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1 Secular variation in seawater redox state during the  
2 Marinoan Snowball Earth event and implications for  
3 eukaryotic evolution

4 **Weibing Shen<sup>1</sup>, Xiangkun Zhu<sup>1\*</sup>, Bin Yan<sup>1</sup>, Jin Li<sup>1</sup>, Pengju Liu<sup>1</sup>, Simon W.**  
5 **Poulton<sup>2</sup>**

6 *<sup>1</sup>MNR Laboratory of Isotope Geology, Institute of Geology, Chinese Academy of*  
7 *Geological Sciences, Beijing 100037, China.*

8 *<sup>2</sup>School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK.*

9 *\*Corresponding author: [xiangkunzhu@163.com](mailto:xiangkunzhu@163.com)*

10 **ABSTRACT**

11 The ocean is hypothesized to have been anoxic throughout the Marinoan  
12 ‘Snowball Earth’ event, from ca. 649-635 million years ago (Ma), with potentially  
13 catastrophic implications for the survival of eukaryotic life. However, the precise nature  
14 of ocean redox chemistry across this critical interval, and hence the factors that  
15 governed the persistence of eukaryotes, remain unknown. Here, we report records of  
16 pyrite Fe- and S-isotopes, combined with Fe-speciation, for glaciogenic diamictites  
17 from the Nantuo Formation of South China. These data provide constraints on seawater  
18 redox state across the Marinoan glaciation, and reveal that the redox state of the ocean  
19 fluctuated in concert with waxing and waning in the extent of glaciation, to include  
20 intervals of expanded oxygenation. The input of meltwater-derived oxygen provides a  
21 potential explanation for the persistence of eukaryotes through the Cryogenian  
22 ‘Snowball Earth’ events, which ultimately paved the way for subsequent intervals of  
23 rapid biological innovation.

24 **INTRODUCTION**

25 The Cryogenian Period is marked by two low-latitude glaciations, namely the  
26 Sturtian and Marinoan glaciations (Hoffman et al., 1998; Rooney et al., 2020). During  
27 these ‘Snowball Earth’ events, the ocean is generally considered to have been isolated  
28 from the atmosphere (Hoffman et al., 2017a). As such, the spatial development and  
29 persistence of anoxia, which was a prevalent feature of the deeper ocean prior to the  
30 glaciations (Canfield, 2008; Guilbaud et al., 2015), would have been exacerbated. The  
31 consequent global development of oceanic anoxia during the glacial period has been

32 proposed as a major constraint on the persistence of eukaryotes (Runnegar, 2000;  
33 Hoffman, et al., 2017a). However, molecular clock and biomarker evidence suggests  
34 major eukaryotic assemblages that had evolved before the Sturtian glaciation persisted  
35 through the Cryogenian (Love et al., 2009; Erwin, 2015). The fossil record, although  
36 sparse, has also verified that some extant eukaryotes, such as macroalgae and possible  
37 sponges (Ye et al., 2015; Turner 2021), survived the glaciations, resulting in an absence  
38 of any apparent eukaryotic bottleneck during the Cryogenian Period (Erwin, 2015).

39 Various ‘refugia’ have been proposed as a potential solution to this apparent  
40 paradox, including small and perhaps intermittent open-water systems and ice shadows  
41 (Hoffman, 2016), but the suitability and full extent of these habitats for eukaryotes have  
42 been questioned (Moczyłowska et al., 2008; Hawes, et al., 2018). Here, we address  
43 this issue via pyrite Fe-S isotope and Fe-speciation analyses of glacial diamictite from  
44 the Nantuo Formation, South China, which allows a detailed reconstruction of oceanic  
45 redox state across the Marinoan glaciation.

## 46 **GEOLOGICAL SETTING AND SEDIMENTARY INTERPRETATION**

47 The Nantuo Formation is widely preserved on the Yangtze block, South China (Fig.  
48 1; Text S1 in Supplementary Materials). Zircons from tuffaceous units constrain  
49 deposition to between ca.  $649 \pm 2.4$  Ma and ca.  $635 \pm 0.6$  Ma, corresponding to the  
50 Marinoan glaciation (Condon et al., 2005; Zhou et al., 2018). We focus our analyses on  
51 well-preserved samples from drill core ZK01, located in Taojiang city, Hunan Province.  
52 In drill core ZK01, the Nantuo Formation has a conformable contact with both the  
53 underlying interglacial deposits and the overlying post-glacial deposits, and can be

54 divided into four units (Fig. 2). Unit I is composed of pebbly sandstone/siltstone  
55 underlying diamictite, showing a shallowing sequence, whereas Unit II consists of  
56 pebbly siltstone and mudstone/carbonate overlying diamictite, reflecting a deepening  
57 sequence. Similarly, units III and IV change from lower siltstone and pebbly sandstone  
58 through middle diamictite to upper pebbly sandstone/siltstone, recording another  
59 sedimentary cycle. These sedimentary cycles as recorded in drill core ZK01 are a  
60 common phenomenon on the Yangtze block, as well as on other continents (Fig. 1b;  
61 Shen et al., 2021).

62 It has been proposed that such facies change in glacial deposits may have been  
63 induced by excessive topography relief during the global glaciation (Hoffman et al.,  
64 2017b). In this scenario, deposition of diamictite during ice sheet melting may have  
65 both created and destroyed topography within a short distance, leading to small-scale  
66 migration of the depocenter and complexity in the stratigraphic detail of glacial deposits  
67 (Hoffman et al., 2017b). However, this scenario does not appear to explain the facies  
68 variability in the Nantuo Formation, which can be correlated across the Yangtze block  
69 (Fig. 1b; Lang et al., 2018a). In particular, the thick sequence of siltstone/mudstones  
70 and carbonate beds in the Nantuo Formation cannot be simply interpreted as deposits  
71 during ice sheet melting (Fig. 1b; Shen et al., 2021). Rather, the Nantuo diamictites and  
72 pebbly sandstone/siltstone are generally considered to reflect deposition in a glacial  
73 marine environment, representing proximal glaciomarine and distal glaciomarine facies,  
74 respectively, whereas the pebble-free mudstone and carbonate may represent normal  
75 marine deposition without the influence of glaciation (Allen and Etienne, 2008; Lang

76 et al., 2018a). Thus, the repetition of glacially influenced units separated by non-glacial  
77 units in the Nantuo Formation appears to record ice-sheet advancing-retreating cycles  
78 and sea-level fluctuations (Figs. 1b and 2; Shen et al., 2021), suggesting Marinoan  
79 glaciation dynamics (Text S2; Liu et al., 2020).

## 80 **SAMPLING AND METHODS**

81 Thin sections were prepared to guide the sampling of pyrite and fine-grained  
82 siliciclastic components (matrix). To avoid large-sized clasts in diamictites, matrix  
83 samples were obtained using a handheld drill. Under the optical and scanning electron  
84 microscope, pyrite morphologies are dominated by euhedral, subhedral, aggregates,  
85 and disseminated pyrite (Fig. 2), indicating a diagenetic origin rather than detrital pyrite.  
86 For total organic carbon (TOC) analyses, sample powders were combusted in a pure  
87 oxygen atmosphere and analyzed via a LECO CS-230. Fe speciation was performed  
88 via standard techniques (Poulton, 2021), with analysis via AAS. For Fe isotope ( $\delta^{56}\text{Fe}_{\text{py}}$ )  
89 measurements, large euhedral pyrite grains were hand-picked, and Fe was purified  
90 using ion-exchange chromatography and measured via Nu-MC-ICP-MS. For in situ S  
91 isotope ( $\delta^{34}\text{S}_{\text{py}}$ ) analyses, euhedral pyrite ( $> 50 \mu\text{m}$ ) was selected and measured via LA-  
92 MC-ICP-MS. More detailed methods are provided in the Supplementary Materials.

## 93 **RESULTS**

94 TOC concentrations are low throughout the section, whereas  $\delta^{56}\text{Fe}_{\text{py}}$ ,  $\delta^{34}\text{S}_{\text{py}}$  and  
95 Fe-speciation systematics show distinct variability (Fig. 3). In the lower part of Unit I,  
96  $\delta^{56}\text{Fe}_{\text{py}}$  values overall are negative, while  $\delta^{34}\text{S}_{\text{py}}$  values decrease upwards. Highly  
97 reactive Fe ( $\text{Fe}_{\text{HR}}$ ) to total Fe ( $\text{Fe}_{\text{T}}$ ) ratios are particularly low ( $0.14 \pm 0.01$ ) throughout

98 this interval. The extent of pyritization of  $\text{Fe}_{\text{HR}}$  is also low, and while the proportion of  
99 ferric (oxyhydr)oxides ( $\text{Fe}_{\text{ox}}/\text{Fe}_{\text{HR}}$ ) shows an overall peak in the lower part of Unit I,  
100 ratios are low throughout the section. The upper part of Unit I is characterized by  
101 intermediate and fluctuating  $\delta^{56}\text{Fe}_{\text{py}}$  values, a positive trend in  $\delta^{34}\text{S}_{\text{py}}$  values, slightly  
102 increased average  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$  ratios, low  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$  ratios, and low  $\text{Fe}_{\text{ox}}/\text{Fe}_{\text{HR}}$  ratios that  
103 decrease through the interval (Fig. 3).

104 In Unit II, the majority of  $\delta^{56}\text{Fe}_{\text{py}}$  values are positive (Fig. 3).  $\delta^{34}\text{S}_{\text{py}}$  values show  
105 a general decrease, while  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$  and  $\text{Fe}_{\text{ox}}/\text{Fe}_{\text{HR}}$  ratios slightly increase through Unit  
106 II, coincident with a general decrease in  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$ . In units III and IV,  $\delta^{56}\text{Fe}_{\text{py}}$  values  
107 show considerable variability, but there is a distinct shift from negative values to  
108 positive values, followed by a decrease to negative values, while  $\delta^{34}\text{S}_{\text{py}}$  values show an  
109 inverse trend (Fig. 3).  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$  ratios progressively increase through units III and IV,  
110 while  $\text{Fe}_{\text{ox}}/\text{Fe}_{\text{HR}}$  ratios show the opposite trend, and  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$  ratios increase  
111 considerably towards the top of the section.

## 112 **DISCUSSION**

### 113 **Variability in Seawater Redox State**

114 Sedimentary pyrite Fe isotope data provide a first-order indication of seawater  
115 redox state (Zhang et al., 2015). In particular, positive  $\delta^{56}\text{Fe}_{\text{py}}$  values are indicative of  
116 ferruginous conditions, whereas negative to near-zero  $\delta^{56}\text{Fe}_{\text{py}}$  values can be observed  
117 under a variety of redox conditions (Text S4; Severmann et al., 2008; Planavsky et al.,  
118 2012). We thus interpret the large stratigraphic variability in  $\delta^{56}\text{Fe}_{\text{py}}$  values to document  
119 variations in redox state (Fig. 3). Furthermore, the positive  $\delta^{56}\text{Fe}_{\text{py}}$  values observed for

120 many of the samples likely reflect ferruginous conditions, with partial oxidation of  
121 ferrous to ferric iron in the water column followed by reduction and transformation of  
122 ferric (oxyhydr)oxides into pyrite during early diagenesis. By contrast, the negative to  
123 near-zero  $\delta^{56}\text{Fe}_{\text{py}}$  values for some samples may have developed under either euxinic or  
124 oxic conditions.

125 Fe-speciation systematics (Text S4; Raiswell and Canfield, 1998; Poulton, 2021)  
126 allow a more nuanced evaluation of the precise nature of redox variability.  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}} >$   
127 0.38 generally provides a robust indication of water column anoxia (Raiswell and  
128 Canfield, 1998), whereas ratios for oxic conditions are generally significantly lower  
129 ( $0.14 \pm 0.08$ ; Poulton and Raiswell, 2002). However, due to inherent variability in the  
130 source rocks deposited in a particular region, wherever possible, an oxic baseline should  
131 be derived for the precise rocks being analysed (Poulton, 2021). This is particularly  
132 significant, since rapid deposition (as would likely be the case for the Nantuo Formation  
133 diamictites) may mask the  $\text{Fe}_{\text{HR}}$  depositional flux from an anoxic water column. Where  
134 samples show evidence of anoxic deposition,  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$  ratios above 0.6–0.8 distinguish  
135 a euxinic water column from ferruginous depositional conditions (Poulton, 2021).

136 The negative  $\delta^{56}\text{Fe}_{\text{py}}$  values in the lower part of Unit I coincide with very low  
137  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$  ratios and peak  $\text{Fe}_{\text{ox}}/\text{Fe}_{\text{HR}}$  ratios, strongly supporting oxic deposition and  
138 allowing an oxic  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$  baseline ratio ( $0.14 \pm 0.01$ ) to be defined for the Nantuo  
139 Formation (Fig. 3). The  $\delta^{56}\text{Fe}_{\text{py}}$  values for the lower part of Unit I can thus be considered  
140 to document oxic depositional conditions followed by conversion of a proportion of the  
141 Fe (oxyhydr)oxide pool to pyrite during diagenesis.  $\delta^{56}\text{Fe}_{\text{py}}$  values in the upper part of



142 Unit I fluctuate between negative and positive, while  $Fe_{HR}/Fe_T$  ratios are either similar  
143 to, or slightly above, the oxic baseline. We interpret these samples to represent a  
144 fluctuating redox state, with low  $Fe_{py}/Fe_{HR}$  ratios supporting oxic through to  
145 ferruginous conditions. This overall more reducing state relative to the lower part of  
146 Unit I is also supported by a general decrease in the preservation of Fe (oxyhydr)oxides  
147 (i.e., lower  $Fe_{ox}/Fe_{HR}$ ).

148 More stable (but potentially fluctuating) ferruginous anoxia is then indicated  
149 throughout Unit II (positive  $\delta^{56}Fe_{py}$  values, combined with slightly elevated  $Fe_{HR}/Fe_T$   
150 and low  $Fe_{py}/Fe_{HR}$ ), but a transition to dominantly oxic conditions is indicated at the  
151 base of Unit III (negative  $\delta^{56}Fe_{py}$  values, combined with a progressive increase in  
152  $Fe_{ox}/Fe_{HR}$ ) (Fig. 3). The main part of Unit III shows a clear redox progression (Fig. 3),  
153 with the initial development of stable ferruginous conditions (positive  $\delta^{56}Fe_{py}$  values,  
154 combined with a transition to highly elevated  $Fe_{HR}/Fe_T$ , lower  $Fe_{ox}/Fe_{HR}$ , and  
155 persistently low  $Fe_{py}/Fe_{HR}$ ). Subsequently, however, the transition to negative  $\delta^{56}Fe_{py}$   
156 values, combined with highly elevated  $Fe_{py}/Fe_{HR}$  ratios in Unit IV, indicates the  
157 development of water column euxinia. Here, the negative to near-zero  $\delta^{56}Fe_{py}$  values  
158 indicate near-quantitative uptake of ferrous Fe into pyrite.

159 The seawater redox variability we document is further supported by  $\delta^{34}S_{py}$  data.  
160 Generally, relatively heavy  $\delta^{34}S_{py}$  values suggest a smaller seawater sulfate reservoir  
161 (SSR), which may be driven by the expansion of anoxia (Text S4; Canfield, 1998;  
162 Habicht et al., 2002). Thus, gradually decreasing  $\delta^{34}S_{py}$  values in Unit II and the lower  
163 part of Unit I suggest an expanding SSR, which is likely tied to our evidence for an

164 increase in seawater oxygenation through these intervals. Conversely, gradually  
165 increasing  $\delta^{34}\text{S}_{\text{py}}$  values in units III-IV and in the upper part of Unit I support a  
166 diminishing SSR due to expanded anoxia (Fig. 3).

### 167 **Mechanisms for Seawater Redox Evolution**

168 This dynamic redox history, particularly the intervals of expanded seawater  
169 oxygenation, is perhaps surprising given the prevalence for the development of ocean  
170 anoxia during ‘Snowball Earth’ events (Hoffman et al., 2017a). However, there are  
171 several potential explanations for redox instability. Firstly, fluctuations in sea-level,  
172 may have brought the site of sedimentation into and out of a more oxygenated surface  
173 ocean. However, there is an apparent contradiction between seawater redox state and  
174 sea-level, whereby seawater oxygenation corresponds to rising sea-levels in Unit II (Fig.  
175 3; Text S5), suggesting that this is an unlikely explanation.

176 Another possible control on the dynamic redox history concerns the periodic  
177 development of open water, leading to enhanced productivity and  $\text{O}_2$  production (Ye et  
178 al., 2015), as well as exchange of  $\text{O}_2$  between the atmosphere and ocean (Johnson et al.,  
179 2017). However, while these two scenarios may have contributed to the redox dynamics,  
180 we note that there is no significant shift in TOC burial (albeit on a highly local scale)  
181 that might otherwise indicate enhanced oxygen production (Fig. 3). Furthermore, rapid  
182 equilibration between the atmosphere and ocean due to the periodic open water may be  
183 expected to lead to abrupt intervals of seawater oxygenation (Le Hir et al., 2008). Thus,  
184 while such a process may explain the more rapid fluctuations in oxygenation observed  
185 in upper part of Unit I, it does not provide a compelling explanation for the progressive

186 changes recorded in other parts of the Nantuo Formation.

187 We thus additionally consider that during the ‘Snowball’ glaciation, air bubbles  
188 would have been readily trapped within the snow (meteoric ice) and subsequently  
189 incorporated into glacial ice (Hoffman et al., 2017a). Upon melting of the glacier, O<sub>2</sub>  
190 derived from the air bubbles would lead to the formation of oxygenated meltwater.  
191 When subglacial drainage was channeled, oxygenated meltwater would have short  
192 residence time and would be transported to ice shelf waters (Jenkins, 1999), resulting  
193 in oxidized seawater (Lechte et al., 2019). Conversely, the distributed drainage and  
194 longer residence time of oxygenated meltwater may have had little influence on  
195 subglacial seawater anoxia (Tranter, 1997; Lechte et al., 2019). The sedimentology of  
196 the studied Marinoan deposits appears to record ice-sheet advancing-retreating cycles,  
197 controlling meltwater supply and subglacial drainage scale (Fig 2; Text S2; Shen et al.,  
198 2021), and hence seawater redox. Specifically, during ice sheet retreat, ice thinning and  
199 sufficient meltwater favored formation of an interconnected drainage system, likely  
200 driving expanded oxygenation of the ocean, whereas the meltwater supply and drainage  
201 system during ice sheet advance were far less efficient, leading to possible ocean  
202 deoxygenation (Fig. 4).

203 The ice-sheet dynamics and associated fluctuations in meltwater-derived O<sub>2</sub> influx  
204 provide a compelling explanation for longer-term changes in seawater redox state  
205 observed in the Nantuo Formation. During the first ice retreat, a relative increase in  
206 meltwater-derived O<sub>2</sub> influx controlled the seawater oxygenation documented in Unit  
207 II (Fig. 3), and ultimately resulted in oxic conditions at the base of Unit III. By contrast,

208 the seawater deoxygenation recorded in Unit III and the upper part of Unit I may have  
209 been linked to a decrease in meltwater-derived O<sub>2</sub> influx during the second and first ice  
210 advances, respectively (Fig. 3). The euxinic conditions recorded in Unit IV, even with  
211 increasing meltwater-derived O<sub>2</sub> during the second ice retreat, were mainly driven by  
212 significant sulfate reduction in the water column (Lang et al., 2018b).

### 213 **Implications for Eukaryotic Evolution**

214 While the secular variation in seawater redox state we document was likely  
215 linked to a variety of factors, including potential changes in productivity and air-sea O<sub>2</sub>  
216 exchange during intervals of open water, a dynamic meltwater-derived O<sub>2</sub> influx due to  
217 Marinoan glaciation dynamics was likely more important and of widespread  
218 significance (Fig. 4). The oceanic influx of meltwater-derived O<sub>2</sub>, although decreased  
219 during ice-sheet advance, was long-lived and widespread throughout the glaciation,  
220 thus meeting the basic requirement for survival of subglacial eukaryotic assemblages.  
221 This persistence of eukaryotic life ultimately paved the way for the subsequent shift in  
222 ecosystem complexity (e.g., the Lantian biota; Yuan et al., 2011) witnessed shortly after  
223 the terminal Marinoan glaciation.

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### 333 **FIGURE CAPTIONS**

334 **Fig. 1. a)** Late Neoproterozoic tectonic division and facies distribution in South China.  
335 **b)** Cyclicity in the Nantuo Formation at a basin-to-platform scale. Photographs of  
336 the Nantuo Formation showing **c)** diamictites, **d)** dropstone, **e)** lonestone, and **f)**  
337 shale.

338 **Fig. 2** Sedimentology and petrography characteristics of the Nantuo Formation in drill

339 core ZK01. Radiometric ages from Condon et al. (2005) and Zhou et al. (2018).

340 **Fig. 3.** Geochemistry related to sedimentary records through the Nantuo Formation in  
341 drill core ZK01.

342 **Fig. 4.** Schematic diagram showing seawater redox evolution during the Marinoan  
343 glaciation. **a)** During ice-sheet advance, anoxic conditions prevailed in the ice-  
344 covered ocean. **b)** During ice-sheet retreat, an abundant influx of meltwater-  
345 derived O<sub>2</sub> led to expanded seawater oxygenation.