INTRODUCTION

The reconstruction of ocean redox conditions in the past has long been a focus of paleoenvironmental research and is critical for examining links between ocean chemistry and the evolution of the biosphere and atmosphere. For example, there is widespread (but not universal) support for the suggestion that delayed oxygenation of the ocean after the first rise of atmospheric oxygen (the Great Oxidation Event, GOE; Holland 1984) ~2.4 billion years ago (Ga) restricted eukaryote evolution and limited primary productivity (potentially restricting organic carbon burial and hence oxygen production; Anbar and Knoll 2002). In this view, it was only after a second rise in oxygen about 800 million years ago that oxygenation of the deep ocean occurred, paving the way for the subsequent rapid evolution of the first large multicellular animals (Canfield et al. 2007, 2008). At the opposite end of the spectrum, periods of ocean anoxia in the Paleozoic have been implicated in several prominent episodes of mass extinction (see Meyer and Kump 2008), while Mesozoic ocean anoxic events (OAEs) have been linked to rapid radiation and turnover in marine plankton (Leckie et al. 2002).

In this regard, our understanding of the links between ocean chemistry and evolution of the biosphere relies on detailed knowledge of the precise nature of ocean oxidations–reduction (redox) conditions. In many cases, largely as a result of the available geochemical toolbox, reconstructions of ocean redox conditions have tended to focus on the extreme case of euxinia (anoxic and sulfidic). However, the redox state of the ocean can vary widely (both temporally and spatially), from various levels of oxygen depletion, through anoxic and non-sulfidic conditions, to fully euxinic. It is during anoxic, non-sulfidic conditions, which can essentially be considered an intermediate state between the oxic and euxinic end-members, that the environmental behavior of iron takes central stage. In this situation, iron may be mobilized as ferrous iron [Fe(II)] resulting in the development of ferruginous water column conditions. Here, we highlight recent research which suggests that ferruginous conditions may have been a dominant feature of anoxic oceanic intervals throughout much of Earth’s history.

Key words: iron, ferruginous, euxinic, iron speciation, paleoredox conditions, anoxic, iron-rich (ferruginous) oceanic conditions often goes unrecognized, but refined techniques are currently providing evidence to suggest that ferruginous deep-ocean conditions were likely dominant throughout much of Earth’s history. The prevalence of this redox state suggests that a detailed appraisal of the influence of ferruginous conditions on the evolution of biogeochemical cycles, climate, and the biosphere is increasingly required.

SOURCES AND SINKS OF WATER COLUMN IRON

Our understanding of the processes that may lead to ferruginous water column conditions is firmly rooted in studies of the modern global iron cycle. Over the last decade or so, considerable effort has been targeted at quantifying the operation of the global iron cycle. Major advances have resulted from studying iron minerals that are biogeochemically reactive in surface and near-surface environments (Raiswell and Canfield 1998; Poulton and Raiswell 2002; Raiswell et al. 2006). Here, we briefly discuss the pathways for the generation of water column iron that were likely significant during ancient anoxic periods. In this context, dissolved ferrous iron may enter the ocean from two main sources: from hydrothermal vents and from sediments during anoxic diagenesis (or potentially also from particulates during transport and deposition in anoxic settings) (Poulton and Raiswell 2002; Raiswell 2006).

In the modern oceanic, the vast majority of Fe(II) released from deep sea hydrothermal vents either reacts rapidly with dissolved sulfide and is deposited close to the vents as pyrite (FeS₂) or is oxidized to ferric (oxyhydr)oxide minerals. Iron(II) generated by reductive dissolution of reactive ferric (oxyhydr)oxide minerals during marine sediment diagenesis may also be released to the overlying water column. As with the hydrothermal source, a large fraction of this Fe(II) is rapidly reoxidized and deposited, but for both sources, some Fe(II) may escape precipitation and hence contribute to the oceanic dissolved-iron inventory (Raiswell 2006; Tagliabue et al. 2010).
Under anoxic oceanic conditions, however, the role of hydrothermal and diagenetic dissolved-Fe(II) sources is much more significant. Reduced iron released by these pathways is essentially stable until transported to an environment where precipitation and deposition can occur. In the case of euxinic settings, Fe(II) is rapidly titrated when it encounters water column sulfide, resulting in an additional flux (and hence enrichment) of pyrite to the deposited sediment (Raiswell and Canfield 1998). Lyons and Severmann (2006) suggested that sediment iron enrichments following water column precipitation in anoxic environments are a unique feature of euxinic depositional conditions. However, recent work on ancient sediments (Poulton et al. 2004, 2010; Canfield et al. 2007, 2008; März et al. 2008; Johnston et al. 2010; Li et al. 2010) has demonstrated that sediment iron enrichments also readily occur during anoxic ferruginous deposition; in this case, however, the additional iron flux occurs due to water column formation of unsulfidized minerals, such as ferric (oxyhydr)oxides (e.g. ferrihydrite) and/or ferrous carbonates (e.g. siderite). These minerals may readily react with dissolved sulfide and are often partially sulfidized during diagenesis. Nevertheless, the tendency for euxinic iron enrichments to be dominated by pyrite, while under ferruginous conditions, a significant proportion of the authigenic iron minerals may remain unsulfidized (e.g. Poulton et al. 2004; Canfield et al. 2008).

RECOGNIZING FERRUGINOUS CONDITIONS

In contrast to euxinic conditions, where a range of trace metal, isotope, and biomarker proxies have the potential to detect free sulfide in the water column (albeit with varying levels of success), the toolbox for identifying ferruginous conditions is much more limited. From the above discussion, it is clear that the identification and mineralogical characterization of sediment iron enrichments are the key factors for recognizing ferruginous deposition. For some periods of Earth history this is relatively straightforward. For example, at certain times during the Precambrian, extensive deposition of marine chemical sediments enriched in iron (banded iron formation, BIF; Fig. 1) points to at least episodic ferruginous oceanic conditions (see below). However, the spatially and temporally restricted nature of these deposits severely limits their use for the identification of ferruginous conditions over much of Earth’s history.

Instead, a geochemical technique for recognizing iron enrichments in normal marine shales is more appropriate. The use of Fe/Al ratios has significant potential for identifying authigenic enrichments in sediment iron and has been successfully used in a number of cases (see Lyons and Severmann 2006). However, while this technique is useful for detecting anoxic conditions, particularly when anoxic baseline Fe/Al ratio can be readily defined for a particular setting (Lyons and Severmann 2006; Poulton et al. 2010), it does not allow euxinic conditions to be distinguished from ferruginous conditions. In this regard, Poulton and Canfield (2005) developed a new sequential extraction technique for iron, based on a refinement of existing redox proxies centered on the mineralogy and biogeochemical behavior of iron (e.g. Raiswell and Canfield 1998). This technique allows full evaluation of the iron minerals that are considered to be highly reactive ($Fe_{hr}$) towards biological and abiological reduction under anoxic conditions. The iron is broadly apportioned into four different pools: (1) iron associated with carbonate minerals ($Fe_{carb}$; siderite, ankerite); (2) ferric (oxyhydr)oxide minerals ($Fe_{ox}$; ferrihydrite, lepidocrocite, goethite, hematite); (3) magnetite ($Fe_{mag}$); and (4) Fe sulfide ($Fe_{py}$; pyrite). The sum of these pools gives the total concentration of highly reactive Fe ($Fe_{hr} = Fe_{carb} + Fe_{ox} + Fe_{mag} + Fe_{py}$).

Extensive studies of modern (Raiswell and Canfield 1998) and Phanerozoic (Poulton and Raiswell 2002) marine sediments have demonstrated that $Fe_{hr}/Fe_{r}$ ratios do not exceed 0.38 during normal deposition under oxic water column conditions ($Fe_{mg}$ is normalized to total Fe, $Fe_{r}$, to allow for variable dilution of absolute $Fe_{hr}$ concentrations by organic matter, silica and/or carbonate precipitation, and to minimize variations associated with different grain-size distributions). By contrast, values above this threshold are commonly found when deposition occurs under anoxic conditions. In fact, the 0.38 ratio represents an extreme upper value for oxic deposition, and work on Phanerozoic shales (Poulton and Raiswell 2002) has shown that ancient sediments deposited from an oxic ocean have average $Fe_{hr}/Fe_{r}$ ratios of 0.14 ± 0.08. These observations allow anoxic ($Fe_{mg}/Fe_{r}$ > 0.38) and oxic ($Fe_{mg}/Fe_{r}$ < 0.22) depositional conditions to be distinguished (Fig. 2). Intermediate $Fe_{hr}/Fe_{r}$ values may still reflect anoxic depositional conditions, but in these cases, water column iron enrichments may have been masked by rapid sedimentation, as is common during turbidite deposition (Raiswell and Canfield 1998; Poulton et al. 2004), or the $Fe_{hr}$ pool may have been depleted due to conversion of a proportion of the unsulfidized minerals to less reactive sheet silicate minerals during burial diagenesis or metamorphism (Poulton and Raiswell 2002; Lyons and Severmann, 2006; Poulton et al. 2010). This latter case can, in part, be evaluated by an additional iron extraction aimed at determining sheet silicate minerals that are poorly reactive towards dissolved sulfide (see Poulton et al. 2010). It should also be noted that, unless reactive iron enrichments are solely a consequence of an enhanced hydrothermal iron flux, sediment iron enrichments cannot occur throughout an anoxic ocean (i.e. simple mass balance constraints require that some sediments have to be depleted in reactive iron to account for enrichments elsewhere). However, because marine sediments display a wide variability in $Fe_{hr}/Fe_{r}$ below 0.38 (i.e. below the lower limit for anoxia), depletions in $Fe_{hr}/Fe_{r}$ due to mobilization of $Fe_{hr}$ are difficult to recognize. This is likely further enhanced by the fact that reactive iron enrichments occur in specific environ-
ments that promote water column iron precipitation (which commonly happens during upwelling onto continental slopes and shelves). Hence, only minor mobilization (i.e. loss) of reactive iron from global oceanic sediments is required to explain significant spatially restricted enrichments elsewhere.

Ferruginous conditions can be distinguished from euxinic conditions by considering the extent of pyritization of the highly reactive iron pool \( \left( \frac{\text{Fe}_{\text{py}}}{\text{Fe}_{\text{T}}} \right) \) in sediments showing clear evidence of anoxic deposition (Fig. 2). Observations on the extent of highly reactive iron pyritization in Black Sea sediments suggest that \( \frac{\text{Fe}_{\text{py}}}{\text{Fe}_{\text{HR}}} = 0.8 \) characterizes the upper limit for ferruginous deposition (Anderson and Raiswell 2004). However, this value was defined using an extraction scheme for iron which does not fully quantify \( \text{Fe}_{\text{org}} \) or \( \text{Fe}_{\text{mag}} \) and recent work on Phanerozoic sediments suggests that an upper threshold of 0.7 may be more appropriate for distinguishing ferruginous conditions (März et al. 2008; Fig. 2).

THE PRECAMBRIAN

Early Archean to Late Paleoproterozoic (\( >3.8 \) to \( ~1.9 \) Ga)

The widespread deposition of BIF early in Earth’s history is a dominant feature of the Precambrian rock record. There is no modern equivalent for these enigmatic deposits, and considerable effort is still being made to understand the mechanisms involved in their genesis and also to extract the environmental information recorded by their geochemistry. Nevertheless, the one factor that has received near-universal accord concerns their formation following transport of dissolved Fe(II) under anoxic oceanic conditions (e.g. Holland 1984). It is commonly assumed, based on indirect evidence from rare earth element and Nd isotope data (e.g. Derry and Jacobsen 1990), that the majority of the Fe(II) required for BIF formation originated from hydrothermal sources, but a significant contribution from terrestrial runoff (Holland 1984) and diagenetic iron cycling remains a possibility (see Raiswell 2006).

The distribution of BIF deposition from the early Archean to the late Paleoproterozoic is shown in Figure 3. With the exception of a temporally restricted episode of deposition associated with extensive glaciations in the late Neoproterozoic, major BIF deposition ceased at \( ~1.8 \) Ga (Isley and Abbott 1999). It is thus tempting to suggest that anoxic ferruginous conditions reigned supreme from the early Archean to the late Paleoproterozoic, but in fact BIF deposition occurred in pulses that were associated with periods of enhanced volcanism (Isley and Abbott 1999). Iron enrichments in late Archean marine shales provide some evidence for persistent ferruginous conditions between these pulses of BIF formation (Reinhard et al. 2009; Kendall et al. 2010), but in general, little is known about the nature of ocean chemistry between many of the major episodes of BIF deposition.

Recent high-resolution reconstructions of ocean redox conditions have also documented a gradual evolution from an ocean characterized by ferruginous conditions throughout to an ocean exhibiting a more detailed redox structure (Fig. 4). Based on a number of redox proxies, it is increasingly apparent that dissolved oxygen began to accumulate in the ocean (possibly transiently) prior to the Great Oxidation Event and that oxygenated or partially oxygenated surface waters were present by \( ~2.7 \) Ga (e.g. Reinhard et al. 2009; Kendall et al. 2010). This early oxygenation also had a major impact on the sulfur cycle, increasing the oxidation of pyrite (probably during transport and deposition) and hence the supply of sulfate to the ocean. In some continental slope environments, this apparently led to the formation of transient, spatially restricted episodes of water column euxinia (Reinhard et al. 2009), a concept which we explore in more detail below. However, although the redox structure of the ocean began to evolve in the late Archean, it remains likely that this immense period of time was dominantly characterized by deep-water, ferruginous conditions (Fig. 4).

Late Paleoproterozoic to Late Neoproterozoic (\( ~1.9 \) to \( ~0.58 \) Ga)

The notion of widespread euxinic conditions in the mid-Proterozoic, as invoked by Canfield (1998), has received considerable attention, with geochemical studies providing abundant evidence for euxinia at this time (e.g. Poulton et al. 2004; Scott et al. 2008). Such conditions would have titrated dissolved Fe(II) from the ocean (as pyrite), thus spelling an end to the global deposition of BIF. Recently, however, a detailed reconstruction of ocean redox structure at a time coincident with the global termination of BIF deposition at \( ~1.8 \) Ga suggests that although euxinic conditions were prevalent in continental margin/slope settings (extending at least 100 km from the paleoshoreline), the deep ocean remained anoxic and ferruginous (Fig. 4;
Poulton et al. 2010). Such conditions would have nevertheless resulted in the termination of BIF deposition, as upwelling Fe(II) would have been precipitated (as pyrite) on the euxinic continental margins.

At present, no other studies have evaluated the redox structure of the mid-Proterozoic ocean in such detail. It thus remains possible that at certain times in the mid-Proterozoic, euxinic conditions were even more widespread (Fig. 4). However, Scott et al. (2008) suggested that euxinic conditions were increasingly difficult to maintain through this period as a result of a nutrient-limiting feedback associated with molybdenum removal under euxinic conditions, while Canfield (2004) suggested that the temporal extent of such conditions would have been limited by the subduction of sedimentary sulfides and hence a reduction in the size of the Earth-surface sulfur pool. Indeed, in a global study of late Neoproterozoic marine sediments, Canfield et al. (2008) found overwhelming evidence for widespread ferruginous deep-ocean conditions (consistent with a return to BIF deposition associated with Neoproterozoic glaciations) and only occasional evidence for euxinic conditions, prior to widespread deep-ocean oxygenation at ~0.58 Ga (Canfield et al. 2007). Building upon these observations, Johnston et al. (2010) and Li et al. (2010) suggested that deep-water ferruginous conditions were dominant at this time, with some areas experiencing either persistent or transient mid-depth euxinia. The similarity in redox structure proposed for the early and late stages of this period (Poulton et al. 2010; Johnston et al. 2010; Li et al. 2010) suggests that this may have been the dominant structure of the ocean throughout the period, although further detailed studies are required to evaluate the evolution of oceanic redox structure over this interval. Nevertheless, the available data suggest that ferruginous deep-water conditions were likely a major feature of this time period.

**THE PHANEROZOIC**

Taken as a whole, the Phanerozoic ocean has been generally well oxygenated. However, numerous examples of anoxic oceanic intervals have been documented throughout the Paleozoic and Mesozoic. Many of these intervals provide strong evidence for euxinia, although ferruginous conditions have been reported for the early Cambrian (Canfield et al. 2008). Furthermore, as reviewed by Meyer and Kump (2008), Paleozoic sections are heavily biased towards shallow, epicontinental sea environments, and thus the spatial and temporal extents of euxinia are often unclear. In addition, low-resolution studies tend to overestimate the significance of euxinic conditions. For example, rapid redox changes, from euxinic through to oxic depositional conditions, have recently been advocated for late Paleozoic (Pennsylvanian) strata from the Midcontinent US, challenging the assumption of persistent euxinia as indicated by bulk geochemical proxies (see Schultz 2004). Thus it appears likely that euxinic intervals were short-lived, and rapid redox cycling resulting in ferruginous intervals remains a distinct possibility.

This suggestion finds support in recent studies of Mesozoic oceanic anoxic events (OAES). The well-documented Toarcian (early Jurassic) and Cretaceous OAEs display abundant, but not ubiquitous, evidence for euxinic deposition (see Meyer and Kump 2008). However, a recent high-resolution study of Cretaceous OAE3 sediments from Demerara Rise found rapid and cyclic changes in deep-ocean redox conditions (März et al. 2008). In this case, euxinic conditions dominated, but after ~90–100 ky these conditions were punctuated by ferruginous bottom waters that lasted for ~15–20 ky. These observations suggest that ferruginous intervals during Phanerozoic anoxic periods may have been more prevalent than generally recognized, but the significance of these conditions is only just beginning to be appreciated.

**CONTROLS ON FERRUGINOUS VERSUS EUXINIC CONDITIONS**

The above observations highlight the hypothesis that ferruginous conditions were likely a major feature of the ocean throughout many periods of water column anoxia. But what controls the temporal and spatial extents of ferruginous and euxinic conditions? At the broadest scale, the oceanic budgets of S and Fe(III) (or Fe(II)) determine whether a specific redox condition is possible (or favorable) when the ocean is in an anoxic state, and thus quantification of these budgets provides primary insight into potential controls on redox variability through time. The global fluxes of S and Fe(III) to the modern ocean (Table 1) are dominated by continental-weathering inputs and by hydrothermal
activity (Poulton and Raiswell 2002; Raiswell et al. 2006). In terms of Fe\textsubscript{HR} sinks, a large proportion of riverine Fe\textsubscript{HR} (~85%) is trapped in flood plains and lagoons (Poulton and Raiswell 2002). The remaining riverine Fe\textsubscript{HR} is deposited in the ocean and is augmented by Fe\textsubscript{HR} from aeolian, glacial, and hydrothermal inputs (Poulton and Raiswell 2002; Raiswell et al. 2006).

In quantifying the inner-shore S sink, we assume that Fe\textsubscript{HR} in these environments reflects the global riverine particulate composition (1.9 wt%; Poulton and Raiswell 2002) and that average sulfur contents are similar to adjacent oxic shallow-shelf concentrations (0.2 wt%; Berner 1982). Combining these Fe\textsubscript{HR} and S contents yields a molar S:Fe\textsubscript{HR} ratio of 0.18:1, and combining this with the depositional flux of Fe\textsubscript{HR} in inner-shore environments yields a S flux of \(-1.0 \times 10^{12}\) mol y\(^{-1}\) (Table 1). The remaining sulfur flux (\(2.3 \times 10^{12}\) mol y\(^{-1}\)) deposits on the continental margins and in the deeper ocean.

The resulting molar S:Fe\textsubscript{HR} ratios (Table 1) show whether euxinic or ferruginous conditions are favorable. Therefore, with S:Fe\textsubscript{HR} > 1.8 (the typical molar S:Fe\textsubscript{HR} ratio observed during euxinic deposition; Poulton et al. 2004, 2010), there is sufficient S to overwhelm the Fe\textsubscript{HR} flux and potentially drive an anoxic system to euxinia. By contrast, sulfur is limiting with S:Fe\textsubscript{HR} < 1.8, favoring the development of ferruginous conditions. Our budget calculations yield a S:Fe\textsubscript{HR} ratio of 1.8, suggesting that when the ocean is anoxic, the global ocean system is precariously balanced between ferruginous and euxinic conditions.

Although internal dynamics exert a major influence on the precise redox structure of the ocean, this simple oceanic budget suggests that minor variations in the relative fluxes of sulfur and Fe\textsubscript{HR} through time would favor either euxinic or ferruginous conditions. Prior to the onset of oxidative weathering early in Earth’s history, sulfur was primarily locked in sulfide minerals, and thus oceanic sulfate fluxes and concentrations were very low (Canfield 1998). Coupled with enhanced hydrothermal iron inputs to the deep ocean, low seawater sulfate would promote widespread ferruginous conditions, as evident from the rock record. With the onset of oxidative weathering, increased oceanic sulfate fluxes would allow the potential development of euxinic conditions in continental margin settings, but removal of sulfate in these environments would also restrict the spatial extent of euxinia (Poulton et al. 2010). Transient increases in the flux of sulfate to the ocean have also been implicated in the potential for development of euxinic conditions during Cretaceous OAEs (Adams et al. 2010), and the fine balance between the oceanic Fe\textsubscript{HR} and sulfur budgets would readily drive cycling between euxinic and ferruginous conditions (e.g. März et al. 2008) as oceanic sulfate concentrations were progressively depleted under euxinic conditions.

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**CONCLUDING REMARKS AND FUTURE DIRECTIONS**

There is a growing body of evidence to suggest that ferruginous conditions were a major feature of anoxic oceanic intervals throughout Earth’s history. However, the temporal and spatial records are currently sparse and despite decades of research, detailed (preferably high-resolution) reconstructions of paleoceanic redox conditions are still needed. In many regards, the consequences of ferruginous conditions are poorly understood. Implications for the evolution of the biosphere are profound and require careful consideration, as do feedback mechanisms associated with the potential for enhanced macro- and micronutrient drawdown under ferruginous conditions (e.g. März et al. 2008).

In this context, a focus on biogeochemical cycling in modern ferruginous environments is required in order to evaluate process controls in ancient settings. Researchers often bemoan the rarity of modern-day euxinic environments for evaluating ancient euxinic intervals—the Black Sea and the Cariaco Basin are the most significant examples of modern euxinic environments. The situation is even more severe with regard to modern ferruginous environments. Nevertheless, ferruginous settings do exist, and ongoing research is providing valuable new insights into the nature of biogeochemical cycling under such conditions (e.g. Crowe et al. 2008).

**TABLE 1**

Global Highly Reactive Iron (Fe\textsubscript{HR}) and Sulfur (S) Budgets for the Modern Ocean

<table>
<thead>
<tr>
<th>Fluxes (× 10^{12} mol y(^{-1}))</th>
<th>Fe\textsubscript{HR}</th>
<th>S</th>
<th>S:Fe\textsubscript{HR}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Continental sources(^{*})</td>
<td>6.5 ± 1.7</td>
<td>2.6 ± 0.6</td>
<td>1.8</td>
</tr>
<tr>
<td>Hydrothermal(^{*})</td>
<td>0.3 ± 0.1</td>
<td>0.5 ± 0.4</td>
<td>1.5</td>
</tr>
<tr>
<td>Volcanic(^{#})</td>
<td>-</td>
<td>0.2 ± 0.1</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>6.8 ± 1.7</td>
<td>3.3 ± 0.7</td>
<td>1.5</td>
</tr>
</tbody>
</table>

| Sinks (× 10^{12} mol y\(^{-1}\)) | Inner-shore areas\(^{†}\) | 5.5 ± 0.6 | 1.0 | 0.2 |
| Global ocean\(^{†}\) | 1.3 ± 0.3 | 2.3 | 1.8 |

\(^{*}\) Fe\textsubscript{HR} budgets from Poulton and Raiswell (2002) and Raiswell et al. (2006)

\(^{#}\) For sulfur fluxes see Canfield and Farquhar (2009).

\(^{†}\) Uncertainties on S sinks are not reasonably definable.


