

Sedimentologic and geochemical markers of marine incursion to the interior Laurentian Oronto Group
basin at ca. 1.08 Ga

By

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Table of Contents

Abstract	vii
Acknowledgements	viii
Financial and Material Support	viii
CRedit Author Statements for published and in preparation manuscripts	ix
Chapter 1: The end-Mesoproterozoic (ca. 1.08 Ga) epeiric seaway of the Nonesuch Formation, Wisconsin and Michigan, USA	1
ABSTRACT	2
INTRODUCTION.....	3
GEOLOGIC SETTING.....	4
AGE CONSTRAINT	5
METHODS	5
LITHOFACIES ASSOCIATIONS AND STRATIGRAPHIC FRAMEWORK	6
Lithofacies Association A	6
Lithofacies Association B	7
Lithofacies Association C	9
Lithofacies Association D	12
Lithofacies Association E	14
Lithofacies Association F	14
Formation Lithostratigraphy	16
<i>Copper Harbor Conglomerate</i>	16
<i>Lower Nonesuch Formation</i>	17
<i>Upper Nonesuch Formation</i>	18
<i>Freda Formation</i>	19
Sequence Stratigraphic Surfaces	19
<i>Transgressive Surface</i>	19
<i>Maximum Flooding Surface</i>	20
<i>Sequence Boundary</i>	21
DISCUSSION.....	22
Depositional Model.....	22
A Changing Balance Between Accommodation Space and Sedimentation Rates.....	25

The Nonesuch Inland Sea: Implications of Marine Influence on Global Paleogeographic and Environmental Reconstructions	29
Latest Mesoproterozoic Ecosystems	31
CONCLUSIONS	34
ACKNOWLEDGEMENTS	35
REFERENCES	35
FIGURES and TABLES.....	44
Figure 1. location	44
Figure 2. Stratigraphic correlation panel, Ashland Syncline	45
Figure 3. Stratigraphic correlation diagram, Keweenaw Peninsula	47
Figure 4. lithofacies associations A and C	48
Figure 5. lithofacies association B	49
Figure 6. lithofacies association C	51
Figure 7. evaporite textures, lithofacies association D.....	53
Figure 8. lithofacies association D.....	55
Figure 9. lithofacies association E	57
Figure 10. lithofacies association F, Freda Fm.....	59
Table 1. Summary of lithofacies of the lower Oronto Group with focus on the Nonesuch Formation ..	62
Chapter 2: A restricted sea in the Laurentian interior: carbonate C-O-Sr isotope geochemistry of the ca. 1081 Ma Nonesuch Formation, Midcontinent Rift, USA	65
ABSTRACT	66
INTRODUCTION.....	67
REGIONAL GEOLOGIC SETTING	69
SEDIMENTOLOGY STRATIGRAPHY	70
METHODS	72
RESULTS	73
Petrography.....	73
<i>Molar tooth microspar within molar tooth structures</i>	<i>73</i>
<i>MT microspar within carbonate-rich layers</i>	<i>74</i>
<i>Veins and Concretions</i>	<i>74</i>
MAJOR- AND TRACE-ELEMENT GEOCHEMISTRY	75
ISOTOPE GEOCHEMISTRY	75
Carbon and Oxygen Isotopes	75
Rubidium and Strontium Isotope Composition	76

DISCUSSION.....	76
Evaluating Diagenetic Alteration.....	76
<i>Calcite microspar within MT structures</i>	77
<i>Calcite microspar within carbonate-rich layers</i>	78
<i>Tracking diagenesis with Sr and O isotopes</i>	79
Carbon Remineralization and the Influence of Early Cementation.....	82
Restricted, Evaporitic Conditions in the Nonesuch Seaway Suggested by C, O Isotopes.....	84
Implications For the Global Marine Sr Composition at Ca. 1081 Ma.....	86
CONCLUSIONS.....	90
ACKNOWLEDGEMENTS.....	91
REFERENCES.....	91
FIGURES.....	99
Figure 1. location.....	99
Figure 2. generalized stratigraphy.....	100
Figure 3. carbonate petrography.....	101
Figure 4. C and O isotopes.....	103
Figure 5. Rb-Sr isotopes.....	104
Figure 6. tests for diagenetic alteration.....	105
Figure 7. Late Mesoproterozoic marine $^{87}\text{Sr}/^{86}\text{Sr}$ compilation.....	106
Table 1. ICPMS element analysis.....	107
Table 2. Rb-Sr isotope composition.....	108
Table 3. Carbon and oxygen isotope compositions.....	110
Chapter 3: Shale and carbonate geochemistry track redox cycling, productivity, and salinity in the late Mesoproterozoic Laurentian inland sea of the Nonesuch Formation, Wisconsin and Michigan, USA	112
ABSTRACT.....	113
INTRODUCTION.....	114
BACKGROUND.....	115
Proxies for redox and productivity from whole rock geochemistry of fine-grained rocks.....	115
Carbonate REY distribution as a salinity proxy.....	117
GEOLOGIC SETTING.....	119
Plateau and Rift-stage volcanism.....	120
Transition from magmatism to sedimentation.....	122
Deposition within subsiding sub-basins.....	123

The Freda Formation and a change from focused to broadly distributed subsidence.....	126
Reverse faulting during Ottawa and Rigolet phases of the Grenvillian orogeny	127
MATERIALS AND METHODS	128
RESULTS	129
Geochemistry of siliciclastic strata	129
Geochemical patterns tied to stratigraphy from core WC-14.....	130
Carbonate REY distributions	132
DISCUSSION.....	133
Sediment provenance and weathering	133
Chemostratigraphic evidence for a revised sequence stratigraphic framework.....	135
Chemostratigraphic evidence for evolving basin productivity and restriction.....	136
Paleosalinity preserved in carbonate REY patterns?	140
<i>Assessing the impact of diagenesis on REY patterns in the Nonesuch Formation</i>	140
<i>Early diagenetic evolution of Nonesuch basin pore water</i>	142
Paleosalinity preserved in shales	144
Midcontinent subsidence, marine incursion, and Oronto Group deposition.....	146
Implications for early eukaryote habitat	147
CONCLUSIONS.....	148
ACKNOWLEDEMENTS.....	149
REFERENCES	149
FIGURES AND TABLES.....	162
Figure 1. location	162
Figure 2. generalized stratigraphy and sample locations	163
Figure 3. siliciclastic REY distributions	165
Figure 4. Sm-Nd	166
Figure 5. chemostratigraphy of detrital proxies	167
Figure 6. chemostratigraphy of redox and productivity proxies	168
Figure 7. carbonate REY distributions	169
Figure 8. weathering and provenance.....	170
Figure 9. relationship between Fe and P.....	171
Figure 10. Mo and U enrichment.....	172
Figure 11. total REY versus $\delta^{18}\text{O}$	173
Figure 12. REY anomalies versus Y/Ho	174

Figure 13. REY anomalies versus $\delta^{13}\text{C}$	175
Figure 14. REY anomalies versus total REY	176
Figure 15. Distribution of S and TOC	177
Table 1. Sm-Nd.....	178
Table 2. REE concentrations (ppm)	179
APPENDIX 1: Supplemental information for Chapter 1 (Stewart et al., 2024)	180
Supplementary Table S1: Core and outcrop locations	180
Supplementary Table S2: Compiled microfossil and core data	191
Appendix 2: Supplementary information for chapter 2	195
SAMPLE PREPARATION	195
Carbon and Oxygen Isotope Analysis	195
<i>University of Michigan Stable Isotope Laboratory</i>	195
<i>Scottish Universities Environmental Research Centre</i>	195
Sample Pre-Leach and Leaching For Rb-Sr Isotope and Major- And Trace-Element Analysis.....	195
<i>Methanol pre-leach</i>	195
<i>Ammonium acetate pre-leach</i>	195
<i>Acetic acid leach</i>	196
Column Chemistry	196
SR and RB ISOTOPE ANALYSIS	196
ICPMS ELEMENT ANALYSIS	197
EPMA ELEMENT ANALYSIS	197
ESTIMATING INGROWTH OF ^{87}Sr IN WEATHERED BASALT	198
REFERENCES	198
FIGURES and TABLES	200
Table S1. Sample locations.....	200
Table S2. EPMA major and trace element chemistry.....	203
Figure S1	204
Appendix 3: Supplementary information for chapter 3	205
SAMPLE PREPARATION	205
Carbon and Oxygen Isotope Analysis	205
Sample Pre-Leach and Leaching for Rb-Sr Isotope and Major- And Trace-Element Analysis	205
<i>Methanol pre-leach</i>	205
<i>Ammonium acetate pre-leach</i>	205

<i>Acetic acid leach</i>	206
ICPMS element analysis of carbonate.....	206
Sm-Nd isotope analysis	206
Whole rock geochemical analysis	207
WC-14- COMMENTS ON CORE DESCRIPTION	208
SEDIMENT PROVENANCE and WEATHERING	208
REFERENCES	210
REY ANOMALY EQUATIONS.....	211
FIGURES and TABLES	212
Figure S1. Sediment classification.....	212
Figure S2. Major element composition	213
Figure S3. Trace element distribution	214
Figure S4. La – Th- Sc ternary diagram and cross-plot of Th/Sc vs. Zr/Sc.....	215
Figure S5. Th – Zr/10 – Sc ternary diagrams by location.....	216
Figure S6. A – CN – K ternary diagram	217
Figure S7. Characterization of REY patterns	218
Figure S8. REY anomalies vs. initial $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}$	219
Table S1. REY sample locations	220
Table S2: Core locations	221
Table S3. Whole rock geochemistry	221

Abstract

The late Mesoproterozoic Oronto Group, Wisconsin and Michigan, preserves an extensive and continuous record of depositional environment and related microbial habitat. Over three kilometers of siliciclastic sediments with minor authigenic calcite record physical and biogeochemical processes acting within the Oronto Group basin at the time of deposition and early diagenesis. In this dissertation I explore the sedimentologic and geochemical signature of the lower Oronto Group (Copper Harbor Conglomerate, Nonesuch, and Freda Formations) with the goal of re-evaluating and refining evolving depositional conditions. Chapter 1 presents a revised sedimentologic and stratigraphic framework and evaluates published geochemical redox proxies and microfossil assemblages within this framework. Sedimentary facies indicate a pervasive shallow marine and tidal influence on deposition, requiring marine incursion to the Laurentian continental interior at ca. 1.08 Ga. Chapter 2 investigates the degree of marine connectivity to the Oronto Group basin using C, O, and Rb-Sr isotope compositions of calcite microspar in molar tooth (MT) structures and carbonate laminae of the Nonesuch Formation. Combined, these data show deposition within a restricted-marine epeiric setting where organic matter remineralization drove ^{13}C depletion, evaporative conditions drove ^{18}O enrichment, and $^{87}\text{Sr}/^{86}\text{Sr}$ reflects marine mixing with continental runoff. Chapter 3 evaluates conditions of salinity, redox, and productivity using whole rock geochemistry of fine-grained siliciclastics and rare earth element + yttrium (REY) distributions of calcite microspar. Shale geochemistry reveals deposition within an oxidized basin with a deep, fluctuating chemocline and expansion of anoxic and euxinic conditions during maximum flooding and base level lowstand. REY distributions of calcite microspar preserve an early diagenetic estuarine signal. Shale geochemistry and carbonate REY distributions bring into focus the prevalence of particle shuttling between the water column and shallow sediments that likely enhanced and focused nutrient P bioavailability, analogous to modern estuarine nutrient cycling. Collectively, these studies provide a richer understanding of late Mesoproterozoic environmental conditions that influenced early eukaryote ecology.

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Chapter 1: The end-Mesoproterozoic (ca. 1.08 Ga) epeiric seaway of the Nonesuch Formation, Wisconsin and Michigan, USA

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The end-Mesoproterozoic (ca. 1.08 Ga) epeiric seaway of the Nonesuch Formation, Wisconsin and Michigan, USA

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ABSTRACT

The Nonesuch Formation and related sedimentary units of the Oronto Group, southern Lake Superior region, USA, are commonly held to have been deposited in a lacustrine rift basin within interior continental Laurentia. Here we present new sedimentological and stratigraphic evidence that shows a marine influence on deposition. Tidally influenced shallow-marine sandstone and evaporitic, sandy and muddy tidal flat facies pass upward into fine-grained estuarine and sandy turbidite deposits, which are sharply overlain by mixed sandy and muddy tidal flat and flood plain deposits. These observations are evidence that the lower Oronto Group was deposited in an epeiric seaway, one of several such seaways that developed during the final amalgamation of Rodinia at a time of globally high sea level. Retrogradational-aggradational-progradational-degradational stratal architecture records changes in the relative balance between generation of accommodation space and sedimentation rates, which we interpret to reflect the combined influence of Grenvillian Ottawa Phase tectonic subsidence and thermal subsidence from earlier Midcontinent Rift magmatism.

We use this revised stratigraphic framework to show that the geochemical proxies of the Nonesuch Formation are tied closely to sedimentary facies and reflect intrabasinal redox heterogeneity rather than global anoxia at the end-Mesoproterozoic. Further, our sedimentology shows that purported lacustrine microfossils recovered from the Nonesuch rocks are primarily

associated with tidal flat facies. The combined influence of marine and local non-marine conditions must be considered when invoking the Nonesuch Formation, or similar marine-influenced interior basin deposits, as global analogues.

INTRODUCTION

The ~1.1 Ga Oronto Group (Figure 1) is among the oldest, best-preserved records of Mesoproterozoic microbial habitat. Stromatolites and a variety of well-preserved microfossils including bacteria and organic-walled microfossils are reported from the upper Copper Harbor Conglomerate and Nonesuch Formation, lower Oronto Group (Elmore, 1983; Wilmeth et al., 2014; Fedorchuk et al., 2016; Strother and Wellman, 2021), raising the question: To what degree are these units an analogue for latest Mesoproterozoic global conditions of habitat, oxygenation, and nutrient availability that set the stage for Neoproterozoic eukaryote evolution? Critically, assessment of environmental conditions recorded by the lower Oronto Group is complicated by conflicting interpretations of depositional environment such that the Nonesuch Formation is alternately thought of as fully lacustrine and anoxic (Cumming et al., 2013), a stratified lake with anoxic bottom waters and oxic surface waters (Suszek, 1997; Slotznick et al., 2018), a lake with an uncertain degree of marine influence (Elmore et al., 1989; Stewart and Mauk, 2017), a marine embayment or estuary (Hieshima and Pratt, 1991; Stüeken et al., 2020), and a tide- and wave-influenced, evaporitic shallow-marine environment (Jones et al., 2020). Resolving the depositional setting for the lower Oronto Group will clarify the degree to which these rocks record global versus local conditions, allowing nuance in how they can be used to constrain latest Mesoproterozoic Earth system development, from plausible levels of atmospheric oxygenation to the nature of microbial ecosystems on land.

We present a new sedimentologic and stratigraphic framework for the lower Oronto Group, with a focus on the Nonesuch Formation. We have significantly expanded the database of outcrop, core and well log information to span the entirety of the known occurrences of the Nonesuch. Our framework uses 39 cores, three historic logs, and six outcrop localities totaling over 14,080 m of stratigraphic section to identify and correlate genetically related stratal packages across ~250 km from the Ashland Syncline, Wisconsin, to the Keweenaw Peninsula, Michigan (Figure 1). This revised framework demonstrates the combined influence of tectonically driven subsidence and marine incursion on deposition of the lower Oronto Group. We place microfossils previously reported from the Nonesuch Formation (Wellman and Strother, 2015; Strother and Wellman, 2016, 2021) into this stratigraphic context.

GEOLOGIC SETTING

The Stenian Oronto Group is part of what has been termed the North American Midcontinent Rift System (MRS), a continental-scale feature whose geophysical trace extends for 2,200 km from Kansas north to Lake Superior and southeast to southern Michigan (Figure 1; Hinze and Chandler, 2020). The MRS evolved through a series of volcanic, sedimentary, and compressional stages spanning from c. 1112 to 1060 Ma and thought to be related to the combined effects of a mantle plume, continental extension, and the Grenvillian Orogeny (Woodruff et al. 2020 and references therein). The Copper Harbor Conglomerate, Nonesuch, and Freda Formations of the Oronto Group are interpreted as recording late-rift and post-rift stages and overlie thick accumulations of mostly mafic volcanic and intrusive rocks (Figure 1). These crop out along river cuts in northeastern Wisconsin and the Keweenaw Peninsula, Michigan, and are preserved in mineral exploration drill core (Figure 1, Supplementary Table S1). Seismic reflection data inform the regional distribution of these units and suggest the Oronto Group

onlaps MRS basalts and pinches out against antecedent topography that partitions volcanic sub-basins (Allen et al., 1997). Deposition of the Oronto Group within subbasins separated by basement highs is further supported by geologic mapping on the Keweenaw Peninsula (White and Wright, 1960; White et al., 1971) and observation of cores within the Ashland Syncline (Moerlein, 1963; Stewart and Mauk, 2017). The lithofacies distribution and stratal stacking patterns presented below largely support this basin geometry.

AGE CONSTRAINT

A U-Pb zircon age from an andesitic interflow within the lower Copper Harbor Conglomerate places a lower age constraint on the Oronto Group of 1085.57 ± 0.25 Ma (Fairchild et al., 2017). A Pb-Pb isochron date of 1081 ± 9 Ma is reported from a carbonate bed near the base of the Nonesuch Formation (Ohr, 1993), consistent with a Re-Os isochron date of 1040 ± 78 Ma from the lower part of that formation sampled along the Big Iron River (Figure 1) (Cumming et al., 2013). Rb-Sr ages of 1047 ± 37 Ma (Rb-Sr, Ruiz et al., 1984) on calcite veins that crosscut the Nonesuch Formation in the White Pine Mine provide a minimum depositional age constraint.

METHODS

Here we present sedimentologic and stratigraphic interpretation of the lower Oronto Group based on observation of cores from the Ashland Syncline (Wisconsin) and Presque Isle/Copperwood basin, White Pine basin, and Calumet area (Michigan), and outcrop sections exposed along river cuts in eastern Wisconsin and the Keweenaw Peninsula of Michigan (Figures 2 and 3). Locations for cores, measured sections, and locations mentioned in the text are shown on Figure 1 and coordinates are provided in Supplementary Table S1. All cores were drilled vertically. Bedding measured from planar-parallel laminations in all cores except CW-17

and JBY-002 are subhorizontal ($<10^\circ$). Bedding in CW-17 dips 30° while bedding in JBY-002 dips 25° , and true vertical thickness for these cores was calculated by taking the cosine of the dip angle multiplied by core thickness. Additionally, faults result in repeated section in drill cores WPB-2 and WPB-7 and, to a minor degree, at the Presque Isle River south section. Where possible, repeated section is excluded from the core description with the goal of representing the most accurate true thickness of each unit.

LITHOFACIES ASSOCIATIONS AND STRATIGRAPHIC FRAMEWORK

The lower Oronto Group is composed of fifteen lithofacies grouped into six associations, A through F, which we summarize below and in more detail in Table 1. First, each facies association description is followed by an interpretation of its depositional environment. Next, we describe formation lithostratigraphy (Copper Harbor Conglomerate, upper and lower Nonesuch Formation, Freda Formation, Figure 1) to facilitate building from and referencing back to over 100 years of prior work on the sedimentology and stratigraphy of the Oronto Group (e.g., Irving, 1883; Lane and Seaman, 1907; Van Hise and Leith, 1909; Thwaites, 1912; White and Wright, 1960; Elmore 1983; Kalliokoski and Welch, 1985; Kalliokoski, 1986; Elmore et al., 1989; Suszek, 1997; Stewart and Mauk, 2017; Jones et al., 2020). We then identify regionally correlative sequence stratigraphic surfaces, which diverge from formation boundaries and provide a framework for discussing a depositional model that links to the broader tectonic and geographic setting of Laurentia at the time of deposition.

Lithofacies Association A

Lithofacies association A (Figures 2, 3, and 4) consists of mostly cobble conglomerate (A1) and cross-bedded lithic sandstone (A2) with lesser planar- to ripple-laminated siltstone to sandstone (A3). Conglomeratic clast compositions of A1 match that of underlying rhyolite

domes and comprise conglomerate lenses that thin away from the edges of the domes (Cornwall, 1954; White and Wright, 1960).

Facies association A has long been interpreted as alluvial fan, braided stream, and overbank deposits (e.g. White and Wright, 1960; Elmore 1983, 1984; Elmore et al., 1989). Composition and spatial relationships of conglomerate lenses (A1) indicate they were derived from underlying rhyolite domes (Cornwall, 1954; White and Wright, 1960) and deposited as alluvial fans (Elmore, 1983; Elmore et al., 1989). Cross-bedded lithic sandstone and associated planar-laminated sandstone through siltstone (A2) are interpreted as braided stream and flood plain deposits while intercalated planar-laminated siltstone and sandstone (A3) preserve deposition within ponds on the alluvial braid plain. These facies may be observed at multiple localities and are present in close succession at the Potato River Falls section immediately below the lower Nonesuch Formation contact (labeled PR on Figures 1 and 2).

Lithofacies Association B

This lithofacies association is characterized by low-angle, small- to large-scale dunes (dm- to m-scale dune heights, Ashley, 1990, Reynaud and Dalrymple, 2011) with notably consistent geometry (B1, Figure 5). It is composed of medium- to fine-grained sandstone organized into low-angle trough cross-beds (Figure 5A, 5B) or low-angle planar cross-bed sets capped by ripple-laminated sandstone to siltstone (Figure 5E – G). Trough cross-bed tops have abundant current lineations and locally have mud drapes, mud clasts, mud cracks, and interference ripples. Load casts and ripples are common in interbedded, planar laminated sandstone and siltstone. The ripples locally have mud drapes and rarely ripple foresets dip opposite to a truncating reactivation surface. Thick, laterally continuous accumulations of lithofacies association B are restricted to basinward settings, along the Black River and Presque

Isle River and the axis of the Ashland Syncline (locations BH, PI, 4, and 5 on Figure 1, PI on Figure 3, see also Supplementary Table S1). We note the lateral (>200 m, outcrop exposure) and vertical continuity (at least 130 m) of this facies and remarkable consistency in grain size (medium- to fine- grained) and dune geometry at each outcrop (compare Figure 5A, 5B, and 5G). Also notable is the absence of conglomerate interbeds, channel forms, or significant scouring on basal bedding surfaces.

Previous interpretations of lithofacies associations B follow from the assumption that the alluvial fan deposits of lithofacies A prograded into a lacustrine basin (White and Wright, 1960; Elmore, 1984). Driven by the interpreted lacustrine setting, the low-angle cross-bedded sandstone is considered to have been deposited as migrating dunes, longitudinal bars, and channel lags during flash flood events on a medial alluvial fan (Elmore, 1984). However, lithofacies B lacks evidence for alternating unconfined and channelized flow characteristic of aggrading alluvial fans (Parker et al., 1998; Whipple et al., 1998; Clarke, 2015), evidence which would include poor or even chaotic preservation of facies or distinct channel and overbank deposits (Blair and McPherson, 1994; Clark, 2015; Moscariello, 2018; Ghinassi and Ielpi, 2018). Laterally continuous, vertically stacked facies are reported from alluvial fans that developed in endorheic, or internally drained, basins, but these facies are composed of sheets of poorly sorted conglomerate and sandstone with only weakly developed cross-bedding (Ventra and Nichols, 2014), distinct from lithofacies association B.

We suggest lithofacies association B was deposited in a tidally influenced shallow-marine setting rather than by flash flood events on an alluvial apron. Thick successions of dunes with regular geometry characterized by vertically stacked cross-bed sets of similar size, like those that compose lithofacies association B, are typical of tidal seaways (Dalrymple and Choi,

2007; Olariu et al., 2012; Reynaud and Dalrymple, 2011). Preservation of over 100 meters of laterally continuous, stacked, small- to large-scale dunes with regular geometry requires prolonged deposition in at least several meters water depth in a high accommodation setting. The local presence of sedimentary structures indicative of fluctuating tidal currents, most commonly mud draped ripples and rarely bi-modal current ripples with reactivation surfaces, support a tidally influenced shallow-marine interpretation (e.g., Jones et al., 2020). Other than these localized, small-scale sedimentary structures, the dune cross-bedding lacks indication of bi-modal or fluctuating currents because dunes migrate on timescales longer than timescales of daily tidal cycles (Allen, 1980; Ashley, 1990; Reynaud and Dalrymple, 2011). Local development of mud cracks, mud drapes, and interference ripples on cross-bed tops indicates shoaling and subaerial exposure of dunes. The geographic restriction of thick accumulation of lithofacies association B to basinward locations is characteristic of dune deposition within tidally influenced estuaries, where muddy and mixed tidal flat facies typically rim shorelines and sand dunes are common in deeper settings away from estuarine coastlines (Dalrymple and Choi, 2007).

Lithofacies Association C

Lithofacies association C shown in Figures 4c, 4d, and 6 and its spatial distribution is shown in Figures 2 and 3. It is composed of ripple and planar-laminated mud-draped and mud-cracked sandstone to siltstone (C1, Figure 4c and 4d), flaser to lenticular-bedded sandstone through shale (C2, Figure 6), and cross-bedded sandstone and pebble conglomerate (C3). Elmore (1984) notes bimodal, northeast- and southwest-directed paleoflow in ripple-laminated to low-angle, cross-bedded sandstone and siltstone (C1). Elmore (1983, 1984) and Elmore et al. (1989) provide excellent descriptions of minor stromatolitic intervals associated with ripple and planar-

laminated sandstone to siltstone exhibiting clast-rimming carbonate cement, evaporite textures and pseudomorphs, mud-drapes, and mud cracks (C1), which are further developed by Kalliokoski (1986), Wilmeth et al. (2014), Fedorchuk et al. (2016) and Jones et al. (2020).

Laterally continuous (at outcrop scale, >100 m), cm-thick, planar siltstone to very fine-grained sandstone beds are notable for their lenticular, wavy, and flaser bedding and abundant current ripples with mud-draped foresets and reactivation surfaces (C2, Figure 6). Locally, flaser to lenticular-bedded sandstone through shale (C2) is mud-cracked with soft-sediment deformation. Mud drapes line ripple foresets and reactivation surfaces, or mud is present as thicker (a few mm to cm), structureless laminae or thin beds.

Coarse- to medium-grained, cross-bedded sandstone or conglomerate (C3) occurs as dm- to m-thick intercalations. Cross-bed sets commonly have scoured bases and fine upward from pebble conglomerate to sandstone with local occurrences of mud chips draping cross-bed foresets and overlying scour surfaces. Mud balls are rarely associated with cross-bedded sandstone (Figure 6). Intervals of coarse- to medium-grained, cross-bedded sandstone are commonly several decimeters to meters thick. Conglomerate clasts are predominantly rounded rhyolite pebbles, though locally are angular.

Similar to lithofacies association B, previous interpretations of lithofacies association C are based on a depositional model of alluvial fans rimming a lacustrine rift basin. Following this model, the ripple and planar-laminated, mud-draped and mud-cracked sandstone to siltstone (C1, Figure 4c, 4d) is considered to be the lateral, basinward equivalent to lithofacies association B, preserving flash flood deposits on a distal alluvial fan (Elmore, 1984). White and Wright (1960) interpret south-directed flow observed in C1 (their “red facies”) to record sediment transport on a nearly flat-lying flood plain towards the toe of piedmont fans. Elmore (1984) interprets planar-

laminated sandstone, mud drapes, and bi-modal paleocurrents to have been deposited by waning, flashy sheet floods on the toes of alluvial fans. The flaser to lenticular-bedded sandstone through shale (C2) and cross-bedded sandstone and pebble conglomerate (C3) are interpreted as sandflat-mudflat deposits (Elmore et al., 1989).

In contrast to a purely non-marine setting, we interpret much of lithofacies association C to have been deposited in a muddy and mixed sand-mud tidal flat setting. Recent work emphasizes sedimentary structures and textures that support a tidal marine interpretation for the ripple- and planar-laminated, mud-draped and mud-cracked sandstone to siltstone facies (C1). At Horseshoe Harbor on the Keweenaw Peninsula (labeled HH on Figure 1), stromatolites are associated with sedimentary structures indicative of tidal modification (Davis, 2011) including bundled, rhythmically thickening and thinning sets of laminated siltstone-shale, and stacked sets of bimodal, mud-draped ripples and reactivation surfaces (Jones et al., 2020). Lenticular, wavy, and flaser bedding, mud-draped current ripples, and reactivation surfaces of facies C2 are also characteristic of tidal deposits (Reineck and Wunderlich, 1968; Klein, 1970; Dalrymple and Choi, 2007; Flemming, 2011). While heterolithic bedding composed of both coarse and fine sediment may form in any environment with both high and low depositional energy, the ubiquitous, laterally continuous, stacked tabular sets of flaser, wavy, and lenticular bedding together with bi-modal paleocurrents strongly suggest cyclic alterations of depositional energy characteristic of tides (Davis, 2011). Thicker mud laminations and thin very fine-grained beds (greater than a few mm thickness) that lack internal silt or sand partings may have been deposited as fluid muds that develop in estuaries due their density stratification of fresh river water and saline seawater (Dalrymple and Choi, 2007). Cross-bedded sandstone and pebble conglomerate (C3) intercalated with laminated or flaser bedded sandstone and shale (C2, D2) is

interpreted as dunes, ripples, and bars that formed within small distributary channels on the tidal flat. The presence of mud balls associated with cross-bedded sandstone and pebble conglomerate (C3) supports a tidal flat distributary channel interpretation, as these are common deposits in tide-dominated or tide-influenced channels (Dalrymple and Choi, 2007; Wellner et al., 2017).

Lithofacies Association D

Lithofacies association D is characterized by laminated, dark gray siltstone with variable interlaminated carbonate, clay, and sandstone. It includes laminated siltstone, carbonate, and shale (D1), finely laminated siltstone and shale (D2), and carbonate laminite (D2). Sedimentary structures and textures consistent with replacement of evaporite minerals are common (Figure 7), including micro-chicken-wire texture (see also Jones et al., 2020), swallow tail and Christmas-tree shaped pseudomorphs, and possible pseudomorphs after nodular and laminar gypsum or anhydrite (see also Elmore et al., 1989).

Repetitively thickening and thinning siltstone, carbonate, and shale laminations of facies D1 (Figure 7D) are bundled into cm-thick beds with common sand-starved ripples that are often carbonate-cemented. This facies forms a distinctive marker unit on the Keweenaw Peninsula (Figure 1) known as “stripey” in the mining literature (Bornhorst and Williams, 2013).

Finely laminated, dark gray siltstone and shale (D2) commonly lacks sedimentary structures or is locally characterized by very small (<1 mm) carbonate blebs (micro-chicken wire fabric), carbonate concretions that deform surrounding laminae, mud cracks, microbially induced sedimentary structures (MISS) or molar tooth (MT) structures (Figure 8). Mud cracks are relatively rare. Finely laminated, dark gray siltstone and shale (D2) is locally present intercalated with lithofacies association C and as minor layers associated with lithofacies association E (described below). We include finely laminated, dark gray siltstone and shale (D2) in lithofacies

association D because it is present in greatest abundance associated with laminated siltstone, carbonate, and shale (D1) and carbonate laminite (D3).

Carbonate laminite (D3) is a distinctive, laterally continuous unit that is gradational and intercalated with finely laminated siltstone and shale (D2). Everywhere it is preserved, carbonate laminite (D3) is notable for its fine (<mm to mm-thick), sharply interlaminated carbonate and shale with characteristic pellet-shaped microspar infilling MT cracks and locally composing laminae (Figure 8F, 8G; Stewart and Mauk, 2017), relatively high organic carbon (Elmore et al., 1989) and sulfur content (Imbus et al., 1992; Stewart and Mauk, 2017), and mineral assemblages and textures that indicate reducing pore water conditions (Elmore et al., 1989; Slotznick et al. 2018). Carbonate laminite (D3) is locally present interbedded with finely laminated siltstone and shale (D2) and graded sandstone through shale (lithofacies association E, described below).

Facies association D is interpreted to have been deposited under moderate to low energy, evaporative conditions. Laminated siltstone, carbonate, and shale (D1) are interpreted as shallower-water deposits while carbonate laminite (D3) is interpreted as deeper-water deposits. The planar lamination and finer grain size indicates deposition under lower energy conditions. Lateral continuity of interlaminated to thinly interbedded carbonate and shale and association and minor intercalation with lithofacies association E, interpreted as turbidites (described below), supports a setting below wave base (Figures 2 and 3, Flügel, 2004). Kriscautzky et al. (2022) note that MT cracks and their characteristic carbonate microspar are most abundant in sediments deposited near the sediment-water interface of shallow-marine, especially intertidal to shallow subtidal, settings. Thick-thin carbonate laminations (D1) may be pseudomorphs after laminar gypsum, and together with other evaporite textures and pseudomorphs, including chicken wire fabric, swallow tail and Christmas tree-shaped pseudomorphs, and nodular gypsum indicate

desiccation of a saline water body (Elmore, 1983; Rodríguez-Aranda, 1995; Flügel, 2004; Sanz-Montero et al., 2006; Jones et al., 2020). Based on the tidal marine interpretation of lithofacies association A and B, we interpret lithofacies association D as estuarine deposits that experienced evaporitic conditions (Flügel, 2004; Babel, 2007; Warren, 2010) as evident from the presence of evaporite pseudomorphs.

Lithofacies Association E

Lithofacies association E (Figure 9) includes graded sandstone and shale (E1) and massive sandstone with floating pebbles and cobbles (E2). Graded beds (E1) typically have a scoured base overlain by structureless, medium- to fine-grained sandstone that fines upward into low-angle cross-bedded, rippled, or laminated sandstone, siltstone, or shale. Flute casts, load casts, and linear sole marks are common sedimentary structures imprinted on the base of massive sandstone beds. Massive sandstone beds with floating pebbles and cobbles (E2) are organized into dm- to m-thick, lenticular beds with scoured bases.

Normally graded sandstone and shale (E1) is interpreted as turbidite lobe deposits, consistent with previous interpretations (Elmore et al., 1989; Suszek, 1997; Stewart and Mauk, 2017). Internally structureless sandstone with flutes and other tool marks overlain by upward fining planar laminated to ripple laminated sandstone, siltstone, and shale are interpreted as Bouma Ta through Te layers (Kuenen, 1953; Bouma, 1962; Dott, 1963; Lowe, 1981; Shanmugam, 1997; Peakall et al., 2020). Massive sandstone with floating pebbles and cobbles (E2) are interpreted as channelized sandy debrite deposits (Postma et al., 1988; Shanmugam, 1997).

Lithofacies Association F

Lithofacies association F (Figure 10) is notably red due to abundant hematite and includes soft-sediment deformed sandstone through shale (F1), thin-bedded shale through sandstone (F2), and lenticular sets of cross-bedded sandstone and conglomerate (F3). Soft-sediment deformed sandstone through shale (F1) is characterized by its poor sorting, abundant soft-sediment deformation, locally abundant flaser bedding, mud roll ups, tepee structures, and cm- to dm-thick intercalations of cross-bedded sandstone. Thin-bedded shale through sandstone (F2) is recognized by distinctive reduced intervals (1 to <4 cm thick) characterized by green to gray poorly sorted sandstone with mm- to cm-scale, rounded carbonate nodules overlain by laminated siltstone and clay with angular, broken clay laminae, tepee structures, mud chips, and locally capped by mm- to cm-scale mud-cracked shale. Cross-bedded sandstone and conglomerate (F3) is organized into upward-fining composite sets above an erosive, lenticular basal surface. The basal surface may be overlain by a pebble lag, conglomerate, or cross-bedded sandstone. Sets of cross-bedded sandstone or conglomerate are commonly overlain by thin planar bedded to planar laminated fine-grained sandstone, siltstone, and shale. Cross-bedded sandstone and conglomerate (F3) are relatively minor constituents of lithofacies association F, locally present in intervals several meters to 10s of meters thick, and interbedded with lithofacies F1 and F2.

Lithofacies association F is interpreted to represent floodplain deposition with lesser fluvial and overbank deposits and tidal reworking. Abundant soft-sediment deformation, scour surfaces overlain by pebbles or mud chips, and upward-fining beds characteristic of F1 may have been produced by liquefaction, dewatering and/or shear stress during emplacement of the overlying bed, or waning flow driven by rapid deposition during flooding events (Owen, 1987; Bridge, 2006). Desiccation cracks, clay roll ups, and tepee structures indicate periods of

subaerial exposure (Asserto and Kendall 1977; Kendall and Warren, 1987; Weinberger, 1998). Locally abundant flaser bedding suggests periods of tidal modification (Reineck and Wunderlich, 1968; Dalrymple and Choi, 2007; Flemming, 2011). Soft sediment deformed sandstone through shale (F1) is interpreted as floodplain deposits along the margin of a tidally influenced estuary that was frequently modified by fluvial or marine flooding and tidal reworking.

Thin-bedded shale through sandstone (F2) is likely the lateral equivalent to soft-sediment deformed sandstone through shale (F1), deposited landward of tidal flats. Centimeter-thick, laterally continuous (meters to tens-of-meters) planar beds composed of poorly sorted fine-grained sandstone, siltstone, and clay with abundant sand-filled mud cracks typical of F2 demonstrate subaerial deposition. Sandstone beds may be levee and crevasse splay deposits while fine-grained interbeds are flood plain deposits (Bridge, 1984, 2006; Kraus, 1986). Green to gray, cm-thick sandstone intervals with carbonate nodules and associated overlying teepee structures, mud cracks, mud chip curl ups are incipient soil horizons (Asserto and Kendall 1977; Kraus, 1986; Brown and Kraus, 1986; Kendall and Warren, 1987). Stacked, meters-thick, lenticular sets of cross-bedded sandstone (F3) locally intercalated with F1 and F2 are interpreted as fluvial channel fill (Bridge, 2006).

Formation Lithostratigraphy

Copper Harbor Conglomerate

The Copper Harbor Conglomerate underlies the Nonesuch Formation is mostly composed of lithofacies associations A (Figures 2 and 3). Facies association B is locally significant and spatially restricted to the axis of the Ashland Syncline, between Black River Harbor and the Presque Isle River, and along the Big Iron River (labeled Ashland Syncline, BH and PI on Figures 1 and 3). Lithofacies C1 is locally present, for example at Horseshoe Harbor and in the

JBY-002 core near Calumet, MI (labeled HH and 10 on Figure 1, JBY-002 on Figure 2, see also Supplementary Table S1).

Lower Nonesuch Formation

The lower Nonesuch Formation is observed in all drill core and measured sections (Figures 2 and 3). Historically the base of the Nonesuch Formation has been placed at a relatively abrupt (cm- to dm- scale) transition from red, cross-bedded sandstone or conglomerate with abundant mud chips and carbonate cement (lithofacies association A and lithofacies C1) to gray or green sandstone or shale (lithofacies associations C and D; Moerlein, 1963; White, 1972; Suszek, 1997). Locally, for example at the Presque Isle River south section (labeled PI on Figures 1 and 3, also see Supplementary Table S1), the basal contact is placed at the abrupt contact between a thick succession of low-angle cross-bedded sandstone (lithofacies association B) and overlying finely laminated siltstone and shale (lithofacies association D).

Above the basal Nonesuch contact, lithofacies association C passes into D, which is sharply overlain by E (Figures 2 and 3). Flaser- to lenticular-bedded siltstone, shale, and sandstone (C2), cross-bedded sandstone and pebble conglomerate (C3), and finely laminated siltstone and shale (D2) intercalate and pass upwards into laminated siltstone, carbonate, and shale (D1), finely laminated siltstone and shale (D2), and carbonate laminite (D3). Carbonate laminite is present at about the same stratigraphic level relative to the base Nonesuch Formation across most of the Ashland Syncline and the Presque Isle and Western Syncline and White Pine areas on the Keweenaw Peninsula (labeled Ashland Syncline, PI, WS, and WP on Figure 1). Carbonate laminite is absent in the Copper Falls and Potato River Falls sections and cores JBY-002 and WC-25 (labeled CF, PR, 10, and 1 on Figure 1, see also Figures 2 and 3, Supplementary Table S1).

Lithofacies association E is a distinctive, thick (tens-of-meters), laterally continuous interval at the top of the lower Nonesuch Formation in most locations (Figures 2, 3, and 9). The base of this interval is sharp and locally associated with soft-sediment deformation. At the Potato River Falls section (labeled PR on Figures 1 and 2, also see Figure 9), meter-scale sand-filled dikes cut beds of flaser- to lenticular-bedded siltstone, shale, and sandstone (C2) that underlie the lowermost bed of normally graded sandstone (E1). At a few localities (CW-17-190, Potato River Falls, WC-9, labeled 8, PR, and 7 on Figure 1, see also Figures 2 and 3, Supplementary Table S1), a relatively thin interval (~10 m) of normally graded sandstone (E1) underlies about three meters of finely laminated dark gray siltstone and shale (D2) and carbonate laminite (D3), which in turn is overlain by relatively thick (~60 m) normally graded sandstone (E1).

Upper Nonesuch Formation

The upper Nonesuch Formation is present at all locations except the Copper Falls locality and cores JBY-002 and WC-25 (labeled CF, 10 and 1 on Figure 1, see also Figures 2 and 3, Supplementary Table S1) and is mostly composed of lithofacies associations B and C. The contact between the upper and lower Nonesuch Formation is sharp and most easily recognized where flaser- to lenticular-bedded sandstone-shale (C2), locally with mm-scale sand-filled mud cracks and micro-chicken-wire fabric, tepee structures, and carbonate-replaced former sulphate nodules ('cauliflowers', e.g. core WC-14, labeled 2 on Figure 1), overlies lithofacies association E. The contact between the lower and upper Nonesuch Formation is difficult to identify where lithofacies association B overlies E, for example, at the Big Iron River and in cores PI-2 and WC-9 (labeled BI, 8, and 7 on Figure 1, see also Supplementary Table S1).

Freda Formation

The Freda Formation is present at all locations and is mostly composed of lithofacies association F. Traditionally, the basal Freda contact is defined by a color change from gray to red and an increase in white mica content across a gradational contact several tens to as much as 100 meters thick (White et al., 1953; Moerlein, 1963; Suszeck, 1997; Daniels, 1982). Geologic maps and historic mineral exploration reports describe a conglomerate marker bed within the lower Freda Formation (Cannon et al., 1996; Moerlien, 1963). We do not observe such a marker unit and instead note stacked sets of conglomeratic and cross-bedded sandstone (F3) locally intercalated with thin-bedded shale through sandstone (F2) throughout the Freda Formation.

Sequence Stratigraphic Surfaces

Regionally correlative stratigraphic surfaces diverge from formation lithostratigraphic boundaries and are identified based on retrogradational, aggradational, progradational, and degradational lithofacies stacking patterns (Neal and Abreu, 2009). These provide a framework for interpreting allogenic drivers of basin evolution (Catuneanu, 2022). Our stratigraphic framework expands upon and refines the framework presented by Stewart and Mauk (2017) to create and extend a depositional framework across the entirety of the Nonesuch Formation in both outcrop and subsurface.

Transgressive Surface

A transgressive surface separates fluvial and alluvial sedimentary rocks (lithofacies association A) of the Copper Harbor Conglomerate from shallow-marine facies (lithofacies associations B, C, and D) of the upper Copper Harbor Conglomerate and lower Nonesuch Formation (labeled 1 on Figures 2 and 3). At most locations, this surface coincides with the base Nonesuch Formation and separates tidal and mud flat shale and siltstone (lithofacies association C) from underlying conglomeratic or cross-bedded sandstone alluvial and fluvial deposits

(lithofacies association A). At locations where the basal Nonesuch contact is present between low-angle, cross-bedded tidally influenced shallow-marine sandstone (lithofacies association B) and tidal and mud flat deposits (lithofacies associations C and D), the transgressive surface is at the base of the marine deposits (facies B1) within the upper Copper Harbor Conglomerate, for example at the Presque Isle River and Big Iron River sections, labeled PI and BI on Figures 1 and 3, see also Supplementary Table S1).

Maximum Flooding Surface

A maximum flooding surface can be identified throughout the Ashland Syncline and across the Keweenaw Peninsula (labelled 3 on Figures 2 and 3). In most locations, it is placed at the base of the carbonate laminite deposits (facies D3, also see Stewart and Mauk, 2017). In locations thought to be underlain by older Precambrian basement topographic highs (White and Wright, 1960; Allen et al., 1997; WC-25, Copper Falls, Potato River Falls, JBY-002, labeled 1, CF, PR, and 10 on Figure 1, see also Figures 2 and 3, Supplementary Table S1), the carbonate laminite is not developed and instead the interval is marked by finely laminated shale. In these instances, the maximum flooding surface is placed at the base of the shale. Stratal stacking patterns change from retrogradational to aggradational across this surface (Figures 2 and 3).

The thick interval of turbidite deposits (lithofacies association E) that sharply overlies the carbonate laminite and finely laminated shale units (~60 meters thick in core WC-9, labeled 7 on Figure 1 and the Presque Isle River south measured section, labeled PI on Figure 1, Figures 2, 3) marks a change from aggradational to progradational stratal stacking patterns. The abrupt, regional nature of this change and marked increase in sandy sediments, along with presence of injectites and abundant soft-sediment deformation, demonstrate sudden, rapid onset and enhanced rates of sedimentation.

Sequence Boundary

A sequence boundary (labeled 4 on Figures 2 and 3) caps strata with aggradational-progradational-degradational stratal stacking patterns (Neal and Abreau, 2009) based on the observation of a basinward shift in facies (shoreward facies unconformably above basinward facies) and erosion and non-deposition associated with subaerial exposure. At more basinward locations the surface separates tidally influenced nearshore sandstone or tidal flat and flood plain deposits (lithofacies associations B, C, F) of the upper Nonesuch and Freda Formations from underlying turbidite deposits (lithofacies association E, for example, cores WC-9, PC-1 and WPB-2 and the Presque Isle River and Big Iron River sections, labeled 7, 8, 9, PI, BI on Figure 1, also see Supplementary Table S1, Figures 2 and 3). Here, the surface marks a facies incongruity with a basinward shift in facies. At shoreward locations (cores WC-25 and WC-14, Copper Falls State Park, and core JBY-002, labeled 1, 2, CF, 10 on Figure 1, also see Supplementary Table S1 and Figures 2 and 3), tidal flat, flood plain, and fluvial facies with evaporite textures and soil horizons (lithofacies association F) of the Freda Formation are juxtaposed across the sequence boundary against tidal flat facies (lithofacies association C) of the lower Nonesuch Formation, and carbonate laminite (facies D3) and turbidite deposits (lithofacies association E) are absent. The thinner stratigraphic section and subaerial facies here are consistent with non-deposition, erosion, and a degradational stratal stacking pattern.

Using the base Nonesuch Formation as a datum, the sequence boundary has several tens of meters of apparent vertical relief across the study area (Figures 2 and 3). In some locations it is present ~90 to 140 meters above the base Nonesuch Formation (e.g. WC-9, PI-2, Presque Isle River, labeled 7, 8, PI on Figure 1) whereas in others its height above the base Nonesuch ranges from ~ 60 to as little as 20 meters (e.g. WC-25, WC-14, Copper Falls State Park, Big Iron River,

JBV-002, labeled 1, 2, CF, BI, 10 on Figure 1, also see Supplementary Table S1 and Figures 2 and 3). Locally, for example in the Presque Isle area (labeled PI on Figure 1), the sequence boundary has as much as ~ 20 to 40 meters of apparent vertical relief over lateral distances of 0.5 to 2.5 km. Above the sequence boundary, conformable, aggradational to progradationally stacked, tidally influenced nearshore sandstone, tidal flat, and fluvial to floodplain facies of the upper Nonesuch and Freda Formations record progradation of a broad, flat floodplain and associated fluvial deposits over estuarine deposits.

DISCUSSION

Depositional Model

The upper Copper Harbor Conglomerate, Nonesuch, and lowermost Freda Formations preserve a vertical facies assemblage that records deposition within a tidally influenced, shallow-marine setting. The same vertical facies assemblage is observed across ~250 km from the Ashland Syncline to the eastern Keweenaw Peninsula. The upper Copper Harbor Conglomerate and lower Nonesuch Formation is a transgressive succession of tidally influenced sandy nearshore, tidal flat, evaporative estuarine, and carbonate laminite deposits. The carbonate laminites are capped by relatively thick sandy turbidites. The upper Nonesuch Formation sharply overlies the turbidites and records a return to a tidally influenced shallow-marine environment including tidally reworked nearshore sandstone and tidal flat deposits. In landward settings (WC-25, Copper Falls State Park sections, and JBV-002, labeled 1, CF, and 10 on Figure 1, see also Supplementary Table S1 and Figures 2 and 3), flood plain and fluvial deposits of the upper Nonesuch and Freda Formations directly overlie tidal flat deposits of the lower Nonesuch Formation.

The presence of tidal flat, estuarine, and tidally influenced nearshore facies require marine flooding several hundred kilometers into the interior of Laurentia. A depositional model that most parsimoniously accounts for these features is a geographically restricted basin with connection to the ocean, in other words an epeiric sea. The marine incursion onto interior Laurentia initially flooded alluvial and braided stream deposits of the Copper Harbor Conglomerate. Tidally modified nearshore sandstone was deposited in areas of greatest differential subsidence, along the axis of the Ashland Syncline and near the Presque Isle River on the Keweenaw Peninsula (e.g. Stewart and Mauk, 2017, labeled Ashland Syncline and PI on Figure 1). Away from these areas, siltstone, shale, and very fine-grained sandstone were deposited in tidal flats. In the Ashland Syncline, cross-bedded, conglomeratic sandstone was deposited within distributary channels that cut across the tidal flats of the lower Nonesuch Formation. The thickness and frequency of these deposits is greatest towards the northwest flank of the Syncline, (towards locations 1 and 2 on Figure 1) and indicating sediment was sourced from the north and transported to the southeast (Moerlein, 1963; Stewart and Mauk, 2017).

Relative base level rise continued during deposition of the lower Nonesuch Formation, marked by estuarine and shallow-marine siltstone, shale, and carbonate laminites that backstep over tidal flat and nearshore sandstones. These settings were characterized by repetitive evaporative conditions typified by laminated carbonate and associated siltstone, shale, and sand-starved ripples passing up section into laminated shale with common micro-chicken-wire fabric and rare carbonate pseudomorphs.

Deeper-water carbonate laminite deposits and associated laminated shale aggraded above shallower-water estuarine strata across the maximum flooding surface. Organic carbon content, carbon and sulfur isotopes (Elmore et al., 1989; Imbus et al., 1992; Stewart and Mauk, 2017),

magnetic mineral facies, and petrographic observations (Slotznick et al., 2018) indicate deposition occurred in reducing, quiet water conditions. Alternating carbonate/clay laminae reflect fluctuating alkalinity perhaps driven by uptake of CO₂ via photosynthesis (Elmore et al., 1989). A chemocline could have existed in deeper settings, favoring preservation of organic carbon, microbial reduction of iron oxide mineral phases, and formation of early diagenetic pyrite (e.g., Elmore et al., 1989; Slotznick et al., 2018; Rico et al., 2019). Alternatively, anoxic conditions could have developed in shallow pore waters below the sediment-water interface (Slotznick et al., 2018). The water column and pore water chemistry interpreted from this interval reflects basin-specific geomorphology and changes in alkalinity and redox conditions perhaps caused by the combined effects of deposition within a basin that was episodically restricted from open marine water (Warren 2010) and experienced relatively high photosynthetic productivity, as suggested by Elmore et al. (1989).

The lateral continuity of the carbonate laminite unit and its near-constant stratigraphic position above the base Nonesuch across the study area indicates its deposition was linked to maximum transgression that flooded the landscape. Local areas of pre-existing topographic highs were present, though, at the northwest flank of the Ashland Syncline (towards locations 1 and 2 on Figure 1, near the Copper Falls, Potato River, and Parker Creek localities at the Wisconsin-Michigan border (labeled CF, PR, and PC on Figure 1), and east of the White Pine area on the Keweenaw Peninsula (labeled WP on Figure 1, see also Supplementary Table S1 and Figures 2 and 3, White and Wright 1960; Moerlein, 1963; Allen et al., 1997).

Aggradation of carbonate laminite deposits was replaced by sandy turbidite flows that accumulated 10 to 200 meters of stacked turbidite deposits. Above the turbidites, a regional drop in base level is marked by development of a sequence boundary and basinward shift from

turbidite deposits of the lower Nonesuch Formation to shoreface sandstone and tidal flat deposits of the upper Nonesuch Formation. These shallow-water deposits pass conformably into several kilometers of low-relief floodplain deposits with local tidal reworking, soil development, and cross-cutting fluvial channel fills of the Freda Formation.

A Changing Balance Between Accommodation Space and Sedimentation Rates

The stratigraphic architecture of the lower Oronto Group records a changing balance between the generation of accommodation space and sedimentation rates that links to the broader tectonic and geographic setting of Laurentia at ca. 1080 Ma. Because these rocks were deposited on continental crust well within the interior of Laurentia, basin morphology would have strongly influenced accommodation space, similar to modern and ancient lakes and inland seas (e.g., Carroll and Bohacs, 1999; Major et al., 2002; Bohacs et al., 2003; Babel, 2007; Warren, 2010). Specifically, accommodation was defined by the elevation difference between the basin floor and its margins, and modified by some combination of basin floor subsidence, margin uplift, and/or global sea level change. Subsidence is traditionally attributed to thermal subsidence after MRS volcanism (Cannon, 1992; Swanson-Hysell et al., 2019; Hinze and Chandler, 2020). Below we develop the idea that deposition of the lower Oronto Group took place within an epeiric seaway whose accommodation and restriction from open marine water was modulated by tectonic subsidence and margin uplift related to the Ottawan phase of the Grenvillian Orogeny superimposed on areas of preexisting crustal weakness created by earlier extensive MRS magmatism.

At first, sedimentation rates exceeded generation of accommodation space, causing conglomerate and coarse-grained sandstone of the Copper Harbor Conglomerate to prograde from highlands and coalesce into broad alluvial fans (Stewart and Mauk, 2017). Initial marine

flooding over coalesced alluvial fan deposits records a regional increase in the generation of accommodation space relative to sedimentation rates. Accommodation space continued to increase relative to sedimentation rates through deposition of most of the lower Nonesuch Formation. The maximum flooding surface marks the time of maximum transgression when available accommodation space mostly exceeded sedimentation rates. Aggradation of carbonate laminites and laminated dark shale above the maximum flooding surface records a quasi-steady state between generation of accommodation space and sedimentation rates.

Turbidite deposition above the carbonate laminites preserves a sustained, basin-wide shift from aggradation to progradation. Although the onset of turbidites at the top of the lower Nonesuch Formation represents a prolonged, basin-wide increase in sediment flux, the imbalance between rates of generation of accommodation space and sedimentation continued.

The sequence boundary at the top of the lower Nonesuch Formation preserves a transition in the balance between generation of accommodation space and sedimentation rates. Across the sequence boundary the balance shifted such that generation of accommodation space slowed relative to sedimentation rates. By upper Nonesuch and Freda time, broadly distributed subsidence was paced by sedimentation, resulting in aggradation of mostly shallow-marine nearshore sandstone and tidal flat facies overlain by flood plain deposits with soil horizons.

Traditionally, space to accommodate deposition of the Oronto Group is interpreted to be driven by thermal subsidence that kept pace with sedimentation after earlier volcanism and extension stopped (Cannon, 1992). Thermal subsidence would be expected to gradually decay through time resulting in progradational stacking patterns, inconsistent with our observation of retrogradational stacking patterns in the upper Copper Harbor and lower Nonesuch formations. The changing balance between generation of accommodation space and sedimentation rates

indicates another process superimposed on thermal subsidence that influenced deposition of the Oronto Group. Tectonic subsidence and global sea level rise are possible controls on basin subsidence and sedimentation rates that we explore below. Climate-driven changes in sediment and water supply also potentially influenced the balance between rates of change in accommodation space and sedimentation (Carroll and Bohacs, 1999), but poor age resolution makes this hard to test, and we do not further discuss climate.

Coeval with the basin-wide changes in accommodation and sediment flux recorded by the Oronto Group was the Ottawa Phase of the collisional Grenvillian Orogeny (ca. 1090 – 1020 Ma; Rivers, 2008). This temporal link indicates changes in accommodation and sedimentation during Oronto Group deposition could have been controlled by flexural subsidence in response to crustal thickening during Ottawa Phase deformation. Tectonic subsidence at least 600 km west of the Grenville Front may have been focused where the crust was weakened by earlier MRS volcanism and could have modulated deposition of the Oronto Group.

A similar combined influence of the Grenvillian Orogeny and MRS magmatism is thought to have controlled deposition within other latest Mesoproterozoic to early Neoproterozoic Laurentian sedimentary basins. The Jacobsville Formation ($<992.51 \pm 0.64$ Ma CA-ID-TIMS detrital zircon maximum depositional age, Hodgin et al., 2022), which overlies the Oronto Group on the Keweenaw Peninsula (Figure 1), and the Middle Run Formation ($<1016 \pm 12$ Ma LA-ICPMS detrital zircon maximum depositional age, Clay et al., 2021), present in the subsurface of Ohio, Kentucky, and Indiana of the eastern US Midcontinent, are interpreted to have been deposited in basins that developed in the Grenville foreland in response to the younger Rigolet Phase (ca. 1000 – 980 Ma; Rivers, 2008) of the Grenvillian Orogeny (Santos et al., 2002; Baranoski et al., 2009; Moecher et al., 2018; Clay et al., 2021; Hodgin et al., 2022). Farther

away, strata within the Bylot (Re-Os isochron ages of 1046 ± 16 Ma and 1048 ± 12 Ma, Gibson et al., 2019 and 1087.1 ± 5.9 Ma, Greenman et al., 2021) and Amundsen basins (Re-Os isochron age 1067.3 ± 13.5 Ma, Rainbird et al., 2020), Arctic Canada were deposited coeval to several tens of millions of years after the Oronto Group. These strata are interpreted to have been deposited in extensional basins (Gibson et al., 2019; Greenman et al., 2023) punctuated by periods of uplift (Sherman et al., 2002; Turner et al., 2016; c.f. Gibson et al., 2019) that developed as a result of Grenvillian orogenic far-field stresses (Turner et al., 2016) or by reactivation of older structures in response to a thermal anomaly associated with the MRS (Greenman et al., 2021).

The terminal Mesoproterozoic (ca. 1.0 Ga) is a time of high global sea level and marine flooding of continents with deposition in epeiric seaways (e.g., Kah et al., 2012; Gilleaudeau and Kah, 2013a, 2013b, 2015; Peters et al., 2017; Rainbird et al., 2020; Kah and Bartley, 2022). Evidence for broad, shallow epeiric seas on the growing Rodinian supercontinent are preserved in the Amundsen and Bylot basins (Rainbird et al., 2020), the Taoudeni Basin of Mauritania, Mali, and Algeria in west Africa (Kah et al., 2012) and the Oronto Group (Hieshima and Pratt, 1991; Jones et al., 2020; Stüeken et al., 2020; this study). Just as early Paleozoic expansion of epicontinental seas has been linked to the evolution of biomineralization (Peters and Gains, 2012), expansion of latest Mesoproterozoic to early Neoproterozoic epeiric seas may have created widespread conditions favorable to eukaryote diversification, including low or fluctuating salinity (Sanchez-Barcaldo, 2015; Sanchez-Barcaldo et al., 2017; Gibson et al., 2019; Stüeken et al., 2021) and greater bioessential trace metal availability (Anbar and Knoll, 2002; Gilleaudeau and Kah 2013b; Stüeken, 2013).

The Nonesuch Inland Sea: Implications of Marine Influence on Global Paleogeographic and Environmental Reconstructions

Notwithstanding the uncertainty of paleogeography at c. 1080 Ma, the lower Oronto Group is commonly interpreted to have been deposited within an intracontinental lacustrine rift basin because of the perception that it is located too far into the interior of the Laurentian margin to have had an oceanic connection (Elmore et al., 1989; Ojakangas 2001). However, the sedimentological and geochemical evidence indicates deposition in an inland seaway with shorelines marked by broad, shallow estuaries and tidal flats, water bodies having fluctuating salinities, and with enough of a connection to the open ocean to experience significant tidal forcings (Hieshima and Pratt, 1991; Jones et al., 2020; Stüeken et al., 2020; this study). This latest Mesoproterozoic marine-influenced basin was one of several approximately coeval epeiric seaways within Laurentia that host well preserved, diverse microfossil assemblages, (Gibson et al., 2018, 2019; Loron et al., 2019a, 2019b; Rainbird et al., 2020), including the oldest occurrence of fungi (Loren et al., 2019) and photosynthetic eukaryote microfossils (Gibson et al., 2018) preserved in the fossil record.

Accurate interpretation of depositional environment is a prerequisite for any meaningful inferences from the Nonesuch Formation about global evolutionary or environmental conditions. Basin morphology, dominant processes (tide, wave, fluvial, biogeochemical, mineralogical), and differences in rates of accommodation versus sedimentation are primary variables that control the distribution of physical rock properties (grain size, organic carbon content, sediment geochemistry and mineralogy, stratigraphic segmentation), which are the basis for interpreting ancient environmental conditions (e.g., Ainsworth et al., 2011; Swanner et al., 2020; Khan et al., 2021 and references therein). Because the defining variables of inland seas differ from open-

marine settings, and because inland seas are more likely influenced by local conditions, direct extrapolation of environmental conditions interpreted from the Oronto Group to global conditions is tenuous.

Sulfur and iron speciation data are common geochemical tools for linking global Mesoproterozoic redox conditions, nutrient cycling, and evolution (Gilleaudeau and Kah, 2015; Guilbaud et al., 2015). The elevated abundances of redox sensitive, bioessential elements in the Nonesuch Formation reflects their elevated abundance in the surrounding basement rocks rather than and in addition to authigenic enrichment under reducing conditions (Slotznick et al., 2018; Rico et al., 2019; Stüeken et al., 2021). Parsing whether these and other local basins record chemistry relevant for understanding global marine conditions is dependent on placing geochemical trends in stratigraphic context. Globally anoxic non-marine conditions inferred from iron speciation data sampled from the estuarine carbonate laminite facies of core PI-1 (Cumming et al. 2013; labeled 8 on Figure 1, see also Supplementary table S1) do not adequately account for depositional setting or sediment provenance. When corrected for stratigraphic position, the Fe speciation data from PI-1 is consistent with that from the Ashland Syncline (Slotznick et al., 2018; Rico et al., 2019), indicating predominantly oxic conditions, with possibly anoxic conditions limited to the deeper estuarine facies. Notably, Fe speciation data from tidal flat and fluvial facies of the upper Nonesuch and Freda Formations suggests anoxic conditions, but this reflects elevated detrital hematite in those units, consistent with their redder color (Slotznick et al., 2018). Geochemical trends in the Nonesuch Formation therefore primarily reflect intrabasinal variations caused by the interplay between sediment provenance, water column, pore water, and biogeochemical processes that are not directly correlative to possible global marine redox conditions. Local conditions, however, likely set the stage for the

accumulation and exceptional preservation of late Mesoproterozoic microfossil assemblages (Wellman and Strother, 2015; Strother and Wellman, 2016, 2021; Gibson et al., 2019).

Latest Mesoproterozoic Ecosystems

A well-preserved, diverse microfossil assemblage is reported from the Nonesuch Formation (Strother and Wellman, 2021). This documented biodiversity and interpreted lacustrine rift setting was the basis for offering hypotheses that non-marine settings favored early eukaryote evolution (Wellman and Strother, 2015; Strother and Wellman, 2016). Paleoecologic interpretation is inextricably tied to the depositional setting of the rocks that host the fossils, and in the case of the Nonesuch palynomorphs the depositional setting is marginal marine. This marginal marine setting, and the discovery of a notably diverse fossil assemblage, including fungi and photosynthetic algae from marine-influenced strata of the Amundsen and Bylot basins (Gibson et al., 2018, 2019; Loron et al., 2019a, 2019b; Rainbird et al., 2020) calls into question their use as evidence to postulate that lacustrine settings were refugia for eukaryote evolution during the latest Mesoproterozoic.

Placing the palynomorphs documented in the literature from the Nonesuch Formation within our stratigraphic context demonstrates that most were recovered from shallow, tidally influenced shoreface and tidal flat deposits of the upper Nonesuch Formation (Figure 3, Supplementary Table S2). Published descriptions of microfossils are reported from seven cores from the White Pine and Presque Isle areas and from outcrops of the Presque Isle and Big Iron Rivers, Michigan (Wellman and Strother, 2015; Supplementary Table S2, labeled 9, 8, and BI on Figure 1). Of these, specific location information that allows samples to be linked to stratigraphic position and depositional setting are provided for 26 individual cells or cell clusters separated from one outcrop sample and 13 samples collected from four drill cores (Wellman and Strother,

2015; Strother and Wellman, 2016, Supplementary Table S2). Seven samples were taken from the upper Nonesuch Formation tidal flat facies, one was collected from tidal flat to flood plain deposits from the upper Nonesuch to Freda transitional zone, two were sampled from siltstone and shale interbedded with low-angle, cross-bedded shoreface sandstone from the upper Nonesuch Formation, three were collected from estuarine facies from the middle part of the lower Nonesuch Formation, and one was sampled from tidal flat facies from the lower part of the lower Nonesuch Formation. Notably, the species *Eohalothece lacustrina* was defined with type locality and paratype collected from mixed tidal flat and floodplain facies within the transitional zone between the uppermost Nonesuch and Freda Formations in core PC-1 (Strother and Wellman, 2016; labeled 8 on Figure 1, see also Figure 3 and Supplementary Table S1 for location). Additional examples of *E. lacustrina* are reported from an outcrop sample of low-angle, cross-bedded, tidally influenced shoreface sandstone along the Presque Isle River near where it empties into Lake Superior (labeled PI on Figure 1, also see Supplementary Table S1 and Figure 3, Figure 5G shows outcrop photo) and from tidal flat facies from both the uppermost upper Nonesuch Formation and lower Nonesuch Formation sampled from core WPB-4. Although the Latin name derivation means “of the lakes,” all the reported samples that can be tied to location information were collected from sedimentary facies with clear tidal indicators or associated floodplain deposits, demonstrating this species lived in shallow-marine-influenced and adjacent settings. Furthermore, Loron et al. (2019b) suggests *E. lacustrina* is the same taxon as *Eosynochococcus* collected from marginal marine facies of the Amundsen basin, Arctic Canada.

Most microfossils were recovered from the upper Nonesuch Formation, which may have paleoecologic significance, or alternatively, it may represent preservation bias. During deposition

of the carbonate laminite facies of the lower Nonesuch Formation, relatively elevated biologic productivity may have resulted in fluctuating alkalinity and suboxic to anoxic water column or pore water conditions via photosynthetic removal of dissolved CO₂ and remineralization of organic matter by microbial respiration. Well-preserved palynomorphs may be less common in the carbonate laminite facies because they were consumed by microbes as they sank through the water column to the sediment-water interface. Enhanced preservation of a variety of microfossils within nearshore deposits of the upper Nonesuch Formation may reflect an optimal balance between sedimentation rates, microbial productivity, and microbial respiration. Additionally, a favorable interplay between subsidence and sedimentation during deposition of the Oronto Group may have caused unusually complete preservation of shallow tidal flat and flood plain facies that hosted these early palynomorph assemblages.

While nearly all the reported microfossils from the Nonesuch Formation were recovered from facies with tidal sedimentary structures, the hypothesis that non-marine settings favored eukaryote evolution remains intriguing. The lower Oronto Group was deposited in a marginal marine setting that was significantly influenced by local conditions on land. Sediment was predominantly sourced from proximal mafic volcanic rocks with elevated abundances of bioessential nutrients, freshwater input from fluvial systems likely significantly diluted saline water, and basin morphology may have inhibited sulfidic conditions that are thought to have developed along productive Mesoproterozoic marine margins (e.g. Lyons et al., 2014; Gibson et al., 2019; Rainbird et al., 2020). While it is tempting to take a dichotomous view on the depositional setting of the lower Oronto Group – i.e., lake or seaway-- the reality was more nuanced. The lower Oronto Group was deposited in a marginal marine setting that reflects the important influence of both marine and local non-marine conditions.

CONCLUSIONS

- The upper Copper Harbor Conglomerate, Nonesuch Formation, and lowermost Freda Formation (lower Oronto Group) include sedimentary facies that were deposited in tidal marine to estuarine settings, requiring marine incursion into the Nonesuch basin. This incursion was coeval with development of a broad, shallow epeiric sea preserved in the Bylot and Amundson basins, Arctic Canada at a time of high global sea level.
- Sedimentary facies and stratal architecture of the lower Oronto Group are consistent over several hundred kilometers from the Ashland Syncline, Wisconsin, to the Keweenaw Peninsula, Michigan, and record marine transgression-regression.
- Geochemical proxies of water column anoxia reported in the literature vary consistently by lithofacies within a predictable stratal architecture, reflecting intrabasinal redox heterogeneity that was influenced by local circumstances of the Nonesuch inland sea.
- Transgressive-regressive stratal stacking patterns were driven by tectonic loading of the Ottawa phase of the Grenvillian Orogeny, which modulated ongoing thermal subsidence and isostatic adjustment caused by emplacement of the underlying MRS volcanic and intrusive rocks.
- The microfossil assemblage reported from the Nonesuch Formation was primarily sampled from tidally influenced shoreface and tidal flat environments, demonstrating these organisms thrived in a marginal marine setting. Marine influence on deposition of this strata contradicts the commonly held interpretation that the fossils recovered from the Nonesuch Formation lived in a landlocked lacustrine rift basin.

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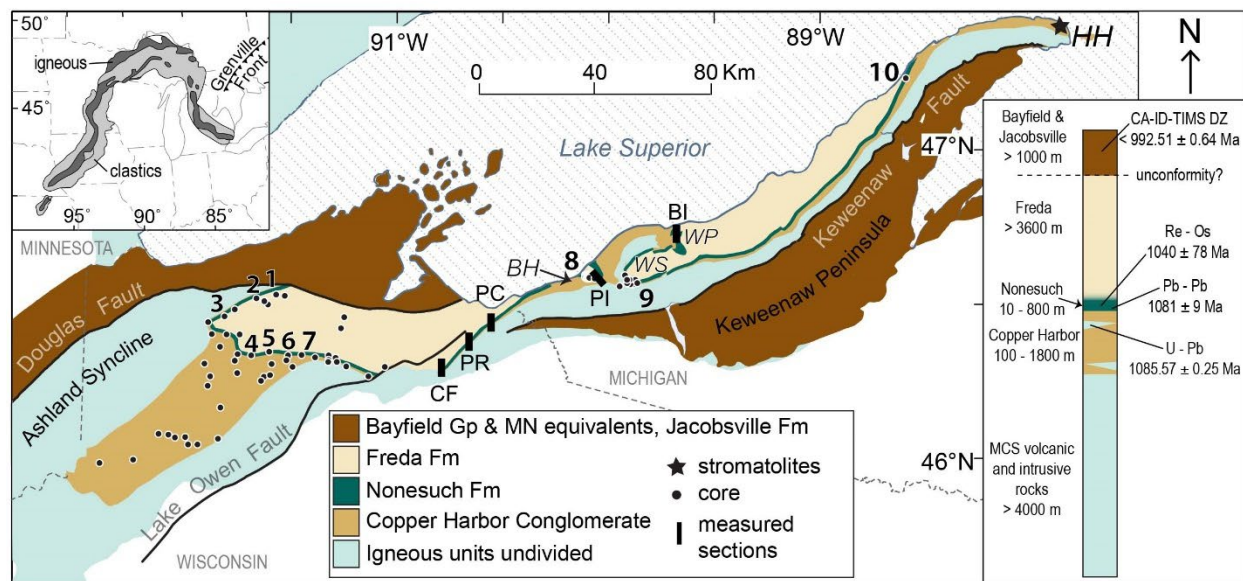
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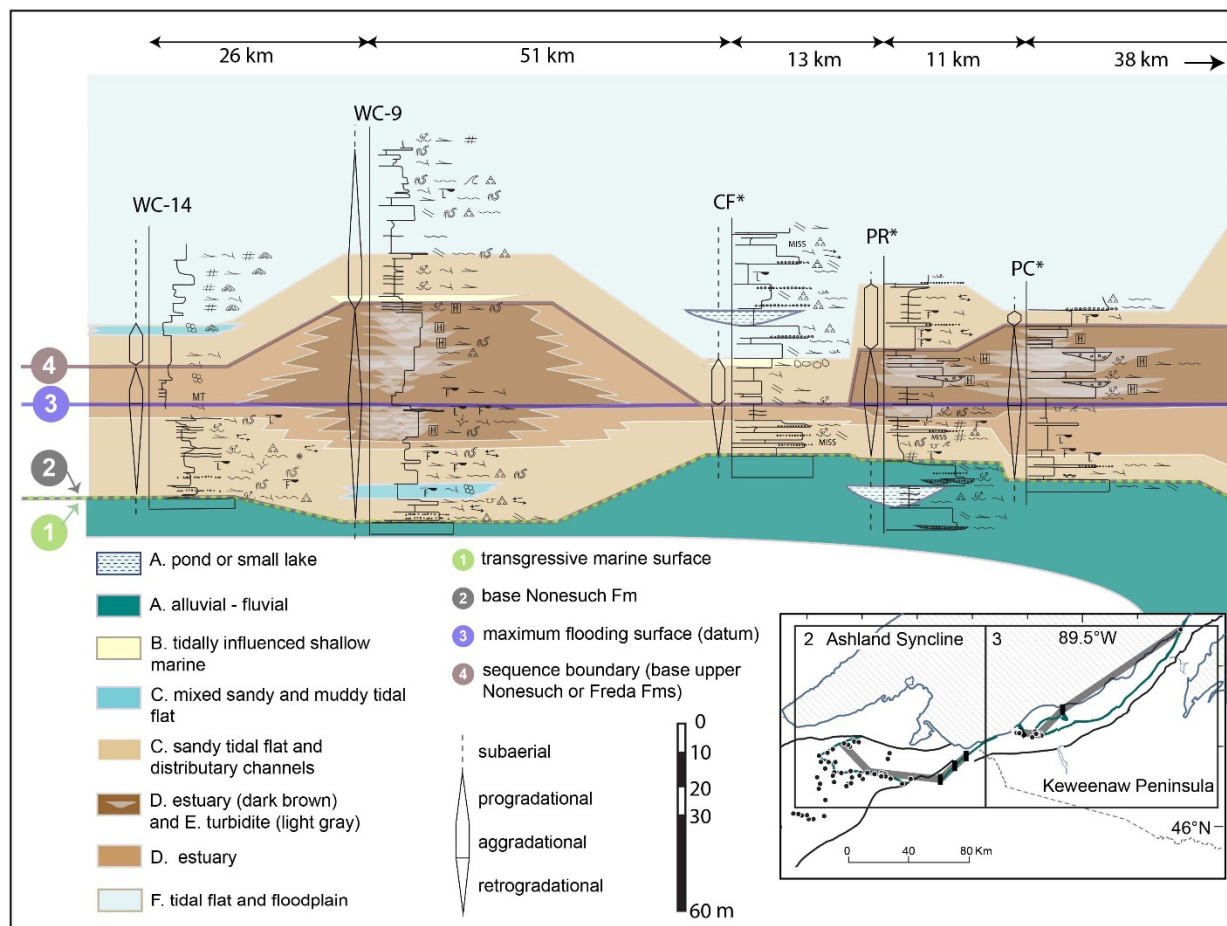
FIGURES and TABLES

Figure 1. location



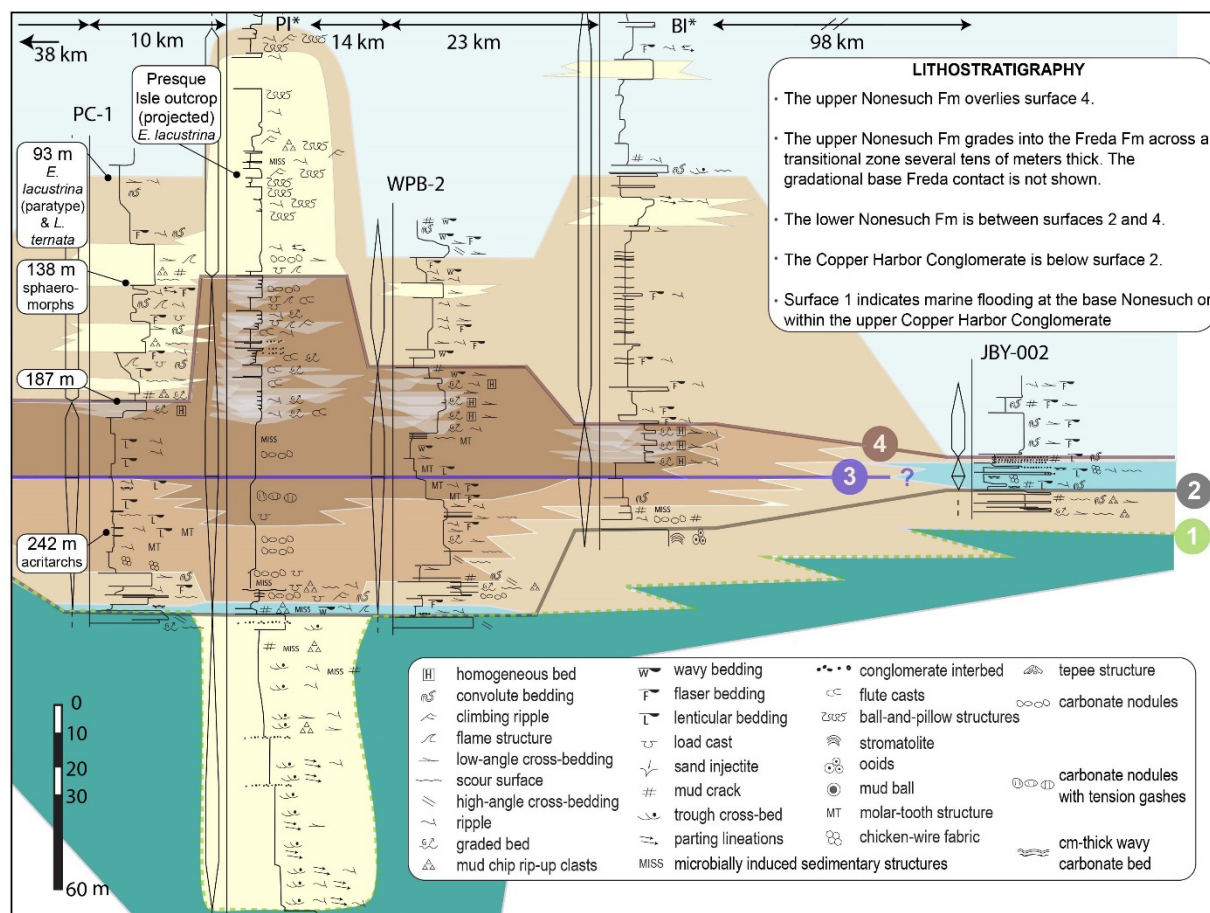
Map of Midcontinent Rift System (MRS) bedrock units. Numbers locate drill cores mentioned in this study: 1: WC-25, 2: WC-14, 3: DO-5, 4: WC-18, 5: WC-13, 6: WC-22, 7: WC-9, 8: (Presque Isle/Copperwood area) PI-1, P1-2, PC-1, PC-5, PC-6, CW-17-190, 9: (White Pine area) WPB-2, WPB-7, WPB-4, WPB-5, WPB-1, 10: (Calumet area) JBY-002. Abbreviations: CF: Copper Falls State Park, PR: Potato River County Park, PC: Parker Creek, BH: Black River Harbor, PI: Presque Isle River, BI: Big Iron River, WS: Western Syncline, WP: White Pine Basin, HH: Horseshoe Harbor, Fm: formation, Gp: Group, MN: Minnesota. Inset map (upper left) shows MRS extent. Modified after Ojakangas et. al (2001) and Stewart and Mauk (2017). Geology from Cannon et al. (1999) and Jirsa et al. (2012). See Supplementary Table S1 for precise location information. Age constraints from Ohr (1993), Cumming et al. (2013), Fairchild et al. (2017), and Hodgins et al. (2022). Thicknesses estimated from Daniels (1982), Elmore et al. (1989), and this study.

Figure 2. Stratigraphic correlation panel, Ashland Syncline



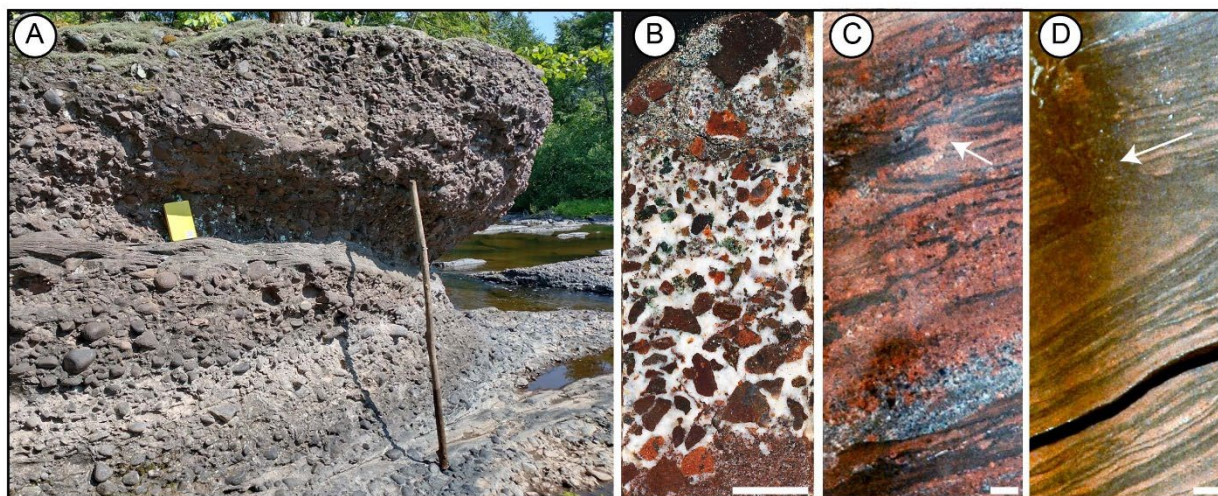
Stratigraphic correlation diagram, Ashland Syncline based on core description and measured sections of outcrops (asterisks denote measured sections). Sedimentary structures are defined in Figure 3. Note different lateral and vertical scales. Datum used is the maximum flooding surface. Colored shading indicates lithofacies associations A through F, which are described in the text. Abbreviations: Fm – Formation, m – meters, CF: Copper Falls State Park, PR: Potato River County Park, PC: Parker Creek. The Copper Harbor Conglomerate occurs below surface 2. The basal Freda Formation contact is not shown because it is gradational over several tens to as much as 100 meters (White et al., 1953; Moerlein, 1963; Suszeck, 1997; Daniels, 1982). Inset map (lower right) locates figures 2 (box 2, Ashland Syncline) and 3 (box 3, Keweenaw Peninsula). The correlation line is shown by the thick gray lines. The Nonesuch Formation is shown in green. The outline of Lake Superior is in blue, and faults are black lines. Cores are black circles, and measured sections are black rectangles. Also see Figures 1 and 3.

Figure 3. Stratigraphic correlation diagram, Keweenaw Peninsula



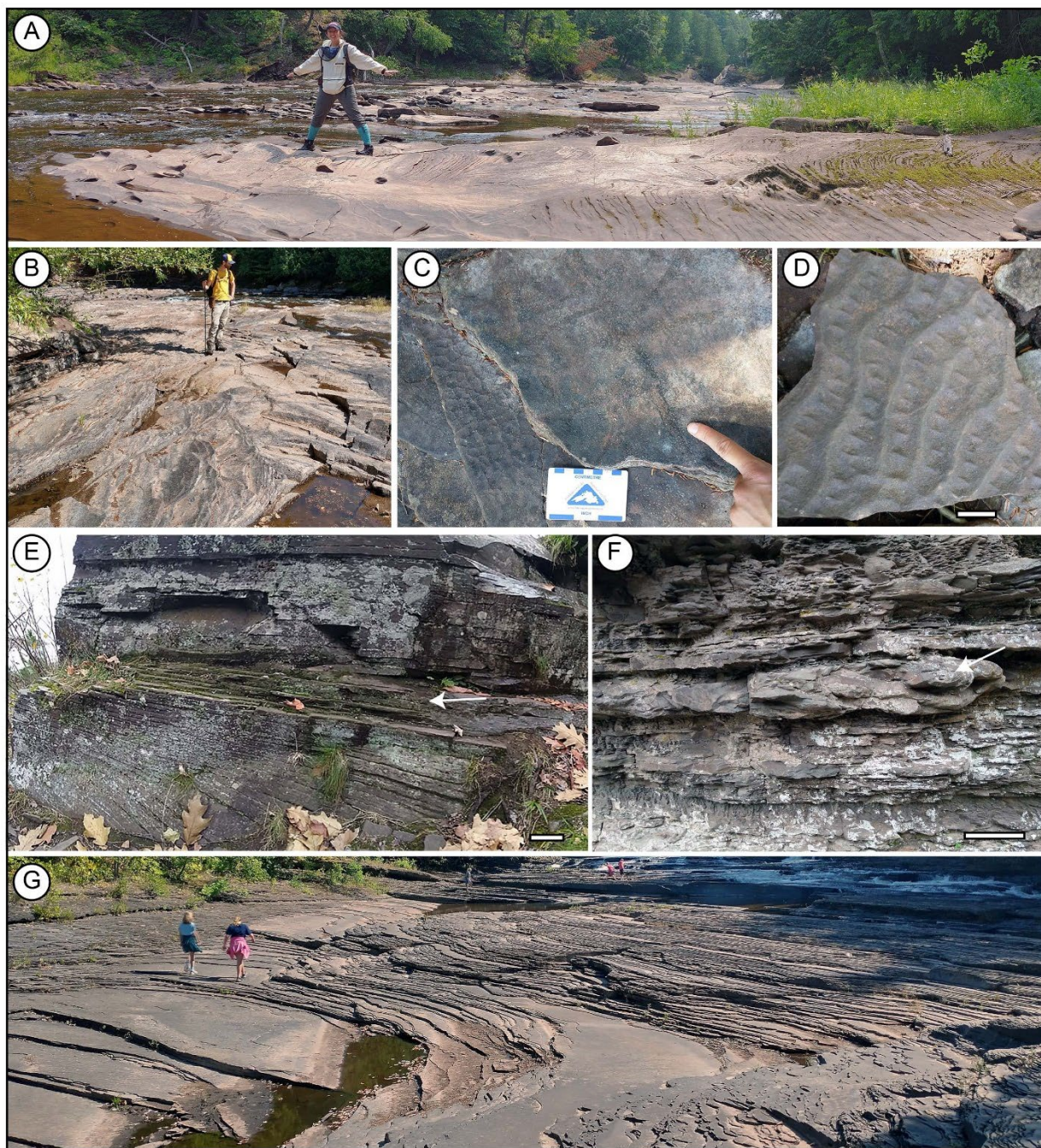
Stratigraphic correlation diagram, Keweenaw Peninsula based on core description and measured sections of outcrops (asterisks denote measured sections). See Figures 1 and 2 and Supplementary Table S1 for core and outcrop locations. Note different lateral and vertical scales. White boxes locate paleontology samples reported by Strother and Wellman (2016). Sample depth and species or acritarch are noted where relevant. See Supplementary Table S2 for more complete sample descriptions. Colors and surfaces as defined on Figure 2. Abbreviations: Fm: formation, m: meters; PI: Presque Isle River, BI: Big Iron River.

Figure 4. lithofacies associations A and C



Outcrop and core photos of facies deposited in alluvial fan, fluvial, and tidal flat settings from the Copper Harbor Conglomerate (lithofacies associations A and C). (A) Cobble conglomerate (A1) forms dm- to m-scale, lenticular beds in the lower and upper parts of the outcrop. Field book (19 cm tall) is resting on recessive interbed of cross-bedded lithic sandstone (A2). These facies were deposited in alluvial fan and braid plain environments. Photo taken along the Presque Isle River 155 meters below the base Nonesuch Formation contact. (B) Core scan showing calcite cement (white) surrounding angular to subangular rhyolite clasts (red) and lithic sandstone matrix (red, lower right behind scale bar), cross-bedded lithic sandstone facies (A2) deposited on an alluvial braid plain. Core DO-5 measured depth 318 m (1044 ft). (C, D) Core photos of ripple and planar-laminated, mud-draped and mud-cracked sandstone to siltstone facies (C1) from core JBY-002, measured depth 129.5 meters (40 ft) and 129 meters (39 ft), about 2 meters below the basal Nonesuch Formation contact. These sediments were deposited on a tidal flat with periodic exposure and desiccation. Arrows point to mm-scale sand-filled mud crack (C) and cm-scale silt-filled mud crack (D). Note wide range in grain size from very coarse-grained, lithic sandstone (red and light gray) to clay or silt drapes on ripple foresets (gray, dipping to the right just below arrowhead on C) and as wavy laminations (gray, dipping to the left in the lower part of D). White scale bars are 1 cm.

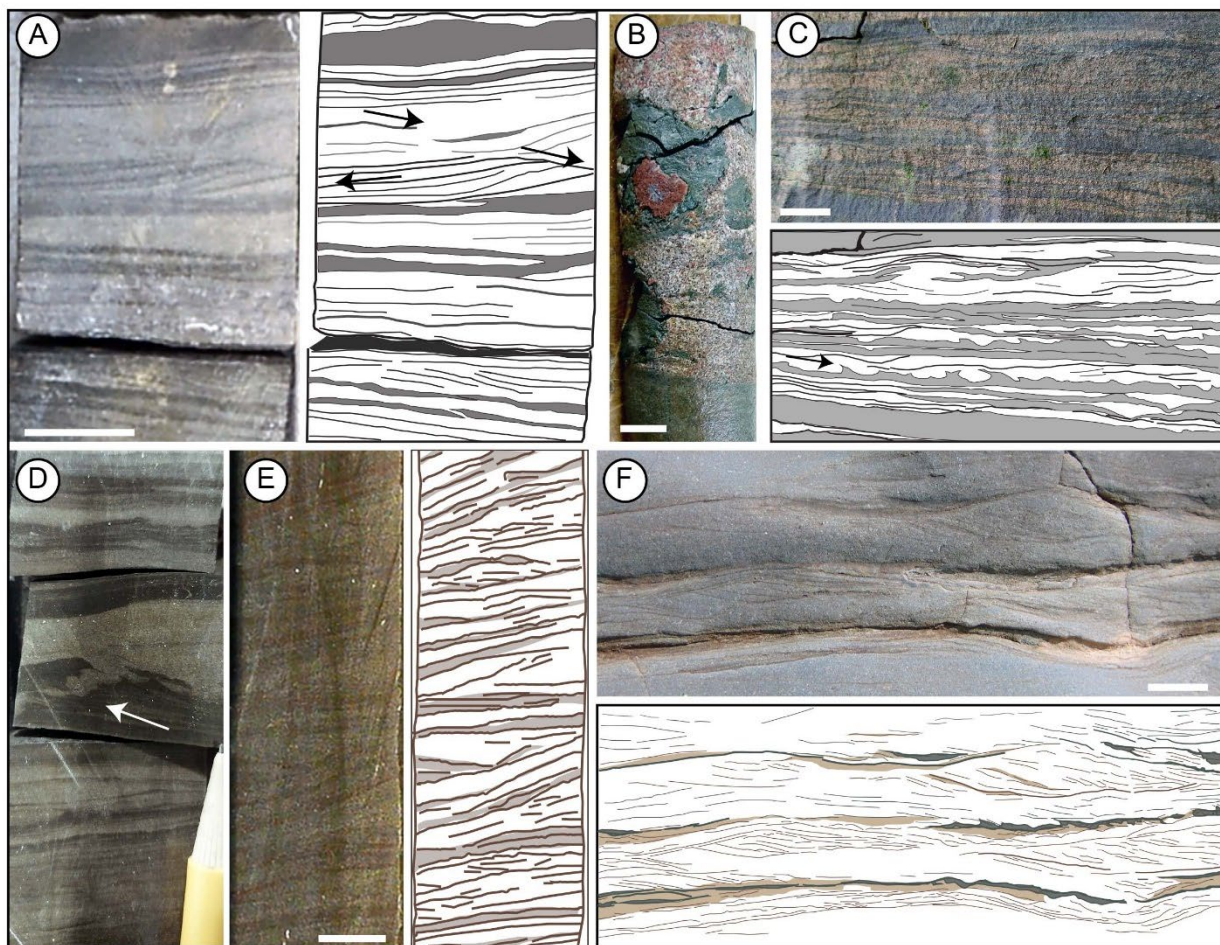
Figure 5. lithofacies association B



Low-angle, cross-bedded sandstone facies from the Copper Harbor Conglomerate and upper Nonesuch Formation (Lithofacies association B). Thick successions of dunes with regular geometry characterized by vertically stacked cross-bed sets of similar size, like those that compose lithofacies association B, are typical of tidal seaways. (A, B) Outcrop views looking down onto the tops of gently tilted, dm- to meter-

scale, low-angle cross-beds in the Copper Harbor Conglomerate just below the contact with the overlying Nonesuch Formation. (A) Black River Harbor locality. Person is 1.7 m (5.5 ft) tall. (B) Presque Isle River south locality. Person is 1.8 m (6 ft) tall. (C, D) Mud cracks and ripples on bed tops of low-angle, cross-bedded sandstone, Copper Harbor Conglomerate, exposed along Presque Isle River south section. (C) Person is pointing to cm-scale, sand-filled mud crack. Millimeter-scale, polygonal mud cracks on top of underlying bed. (D) Interference ripples. White scale bar, lower right, is 2 cm long. (E, F, G) Low-angle, cross-bedded sandstone from the upper Nonesuch Formation exposed along the Presque Isle River downstream of Manabezho Falls within the Porcupine Mountains State Wilderness Area. (E) Profile view showing association of low-angle, cross-bedded sandstone (bottom and top of outcrop) with siltstone and shale (arrow pointing to recessive bed in middle of outcrop). White scale bar is ~20 cm long. (F) Ball-and-pillow structures (arrow) and associated planar-tabular siltstone and very fine-grained sandstone. White scale bar is 10 cm long. (G) View looking down on gently tilted tops of low-angle cross-bed sets. People are ~1.7 m (5.5 ft) tall.

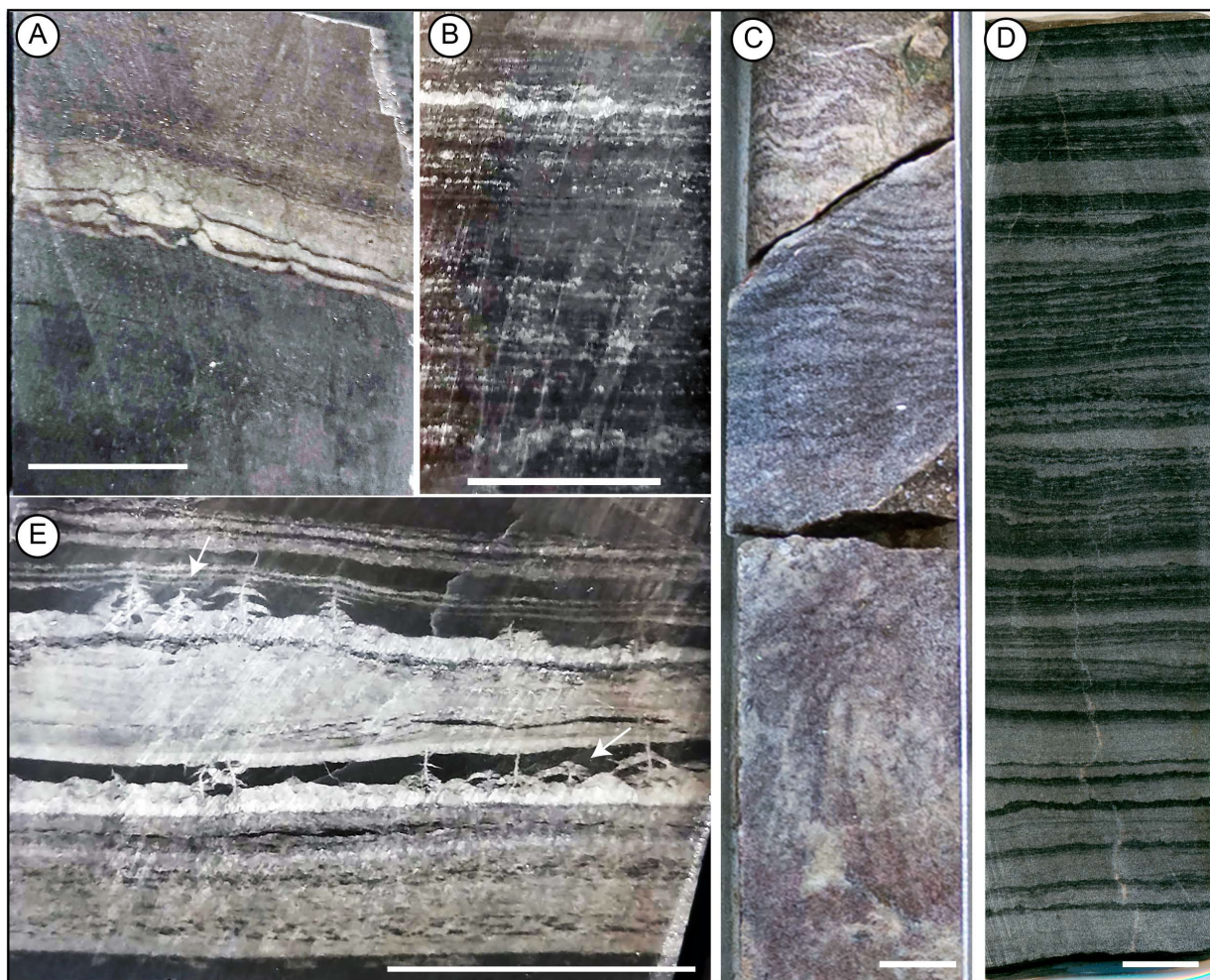
Figure 6. lithofacies association C



Lithofacies association C: Tidal Flat. All images show examples of facies C2, flaser to lenticular-bedded sandstone through shale except for (B), which shows facies C3, cross-bedded sandstone and pebble conglomerate. (A) Core photograph (left) and line drawing (right). Thin clay beds and drapes are darker gray. Very fine-grained sandstone and sandy siltstone is light gray on core photo and white on the line drawing. Note common mud drapes on ripple laminae and as bundles of thin-thick planar laminae and thin beds. Arrows point to bi-directional ripples: Mud-draped ripple foresets dip to the left (bottom arrow) while the reactivation surface truncating the top of the ripple dips to the right (middle arrow). Overlying ripple (top arrow) also dips to the right. Core WC-9, 498 m (1635 ft) measured depth. (B) Core photograph. Dark gray shale to siltstone is overlain by very coarse-grained lithic sandstone with gray mud clasts and mud balls. Note the large (~2 cm diameter) mud ball with subangular rhyolite clast at its core.

(C) outcrop photograph (top) and line drawing (bottom) from the Potato River Falls locality. Clay is dark gray. Fine-grained sandstone to siltstone is beige (photograph) or white (line drawing). Note abundant clay drapes and thin beds. Arrow on line drawing points to flame structures along a clay bed. (D) core photograph showing sand ripples, clay drapes, and thin clay beds, lower Nonesuch Formation. Arrow points to sand-filled mud crack. Core WPB-7, 485 m (1590 ft) measured depth. (E) Core photo showing fine-grained sand ripples with clay drapes (left) and line drawing (right), upper Nonesuch Formation. Core PI-2, 131 m (429 ft) measured depth. (F) Outcrop photo showing combined flow ripples with clay drapes on foresets and reactivation surfaces, upper Nonesuch Formation, Big Iron River about 57 m from base Nonesuch Formation. White bars indicate 1 cm.

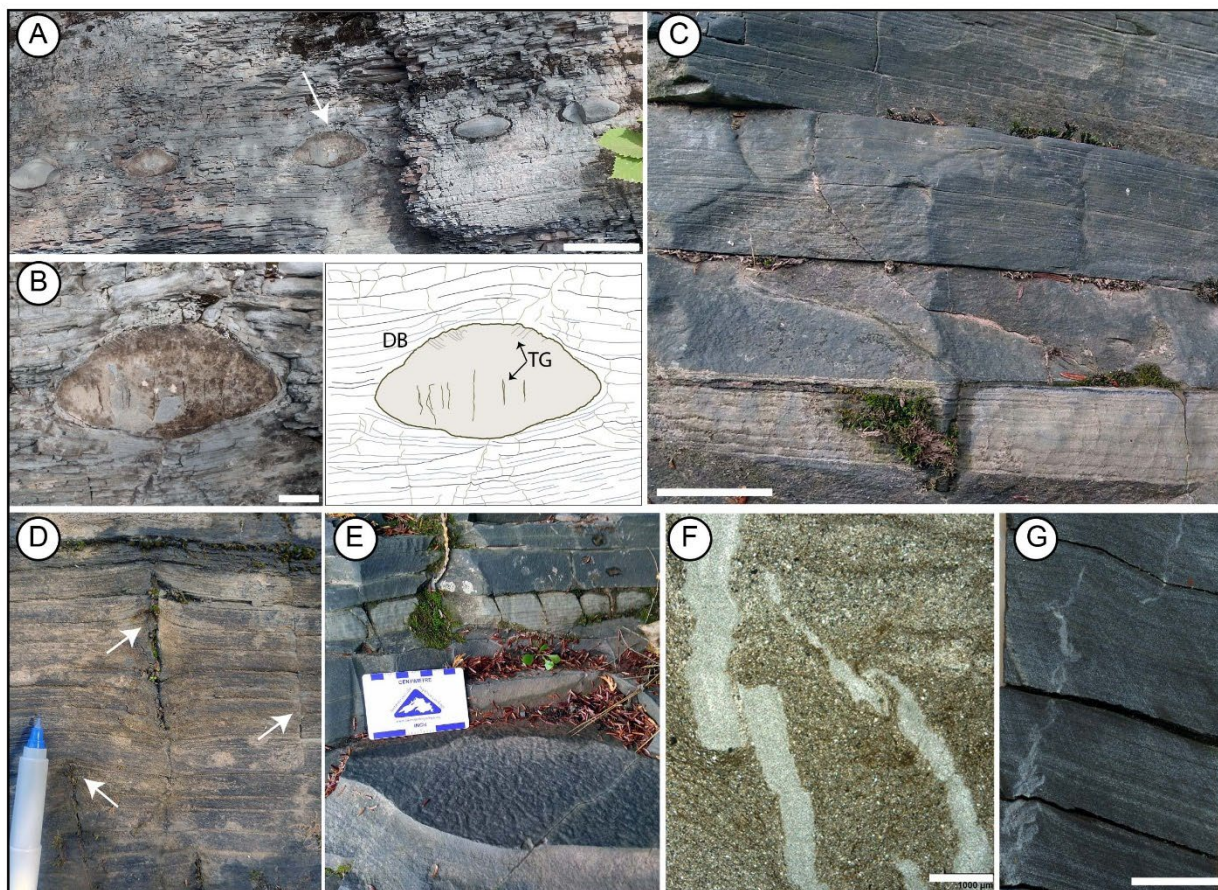
Figure 7. evaporite textures, lithofacies association D



Core photographs of probable evaporite textures in lithofacies association D: Planar carbonate interbeds in A and D may represent calcite replacement of laminar gypsum while micro-chicken wire, swallow tail, and Christmas-tree morphologies (B and E) suggest calcite pseudomorphs after gypsum. (A) The informal Jr marker bed (white) within the finely laminated siltstone and shale facies (D2). Note the wrinkly- to disrupted interlaminae of carbonate (white) and lesser shale (dark) that compose the marker bed. Photo from core PI-1, measured depth 107 m (350 ft), about 0.6 meters (2 feet) above the base of the Nonesuch Formation. (B) Micro-chicken wire fabric (white speckles) within the finely laminated siltstone and shale facies (D2). Photo from core PI-2, measured depth 244 m (800 ft), lower Nonesuch Formation. (C) Part of an eight-meter-thick carbonate interval at the contact between the Nonesuch and

Freda Formations, core WC-25, 666 m (2186 ft) measured depth. Carbonate is likely replacing gypsum or anhydrite with nodular (lower core piece) and layered (upper core pieces) texture. (D) laminated siltstone, carbonate, and shale (D1). Carbonate is light gray; siltstone and clay are dark gray. Photo from core WC-13 measured depth 953 m (3125 ft). (E) Calcite pseudomorphs after evaporite (gypsum?) within the finely laminated siltstone and shale facies (D2). Photo from core PI-1, measured depth 61 m (200 ft), lower Nonesuch Formation. Arrows point to swallow tail and Christmas-tree shaped pseudomorphs characteristic of gypsum. White scale bar represents 1 cm in all images.

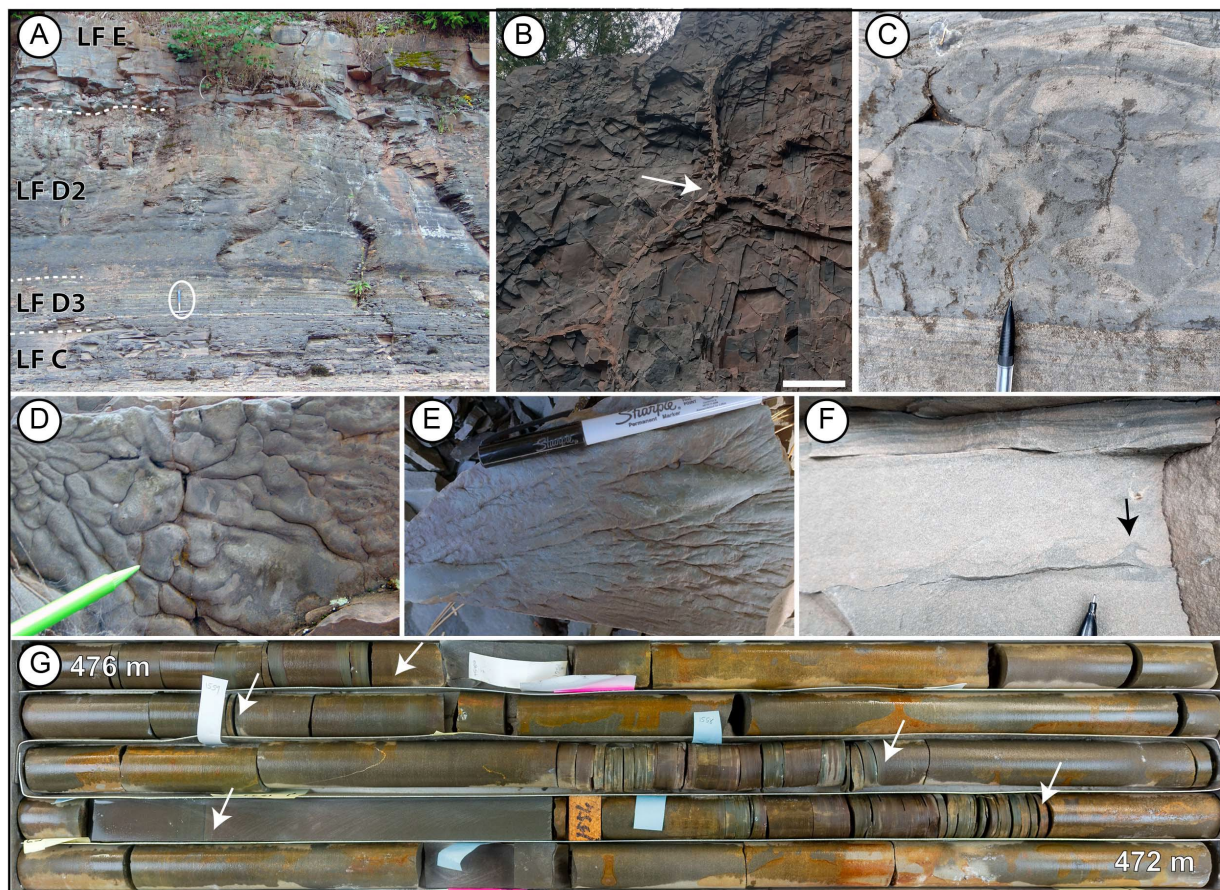
Figure 8. lithofacies association D



Outcrop, core, and thin section images of concretions, molar tooth (MT) structures in lithofacies association D. (A) Layer of earliest diagenetic concretions within thinly bedded to laminated siltstone (D2) exposed about 50 m above the base of the Nonesuch Formation at the Presque Isle River south locality. Each concretion is about 25 cm across. Thin beds and laminae are deformed around the concretions, indicating the concretion grew prior to sediment lithification. Arrow points to concretion shown in B. Scale bar, lower right, is 24 cm long. (B) Close up of concretion shown in A (left) and line drawing (right) highlighting bedding geometry and extensional features that demonstrate growth of concretion during early diagenesis. Note tension gashes (TG) and deflected bedding (DB), which indicate rapid lithification of concretion within soft sediment. White scale bar is 5 cm. (C) Outcrop photo showing carbonate laminite (D3) interbedded with planar-laminated siltstone (D2) from Big Iron River about 24 m above the base Nonesuch Formation. A beige carbonate laminite bed in the lower part of the photo

pinches to the left and is composed of wavy, thickly laminated carbonate, silt, and clay. The overlying bed is composed of apparently internally structureless siltstone to very fine-grained sandstone. The upper two carbonate laminite beds are composed of planar-laminated carbonate, siltstone, and shale. Scale bar is 5 cm. (D) Arrows point to MT cracks within carbonate laminite (D3) exposed about 55 m above the base Nonesuch Formation, Presque Isle River south locality. Note how carbonate laminite laminations deflect both up and down around the tips of the MT cracks. (E) Interbedded carbonate laminite (D3) and planar-laminated siltstone (D2) with microbially induced sedimentary structures (MISS) exposed about 70 m above the base Nonesuch Formation, Presque Isle River south locality. Note elephant skin texture (MISS) on bedding surface just below scale card. (F, G) Thin section and core image of MT cracks within carbonate laminite (D3), core DO-5, 266 m (874 ft) measured depth. (F) Transmitted light photomicrograph under cross-polars. MT cracks are filled with $\sim 15\ \mu\text{m}$ carbonate microspar (see also Stewart and Mauk, 2017). Note how surrounding matrix, composed of siltstone and clay, deflects around tips of MT cracks. Scale bar is $1,000\ \mu\text{m}$. (G) Core scan of MT crack shown in F. Carbonate laminite surrounding MT crack is composed of planar, carbonate-rich (light gray) and siltstone-rich (dark gray) laminations. Scale bar is 1 cm.

Figure 9. lithofacies association E

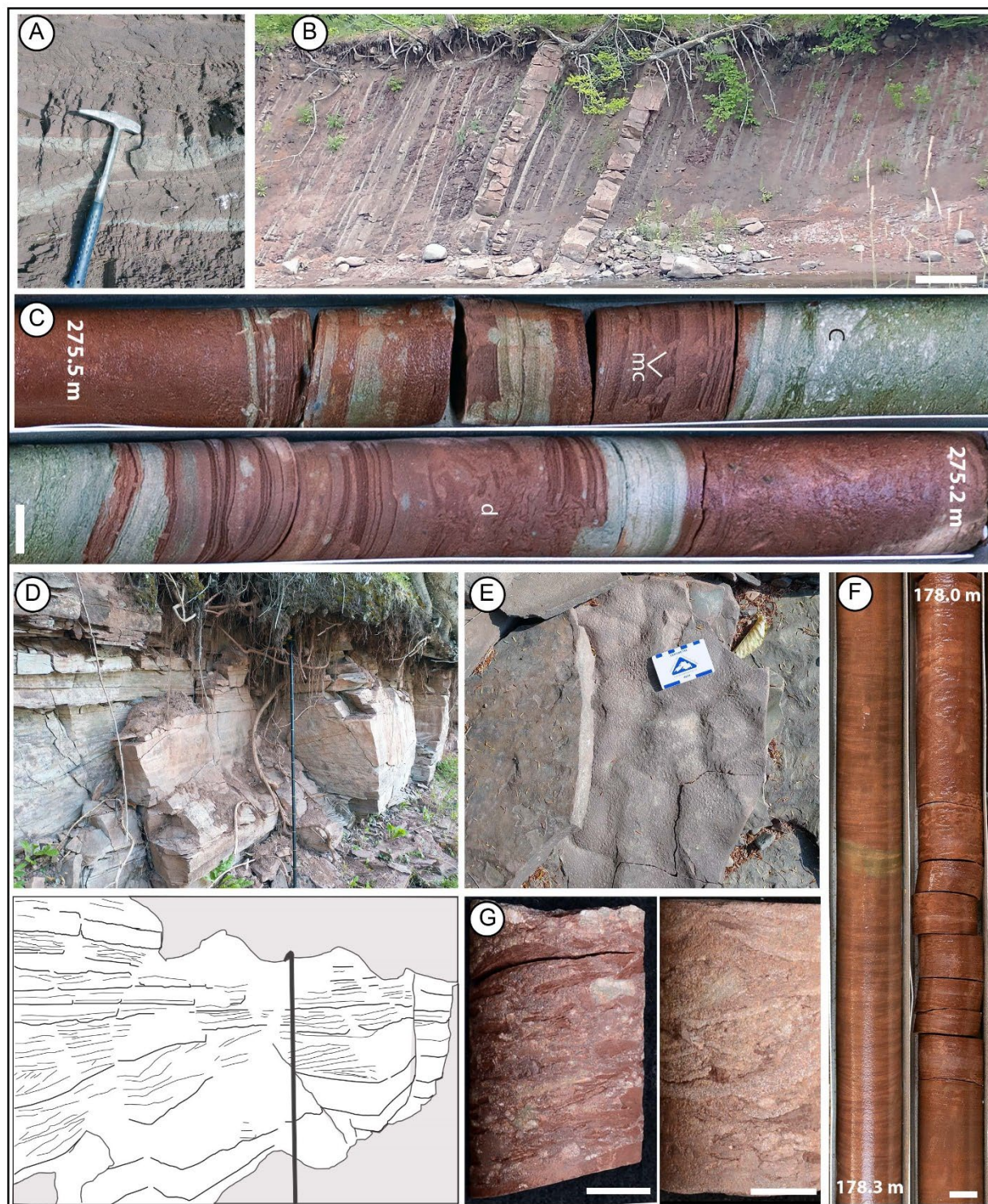


Outcrop and core photos of lithofacies association E and immediately underlying facies. (A) outcrop photo showing graded sandstone through shale (E1) sharply overlying laminated siltstone and shale (D2) and carbonate laminite (D3) from the lower Nonesuch Formation exposed along the Big Iron River about 29 m above the base Nonesuch Formation. Rock hammer (circled in white) is 33 cm tall. (B) Sandstone dikes injected into cross-bedded sandstone and conglomerate interbed (C3) about four meters below the base of the graded sandstone through shale facies (E1) along the Potato River about 14 m above the base Nonesuch Formation. The photo is looking up at the base of a steeply-dipping bed. Arrow points to sandstone dike that cuts across the base of the bed. Scale bar is 50 cm long. (C) Photo of the sharp contact between the graded sandstone through shale facies (E1) and underlying flaser- to lenticular-bedded sandstone – shale (C2). The pencil tip is at the contact. Note well-developed soft-sediment deformation within the sandstone above the contact. Potato River Falls section 18 m above the base Nonesuch

Formation. (D) Load casts on a sandstone bed, normally graded sandstone through shale facies (E1).

Photo from outcrop along the Big Iron River about 29 m above the base Nonesuch Formation. (E) Linear sole marks on the base of a sandstone bed, graded sandstone through shale facies (E1), Presque Isle River south locality about 100 m above the base Nonesuch Formation. (F) Photo showing flame structures and symmetric ripples defined by subtle gray color due to slightly greater clay content within otherwise homogeneous sandstone bed, normally-graded sandstone through shale facies (E1), Presque Isle River south locality about 117 m above the base Nonesuch Formation. (G) Core photograph of normally-graded sandstone-shale facies highlighting graded beds. Arrows point to base of graded bed. Core WC-18 (Ashland Syncline). Core reads from upper left (476 m) to lower right (472 m); depths are relative to land surface elevation.

Figure 10. lithofacies association F, Freda Fm.



Field and core photographs of lithofacies association F from the Freda Formation. (A) thin-bedded shale, siltstone, and sandstone (F2). Close up of fine-grained portion of outcrop shown in B. Red, fissile, sandy

siltstone and shale with green to beige, medium- to fine-grained sandstone infilling cm-scale channel forms. Hammer for scale. (B) Outcrop exposed along the bank of the Bad River within Copper Falls State Park. Alternating thin beds (cm- to dm-thick) of fine-grained red siltstone, clay, and green sandstone (F2) with lesser, 30 to 50 cm-thick broadly lenticular sandstone interbeds (F3). This outcrop records deposition on a floodplain cut by small-scale, ephemeral streams and larger-scale fluvial channels. (C) Core photograph highlighting floodplain deposits with soil horizons (F2). Core WC-18, depth 275.5 – 275.2 m measured depth. Core reads from top left to bottom right. Red, very fine-grained sandstone at 275.5 m passes up section into red and green, thin-bedded to interlaminated sandstone, siltstone, and clay. Clay is darkest red and cut by sand-filled mud cracks (labeled mc). Mud-cracked interval is overlain by white and green, convolute-bedded sandstone, siltstone, and clay with white, rounded carbonate nodules (labeled C) that may be soil concretions. The green, convolute interval is overlain by interlaminated sandstone through clay with rare, mm-scale mud cracks, white to green bleached intervals, and intervals of disrupted bedding with upturned and convolute bedding (labeled d). White scale bar is 1 cm. (D) Outcrop photo (top) and line drawing (bottom) of lenticular sets of cross-bedded sandstone (F3) exposed along the Presque Isle South locality. Jacob staff is 1.5 m. Twenty to 50 cm-thick, lenticular beds of cross-bedded, fine- to medium-grained sandstone (base of photo) preserves fluvial channel-fill deposits and are overlain by thin, planar-bedded sandstone and siltstone that record overbank deposition. (E) Mud chips, sand-filled mud cracks, and ripples with raindrop marks preserved on sandstone bed surfaces associated with lenticular sets of cross-bedded sandstone (F3) exposed along the Presque Isle South locality. Mud chips and sand filled mud cracks are preserved on upper bed (left side of photo, below the E) while ripple marks with superimposed raindrop marks are preserved on the lower bed with scale card. (F) Photo of core WC-22 from depths 178.3 m to 178.0 m measured depth highlighting transitional zone between upper Nonesuch and Freda Formations. Core reads from bottom left to upper right. Red, ripple-laminated, very fine-grained sandstone and siltstone with dark red clay drapes passes up section convolute-bedded interval with abundant red, flakey clay laminae (F1). White scale bar is 1 cm. (G) Photos of core WC-13,

depths 359 m (left) and 338 m (right) showing probable soil horizons (F2). Note white, rounded carbonate nodules, red, disrupted clay laminae, and laminae upturned into tepee structures. White scale bar is 1 cm.

Table 1. Summary of lithofacies of the lower Oronto Group with focus on the Nonesuch Formation

<i>Unit*</i>	Lithofacies association	Description	Depositional environment
<i>LITHOFACIES ASSOCIATION F: FLOOD PLAIN and TIDAL FLAT</i>			
<i>FF</i>	F3: lenticular sets of cross-bedded sandstone and conglomerate	Red to pink, dm- to m-scale lenticular sets of medium- to coarse-grained, trough cross-bedded, micaceous sandstone and lesser conglomerate. Beds are commonly stacked into upward-fining sets typically 0.5-1.5 m thick and capped by planar laminated siltstone and shale with local cm-scale current and symmetrical ripples. Local raindrop impressions on rippled bed tops.	Fluvial channel and overbank
<i>FF</i>	F2: thin- bedded shale through sandstone	Red, poorly sorted, laminated to thin-bedded shale, siltstone, and fine-grained sandstone. Clay laminae have distinctive flakey texture; local mm- to cm-scale sand-filled mud cracks, clay roll ups, tepee structures; green to gray horizons with carbonate nodules and disrupted, angular clay chips and laminae; local, cm-thick current rippled, cross-bedded, or soft-sediment deformed fine- to medium-grained sandstone; scours overlain by cm- to mm-scale, angular mud chips.	Flood plain with common soil horizons and ephemeral channels
<i>FF</i>	F1: soft-sediment deformed sandstone through shale	Red sandstone through shale with abundant soft-sediment deformation. Beds organized into dm- to m-scale upward-fining sets capped by siltstone to shale; fine- to medium-grained, lenticular beds of trough, planar, and low angle cross-bedded, micaceous sandstone; locally abundant flaser bedding; local scour surfaces overlain by pebble or mud chip lags, mm- to cm-scale sand-filled mud cracks, clay roll ups, tepee structures.	mixed tidal flat and flood plain with ephemeral channels
<i>LITHOFACIES ASSOCIATION E: TURBIDITE</i>			
<i>NFl</i>	E2: massive sandstone with floating pebbles and cobbles	Gray, structureless, medium-grained sandstone with floating, rounded pebbles to cobbles. Dm- to m-scale lenticular beds with scoured bases; internally structureless sandstone with local, poorly developed cross-bedding and pebbles to cobbles floating in sandstone matrix.	Sandy debrites; turbidite channels
<i>NFl</i>	E1: Graded sandstone through shale	Gray, medium- to fine-grained sandstone through shale organized into cm- to m-scale graded beds. Sharp bases overlain by 1 to several cm-thick beds of internally structureless sandstone and locally associated with soft-sediment deformation; structureless sandstone commonly passes into low-angle cross-bedded, rippled, or laminated sandstone and is locally capped by cm-thick laminated or rippled siltstone to shale; graded beds commonly partially preserved, for example as stacks of internally structureless to low-angle cross-bedded sandstone bounded by scour surfaces; flute casts common.	Turbidite lobes

LITHOFACIES ASSOCIATION D: ESTUARY

NFI	D3: carbonate laminite	Gray, finely (mm- to sub-mm scale) interlaminated carbonate and organic-rich shale to siltstone. Common molar tooth (MT) cracks infilled with micro-carbonate spar and lesser silt- and clay-sized clastic grains.	Relatively deep, subtidal estuary
NFI, NFU	D2: finely laminated siltstone and shale	Dark gray to black, finely laminated siltstone and shale. Planar, cm-thick beds. May include common MISS, local to rare mm- to cm-scale sand-filled mud cracks, mm-scale carbonate blebs (micro-chicken wire fabric), MT cracks, and cm-scale carbonate concretions that locally deform adjacent laminae and in one location (Big Iron River) preserve MT cracks and cross-cutting mud cracks on concretion surface. Includes the “Jr” and “Galaxy” marker beds (Bornhorst and Williams, 2013).	Muddy, evaporitic tidal flat or low energy estuary
NFI	D1: laminated siltstone, carbonate, and shale	Gray, coarsely-laminated siltstone, carbonate, and shale. Repetitively thickening and thinning laminations 1 to 4 mm thick bundled into cm-scale beds. Local fine-grained sandstone interbeds with sand starved ripples are commonly carbonate cemented. This facies composes the “Stripey” marker bed (Bornhorst and Williams, 2013)	Shallow, evaporitic estuary

LITHOFACIES ASSOCIATION C: TIDAL FLAT

NFI	C3: cross-bedded sandstone and pebble conglomerate	Gray, medium- to coarse-grained, steep- to low-angle cross-bedded sandstone and interbedded conglomerate. Scour surfaces overlain by coarse-grained sandstone to conglomerate organized into cm-thick lenticular beds; cm- to m-scale upward fining sets of conglomerate or coarse-grained through medium-grained sandstone; common mm- to cm-diameter, rounded, well to poorly sorted rhyolite clasts. Locally common mud chips, rare armored mud balls. Includes the “Upper sandstone” and “Tiebol” marker beds (Bornhorst and Williams, 2013).	Distributary tidal-flat channels
NFI, NFU	C2: flaser to lenticular-bedded sandstone- shale	Gray siltstone, shale, and very fine-grained sandstone. Planar, cm-thick, laterally continuous beds on outcrop scale (10s of m); commonly planar-laminated siltstone with locally abundant lenticular bedding and current ripples, mud-drapes on ripple foresets and reactivation surfaces, local scour surfaces overlain by coarser-grained sandstone lags or thin beds, thin lenses and starved ripples of fine-grained gray sandstone through coarse-grained, rhyolite-lithic sandstone, flame structures, soft-sediment deformation; local carbonate cementing matrix of sandstone lenses and ripples, rare, cm- to mm-scale sand injectites, mm- to cm-scale sand-filled mud cracks, and bi-directional current ripples with foresets dipping opposite to reactivation surfaces. Ripples indicate both north- and south-directed flow ⁺ (Elmore et. al, 1989).	Sandy tidal flat
CHC	C1: ripple- and planar-laminated, mud-draped and	Red, platy, ripple- and planar-laminated fine-grained sandstone to siltstone. Abundant current, symmetric, and interference ripples, mud drapes, mud chip clasts, and desiccation cracks; stacked current ripples with mud-drapes on reactivation surfaces and foresets locally preserve bi-modal	Mixed sandy and muddy tidal flat

mud-cracked sandstone to siltstone	transport directions; planar laminated sandstone to siltstone locally bundled into repetitive thickening-thinning sets, locally stromatolitic (Jones et al., 2020). Cross-bedding, ripples, and lineations indicate both north- and south-directed flow ⁺ (White and Wright, 1960; Elmore, 1984).
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LITHOFACIES ASSOCIATION B: TIDALLY INFLUENCED SHALLOW MARINE

NFu, NFI CHC	B1: low-angle cross-bedded sandstone	Gray to pink, medium- to fine-grained, low-angle cross-bedded sandstone. Cm-thick, broad (dm- to m-length), low-angle trough and planar cross-beds organized into stacked, dm- to m-thick sets with scoured bases; locally sandstone sets are stacked or fine upwards and are capped by planar to wavy laminated fine-grained sandstone, siltstone, and shale; locally abundant current ripples with mud-drapes along ripple reactivation surfaces; abundant parting lineations; locally, ripple foresets dip in opposite direction to reactivation surfaces, locally abundant interference ripples and symmetric ripples, mud cracks, MISS, and mud roll up structures on cross-bed tops near contact with NFI; locally abundant intervals with soft-sediment deformation and ball and pillow structures (NFu only); local cm-scale mud chip clasts, flame structures. Cross-bedding and parting lineations indicate south- and north-directed flow ⁺ (Elmore, 1984).	Tidally influenced shallow marine
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LITHOFACIES ASSOCIATION A: ALLUVIAL-FLUVIAL

CHC, FF	A3: planar to ripple laminated siltstone to sandstone	Gray siltstone to fine-grained sandstone and thinly interbedded medium- to coarse-grained sandstone. Planar-laminated to thin-bedded, local ripples, basal scours overlain by angular mud chip clasts. Present locally as minor intercalations in facies associations A and F.	Pond or small lake
CHC	A2: cross-bedded lithic sandstone	Red, medium- to coarse-grained, lithic, trough cross-bedded sandstone, lesser medium- to fine-grained ripple- and planar-laminated sandstone, siltstone, and shale; cm-scale beds organized into dm- to m-thick sets, locally upward-fining; local parting lineations, mud cracks, mud drapes, and mud chips. Trough cross-bedding indicates north-directed flow ⁺ (White and Wright, 1960; Hamblin and Horner, 1961; Elmore, 1984).	Fluvial braid plain
CHC	A1: cobble conglomerate	Interbedded red conglomerate through shale. Massive or upward-fining cobble to pebble conglomerate, poorly to moderately sorted, local cast imbrication, rounded to subrounded clasts composed of rhyolite and lesser basalt, rare gneiss and slate and other metasedimentary rocks; local thin beds of cross-bedded, planar- and ripple- laminated sandstone through mudstone; parting lineations, mud cracks; local carbonate coatings on clasts and cementing matrix. Clast imbrication indicates north-directed flow ⁺ (White and Wright, 1960; Hamblin and Horner, 1961; Elmore, 1984)	Alluvial fan

*Lithostratigraphic units: FF: Freda Formation, NFI: lower Nonesuch Formation, NFU: upper Nonesuch Formation, CHC: Copper Harbor Conglomerate.

+All paleocurrents measured from outcrops east of the Ashland Syncline

Chapter 2: A restricted sea in the Laurentian interior: carbonate C-O-Sr isotope geochemistry of the ca. 1081 Ma Nonesuch Formation, Midcontinent Rift, USA

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A restricted sea in the Laurentian interior: carbonate C-O-Sr isotope geochemistry of the ca. 1081 Ma Nonesuch Formation, Midcontinent Rift, USA

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ABSTRACT

The late Mesoproterozoic Nonesuch Formation comprises up to ~800 meters of siliciclastic sediments, minor authigenic calcite, and well-preserved microfossils that were deposited within an interior Laurentian sea, preserving a continuous record of microbial habitat. Environmental heterogeneity inherent to inland seas may have promoted expansion of microbes to new habitat and their related evolution, motivating re-evaluation of the varied depositional conditions of the Nonesuch Formation. Here we explore marine connectivity using C, O, and Rb-Sr isotope compositions of calcite in molar tooth (MT) structures and carbonate laminae. Diagenesis links to lower $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}$ values and greater carbonate recrystallization. Carbon isotope values group by facies and are uncorrelated with $\delta^{18}\text{O}$, reflecting facies-dependent diagenetic pore water evolution and timing of calcite precipitation. The $\delta^{13}\text{C}$ (-3.9 to -2.0‰) and $\delta^{18}\text{O}$ (-6.7 to -3.6‰) values of calcite from MT structures overlap values of contemporaneous restricted-marine epicratonic carbonates, reflecting *in situ* microbial carbon cycling and evaporative conditions, respectively. Similarly, the $^{87}\text{Sr}/^{86}\text{Sr}$ of least-altered calcite (~0.7068 to 0.7069) is more radiogenic than previous late-Mesoproterozoic seawater estimates (0.7051 to 0.7066), reflecting the influence of continental runoff and concurrent Grenvillian

orogenesis. Our data corroborate an emerging pattern of fluctuations in the late-Mesoproterozoic seawater Sr isotope curve that we likewise attribute to both global expansion of epeiric seas during sea-level highstand and enhanced continental runoff. Expansion of such seas would have increased marginal marine settings and related basin conditions of freshwater input, evaporation, variable redox structure, and nutrient availability, perhaps influencing early eukaryote habitat expansion and related diversification.

INTRODUCTION

The late Mesoproterozoic was a time of global sea level highstand characterized by expansion of inland seas (Kah et al., 2012; Gilleadeau and Kah, 2013; Rainbird et al., 2020). Although the influence of evolving Proterozoic environmental conditions remains unclear (Butterfield, 2015; Brocks et al., 2023; Porter and Riedman, 2023), environmental heterogeneity inherent to inland seas may have influenced microbial habitat transitions and related evolution of early eukaryotes. Successful adaptation to new environments is an important driver of evolution, and adaptation to marginal marine environments with varied salinity is considered one of the most difficult barriers to habitat expansion (Jamy et al., 2022). As suggested by Reidman et al. (2023) the importance of nearshore environments for early eukaryote habitat may be underappreciated, providing motivation to study links between early eukaryote ecology and water column conditions of freshwater input, evaporation, and nutrient availability typical of marginal marine settings. Strata of the Nonesuch Formation (Midcontinent USA) provide an opportunity to investigate the connection between late Mesoproterozoic microorganism habitat and environmental heterogeneity inherent to inland seas. A relatively diverse, well preserved microfossil assemblage from these rocks is pointed to as evidence that early eukaryotes had inhabited redox-stratified lacustrine habitats by the end-Mesoproterozoic (Elmore et al., 1989;

Cumming et al., 2013; Strother and Wellman, 2021; Slotznick et al., 2024). Although recent sedimentologic and geochemical investigations demonstrate marine influence on deposition (Jones et al., 2020; Stüeken et al., 2020; Stewart et al., 2024; see also Hieshima and Pratt, 1991), the inference holds that by the end Mesoproterozoic early eukaryotes were tolerant of ecologically variable habitats, including subaerial settings (Strother and Wellman, 2011).

Here we present new C, O, and Rb-Sr isotope as well as major and trace element geochemistry from molar tooth (MT) calcite microspar extracted from MT structures and associated carbonate-rich layers of the Nonesuch Formation to constrain the degree of marine connectivity to the Nonesuch basin. Molar tooth structures are carbonate microspar-filled voids that developed in unlithified sediments with occurrences peaking in the late Mesoproterozoic to early Neoproterozoic (Kuang, 2014; Kriscautzky et al., 2022). These structures are interpreted to archive the isotopic and elemental composition of depositional fluids or shallow, earliest diagenetic pore fluids (Kuang, 2014; Zhou et al., 2020; Kriscautzky et al., 2022).

While our focus is on MT calcite microspar, carbonate in the Nonesuch Formation is present in several additional fabrics that precipitated at or shortly after deposition and during early to late burial diagenesis and later faulting. We use multiple parameters including patterns in $^{87}\text{Sr}/^{86}\text{Sr}$, trace element concentrations, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values, and petrographic evidence for recrystallization from all these carbonate fabrics to constrain the impact of postdepositional diagenetic alteration on carbonate geochemistry, a prerequisite for meaningful interpretation of primary basin conditions. Our geochemical datasets paired with petrographic observation and integrated with sedimentologic-stratigraphic data (Stewart et al., 2024) allow us to make inferences about the chemistry of shallow pore fluids and the overlying water column and interpret connectivity of the Nonesuch interior seaway to the late Mesoproterozoic ocean. We

identify least-altered isotopic compositions and compare those to values reported from other late Mesoproterozoic marine carbonates. Carbon and oxygen isotopes provide insight into the timing of carbonate precipitation and importance of organic carbon remineralization within shallow pore fluids as well as aspects of basin restriction and evaporation. Strontium isotope compositions inform on the combined contribution of global seawater and continental water sources (Brand et al., 2009; Kuznetsov et al., 2012; Paula-Santos et al., 2017; Deußen et al., 2024), but care is required to understand how those values have been influenced by basin restriction and potential decoupling of isotopic values from the open ocean. Comparison of Nonesuch Formation Sr compositions to other late Mesoproterozoic marine carbonates offers an opportunity to evaluate the significance of restricted marine basins on construction of a late Mesoproterozoic global seawater curve during a time of postulated high sea-level and continental flooding (Kah et al., 2012; Rainbird et al., 2020).

REGIONAL GEOLOGIC SETTING

The Nonesuch Formation is part of the lower Oronto Group, a sedimentary succession that overlies thick accumulations of basalt, rhyolite flows, and intrusions of the North American Midcontinent Rift System (MCS). The MCS evolved as a series of basins that are known from regional gravity data to extend 2200 km from Kansas through Lake Superior to Michigan (Figure 1; Woodruff et al., 2020). In the Lake Superior region, volcanism between ca. 1112 – 1090 Ma resulted in development of several sub-basins infilled with subaerial basalt flows and intrusions and separated by older basement highs (Allan, 1997). As volcanism waned by ca. 1083 Ma, deposition of the overlying Oronto Group was accommodated by continued subsidence, resulting in thicker deposits towards basin centers and onlapping of the Copper Harbor Conglomerate, Nonesuch Formation, and lower Freda Formation against underlying volcanic rocks and older

basement highs along basin margins (Stewart et al., 2024). The age of the lower Oronto Group is constrained by a U-Pb zircon age of 1085.57 ± 0.25 Ma from an andesite flow within the lower Copper Harbor Conglomerate (Fairchild et al., 2017), a Pb-Pb isochron age of 1081 ± 9 Ma from a carbonate bed in the basal Nonesuch Formation (Ohr, 1993), and a Re-Os isochron age of 1040 ± 78 Ma from dark shales in the lower Nonesuch Formation (Figure 1; Cumming et al., 2013). Ruiz et al. (1984) report a Rb-Sr age of 1047 ± 37 Ma for crosscutting carbonate veins.

SEDIMENTOLOGY STRATIGRAPHY

The upper Copper Harbor Conglomerate and Nonesuch Formation comprise three transgressive-regressive cycles whose preservation is controlled by proximity to basin margin settings (Figure 2; Stewart et al., 2024). The lowest cycle is locally preserved in areas of greatest subsidence where thick accumulations of tidal-marine sandstone in the upper Copper Harbor conglomerate shoal into tidal flat and distributary channel deposits in the lower Nonesuch Formation. At most locations, only the middle and upper cycles are preserved (as shown in Figure 2). At these more landward positions, alluvial and fluvial deposits of the Copper Harbor Conglomerate are abruptly overlain by tidal flat shale, siltstone, and sandstone of the Nonesuch Formation, which transition up section into estuarine deposits composed of laminated to thin-bedded fine-grained sandstone, siltstone, shale. The distribution of authigenic carbonate cement targeted for this study is highlighted by the calcium curves shown in Figure 2. Carbonate is present in the tidal flat facies and becomes more common in the overlying estuarine facies. In Michigan, the informal Junior member is recognized as a regional, cm-thick sedimentary calcite marker bed within tidal flat facies of the middle cycle (Mauk et al., 1992; Jones et al., 2023). The estuarine facies is broadly equivalent to the carbonate-rich facies of Imbus et al. (1992) and the anoxic magnetic mineral facies of Slotznick et al. (2024). Turbidite deposits composed of

normally graded sandstone, siltstone, and shale are interbedded with upper estuarine deposits. A sequence boundary caps the middle cycle and records an abrupt, basinward shift in facies that juxtaposes tidal flat deposits above relatively deep-water estuary and turbidite deposits. In areas of greatest subsidence, the middle cycle is capped by a sequence boundary or its correlative conformity and overlain by shallow marine sandstone. Above the sequence boundary, shallow marine to shoreline deposits pass upwards into mixed tidal flat, floodplain, and fluvial deposits of the lower Freda Formation. In basin margin settings, the sequence boundary truncates the middle cycle such that shallow marine, tidal flat, or floodplain deposits of the upper cycle directly overlie tidal flat or lower estuarine deposits of the middle cycle.

Sedimentary calcite comprises a minor component (<1%) of the Nonesuch Formation. One thin (mm- to cm-thick) calcite marker bed informally named the Junior member is present along the Keweenaw Peninsula and interpreted as sedimentary calcite (Ohr, 1991; Mauk et al., 1992; Jones et al., 2023). Molar tooth calcite microspar infills mm- to cm-scale MT structures and is present within carbonate-rich laminae (Stewart and Mauk, 2017). Concretions formed during early (pre-compactional) and later (syn- to post-compactional) burial diagenesis, while interstitial calcite cement precipitated during advanced stages of burial, and calcite veins are related to faulting during the Grenvillian orogeny (Ruiz et al., 1984; Mauk, 1992; Jones et al., 2023; Hodgins et al., 2024). This contribution focuses on the geochemistry of MT calcite microspar.

Across the entire lateral extent of the Nonesuch Formation, MT calcite microspar is present as two distinct fabrics: carbonate-rich layers and MT structures (see Kriskautzky et al. 2022 for a review of MT microspar). Carbonate-rich layers are composed of cm- to mm-thick carbonaceous beds and laminae intercalated with mm-thick laminae of organic-rich (<2%, Imbus

et al., 1992) argillaceous material and quartz silt (Figure 3a, d, e, f, g, h). MT structures are cracks and pockets that crosscut and distort bedding and are infilled with characteristic MT calcite microspar (Stewart and Mauk, 2017; Kriscautzky et al., 2022; Figure 3a, b, c, e). MT structures and carbonate-rich layers are most common within the estuarine facies and less common within tidal flat deposits (Figure 2), and locally mm-scale carbonate rip up clasts are incorporated into turbidite facies.

METHODS

Samples for this study were collected from drill core from northern Wisconsin and the Keweenaw Peninsula of Michigan and the Big Iron River outcrop section and tied to sedimentary facies described in Stewart et al. (2024; see Supplemental table S1 for sample locations). Calcite MT microspar from the Nonesuch Formation, the focus of this study, was targeted for analysis from carbonate-rich laminae and MT structures. Diagenetic interstitial carbonate and carbonate veins and concretions were also analyzed to evaluate potential post-depositional alteration. Several samples of the Junior member were collected from outcrops along the Big Iron River for C and O isotope analysis only. Carbonate phases, alteration, and recrystallization were assessed by petrographic observation of thin sections and geochemical composition.

Most carbonates were milled from thick sections, powdered, and split into two aliquots. One aliquot was reserved for carbon and oxygen isotope analysis at the University of Michigan Stable Isotope laboratory. The other aliquot was processed for Rb-Sr isotope and major and trace element analysis at the University of Wisconsin ICP-TIMS laboratory. A selection of thin sections was characterized at the University of Wisconsin Electron Microbeam laboratory. Additional samples were collected from outcrop exposure along the Big Iron River and analyzed for carbon and oxygen isotopes at the Scottish Universities Environmental Research Centre.

Carbon and O isotope compositions are reported in delta per mil (‰) notation relative to VPDB (see supplements for detailed methodology).

RESULTS

Petrography

Here we present petrographic observations with an emphasis on MT calcite microspar. Diagenetic carbonate, including calcite concretions, interstitial calcite, and calcite veins, are also considered to constrain the degree of alteration of MT microspar.

Molar tooth microspar within molar tooth structures

Under transmitted light, calcite microspar infilling MT structures is composed of clear, equant crystals (5 to 10 μm) with planar, noninterlocking crystal boundaries (Figure 3b, c). Molar tooth microspar is composed of cores and rims that are indistinguishable under transmitted light because they are in optical continuity while backscatter electron imagery locally distinguishes dull, peloidal-shaped cores from brighter rims (Bishop and Sumner, 2006; Kriskautzky et al, 2023). Trace element ratios indicate MT carbonate is composed of calcite with minor Fe and Mn (Table 1, Supplementary table S2), while Energy Dispersive X-ray Spectroscopy (EDS) confirms cores are composed of calcite while rims include minor abundances (< 2 weight %) of Fe, Mn, and Mg. In some samples, minor recrystallization of microspar within MT structures results in patches of coarser crystals that have less well-defined crystal boundaries (long axis length of patchy recrystallization about 0.03 to 0.07 mm, Figure 3d). In these samples, MT microspar has interlocking crystal boundaries. Detrital sediments are absent or locally incorporated into MT structures (see Figure 8a of Stewart and Mauk, 2017). The edges of MT structures are distinct (Figure 3a, b, c, e), making them readily identified and physically isolated. Encasing sedimentary laminae bend around MT structures (Figure 3a, e), demonstrating the structures developed before sediment compaction. MT structures show local

brittle deformation (Figure 3e) indicating early carbonate cementation prior to sediment compaction and lithification of the surrounding sediments.

MT microspar within carbonate-rich layers

Carbonate-rich layers include significant intermixed detrital material (Figure 3h). Fine-grained carbonate composes 90 – 95% of framework grains and shows irregular crystal boundaries and unevenly distributed crystal sizes between 5 to 50 μm (Figure 3d, f, g, h). Partially recrystallized MT microspar is concentrated in pockets that locally load into underlying detrital-rich laminae (Figure 3d). Molar tooth microspar is more common in carbonate-rich laminae of estuary, and especially evaporitic estuary facies while euhedral to anhedral calcite cement is most common in carbonate-rich laminae of the tidal flat facies. Pervasive carbonate recrystallization results in varied crystal sizes from blocky, equant, well-twinned carbonate crystals to small, bubbly carbonate partially replacing detrital quartz and clay. One sample with mm-scale displacive evaporite fabric is composed of large (long axis length about 0.50 to 0.80 mm), euhedral, well-twinned carbonate crystals (Figure 3f, g). Original bedding is well- to poorly preserved.

Veins and Concretions

Concretions are typically ellipsoidal and deflect or crosscut the surrounding sedimentary laminae, indicating their development spans early (pre-compaction) and later (post-compaction) burial diagenesis (Mauk et al., 1992; Jones et al., 2023). Calcite within concretions partially to completely replaces detrital sediments. Carbonate crystal size is variable, and in some samples crystal size and shape appears to vary with original sedimentary bedding. Calcite veins are associated with faults and composed of coarse, blocky, subhedral to euhedral, twinned calcite and massive, anhedral calcite (Ruiz et al., 1984; Carpenter, 1963; Mauk et al., 1992; Jones et al., 2023).

MAJOR- AND TRACE-ELEMENT GEOCHEMISTRY

Overall, carbonates record minor variation in Rb and Sr concentrations and in Mg/Ca, Mn/Sr, and Fe/Sr (Tables 1, 2). Strontium concentrations of carbonate sampled from MT structures and carbonate-rich layers are 92-552 ppm and 110-505 ppm, respectively. Strontium concentrations of veins and concretions are 110 and 172 ppm. The range and magnitude of Rb concentrations is larger for carbonate-rich layers (0.28 – 5.35 ppm) compared to MT structures (0.09 – 2.88 ppm) and veins and concretions (0.06 – 1.91 ppm). Mg/Ca, Mn/Sr, and Fe/Sr are lower for carbonate sampled from MT structures (<0.0047, <38, <15, respectively) compared to carbonate sampled within bedding (<0.017, <104, <28, respectively). Concretions have low Mg/Ca (0.0050) while Mn/Sr and Fe/Sr are elevated (45 and 68, respectively).

ISOTOPE GEOCHEMISTRY

Carbon and Oxygen Isotopes

The $\delta^{13}\text{C}$ values of all MT structures and carbonate-rich layers fall between -0.4‰ to -10.5‰ (Table 3, Figure 4). $\delta^{13}\text{C}$ values group by sedimentary facies such that tidal flat facies have lower $\delta^{13}\text{C}$ than estuary and evaporitic estuary facies. Furthermore, within the estuary and tidal flat facies, MT structures have a narrower range of $\delta^{13}\text{C}$ (-0.4 to -4.9‰ and -6.2 to -6.4‰, respectively) compared to carbonate-rich layers (-2.3 to -6.9‰ and -8.8 and -10.5‰, respectively). $\delta^{13}\text{C}$ values of MT structures and carbonate-rich layers of the evaporitic estuary facies and the Junior member is between -2.0 to -3.9‰ with no clear distinction between carbonate texture. Cross-cutting veins and concretions record values between -3.2 to -23.9‰.

Oxygen isotope values of MT structures and carbonate-rich layers range from -3.6‰ to -13.9‰. For all facies, carbonate sampled from MT structures define a heavier, narrower range of $\delta^{18}\text{O}$ from -3.6 to -6.7‰. Except for the Junior member, all samples from the Big Iron River

location (see Figure 1 for location) have oxygen isotope values less than -9‰. Excluding the Big Iron River location, all samples except two have $\delta^{18}\text{O}$ greater than -9‰. Veins and concretions are skewed towards lighter values (-15.0 to -10.3‰ and -10.3 to -8.1‰, respectively).

Rubidium and Strontium Isotope Composition

Initial $^{87}\text{Sr}/^{86}\text{Sr}$ of all MT structures and carbonate-rich layers calculated to 1081 Ma span 0.70502 to 0.70693 ($n = 26$, Table 2). Initial $^{87}\text{Sr}/^{86}\text{Sr}$ of crosscutting veins and concretions span 0.70267 to 0.70655 ($n = 5$). Measured whole-rock $^{87}\text{Sr}/^{86}\text{Sr}$ for siliciclastic samples from the Nonesuch Formation are significantly more radiogenic, between 0.74048 and 0.78453 (Ruiz et al., 1984; Ohr, 1993). Incorporation of even small amounts of detrital material during sample preparation could alter the Sr isotope composition of the leachate towards more radiogenic values. A positive correlation between $^{87}\text{Rb}/^{86}\text{Sr}$ and Sr isotope composition would indicate incorporation of Rb and Sr associated with clay and other detrital sediments during sample preparation; such a correlation is absent in our data (Figure 5).

DISCUSSION

Evaluating Diagenetic Alteration

Several generations of carbonate are present within the Nonesuch Formation, representing a paragenetic history spanning deposition through maximum burial and subsequent uplift during Grenvillian orogenesis (Ruiz et al., 1984; Mauk et al., 1992; Jones et al., 2023; Hodgins et al., 2024). The relative timing of different carbonate generations is based on observation of authigenic mineral relationships (Jones et al., 2023). Maximum burial temperature is determined from illite-smectite expandability, illite crystallinity, organic thermal maturity, and carbonate clumped isotopes and falls within the range of ~100 - 160°C (Price and McDowell, 1993; Price et al., 1996; Gallagher et al., 2017; Jones et al., 2023). Reported geothermal gradients

for the MRS span 45 to 55°C km⁻¹ based on constraints from actinolite in volcanic rocks underlying the Oronto Group and illite/smectite expandability from the Oronto Group (Price and McDowell, 1993; Wirth et al., 1997). Maximum temperature of calcite vein formation is interpreted from carbonate clumped isotopes at ~55°C and ~1 km depth using an estimated surface temperature of ~30°C and geothermal gradient of 35°C km⁻¹ (Hodgin et al., 2024).

We focus on MT calcite microspar because that carbonate texture is present in the Nonesuch Formation across its entire lateral extent, and it is thought to have precipitated in shallow pore fluids and perhaps bottom water at or shortly after deposition (Kriskautzky et al., 2022). The chemistry preserved by MT microspar thus reflects that of shallow pore water and perhaps bottom water, and it may have been altered by fluid-rock interactions during burial diagenesis. In the following discussion we assess the impact of burial diagenesis to identify C, O, and Sr isotopic compositions that best reflect the composition of the water column or shallow pore fluids near the time of deposition. We first consider petrographic, trace element, and O isotopic evidence for diagenetic alteration of MT microspar within MT structures compared to carbonate-rich laminae. Next, we use Rb-Sr and O isotopes to assess carbonate alteration via fluid-rock interactions during burial diagenesis.

Calcite microspar within MT structures

Textural relationships between MT structures and encasing detrital sediments, including incorporation of detrital sediments from, and displacement of adjacent detrital laminae, brittle displacement of MT structures during sediment compaction (Figure 3a, e), and minor redeposited carbonate breccia, are consistent with MT voids and their infilling microspar developing penecontemporaneously in unlithified sediment near the sediment-water interface (Kriskautzky et al., 2022). Calcite microspar within MT structures of the Nonesuch Formation shows minimal

petrographic evidence for pervasive alteration. Microspar mostly retains the characteristic petrographic features of MT microspar including clear, uniform, small crystals with planar, non-interlocking crystal boundaries with only minor patchy recrystallization. Low Rb and Mg/Ca, Mn/Sr, and Fe/Sr are consistent with petrographic evidence for minimal alteration and clastic contamination (Brand and Veizer, 1980; Chen et al., 2022). The few MT structures with significant detrital material also have greater Rb, Mg/Ca, Mn/Sr, and Fe/Sr. The narrow range in $\delta^{18}\text{O}$ of microspar sampled from MT structures (-3.6 to -6.7‰) compared to associated carbonate-rich laminae (-5.5 to -13.9‰) supports petrographic evidence that these samples experienced minimal postdepositional diagenetic alteration (Brand and Veizer, 1981; Swart, 2015). Pervasive alteration through contact with a single diagenetic fluid cannot reasonably explain this narrow range in $\delta^{18}\text{O}$ values because (1) textural relationships between MT structures and encasing sediments indicate MT structures and their infilling microspar developed at or near the sediment-water interface during deposition and earliest burial, before sediment compaction; (2) microspar within MT structures shows minimal petrographic evidence for recrystallization compared to surrounding carbonate-rich laminae; and (3) carbonate from associated carbonate-rich laminae preserves a wider range of $\delta^{18}\text{O}$ values and shows greater petrographic evidence for carbonate alteration.

Calcite microspar within carbonate-rich layers

Compared to calcite microspar within MT structures, calcite within carbonate-rich layers is associated with more detrital grains and shows greater petrographic evidence for recrystallization, including irregular crystal boundaries and variable crystal-size distributions. Elevated Rb concentrations and Mg/Ca, Mn/Sr, and Fe/Sr, and lower $\delta^{18}\text{O}$ values (-5.5 to -13.9‰), correspond directly to petrographic evidence for carbonate recrystallization and detrital

contamination. Furthermore, samples collected from the Big Iron River location have exceptionally low $\delta^{18}\text{O}$ values: Carbonate-rich layers fall between -9.1 and -13.9‰ while the Junior member is -7.7 to -9.5‰. Such low values are indicative of alteration controlled by temperature and fluid-rock interactions (Sheppard, 1986; Swart, 2015), which is unsurprising at this location due to the prevalence of mapped folds and faults (Cannon et al., 1995) and the proximity to the White Pine mine with its extensive Cu mineralization.

The combined petrographic, trace element, and $\delta^{18}\text{O}$ constraints demonstrate that calcite microspar within MT structures is less impacted by dissolution, recrystallization, and contamination by detrital material during diagenesis than carbonate within carbonate-rich layers. The most altered samples, regardless of carbonate fabric, were collected from the Big Iron River location near well documented Cu mineralization and faulting at White Pine.

Tracking diagenesis with Sr and O isotopes

Molar tooth microspar precipitated from shallow pore fluids whose composition may have evolved from that of the overlying water column through microbially mediated redox reactions and exchange with surrounding detrital sediments at or shortly after deposition (Kriskautzky et al., 2022). Additionally, later generations of carbonate precipitated in available pore space and locally overprinted or replaced earlier carbonate during burial diagenesis. The water from which these carbonates precipitated or recrystallized may represent a combination of mixing fluids with distinct compositions and evolving fluid composition driven by temperature-dependent fluid-rock interactions.

Paired O isotope and Rb-Sr isotope systematics of the Nonesuch Formation presents an opportunity to evaluate the impact of water-rock interactions on the composition of pore water that potentially precipitated or altered MT microspar. In typical depositional settings, the

sediments that would contribute to diagenetic alteration of carbonate have $^{87}\text{Sr}/^{86}\text{Sr}$ compositions that are more radiogenic than the fluids from which the carbonates precipitated. Therefore, the least radiogenic values from a suite of carbonates are commonly interpreted as least-altered (e.g. Gorokhov et al., 1995; Shields and Veizer, 2002). The opposite is true for the Nonesuch Formation because the underlying basalts, which were the primary source for most of the Nonesuch Formation detrital sediments (Cullers and Berendsen, 1998), have less radiogenic initial (1081 Ma) $^{87}\text{Sr}/^{86}\text{Sr}$ (~ 0.7032 ; Paces and Bell, 1989; Nicholson and Shirey, 1990) than the initial $^{87}\text{Sr}/^{86}\text{Sr}$ of Nonesuch carbonates (~ 0.7069) and previously reported values of the late Mesoproterozoic marine system (~ 0.7051 to 0.7066 ; Gorokhov et al., 1995; Semikhatov et al., 2002; Shields and Veizer, 2002; Kuznetsov et al., 1997 2003; 2006; 2008; 2017; 2019; Cox et al., 2016; Gibson et al., 2019; Zhou et al., 2020). Nonesuch carbonate samples show a weak negative correlation between initial $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$ ($R^2 = 0.52$) that tracks diagenetic incorporation of less radiogenic Sr from the underlying basalts (Figure 5), like patterns observed in interstitial pore water of modern marine sediments (Elderfield and Gieskes, 1982; Gieskes et al., 1986). Because carbonate diagenesis leads to a decrease in Sr concentration and lighter $\delta^{18}\text{O}$ values of carbonate (Brand and Veizer, 1980; 1981; Swart, 2015), we can cross-plot these variables against initial $^{87}\text{Sr}/^{86}\text{Sr}$ as an independent test for carbonate diagenesis. Our data show positive correlations between $\delta^{18}\text{O}$, Sr concentration, and initial $^{87}\text{Sr}/^{86}\text{Sr}$ consistent with diagenetic alteration of Nonesuch carbonates towards less radiogenic Sr isotope compositions. (Figure 6a, Supplemental figure A1).

We next consider how carbonate diagenesis may have been affected by the strontium isotope composition of Nonesuch detrital sediments weathered from the underlying basalts. Previous Rb-Sr isotope measurements of the detrital lithic sediment and clays in the Nonesuch

Formation (Ruiz et al., 1984; Ohr, 1993) yield an initial $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.7068 and model age of 1048 Ma. We interpret this age to indicate resetting of the Rb-Sr system by fluids associated with late Mesoproterozoic Grenvillian orogenesis. Because the Rb-Sr isotope systematics of the Nonesuch detrital sediments were reset during this event, we instead consider diagenesis driven by interaction with weathered basalt as a proxy for sediment compositions prior to Grenvillian overprinting.

Diagenetic alteration shifts Nonesuch carbonate initial $^{87}\text{Sr}/^{86}\text{Sr}$ towards less radiogenic values. Most of the data (16 of 26 samples) fall along a linear array that extends from least-altered initial $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.70693 and very low (0.00090) $^{87}\text{Rb}/^{86}\text{Sr}$ towards most-altered initial $^{87}\text{Sr}/^{86}\text{Sr}$ of ~ 0.7050 (see dashed arrow labeled ‘diagenesis’ on Figure 5b). Samples that plot above this array have elevated $^{87}\text{Rb}/^{86}\text{Sr}$ (>0.013) and initial $^{87}\text{Sr}/^{86}\text{Sr}$ greater than 0.7050, which is more radiogenic than the $^{87}\text{Sr}/^{86}\text{Sr}$ of underlying basalts at 1081 Ma (~ 0.7032 ; Paces and Bell 1989; Nicholson and Shirey 1990). The lowest initial $^{87}\text{Sr}/^{86}\text{Sr}$ (~ 0.705 to ~ 0.706) recorded in diagenetically altered Nonesuch carbonates could be explained by accumulation of radiogenic Sr in relatively high-Rb/Sr early diagenetic clays that developed from weathering of the basalt (See supplemental material for details of this estimation). Based on Rb-Sr isotope systematics, the timing of carbonate diagenesis was relatively early because accumulation of radiogenic Sr during diagenetic clay mineral growth occurred in the 12 to 4 Myr between eruption of the basalts and deposition of the Nonesuch Formation (Li et al., 1995; Fairchild et al., 2017; Swanson-Hysell et al., 2019). When paired with other traditional proxies like carbon and oxygen, Rb-Sr isotope systematics can be used to evaluate early diagenetic trends that are otherwise indistinguishable with any one proxy.

Carbon Remineralization and the Influence of Early Cementation

From petrographic characteristics paired with oxygen isotope values, we determined microspar within MT structures precipitated from shallow pore fluids before sediments lithified and compacted, while carbonate within carbonate-rich layers represents early phases that were variably overprinted during diagenesis. Most-altered $^{87}\text{Sr}/^{86}\text{Sr}$ of ~ 0.705 to ~ 0.706 place constraints on the timing of carbonate diagenesis to be within 4 to 12 million years of eruption of the underlying basalts, essentially during deposition of the Nonesuch Formation. These combined observations are consistent with previous work (Imbus et al., 1992; Mauk et al., 1992; Jones et al., 2023) suggesting the geochemistry of MT structures and carbonate-rich layers tracks diagenetic evolution of pore fluids during deposition and burial of the Nonesuch Formation. The chemistry of veins, concretions, and some carbonate-rich layers reflects later burial diagenetic processes including hydrocarbon generation and migration (Imbus et al., 1992) and migration of copper-mineralizing fluids (Mauk et al., 1992; Jones et al., 2023) as well as Grenvillian deformation (Hodgin et al., 2024).

To test if carbonate from MT structures and carbonate-rich layers records the evolution of pore fluids during Nonesuch deposition, we first consider $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ compositions, separated by facies. During diagenesis, oxygen is more susceptible to fluid alteration than carbon (Brand and Veizer, 1981; Swart, 2015), so we expect greater variability in $\delta^{18}\text{O}$ compared to $\delta^{13}\text{C}$. Nonesuch $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are uncorrelated (Figure 4), and $\delta^{18}\text{O}$ values span a wide range across all sedimentary facies. This signal preserves a range of depositional fluid compositions that may reflect a combination of fluid mixing between meteoric, connate, and deep basinal water and evolving fluid composition driven by temperature-dependent fluid-rock interactions especially at the Big Iron River location. In contrast, $\delta^{13}\text{C}$ values vary by lithofacies suggesting buffering by surrounding sediments or rocks (Kah et al., 1999). The variability in $\delta^{13}\text{C}$ is

interpreted to reflect facies-dependent composition of dissolved inorganic carbon in pore fluids, which ties to organic matter oxidation and authigenic carbonate precipitation (e.g., Imbus et al., 1992; Mauk et al., 1992). Away from the Big Iron River location, only two samples have $\delta^{13}\text{C}$ values less than -6.5‰ (labeled ‘most altered’ on Figure 4). These most-altered samples have $\delta^{18}\text{O}$ values less than -8‰ and show direct petrographic evidence for alteration including large, well-twinned carbonate within layers that show displacive evaporite texture (Figure 3g) or abundant detrital material and large, well-twinned, blocky carbonate crystals within poorly defined carbonate-rich laminae. Dissolution and precipitation of carbonate at higher temperatures during later stages of burial diagenesis, associated hydrocarbon generation and migration (Imbus et al., 1992), and fluid migration during Grenvillian orogenesis likely contributed to the relatively light values observed in the most altered samples, as well as for veins and concretions (Ruiz et al., 1984; Mauk et al., 1992; Jones et al., 2023). Later diagenetic features are thus clearly identified with petrographic evidence and oxygen isotope compositions. Next, considering Sr and C isotopes together provides insight into the evolution of pore fluid chemistry during early diagenesis and allows us to infer the composition of the overlying waterbody during deposition of the Nonesuch Formation.

Covariation of initial $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{13}\text{C}$ relates to the timing of carbonate precipitation and the degree of recrystallization. Rapid, early cementation would occlude porosity, minimizing incorporation of remineralized and recycled organic carbon and exchange of Sr between pore fluids and surrounding clays. Conversely, protracted cementation or recrystallization would allow for biogeochemical evolution of pore water compositions. In the Nonesuch basin, microbial recycling of organic matter, remineralization of organic carbon, and cation exchange with surrounding detrital material should drive pore fluids towards lighter $\delta^{13}\text{C}$ values and less

radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ compositions. Initial $^{87}\text{Sr}/^{86}\text{Sr}$ of Nonesuch carbonate show a weak positive correlation with $\delta^{13}\text{C}$ (Figure 6b). Samples from the evaporitic estuary facies cluster within a relatively narrow range of $^{87}\text{Sr}/^{86}\text{Sr}$ (0.70634 to 0.70684) and $\delta^{13}\text{C}$ values (-4.0 to -2.0‰). Samples from estuary facies are aligned with the evaporitic estuarine samples and extend to less radiogenic Sr (0.70502 to 0.70684) and lighter $\delta^{13}\text{C}$ (-6.1 to -0.5‰) values. Tidal flat facies show greater scatter towards less radiogenic Sr (0.70576 to 0.70668) and lighter $\delta^{13}\text{C}$ (-10.5 to -6.0‰) values. This clustering by facies and overall covariation of $^{87}\text{Sr}/^{86}\text{Sr}$ with $\delta^{13}\text{C}$ is consistent with facies-dependent differences in the timing of carbonate cementation. Rapid cementation of the evaporitic estuary facies captured pore fluid composition closer to the composition of the overlying estuarine waterbody. In contrast, carbonate of the estuary and especially the tidal flat facies precipitated from pore fluids that had variably evolved compositions. In particular, the coarser grain size and greater porosity of the relatively sandy tidal flat facies likely favored diagenetic carbonate precipitation during early burial diagenesis.

Restricted, Evaporitic Conditions in the Nonesuch Seaway Suggested by C, O Isotopes

Carbon isotope values from the Nonesuch formation expectedly fall below typical late Mesoproterozoic marine carbonate values of 2 to 4‰ (Kah et al., 1999, 2012; Bartley et al., 2001; Bartley and Kah, 2004; Silva-Tamayo et al., 2018; George et al., 2018; Li et al. 2022) because they represent deposition within an epeiric seaway. The light $\delta^{13}\text{C}$ values (-4.0 to -2.0‰) of Nonesuch Formation carbonates of the evaporitic estuary facies is consistent with oxidation of organic carbon within the water column or shallow sediments, as previously suggested by Elmore et al. (1989) and Imbus et al. (1992). Other late Mesoproterozoic epeiric basins also record $\delta^{13}\text{C}$ values that are 2 to 5‰ lighter than coeval open-marine facies and are similarly

interpreted to record *in situ* remineralization of organic matter (Gilleaudeau and Kah, 2013; Paula-Santos et al., 2021).

Although the oxygen isotope composition of Precambrian marine carbonate remains difficult to interpret because of pervasive overprinting and possible secular variation of the composition of seawater (Galili et al., 2019), least altered Mesoproterozoic marine carbonate $\delta^{18}\text{O}$ values are commonly -6 to -9‰ while values from restricted, evaporitic basins are a few per mil heavier, to about -3‰ (Frank and Lyons, 2000; Kah, 2000; Bartley et al., 2007; Gilleaudeau and Kah, 2013). Most $\delta^{18}\text{O}$ values of Nonesuch carbonate overlap with these values. Samples of carbonate from MT structures that show the least petrographic evidence for alteration (labeled least altered on Figure 4) cluster between -3.6 and -5.7‰, consistent with sedimentologic evidence for mildly evaporitic conditions (Jones et al., 2020). These values may be close to the primary oxygen isotope composition of the Nonesuch basin. Furthermore, excluding the Big Iron River location, $\delta^{18}\text{O}$ values of all samples except two (labeled most altered on Figure 4) are heavier than -9‰. Although the $\delta^{18}\text{O}$ values of these samples clearly reflects decreasing carbonate $\delta^{18}\text{O}$ values caused by fluid-rock interactions during burial diagenesis (Figure 6a), they remained within the range of typical least-altered Mesoproterozoic marine systems.

We can test our estimated timing of early carbonate diagenesis (approximately contemporaneous with deposition based on Rb-Sr isotope systematics, described above and in supplements) by considering temperature controls on $\delta^{18}\text{O}_{\text{carbonate}}$ values during burial diagenesis. From the paragenetic history presented in Jones et al. (2023) and Hodgin et al. (2024), and estimated surface temperature (20°C) and geothermal gradient (55°C km⁻¹), five carbonate generations are interpreted to have precipitated at the following stages of deposition and burial:

- (1) MT microspar and Junior member calcite bed (sedimentation and earliest burial, near

sediment-water interface); (2) early concretions (pre-compaction, surface to ~0.5 km, ~20 - 48°C); (3) late concretions (syn- to post-compaction, ~1.0 km, ~75°C, the boundary between early and intermediate diagenesis; Hess and Schacht, 2011); (4) interstitial cement (near maximum burial, ~2.2 km, ~140°C); and (5) calcite veins (Grenvillian faulting and uplift, ~0.6 km, ~55°C). Assuming carbonate diagenesis was driven by equilibrium reactions between a single pore fluid and calcite under increasing temperature conditions with burial, average primary $\delta^{18}\text{O}_{\text{carbonate}}$ (-5‰) from least altered MT microspar in MT structures, and fractionation constraints of Zheng (1999), the lowest $\delta^{18}\text{O}_{\text{carbonate}}$ (-9‰) corresponds to 37°C and 0.3 km burial depth. This depth is consistent with early diagenetic carbonate precipitation or recrystallization during burial diagenesis within ~1 to 3 million years of deposition, assuming a subsidence rate on the order of 0.1 km Myr⁻¹. A component of mixing with meteoric water, which typically has lower $\delta^{18}\text{O}$ values (Swart, 2015), would be compatible with more shallow burial depths and lower temperatures.

Implications For the Global Marine Sr Composition at Ca. 1081 Ma

Sedimentologic and geochemical constraints demonstrate an estuarine depositional setting for the Nonesuch Formation (Hieshima and Pratt, 1991; Jones et al., 2020; Stüeken et al., 2020; Stewart et al., 2024). The initial $^{87}\text{Sr}/^{86}\text{Sr}$ of least-altered Nonesuch carbonates (0.70683 - 0.70693) are interpreted to record the composition of shallow pore fluids in connection with the overlying estuarine waterbody. The combined petrographic and geochemical evidence indicates rapid carbonate precipitation from these fluids soon after deposition, so pore fluid composition is interpreted to be minimally evolved. The Sr isotope composition of marginal basins is shown to track global seawater compositions (Brand et al., 2009; Kuznetsov et al., 2012), although restricted intracontinental basins may reflect contribution from continental sources (Paula-Santos et al., 2017; Deußen et al., 2024). While the Nonesuch basin was located well within the

Laurentian continental interior, tidal sedimentary structures (Jones et al., 2020; Stewart et al., 2024) demonstrate a significant marine connection, as tidal forcing is likely diminished within the interior of epeiric seaways (Schieber, 2015). Thus, the $^{87}\text{Sr}/^{86}\text{Sr}$ of least-altered Nonesuch carbonates could plausibly approximate the global seawater composition at ca. 1081 Ma. Alternatively, it could represent mixing of seawater $^{87}\text{Sr}/^{86}\text{Sr}$ with local sources. We explore each scenario below.

Initial $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.70683 to 0.70693 from least-altered samples is more radiogenic than previously reported values between 0.70513 and 0.70656 for the late Mesoproterozoic (Gorokhov et al., 1995; Semikhatov et al., 2002; Shields et al., 2002; Kuznetsov et al., 1997 2003; 2006; 2008; 2017; 2019; Cox et al., 2016; Gibson et al., 2019; Zhou et al., 2020). This Initial $^{87}\text{Sr}/^{86}\text{Sr}$ could reflect influence of drainage systems overlying Archean- and Paleoproterozoic-cored uplands that fed into the Nonesuch basin. In support of this view, 80 to 90 percent of lower Oronto Group sediments were sourced from underlying basalts and the remaining 10 to 20 percent from presumably older granitoids (Cullers and Berendsen 1998). However, the average $^{87}\text{Sr}/^{86}\text{Sr}$ contributed to the Nonesuch basin is difficult to constrain because large geographic differences in bedrock $^{87}\text{Sr}/^{86}\text{Sr}$ result in widely variable $^{87}\text{Sr}/^{86}\text{Sr}$ of continental runoff (Beard and Johnson, 2000; Bataille and Bowen, 2012).

Alternately, the radiogenic initial $^{87}\text{Sr}/^{86}\text{Sr}$ of least-altered Nonesuch microspar could reflect an increase in the global seawater $^{87}\text{Sr}/^{86}\text{Sr}$ composition linked to uplift and erosion at the beginning of Ottawa phase Grenvillian orogenesis. The late Mesoproterozoic global seawater strontium curve is characterized by fluctuations between values close to 0.705 and 0.706, both within and between basins (Figure 7). Previous compilations (Semikhatov et al., 2002; Cox et al., 2016; Zhou et al., 2020; Chen et al., 2022) have noted relatively unradiogenic seawater strontium

compositions near ~ 0.705 coincident with assembly of Rodinia during the Grenvillian Orogeny and subsequent early Neoproterozoic rifting and have attributed these values to weathering of unradiogenic mantle and pulses of increased mafic magmatism. Gibson et al. (2019) propose the trend of rising seawater strontium values they observe from the Bylot basin, Canada ties to increased weathering of more radiogenic, old crust during the peak Grenvillian orogeny. While it is possible that the Nonesuch Formation records a similar record of increased weathering during early stages of the Grenvillian orogeny, the least-altered strontium isotope values of 0.70683 to 0.70693 are significantly more radiogenic than any other reported late Mesoproterozoic record. In fact, the global marine strontium isotope curve does not conclusively reach these values until the early Cryogenian (Cox et al., 2016; Chen et al., 2022). For this reason, the least-altered Nonesuch values most likely reflect mixing of seawater strontium with continental runoff in a restricted marine basin. The possibility of a positive excursion to ~ 0.7069 at ca. 1081 Ma in the global marine strontium isotope curve remains an intriguing possibility.

The emerging pattern of repeated fluctuation in the late Mesoproterozoic seawater strontium curve between ~ 0.7052 and ~ 0.7069 has implications for understanding continental weathering fluxes, carbon burial, and global climate feedbacks (e.g. Cox et al., 2016; Zhou et al., 2020), yet the spatial and temporal resolution remains too coarse to tell whether variability in the curve is due to local effects or large oscillations in global seawater strontium values on several millions- to tens-of-million-year timescales. While $^{87}\text{Sr}/^{86}\text{Sr}$ of epeiric seaways is thought to match global marine values (Brand et al., 2009; Kuznetsov et al., 2012), the greater significance of authigenic carbonate precipitation in shallow pore fluids during the Precambrian (Kriscautzky et al., 2022; Wang et al., 2023) and propensity for alteration of matrix carbonate (Brand et al., 2009) may have enhanced preservation of local effects in the Mesoproterozoic global marine

strontium record. This is because authigenic carbonate precipitation in pore fluids would preserve an early diagenetic signal that incorporates strontium from shallow pore fluids reacting with the surrounding sediments, groundwater recharge, and the overlying waterbody during deposition and diagenesis. The impact of local effects on the Proterozoic marine Sr isotope record may be reduced with petrographic characterization to identify diagenetic alteration and strategies against incorporation of non-authigenic Sr, such as appropriate sample cleaning and leaching protocols and determination of Rb concentrations for calculating initial Sr isotope compositions.

The late Mesoproterozoic global Sr seawater curve shows an emerging pattern of interbasinal and intrabasinal fluctuations that may reflect regional signals imparted by continental runoff to restricted marine basins during a time of postulated high sea level and continental flooding (Kah et al., 2012; Rainbird et al., 2020). Restricted circulation between epeiric seas and bordering oceans, their smaller water volumes, and a greater influence of continental runoff all contribute to local differences in water chemistry of epeiric seaways (Holmden et al., 1998; Gilleadeau et al., 2023) capable of decoupling the strontium isotope record of restricted epeiric seas and their coeval marine basins (Paula-Santos et al., 2017; Deußen et al., 2024). Thus, large fluctuations in the Proterozoic Sr seawater curve may signal expansion of epeiric seas and the development of restricted marine basins within continental interiors. Development of such seas would have resulted in greater regional and temporal variability in factors like fluvial contribution and basin circulation and stratification which should be considered when using analogues to interpret global signals. Importantly, expansion of epeiric seas would have increased the extent of marginal marine habitat with varied conditions of salinity, redox, and nutrient input, providing a broader range of ecological niches for early

eukaryotes to colonize (Jamy et al., 2022). Adaptation to these widely variable environmental conditions could be an important driver of early eukaryote evolution and radiation.

CONCLUSIONS

New C, O, and Rb-Sr isotope and major- and trace-element geochemistry from MT structures and associated carbonate-rich layers of the Nonesuch Formation track the composition of shallow pore fluids of the Nonesuch epeiric seaway. Rapid cementation of shallow pore space of the evaporitic estuary facies and Junior member captured pore fluid $\delta^{13}\text{C}$ values close to the composition of the overlying estuarine waterbody ($\delta^{13}\text{C}$ of -2.0 to -3.9‰). These values are 2 to 5‰ lighter than reported values for late Mesoproterozoic marine carbonate and are interpreted to record *in situ* remineralization of organic matter in a restricted seaway. In contrast, carbonate of the estuary and tidal flat facies ($\delta^{13}\text{C}$ of -0.5 to -10.5‰) precipitated from variably evolved pore fluids. Away from the Big Iron River location, $\delta^{18}\text{O}$ values of Nonesuch carbonate overlap the range of reported values for least-altered Mesoproterozoic marine and restricted marine carbonates, although $\delta^{18}\text{O}$ values clearly preserve a signal of diagenetic overprinting. Least altered MT microspar preserves values between -3.6 and -5.7‰, interpreted as the primary oxygen isotope composition of the Nonesuch basin and consistent with sedimentologic evidence for mildly evaporitic conditions. Least altered initial $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.70683 to 0.70693 are more radiogenic than existing estimates of late Mesoproterozoic seawater values. Because diagenetic alteration of Nonesuch carbonates pulls their strontium isotope composition towards less radiogenic values, least-altered $^{87}\text{Sr}/^{86}\text{Sr}$ likely records regional input of radiogenic Sr sourced from Archean and Paleoproterozoic highlands that drained into the Nonesuch basin and perhaps an increase in global continental weathering during initial stages of the Ottawan phase of the Grenvillian orogeny.

The late Mesoproterozoic seawater strontium curve shows an emerging pattern of fluctuation between ~ 0.7052 and ~ 0.7069 . These fluctuations may reflect expansion of restricted, epeiric seaways during sea-level highstand. In this view, the large fluctuations in $^{87}\text{Sr}/^{86}\text{Sr}$ within and between late Mesoproterozoic basins reflect restriction from open seawater and the regional influence of continental runoff to each basin. Global expansion of epeiric seaways would have broadened the extent of marginal marine environments that are increasingly viewed as important early eukaryote habitat (Riedman et al., 2023; Brocks et al., 2023), perhaps establishing environmental conditions that allowed for early eukaryote niche expansion and resulting diversification (Jamy et al. 2022).

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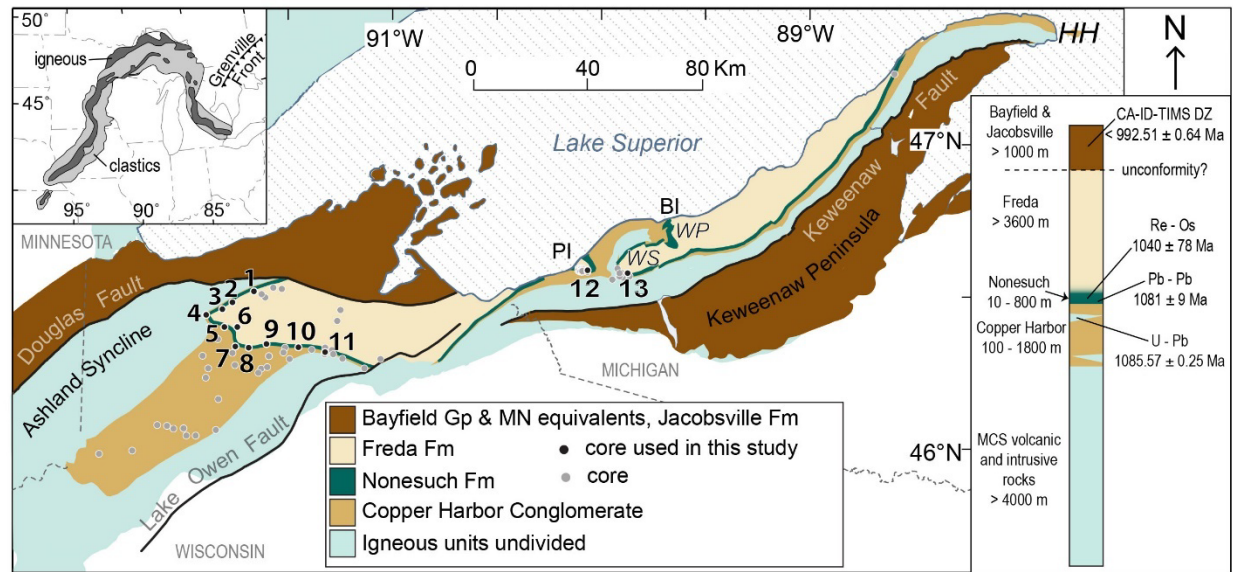
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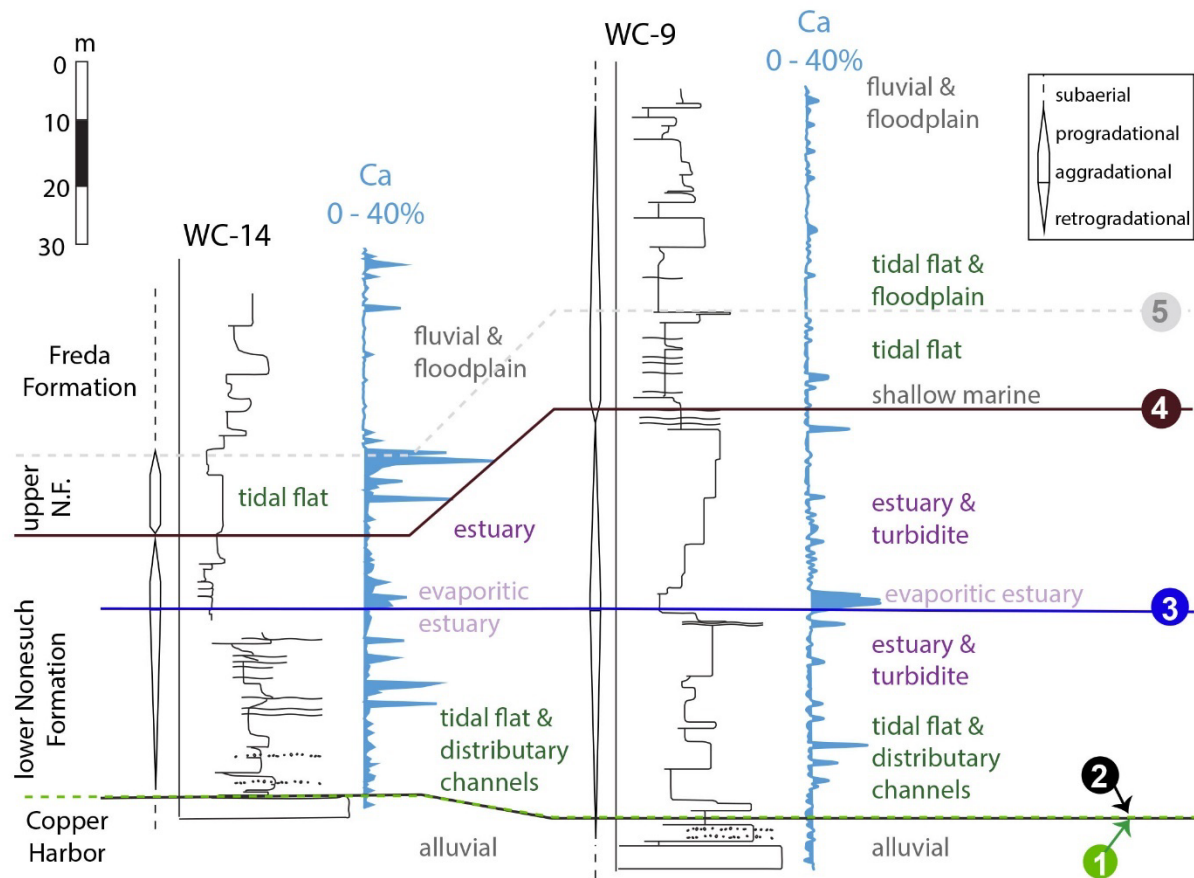
FIGURES

Figure 1. location



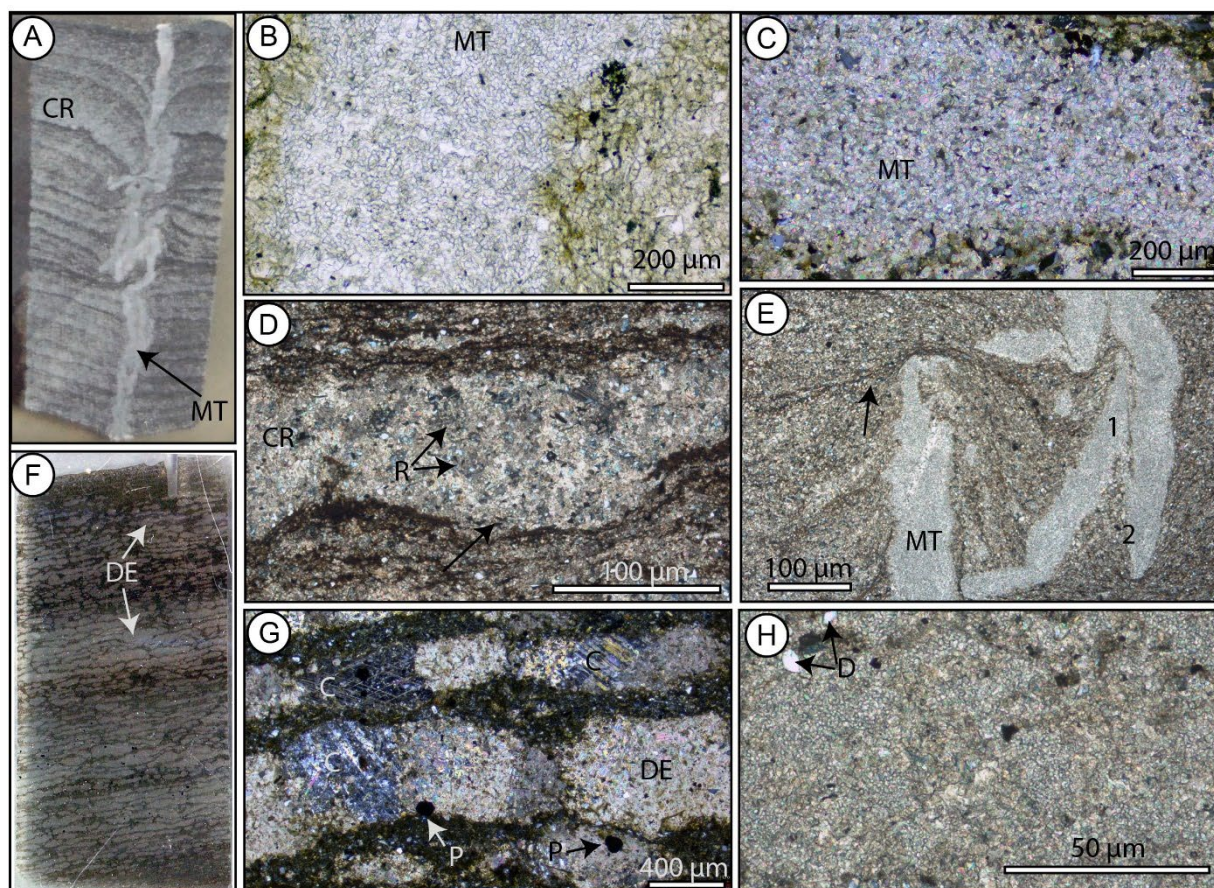
Map of Midcontinent Rift bedrock units. Numbers locate drill cores: 1: WC-14, 2: DO-6, 3: DO-5, 4: DO-10, 5: DO-13, 6: DO-14, 7: DO-8, 8: WC-18, 9: WC-13, 10: WC-9, 11: WC-2, 12: (Presque Isle/Copperwood area) PI-2, 13: (White Pine area) WPB-2. PI: Presque Isle River, WS: Western Syncline, WP: White Pine Basin, Fm: formation, Gp: Group, MN: Minnesota. Inset map (left) shows Midcontinent Rift extent, modified from Ojakangas et al (2001). Age constraints from Ohr (1993), Cumming et al. (2013), Fairchild et al. (2017), and Hodgkin et al. (2022). Thicknesses estimated from Daniels (1982), Elmore et al. (1989), and Stewart et al. (2024). Modified after Stewart et al. (2024). See Supplementary Table A1 for drill core location coordinates.

Figure 2. generalized stratigraphy



Stratigraphic correlation of the Nonesuch Formation from proximal (WC-14) to distal (WC-9) settings. Sedimentary facies and stratigraphy from Stewart et al. (2024), calcium curve from Stewart and Mauk (2017). Stratigraphic surfaces- 1: transgressive marine surface; 2: base Nonesuch Formation (a lithostratigraphic surface); 3: maximum flooding surface (datum); 4: sequence boundary (base upper Nonesuch or Freda formations); 5: base Freda Formation (a gradational, lithostratigraphic surface).

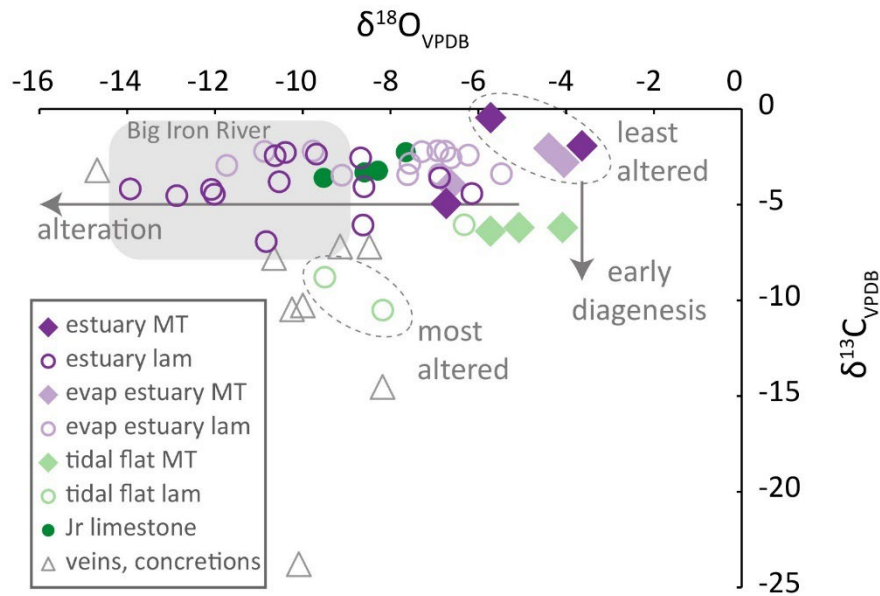
Figure 3. carbonate petrography



Nonesuch Formation carbonate petrography. A – C) least-altered microspar within molar tooth structures (MT). A) sample DO6-1365 showing MT structure cross-cutting carbonate-rich layers (CR). Detrital sediments are dark gray, and carbonate is light gray. B) Photomicrograph (plain polars) of MT structure shown in (A). C) sample DO6-1369. D) Photomicrograph (plain polars) of carbonate-rich layer (CR) with sedimentary loading (arrow) and partially recrystallized carbonate (R), sample WC9-1571 ft. E) Photomicrograph (cross polars) showing bedding deflecting around MT structures (arrow) and brittle deformation of MT structures (1 displaced from 2), sample DO5-874. F) thin section scan and G) photomicrograph (cross polars), sample WC14-1529, showing displacive evaporite textures (DE), euhedral, twinned carbonate (C) and pyrite (P). H)

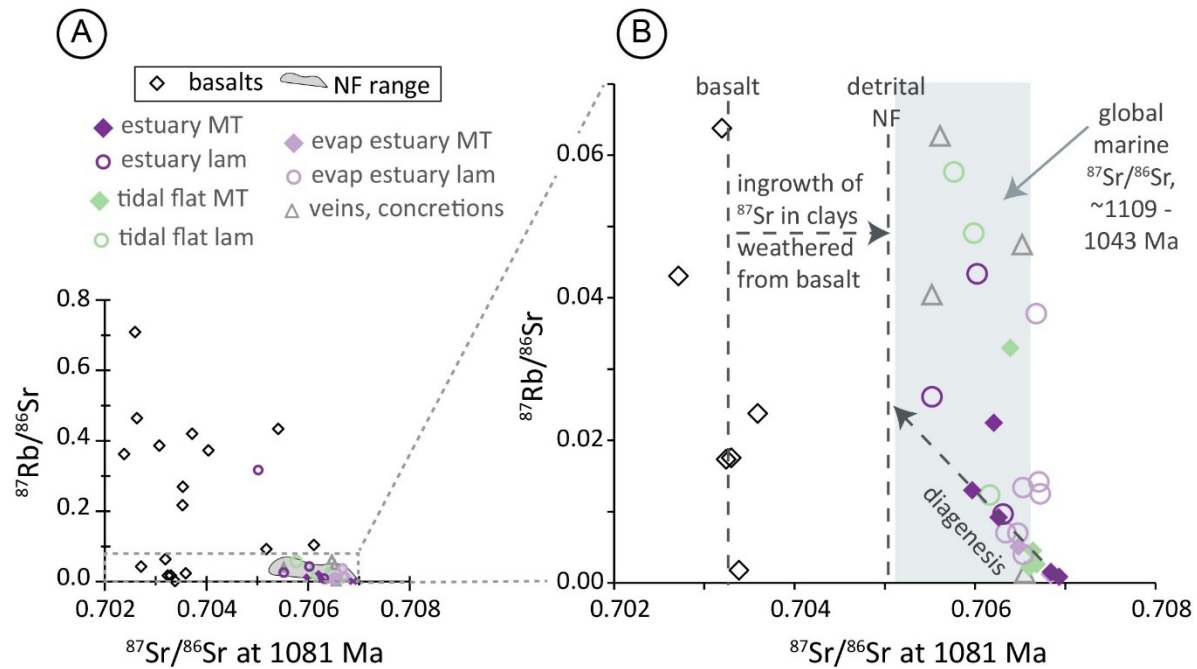
Photomicrograph (cross polars) of carbonate-rich layer, sample DO13-820 showing partial carbonate recrystallization and association with detrital minerals (D).

Figure 4. C and O isotopes



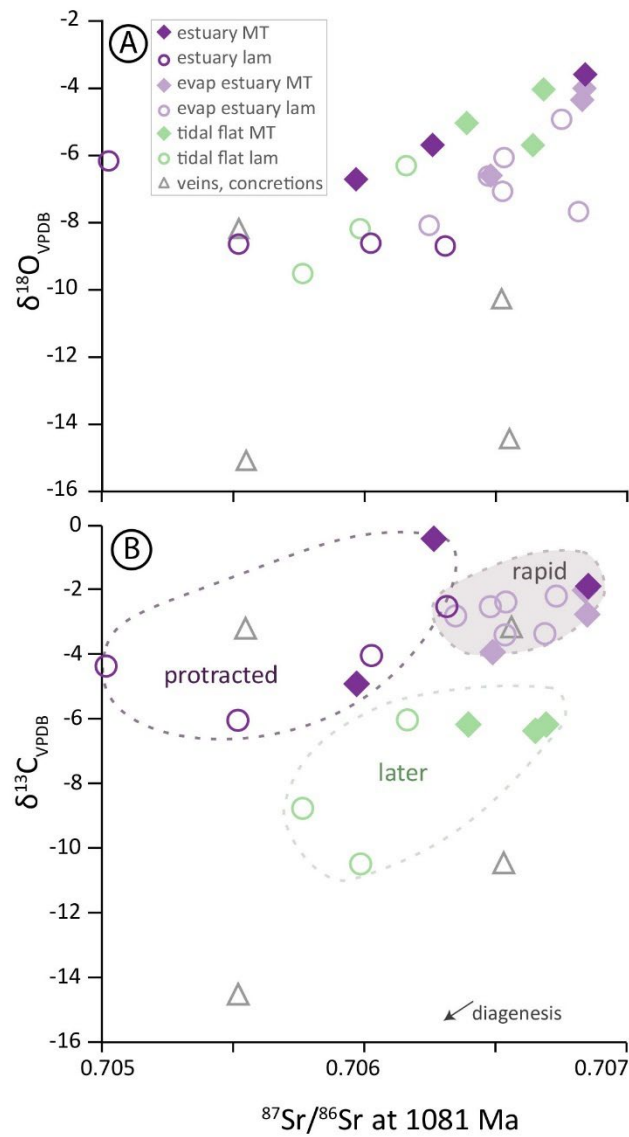
$\delta^{18}\text{O}$ versus $\delta^{13}\text{C}$ of Nonesuch carbonates. Estuary, evaporitic (evap) estuary, and tidal flat indicate depositional facies from which Nonesuch carbonate was sampled. Excluding the Junior member samples from the Big Iron River location noted with gray box. Least and most altered samples (excluding Big Iron River) noted with dashed circles. Molar tooth- MT, lam- laminae.

Figure 5. Rb-Sr isotopes

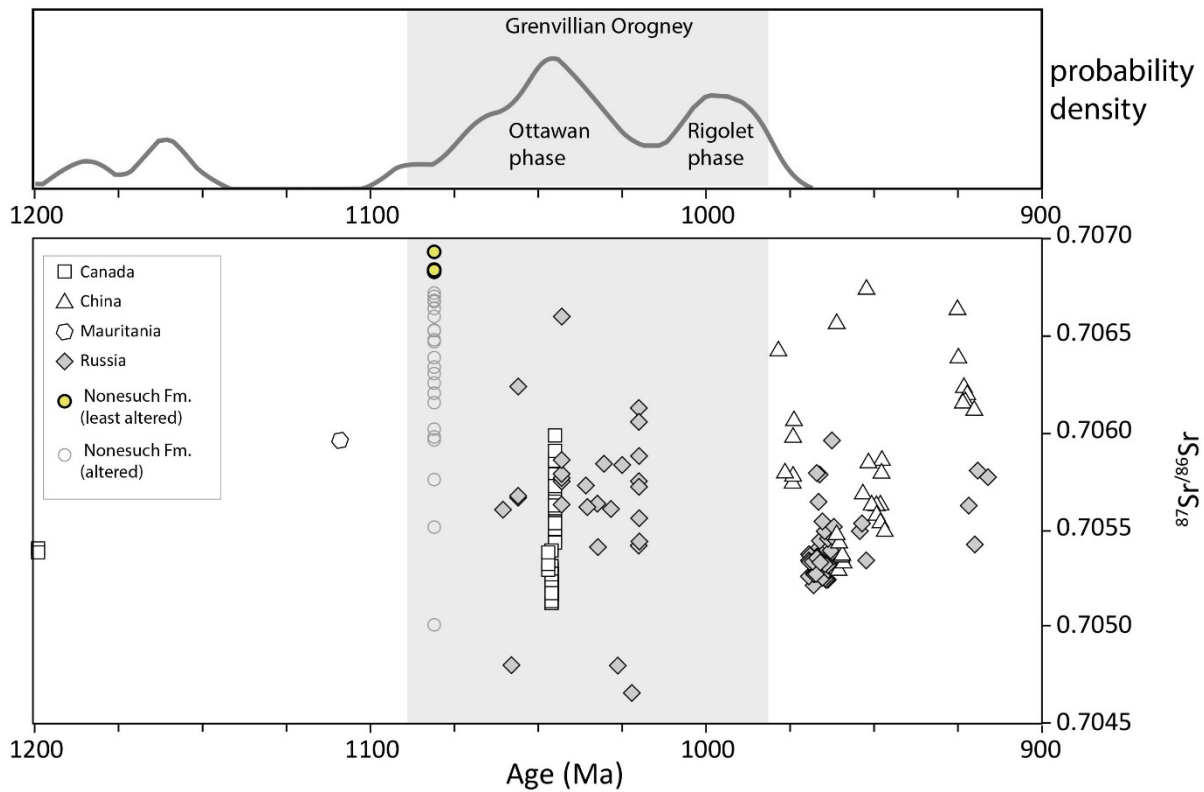


Initial $^{87}\text{Sr}/^{86}\text{Sr}$ at 1081 Ma versus $^{87}\text{Rb}/^{86}\text{Sr}$ of Nonesuch Formation carbonates and the underlying basalt. (A) full distribution of basalt values, with zoom in (B) to carbonates. (B) The gray rectangle indicates the range of global marine $^{87}\text{Sr}/^{86}\text{Sr}$ composition at 1043-1109 Ma (compiled in Chen et al., 2022). The offset between average initial $^{87}\text{Sr}/^{86}\text{Sr}$ of basalt and estimated initial $^{87}\text{Sr}/^{86}\text{Sr}$ of Nonesuch Formation detrital sediments (dashed lines) represents radiogenic ingrowth of ^{87}Sr in clays derived from weathering of the basalt. Early diagenetic alteration modified Nonesuch carbonates to less radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ buffered by high Rb/Sr clays. Gray bar shows global marine $^{87}\text{Sr}/^{86}\text{Sr}$. Estuary, evaporitic estuary, and tidal flat indicate depositional facies. Basalt values from the Portage Lake Volcanic Group (Paces and Bell 1989; Nicholson and Shirey, 1990). Molar tooth- MT, lam- laminae, NF- Nonesuch Formation.

Figure 6. tests for diagenetic alteration



$^{87}\text{Sr}/^{86}\text{Sr}$ versus (A) $\delta^{18}\text{O}$ and (B) $\delta^{13}\text{C}$. Arrow indicates direction of diagenetic alteration. Rapid, protracted, and later indicate timing of carbonate cementation. Concretion WC9-1407 is not shown.

Figure 7. Late Mesoproterozoic marine $^{87}\text{Sr}/^{86}\text{Sr}$ compilation

Timing of Grenville Province metamorphism (top panel) indicated by continuous probability density curve of compiled metamorphic zircon and monazite U-Pb dates (from Swanson-Hysell et al., 2023). $^{87}\text{Sr}/^{86}\text{Sr}$ of late Mesoproterozoic marine carbonate (bottom panel) showing Nonesuch Formation initial $^{87}\text{Sr}/^{86}\text{Sr}$ at 1081 Ma (yellow filled circles) and measured $^{87}\text{Sr}/^{86}\text{Sr}$ values compiled by Chen et al., 2022. Data from Gorokhov et al., 1995; Knoll et al. 1995; Kuznetsov et al., 1997, 2003, 2006, 2017, 2019; Bartley et al., 2001; Semikhatov et al., 2002; Shields et al., 2002; Cox et al., 2016; Gibson et al., 2019; and Zhou et al., 2020. Gray bar shows Grenvillian Orogeny duration.

Table 1. ICPMS element analysis

sample name	Mg/Ca	Mn/Ca	Fe/Ca	Na/Ca	K/Ca	Sr/Ca	Mn/Sr	Fe/Sr	texture	facies
PI2-675	0.00503	0.0713	0.0197	0.00091	0.00091	0.000291	245	68	concretion	estuary
DO14-3068LAM	0.00649	0.00684	0.00570	0.00160	0.000285	0.000697	9.81	8.2	laminae	evaporitic estuary
WPB-21647MT	0.001258	0.010	0.00192	0.00091	0.000199	0.000272	38.43	7.1	MT	estuary
WPB2-1650	0.001832	0.0326	0.0069	0.00114	0.000478	0.000314	104	22.1	laminae	estuary
DO10-374MT	0.001037	0.00560	0.000346	0.00137	0.000138	0.000504	11.1	0.69	MT	tidal flat
DO14-3071MT	0.00466	0.0121	0.00366	0.00114	0.000236	0.000615	19.7	5.95	MT	evaporitic estuary
DO14-3071LAM	0.01727	0.0291	0.0171	0.0057	0.00079	0.000822	35.5	20.8	laminae	evaporitic estuary
DO10-312	0.00646	0.0225	0.0117	0.00137	0.00075	0.000423	53.1	27.5	laminae	tidal flat
PI2-660 MT	0.00200	0.00476	0.00376	0.000457	0.000230	0.000254	18.8	14.8	MT	estuary
DO61369MT	0.00441	0.00239	0.00209	0.000457	0.000149	0.00134	1.78	1.56	MT	evaporitic estuary
DO6-1365MT	0.00393	0.00280	0.00189	0.00069	0.000070	0.00119	2.35	1.59	MT	evaporitic estuary
DO6-1365LAM	0.00570	0.00249	0.00336	0.00069	0.000219	0.000740	3.36	4.54	laminae	evaporitic estuary
WC18-1836MT	0.00312	0.0232	0.00208	0.00069	0.000245	0.000798	29.1	2.60	MT	tidal flat
WC18-1835MT	0.00438	0.0170	0.0068	0.000457	0.000175	0.00109	15.6	6.29	MT	tidal flat
uncertainty	5%	10%	15%	20%	15%	10%	14%	18%		

Table 2. Rb-Sr isotope composition

Sample name	texture	facies	$^{87}\text{Sr}/^{86}\text{Sr}^*$	Rb (ppm)	Sr (ppm)	$^{87}\text{Rb}/^{86}\text{Sr}^{**}$	$^{87}\text{Sr}/^{86}\text{Sr}$
			measured				initial at T 1081 Ma
WC14-1623 MT	MT	estuary	0.706945	0.1202	545	0.0009022	0.70693
DO8-1264 MT	MT	estuary	0.706554	0.912	166.0	0.02248	0.70621
DO8-1264 lam	laminae	estuary	0.706694	5.35	505	0.04341	0.70602
DO5-874	MT	estuary	0.706865	0.2124	552	0.0015747	0.70684
WC9-1570	laminae	estuary	0.706457	0.618	260.5	0.009715	0.70631
WPB-2-1647 MT	MT	estuary	0.706169	0.3354	105.5	0.013023	0.70597
WPB2-1650	laminae	estuary	0.705924	0.702	110.0	0.02616	0.70552
WPB7-1250	laminae	estuary	0.710013	4.149	52.4	0.3229	0.70502
WC2 781	vein	estuary	0.706574	0.0604	171.7	0.0014414	0.70655
WC2 781_r1	vein	estuary	0.706519	0.1381	169.2	0.06272	0.70555
PI2-660 MT	MT	estuary	0.706402	0.2085	92.4	0.009240	0.70626
PI2-675	concretion	estuary	0.706146	1.090	110.5	0.04044	0.70552
WC14-1529	laminae	tidal flat	0.706742	1.674	139.5	0.04913	0.70598
WC-18-1836 MT	MT	tidal flat	0.706899	2.885	357.8	0.03300	0.70639
DO-10-374 MT	MT	tidal flat	0.706723	0.1239	191.1	0.002654	0.70668
DO10-312	laminae	tidal flat	0.706350	0.4626	152.8	0.012394	0.70616
WC18-1836 MT	MT	tidal flat	0.706712	0.4029	361.1	0.004567	0.70664
WC18-1835 MT	MT	tidal flat	0.706635	0.0946	176.1	0.002200	0.70660
WC9-1651B	laminae	tidal flat	0.706656	2.063	146.4	0.05770	0.70576
WC9-1669	concretion	tidal flat	0.707257	1.915	164.9	0.04750	0.70652
WC9-1407	concretion	tidal flat	0.744814	12.55	17.97	2.724	0.70267
WC13-3125	laminae	evaporitic estuary	0.706923	0.740	212.8	0.014232	0.70670
DO13-820	laminae	evaporitic estuary	0.707261	1.107	119.8	0.03781	0.70668
DO13-756	laminae	evaporitic estuary	0.706914	0.982	320.1	0.012551	0.70672
DO-14-3068 lam	laminae	evaporitic estuary	0.706450	0.487	282.1	0.007073	0.70634
DO-14-3071 MT	MT	evaporitic estuary	0.706560	0.3418	272.2	0.005140	0.70648
DO-14-3071 lam	laminae	evaporitic estuary	0.706734	1.115	340.1	0.013418	0.70653
DO6-1369 MT	MT	evaporitic estuary	0.706848	0.1493	486.8	0.0012553	0.70683
DO6-1365 MT	MT	evaporitic estuary	0.706855	0.1278	460.7	0.0011349	0.70684

DO6-1365 lam	laminae	evaporitic estuary	0.706592	0.2755	279.9	0.0040305	0.70653
DO6-1364	laminae	evaporitic estuary	0.706580	0.4485	260.9	0.0070388	0.70647

*Uncertainty estimated as 0.00002 (2SD) based on reproducibility of SRM987 standard

**Uncertainty estimated as 0.6% (2SD)

Initial $^{87}\text{Sr}/^{86}\text{Sr}$ is calculated using a decay constant of 1.42×10^{-11} (Steiger and Jäger, 1977)

Table 3. Carbon and oxygen isotope compositions

sample name	texture	$\delta^{13}\text{C}/^{12}\text{C}$ VPDB	$\delta^{18}\text{O}/^{16}\text{O}$ VPDB	facies
DO8-1264 lam	laminae	-4.0	-8.5	estuary
DO8-1264 lam	laminae	-4.1	-8.7	estuary
DO5-874	MT	-1.9	-3.6	estuary
WPB-2-1647 MT	MT	-4.9	-6.7	estuary
WPB2-1650	laminae	-6.1	-8.6	estuary
WPB7-1250	laminae	-4.4	-6.2	estuary
WPB7-1251	laminae	-4.4	-6.1	estuary
BI-676	laminae	-2.4	-10.6	estuary
BI-676	laminae	-2.3	-9.7	estuary
BI-676	laminae	-2.3	-10.4	estuary
BI-680	laminae	-4.2	-12.1	estuary
BI-685	laminae	-4.2	-13.9	estuary
WC9-1570	laminae	-2.5	-8.7	estuary
WC2_781_r1	vein	-3.2	-15.0	estuary
WC-2 781	vein	-3.2	-14.4	estuary
PI2-660 MT	MT	-0.4	-5.7	estuary
BI-673	laminae	-6.9	-10.8	estuary
BI-673	laminae	-4.3	-10.1	estuary
BI-673	laminae	-3.3	-11.0	estuary
BI-673	laminae	-4.5	-12.9	estuary
BI- 21.42	laminae	-4.4	-12.0	estuary
WC-14 1679	laminae	-3.6	-6.9	estuary
BI-673	vein	-8.4	-11.0	estuary
BI-673	vein	-7.2	-10.3	estuary
PI2-675	concretion	-14.6	-8.3	estuary
PI2-675	concretion	-14.4	-8.1	estuary
BI- 19.43	concretion	-7.2	-9.2	estuary
BI- 23.13	concretion	-10.3	-10.0	estuary
WC14-1529	laminae	-10.5	-8.2	tidal flat
WC14-1529	laminae	-10.5	-8.2	tidal flat
WC-18-1836 MT	MT	-6.2	-5.1	tidal flat
DO-10-374 MT	MT	-6.2	-4.1	tidal flat
DO10-312	laminae	-6.0	-6.3	tidal flat
WC18-1836 MT	MT	-6.4	-5.7	tidal flat
WC9-1651B	laminae	-8.8	-9.4	tidal flat
WC9-1651B	laminae	-8.8	-9.6	tidal flat
WC9-1669	concretion	-10.5	-10.3	tidal flat
WC9-1669	concretion	-10.4	-10.2	tidal flat
BI- 4.01	concretion	-7.2	-8.6	tidal flat
WC9-1407	concretion	-23.9	-10.1	tidal flat
WC9-1407	concretion	-23.9	-10.1	tidal flat

BI- 9.6	laminae	-3.6	-9.5	tidal flat (Jr limestone)
BI- 9.25	laminae	-3.3	-8.6	tidal flat (Jr limestone)
BI- 10.55	laminae	-2.2	-7.7	tidal flat (Jr limestone)
BI- 11.62	laminae	-3.2	-8.3	tidal flat (Jr limestone)
DO13-820	laminae	-3.4	-5.5	evaporitic estuary
DO13-756	laminae	-2.2	-7.3	evaporitic estuary
DO-14-3068 lam	laminae	-2.8	-7.6	evaporitic estuary
DO-14-3071 MT	MT	-3.9	-6.6	evaporitic estuary
DO-14-3071 lam	laminae	-3.4	-6.9	evaporitic estuary
DO6-1369 MT	MT	-2.0	-4.4	evaporitic estuary
DO6-1365 MT	MT	-2.8	-4.1	evaporitic estuary
DO6-1364	laminae	-2.5	-6.6	evaporitic estuary
DO6-1365 lam	laminae	-2.4	-6.2	evaporitic estuary
WC14_1636_r1	laminae	-2.2	-6.8	evaporitic estuary
WC-14 1636	laminae	-2.2	-6.9	evaporitic estuary
BI- 19.66	laminae	-2.2	-10.9	evaporitic estuary
BI- 20.8	laminae	-3.4	-9.1	evaporitic estuary
BI- 20.8	laminae	-2.2	-9.8	evaporitic estuary
BI-692	laminae	-2.9	-11.7	evaporitic estuary
WC13-3125	laminae	-3.4	-7.6	evaporitic estuary

Chapter 3: Shale and carbonate geochemistry track redox cycling, productivity, and salinity in the late Mesoproterozoic Laurentian inland sea of the Nonesuch Formation, Wisconsin and Michigan, USA

Shale and carbonate geochemistry track redox cycling, productivity, and salinity in the late Mesoproterozoic Laurentian inland sea of the Nonesuch Formation, Wisconsin and Michigan, USA

ABSTRACT

The Oronto Group (Copper Harbor Conglomerate, Nonesuch Formation, Freda Formation) was deposited in an interior sea well within the Laurentian continent at the end Mesoproterozoic (ca. 1081 – 1052 Ma) during a time of global sea level high stand. Marginal marine settings are increasingly recognized as important early eukaryote habitat, and expansion of interior seas like the Oronto Group basin may have shaped eukaryote evolution by increasing habitat and enhancing selective evolutionary pressures. In this chapter I characterize conditions of salinity, redox, and productivity in the Oronto Group basin to constrain environmental conditions that supported cyanobacteria and early eukaryotes.

Shale geochemistry including enrichment in S, TOC, Mo, and U and local depletion in Ba and P demonstrate deposition of the Nonesuch Formation in an oxidized basin with a deep, fluctuating chemocline. Anoxic and euxinic conditions developed in shallow pore water and locally extended to the bottom water column in distal parts of the basin especially during times of maximum flooding or base level lowstand. Rare earth element + yttrium (REY) distributions of calcite microspar from molar tooth (MT) structures and carbonate laminae preserve an early diagenetic estuarine signal. Weakly developed characteristic marine REY distributions, including positive La anomaly, Y/Ho, and heavy rare earth element enrichment demonstrate deposition of the Nonesuch Formation under brackish conditions while positive Ce anomalies indicate redox cycling between an oxic water column and reduced pore water. Sediments were predominantly sourced from Midcontinent Rift basalts and intermediate volcanic rocks, which provided

enhanced nutrient delivery to the Oronto Group basin, likely promoting microbial blooms that influenced basin redox structure. These microbial communities, including early eukaryotes, thus inhabited an estuarine setting where significant freshwater inputs from rivers and runoff (regional signals) mixed with seawater (a global signal).

INTRODUCTION

At the end Mesoproterozoic (ca. 1.1 – 1.0 Ga), cratonic basins with intermittent marine connection were widespread across the supercontinent Rodinia (Li et al., 2008; Kah et al., 2012; Gilleaudeau and Kah 2013a, b; Rainbird et al., 2017; 2020; Gibson et al., 2018; 2019; Loron et al., 2019a, b; Greenman et al., 2021; Jones et al., 2020; Stüeken et al., 2020). The fossil record suggests marginal marine environments had particular importance as early eukaryote ecosystems (Riedman et al., 2023), although the role of fluctuating freshwater and nutrient input, redox structure, and desiccation -- all characteristic of these dynamic settings -- remains unclear (Gibson et al., 2019; Lyons et al., 2021; Brocks et al., 2023; Nielson et al., 2024; Tang et al., 2025).

The Oronto Group, Wisconsin and Michigan, USA (Figure 1) is a latest Mesoproterozoic siliciclastic succession that is commonly held to record several kilometers of fluvial, alluvial, and lacustrine deposition (Daniels et al., 1982; Elmore, 1983, 1984; Elmore et al., 1989; Suszek, 1997; Slotznick et al., 2024). These rocks also preserve some of the oldest well-preserved assemblages of cyanobacteria and eukaryotes, motivating hypotheses that early eukaryotes evolved in freshwater, continental settings (Strother and Wellman, 2021). However, growing sedimentologic and geochemical evidence indicate a marine influence on deposition of parts of the Oronto Group (Hieshima and Pratt, 1991; Jones et al., 2020; Stüeken et al., 2020; Stewart et al., 2024).

Here, I evaluate conditions of salinity and redox structure of the ancient Oronto Group basin using shale trace element chemistry and rare earth element + yttrium (REY) distributions of MT calcite microspar. Chemostratigraphic trends from one core (WC-14) provide insight to evolution of redox conditions during transgression-regression. The emerging picture of a brackish, oxic water column and fluctuating, deep chemocline captures environmental conditions of early eukaryote habitat.

BACKGROUND

Proxies for redox and productivity from whole rock geochemistry of fine-grained rocks

Redox-sensitive trace element enrichment develops in shales through particle cycling across redox boundaries, diffusion across the sediment-water interface, or repartitioning across redox gradients in shallow sediments (Tribovillard et al., 2006; Algeo and Maynard, 2008). Processes that control sediment trace element enrichment include precipitation of sulfides or oxyhydroxide particles, particle adsorption, and complexation of trace metals and organic molecules. These processes link to redox conditions that develop in the water column and shallow sediments during deposition and early diagenesis. In addition to these abiotic processes, nutrient trace elements are incorporated into organic matter through biotic processes. Thus, sediment trace element enrichment patterns allow reconstruction of redox and productivity in ancient basins (e.g., Algeo and Maynard, 2004; Turner et al., 2016; Gilleaudeau et al., 2023).

Because many trace elements adsorb to iron (Fe)- and manganese (Mn)-oxyhydroxides, particle transport of Fe- and Mn-oxyhydroxides to the shallow sediments is an important pathway for trace element enrichment. Sediment trace element enrichment develops through recycling of insoluble Fe/Mn-oxyhydroxides and soluble, reduced Fe^{2+} / Mn^{2+} across redox fronts (Calvert and Pederson, 1996; Algeo and Tribvillard, 2009).

Ratios of molybdenum (Mo) and uranium (U) enrichment leverage the different behavior of Mo and U under oxic, anoxic, and euxinic (anoxic + sulfidic) conditions (Algeo and Tribovillard, 2009). Authigenic molybdenum (Mo) enrichment follows different pathways depending on basin redox structure. In basins with fluctuating suboxic to weakly sulfidic bottom water, authigenic Mo enrichment follows a particle shuttle pathway (Algeo and Tribovillard et al., 2009). Dissolved Mo in the oxic water column adsorbs to Mn/Fe-oxyhydroxides, which accumulate at the sediment-water interface. If the redox boundary rises into the lower water column, Mn/Fe-oxyhydroxides at the sediment water interface dissolve and release aqueous Mo. Under euxinic conditions, Mo reacts with HS^- to form particle reactive compounds (thiomolybdates) that are scavenged by sulfur-rich organic matter and Fe-rich particles, resulting in sediment authigenic Mo enrichment (Algeo and Lyons, 2006; Algeo and Tribovillard, 2009). In restricted, silled basins, Mo content can become depleted as Mo trapped in sediments is not replenished by marine incursion. In contrast, authigenic uranium (U) enrichment develops under suboxic to anoxic conditions within shallow sediments and is not controlled by euxinia or scavenging by Fe- or Mn-oxyhydroxides. Thus, authigenic sediment U enrichment exceeds Mo enrichment under suboxic conditions (Tribovillard et al., 2006).

Phosphorus (P) and barium (Ba) are common productivity proxies, though their accumulation in sediments is modulated by redox conditions. Barium is mainly delivered to modern oceans by rivers, where it reacts with sulfate to form barite (BaSO_4) in association with particulate organic matter, which is buried in marine sediments (Tribovillard et al 2006; Schoepfer et al., 2015; Wei and Algeo, 2020; Wei et al, 2021). Barite is relatively unreactive in sediments except under euxinic conditions, which dissolve barite and release Ba to pore water. Under oxic conditions, P is also sourced to the ocean from weathering, where it is taken up into

organic matter or removed by particle transport, especially by Fe- and Mn-oxyhydroxides (Tribovillard et al., 2006; Schoepfer et al., 2015; Guilbaud, 2024). Authigenic apatite ($\text{Ca}_5(\text{PO}_4)_3$) formed in the water column or pore fluids is an additional pathway for sediment trapping of P. Organic matter remineralization releases P to the water column, as does dissolution of Fe-oxyhydroxides under anoxic conditions. Authigenic Fe-oxyhydroxides may reprecipitate along redox boundaries, trapping P in shallow sediments before it is released to the water column. Under euxinic conditions, dissolution of Fe-oxyhydroxides and organic matter releases P to pore water and the overlying water column.

Carbonate REY distribution as a salinity proxy

Carbonates record the rare earth element and yttrium (REY) composition of the fluids from which they precipitate, and these REY compositions are resistant to subsequent alteration including dolomitization (Zhao et al., 2022; 2021; Banner et al., 1990). Carbonate in the Nonesuch Formation is present as calcite infilling MT structures and associated mm- to cm-thick laminae. Molar tooth structures are carbonate microspar-filled voids that formed in unlithified sediments with occurrences peaking in the late Mesoproterozoic to early Neoproterozoic and are considered archives of basin or earliest diagenetic pore water compositions (Kuang, 2014; Zhou et al., 2021; Kriscautzky et al., 2022). REY contents of MT structures and associated carbonate-rich layers potentially record evolution of shallow pore fluids from the overlying water and may preserve paleoredox conditions, hydrothermal input, salinity, and nutrient cycling.

Shale-normalized REY patterns observed in modern rivers and lakes are variable, controlled by preferential scavenging of LREE and MREE by particle adsorption and complexation of HREE with carbonate ions (Junqueira et al., 2024; Jiang et al., 2022; Lawrence and Kamber, 2006; Elderfield et al., 1990). In contrast, seawater has a typical REY profile

characterized by smooth, progressive enrichment in HREE that results from preferential complexation of HREE with carbonate ions and particle adsorption of LREE (Lawrence and Kamber, 2006; Sholkovitz et al., 1994; Stanley and Bryne, 1990). Anomalies along this trend are caused by the unique chemical properties that control solubility and scavenging by particle adsorption of La, Ce, Eu, and Y. Elevated Y/Ho ratios are caused by preferential scavenging of Ho over Y onto particles (Nozaki et al., 1997), while La is unusually stable in seawater and estuaries compared to the other LREE (Albio and Nozaki 1998; Lawrence and Kamber, 2006). Negative Ce anomalies develop through precipitation of oxidized Ce^{+4} (Ohta and Kawabe 2001) while positive Eu anomalies are likely derived from hydrothermal input of reduced Eu^{2+} (Kamber and Webb, 2001; Danielson et al., 1992) or from groundwater in basalt source terranes (Nelson et al., 2004). The characteristic marine REY pattern develops during estuarine mixing through the combined effect of salt-induced coagulation and flocculation of Fe- and organic particles that preferentially scavenge LREE and MREE, and complexation of HREE with carbonate ions (Elderfield et al., 1990; Sholkovitz, 1992; Sholkovitz and Szymzak, 2000; Lawrence and Kamber, 2006). Modern marine REY profiles have a negative Ce anomaly that developed through removal of particulate Ce-oxides in the water column.

REY are released to pore waters during diagenesis resulting in fractionation and a high concentration gradient between pore water and the overlying waterbody (Sholkovitz et al., 1989; Haley et al., 2004; Soyol-Erdene and Huh, 2015; Johannesson et al., 2017). REY cycling in pore water is mostly controlled by (1) scavenging and transport of particulate organic carbon (POC) and Fe/ Mn- and Ce-oxides in the water column and (2) particulate oxide reduction and disintegration of POC in pore fluids (Haley et al., 2004; Chen et al., 2015; Skinner et al., 2019). These processes result in three different characteristic pore water REY distributions: flat, MREE-

enriched, and HREE-enriched. Flat pore water REY distributions are attributed to preferential release of LREE through POC remineralization in shallow oxic to suboxic sediments (Haley et al., 2004). MREE-enriched distributions are a common pore water feature with several possible mechanisms involving adsorption and desorption of primarily LREE and MREE with Fe/Mn oxyhydroxides (Haley et al., 2004; Soyol-Erdene and Huh, 2013) and dissolution of phosphate minerals (Hannigan and Sholkovitz, 2001). HREE-enriched distributions are linked to preferential complexation of HREE with dissolved carbonate ions derived from remineralized organic carbon (Haley et al., 2004) or the combined effect of low concentration DOC and Fe inhibiting REY particle adsorption and solution complexation of REY with carbonate ions weathered from basalt (Neslon et al., 2004; Johannesson et al., 2017). Negative Ce anomalies are less pronounced, absent, or positive due to dissolution of Ce oxides in anoxic pore waters.

GEOLOGIC SETTING

The Oronto Group is part of the North American Midcontinent Rift system (MRCS), a continental-scale feature that extends 2,200 km from Kansas north to Lake Superior and southeast into southern Michigan (Figure 1, Van Schmus and Hinze, 1985; Hinze and Chandler, 2020). The Midcontinent Rift is buried beneath younger rocks and sediments for most of its extent and is exposed in the Lake Superior Region of northern Minnesota, Wisconsin, and Michigan, USA, and southern Ontario, Canada (Woodruff et al., 2020). Although it is mostly overlain by younger sedimentary cover, the rift's geophysical signature crosscutting Laurentia is striking in aeromagnetic and gravity anomaly maps due to its spatial extent and the enormous volume of igneous and sedimentary rocks.

Midcontinent Rift development is broadly subdivided into an early Plateau stage of volcanism, a main Rift stage of volcanism, a transitional stage between volcanism and

sedimentation, and a later stage of sedimentation and compression related to Grenvillian orogenesis (Woodruff et al., 2020). The sedimentary rocks are divided into the Oronto Group, the focus of this paper, and overlying Bayfield Group and Jacobsville Formation. The Oronto Group includes the Copper Harbor Conglomerate, Nonesuch and Freda Formations, each described below. Within $\lesssim 40$ Myr of deposition, during early diagenetic compaction and coeval to younger Grenvillian deformation, migration of mineralizing brines caused copper and lesser silver deposits to form within the uppermost Copper Harbor Conglomerate and lower Nonesuch Formation and within basalt flow-top vesicles and permeable zones in the Copper Harbor Conglomerate (Butler and Burbank, 1929; White and Wright, 1954; 1966; Bornhorst et al., 1988; Mauk and Hieshima, 1992; Swenson et al., 2004; Bornhorst and Williams, 2013; Symons and Kawasaki, 2019; Bodden et al., 2022; Jones et al., 2023).

Plateau and Rift-stage volcanism

Between ca. 1112 – 1105 Ma, subaerial basalt flowed from fissures and shield volcanoes to form a broad volcanic plateau up to 10 km thick that likely extended well beyond the present-day erosional remnants of the MRCS (Green, 1983; 1989; Woodruff et al., 2020). Associated intrusive sills and plutons are today exposed along the northern Lake Superior shoreline and include the Coldwell complex, early intrusions of the Duluth complex, and Logan and Nipigon sills while geophysical and geochronological constraints indicate emplacement of Midcontinent Rift intrusions in southern Minnesota, northern Iowa, and southern Wisconsin (Miller and Ripley, 1996; Heaman et al., 2007; Drenth et al., 2020; Holm et al., 2020; Good et al., 2021). Seismic and outcrop relationships around Lake Superior suggest extension was accommodated through development of sag basins rather than grabens bounded by normal faults that penetrate and offset the lower crust (Green, 1983, 1989; Allen, 1994; Allen et al., 2006). Based on

observation of two seismic reflection lines, Cannon et al. (1989) argue that crustal downwarping was augmented by normal faulting. Most subsequent interpretations of Midcontinent Rift system evolution build from this model, emphasizing the development of normal-fault-bounded half grabens that were reactivated as reverse faults during Grenvillian orogenesis (e.g. Cannon, 1992; Thomas and Teskey, 1994; Dickas and Mudrey, 1997; Stein et al., 2015, 2018; Hodgins et al., 2024)

Following a several-million-year pause in volcanism in western Lake Superior (Swanson-Hysell et al., 2014), extensive subaerial flood basalts infilled subsiding volcanic basins beneath what is now Lake Superior and the Ashland Syncline of northern Wisconsin. Enormous volumes of basalt erupted during this rift-stage of magmatism between ca. 1102 – 1090 Ma (Woodruff et al., 2020). Volcanism kept pace with subsidence, resulting in stacked, flat subaerial flows with remarkable lateral extent and volume (White, 1960; Green, 1983). As rift-stage volcanism progressed, erupted flows gradually flexed into subsiding volcanic basins that developed around older basement-cored ridges, accumulating to thicknesses of 14 km or greater beneath Lake Superior (Allen, 1994; Allen et al., 1997). Large mafic intrusions are associated with rift-stage magmatism, including the Duluth Complex and Beaver Bay Complex in Minnesota and Mellon Complex in Wisconsin (Miller and Chandler, 1999; Miller et al., 2002; Zhang et al., 2021). At the end of the rift-stage, spatially limited central volcanoes developed that tapped upper crustal magma chambers and produced intermediate and rhyolitic rocks (Nicholson et al., 1997). The most significant of these are preserved on Michipicoten Island and in the Porcupine Mountains of Michigan (Green, 1983).

Transition from magmatism to sedimentation

Between ca. 1090 – 1083 Ma, volcanism waned, and long-lasting siliciclastic deposition became established (Woodruff et al., 2020). Along the southern Lake Superior shoreline and on Isle Royale, the lower part of the Copper Harbor Conglomerate overlies and locally interfingers with basalt and andesite flows dated at 1085.57 ± 0.25 Ma (Fairchild et al., 2017). In some locations, the Copper Harbor Conglomerate broadly fines upward from interbedded arkosic sandstone and conglomerate with abundant rhyolite clasts to cross-bedded and ripple-laminated sandstone (White and Wright, 1960, Elmore, 1984). The cross-bedded and rippled sandstone facies gradually fines and shoals upward, with interference ripples and desiccation cracks developed in the uppermost 20 meters of this facies where it is exposed along the Presque Isle River (Stewart et al., 2024). The upward fining and shoaling low-angle cross-bedded sandstone succession is best developed between Black River Harbor and the Presque Isle River on the Keweenaw Peninsula. Elsewhere, cobble conglomerate and interbedded cross-bedded and heterolithic sandstone-siltstone-shale compose the upper Copper Harbor Conglomerate. Near the eastern tip of the Keweenaw Peninsula, this facies includes well-developed domal stromatolites and microbial structures (Elmore, 1983; Wilmeth et al., 2014; Fedorchuk et al., 2016). The lower conglomerate and conglomerate-sandstone facies represent braided stream deposits above coalesced alluvial fans (Elmore, 1984). The upper conglomerate and associated cross-bedded sandstone and heterolithic sandstone-siltstone-shale have also been interpreted as alluvial and fluvial deposits on a lacustrine shoreline (Elmore, 1984). Jones et al. (2020) note sedimentary structures indicative of tidal modification associated with stromatolites in these facies and instead propose a shallow marine setting. The upper cross-bedded and ripple-laminated sandstone facies has been interpreted as sheet flood deposits on the broad, sandy toes of alluvial fans (Elmore, 1984). Stewart et al. (2024) present an alternate interpretation of tidally influenced,

shallow-marine dunes based on vertical continuity (at least 130 m), remarkable consistency in grain size and dune morphology, and an absence of conglomerate interbeds, channel forms, or significant scouring on basal bedding surfaces.

Deposition within subsiding sub-basins

The Copper Harbor Conglomerate and overlying Nonesuch Formation were deposited within subsiding basins that formed above older rift-stage volcanic basins (Allen et al., 1997). Seismic, gravity, and aeromagnetic data indicate that beneath Lake Superior these basins are separated by older, likely Archean-cored basement ridges. Rift-stage volcanic rocks and overlying strata of the Copper Harbor Conglomerate and Nonesuch Formation infill the basins, onlapping onto the ridges with little evidence for substantial faulting. Synsedimentary normal faults with several meters to < 50 m displacement are documented in the Copper Harbor and Nonesuch Formation near White Pine (Mauk and Hieshima, 1992; Mauk et al., 1992; Jones et al., 2023). Onshore, stratigraphic thinning and facies changes demonstrate similar infill of sedimentary basins that subsided largely after deposition of the lower Copper Harbor Conglomerate. Along the Keweenaw Peninsula, White and Wright (1960) note that tilting of the lower Copper Harbor Conglomerate and underlying volcanic flows formed topographic ridges that were onlapped by upper Copper Harbor Conglomerate strata. Similar stratigraphic thinning and facies changes onto an older bedrock ridge is observed near Copper Falls State Park in northeast Wisconsin (Suszek, 1997; Swanson-Hysell et al., 2019; Slotznick et al., 2024; Stewart et al., 2024). Further west within the Ashland Syncline, bedding orientations of volcanic flows and overlying sedimentary strata suggest a similar subsidence history, locally modified by later movement along the Douglas and Lake Owen Faults: The rift-stage Chengwatana volcanics and overlying strata of the lower Copper Harbor Conglomerate dip 10 to 30° towards the syncline

axis (Figure 1; Nicholson et al., 2006), yet strata of the upper Copper Harbor Conglomerate and younger Nonesuch and Freda Formations preserved in drill core is flat to dipping less than 5° (Stewart and Mauk, 2017). Stratal thinning and facies changes of the lower Oronto Group along the northwest limb of the Ashland Syncline is accompanied by a shift in composition of Nonesuch sediments from predominantly mafic and intermediate volcanic rock fragments to felsic volcanic fragments, further supporting onlap onto an older basement-cored ridge (Suszek, 1997).

Strata of the upper Copper Harbor Conglomerate, Nonesuch Formation, and lower Freda Formation (lower Oronto Group) compose three upward shoaling cycles (Stewart et al., 2024). The lowest cycle is present within the upper Copper Harbor Conglomerate while the middle and upper cycles are within the lower Nonesuch Formation and upper Nonesuch to lower Freda Formations, respectively. Cycles are best developed in areas that experienced greatest subsidence, especially near the Presque Isle River in Michigan (Suszek, 1997; Stewart and Mauk, 2017; Slotznick et al., 2024; Stewart et al., 2024). Away from this area, the lower cycle is poorly developed or absent, and the middle cycle directly overlies conglomerate facies of the Copper Harbor Conglomerate. The middle and upper cycles thin in the paleo-landward direction due to combined non-deposition and erosion. In most landward positions along the northwest limb of the Ashland Syncline, at Copper Falls State Park in northwest Wisconsin, and near the eastern tip of the Keweenaw Peninsula, only the middle cycle is present, and it is thinned or truncated beneath the overlying Freda Formation.

The lower Nonesuch Formation is composed of dark laminated shale, local interbeds of cross-bedded sandstone, and heterolithic sandstone-siltstone-shale with mud drapes, desiccation cracks, bimodal ripples, flaser, and wavy bedding (Figure 2). This assemblage fines upward into

dark laminated shale, siltstone, and carbonate laminite (Elmore et al., 1984; Suszek, 1997; Stewart and Mauk, 2017; Jones et al., 2020; Stewart et al., 2024). The age of the Nonesuch Formation is constrained by a Pb-Pb isochron age of 1081 ± 9 Ma from a carbonate bed in the basal Nonesuch Formation (Ohr, 1993) and a Re-Os isochron age of 1040 ± 78 Ma from dark shales in the lower Nonesuch Formation (Figure 1; Cumming et al., 2013). Heterolithic sandstone-shale is interpreted as mudflat and sheetflood deposits on a lacustrine shoreline (Elmore et al., 1984) or tidal flat deposits (Jones et al., 2020; Stewart et al., 2024). Dark laminated shale, siltstone, and carbonate laminite are interpreted as deepwater deposits of a stratified lake (Elmore et al., 1984) or estuary (Jones et al., 2020; Stewart et al., 2024). In more basinward settings, stacked, meter-scale upward fining sandstone-siltstone packages, interpreted as turbidite deposits, are associated with the dark laminated shale and siltstone (Elmore et al., 1984; Suszek, 1997; Stewart and Mauk, 2017; Stewart et al., 2024).

The upper Nonesuch Formation is composed of heterolithic sandstone-siltstone-shale, low-angle cross-bedded sandstone, and lesser dark laminated shale and siltstone. The upper Nonesuch Formation grades upward into reddish sandstone, siltstone, and shale of the Freda Formation. The heterolithic sandstone-siltstone-shale and low-angle cross-bedded sandstone facies are interpreted as sheetflood deposits on a distal alluvial apron along a lacustrine shoreline (Elmore et al., 1989) or tidal flat and tidally influenced shallow marine deposits (Jones et al., 2020; Stewart et al., 2024). The reddish sandstone, siltstone and shale of the lower Freda Formation are interpreted as fluvial floodplain and channel deposits (Elmore et al., 1989) with local tidal modification (Stewart et al., 2024).

The Freda Formation and a change from focused to broadly distributed subsidence

The Freda Formation is the uppermost Formation in the Oronto Group, reaching thicknesses of greater than 3,600 m (Daniels et al., 1982). A youngest detrital zircon U-Pb age constrains deposition of the upper Freda Formation to less than 1051.58 ± 1.11 Ma (Hodgin et al., 2024). Detailed study of the Freda Formation is limited, and the entire package is typically described as fluvial sandstone and finer-grained floodplain deposits (Hamblin, 1961a; Daniels et al., 1982; Ojakangas et al., 2001). Hite (1968) interpreted the Freda Formation to record a transition from fluvial to shoreline and tidal flat environments up stratigraphic section, and Hamblin (1961b) interpreted predominantly floodplain and lacustrine deposition. Stewart et al. (2024) note fluvial channel fill and overbank deposits as well as sedimentary structures indicative of tidal processes and probable soil horizons. The kilometers-thick Freda Formation clearly records evolving depositional conditions during an interval of the latest Mesoproterozoic that is notable for preserving the earliest known fossils of multicellular green and red algae in North China (Tang et al., 2020) and northeast Canada (Gibson et al., 2018), and detailed stratigraphic study of this unit is needed.

Unlike the focused subsidence over older volcanic sub-basins during Copper Harbor and Nonesuch time, subsidence to accommodate the Freda Formation was widespread. Based on correlation of seismic reflection data and onshore geology, Allen et al. (1997) documents Freda Formation directly overlying Archean-cored ridges that were onlapped by the older volcanic and sedimentary strata. A similar pattern is observed onshore: the Copper Harbor Conglomerate and Nonesuch Formation thin, and the base Freda drops down stratigraphic section, towards areas underlain by older basement ridges (see Fig. 4 in Stewart and Mauk, 2017; Fig. 2 in Slotznick et al., 2024). In many locations, the lower Freda Formation is conformable with the Nonesuch

Formation based on its gradational lower contact (Daniels et al., 1982; Elmore et al., 1989; Suszek et al., 1997; Stewart and Mauk, 2017; Slotznick et al., 2020, 2024). Stewart and Mauk (2017) suggest a sequence boundary is present within the lower Freda Formation. Stewart et al. (2024) place a sequence boundary at the base of the upper Nonesuch or base of the Freda Formation where that unit directly overlies lower Nonesuch Formation strata and interpret variable nondeposition and erosion of upper Nonesuch and likely lower Freda strata below this boundary. These relationships suggest a significant change in the extent and style of basin subsidence and sedimentation happened during lower Freda time.

Reverse faulting during Ottawan and Rigolet phases of the Grenvillian orogeny

The Oronto Group is overlain by the Bayfield Group and Jacobsville Formations, which were deposited after ca. 995 and 992 Ma, respectively (Hodgin et al., 2024; 2022) across a probable angular unconformity (Daniels et al., 1982; Adamson, 1997). These units are not discussed further here, except in the context of regional faulting.

Several reverse faults offset Midcontinent Rift volcanic and sedimentary rocks along the south shore of Lake Superior. The most prominent of these are the Douglas and Lake Owen Faults, which offset rocks deposited within the Ashland Syncline, Wisconsin; the Pelton Creek and Marenisco faults, which formed the Montreal River Monocline along the Wisconsin-Michigan border; and the Keweenaw Fault, Keweenaw Peninsula, Michigan (Cannon et al., 1993; Allen et al., 1996; DeGraff and Carter, 2022; Hodgin et al., 2022; 2024). Cannon et al. (1993) demonstrate exhumation of Archean basement and overlying Midcontinent Rift volcanic and Oronto Group strata along the Montreal River monocline at ca. 1060 ± 20 Ma based on biotite Rb-Sr ages. In the Ashland Syncline area of Wisconsin, U-Pb dates from vein calcite collected from the fault zone in the hanging wall of the Douglas Fault constrain movement to

1049 $\pm$ 13 Ma, during the Ottawa Phase of the Grenvillian Orogeny and within uncertainty of the maximum depositional age of the upper Freda Formation (Hodgin et al., 2024). Calcite veins from fault zones in the hanging wall of the Keweenaw fault yield similar U-Pb ages (1052 $\pm$ 36 Ma and 1048 $\pm$ 87 Ma; Hodgin et al., 2022; 2024). Ruiz et al. (1984) report a Rb-Sr age of 1047 $\pm$ 37 Ma for carbonate veins that crosscut the Nonesuch Formation in the White Pine mine. Strata of the Bayfield Group and Jacobsville Formation are deformed in the footwalls of the Douglas and Keweenaw Faults, respectively, constraining fault reactivation to after deposition at ca. 995 and 992 Ma (Hodgins et al., 2024). A calcite vein from the damage zone in the hanging wall of the Keweenaw Fault has a U-Pb age of 985.5 $\pm$ 35.8 Ma, indicating reactivation during the Rigolet phase of Grenvillian orogenesis (Hodgins et al., 2022).

MATERIALS AND METHODS

Samples for this study were collected from drill core from northern Wisconsin and the Keweenaw Peninsula of Michigan and the Big Iron River outcrop section (Supplemental tables S1, S2). Whole rock geochemical samples were analyzed by Australian Laboratory Services (ALS). Additional whole rock geochemistry was compiled from the USGS National Geochemical Database and published datasets (Nicholson and Shirey, 1990; Nicholson et al., 1997; Wirth et al., 1997; Stüeken et al. 2020; <https://www.usgs.gov/centers/gggsc/science/national-geochemical-database>; USGS unpublished data). For eight samples of the lower and upper Nonesuch and Freda Formations, new ^{147}Sm - ^{143}Nd isotope analyses were performed on splits of the same powders that were analyzed for whole rock geochemistry. Additionally, calcite from the Nonesuch Formation was targeted for analysis from carbonate-rich laminae and MT structures. Carbonate veins and concretions were also analyzed to evaluate potential post-depositional alteration. Carbonate phases, alteration, and

recrystallization were assessed by petrographic observation of thin sections and geochemical composition. New carbonate REY analyses were collected from the same powders that were analyzed for chemical and C, O, and Sr isotope compositions in chapter 2 of this dissertation. Carbonates were milled from thick sections, powdered, and split into two aliquots. One aliquot was reserved for carbon and oxygen isotope analysis at the University of Michigan Stable Isotope laboratory. The other aliquot was processed for Rb-Sr isotope and major and trace element analysis, including REY, at the University of Wisconsin ICP-TIMS laboratory. A selection of thin sections was characterized at the University of Wisconsin Electron Microbeam laboratory. Carbon and O isotope compositions are reported in delta per mil (‰) notation relative to VPDB (see supplements for detailed methods).

RESULTS

Geochemistry of siliciclastic strata

The following section describes whole rock geochemistry and Sm-Nd isotope composition of siliciclastic strata sampled from cores from the Ashland Syncline and Keweenaw Peninsula. The whole rock geochemistry represents a compilation of published and new data (Supplemental Table S3). Most lower Oronto Group sediments are classified as shales or wackes, with lesser Fe-sandstone, lithic arenite, and arkose following Herron (1988; see supplemental figure S1). The Freda Formation is a distinct population on variation diagrams of major oxide composition, with shales having on average greater weight percent SiO₂, Al₂O₃, Fe₂O₃, K₂O, and TiO₂ and lesser MgO, CaO, MnO, and P₂O₅ compared to shales of the Nonesuch Formation (supplementary Figure S2).

The upper continental crust (UCC, Rudnick and Gao, 2003)-normalized trace element distribution of sediments from the Copper Harbor Conglomerate, Nonesuch Formation, and

Freda Formation are similar (supplementary Figure S3). Large ion lithophile elements (LILE) Rb and Cs are spread around the average of UCC while Sr is depleted, and Ba is both depleted and enriched. High field strength elements (HFSE) Zr, Hf, Nb, Ta, and U are at or slightly above average UCC, with U having greater spread. Transition metals V, Cr, Co, Ni, Zn, and Ga are also at or slightly above average UCC. Mo, Cu, and Pb range between depleted and significantly (>10x) enriched levels, and S is significantly enriched relative to UCC.

Rare earth elements normalized to PAAS (Post-Archean Australian Shale, Taylor and McLennan, 1985) of lower Oronto Group shales and wackes also have similar distribution patterns (Figure 3). Light rare earth elements (LREE, La to Eu) have a positive slope with pronounced depletion of La and Ce, Pr and Nd varying about the mean of PAAS, and enrichment of Sm and Eu. Heavy rare earth elements (HREE, Gd to Lu) generally have a flat, enriched pattern.

$^{147}\text{Sm}/^{144}\text{Nd}$ of all the samples spans 0.1157 to 0.1354 ($n = 8$, Table 1, Figure 4). At 1081 Ma, ϵNd ranges between ~ -0.9 to -1.6 . Depleted mantle model ages (Bouvier et al., 2008) fall between ~ 2.0 and 1.6 Ga, though most ages ($n = 5$) are ~ 1.8 to 1.9 Ga.

Geochemical patterns tied to stratigraphy from core WC-14

Chemostratigraphic trends are shown in Figures 5 and 6 for core WC-14 from the Ashland Syncline sub-basin. Zirconium concentration gradually increases from $\sim 130 - 220$ ppm from near the base of the lower Nonesuch Formation until about 1620 feet. In the same interval, Rb concentrations are widely scattered with no clear trend between $\sim 55 - 120$ ppm. Between 1620 and ~ 1570 feet, Zr and Rb concentrations around 200 and ~ 100 ppm, respectively before declining to values near 155 and 80 ppm, respectively, at the sequence boundary (1540 feet). In the 20 feet above the sequence boundary (1540 to 1520 feet), Zr abruptly increases with

considerable scatter (~235 and 615 ppm) while Rb gradually increases. The provenance proxy $\ln(K_2O/MgO)$ (Lipp et al., 2020) has a subtle increasing trend throughout the lower Nonesuch Formation from ~ -0.55 in the basal Nonesuch Formation to 0.27 at the sequence boundary (1540 feet). In the upper Nonesuch Formation between 1540 and 1510 feet, $\ln(K_2O/MgO)$ has considerable scatter between -0.64 and -0.18. Above 1510 feet, $\ln(K_2O/MgO)$ has less scatter with gently declining values from ~0.10 to 0.04. Throughout the core, Ca is generally below 2.5% with a few exceptions, most notably within the evaporitic estuary facies between 1630 - 1600 feet and 1540 -1530 feet.

Total S is elevated above 0.25% within much of the estuary and evaporitic estuary facies (depths 1632 – 1522 and 1566 – 1495, respectively), with values reaching 1.5 %. Total S content of the basal Nonesuch Formation to 1646 feet fluctuates between 0.02 – 0.14, with one sample at 0.3 % (Figure 6). Above the sequence boundary at 1420 feet, S is consistently below 0.03%. Total organic carbon (TOC) is near zero (0.03 – 0.13%) within the tidal flat facies of the lower Nonesuch Formation while organic carbon content of the estuary and evaporitic estuary facies is typically higher, between 0.17 and 0.87%. Across the sequence boundary (1540 – 1522 feet), TOC increases to as much as 4.36%, and by 1416 feet, TOC returns to consistent near-zero values (0.03 – 0.07%).

Molybdenum is mostly below 2.5 ppm with scattered elevated values (<8.32 ppm) between 1630 – 1593 feet and consistently elevated values of 9.70 decreasing to 3.15 between 1555 – 1543 feet. Barium decreases from 374 – 330 ppm between the basal Nonesuch Formation and 1630 feet, abruptly drops to 200 ppm at 1628 feet and then increases to fluctuating values between ~250 and 490 ppm with outliers to 750 ppm between 1610 – 1506 feet. Above 1506 feet, Ba drops to values between 320 – 471 ppm. Manganese has generally low values near 700

ppm from the basal Nonesuch Formation to 1588 feet. Between 1588 – 1550 Mn increases sharply to values as high as 3470 ppm. Above 1500 ft, Mn drops to values near 600 ppm. In the lower Nonesuch Formation P gently declines from values near 0.09% in the basal Nonesuch Formation to 0.07% below the sequence boundary at 1540 feet. Between 1540 – 1510 feet, P decreases to values as low as 0.04%. Above 1510 feet, P increases to 0.07%.

Carbonate REY distributions

Molar tooth structures and carbonate-rich layers sampled from several cores from the Ashland Syncline and Keweenaw Peninsula have Σ REY abundances between 41.6 to 256.8 ppm (Table 2). Total REY of carbonate from the evaporitic estuary facies is lower (41.6 – 170.9 ppm) than carbonate from estuary and tidal flat facies (97.8 – 256.8 ppm). Because the REY distribution of lower Oronto Group shales and wackes are distinct from PAAS (Figure 3), I normalize Nonesuch carbonate REY to average Nonesuch REY (REY_{NF}). Equations used to calculate REY anomalies are from Lawrence and Kamber (2006) and available in the supplements.

Carbonate REY distributions fall into three groups. Three samples have an LREE-enriched distribution (Figure 7a), with shale-normalized MREE enrichment (bell shaped index, BSI, see supplements for equations) between 1.12 to 1.15, LREE/HREE between 1.88 to 2.68, positive La anomalies between 1.08 – 1.44, positive Ce anomalies between 1.11 – 1.27, positive Eu anomalies between 1.10 – 1.24, and Y/Ho between 31 – 35. Five samples have a flat distribution (Figure 7b) with BSI between 0.76 to 1.06, LREE/HREE between 0.08 to 1.24, La anomalies between 0.86 to 1.64, Ce anomalies between 0.92 to 1.52, flat to positive Eu anomalies between 1.04 to 1.27, and Y/Ho between 27 to 34. Six samples have slightly enriched HREE distributions (Figure 7c), with BSI between 0.81 to 0.96, LREE/HREE between 0.66 to

0.94, positive La anomalies between 1.11 – 1.69, positive Ce anomalies between 1.02 – 1.44, flat to positive Eu anomalies between 1.06 – 1.47, and Y/Ho between 28 – 30. These REY distributions are differentiated on a cross-plot of shale-normalized MREE enrichment plotted against LREE/HREE (Figure 7d). Most samples (8 of 13) have no MREE enrichment ($BSI < 1$) and show increasing ΣREY with decreasing LREE/HREE (supplemental figure S4). These samples either have flat REY distributions with slight LREE depletion (circled in Figure 7 b) or slight HREE enrichment (Figure 7c). Five samples have flat or LREE enriched distributions (Figure 7d). These samples have generally lighter $\delta^{13}C$ values and show no trend with ΣREY (supplemental Figure S4). There is no clear correlation between initial $^{87}Sr/^{86}Sr$ or $\delta^{18}O$ and REY distributions. One concretion was analyzed as a diagenetic endmember. It has a flat REY distribution (Figure 7b carbREY) with significantly elevated total REY (680 ppm), Y/Ho of 34, and positive La and Ce anomaly (1.24 each) and no Eu anomaly (1.04).

DISCUSSION

Sediment provenance and weathering

Shale geochemistry reported herein substantiates decades of previous work that demonstrates the Oronto Group was mainly sourced from underlying MRCS basalts with lesser felsic contribution and sediment composition shifted to more felsic, mature compositions up stratigraphic section (Ojakangas et al., 2001; Berendsen and Barczuk, 1993; Suszek, 1997; Cullers and Berendsen, 1998; Mitchel and Sheldon, 2016; Craddock et al., 2013; see supplemental text for more detailed description). Weathering intensity (ω) and provenance (ψ) are evaluated through the oxide composition of lower Oronto Group shales and wackes following the model presented by Lipp et al. (2020). The range of weathering intensity for the Nonesuch and Freda Formations (ω values between 0.5 – 2, low to intermediate; Figure 8) is

consistent across the lower Oronto Group and corresponds to chemical index of alteration between ~50 - 75 (supplemental Figure S7). Provenance composition values ψ are relative to UCC, with -2 and +2 corresponding to basalt and rhyolite compositions, respectively. Most upper Nonesuch and Freda Formation samples have ψ values between -0.2 to 0.2 while ψ values of most lower Nonesuch shales are between -0.2 to -0.8 indicating a shift to more felsic sediment sources with time.

Shale REY distributions also indicate a dominantly mafic source based on depletion of LREE and flat to slightly enriched HREE for all lower Oronto Group shales and wackes (Figure 3). Likewise, the $^{147}\text{Sm}/^{144}\text{Nd}$ of the lower Nonesuch and Freda Formation (0.1157 to 0.1354) is consistent with a mixed provenance derived from mafic to intermediate MRCS rocks: the range in ϵNd (1081 Ma) between -1.56 to 0.87 is comparable to ϵNd (1081 Ma) reported for Portage Lake Volcanic basalts and intermediate volcanics (Figure 4; Nicholson and Shirey, 1990). Similarly, depleted mantle model ages predominantly between ~1.9 to 1.8 Ga (full range from ~2.0 to 1.6 Ga) is consistent with depleted mantle model ages of ~2.4 to 1.8 Ga Ma for the Portage Lake basalts and intermediate volcanics (Nicholson and Shirey, 1990).

Continental flood basalts like those of the MRCS (e.g. Green, 1984) are enriched in P relative to average UCC, and basalt weathering could have stimulated primary production within the Oronto Group basin (Horton, 2015; Cox et al., 2016). Basalt weathering and enhanced nutrient delivery would have been most pronounced during lower Nonesuch time and persisted through deposition of the lower Freda Formation, and this is broadly consistent with P concentrations. Average P contents of the lower Nonesuch Formation is 0.09% (0.06 – 0.11, n=207) compared to 0.07% (0.06 – 0.08, n=36) for the upper Nonesuch, 0.07% (0.04 – 0.09, n=20) for the Freda, and 0.07% for UCC (Rudinick and Gao, 2003). Covariation between Fe and

P for Nonesuch shales indicates that much of the P delivered to the basin was scavenged by Fe oxides, limiting its bioavailability (Figure 8; Laasko and Schrag, 2014). Despite the association between Fe and P_2O_5 , the rock record indicates pulses of enhanced productivity: carbonate laminite associated with elevated TOC within the lower Nonesuch Formation has been attributed to intense organic production during seasonal algal blooms (Elmore, 1989; Imbus et al., 1992; Suszek, 1996). In the next section I consider elemental variation preserved in core WC-14 to evaluate trends in basinal redox and productivity.

Chemostratigraphic evidence for a revised sequence stratigraphic framework

In core WC-14, the steady yet subtle increase in Zr through much of the lower Nonesuch Formation corresponds to gradually decreasing grain size, from wackes composed of shale and fine- to very fine-grained sandstone to predominantly shale and siltstone (Figure 5). This increasing Zr concentration cannot be explained by greater contribution of coarse-grained sediments (e.g. McLennan et al., 1993; Turner et al., 2016; Dypvik and Harris, 2001; LaGrange et al., 2020) and instead may reflect a gradual shift to a more felsic sediment source. The steady increase in provenance proxy $\ln(K_2O/Mg)$ throughout the lower Nonesuch Formation supports this interpretation and is also consistent with greater ψ coefficients for the upper Nonesuch and Freda Formations compared to the lower Nonesuch Formation (Figure 8; Lipp et al., 2020; supplemental text). The abrupt increase in both Zr and Rb concentrations and decrease in $\ln(K_2O/MgO)$ above the sequence boundary at 1540 ft indicates greater delivery of continentally derived sediments with a more mafic provenance. Above 1520 feet, the abrupt drop in Zr to values around 200 ppm, increase in $\ln(K_2O/MgO)$ to values near 0.1, and increase in Rb to values above 120 ppm correspond to shaley siltstone and sandstone of the lower Freda Formation (Figure 5). Based only on visual core inspection and stratal stacking patterns I interpreted the

shale between 1540 – 1520 feet as muddy deposits on or adjacent to a tidal flat setting (Stewart et al., 2024). As elaborated below, geochemical indicators of anoxia and productivity suggest these shales are better interpreted as a progradational-aggradational succession of distal basin lowstand deposits that developed when base level was at a minimum and increasing. Following this interpretation, the abrupt shift from relatively distal black laminated shale to continental deposits of the Freda Formation requires development of a second sequence boundary at 1420 feet.

Chemostratigraphic evidence for evolving basin productivity and restriction

Elevated organic carbon and total S concentrations are associated with black laminated shale, siltstone, and carbonate laminites in the Nonesuch Formation (Figure 6, Imbus et al., 1988; Stewart and Mauk, 2017). Organic carbon, total sulfur, and redox sensitive trace elements are generally enriched under euxinic conditions (Tribolivard et al., 2006) and based on magnetic mineral assemblages of this facies (pyrite, titanium oxide, and absence of detrital iron oxide minerals), Slotznick et al. (2018, 2023) demonstrate the development of anoxic and sulfidic pore water possibly extending to the overlying bottom water. Sediment enrichment in Mo and U should track with conditions of reducing pore or bottom water because solubility of these metals decreases under reducing conditions, resulting in authigenic sediment enrichment (Algeo and Maynard, 2004; Algeo and Lyons, 2006). By cross plotting data from many cores in the White Pine and Western Syncline areas, Keweenaw Peninsula, Stüeken et al (2020) document sediment enrichment of Mo and U that is uncorrelated with Zr/Ti, a proxy for detrital input and provenance. Evaluating stratigraphic trends in total S, organic carbon, Mo, U, Ba, P, and Mn from core WC-14 complements and adds new dimension to these observations.

In core WC-14, two intervals are associated with total S greater than 0.75% and total organic carbon >0.25% (1633 – 1592 and 1547 – 1520 feet, labeled A and B on Figures 5 and 6). Total organic carbon is greater in unit B (average 1.31%, 0.16 – 4.36%, n=10) than unit A (average 0.39%, 0.06 – 0.74%, n=21). Both intervals have Mo and U concentration locally exceeding 3 ppm. Elevated concentrations are generally greater in the upper unit B (Mo: average 1.92 ppm, 0.48 – 5.02 ppm, U: average 4.1 ppm, 2.9 – 9.6 ppm, n=14) compared to unit A (Mo: average 1.89 ppm, 0.43 – 8.32 ppm, U: average 2.8 ppm, 2.1 – 4.3 ppm, n=21).

Strong Mo enrichment relative to U reflects conditions of fluctuating redox dominated by suboxic to weakly sulfidic deepwaters (Algeo and Tribovillard et al., 2009). Rico et al. (2019) note high Mo relative to U enrichment in the Nonesuch Formation, which they attribute to particle shuttling of Mo under anoxic – but not euxinic- conditions. Enrichment factors for Mo and U in core WC-14 follow the same pattern (Figure 10a). Mo and U enrichment patterns suggest the dominant control on Mo enrichment was the particulate shuttle pathway, and the presence of pyrite, titanium oxide, and absence of detrital iron oxide minerals in black laminated shale, siltstone, and carbonate laminite facies indicates development of sulfidic pore water (Slotznick et al., 2018, 2024). Notably, some samples from unit B fall off the particulate shuttle trend, with Mo_{EF}/U_{EF} below 0.3 x seawater. Lower Mo_{EF}/U_{EF} could be attributed to (a) deposition under suboxic conditions; (b) deposition within a restricted, silled basin where Mo drawdown in sediments is not replenished; (Algeo and Lyons, 2006; Algeo and Tribovillard, 2009) or (c) detrital contribution of U in zircons. Enrichment factors calculated relative to Zr rather than Al suggests some excess U is hosted by zircons, however the two trends remain (Figure 10b). The consistent slope of the $Mo_{EF}(Zr)/U_{EF}(Zr)$ trend below 0.3 x SW suggests

deposition under suboxic conditions. Enrichment trends of Ba, P, and Mn in core WC-14 allows a more nuanced view of the Nonesuch basin redox structure.

Manganese concentrations are greatest in the interval between units A and B (average: 1187 ppm, 640 – 3470 ppm, n=23) compared to unit A (average 861 ppm, 569 – 3020 ppm, n=21), B (average: 525 ppm, 482 – 844 ppm, n=14), or the rest of the core (average: 801, 482 – 3317 ppm, n=26). Barium reaches lowest values within units A (average: 284 ppm, 200 – 410 ppm, n=21) and B (average: 360 ppm, 260 – 620 ppm, n=14) compared to the rest of the studied core interval (average: 424 ppm, 280 – 831 ppm, n=49) (Figure 6). Between units A and B, Ba steadily increases from ~350 ppm, reaching concentrations as high as 750 ppm at the base of unit B. In contrast to Mn and Ba, P concentrations decline throughout the Nonesuch Formation, though with scatter. Within unit A, P has no clear trend around an average value of 815 ppm with scatter between 730 – 900 ppm (n=21). Within unit B, P declines sharply from an average of 768 ppm (720 – 820 ppm, n=4) to average 679 ppm (570 – 840 ppm, n=14) across the sequence boundary at 1540 feet.

The combined trends in Mn, Mo, U, Ba and P indicate development of Mn-oxyhydroxide particle shuttle in an oxygenated water column and episodic development of euxinia in sediments or deep water. Manganese enrichment below unit B suggests cycling of Mn-oxyhydroxides across a redox front that developed within shallow sediments. Increasing Ba concentrations between units A and B further support development of more oxygenated pore water in that interval. Likewise, the relative depletion of Ba within units A and B suggests development of euxinic pore waters during deposition of these intervals. Carbonate laminite and associated MT structures are characteristic of the evaporitic estuary facies within units A and B. Carbonate likely precipitated in these units because of increased carbonate alkalinity from microbial sulfate

or iron reduction in shallow sediments. Relative depletion in P and elevated TOC in the upper part of unit A further supports release of P from sediments under euxinic conditions.

The evolving redox conditions preserved in core WC-14 may be understood within a sequence stratigraphic framework. The lower Nonesuch Formation preserves retrogradational stacking of estuary over tidal flat facies (Stewart and Mauk, 2017; Stewart et al., 2024). During maximum transgression marked by the maximum flooding surface at ~1635 feet near the base of unit A, the chemocline rose to the bottom of the water column and euxinic conditions developed in pore waters and the deeper water column. As sedimentation increased relative to generation of accommodation in the overlying highstand systems tract, shallow sediments transitioned from euxinic to anoxic conditions. This change from euxinic to anoxic pore water is reflected by rising Ba concentrations from the base of unit A to the sequence boundary at 1540 feet. Enrichment in Mn in the 40 feet below the sequence boundary further supports cycling of Mn and associated trace elements across an anoxic-oxic boundary within the sediments or at the sediment water interface at the top of the highstand systems tract. The abrupt shift to lower Mn, P, Ba, and Mo concentrations across the sequence boundary is consistent with development of more pronounced anoxia as base level was at its lowest point and rising, during deposition of the lowstand systems tract. TOC is greatest and P concentrations are lowest in this interval, indicating development of euxinia in pore waters that may have extended into the overlying bottom waters. Basin geometry characterized by development of subsiding sag basins separated by basement ridges (White and Wright, 1960; Allen et al., 1997; Suszek, 1997; Slotznick et al., 2004; Stewart et al., 2004) may have promoted development of restricted conditions during lowstand deposition. Flood plain and fluvial deposits of the overlying Freda Formation represent a dramatic basinward shift in facies across a second sequence boundary.

Palaeosalinity preserved in carbonate REY patterns?

Assessing the impact of diagenesis on REY patterns in the Nonesuch Formation

Work in modern estuaries and nearshore marine settings demonstrates that shallow sediments and groundwater-seawater mixing zones are significant sources of trace elements, including REY, to the ocean (Sholkovitz et al., 1989; Charette and Sholkovitz, 2005; Chevis et al., 2015; Johannesson et al., 2017). In the shallow pore waters of the Nonesuch basin, organic carbon remineralization and cation exchange with surrounding detrital material drove pore fluids towards lighter $\delta^{13}\text{C}$ values and less radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ compositions (see chapter 2), and more generally, carbonate diagenesis leads to lighter $\delta^{18}\text{O}$ values (Brand and Veizer, 1980; 1981). We can cross-plot ΣREY against these variables to assess REY cycling during early diagenesis. Total REY contents of Nonesuch carbonates (excluding the concretion) anticorrelate with initial $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{13}\text{C}$ and are at best weakly anticorrelated with $\delta^{18}\text{O}$ (Figure 11). Release of REY from particles and remineralized organic carbon increased REY concentrations in pore fluids during early diagenesis of Nonesuch Formation sediments. Diagenetic alteration associated with lighter $\delta^{18}\text{O}$ values had little impact on ΣREY .

I next consider processes that may have produced REY distributions of Nonesuch carbonate. The LREE enriched distribution characteristic of three Nonesuch Formation carbonates (Figure 7a) is unlike common diagenetic REY distributions (Haley et al., 2004; Chen et al., 2015; Skinner et al., 2019; Zhao et al., 2021). These samples are characterized by a flat LREE distribution around the average of Nonesuch Formation sediments and coherent MREE and HREE depletion interrupted by a subtle increase in Y/Ho. Some of the LREE enrichment relative to HREE may have developed in part through a dominant process of POC degradation and reduction of Fe/Mn oxyhydroxides in anoxic pore fluids, consistent with their positive Ce anomalies and lighter $\delta^{13}\text{C}$ values (-4.9 to -6.2 ‰), but this does not explain the MREE and

HREE depletion. LREE enrichment and HREE depletion has been attributed to carbonate precipitation from Ca-poor hydrothermal fluids (Debruyne et al., 2016) or plagioclase weathering and associated precipitation of secondary calcite (Mathurin et al., 2014). Although REY abundance and distribution broadly reflect the dominant processes acting in the water column and pore waters, they capture local conditions that may vary over short distances and timescales (Elderfield et al., 1990; Sholkovitz and Szymczak, 2000). The observed LREE-enriched distribution may primarily reflect localized diagenetic influences.

The characteristic flat and HREE-enriched REY patterns of Nonesuch carbonates (Figure 7b, c) are like the patterns first recognized by Haley et al. (2004) as pore water features that developed through particle adsorption/desorption, organic matter degradation, and complexation with carbonate ions during early diagenesis in shallow marine sediments. Four samples have a flat REY distribution that likely represents a mix of dominant processes in shallow pore fluids. One sample from a carbonate-rich layer of the tidal flat facies has a flat distribution that reflects equilibration to the REY contents of Nonesuch siliciclastic sediments during diagenesis. Two samples from the evaporitic estuary facies have progressive LREE depletion from La to Sm, flat to slight HREE enrichment, weak to no Ce anomalies, and positive La and Eu anomalies. This pattern resembles a muted marine distribution and is consistent with evolution of estuarine pore fluids: Remineralization of POC released LREE and dissolved inorganic carbon, resulting in flatter LREE patterns and slight HREE enrichment (Haley et al., 2004). One sample from the estuary facies has a flat REY distribution like the three evaporitic estuary facies samples but with a MREE bulge, which is commonly attributed to reductive dissolution of Fe/Mn oxyhydroxides (Haley et al., 2004; Soyol-Erdene and Huh, 2013). Six samples have slightly HREE-enriched distributions that are like the three evaporitic estuary samples with flat REY distributions, but

with more pronounced HREE enrichment ($\text{Pr}/\text{Er}_{\text{NF}} < 1$; Figure 7c, d). They likely reflect similar shallow marine-influenced diagenetic processes.

Despite clear evidence for diagenetic signals in Nonesuch carbonate REY distributions, most samples (8 of 13) preserve features of the characteristic marine REY distribution, including positive La anomalies, elevated Y/Ho, and HREE enrichment. I next consider whether these features might preserve signals that developed in the estuarine water column. La and Ce anomalies (but not Eu) covary with Y/Ho ratios (Figure 12). The trend extends from Y/Ho values near 35 and positive La (1.65) and Ce (1.49) anomalies to the crosshairs defining the Nonesuch Formation siliciclastic sediment values and is most pronounced for samples from the evaporitic estuary facies. Contribution of REY from siliciclastics can potentially alter REY patterns towards flat shale-normalized distributions, resulting in covariation between REY anomalies (Kamber et al., 2004). Rb-Sr isotopes show no evidence for sample contamination by leaching of siliciclastics during sample preparation (see chapter 2). An alternative explanation for the covariation between La and Ce anomalies with Y/Ho is that these anomalies became enhanced during pore water evolution at or shortly after deposition, an idea I explore below.

Early diagenetic evolution of Nonesuch basin pore water

Early diagenetic microbial oxidation of organic matter lowered $\delta^{13}\text{C}$ values of Nonesuch pore water, while cation exchange with detrital material derived from unradiogenic basalt in shallow pore fluids drove initial $^{87}\text{Sr}/^{86}\text{Sr}$ to less radiogenic values (see chapter 2). Therefore, plotting REY anomalies against C, O, and Rb-Sr isotopes provides an independent test for diagenetic evolution of REY distributions in pore water. La and Ce anomalies and Y/Ho of samples only from the evaporitic estuary facies anticorrelate with $\delta^{13}\text{C}$ (Figure 13) and are uncorrelated with $\delta^{18}\text{O}$ or $^{87}\text{Sr}/^{86}\text{Sr}$ (supplemental Figure S9). In contrast, Eu anomalies of all

samples correlate with initial $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}$ and are uncorrelated with $\delta^{13}\text{C}$. Lower $\delta^{13}\text{C}$ values link to greater diagenetic microbial remineralization of organic matter, which would have increased pore water alkalinity, enhancing La anomalies and Y/Ho. Anoxia commonly develops in shallow pore water as oxygen is depleted through microbial metabolism of organic matter, a process that is captured by Ce anomalies of the evaporitic estuary facies. Development of positive Ce anomalies tied to lower $\delta^{13}\text{C}$ values demonstrates removal of Ce from the overlying water column to Ce-oxide particles, which accumulated in shallow sediments and were subsequently reduced in suboxic to anoxic pore fluids.

Positive Eu anomalies relative to the average composition of Nonesuch Formation indicate hydrothermal input to the Nonesuch basin. Correlation between Eu anomalies and initial $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}$ (supplemental Figure S9) suggest that Eu anomalies were diagenetically altered towards the Eu content of the Nonesuch detrital material.

Cross-plotting REY anomalies against ΣREY concentration allows another view into evolution of REY patterns during early diagenesis (Figure 14). Lanthanum anomalies are uncorrelated with ΣREY . Cerium anomalies and Y/Ho of evaporitic estuary facies are weakly correlated with ΣREY while these features are uncorrelated in carbonates from other facies. Europium anomalies from all samples are anticorrelated with ΣREY . Correlation between Ce anomalies and ΣREY corroborates Ce cycling through an oxygenated water column and reduced pore fluids. Increased ΣREY links to more pronounced HREE enrichment and elevated Y/Ho (Figure 7d, 14), suggesting development of greater carbonate alkalinity in shallow sediments.

The characteristic marine anomalies are least developed for samples with minimal petrographic and isotopic evidence for diagenesis. This implies the combined influence of (1) low salinity in the Nonesuch basin water column and (2) earliest diagenetic processes involved

release of LREE and MREE by reductive dissolution of Fe/Mn oxyhydroxides, which acted to flatten positive REY distributions. As early diagenesis progressed, pore water gained Σ REY and La and Ce anomalies, Y/Ho, and HREE enrichment all increased, indicating an increase in salinity. Release of DIC during organic carbon remineralization may have enhanced these signals but is unlikely to generate them given the abundance of Fe, Mn and organic matter in the water column during deposition (Neslon et al., 2004; Johannesson et al., 2017). The most parsimonious explanation for muted marine REY distributions is pore water evolution from a brackish water column. Pore water from modern estuaries and salt marshes also show elevated salinity compared to the overlying water column, with considerable spatial and temporal variability (Charette and Sholkovitz, 2005; Hughes et al., 2012; Hossain and Marshall, 2014). Nonesuch carbonate REY patterns are thus consistent with precipitation from pore water that evolved from a brackish estuarine water column. These results align with sedimentologic and stratigraphic evidence for estuarine and tidal flat depositional settings (Jones et al., 2020; Stewart et al., 2024).

Paleosalinity preserved in shales

Geochemical salinity proxies applied to fine-grained detrital sediments provide an independent test for salinity conditions of the Nonesuch basin. Published paleosalinity proxy data for the Nonesuch Formation and lower Freda Formation suggest deposition under brackish to marine conditions (Hieshima and Pratt, 1991; Stüeken, 2021; Liu et al., 2024). Elevated S/TOC above values typical of modern marine shales (0.1 – 0.3, Berner and Raiswell, 1983; Liu et al., 2024) indicate a sulfate source in the water column and bacterial sulfate reduction in pore water (Figure 15; Hieshima and Pratt, 1991; Imbus et al., 1992; c.f. Cumming et al., 2013). Likewise, Mo enrichment in the Nonesuch formation is consistent with Mo sourced from a saline waterbody and trapped in sediments under fluctuating redox conditions dominated by suboxic to

weakly sulfidic deepwaters (Stüeken et al., 2020; Rico et al., 2019; this paper). The Sr/Ba proxy mostly falls above 0.2, a proposed threshold for marine salinity for Proterozoic shales (Stüeken et al., 2020; Liu et al., 2024). These proxies corroborate carbonate REY evidence for brackish conditions in the Nonesuch basin.

Although shale salinity proxies suggest non-freshwater salinity during Nonesuch deposition, proxies that depend on aqueous exchange with clays may have been overprinted during migration of Cu-mineralizing brines and should be interpreted with caution. While S/TOC and Mo enrichment are dependent on variables including redox, the Sr/Ba proxy is governed by exchange of aqueous Sr with clays (Liu et al., 2024; Wei and Algeo, 2020). Validity of the Sr/Ba proxy depends on the assumption that excess Sr taken up by clays in sediments is controlled by the aqueous Sr concentration in the water column during deposition. However, lower Oronto Group sediments may have gained Sr after deposition from migrating hydrothermal fluids, including Cu-mineralizing brines. Published Rb-Sr isotope measurements of Nonesuch Formation detrital sediment (Ruiz et al., 1984; Ohr, 1993) yield a model age of about 1048 Ma. Likewise, the Rb-Sr isotope composition of gangue minerals associated with native copper deposits in Midcontinent Rift basalts and overlying Copper Harbor Conglomerate (microcline, calcite, epidote and chlorite) have model ages of about 1060 and 1048 Ma (Bornhorst et al., 1988). Hydrothermal fluids associated with late Mesoproterozoic Grenvillian orogenesis and copper mineralization reset the Rb-Sr system 20 to 40 million years after Nonesuch deposition (Ruiz et al., 1984; Bornhorst et al., 1988; Ohr, 1993). Furthermore, Ba may be enriched in organic-rich sediments (Tribovillard et al., 2006), and the Nonesuch Formation shows evidence for localized Ba enrichment, which would depress Sr/Ba ratios for those intervals. The Sr/Ba values of the lower Oronto Group likely do not record salinity of the primary depositional

waterbody or early diagenetic pore water. They instead reflect elevated Sr in younger hydrothermal fluids, which included oxidized brines necessary to transport Cu leached from Midcontinent Rift basalts (Brown, 2006; Hitzman et al., 2010). Nevertheless, S/TOC and elevated Mo concentrations are consistent with sedimentologic and carbonate REY evidence for deposition under brackish conditions.

Midcontinent subsidence, marine incursion, and Oronto Group deposition

Many early workers interpret the lower Oronto Group to record deposition within and along the shorelines of a stratified lake based on analogy to the modern East African Rift, interpretation of several km-thick alluvial and fluvial deposits in the underlying Copper Harbor Conglomerate and overlying Freda Formation, and location within the interior of the Laurentian continent (Daniels et al., 1982; Elmore et al., 1984; Suszek, 1997; Ojakangas et al., 2001). More recent work highlights sedimentologic evidence for deposition within a tidally influenced marginal marine setting for at least parts of the upper Copper Harbor Conglomerate, Nonesuch Formation, and Freda Formation (Jones et al., 2020; Stewart et al., 2024, see also Hite, 1969). Geochemical evidence including organic carbon and total sulfur contents, Mo enrichment, and salinity proxy B/Ga support episodic mixing between freshwater and saltwater during Nonesuch deposition (Hieshima and Pratt, 1991; Stüeken et al., 2020; Liu et al., 2025).

Despite sedimentologic and geochemical evidence for tidal modification of sediments deposited under brackish conditions, the nature of a connection between the open ocean and Nonesuch interior basin remains in question. Slotznick et al. (2024) assert that a transient marine incursion to the interior of continental Laurentia at the start of thermal subsidence is implausible and favor deposition within a saline lake setting. Stewart et al. (2024) suggest episodic marine incursion to interior Laurentia may have been driven by the combined influence of thermal

subsidence and tectonic loading during early stages of the Ottawa phase of the Grenvillian orogeny. Geochronology constrains most thrusting on the Keweenaw and Douglas Faults as contemporaneous with deposition of the upper Freda Formation up to ~15 Myr after (Hodgin et al., 2024), consistent with an important Ottawa phase tectonic control on subsidence during Oronto Group deposition. In addition to thermal subsidence and subsidence related to Grenvillian orogenesis, syn-magmatic basin subsidence noted by many others likely had a density-driven component (White, 1971; Green, 1984; 1989; Allen et al., 1997), similar to subsidence on the Neogene-Quaternary Eastern Snake River Plain, Idaho (McQuarrie and Rodgers, 1998; Rodgers et al., 2002; McCurry and Rodgers, 2008; Rodgers and McCurry, 2008; Schusler et al., 2020). Combined, these mechanisms could have resulted in marine incursion to the interior Oronto Group basin.

Review of the existing literature thus suggests subsidence to accommodate Oronto Group deposition was generated through the combined influence of thermal subsidence, density-driven subsidence, and Ottawa phase Grenvillian orogenesis, rather than only thermal subsidence as is commonly asserted. Likewise, the Copper Harbor Conglomerate and Freda Formations include significant intervals of shallow marine strata, rather than preserving several kilometers of fluvial and alluvial deposits most frequently cited in the literature. These realizations highlight the plausibility of marine incursion to the interior of Laurentia and provide motivation for in-depth investigation into mechanisms of basin subsidence and the depositional setting of the Freda Formation and overlying Bayfield Group.

Implications for early eukaryote habitat

The Oronto Group preserves a substantial record of marginal marine environments. While some of the microfossils preserved in these rocks could have been fluvially transported

from lacustrine settings after their death, many likely lived near where they were ultimately preserved within marine-influenced facies of the Nonesuch Formation. The combined geochemical evidence indicates this environment was characterized by an oxygenated, brackish water column with anoxic and euxinic conditions locally developing in shallow sediments during diagenesis and extending to the deeper water column in distal parts of the basin. Although adsorption to Fe-oxides limited bioavailability of enhanced P delivery from weathered basalts, elevated P may have promoted microbial blooms as evidenced by carbonate laminites in the Nonesuch Formation. The organisms that lived in the Oronto Group basin would have tolerated conditions of low, and likely fluctuating salinity, a largely oxygenated water column and abundant nutrient supply. Particle shuttling of Fe and Mn oxyhydroxides between the water column and anoxic pore water and bottom water could have enhanced or focused nutrient availability through concentration and release of bioessential elements including P, analogous to modern estuarine nutrient cycling (e.g., Chanvalon et al., 2016).

CONCLUSIONS

The lower Oronto Group preserves marginal marine sediments that were deposited in an oxidized, brackish water column. Enhanced nutrient delivery from weathered basalt promoted microbial blooms, which impacted redox conditions in distal settings. In deeper parts of the basin, suboxic to weakly sulfidic conditions developed and the chemocline likely fluctuated between the bottom water and shallow sediments. Particle shuttling of Fe and Mn oxyhydroxides between the water column and anoxic pore water and bottom water likely enhanced and focused nutrient availability through concentration and release of nutrient P. These results provide a fuller picture of the processes that controlled variable environmental conditions of early eukaryote habitat.

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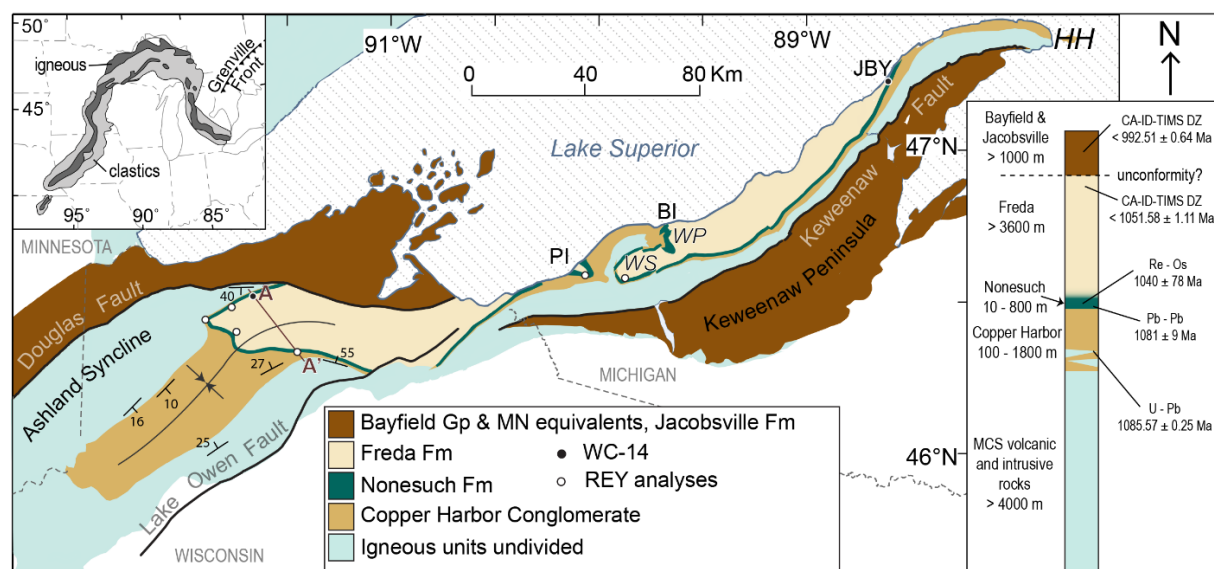
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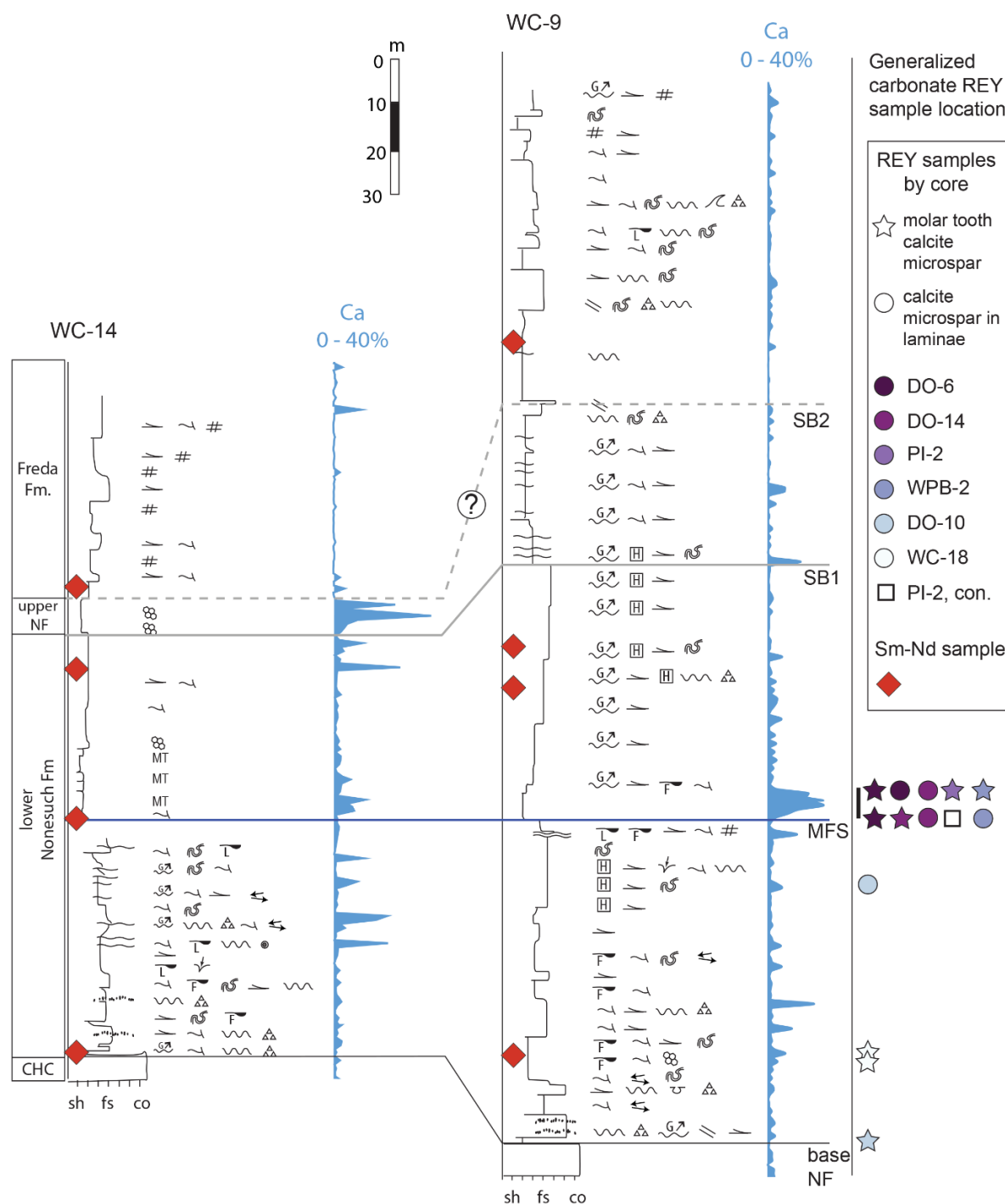
FIGURES AND TABLES

Figure 1. location



Map of Midcontinent Rift bedrock units showing location of core WC-14 and cores sampled for carbonate REY. New and compiled whole rock geochemical data were sampled from these cores as well as cores from the Presque Isle Syncline (PI), Western Syncline (WS), White Pine (WP), and JBY core. Line A-A' locates cores shown in Figure 2. Select strikes and dips are shown for the Ashland Syncline from Nicholson et al., 2006. Inset map (left) shows Midcontinent Rift extent, modified from Ojakangas et al (2001). Age constraints on generalized stratigraphic column (right) are from Ohr (1993), Cumming et al. (2013), Fairchild et al. (2017), and Hodgin et al. (2022, 2024). Thicknesses estimated from Daniels (1982), Elmore et al. (1989), and Stewart et al. (2024). Modified after Stewart et al. (2024). See Supplementary Table A1 for drill core location coordinates.

Figure 2. generalized stratigraphy and sample locations



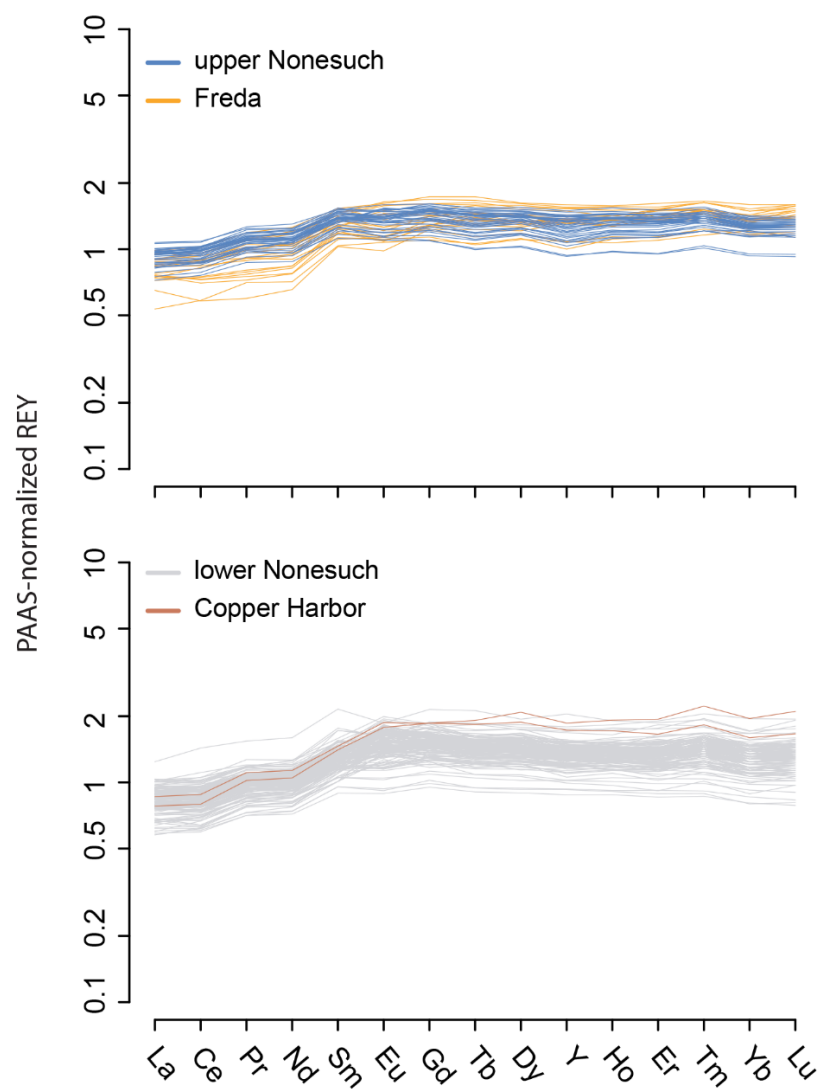
Stratigraphic correlation of proximal (WC-14) and distal (WC-9) cores from the Ashland

Syncline. Left panel: core log showing grain size increasing to the right (sh: shale, fs: fine-

grained sandstone; co: conglomerate). See Figure 6 for stratigraphic and sedimentary structure

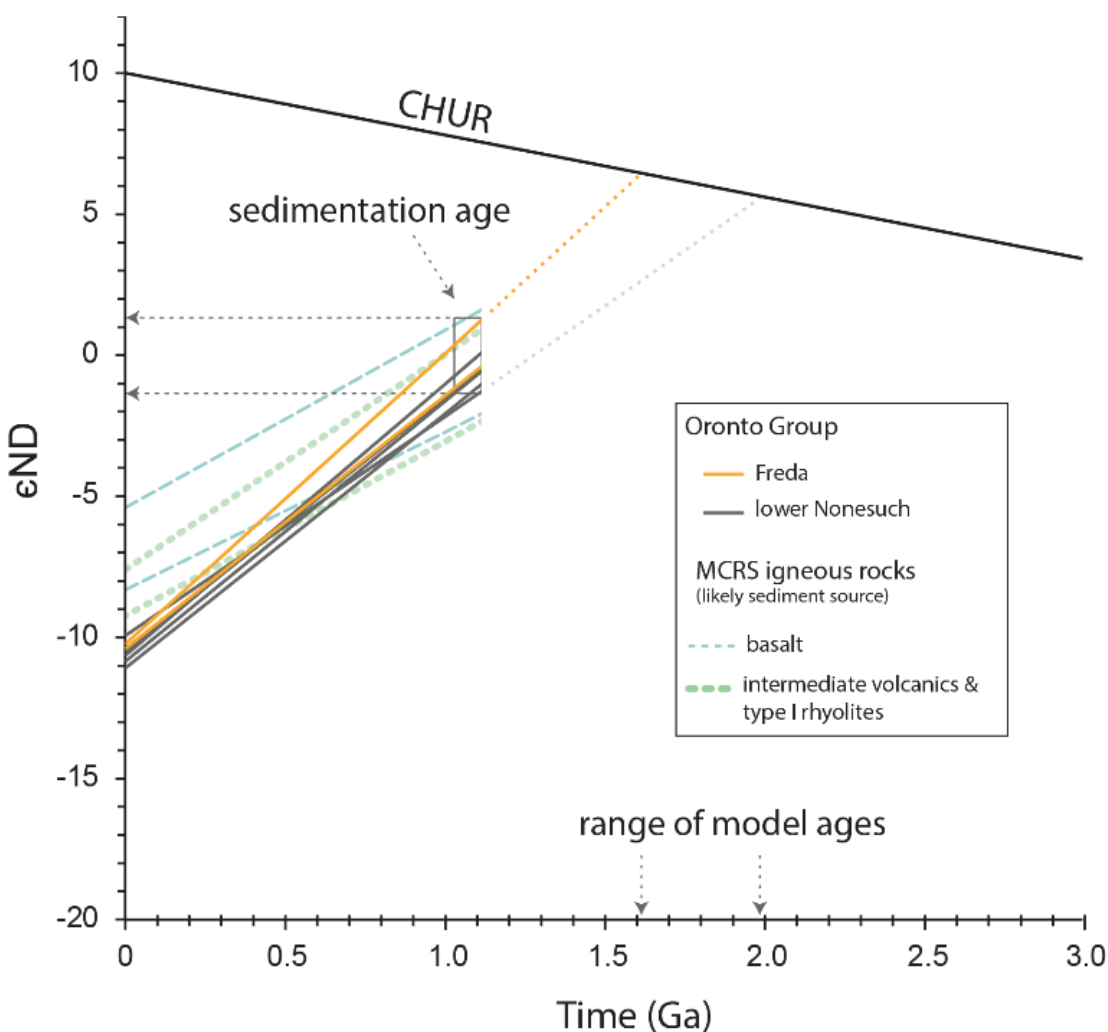
key. The blue curve shows Ca concentration measured every 2 feet with a handheld XRF as a screen for Ca carbonate present as calcite microspar in mm-scale MT cracks and laminae and early diagenetic concretions (Stewart and Mauk, 2017). The rightmost panel shows the generalized stratigraphic location of carbonate REY samples from multiple cores across WI and MI (core name indicated in key, see supplemental table for location coordinates). Most samples are from the carbonate-rich interval above the MFS. The black box is an early diagenetic concretion (conc.)

Figure 3. siliciclastic REY distributions



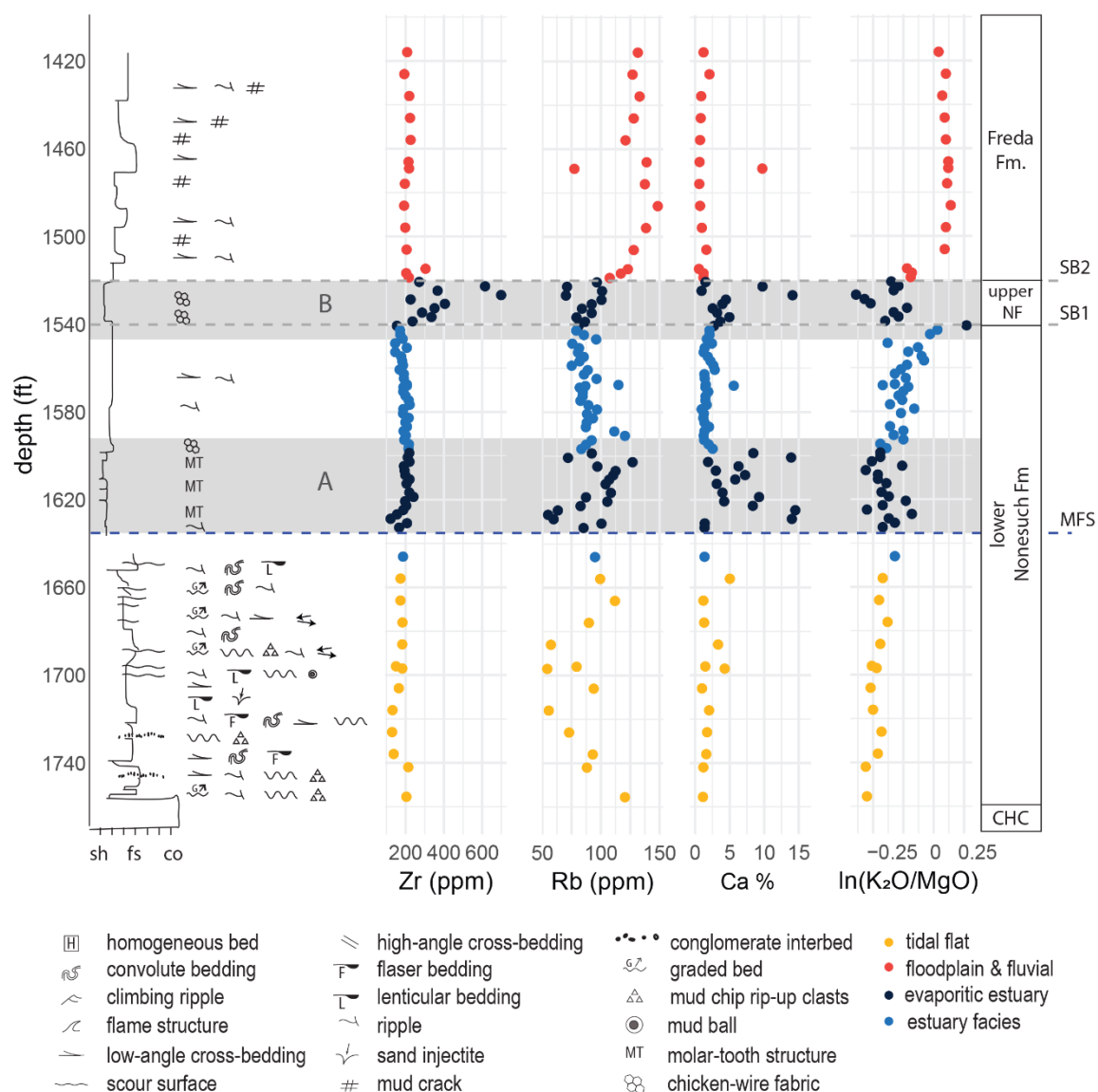
PAAS-normalized (Taylor & McLennan 1985) REY patterns of lower Oronto Group shales and wackes. LREE depletion and flat to slightly enriched HREE indicate a mafic source for all units.

Figure 4. Sm-Nd



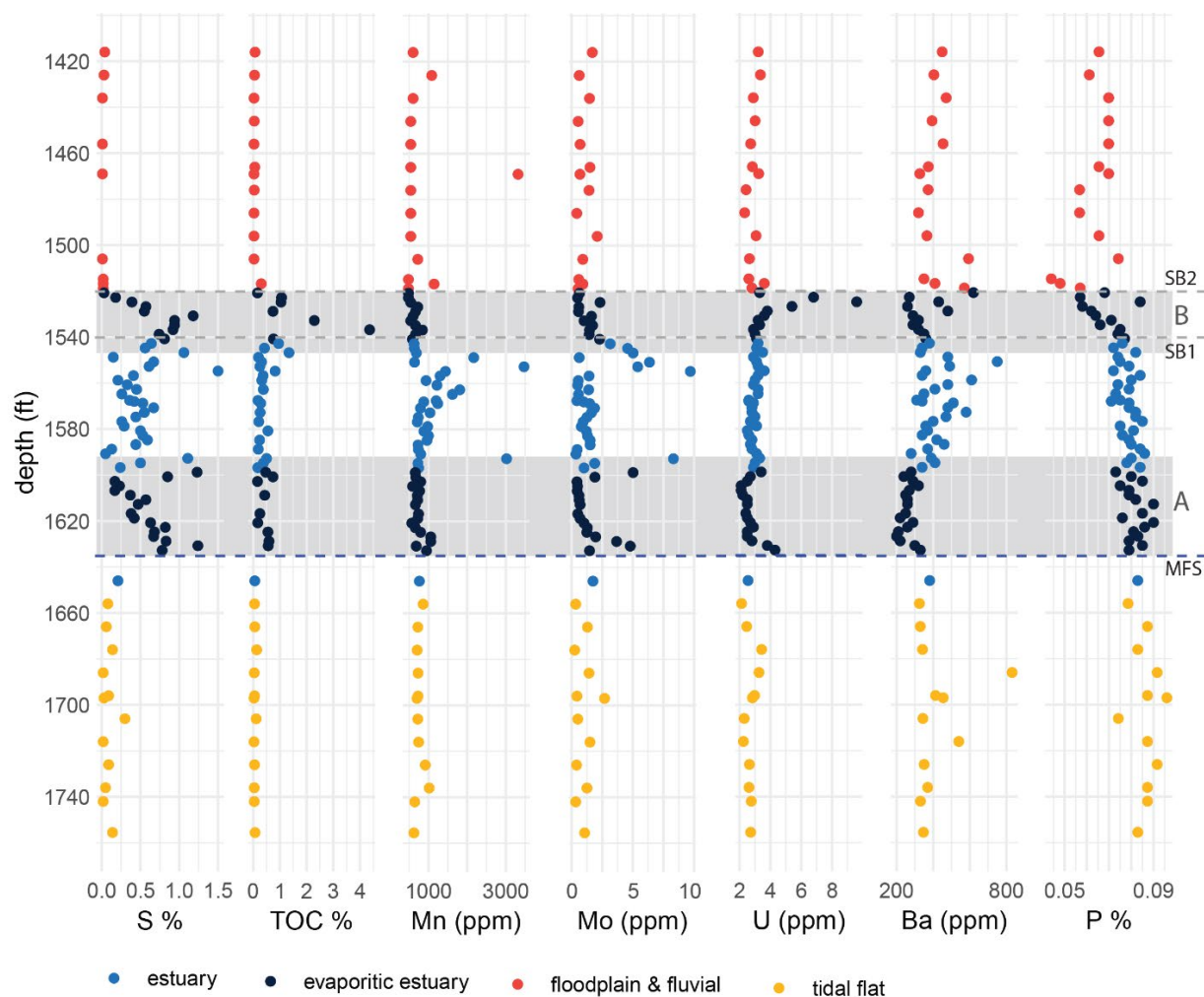
ϵ_{Nd} versus time plot for Nd isotope data from the Nonesuch and Freda Formations, Ashland Syncline, WI. Depleted mantle model is from Goldstein et al (1984) and assumes a linear depletion of the mantle from $\epsilon_{Nd} = 0$ at 4560 Myr to $\epsilon_{Nd} = +10$, MORB composition, at 0 Myr. The range of depleted mantle model ages ($\sim 1.6 - 2.0$ Ga) are determined from the intersection of the sample field with the depleted mantle model (vertical arrows). The range of ϵ_{Nd} at 1081 Ma is about -1.65 to 0.87 (horizontal arrows).

Figure 5. chemostratigraphy of detrital proxies



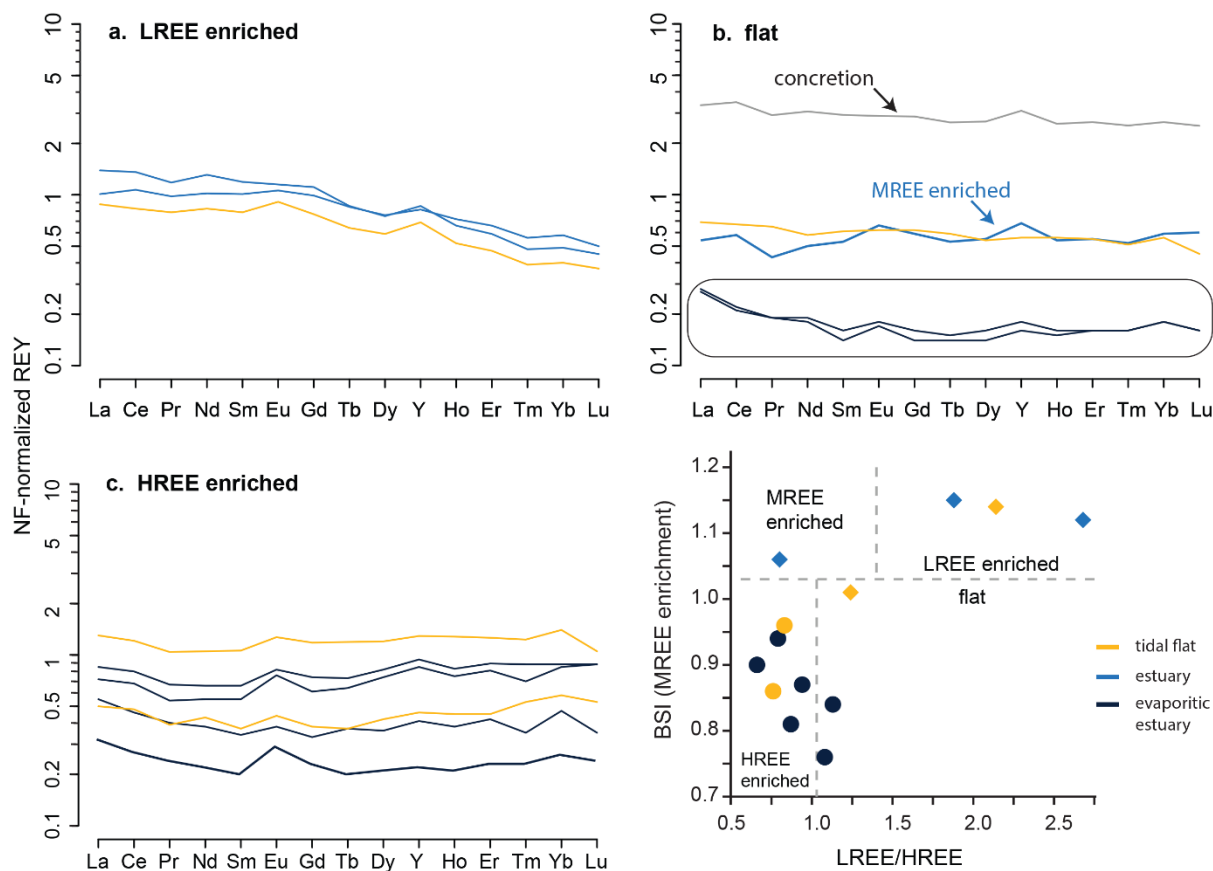
Stratigraphic plot for core WC-14 showing core log (left), detrital proxies Zr and Rb, provenance proxy $\ln(K_2O/MgO)$ and carbonate proxy Ca. Shaded intervals A and B highlight strata with best developed evidence for anoxic and euxinic shallow pore water (see Figure 6 and text for explanation). The Freda Formation overlies sequence boundary 2 (SB2). CHC: Copper Harbor Conglomerate, NF: Nonesuch Formation, Fm: Formation, MFS: maximum flooding surface, SB: sequence boundary

Figure 6. chemostratigraphy of redox and productivity proxies



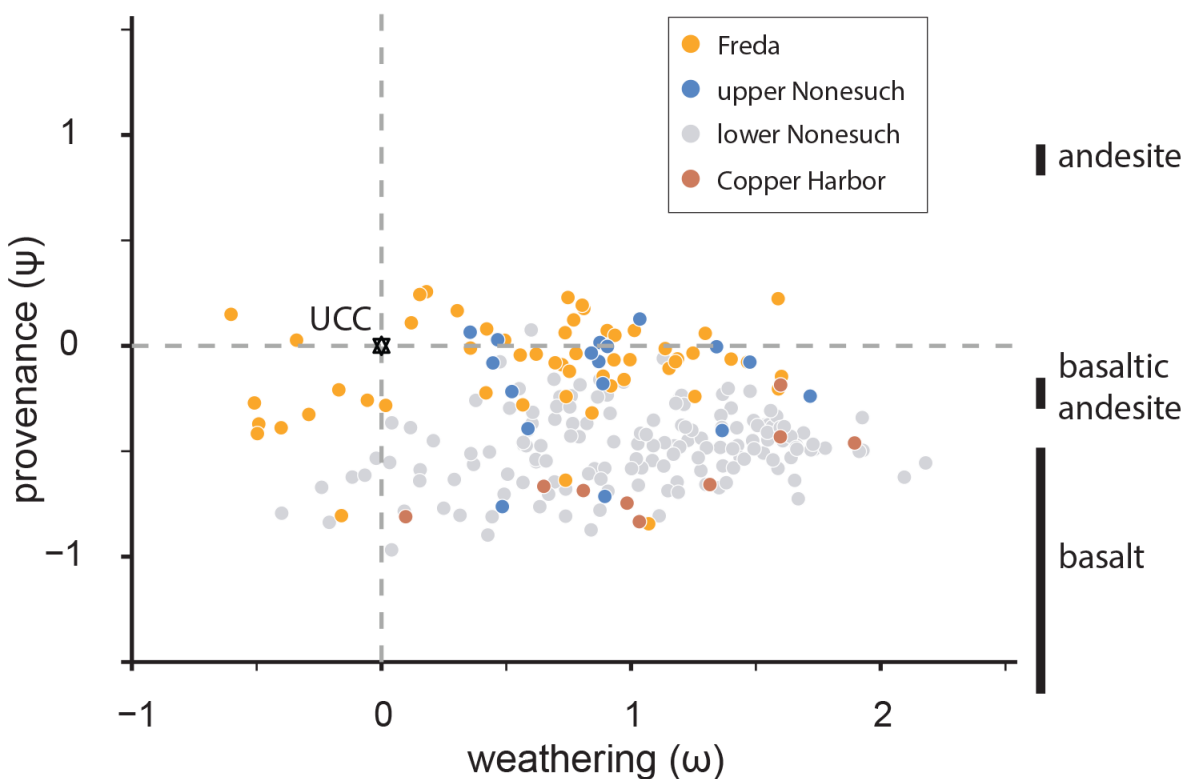
Stratigraphic plots for core WC-14 showing paleo-redox proxies S, TOC, Mo, Mn, U and paleo-productivity proxies Ba and P. Colors indicate depositional facies. Units A and B highlight strata with best developed evidence for anoxic and euxinic shallow pore water. Sequence boundary 1 (SB1) separates the lower and upper Nonesuch Formation. The Freda Formation overlies sequence boundary 2 (SB2). MFS: maximum flooding surface.

Figure 7. carbonate REY distributions



REY distributions of calcite from Nonesuch Formation MT structures and carbonate laminae normalized to the average composition of Nonesuch Formation (NF) shale. a) LREE enriched distributions; b): flat distribution; c): HREE enriched distribution. d) characterization of REY patterns by MREE enrichment (BSI) versus LREE/HREE. Circles indicate samples with components of a marine REY distribution. These samples have BSI < 1 and include all samples with HREE enriched REY distributions (c) and two samples with flat distributions (circled in b). Note that the two circled samples in (b) are from a MT crack and surrounding carbonate laminae from the same depth interval and core. Diamonds indicate samples that lack components of a marine REY distribution. Colors indicate facies.

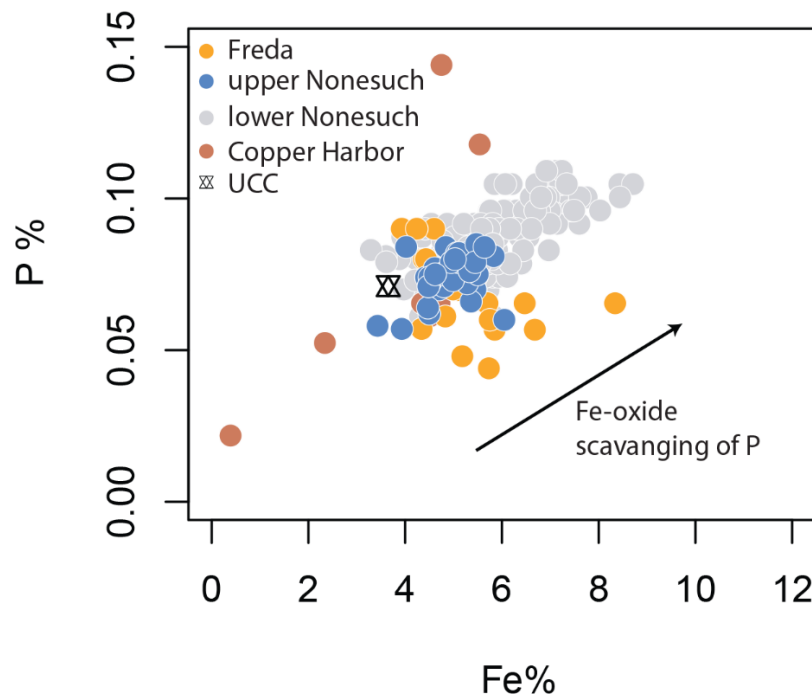
Figure 8. weathering and provenance



Variation in weathering intensity (ω) and provenance (ψ) of lower Oronto Group shale and wacke. The range of MRS igneous rocks is shown for comparison (Nicholson & Shirey, 1990, Nicholson et al., 1997, Wirth et al., 1997). Positive ω and ψ values are more weathered or felsic than UCC (Rudnick and Gao, 2003), respectively. ω values of 0 and 2 correspond to chemical index of alteration values of ~ 45 and 75, respectively (compare to supplemental Figure S7).

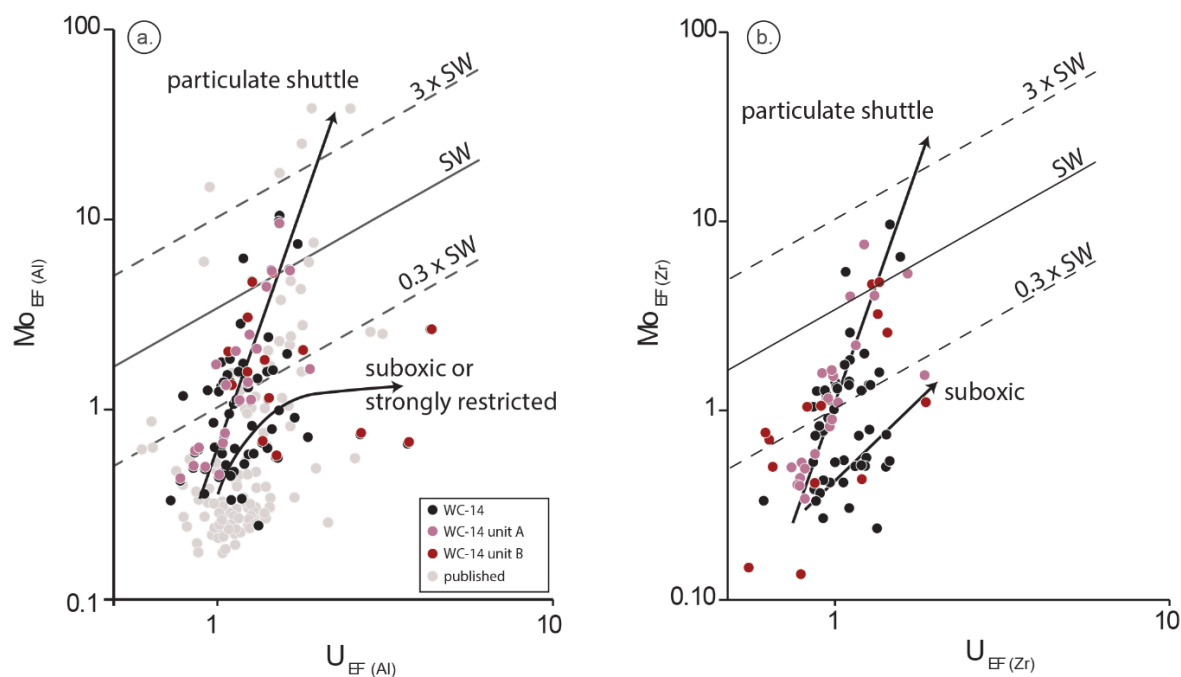
After Lipp et al. (2020).

Figure 9. relationship between Fe and P

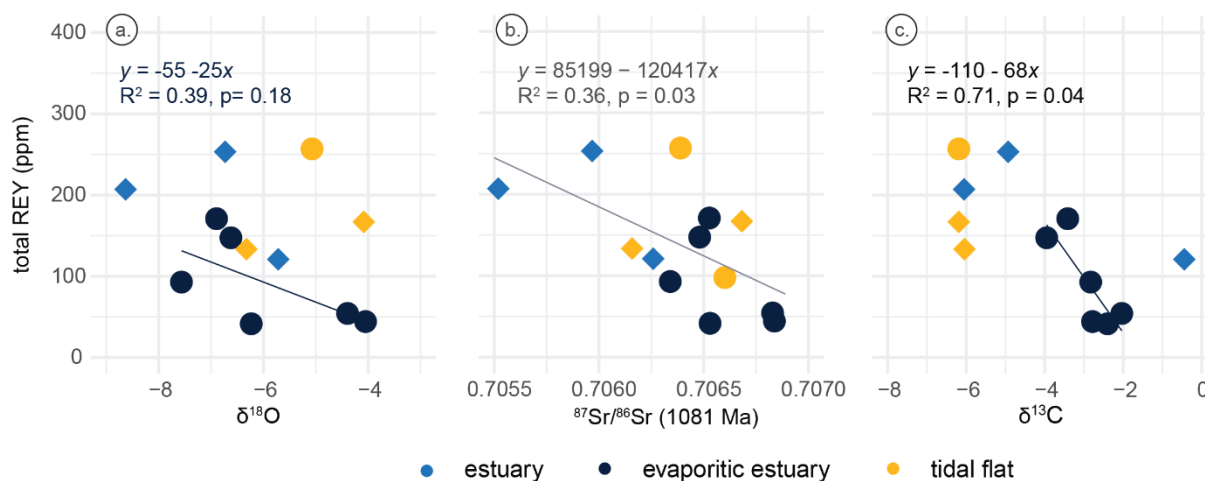


Plot showing distribution of P vs Fe by stratigraphy for shale samples. P covaries with Fe in the lower Nonesuch Formation, consistent with sourcing from basalts (black circles) and suggesting adsorption of P to Fe-oxides.

Figure 10. Mo and U enrichment

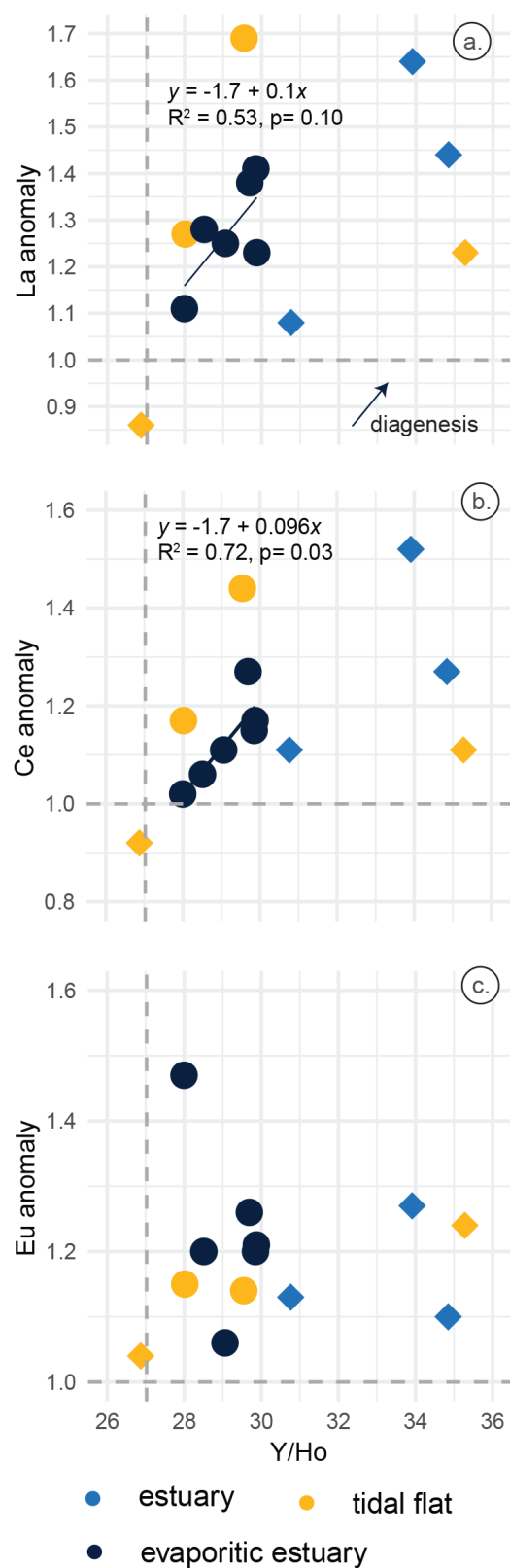


Plot of Mo versus U enrichment factors for Nonesuch Formation from core WC-14 and published values from the Ashland Syncline and Keweenaw Peninsula (Rico et al., 2019). Units A and B from core WC-14 are highlighted because these show independent evidence for development of euxinic conditions. Diagonal lines show the Mo: U ratio of modern seawater (3.4, Algeo and Tribovillard, 2009), 3 x seawater, and 0.3 x seawater. Enrichment factors are calculated as $(\text{element}/Al)_{\text{sample}} / (\text{element}/Al)_{UCC}$ (a) and $(\text{element}/Zr)_{\text{sample}} / (\text{element}/Zr)_{UCC}$ (b). Because Mo and U concentration of basalt are lower than UCC (Rudnick and Gao, 2003; Gale et al., 2013; Fang et al., 2022), Mo_{EF} and U_{EF} shown here are conservative. The arrows highlight two enrichment pathways, a dominant particulate shuttle pathway and a subordinate pathway with lesser Mo_{EF}/U_{EF} that may reflect deposition under suboxic conditions or evolving water chemistry resulting in Mo depletion in a restricted, silled basin. Modified after Algeo and Tribovillard, (2009) and Rico et al. (2019).

Figure 11. total REY versus $\delta^{18}\text{O}$ 

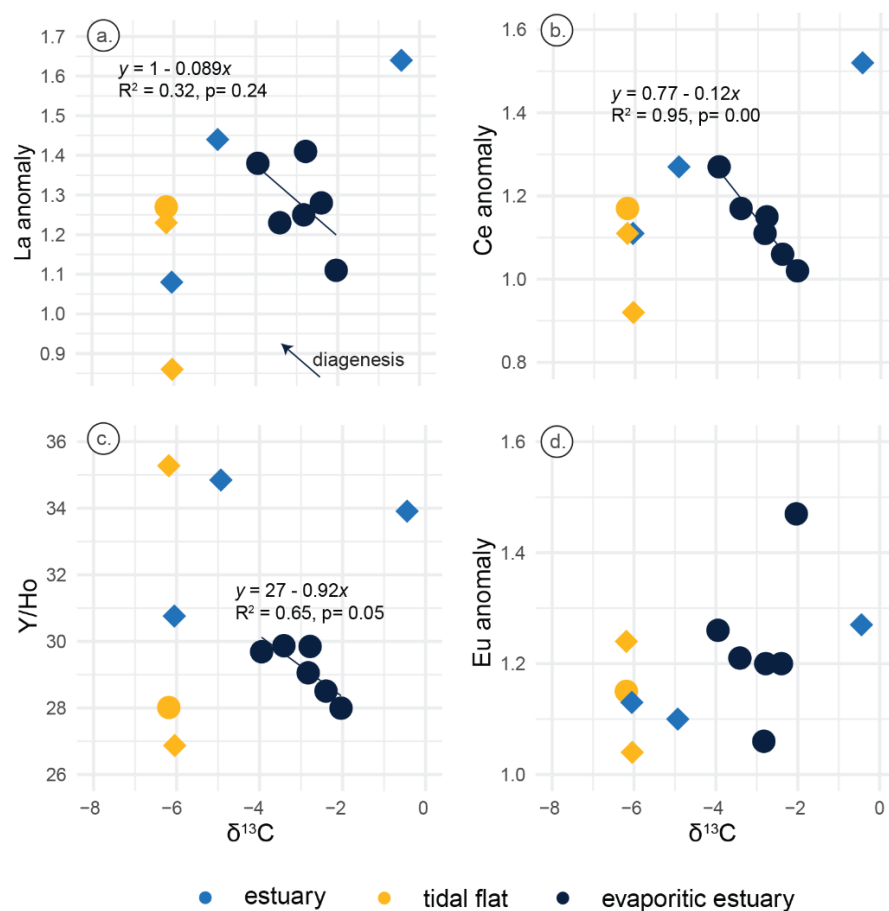
Tests of carbonate diagenetic effects on total REY abundance. a) Overall, samples are uncorrelated with $\delta^{18}\text{O}$. Best fit line for evaporitic estuary facies suggests a weak anticorrelation. b) Total REY of all facies are anticorrelated with initial $^{87}\text{Sr}/^{86}\text{Sr}$. Best fit line for all data. c) Total REY anticorrelates with $\delta^{13}\text{C}$ only for samples from the evaporitic estuary facies. Best fit line for evaporitic estuary facies.

Figure 12. REY anomalies versus Y/Ho



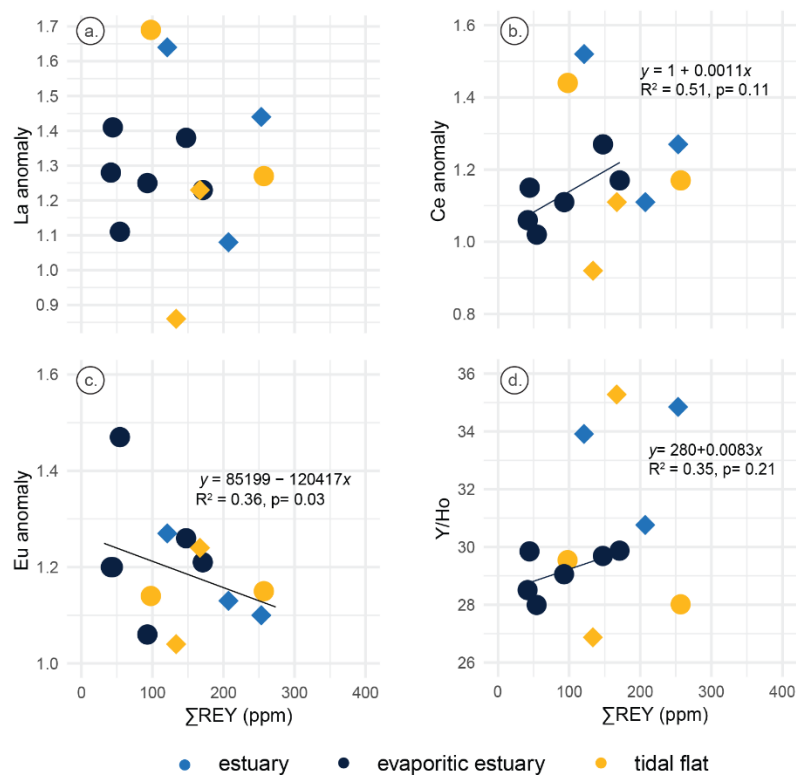
Tests for diagenetic pore water evolution or excess siliciclastic leaching during sample preparation.

Excess leaching would drive anomalies and Y/Ho towards the composition of average Nonesuch Formation shales and wackes (dashed lines). La and Ce anomalies covary with Y/Ho for samples from the evaporitic estuary facies (a, b) and there is no correlation between Eu anomalies and Y/Ho (c).

Figure 13. REY anomalies versus $\delta^{13}\text{C}$ 

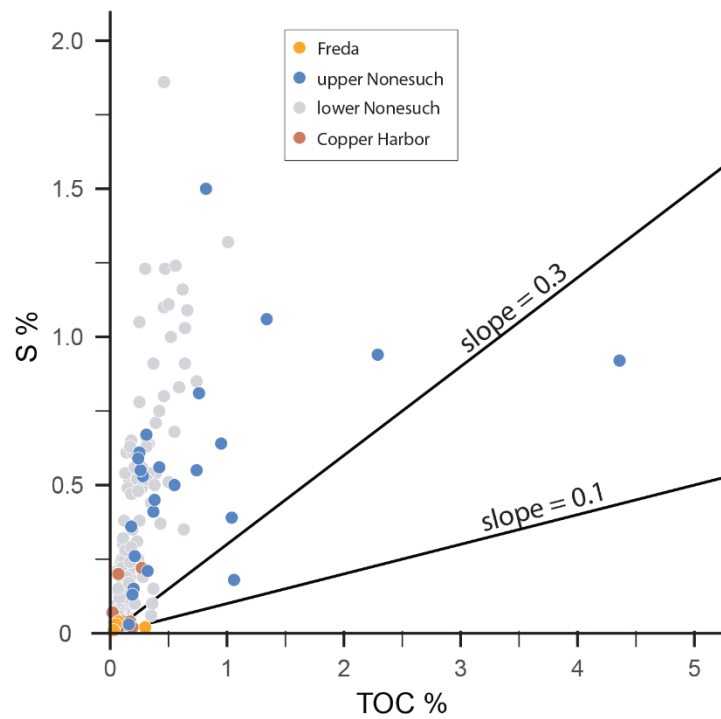
Tests of carbonate diagenetic effects on REY anomalies. La and Ce anomalies and Y/Ho anticorrelate with $\delta^{13}\text{C}$ (a, b, c) only for samples from the evaporitic estuary facies (best fit lines). The Eu anomaly shows no correlation with $\delta^{13}\text{C}$ (d). Diagenesis links to lower $\delta^{13}\text{C}$, see text for details.

Figure 14. REY anomalies versus total REY



Tests of carbonate diagenetic effects on REY anomalies. Total REY is the independent variable (x axis) and REY anomalies normalized to average Nonesuch Formation are the dependent variable (y axis). Diamonds indicate samples with BSI>1 (flat and LREE enriched distributions). Best fit lines are for the evaporitic estuary facies (b, d) or all samples (c).

Figure 15. Distribution of S and TOC



Plot showing distribution of total S versus TOC (%) by stratigraphy for shale samples of the lower Oronto Group. The diagonal lines show average S:TOC ratio of modern marine sediments (pyrite S vs TOC, 0.3, Berner and Raiswell, 1983; total S vs TOC, 0.1, Wei and Algeo, 2020).

Table 1. Sm-Nd

sample #	core	depth (ft)	Sm ppm	Nd ppm	$^{147}\text{Sm}/^{144}\text{Nd}$	2SD	$^{143}\text{Nd}/^{144}\text{Nd}$	2-SE	ϵNd	Sm/Nd	$^{143}/^{144}$ initial Nd	$\epsilon\text{Nd t}$	2-SD	T Chur Ma	Fm.
WC9-1343	WC-9	1343	6.8230	32.7111	0.1261	0.0006	0.512097	0.000006	-10.4	0.2086	0.511202	-0.72	0.28	1833	Freda
WC9-1494	WC-9	1494	6.9705	33.2882	0.1266	0.0006	0.512097	0.000005	-10.4	0.2094	0.511199	-0.80	0.28	1844	lower NF
WC9-1504	WC-9	1504	6.0297	28.9564	0.1259	0.0006	0.512093	0.000005	-10.5	0.2082	0.511200	-0.78	0.28	1836	lower NF
WC9-1685	WC-9	1685	6.6960	32.1965	0.1257	0.0006	0.512062	0.000004	-11.1	0.2080	0.511170	-1.36	0.27	1886	lower NF
WC14-1555	WC-14	1555	7.2474	35.2890	0.1241	0.0006	0.512074	0.000005	-10.8	0.2054	0.511193	-0.91	0.28	1832	lower NF
WC14-1515	WC-14	1515	7.4808	39.0707	0.1157	0.0006	0.512105	0.000005	-10.2	0.1915	0.511284	0.87	0.29	1627	Freda
WC14-1631	WC-14	1631	6.9657	31.0915	0.1354	0.0007	0.512120	0.000005	-9.9	0.2240	0.511159	-1.56	0.27	2005	lower NF
WC14-1756	WC-14	1756	9.3203	46.5498	0.1210	0.0006	0.512084	0.000007	-10.6	0.2002	0.511226	-0.27	0.30	1754	lower NF
BCR-2	ref. mat.		6.2007	27.0927	0.1384	0.0007	0.512636	0.000005	0.1	0.2289					

Calculations shown in this table are based on the ^{147}Sm decay constant of 6.54×10^{-12} (Lugmair and Marti, 1978), $^{147}\text{Sm}/^{144}\text{Nd} = 0.196$, and $^{143}\text{Nd}/^{144}\text{Nd} = 0.51263$ (Bouvier et al., 2008). $\epsilon\text{Nd t}$ 2-SD is a propagated uncertainty calculated based on equations of Ickert (2013).

Table 2. REE concentrations (ppm)

sample name	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	carbonate texture	facies
PI2-675	108.0	237.2	25.7	106.2	21.2	4.6	19.7	2.9	17.7	110.6	3.5	10.1	1.4	9.6	1.4	conc.	
DO14-3068 LAM	17.7	31.6	3.5	13.1	2.5	0.6	2.3	0.4	2.4	14.7	0.5	1.6	0.2	1.7	0.2	laminae	evaporitic estuary
WPB-21647 MT	44.8	92.4	10.4	45.4	8.6	1.8	7.6	0.9	5.0	30.8	0.9	2.2	0.3	1.8	0.3	MT	estuary
WPB2-1650	32.7	73.1	8.7	35.2	7.3	1.7	6.8	0.9	5.0	29.4	1.0	2.5	0.3	2.1	0.3	laminae	estuary
DO10-374 MT	28.3	56.9	6.9	28.8	5.8	1.4	5.3	0.7	3.9	24.6	0.7	1.8	0.2	1.4	0.2	MT	tidal flat
DO14-3071 MT	23.4	46.3	4.8	19.2	4.0	1.2	4.2	0.7	4.9	30.6	1.0	3.1	0.4	3.1	0.5	MT	evaporitic estuary
DO14-3071 LAM	27.6	54.6	5.9	22.9	4.8	1.3	5.1	0.8	5.4	33.8	1.1	3.4	0.5	3.2	0.5	laminae	evaporitic estuary
DO10-312	22.5	45.6	5.7	20.2	4.4	1.0	4.2	0.6	3.6	20.2	0.8	2.1	0.3	2.0	0.3	laminae	tidal flat
PI2-660 MT	17.4	39.3	3.8	17.5	3.8	1.1	4.1	0.6	3.6	24.2	0.7	2.1	0.3	2.2	0.3	MT	estuary
DO6-1369 MT	10.4	18.6	2.1	7.7	1.5	0.5	1.6	0.2	1.4	8.0	0.3	0.9	0.1	0.9	0.1	MT	evaporitic estuary
DO6-1365 MT	9.0	15.3	1.7	6.6	1.1	0.3	1.1	0.2	1.1	6.3	0.2	0.6	0.1	0.7	0.1	MT	evaporitic estuary
DO6-1365 LAM	8.7	14.4	1.7	6.3	1.0	0.3	0.9	0.1	1.0	5.6	0.2	0.6	0.1	0.7	0.1	laminae	evaporitic estuary
WC18-1836 MT	42.1	82.7	9.2	36.7	7.7	2.0	8.1	1.3	7.9	46.3	1.7	4.8	0.7	5.1	0.6	MT	tidal flat
WC18-1835 MT	16.1	32.9	3.4	15.1	2.7	0.7	2.6	0.4	2.8	16.4	0.6	1.7	0.3	2.1	0.3	MT	tidal flat

Uncertainties are estimated to be 10%.

APPENDIX 1: Supplemental information for Chapter 1 (Stewart et al., 2024)

Supplementary Table S1: Core and outcrop locations

Wid (WI unique ID)	LatDd	LonDd	Site Name	short_name	type
4000217	46.4160	-91.2996	Bear Creek Mining Co. WC-9	WC-9	core
4000218	46.5748	-91.4587	Bear Creek Mining Co. WC-10	WC-10	core
4000219	46.3853	-91.4379	Bear Creek Mining Co. WC-11	WC-11	core
4000220	46.5854	-91.4765	Bear Creek Mining Co. WC-12	WC-12	core
4000234	46.3820	-90.9157	Bear Creek Mining Co. WC-24	WC-24	core
4000235	46.6076	-91.4232	Bear Creek Mining Co. WC-25	WC-25	core
4000214	46.3438	-91.4720	Bear Creek Mining Co. WC-6	WC-6	core
4000216	46.4154	-91.1746	Bear Creek Mining Co. WC-8	WC-8	core

4000221	46.4239	-91.4489	Bear Creek Mining Co. WC-13	WC-13	core
4000223	46.6037	-91.3821	Bear Creek Mining Co. WC-15	WC-15	core
4000225	46.4089	-91.2381	Bear Creek Mining Co. WC-17	WC-17	core
4000230	46.4132	-91.3622	Bear Creek Mining Co. WC-22	WC-22	core
4000232	46.4132	-91.3622	Bear Creek Mining Co. WC-22 (to end)	WC-22 (to end)	core
4000209	46.3955	-91.1760	Bear Creek Mining Co. WC-1	WC-1	core
4000210	46.4015	-91.1752	Bear Creek Mining Co. WC-2	WC-2	core
4000211	46.3816	-91.0937	Bear Creek Mining Co. WC-3	WC-3	core
4000212	46.5030	-91.1191	Bear Creek Mining Co. WC-4	WC-4	core

4000226	46.4121	-91.5336	Bear Creek Mining Co. WC-18	WC-18	core
4000227	46.3979	-91.3694	Bear Creek Mining Co. WC-19	WC-19	core
4000228	46.3496	-91.4448	Bear Creek Mining Co. WC-20	WC-20	core
4000229	46.3317	-91.4846	Bear Creek Mining Co. WC-21	WC-21	core
4000213	46.3770	-91.3412	Bear Creek Mining Co. WC-5	WC-5	core
4000215	46.4081	-91.1428	Bear Creek Mining Co. WC-7	WC-7	core
4000222	46.5935	-91.5129	Bear Creek Mining Co. WC-14	WC-14	core
4000224	46.3951	-91.1369	Bear Creek Mining Co. WC-16	WC-16	core

4000231	46.3853	-91.4381	Bear Creek Mining Co. WC-11 (to end)	WC-11 (to end)	core
4000233	46.3505	-90.9903	Bear Creek Mining Co. WC-23	WC-23	core
7000772	46.0573	-92.2193	Bear Creek Mining Co. BU-2	BU-2	core
7000771	46.0709	-92.0646	Bear Creek Mining Co. BU-1	BU-1	core
16000454	46.4152	-91.5960	Bear Creek Mining Co. DO-8	DO-8	core
16000455	46.4366	-91.6768	Bear Creek Mining Co. DO-9	DO-9	core
16000456	46.5149	-91.7351	Bear Creek Mining Co. DO-10	DO-10	core
16000457	46.3818	-91.7482	Bear Creek Mining Co. DO-11	DO-11	core
16000449	46.2431	-91.6695	Bear Creek Mining Co. DO-3	DO-3	core

16000451	46.5341	-91.6604	Bear Creek Mining Co. DO-5	DO-5	core
16000453	46.3931	-91.6085	Bear Creek Mining Co. DO-7	DO-7	core
16000458	46.4777	-91.7174	Bear Creek Mining Co. DO-12	DO-12	core
16000460	46.4779	-91.5876	Bear Creek Mining Co. DO-14	DO-14	core
16000447	46.3113	-91.7306	Bear Creek Mining Co. DO-1	DO-1	core
16000448	46.3423	-91.7195	Bear Creek Mining Co. DO-2	DO-2	core
16000450	46.3546	-91.5957	Bear Creek Mining Co. DO-4	DO-4	core
16000452	46.5568	-91.6120	Bear Creek Mining Co. DO-6	DO-6	core
16000459	46.4771	-91.6491	Bear Creek Mining Co. DO-13	DO-13	core
66000091	46.1235	-91.7715	Bear Creek Mining Co. WA-1	WA-1	core

66000092	46.1228	-91.8159	Bear Creek Mining Co. WA-2	WA-2	core
66000093	46.1471	-91.8290	Bear Creek Mining Co. WA-3	WA-3	core
66000094	46.1446	-91.8751	Bear Creek Mining Co. WA-4	WA-4	core
66000095	46.1536	-91.9059	Bear Creek Mining Co. WA-5	WA-5	core
66000096	46.1554	-91.9517	Bear Creek Mining Co. WA-6	WA-6	core
66000097	46.1432	-91.6780	Bear Creek Mining Co. WA-7	WA-7	core
N/A	46.5380	-91.1052	Terra-Patrick # 7-22	Terra-Patrick	geophysical logs and cuttings
N/A	46.6754	-89.9847	Bear Creek Mining Co. PC-9	PC-9	core
N/A	46.6755	-89.9799	Bear Creek Mining Co. PC-10	PC-10	core
N/A	46.6755	-89.9888	Bear Creek Mining Co. PC-8	PC-8	core

N/A	46.6785	-89.9887	Bear Creek Mining Co. PC-7	PC-7	core
N/A	46.6786	-89.9845	Bear Creek Mining Co. PC-6	PC-6	core
N/A	46.6786	-89.9798	Bear Creek Mining Co. PC-5	PC-5	core
N/A	46.6783	-89.9749	Bear Creek Mining Co. PC-1	PC-1	core
N/A	46.6788	-89.9702	Bear Creek Mining Co. PC-2	PC-2	core
N/A	46.6755	-89.9704	Bear Creek Mining Co. PC-3	PC-3	core
N/A	46.6755	-89.9751	Bear Creek Mining Co. PC-4	PC-4	core
N/A	46.6722	-89.9779	Bear Creek Mining Co. PC-13	PC-13	core
N/A	46.6722	-89.9739	Bear Creek Mining Co. PC-12	PC-12	core
N/A	46.6693	-89.9789	Bear Creek Mining Co. PC-16	PC-16	core

N/A	46.6690	-89.9741	Bear Creek Mining Co. PC-15	PC-15	core
N/A	46.6689	-89.9697	Bear Creek Mining Co. PC-14	PC-14	core
N/A	46.6664	-89.9697	Bear Creek Mining Co. PC-21	PC-21	core
N/A	46.6675	-89.9742	Bear Creek Mining Co. PC-20	PC-20	core
N/A	46.6684	-89.9790	Bear Creek Mining Co. PC-23	PC-23	core
N/A	46.6688	-89.9836	Bear Creek Mining Co. PC-19	PC-19	core
N/A	46.6703	-89.9887	Bear Creek Mining Co. PC-22	PC-22	core
N/A	46.6723	-89.9888	Bear Creek Mining Co. PC-18	PC-18	core
N/A	46.6719	-89.9839	Bear Creek Mining Co. PC-17	PC-17	core
N/A	46.6722	-89.9702	Bear Creek Mining Co. PC-11	PC-11	core

N/A	46.6722	-89.9444	Bear Creek Mining Co. PI-2	PI-2	core
N/A	46.6672	-89.9451	Bear Creek Mining Co. PI-1	PI-1	core
N/A	46.6776	-89.8047	Bear Creek Mining Co. WPB-6	WPB-6	core
N/A	46.6633	-89.7574	Bear Creek Mining Co. WPB-2	WPB-2	core
N/A	46.6524	-89.7467	Bear Creek Mining Co. WPB-4	WPB-4	core
N/A	46.6487	-89.7790	Bear Creek Mining Co. WPB-5	WPB-5	core
N/A	46.6488	-89.7683	Bear Creek Mining Co. WPB-1	WPB-1	core
N/A	46.6525	-89.7948	Bear Creek Mining Co. WPB-9	WPB-9	core

N/A	46.6562	-89.7841	Bear Creek Mining Co. WPB-3	WPB-3	core
N/A	46.6633	-89.7843	Bear Creek Mining Co. WPB-8	WPB-8	core
N/A	46.6634	-89.7947	Bear Creek Mining Co. WPB-7	WPB-7	core
N/A	46.6415	-89.8286	possible Bear Creek core? 25-11	25-11	core
N/A	47.2965	-88.4833	JBV-002	JBV-002	core
N/A	46.6742	-89.9770	Copperwood-17-190	CW-17-190	core
N/A	46.4590	-90.5259	Potato River Falls County Park	N/A	measured section
N/A	46.3760	-90.6399	Copper Falls State Park	N/A	measured section
N/A	46.3885	-90.6407	Copper Falls State Park north (Freda Fm. exposure)	N/A	outcrops

N/A	46.8251	-89.5701	Big Iron River	N/A	measured section
N/A	46.5241	-90.4199	Parker Creek	N/A	measured section
N/A	46.6614	-89.9420	Presque Isle River South	N/A	measured section
N/A	46.7083	-89.9721	Presque Isle River in park	N/A	outcrops
N/A	46.6546	-90.0457	Black River Harbor	N/A	outcrops

Supplementary Table S2: Compiled microfossil and core data

core	depth (m)	name	description (Strother & Wellman, 2016 or Wellman and Strother, 2015)	Formation (this publication)	Lithofacies (this publication)	reference	notes from Strother and Wellman (2016) or Wellman and Strother (2015)
PC-1	138	sphaeromorph	unnamed sphaeromorph with included organic blebs	upper Nonesuch	C: tidal flat	Wellman and Strother (2015)	
PC-1	138	sphaeromorph	sphaeromorph with a striate wall structure similar to that of <i>Valeria</i>	upper Nonesuch	C: tidal flat	Wellman and Strother (2015)	
PC-1	138	ellipsoidal form	unnamed ellipsoidal form covered in a microreticulate wall	upper Nonesuch	C: tidal flat	Wellman and Strother (2015)	
WPB-4	105	<i>Simia</i> sp.		upper Nonesuch	C: tidal flat	Wellman and Strother (2015)	
PC-1	93	sphaeromorph	unnamed discoidal sphaeromorph possessing a medial split	upper Nonesuch or within upper Nonesuch to Freda transition zone	F: floodplain or tidal flat	Wellman and Strother (2015)	sample NON09-3B (this sample includes paratype for <i>Eohalothece lacustrina</i>)
WPB-4	83.5	<i>Valeria lophostriata</i>		upper Nonesuch	B & C: nearshore sandstone and tidal flat	Wellman and Strother (2015)	
WPB-4	54.5	<i>Symplassophaeridium</i> sp.	cluster of spherical cells	upper Nonesuch or within upper Nonesuch to Freda transition zone	F: tidal flat or floodplain	Wellman and Strother (2015)	
WPB-4	105	protist	unnamed protistian microfossil with longitudinal folds, a basal thickening, and acuminate apex	lower part of upper Nonesuch?	C: tidal flat	Wellman and Strother (2015)	
WPB-4	50	unnamed	unnamed chain of large ellipsoidal cells, which is distinct from <i>Archaeoellipsoides</i> in the sense of Tomitani et al (2006)	upper Nonesuch or within upper Nonesuch to Freda transition zone	F: tidal flat or flood plain with soil horizons	Wellman and Strother (2015)	

PC-1	187	filament	large filament with tapered ends	upper Nonesuch	C: tidal flat	Wellman and Strother (2015)	
PC-1	187	unnamed	unnamed pseudo-branching structure exhibiting a modular arrangement of attached cells (?)	upper Nonesuch	C: tidal flat	Wellman and Strother (2015)	
PC-1	187	unnamed	pseudo-branching form, each cell possessing an open linear extrusion	upper Nonesuch	C: tidal flat	Wellman and Strother (2015)	
PC-1	138	unnamed	somewhat irregular linear chain of cells with associated organic matter, distinct from <i>Chorogloeaopsis</i> Maithy, 1975	upper Nonesuch	C: tidal flat	Wellman and Strother (2015)	
WPB-4	136	ellipsoidal form	large ellipsoidal cell pair, distinct from typical <i>Archaeoellipsoides</i>	lower Nonesuch	D: estuary, carbonate laminite or laminated siltstone-clay	Wellman and Strother (2015)	
WPB-1	92.5	possible cyanobacteria	small elliptical cells, possibly cyanobacteria in close association with sheaths derived from a microbial mat rip-up	lower Nonesuch	D: estuary, carbonate laminite or laminated siltstone-clay	Wellman and Strother (2015)	
WPB-1	92.5	unnamed	unnamed linear tapered form	lower Nonesuch	D: estuary, carbonate laminite or laminated siltstone-clay	Wellman and Strother (2015)	

PC-1	93	<i>Eohalotheca lacustrina</i> sp. nov.	bacteria; species typically occurs in clusters of what appear to be genetically related populations of cells; subelliptical cells with some somewhat tapered ends; probable cyanobacteria;	upper Nonesuch or within upper Nonesuch to Freda transition zone	F: floodplain or tidal flat	Strother and Wellman 2016	sample NON09-3B was located near the top of the section, 19.8 m below the contact with the overlying Freda Sandstone. This species observed in cores PC-1, PI-2, WPB-2, WPB-5, WPB-7, WPB-8. It occurs in samples of Nonesuch Formation collected from outcrop below Manido Falls on a dry branch of the Presque Isle River (46°42.4980N 89°58.3250W)
WPB-5	89	<i>L. ternata</i> and <i>lacustrina</i>	associated with amorphous organic matter, which is a possible biofilm fragment	upper Nonesuch or within upper Nonesuch to Freda transition zone	F: floodplain or tidal flat	Strother and Wellman 2016	sample NON12-22
PC-1	93	<i>L. ternata</i> and <i>E. lacustrina</i> paratype	associated with amorphous organic matter, possibly the remains of biofilm	upper Nonesuch or within upper Nonesuch to Freda transition zone	F: floodplain or tidal flat	Strother and Wellman 2016	sample NON09-3B (this sample includes paratype for <i>Eohalotheca lacustrina</i>)
PC-1	93	<i>Eohalotheca lacustrina</i> (paratype)	large colony with irregular globular overall form	upper Nonesuch or within upper Nonesuch to Freda transition zone	F: floodplain or tidal flat	Strother and Wellman 2016	sample NON09-3B (this sample includes paratype for <i>Eohalotheca lacustrina</i>)
PC-1	93	<i>Eohalotheca lacustrina</i> (paratype)	large colony with ovoid overall form	upper Nonesuch or within upper Nonesuch to Freda transition zone	F: floodplain or tidal flat	Strother and Wellman 2016	sample NON09-3B (this sample includes paratype for <i>Eohalotheca lacustrina</i>)

WPB-4	54.5	<i>Eohalotheca lacustrina</i>	large colony displaying clathrate form similar to that found in planktonic freshwater species of <i>Microcystis</i> today	upper Nonesuch or within upper Nonesuch to Freda transition zone	F: floodplain or tidal flat	Strother and Wellman 2016	sample NON09-24B
WPB-4	59.5	<i>Eohalotheca lacustrina</i>	distributed colony adhering to flat organic fragment	upper Nonesuch	C: tidal flat	Strother and Wellman 2016	sample NON09-25B
WPB-4	164	<i>Eohalotheca lacustrina</i>	oddly shaped fragment comprised of amorphous organic matter with embedded population of <i>E. lacustrina</i>	lower Nonesuch	C: tidal flat	Strother and Wellman 2016	sample NON09-34C
PC-1	242	<i>acritarchs</i>	contains a well-preserved acritarch assemblage	lower Nonesuch	D: estuary	Strother and Wellman 2016	sample NON09-18 occurs 31m (102 feet) above the CHC contact
outcrop along Presque Isle River	46° 42.498	<i>Eohalotheca lacustrina</i>		upper Nonesuch	B: low-angle cross-bedded nearshore sandstone and associated siltstone-shale.	Strother and Wellman 2016	sample collected on Presque Isle just below Manabehzo Falls along Presque Isle River near Lake Superior

Appendix 2: Supplementary information for chapter 2

SAMPLE PREPARATION

Carbon and Oxygen Isotope Analysis

University of Michigan Stable Isotope Laboratory

A subset of samples was analyzed at the University of Michigan Stable Isotope Laboratory, Ann Arbor, Michigan. Carbonate samples weighing a minimum of 10 micrograms were transferred to individual borosilicate reaction vessels and reacted at $77^{\circ} \pm 1^{\circ}\text{C}$ with 4 drops of anhydrous phosphoric acid for 8 minutes in a Finnigan MAT Kiel IV preparation device coupled directly to the inlet of a Finnigan MAT 253 triple collector isotope ratio mass spectrometer. ^{17}O -corrected data are corrected for acid fractionation and source mixing by calibration to a best-fit regression line defined by two NBS standards, NBS 18 and NBS 19. Data are reported in permil (‰) notation relative to VPDB. Precision and accuracy of data were monitored through analysis of at least four powdered carbonate reference materials. Measured precision was better than 0.1 ‰ for both carbon and oxygen isotope compositions.

Scottish Universities Environmental Research Centre

A subset of analyses for carbonate carbon and oxygen isotopes were performed at the Scottish Universities Environmental Research Centre, East Kilbride, Scotland, using an Analytical Precision 2003 continuous flow triple collector mass spectrometer coupled to an individual acid bath system carbonate injector. Samples were cut and cleaned and micro-drilled to obtain about 1 mg of carbonate powder that was placed in an Exetainer and dissolved using supersaturated 103% phosphoric acid. Following methods modified slightly from McCrea (1950), the resulting carbon dioxide was purified and passed into the mass spectrometer. Each Exetainer was sampled four times, bracketed by pulses of reference carbon dioxide of known isotopic composition, and a laboratory reference material carbonate (MAB marble from Carrara, Italy) bracketed every five unknowns. Oxygen isotope fractionation factors between carbonate and carbon dioxide were taken from Rosenbaum and Sheppard (1986) and calibrated to internationally accepted standards through analysis of NBS 19. Precision at 1σ is better than 0.2‰ for both oxygen and carbon, which are reported in delta per mil notation relative to Vienna Pee Dee belemnite (V-PDB).

Sample Pre-Leach and Leaching For Rb-Sr Isotope and Major- And Trace-Element Analysis

Carbonate vein samples WC2 781 and WC2 781_r1 were leached in 1 M acetic acid. For all other samples, ten- to thirty-mg aliquots of powdered sample were treated with methanol and ammonium acetate pre-leaches and then leached with 0.5 M acetic acid following Gao et al. (1996), Bailey et al. (2000), and McArthur et al. (2006).

Methanol pre-leach

Sample powders were agitated three times in 50% methanol solution to suspend and remove insoluble, high-Rb/Sr clay. Sample powders were suspended in the methanol solution using a vortex mixer for 15 seconds, then placed in an ultrasonic bath for 15 minutes, and then mixed in the vortex mixer again for 15 seconds. The samples were allowed to settle for 30 seconds to 1 minute and then the methanol solution was removed by pipetting. This process was repeated three times, and then the sample powders were dried and weighed.

Ammonium acetate pre-leach

Next powders were treated with ammonium acetate to exchange Sr not structurally bound in carbonate with ammonium. Sample powders were first suspended in 1 mL of 1 M ammonium acetate solution using a vortex mixer for 15 to 30 seconds, then placed in an ultrasonic bath for three hours, then

mixed a second time using a vortex mixer for 15 to 30 seconds and lastly centrifuged for 5 minutes. After centrifuging, the ammonium acetate waste was removed. The ammonium acetate wash was repeated three times.

After treating with ammonium acetate, the samples were washed in ultrapure (18.2 M Ω) water, dried, and weighed. Samples were first suspended in 1 mL of ultrapure water for 15 to 30 seconds using a vortex mixer, then placed in an ultrasonic bath for one hour, then mixed again using a vortex mixer for 15 to 30 seconds, and lastly centrifuged for 5 minutes. The waste was removed by decanting or with a pipette. This step was repeated three times, and then the sample powders were dried and weighed.

Acetic acid leach

Powders were leached in acetic acid to dissolve the carbonate fraction. Powders were suspended in 1 mL of 0.5 M acetic acid using a vortex mixer for 15 seconds, placed in an ultrasonic bath for 30 minutes, mixed using the vortex mixer for 15 seconds, again placed in an ultrasonic bath for 30 minutes followed by mixing in a vortex mixer for 15 seconds, and lastly centrifuged for three minutes to separate the dissolved carbonate from insoluble residue. The leached liquid was pipetted into a clean 7 mL beaker, taking care to avoid the meniscus while pipetting.

Next, the residue was washed two times in water. One mL of ultrapure (18.2 M Ω) water was added to the residue and any remaining acetic acid leach. This mixture was agitated in a vortex mixer for 15 seconds and then centrifuged for three minutes. The liquid was carefully pipetted into the beaker avoiding any solid particles. This water wash step was repeated a second time so that the sample beaker contained 1 mL of acetic acid leach and 2 mL of water wash. The residues were dried, and the mass of the leached material was determined by subtraction. A mixed ^{87}Rb - ^{84}Sr enriched tracer solution was added to the leached sample aliquot reserved for Rb-Sr isotope analysis to determine accurate Rb and Sr concentrations by isotope dilution mass spectrometry.

Column Chemistry

Samples were evaporated and redissolved in 4 M HNO_3 in preparation for column chemistry. Strontium was separated from the sample solution utilizing ~ 200 μL of Eichrom Sr-spec resin (50-100 μm). After the sample was loaded on the column, the matrix including Rb was separated by adding 4 M HNO_3 . Sr was then eluted using 2% HNO_3 .

The Rb split was then dried, redissolved in 1 M HNO_3 , and loaded onto ~ 750 μL columns containing Eichrom DGA resin (normal, 50-100 μm). DGA resin was used for its effectiveness separating any remaining Sr and Ca present in the sample as those elements are retained on the resin while Rb was eluted from the column in 1 M HNO_3 . Rb and Sr cuts were then evaporated in preparation for mass spectrometry analysis.

SR and RB ISOTOPE ANALYSIS

Strontium was analyzed on a Micromass Sector 54 thermal ionization mass spectrometer (TIMS) in the ICP-TIMS lab at the University of Wisconsin-Madison. Samples were dissolved in dilute HCl and ~ 100 -200 ng Sr was loaded onto outgassed rhenium filaments with a TaF solution (Charlier et al., 2006) and dilute H_3PO_4 . Samples were analyzed in a three-step multi-dynamic method with 10 cycles per block and 12 total blocks for a total of 120 dynamic ratios while maintaining an $\sim 3 \times 10^{-11}$ A ^{88}Sr signal. An exponential correction was applied to correct for instrumental mass bias using an assumed $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$. Rubidium interference was monitored at mass 85 and data rejected if the magnitude of the correction was greater than the correction applied during the analysis of the standard which contained no Rb. Data was reduced and the average and 2SD were calculated using the Tripoli program. The standard SRM987 was loaded at two different concentrations (42 ng Sr and 210 ng Sr) and repeatedly analyzed over the duration of analytical sessions yielding an $^{87}\text{Sr}/^{86}\text{Sr}$ (0.710267 ± 0.000018 2SD, $n = 83$)

consistent with the long-term value for the lab. Three aliquots of USGS EN-1 carbonate standard were dissolved in dilute HCl and processed in the same manner as samples and yielded an average $^{87}\text{Sr}/^{86}\text{Sr}$ (0.709202 ± 0.000020 2SD, $n = 34$) also consistent with the long-term values for the lab. Strontium blanks were monitored during each session and ranged from 19.0-53.3 pg Sr with a mean of 29.6 pg. No blank correction was applied. For samples, the quoted uncertainty on the $^{87}\text{Sr}/^{86}\text{Sr}$ is the greater value between the internal precision of the measurement or the 2SD reproducibility of the SRM987 standard.

Rubidium was analyzed on a Nu Plasma II multi-collector thermal ionization mass spectrometer (MC-ICP-MS) in the ICP-TIMS lab at the University of Wisconsin Madison. Samples were dissolved in dilute nitric acid and diluted to approximately 20 ppb Rb. Sample solutions were introduced to the mass spectrometer via an CETAC ASX-112FR autosampler outfitted with a Savillex 50 $\mu\text{l}/\text{minute}$ self-aspirating nebulizer and introduced via a CETAC Airdus II desolvating nebulizer. SRM 984 was used as the bracketing standard and analyzed every 2-3 unknowns and a correction factor was applied to all unknown samples based on the natural $^{87}\text{Rb}/^{85}\text{Rb}$ of 0.3855. A zirconium standard solution (sourced from High Purity Standards or HPS) was added to all standard and sample solutions and the stable $^{90}\text{Zr}/^{91}\text{Zr} = 4.5874$ was used to correct for instrumental mass bias using an exponential correction following the method of Waight et al. (2002). Measurements consisted of 40 cycles with a 5 sec integration period. All ion signals were collected in faraday collectors. A second Rb solution (HPS) was used as a quality control standard to check analysis method accuracy. Strontium interference was monitored at mass 88 and a correction was applied to mass 87 based on the measured Sr isotopic composition of the sample. The magnitude of this correction is generally smaller than the uncertainty of the measurement though to ensure this correction produced accurate results a second rubidium standard was doped with 0.5 ppb SRM 987 Sr. This doped solution returned average $^{87}\text{Rb}/^{85}\text{Rb}$ values in agreement with the non-doped standard.

ICPMS ELEMENT ANALYSIS

Aliquots of the same leached carbonate that was processed for Rb-Sr isotope analysis were analyzed on an Agilent 8900 ICPMS in the ICP-TIMS lab at the University of Wisconsin Madison. Samples were dissolved in dilute HNO_3 and introduced via micromist nebulizer. Analysis was performed in both no gas and O_2 MS/MS modes and consisted of 25 replicates with 25 sweeps per replicate and a three-point defined Q2 peak pattern. Indium was used as the internal standard. A multi-element solution (HPS) was used as the calibration standard. Concentrations were calculated using the Agilent MassHunter software. The method was checked for accuracy utilizing two in-house carbonate synthetic solutions and three dissolved carbonate rock standards from the China National Analysis Center for Iron and Steel. Uncertainty is estimated based on the accuracy of those reference solutions.

EPMA ELEMENT ANALYSIS

Chemical composition was measured from analysis of carbon-coated thin sections using a Cameca SX-Five Field Emission Electron Probe Microanalyzer (FE-EPMA) at UW-Madison. Spot measurements were acquired using 15 kV accelerating voltage and 50 nA beam current with 10 μm defocused beam. Five Wavelength Dispersive Spectrometers (WDS) were used to measure Mg, Mn, Fe, and Sr (Sr was measured on two spectrometers and aggregated). A Thermo Ultra EDS detector was used to analyze Ca, which was measured with reduced aperture to maintain detector deadtime less than 10%. A Mean Atomic Number (MAN) background correction with 300 s counting time was used for Mg, Mn, and Fe, while an off-peak background correction with 160 s counting on-peak and 80 s on high and low backgrounds was used for Sr, which yielded average detection limits of 10 ppm Mg, 70 ppm Mn, 76 ppm Fe, and 53 ppm Sr. A Time-Dependent Intensity correction was applied to account for effects of beam damage which was observed to be substantial at these conditions. Carbonate standards calcite (NMNH 136321), dolomite (NMNH R10057), siderite (NMNH R2460), strontianite (NMNH R10065) (Jarosewich et al. 1983; 1987), and rhodochrosite were used for peaking and calibration. High purity synthetic oxides

and metals were used as MAN standards. Calcite (Callendar) was used as a secondary standard. The composition of eight samples was analyzed with four closely spaced measurements from three different locations.

EPMA spot measurements of Mg, Mn, Fe, and Sr contents yielded intra-grain variability that was substantially higher than the measurement precision, making it difficult to determine an average value for each grain. For this reason, and because of differences in the sample size of leached carbonate and microbeam spot analyses, the directional trends of elemental ratios determined from ICPMS and EPMA are meaningful, though only the ratios from ICPMS and TIMS are verifiably accurate.

ESTIMATING INGROWTH OF ^{87}Sr IN WEATHERED BASALT

Li et al. (1995) document early diagenetic mixed illite-smectite and chlorite matrix clay in the Nonesuch Formation, which they interpret as developing during earliest weathering after eruption of the basalts. Assuming the Nonesuch Formation detritus is primarily sourced from the immediately underlying basalts, which erupted between ca. 1093 and 1085 Ma (Fairchild et al., 2017; Swanson-Hysell et al., 2019) and the clay matrix largely developed by deposition of the Nonesuch Formation at ca. 1081, the duration of radiogenic strontium ingrowth within the clays is constrained between 12 and 4 Ma. Assuming typical $^{87}\text{Rb}/^{86}\text{Sr}$ of ~ 10 to 50 for clays (e.g. Gorokhov et al., 1994; Clauer et al., 1997; Kirsimäe and Jorgensen, 2000), accumulation of radiogenic ^{87}Sr in diagenetic clays could increase the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the Nonesuch detrital sediments from ~0.703 to ~0.706. Therefore, the lowest initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of ~0.705 to ~0.706 recorded in diagenetically altered Nonesuch carbonates could be explained by exchange with relatively high-Rb/Sr clays that developed from weathering of the basalts. The $^{87}\text{Sr}/^{86}\text{Sr}$ of these clays requires that carbonate diagenesis occurred on this same timescale.

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FIGURES and TABLES

Table S1. Sample locations

Sample name	sample type	depth core (ft), outcrop (m)	WID (WI unique ID)	LatDd	LonDd	Site Name	facies
WPB7-1250	core	1250	N/A	46.6634	-89.7947	Bear Creek Mining Co. WPB-7	estuary
WPB2-1650	core	1650	N/A	46.6633	-89.7574	Bear Creek Mining Co. WPB-2	estuary
WPB-2-1647 MT	core	1647	N/A	46.6633	-89.7574	Bear Creek Mining Co. WPB-3	estuary
WC9-1669	core	1669	4000217	46.4160	-91.2996	Bear Creek Mining Co. WC-9	tidal flat
WC9-1651B	core	1651	4000217	46.4160	-91.2996	Bear Creek Mining Co. WC-9	tidal flat
WC9-1570	core	1570	4000217	46.4160	-91.2996	Bear Creek Mining Co. WC-9	estuary
WC9-1407	core	1407	4000217	46.4160	-91.2996	Bear Creek Mining Co. WC-9	tidal flat
WC2 781_r1	core	781	4000210	46.4015	-91.1752	Bear Creek Mining Co. WC-2	estuary
WC2 781	core	781	4000210	46.4015	-91.1752	Bear Creek Mining Co. WC-2	estuary
WC-18-1836 MT	core	1836	4000226	46.4121	-91.5336	Bear Creek Mining Co. WC-18	tidal flat
WC18-1836 MT	core	1836	4000226	46.4121	-91.5336	Bear Creek Mining Co. WC-18	tidal flat
WC18-1835 MT	core	1835	4000226	46.4121	-91.5336	Bear Creek Mining Co. WC-18	tidal flat
WC14-1623 MT	core	1623	4000222	46.5935	-91.5129	Bear Creek Mining Co. WC-14	estuary
WC14-1529	core	1529	4000222	46.5935	-91.5129	Bear Creek Mining Co. WC-14	tidal flat
WC14_1636_r1	core	1636	4000222	46.5935	-91.5129	Bear Creek Mining Co. WC-14	evaporitic estuary
WC-14 1679	core	1679	4000222	46.5935	-91.5129	Bear Creek Mining Co. WC-14	tidal flat
WC-14 1636	core	1636	4000222	46.5935	-91.5129	Bear Creek Mining Co. WC-14	evaporitic estuary

WC13-3125	core	3125	4000221	46.4239	-91.4489	Bear Creek Mining Co. WC-13	evaporitic estuary
PI2-675	core	675	N/A	46.6722	-89.9444	Bear Creek Mining Co. PI-2	estuary
PI2-675	core	675	N/A	46.6722	-89.9444	Bear Creek Mining Co. PI-2	estuary
PI2-660 MT	core	660	N/A	46.6722	-89.9444	Bear Creek Mining Co. PI-2	estuary
DO8-1264 MT	core	1264	16000454	46.4152	-91.5960	Bear Creek Mining Co. DO-8	estuary
DO8-1264 lam	core	1264	16000454	46.4152	-91.5960	Bear Creek Mining Co. DO-8	estuary
DO6-1369 MT	core	1369	16000452	46.5568	-91.6120	Bear Creek Mining Co. DO-6	evaporitic estuary
DO6-1365 MT	core	1365	16000452	46.5568	-91.6120	Bear Creek Mining Co. DO-6	evaporitic estuary
DO6-1365 lam	core	1365	16000452	46.5568	-91.6120	Bear Creek Mining Co. DO-6	evaporitic estuary
DO6-1364	core	1364	16000452	46.5568	-91.6120	Bear Creek Mining Co. DO-6	evaporitic estuary
DO5-874	core	874	16000451	46.5341	-91.6604	Bear Creek Mining Co. DO-5	estuary
DO-14-3071 MT	core	3071	16000460	46.4779	-91.5876	Bear Creek Mining Co. DO-14	evaporitic estuary
DO-14-3071 lam	core	3071	16000460	46.4779	-91.5876	Bear Creek Mining Co. DO-14	evaporitic estuary
DO-14-3068 lam	core	3068	16000460	46.4779	-91.5876	Bear Creek Mining Co. DO-14	evaporitic estuary
DO13-820	core	820	16000459	46.4771	-91.6491	Bear Creek Mining Co. DO-13	evaporitic estuary
DO13-756	core	756	16000459	46.4771	-91.6491	Bear Creek Mining Co. DO-13	evaporitic estuary
DO-10-374 MT	core	374	16000456	46.5149	-91.7351	Bear Creek Mining Co. DO-10	tidal flat
DO10-312	core	312	16000456	46.5149	-91.7351	Bear Creek Mining Co. DO-10	tidal flat
BI-692	outcrop	692	N/A	46.8247	-89.5694	Big Iron River	evaporitic estuary
BI-685	outcrop	685	N/A	46.8227	-89.5708	Big Iron River	estuary
BI-680	outcrop	680	N/A	46.8233	-89.5704	Big Iron River	estuary
BI-676	outcrop	676	N/A	46.8243	-89.5695	Big Iron River	estuary
BI-676	outcrop	676	N/A	46.8243	-89.5695	Big Iron River	estuary
BI-676	outcrop	676	N/A	46.8243	-89.5695	Big Iron River	estuary
BI-673	outcrop	673	N/A	46.8247	-89.5690	Big Iron River	estuary
BI-673	outcrop	673	N/A	46.8247	-89.5690	Big Iron River	estuary
BI- 9.6	outcrop	9.6	N/A	46.82054	-89.57290	Big Iron River	tidal flat
BI- 9.25	outcrop	9.25	N/A	46.82054	-89.57290	Big Iron River	tidal flat
BI- 4.01	outcrop	4.01	N/A	46.82108	-89.57291	Big Iron River	tidal flat
BI- 23.13	outcrop	23.13	N/A	46.82040	-89.57283	Big Iron River	estuary
BI- 21.42	outcrop	21.42	N/A	46.82040	-89.57283	Big Iron River	estuary

BI- 20.8	outcrop	20.8	N/A	46.82040	-89.57283	Big Iron River	evaporitic estuary
BI- 20.8	outcrop	20.8	N/A	46.82040	-89.57283	Big Iron River	evaporitic estuary
BI- 19.66	outcrop	19.66	N/A	46.82040	-89.57283	Big Iron River	evaporitic estuary
BI- 19.43	outcrop	19.43	N/A	46.82040	-89.57283	Big Iron River	estuary
BI- 11.62	outcrop	11.62	N/A	46.82054	-89.57290	Big Iron River	tidal flat
BI- 10.55	outcrop	10.55	N/A	46.82054	-89.57290	Big Iron River	tidal flat

Table S2. EPMA major and trace element chemistry

sample	Mg ppm	Fe ppm	Ca WT%	Sr ppm	Mn ppm	Mn/Sr (g/g)	Fe/Sr (g/g)	Mg/Ca (g/g)	texture	facies
WPB-2-1647_location1	823	861	42.23	76	2774	36	11	0.002	MT	estuary
WPB-2-1647_location2	535	260	43.37	61	1647	27	4	0.001	MT	estuary
WPB-2-1647_location3	754	634	43.23	78	2633	34	8	0.002	MT	estuary
PI2-660 MT location 1	549	1623	42.13	122	871	7	13	0.001	MT	estuary
PI2-660 MT location 2	507	1500	42.23	126	876	7	12	0.001	MT	estuary
PI2-660 MT location 3	698	1945	41.81	89	1154	13	22	0.002	MT	estuary
PI2-675_location 1	853	2532	39.27	89	8928	100	28	0.002	concretion	estuary
PI2-675_location 2	2611	8790	38.36	5	34573	6730	1711	0.007	concretion	estuary
PI2-675_location 3	2107	7054	37.78	81	31027	384	87	0.006	concretion	estuary
WPB2-1650_location 1 lam	967	2334	40.53	72	16295	227	33	0.002	laminae	estuary
WPB2-1650_location 2 lam	1061	2481	40.27	77	14589	191	32	0.003	laminae	estuary
WPB2-1650_location 3 lam	940	2277	40.25	30	12378	418	77	0.002	laminae	estuary
DO5-874_location1 (MT)	1884	1130	40.57	726	312	0.4	2	0.005	MT	estuary
DO5-874_location2 mt	1184	515	41.20	746	135	0.2	1	0.003	MT	estuary
DO5-874_location3 mt	1631	728	41.07	763	226	0.3	1	0.004	MT	estuary
DO8-1264_location2 lam	3833	3004	39.48	182	2646	15	16	0.010	laminae	estuary
DO8-1264_location3 MT	983	1207	40.39	135	1397	10	9	0.002	MT	estuary
DO8-1264_location1 MT	2672	2531	39.82	138	1941	14	18	0.007	MT	estuary
WC14 1623 MT_location1	892	538	40.82	641	340	1	1	0.002	MT	estuary
WC14 1623 MT_location2	1106	629	40.25	491	359	1	1	0.003	MT	estuary
WC14 1623 MT_location3	1049	1031	40.79	617	676	1	2	0.003	MT	estuary
WC9 1570 LAM_location1	2595	2590	39.84	217	6109	28	12	0.007	laminae	estuary
WC9 1570 LAM_location2	3255	2096	40.07	251	1989	8	8	0.008	laminae	estuary
WC9 1570 LAM_location3	3592	3311	39.50	307	5197	17	11	0.009	laminae	estuary

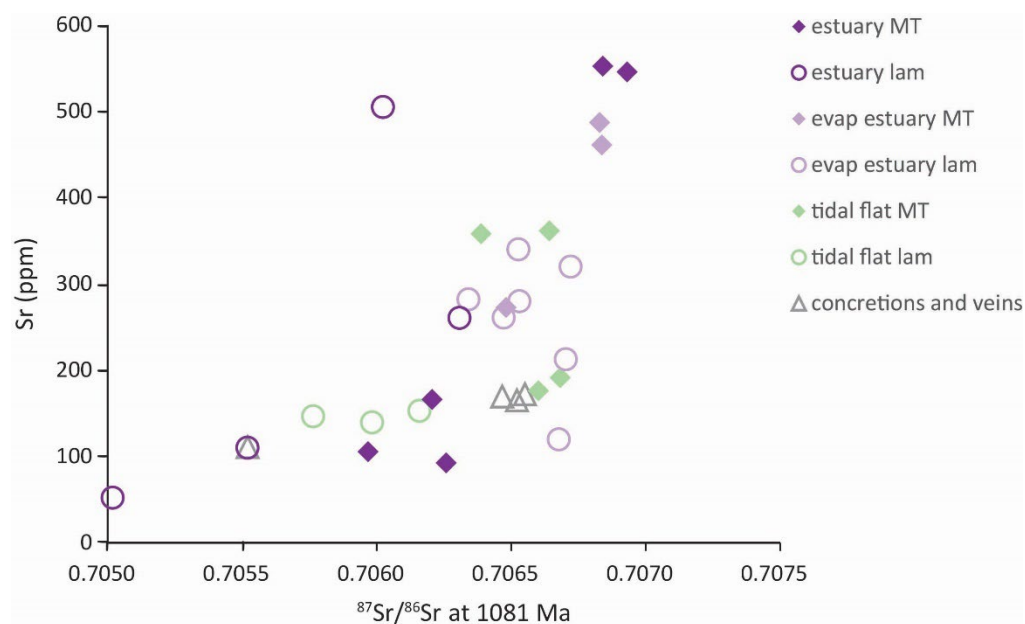


Figure S1

Plot of initial $^{87}\text{Sr}/^{86}\text{Sr}$ versus Sr (ppm) shows a positive correlation, indicating that diagenesis resulted in a loss of strontium and decrease in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. This trend breaks down for samples with strontium concentrations less than about 200 ppm.

Appendix 3: Supplementary information for chapter 3

SAMPLE PREPARATION

Carbon and Oxygen Isotope Analysis

Sample powders were analyzed at the University of Michigan Stable Isotope Laboratory, Ann Arbor, Michigan. Carbonate samples weighing a minimum of 10 micrograms were transferred to individual borosilicate reaction vessels and reacted at $77^{\circ} \pm 1^{\circ}\text{C}$ with 4 drops of anhydrous phosphoric acid for 8 minutes in a Finnigan MAT Kiel IV preparation device coupled directly to the inlet of a Finnigan MAT 253 triple collector isotope ratio mass spectrometer. ^{17}O -corrected data are corrected for acid fractionation and source mixing by calibration to a best-fit regression line defined by two NBS standards, NBS 18 and NBS 19. Data are reported in permil (‰) notation relative to VPDB. Precision and accuracy of data were monitored through analysis of at least four powdered carbonate reference materials. Measured precision was better than 0.1 ‰ for both carbon and oxygen isotope compositions.

Sample Pre-Leach and Leaching for Rb-Sr Isotope and Major- And Trace-Element Analysis

Ten- to thirty-mg aliquots of powdered sample were treated with methanol and ammonium acetate pre-leaches and then leached with 0.5 M acetic acid following Gao et al. (1996), Bailey et al. (2000), and McArthur et al. (2006). An aliquot of leached material was reserved for Rb-Sr isotope analysis, described in chapter 2. Another aliquot was reserved for major and trace element analysis of carbonates, described below.

Methanol pre-leach

Sample powders were agitated three times in 50% methanol solution to suspend and remove insoluble, high-Rb/Sr clay. Sample powders were suspended in the methanol solution using a vortex mixer for 15 seconds, then placed in an ultrasonic bath for 15 minutes, and then mixed in the vortex mixer again for 15 seconds. The samples were allowed to settle for 30 seconds to 1 minute and then the methanol solution was removed by pipetting. This process was repeated three times, and then the sample powders were dried and weighed.

Ammonium acetate pre-leach

Next powders were treated with ammonium acetate to exchange Sr not structurally bound in carbonate with ammonium. Sample powders were first suspended in 1 mL of 1 M ammonium acetate solution using a vortex mixer for 15 to 30 seconds, then placed in an ultrasonic bath for three hours, then mixed a second time using a vortex mixer for 15 to 30 seconds, and lastly centrifuged for 5 minutes. After centrifuging, the ammonium acetate waste was removed. The ammonium acetate wash was repeated three times.

After treating with ammonium acetate, the samples were washed in ultrapure (18.2 MΩ) water, dried, and weighed. Samples were first suspended in 1mL of ultrapure water for 15 to 30 seconds using a vortex mixer, then placed in an ultrasonic bath for one hour, then mixed again using a vortex mixer for 15 to 30 seconds, and lastly centrifuged for 5 minutes. The waste was removed by decanting or with a pipette. This step was repeated three times, and then the sample powders were dried and weighed.

Acetic acid leach

Powders were leached in acetic acid to dissolve the carbonate fraction. Powders were suspended in 1 mL of 0.5 M acetic acid using a vortex mixer for 15 seconds, placed in an ultrasonic bath for 30 minutes, mixed using the vortex mixer for 15 seconds, again placed in an ultrasonic bath for 30 minutes followed by mixing in a vortex mixer for 15 seconds, and lastly centrifuged for three minutes to separate the dissolved carbonate from insoluble residue. The leached liquid was pipetted into a clean 7mL beaker, taking care to avoid the meniscus while pipetting.

Next, the residue was washed two times in water. One mL of ultrapure (18.2 M Ω) water was added to the residue and any remaining acetic acid leach. This mixture was agitated in a vortex mixer for 15 seconds and then centrifuged for three minutes. The liquid was carefully pipetted into the beaker avoiding any solid particles. This water wash step was repeated a second time so that the sample beaker contained 1mL of acetic acid leach and 2 mL of water wash. The residues were dried, and the mass of the leached material was determined by subtraction. A mixed ^{87}Rb - ^{84}Sr enriched tracer solution was added to the leached sample aliquot reserved for Rb-Sr isotope analysis to determine accurate Rb and Sr concentrations by isotope dilution mass spectrometry.

ICPMS element analysis of carbonate

Aliquots of the same leached carbonate that was processed for Rb-Sr isotope analysis (see chapter 2) were analyzed on an Agilent 8900 ICPMS in the ICP-TIMS lab at the University of Wisconsin Madison. Samples were dissolved in dilute HNO_3 and introduced via micromist nebulizer. Analysis was performed in both no gas and O_2 MS/MS modes and consisted of 25 replicates with 25 sweeps per replicate and a three-point defined Q2 peak pattern. Indium was used as the internal standard. A multi-element solution (HPS) was used as the calibration standard. Concentrations were calculated using the Agilent MassHunter software. The method was checked for accuracy utilizing two in-house carbonate synthetic solutions and three dissolved carbonate rock standards from the China National Analysis Center for Iron and Steel. Uncertainty is estimated based on the accuracy of those reference solutions.

Sm-Nd isotope analysis

Samples were prepared from splits of sample powders used for whole rock geochemical analysis of major and trace elements for cores WC-9 and WC-14. About 50 mg of sample powder was weighed and transferred to precleaned Savillex beakers and dissolved in ~2.5 ml of a 4:1 mixture of concentrated HF and HNO_3 on a hotplate at ~140°C for 48 hours. Following dissolution, the HF and HNO_3 was evaporated and ~3 ml of 8M HCl was added and the capped beakers were placed on a hotplate overnight. Following the HCl treatment the samples were checked to ensure that all material was dissolved and then a mixed tracer solution enriched in ^{149}Sm - ^{150}Nd was added to each sample. Samples were then evaporated to dryness to begin ion exchange separation of Sm and Nd.

Samples were processed through a cation exchange column using HCl to collect a bulk REE cut that was then processed using cation exchange resin and 2-methylactic acid to isolate Sm and Nd. Total procedural blanks were 12 and 32 pg for Sm and Nd, respectively. These blanks are insignificant, and no blank corrections were applied.

Samarium and Nd were analyzed using a Nu Instruments multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS) with enhanced sensitivity interface with samples diluted to a concentration of 50 ppb Nd in 2% HNO₃. A Cetac Aridus II fitted with a Savillex 50µl/min concentric flow nebulizer was used to aspirate the sample into the instrument; this produced a typical ¹⁴⁴Nd⁺ ion signal of $\sim 7 \times 10^{-11}$ A. Neodymium isotope ratio measurement used static multi-collector analysis routine consisting of collecting 40 ratios (10s of integrations) with an initial on-peak-zero subtraction based on a one minute analysis of the 2% HNO₃ blank acid conducted before the Nd isotope analysis. Instrumental mass bias was corrected by exponential normalization to a ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219. The USGS rock standard BCR-2 was processed through the entire ion exchange routine and analyzed for Sm-Nd isotopes. Every third sample was a bracketing standard consisting of the internal UW Ames II Nd isotope standard. A second internal standard (Ames I) and external standard (JNdi) were analyzed repeatedly during the run to ensure measurement accuracy and the measured values are in agreement with the long-term values for the lab. The ¹⁴³Nd/¹⁴⁴Nd ratio and errors reported for the Nd isotope analyses done using the NP2 are the average and 2 standard deviation based on three replicate analyses. The average internal error (2SE) was reported if it was larger than 2SD of the replicate analysis. Epsilon Nd values were calculated using a ¹⁴³Nd/¹⁴⁴Nd of 0.512634 for modern CHUR. Samarium isotope composition was measured using the same instrument configuration as Nd and using an in-house Ames Sm solution as the bracketing standard. Mass bias was corrected by exponential normalization to ¹⁴⁹Sm/¹⁴⁷Sm of 0.9216.

Whole rock geochemical analysis

New whole rock geochemistry reported here was analyzed by the USGS in 2015 and ALS in 2021 and 2022. Handheld XRF (pXRF) measurements of Si concentrations are included for a subset of samples that lack whole rock SiO₂ analyses. The pXRF analyses are semiquantitative (Stewart and Mauk, 2017) and only used to classify sediments as shales, wackes, or sandstones following Herron (1988, see figure S1). All other whole rock geochemistry was compiled from published sources.

All analyses from core WC-14 were performed by ALS. Samples were pulverized up to 250 g 85% < 75 µm. Samples from depths 1514.75 – 1632.75 were analyzed with package ME-MS61r in 2021. Samples were dissolved with a four acid digestion and analyzed by ICP-MS. Barite and rare earth oxides may not fully digest under this method. Samples from depths 1514.75 – 1632.75 feet were analyzed with packages C-IR07 (total carbon) and C-IR06a (non-carbonate carbon) in 2022. Total carbon was measured by induction furnace/ IR. Non-carbonate carbon was leached in 25% HCl at high temperature for 1 hour to expel carbonates as CO₂ and the residue was analyzed for C by induction furnace/IR. Carbonate carbon was calculated by difference. Samples from depths 1416 – 1506 feet and 1646 – 1755.5 feet were analyzed with packages CCP-PKG05 and C-IR06a in 2022. Package CCP-PKG05 combines whole rock analysis, trace elements by fusion, and aqua regia digestion for volatile trace elements, and carbon and sulfur by combustion analysis. Major element oxides were analyzed by ICP-AES. Trace elements were analyzed by ICP-MS. Samples from cores DO-13 and WC-9 were analyzed by the USGS. Samples were pulverized, major element oxides were analyzed by WDXRF, and trace elements were analyzed by ICP-AES.

WC-14- COMMENTS ON CORE DESCRIPTION

Depositional facies and stratigraphic surfaces were determined through visual inspection of the drill core. The sequence boundary falls within a black laminated shaley siltstone and was difficult to place precisely based on visual core inspection alone. Chemostratigraphic trends presented in the main text clarify placement of this surface. Depths are given in feet relative to land surface to maintain consistency with documentation collected at the time the cores were drilled. The proxy $\ln(K_2O/MgO)$ approximates the sediment provenance coefficient ψ (Lipp et al., 2020) and is used to evaluate provenance trends in core WC-14 because analyses of SiO_2 necessary to calculate ψ were collected for only a partial section of that core.

An interval of Copper Harbor Conglomerate that is boxed out of stratigraphic order within the middle to upper part of the Nonesuch Formation. This interval is labeled as coming from the bottom of the hole (1765 to 1771 feet), yet it is placed in the core box below Nonesuch Formation strata with a depth marker indicating recovery from 1562 feet below land surface and above similar Nonesuch Formation strata with depth marker indicating recovery from about 1567 feet. No original core logs are available for this core that might clarify why this interval was boxed out of order. While it could represent faulted repetition of the Copper Harbor Conglomerate, in other cores faulted intervals are labeled with continuous measured depths relative to land surface. There is no obvious indication of faulting: Bedding in the Nonesuch Formation is flat, and there are no significant carbonate veins or slickensides. Core depth markers in the Nonesuch Formation above and below this interval of Copper Harbor Conglomerate are continuous, and there are no obvious visual changes in the Nonesuch strata at ~1570 to 1550 feet that would indicate a discontinuous succession. Based on these observations I conclude that the core was boxed out of order here, and the Nonesuch Formation above and below this interval of Copper Harbor Conglomerate is a continuous succession. However, this out of place interval of Copper Harbor Conglomerate adds uncertainty to interpretation of the sequence stratigraphy and chemostratigraphy.

SEDIMENT PROVENANCE and WEATHERING

Existing studies focus on distinguishing provenance of the Oronto Group, Bayfield Group, and Jacobsville Sandstone. Ojakangas and Morey (1982) and Berendsen and Barczuk (1993) document north directed paleocurrents and lithic to arkosic arenite composition for lower Oronto Group sandstones along southern Lake Superior. Berendsen and Barczuk (1993) report pyroclastic quartz, microcline, and metamorphic lithic clasts from Nonesuch Formation sandstones and note chlorite replacing detrital biotite and volcanic glass. Cullers and Berendsen (1998) interpret whole rock geochemistry of Copper Harbor Conglomerate and Nonesuch Formation sandstone to indicate a proximal MCR basalt and lesser felsic source. In contrast, Mitchel and Sheldon (2016) use elemental abundances of Copper Harbor Conglomerate sandstone on the Keweenaw Peninsula to interpret a distal felsic recycled basement provenance. Craddock et al. (2013) interpret a shift from proximal to more distal detrital zircon sources within the Oronto Group. Copper Harbor Conglomerate zircon ages are primarily Midcontinent Rift/ Grenvillian with lesser contribution from the relatively distal Wolf River batholith, Penokean orogenic belt, and Archean basement. The age distribution of detrital zircons in the Freda Formation is dominated by Penokean and Archean ages with lesser Midcontinent Rift/ Grenvillian and Wolf River batholith ages.

Trace element discriminant diagrams leverage immobile trace element relationships to evaluate sediment provenance (Bhatia and Crook, 1986; McLennan and Taylor, 1991). Most lower Oronto Group fine-grained sediments plot in a linear array on a lanthanum-scandium-thorium (La-Sc-Th) plot (Figure S4a) parallel to the array of Midcontinent Rift basalts and offset towards the Th axis. On the same plot, coarse-grained sediments are relatively enriched in La and overlap with andesite. These patterns are consistent with Midcontinent Rift basalts readily weathering to clays while intermediate volcanic rocks, which are more resistant to chemical weathering, are preserved in the coarser sediment fractions. Most shales cluster on a thorium-zirconium/10-scandium (Th-Zr/10-Sc) plot (Figure S4b) in a population that falls along the Zr/10 - Sc axis between Kallander Creek type 3 basalt and Porcupine Volcanics basalt (dashed circle) while coarser-grained sediments extend towards Zr/10. Covariation of Th/Sc with Zr/Sc indicates igneous differentiation of the source area is the primary control on Zr abundance in sediments and zircon enrichment through sedimentary sorting is not a dominant process (Figure S4c; McLennan et al. 1993). The simplest interpretation is that most lower Oronto Group sediments were sourced from Midcontinent Rift basalts with compositions similar to the suite with compositional endmembers Kallander Creek type 3 basalt and Porcupine Volcanics basalt (dashed circle on Figure S4 a,b) mixed with andesite, dacite, and rhyolite. Zircons, the main source of Zr, are concentrated in coarser-grained sediments and mostly derived from Midcontinent Rift intermediate volcanics and rhyolite. Although detrital zircon ages demonstrate some of the sediments were recycled from older basement terranes, this was likely a minor fraction. If the degree of recycling from these older sources was significant, lower Oronto Group sediments would be sufficiently enriched in zircons that they would fall off the Th/Sc versus Zr/Sc trend (McLennan et al., 1993).

Lower Oronto Group shales show slight separation by formation and location when plotted on Th-Zr/10-La diagrams (Figure S5). In the Ashland Syncline, the lower Nonesuch Formation is relatively enriched in Zr, the upper Nonesuch Formation is relatively enriched in Th, and the Freda Formation is relatively enriched in Sc. In contrast, shales from the Keweenaw Peninsula have overlapping populations with the lower Nonesuch Formation relatively enriched in Sc, the Freda Formation relatively enriched in Zr/10, and the upper Nonesuch Formation transitional between the lower Nonesuch and Freda. During deposition of the lower Oronto Group, the Ashland Syncline and Keweenaw Peninsula were separate sub-basins that received sediment from different sources of Midcontinent Rift igneous Rocks, consistent with petrographic observations of Suszek (1997). In each sub-basin, sediment sources shifted throughout deposition of the lower and upper Nonesuch Formation and Freda Formation.

Chemical weathering intensity and trends are commonly evaluated through the Chemical Index of Alteration (CIA) and A-K-CN (molar $\text{Al}_2\text{O} - \text{Ca}_2\text{O}^* + \text{Na}_2\text{O} - \text{K}_2\text{O}$) ternary plots, which track the breakdown of feldspars into clay minerals (Nesbitt and Young, 1982). All calculations are on a molar basis. Lower Oronto Group shales and wackes have a linear trend on an A-K-CN plot (Figure S7). Ca_2O^* was calculated to correct for phosphate and carbonate CaO. Ca_2O^* was calculated by first subtracting phosphate CaO based on P_2O_5 content ($\text{CaO}_{\text{non-phosphate}} = \text{CaO}_{\text{total}} - 10/3 \times \text{P}_2\text{O}_5$). Further adjustment for carbonate CaO was made by assuming detrital siliciclastics were derived from a mixture of MCS basalts and intermediate volcanic rocks with average molar $\text{CaO}/\text{Na}_2\text{O} \sim 1.5$ (Nicholson & Shirey, 1990). If $\text{CaO}_{\text{non-phosphate}} > 1.5 \times \text{Na}_2\text{O}$ then CaO^* is equal to $1.5 \times \text{Na}_2\text{O}$, otherwise $\text{CaO}^* = \text{CaO}_{\text{non-phosphate}}$. This correction will underestimate CIA for samples derived from more felsic sources. Molar $\text{CaO}/\text{Na}_2\text{O}$ of MCS basalt ranges from 5.5 – 1.9

(Nicholson and Shirey, 1990; Nicholson et al, 1997), and the CaO* correction will overestimate CIA of samples derived predominantly from these lithologies.

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REY ANOMALY EQUATIONS

Bell-shaped index (BSI), measures MREE enrichment (Tostevin et al., 2016)

$$BSI = \frac{2 * ([Sm]_{SN} + [Gd]_{SN} + [Dy]_{SN})/3}{([La]_{SN} + [Pr]_{SN} + [Nd]_{SN})/3 + ([Ho]_{SN} + [Er]_{SN} + [Tm]_{SN} + [Yb]_{SN} + [Lu]_{SN})/5}$$

LREE/HREE, measures relative depletion of LREE compared to HREE (Skinner et al., 2019)

$$LREE/HREE = \frac{([Pr]_{SN} + [Nd]_{SN})/2}{([Yb]_{SN} + [Lu]_{SN})/2}$$

Cerium anomaly (Lawrence and Kamber, 2006)

$$(Ce/Ce^*)_{SN} = \frac{[Ce]_{SN}}{[Pr]_{SN} * ([Pr]_{SN} / [Nd]_{SN})}$$

Europium anomaly (Lawrence and Kamber, 2006)

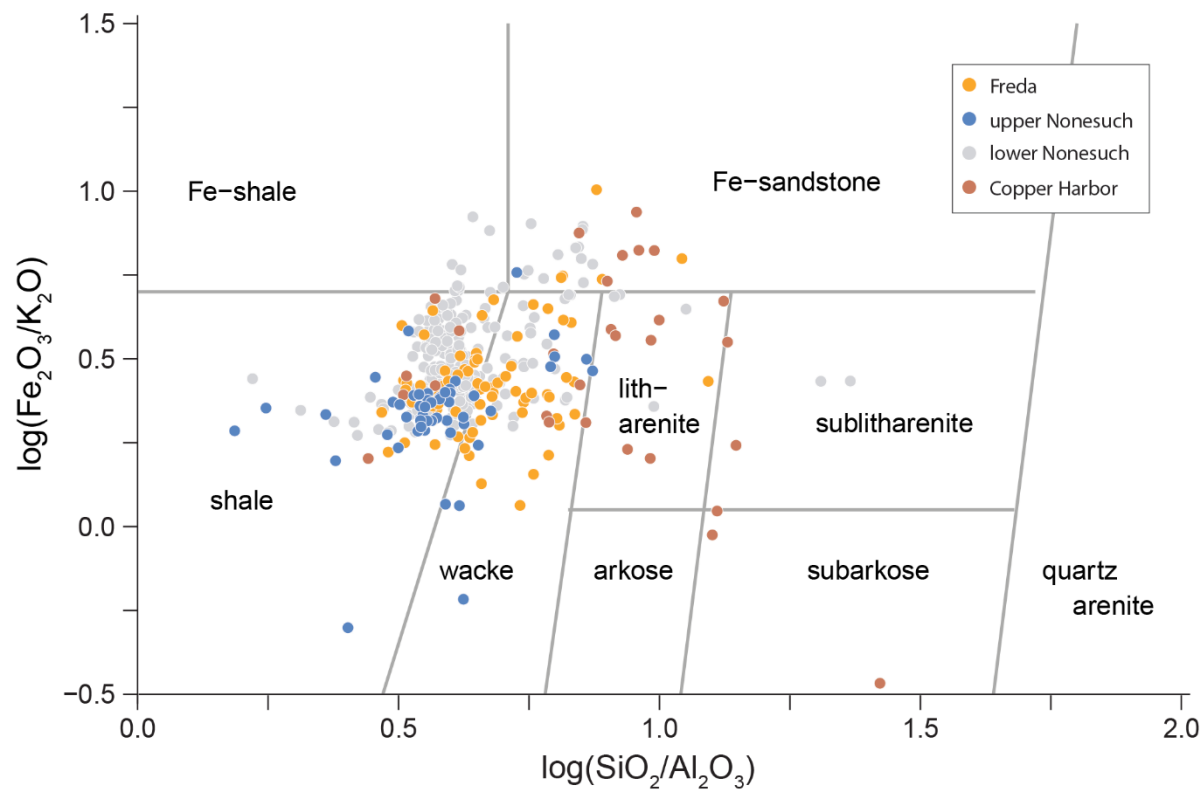
$$(Eu/Eu^*)_{SN} = \frac{[Eu]_{SN}}{([Sm]_{SN})^2 * ([Tb]_{SN})^{1/3}}$$

Lanthanum anomaly (Lawrence and Kamber, 2006)

$$(La/La^*)_{SN} = \frac{[La]_{SN}}{[Pr]_{SN} * ([Pr]_{SN} / [Nd]_{SN})^2}$$

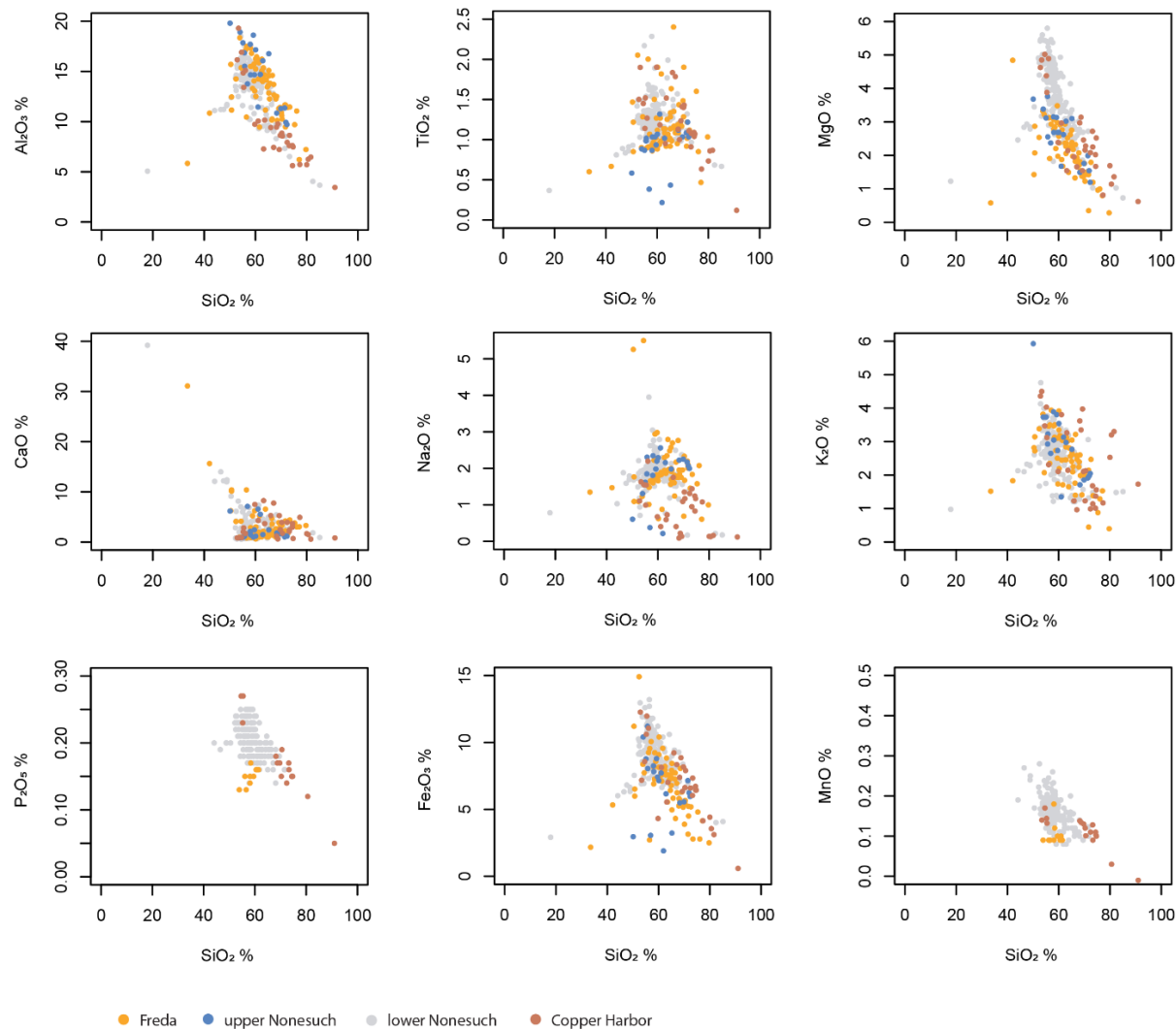
FIGURES and TABLES

Figure S1. Sediment classification



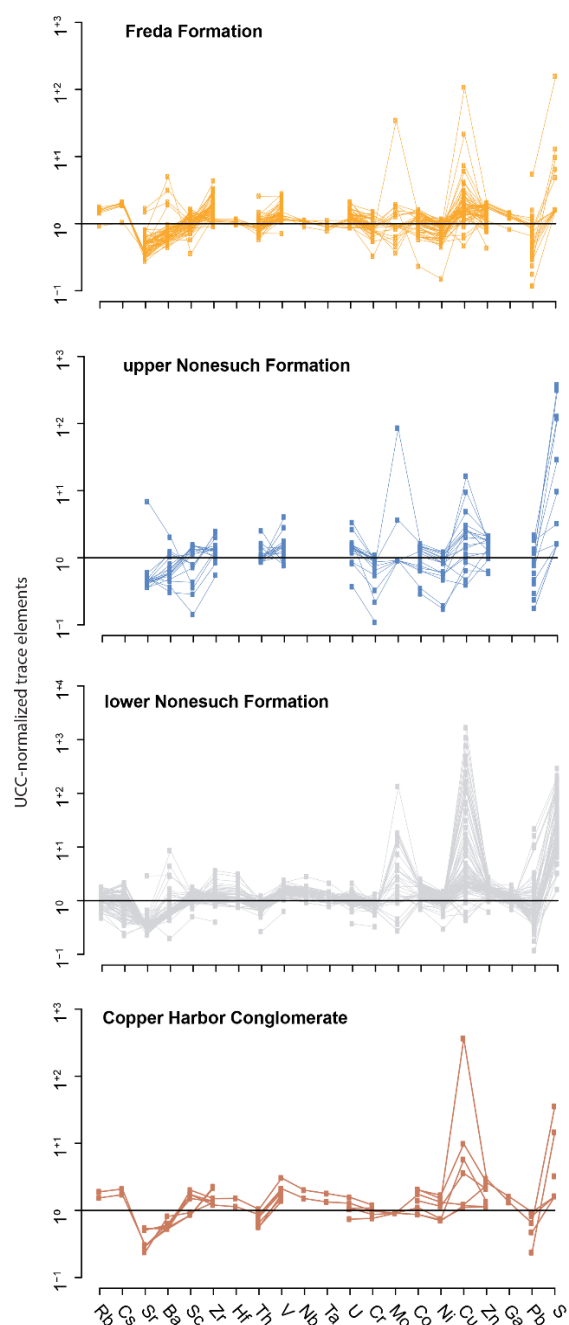
Siliciclastic sediment classification (modified after Herron, 1988).

Figure S2. Major element composition



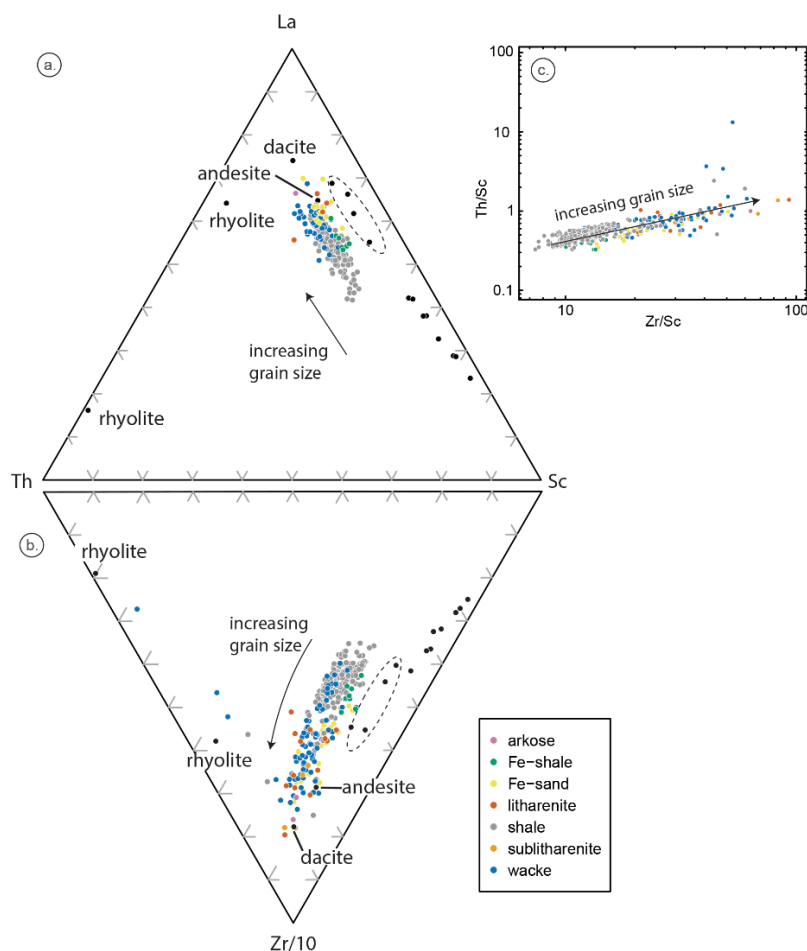
Scatterplots showing major element composition against SiO_2 for the lower Oronto Group. Note P_2O_5 , MnO , and Na_2O analyses were not collected for some samples.

Figure S3. Trace element distribution



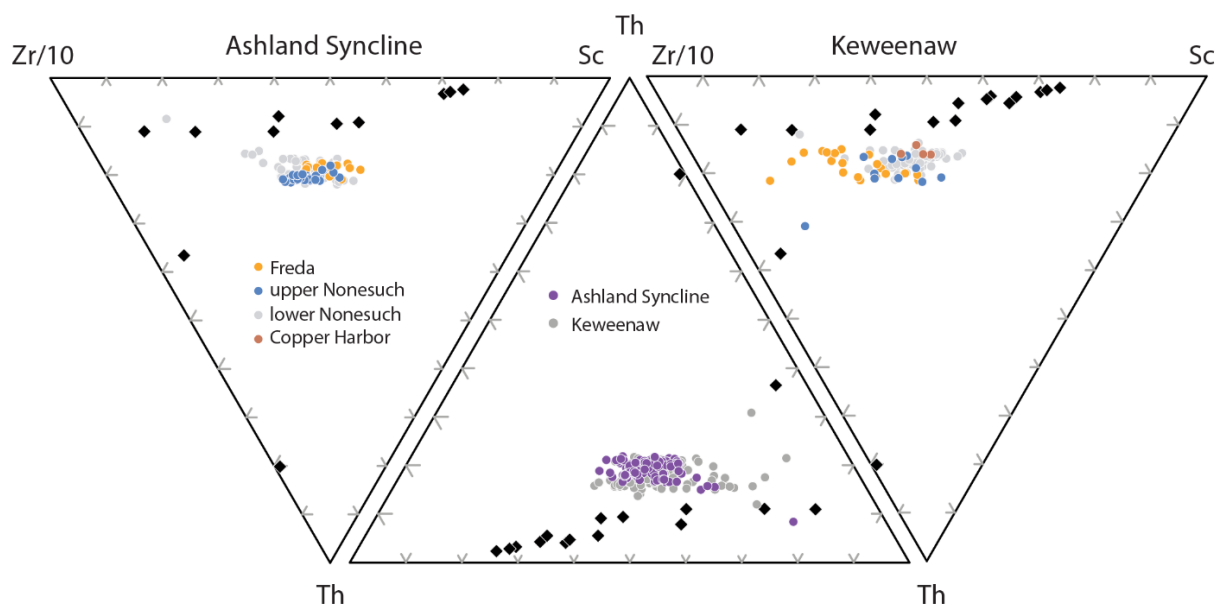
Trace element distributions for lower Oronto Group sediments normalized to upper continental crust (Rudnick and Gao, 2003).

Figure S4. La – Th- Sc ternary diagram and cross-plot of Th/Sc vs. Zr/Sc



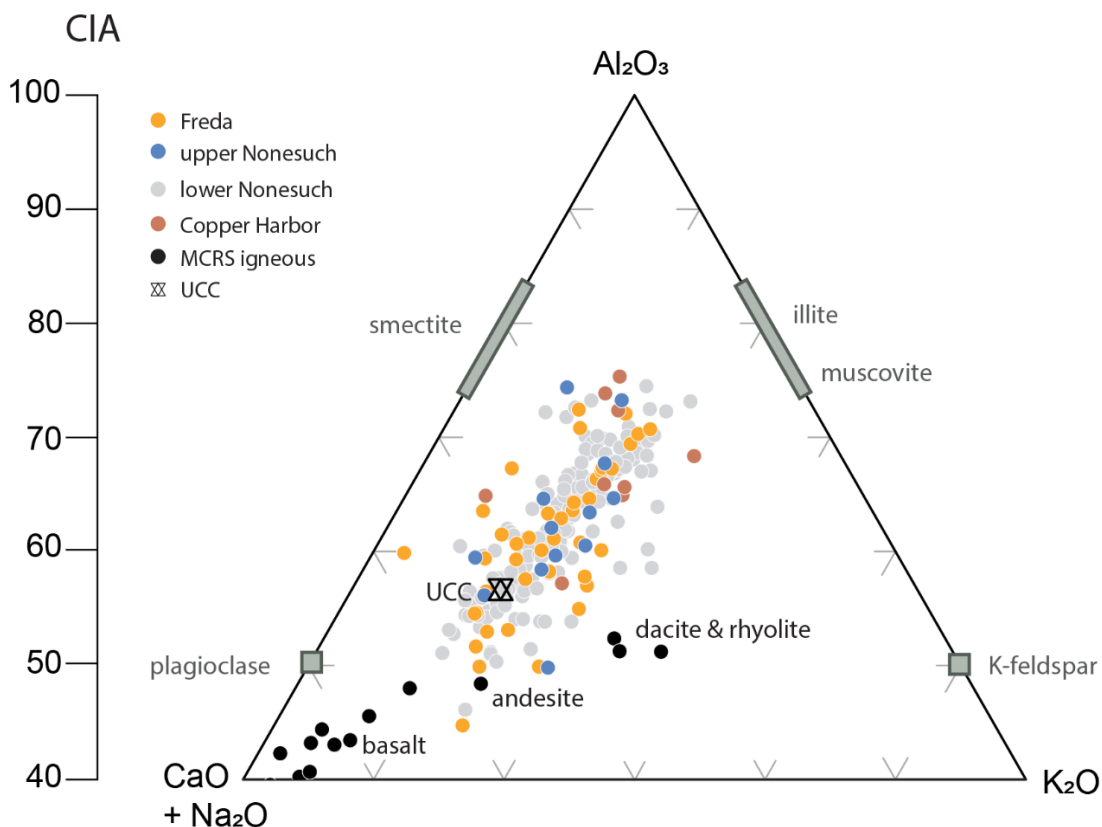
Sediment source and recycling discrimination ternary plots La-Sc-Th (a) and Th-Zr/10-Sc (b) of lower Oronto Group sediments (Bhatia and Crook, 1986). Black circles are MCS igneous rocks (Nicholson et al., 1997; Nicholson and Shirey, 1990; Nicholson, 1990; Wirth et al., 1997). Dashed circle identifies igneous rock compositions most similar to lower Oronto Group sediments and includes Kallander Creek type 3, basaltic andesite, Seimens Creek type 1, and Porcupine Volcanics basalt. c) Test of the influence of sedimentary sorting and recycling on Zr abundance (after McLennan et al., 1993). Samples are compiled from new and published data for the lower Oronto Group across the Ashland Syncline and Keweenaw Peninsula. Note that (a) shows fewer samples, as La analyses are unavailable for some samples.

Figure S5. Th – Zr/10 – Sc ternary diagrams by location



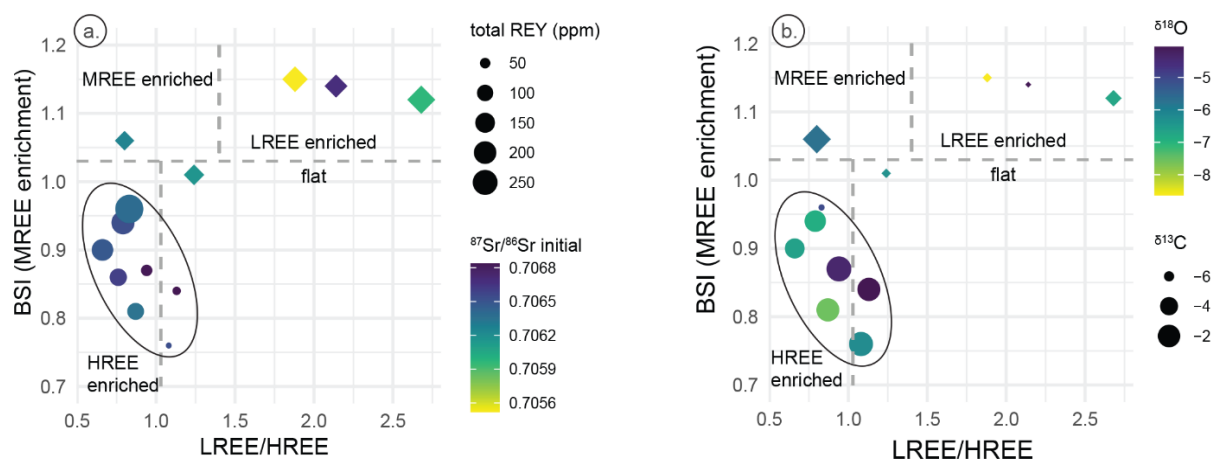
Sediment source and recycling discrimination Th-Zr/10-Sc ternary plots of lower Oronto Group shales (Bhatia and Crook, 1986) suggest different local sediment sources for the Ashland Syncline (a) and Keweenaw Peninsula (b, c). Plots (a) and (c) colored by stratigraphic unit. Plot (b) is colored by sample location. Black diamonds are MCR igneous rocks (Nicholson et al., 1997; Nicholson and Shirey, 1990; Wirth et al., 1997).

Figure S6. A – CN – K ternary diagram

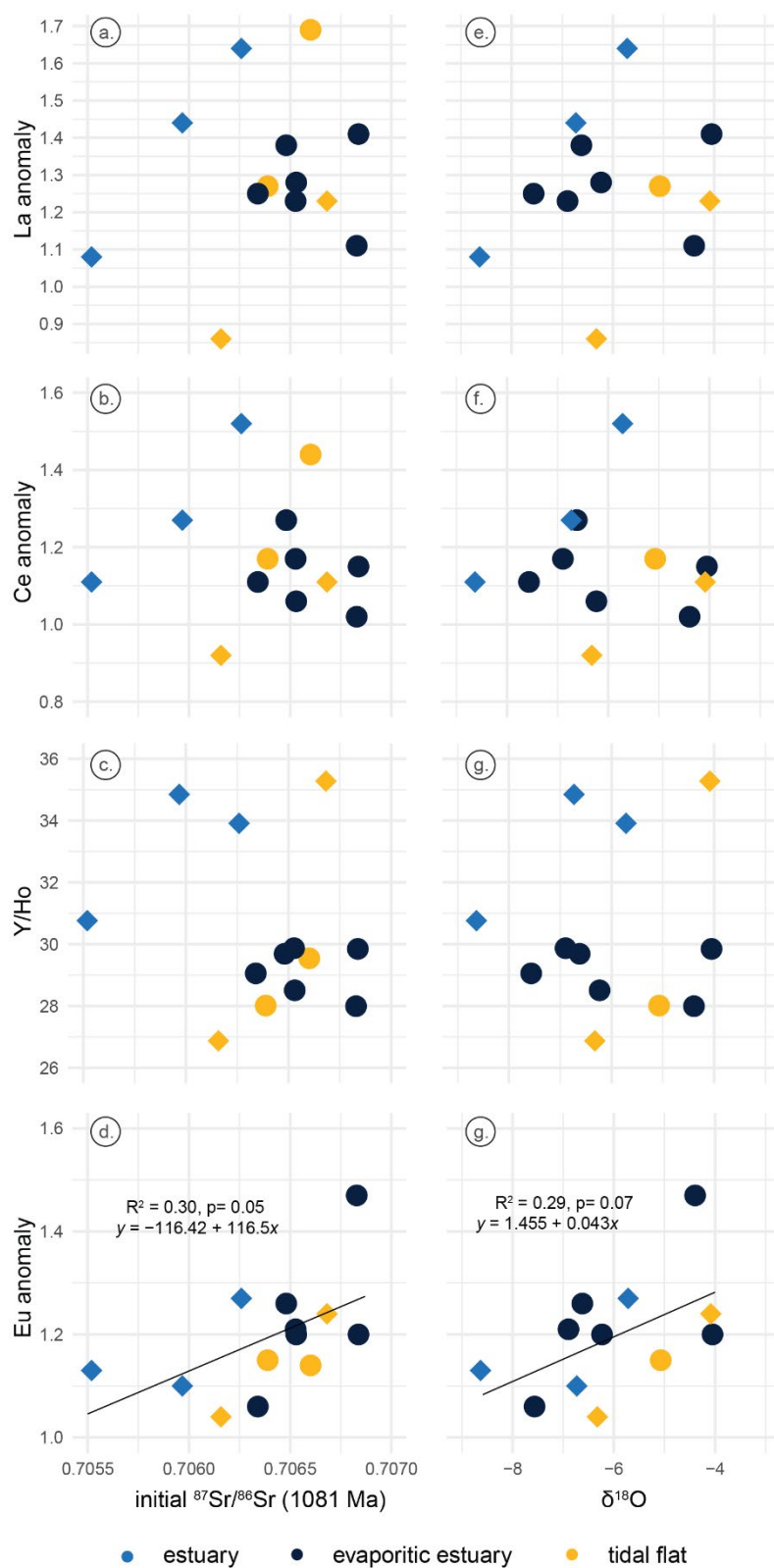


ACNK ternary plot showing weathering trends and chemical index of alteration (CIA) for lower Oronto Group shales and wackes. The apices are the molar proportions of Al_2O_3 , $\text{CaO}^* + \text{Na}_2\text{O}$, and K_2O in a sample. CaO^* was adjusted for phosphate and carbonate CaO . (see supplemental text for details). The gray boxes show the compositional fields of common minerals (modified after Algeo et al., 2025). MCS igneous rocks, the source of lower Oronto Group sediments, are shown for reference (Nicholson et al., 1997; Nicholson and Shirey, 1990; Wirth et al., 1997). Upper continental crust (UCC) from Rudnick and Gao, 2003. Note the diagram is truncated at $\text{CIA} < 40$.

Figure S7. Characterization of REY patterns



Characterization of REY patterns shown in Figure 7 by MREE enrichment (BSI) versus LREE/HREE (Pr/Er_{NF}). Samples with components of a marine REY distribution have BSI < 1 (circled). Samples show no clear correlation between REY distribution and initial ⁸⁷Sr/⁸⁶Sr (a) or ^δ18O (b). Total REY increases with increasing HREE enrichment for samples with BSI < 1 (a) while flat and LREE enriched samples with BSI > 1 have lightest ^δ13C values (b).

Figure S8. REY anomalies vs. initial $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}$ 

Tests for pore water evolution or sample contamination during leaching. Best fit lines in d and g are for all samples.

Table S1. REY sample locations

Sample name	sample type	depth (ft)	WID (WI unique ID)	LatDd	LonDd	Site Name	facies
WPB2-1650	core	1650	N/A	46.6633	-89.7574	Bear Creek Mining Co. WPB-2	estuary
WPB-2-1647 MT	core	1647	N/A	46.6633	-89.7574	Bear Creek Mining Co. WPB-3	estuary
WC18-1836 MT	core	1836	4000226	46.4121	-91.5336	Bear Creek Mining Co. WC-18	tidal flat
WC18-1835 MT	core	1835	4000226	46.4121	-91.5336	Bear Creek Mining Co. WC-18	tidal flat
PI2-675	core	675	N/A	46.6722	-89.9444	Bear Creek Mining Co. PI-2	estuary
PI2-660 MT	core	660	N/A	46.6722	-89.9444	Bear Creek Mining Co. PI-2	estuary
DO6-1369 MT	core	1369	16000452	46.5568	-91.6120	Bear Creek Mining Co. DO-6	evaporitic estuary
DO6-1365 MT	core	1365	16000452	46.5568	-91.6120	Bear Creek Mining Co. DO-6	evaporitic estuary
DO6-1365 lam	core	1365	16000452	46.5568	-91.6120	Bear Creek Mining Co. DO-6	evaporitic estuary
DO-14-3071 MT	core	3071	16000460	46.4779	-91.5876	Bear Creek Mining Co. DO-14	evaporitic estuary
DO-14-3071 lam	core	3071	16000460	46.4779	-91.5876	Bear Creek Mining Co. DO-14	evaporitic estuary
DO-14-3068 lam	core	3068	16000460	46.4779	-91.5876	Bear Creek Mining Co. DO-14	evaporitic estuary
DO-10-374 MT	core	374	16000456	46.5149	-91.7351	Bear Creek Mining Co. DO-10	tidal flat
DO10-312	core	312	16000456	46.5149	-91.7351	Bear Creek Mining Co. DO-10	tidal flat

Table S2: Core locations

Wid (WI unique ID)	LatDd	LonDd	Site Name	short_name	type
4000217	46.4160	-91.2996	Bear Creek Mining Co. WC-9	WC-9	core
4000222	46.5935	-91.5129	Bear Creek Mining Co. WC-14	WC-14	core

Table S3. Whole rock geochemistry

Please see Excel file