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1 **Anoxia in the terrestrial environment during the late** 2 **Mesoproterozoic**

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4

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10

11 **ABSTRACT**

12 **A significant body of evidence suggests that the marine environment remained largely**
13 **anoxic throughout most of the Precambrian. In contrast, the oxygenation history of**
14 **terrestrial aquatic environments has received little attention, despite the significance of**
15 **such settings for early eukaryote evolution. To address this, we provide here a**
16 **geochemical and isotopic assessment of sediments from the late Mesoproterozoic**
17 **Nonesuch Formation of central North America. We utilize rhenium-osmium (Re-Os)**
18 **geochronology to yield a depositional age of 1078 ± 24 Ma, while Os isotope**
19 **compositions support existing evidence for a lacustrine setting. Fe-S-C systematics**
20 **suggest that the Nonesuch Formation was deposited from an anoxic Fe-rich**
21 **(ferruginous) water column. Thus, similar to the marine realm, anoxia persisted in**
22 **terrestrial aquatic environments in the mid-late Proterozoic, but sulfidic water column**
23 **conditions were not ubiquitous. Our data suggest that oxygenation of the terrestrial**
24 **realm was not pervasive at this time and may not have preceded oxygenation of the**

25 **marine environment, signifying a major requirement for further investigation of links**
26 **between the oxygenation state of terrestrial aquatic environments and eukaryote**
27 **evolution.**

28 **Keywords:** oxygenation; Precambrian; terrestrial environment; Re-Os; Fe speciation

29

30 **INTRODUCTION**

31 Recent reconstructions suggest that the global ocean remained anoxic between Earth's
32 two major periods of rising atmospheric oxygen at either end of the Proterozoic Eon (2500 –
33 542 Ma). In detail, sulfidic water column conditions were prevalent along productive
34 continental margins, overlying deeper waters that contained dissolved Fe (ferruginous)
35 (Canfield et al., 2008; Poulton et al., 2010; Poulton and Canfield, 2011; Planavsky et al.,
36 2011). However, in contrast to these advances in our understanding of the evolution of mid-
37 Proterozoic ocean chemistry, much less is known about oxygenation of terrestrial aquatic
38 environments during this period.

39 Recently, the determination of sulfur isotope fractionations between sulfate and
40 sulfide ($\Delta^{34}\text{S}$) of >50‰ in lacustrine sediments from the Mesoproterozoic Torridon and Stoer
41 Groups of NW Scotland, were interpreted to suggest that oxygenation of terrestrial aquatic
42 environments preceded oxygenation of the oceans (Parnell et al., 2010). Such fractionations
43 are generally considered to require an active oxidative sulfur cycle driven by
44 disproportionation reactions involving sulfide-oxidising bacteria, and are interpreted to reflect
45 a major rise in oxygen in the late Neoproterozoic (Canfield and Teske, 1996). If correct, this
46 suggests that, unlike the marine realm, late Mesoproterozoic terrestrial aquatic environments
47 were sufficiently oxidized to support a complex biota adapted to an oxygen-rich atmosphere
48 (Parnell et al., 2010). However, $\Delta^{34}\text{S}$ fractionations of 60-70‰ have recently been measured
49 in an anoxic, low sulfate lake in the absence of oxidative sulfur cycling (Canfield et al.,

50 2010). This builds upon theoretical calculations of the magnitude of fractionation possible by
51 bacterial sulfate reduction alone (Brunner and Bernasconi, 2005), and is supported by direct
52 measurements of fractionations obtained during growth of a pure culture of bacterial sulfate
53 reducers (Sim et al., 2011).

54 Considering the evolutionary significance of possible early oxygenation of terrestrial
55 environments, coupled with these recent developments in our understanding of sulfur isotope
56 fractionation, a more direct assessment of the redox state of the terrestrial realm during the
57 late Mesoproterozoic is clearly warranted. Our focus is on the Nonesuch Formation,
58 deposited within the ~1100 Ma intracratonic Mid-Continent Rift System of central North
59 America (Ojakangas et al., 2001). Like the Torridon Group of NW Scotland, the Nonesuch
60 Formation contains a rich record of eukaryotic life (Pratt et al., 1991; Strother and Wellman,
61 2010) and thus represents an ideal locality to assess possible links to early terrestrial
62 oxygenation. We utilize Fe-S-C systematics to assess water column redox conditions,
63 coupled with Re-Os geochronology to provide a depositional age for the Nonesuch
64 Formation, and Os isotope systematics to yield insight into the nature of the depositional
65 setting.

66

67 **GEOLOGICAL SETTING**

68 The Mid-Continent Rift System of central North America was one of the world's
69 largest continental rifts (Ojakangas et al., 2001). In the Lake Superior region, up to 30 km of
70 volcanic and sedimentary rift-fill sequences make up the Keweenaw Supergroup
71 (Ojakangas et al., 2001; Fig. 1). The Oronto Group consists of fluvial and alluvial
72 volcanoclastics, with the exception of the Nonesuch Formation, a 40 to 200 m thick
73 succession of organic-rich siliciclastics. Geochronology of the Keweenaw Supergroup is
74 based upon U-Pb zircon ages of rift-related volcanics, with the overlying post-rift sediments

75 poorly constrained temporally. An existing U-Pb zircon age of 1087.2 ± 1.6 Ma from the
76 final andesite flow in the Copper Harbour Conglomerate (Davis and Paces, 1990; Fig. 1)
77 provides a maximum age for the Nonesuch Formation.

78 To allow redox assessment using Fe-S-C systematics we have sampled well-preserved
79 drillcore (PI-1) across a 60 m interval that covers the entire Nonesuch Formation (Pratt et al.,
80 1991). These samples are augmented by Re-Os geochronology and Os isotope analyses of
81 outcrop samples collected ~30 m above the Copper Harbour Conglomerate (Fig. 1; full
82 details of the sampling and analytical protocols are provided in the GSA Data Repository).
83 The Re-Os age for all the outcrop samples is 1040 ± 78 Ma (2σ , $n = 16$, Mean Squared of
84 Weighted Deviation [MSWD] = 10.6; Fig. DR1; Table DR1). The large MSWD and
85 uncertainty on this Re-Os date is due to variation in the initial $^{187}\text{Os}/^{188}\text{Os}$ (Os_i) values rather
86 than disturbance to the isotope system, as suggested by the isochronous nature of the samples
87 and agreement with the underlying U-Pb date (see GSA Data Repository). In fact, the Os_i
88 values form two distinct groups, with eleven of the 16 samples yielding the most precise
89 depositional age of 1078 ± 24 Ma (2σ , $n = 11$, MSWD = 1.05; Fig. DR1).

90

91 **DEPOSITIONAL ENVIRONMENT**

92 Sedimentological characteristics of the Nonesuch Formation and proximity to
93 continental red-beds (Fig. 1), coupled with paleogeographic reconstructions suggesting that
94 the nearest coastline was ~800 km away, indicating that the Nonesuch Formation was likely
95 deposited in a lacustrine environment (Elmore et al., 1989; Imbus et al., 1992; Ojakangas et
96 al., 2001). However, a marine embayment or estuarine environment has also been suggested
97 based on the presence of specific biomarkers and S/C ratios (Pratt et al., 1991; Hieshima and
98 Pratt, 1991). Biomarkers extracted from the Nonesuch Formation include low levels of 24-*n*-
99 propylcholestane (Pratt et al., 1991), which is commonly, but not uniquely, found in rocks of

100 marine origin (Moldowan et al., 1990) and may in fact relate to the presence of eukaryotic
101 organisms in the Nonesuch Formation. Thus, the presence of 24-*n*-propylcholestane at low
102 concentration does not unambiguously denote a marine depositional setting for the Nonesuch
103 Formation.

104 Enrichments in S/C ratios have previously been interpreted to reflect deposition of the
105 Nonesuch Formation under sulfate-rich marine conditions (Fig. DR2; Hieshima and Pratt,
106 1991; Imbus et al., 1992). However, enhanced fixation of sulfide as a result of the absence of
107 bioturbation in the Precambrian and (potentially) non-Fe limited conditions during
108 ferruginous deposition, combined with differences in the metabolisability of Precambrian
109 organic matter, could readily lead to the observed enrichments in sulfur and decoupling
110 between sulfur and carbon under lacustrine conditions (e.g., Raiswell and Canfield, 2012).

111 Application of Re-Os geochronology provides an additional, novel constraint on the
112 nature of the depositional environment by yielding the Os_i composition of the water column
113 at the time of deposition, which can be used to distinguish between lacustrine and marine
114 settings (Poirier and Hillaire-Marcel, 2011; Cumming et al., 2012). The Os_i derived from the
115 Re-Os isochrons are 0.81 ± 0.28 and 0.49 ± 0.13 (Fig. DR1), a variation reflecting a balance
116 between weathering of radiogenic Archean-Proterozoic cratonic lithosphere (~ 1.01 ; upper
117 continental crust calculated at 1100 Ma; Esser and Turekian, 1993) and unradiogenic rift-
118 related flood basalts (~ 0.13 ; Allegre et al., 1999). At 1100 Ma, seawater $^{187}Os/^{188}Os$ was
119 relatively unradiogenic at ~ 0.3 (a value derived from two separate margins; Rooney et al.,
120 2010; Azmy et al., 2008), and therefore the more radiogenic values measured for the
121 Nonesuch Formation (0.81 and 0.49) suggest that minimal Os was sourced from the marine
122 realm. Thus, the Os isotope data support sedimentological and paleogeographic evidence for
123 lacustrine depositional conditions.

124

125 **REDOX CONDITIONS**

126 Water column redox conditions during deposition of the Nonesuch Formation were
127 evaluated using Fe speciation. A biogeochemically 'highly reactive' Fe pool (Fe_{HR}) is
128 analysed through a series of extractions (Poulton and Canfield, 2005). Modern and ancient
129 sediments deposited under anoxic conditions commonly have $Fe_{HR}/total\ Fe\ (Fe_T)$ ratios
130 >0.38 , in contrast to oxic depositional conditions, where ratios are consistently below 0.22
131 (Poulton and Canfield, 2011). About 40% of drill core samples (Fig. 2), and all outcrop
132 samples (Table DR2), were clearly deposited from an anoxic water column with Fe_{HR}/Fe_T
133 >0.38 , while others fall within the equivocal range ($Fe_{HR}/Fe_T = 0.22-0.38$). These equivocal
134 samples may reflect the masking of water column Fe_{HR} enrichments due to rapid
135 sedimentation or transformation of non-sulfidized Fe_{HR} to clay minerals during burial
136 diagenesis or metamorphism (Poulton and Raiswell, 2002; Poulton et al., 2010). The latter
137 possibility can be evaluated by considering Fe/Al ratios (Fig. 2), whereby significant
138 enrichments in Fe relative to both average shale (Lyons and Severmann, 2006) and typical
139 oxic lacustrine sediments (e.g., Kemp and Thomas, 1976; Fagel et al., 2005) throughout the
140 Nonesuch Formation provide strong evidence for anoxic depositional conditions. Post-
141 depositional loss of Fe_{HR} can also be assessed through an extraction that targets Fe associated
142 with clay minerals (termed poorly reactive silicate Fe; Fe_{PRS}) (Poulton et al., 2010). Extreme
143 enrichment in Fe_{PRS} in the Nonesuch Formation (Fe_{PRS}/Fe_T values are well above the modern
144 and Phanerozoic averages; Fig. 2; Poulton and Raiswell, 2002) suggests that significant loss
145 of Fe_{HR} through authigenic clay mineral formation was responsible for reducing original
146 depositional Fe_{HR}/Fe_T ratios (Poulton et al., 2010), supporting anoxic deposition for all
147 Nonesuch Formation samples.

148 For samples showing evidence of anoxic deposition, the extent to which the Fe_{HR} pool
149 has been pyritized (Fe_{py}/Fe_{HR}) can then distinguish euxinic ($Fe_{py}/Fe_{HR} >0.7-0.8$) from

150 ferruginous ($Fe_{py}/Fe_{HR} < 0.7-0.8$) depositional conditions (Poulton and Canfield, 2011). All of
151 the Nonesuch Formation samples have Fe_{py}/Fe_{HR} ratios well below the euxinic threshold (Fig.
152 2), indicating anoxic ferruginous depositional conditions throughout and thus refuting the
153 suggestion of a possible euxinic depositional setting (c.f. Imbus et al., 1992).

154

155 **IMPLICATIONS FOR TERRESTRIAL BIOSPHERIC OXYGENATION**

156 The upper Nonesuch Formation comprises fining and coarsening upward packages
157 interpreted to be the transition between lacustrine deposition and fluvial conditions of the
158 conformably overlying Freda Sandstone (Elmore et al., 1989). This suggests that the
159 Nonesuch Formation was likely deposited under progressively more oxic conditions as water
160 depth decreased towards the top of the succession (Elmore et al., 1989). Oxygenated surface
161 waters in ~1.1 Ga terrestrial aquatic environments would be expected, particularly since
162 shallow marine waters were apparently oxygenated much earlier in Earth history (~2.7 Ga;
163 Kendall et al., 2010; Zerkle et al., 2012). However, we find no evidence for oxic deposition in
164 core PI-1, suggesting that anoxia was a persistent feature throughout the depositional period,
165 and any oxygenation was likely restricted to surface waters.

166 The observation of persistent ferruginous water column conditions suggests that the
167 flux of Fe_{HR} to the lake overwhelmed the flux of sulfate (Poulton and Canfield, 2011). We
168 note here that our Os_i values suggest that any hydrothermal fluid contribution to the lake from
169 rifting or extensive weathering of rift-related basalts would have been negligible, as Os_i
170 values closer to ~0.13 (Allegre et al., 1999; Miesel et al., 2001) would otherwise be expected.
171 In consequence, there is no evidence to support a particularly enhanced influx of Fe due to
172 rifting. Instead, the prevalence of ferruginous water column conditions is consistent with low
173 rates of oxidative pyrite weathering driven by only modest levels of atmospheric oxygen
174 (Canfield and Raiswell, 1999). Although it is not possible to directly determine water column

175 sulfate concentrations, we note that pyrite sulfur isotope compositions are relatively heavy
176 ($8.5 \pm 6.3\text{‰}$) throughout most of the Nonesuch Formation (Fig. 2), while a compilation of
177 pyrite sulfur isotope data for the Nonesuch Formation shows a similar distribution (possibly
178 skewed towards slightly heavier values) to 1.5 - 1.0 Ga marine sediments (Fig. 3). This is
179 entirely consistent with a relatively low sulfate environment (e.g., Canfield and Raiswell,
180 1999), and further supports efficient trapping of sulfide (and hence high S/C ratios; Fig. DR2)
181 driven by a lack of bioturbation, and deposition from a ferruginous system which was sulfur
182 (rather than reactive Fe) limited (e.g., Raiswell and Canfield, 2012).

183 The distribution of the Nonesuch Formation sulfur isotope data is very different to
184 that observed for 1.18-1.0 Ga lacustrine sediments from NW Scotland (Fig. 3), with no
185 indication of large-scale fractionations that would indicate significant oxidative sulfur cycling
186 through microbial disproportionation. This is likely a consequence of the restriction of oxic
187 conditions to surface waters, and limitation of sulfate reduction to sediment porewaters
188 beneath the ferruginous water column of the Nonesuch basin. Together, this would limit
189 formation of the oxidized sulfur species required for disproportionation (Thamdrup et al.,
190 1993). In addition, the low sulfate concentrations inferred for the Nonesuch basin would limit
191 the maximum expression of sulfur isotope fractionation even if oxidative sulfur cycling and
192 disproportionation reactions were prevalent (Canfield and Raiswell, 1999). This is consistent
193 with multiple ($^{32/33/34}\text{S}$) sulfur isotope systematics in marine sediments, which suggest that
194 microbial sulfur disproportionation was prevalent by at least 1.3 Ga (Johnston et al., 2005),
195 but was only manifest in the major ($^{32/34}\text{S}$) sulphur isotope record after a later Neoproterozoic
196 rise in atmospheric oxygen led to a significant increase in seawater sulfate concentrations
197 (Canfield and Teske, 1996). Thus, rather than reflecting high sulfate concentrations
198 (Hieshima and Pratt, 1991) potentially attributable to extensive oxygenation of the continents

199 under high atmospheric oxygen, Fe-S-C systematics in the Nonesuch Formation suggest low
200 sulfate concentrations, ferruginous conditions and only modest atmospheric oxygenation.

201 In light of this, the sulfur isotope data for the Stoer and Torridon Groups may reflect
202 either an unusually sulfate-rich environment that allowed maximum expression of sulfur
203 isotope fractionations (Parnell et al., 2010), or the preservation of large sulfur isotope
204 fractionations through bacterial sulfate reduction alone (Canfield et al., 2010; Sim et al.,
205 2011). Thus, while it remains possible that sulfur isotope systematics in the Stoer and
206 Torridon Groups may be providing an early record of terrestrial oxygenation; our redox and
207 sulfur isotope data for the Nonesuch Formation suggest that early terrestrial oxygenation was
208 not a pervasive feature of localities that preserve evidence for diverse eukaryotic life. Instead,
209 the redox characteristics display strong similarities to the marine realm (Poulton and
210 Canfield, 2011), implying that in terms of water column and atmospheric oxygenation,
211 terrestrial environmental conditions were likely no more pre-disposed towards eukaryote
212 evolution than shallow marine environments. We suggest that the identification and detailed
213 redox evaluation of other late Mesoproterozoic terrestrial sediments should be a priority in
214 order to more precisely evaluate potential links between the redox evolution of aquatic
215 systems and the rich terrestrial biological record.

216

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222

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324 **FIGURE CAPTIONS**

325 **Figure 1:** A. Geological map of the Lake Superior region showing the location of the main
326 Keweenawan Supergroup units. The Nonesuch Formation is part of the Oronto Group
327 situated between continental red-beds of the Copper Harbour Conglomerate and the Freda
328 Sandstone and outcrops on the southern shores of Lake Superior. B. Schematic stratigraphy
329 of the Keweenawan Supergroup, focusing on post-rift sediments. The right hand panel
330 illustrates depth variations for each unit. Locations of the Re-Os (1078 ± 24 Ma; this study)
331 and U-Pb (1087.2 ± 1.6 Ma; Davis and Paces, 1990) ages are labelled. Figures adapted from
332 Elmore et al. (1989) and Ojakangas et al. (2001).

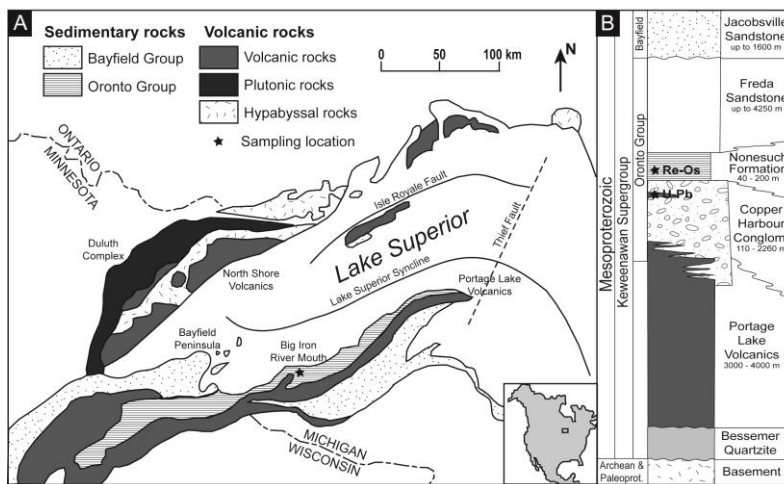
333

334 **Figure 2:** Geochemical profiles for the Nonesuch Formation core samples. For the Fe_{HR}/Fe_T
335 and Fe_{Py}/Fe_{HR} graphs the dashed lines show the fields for oxic or anoxic deposition and
336 ferruginous or euxinic deposition, respectively (Poulton and Canfield, 2011). On the Fe_T/Al
337 graph the dashed line represents average anoxic shale (Lyons and Severmann, 2006). On the
338 Fe_{PRS}/Fe_T graph the dashed lines represent modern (Raiswell and Canfield, 1998) and
339 Phanerozoic (Poulton and Raiswell, 2002) averages. CHC stands for Copper Harbour
340 Conglomerate.

341

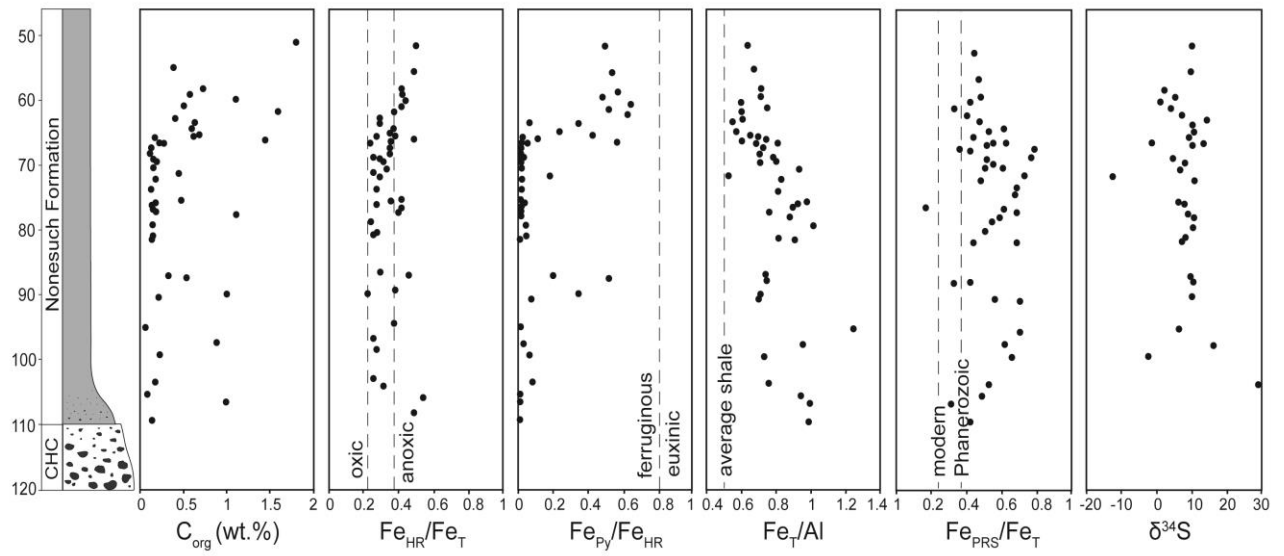
342 **Figure 3:** Probability density plot of pyrite sulfur isotope data for the Nonesuch Formation
 343 (this study; Imbus et al., 1992), the Torridon and Stoer Groups (Parnell et al., 2010) and 1.5 –
 344 1.0 Ga marine sediments (Canfield and Raiswell, 1999).
 345
 346 ¹GSA Data Repository item 2009xxx, which includes a detailed sampling and methodology
 347 section, a detailed Re-Os geochronology results section and results tables, is available online
 348 at www.geosociety.org/pubs/ft2009.htm, or on request from editing@geosociety.org or
 349 Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

350
 351 **FIGURE 1**



352
 353
 354 **FIGURE 2**

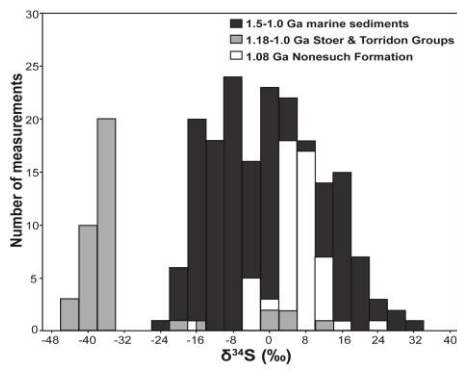
355



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358 **FIGURE 3**



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