



## Joining forces: Combined biological and geochemical proxies reveal a complex but refined high-resolution palaeo-oxygen history in Devonian epeiric seas

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### ABSTRACT

Two Devonian black shale intervals were analysed using a carefully integrated palaeontological–geochemical approach to interpret relative bottom water oxygen levels at a resolution and sensitivity possible only through the combined approach. Biological data presented as both trace and body fossil abundance and size suggest generally low bottom water oxygen conditions. The frequently laminated sediments would be viewed traditionally as recording appreciable intervals of anoxic and/or euxinic (anoxic and H<sub>2</sub>S-containing) bottom waters. The inclusion of parallel geochemical results, however, refines this perspective.

Well-established iron proxies for depositional redox tell us that anoxic and euxinic conditions were intermittent and short-lived, if present at all. Manganese and molybdenum data point to conditions with a likelihood of very low oxygen in bottom waters during intervals with high pore-water concentrations of hydrogen sulphide near the sediment–water interface. These elevated sulphide concentrations under iron limited diagenetic conditions varied with organic content and may have further inhibited benthic colonization, and an active infaunal community more specifically. The combined palaeontological and geochemical data sets point to depleted bottom water oxygen contents with evidence for hydrogen sulphide limited dominantly or exclusively to the pore waters. Anoxia and euxinia, if present, occurred only intermittently and lasted only briefly, perhaps on seasonal time scales tied to primary productivity cycles or climatically induced variation in water column stratification. The time scales and mechanisms of rapid redox variation remain to be studied. The details of such transitional and dynamic settings are best viewed from a multi-proxy, biogeochemical and palaeoecological perspective. As an important byproduct, geochemical methods refined in multi-proxy studies of Phanerozoic shales can then be extended with greater utility to Precambrian strata without trace and body fossils.

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### 1. Introduction

Geochemical proxies are important in the reconstruction of ancient depositional settings and are particularly valuable when applied to fine-grained siliciclastic sediments. In the past few decades increased study of black shales, due in part to their economic potential and their value as archives of early biospheric evolution, has led to developments in geochemical techniques with an emphasis on palaeo-oxygenation histories (e.g., Calvert and Pedersen, 1993; Arthur and Sageman, 1994; Jones and Manning, 1994; Wignall, 1994; Schieber, 1998; Raiswell et al., 2001; Algeo and Maynard, 2004; Sageman and Lyons, 2004; reviewed in Lyons et al., 2009). The behaviours of many tracers of depositional redox conditions, iron and molybdenum in particular, have been well calibrated in modern environments, including the Black Sea, Cariaco Basin, Orca Basin,

California borderlands, and anoxic fjords, representing a wide range of oxygen-deficient bottom water conditions (e.g., Calvert and Pedersen, 1993; Calvert et al., 1996; Lyons, 1997; Raiswell and Canfield, 1998; Lyons et al., 2003; Algeo and Lyons, 2006; Lyons and Severmann, 2006; Lyons et al., 2009). These studies have yielded refined calibrations between measurable geochemical conditions in modern depositional settings (e.g., the presence of H<sub>2</sub>S) and proxy records with strong preservation potential in the ancient record. However, the interpretation of geochemical signals preserved in ancient strata can be complicated by transitional states and short-term variations (e.g., intermittent anoxia) that are best viewed through the lens of an integrated geochemical–palaeoecological multi-proxy approach.

Certain geochemical proxies can provide a clear record of specific redox conditions. For example, signals of euxinia (anoxic and sulphidic bottom waters) captured in modern settings are effectively extrapolated to analogous conditions in the geologic record because of the unique geochemical signatures generated and preserved under a sulphidic water column. These signatures include diagnostic C–S–Fe properties as well as molybdenum and other trace metal concentrations, among

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other organic and inorganic proxies (e.g., Raiswell and Canfield, 1998; Lyons and Severmann, 2006; Meyer and Kump, 2008; Lyons et al., 2009). Anoxic but non-sulphidic bottom waters (e.g., Fe-rich) can also be identified in the stratigraphic record through distinctive Fe enrichment patterns in combination with integrated trace metal records (also Gobeil et al., 1997; Morford and Emerson, 1999; Turgeon, and Brumsack, 2006) (Fig. 1). Dysoxic bottom waters, as used in this paper, are characterized by low to trace levels of oxygen and the redox boundary (first appearance of  $H_2S$ ) below the sediment–water interface (consistent with Tyson and Pearson, 1991). Such settings, also referred to as suboxic, have diagnostic biological signals that are preserved in ancient sediments (e.g., Rhoads and Morse, 1971; Savrda, 1992; Wignall, 1994). Although dysoxic and/or fluctuating relative bottom water oxygen conditions are expected in the rock record, our calibration of the geochemical signatures of reduced but non-zero bottom water oxygen levels remains comparatively incomplete and tied most successfully to trends for rhenium, manganese, molybdenum, and uranium. The geochemical signals of persistent euxinia and anoxia are well known and generally unambiguous relative to each other and the oxygen-containing end members, but straightforward geochemical indications of specifically low (but non-zero) and variable oxygen conditions independent of body or trace fossil data can be elusive (Fig. 1).

Biological components of marine systems are highly sensitive in predictable ways to environmental fluctuations, particularly to variations in bottom water oxygen levels, as studied extensively in modern settings (Parker, 1964; Thompson et al., 1985; Wu, 2002; Levin, 2003). In part due to the responsiveness of marine ecosystems to small-scale variability in depositional conditions (Cannariato et al., 1999; Kitamura, 2004), as well as the excellent preservation of fossils under reduced oxygen conditions (Canfield and Raiswell, 1991), trace and body fossil models are used widely to distinguish anoxic, dysoxic, and oxic settings preserved in Phanerozoic strata (e.g., Rhoads and Morse, 1971; Savrda and Bottjer, 1986; Sageman et al., 1991; Wignall, 1994; Allison et al., 1995; Hoffman et al., 1998; Martin, 2004). More specifically, as relative bottom water oxygen levels decrease, there is a correlative decrease in diversity, abundance, and size of individual organisms (e.g., Rhoads and Morse, 1971; Thompson et al., 1985; Wu, 2002). This trend is recognized in the rock record as a decrease in macrofaunal species richness and within the infaunal community as a decrease in relative amount of bioturbation and relative size of burrows—culminating with preserved, nonfossiliferous strata under the extreme of anoxia. A combined high resolution trace and body fossil approach allows variations in relative oxygen to be recognized on a microstratigraphic scale (Savrda, 1992; Boyer and Droser, 2009); however, magnitudes and durations of anoxia can be difficult to constrain and potentially overestimated in the absence of complementary geochemical data.

Previous studies emphasizing the geochemistry of analogous Devonian black shales from the same region, including samples from the same formations, have identified euxinia persistent over a range of estimated time scales and attributed variations in redox

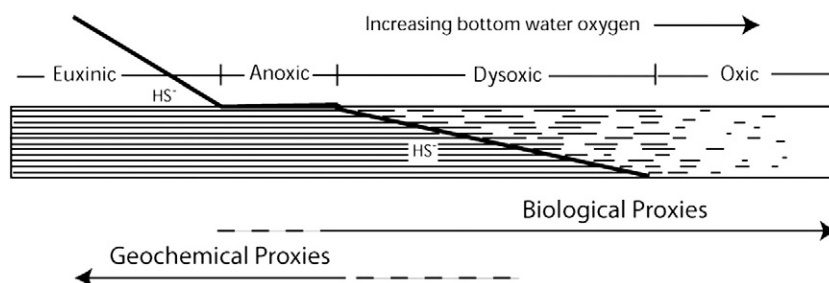
conditions to sea-level change, variation in carbonate/siliciclastic input, and seasonal stratification and mixing (Murphy et al., 2000a; Werne et al., 2002; Sageman et al., 2003). These studies, however, were investigating patterns on broad stratigraphic scale and without the same attention to faunal relationships present in this study. In modern low oxygen settings, such as oxygen minimum zones (OMZ), conditions fluctuate through a broad range of relative bottom water oxygen levels, from euxinic to anoxic to dysoxic, over short time scales, and the sedimentary response to these fluctuations has been studied in detail (e.g., Thamdrup and Canfield, 1996; Zheng et al., 2000; Nameroff et al., 2004; Vargas et al., 2004). Included in these studies are feedbacks, such as loss of fixed nitrogen through denitrification, that allow for persistently low to zero oxygen conditions but insufficient export production to establish or sustain euxinia (Canfield, 2006).

Our study emphasizes geochemical and biological data from two continuously sampled black shale intervals collected at very high resolution to explore a range of redox conditions, including high frequency fluctuations in bottom water oxygen. Palaeontological data are sensitive to variations through a range of dysoxic conditions but cannot distinguish anoxia from euxinia nor clearly delineate the temporal stability of extreme oxygen deficiency—a strength of the geochemical proxies. Few studies have attempted to bridge palaeontological and geochemical data at a very fine scale (cm-by-cm continuous sampling), despite the potential reward of highly refined palaeoenvironmental perspectives and the certain value of intercalibration of palaeontological data with important, frequently used geochemical proxies, including degree of pyritization, total organic carbon, trace metal compositions, and sulphur isotope data. The result is a much better view of bottom water redox chemistry across gradients in time and space (Fig. 1).

## 2. Geologic setting

Devonian-aged strata of the Appalachian Basin are preserved in an eastward thickening succession of mixed carbonate and siliciclastic units that represent deposition in a broad shallow epeiric seaway (Ettensohn, 1985; Brett, 1986). This mixed lithologic succession is interpreted to represent several transgressive/regressive cycles coupled with uplift and variable siliciclastic input into the basin (Woodrow and Sevon, 1985; Kirchgasser et al., 1988). Black shales within these basins have been well studied and largely preserve original geochemical signals unaltered by metamorphism or other diagenetic processes (Woodrow and Sevon, 1985; Gutschick and Sandberg, 1991; Martini et al., 2003; Sageman et al., 2003). The shales are widely interpreted to reflect dysoxic through euxinic depositional conditions (Thayer, 1974; Thompson and Newton, 1987; Murphy et al., 2000a,b; Werne et al., 2002).

Devonian-aged black shales were explored in this study because numerous dysoxic intervals have been identified previously based on reduced fossil diversity, trace fossil abundance, and sedimentary fabrics (e.g. Brett et al., 1991; Baird et al., 1999; Sageman et al., 2003;



**Fig. 1.** Schematic representation of how the combination of biological and geochemical proxies expand the resolution of bottom water oxygen conditions for the interpretation of ancient depositional conditions.

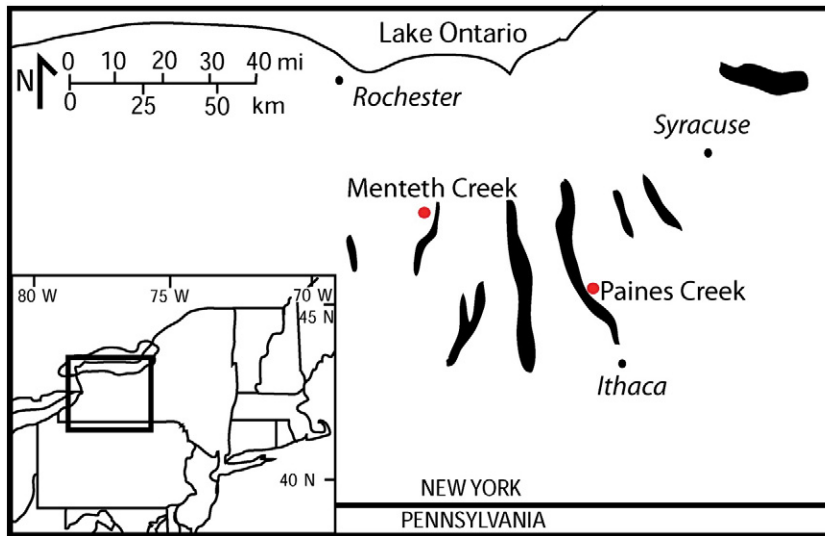


Fig. 2. Locality map showing the two field locations in western New York State.

Brett et al., 2007). The specific units we studied were selected because they preserve a robust biological signal, including a consistent trace fossil record through the dysaerobic zone as well as common and abundant dysaerobic (dysoxic) body fossils within the sampled units. Devonian black shales are well exposed in central New York and are well studied for their biostratigraphic and palaeoecologic properties (Brett, 1986; Thompson and Newton, 1987; Kirchgasser et al., 1988; Brett et al., 2007). Two localities in central New York at Paines Creek (Lat. 42°43'37"N, Long. 76°41'09"W) and Menteth Creek (Lat. 42°48'43"N, Long. 77°19'38") expose the Middle Devonian Ledyard Shale of the Ludlowville Formation and Upper Devonian Penn Yan Shale of the Genesee Formation, respectively (Figs. 2 and 3). These silty shale units are lithologically very similar—composed primarily of clay, dominantly illite, with a smaller fraction of sub-rounded to angular quartz silt grains. Sampled intervals within thick (tens of metres) successions of black shale were selected because of the range of biological data contained within them. We sampled from streambeds to procure fresh materials free of the detrimental effects of weathering.

3. Methods

Hand samples were collected continuously through vertical sections at each locality to capture the full range of geochemical and biological variability. Sampled intervals were selected from freshly exposed, unweathered surfaces in stream beds. The samples were cut perpendicular to bedding to evaluate the ichnological record. The ichnofabric index (ii) was used as a way to quantify relative amounts of bioturbation, with an ii of 1 indicating laminated sediments and ranging up to ii5 for fully bioturbated sediments (Droser and Bottjer, 1986). Ichnofabric values were averaged through each vertical cm. The size of individual burrows expressed as width and depth of penetration was also noted. Maximum burrow width is specifically meaningful in that it preserves a record of the largest infaunal organism present at a given time. Relative oxygen levels correlate with body size through physiological oxygen demands (Savrdá, 1992). However, the ii is used as the primary trace fossil metric because individual measurable burrows are not abundant and the diversity of individual trace fossils, widely used to infer relative oxygen levels, is prohibitively low throughout these intervals. In contrast, disruption of primary lamination, quantifiable by ii values, can be collected continuously through the succession, and, when present, burrow size varies in concert with the ii data. For the interpretation of relative oxygen levels from trace fossil data it is essential

to recognize that individual burrows reflect conditions at the sediment-water interface; as such, inferences from trace fossil data are correlated with the horizon of burrow origination (sediment–water

	Stage	Formation	Member
Givetian	Frasnian	Genesee	Penn Yan Shale *
			Genesee Sh.
	Hamilton Group	Moscow	Tully Ls.
			Windom Sh.
		Ludlowville	Kashong Sh.
			Jaycox Sh.
	Eifelian	Marcellus	Wanakah Shale
			Ledyard Shale *
			Centerfield Ls.
	Eifelian	Skaneateles	Levanna Shale
Butternut Pompey Delphi Station Stafford Mottville			
Eifelian	Onondaga	Oatka Creek Shale	
		Union Springs	

Fig. 3. Stratigraphy of studied intervals. Stars indicate intervals from which samples were collected. The Ledyard Shale is exposed at Paines Creek and the Penn Yan Shale at Menteth Creek.

interface). This approach was relatively straightforward in these sections because burrows typically penetrate less than 0.5 cm below the interface (Boyer and Droser, 2009).

Data for body fossil diversity were also collected along the bedding planes and analysed for trace fossil properties. The taphonomic conditions of the shells were recorded, and we used only those interpreted to represent a local signal—i.e., lacking evidence such as fragmentation, sorting, or abrasion from extensive transport.

Samples were collected for whole-rock geochemical analysis in correlation with the biological data at every cm interval and representing a total sample thickness of no more than 3 mm. Samples were completely trimmed prior to powdering to ensure the least altered materials possible. If the samples were badly altered on outcrop we would expect to see oxidized pyrite as elemental sulphur and secondary iron oxides. Total carbon (TC) and total sulphur (TS) were measured by combustion of 100 mg of dry sample on an Eltra CS-500 carbon/sulphur analyser with high-temperature furnace. Total inorganic carbon (TIC) is measured using an acidification module in combination with the Eltra and total organic carbon (TOC) is calculated by the difference.

We used a standard chromium-reducible sulphur (CRS) method to quantify pyrite concentration (Canfield et al., 1986). Specifically,  $S_{\text{pyrite}}$  was extracted in an acidic (0.5 M HCl)  $\text{CrCl}_2$  solution for 2 hours, which evolves  $\text{H}_2\text{S}$  that is reprecipitated as zinc sulphide ( $\text{ZnS}$ ) in a 1.48 M  $\text{NH}_4\text{OH}$  and 0.03 M zinc acetate solution. The precipitated  $\text{ZnS}$  was quantified by titration with a 0.1 M  $\text{KIO}_3$  solution in the presence of excess KI and starch (Canfield et al., 1986), yielding wt.%  $S_{\text{pyrite}}$  within the sample. For isotopic analysis,  $\delta^{34}\text{S}_{\text{pyrite}}$  was reprecipitated as  $\text{Ag}_2\text{S}$  using the same acidic  $\text{CrCl}_2$  method but with a 1.48 M  $\text{NH}_4\text{OH}$  and 30 mM  $\text{AgNO}_3$  trap solution. The precipitated  $\text{Ag}_2\text{S}$  was filtered, homogenized, and weighed into pressed tin capsules. The samples were combusted by EA coupled, through a continuous flow, to a Delta V Thermo IRMS (Isotope Ratio Mass Spectrometer). The isotope ratio ( $^{34}\text{S}/^{32}\text{S}$ ) was calculated as  $\delta^{34}\text{S}_{\text{‰}} = ([^{34}\text{S}/^{32}\text{S}_{\text{sample}}]/[^{34}\text{S}/^{32}\text{S}_{\text{standard}}] - 1) \times 10^3$ . The samples were corrected using a series of standards (IAEA S-1, S-2, and S-3) and Vienna Canyon Diablo Triolite (VCDT) with a long term standard error of  $\pm 0.2\text{‰}$  in the Lyons' stable isotope lab.

Degree of pyritization (DOP) determination requires two separate extractions.  $S_{\text{pyrite}}$  is determined using the aforementioned  $\text{CrCl}_2$  method. Residual reactive Fe ( $\text{Fe}_{\text{HCl}}$ ),  $(\text{Fe}_{\text{HCl}})_{\text{res}}$ —that is, Fe with the potential to form pyrite, but still unreacted with sulphide—was estimated using 100 mg of powdered sample and 5 ml of boiling, concentrated HCl. We quantified the extracted  $\text{Fe}_{\text{HCl}}$  using the ferrozine spectrophotometer method (Stookey, 1970; Viollier et al., 2000). DOP (Raiswell et al., 1988), an approximation of the extent to which reactive Fe is converted to pyrite, is defined as:  $\text{DOP} = \frac{\text{Fe}_{\text{HCl}} + \text{Fe}_{\text{pyrite}}}{\text{Fe}_{\text{pyrite}}}$ .

We also present detailed iron speciation data, which operationally define reactive iron as pyrite Fe ( $\text{Fe}_{\text{py}}$ ), Fe carbonate ( $\text{Fe}_{\text{carb}}$ ), and Fe oxides ( $\text{Fe}_{\text{ox}}$ ). To calculate highly reactive iron ( $\text{Fe}_{\text{HR}}$ ) as  $\text{Fe}_{\text{py}} + \text{Fe}_{\text{carb}} + \text{Fe}_{\text{ox}}$ , we use pyrite sulphur concentrations from the chromium reduction procedure described above and calculate  $\text{Fe}_{\text{py}}$  assuming a stoichiometry of  $\text{FeS}_2$ .  $\text{Fe}_{\text{carb}}$  and  $\text{Fe}_{\text{ox}}$  were extracted sequentially as described by Pouton and Canfield (2005). Briefly, a 100 mg sample was weighed into a 15 ml centrifuge tube and extracted sequentially as follows: Step 1, 1 M sodium acetate extraction adjusted to pH = 4.5 for 48 h with constant shaking ( $\text{Fe}_{\text{carb}}$ ), and Step 2, the sample residue was extracted for its iron oxide content ( $\text{Fe}_{\text{ox}}$ ) using 50 g/L sodium dithionite buffered to pH = 4.8 for 2 h while shaking. All extracts were diluted 100-fold in 2%  $\text{HNO}_3$  and analysed for Fe concentrations using ICP-MS (see below).

For trace element contents, powdered samples were weighed (~400 mg) into a ceramic crucible and placed in a furnace for 12 hours at ~850 °C to volatilize organic material and then cooled and weighed to determine the loss on ignition (LOI). 50–75 mg of ashed sample was then weighed into screw top Teflon vials to digest by a standard three acid sequential protocol using  $\text{HNO}_3/\text{HCl}/\text{HF}$  at ~150 °C. All acids used

in this method were Aristar/trace metal clean. Samples were initially treated with 1 ml of 8 M  $\text{HNO}_3$  for 2 h to dissolve carbonate phases to minimize the possibility of CaF precipitation during subsequent steps. The samples are then centrifuged, decanted ( $\text{HNO}_3$ -soluble fraction), and treated with 1 ml of 50%  $\text{HF}/\text{HNO}_3$  for 2 h to dissolve all silicate phases. The remaining solid phases were then dried down and treated with 2 ml of 6 M HCl for 2 h to dissolve any remaining solid phase. The decanted  $\text{HNO}_3$ -soluble fraction was then added back to the completely dissolved sample and dried down. This solution was then diluted to ~5 ml using 2%  $\text{HNO}_3$ . Concentrations of major and minor elements (Ca, Mg, Sr, P, Mn, Fe, Al, Mo, V, Ni, Cu, and U) were measured on an Agilent 7500ce ICP-MS (Inductively Coupled Plasma-Mass Spectrometer). Most samples were measured using two isotopes and in the optimal mode for that element, ranging from no gas,  $\text{H}_2$ , and He in the collision cell; typical analyses had an error of less than 5%. Standard reference materials (SDO-1 and SCO-1 shales) were digested and analysed with each set of digestion extractions and in all cases were within the accepted analytical error for all elements.

## 4. Results

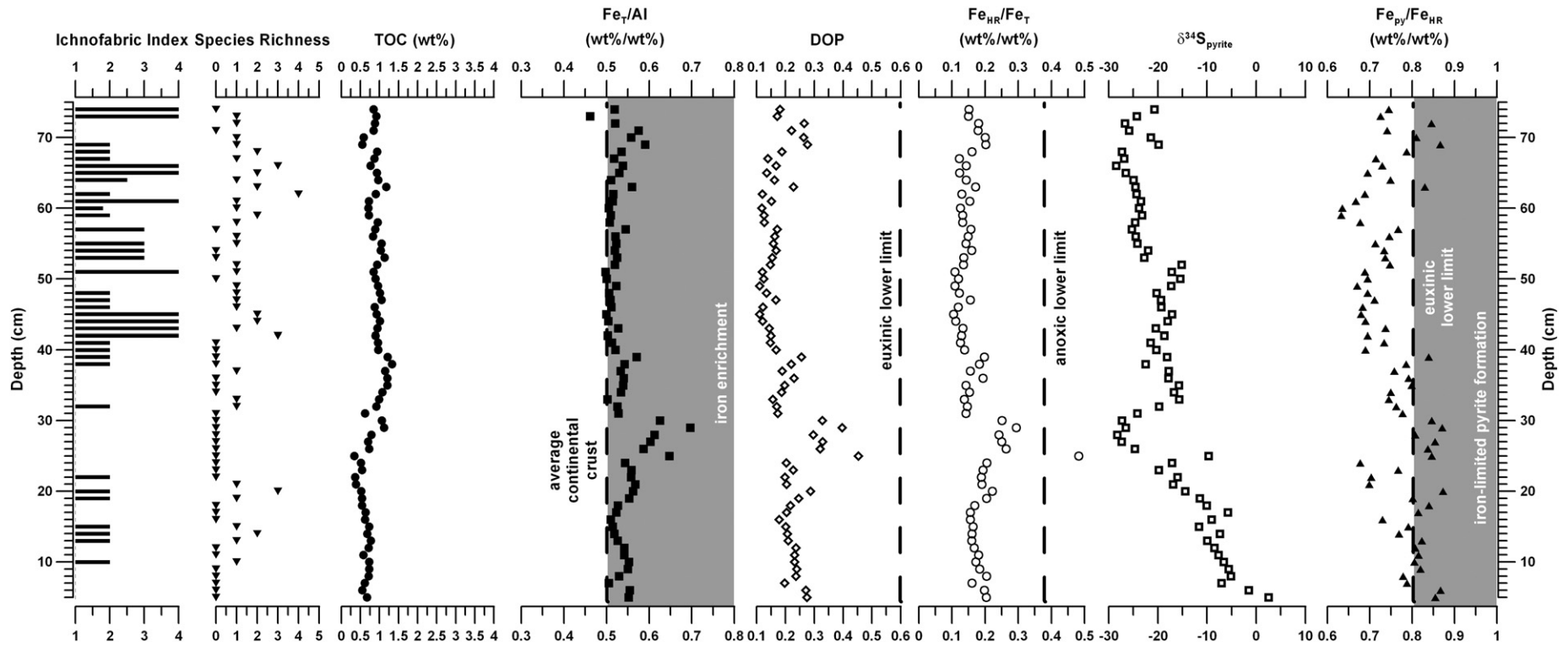
### 4.1. Biological data

The trace fossils are consistently small, and ichnofabrics range from laminated sediments (ii1) to nearly fully bioturbated (ii4). In other Devonian-aged black shales, burrows can reach 10 cm in depth (e.g. Jordan, 1985); however, within our samples, over 90% of all burrows are smaller than 0.5 cm in both depth and width. Nearly all of the trace fossils are assigned to the ichnogenus *Planolites*; however, it should be noted that many biological disruptions in the primary sedimentary structure (i.e., breaks in lamination) are not readily identifiable as a specific ichnogenus. Laminated intervals are common but not stratigraphically persistent for more than 7 cm. Benthic species richness values range from zero to a total diversity of four species along an individual bedding plane. Benthic macrofauna are uncommon and dispersed along individual bedding planes throughout these units with the exception of two bedding planes at the Menteth locality with abundant, densely packed fossils. The two sampled localities differ in their biological signals as indicated below.

The ichnofabric of the Paines Creek section ranges from laminated (ii1) through nearly fully bioturbated (ii4), although individual trace fossils are rare (Figs. 4 and 6). Eight individual burrows measured from this locality ranged in depth of penetration from 0.05 to 0.23 cm and from 0.03 to 0.34 cm in maximum burrow width. There are mottled intervals between 60 and 70 cm above the base of the section that are almost fully bioturbated with no individual recognizable burrows. Body fossils at the Paines Creek locality total 166 individuals collected through 70 cm of exposure with a total diversity through the section of nine macrofaunal benthic species. The brachiopod species *Eumtabolotoechia multicosata*, of the family Camarotoechioidea is the most common individual—making up 89% of the total fauna—with other uncommon brachiopods, trilobites, and bivalves observed. Fossils are dispersed and well preserved on individual bedding planes as molds with little fragmentation or abrasion. The lower half of this section, from 0 to 36 cm above the base, preserves several intervals with ii1 and a species richness of zero, which we interpret to be anoxic intervals based on the palaeontology. Although fluctuating, values for ii and species richness increase up section and are interpreted to represent a relative increase in bottom water oxygen levels.

Laminated intervals (ii1) and broken laminations (ii2) are common in the Menteth Creek section (Figs. 5, 7). The most intensely burrowed interval is associated with ii3, which is a lower value than the most intensely burrowed interval found at the Paines Creek section. Ichnofabric indices mostly fluctuate between ii1 and ii2 with uncommon laminated intervals. Ten individual burrows ranging from 0.02 to 0.17 cm in burrow depth and 0.02 to 0.65 cm in maximum





**Fig. 4.** Biological data as ichnofabric and species richness data along with C-Fe-S proxy data from the Paines Creek locality. Dashed line on the  $\text{Fe}_T/\text{Al}$  plo indicates a modern average. Dashed line on degree of pyritization (DOP) indicates enrichment compared to modern values. Dashed line on the DOP plot delineates the lower anoxic/euxinic threshold value of 0.6. Dashed line on the  $\text{Fe}_{\text{HR}}/\text{Fe}_T$  plot at 0.38 indicates modern upper threshold for oxic conditions, and dashed line on  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$  plot the modern average. See text for discussion and references.

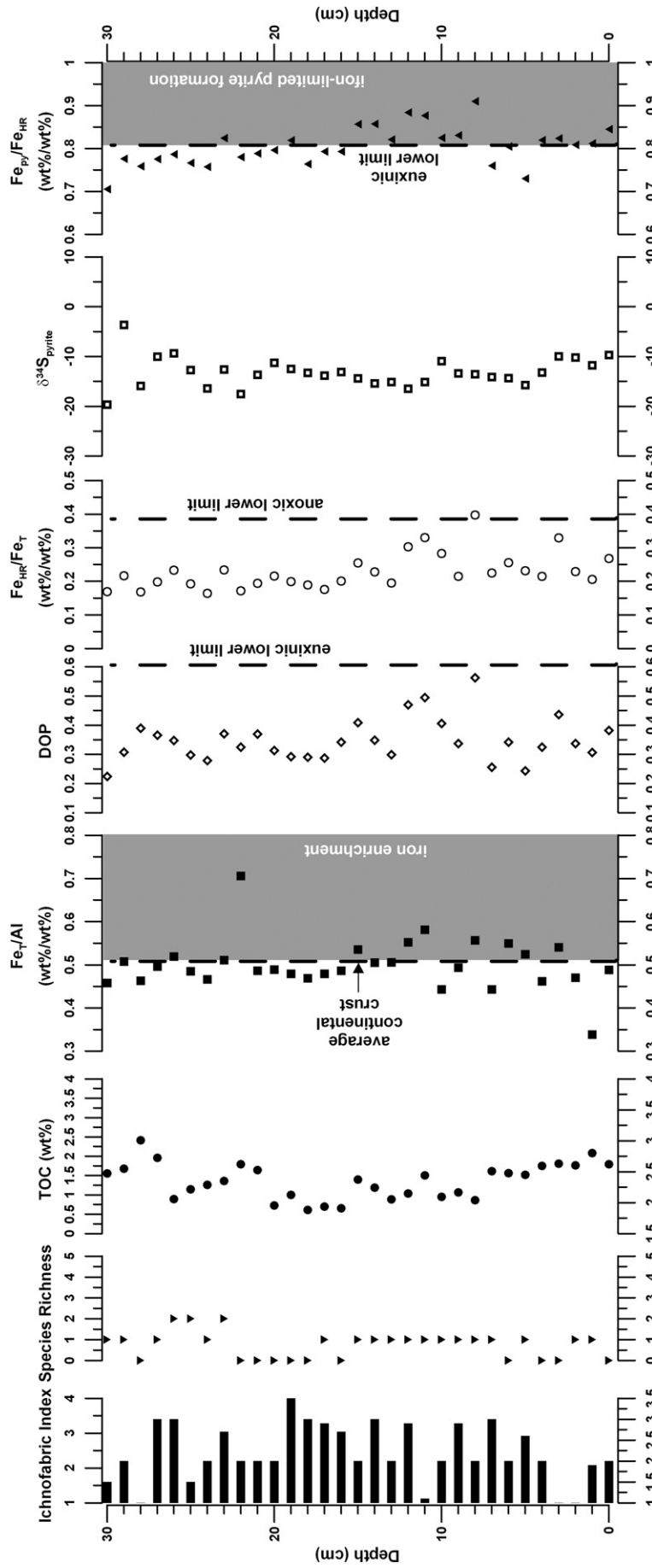


Fig. 5. Biological data as ichnofabric and species richness data along with C–Fe–S proxy data from the Menteth Creek locality. See Fig. 4 for description of plots.

burrow width occur through the measured interval. Body fossils are rare at the Menteth Creek locality, typically occurring as single individuals on a bedding plane, with the exception of several bedding planes with abundant fossils. A total of 238 individual specimens were collected at this locality with a total specific diversity of three brachiopods. One brachiopod species, *Leiorhynchus sinuata* of the family Camarotoechioidea, makes up 98% of the total macrofauna. Species richness values range from 0 to 2, but it should be noted that increases in species richness in this section are due to the presence of a single individual of a different species along a bedding plane. There are two intervals with ii1 and no body fossils preserved, which are interpreted as anoxic based on biological signals.

#### 4.2. Carbon–sulphur–iron proxy data

TOC values are consistently low, at the Paines Creek locality, ranging from 0.61 to 1.39 wt.% (mean: 0.81 wt.%), while the Menteth Creek locality has higher values from 1.90 to 2.99 wt.% (mean: 2.35 wt.%) (Table 1). These values are in agreement with data from other studies of these and similar units using both drill core and outcrop samples (Murphy et al., 2000b; Sageman et al., 2003). TIC contents range from 0.11 to 1.75 wt.% with a mean value of  $0.55 \pm 0.23$  wt.% at the Paines Creek locality (assuming all of the inorganic carbon is present as  $\text{CaCO}_3$ , this range equates to 0.96 to 14.55 wt.%  $\text{CaCO}_3$ ) with all but one sample less than 1 wt.% TIC. Total inorganic carbon values are slightly higher at the Menteth Creek locality, ranging from 1.14 to 2.23 wt.% (9.50 to 18.60 wt.%  $\text{CaCO}_3$ ) with a mean value of  $1.60 \pm 0.21$  wt.%.

DOP values at the Paines Creek locality range from 0.11 to 0.45, with an average of  $0.20 \pm 0.07$  (Fig. 4); the Menteth Creek locality ranges from 0.22 to 0.56, with an average of  $0.35 \pm 0.07$  (Fig. 5). Many values from both localities fall within a range typically ascribed to oxic bottom waters (–0.0 to 0.3; Raiswell et al., 1988; Lyons et al., 2009), but the highest values approach those typical of euxinic deposition (–0.6 to 1.0). Intermediate values are attributed to either sulphide-rich (and therefore organic-rich) pore waters below oxic bottom waters, rapid euxinic deposition, or fluctuating redox conditions (Lyons and Severmann, 2006; Lyons et al., 2009, and references therein). The DOP values are relatively invariant through the entire Paines Creek section with the exception of slightly elevated values associated with PC 25–30, an interval dominated by laminated sediments and associated with no body fossils. The DOP values are slightly higher at the Menteth Creek locality but show very little variation. The highest DOP values (0.56) within the Menteth Creek section are associated with a species richness of 1 and ii2.

In order to tease apart the details of the reactive iron pool more specifically, we use the ratio of highly reactive Fe to total iron ( $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$ ;  $\text{Fe}_{\text{HR}} = \text{Fe}_{\text{py}} + \text{Fe}_{\text{carb}} + \text{Fe}_{\text{ox}}$ ), where modern oxic sediments have an average of  $0.26 \pm 0.08$  (ranges of 0.06 to 0.38). This range defines a modern siliciclastic background flux with 0.38 as a conservative upper limit for oxic deposition (but fails to discriminate variation across a wide range of possible  $\text{O}_2$  concentrations). Specifically because DOP calculations can overestimate the highly reactive iron pool (Lyons and Severmann, 2006), we calculated  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$  through these intervals as an independent measure of depositional redox conditions. Anoxic (and euxinic) intervals commonly show enrichments in  $\text{Fe}_{\text{HR}}$  relative to oxic marine sediments (Raiswell and Canfield, 1998) and as also expressed in elevated  $\text{Fe}_{\text{T}}/\text{Al}$  ratios compared to average continental crust (Lyons and Severmann, 2006). Our  $\text{Fe}_{\text{T}}/\text{Al}$  values range from 0.46 to 0.70 through the PC section. The higher values are concentrated within the interval between 25 and 30 cm above the base, which coincides with the longest interval of persistent lamination. However, our average throughout the section is 0.54 which is only slightly higher than the mean value for Palaeozoic shales ( $0.53 \pm 0.11$ ; Raiswell et al., 2008a,b) and average continental crust more generally. Overall, there are elevated values for DOP,  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$ , and  $\text{Fe}/\text{Al}$  in the 25 to 30 cm interval above the base at the Paines Creek section. While

Menteth Creek,  $\text{Fe}_{\text{T}}/\text{Al}$  values fall between 0.4 and 0.6 (average of 0.5), with two exceptions of 0.34 and 0.71. The interval between 25 and 30 cm at Paines Creek correlates with a portion of the section interpreted to reflect anoxia based on the biological signal (ii1 and species richness of 0). One way to evaluate iron limitations is to evaluate the degree to which the highly reactive iron pool has been pyritized ( $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$ ). Values above 0.8 are convincing evidence for euxinia when coupled with high values of  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$  fingerprinting anoxia, but when observed in concert with low values of  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$  can indicate Fe limitation in  $\text{H}_2\text{S}$ -rich pore fluids beneath an oxygen-containing water column.

$\delta^{34}\text{S}$  values for pyrite ( $\delta^{34}\text{S}_{\text{py}}$ ) at both localities are all depleted compared to mean estimates for the coeval seawater sulphate composition of ~20 and ~23‰ for the Givetian (Paines Creek) and Frasnian (Menteth Creek), respectively (Claypool et al., 1980; Strauss, 1997; Kampschulte and Strauss, 2004).  $\delta^{34}\text{S}_{\text{pyrite}}$  values at Paines Creek range from –28.3 to +2.6‰, and both the highest and lowest values are associated with intervals interpreted to be anoxic or euxinic from the biological data (Fig. 4). There is a trend of increasingly depleted  $\delta^{34}\text{S}_{\text{pyrite}}$  values through the bottom half of the Paines Creek locality, which coincides with laminated intervals. The values in the top half of the section remain depleted between approximately –15.0 and –28.5‰. At the Menteth Creek locality,  $\delta^{34}\text{S}_{\text{pyrite}}$  values are less variable and range from –19.7 to –3.7‰ (Fig. 3). These high and low values are found in successive beds less than 1 cm apart.

#### 4.3. Molybdenum and manganese data

Trace metal concentrations are reported in Table 1. Molybdenum values at these two localities range from typical crustal values (1–2 ppm) to a maximum enrichment of 34.5 ppm. At the Paines Creek locality, the values are consistently close to crustal through the entire succession, with the most elevated values (2.7 to 3.3 ppm) within the interval 29–30 cm above the base of the section (Fig. 6). The Mo data from Menteth Creek are relatively enriched, with all Mo concentrations greater than 10 ppm and a maximum value of 34.5 ppm. The samples from 8 and 11 cm above the base of the section at Menteth Creek show maximum enrichments yet are associated with trace and body fossils (Fig. 7). These Mo values are most consistent with sulphide accumulation limited to the pore waters (Lyons et al., 2009). Manganese concentrations at these localities range from 448 to 893 ppm and 507 to 804 ppm at the Paines Creek and Menteth localities, respectively. Normalized Mn/Al values are depleted relative to average continental crust (Turekian and Wedepohl, 1961; Taylor and McLennan, 1985) through both of these sections, with the exception of one sample at the Paines Creek locality (Figs. 6, 7).

### 5. Discussion

The overall low macrofaunal diversity, maximum species richness of four, and lack of completely bioturbated and homogenized sediments (ii5) supports the persistent influence of oxygen stress during deposition of these strata. The details of the biological data reveal that relative bottom water oxygen levels fluctuated between what is interpreted as anoxic—preserved as laminated intervals with no body fossils—to increased oxygenation, preserved as ii4 indicative of an active infauna associated with numerous large shelly epibenthos. The distribution of macrobenthos is consistent with faunal assemblages interpreted to represent ‘episodically dysaerobic’ (Wignall and Myers, 1988), poikiloaerobic (Oschmann, 1991), or intermittently euxinic (Kenig et al., 2004) depositional conditions. Exaerobic conditions are defined by the presence of macrobenthos occurring repeatedly within laminated strata and are interpreted to represent conditions with the redox boundary fixed at the sediment–water interface (Savrdá and Bottjer, 1986). Although body fossils occur within laminated sediments in these units, the repeated occurrence of these same taxa associated





Table 1 (continued)

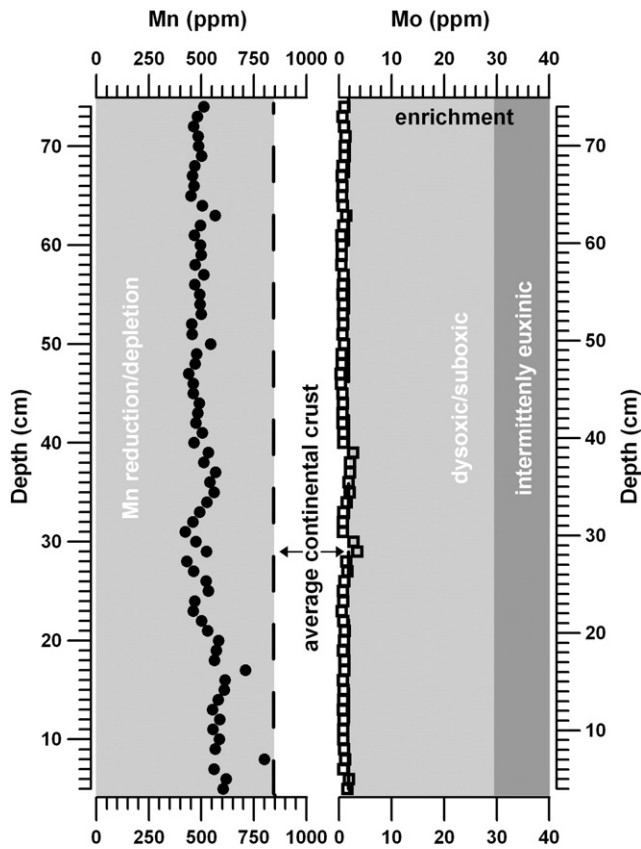
Height (cm)	Ichnofabric index	Species richness	TOC (wt.%)	TIC (wt.%)	Al (wt.%)	Mn (ppm)	Fe <sub>T</sub> (wt.%)	Mo (ppm)	Fe <sub>pyrite</sub> (wt.%)	Fe <sub>HR</sub> (wt.%)	Fe <sub>T</sub> /Al (wt.%/wt.%)	DOP	Fe <sub>HR</sub> /Fe <sub>T</sub> (wt.%/wt.%)	Fe <sub>pyrite</sub> /Fe <sub>HR</sub> (wt.%/wt.%)	d <sup>34</sup> S <sub>pyrite</sub>
<i>Manteth Creek</i>															
0	2	0	2.62	1.57	8.74	534.23	4.27	15.12	0.97	1.14	0.49	0.38	0.27	0.84	−9.74
1	1.9	1	2.80	1.59	12.52	504.74	4.24	12.53	0.71	0.87	0.34	0.31	0.21	0.81	−11.80
2	1	1	2.60	1.61	8.43	510.30	3.96	13.32	0.73	0.90	0.47	0.34	0.23	0.81	−10.23
3	1	0	2.63	1.72	8.08	542.59	4.36	17.36	1.18	1.44	0.54	0.44	0.33	0.82	−9.98
4	2	0	2.59	1.72	8.65	520.20	4.00	15.98	0.70	0.86	0.46	0.32	0.21	0.82	−13.25
5	2.6	1	2.45	1.61	5.76	128.55	3.02	29.51	0.51	0.70	0.52	0.24	0.23	0.73	−15.79
6	2	0	2.48	1.62	5.47	141.82	3.01	30.93	0.62	0.77	0.55	0.34	0.26	0.80	−14.36
7	3	1	2.51	1.81	7.67	464.85	3.40	13.05	0.58	0.76	0.44	0.26	0.22	0.76	−14.17
8	2	1	2.04	2.23	9.05	697.54	5.03	26.11	1.82	2.00	0.56	0.56	0.40	0.91	−13.60
9	2.9	1	2.16	1.88	8.86	613.28	4.37	14.61	0.78	0.94	0.49	0.34	0.21	0.83	−13.45
10	2	1	2.09	1.85	8.22	490.77	3.64	15.00	0.85	1.03	0.44	0.41	0.28	0.82	−10.97
11	1.1	1	2.44	1.24	8.38	523.10	4.87	30.15	1.41	1.60	0.58	0.49	0.33	0.88	−15.16
12	2.9	1	2.14	1.14	8.90	452.69	4.91	21.99	1.31	1.48	0.55	0.47	0.30	0.88	−16.49
13	2	1	2.05	1.26	8.47	462.56	4.28	15.91	0.68	0.83	0.51	0.30	0.19	0.82	−15.17
14	3	1	2.24	1.63	8.09	504.93	4.09	15.65	0.80	0.93	0.50	0.35	0.23	0.86	−15.44
15	2	1	2.37	1.73	8.20	530.42	4.39	16.22	0.96	1.12	0.54	0.41	0.25	0.86	−14.40
16	2.7	0	1.91	1.43	8.71	478.51	4.23	10.47	0.67	0.85	0.49	0.34	0.20	0.79	−13.15
17	2.9	1	1.94	1.49	8.90	596.19	4.26	11.67	0.59	0.75	0.48	0.29	0.18	0.79	−13.88
18	3	0	1.88	1.60	8.38	510.09	3.93	9.31	0.57	0.74	0.47	0.29	0.19	0.76	−13.31
19	3.5	0	2.12	1.72	8.05	516.82	3.86	12.77	0.63	0.77	0.48	0.29	0.20	0.82	−12.51
20	2	0	1.95	1.69	8.23	510.05	4.02	12.15	0.69	0.87	0.49	0.31	0.22	0.80	−11.31
21	2	0	2.53	1.55	8.66	533.10	4.21	18.01	0.64	0.82	0.49	0.37	0.19	0.79	−13.71
22	2	0	2.62	1.61	6.55	442.88	4.62	25.40	0.62	0.79	0.71	0.32	0.17	0.78	−17.57
23	2.7	2	2.35	1.40	8.41	471.35	4.30	19.83	0.83	1.00	0.51	0.37	0.23	0.82	−12.62
24	2	1	2.28	1.43	8.71	479.79	4.06	13.77	0.50	0.66	0.47	0.28	0.16	0.76	−16.42
25	1.5	2	2.21	1.44	8.48	509.57	4.11	14.39	0.60	0.79	0.48	0.30	0.19	0.77	−12.77
26	3	2	2.06	1.47	8.12	511.08	4.21	15.25	0.77	0.98	0.52	0.35	0.23	0.79	−9.42
27	3	1	2.72	1.67	8.27	500.47	4.10	13.29	0.63	0.81	0.50	0.37	0.20	0.78	−10.05
28	1	0	3.01	1.55	8.75	479.67	4.05	12.54	0.52	0.68	0.46	0.39	0.17	0.76	−15.95
29	2	1	2.55	1.56	8.24	499.02	4.18	13.84	0.70	0.90	0.51	0.31	0.22	0.78	−3.68
30	1.5	1	2.47	1.65	8.15	468.73	3.73	11.46	0.45	0.63	0.46	0.22	0.17	0.71	−19.68
Average	2.20	0.74	2.35	1.60	8.33	488.06	4.12	16.70	0.77	0.95	0.50	0.35	0.23	0.80	−13.23
Standard deviation	0.69	0.63	0.29	0.21	1.14	106.63	0.45	5.89	0.30	0.30	0.06	0.07	0.05	0.04	3.01

with bioturbated intervals interpreted to represent dysoxic to oxic depositional conditions, makes these groups unlikely as exaerobic specialists restricted to extremely depleted oxygen levels (Savrda and Bottjer, 1986). Inferred fluctuations in the relative concentrations of oxygen in the bottom waters are observed on a very fine stratigraphic scale. For example, the shift from ii1 to ii4 back to ii1 all within 2 cm (PC 50–52) supports the contention that bottom water oxygen levels were not stable and shifted over relatively short time scales (Figs. 4 and 6)—thus explaining the diversity of palaeontological observations, including a wide range of ii values, macrofaunal diversity, and even macrofauna associated with laminated intervals.

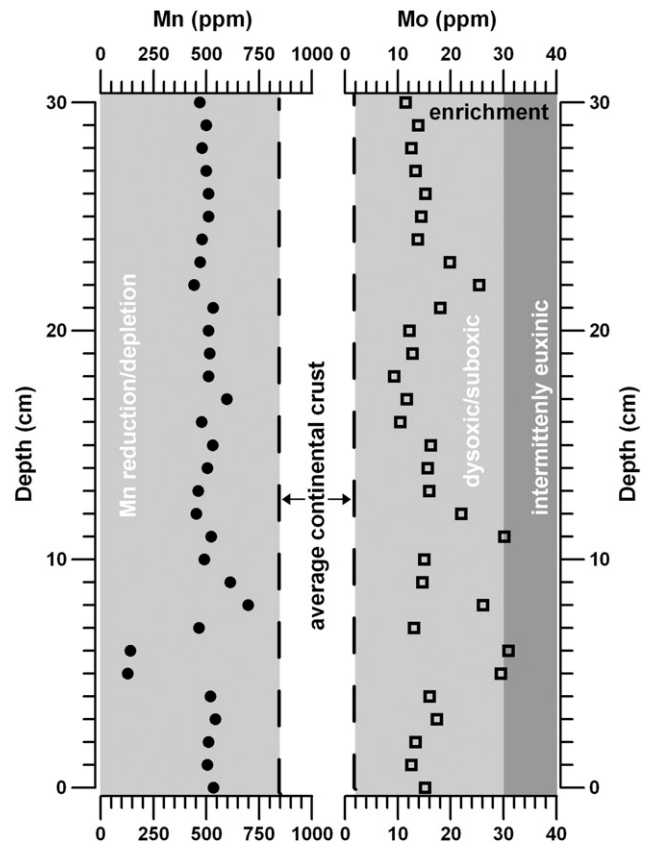
The lower ii values, overall lower diversity and low abundance of body fossils on most bedding planes at the Menteth Creek locality points to conditions that were relatively oxygen-poor. Based on the palaeontology alone, it is likely that bottom water oxygen fluctuated between anoxic and dysoxic throughout this section, as persistent dysoxia would result in total disruption of the sediment. Even extremely small infaunal organisms, under stable conditions, can completely homogenize the sedimentary fabric under extremely reduced oxygen conditions (Levin, 2003). However, in this section there are no intervals of laminated strata (ii1) greater than 2 cm thick, supporting the hypothesis that there were not extensive intervals of anoxia and, therefore, conditions were not reducing enough for euxinia. In contrast, the Paines Creek locality, although preserving a wide range of relative oxygen levels inferred from the biology, has more persistent intervals of anoxia interpreted from several intervals of laminated strata (ii1) that are continuous over >5 cm. Other intervals at Paines Creek are interpreted to preserve higher relative oxygen levels inferred from the combination of higher ii values and increased species richness. Both of these sections preserve macrofaunal signals of fluctuating relative bottom water oxygen conditions but without clear evidence for fully oxygenated or euxinic conditions.

The biological signal allows detailed analysis of relative oxygen contents from dysoxic through oxic conditions; however, the method stumbles when trying to distinguish between anoxic and/or euxinic conditions. Also a challenge is recognizing extremely low palaeo-O<sub>2</sub> and intermittent anoxia/euxinia if they were sufficient to preclude stable benthic communities. Geochemistry can help in these particular situations. As outlined above, reactive iron is typically enriched under pervasive anoxic and euxinic conditions—preserved as elevated Fe<sub>HR</sub>/Fe<sub>T</sub> and Fe<sub>T</sub>/Al (Lyons and Severmann, 2006). High DOP values and Fe<sub>pyrite</sub>/Fe<sub>T</sub> ratios then point to euxinia. The multiple iron proxy data are roughly comparable in both units and do not support persistent euxinia or anoxia, but rather indicate mostly oxic to dysoxic conditions—which is consistent, in an overarching sense, with the dominant biological signals. There are frequent suggestions of anoxia in biological data at Paines Creek, but the geochemistry tells us that conditions did not become anoxic/euxinic at either locale for any appreciable duration. In other words, the palaeontologically inferred episodes of anoxia did not result in the telltale Fe or Mo fingerprint of anoxia/euxinia, suggesting fluctuating redox conditions and/or trace oxygen levels that were sufficiently brief and/or low to preclude colonization.

One interval at the Paines Creek locality (PC 25–30) preserves slight enrichments expressed in Fe<sub>HR</sub>/Fe<sub>T</sub>, Fe<sub>T</sub>/Al, Fe<sub>py</sub>/Fe<sub>HR</sub>, and higher DOP values, consistent with at least brief anoxia or euxinia, but this geochemical pattern is not associated with other thinner laminated intervals through the succession. Also, the classic Fe proxy thresholds are not exceeded, suggesting, at the most, brief anoxia/euxinia with resulting signals diluted by return to oxic/dysoxic bottom waters. At both localities, DOP values range from 0.1 to 0.6, and associated Fe<sub>HR</sub>/Fe<sub>T</sub> values are between 0.1 and 0.4; these ranges are most parsimoniously interpreted as reflecting oxic depositional conditions in both modern and ancient settings with possible transitions into



**Fig. 6.** Mo and Mn proxy data from the Paines Creek locality. Dashed lines indicate crustal values and shaded areas indicate values associated with dysoxic and euxinic depositional conditions. See text for discussion.



**Fig. 7.** Mo and Mn proxy data from the Menteth Creek locality. Dashed lines indicate crustal values and shaded areas indicate values associated with dysoxic and euxinic depositional conditions. See text for discussion.

brief episodes of anoxia and euxinia (Raiswell et al., 1988; Lyons and Severmann, 2006). Overall, the generally low mean values for these Fe parameters with only minor exceptions are best interpreted as normally oxic to dysoxic conditions with only minor expressions of transient anoxia/euxinia, despite the abundance of lamination. The combined data, therefore, are telling us that oxygen conditions could have been low and variable enough to limit the macrofauna, without full-on establishment of stable anoxia.

Concentrations of redox-sensitive elements such as Mo are often used to infer variations in the oxygen content of bottom waters (Arthur and Sageman, 1994; Wignall, 1994; Rimmer, 2004). Under reducing conditions ( $H_2S$  present), Mo levels are enriched under persistently low oxygen settings (Morford and Emerson, 1999; Scott et al., 2008). Specifically, Mo can be enriched beneath dysoxic waters with values between ~2 and 30 ppm (McManus et al., 2006) and beneath intermittent euxinia in the same range or higher depending on water column Mo availability and the persistence of euxinia (Murphy et al., 2000a; Lyons et al., 2009). Greatly enriched Mo values (up to and even exceeding 200 ppm) have been reported from other studies of Devonian black shales from the same region and interpreted to represent euxinia (Werne et al., 2002; Sageman et al., 2003; Gordon et al., 2009).

The Menteth Creek locality shows signs of Mo enrichment relative to typical crustal shale values (1–2 ppm). Such levels of enrichment, based on modern analogs (see Lyons et al., 2009), suggest  $H_2S$  accumulation in appreciable quantities within the sediments without extending into the water column or temporally unstable establishment of euxinia on relatively short time scales. These moderate Mo enrichments are consistent with elevated  $Fe_{py}/Fe_{HR}$ , which can occur in either sulphidic pore waters beneath  $O_2$ -containing bottom waters or in the presence of euxinia. The former is favored by higher organic

contents in the sediments, as we see (subtly) at the Menteth section, although any accumulation of  $H_2S$  in the pore fluids did not preclude infaunal activity at this site. The biological data, with ii's of 3 and 4 suggesting oxygenation, are consistent with dominantly oxic deposition, perhaps with variable redox conditions. The Paines Creek section shows no Mo enrichment, with values hovering around the oxic shale baseline of 2 ppm. This relationship argues against appreciable accumulation of  $H_2S$  in the pore waters, as is also suggested by the relatively low TOC contents and  $Fe_{py}/Fe_{HR}$  ratios, and demands very little or no presence of sulphide in the water column. (Appreciable pore water dissolved sulphide is a prerequisite for diagenetic Mo enrichment.) Although not reflected in the low Mo concentrations—there is some suggestion, especially in the lower part of the Paines Creek section, for Fe-limited pore waters (higher  $Fe_{py}/Fe_T$ ) and thus free  $H_2S$ . The corresponding decrease in mean ii over the same interval could reflect this  $H_2S$  and its impact on infaunal habitability. Pore water dissolved sulphide is common but demanded beneath low oxygen bottom waters.

Manganese concentrations can be depleted in dysoxic to anoxic settings compared to the average crustal value of ~850 ppm because of reduction under dysoxic to anoxic conditions in the sediments or water column and loss to the  $O_2$ -lean water column (Calvert and Pedersen, 1993; Morford and Emerson, 1999; Turgeon and Brumsack, 2006). Mn values in our sections are moderately depleted at both sections (Figs. 6, 7), consistent with very low to zero oxygen conditions in the water column, at least intermittently. Bacterial Mn reduction occurs early in the sequence of microbial reactions in the complete or near absence of oxygen but before the onset of bacterial sulphate reduction—that is, under classically suboxic conditions (Froelich et al., 1979). Collectively, our geochemical data point to suboxic/dysoxic conditions, punctuated perhaps by episodes of anoxia

and euxinia and even times of higher O<sub>2</sub> content. Evidence for deposition at the redox extremes—i.e., persistent of either anoxia/euxinia or fully oxygenated bottom waters—is weak, particularly if pushed beyond arguments for only brief episodes of either.

Interestingly, sulphur isotope values for the entire Menteth section and the lower portion at Paines Creek cluster around -10‰, which are offset from coeval seawater sulphate by roughly 30‰ (Figs. 5, 6)—although the data at Paines Creek are more variable. Relatively small fractionations, rather than the extreme fractionations of up to and exceeding 60‰ associated with open conditions of bacterial sulphate reduction and water column pyrite formation that dominate euxinic settings (e.g., Lyons, 1997; Sageman and Lyons, 2004), are consistent with bacterial sulphate reduction and pyrite formation within sediments during diagenesis. In support of this model, these intervals show low ichnofabric indices that suggest ineffective mixing of the sediment and, therefore, dominantly diffusional transport of sulphate into the sediments. In other words, bioturbational mixing and bioirrigation played little or no role in enhancing transport of sulphate from the water column to the sediments. In contrast to what we see in our rocks, bio-enhanced sulphate delivery can lead to less sulphate-limited conditions and therefore larger net sulphur isotope fractionation during bacterial sulphate reduction—the first step in sedimentary pyrite formation. An exception to this trend is the kick to more <sup>34</sup>S-depleted values at ~30 cm at Paines Creek, which is also marked by increases in the Fe proxies, although still below the anoxic/euxinic threshold values. Collectively, an episode of euxinia is suggested, but with the muted Fe enrichment and the lack of elevated Mo reflecting the transience of the event.

<sup>34</sup>S values in the upper half of the section at Paines Creek remain comparatively <sup>34</sup>S-depleted, with fractionations relative to parent seawater sulphate of 40 to 50‰ (Fig. 5). Given that increased frequency of euxinia is not suggested by the geochemistry or the biology, we infer that sediment (diagenetic) pyrite formed under more open conditions as would be expected with greater bioturbation. Greater infaunal disturbance is suggested independently by a corresponding increase in the mean ichnofabric index over the same interval. With greater biological mixing and bioirrigation comes enhanced transport of seawater and therefore sulphate into the sediment, yielding more open diagenetic conditions and greater net fractionation during bacterial sulphate reduction.

## 6. For further consideration: the geochemical proxies

We have endeavored to be conservative in our interpretations, weighing the collective data in the most parsimonious way. Nevertheless, there are always additional factors to consider now and down the road. For example, high rates of siliciclastic sedimentation can mute enrichments of the diagnostic geochemical signatures through simple dilution by the high flux of detrital sediment. This effect has been observed for reactive iron and molybdenum, for example, even under modern euxinic conditions (Lyons and Kashgarian, 2005; Lyons and Severmann, 2006). Also, rapid sedimentation can drive the <sup>34</sup>S of diagenetic pyrite toward higher values (smaller offsets from the parent sulphate) through rapid removal from the overlying seawater reservoir. Although high and variable sedimentation rates are not suggested by our biological data, they remain an important consideration in this and other studies.

Enrichments in molybdenum under persistently euxinic conditions and comparatively slow sedimentation are diagnostically high, but they are also variable across a wide range of high concentrations. The observed variability can reflect limited availability of dissolved Mo within the local or global ocean, but there is also a strong coupling to organic content, and so Mo typically covaries with TOC in euxinic settings (Algeo and Lyons, 2006; Scott et al., 2008; Lyons et al., 2009). Given this Mo-TOC relationship, we can surmise that our low Mo

contents might also reflect the scarcity of the TOC host—particularly at Paines Creek.

We also are aware of the risk in over-interpreting geochemical data in terms of widely accepted but not foolproof thresholds or baseline values, such as the lower limits for Fe<sub>HR</sub>/Fe<sub>T</sub> and Fe<sub>py</sub>/Fe<sub>T</sub> used to delineate anoxic and euxinic conditions. The ratios we use here are based on comprehensive studies in modern analogue systems, such as the Black Sea (e.g., Raiswell and Canfield, 1998). Enrichments in Fe<sub>HR</sub> in the Black Sea and elsewhere are inferred to be tied to remobilization and transport ('shuttling') of reactive Fe from the oxic basin margin to the deep basin—providing a fingerprint of the deep anoxic conditions—and the high Fe<sub>py</sub>/Fe<sub>HR</sub> ratios reflect the high degrees of conversion that shuttled Fe<sub>HR</sub> to pyrite in the sulphidic (euxinic) water column (reviewed in Lyons and Severmann, 2006). The Fe<sub>HR</sub>/Fe<sub>T</sub> anoxic threshold can be lowered in thermally altered sedimentary rocks through mineral transformations of Fe<sub>HR</sub> to nonreactive or less reactive Fe during burial alteration, such as transformations among the Fe-bearing silicates—and including metamorphism in the extreme (e.g., Raiswell et al., 2011). The argument is that primary reactive Fe phases transform specifically to minerals no longer captured as Fe<sub>HR</sub> in our Fe extraction. Raiswell et al. (2008a,b), in a study of Ordovician and Devonian shales, argued for lowering the Fe<sub>HR</sub>/Fe<sub>T</sub> limit for anoxic deposition from the modern value of 0.38 to 0.15 because of burial effects.

Interestingly, many of our Fe<sub>HR</sub>/Fe<sub>T</sub> ratios fall near 0.15 or between 0.15 and 0.38, suggesting that we could be underestimating the frequency and persistence of the anoxic signal. We could also be overestimating the extent of euxinia if measured non-pyrite Fe<sub>HR</sub> is falsely low. However, few of our samples test as clearly euxinic (using the Mo proxy and others) even with this possible artifact. Second, our samples have not experienced intense thermal histories, arguing for minimal loss of Fe<sub>HR</sub> during burial. Third, the Fe<sub>HR</sub> enrichments that typify anoxic/euxinic deposition are also manifest in elevated Fe<sub>T</sub>/Al ratios (Lyons and Severmann, 2006), which are obviously impervious to internal mineralogical repartitioning within the total Fe pool. Most of our Fe<sub>T</sub>/Al values fall close to the average for continental crust, which also argues against persistent anoxia/euxinia. Finally, the hyper-aggressive boiling HCl leach of the DOP method will likely extract the Fe from any mineral formed during burial at the expense of primary, unpyritized Fe<sub>HR</sub>, and so our DOP values are not spuriously high. But even if they were elevated by mineral transformations during burial, our DOPs are still exclusively low to intermediate and point away from persistently euxinic deposition. Our highest DOP values suggest, at best, free sulphide within the pore fluids and/or fluctuating redox in the water column.

In light of all due consideration to the caveats intrinsic to the geochemical approaches, the collective geochemical data argue strongly for a system poised at but not dominantly beyond the door to persistent anoxia and specifically euxinia. Nevertheless, that anoxic/euxinic threshold was close enough and crossed frequently enough, albeit briefly, that benthic community development was strongly inhibited. In fact, absent the refinements that come with the geochemistry, one might surmise that persistent anoxia and euxinia dominated long intervals of deposition.

## 7. Conclusion

Independent analyses of the biological and geochemical data lead to similar interpretations of depositional conditions, but each perspective is strengthened by the presence of the other. Interpretation of the biological data suggests that persistent anoxic or even euxinic conditions alternated with intervals of dysoxic to mildly oxic conditions. The geochemical data on the other hand point to dominantly oxic conditions but likely at very low levels with variable amounts of free hydrogen sulphide in the sediments and the possibility of brief episodes of anoxia and even euxinia. Sustained,



trace levels of oxygen (suboxia) with intermittent, perhaps seasonal, anoxia/euxinia are consistent with observations in modern OMZ settings where high productivity but corresponding negative feedbacks (e.g., loss of fixed nitrogen required for primary production via denitrification) work to sustain a sensitive balance that disfavors persistent anoxia and euxinia (Canfield, 2006). (In contrast, high export of organic matter to the deep waters favors anoxia and even euxinia through high respiratory demand on oxygen at depth.) There is every reason to think that biogeochemically analogous conditions could occur in epicontinental settings with short- and longer-term climatic drivers of redox variability. The biological data (specifically the laminated intervals) cannot resolve whether sulphide was enriched in the water column in the absence of bottom water oxygen; however, the ichnofabrics do tell us that oxygen, when present, was not high—something we cannot tell from the Fe–Mo data alone. The high-resolution biological data at these localities support extremely reduced and rapidly fluctuating bottom water oxygen conditions with some intervals of anoxia and even euxinia. The rapid fluctuations between dysoxic and anoxic conditions are not captured cleanly with the geochemical data, suggesting that the latter intervals were brief. The combined approaches, with their complementary but also unique strengths, allow us to define a highly transitional and likely dynamic system that operated near threshold states at the low end of the depositional redox spectrum. Much work lies ahead, including better use of a broader spectrum of trace metals. But the picture to emerge already may not be an uncommon one, if analogous conditions in modern oxygen minimum settings and their prevailing biogeochemical controls are any guide. Minimally, this study invites more and better integrations of rigorous palaeobiological and biogeochemical approaches.

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