Redox chemistry and molybdenum burial in a Mesoproterozoic lake

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Key Points:

- Fe, Mo, and U sediment geochemistry of the Nonesuch Formation (~1.1 Ga; USA) indicate fluctuating oxic and anoxic redox chemistry
- Mo and U covariation in the Nonesuch Formation and modern analogue sediments confirm euxinia is not necessary for moderate Mo burial
- Comparison of Nonesuch Formation and modern analogue indicates that Proterozoic lakes are unlikely to constrain atmospheric oxygen

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Abstract

While marine sediments have been used to constrain a history of redox chemistry throughout the Precambrian, far fewer data have been generated from lakes. With major biological innovations thought to have occurred in Proterozoic lakes, understanding their chemistry is critical for understanding the evolution of eukaryotic life. We use sediment geochemistry to characterize the redox conditions of the Nonesuch Formation (~1.1 Ga) and a modern analogue for the Proterozoic: the Middle Island Sinkhole (MIS) in Lake Huron (USA). Iron speciation, Mo contents, and Mo-U covariation demonstrate oxic and anoxic—not euxinic—environments, with no clear indicators of enhanced biological productivity in the Nonesuch Formation. Moderate Mo enrichments observed in the Nonesuch Formation are not attributed to euxinia, but instead to an authigenic particulate shuttle. We suggest that the Fe and Mo sediment geochemistry of these lacustrine systems reflect only local water column and sediment burial conditions, and not atmospheric oxygenation.

Plain language summary

Lakes are proposed to have been critical environments for the evolution of life during the Proterozoic (~2.5 to 0.5 billion years ago). However, relatively little is known about the chemistry of ancient lakes, including the availability of oxygen for biological productivity, and how local oxygen availability can be extrapolated to understand global oxygen availability. In addition, with no lakes remaining from the Proterozoic, the only way to study ancient lakes is to use the chemistry of the sediments left behind. This study uses the sediment chemistry of elements that are sensitive to oxygen to understand oxygen availability in a Proterozoic lake environment. This data was then compared to modern lake environments with known chemistry and oxygen levels in order to interpret the results better. We found that oxygen availability in the Proterozoic lake was variable, with no clear indicators of abundant biological productivity. We conclude that ancient lake sediments only constrain the chemistry of the local environment, with no major implications for global or even regional atmospheric oxygenation.

1 Introduction

Geochemical characterizations of ancient marine sediments have been used successfully to investigate shifts in atmospheric oxygenation throughout the Precambrian (e.g. Farquhar, Bao, & Thiemens, 2000). For the mid-Proterozoic, ocean redox chemistry and atmospheric oxygenation has been hotly debated, with geochemical methods indicating variable marine redox conditions, and subsequently, various interpretations of atmospheric oxygenation (e.g. Sperling et al., 2014; Planavsky et al., 2018). In comparison, fewer geochemical data have been generated from Proterozoic lakes to constrain the redox chemistry of terrestrial environments. However, there is increasing evidence that Proterozoic lakes—not oceans— may have been critical habitats for biological evolutions (e.g. the diversification of cyanobacteria and early eukaryotic life; Blank & Sánchez-Baracaldo, 2010; Strother et al., 2011; Blank, 2013). As a result, it becomes increasingly important to understand the habitats wherein these major evolutions took place. Constraining the geochemistry of Proterozoic lake environments can help to characterize the conditions wherein multicellular life may have evolved. Molybdenum (Mo), a redox-sensitive trace element, has been intensively used as a paleo redox proxy, mostly to identify periods of past anoxia (Chappaz, Glass, & Lyons, 2018; Hardisty et al., 2018). In presence of sulfide ($\sum$S(–II) = $H_2S + HS^- + S^{2-}$), Mo can be scavenged in sediment via two pathways: (1) through association with Fe–S minerals (e.g. Chappaz et al., 2014; Helz and Vorlieck, 2019) and (2)

through interactions with organic matter (e.g. Ardakani, Chappaz, Sanei, & Mayer, 2016; Wagner, Chappaz, & Lyons, 2017; Tessin, Chappaz, Hendy, & Sheldon, 2018). As a consequence, Mo enrichments can exceed crustal levels by two orders of magnitude when ∑S(–II) is present within the water column (euxinia; Scott and Lyons, 2012). In addition, Mo is a cofactor in many metabolic pathways and has consequently played a key role in biospheric evolution (Lyons, Reinhard, & Planavsky, 2014). Geobiologically speaking, Mo is an essential micronutrient strongly integrated into the nitrogen cycle, including vital roles in N_2 fixation and fixed nitrogen assimilation, and is a key element limiting primary productivity in lakes (Goldman, 1960; Howarth & Cole, 1985; Glass et al., 2012).

The relationship between geochemistry and biological evolution in Mesoproterozoic lakes has been studied using the Stoer Group (1.18 Ga) of the Torridonian Supergroup, UK (Parnell, Boyce, Mark, Bowden, & Spinks, 2010; Parnell, Spinks, Andrews, Thayalan, & Bowden, 2015). Based upon ample burial of Mo in Stoer Group sediments, Parnell et al. (2015) concluded that oxygenation of terrestrial environments increased oxidative weathering and sulfate delivery to lakes, allowing for widespread euxinia to develop and for abundant nutrients that spurred enhanced biological productivity. However, Mo and Sr isotope data indicate that much of the Stoer Group is marine or marine-influenced, and not strictly lacustrine (Stüeken et al., 2017). Therefore, if the Stoer Group is not appropriate for understanding redox chemistry Proterozoic lakes, we must consider other systems to investigate Mesoproterozoic lacustrine geochemistry. Here, we examine the Fe and Mo geochemistry of the Nonesuch Formation (~1.1 Ga; Figure 1a) of the Keweenaw Supergroup, as well as two modern analogues for Proterozoic waters—the low-oxygen Middle Island Sinkhole (MIS) and an oxic Lake Huron control site (LH; Figure 1b) —to test the conclusions made by Parnell et al. (2015) and to assess whether euxinia and enhanced biological productivity were widespread during the Mesoproterozoic in terrestrial environments.

2 Site Descriptions

2.1 The Nonesuch Formation

The Nonesuch Formation is comprised of sandstones, mudstones, and rare limestone interbeds that were deposited as part of the Midcontinent Rift System (Elmore, Milavec, Imbus, & Engel, 1989). This formation—which is bookended by alluvial fan and fluvial depositional environments, and incorporates one or possibly a series of rift lakes (Suszek, 1997)—includes diverse freshwater phytoplankton microfossils (Wellman & Strother, 2015). Further, the Nonesuch Formation interfingers in places with the Copper Harbor Conglomerate (1.09 Ga), which features alluvial fan and fluvial facies, and lacustrine stromatolite mounds (Elmore, 1983; Wilmeth, Dornbos, Isbell, & Czaja, 2014; Fedorchuk et al., 2016). Therefore, there is an abundance of evidence that the Nonesuch Formation is comprised of fluctuating freshwater environments, and lacks significant marine influence. This work uses samples from cores DO-6, PI-2, and WPB-4(Figure 1a), incorporating shore-proximal and shore-distal lacustrine units possibly from two different lake sub-basins (Suszek, 1997). This work includes samples from mudstone beds with consistent stratigraphic spacing (roughly every 1–5 m) for each of these three cores. Nonesuch Formation geochemical data and interpretations of redox chemistry are compared to that of core PI-1 (Cumming, Poulton, Rooney, & Selby, 2013), and DO-8 and WC-9 (Slotznick, Swanson-Hysell, & Sperling, 2018), which also may also encompass additional lake sub-basins.

2.2 The Middle Island Sinkhole (MIS)

Located in Lake Huron (Figure 1b), the Middle Island Sinkhole is a 23 m deep karst feature wherein low-oxygen high-sulfate groundwater seeps into the sinkhole, resulting in low (<5%) dissolved oxygen and 7.8 mM sulfate that persists 1–3 meters above the sediment-water interface (Ruberg et al. 2008).This water chemistry is comparable to proposed levels for mid-Proterozoic waters, which are inferred to have little to no oxygen (e.g. Shen, Canfield, & Knoll, 2002; Lyons et al., 2014), and sulfate concentrations in the range of <2 mM to ~10 mM (Olson, Reinhard, & Lyons, 2016; Blättler et al., 2018. As a result of this water chemistry, dynamic microbial mats grow at this interface, including cyanobacteria that conduct both oxygenic and anoxygenic photosynthesis (Voorhies et al., 2012), and are therefore similar to the versatile cyanobacteria proposed to have dominated Proterozoic aquatic systems (Johnston, Wolfe-Simon, Pearson, & Knoll, 2009; Voorhies et al., 2012). Redox chemistry of MIS allows for the burial of nutrient- and metal-rich sediments below the microbial mat (Nold et al., 2013; Kinsman-Costello et al., 2017; Rico & Sheldon, 2019). With water chemistry and microbiology similar to what has been inferred for the Proterozoic, MIS has been considered an analogue to interpret biogeochemical cycling in shallow Proterozoic waters (Voorhies et al., 2012; Kinsman-Costello et al., 2017; Rico & Sheldon, 2019).

A Lake Huron (LH) control site of comparable depth to MIS is used to provide an oxic endmember. LH, which is 0.6 km away from MIS (Figure 1b), is comprised of mudstones like MIS, but has limited groundwater influence and no evidence of a microbial mat at the sediment water interface (Kinsman-Costello et al., 2017). Porewater and sediment geochemistry, and microbial community assemblage, differ between MIS and LH (Kinsman-Costello et al., 2017; Rico & Sheldon, 2019). For MIS and LH, samples encompass surficial sediments (<25 cm depth).

3 Methods

MIS (n = 56), LH (n = 22) Mo, U, and Al contents, and Nonesuch Formation (n = 113) Mo, Fe, U, Al, S, and P concentrations were analyzed at ALS Laboratories in Vancouver, British Columbia, where samples were digested with perchloric, hydrofluoric, nitric, and hydrochloric acids, and concentrations were determined by ICP-OES and ICP-MS calibrated using internal standards. Major element precision was better than 0.2 wt.%. A single outlier for LH with respect to Mo was excluded from this work. To compare the respective enrichments of Mo and U in the study locations, trace metal concentrations are given in the form of enrichment factors (EFs), which were calculated as:

$$X_{EF} = [(X/Al)_{sample}/(X/Al)_{background}] \quad (1)$$

where X and Al represent the weight percent concentrations of elements X and Al, respectively. For the Nonesuch Formation, samples are normalized using the post-Archean average shale (PAAS) compositions of Taylor and McLennan (1985). LH and MIS samples were normalized using average Lake Huron background values of Mo (0.25 ± 0.05 ppm), U (1.02 ± 0.15 ppm), and Al (3.1 ± 1.1 wt. %; after Chappaz, Gobeil, & Tessier, 2008). While there are potential pitfalls with any normalization (e.g. PAAS may not be representative of local sediments; Van der Weijden, 2002), because this study aims to compare respective enrichments of Mo and U, the

differences in reference material between our study sites should not have major implications for our overall interpretations.

For total organic carbon (TOC) analyses, Nonesuch Formation samples (n = 112) were washed with a 1–2N HCl solution to remove carbonates, rinsed, and oven-dried overnight at 50°C. In order to get TOC of the bulk sample, acidified and unacidified sample pairs were loaded into tin capsules, and analyzed using a Costech ECS4010 elemental analyzer in UM's Earth System Science Lab. Acetanilide (%C = 71.09, %N = 10.36) was used to calibrate elemental composition.

Fe speciation for the Nonesuch Formation (n = 55) samples was determined using a three-step sequential extraction developed by Poulton and Canfield (2005). Pyrite concentrations were stoichiometrically determined via titration of chromium reducible sulfide precipitated as ZnS (Canfield, Raiswell, Westrich, Reaves, & Berner, 1986). The total highly reactive pool of iron (iron that is highly reactive towards sulfide; Fe_{HR}; Poulton & Canfield, 2005) represents the sum of these four extractions. Detailed methods are given in Table S1 in the supporting information. Iron in the Nonesuch Formation sequential extraction solutions were analyzed by ICP-MS within the STARLAB at Central Michigan University. Uncertainties for all Fe pools were less than 0.2 wt. %. All of the sediment geochemical data (this work) are presented in Tables S2–S3 in the Data Repository.

To calibrate "normal" distributions of Mo and U in large lakes, water column samples were collected at three stations in August 2014 at 10 different depths using Niskin bottles aboard R/V Blue Heron in Lake Superior. Within 1 hour and in a clean environment, all water samples were filtered with 0.45 µm syringe nylon filters and transferred into 50 mL HDPE (previously acid washed) tubes filled with 1 mL of HNO_3 high purity (Optima, 2% v/v). Molybdenum and U concentrations were determined at the STARLAB at Central Michigan University using ICP-MS analysis and external calibration.

4 Results and Discussion

4.1 Redox chemistry of the Nonesuch Formation

Analysis of Fe speciation uses Fe_{HR}/Fe_T and Fe_{py}/Fe_{HR} to differentiate between oxic, ferruginous (Fe(II) within the water column), anoxic ($\sum$S(–II) only present in the porewater) and euxinic conditions (e.g. Tessin, Sheldon, Hendy, & Chappaz, 2016). Previous Fe speciation data for the Nonesuch Formation from a nearby core (Figure 1) to the ones examined herein indicate predominantly ferruginous conditions (Cumming et al., 2013; Figure S1). In contrast, magnetic Fe mineralogy and petrographic data from two cores in Northern Wisconsin have been interpreted to indicate that the Nonesuch Formation there featured oxic water columns (Slotznick et al., 2018). Thus, one possibility for this discrepancy is that the proxies are not reliably recording water column oxygenation. However, modern sequential Fe extraction results appropriately define MIS as ferruginous and LH as oxic (Figure 2; Rico & Sheldon, 2019), matching their known oxygen levels, so we consider the Fe-based proxies to be reliable. The new Nonesuch Formation data mostly indicate oxic or possibly anoxic conditions (Figure 2), with significant overlap between individual cores (DO-6, PI-2, WPB-4; Figure S1). Notably, Fe speciation results indicate that the oxic LH sediments are more anoxic than the majority of the Nonesuch Formation samples. This is driven by an Fe limitation in LH; there is a much higher relative abundance (~5x LH) of Fe_T in the Nonesuch Formation. As cautioned by Raiswell et al. (2018), this work suggests that discrepancies in local Fe enrichments need to be considered when comparing Fe speciation results for spatially or temporally separate aquatic systems.

Iron speciation results for much of the Nonesuch Formation sediments indicate a high degree of pyritization with oxic deposition (Figure 2), which is rare for modern systems (Tables S2 and S3). However, especially with limited oxygen availability in the mid-Proterozoic (e.g. Planavsky et al., 2018), reduced chemical species such as pyrite are to be expected when oxygen is consumed. In contrast, MIS does not display a high degree of pyritization, likely attributed to a sulfide limitation in porewater (which fluctuates between 0–7 mM H_2S; Kisman-Costello et al., 2017). Given that the Nonesuch Formation is likely comprised of a series of rift basins (Suszek, 1997), data from this study could incorporate separate lake systems that overlap with those of previously published data from Cumming et al. (2013) and Slotznick et al. (2018). Taken together, variability in interpretations of Fe geochemistry in the Nonesuch Formation could in part reflect real spatial and temporal variability in water chemistries and depths of the sedimentary environments.

4.2 Molybdenum burial in the Nonesuch Formation

The modern anoxic analogue and oxic lake sediments exhibit a large range in organic C contents (0.3–10.4%), whereas their Mo contents are consistently low (<1 ppm; Figure 3), regardless of redox conditions. In comparison, the Nonesuch Formation samples exhibit a smaller range in organic C (0–1.7%) but feature higher Mo concentrations (0.12–40 ppm; Figure 3). However, both the modern systems and the Nonesuch Formation exhibit Mo contents far below what is anticipated for euxinic conditions (e.g. as in the Stoer Group; Figure 3).

The highest accumulation of authigenic Mo is conventionally attributed to the presence of free sulfide ($\sum$S(–II); i.e. euxinic conditions) and subsequent formation of thiomolybdates (Erickson & Helz, 2000; Vorlicek et al., 2015). Some Nonesuch Formation samples exhibit Mo enrichments relative to the modern systems (Figure 3), yet there is no evidence for persistent euxinia in any of the lake environments (Table 1; Figures 2 and 3). To refine the mechanisms that could control Mo burial, the Mo-U covariation was evaluated across all of our sites.

Trends in Mo-U covariation for modern and ancient marine systems have been linked to the controls on Mo deposition in sediments (Algeo & Tribovillard, 2009; Tribovillard, Algeo, Baudin, & Riboulleau, 2012). Molybdenum enrichments can occur: 1) via a "particulate shuttle" wherein authigenic Mo is scavenged by metal hydroxides (e.g. Mn and Fe), transported through the water column, and buried in sediments (authigenic U does not get scavenged in this process, resulting in a high Mo_{EF} and comparably low U_{EF}) or 2) via a shift from suboxic to anoxic to euxinic water chemistry, enabling an enrichment in U under suboxia, and then enhanced burial of Mo in the presence of free sulfide (i.e. the "unrestricted marine" trend wherein U_{EF} increases then Mo_{EF} increases; Algeo & Tribovillard, 2009). The Mo_{EF}/U_{EF} method uses mass ratios from modern seawater to designate threshold concentrations that can be related to depositional processes. Average seawater concentrations for Mo and U are 10.6 and 3.1 ppb, respectively (Mo/U = 3.4 Algeo & Tribovillard, 2009). Throughout the entire water column at three different stations in Lake Superior (max depth of 315 m), average concentrations for Mo and U are 0.13 and 0.04 ppb, respectively (n = 30; Mo/U = 3.3; Table S4). Given that the Mo_{EF}/U_{EF} method is based on ratios (not total concentration), the fact that $Mo/U_{seawater}$ is almost identical to the $Mo/U_{Lake\ Superior}$ (3.4 vs. 3.3) implies that the approach developed by Algeo and Tribovillard (2009) can be applied to our lacustrine systems.

As a fully oxygenated system, LH sediments are anticipated to have little Mo and U enrichment; this is corroborated by low EFs in Figure 4. MIS sediments are more enriched in Mo and U relative to LH sediments, with no overlap, and may follow the "particulate shuttle"

pathway of Mo burial (Figure 3). In comparison, ~30% of the Nonesuch Formation data are enriched (EF > 1) for Mo and U, with only a few samples exhibiting substantial enrichment (EF > 10). However, the samples that are enriched fall along the "particulate shuttle" pathway (Figure 4). This suggests that for the Nonesuch Formation, euxinic conditions are not directly causing Mo enrichments. Instead, the dominant burial mechanism for Mo is the "particulate shuttle" pathway; enrichments in Fe_T and Fe_{ox} (Table S3) may have favored Mo enrichments via this pathway relative to MIS and LH.

4.3 Implications for biological productivity and atmospheric oxygen

Based upon sediment Mo geochemistry in the Mesoproterozoic Stoer Group, Parnell et al. (2015) hypothesized that high atmospheric pO_2 in the Mesoproterozoic would have increased delivery of sulfate, resulting in 1) sulfate reduction and significant Mo burial via sulfides in lakes (i.e. widespread euxinia), and 2) no nutrient limitation and therefore high levels of biological productivity. While the Stoer Group is marine-influenced, and not strictly lacustrine (Stüeken et al., 2017), Parnell et al. (2015) provide a testable hypothesis for Mesoproterozoic lake environments. The Stoer Group Mo contents are greater than both those of the Nonesuch Formation and the modern systems (Figure 3) and could be the result of post depositional processes remobilizing and enriching Mo (e.g. Ardakani et al., 2016). When combining our different approaches (Fe speciation and Mo-U covariation), there is no evidence that euxinia was widespread across terrestrial environments during the Mesoproterozoic, nor any clear indicators for abundant nutrient availability that would help to sustain biological activity (Figures 2 and 4). The Nonesuch Formation sediments feature organic C contents similar to a modern biologically productive environment (LH; Figure 3) and experienced a relatively mild thermal history (<150 °C; Gallagher et al., 2017) suggesting that their C contents are not substantially lower than they were at the time of deposition. However, it is unclear whether this organic C burial can be attributed to an increase in biological productivity or a shift to greater carbon preservation. Well-preserved eukaryotic remains are most abundant and diverse in discrete horizons, which may indicate that pelagic productivity occurred in episodic bursts (Wellman & Strother, 2015), but do not correspond to the observed Mo enrichments. This would be consistent with intermittent nutrient limitation, impacting the extent of biological productivity, and ultimately contrasting with the model of Parnell et al. (2015). Without high enough Mo to indicate significant sulfate weathering, this study provides no clear indicator of Mesoproterozoic atmospheric oxygenation levels. Differences were observed in Fe geochemistry between various Nonesuch Formation rift basin lakes and in the apparent degree of oxygenation from anoxic to oxic. This variability occurred in sediments that were formed penecontemporaneously and therefore under approximately the same atmospheric pO_2, indicating that oxygen availability was locally controlled in the water column and sediments (e.g. by biological production and consumption of oxygen, or physically via stratification) rather than by the atmosphere. In the modern analogue setting, an oxygenated atmosphere coexists with both oxic and ferruginous sediment chemistry (Table 1). Taking all of this together, the most parsimonious explanation of the Nonesuch Formation Mo geochemistry is that it reflects fluctuating redox conditions and intense cycling of Fe and Mn oxyhydroxides within the water column, raising questions about attempts to use ancient lakes to reconstruct atmospheric oxygen levels. Indeed, the modern analogue system records ferruginous conditions reflective of a steep redoxcline at depth even in a fully oxygenated atmosphere and thus reflects only a portion of the water column, and not the part that is in contact with the atmosphere.

5 Conclusions

It has been proposed that Mo enrichments in Mesoproterozoic lake deposits would indicate widespread euxinia, no nutrient limitation in terrestrial systems, and high levels of atmospheric oxygen. Iron speciation, low Mo contents, and Mo-U covariation of the 1.1 Ga old Nonesuch Formation contradict this model of widespread lacustrine euxinia, and do not provide any indication of enhanced biological productivity or provide a useful constraint on atmospheric oxygenation during the Mesoproterozoic. Sediment geochemistry of Proterozoic terrestrial environments may only demonstrate *in situ* water column and sediment chemistry. Whether or not Mo geochemistry of Mesoproterozoic lakes record biological productivity and global atmospheric oxygenation remains unresolved.

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477 **Table 1**. Percentage of Fe speciation data indicative of a given redox regime

Location	Percent oxic (%)	Percent possibly anoxic (%; ancient sediments only)	Percent ferruginous (%)	Percent possibly euxinic (%)	Percent euxinic (%)
Middle Island Sinkhole	16	--	78	5	0
Lake Huron	100	--	0	0	0
Nonesuch Formation	73(40)[1]	25(45)	0(14)	0	<1(<1)

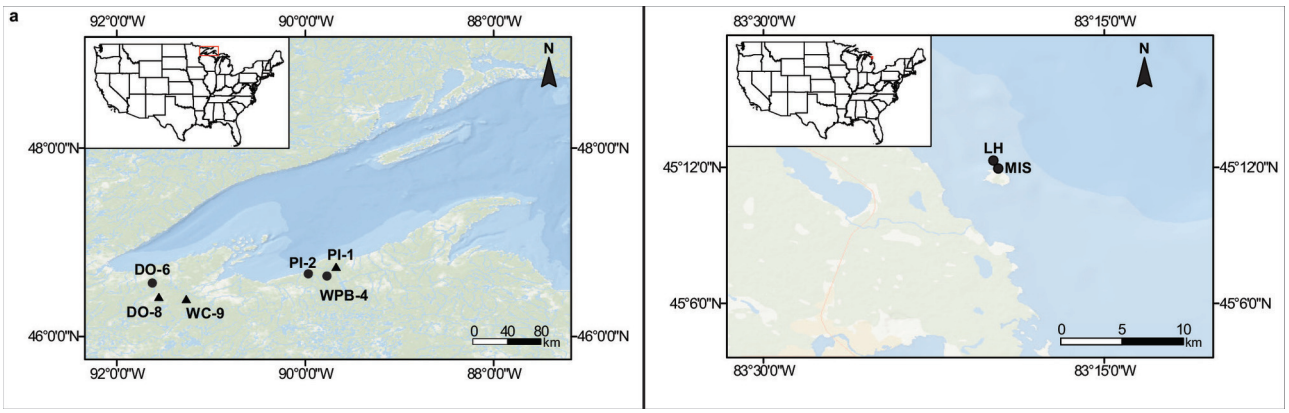
478 [1]Values are given for MIS, LH, and the Nonesuch Formation from *this work*, with parenthetical values including
479 both *this work* and previously published data from Cumming et al. (2013; Figure S1).
480
481

Figure 1. Sample localities for the a) DO-6, PI-2, and WPB-4 cores of the Nonesuch Formation and b) Middle Island Sinkhole (MIS) and Lake Huron control site (LH). The PI-1 core was previously examined for Fe speciation by Cumming et al. (2013), and the DO-8 and WC-9 cores were previously examined by Slotznick et al. (2018).

Figure 2. Cross plot of the ratios of iron in pyrite (Fe_{py}) to highly reactive iron (Fe_{HR}) versus Fe_{HR} to total iron (Fe_T) for Middle Island Sinkhole (dark blue circles) Lake Huron (yellow circles), and Nonesuch Formation (red circles) sediments. These Fe ratios can distinguish the redox chemistries of aquatic environments as oxic, ferruginous, or euxinic (Raiswell and Canfield, 2012; Raiswell et al., 2018). Solid gray lines are recommended boundaries whereas dashed gray line is suggested only for ancient sediments (after Raiswell et al., 2018). Middle Island Sinkhole and Lake Huron data is from Rico and Sheldon (2019).

Figure 3. Mo (ppm) versus $\%C_{org}$ contents for Middle Island Sinkhole (blue circles), Lake Huron (yellow circles), and Nonesuch Formation (red circles). Stoer Group data (gray circles; Parnell et al., 2015) are also included as a comparative euxinic endmember. Dashed lines indicate thresholds for oxic, anoxic, and euxinic conditions based upon Mo enrichments (Scott and Lyons, 2012). Inset plot highlights Lake Huron and Nonesuch Formation data. Middle Island Sinkhole and Lake Huron organic C data is from Rico and Sheldon (2019).

Figure 4. Cross plot of the enrichment factors (EFs) of Mo and U for the Nonesuch Formation sediments (red circles), MIS sediments (blue field) and Lake Huron sediments (yellow field) for samples enriched in Mo and U relative to their reference value (EF > 1). Diagonal lines represent the Mo:U ratio of present-day seawater and fractions thereof. Large arrows depict the particulate shuttle and unrestricted marine pathways of Mo and U deposition in marine sediments. Similar Mo/U ratios between Lake Superior (3.3) and average seawater (3.4) allow us to use this marine approach (after Algeo & Tribovillard, 2009) with the lacustrine sediments.



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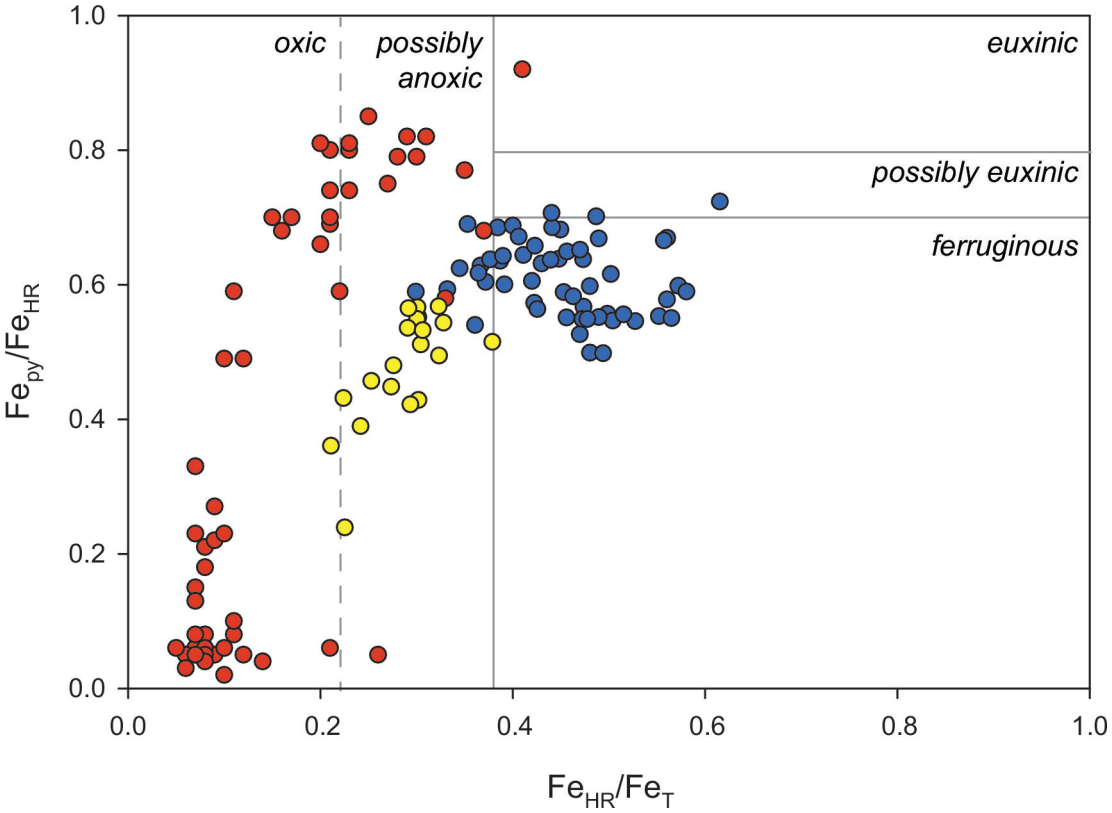

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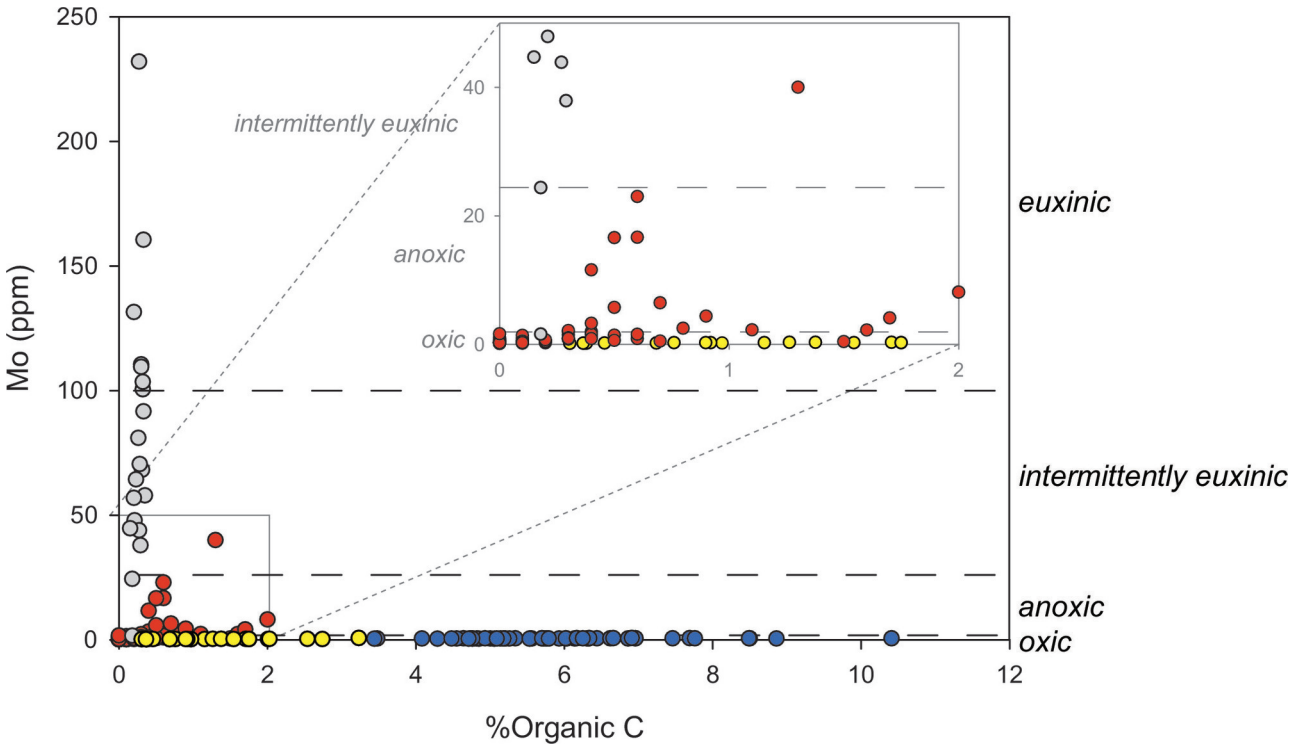

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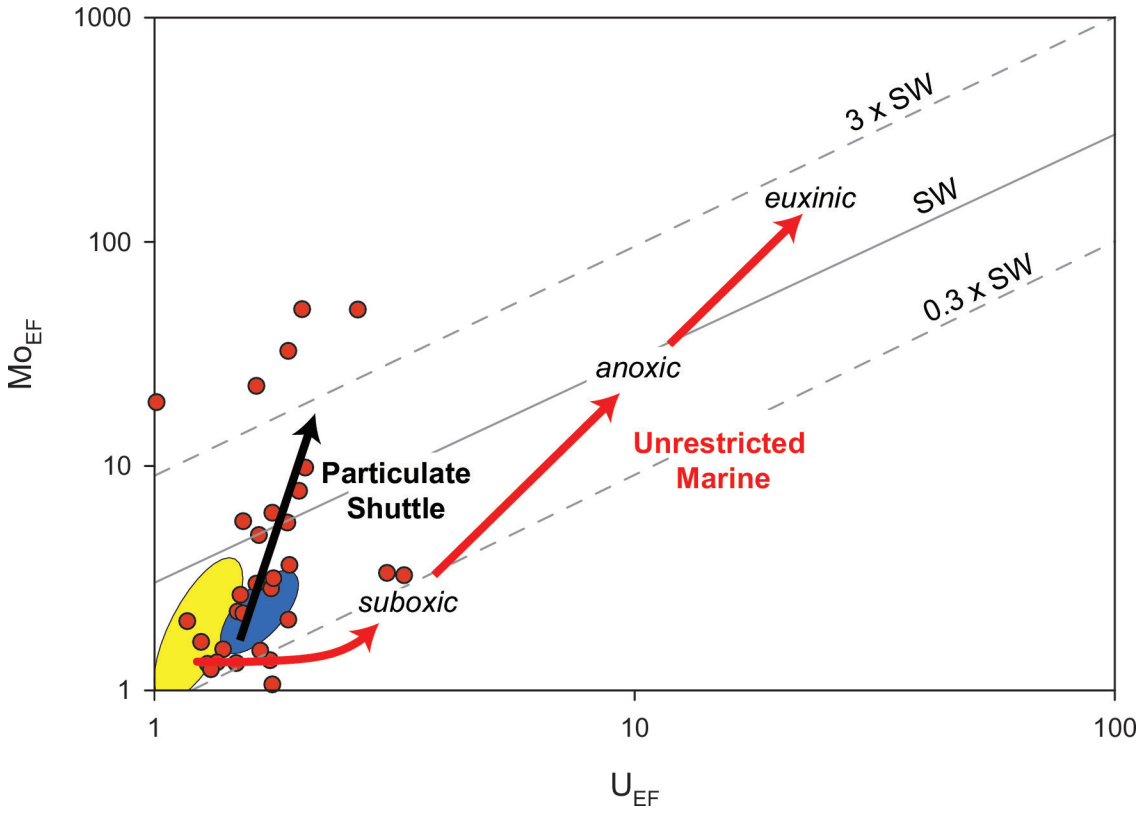

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