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# 1 **Anoxia in the terrestrial environment during the late**

## 2 **Mesoproterozoic**

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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  $1078 \pm 24$  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.,

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

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

66

## 67 **GEOLOGICAL SETTING**

The Mid-Continent Rift System of central North America was one of the world's largest continental rifts (Ojakangas et al., 2001). In the Lake Superior region, up to 30 km of volcanic and sedimentary rift-fill sequences make up the Keweenaw Supergroup (Ojakangas et al., 2001; Fig. 1). The Oronto Group consists of fluvial and alluvial volcanoclastics, with the exception of the Nonesuch Formation, a 40 to 200 m thick succession of organic-rich siliciclastics. Geochronology of the Keweenaw Supergroup is 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  $1087.2 \pm 1.6$  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  $1040 \pm 78$  Ma ( $2\sigma$ ,  $n = 16$ , 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  $^{187}\text{Os}/^{188}\text{Os}$  ( $\text{Os}_i$ ) 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  $\text{Os}_i$   
88 values form two distinct groups, with eleven of the 16 samples yielding the most precise  
89 depositional age of  $1078 \pm 24$  Ma ( $2\sigma$ ,  $n = 11$ , 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  $0.81 \pm 0.28$  and  $0.49 \pm 0.13$  (Fig. DR1), a variation reflecting a balance  
116 between weathering of radiogenic Archean-Proterozoic cratonic lithosphere ( $\sim 1.01$ ; upper  
117 continental crust calculated at 1100 Ma; Esser and Turekian, 1993) and unradiogenic rift-  
118 related flood basalts ( $\sim 0.13$ ; Allegre et al., 1999). At 1100 Ma, seawater  $^{187}Os/^{188}Os$  was  
119 relatively unradiogenic at  $\sim 0.3$  (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 ( $1078 \pm 24$  Ma; this study)  
331 and U-Pb ( $1087.2 \pm 1.6$  Ma; Davis and Paces, 1990) ages are labelled. Figures adapted from  
332 Elmore et al. (1989) and Ojakangas et al. (2001).

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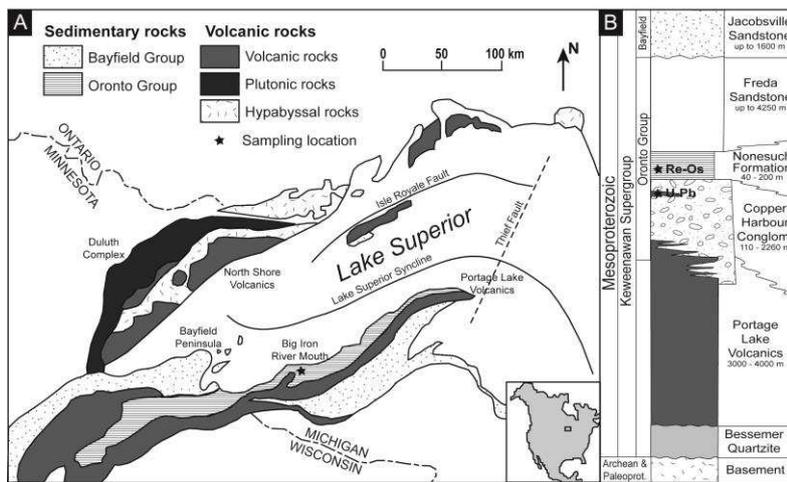
334 **Figure 2:** Geochemical profiles for the Nonesuch Formation core samples. For the  $Fe_{HR}/Fe_T$   
335 and  $Fe_{Py}/Fe_{HR}$  graphs the dashed lines show the fields for oxic or anoxic deposition and  
336 ferruginous or euxinic deposition, respectively (Poulton and Canfield, 2011). On the  $Fe_T/Al$   
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 <sup>1</sup>GSA 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](http://www.geosociety.org/pubs/ft2009.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or  
 349 Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

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351 **FIGURE 1**

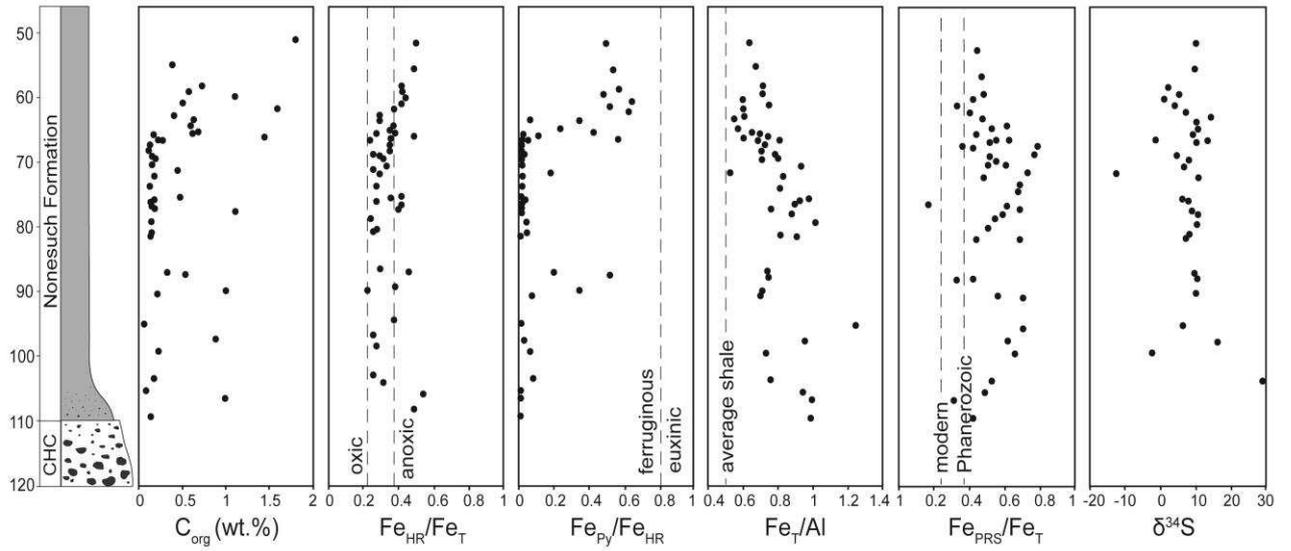


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353

354 **FIGURE 2**

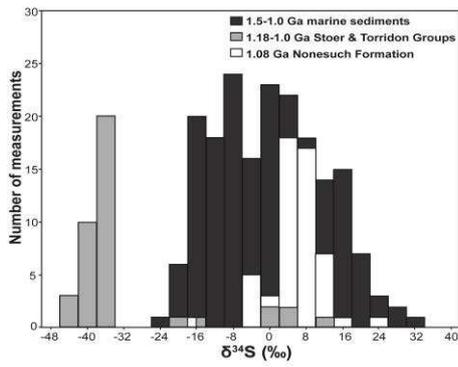
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358 **FIGURE 3**



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