Science Bulletin 65 (2020) 2141–2149

Contents lists available at ScienceDirect

Science Bulletin

journal homepage: www.elsevier.com/locate/scib

Review

The redox structure of Ediacaran and early Cambrian oceans and its controls

Chao Li [a,*], Wei Shi [a], Meng Cheng [a], Chengsheng Jin [b], Thomas J. Algeo [a,c,d]

[a] *State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan 430074, China*
[b] *Yunnan Key Laboratory for Palaeobiology, Yunnan University, Kunming 650091, China*
[c] *State Key Laboratory of Geological Process and Mineral Resources, China University of Geosciences, Wuhan 430074, China*
[d] *Department of Geology, University of Cincinnati, Cincinnati OH45221, USA*

ARTICLE INFO

Article history:
Received 23 July 2020
Received in revised form 24 August 2020
Accepted 25 August 2020
Available online 19 September 2020

Keywords:
Redox stratification
Oceanic oxygenation
Euxinia
Early animal
Cambrian Explosion

ABSTRACT

The rapid diversification of early animals during the Ediacaran (635–541 Ma) and early Cambrian (ca. 541–509 Ma) has frequently been attributed to increasing oceanic oxygenation. However, the pattern of oceanic oxygenation and its relationship to early animal evolution remain in debate. In this review, we examine the redox structure of Ediacaran and early Cambrian oceans and its controls, offering new insights into contemporaneous oceanic oxygenation patterns and their role in the coevolution of environments and early animals. We review the development of marine redox models which, in combination with independent distal deep-ocean redox proxies, supports a highly redox-stratified shelf and an anoxia-dominated deep ocean during the Ediacaran and early Cambrian. Geochemical and modeling evidence indicates that the marine redox structure was likely controlled by low atmospheric O_2 levels and low seawater vertical mixing rates on shelves at that time. Furthermore, theoretical analysis and increasing geochemical evidence, particularly from South China, show that limited sulfate availability was a primary control on the attenuation of mid-depth euxinia offshore, in contrast to the existing paradigm invoking decreased organic carbon fluxes distally. In light of our review, we infer that if oceanic oxygenation indeed triggered the rise of early animals, it must have done so through a shelf oxygenation which was probably driven by elevated oxidant availability. Our review calls for further studies on Ediacaran-Cambrian marine redox structure and its controls, particularly from regions outside of South China, in order to better understand the coevolutionary relationship between oceanic redox and early animals.

1. Introduction

The appearance of animals (metazoans) in the Cryogenian and their subsequent radiations in the Ediacaran (635–541 Ma) and early Cambrian (~541–509 Ma; i.e., "Cambrian Explosion") are among the most important biotic events in Earth history [1–5]. Because early animals lived in seawater and required O_2, which was linked to greater aerobic requirements with increasing organismal complexity and activity levels [6–8], the history of oceanic oxygenation is central to an understanding of early animal evolution (note: we define "oceanic oxygenation" as buildup in seawater of dissolved O_2 as well as other oxidants). However, the relationship of early animal evolution to Ediacaran-Cambrian oceanic oxygenation remains strongly debated. Conventional coevolution hypotheses argue that a significant increase in deep-ocean oxygen levels (i.e., a so-called deep-ocean ventilation; note: "deep ocean" in this study signifies subsurface waters ranging from continental shelves to abyssal plains, unless otherwise specified) associated with the Neoproterozoic Oxidation Event (NOE) triggered the rise of early animals (Fig. 1a) [9–13], whereas non-coevolution hypotheses argue that limited oceanic oxygenation [14–16] or the low metabolic O_2 requirements of early animals [e.g., 6] precluded significant oceanic oxygenation serving as an evolutionary stimulus, and, therefore, that genetic or ecological factors were more important in the rise of early animals (Fig. 1b). Recently, stratified marine redox models emphasizing significant spatial heterogeneity of marine redox, particularly in shelf oceans, have been proposed [e.g., 17–19]. In the context of a redox-stratified ocean, a new coevolution hypothesis, in which oxygenation led to dynamic expansion of the oxic ocean-surface layer in shelf settings, has been proposed to account for the spatiotemporal radiation of animals in the Ediacaran and early Cambrian (Fig. 1c) [20–25]. Therefore, the redox structure of Ediacaran-Cambrian

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* Corresponding author.
E-mail address: chaoli@cug.edu.cn (C. Li).

https://doi.org/10.1016/j.scib.2020.09.023

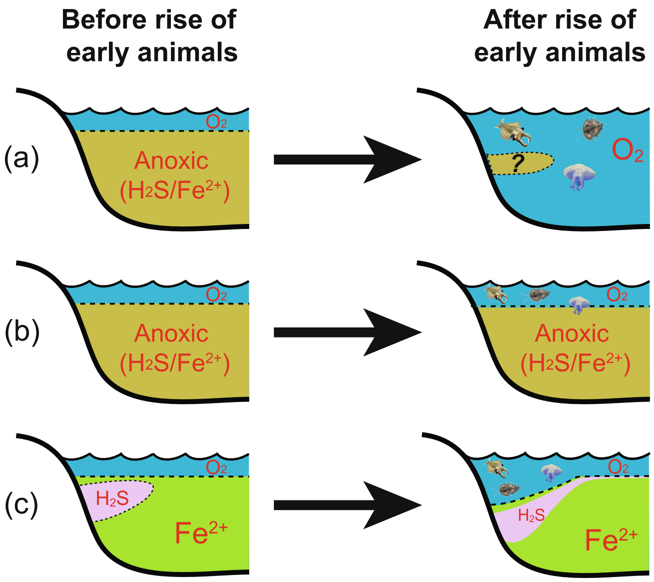

Fig. 1. Alternative hypotheses for the relationship between oceanic oxygenation and early animal evolution during the Ediacaran and early Cambrian. (a) Conventional coevolution hypotheses postulating control of early animal evolution by a significant deep-ocean oxygenation or oxygenic ventilation. (b) Non-coevolution hypotheses postulating that oceanic oxygenation was (very) limited and had no direct relationship to the rise of early animals. (c) New coevolution hypotheses in which dynamic shelf oxygenation was spatiotemporally coupled with early animal evolution. O_2, Fe^{2+} and H_2S denote oxic, ferruginous and sulfidic (or euxinic) conditions, respectively.

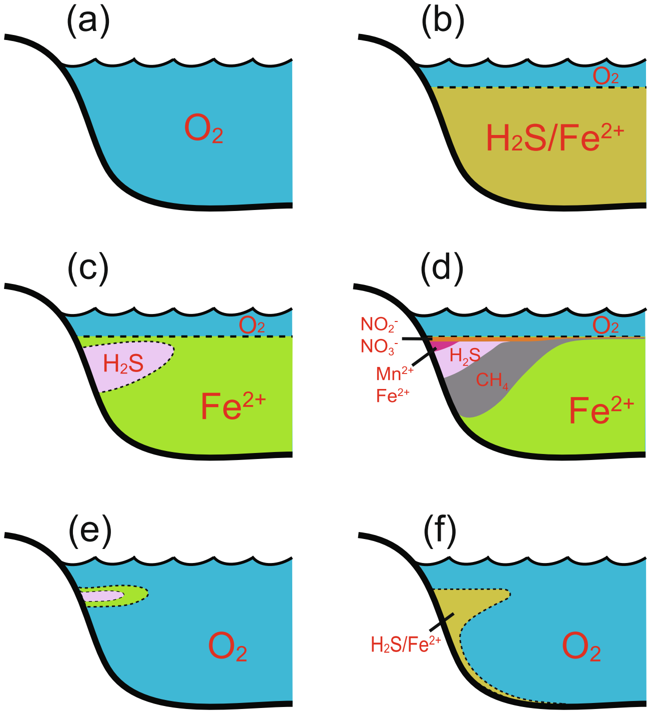

Fig. 2. Alternative models for the redox structure of Ediacaran and early Cambrian oceans. Redox-homogeneous ocean models with (a) an oxic deep ocean [26,27] or (b) a euxinic [28,29] or ferruginous [30] deep ocean; redox-heterogeneous deep-ocean models including (c) the euxinic wedge model [17] or (d) a multi-layer model [18]; and modern-like ocean redox models, including (e) a standard oxygen-minimum zone model [31] and (f) a modified oxygen-minimum zone model [32,33].

oceans is a key to evaluating alternative hypotheses regarding co-evolutionary relationships between early animals and their environment. In this review, we focus on the development of marine redox structure models for Ediacaran and early Cambrian oceans and their controls, offering new insights into the co-evolutionary history of the marine redox environment and early animals.

2. Evolving models of redox structure in Ediacaran and early Cambrian oceans

Based largely on geological evidence such as the disappearance of banded iron formations, the deep ocean was long regarded as oxic after 1.8 Ga (Fig. 2a) [26,27]. Subsequently, a model invoking a dominantly ferruginous (i.e., anoxic and Fe^{2+}-bearing) deep ocean after ~740 Ma was proposed based on global iron speciation and sulfur isotope data (Fig. 2b) [30]. However, a euxinic (i.e., anoxic and H_2S-bearing, or sulfidic) deep ocean during the Ediacaran and early Cambrian has also been inferred (Fig. 2b) [e.g., 28,29]. In 2010, the "euxinic wedge model", in which a mid-depth euxinic watermass coexisted dynamically with an oxic surface (i.e., the atmospheric O_2-enriched layer) and deep ferruginous waters, was proposed for Ediacaran oceans based on unique patterns of Fe-S-C-trace metal chemistry of the Doushantuo Formation on the Yangtze Platform, South China [17] (Fig. 2c). In this model, the "mid-depth" euxinic wedge dynamically developed within a variable range of water depths between the oxic surface layer and the deep ferruginous watermass (i.e., from shelf to slope and basinal settings). Its size and location depended on local Fe-S-C biogeochemical balances that were influenced by tectonic, climatic, paleogeographic and other factors (see Section 3.2). One important feature of this model, i.e., strong spatial heterogeneity of redox conditions in Ediacaran shelf oceans, is significant in (1) accounting for conflicting redox records that imply co-occurrence of oxic, ferruginous, and/or euxinic conditions [e.g., 26–30], and (2) establishing a co-evolutionary link with early animal evolution, which occurred mainly on continental shelves rather than in the deep ocean [17]. Based on more detailed paleofacies analysis of the Ediacaran Doushantuo Formation on the Yangtze Platform [34,35], it was proposed that the mid-depth euxinic wedge was likely a euxinic intra-shelf basin/lagoon behind a rimmed platform margin [36,37]. However, later studies suggested that the euxinic wedge model was applicable to both Ediacaran and early Cambrian oceans [e.g., 11,14,20,22,38–45], and possibly also to other Proterozoic intervals [e.g., 46–50]. The development of the mid-depth euxinic wedge model was important in fostering an emerging concept—redox heterogeneity in our understanding of Ediacaran and early Cambrian oceans.

In 2015, an idealized chemical zonation (or "multi-layer") model, representing an update of the earlier euxinic wedge model, was proposed for >510-Ma oceans [18]. In this model, the water column below the oxic ocean-surface layer was comprised of multiple reducing zones that mirrored the redox zonation observed in modern sedimentary porewaters [51] and in some restricted basins (e.g., the Black Sea) [52]: (1) a nitrogenous zone (i.e., with nitrate reduction and NO_3^-–NO_2^- enrichment), (2) a manganous-ferruginous zone (i.e., with Mn-Fe reduction, leading to Mn^{2+}-Fe^{2+} enrichment), (3) a sulfidic (euxinic) zone (i.e., the euxinic wedge with sulfate reduction, leading to H_2S enrichment), (4) a methanic zone (i.e., with CH_4 enrichment through organic matter disproportionation), and (5) a ferruginous deep-water zone (i.e., with hydrothermal Fe^{2+} supply) (Fig. 2d). This redox zonation pattern was hypothesized to have existed not only vertically within the water column but also as a proximity gradient across continental shelves (Fig. 2d). The development of multiple redox layers in this model depended on the supply and, thus, availability of various oxidants in seawater [18].

A number of recent studies have examined the applicability of the multi-layer model to Ediacaran and early Cambrian marine systems. Hammarlund et al. [53] found that their integrated Fe speciation, N isotope and trace-metal data supported the existence of a nitrogenous zone immediately below the oxic surface layer, enhancing conditions for preservation of the early Cambrian Chengjiang Biota. Tostevin et al. [19] reported that cerium (Ce) anomaly proxy data from the Ediacaran Nama Group (~550–541 Ma) in Namibia supported the existence of manganous-ferruginous zone below the oxic surface layer of the late Ediacaran ocean. Cheng et al. [54] found that Fe-Mn-Mo-U-C data from black shales of the lower Cambrian Niutitang Formation provided evidence of Mo cycling within a manganous-ferruginous zone above the euxinic wedge on the early Cambrian Yangtze shelf margin (South China). Zhang et al. [42] reported that integrated Fe-Mo-U-S-N-C data from lower Cambrian black shales of Qingxi Formation supported the co-existence of multiple redox zones on the southeastern (Cathaysian) margin of the early Cambrian Nanhua Basin (South China). These individual cases from various geographic locations indicate that Ediacaran and early Cambrian oceans were likely highly redox-stratified below the oxic surface layer, particularly on continental shelves.

Recently, ocean redox structure models based on modern oceanic oxygen-minimum zones (OMZ) have been proposed for Ediacaran and early Cambrian oceans. These models invoke a deep ocean that was largely oxic rather than anoxic, as in the stratified redox models above (Fig. 2). For example, Guilbaud et al. [31] hypothesized OMZ-like conditions on the productive margin of an oxic deep ocean in the early Cambrian based on Fe speciation and trace element data from the Baltic Basin (Fig. 2e). However, we realize that the stratigraphic correlations in this study actually indicate that the strata of distal sections yielding oxic deep-water signals were older than those of the proximal sections exhibiting OMZ development, thus casting doubt on this model. Based on N-isotope data from the Yangtze Platform, Wang et al. [32,33] proposed a modified OMZ model for Ediacaran and early Cambrian oceans (Fig. 2f). This model is similar to the modern ocean in having an oxic deep ocean (as inferred from modern-like δ^{15}N values, implying a similarly sized seawater NO_3^- reservoir) as well as an OMZ on productive shelf margins, but it differs in having a thin anoxic bottom-water layer in distal deep waters inferred from local Fe speciation and redox-sensitive trace-element data. However, the N-isotope data demonstrate significant spatial heterogeneity in both Ediacaran [32] and lower Cambrian units [55] of the Yangtze Platform, consistent with an aerobic N cycle dominant in shallow waters and an anaerobic N cycle dominant in distal waters and, thus, with an anoxic deep ocean. Therefore, the assumption of an oxic deep ocean in these OMZ models is still unproven.

A major hurdle to analysis of redox conditions in distal deep oceans of the Ediacaran and early Cambrian is that nearly all oceanic crust and overlying marine sediments of those ages have been subducted, limiting investigations to continental shelf, cratonic, and marginal sea deposits. However, independent evidence indicates a generally anoxic deep ocean despite increasing O_2 concentrations during the Ediacaran and early Cambrian. For example, the average $Fe^{3+}/\Sigma Fe$ of oceanic basalts and $Fe^{3+}/\Sigma Fe$ plus V/Sc of island arc rocks indicate that the global deep ocean was not fully oxygenated until the Devonian [56,57], when land plants spread rapidly and vertebrates radiated [58,59]. Late deep-ocean oxygenation is consistent with the rise of atmospheric O_2 to modern levels for the first time in the Devonian [60], and it is also supported by global compilations of redox proxies such as Mo isotopes and concentrations [61], Fe speciation [15], and carbonate-associated Ce anomalies [62]. In addition, marine U isotopes provide evidence for strongly fluctuating global-ocean redox conditions, and not fully oxygenated deep ocean during the Ediacaran and early Cambrian [12,13,63,64]. In summary, existing observations suggest that global deep oceans of the Ediacaran and early Cambrian were anoxia-dominated, whereas contemporaneous continental shelf watermasses had a stratified redox structure.

3. Mechanisms for stratified ocean-redox structure in Ediacaran and early Cambrian oceans

3.1. Why anoxic and stratified?

Our review of the development of ocean-redox structure models indicates that shelf redox stratification and dominance of deep-ocean anoxia were major features of Ediacaran and early Cambrian oceans. The prevalence of anoxia in deep-ocean watermasses was probably related to low atmospheric pO_2 during the Ediacaran (<1%–40% PAL, or present atmospheric level) and early Cambrian (~10%–40% PAL), although O_2 levels were significantly higher than those during the preceding billion years [65]. Biogeochemical modeling indicates that a combination of low atmospheric O_2 levels and an active biological pump inevitably results in deep-ocean anoxia due to respiratory O_2 demand exceeding the resupply of O_2 to deep oceans through vertical mixing and diffusion [65–67]. Modeling results also show that even at higher pO_2, deep-ocean anoxia can potentially be maintained through strong respiratory O_2 consumption related to high productivity and organic matter sinking fluxes without requiring reduced vertical mixing of seawater, as in some modern OMZs [68].

The persistence of strong redox stratification in shelf oceans for an interval > 10^8 years during the Ediacaran and early Cambrian was likely due to lower vertical mixing rates than in the modern ocean. Key evidence for this inference is the long-term existence of stable vertical and/or lateral gradients in C-S-N isotopes and/or concentrations in marine shelf deposits of those ages [e.g., 17,21,22,32,69,70]. Here, we focus on gradients in seawater sulfate concentrations ($[SO_4^{2-}]_{sw}$) and isotopic compositions ($\delta^{34}S_{sulfate}$). In modern marine sediments in which fluid advection is limited, sulfate exhibits pronounced concentration and isotopic gradients with depth below the sediment–water interface [68]. Geochemical gradients of sulfate have also been reported in the water columns of hydrologically restricted modern watermasses, e.g., coastal ponds in the northeastern USA in which microbial sulfate reduction (MSR) is the dominant process of organic remineralization [71]. However, modern oceans contain high concentrations of sulfate (~29 mmol/L) [72,73], and modern open-shelf areas are subject to physical processes (e.g., baroclinic pressure gradients, eddy mixing, tidal friction mixing, and wave breaking) that promote vertical mixing within the water column [74], preventing the formation of such geochemical gradients.

In order to quantitatively evaluate the effect of vertical mixing on the distribution of sulfate in the water column of Ediacaran and early Cambrian oceans, we developed a one-dimensional, depth-dependent geochemical model. In this model, sulfate concentration (S) at depth x varies with time (t) according to the following equation (Eq. (1)), which considers the physical processes of diffusion and advection, as well as the depth-dependent rate of sulfate reduction [75]:

$$\frac{dS}{dt} = D\frac{d^2S}{dx^2} - v\frac{dS}{dx} - LkG\exp\left[-\left(\frac{k}{v}\right)x\right], \tag{1}$$

where D is the diffusion coefficient, v is the advective velocity, L is the stoichiometric coefficient equal to the number of sulfate molecules reduced for each carbon atom oxidized (i.e., 1/2), k is the carbon oxidation rate constant for sulfate-reducing microorganisms, and G is the concentration of organic carbon that can be utilized for MSR. In this approximation, we assume that v is constant with depth, and we ignore other processes (e.g., precipitation or dissolution of sulfate minerals, and bacterial oxidation of sulfide to sulfate) that were not important in Ediacaran-early Cambrian shelf oceans [71,75]. We can further calculate the $\delta^{34}S_{sulfate}$ at depth x ($\delta^{34}S_x$) through a mass balance equation (Eq. (2)) when $[SO_4^{2-}]_{sw}$ is known at 0 m ($[SO_4^{2-}]_0$) and x m ($[SO_4^{2-}]_x$).

$$\delta^{34}S_x = \left(\left[SO_4{}^{2-}\right]_0 \delta^{34}S_0 - \left[SO_4{}^{2-}\right]_{MSR}\left(\delta^{34}S_0 - \Delta^{34}S\right)\right) / \left[SO_4{}^{2-}\right]_x, \qquad (2)$$

where $[SO_4^{2-}]_{MSR} = [SO_4^{2-}]_0 - [SO_4^{2-}]_x$ and $\Delta^{34}S = 7.03\ \ln([SO_4^{2-}]_x) + 21.22$ [76]. In this model, we prescribed the initial boundary conditions for sulfate concentrations ($[SO_4^{2-}]_0$ = 2 mmol/L) [77] and isotope composition ($\delta^{34}S_0$ = ~27‰) [78] in the surface layer of Ediacaran and early Cambrian shelf oceans. Because an increase in the vertical mixing rate is equivalent to an increase in D in terms of its effect on sulfate distribution in the water column, we varied the value of D in this model to simulate scenarios ranging from a restricted-basin setting (initialized to bottom waters of the modern Black Sea, i.e., D_{BS}) to an open-shelf setting (expressed as multiples of D_{BS}). The parameters used in our model are listed in Table 1, and more details of the model can be found in the Supplementary materials (online).

Our model results confirm that lower vertical mixing rates result in gradients of sulfate concentrations and isotopic compositions in shelf oceans [17,21,22,83], whereas higher vertical mixing rates eliminate such gradients (Fig. 3). A remarkable observation in our modeling is that vertical mixing rates theoretically lower than a certain threshold cause the complete depletion of deep-water sulfate. In the current parameter framework, $D < 2.06 \times D_{BS}$ results in a zero sulfate concentration (Fig. 3a) and an infinitely positive sulfate isotopic composition (Fig. 3b; but note that $\delta^{34}S$ is meaningless in the context of $[SO_4^{2-}]_{SW}$ = 0 mmol/L) at depths ≥ ~200 m below the chemocline. An absence of deep-water sulfate is consistent with the inferred existence of a large dissolved organic carbon (DOC) reservoir in the Ediacaran deep ocean [84–86]. A large deep-ocean DOC reservoir, which does not exist in the modern, could not have been maintained theoretically for millions of years during the Ediacaran if dissolved sulfate had been available for MSR.

The hypothesis that strong redox stratification of Ediacaran and early Cambrian shelf oceans was likely due to low vertical mixing rates is thus supported by current geochemical and modeling evidence. Low mixing rates may have been related to hydrological restriction of contemporaneous marginal seas [e.g., 34,87] and/or to equator-to-pole temperature gradients that were flatter than in the modern or inverted (e.g., linked to high (>54°) axial obliquity; [88]). However, these hypotheses are speculative at present, and the underlying mechanisms for low mixing rates remain uncertain, with further research from a physical oceanography perspective needed. We note that most existing evidence for spatial gradients in C-S-N isotopes and/or concentrations is from South China, where sedimentary paleogeography and correlations of Ediacaran and lower Cambrian strata are complex and sometimes controversial [e.g., 17,20,34–37,89,90]. Thus, more data, especially from regions outside of South China, are also needed to test the existence of such gradients.

Table 1
Model input parameters.

Parameter	Symbol	Value	Source
Carbon oxidation rate constant for sulfate reducing bacteria (Black Sea)	k	1.4×10^{-10} s^{-1}	[79,80]
Advective velocity (Limfjorden)	v	0.6×10^{-8} cm s^{-1}	[81]
Diffusion coefficient (4 °C bottom waters of Black Sea)	D	~0.8×10^{-5} cm^2 s^{-1}	[82]
Utilizable organic carbon concentration (Santa Barbara Basin)	G	2.6×10^{-4} mol cm^{-3}	[80]

3.2. Why mid-depth euxinia?

3.2.1. Theoretical controls on euxinia in Ediacaran and early Cambrian oceans

Although some of the redox zones predicted by Li et al. [18] to have been present in Ediacaran and early Cambrian shelf oceans remain unproven, the existence of a mid-depth euxinic zone in Precambrian oceans has been widely recognized [e.g., 46–49,91–95]. One unresolved issue is why this euxinic wedge disappeared in the distal (oceanward) direction. In oceanic systems, sinking organic carbon (OC) generated by photoautotrophs in the ocean-surface layer tends to be oxidized sequentially by O_2, NO_3^-, Mn^{4+}, Fe^{3+}, and SO_4^{2-} due to the progressively lower energy yields of these reactions [68]. However, the theoretically low levels of most of these oxidants (e.g., O_2, NO_3^-, Mn^{4+} and Fe^{3+}) in the Ediacaran and early Cambrian anoxic deep ocean allowed sulfate to play a dominant role in OC degradation [18]. In anoxic waters in which sulfate serves as the main electron acceptor, the two main reactions influencing the development of euxinia are: (1) MSR, which consumes SO_4^{2-} and generates HS^- (or H_2S; note: $H_2S = HS^- + H^+$) via the reaction of OC with SO_4^{2-} (Eq. (3)), and (2) pyrite formation, which generates FeS_2 via reaction of HS^- (or H_2S) with Fe^{2+} (Eq. (4)), although other reactions (e.g., H_2S reoxidation) play a minor role [71]. In such systems, the watermass becomes euxinic when the HS^- or H_2S flux exceeds two times of the Fe^{2+} flux (i.e., the ratio of S to Fe in stoichiometric pyrite), but otherwise ferruginous conditions develop. At a given concentration of aqueous Fe^{2+}, the relative availability of OC versus SO_4^{2-} determines the magnitude of the HS^- or H_2S flux and, thus, whether euxinic or ferruginous conditions develop. At higher Fe^{2+} concentrations, larger fluxes of sulfate and organic matter are required for euxinia to develop. The quantitative relationships of Fe:S:C in Eqs. (3) and (4) suggest that, for euxinia to develop in a watermass in which MSR is the dominant process of OC remineralization, two quantitative conditions must be met: (1) $\left[SO_4{}^{2-}\right]_{local} > 2\left[Fe^{2+}\right]_{local}$, and (2) $[OC]_{local} > 4\left[Fe^{2+}\right]_{local}$; all fluxes are in units of moles.

$$2CH_2O + SO_4^{2-} \rightarrow HS^- + H_2O + CO_2 + HCO_3^-, \qquad (3)$$

$$2HS^- + Fe^{2+} \rightarrow FeS_2 + H_2, \qquad (4)$$

$$CH_2O + 4Fe(OH)_3 \rightarrow 4Fe^{2+} + 3H_2O + 7OH^- + HCO_3^-. \qquad (5)$$

In modern oxic oceans, iron concentrations are extremely low (< ~4 nmol/L) [96]. However, thermodynamic modelling indicates that Fe^{2+} concentrations must have been > 50 μmol/L in the anoxic Precambrian oceans in which banded iron formations precipitated [97]. Fe^{2+} in Ediacaran and early Cambrian oceans may have been sourced from subaerial reduction of Fe^{3+} (Eq. (5)) or hydrothermal emissions of Fe^{2+} (Fig. 4). Although Fe^{3+} availability (and thus the Fe^{2+} flux from its reduction) would have been limited in a generally reducing Earth-surface environment, Fe^{2+} fluxes from hydrothermal venting are thought to have been high during the Ediacaran and early Cambrian [98], and generally ferruginous deep-ocean conditions have been inferred for this interval [17,22,30,39,99]. Thus, in theory, both sulfate and OC availability were important factors controlling the development of euxinia in Ediacaran and early Cambrian shelf oceans.

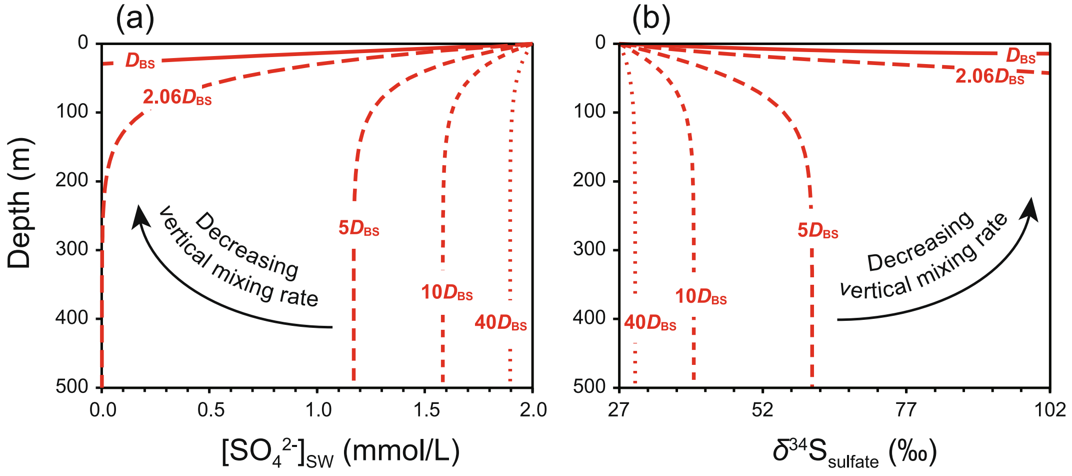

Fig. 3. (Color online) Quantitative modeling of the effect of variable vertical mixing rates on the distribution of sulfate (a: concentration, b: isotopic composition) in the water column of Ediacaran and early Cambrian shelf oceans. Note: the 0 m level represents the oxic/anoxic chemocline of the water column. See text, Table 1 and Supplementary materials (online) for modeling details. D_{BS}: diffusion coefficient of Black Sea bottom waters (4 °C) = ~0.8 × 10^{-5} cm^2 s^{-1} [82].

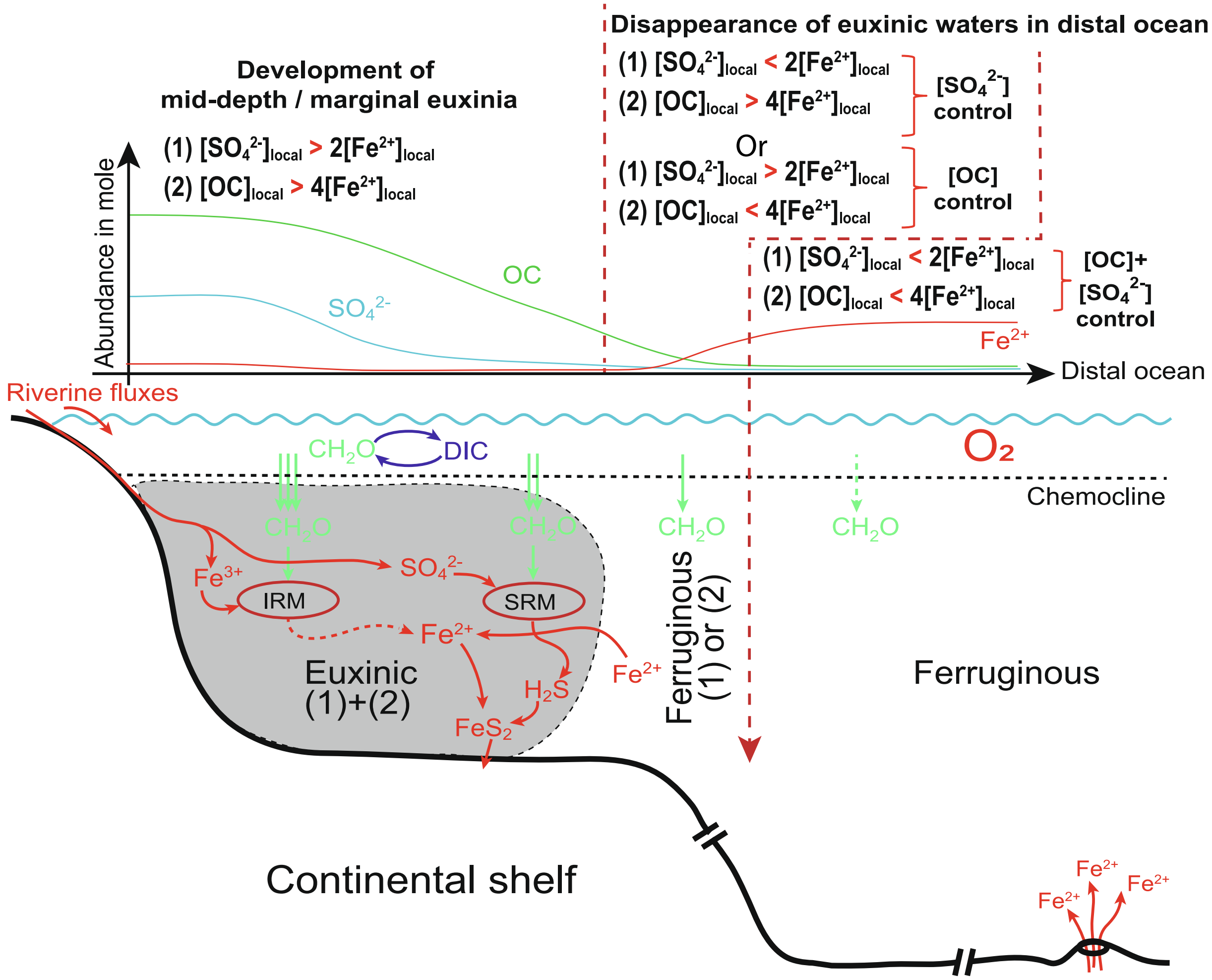

Fig. 4. (Color online) Theoretical controls on the disappearance of the mid-depth euxinic wedge distally in Ediacaran and early Cambrian oceans. The availabilities of both sulfate and organic carbon (OC) were probably key factors controlling development of euxinia in Ediacaran and early Cambrian shelf oceans. DIC: dissolved inorganic carbon; IRM: iron-reducing microbes, SRM: sulfate-reducing microbes.

3.2.2. Sulfate availability as a primary control on development of mid-depth euxinia

The standard paradigm for development of euxinia in Precambrian oceans is that OC sinking fluxes consumed water-column O_2, allowing deep-water H_2S buildup [e.g., 65,67]. In this scenario, the attenuation of euxinia in the distal deep ocean was linked to decreasing OC sinking fluxes offshore. This model is applicable to modern oceans, in which continental margins are highly productive (>40% of global net production despite being only ~6% of total ocean area; [100]) due to nutrient inputs from continents and/or upwelled deep waters, and in which dissolved sulfate is present in high concentrations (~29 mmol/L) throughout the ocean. For example, the formation of OMZs on modern ocean margins is widely associated with high OC sinking fluxes. The proposals for OC-driven marine euxinia in Precambrian oceans have been based mainly on observations linking euxinic conditions with elevated sediment total OC (TOC) content [e.g., 46,92,93]. However, euxinic conditions alone would have strongly enhanced organic preservation in Precambrian sediments [e.g., 101], and, thus, high TOC content is not necessarily an indication of elevated primary productivity or OC sinking fluxes. Thus, the mechanism of OC-driven marine euxinia that is characteristic of modern oceans cannot be assumed to have applied to Precambrian oceans because of their much lower dissolved sulfate concentrations [77,78].

Given a generally anoxic stratified ocean as outlined in Section 2, seawater sulfate concentrations are theoretically expected to have been low in Ediacaran and early Cambrian oceans (i.e., a small sulfate reservoir), particularly in the distal anoxic deep ocean where dissolved sulfate would have been consumed rapidly whenever OC was available. Accordingly, continental weathering fluxes are likely to have been the major source of sulfate to Ediacaran and early Cambrian oceans. Furthermore, given low vertical mixing rates (Section 3.1) and deep-water MSR consumption (Section 3.2.1), the flux of riverine sulfate would have theoretically led to maximum sulfate concentrations in proximal areas of continental shelves and generated a gradient toward lower concentrations offshore (Fig. 4). These inferences are supported by published estimates of < 2 mmol/L for seawater sulfate concentrations in shallow carbonate platforms and even lower values for distal shelves of Ediacaran and early Cambrian oceans, based on the S-isotopic compositions of coexisting sedimentary carbonate-associated sulfate ($\delta^{34}S_{CAS}$) and pyrite ($\delta^{34}S_{py}$) from South China, Oman, Mexico, and the United States [17,73,77,102]. In this context, the availability of both OC and sulfate must have sufficient to generate a H_2S flux that exceeded the 2 times of Fe^{2+} flux in the mid-depth euxinic watermass (Section 3.2.1), but both OC and sulfate availability probably declined further oceanward, and, at some point, an increasing Fe^{2+} supply from deep-water hydrothermal sources would have resulted in a transition to a ferruginous deep ocean due to an insufficiency of OC and/or sulfate (Fig. 4).

Low sulfate concentrations distally in Ediacaran and early Cambrian oceans do not mean that sulfate was available only in shallow shelf areas, as sulfate availability can be influenced by local factors such as riverine inputs, marine productivity, and estuary changes etc. [e.g., 39]. There is increasing evidence to support a large-scale sulfate gradient in the Ediacaran and early Cambrian oceans of South China. Li et al. [17] reported large differences in $\delta^{34}S_{py}$, ε_{MSR} (=$\delta^{34}S_{CAS}$–$\delta^{34}S_{py}$; i.e., the S-isotopic fractionation of MSR), and C/S ratios of Ediacaran Doushantuo Formation between the intra-shelf Jiulongwan and shelf-margin Zhongling sections on the Upper Yangtze Block that are consistent with lower sulfate concentrations offshore. As supported by recent advances in dating of the Doushantuo Formation [e.g, 103,104], this sulfate gradient was confirmed by quantitative estimates of seawater sulfate based on paired $\delta^{34}S_{CAS}$ and $\delta^{34}S_{py}$ data from the mid-Ediacaran strata of this formation, which yielded higher concentrations for the intra-shelf Jiulongwan section than for the upper-slope Siduping section [21]. Significantly, this study also demonstrated pulsed inputs of sulfate at both sites that were likely linked to increased continental weathering fluxes, which is consistent with control of sulfate availability in Ediacaran shelf oceans by weathering intensity [21]. Declining sulfate concentrations offshore were also suggested by generally heavier $\delta^{34}S_{py}$ values in deep-water (slope to basinal) Ediacaran sections of the Lower Yangtze Block [105] and lower Cambrian sections of the Upper Yangtze Block [22,39,83]. These observations support limited sulfate availability as a possible primary cause for the distal disappearance of mid-depth euxinia in Ediacaran and early Cambrian oceans.

Sulfate availability as a primary control on development of the mid-depth euxinic wedge in Ediacaran-Cambrian oceans was formally proposed by Feng et al. [39]. In that study, sulfate limitation of MSR in distal deep-water sections of the early Cambrian Yangtze Platform was supported by weak correlations ($R^2 \leq 0.22$) between euxinic extent (given as the ratio of pyrite Fe versus highly reactive Fe) and TOC contents for anoxic deep-water sections as well as high TOC contents (averaging 6%) in the deepest ferruginous sections. This inference was reinforced by the more comprehensive study of Jin et al. [22], who studied redox conditions of eight early-Cambrian sections along two shelf-to-basin transects of the Yangtze Platform. Recently, Li et al. [83] undertook a comparative analysis of redox conditions on the northwestern (Yangtze Block) and southeastern (Cathaysia Block) margins of the early Cambrian Nanhua Basin, documenting more extensive development of mid-depth euxinia on the Cathaysian margin. They also found evidence of higher continental weathering intensity on the same margin, and, because riverine sulfate fluxes are enhanced through oxidation of sulfide minerals which are increasingly exposed by enhanced subaerial weathering of their host silicates in continents, their findings are consistent with the hypothesis that weathering-derived sulfate fluxes likely were the primary control on the spatial development of marine euxinia in the early Cambrian Nanhua Basin. Because most evidence to date for sulfate gradients and the sulfate control on the development of mid-depth euxinic wedge during the Ediacaran to early Cambrian is from the Nanhua Basin, additional data are needed from regions outside of South China in order to test if the model of sulfate-driven marine euxinia is generally applicable to Ediacaran and early Cambrian oceans.

4. Implications for early animal evolution

Our review demonstrates that a highly redox-stratified shelf ocean and an anoxia-dominated deep ocean were major features of the Ediacaran and early Cambrian, and that the spatial distribution of euxinia was probably controlled by sulfate availability. These features are consistent with oxidant control of marine redox stratification as proposed in the multi-layer model for >510-Ma-old oceans [18]. These inferences have important implications for competing hypotheses regarding the relationship between oceanic oxygenation and early animal radiation (Fig. 1).

First, given the anoxia-dominated nature of contemporaneous deep oceans, the early radiation of animals during the Ediacaran and the subsequent “Cambrian Explosion” were most likely not related to significant oxygenation or ventilation of the global deep ocean, as suggested in conventional co-evolution hypotheses (Fig. 1a) [9–11,13,33]. Such hypotheses seem inherently unreasonable given that early animals mainly or exclusively occupied shallow continental shelves [106,107], meaning that oxygenation of the global deep ocean was not a necessary precondition for metazoan diversification.

Second, if oceanic oxygenation indeed triggered the rise of early animals, it must have done so through shelf oxygenation, which was probably driven by increased oxidant availability (Fig. 1c), as inferred from the existence of oxidant-driven ocean-redox stratification in shelf settings (see Section 3) and concurrent dominance of anoxia in the deep ocean (see Section 2). Many lines of elemental and isotopic evidence support significant oceanic oxygenation during the Ediacaran and early Cambrian [9–11,13,23,33,108–114]. However, other studies have inferred limited oceanic oxygenation at that time [14,15]. If the oxygenation process was limited primarily to shelf oceans, these conflicting inferences can be reasonably reconciled. Recent work has documented strong spatiotemporal heterogeneity of redox conditions in Ediacaran-early Cambrian shelf oceans, which may have profoundly shaped the local ecosystems of early animals [24]. Furthermore, a recently published co-evolution hypothesis: the "dynamic shelf oxygenation hypothesis" [24,25], argues that pulsed or stepwise shelf oxygenation driven by increases either in local primary productivity (thus photosynthetic O_2 production) and weathering oxidant fluxes (mainly sulfate) or in atmospheric pO_2 and ocean-surface O_2 concentrations may have stimulated early animal radiations during the Ediacaran and early Cambrian (Fig. 1c). This hypothesis is consistent with the major features of Ediacaran-early Cambrian ocean-redox structure and its controls, as outlined in this review, providing a framework for understanding the relationship between the process of oceanic oxygenation and the evolutionary development of early animals that can be qualitatively and quantitatively investigated further in future studies.

5. Summary and perspective

Our review of the development of marine redox structure models for the Ediacaran and early Cambrian highlights the existence of highly redox-stratified shelf oceans and anoxia-dominated deep oceans. Dominance of anoxia in the deep ocean was the product of generally low atmospheric O_2 levels in combination with strong shelf redox stratification that was likely linked to low vertical mixing rates. Theoretical analysis and geochemical evidence, particularly from South China, show that the distal disappearance of the mid-depth euxinic watermass was probably controlled to a greater degree by oceanward decreases in sulfate availability rather than in organic carbon sinking fluxes, as previously hypothesized. Continental weathering intensity and riverine sulfate fluxes were likely key controls on seawater sulfate availability and in turn, the spatial distribution of mid-depth euxinic watermass in Ediacaran and early Cambrian oceans. Our review supports the hypothesis that dynamic shelf oxygenations, likely driven by elevated but dynamically variable local oxidant availability, must have been responsible for the radiations of early animals. Our findings highlight the need for continued studies on marine redox structure and its controlling mechanisms—particularly in terms of quantification and global scope, and with a focus on regions outside of South China—in order to better understand the coevolutionary history of ocean-redox conditions and early animals.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

This work was supported by the National Natural Science Foundation of China-Research Councils United Kingdom_Natural Environment Research Council Program (41661134048), the National Natural Science Foundation of China (41825019, 41821001), the National Key Research & Development Program of China (2016YFA0601100), and 111 Project of China (BP0820004) to Chao Li. Meng Cheng and Chengsheng Jin acknowledge support from the National Natural Science Foundation of China (41703008, 41902027), respectively. We thank Maoyan Zhu (Nanjing Institute of Geology and Palaeontology, Chinese Academy of Sciences (CAS)), Xuelei Chu (Institute of Geology and Geophysics, CAS), Xingliang Zhang (Northwest University, China), Ping'an Peng (Guangzhou Institute of Geochemistry, CAS), Timothy Lyons (University of California-Riverside, USA), Graham Shields (University College London, UK) and Simon Poulton (University of Leeds, UK) for helpful discussion, which refined the ideas presented in the manuscript. We are also grateful to Dr. Huan Cui (Free University of Brussels, Belgium) and other two anonymous reviewers for their comments, which greatly improved this manuscript.

Author contributions

Chao Li designed research and wrote the paper with inputs from all coauthors. All authors collected and analyzed data.

Appendix A. Supplementary materials

Supplementary materials to this article can be found online at https://doi.org/10.1016/j.scib.2020.09.023.

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Chao Li is a professor of Biogeochemistry, group leader of Precambrian Geobiology at State Key Laboratory of Biogeology and Environmental Geology (BGEG), and the deputy director of BGEG, China University of Geosciences (Wuhan). His research focuses on the biogeochemical processes and mechanisms in early oceans, particularly on Cambrian and Proterozoic ocean redox chemistry evolution and its coevolution with life.