

Geochemical fingerprints of seawater in the Late Mesoproterozoic Midcontinent Rift, North America: life at the marine-land divide

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Abstract

The 1.1 Ga Midcontinent Rift (MCR) is a thick volcanic-sedimentary succession that forms a curvilinear belt through central North America and crops out along its northern apex around Lake Superior. Sedimentary units of the MCR have been long interpreted as fluvial-lacustrine and invited a number of studies on the early evolution of life in non-marine habitats. One of the key units is the siliciclastic Nonesuch Formation, thought to record deposition in a large lake. However, recent sedimentological observations indicate the presence of marine incursions. To further test this interpretation, we analysed trace element abundances in a broad suite of samples from multiple drill cores through the Nonesuch Formation. We aimed to differentiate geochemical influences of sediment provenance from post-depositional hydrothermal overprint and thereby identify authigenic enrichments in fluid-mobile elements that are indicators of primary environmental conditions. Our results reveal discrete enrichments in Mo and U in organic- and sulphide-rich horizons, which are most parsimoniously interpreted as marine signatures. This conclusion is supported by Sr/Ba ratios, which suggest mixing between freshwater and saltwater, and by rare cm-thick gypsum in the upper Copper Harbor Formation immediately below the Nonesuch rocks. The gypsum displays $\delta^{34}\text{S}$ values of $+25.9 \pm 0.6\%$, consistent with input of marine sulphate at least during parts of the basin's history. Collectively, our geochemical data support the sedimentological interpretation that this portion of the MCR archives a marine-influenced estuarine system. Although this conclusion rules out that microbial life documented from the MCR was living in exclusively freshwater habitats, the Nonesuch Fm and associated rocks still hold important clues about organisms that were capable of withstanding salinity gradients and bridging the gap between the marine and non-marine environments of the mid-Proterozoic.

1. Introduction

The Keweenawan Supergroup in the North American Midcontinent Rift (1.1 Ga, Stein et al., 2018) has been long interpreted as one of the great lakes of the late Mesoproterozoic (Cumming et al., 2013; Suszek, 1997), along with rocks of the Torridonian Supergroup in NW Scotland (1.2-

1.0 Ga, Stewart, 2002) and parts of the Borden Basin in northern Canada (1.1 Ga, Hahn et al., 2015). Occurrences of eukaryotic microfossils and biomarkers in some of these strata (Pratt et al., 1991; Wellman and Strother, 2015) have nurtured the hypothesis that freshwater habitats were the cradles of complex life (Sánchez-Baracaldo et al., 2017), which has motivated a number of studies addressing the redox landscape and nutrient inventory of these key habitats (Cumming et al., 2013; Parnell et al., 2015; Slotznick et al., 2018).

However, in the absence of diagnostic fossils, the non-marine nature of Precambrian depositional environments is difficult to prove. In the case of the Midcontinent Rift, mudrocks of the Nonesuch Formation (an extensive fine-grained siliciclastic unit, dated to c. 1.08 Ga with Re-Os and U-Pb geochronology, Cumming et al., 2013; Fairchild et al., 2017) have been interpreted as lacustrine because of (a) their close association with demonstrably fluvial rocks in the underlying Copper Harbor Formation and overlying Freda Formation (Fig. 1) (Elmore, 1984), (b) the intra-continental setting of the basin, and (c) an initial $^{187}\text{Os}/^{188}\text{Os}$ ratio that differs from that of unambiguously marine sedimentary rocks of potentially similar age (Cumming et al., 2013). While these arguments are indeed consistent with a lacustrine interpretation, they cannot rule out a marine influence. Jones *et al.* (2020) recently documented sedimentary features, including hummocky cross-stratification and tidal indicators, that are most parsimoniously explained by an open connection to the global ocean. The modern geographic setting of the basin does not prohibit a marine connection during the time of basinal deposition, perhaps akin to large modern bays and seaways.

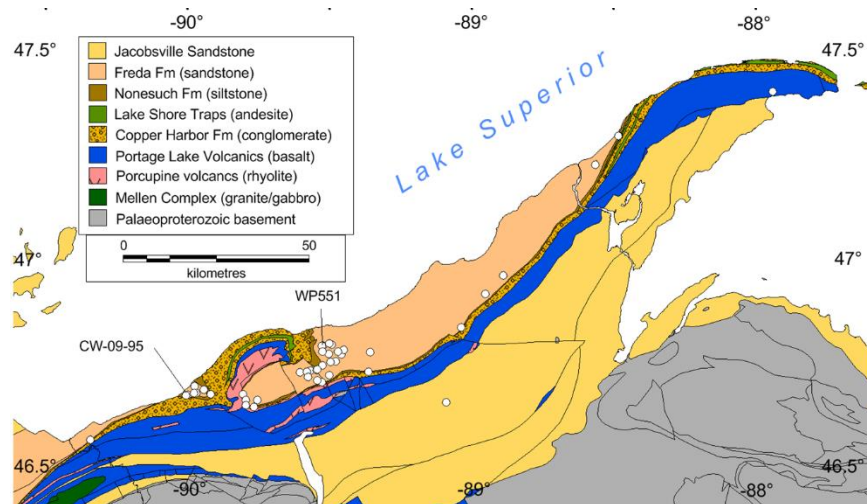


Figure 1: Locality map. Geographic positions of drill cores are listed in Table S5. The White Pine mine is close to core WP551.

To further inform the depositional setting, we collected a large set of grey siltstones and black shales dispersed through the Nonesuch Formation (Fig. 1) and investigated their bulk elemental composition. This dataset allows us to identify the fingerprints of sedimentary provenance and hydrothermal mineralisation, sufficient to isolate those elements that reflect primary authigenic enrichments indicative of environmental conditions during the time of deposition. We also explore previous reports of gypsum in the Copper Harbor Formation (Elmore et al., 1989) to investigate their origin and spatial extent.

2. Materials and Methods

2.1. Sample selection

We collected 263 samples from 47 exploration drill cores through the Nonesuch and upper part of the Copper Harbor formations, including samples proximal to the world-class copper deposit at White Pine, distal to this mineralisation, and intersecting unmineralised strata elsewhere on the Keewenaw peninsula. Sampling was largely driven by availability and accessibility of cores. As most cores have been drilled for exploration purposes, we have a relatively higher density of samples close to the White Pine ore body (Fig. 1). However, these cores include thick unmineralised packages. Furthermore, by including samples proximal and distal to the mineralisation front, we are able to identify the effects of mineralisation on primary environmental signatures (see below). Our sample set also spans a range of sedimentary facies, including dark shales, grey siltstones and fine sandstones, to detect geochemical imprints of sedimentary provenance. These signatures may be more pronounced in coarser-grained strata with high sedimentation rates, where authigenic enrichments of organic carbon, sulphur and redox-sensitive trace elements are minimal. Our sampling density per core is coarser than that of previous studies focused on high-resolution records in single cores (Cumming et al., 2013; Rico et al., 2019). Our approach, in contrast, enables identification of potential biases caused by mineralisation and detrital provenance as well as determination of potential marine geochemical signatures spanning the basin, unrestricted to a particular lithofacies at a single location.

2.2. Analytical methods

The outer ~0.5-1cm of the samples were removed with a rock saw and the interior was pulverised with an agate ball mill. For bulk geochemical analyses, an aliquot of powder was sent to Australian Laboratory Services (ALS) where the samples were dissolved in HNO₃, HF, HClO₄ and HCl and analysed by ICP-MS for minor elements and ICP-OES for major elements. Analytical reproducibility for samples is 4% or better (1SD/average). Accuracy, assessed with the international reference materials OREAS-46 and OREAS-920, was better than 10% for Mo and better than 5% for all other elements of interest.

Measurements of total organic carbon (TOC) and sulphur isotopes were conducted on a subset of samples at the University of St Andrews, Scotland. These analyses were focused on fine-grained grey and black shales. For a higher-resolution study, we selected core WP551, which is close to the White Pine ore body but contains a long section above the mineralized horizon. Rock powders were first decarbonated with 2M HCl at 60°C overnight, washed three times with DI-H₂O (18 MΩ cm⁻¹) and dried in a closed oven. Gypsum was extracted with a scalpel and pulverised with pestle and mortar. The dry powders were weighed into tin capsules and analysed with an elemental analyser (EA IsoLink) coupled to a MAT253 isotope ratio mass spectrometer. TOC was calibrated with the peak area of an array of USGS-41 standards. Sulphur isotopes of gypsum were calibrated with IAEA-SO6 and NBS-127. Results are expressed in delta notation relative to VCDT ($\delta^{34}\text{S} = [({}^{34}\text{S}/{}^{32}\text{S})_{\text{sample}}/({}^{34}\text{S}/{}^{32}\text{S})_{\text{VCDT}} - 1] \times 1000$). Analytical reproducibility was 0.5‰ (1SD). Accuracy was tracked with IAEA-SO5 and was better than 0.6‰ (maximum offset).

3. Results

Gypsum was found in three drill cores of the Copper Harbor Formation as cm-thick stratiform laminae (Fig. 2a), and gypsum pseudomorphs (now calcite) are preserved in numerous cores of the upper Copper Harbor and Nonesuch formation (Jones et al., 2020). The $\delta^{34}\text{S}$ values of the gypsum cluster tightly around $+25.9 \pm 0.6$ ‰ (n = 6). In siliciclastic rocks of the Nonesuch Formation, ratios of Sr/Ba, which have been proposed as an indirect sulphate proxy (Wei and Algeo, 2019), range from 0.06 to 2 with a median of 0.3 (+0.3/-0.2). Sr/Ba ratios are not strongly correlated with Ca (Fig. 3i). The Ca content (median 1.7%) is mostly lower than that of average upper continental crust (2.6% Ca, Rudnick and Gao, 2003).

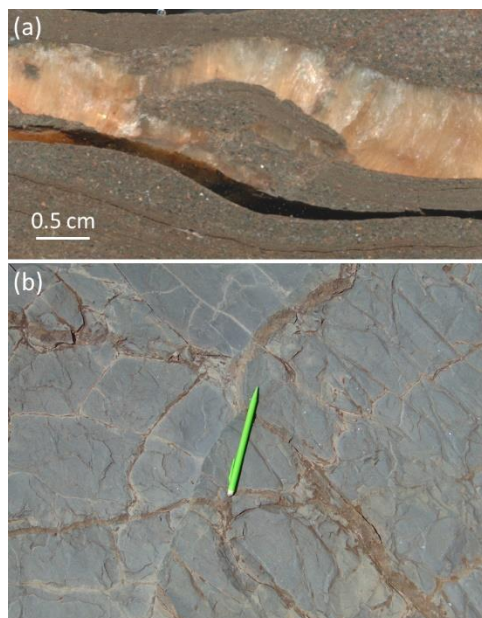


Figure 2: Photographs. (a) Evaporitic gypsum within the upper Copper Harbor Formation, core CW-09-95, 131.84m (see Fig. 1). (b) Desiccation cracks in the Nonesuch Formation; these are typical of those found across the Nonesuch Formation outcrop belt.

The Nonesuch Formation is known for significant stratiform Cu mineralisation (Bornhorst and Williams, 2013; Ho and Mauk, 1996), which we consider a proxy for secondary overprint by oxidised Cu-rich brines. In bulk rocks across the basin, Cu shows strong covariance with Ag (Fig. 3a). In contrast, correlations between Cu and other fluid-mobile metals (Mo, U, Ni, Co, Zn, V) are absent (Fig. 3b, S2). When Cu is plotted against TOC and S, it shows two populations, above and below ~1000 ppm Cu, with distinct covariances (Fig. 3c, d).

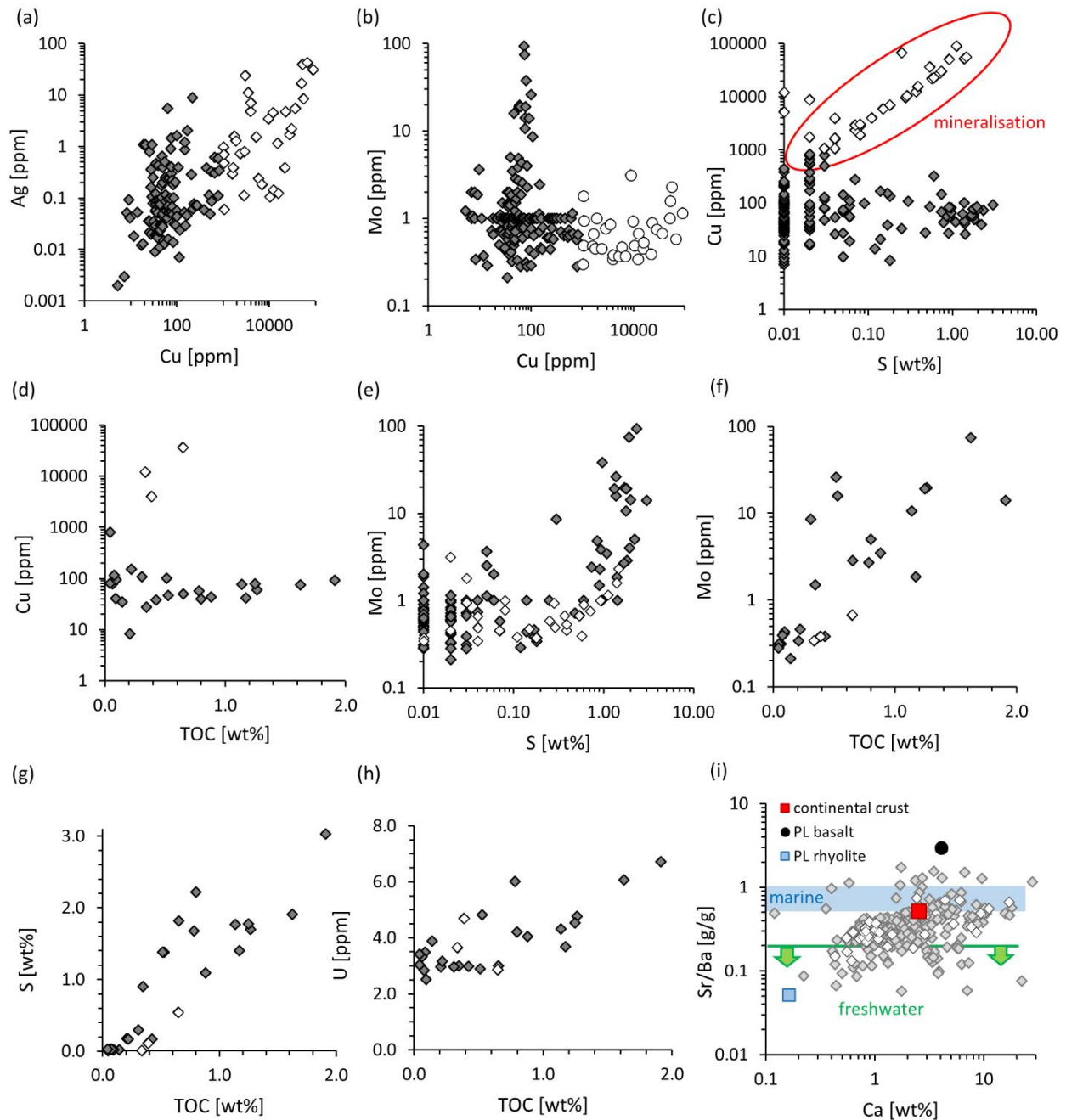


Figure 3: Tests of mineralisation effects and primary authigenic enrichments. All data points are from the Nonesuch Formation. Dependent variables are plotted on the y-axes, independent variables on the x-axes. White diamonds = $\text{Cu} > 1,000$ ppm. Silver (a) was likely enriched by the same mineralising fluids that carried Cu, but Mo (b) was not. The Cu mineralisation likely also introduced additional S (c), but a second population of S data is uncorrelated with Cu. Covariances between Mo, S and TOC (e, f, g) as well as U and TOC (h) are most parsimoniously explained by primary authigenic enrichments under anoxic conditions from a relatively Mo- and U-rich marine reservoir. Sr/Ba ratios scattered between freshwater and marine values may reflect mixing of water masses in an estuarine setting (i). PL = Portage Lake Volcanics, taken from Nicholson and Shirey (1990).

Fe/Al ratios, a common redox indicator in shales (Lyons and Severmann, 2006), range from 0.1 to 2.2 and anticorrelate with Zr/Ti ratios, which are fluid-immobile elements (Fig. 4a). Most of the measured range in Zr/Ti ratios falls between average continental crust and Portage Lake volcanic rocks, a suite of mostly tholeiitic basalts that occur below the Copper Harbor Formation and may have eroded locally (Nicholson and Shirey, 1990). Cu in Nonesuch Formation mudrocks is not correlated with Zr/Ti (Fig. 4d), but V, Ni and Co (i.e., other fluid-mobile transition metals, Ptáček et al., 2020) are (Fig. 4b, c, S1). V, Ni and Co show no covariance with S and TOC (Fig. S2). Mo and U (two commonly-used redox indicators, Tribovillard et al., 2006) are uncorrelated with Zr/Ti (Fig. 4e, f), but Mo is moderately correlated with S and TOC (Fig. 3e, f, h), which in turn are co-correlated (Fig. 3g). The Mo data plotted against Zr/Ti thus reveals two populations: one group of samples with high Mo-enrichments and a second group with flat Mo concentrations over a wide range of Zr/Ti ratios (Fig. 4f). Samples from the first group of data points correspond to those that are enriched in TOC (> 0.3 wt. %, Fig. 3f) and/or TS (> 0.5 wt. %, Fig. 3e), while the second set shows no TOC enrichments. It is therefore a combination of organic carbon abundance and redox chemistry (TOC, TS) rather than sedimentary provenance (Zr/Ti) that is controlling the behaviour of Mo.

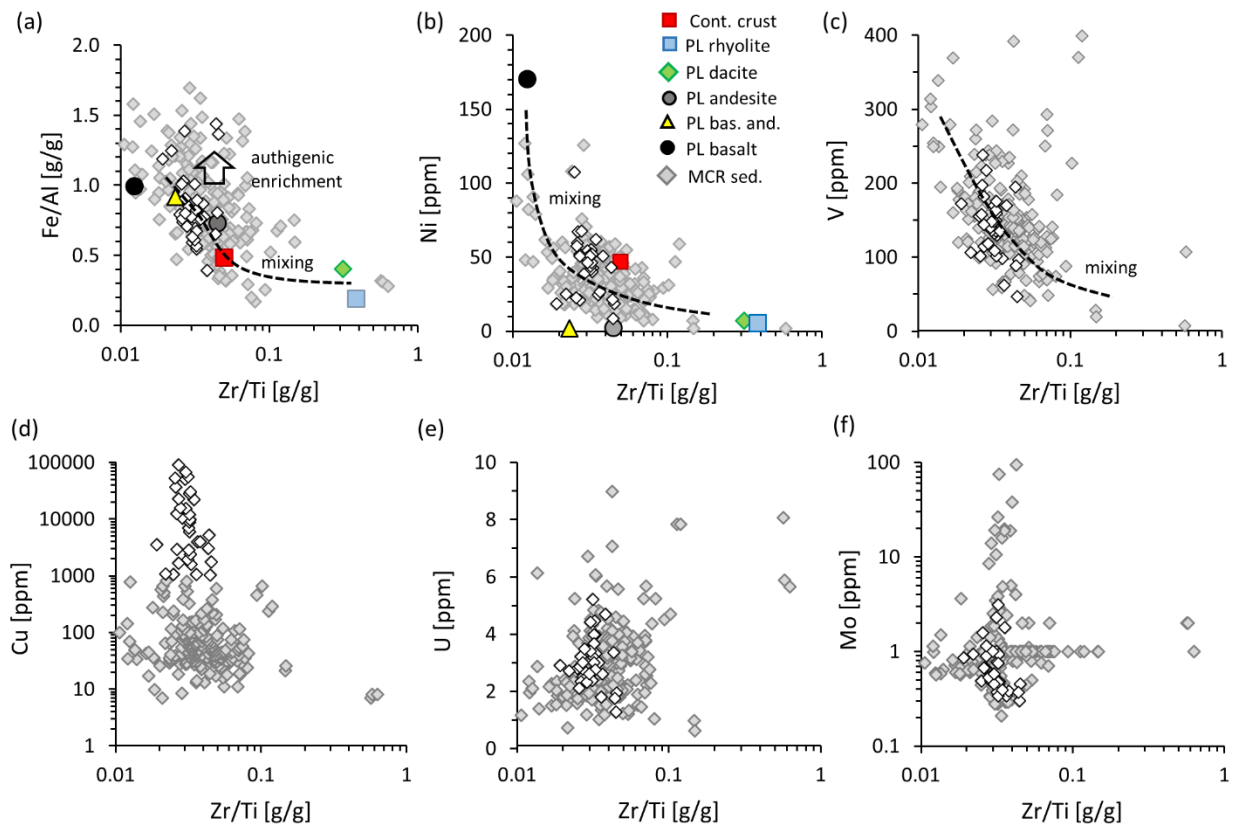


Figure 4: Tests of sediment provenance effects. All samples are from the Nonesuch Formation. White diamonds = Cu > 1,000 ppm. Covariances with Zr/Ti shown by Fe/Al (a), Ni (b) and V (c) suggest that provenance, i.e. mixing of detritus from geochemically distinct source rocks, imparted a strong control on these elements. In contrast, Cu (d), U (e) and Mo (f) are not controlled by provenance. bas. and. = basaltic andesite, MCR = Midcontinent Rift.

4. Discussion

4.1. Entrainment of Marine Sulphate

The mean $\delta^{34}\text{S}$ value of $+25.9 \pm 0.6$ ‰ for gypsum layers in the upper Copper Harbor Formation falls within the range of late Mesoproterozoic seawater ($+26 \pm 6$ ‰, Johnston et al., 2005; Strauss, 1993). The isotopic offset between gypsum and sulphide minerals in the Nonesuch Formation (Cumming et al., 2013; Imbus et al., 1992) is thus up to 30‰ and mostly around 20‰, which may indicate a moderate reservoir of sulphate that was rarely depleted. One occurrence of gypsum has been reported previously in the Nonesuch rocks (Elmore et al., 1989). Hence, although Ca-sulfate pseudomorphs and evaporite fabrics can be observed in numerous cores along the length of the Keweenaw peninsula (Jones et al., 2020), the absence of thick evaporite deposits throughout the succession, despite many occurrences of desiccation cracks (Fig. 2b), suggests that the water column was likely not highly saline for long periods of time. Such conditions are consistent with an estuarine setting.

The Sr/Ba ratios of the Nonesuch Formation also are consistent with at least intermittent presence of sulphate in the water column. The Sr/Ba proxy is sensitive to salinity on the basis that riverine Ba reacts rapidly with SO_4^{2-} as it encounters seawater and precipitates as highly insoluble barite in estuaries (Wei and Algeo, 2019). Sr is more soluble than Ba and thus becomes relatively enriched in seawater. Both elements become incorporated into authigenic clays. A recent compilation of data suggests that marine shales tend to show enrichments in Sr/Ba ratios around 0.5-1.0 compared to ratios below 0.2 in non-marine settings (Wei and Algeo, 2019). The bulk of our values are above the freshwater value and partly overlap with the marine range (Fig. 3i). The depletion in Ca relative to average crust and Portage Lake basalt, which is a significant contributor to detrital sediments in the Nonesuch Formation (see below), suggests that Ca was mostly leached from silicate minerals during weathering of the hinterland and did not accumulate as carbonate phases in these rocks. Hence carbonate is most likely not responsible for raising Sr levels over Ba (cf. Wei and Algeo, 2019). Although use of the Sr/Ba proxy is in its infancy, our data are consistent with a setting that fluctuated between fresh or brackish (low Sr/Ba) and saline (high Sr/Ba), again compatible with a tidal estuary setting (Dalrymple and Choi, 2007).

4.2. Provenance Effects on Transition Metals

Midcontinent Rift mineralization (*i.e.*, ore formation) has clearly impacted the distribution of not only Cu but also Ag in the Nonesuch Formation as suggested by strong covariance between these two elements. However, many other transition metals appear to have been less affected given their lack of correlation with Cu abundances. Instead, their covariances with Zr/Ti (Fig. 4a-f, S1) suggest that provenance imparted a first-order control on metal abundances in these rocks. Zr and Ti are both fluid immobile under environmental conditions with circumneutral pH, but the Zr/Ti ratio is lower in titanomagnetite-rich mafic rocks of the Portage Lake volcanic suite (0.01 g/g, Nicholson and Shirey, 1990) than in more-zirconiferous, intermediate-composition global average continental crust (0.05g/g, Rudnick and Gao, 2014). In contrast, Fe/Al ratios are higher in Portage Lake basalts (0.99 g/g) than in continental crust (0.48 g/g). Hence detrital sediments likely represent a mixture of regional continental crust and local mafic volcanic rocks from the Portage Lake volcanic suite (Nicholson and Shirey, 1990) (Fig. 4a). A volcanic detrital endmember also

can explain the covariance of Zr/Ti with Ni, Co and Zn (Fig. 4b, S1), all of which tend to be enriched in mafic minerals (White and Klein, 2014). The covariance between Zr/Ti and V (Fig. 4c) may indicate contributions of detrital magnetite, which is a significant host mineral of V in mafic rocks (Huang et al., 2015). Vanadium shows only a very subtle covariance with TOC (not shown), indicating that it is overwhelmingly controlled by detrital input rather than redox chemistry in this basin. High abundances of magnetite in the Nonesuch Formation have been documented by Cumming *et al.* (2013), who interpreted these as authigenic enrichments. However, if a large fraction of the magnetite is detrital in origin, Fe/Al ratios and Fe speciation cannot be used as reliable redox proxies, because these proxies have been calibrated empirically relative to average continental crust (Raiswell et al., 2019). Only the degree of pyritisation of reactive iron (including iron oxides, carbonates and sulphides) may be applicable. Previous studies have documented a wide range from 0% to 80% pyritisation (Cumming et al., 2013; Rico et al., 2019), and the higher values may indicate sulfidic pore waters. Indeed, in the data presented by Cumming et al. (2013), pyrite abundance anticorrelates with magnetite abundance, which may reflect conversion of magnetite to pyrite during diagenesis. However, the redox state of the water column cannot be assessed with this metric alone.

4.3. Authigenic Metal Enrichments

Elements that do not show noticeable covariance with Zr/Ti (besides Cu) are Mo and U (Fig. 4e,f), which is consistent with their generally low concentrations in mafic rocks (White and Klein, 2014; Willbold and Elliott, 2017). Lack of covariance with Cu further indicates that they were not significantly affected by the same mineralizing fluids. Further, their correlation with S and TOC (Fig. 3e-h), as noted by Rico *et al.* (2019), is typical for the primary behaviour of these elements in low-temperature systems. Under anoxic conditions, both Mo and U become enriched in sediments if the overlying water column contains a significant dissolved reservoir of these elements (Algeo and Lyons, 2006; Tribovillard et al., 2006). The mid-Proterozoic Mo concentration is estimated to be 5-10 nM compared to 107 nM today (Reinhard et al., 2013), but those levels were sufficient to create sedimentary Mo enrichments of several tens of ppm (Reinhard et al., 2013). Higher enrichments of up to 200 ppm have been observed under evaporitic marine conditions in the mid-Proterozoic Stoer Group in NW Scotland (Stüeken et al., 2017). Modern lake waters show a range of Mo concentrations from <0.1 nM to 13 nM, with higher values restricted to saline lakes (Glass et al., 2012). Even under anoxic conditions, sediments from modern lakes may show no significant Mo enrichment (<1 ppm) (Rico et al., 2019); the one exception was interpreted as resulting from an unusually high influx of particulate FeMn oxides (Glass et al., 2013). In the case of the Nonesuch Formation, particulate Fe phases would have been derived from Mo-poor basaltic sources. Further, such a detrital Mo source could not explain the strong covariance between Mo and TOC in the shale facies (Fig. 3f). The high Mo enrichments in the Nonesuch Formation are thus indicative of a significant dissolved Mo reservoir of at least several nM, which would be consistent with either a saline lake or seawater. Importantly, Mo enrichments above 3 ppm, which is a conservative threshold relative to the likely Mo-poor detrital flux, occur in cores throughout the basin (Fig. 5a) implying that this Mo-bearing water mass was not paleogeographically restricted.

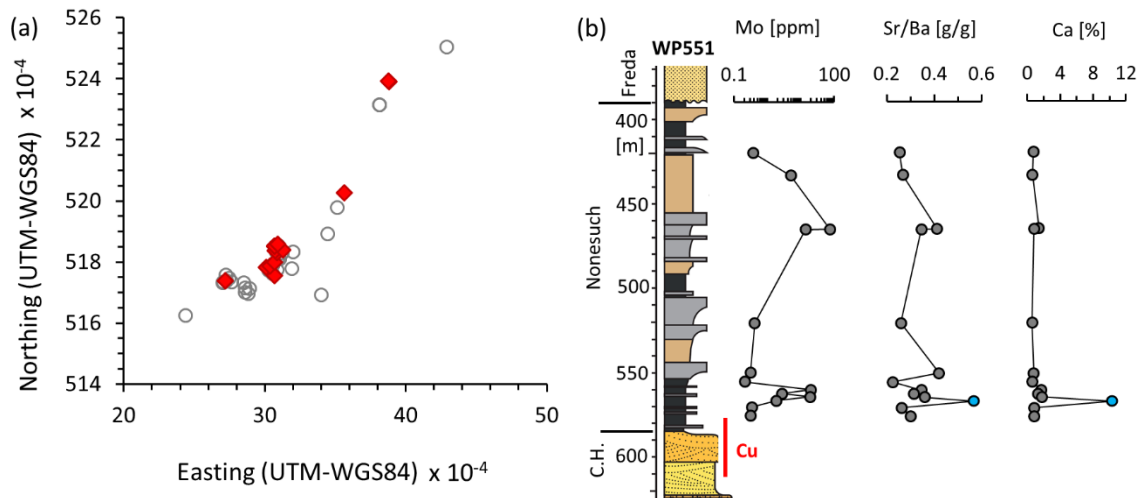


Figure 5: Geographic (a) and stratigraphic (b) location of Mo enrichments. (a) Plotted are the geographic locations of all drill cores investigated in this study. Those with a Mo detection above 3ppm are highlighted in red. (b) Geochemical data from core WP551 for which we have the most data points. C.H. = Copper Harbor Formation. Cu = zone of copper mineralisation. The data point marked in blue is carbonate rich. In all other samples, elevated Sr/Ba ratios above 0.2 g/g likely reflect saline water conditions. These conditions coincide with intervals of Mo enrichments.

Although we have no independent control on the redox state of the water column from other proxies, such as iron speciation, Rico *et al.* (2019) reported Mo values above 3 ppm only in samples where at least 60% and mostly more than 70% of all highly reactive iron was present as pyrite. The 70% threshold is posited as an indicator of euxinic conditions (Poulton and Canfield, 2011), but those appear to have been rare in the Nonesuch basin (Cumming *et al.*, 2013; Rico *et al.*, 2019; Slotznick *et al.*, 2018), probably because it is mostly a shallow-water setting with frequent subaerial exposure and wave action (Jones *et al.*, 2020). It is therefore possible that we are under-sampling the true Mo reservoir of the water column because conditions may simply not have been conducive towards efficient trapping of Mo in underlying sediments. However, we note that in core WP551, from which we have the most Mo data points (13 in total), Mo enrichments show a broad covariance with Sr/Ba ratios (Fig. 5b), which may point towards salinity fluctuations in the water column.

Combined, the marine $\delta^{34}\text{S}$ values of Copper Harbor gypsum (Fig. 2a), elevated Sr/Ba ratios (Fig. 3i), and Mo enrichments (Fig. 3f) (Rico *et al.*, 2019) in Nonesuch rocks, paired with the widespread presence of desiccation cracks (Fig. 2b), evaporite pseudomorphs and tidal sedimentary structures throughout much of the Nonesuch Formation (Jones *et al.*, 2020) is most consistent with a shallow-marine, tidally influenced estuarine setting.

4.4. Life at the marine-land divide

Although the lack of age constraints and the lateral facies variability so far prohibit a detailed reconstruction of discrete marine incursions into the Midcontinent Rift, our results impact understanding of biosignatures that have been reported from the Nonesuch Formation (Wellman and Strother, 2015). An important characteristic of estuaries is that they experience frequent desiccation and salinity fluctuations (Dalrymple and Choi, 2007). Such salinity fluctuations result

from the inward and outward migration of the marine ‘salt wedge’. Organisms living in estuarine habitats therefore need to be adapted to constant changes in the osmotic pressure that is acting on their cells. Indeed, among prokaryotes, the genetic adaptations that are necessary to adapt to changes in salinity are so characteristic that they have led to the proposal of a ‘terrabacterial’ clade (Battistuzzi and Hedges, 2008). Cavalier-Smith (2009) points out that the “sharp differentiation into marine and non-marine forms is one of the strongest features of biodiversity of all microbes, including bacteria.” Evidence for eukaryotic life in the Midcontinent Rift thus implies that at least some complex organisms had evolved strategies to overcome the salinity barrier by 1.1 Ga. This recognition has implications for our understanding of how early eukaryotes may have colonized the planet. It has been proposed that eukaryotic algae evolved in freshwater, based on the phylogeny of plastids (Sánchez-Baracaldo et al., 2017) and of the enzymatic machinery that regulates osmotic pressure (Cavalier-Smith, 2009). If so, our results suggest that some of the earliest eukaryotes already had developed coping strategies to migrate from land to sea.

Conversely, certain marine organisms likely had the ability to adapt to low-salinity conditions and expand into freshwater habitats. Throughout the Precambrian, some key nutrients, including nitrate, phosphate and many transition metals, were either unstable or poorly soluble under anoxic marine conditions (Reinhard et al., 2017; Robbins et al., 2016; Stüeken et al., 2016). In contrast, oxic Proterozoic river waters may have been relatively nutrient rich, because weathering of phosphatic minerals was likely very efficient when atmospheric CO₂ was higher (Hao et al., 2017), and the breakdown of extensive microbial mats on land may have delivered bioavailable nitrogen (Thomazo et al., 2018). Today, the land-derived nutrient flux makes estuaries some of the most productive ecosystems on Earth with diverse suites of primary and secondary producers (Correll, 1978). Our results indicate that such settings already existed in the Proterozoic and may have been important cradles for biological innovation.

5. Conclusions

Our data suggest a sequence of processes that shaped the observed geochemical patterns in the upper Copper Harbor and Nonesuch formations:

- (1) The sediment provenance – a combination of local volcanic rocks and crustal hinterland – created variable enrichments in Fe, Ni, Co, Zn and V. Vanadium in particular may reflect detrital magnetite derived from basalts, consistent with reports of high magnetite abundances in Nonesuch shales (Cumming et al., 2013; Slotznick et al., 2018).
- (2) Enrichments of Mo and U in organic-rich shales, which are characteristic of anoxic marine sediments (Partin et al., 2013; Scott and Lyons, 2012; Scott et al., 2008), reflect a marine influence on the water chemistry of this basin. The covariance with TOC indicates that Mo and U enrichments are authigenic in nature, and covariance between Mo and S suggests sulphidic conditions in pore waters or in the lower water column during deposition (Tribovillard et al., 2006). However, if euxinia was rare (Cumming et al., 2013; Slotznick et al., 2018), we are likely under-sampling the true dissolved Mo reservoir. Our interpretation of a Mo-bearing water column is thus conservative. A marine influence also is indicated by gypsum evaporites with a marine sulphur isotopic composition in the upper Copper Harbor Formation and consistent with slightly elevated Sr/Ba ratios that suggest brackish water conditions.
- (3) After sediment deposition, mineralising fluids introduced Cu and Ag along with some additional S (Fig. 3a,c). These fluids did not significantly perturb geochemical indicators of

provenance (Zr/Ti, Fe, Ni, Co, V) nor signatures of authigenic enrichments of elements that are depleted in basalts (Mo, U).

Collectively, these observations lead us to conclude that this portion of the Midcontinent Rift was an estuary experiencing frequent seawater influx. This interpretation is compatible with documented Os isotope discrepancies between the Nonesuch Formation and other contemporaneous marine sections (Cumming et al., 2013) because (a) Os isotope values may have been highly heterogeneous in space and time in the anoxic Proterozoic ocean (Kendall et al., 2009), and (b) they could reflect a brackish endmember in the estuary. An estuarine setting for the Midcontinent Rift has important implications for our understanding of eukaryotic evolution, because it implies that organisms had already evolved the ability to overcome the osmotic barrier that exists between freshwater and salt water habitats by the late Mesoproterozoic. Our findings thus lend credence to the proposition that eukaryotic organisms migrated between habitats relatively early in their evolution.

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