

A theoretical prediction of chemical zonation in early oceans (>520 Ma)

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Early oceans (>520 Ma) were characterized by widespread water-column anoxia, stratification, and limited oxidant availability, which are comparable to the chemical characteristics of modern marine sedimentary pore-waters in productive continental margins. Based on this similarity and our current understanding of the formation mechanism of early Earth ocean chemistry, we propose an idealized chemical zonation model for early oceans that includes the following redox zones (from shallow nearshore to deep offshore regions): oxic, nitrogenous (NO_3^- - NO_2^- -enriched), manganous-ferruginous (Mn^{2+} or Fe^{2+} -enriched), sulfidic (H_2S -enriched), methanic (CH_4 -enriched), and ferruginous (Fe^{2+} -enriched). These zones were dynamically maintained by a combination of processes including surface-water oxygenation by atmospheric free oxygen, nitrate reduction beneath the chemocline, nearshore manganese-iron reduction, sulfate reduction, methanogenesis, and hydrothermal Fe^{2+} inputs from the deep ocean. Our modified “euxinic wedge” model expands on previous versions of this model, providing a more complete theoretical framework for the chemical zonation of early Earth oceans that helps to explain observations of unusual Mo-S-C isotope patterns. This model may provide a useful foundation for future studies of ocean chemistry evolution and elemental biogeochemical cycles in early Earth history.

Proterozoic, early Cambrian, oceanic redox chemistry, anoxia, euxinia

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Oceanic redox conditions, which substantially affect elemental biogeochemical cycles and biological evolution on Earth (e.g., Anbar and Knoll, 2002; Li et al., 2010), are controlled by relative fluxes of oxidants and reductants into the oceans (Raiswell and Canfield, 2012). Earth's oceans underwent a redox transition from an anoxic state in early eons to the modern oxic state that shows a close relationship with the history of rising atmospheric O_2 levels (Lyons et al., 2014). Broadly viewed, the oxygenation of Earth's oceans was the consequence of photosynthetic oxygen production and a resulting oxidation of reducing agents in seawater.

However, at more localized scales (in a specific region at a given time), the oceanic redox conditions were determined mainly by the mass balance between organic production and oxidant availability (Johnston et al., 2010; Li et al., 2012; Feng et al., 2014). Dissolved O_2 is the most important oxidant in the ocean. Based on dissolved O_2 levels, water redox conditions can be classified simply as oxic ($[\text{O}_2] > 2 \text{ mL/L}$), suboxic ($2 \text{ mL/L} > [\text{O}_2] > 0.2 \text{ mL/L}$), and anoxic ($[\text{O}_2] < 0.2 \text{ mL/L}$), respectively (Wright et al., 1995). However, given the numerous other oxidants (e.g., SO_4^{2-} , Fe^{3+}) consumed during organic remineralization in natural oceanic environments, seawater redox conditions are more complex than indicated by this simple tripartite scheme.

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Oxic waters account for ~90% of the modern ocean by volume due to high present-day atmospheric O₂ concentrations (21%), with anoxic or euxinic waters limited to settings in which water circulation is restricted or dissolved O₂ is rapidly consumed by high production fueled by high nutrient availability (e.g., upwelling regions) (Kendall et al., 2009; Scott et al., 2008). Sedimentary pore-waters in such productive continental shelf areas exhibit a redox transition downward from oxic to anoxic conditions due to consumption of dissolved O₂ by sedimentary organic matter and limited diffusion of O₂ from the sediment-water interface. This redox transition is usually characterized by multiple chemical zones that are driven by anaerobic remineralization of sedimentary organic matter by different oxidants (Canfield and Thamdrup, 2009). A similar pattern of redox zonation is observed within the water column of a few restricted, anoxic marine basins such as the Black Sea (Konovalov et al., 2005; Murray et al., 2005) and Cariaco Basin (Ho et al., 2004).

Available studies on ancient ocean chemistry show that Precambrian and early Cambrian oceans (>520 Ma; hereafter termed “early oceans”) were characterized by widespread water-column anoxia and stratification (Canfield et al., 2008; Li et al., 2010; Lyons et al., 2014; Poulton and Canfield, 2011). Such conditions are comparable to those in modern sedimentary pore-waters, in which limited downward penetration of dissolved O₂ leads to anaerobic remineralization of organic matter by other oxidants at depth. The differential distribution of oxidants in the early oceans is likely to have produced a similar chemical zonation. For example, euxinic zones were found to have dynamically developed on productive continental margins due to higher sulfate availability in nearshore areas by riverine input relative to distal oceans (Li et al., 2010; Feng et al., 2014) or to higher marine organic production on continental margins (Johnston et al., 2010; Poulton et al., 2010; Poulton and Canfield, 2011). Therefore, chemical zonation in the early oceans can be compared to that of sedimentary pore-waters in modern productive continental margins.

In this contribution, we explore possible chemical zonation of the early oceans based on our understanding of chemical zonation in modern sedimentary pore-waters and of early ocean chemistry. This study is intended to provide a robust framework for interpretation of geochemical data in studies of early ocean chemistry, its long-term evolution, and its relationship to elemental biogeochemical cycles.

1 Water-column anoxia and sedimentary pore-water chemical zonation in modern oceans

The remineralization of organic matter in the oceans generally involves multiple energy-yielding redox reactions using various oxidants and mediated by marine organisms in search of energy. In order of decreasing energy yield, these oxidants are oxygen, nitrate, Mn⁴⁺, Fe³⁺, sulfate, and even

organic matter itself (through disproportionation into oxidized and reduced fractions), corresponding to a series of redox reactions, i.e., aerobic respiration, denitrification, manganese reduction, iron reduction, sulfate reduction, and fermentation, respectively (Table 1). Marine organisms preferentially oxidize organic matter using the oxidant with the highest energy for as long as that oxidant is biologically available. Aerobic respiration is dominant in modern well-oxygenated oceans, restricting anaerobic respiration mostly to the sediment column, where dissolved O₂ levels fall to zero (Berner, 1982). However, increases in marine production can cause substantial decreases in water-column dissolved O₂ (e.g., within the oxygen minimum zone of modern oceans). Along the western coast of Peru, for example, strong upwelling of nutrients enhances organic production that, in turn, consumes dissolved O₂ in the water column (Scholz et al., 2011). Where dissolved O₂ concentrations are low, microbes engage in metabolic strategies that involve reduction of other oxidants, such as nitrate, Mn⁴⁺, Fe³⁺, sulfate, and even organic matter (Canfield and Thamdrup, 2009; Schunck et al., 2013). In addition, in hydrographically restricted settings such as the Black Sea, limited vertical exchange reduces the resupply of atmospheric O₂ to deep waters, contributing to lower dissolved O₂ levels in the water column (Neubert, et al., 2008).

In modern oceans, depletion of dissolved O₂ in sedimentary pore-waters is rapid, especially on productive continental shelves (Libes, 2009). The downward penetration of dissolved O₂ from the overlying water column is limited by sediment permeability and bio-irrigation intensity. As sediments are buried, microbial decay of organic matter first utilizes dissolved O₂ as an oxidant. When dissolved O₂ is depleted, other oxidants are subsequently consumed in a sequence determined by their energy yields per mole of organic carbon, resulting in successive enrichments of different

Table 1 Energy yield from various oxidation reactions^{a)}

Oxidation reaction	Energy yield (kcal/mole CH ₂ O)
Aerobic respiration	
CH ₂ O+O ₂ →CO ₂ +H ₂ O	119.6
Denitrification	
CH ₂ O+4/5NO ₃ ⁻ +4/5H ⁺ →2/5N ₂ +7/5H ₂ O+CO ₂	113.6
Manganese respiration	
CH ₂ O+2MnO ₂ +4H ⁺ →2Mn ²⁺ +CO ₂ +3H ₂ O	98.4
Iron respiration	
CH ₂ O+4Fe(OH) ₃ +8H ⁺ →4Fe ²⁺ +CO ₂ +11H ₂ O	50.4
Sulfate reduction	
CH ₂ O+1/2SO ₄ ²⁻ +1/2H ⁺ →1/2HS ⁻ +CO ₂ +H ₂ O	24.4
Methane fermentation	
CH ₂ O→1/2CO ₂ +1/2CH ₄	22.4

a) After Libes, 2009.

reduced products with increasing burial depth (Figure 1).

The chemical zones illustrated in Figure 1 are not completely discrete. More commonly, these chemical zones exhibit spatial overlap. For example, denitrification can occur in pore waters with low dissolved O_2 concentrations (Jensen et al., 2008), and iron reduction can occur concurrently with sulfate reduction (Canfield et al., 1993). The chemical zonation in sediments is always maintained dynamically because the reduced products of each chemical zone can diffuse vertically or be consumed in other redox reactions. For example, H_2S produced in the sulfate reduction zone can migrate upward and react with Fe^{2+} to form pyrite (Raiswell and Canfield, 2012), and Mn^{2+} can be reoxidized to Mn^{4+} when it diffuses back into the oxic zone (Canfield et al., 1993).

2 Early oceans versus modern sedimentary pore-waters and anoxic marine basins

Today's well-oxygenated atmosphere evolved from a reducing atmosphere in early Earth history that was followed by a long interval (~2.4–0.6 Ga) of low O_2 concentrations (Canfield, 2005; Holland, 2006). Recent studies have documented some variation in O_2 levels during this interval, with a transient peak of ~1% PAL (present atmospheric level) at ~2.1 Ga (Planavsky et al., 2012; Canfield et al., 2013), followed by a decline to ~0.1% PAL at 1.8–0.8 Ga (Planavsky, et al., 2014). At such low atmospheric O_2 levels, the sub-surface waters of early oceans would have remained anoxic even though surface waters were oxygenated. A modeling study inferred that widespread oceanic anoxia will occur when atmospheric O_2 concentrations fall to <60%–70% PAL (Ozaki and Tajika, 2013). In addition, geological S-isotope

records and modeling results indicate that oceanic sulfate concentrations were still low (<2 mmol/L compared to 28 mmol/L in modern seawater) in the early Cambrian (542–520 Ma) (Loyd et al., 2012; Feng et al., 2014), which is consistent with weak oceanic oxygenation. Geological Mo-isotope records suggest that full oceanic oxygenation might have been delayed until around the early/middle Cambrian boundary (~521 Ma; Chen et al., 2015) or even until the Devonian (Dahl et al., 2010). Thus, we infer that early oceans may have exhibited similar chemical characteristics and redox zonation to sedimentary pore-waters in the modern oceans.

Although the sequence of chemical redox zones observed in sedimentary pore-waters and anoxic marine basins is identical, these systems show considerable differences in the thicknesses of individual zones. In sediment columns, the suboxic zone (comprising the nitrogenous, manganous, and ferruginous zones) is often quite thin (i.e., a few millimeters to tens of millimeters) owing to low pore-water concentrations of the corresponding oxidants (Thamdrup, 2000). The thinness of these zones is maintained, in part, by the near-absence of fluid flow in low-permeability pore-water systems, in which solute transport may occur dominantly through diffusion (Li and Gregory, 1974). In contrast, the underlying sulfidic zone can be much thicker (i.e., tens of meters or more) owing to the comparatively high pore-water concentrations of dissolved sulfate. In an open vertically stratified water column, the suboxic zone can be much thicker, e.g., ~30 m in the Black Sea (Konovalov et al., 2005; Murray et al., 2005) and ~100–150 m in the Cariaco Basin (Ho et al., 2004). In these modern marine systems, the nitrogenous, manganous, and ferruginous zones partially overlap, although the latter two tend to be thinner owing to

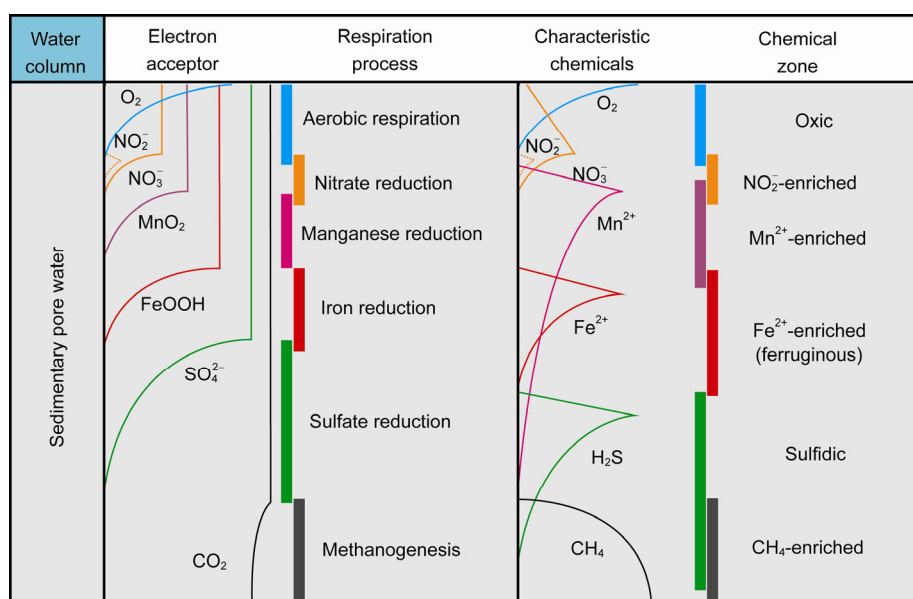


Figure 1 An idealized model of chemical zonation in modern ocean sediments (modified from Canfield and Thamdrup, 2009).

low Mn and Fe concentrations in seawater. The thickness of the suboxic zone is quite variable particularly in the Cariaco Basin, which is subject to greater vertical mixing than the Black Sea. In considering lateral (or slanted) redox zonation in early oceans with strong lateral chemical gradients (see Section 3 and 4), the equivalent zones must have been significantly wider, probably on the order of hundreds of meters to hundreds of kilometers because lateral fluid mixing is much easier than vertical mixing in a vertically stratified ocean. For example, Poulton et al (2010) found that the sulfidic zone had extended over 100km from the palaeoshoreline in the 1.88–1.83 Ga Animikie Basin (Superior region, North America). Despite differences in physical dimensions, the chemical processes associated with each redox zone were probably the same as those observed in modern sedimentary pore-waters and anoxic marine basins.

3 Mechanism for development of euxinia in early oceans and the “euxinic wedge” model

It is well known that, during organic matter decay under anoxic conditions, sulfate-reducing bacteria convert dissolved sulfate to hydrogen sulfide (H_2S), which can subsequently react with Fe^{2+} to form pyrite (Johnston et al., 2010). Euxinia develops when H_2S is able to accumulate in sediment pore-waters or the overlying water column. In general, development of euxinia is favored by the presence of ample organic matter and dissolved sulfate. In modern oceans, seawater sulfate concentrations are ~ 28 mmol/L, which is sufficiently high to make organic matter availability the limiting factor for development of euxinia. Euxinic waters can develop in upwelling regions of the modern oceans because the influx of abundant nutrients enhances productivity,

which subsequently exhausts dissolved O_2 , nitrate, and Fe-Mn oxides, leading to conditions of sulfate reduction (Canfield and Thamdrup, 2009; Schunck et al., 2013). This high-sulfate scenario reflects an organic productivity control on development of anoxia and euxinia in the modern oceans. In contrast, sulfate concentrations in pre-520-Ma oceans may have been much lower than at present (Kah et al., 2004; Li et al., 2010; Loyd et al., 2012) because of greater microbial sulfate reduction owing to widespread seawater anoxia, and high pyrite burial rates (Kah et al., 2004; Canfield and Farquhar, 2009). Thus, the development of euxinia in early oceans might have been linked to organic matter fluxes (Johnston et al., 2010; Poulton et al., 2010), sulfate supply (Feng et al., 2014; Jin et al., 2014; Li et al., 2010), or both (Li et al., 2012; Li et al., 2015).

Continental margins are the most productive areas in oceans due to relatively high nutrient inputs from continents. Today, marginal oceans, with only $\sim 6\%$ of marine surface area, contribute more than 40% of global net production (Ducklow and McCallister, 2004). Similar high productivity is likely to have existed on the continental margins of early oceans. Under conditions of low oceanic sulfate availability but ample organic carbon supply, the continental margins would have been the most likely places for euxinia to develop because of localized sulfate inputs from rivers. Given the pattern of mixing of low-salinity river waters with high-salinity seawater, delivery of riverine sulfate to the oceans would have favored development of wedge-shaped euxinic water masses in shelf areas (Li et al., 2010, 2012; Feng et al., 2014; Figure 2). Due to water-gas equilibrium, surface waters were continuously re-oxygenated by atmospheric O_2 , limiting expansion of the euxinic zone in the shoreward direction. In the oceanward direction, expansion of the euxinic zone was constrained by decreasing sulfate availability and increasing

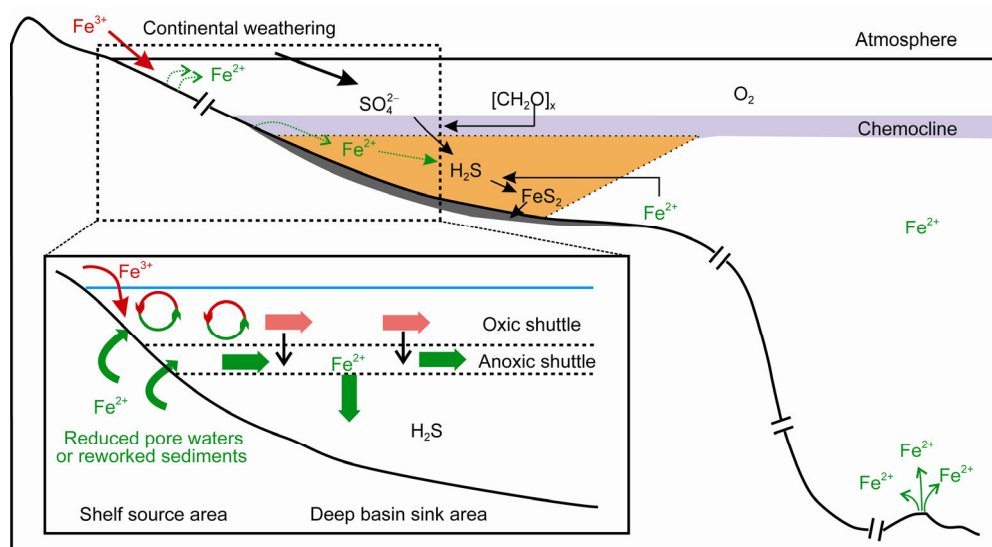


Figure 2 The “euxinic wedge” model for early oceans and modes of iron remobilization on shelves. Modified from Li et al. (2010) and Raiswell and Canfield (2012).

hydrothermal Fe^{2+} inputs from submarine hydrothermal ridges, causing the deep oceans to remain ferruginous (Poulton and Canfield, 2011). The term “euxinic wedge” has been applied to this distinctive chemical zonation pattern in the early oceans (Li et al., 2010).

Several considerations pertaining to the “euxinic wedge” model warrant mention. First, the wedge-shaped euxinic zone was not spatially equivalent to the region of microbial sulfate reduction. This is because development of euxinia is controlled by a combination of the relative fluxes of H_2S generated by microbial sulfate reduction and reactive Fe supplied from riverine and hydrothermal sources (Johnston et al., 2010). Once the dissolved O_2 , NO_3^- , MnO_2 , and Fe_2O_3 in seawater are exhausted, H_2S begins to be generated through microbial reduction of dissolved sulfate, provided that there is excessive organic matter in the system. If reactive Fe (here defined as Fe that can potentially react with H_2S to form pyrite in the water column or during early diagenesis; Raiswell and Canfield, 1998) is available, then the generated H_2S will react with it to form pyrite at a 2:1 molar ratio. Therefore, euxinia only develops when the H_2S flux is at least two times higher than that of reactive Fe. For this reason, the region of sulfate reduction is generally larger than the “euxinic wedge” itself. Second, Fe in the ferruginous deep water mass of early oceans came mainly from submarine hydrothermal inputs. Although Fe in most regions of the modern ocean is derived mainly from riverine fluxes, eolian dust, and icebergs (Raiswell and Canfield, 2012), the widespread occurrence of iron formations (Isley and Abbott, 1999) and contemporaneous hydrothermal activity (Kump and Seyfried, 2005) suggest stronger hydrothermal Fe inputs into the deep water mass of early oceans. Thus, the intensity of submarine hydrothermal activity may

have served to delimit the oceanward boundary of the “euxinic wedge” in early oceans.

4 Theoretical predictions of chemical zonation in early oceans

Based on our analysis of the formation mechanisms of euxinic waters in early oceans (Section 3) and the comparison of chemical characteristics between modern sedimentary pore-waters and the early oceans (Section 2), we propose an idealized chemical zonation model for early Earth oceans. This model includes oxic, nitrogenous (NO_3^- - NO_2^- -enriched), manganous-ferruginous (Mn^{2+} or Fe^{2+} -enriched), sulfidic (H_2S -enriched), methanic (CH_4 -enriched), and ferruginous (Fe^{2+} -enriched) zones, developed sequentially from shallow nearshore to deep distal waters (Figure 3). These zones were dynamically maintained by a combination of processes including surface-water oxygenation by atmospheric free oxygen, nitrate reduction beneath the chemocline, nearshore manganese-iron reduction, sulfate reduction, methanogenesis, and hydrothermal Fe^{2+} inputs from the deep ocean. The formation of the surface oxic zone, the mid-depth euxinic wedge, and the distal deep ferruginous waters have been elucidated in Section 3. Here, we focus on the possible formation of nitrogenous, manganous-ferruginous, and methanic zones in the early oceans, which have received no attention in earlier paleoceanic studies.

4.1 Nitrogenous zone

Nitrate in modern oceans mainly derives from riverine input, aeolian dust, and microbial decomposition of marine organic

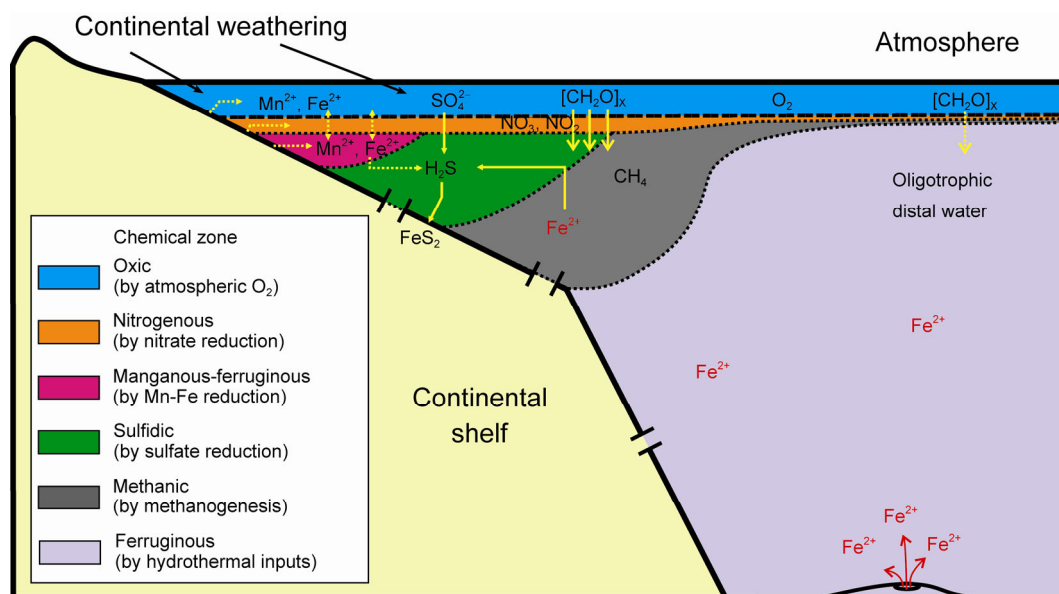


Figure 3 A conceptual model for the chemical zonation in early oceans. The sizes of chemical zones in this figure are only for conceptual presentation and may not be in actual relative scale in early oceans.

matter (Libes, 2009). Although anaerobic respiration is enhanced in stratified anoxic waters, biomass produced in the photic zone is mainly degraded through aerobic respiration in oxic surface waters, resulting in a NO_3^- -enriched zone immediately beneath the chemocline (Libes, 2009). In theory, NO_3^- was distributed across both nearshore and distal areas of early oceans but with a higher concentration on productive shelves. Because of low dissolved O_2 concentrations below the chemocline, marine biomass would be preferentially degraded by NO_3^- (i.e., through denitrification), generating N_2 as a byproduct (Table 1). However, due to the low solubility of N_2 , the intermediate product NO_2^- of the denitrification process would be relatively concentrated and, thus, a NO_3^- - NO_2^- -enriched zone would have been generated beneath the oxic surface waters of early oceans. Oxidation by NO_3^- reduction accounts for up to 69% of organic carbon degradation on productive shelves and 4.4% in oligotrophic distal waters in modern oceans (Libes, 2009). However, it should be noted that NO_3^- is significant in the distal oceans regarding to anaerobic oxidation of organic carbon although the oxidation ratio is relatively low because the limited organic production can usually only support anaerobic oxidation of organic matter by NO_3^- . Taken together, although NO_3^- concentrations may have been low in early oceans (Fennel et al., 2005), the NO_3^- - NO_2^- -enriched zone marked by strong denitrification is likely to have been important in biogeochemical nitrogen cycling.

4.2 Manganous-ferruginous zone

In modern oceans, Mn^{4+} and Fe^{3+} reduction occurs mainly in sedimentary pore-waters, where Mn- and Fe-oxides derive from the particulate sediment, rather than in seawater, in which Mn- and Fe-oxides are present in low concentrations owing to their low solubility. However, studies of Fe shuttles in anoxic basins (see review by Raiswell and Canfield, 2012) indicate two processes of Fe migration from basin margins to depocenter (see insert in Figure 2): (1) Fe^{2+} that is remobilized from reduced pore-waters or reworked sediments is re-oxidized in surface waters to nano-size Fe-oxide or Fe-hydroxide particles that are then transported into distal anoxic basins where they undergo reduction and redeposition (i.e., oxic shuttle); and (2) remobilized Fe^{2+} is transported to distal basins via anoxic subsurface waters and is redeposited without re-oxidation (i.e., anoxic shuttle). Mn behaves in a similar manner and can be transported via these two modes.

In early oceans, a Mn^{2+} - and Fe^{2+} -enriched zone is likely to have formed in anoxic nearshore waters through Mn^{4+} and Fe^{3+} reduction that may have depressed the sulfate re-

duction in early oceans. In fact, there may well have been separate zones of Mn^{2+} and Fe^{2+} enrichment owing to small differences in the redox potentials at which Mn^{4+} and Fe^{3+} are reduced. With declining redox potential Mn^{4+} reduction occurs first (Scott and Lyons, 2012), resulting in the zone of Mn^{2+} enrichment being located above that of Fe^{2+} enrichment in sediment pore-waters and shoreward of the Fe^{2+} -enriched zone in chemically zoned early oceans. However, given low atmospheric O_2 levels at >520 Ma, the fluxes of Mn- and Fe-oxides into the early oceans were low, limiting the size (width) of the Mn^{2+} - and Fe^{2+} -enriched zones. Furthermore, because these two oxidants behave similarly and it is difficult to differentiate these zones in actual work, we combine them into one zone, termed the ‘manganous-ferruginous zone’.

Although the manganous-ferruginous zone was likely of small size in early oceans, as discussed above, the development of this zone was significant for the oxidation of organic carbon because of the prevalence of Fe and Mn in the Earth-surface system. For example, organic carbon oxidation by Mn^{4+} and Fe^{3+} accounts for organic matter degradation up to 6.9% and 20% on productive shelves of the modern oceans, respectively (Libes, 2009). In addition, the global development of this zone may also have been significant for the biogeochemical cycles of redox-sensitive elements in the early oceans. For example, it is well known that isotopically light molybdenum (Mo) can be preferentially absorbed by Fe-Mn oxides and subsequently released when these oxides are reduced (i.e., Fe-Mn shuttle) (Algeo and Tribovillard, 2009; Cheng et al., 2015a). Studies of the Mo isotopic composition ($\delta^{98}\text{Mo}$) of euxinic shales deposited in early oceans suggest that late Neoproterozoic-early Cambrian oceans had similar seawater $\delta^{98}\text{Mo}$ to modern oceans ($\sim 2.3\text{‰}$) (Lehmann et al., 2007; Wen et al., 2011, 2015; Kendall et al., 2015), which is consistent with full oxygenation of the oceans at that early stage (Chen et al., 2015). However, such an inference is contradictory to other geochemical records that suggest widespread water column anoxia and/or euxinia in early oceans (Goldberg et al., 2007; Wille et al., 2008; Li et al., 2010; Och et al., 2013; Feng et al., 2014; Wen et al., 2014). Recent studies have inferred that heavy seawater $\delta^{98}\text{Mo}$ in early oceans was likely caused by global development of the manganous-ferruginous zone, in which Fe-Mn shuttles transported large quantities of isotopically light Mo toward nearby euxinic wedges for deposition, leaving seawater enriched in ^{98}Mo (Kendall et al., 2015; Wen et al., 2015)¹⁾.

4.3 Methanic zone

By analogy with modern sedimentary pore-waters, we predict

1) Cheng M, Li C, Zhou L, Algeo T J, Jin C, Lei L, Feng L, Jiang S. 2015b. The euxinic-wedge model: Linkage of Fe-Mn shuttles, Mo cycling, and seawater sulfate in the early Cambrian ocean. *Geochim Cosmochim Acta*, submitted.

that a methanic zone developed below the wedge-shaped euxinic zone in early oceans whenever other oxidants were exhausted while organic carbon was still available. This would have led to the methane fermentation of organic matter (Table 1). The methanic zone might have overlapped with distal deep ferruginous waters to some extent, and it would have gradually disappeared distally within oligotrophic oceans as organic production became extremely low. The presence of a deep-water methanic zone in early oceans is consistent with widespread preservation of organic matter characterized by extremely low C-isotopic compositions ($\delta^{13}\text{C} < -40\text{‰}$) (Eigenbrode and Freeman, 2006). Further, this hypothesis may help to explain the enigmatically low $\delta^{13}\text{C}$ of carbonates preserved in deep facies of the early oceans. For example, carbonates preserved in basal facies of the Ediacaran Doushantuo Formation (635–551 Ma) yielded $\delta^{13}\text{C}$ of $< -8\text{‰}$ (Jiang et al., 2007). This phenomenon can be readily explained as a consequence that the isotopically light methane in the methanic zone diffusing up to surface oxic waters was oxidized to dissolved inorganic carbon which may have contributed to the formation of carbonates.

4.4 Theoretical considerations

Several considerations regarding the proposed chemical zonation model for early oceans should be noted. (1) This is a theoretical model in which ideal conditions would be required for all model zones to develop. In fact, whether or not a given zone developed would depend on the specifics of geochemical fluxes and redox processes in an actual depositional system. For example, the development of a wedge-shaped euxinic zone is determined by the dynamic balance between Fe, S and C fluxes (see Section 3). (2) The ferruginous zone developing above the euxinic wedge is different in nature from the distal deep ferruginous zone. Firstly, Fe in the nearshore ferruginous zone is derived mainly from reduction of detrital Fe oxides, whereas Fe in the distal deep ferruginous zone is sourced mainly from seafloor hydrothermal inputs. Secondly, the fermentation of organic matter occurring in distal deep ferruginous waters cannot happen in the nearshore ferruginous zone due to the relatively high abundance of other oxidants such as Fe oxides and sulfate. Thirdly, the distal deep ferruginous waters in this model (not including ferruginous waters close to the oxic surface oxic watermass) may contain oxidants at very low concentrations, making this zone the most reduced in theory. (3) An ample supply of organic carbon is a prerequisite for the development of each chemical zone in this idealized model with the exception of the distal deep ferruginous waters. With an ample organic carbon supply, the development of each zone is controlled only by the availability of each type of oxidant. However, if the organic carbon supply is not adequate, the deep-water chemical zones (not including the distal ferruginous zone) may not develop.

5 Biogeochemical implications of the proposed chemical zonation for early oceans

The chemical zonation proposed for the early oceans likely reflects spatial patterns of oceanic oxygenation by rising atmospheric O_2 levels. The oxygenation of early oceans generally was a long-term consequence of direct oxygenation by atmospheric O_2 from surface waters to bottom waters and indirect oxygenation by atmospheric O_2 through input of continental weathering oxidants from nearshore shallow waters to distal deep waters. For example, although the solubility of Fe-Mn oxides is low in seawater, their repeated reduction and oxidation during oceanward transport (see Section 4 and Figure 2) effectively conveyed these oxidants from nearshore shallow waters to distal deep waters. In addition, the wedge-shape euxinic zone that separated nearshore shallow oxic waters from distal deep anoxic waters likely played a key role in preventing reducing agents (especially Fe^{2+}) from deep waters reaching nearshore waters through upwelling. Additionally, rising atmospheric O_2 levels also enhanced continental weathering, leading to higher nutrient fluxes that stimulated oceanic production, resulting in the release of yet more photosynthetic O_2 . Enhanced oceanic production may also have helped to maintain the predicted chemical zonation of the early oceans (see Section 4). For example, widespread development of euxinic waters may have greatly enhanced the burial of organic matter and pyrite, both of which contributed to buildup of O_2 in the atmosphere (Canfield, 2005). Therefore, the development of chemical zonation in the early oceans not only reflects the spatial pattern of oceanic oxygenation by atmospheric O_2 , but is also likely to have facilitated the buildup of atmospheric O_2 through a positive feedback. This mechanism linking chemical zonation of early oceans to the oxygenation history of the Earth's atmosphere may be a key for understanding the nature of long-term ocean-atmosphere coevolution.

The chemical zonation of the early oceans was also important for the biogeochemical cycles of many key elements. (1) Denitrification is an important pathway for the loss of oceanic fixed N, and denitrification associated with the nitrogenous zone may have caused a significant shortage of N in the early oceans, in turn affecting N-related biochemical reactions in marine organisms (Ader et al., 2014). (2) Oxidation and reduction of Mn and Fe in the manganous-ferruginous zone may have adsorbed and released a number of bioessential metals (e.g., Mo, V, Ni), resulting in remobilization and redistribution of these elements, contributing to their spatial heterogeneity in the early oceans (e.g., Dellwig et al., 2010; Goldberg et al., 2009; also see Section 4). (3) Fe oxides can effectively remove phosphorus, an important nutrient element for marine productivity, from seawater via absorption (Tyrrell, 1999). Fe oxides can thus significantly control the biogeochemical behavior of P via oxidation and reduction of Fe associated with the manganous-ferruginous

zone. (4) Redox-sensitive elements (e.g., Mo, U, Zn, Pb, V) can be significantly enriched in sediments under euxinic conditions, substantially reducing their inventories in early oceans in which widespread euxinia existed (Scott et al., 2008). (5) Chemical zonation of the early oceans may have contributed to the isotopic heterogeneity of many elements observed in paleomarine systems. For example, the spatial gradients of S- and C-isotopes observed in late Neoproterozoic-early Cambrian oceans in South China have been inferred to be related to spatial heterogeneity in the marine S- and C-cycles caused by chemical zonation in the early oceans (Jiang et al., 2010; Li et al., 2010; Feng et al., 2014).

In summary, the proposed chemical zonation in early oceans could potentially have had strong effects on oceanic and atmospheric oxygenation and elemental biogeochemical cycles. Thus, it will be important to consider this chemical zonation framework in future studies of ocean chemistry evolution and elemental biogeochemical cycles in early Earth history.

6 Summary

The early oceans (>520 Ma) are likely to have exhibited a chemical zonation similar to that observed in sedimentary pore-waters on productive continental shelves of modern oceans. However, the equivalent zones must have been significantly wider (up to hundreds of kilometers) given the lateral chemical zonation in early oceans. In light of our current understanding of ocean redox dynamics, we propose an idealized chemical zonation model for the early oceans, in which oxic, nitrogenous (NO_3^- - NO_2^- -enriched), manganous-ferruginous (Mn^{2+} or Fe^{2+} -enriched), sulfidic (H_2S -enriched), methanic (CH_4 -enriched), and ferruginous (Fe^{2+} -enriched) redox zones developed sequentially from shallow nearshore to deep distal waters. These zones were dynamically maintained by a combination of processes including surface-water oxygenation by atmospheric free oxygen, nitrate reduction beneath the chemocline, nearshore manganese-iron reduction, sulfate reduction, methanogenesis, and hydrothermal Fe^{2+} inputs from the deep ocean. These chemical zones may have overlapped spatially with each other, consistent with the emerging picture of early oceans that were spatially heterogeneous and temporally dynamic in water redox chemistry. This chemical zonation framework likely reflects the progressive ventilation of the early oceans by rising atmospheric O_2 , with oxygenation proceeding from shallow nearshore to deep distal waters. Our modified “euxinic wedge” model provides a robust theoretical framework for future studies of ocean chemistry evolution and elemental biogeochemical cycles in early Earth history.

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