

如 43 亿年的锆石氧同位素特征指示地表在冥古宙时期存在液态水(Mojzsis *et al.*, 2001; Wilde *et al.*, 2001); 太古宙大量 38~35 亿年富水环境下形成的沉积岩也表明太古宙时期地表已经存在大量液态水(Lowe, 1980; Walker, 1982; Walker *et al.*, 1983; Fowler *et al.*, 2002; Eriksson *et al.*, 2004; Benn *et al.*, 2006); 此外, 35~25 亿年岩石中微体生物化石和叠层石的发现证明在太古宙时期已存在微生物(Barghoorn and Schopf, 1966; Altermann and Kazmierczak, 2003; Schopf, 2006)。因此, 地球早期地表温度不会一直低于零度, 还需要有其它热源来抵

消太阳光度的影响。有学者认为早期地球大气中的高 CO_2 浓度可以解释这一矛盾,和现今大气不同,地球早期大气极度贫氧,其含量小于现今大气中氧含量的百万分之一,然而地球早期大气 CO_2 含量是现今大气的 $10\sim 2\,500$ 倍,由此造成的温室效应可以抵消早期太阳光度不足对地表气候的影响(Owen *et al.*, 1979; Walker *et al.*, 1981; Kuhn and Kasting, 1983; Zahnle, 2006; Feulner, 2012; Catling and Zahnle, 2020)。

前文论述表明,早期板块构造阶段,地幔具有更高的热流值,俯冲板块中的碳大部分都会通过岛弧火山释放到大气中。Nakamura 和 Kato (2004) 对西澳大利亚皮尔巴拉克拉通东部的太古宙 (3.46 Ga) 热液蚀变玄武质岩石研究表明,这一时期进入俯冲带的碳可以达到每年 3.8×10^{13} mol (约合每年 1.7×10^{15} g CO_2)。Shibuya 等(2012)对西澳大利亚皮尔巴拉克拉通 Cleaverville 地区的中太古代绿岩带岩石进行了详细的研究,根据这些岩石的热液碳酸盐化作用估算得出在中太古代时期通过海底热液蚀变作用 ($\text{CO}_2 + \text{CaSiO}_3 \rightarrow \text{CaCO}_3 + \text{SiO}_2$), 每年大约有 1.5×10^{14} mol 的碳进入洋壳岩石。如果这些碳在洋壳俯冲作用过程中全部通过岛弧火山释放到大气中,那么太古宙时期岛弧火山释放的碳通量将比现今的高 $1\sim 2$ 个数量级,这为地球早期的温室效应提供了有力的证据(Dasgupta and Hirschmann, 2010; Dasgupta, 2013)。

已有大量证据表明,地球早期大气缺氧状态一直持续到 2.45 Ga,而在 2.4~2.0 Ga 间,大气和表层海水中的氧气开始快速增加,从小于 $10^{-7}\sim 10^{-5}$ PAL (present atmospheric levels, 现今大气水平) 增长到 $10^{-4}\sim 10^{-2}$ PAL (Bekker *et al.*, 2004; Lyons *et al.*, 2014; Lee *et al.*, 2016; Gumsley *et al.*, 2017), 这一事件被称为大氧化事件 (GOE, great oxidation event)。地质证据包括这时期地层中红层、富 CaSO_4 蒸发岩、氧化的浅水铁层普遍发育,硫同位素非质量平衡分馏现象消失等 (Chandler, 1980, 1988; El Tabakh *et al.*, 1999; Farquhar *et al.*, 2000; Bekker *et al.*, 2004)。关于大氧化事件形成的确切机制目前还存在争议。地球目前的含氧大气是光合作用的结果,但是生命本身甚至光合作用并不能保证有一个含氧大气,27 亿年前沉积地层中蓝藻细菌的发现表明大氧化事件发生之前地球就有光合作用存在 (Canfield, 2005; Anbar *et al.*, 2007; David and

Alm, 2011; Crowe *et al.*, 2013; Planavsky *et al.*, 2014), 然而光合作用的出现并没有使大气氧含量迅速增加。有研究者认为早期大气富含 CH_4 和 H_2 等还原性气体,光合作用产生的氧气大部分都会被还原性气体消耗,使氧气增长缓慢,而随着 CH_4 和 H_2 向地球外逃逸,大气中的氧才开始快速增加 (Kasting *et al.*, 1993; Catling *et al.*, 2001; Catling and Claire, 2005; Kadoya *et al.*, 2020)。然而,如果 CH_4 和 H_2 一直不断地向地球外逃逸,地幔和大气将变得越来越氧化,但是大氧化事件之后的一段时间,大气的氧含量平稳地保持了很长时间 (图 6a), 并没有一直增加。Lee 等 (2016) 提出一个大气氧含量的两阶段增长模型。第 1 阶段,大陆地壳成分由富铁镁质向富长英质转变,由于富铁镁质基性岩石相对长英质岩石富集 Fe^{2+} 和 S^{2-} , 容易和大气中的氧发生氧化还原反应,因此这一过程减弱了大陆地壳对大气氧的消耗,这是氧气可以在大气中逐渐积累的前提条件;第 2 阶段,随着大陆地壳的增长,风化作用增强,导致无机碳酸盐增多,此外风化作用可以为海洋生物提供大量的营养物质,促使光合作用产氧量增加,因此,地表的总碳量 (包括碳酸盐、有机碳和大气二氧化碳) 将逐渐增加,地表碳同位素数据表明太古宙以来有机碳占总碳的百分比大部分时间都稳定在 20% 左右 (Krissansen-Totton *et al.*, 2015), 因此如果地表总碳量增加,那么大气中的氧含量也会增加。此外,沉积物黄铁矿的埋藏可以减弱大陆地壳对大气氧的消耗,它也是促进大气氧含量增加的重要因素 (Berner, 1982)。然而,尽管大量有机碳的埋藏可以使大气氧快速增加,但是这些埋藏的有机碳在受到岩浆热事件的影响时,很容易重新氧化消耗大气氧 (Ganino and Arndt, 2009), 因此需要有其它机制将有机碳长期存储起来,才能使大气氧浓度维持在一个稳定的区域。Galvez 等 (2020) 研究认为有机碳转变为石墨后可以长期稳定在岩石圈中, Duncan 和 Dasgupta (2017) 的高温高压实验表明石墨有机碳在俯冲板块流纹质熔体中的溶解度很低,含有机碳的大洋板块不论是沿着现代俯冲地热梯度还是太古宙高温地热梯度俯冲,其中的有机碳只有很少部分会通过岛弧火山释放回地表,大部分有机碳可以被带入地球深部,长时间存储在深部地幔中,促使地表氧浓度升高。在此基础上, Eguchi 等 (2020) 进一步提出了有机碳和无机碳的差异循环模型 (图 7), 用来解释俯冲带深部碳循

环和大氧化事件及地表碳酸盐碳同位素变化之间的关系。该模型显示板块构造运动的发生导致岛弧火山 CO_2 释放,使大气中 CO_2 含量迅速增加,可以使地表沉积的碳酸盐和有机物含量都显著增加,进而导致大气氧含量升高。该模型表明俯冲带碳酸盐矿物和石墨有机碳的物理化学行为有显著差别,在早期板块构造阶段,高的俯冲地热梯度使得碳酸盐矿物在岛弧深度几乎可以全部脱出去,而石墨有机碳只发生少量的脱碳作用,大部分将被带入地幔深

部,参与深部地幔碳循环作用,最后随着地幔柱的上涌从洋岛或洋中脊释放回地表,因此有机碳的释放相对无机碳酸盐滞后 1 亿年左右,这可以用来解释为什么大氧化事件比拉玛岗地-瓦图里事件 (Lomaundi-Jatuli Event; Baker and Fallick, 1989a, 1989b; 该事件以全球性 $\delta^{13}\text{C}_{\text{carb}}$ 正漂移为特征,图 6b) 早发生大约 1 亿年 (Bekker *et al.*, 2004, 2008; Bekker *et al.*, 2006; Luo *et al.*, 2016), 并且全球性 $\delta^{13}\text{C}_{\text{carb}}$ 正漂移发生不久就重新回到了零左右。

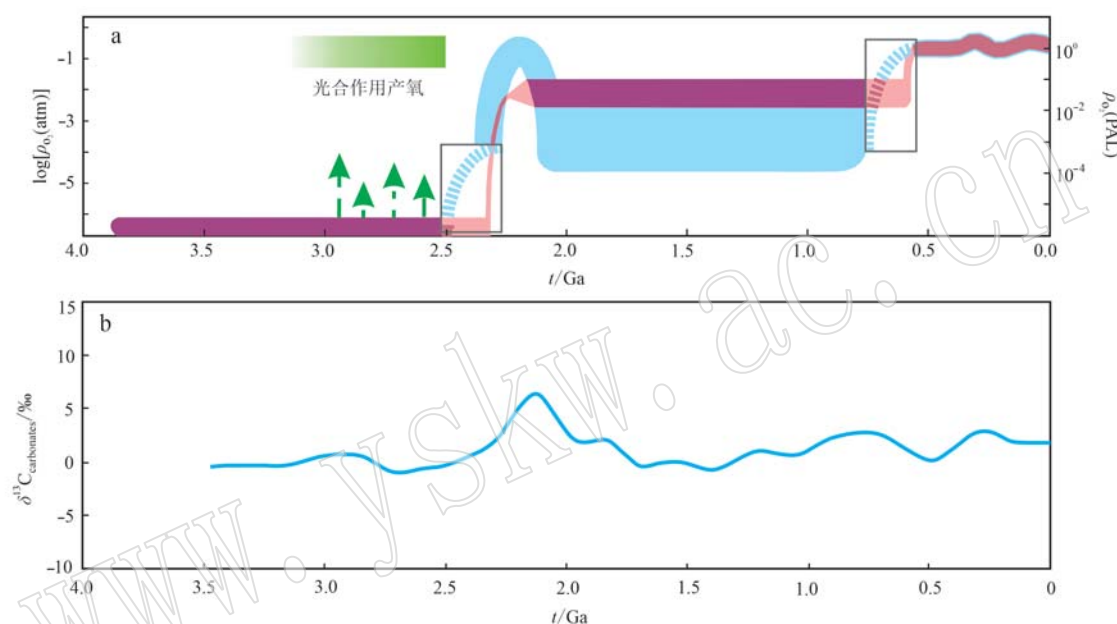


图 6 地球大气氧含量随时间演变规律 [a, 据 Lyons 等 (2014) 修改] 和地表碳酸盐碳同位素随时间演变规律 [b, 据 Krissansen-Totton 等 (2015) 修改]

Fig. 6 Evolution of Earth's atmospheric oxygen content through time (a, modified after Lyons *et al.*, 2014) and Earth's surface carbonate $\delta^{13}\text{C}$ through time (b, modified after Krissansen-Totton *et al.*, 2015)

综上所述,地球早期碳循环作用和大氧化事件具有紧密的联系,大气中 CO_2 含量的升高、有机物的埋藏、无机碳酸盐和有机碳俯冲循环效率的差异等都是形成大氧化事件的关键因素。然而,地球早期碳循环作用并不是导致大氧化事件的直接原因,例如地球在岩浆海时期也存在着大气-地幔-地核之间的碳循环过程,但并没有形成富氧的大气。另一方面大氧化事件也不能脱离碳循环而独立发生,大气氧的产生需要 CO_2 作为原材料,需要碳基生命的光合作用。地球碳循环和大氧化事件之间有交集,但并非包含和因果关系。在地球的不同演化时期,其碳循环作用存在显著的差异。在冥古宙时期,地球碳循环主要通过地球核-幔分异过程进行 (Dasgupta, 2013); 在太古宙时期,地球主要通过深源地

幔柱和浅部软流圈的上涌实现地球深部和浅部之间碳的循环过程 (Dasgupta, 2013); 在太古宙之后,地球开始有了板块构造运动 (Cawood *et al.*, 2018; Brown and Johnson, 2019; Holder *et al.*, 2019; 孙卫东等, 2021), 此时地球主要通过板块俯冲进行地表和地球深部之间的碳循环过程 (Berner, 2003; Dasgupta, 2013; Kelemen and Manning, 2015; 张立飞等, 2017; 刘勇胜等, 2019; Plank and Manning, 2019)。从地质时间尺度上来看,大氧化事件发生的时间 (2.4~2.3 Ga, Bekker *et al.*, 2004; Lyons *et al.*, 2014; Lee *et al.*, 2016; Gumsley *et al.*, 2017) 正好对应板块俯冲作用开始的时间, Eguchi 等 (2020) 提出的碳循环模型比较合理地解释了大氧化事件和俯冲碳循环之间的联系。板块俯冲作用的发生,地球

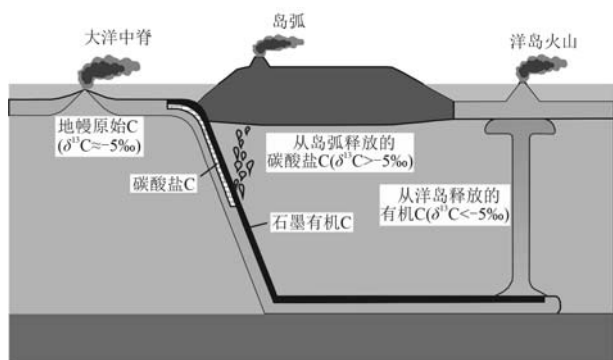


图7 俯冲带有机碳和无机碳的差异循环模式图

Fig. 7 A schematic diagram showing different cycle process of organic and inorganic carbon in subduction zones

构造体制的转变可能是大氧化事件发生的前提条件,但具体哪些因素控制着大氧化事件的形成还需要进一步的研究工作。

4 结论

(1) 地球是从太阳星云中通过星子吸积增生演化形成的,地球上的碳有一部分来自于地球的初始组成物质,还有一部分是通过大碰撞事件以及后期增生过程获得的。

(2) 在地球形成之初的岩浆海时期,地核和地幔之间的分异作用会使地核富集碳而地幔极度亏损碳;岩浆海和地球早期大气之间的相互作用可以把大气中的碳循环带入地幔中。

(3) 在早期板块构造阶段,高的地热梯度使俯冲的蚀变洋壳和洋底沉积物在很浅部通过脱碳反应或者熔融作用发生完全的脱碳作用,只有少量的碳可以通过碳酸盐化橄榄岩带入地球深部,由此造成的温室效应可以抵消早期太阳光度不足对地表气候的影响。

(4) 地球早期碳循环作用和大氧化事件具有紧密的联系,大气中 CO_2 含量的升高、有机物的埋藏、无机碳酸盐和有机碳俯冲循环效率的差异是形成大氧化事件的关键因素。

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