The Hyper-Enrichment of V and Zn in Black Shales of the Late Devonian-Early Mississippian Bakken Formation (USA)

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Abstract

Black shales of the Late Devonian to Early Mississippian Bakken Formation are characterized by high concentrations of organic carbon and the hyper-enrichment (>500 to 1,000s of mg/kg) of V and Zn. Deposition of black shales resulted from shallow seafloor depths that promoted rapid development of euxinic conditions. Vanadium hyper-enrichments, which are unknown in modern environments, are likely the result of very high levels of dissolved H₂S (~10 mM) in bottom waters or sediments. Because modern hyper-enrichments of Zn are documented only in Framvaren Fjord (Norway), it is likely that the biogeochemical trigger responsible for Zn hyper-enrichment in Framvaren Fjord was also present in the Bakken basin. With Framvaren Fjord as an analogue, we propose a causal link between the activity of phototrophic sulfide oxidizing bacteria, related to the development of photic-zone euxinia, and the hyper-enrichment of Zn in black shales of the Bakken Formation.

Keywords: Black shales, trace metals, euxinia, molybdenum, vanadium, zinc

1. Introduction

Black shales are fine-grained sedimentary rocks containing appreciable amounts of organic carbon (>0.5 wt.% total organic carbon (TOC)). In addition, black shales tend to be enriched in sulfur (S; 0.1 to 5 wt.%), iron (Fe; 0.1 to 5 wt.%), and a variety of trace metals (TMs; e.g., Mo, V, Zn, Ni, Cu, Cr, and U in the range of 10s to 1,000s of mg/kg). These components, C-S-Fe-TMs, represent the principal biogeochemical constituents of black shales and are the focus of this study. Here we use whole-rock geochemical data for these components to reconstruct the redox conditions during deposition of Bakken Formation black shales, with each constituent providing a unique set of environmental constraints. Three important features of black shales motivate this study: (1) they constitute source rocks for most oil and many natural gas deposits (e.g., Lillis, 2013); (2) they are host rocks for a variety of important mineral deposits (e.g., Scott et al., 2014); and (3) they preserve a record of sea water chemistry with implications for changing surface redox states and the evolution of life (e.g., Scott et al., 2008; Sahoo et al., 2012; Partin et al., 2013; Scott et al., 2013; Planavsky et al., 2014).

The key feature of black shales is the presence of organic matter (OM), yet debate persists as to how OM is preserved (Arthur and Sageman, 1994; Wignall, 1994; Smith and Bustin, 1998; Sageman et al., 2003). This debate typically emphasizes one of two controlling variables: (1) increased productivity leads to an increase in net OM burial, or (2) basin restriction promotes the preservation of OM due to a reduction in the supply of O_2 . There are good reasons to frame the debate in this manner. High TOC concentrations are well documented within the sediments of some modern nutrient-rich upwelling zones (e.g., Peru margin, Scholz et al., 2011; Namibian shelf, Brongersma-Sanders et al., 1980) and in some restricted marine basins and

fjords (Black Sea, Lyons and Berner, 1992; Cariaco Basin, Lyons et al., 2003; Werne et al., 2002; Framvaren Fjord, Skei et al., 1988; Sannich Inlet, Francois, 1988). However, increased productivity or basin restriction are not absolute requirements for the formation of black shales, and the possibility that black shales form under normal rates of primary productivity and in the absence of basin restriction has been largely ignored. Significantly, many of the black shales found in Phanerozoic successions were deposited in epicontinental seas and thus lack appropriate modern analogues (Wignall, 1994). For this reason it seems likely that the binary production-basin restriction framework is a poor model for the deposition of some—and perhaps many—ancient black shales. Here we build upon our understanding of the biogeochemistry (C-S-Fe-TMs) of black shales and describe an alternative model for their deposition within the Late Devonian-Early Mississippian Bakken basin.

2. Bakken Formation

The Bakken Formation occurs in the Williston Basin of Montana, North Dakota, Saskatchewan, and Manitoba (Fig. 1). Because black shales of this formation represent an important source rock for hydrocarbons, considerable research has been conducted on various aspects of these strata. The Lower and Upper Members of the Bakken are black shales whereas the Middle Member is composed of sandstone, siltstone, and dolostone (Fig. 2; Smith et al., 1995). The Lower and Upper Members are relatively thin, averaging 4 and 2 m, with maxima of 20 and 7 m, respectively (Smith and Bustin, 1998). The Middle Member is 10 m thick on average. The Lower Member is Late Devonian and the Upper Member is Early Mississippian (Holland et al., 1987). Shale units consist primarily of quartz, illite, OM, and alkali feldspar with minor carbonate and pyrite (Smith and Bustin, 1996). Organic matter is amorphous, primarily

Types I and II (reflecting a primarily marine source; Smith and Bustin, 1996); thermal maturity indicators typically place Bakken shales within the oil window.

Early estimates for seafloor depths during deposition of Bakken shales were rather shallow (e.g., 38-180 m; Smith and Bustin, 1996). A more recent depth estimate of greater than 200 m by Smith and Bustin (1996) is based on a common definition of storm wave base (Boggs, 1987) and not on any indicator specific to the Bakken basin. Smith and Bustin (1998) provided a detailed model for the formation of Bakken black shales. Their model requires a deep basin (>200 m water depth) suitable for the establishment of estuarine-like marine circulation, whereby upwelling seawater from the open ocean enters and travels throughout the basin at intermediate depths (100-200 m) and provides a source of nutrients to promote increased rates of primary production. Furthermore, upwelled open ocean water supplied to shallow and intermediate depths would promote stagnation of the deeper basin and increase preservation of OM. Thus, estuarine-like circulation, so described, allows for both increased productivity and decreased OM degradation within a relatively deep basin. Other workers have proposed similar scenarios for black shale deposition elsewhere (e.g., Algeo and Heckle, 2008).

Previous studies of Bakken black shales have identified biomarkers indicative of phototrophic sulfide-oxidizing bacteria (PSOB; Requejo et al., 1992; Jiang et al., 2001). This is a valuable observation because it requires that dissolved H_2S was present in the photic zone. Such photic zone euxinia represents an extreme end-member of anoxic conditions that rarely occurs on a large scale in modern marine settings, with the Black Sea being a notable exception (Manske et al., 2005). Thus, in this respect, as in others described below, Bakken black shales lack a modern analogue.

3. Samples and Methods

Samples of black shale ($n = 114$) were collected from the Lower and Upper Members of the Bakken Formation from six cores drilled in Montana and North Dakota (Fig. 1). The drill cores are housed at the U.S. Geological Survey (USGS) Core Repository Center in Denver, Colo., and additional information, including photographs of the drill cores and thin sections, and data from various analyses (programmed pyrolysis, vitrinite reflectance, x-ray diffraction, etc.) that were not part of this study, are available online at <http://geology.cr.usgs.gov/crc/>. Samples were collected at regular intervals of ca. 30 cm with some limitation owing to missing core. Four of the cores (E701, B659, B832, and B706) intersected both the Lower and Upper Members, one core (R311) captured only the Upper Member, and one core (D306) only the Lower Member. Samples (about 2 cm thick) were homogenized in an alumina ball mill prior to analysis. It is important to note that by homogenizing this thickness of shale, thousands of years of environmental redox conditions are averaged, as reflected by the biogeochemical data examined herein.

All analyses were conducted by SGS Laboratories in Toronto, Ontario. Ten major elements (SiO_2 , Al_2O_3 , CaO , MgO , Na_2O , K_2O , Fe_2O_3 , MnO , P_2O_5 , and TiO_2) were determined by wavelength-dispersive X-ray fluorescence spectrometry (WD-XRF) on rock powders fused with a lithium metaborate/tetraborate flux. The accuracy and precision of the method is about 5% (Taggart and Siems, 2002). Samples were also analyzed for major, trace, and rare earth elements (REE) by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) after decomposition using a sodium peroxide sinter at 450°C , in order to insure complete digestion of refractory minerals such as monazite, zircon, and barite. All major and minor element data discussed in this study are derived from the

ICP analyses. Selenium was analyzed by atomic absorption spectrometry following a four-acid digestion following the method outlined by Hageman et al. (2002). USGS Standards (Ohio Shale SDO-1 and Brush Creek Shale SBC-1) were run to monitor accuracy, and to compensate for matrix effects and internal drifts (Briggs and Meier, 2002; Meier and Slowik, 2002).

Total sulfur was determined using the automated sulfur analyzer method described by Brown and Curry (2002a). Samples were mixed with a vanadium pentoxide flux and combusted in an oxygen atmosphere at 1350°C where sulfur oxidizes to sulfur dioxide; the sulfur dioxide gas is then measured by a solid state infrared detector. Carbonate carbon (coulometric titration after treatment of sample with perchloric acid) subtracted from total carbon (analyzed by combustion/infrared detection) yielded TOC. See Brown and Curry (2002b) and Brown et al. (2002) for more details on these methods.

4. Results

Data generated for this study are total carbon, total inorganic carbon (TIC), TOC, total sulfur (TS), and a suite of 56 major elements, trace elements, and REE. All of the data generated are available in the supplementary data file. The discussion below focuses on TOC, TS, Fe, Mo, V, and Zn concentrations; aluminum concentrations were used to calculate authigenic trace metal fractions (Fig. 3). Total organic carbon concentrations range from <0.1 wt.% to 18.9 wt.% (Fig. 4). Total sulfur is typically in the range of 0.3 wt.% to 4.5 wt.% (Fig. 5), with six samples containing between 6 and 12 wt.%. These six outliers occur primarily in the bottom 0.5 m of the Lower Member.

The range of concentrations obtained for Mo, V, and Zn are typical of Paleozoic black shales in general (e.g., Scott et al., 2008; Sahoo et al., 2012; Scott et al., 2013). Molybdenum concentrations are 1 to 694 mg/kg; one sample contains 1,810 mg/kg. Vanadium ranges from 70 to 2,540 mg/kg. More than 90% of the samples have Zn concentrations between 20 and 4,980 mg/kg; additional samples contain up to 38,000 mg/kg. Globally, Zn concentrations of 1,000 to 3,000 mg/kg are common in Phanerozoic black shales, whereas those having >6,000 mg/kg are rare (Scott et al., 2013).

5. Discussion

5.1. *Identifying authigenic fractions of trace metals*

There are three primary sources of TMs in typical black shales: (1) a detrital fraction derived from continental weathering of terrigenous material; (2) a biological fraction assimilated by organisms during their life cycle and retained to some degree following degradation in the water column and within sediments; and (3) an authigenic fraction that reflects redox processes during early diagenesis, and that is ultimately derived from seawater. Our focus here is on the authigenic fraction of individual TMs and how that fraction informs our understanding of the redox conditions in the depositional environment. To determine what proportion of total TMs is contained in the authigenic fraction, we use the concentrations of TMs and Al in continental crust (8.04 wt.%; Taylor and McLennan, 1995) to calculate the authigenic fractions of Mo, V, and Zn (Fig. 3A-C) based on the formula: $TM_{auth} = TM_{bulk} - (TM/Al)_{crust} * Al_{bulk}$. The concentration of Al in our sample set ranges from 1.4 to 7.6 wt.% and averages 6.6 wt.%.

For Mo, the authigenic fraction is essentially the same as the bulk concentration owing to the low concentration (1.5 mg/kg) of Mo in the crust. In contrast, the authigenic fraction for V is distinct from that of the bulk concentration, but for most samples the terrigenous fraction is <10% of the total. The terrigenous fraction commonly dominates the bulk concentration of Zn in our sample set, and for many of these samples the calculated authigenic fraction is a negative value. This fact demonstrates that there is little or no authigenic enrichment of Zn within many samples of Bakken shales. It also demonstrates that using average crustal values to calculate authigenic fractions introduces a non-trivial degree of ambiguity (cf. Böning et al., 2012). However, where clear authigenic Zn enrichments occur, they exceed the terrigenous contribution by one to two orders of magnitude. To restate, for samples in which total Zn is dominated by the detrital fraction, it is due to little or no authigenic enrichment of Zn and not due to an anomalously high contribution of Zn by the terrigenous fraction which has a maximum value of 67 mg/kg Zn in our sample set.

It seems unlikely that the TM/C ratio of living phytoplankton will remain constant during degradation in the water column and sediments and as OM is consumed and transformed during heterotrophy. Nonetheless, we can use this ratio ($\text{Zn/C} = 0.036 \text{ mmol/mol}$; Little et al., 2015) to obtain a rough estimate of the potential biological contribution to the shale and to calculate an additional authigenic fraction for Zn that takes this contribution into account (Fig. 3C). Zinc is by far the most abundant trace element in living phytoplankton (e.g., Little et al., 2015) yet even in samples in which TOC approaches 20 wt.%, the calculated biological contribution is only ~40 mg/kg. Effects for Mo and V are even smaller. Because evidence exists for both a small continental and biological contribution in most cases (Mo, V, Zn) and because of the potential

for additional uncertainty resulting from calculations of an authigenic fraction (V, Zn), we use the bulk concentrations of TMs in the following discussion.

5.2. *Carbon-Sulfur-Iron Systematics*

Total organic carbon in Bakken black shales ranges from less than 1 wt.% to nearly 20 wt.% and averages 9.6 wt.% (Fig. 4). Because the microbial oxidation of sedimentary OM drives the biogeochemical cycles considered here (Froelich et al., 1979; Canfield et al., 1993), and because black shales having higher TOC hold greater potential to generate large oil and gas deposits, the concentration of TOC in Bakken shales is of singular importance. However, there is no unique set of conditions that promotes OM burial so that TOC alone is a poor indicator of depositional environment. Nonetheless, two generalizations can be made based on the concentration of TOC in Bakken shales. First, the system was not nutrient limited. Second, primary production exceeded oxidation in the water column and sediments. Importantly, neither of these generalizations strictly requires elevated primary productivity nor any special mechanism to supply nutrients to the basin, nor do they require a silled basin or a deep basin.

Black shales typically have an abundance of TMs and commonly display a clear, positive correlation between TOC and the magnitude of TM enrichments (Algeo and Lyons, 2006; Tribovillard et al., 2006, Algeo and Maynard, 2008), but it is reduced sulfur (i.e., dissolved H₂S) that links OM to the authigenic enrichment of most TMs (Breit and Wanty, 1991; Calvert and Pedersen, 1993; Helz et al., 1996). Therefore, the two most important variables to consider regarding TM enrichments in black shales are as follows: (1) where was H₂S accumulating (in the pore waters or the water column), and (2) how much H₂S was present.

The source of reduced sulfur in the system is microbial sulfate reduction (MSR) coupled with the oxidation of OM. This process initially occurs at a depth in the sediments beneath the aerobic and suboxic zones where O_2 , NO_3^- , and metal oxides are being reduced (Froelich et al., 1979; Canfield et al., 1993). However, as OM burial continues, the zone of SO_4^{2-} reduction, and H_2S accumulation, can move upward and into the bottom waters, thus establishing euxinic conditions. This distinction between pore-water H_2S and water-column H_2S is critical to the interpretation of TM enrichments (Scott and Lyons, 2012). The amount of dissolved H_2S that accumulates in the system is controlled by the balance between sulfate reduction (source) and precipitation of metal sulfides and H_2S oxidation (sinks). C-S-Fe systematics can be used to determine the locus of H_2S accumulation but they offer no information on the amount of H_2S within the system.

By comparing the concentrations of TOC with TS in Bakken black shales two distinct populations are observed (Fig. 4). In the first population, samples contain <6 wt.% TOC and <2 wt.% TS. The second population has TOC >7 wt.% and TS between 2 and 4.5 wt.%. Nearly 90 % of the samples are included in these two populations. Most informative is the clear decoupling between TOC and TS where TOC exceeds 7 wt.%. Here, TOC concentrations nearly triple with no associated increase in TS. This relationship highlights the decoupling of OM burial and sulfide preservation rather than sulfide production. This is an important distinction because it follows that the concentration of TS preserved in Bakken shales does not reflect the concentration of dissolved H_2S in the system. Instead, it reflects delivery of reactive Fe to the system.

The formation of Fe sulfide minerals (ultimately preserved as pyrite) is the primary pathway whereby pore-water and water-column H_2S is transferred to sediments and preserved in

black shales (Berner, 1984). It is well demonstrated that a discrete pool of Fe, dominated by Fe³⁺ oxides and oxy-hydroxides and referred to as highly reactive Fe (FeHR), is available for pyrite formation, whereas the pool of Fe delivered in the siliciclastic detrital fraction (nonreactive Fe) is essentially inert with respect to H₂S (Raiswell and Canfield, 1998). If we allow that all S and FeHR in Bakken black shales are in the form of pyrite (an assumption supported by the coupling between total Fe (FeT) and TS; Fig. 5), we can calculate an average non-reactive Fe pool of ~0.6 wt.%. This calculated value is consistent with the minor enrichment of Fe relative to the ratio of Fe/S in pyrite (0.87; Fig. 5). In contrast, pyrite Fe concentrations (Fe_{py}) typically fall in the range of 1 to 4 wt.% Fe (89 % of samples). This magnitude of Fe_{py} enrichment is typical of sulfidic sediments (Lyons et al., 2003) and black shales (e.g., Werne et al., 2002); in contrast, the inferred detrital Fe fraction is well below that of average crust (3.5 wt.%; Taylor and McLennan, 1995).

Figure 5 demonstrates a tight coupling between FeT and TS in Bakken shales. Note that the relationship is strongest where TS exceeds 2 wt.% and is weak or non-existent where TS is less than 2 wt.%. The strong covariance between FeT and TS is expected under euxinic conditions and indicates that the FeHR pool was completely consumed during the formation of pyrite (Raiswell et al., 1988). Euxinic conditions develop when net H₂S production exceeds the delivery of FeHR to the sediments (Johnston et al., 2010). After this condition is reached, further H₂S generation will not drive additional enrichment of TS in the sediments because Fe-sulfides dominate TS (sulfurization of OM and incorporation of ZnS can augment the TS pool but their contribution is small; e.g., Werne et al., 2000; Slack et al. 2015; this study). Thus, the decoupling of TOC and TS and the coupling of TS and FeT in Bakken shales share the same inflection point (at 2 wt.% TS), because they reflect the same phenomenon—euxinic conditions. Since most samples record euxinic conditions, euxinia is inferred to have been widespread and persistent in

the Bakken basin. However, no reliable estimates can be made of the concentration of H₂S in the system using C-S-Fe systematics alone.

It is likely that H₂S generation and accumulation continued after the reactive Fe was exhausted. This scenario raises the question of what is the maximum attainable concentration of H₂S in a system with up to 20 wt.% TOC? Our data set does not provide a direct measure of the availability of sulfate for MSR, but the extreme TM enrichments observed in the Bakken Formation (Fig. 3) require a strong connection to the open ocean reservoir of dissolved metals (e.g., Algeo and Lyons, 2006). This scenario should also be true for SO₄²⁻ and it is unlikely that it was biolimiting. Therefore, Bakken sediments and bottom waters were primed for runaway sulfide production, where the concentration of H₂S increases up to the point where it begins to limit the rate of MSR. Experimental studies demonstrate that limitation occurs where H₂S exceeds ~10 mM (Reis et al., 1992; Wing and Halevy, 2014). Such high concentrations of H₂S would be difficult to achieve in natural environments, because rates of sulfide generation would need to exceed rates of sulfide oxidation in the water column, and concentrations of H₂S above 10 mM are unknown in modern marine environments. However, we argue below that the observed hyper-enrichments of V in Bakken black shales, which are also not observed in modern marine environments, are consistent with the development of hyper-sulfidic conditions in the range of 10 mM H₂S.

5.3. *Molybdenum*

Molybdenum averages 1.5 mg/kg in continental crust (Taylor and McLennan, 1995) but typically occurs at 10s to 100s of mg/kg in black shales (e.g., Wilde et al., 2004; Algeo and Lyons, 2006; Scott et al., 2008) and their modern analogues, sulfidic organic-rich sediments

(e.g., eastern tropical North Pacific, Nameroff et al., 2002; Santa Barbara Basin, Zheng et al., 2000; Cariaco Basin, Lyons et al., 2003; Peru margin, McManus et al., 2006 and Scholz et al., 2011).

Initial enrichment of Mo in sediment occurs at relatively low concentrations of H_2S ($<11 \mu\text{M H}_2\text{S}_{(\text{aq})}$; Helz et al., 1996; Erickson and Helz, 2000). Above this threshold, increased H_2S concentrations do not generate higher Mo concentrations. Instead, maximum Mo enrichments closely track those of TOC and the concentration of Mo in seawater (Algeo and Lyons, 2006). As described in Scott and Lyons (2012), the bulk concentration of Mo in black shales provides important information with respect to the location of sulfide accumulation. Specifically, Mo concentrations of $\leq 25 \text{ mg/kg}$ may be interpreted as indicating that H_2S was restricted to pore waters and that bottom waters were oxic to suboxic. Molybdenum concentrations exceeding 100 mg/kg represent bottom waters that were persistently euxinic (i.e., H_2S present the bottom waters). Lastly, Mo concentrations between 25 and 100 mg/kg reflect an environment that was either intermittently euxinic or experienced an extreme degree of basin restriction.

Using this scheme (Fig. 6) we find that persistently euxinic conditions characterize both the Upper and Lower Member shales in the four northernmost drill cores sampled (B706, B306, E701, R311; Fig. 1). Here, Mo concentrations exceed 100 mg/kg in 90% of samples and have an average concentration of 362 mg/kg and maximum concentrations that exceed 600 mg/kg . Conversely, the two southernmost drill cores (B659 and B832; Fig. 1) represent less-reducing sites within the Bakken basin, where euxinia was more commonly intermittent during deposition of the Lower Member and completely absent in the Upper Member. Similar oxic to suboxic conditions are found on the shelf of the Black Sea (e.g., Lyons and Severmann, 2006) and likely represent shallower depths. All of the non-euxinic samples, as indicated by Mo concentrations of

<25 mg/kg, have TOC <6 wt.% and TS <2 wt.% (Fig. 4). Thus, C-S-Fe systematics and Mo concentrations together suggest predominantly euxinic conditions in the Bakken basin overall, but also clearly identify those sites with non-euxinic (oxic to suboxic) bottom waters.

Egenoff and Fishman (2013) used the presence of purported burrows in Upper Member black shales to argue for a dysoxic depositional environment. The authenticity of these burrows was subsequently challenged by Schieber (2014). It is possible that Egenoff and Fishman (2013) have observed burrows in a non-euxinic horizon. It is also possible that brief periods of dysoxic or even oxic conditions could allow for the colonization of sediments by animals and that subsequent periods of euxinia could overprint a formerly oxic interval with a euxinic biogeochemical signature (e.g., Sperling et al., 2016), keeping in mind that due to sample homogenization our data represent an integration of 100s to 1000s of years of redox conditions. However, the combined input of C-S-Fe and Mo geochemical data provide strong support for the widespread and persistent occurrence of euxinic conditions in the Bakken basin.

A clear covariance exists between the concentrations of Mo and TOC in euxinic intervals of both Lower and Upper Member shales (Fig. 6). This trend is a common feature of euxinic black shales and sediments from modern euxinic basins. Algeo and Lyons (2006) demonstrated that the ratio of Mo/TOC in sediments from euxinic basins correlates positively with the concentration of Mo in the water column. Based on this work, it appears that the concentration of Mo in seawater of the Bakken basin was relatively higher during the Late Devonian (avg. Mo/TOC = 31.3) and relatively lower during the Early Mississippian (avg. Mo/TOC = 26.3) and that during both the Late Devonian and the Early Mississippian the concentration of Mo in Bakken basin seawater was higher than it is in the modern ocean (cf. Algeo and Lyons, 2006). Considering the potential for widespread euxinic deposition to draw down the global Mo

seawater inventory (Scott et al., 2008), the apparently high concentration of dissolved Mo in the Bakken basin is difficult to reconcile with the widespread occurrence of euxinic black shales at this time. Future work is needed to address this paradox.

5.4. *Vanadium*

Based on the range of Al concentrations in our sample set we calculate an average detrital contribution of 89 mg/kg for V, with a maximum of 137 mg/kg. In contrast, average and maximum bulk concentrations are 850 and 2540 mg/kg, respectively (Fig. 3B; <10% of samples lack calculated authigenic enrichments). A comparison of V and TOC reveals two distinct populations that likely represent two distinct modes of enrichment (Fig. 3B). One population exceeds 500 mg/kg V and 7 wt.% TOC. The second population contains less than 500 mg/kg V but a wide range of TOC concentrations. Because V concentrations in modern sediments are below 500 mg/kg (Nameroff et al., 2002; Scholz et al., 2011), samples having greater than 500 mg/kg are referred to here as “hyper-enriched” with respect to V. By comparing V to TS we find that most hyper-enrichments occur in samples with TS between 2 and 4.5 wt.% (Fig. 7), and thus where TS is decoupled from TOC and the highest concentrations of H₂S are expected.

Vanadium exists in two oxidation states in most marine environments (Wanty and Goldhaber, 1992). Vanadium (V) predominates in oxic seawater and is largely unreactive, whereas reduction to particle-reactive V(IV) occurs under moderately reducing conditions (Sadiq, 1988). Authigenic enrichments of 10 to 300 mg/kg are observed in modern suboxic (Nameroff et al., 2002; Scholz et al., 2011) and euxinic (Piper and Dean, 2002; Brumsack, 2006) settings, and likely represent removal of dissolved V as V(IV) (Breit and Wanty, 1991). Thus, although V concentrations exceeding 500 mg/kg are common in Phanerozoic black shales

(Sahoo et al., 2012; max. typically 1000-5000 mg/kg), no modern analogues for this magnitude of enrichment are known.

Previous work on V in black shales (Lewan and Maynard, 1982; Lewan, 1984; Breit and Wanty, 1991; Wanty and Goldhaber, 1992) links V enrichments to the accumulation of excess H_2S in sediments and/or bottom waters where reduction of V(IV) to V(III) occurs. The presence of V in authigenic clays in some V hyper-enriched black shales (e.g., Ripley et al., 1990; Peacor et al., 2000; Kelley et al., 2015) is consistent with reduction to V(III). Wanty and Goldhaber (1992) demonstrated that whereas thermodynamics predicts that V(III) should exceed V(IV) where H_2S exceeds 0.029 mM, very high concentrations of H_2S are required to drive this reduction step on laboratory timescales. The highest concentration of H_2S observed in modern marine settings is 8 mM, measured in Framvaren Fjord (Skei et al., 1988). However, sediments from this basin lack V hyper-enrichments (avg. 41 mg/kg in the deep basin; Jens Skei pers. comm.). Therefore, if H_2S activity is indeed the critical parameter that drives the reduction of V(IV) to V(III), and subsequent hyper-enrichment of V in local sediments, then the concentration of H_2S in coeval bottom-waters or pore-waters must exceed 8 mM.

In section 5.2 we suggested that where TS and TOC are decoupled (TOC >7 wt.% and TS >2 wt.% for Bakken black shales), there is the potential for runaway sulfide generation because neither OM nor sulfate was limiting in the Bakken basin. Under these conditions, H_2S production can continue until it reaches ~10 mM, at which point it begins to depress the forward reaction (Reis et al., 1992; Wing and Halevy, 2014). Two-thirds of the Bakken samples that contain >7 wt.% TOC and >2 wt.% TS (where TOC and TS are decoupled; Fig. 4) also contain >500 mg/kg V, thus supporting a link between decoupling of TOC and TS, elevated H_2S activity, and hyper-enrichment of V (Lewan and Maynard, 1982; Lewan, 1984; Breit and Wanty, 1991; Wanty and

Goldhaber, 1992). Based on this previous work and the data presented here for the Bakken Formation, we propose that V concentrations ≥ 500 mg/kg in Bakken black shales represent hyper-sulfidic conditions in which H_2S approaches or exceeds 10 mM in pore-waters or bottom-waters.

It is important to clarify that even although high activity of H_2S is likely required for the reduction of V(IV) to V(III) (Breit and Wanty, 1991; Wanty and Goldhaber, 1992), and its subsequent hyper-enrichment in black shales, V rarely forms sulfide minerals and occurs in only negligible amounts within pyrite. Rather, in black shales, V is hosted mainly in OM and/or authigenic clays or illite (Ripley et al., 1990; Peacor et al., 2000; Kelley et al., 2015). Thus, although the concentration of TS in black shales provides little insight into H_2S activity in the depositional environment, the concentration of V does potentially yield valuable information, (i.e., $\text{V} > 500$ mg/kg reflects $\text{H}_2\text{S} > 10$ mM) even though V is essentially absent in sulfide minerals.

5.5. *Zinc*

Zinc concentrations are both conspicuously high and conspicuously low in Bakken black shales (Fig. 8). Twenty-five percent of samples contain greater than 500 mg/kg Zn, with several samples exceeding 1000 mg/kg, representing extreme enrichments relative to most modern environments (e.g., Piper and Dean, 2002; Brumsack, 2006; Little et al., 2015). Conversely, 44% of samples have Zn concentrations below that of average crust (71 mg/kg; Taylor and McLennan, 1995) and 48% of samples below that of average shale (95 mg/kg; Turekian and Wedepohl, 1961). Importantly, there is little or no correlation between total Zn and TS despite the fact that ZnS (as sphalerite) and Zn in pyrite are well known in modern sulfidic sediments

and ancient black shales (Ripley et al., 1990; Huerta-Diaz and Morse, 1992; Pašava et al., 1996; Fleurance et al., 2013; Slack et al., 2015; Gregory et al., 2015). To some degree, this lack of correlation is due to the fact that delivery of reactive Fe controls the concentration of TS. However, additional variables likely affect the decoupling observed between Zn and TS.

We identify three classes of Zn concentrations in Bakken shales: (1) little to no enrichment is indicated where Zn is <71 mg/kg (i.e., below the concentration of continental crust; Taylor and McLennan, 1995); (2) Zn concentrations between 71 and 500 mg/kg represent moderate enrichments compared to continental crust and modern sediments; and (3) samples with >500 mg/kg Zn that are termed “hyper-enriched” because they exceed the concentration in all but one known modern environment (Framvaren Fjord, Norway). All three classes are present in both Upper and Lower Members of the Bakken, and in each of the six drill cores studied. This range of Zn concentrations and its decoupling from TS lead to two important questions applicable to black shales in general: how is the lack of Zn enrichment explained for environments where dissolved H_2S was clearly present, and how is the hyper-enrichment of Zn produced?

The concentration of Zn in seawater seems an unlikely control on variable Zn enrichments observed in Bakken shales because we find both minor enrichments (e.g., Cariaco Basin; Little et al., 2015) and hyper-enrichments (Framvaren Fjord; Skei et al., 1988) in modern settings with comparable concentrations of dissolved Zn present in surface waters. Furthermore, if the composition of local seawater is the predominant control, then the variable enrichment of Zn observed in Bakken shales would require extreme fluctuation in seawater Zn concentrations, with no attendant fluctuations in Mo and V. The activity of H_2S also seems an unlikely control. Zinc exists in seawater in a single valence state, Zn(II) , and should precipitate rapidly in the

presence of low levels of H_2S (Algeo and Maynard, 2004) so that where Mo exceeds the crustal average of 1.5 mg/kg (requiring $\sim 10 \mu\text{M} \Sigma\text{H}_2\text{S}$; Helz et al., 1996), ZnS should also be found. However, there is a conspicuous lack of significant Zn enrichments in the euxinic Cariaco basin ($65 \mu\text{M} \text{H}_2\text{S}$; Li et al., 2011; Little et al., 2015) and the Black Sea ($380 \mu\text{M} \text{H}_2\text{S}$; Murray et al., 1989; Little et al., 2015). Thus, the absence of significant authigenic Zn concentrations in many modern sediments and ancient black shales is perplexing and suggests that hyper-enrichment likely requires an additional mechanism beyond the presence of excess H_2S .

We propose that Zn has two distinct authigenic enrichment mechanisms, which we refer to as primary and secondary authigenic enrichments. Primary authigenic enrichment is linked to the accumulation of H_2S in pore waters and in the water column and results in small to moderate amounts of Zn (72 to 500 mg/kg), using sediments of the modern Cariaco Basin as an analogue (Piper and Dean, 2002; Little et al., 2015). The principal host phase for primary authigenic enrichments is likely pyrite with minor amounts of ZnS . Secondary authigenic enrichment requires more than just the presence of dissolved H_2S and results in the hyper-enrichment of Zn. Because Zn hyper-enrichments in the Bakken Formation are decoupled from TS (Fig. 8), and because TS is controlled primarily by the precipitation of FeS_2 , we suggest that secondary enrichments of Zn result in the formation of ZnS and do not reflect increased pyritization of Zn (see Ripley et al., 1990). This scenario implies the formation of ZnS in the water column, a phenomenon that has also been suggested for Cretaceous black shales (Brumsack, 1980).

The only known modern analogue for Zn hyper-enrichment is Framvaren Fjord (Skei et al., 1988). Framvaren is notable for its extreme accumulations of H_2S (up to 8 mM; Skei et al., 1988), abnormal concentrations of dissolved organic matter (Skei et al., 1988), and the presence of PSOB in the water column (Sørensen, 1988). Given these parameters, we propose that the

hyper-enrichment of Zn (>500 mg/kg for Bakken shales specifically) in black shales and sediments is directly related to the activity of PSOB. The production of polysulfides (S_x^{2-}) during sulfide oxidation (e.g., Overmann et al., 1996; Findlay et al., 2014) could provide the necessary enrichment mechanism since polysulfides form relatively stable complexes with Zn (Chadwell et al., 2001).

Although this mechanism for Zn hyper-enrichment is speculative, it is also a testable hypothesis. If this proposed mechanism for the secondary enrichment of Zn is proven correct, then non-epigenetic (i.e., hydrothermal) hyper-enrichments of Zn in ancient black shales could be used as an indicator of photic zone euxinia, even in units where biomarkers are unreliable due to thermal alteration or contamination during drilling (e.g., French et al., 2015).

5.6. *Depositional Environments*

The defining characteristic of Bakken black shales is the high concentrations of TOC (avg. 9.7 wt. %; max. 18.9 wt. %), but these concentrations are difficult to explain. They are greater than those found in most modern environments to include all known euxinic environments (Cariaco Basin, Lyons et al., 2003; Black Sea, Lyons and Berner, 1992; Framvaren Fjord, Skei et al., 1988; Saanich Inlet, Francois, 1988) thus suggesting that the development of euxinic conditions alone is not sufficient to drive such high concentrations of TOC. Total organic carbon concentrations do reach 20 wt. % locally on the Peru margin and Namibian shelf (Brongersma-Sanders et al., 1980; Böning et al., 2004; Scholz et al., 2011) but these high concentrations of TOC are uncommon. Other upwelling zones, such as in the eastern North Pacific offshore from Mexico, generate clear oxygen minimum zones but accumulate just a few wt.% TOC in related sediments (e.g., Nameroff et al., 2002). Nonetheless, considering that the Bakken Formation was deposited in an epicontinental sea removed from the continental margin

(Smith and Bustin, 1996), modern upwelling zones are likely to be poor analogues for the Bakken basin. For these reasons we suggest an alternative model for the accumulation of high concentrations of OM that focuses on shallow depths and the contribution of PSOB, rather than basin restriction or elevated primary productivity.

The key variable in our model is the amount of time that OM is exposed to oxidation in the water column. The focus here is on time rather than redox condition because euxinia follows the burial of OM and should be considered a direct result of OM burial rather than its cause. The ideal water depth for the deposition of OM is the minimum depth that will prevent resuspension. Any increase in water depth beyond this minimum will increase sediment exposure time as it descends through the water column and decrease the likelihood that OM is ultimately buried. In shallower waters, OM is produced closer to the sediment/water interface, but due to resuspension its exposure to oxidation in the water column is longer. This raises the question of what is the minimum depth that would allow for the burial of organic matter.

Smith and Bustin (1996) used a common estimate for storm wave base (200 m; Boggs, 1987) to define a minimum water depth of 200 m for the Bakken basin. This approach is valid in the sense that the fine-grained sediments that characterize black shales are unlikely to accumulate above wave base. However, the estimate of 200 m for storm wave base is inconsistent with modern observations. Peters and Loss (2012) used wave data from the Atlantic and Gulf Coasts of North America to challenge the distinction between fair weather and storm wave base and demonstrated that wave base rarely exceeds 150 m along the Atlantic Coast and is even shallower (generally < 100 m) along the Gulf Coast, despite the influence of multiple large hurricanes. Thus, if we use the concept of wave base to define a minimum depth of deposition in the Bakken basin, a minimum value of 100 m is more appropriate. For the purposes of this

discussion we use an estimated depth of 100 to 150 m rather than > 200m. This is an important distinction because it allows for the sediment water interface to exist close to, or even within, the photic zone.

Black shale deposition commenced in the Bakken basin when depths exceeded 100 m and organic matter began to accumulate on the seafloor. Initially, sulfate reduction would have been restricted to deeper sediments, separated from oxic or suboxic bottom waters by an aerobic/suboxic sediment zone (e.g., Froelich et al., 1979). At this stage, TOC and TS were coupled and Mo concentrations were <25 mg/kg. As OM sedimentation continued, sulfide production ultimately outpaced that of FeHR delivery and euxinic conditions developed (Fig. 9). As a result, TOC and TS were decoupled (Fig. 4), TS was controlled by the delivery of FeHR (Fig. 5), and Mo concentrations exceeded 100 mg/kg (Fig. 6). In the four northernmost drill cores analyzed in this study (Fig. 1), the transition to euxinia occurred rapidly and euxinic conditions persisted throughout shale deposition. However, non-euxinic (i.e. oxic to suboxic) conditions were common in the two southernmost drill cores, perhaps as a consequence of shallower depths.

With an ample supply of organic C and dissolved sulfate, sulfide production continued unabated until H₂S concentrations (~10 mM; Reis et al., 1992; Wing and Halevy, 2014) began to depress rates of sulfide production. Based on the hyper-enrichment of V (Fig. 7), we infer that the concentration of H₂S reached this level—higher than observed in modern marine environments—repeatedly during the deposition of Bakken shales.

The very high concentrations of H₂S inferred for the Bakken basin would be conducive to the activity of PSOB provided that sulfide was present within the photic zone at slightly lower concentrations (H₂S inhibits sulfide oxidation above 2-4 mM; Van Gernerden, 1984). Indeed,

previous biomarker studies have identified the remains of PSOB in Bakken black shales, reflecting the development of euxinia within the photic zone (Requejo et al., 1992; Jiang et al., 2001). To the degree that the activity PSOB promote the hyper-enrichment of Zn in Bakken shales (Section 5.5), we also find evidence for episodic photic-zone euxinia (Fig. 8).

It seems reasonable that the higher the concentration of H_2S at the sediment-water interface, the greater the likelihood of H_2S reaching the photic zone. A plot of V and Zn concentrations in Bakken black shales (Fig. 10) supports this reasoning. The development of photic-zone euxinia, inferred by hyper-enrichment of Zn (>500 mg/kg), requires the development of hyper-sulfidic conditions (probably close to the sediment-water interface) as identified by the hyper-enrichment of V (>500 mg/kg), in essentially all cases. However, the development of hyper-sulfidic conditions does not uniformly result in photic-zone euxinia.

It is important to keep in mind that PSOB fix C in the absence of O_2 and, in our model, lived close to the sediment-water interface. This environment would promote the accumulation of even greater concentrations of TOC within the sediments by the addition of OM that had never been exposed to aerobic degradation. The debate between the relative roles of production and preservation typically focuses on OM produced during oxygenic photosynthesis in the surface waters. However, OM produced by PSOB represents an additional source of OM that has a very high potential for preservation and can explain the high TOC observed in Bakken shales without requiring increased productivity, basin restriction, or anomalously low rates of clastic sedimentation.

To recapitulate, we argue here for increased OM delivery to Bakken sediments as a result of the development of a shallow (100 to 150 m) basin. Euxinia was a product of OM burial and not the cause. Although H_2S accumulated to very high concentrations, it remained close to the

sediment-water interface and only reached the photic zone episodically. We suggest that the activity of phototrophic sulfide-oxidizing bacteria, close to the sediment-water interface, contributed to the high concentrations of TOC within the Bakken Formation by providing an additional source of minimally processed OM.

5.7. *Broader Implications*

The high TOC concentrations and hyper-enrichments of trace metals that characterize Bakken black shales are not observed in modern environments but are common in many Paleozoic black shales of North America (e.g., Coveney and Martin, 1983; Coveney and Glascock, 1989; Hatch and Leventhal, 1992, 1997; Algeo and Maynard, 2004; Algeo et al., 2004; Perkins et al., 2008). Occurrence of metalliferous black shales elsewhere suggests that a common driver was involved in their formation. It seems unlikely that variables unique to individual basins (e.g., basin geometry, estuarine-like circulation, hydrothermal venting of metals) can explain their common occurrence or that multiple mechanisms operated simultaneously in the Paleozoic, whereas none are operating today. Rather, a common denominator is needed to explain the commonality of TM hyper-enriched black shales in the Paleozoic of North America. We propose that this common denominator is a shallow water depth (100 to 150 m) and hence a short transit time of OM through the water column. This mechanism does not require elevated productivity or stagnant bottom waters. However, marine flooding of much of the North American continent during the Paleozoic could explain the local occurrence of hyper-enriched black shales then and their absence now. It is also worth considering the possibility that the high TOC concentrations observed in such black shales represent two sources

of marine primary organic carbon: (1) oxygenic photosynthesis; and (2) primary production associated with the oxidation of H₂S, either photosynthetic or chemosynthetic. Lastly, we stress the concept that euxinia is the product of OM burial and not the cause. For this reason, caution is needed in linking the widespread deposition of black shales to global-scale ocean anoxia. Moreover, it is possible that black shale deposition was, at times, largely decoupled from the degree of ocean oxygenation and was instead the result of the expansion of shallow depositional environments.

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References

- Algeo, T.J., Maynard, J.B., 2004. Trace-element behavior and redox facies in core shales of Upper Pennsylvanian Kansas-type cyclothems. *Chem. Geol.* 206, 289–318.
- Algeo, T.J., Lyons, T.W., 2006. Mo-total organic carbon covariation in modern anoxic marine environments: implications for analysis of paleoredox and paleohydrographic conditions. *Paleoceanogr.* 21, PA 1016, doi:10.1029/2004PA001112.

Algeo, T.J., Heckle, P.H., 2008. The Late Pennsylvanian Midcontinent sea of North America: a review. *Paleogeogr., Paleoclimatol., Paleoecol.* 268, 205–221.

Algeo, T.J., Maynard, J.B., 2008. Trace-metal covariation as a guide to water-mass conditions in ancient anoxic marine environments. *Geosphere* 4, 872–887.

Algeo, T.J., Schwark, L., Hower, J.C., 2004. High-resolution geochemistry and sequence stratigraphy of the Hushpuckney Shale (Swope Formation, eastern Kansas): implications for climato-environmental dynamics of the Late Pennsylvanian Midcontinent seaway. *Chem. Geol.* 206, 259–288.

Arthur, M.A., Sageman, B.B., 1994. Marine black shales: depositional mechanisms and environments of ancient deposits. *Ann. Rev. Earth Planet. Sci.* 22, 499–551.

Berner, R.A., 1984. Sedimentary pyrite formation: an update. *Geochim. Cosmochim. Acta* 48, 605–615.

Boggs, S., 1987. *Principles of sedimentology and stratigraphy*. Merrill Publishing, Columbus, Ohio, 784 pp.

Böning, P., Brumsack, H.-J., Böttcher, M.E., Schnetger, B., Kriete, C., Kallmeyer, J., Borchers, S.L., 2004. Geochemistry of Peruvian near-surface sediments. *Geochim. Cosmochim. Acta* 68, 4429–4451.

Böning, P., Fröllje, H., Beck, M., Schnetger, B., Brumsack, H.-J., 2012. Underestimation of the authigenic fraction of Cu and Ni in organic-rich sediments. *Marine Geol.* 323–325, 24–28.

Breit, G.N., Wanty, R.B., 1991. Vanadium accumulation in carbonaceous rocks: a review of geochemical controls during deposition and diagenesis. *Chem. Geol.* 91, 83–97.

Briggs, P.H., Meier, A.L., 2002. The determination of forty-two elements in geologic materials by inductively coupled plasma-mass spectrometry, in Taggart, J.E., ed., *Analytical methods for chemical analysis of geologic and other materials* U.S. Geological Survey Open-File Report 02–223, pp. I1–I14.

Brongersma-Sanders, M., Stephan, K.M., Kwee, T.G., De Bruin, M., 1980. Distribution of minor elements in cores from the southwest Africa shelf with notes on plankton and fish mortality. *Marine Geol.* 37, 91–132.

Brown, Z., Curry, K.J., 2002a. Total sulfur by combustion, in Taggart, J.E., ed., *Analytical methods for chemical analysis of geologic and other materials*. U.S. Geological Survey Open-File Rept. 02–223, pp. Q1–Q4.

Brown, Z., Curry, K.J., 2002b. Total carbon by combustion, in Taggart, J.E., ed., Analytical methods for chemical analysis of geologic and other materials. U.S. Geological Survey Open-File Report 02–223, pp. R1–R4.

Brown, Z., Papp, C., Brandt, E., Aruscavage, P., 2002. Carbonate carbon by coulometric titration, in Taggart, J.E., ed., Analytical methods for chemical analysis of geologic and other materials, U.S. Geological Survey: U.S. Geological Survey Open-File Report 02–223, pp. S1–S6.

Brumsack, H.-J., 1980. Geochemistry of Cretaceous black shales from the Atlantic Ocean (DSDP Legs 11,14, 36 and 41). *Chem. Geol.* 31, 1-25.

Brumsack, H.-J., 2006. The trace metal content of recent organic carbon-rich sediments: implications for Cretaceous black shale formation. *Palaeogeogr., Palaeoclimatol., Palaeoecol.* 232, 344–361.

Calvert, S.E., Pedersen, T.F., 1993. Geochemistry of Recent oxic and anoxic marine sediments: implications for the geological record. *Marine Geol.* 113, 67–88.

Canfield, D.E., Thamdrup, B., Hansen, J.W., 1993. The anaerobic degradation of organic matter in Danish coastal sediments: iron reduction, manganese reduction, and sulfate reduction. *Geochim. Cosmochim. Acta* 57, 3867–3883.

Chadwell, S.J., Rickard, D., Luther III, G.W., 2001. Electrochemical evidence for metal polysulfide complexes: tetrasulfide (S_4^{2-}) reactions with Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} . *Electroanalysis* 13, 21-29.

Coveney, R.M., Jr., Martin, S.P., 1983. Molybdenum and other heavy metals of the Mecca Quarry and Logan Quarry shales. *Econ. Geol.* 78, 132–149.

Coveney, R.M., Jr., Glascock, M.D., 1989. A review of the origins of metal-rich Pennsylvanian black shales, central U.S.A., with an inferred role for basinal brines. *Applied Geochem.* 4, 347–367.

Egenoff, S.O., Fishman, N.S., 2013. Traces in the dark—sedimentary processes and facies gradients in the Upper Shale Member of the Upper Devonian–Lower Mississippian Bakken Formation, Williston Basin, North Dakota, U.S.A. *J. Sed. Res.* 83, 803–824.

Erickson, B.E., Helz, G.R., 2000. Molybdenum(VI) speciation in sulfidic waters: stability and lability of thiomolybdates. *Geochim. Cosmochim. Acta* 64; 1149-1158.

Findlay, A.J., Gartman, A., MacDonald, D.J., Hanson, T.E., Shaw, T.J., Luther III, G.W., 2014. Distribution and size fractionation of elemental sulfur in aqueous environments: the Chesapeake Bay and Mid-Atlantic Ridge. *Geochim. Cosmochim. Acta* 142, 334-348.

Fleurance, S., Cuney, M., Malartre, F., Reyx, J., 2013. Origin of the extreme polymetallic enrichment (Cd, Cr, Mo, Ni, U, V, Zn) of the Late Cretaceous-early Tertiary Belqa Group, central Jordan. *Palaeogeogr., Palaeoclimatol., Palaeoecol.* 369, 201–219.

Francois, R., 1988. A study on the regulation of the concentrations of some trace metals (Rb, Sr, Zn, Pb, Cu, V, Cr, Ni, Mn and Mo) in Saanich Inlet sediments, British Columbia, Canada. *Marine Geol.* 83, 285–308.

French, K.L., Hallmann, C., Hope, J.M., Schoon, P., Zumberge, J.A., Hoshino, Y., Peters, C., C., George, S.C., Love, G.D., Brochs, J.J., Buick, R., Summons, R.E., 2015. Reappraisal of hydrocarbon biomarkers in Archean rocks. *Proceed. National Acad. Sci.* 112, 5915–5920.

Froelich, P.N., Klinkhammer, M.L., Bender, M.L., Luedtke, N.A., Heath, G.R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B., Maynard, V., 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. *Geochim. Cosmochim. Acta* 43, 1075–1090.

Gregory, D.D., Large, R.R., Halpin, J.A., Baturina, E.L., Lyons, T.W., Wu, S., Danyushevsky, L., Sack, P.J., Chappaz, A., Maslennikov, V.V., Bull, S.W., 2015. Trace element content of sedimentary pyrite in black shales. *Econ. Geol.* 110, 1389–1410.

Hageman, P.L., Brown, Z.A., Welsch, E., 2002. Arsenic and selenium by flow enjection or continuous flow-hydride generation-atomic absorption spectrophotometry, in Taggart, J.E., ed.,

Analytical methods for chemical analysis of geologic and other materials, U.S. Geological Survey: U.S. Geological Survey Open-File Rept. 02-223, pp. L1-L7.

Hatch, J.R., Leventhal, J.S., 1992. Relationship between inferred redox potential of the depositional environment and geochemistry of the Upper Pennsylvanian (Missourian) Stark Shale Member of the Dennis Limestone, Wabaunsee County, Kansas, U.S.A. *Chem. Geol.* 99, 65-82.

Hatch, J.R., Leventhal, J.S., 1997. Early diagenetic partial oxidation of organic matter and sulfides in the Middle Pennsylvanian (Desmoinesian) Excello Shale Member of the Fort Scott Limestone and equivalents, northern Midcontinent region, USA. *Chem. Geol.* 134, 215-235.

Helz, G.R., Miller, C.V., Charnock, J.M., Mosselmans, J.F.W., Patrick, R.A.D., Garner, D.D., Vaughan, D.J., 1996. Mechanism of molybdenum removal from the sea and its concentration in black shales: EXAFS evidence. *Geochim. Cosmochim. Acta* 60, 3631-3642.

Holland, F.D., Jr., Hayes, M.D., Thrasher, L.C., Huber, T.P., 1987. Summary of the biostratigraphy of the Bakken Formation (Devonian and Mississippian) in the Williston Basin, North Dakota. In: Carlson, C.G., Christopher, J.E. (Eds.), 5th International Williston Basin Symposium. *Saskatch. Geol. Soc. Spec. Publ.* 9, pp. 68-76.

Huerta-Diaz, M.A., Morse, J.W., 1992. Pyritization of trace metals in anoxic marine sediments. *Geochim. Cosmochim. Acta* 56, 2681-2702.

- Jiang, C., Maowen, Li., Osadetz, K.G., Snowdon, L.R., Obermajor, M., Fowler, M.G., 2001. Bakken/Madison petroleum systems in the Canadian Williston Basin. Part 2: molecular markers diagnostic of Bakken and Lodgepole source rocks. *Organic Geochem.* 32, 1037–1054.
- Johnston, D.T., Poulton, S.W., Dehler, C., Porter, S., Husson, J., Canfield, D.E., Knoll, A.H., 2010. An emerging picture of Neoproterozoic ocean chemistry: insights from the Chuar Group, Grand Canyon, USA. *Earth Planet. Sci. Letters* 290, 64–73.
- Kelley, K.D., Graham, G.E., Benzel, W.M., 2015. Extent of metalliferous intervals and principal hosts of Mo, Ni, V, and Zn in oil shale of the Mississippian Heath Formation, Montana, USA. In: André-Mayer, A.-S., Cathelineau, M., Muehez, P., Piraid, E., Sindern, S. (Eds.), *Mineral resources in a sustainable world. Proceed. 13th Biennial Mtg., Society for Geology Applied to Mineral Deposits (SGA), Nancy, France, August 24-27, 2015*, v. 4, pp. 1937–1940.
- Lewan, M.D., 1984. Factors controlling the proportionality of vanadium to nickel in crude oils. *Geochim. Cosmochim. Acta* 48, 2231–2238.
- Lewan, M.D., Maynard, J.B., 1982. Factors controlling enrichment of vanadium and nickel in the bitumen of organic sedimentary rocks. *Geochim. Cosmochim. Acta* 46, 2547–2560.

Li, X., Cutter, G.A., Thunell, R.C., Tappa, E., Gihooly III, W.P., Lyons, T.W., Astor, Y., Scranton, M.I., 2011. Particulate sulfur species in the water column of the Cariaco Basin. *Geochim. Cosmochim. Acta* 75, 148–163.

Lillis, P.G., 2013. Review of oil families and their petroleum systems of the Williston Basin. *Mountain Geol.* 50, 5–31.

Little, S.H., Vance, D., Lyons, T.W., McManus, J., 2015. Controls on trace metal authigenic enrichment in reducing sediments: insights from modern oxygen-deficient settings. *Amer. Jour. Sci.* 315, 77–119.

Lyons, T.W., Berner, R.A., 1992. Carbon-sulfur-iron systematics of the uppermost deepwater sediments of the Black Sea. *Chem. Geol.* 99, 1–27.

Lyons, T.W., Severmann, S., 2006. A critical look at iron paleoredox proxies: new insights from modern euxinic marine basins. *Geochim. Cosmochim. Acta* 70, 5698–5722.

Lyons, T.W., Werne, J.P., Hollander, D.J., Murray, R.W., 2003. Contrasting sulfur geochemistry and Fe/Al and Mo/Al ratios across the last oxic-to-anoxic transition in the Cariaco Basin, Venezuela. *Chem. Geol.* 195, 131–157.

Manske, A.K., Glaeser, J., Kuypers, M.M.M., Overmann, J., 2005. Physiology and phylogeny of green sulfur bacteria forming a monospecific phototrophic assemblage at a depth of 100 meters in the Black Sea. *Applied Environ. Microbiol.* 71, 8049–8060.

McManus, J., Berelson, W.M., Severmann, S., Poulson, R.L., Hammond, D.E., Klinkhamer, G.P., Holm, C., 2006. Molybdenum and uranium geochemistry in continental margin sediments: paleoproxy potential. *Geochim. Cosmochim. Acta* 70, 4643–4662.

Meier, A.L., Slowik, T., 2002. Rare earth elements by inductively coupled plasma-mass spectrometry, in Taggart, J.E., ed., *Analytical methods for chemical analysis of geologic and other materials*. U.S. Geological Survey Open-File Rept. 02–223, pp. K1–K8.

Murray, J. W., Jannasch, H. W., Honjo, S., Anderson, R. F., Reeburgh, W. S., Top, Z., Friederich, G. E., Codispoti, L. A., and Izdar, E., 1989. Unexpected changes in the oxic/anoxic interface in the Black Sea: *Nature* 338, 411–413.

Nameroff, T.J., Balistrieri, L.S., Murray, J.W., 2002. Suboxic trace metal geochemistry in the eastern tropical North Pacific. *Geochim. Cosmochim. Acta* 66, 1139–1158.

Overmann, J., Beatty, J.T., Krouse, H.R., Hall, K.J., 1996. The sulfur cycle in the chemocline of a meromictic salt lake. *Limnol. Oceanogr.* 41, 147-156.

Partin, C.A., Bekker, A., Planavsky, N.J., Scott, C.T., Gill, B.C., Podkovyrov, V., Maslov, A., Lalonde, S.V., Love, G.D., Poulton, S.W., Lyons, T.W., 2013. Large-scale fluctuations in Precambrian atmospheric and oceanic oxygen levels from the record of U in shales. *Earth Planet. Sci. Letters* 369–370, 284–293.

Pašava, J., Hladikova, J., Dobes, P., 1996. Origin of Proterozoic metal-rich black shales from the Bohemian massif, Czech Republic. *Econ. Geol.* 91, 63–79.

Peacor, D.R., Coveney, R.M., Zhao, G., 2000. Authigenic illite and organic matter: the principal hosts of vanadium in the Mecca Quarry Shale at Velpen, Indiana. *Clays Clay Min.* 48, 311–316.

Perkins, R.B., Piper, D.Z., Mason, C.E., 2008. Trace-element budgets in the Ohio/Sunbury shales of Kentucky: constraints on ocean circulation and primary productivity in the Devonian-Mississippian Appalachian Basin. *Paleogeogr. Paleoclimatol. Paleoecol.* 265, 14–29.

Peters, S.E., Loss, D.P., 2012. Storm and fair-weather wave base: a relevant distinction? *Geology* 40, 511–514.

Piper, D.Z., Dean, W.E., 2002. Trace-element deposition in the Cariaco Basin, Venezuela shelf, under sulfate-reducing conditions—a history of the local hydrography and global climate, 20 ka to the present. *U.S. Geol. Survey Prof. Paper* 1670, 41 pp.

- Planavsky, N.J., Reinhard, C.T., Wang, X., Thomson, D., McGoldrick, P., Rainbird, R.H., Johnson, R., Fischer, W.W., Lyons, T.W., 2014. Low Mid-Proterozoic atmospheric oxygen levels and the delayed rise of animals. *Science* 346, 635-638.
- Raiswell, R., Canfield, D.E., 1998. Sources of iron for pyrite formation in marine sediments. *American Jour. Sci.* 298, 219–245.
- Raiswell, R., Buckley, F., Berner, R.A., Anderson, T.F., 1988. Degree of pyritization of iron as a paleoenvironmental indicator. *Jour. Sed. Petrol.* 58, 812–819.
- Reis, M.A.M., Almeida, J.S., Lemos, P.C., Carrondo, M.J.T., 1992. Effect of hydrogen sulfide on growth of sulfate reducing bacteria. *Biotechnol. Bioengineer.* 40, 593–600.
- Requejo, A.G., Allan, J., Creaney, S., Gray, N.R., Cole, K.S., 1992. Aryl isoprenoids and diaromatic carotenoids in Paleozoic source rocks and oils from the western Canada and Williston Basins. *Org. Geochem.* 19, 245–264.
- Ripley, E.M., Shaffer, N.R., Gilstrap, M.S., 1990. Distribution and geochemical characteristics of metal enrichment in the New Albany Shale (Devonian-Mississippian), Indiana. *Econ. Geol.* 85, 1790–1807.
- Sadiq, M., 1988. Thermodynamic stability relationships of inorganic vanadium in the marine environment. *Marine Chem.* 23, 87–96.

Sageman, B.B., Murphy, A.E., Werne, J.P., Ver Straeten, C.A., Hollander, D.J., Lyons, T.W., 2003. A tale of shales: the relative roles of production, decomposition, and dilution in the accumulation of organic-rich strata, Middle-Upper Devonian, Appalachian basin. *Chem. Geol.* 195, 229–273.

Sahoo, S.K., Planavsky, N.J., Kendall, B., Wang, X., Shi, X., Scott, C., Anbar, A.D., Lyons, T.W., Jiang, G., 2012. Ocean oxygenation in the wake of the Marinoan glaciation. *Nature* 489, 546–549.

Schieber, J., 2014. Traces in the dark—sedimentary processes and facies gradients in the Upper Shale Member of the Upper Devonian–Lower Mississippian Bakken Formation, Williston Basin, North Dakota, U.S.A. —Discussion. *J Sed. Res.* 84, 837–838.

Scholz, F., Hensen, C., Noffke, A., Rohde, A., Liebertrau, V., Wallmann, K., 2011. Early diagenesis of redox-sensitive trace metals in the Peru upwelling area—response to ENSO-related oxygen fluctuations in the water column. *Geochim. Cosmochim. Acta* 75, 7257–7276.

Scott, C., Lyons, T.W., 2012. Contrasting molybdenum cycling and isotopic properties in euxinic versus non-euxinic sediments and sedimentary rocks: refining the paleoproxies. *Chem. Geol.* 324, 19–27.

Scott, C.T., Lyons, T.W., Bekker, A., Poulton, S.W., Shen, Y., Chu, X., Anbar, A.D., 2008. Tracing the stepwise oxygenation of the Proterozoic ocean. *Nature* 452, 456–460.

Scott, C., Planavsky, N.J., Dupont, C.L., Kendall, B., Gill, B.C., Robbins, L.J., Husband, K.F., Arnold, G.L., Wing, B.A., Poulton, S.W., Bekker, A., Anbar, A.D., Konhauser, K.O., Lyons, T.W., 2013. Bioavailability of zinc in marine systems through time. *Nature Geosci.* 6, 125–128.

Scott, C., Kelley, K.D., Slack, J.F., 2014. The geobiology of sediment-hosted mineral deposits. In: Kelley, K.D., Golden, H.C. (Eds.), *Building exploration capability for the 21st Century*. Society Economic Geologists Spec. Publ. 18, pp. 17–35.

Skei, J., Loring, D.H., Rantala, R.T.T., 1988. Partitioning and enrichment of trace metals in a sediment core from Framvaren, south Norway. *Marine Chem.* 23, 269–281.

Slack, J.F., Selby, D., Dumoulin, J.A., 2015. Hydrothermal, biogenic, and seawater components in metalliferous black shales of the Brooks Range, Alaska: syngenetic metal enrichment in a carbonate ramp setting. *Econ. Geol.* 110, 653–675.

Smith, M.G., Bustin, R.M., 1996. Lithofacies and paleoenvironments of the Late Devonian and Early Mississippian Bakken Formation, Williston Basin. *Canad. Soc. Petrol. Geol. Bull.* 44, 495–507.

Smith, M.G., Bustin, R.M., 1998. Production and preservation of organic matter during deposition of the Bakken Formation (Late Devonian and Early Mississippian), Williston Basin. *Paleogeogr., Paleoclimatol., Paleoecol.* 142, 185–200.

Smith, M.G., Bustin, R.M., Caplan, M.L., 1995. Sequence stratigraphy of the Bakken and Exshaw formations: a continuum of black shale formations in the western Canada sedimentary basin. In: Hunter, L.D.V., Schalla, R.A. (Eds.), 7th International Williston Basin Symposium. Montana Geol. Soc. Spec. Publ., pp. 399–409.

Sørensen, K., 1988. The distribution and biomass of phytoplankton and phototrophic bacteria in Framvaren, a permanently anoxic fjord in Norway. *Marine Chem.* 23, 229–241.

Sperling, E.A., Carbone, C., Strauss, J.V., Johnston, D.T., Narbonne, G.M., Macdonald, F.A., 2016. Oxygen, facies, and secular controls on the appearance of Cryogenian and Ediacaran body and trace fossils in the Mackenzie Mountains of northwestern Canada. *Geol. Soc. Amer. Bull.* 128, 558–575.

Taggart, J.E., Siems, D.F., 2002. Major element analysis by wavelength dispersive X-ray fluorescence spectrometry, in Taggart, J.E., ed., *Analytical methods for chemical analysis of geologic and other materials*. U.S. Geological Survey Open-File Rept. 02–223, pp. T1–T9.

Taylor, S.R., McLennan, S.M., 1995. The geochemical evolution of the continental crust. *Rev. Geophys.* 33, 241–265.

Tribovillard, N., Algeo, T.J., Lyons, T., Riboulleau, A., 2006. Trace metals as paleoredox and paleoproductivity proxies: an update. *Chem. Geol.* 232, 12–32.

Turekian, K.K., Wedepohl, K.H., 1961. Distribution of the elements in some major units of Earth's crust. *Geol. Soc. Amer. Bull.* 72, 175–192.

Van Gernerden, H., 1984. The sulfide affinity of phototrophic bacteria in relation to the location of elemental sulfur. *Arch. Microbiol.* 139, 289–294.

Wanty, R.B., Goldhaber, M.B., 1992. Thermodynamics and kinetics of reactions involving vanadium in natural systems: accumulation of vanadium in sedimentary rocks. *Geochim. Cosmochim. Acta* 56, 1471–1483.

Werne, J.P., Hollander, D.J., Behrens, A., Schaeffer, P., Albrecht, P., Sinninghe Damsté, J.S., 2000. Timing of early diagenetic sulfurization of organic matter: a precursor-product relationship in Holocene sediments of the Cariaco Basin, Venezuela. *Geochim. Cosmochim. Acta* 64, 1741–1751.

Werne, J.P., Sageman, B.B., Lyons, T.W., Hollander, D.J., 2002. An integrated assessment of a “type euxinic” deposit: evidence for multiple controls on black shale deposition in the Middle Devonian Oatka Creek Formation. *Amer. Jour. Sci.* 302, 110–143.

Wignall, P.B., 1994. Black shales. Oxford Monographs on Geology and Geophysics, v. 30, 127 pp.

Wilde, P., Lyons, T.W., Quinby-Hunt, M.S., 2004. Organic carbon proxies in black shales: molybdenum. *Chem. Geol.* 206, 167–176.

Wing, B.A., Halevy, I., 2014. Intracellular metabolite levels shape sulfur isotope fractionation during microbial sulfate respiration. *Proceed. National Acad. Sci.* 111, 18,116–18,125.

Zheng, Y., Anderson, R.F., Van Geen, A.L., Kuwabara, J., 2000. Authigenic molybdenum formation in marine sediments: a link to pore water sulfide in the Santa Barbara Basin. *Geochim. Cosmochim. Acta* 64, 4165–4178.

Figure 1. Extent of Late Devonian to Early Mississippian Bakken Formation (shaded area) in the United States and Canada showing locations of drill cores sampled for this study. Dashed lines indicate the international boundary between the United States and Canada.

Figure 2. A schematic stratigraphic column of the Bakken Formation. After Egenhoff and Fishman (2013).

Figure 3. Comparison of bulk and authigenic concentrations of (A) Mo, (B) V, and (C) Zn in Bakken Formation black shales. Blue crosses represent bulk trace metal concentrations. Black circles represent authigenic concentrations, defined as $TM_{auth} = TM_{bulk} - (TM/Al)_{crust} * Al_{bulk}$. Red circles in C represent authigenic fraction, defined as $TM_{auth} = TM_{bulk} - ((TM/Al)_{crust} * Al_{bulk}) - (TOC * (Zn/TOC)_{phytoplankton})$. The Zn/C ratio of 0.036 mmol/mol for phytoplankton is from Little et al. (2015).

Figure 4. Comparison of total sulfur (TS) and total organic carbon (TOC) contents in Bakken Formation black shales. Green symbols represent samples from Upper Member and gray symbols represent samples from Lower Member. Total sulfur concentrations of data points a, b, and c are 10.5, 11.7, and 12.2 wt.%, respectively.

Figure 5. Comparison of total iron (FeT) and total sulfur (TS) contents in Bakken Formation black shales. Symbols as in Fig. 4. Dashed line represents the ratio of Fe/S by weight in FeS_2 ($\text{Fe/S} = 0.87$).

Figure 6. Comparison of Molybdenum (Mo) and total organic carbon (TOC) contents in Bakken Formation black shales. Symbols as in Fig. 4. Concentration of Mo for point a is 1810 mg/kg.

Figure 7. Comparison of vanadium (V) and total sulfur (TS) contents in Bakken Formation black shales. Symbols as in Fig. 4. The V concentration of data point a is 2540 mg/kg; TS concentrations of data points b, c, and d are 12.2, 11.7, and 10.5 wt. %, respectively.

Figure 8. Comparison of zinc (Zn) and total sulfur (TS) contents in Bakken Formation black shales. Symbols as in Fig. 4. Zinc concentrations for data points a-f are 6910, 3990, 19300, 4980, 6950, and 2800 mg/kg, respectively. Zinc and total sulfur are 38,000 mg/kg and 10.5 wt.% for data point g; 10,400 mg/kg and 11.7 wt. % for data point h; and 7550 mg/kg and 12.2 wt.% for data point i.

Figure 9. Schematic of proposed depositional model for black shales of Bakken Formation. Water depths are less than 150 m and sediments contain between 10 and 20 wt.% TOC. H_2S is present in bottom waters at concentrations high enough (~ 10 mM) to trigger V hyper-enrichment in sediments. H_2S is present at bottom of photic zone, allowing for activity of phototrophic sulfide-oxidizing bacteria and hyper-enrichment of Zn.

Figure 10. Comparison of zinc (Zn) and vanadium (V) contents in Bakken Formation black shales. Symbols as in Fig. 4. Nearly all occurrences of Zn hyper-enrichment (>500 mg/kg) indicating photic-zone euxinia are accompanied by V hyper-enrichments (>500 mg/kg) indicative of hyper-sulfidic bottom waters (~ 10 mM H_2S). Zinc concentrations of data points a-i are 19300, 3900, 38000, 10400, 7550, 6910, 4980, 2800, 6950 mg/kg, respectively. Concentration of V in data point j is 2540 mg/kg.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10