

## **Uranium and molybdenum isotope evidence for an episode of widespread ocean oxygenation during the late Ediacaran Period**

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Manuscript accepted for *Geochimica et Cosmochimica Acta*

2015

<https://doi.org/10.1016/j.gca.2015.02.025>

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1 **Abstract**

2 To improve estimates of the extent of ocean oxygenation during the late Ediacaran  
3 Period, we measured the U and Mo isotope compositions of euxinic (anoxic and sulfidic)  
4 organic-rich mudrocks (ORM) of Member IV, upper Doushantuo Formation, South China. The  
5 average  $\delta^{238}\text{U}$  of most samples is  $0.24 \pm 0.16$  ‰ (2SD; relative to standard CRM145), which is  
6 slightly higher than the average  $\delta^{238}\text{U}$  of  $0.02 \pm 0.12$  ‰ for restricted Black Sea (deep-water Unit  
7 I) euxinic sediments and is similar to a modeled  $\delta^{238}\text{U}$  value of 0.2 ‰ for open ocean euxinic  
8 sediments in the modern well-oxygenated oceans. Because  $^{238}\text{U}$  is preferentially removed to  
9 euxinic sediments compared to  $^{235}\text{U}$ , expanded ocean anoxia will deplete seawater of  $^{238}\text{U}$   
10 relative to  $^{235}\text{U}$ , ultimately leading to deposition of ORM with low  $\delta^{238}\text{U}$ . Hence, the high  $\delta^{238}\text{U}$   
11 of Member IV ORM points to a common occurrence of extensive ocean oxygenation ca. 560 to  
12 551 Myr ago.

13 The Mo isotope composition of sediments deposited from strongly euxinic bottom waters  
14 ( $[\text{H}_2\text{S}]_{\text{aq}} > 11 \mu\text{M}$ ) either directly records the global seawater Mo isotope composition (if Mo  
15 removal from deep waters is quantitative) or represents a minimum value for seawater (if Mo  
16 removal is not quantitative). Near the top of Member IV,  $\delta^{98}\text{Mo}$  approaches the modern seawater  
17 value of  $2.34 \pm 0.10$ ‰. High  $\delta^{98}\text{Mo}$  points to widespread ocean oxygenation because the  
18 preferential removal of isotopically light Mo to sediments occurs to a greater extent in  $\text{O}_2$ -rich  
19 compared to  $\text{O}_2$ -deficient marine environments. However, the  $\delta^{98}\text{Mo}$  value for most Member IV  
20 ORM is near 0‰ (relative to standard NIST SRM 3134 = 0.25‰), suggesting extensive anoxia.  
21 The low  $\delta^{98}\text{Mo}$  is at odds with the high Mo concentrations of Member IV ORM, which suggest a  
22 large seawater Mo inventory in well-oxygenated oceans, and the high  $\delta^{238}\text{U}$ . Hence, we propose  
23 that the low  $\delta^{98}\text{Mo}$  of most Member IV ORM was fractionated from contemporaneous seawater.

24 Possible mechanisms driving this isotope fractionation include: (1) inadequate dissolved sulfide  
25 for quantitative thiomolybdate formation and capture of a seawater-like  $\delta^{98}\text{Mo}$  signature in  
26 sediments or (2) delivery of isotopically light Mo to sediments via a particulate Fe-Mn  
27 oxyhydroxide shuttle.

28 A compilation of Mo isotope data from euxinic ORM suggests that there were transient  
29 episodes of extensive ocean oxygenation that break up intervals of less oxygenated oceans  
30 during late Neoproterozoic and early Paleozoic time. Hence, Member IV does not capture  
31 irreversible deep ocean oxygenation. Instead, complex ocean redox variations likely marked the  
32 transition from  $\text{O}_2$ -deficient Proterozoic oceans to widely oxygenated later Phanerozoic oceans.

33

34

## 1. INTRODUCTION

35

36 High concentrations of environmental oxygen are a physiological requirement for the  
37 evolution of metabolically active metazoans capable of movement and predation (Towe, 1970;  
38 Runnegar, 1991; Knoll and Carroll, 1999; Knoll, 2011). The time when this requirement was met  
39 is not precisely known. Furthermore, there is debate about whether or not environmental  
40 oxygenation is the main driver of trends in early metazoan evolution, once the physiological  
41 requirement was met. Some studies highlight a direct connection between the initial  
42 diversification of Ediacaran metazoans and ocean oxygenation, for example, in the aftermath of  
43 the ca. 635 Ma end-Cryogenian glaciation (Planavsky et al., 2010; Sahoo et al., 2012).  
44 Alternatively, a significant time lag between the attainment of sufficient oxygen levels and the  
45 diversification of metazoans may have arisen from genetic and ecological factors (Erwin et al.,  
46 2011; Mills et al., 2014; Penny et al., 2014; Planavsky et al., 2014). The appearance of more

47 complex eukaryotes, including early metazoans, may have led to more extensive ocean  
48 oxygenation (Butterfield, 2009; Lenton et al., 2014). Environmental and ecological triggers may  
49 have acted in tandem to drive metazoan diversification, culminating in the Cambrian Explosion  
50 (Sperling et al., 2013a). Understanding the relationship between environmental oxygen levels  
51 and metazoan evolution ultimately requires higher resolution geochemical, geochronological,  
52 and biostratigraphic data, as well as improved quantitative constraints on spatiotemporal changes  
53 in atmosphere and ocean redox conditions (e.g., Och and Shields-Zhou, 2012; Lowenstein et al.,  
54 2014; Lyons et al., 2014).

55         Geochemical proxies for the extent of ocean oxygenation during the Ediacaran Period  
56 suggest a time of complicated redox changes. High concentrations of the redox-sensitive metals  
57 Mo and V are found in the earliest Ediacaran (ca. 632 Ma) organic-rich mudrocks (ORM) of the  
58 Doushantuo Formation (South China). The high Mo and V concentrations point to a larger  
59 oceanic Mo and V inventory as a result of increased deep ocean oxygenation (Sahoo et al.,  
60 2012). However, there is no compelling evidence for extensive oxygenation during the remainder  
61 of the early Ediacaran Period. For example, sedimentary Fe speciation, S and Fe isotope data,  
62 and low Mo concentrations in ORM suggest widely anoxic oceans containing low marine sulfate  
63 concentrations (Canfield et al., 2008; McFadden et al., 2008; Li et al., 2010; Fan et al., 2014;  
64 Guan et al., 2014). These data suggest that the oceans largely retained a Proterozoic-style, redox-  
65 stratified character during the early Ediacaran Period.

66         There is geochemical evidence to support episodes of late Ediacaran ocean oxygenation.  
67 Although sedimentary Fe speciation data continue to point to regions of at least locally anoxic  
68 deep oceans (Canfield et al., 2008; Li et al., 2010; Frei et al., 2013; Johnston et al., 2013), the  
69 same proxy suggests that parts of the deep ocean became oxygenated after the end of the ca. 580

70 Ma Gaskiers glaciation (Canfield et al., 2007, 2008; Johnston et al., 2012a). High Mo  
71 concentrations in ca. 560-551 Ma ORM of Member IV, upper Doushantuo Formation (South  
72 China), point to a more globally oxygenated state for the oceans (Scott et al., 2008; Li et al.,  
73 2010; Och and Shields-Zhou, 2012). However, the absence of evidence for late Ediacaran ocean  
74 oxygenation in some ocean basins has led some researchers to question the extent of oxygenation  
75 (Johnston et al., 2013). The isotopic compositions of U and Mo in anoxic and sulfidic (euxinic)  
76 ORM are a promising approach for constraining the global extent of ancient ocean oxygenation  
77 (Arnold et al., 2004; Weyer et al., 2008). Here, we present new U and Mo isotope data from  
78 Member IV ORM that provide further evidence for extensive ocean oxygenation ca. 560-551  
79 Myr ago. We also present an updated Mo isotope compilation for ORM that suggests multiple  
80 transient episodes of widespread ocean oxygenation occurred at the Precambrian-Phanerozoic  
81 transition.

82

## 83 **2. MEMBER IV, DOUSHANTUO FORMATION, SOUTH CHINA**

84

85 The Doushantuo Formation was deposited between 635 and 551 Ma on a passive margin  
86 continental shelf (Nanhua Basin, South China) on the Yangtze Block following the breakup of  
87 Rodinia (Wang and Li, 2003; Jiang et al., 2003). The Doushantuo Formation is underlain by  
88 glacial diamictites of the Nantuo Formation, deposited during the widespread end-Cryogenian  
89 glaciation, and is overlain by carbonates of the latest Ediacaran Dengying Formation. In the  
90 Three Gorges region, located ~30 km west of Yichang (Fig. 1), the Doushantuo Formation was  
91 deposited on the inner shelf (Western Hubei Platform) below wave base (McFadden et al., 2008;  
92 Jiang et al., 2011). Here, the formation is up to 250 m thick and comprises a basal ~5 m thick

93 dolostone (Member I), interbedded ORM and dolostones containing abundant chert nodules  
94 (Member II), dolostone that passes into interbedded limestone and dolomitic mudstone (Member  
95 III), and a ~5-15 m thick interval of ORM (Member IV) (Fig. 2, Zhou and Xiao, 2007;  
96 McFadden et al., 2008; Sawaki et al., 2010; Jiang et al., 2011).

97 Fossil assemblages in the Doushantuo Formation and correlatives include macroscopic  
98 carbonaceous compressions of eukaryotes, multicellular algae, acanthomorph acritarchs, and  
99 possible animal eggs and embryos (Xiao et al., 2002; Yin et al., 2007; McFadden et al., 2008;  
100 Yuan et al., 2011; Schiffbauer et al., 2012; Chen et al., 2014). Alternative interpretations for  
101 these embryo-like fossils, such as non-metazoan holozoans (Huldtgren et al., 2011) or sulfur  
102 bacteria (Bailey et al., 2007), are inconsistent with their morphology, taphonomy and  
103 multicellularity (Xiao et al., 2007, 2012; Schiffbauer et al., 2012; Chen et al., 2014). The  
104 overlying carbonates of the latest Ediacaran Dengying Formation preserve macroscopic  
105 metazoan body fossils, biomineralizing metazoans (e.g., *Cloudina* and *Sinotubulites*), and large  
106 horizontal trace fossils made by motile bilaterians (Xiao et al., 2005; Weber et al., 2007; Chen et  
107 al., 2008).

108 To obtain better quantitative constraints on the extent of late Ediacaran ocean  
109 oxygenation, we measured U and Mo isotope compositions, Fe speciation, and total organic  
110 carbon (TOC) concentrations for the Member IV ORM. Our measurements were obtained from  
111 the well-studied Jiulongwan outcrop section, Three Gorges region (McFadden et al., 2008), plus  
112 a recently drilled core collected 5 km farther southwest (Site 1 of Sawaki et al., 2010) to test  
113 lateral homogeneity of the data and to verify that deleterious oxidative weathering was  
114 negligible. Previous work has revealed high Mo concentrations in Member IV, which most likely  
115 requires a large dissolved Mo reservoir, suggesting both significant ocean oxygenation and a

116 good connection between the Nanhua Basin and open ocean (Scott et al., 2008; Sahoo et al.,  
117 2012).

118         Precise absolute age constraints for the duration of Member IV deposition have been  
119 challenging to obtain. The end of Member IV deposition is well-constrained by a U-Pb zircon  
120 age of  $551.1 \pm 0.6$  Ma (Mean Square of Weighted Deviates [MSWD] = 0.48) from an ash bed  
121 nearly 1 m below the top of the member (from the Jiuqunao section located ~20 km northwest of  
122 the Three Gorges region; Condon et al., 2005). However, the onset of Member IV deposition is  
123 poorly constrained. The top of Member IV (ca. 551 Ma) marks the end of a prominent negative  
124  $\delta^{13}\text{C}$  excursion that began in Member III (Jiang et al., 2007; Zhou and Xiao, 2007; Zhu et al.,  
125 2007; McFadden et al., 2008; Sawaki et al., 2010). This excursion has been correlated with the  
126 Shuram  $\delta^{13}\text{C}$  excursion in Oman (Fike et al., 2006; Le Guerroué, 2010), the Wonoka  $\delta^{13}\text{C}$   
127 excursion in Australia (Calver, 2000; Retallack et al., 2014), and the Krol B  $\delta^{13}\text{C}$  excursion in  
128 India (Kaufman et al., 2006; Jiang et al., 2007). Although there is no absolute age constraint for  
129 the duration of this  $\delta^{13}\text{C}$  excursion in any of these successions, stratigraphic analyses and Sr  
130 isotope data suggest that the Doushantuo-Shuram-Wonoka-Krol isotope anomaly is younger than  
131 the Gaskiers glaciation (Calver, 2000; Fike et al., 2006; Le Guerroué, 2010; Sawaki et al., 2010).  
132 This interpretation is in line with the suggestion that the stratigraphic break at the Member II-III  
133 transition reflects sea-level fall during the Gaskiers glaciation and is thus ca. 580 Ma (Condon et  
134 al., 2005; Tahata et al., 2013). Considering that the Doushantuo Formation (ca. 635–551 Ma)  
135 covers ~90% of Ediacaran time, a simple age extrapolation would place the base of Member IV  
136 at ca. 560 Ma (e.g., Jiang et al., 2007). This estimate is consistent with a Pb-Pb age of  $576 \pm 14$   
137 Ma (MSWD = 0.4) from the upper phosphorite layers (Member III correlative) of the  
138 Doushantuo Formation in Weng'an, located 750 km to the southwest of the Three Gorges region



139 (Chen et al., 2004), and the similarity of acritarch fossils between the Jiulongwan and Weng'an  
140 sections (e.g., Zhou et al., 2007; Xiao et al., 2014).

141         Recently, a Re-Os age of  $595 \pm 22$  Ma (MSWD = 29) was reported from ORM at the  
142 base of Member IV in the Jiulongwan section (Zhu et al., 2013). A more precise Re-Os age of  
143  $591.1 \pm 5.3$  Ma (MSWD = 1.3) was derived from a subset of four analyses that made up the 7-  
144 point Re-Os isochron regression of  $595 \pm 22$  Ma. Zhu et al. (2013) attributed the excess scatter in  
145 the 7-point regression to initial  $^{187}\text{Os}/^{188}\text{Os}$  heterogeneity (i.e., variations in seawater  $^{187}\text{Os}/^{188}\text{Os}$ )  
146 rather than post-depositional disturbance. However, the seven samples were obtained from a  
147 lateral interval of only ~5 to 10 cm thick, raising doubts about whether variations in seawater  
148  $^{187}\text{Os}/^{188}\text{Os}$  can explain the high MSWD. As discussed below, the basal Member IV ORM from  
149 the Jiulongwan section have unusual Mo and U isotope signatures, which may reflect post-  
150 depositional modification that could have had an adverse effect on the Re-Os age of Zhu et al.  
151 (2013). In addition, the Re-Os age of ca. 591 Ma implies that the  $\leq 10$ -m-thick Member IV black  
152 shales span 40 Myr of time. This is unlikely unless a major unconformity or hiatus is found  
153 within Member IV in future studies. Therefore, we prefer to estimate the age of Member IV as  
154 ca. 560–551 Ma.

155

156

### 3. ANALYTICAL METHODS

157

#### 3.1 Uranium isotopes

159         All U and Mo isotope data were obtained at the W. M. Keck Foundation Laboratory for  
160 Environmental Biogeochemistry, School of Earth and Space Exploration, Arizona State  
161 University. Uranium isotope measurements were made following the protocols outlined in

162 Weyer et al. (2008) and Kendall et al. (2013). Powdered sample splits (75-100 mg) were ashed  
163 overnight at 550°C and dissolved completely by HF-HNO<sub>3</sub>-HCl acid digestion. A split of the  
164 sample solution was diluted with 2% HNO<sub>3</sub> and analyzed for U concentrations on a Thermo  
165 Scientific X series quadrupole ICP-MS (inductively coupled plasma mass spectrometer).  
166 Instrument accuracy was verified using secondary standard solutions, including the USGS  
167 Devonian black shale standard SDO-1. Analyte concentration reproducibility was within 5%.

168 Uranium isotope compositions were measured on a Thermo Scientific Neptune multi-  
169 collector ICP-MS using a <sup>236</sup>U:<sup>233</sup>U double spike (IRMM-3636; Verbruggen et al., 2008) to  
170 correct for instrumental mass bias. The spike was equilibrated with sample solutions, and U was  
171 subsequently isolated from the sample-spike mixture using Eichrom® UTEVA resin. Sample  
172  $\delta^{238}\text{U}$  is reported as per mil deviations from the CRM145 standard [ $\delta^{238}\text{U} =$   
173  $(^{238/235}\text{U}_{\text{sample}}/^{238/235}\text{U}_{\text{standard}} - 1) \times 1000$ ]. Repeated measurements of the U isotope standards  
174 SRM950a and CRM129a yielded average  $\delta^{238}\text{U}$  values of  $0.04 \pm 0.06$  ‰ (2SD; n = 38) and –  
175  $1.72 \pm 0.09$  ‰ (2SD; n = 124), respectively. Hence, U isotope data reported relative to CRM145  
176 are statistically identical to U isotope data reported relative to SRM950a (e.g., Weyer et al.,  
177 2008; Montoya-Pino et al., 2010; Brennecka et al., 2011a, b; Kendall et al., 2013). We also  
178 measured four full powder replicates of SDO-1 during the course of this study, and these  
179 analyses gave an average of  $-0.06 \pm 0.04$  ‰ (2SD; n = 17). We report the 2SD uncertainty of a  
180 sample as the 2SD uncertainty of sample replicate measurements or 0.07 ‰ (average of the  
181 uncertainties given above for SRM950a, CRM129a, and SDO-1), whichever is greater.

182

183

184

## 185 3.2 Molybdenum isotopes

186 Molybdenum concentration and isotope data were obtained following the methods  
187 outlined in Kendall et al. (2009a) and Duan et al. (2010). After sample dissolution using the  
188 methods outlined above, samples were purified for Mo using anion and cation exchange  
189 chromatography. For each sample, Mo concentrations were measured before and after  
190 chromatography to verify that column yields were >95%. For optimal precision of column yield  
191 measurements, Mo concentrations were determined by isotope dilution quadrupole ICP-MS, and  
192 all of the digested sample solution was used for column chemistry (hence, separate splits of the  
193 sample powders were used for Mo and U isotope measurements). The Mo isotope compositions  
194 were measured by multi-collector ICP-MS using sample-standard bracketing and a Zr element  
195 spike (prepared from Johnson Matthey Specpure® Zr plasma standard solution; Lot #700193E)  
196 to correct for instrumental mass fractionation (these measurements were done before  
197 implementation of the Mo double spike technique at Arizona State University). Our Mo isotope  
198 data were originally measured relative to the Johnson Matthey Specpure® Mo plasma standard  
199 (Lot #802309E; RochMo2).

200 Sample  $\delta^{98}\text{Mo}$  was re-calculated as per mil deviations from the new international NIST  
201 SRM 3134 standard as follows:  $\delta^{98}\text{Mo} = \left[ \frac{{}^{98/95}\text{Mo}_{\text{sample}}}{{}^{98/95}\text{Mo}_{\text{standard}} * 0.99975} - 1 \right] \times 1000$   
202 (Goldberg et al., 2013; Nägler et al., 2014). The logic behind setting the NIST SRM 3134  
203 standard to 0.25‰ (instead of 0‰) is to retain comparison of sample  $\delta^{98}\text{Mo}$  data with the  
204 "traditional" seawater  $\delta^{98}\text{Mo}$  value of 2.3‰ (Nägler et al., 2014). On this scale, seawater has a  
205 value of  $2.34 \pm 0.10$  ‰, and RochMo2 has a value of  $-0.08 \pm 0.05$  ‰ (Goldberg et al., 2013;  
206 Nägler et al., 2014). For an eighteen month period covering the Mo isotope analyses in this  
207 study, the average  $\delta^{98}\text{Mo}$  for SDO-1, based on five separate powder digestions, was  $0.83 \pm 0.15$

208 ‰ relative to NIST SRM 3134 = 0‰ or  $1.08 \pm 0.15$  ‰ relative to NIST SRM 3134 = 0.25‰  
209 (2SD, n=238). The first value is in excellent agreement with the SDO-1 average of  $0.80 \pm 0.14$   
210 ‰ reported by Goldberg et al. (2013). Given the average uncertainty of SDO-1, we report the  
211 2SD uncertainty of a sample as the 2SD uncertainty of sample replicate measurements or 0.15  
212 ‰, whichever is greater.

213

### 214 **3.3 Sedimentary iron speciation**

215        Preservation of seawater  $\delta^{98}\text{Mo}$  is most likely to occur in ORM deposited beneath  
216 strongly euxinic bottom waters (Barling et al., 2001; Arnold et al., 2004; Neubert et al., 2008;  
217 Gordon et al., 2009). Hence, sedimentary Fe speciation was used to reconstruct local bottom  
218 water redox conditions at the studied localities. Transport, scavenging, and enrichment of Fe  
219 occur in modern anoxic marine basins. The sediments accumulating in such settings have ratios  
220 of biogeochemically highly reactive Fe ( $\text{Fe}_{\text{HR}}$ ) to total Fe ( $\text{Fe}_{\text{T}}$ ) that are higher (typically  $>0.38$ )  
221 compared to modern sediments ( $0.26 \pm 0.08$ ) and Phanerozoic sedimentary rocks ( $0.14 \pm 0.08$ )  
222 deposited from oxygenated bottom waters (Raiswell and Canfield, 1998; Poulton and Raiswell,  
223 2002; Lyons and Severmann, 2006). Biogeochemically highly reactive Fe ( $\text{Fe}_{\text{HR}}$ ) is defined as  
224 pyrite Fe ( $\text{Fe}_{\text{PY}}$ ) and other Fe phases (carbonates [ $\text{Fe}_{\text{Carb}}$ ], ferric oxides [ $\text{Fe}_{\text{Ox}}$ ], and mixed-valence  
225 Fe oxides, primarily magnetite [ $\text{Fe}_{\text{Mag}}$ ]) that will react with sulfide in the water column or in  
226 sediments during early diagenesis. Hence,  $\text{Fe}_{\text{HR}} = \text{Fe}_{\text{PY}} + \text{Fe}_{\text{Carb}} + \text{Fe}_{\text{Ox}} + \text{Fe}_{\text{Mag}}$  (Poulton et al.,  
227 2004; Poulton and Canfield, 2005). The modern baseline for  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$  was derived using  $\text{Fe}_{\text{HR}} =$   
228  $\text{Fe}_{\text{PY}}$  (pyrite) +  $\text{Fe}_{\text{Ox}}$  (ferric oxides) (Raiswell and Canfield, 1998). Although  $\text{Fe}_{\text{HR}}$  has been  
229 expanded to include  $\text{Fe}_{\text{Carb}}$  (carbonates) and  $\text{Fe}_{\text{Mag}}$  (mixed-valence Fe oxides) because of their  
230 importance in ancient ORM (Poulton et al., 2004; Poulton and Canfield, 2005), comparison with

231 the modern baseline is still justified given the scarcity of  $\text{Fe}_{\text{Carb}}$  and  $\text{Fe}_{\text{Mag}}$  in modern sediments.  
232 The extent to which  $\text{Fe}_{\text{HR}}$  has been converted to pyrite ( $\text{Fe}_{\text{PY}}$ ) is used to determine if the bottom  
233 waters were euxinic ( $\text{Fe}_{\text{PY}}/\text{Fe}_{\text{HR}} > 0.7$ ) or ferruginous ( $\text{Fe}_{\text{PY}}/\text{Fe}_{\text{HR}} < 0.7$ ) (some studies use the  
234 older boundary value of 0.8; Anderson and Raiswell, 2004; Poulton et al., 2004; Poulton and  
235 Canfield, 2011).

236 Sedimentary Fe speciation analyses were carried out at the University of California,  
237 Riverside. A sequential extraction method (Poulton and Canfield, 2005), followed by analysis on  
238 an Agilent 7500ce ICP-MS, was used to determine  $\text{Fe}_{\text{Carb}} + \text{Fe}_{\text{Ox}} + \text{Fe}_{\text{Mag}}$  (Li et al., 2010).  
239 Analytical reproducibility was typically within 5%, with the exception of some low-Fe samples  
240 (<0.1 wt%). Pyrite Fe was determined from the weight percent of S extracted during a 2-hour  
241 chromium chloride distillation, assuming a stoichiometry of  $\text{FeS}_2$ .

242

### 243 **3.4 Total organic carbon**

244 Measurements of total organic carbon (TOC) were made at the Japan Agency of Marine-  
245 Earth Science and Technology (JAMSTEC) and are described in Kikumoto et al. (2014). A  
246 known amount of powdered sample was first demineralized by 10 M HCl at 70°C for >24 hours.  
247 Residues were rinsed with pure water and ethanol, dried, weighed, and combusted at 1000°C  
248 with an elemental analyzer (EA) connected to a Finnigan Delta XP mass spectrometer.  
249 Abundances of the resultant  $\text{CO}_2$  gas were measured by a conventional EA-IRMS method.  
250 Additional TOC measurements, derived from the difference between total carbon (determined by  
251 combustion) and total inorganic carbon (determined by acidification), were made using an Eltra  
252 CS-500 carbon/sulfur analyzer at the University of California, Riverside, as described in Scott et

253 al. (2008) and Li et al. (2010). For both methods, the analytical reproducibility of TOC contents  
254 is 0.10 wt% or better based on repeated analyses of standards.

255

256

## 4. RESULTS

257

### 4.1 Sedimentary iron speciation and metal concentrations

259 All samples from the Jiulongwan outcrop section and the Site 1 drill core section have  
260  $Fe_{HR}/Fe_T > 0.38$  and  $Fe_{PY}/Fe_{HR} > 0.7$ , indicating that the inner shelf was persistently covered by  
261 euxinic bottom waters during deposition of Member IV, consistent with prior data (Table 1 and  
262 Fig. 2; Scott et al., 2008; Li et al., 2010). This interpretation is further supported by high Mo  
263 concentrations (25-663 ppm; average = 138 ppm) and U concentrations (5-97 ppm; average = 22  
264 ppm) in the Member IV ORM (Tribovillard et al., 2006; Scott and Lyons, 2012).

265 To further establish local depositional conditions in the Nanhua Basin during Member IV  
266 time, we compared the enrichment factors (EFs) of Mo and U relative to average upper crust.  
267 The EF is calculated as follows (Tribovillard et al., 2006):

$$268 \quad EF_{\text{element X}} = (X/Al)_{\text{sample}} / (X/Al)_{\text{average upper crust}}$$

269 Average upper crust concentrations are Mo = 1.5 ppm, U = 2.8 ppm, and Al = 80,400 ppm  
270 (McLennan, 2001). High EF values for both Mo (35-512; average = 142) and U (5-52; average =  
271 14) indicate a dominance of hydrogenous over detrital contributions of Mo and U to Member IV  
272 ORM. The Mo/U ratios of Member IV ORM consistently exceed those of modern seawater (Fig.  
273 3a). This observation is consistent with the occurrence of locally euxinic bottom waters, and  
274 unrestricted exchange between the local depositional basin and the open ocean (Algeo and  
275 Tribovillard, 2009). High Mo/U ratios in ORM can also be caused by the operation of a

276 particulate Fe-Mn oxyhydroxide shuttle in a weakly restricted basin (as in the modern Cariaco  
277 Basin), which leads to more efficient removal of Mo from the water column to sediments  
278 compared to U (Algeo and Tribovillard, 2009).

279

## 280 **4.2 Uranium and molybdenum isotope compositions**

281 The U and Mo isotope data were not corrected for detrital contributions because of the  
282 dominance of hydrogenous over detrital U and Mo in the Member IV ORM. Despite the  
283 persistence of euxinic bottom waters at the studied localities, the stratigraphic trends of  $\delta^{238}\text{U}$   
284 and  $\delta^{98}\text{Mo}$  are significantly different (Fig. 2), with no significant correlation between them (Fig.  
285 3b). In the Jiulongwan outcrop section, a few samples (HND 30.35, HND 29.5, HND 28.85) at  
286 the base of Member IV have the lowest  $\delta^{98}\text{Mo}$  ( $-1.3$  to  $-0.5$  ‰) and highest  $\delta^{238}\text{U}$  ( $0.4$ - $0.5$ ‰).  
287 The rest of Member IV in the Jiulongwan section has uniform  $\delta^{238}\text{U}$  ( $0.2$ - $0.4$ ‰) except for one  
288 outlier near the top of the section (sample HN-23 =  $-0.4$ ‰). In contrast, the Mo isotope data  
289 show a more complex pattern. The exceptionally low  $\delta^{98}\text{Mo}$  at the base gives way upsection to  
290  $\delta^{98}\text{Mo}$  values between  $-0.4$ ‰ and  $+0.4$ ‰. This trend is followed up section by an excursion to  
291 high  $\delta^{98}\text{Mo}$  (up to  $2.0$  ‰) near the top of Member IV. A return to low  $\delta^{98}\text{Mo}$  values marks the  
292 top of Member IV.

293 Stratigraphic trends in the Site 1 drill core section are similar to the Jiulongwan section  
294 except for the absence of exceptionally low  $\delta^{98}\text{Mo}$  and exceptionally high  $\delta^{238}\text{U}$  at the base of  
295 Member IV. Hence, these few unusual isotopic signatures at the base of the Jiulongwan section  
296 are possible post-depositional artifacts (e.g., modification by surficial fluids concentrated along  
297 the Member III-IV contact) and are not considered further. In the Site 1 drill core, there is  
298 minimal variation in  $\delta^{238}\text{U}$  ( $0.1$ - $0.3$  ‰) except for one outlier at the top of the section (sample

299 40-4-of-12 =  $-0.13\%$ ). The  $\delta^{98}\text{Mo}$  of lower Member IV ranges between  $-0.5\%$  and  $+0.2\%$ . As  
300 in the Jiulongwan section, there is an excursion to high  $\delta^{98}\text{Mo}$  (up to  $1.7\%$ ) near the top of  
301 Member IV, which is followed by a return to lower  $\delta^{98}\text{Mo}$ .

302 Hence, there are two major observations from the isotopic data: (1) dominantly uniform  
303  $\delta^{238}\text{U}$  throughout most of Member IV (average  $\delta^{238}\text{U} = 0.24 \pm 0.16\%$ , 2SD, 34 out of 39  
304 samples; excluding HN-23, HND 30.35, HND 29.5, HND 28.85, and 40-4-of-12) and (2) a  
305 prevalence of  $\delta^{98}\text{Mo}$  values near  $0\%$  in Member IV except for an excursion to high  $\delta^{98}\text{Mo}$  ( $1.7$ -  
306  $2.0\%$ ) near the top of both sections.

307

308

## 5. DISCUSSION

309

### 310 **5.1 Uranium isotopes: evidence for widespread ocean oxygenation at ca. 560-551 Ma**

311 Recent advances in our understanding of the modern marine U isotope budget have led to  
312 the application of U isotope data from ORM and carbonates as a paleoredox proxy (Weyer et al.,  
313 2008; Montoya-Pino et al., 2010; Brennecka et al., 2011a; Asael et al., 2013; Kendall et al.,  
314 2013; Andersen et al., 2014; Dahl et al., 2014). In oxygenated seawater, uranium exists as  
315 dissolved U(VI), primarily as the uranyl carbonate anion ( $\text{UO}_2[\text{CO}_3]_3^{4-}$ ; Langmuir, 1978), and  
316 has a conservative distribution in the oceans with a residence time of  $\sim 400$ - $500$  kyr (Ku et al.,  
317 1977; Dunk et al., 2002). The single major source of U to the oceans is oxidative mobilization of  
318 U from the upper continental crust and transport of dissolved U(VI) to the oceans via rivers  
319 (Dunk et al., 2002). In contrast, there are multiple marine sinks for U. Biogenic carbonates,  
320 sediments deposited beneath anoxic bottom waters, and sediments deposited beneath weakly  
321 oxygenated bottom waters are major sinks. Minor sinks include sediments deposited beneath



322 well-oxygenated bottom waters and the hydrothermal alteration of oceanic crust (Morford and  
323 Emerson, 1999; Dunk et al., 2002; Partin et al., 2013).

324 In anoxic basins, U is primarily removed below the sediment water-interface rather than  
325 in the water column (Anderson et al., 1989; Barnes and Cochran, 1990). Uranium can be  
326 precipitated from sediment pore waters as  $\text{UO}_2$  or adsorbed to organic matter following the  
327 reduction of dissolved U(VI) to U(IV) at the depth of microbial  $\text{Fe}^{3+}$  and  $\text{SO}_4^{2-}$  reduction (see  
328 recent reviews on U marine geochemistry by Algeo and Tribovillard, 2009; Asael et al., 2013;  
329 Partin et al., 2013). The reduction and removal of U to the euxinic sediments of the deep Black  
330 Sea is accompanied by a large volume-dependent equilibrium isotope fractionation that favors  
331 the removal of heavier U isotopes from the water column (Schauble, 2006; Weyer et al., 2008;  
332 Montoya-Pino et al., 2010; Andersen et al., 2014). Taking the offset between the average  $\delta^{238}\text{U}$   
333 of recent Unit I organic-rich sediments deposited from strongly euxinic waters at water depths of  
334  $>2000$  m ( $0.02 \pm 0.12$  ‰) and modern seawater ( $-0.40 \pm 0.03$  ‰), the magnitude of isotope  
335 fractionation is  $\sim 0.4$  ‰ (Weyer et al., 2008; Andersen et al., 2014). A similar offset was  
336 determined between Unit I sediments and seawater at a water depth of 418 m (Weyer et al.,  
337 2008; Montoya-Pino et al., 2010). Given the restricted setting of the Black Sea, with  $\sim 40\%$  U  
338 depletion in the deep euxinic water column (Anderson et al., 1989), the observed offset between  
339 Unit I sediments and seawater is only a minimum for open ocean settings. Using mass balance  
340 modeling, Andersen et al. (2014) suggest that in an open ocean setting characterized by strong U  
341 recharge to locally euxinic bottom waters and U removal from solution below the sediment-  
342 water interface, the U isotope fractionation between euxinic sediments and modern seawater will  
343 be  $\sim 0.6$ ‰, which corresponds to a euxinic sediment  $\delta^{238}\text{U}$  of  $\sim 0.2$ ‰.

344 In contrast to the anoxic sink, the other marine sinks are associated with small U isotope  
345 fractionations. Peruvian continental margin sediments underlying weakly oxygenated waters  
346 have an average  $\delta^{238}\text{U}$  of  $-0.28 \pm 0.19$  ‰, which is only  $\sim 0.1$  ‰ higher than seawater (Weyer et  
347 al., 2008). The surface layers of Fe-Mn crusts in sediments underlying well-oxygenated bottom  
348 waters ( $-0.65 \pm 0.05$  ‰) show an opposite sense of isotope fractionation and have  $\delta^{238}\text{U}$  that is  
349  $\sim 0.24$  ‰ lower than seawater (Weyer et al., 2008; Brennecka et al., 2011b; Goto et al., 2014).  
350 The U isotope fractionation accompanying hydrothermal alteration of oceanic crust may be  
351 minimal if fresh and altered basalts typically have similar  $\delta^{238}\text{U}$  (Noordmann et al., 2010, 2011).  
352 Primary biological and abiological carbonate precipitates show negligible offset from seawater  
353 (Stirling et al., 2007; Weyer et al., 2008; Romaniello et al., 2013; Andersen et al., 2014). An  
354 exception is shallow-water carbonate sediments containing dissolved sulfide in pore waters,  
355 which can have  $\delta^{238}\text{U}$  values of 0.2-0.4 ‰ higher compared to seawater (Romaniello et al.,  
356 2013).

357 Well-oxygenated bottom waters dominate the modern ocean. Because the expression of  
358 U isotope fractionation in oxygenated sediments is small, and the areal extent of weakly  
359 oxygenated to anoxic bottom waters is limited, the  $\delta^{238}\text{U}$  of seawater is only slightly lower  
360 compared to riverine inputs ( $-0.3$  to  $0.0$  ‰; Stirling et al., 2007; Noordmann et al., 2010, 2011).  
361 In contrast, at times of expanded ocean anoxia, seawater  $\delta^{238}\text{U}$  will be lower because of  
362 extensive preferential removal of isotopically heavy U isotopes to euxinic sediments (Weyer et  
363 al., 2008; Montoya-Pino et al., 2010; Brennecka et al., 2011a). Hence, expanded ocean anoxia  
364 should cause the  $\delta^{238}\text{U}$  of ancient euxinic ORM deposited in an open ocean euxinic setting to be  
365 lower than  $\sim 0.2$ ‰ (Andersen et al., 2014).

366 Using this modern framework, we interpret the high average  $\delta^{238}\text{U}$  of  $0.24 \pm 0.16$  ‰ for  
367 most Member IV ORM as evidence for widespread ocean oxygenation ca. 560-551 Myr ago. The  
368 average  $\delta^{238}\text{U}$  value from Member IV is similar to the predicted  $\delta^{238}\text{U}$  for a hypothetical modern  
369 euxinic sediment deposited in an unrestricted ocean basin. High Mo/U and Mo/TOC ratios for  
370 Member IV ORM indicate that water exchange between the local depositional environment and  
371 the open ocean was not severely restricted (Algeo and Lyons, 2006; Algeo and Tribovillard,  
372 2009). The average Mo/TOC ratio of 23 ppm/wt% for Member IV ORM (excluding the three  
373 samples from the base of the Jiulongwan section) is similar to the average of 25 ppm/wt% for the  
374 weakly restricted Cariaco Basin (Algeo and Lyons, 2006). Hence, we suggest that the U isotope  
375 fractionation between the Member IV euxinic sediments and global seawater was close to 0.6 ‰,  
376 thus implying a late Ediacaran seawater  $\delta^{238}\text{U}$  that was near the modern seawater value of –  
377 0.4‰. Our interpretation assumes that riverine  $\delta^{238}\text{U}$  during late Ediacaran time was broadly  
378 similar to modern values of –0.3 to 0.0 ‰. However, Ediacaran rivers may have lower  $\delta^{238}\text{U}$   
379 compared to modern rivers because Precambrian ORM with both high U concentrations and high  
380  $\delta^{238}\text{U}$ , a signature of well-oxygenated oceans, were probably less available for weathering (Partin  
381 et al., 2013). A lower riverine  $\delta^{238}\text{U}$  implies that the seawater  $\delta^{238}\text{U}$  of a well-oxygenated  
382 Ediacaran ocean was lower than modern seawater. Hence, the high average  $\delta^{238}\text{U}$  of euxinic  
383 Member IV ORM suggests extensive ocean oxygenation on a scale similar to or even greater  
384 than today.

385 Our interpretation is consistent with high Mo concentrations in Member IV ORM, which  
386 point to a high seawater Mo inventory in well-oxygenated oceans (Scott et al., 2008), and Fe  
387 speciation evidence for locally oxygenated deep waters in some late Ediacaran ocean basins

388 (Canfield et al., 2008; Johnston et al., 2012). Solitary low  $\delta^{238}\text{U}$  values at the top of both sections  
389 may suggest a transient episode of expanded ocean anoxia during Member IV time.

390 The development of locally anoxic basins in continental margin environments is not  
391 precluded by our data and thus is not incompatible with geochemical evidence for local anoxia in  
392 some late Ediacaran sedimentary basins (e.g., Canfield et al., 2008; Frei et al., 2013; Johnston et  
393 al., 2013). However, our data do indicate that anoxia was comparatively minor relative to ocean  
394 oxygenation at ca. 560-551 Ma. Our interpretations are based on the concentration and isotopic  
395 composition of redox-sensitive trace metals (Mo, U) with long oceanic residence times (400-500  
396 kyr). These geochemical tools, when applied to euxinic ORM, are more favorable for  
397 constraining the global extent of ocean oxygenation and anoxia (Arnold et al., 2004; Weyer et  
398 al., 2008) compared to elements with short oceanic residence times.

399 Extensive ocean oxygenation ca. 560-551 Myr ago is coincident with the later stages of  
400 the Shuram negative carbon isotope excursion (Fig. 4). In South China, the onset of the Shuram  
401 excursion occurs in Member III and ends at the Doushantuo-Dengying transition (Jiang et al.,  
402 2007; Zhou and Xiao, 2007; Zhu et al., 2007; McFadden et al., 2008; Sawaki et al., 2010; Tahata  
403 et al., 2013). Because U isotope data are not available for Member III, we cannot determine if  
404 widespread ocean oxygenation occurred during the entirety of the Shuram excursion. Hence, we  
405 consider it beyond the scope of this paper to delve into the debate surrounding the origin of the  
406 Shuram excursion (Grotzinger et al., 2011).

407

## 408 **5.2 Molybdenum isotopes: Constraints on global and local ocean redox conditions**

409 Molybdenum is oxidatively mobilized from the upper continental crust beneath an  
410 oxygenated atmosphere and is transported to the oceans primarily by rivers as largely unreactive

411  $\text{MoO}_4^{2-}$  (molybdate). Molybdenum behaves conservatively in oxygenated seawater and thus  
412 accumulates in the oceans, leading to a long oceanic residence time of ~440 kyr (Miller et al.,  
413 2011). Upon encountering sulfidic conditions in the water column or sediment pore fluids,  
414  $\text{MoO}_4^{2-}$  is converted to  $\text{MoO}_{4-x}\text{S}_x^{2-}$  (thiomolybdate) (Helz et al., 1996; Erickson and Helz, 2000)  
415 and then, at least in some settings, to reactive Mo-polysulfide species (Dahl et al., 2013). These  
416 species are then scavenged by Fe sulfide minerals (Helz et al., 1996, 2004) and organic particles  
417 (Helz et al., 1996; Tribovillard et al., 2004; Chappaz et al., 2014) or undergo equilibrium  
418 precipitation as a Fe(II)-Mo(VI) sulfide mineral (Helz et al., 2011), thus removing Mo to  
419 sediments.

420       Where marine bottom waters become highly sulfidic (“strongly euxinic”;  $[\text{H}_2\text{S}]_{\text{aq}} > 11$   
421  $\mu\text{M}$ ), the quantitative conversion of  $\text{MoO}_4^{2-}$  to  $\text{MoS}_4^{2-}$  (tetrathiomolybdate) and its removal from  
422 bottom waters can lead to the preservation of seawater  $\delta^{98}\text{Mo}$  in sediments (Barling et al., 2001;  
423 Arnold et al., 2004; Neubert et al., 2008). Doubts have been raised as to whether quantitative Mo  
424 removal is characteristic of highly sulfidic marine basins (Helz et al., 2011). However, a small  
425 isotopic offset between dissolved  $\text{MoS}_4^{2-}$  and authigenic solid Mo ( $\Delta^{98}\text{Mo} \sim 0.5 \pm 0.3\%$ ; Nägler  
426 et al., 2011) suggests the  $\delta^{98}\text{Mo}$  of strongly euxinic sediments will closely approximate seawater  
427 even if Mo removal from bottom waters is not quantitative. The long seawater Mo residence time  
428 means that the  $\delta^{98}\text{Mo}$  of strongly euxinic sediments at a single locality, including basins with  
429 semi-restricted access to the open ocean, can stand as a proxy for global seawater, as shown for  
430 the modern Black Sea (Barling et al., 2001; Arnold et al., 2004; Neubert et al., 2008).

431       Seawater  $\delta^{98}\text{Mo}$  represents an ocean redox proxy because it records the relative  
432 proportion of Mo buried in marine sediments deposited beneath  $\text{O}_2$ -rich and  $\text{O}_2$ -poor waters.  
433 Global seawater today is enriched in heavy Mo isotopes ( $\delta^{98}\text{Mo} = 2.34 \pm 0.10\%$ ; Barling et al.,

434 2001; Siebert et al., 2003; Nakagawa et al., 2012; Nägler et al., 2014) relative to oceanic inputs  
435 (dominated by rivers, average  $\delta^{98}\text{Mo} \sim -0.7\text{‰}$ ; Archer and Vance, 2008). The extent of this  
436 enrichment results largely from the preferential adsorption of light Mo isotopes in seawater onto  
437 Mn oxides in sediments beneath oxygenated waters. The isotope fractionation during this process  
438 is large ( $\sim 3\text{‰}$ ; Barling et al., 2001; Siebert et al., 2003, Barling and Anbar, 2004; Wasylenki et  
439 al., 2008; Poulson Brucker et al., 2009). In contrast, isotope fractionation is often smaller  
440 (typically  $\leq 1\text{‰}$ ) during Mo burial in low- $\text{O}_2$  ( $< 10 \mu\text{M}$ ) and anoxic marine environments where  
441  $\text{H}_2\text{S}$  is present in pore and/or bottom waters (Barling et al., 2001; Arnold et al., 2004; Poulson et  
442 al., 2006; Siebert et al., 2006; Neubert et al., 2008; Poulson Brucker et al., 2009). A notable  
443 exception is weakly euxinic environments ( $[\text{H}_2\text{S}]_{\text{aq}} < 11 \mu\text{M}$ ) where sediments have  $\delta^{98}\text{Mo}$  that is  
444 up to 3.0‰ lower than seawater because of the incomplete conversion of molybdate to  
445 tetrathiomolybdate and the preservation of Mo isotope fractionation during the formation of  
446 intermediate thiomolybdate complexes (Arnold et al., 2004, 2012; Neubert et al., 2008; Dahl et  
447 al., 2010a; Nägler et al., 2011; Azrieli-Tal et al., 2014). In continental margin environments  
448 where bottom waters are mildly oxygenated (e.g., 10-35  $\mu\text{M}$ ) and sediments are characterized by  
449 active Fe-Mn oxide recycling above a deeper zone of dissolved sulfide, sediments have  $\delta^{98}\text{Mo}$   
450 that is intermediate between the well-oxygenated and strongly euxinic end-members (Siebert et  
451 al., 2006; Poulson Brucker et al., 2009; Goldberg et al., 2012). The general picture that emerges  
452 is that high seawater  $\delta^{98}\text{Mo}$  reflects well-oxygenated oceans whereas low seawater  $\delta^{98}\text{Mo}$  points  
453 to extensive ocean anoxia, specifically a greater extent of strongly euxinic waters because it is in  
454 such environments that Mo isotope fractionation between seawater and sediment is smallest. In  
455 this way, the  $\delta^{98}\text{Mo}$  of ancient seawater, as inferred from euxinic ORM, can be used to elucidate

456 past global ocean redox conditions (e.g., Arnold et al., 2004; Dahl et al., 2010b; Kendall et al.,  
457 2011).

458 High  $\delta^{98}\text{Mo}$  values (1.7-2.0‰) near the top of Member IV in both sections approach the  
459 modern seawater value of 2.3‰, which points to widespread oxygenation of the oceans just prior  
460 to 551 Ma (Fig. 1). The highest  $\delta^{98}\text{Mo}$  in Member IV represents a minimum value for seawater  
461 because of the possibility of isotopic fractionation between dissolved  $\text{MoS}_4^{2-}$  and authigenic solid  
462 Mo, which results in preferential removal of light Mo isotopes to sediments.

463 Seawater  $\delta^{98}\text{Mo}$  is determined by the isotopic composition of inputs to the ocean and the  
464 relative proportion of Mo buried into sediments of different redox character. The  $\delta^{98}\text{Mo}$  of the  
465 upper continental crust and riverine inputs is suggested to be broadly uniform during the past 2.7  
466 Ga because no correlation exists between  $\delta^{98}\text{Mo}$  and age for molybdenites, a major source of  
467 oceanic Mo (Hannah et al., 2007). Nevertheless, Ediacaran rivers could have had lower  $\delta^{98}\text{Mo}$   
468 than modern rivers because ORM with both high Mo concentrations and high  $\delta^{98}\text{Mo}$ , indicative  
469 of well-oxygenated conditions, were probably less available for weathering compared to today  
470 (see section 5.3). Hence, an Ediacaran seawater  $\delta^{98}\text{Mo}$  of  $\geq 2.0$  ‰ suggests that the ratio of  
471 dissolved Mo buried in mildly/strongly oxygenated versus low- $\text{O}_2$ /anoxic marine environments  
472 was comparable to or higher than that observed in today's predominantly oxygenated oceans.

473 In the isotopically heavy part of Member IV, the Mo/TOC ratios, which scale with Mo  
474 concentrations in sulfidic bottom waters (Algeo and Lyons, 2006), reach 32-34 ppm/wt%. These  
475 ratios are similar to those of Phanerozoic euxinic ORM, reflecting enrichment under a large  
476 dissolved Mo inventory and an appreciable extent of deep-ocean oxygenation (Scott et al., 2008;  
477 Dahl et al., 2011; Dickson and Cohen, 2012; Sahoo et al., 2012; Reinhard et al., 2013). High

478  $\delta^{98}\text{Mo}$  signatures together with high Mo/TOC provide a compelling case for widespread ocean  
479 oxygenation.

480         Alternative scenarios to explain the combination of high  $\delta^{98}\text{Mo}$  and high Mo/TOC are  
481 unlikely. Large isotopic offsets of up to  $\sim 3\text{‰}$  lower than seawater are observed in modern Black  
482 Sea sediments deposited beneath weakly euxinic waters near the chemocline ( $[\text{H}_2\text{S}]_{\text{aq}} < 11 \mu\text{M}$ ;  
483 Neubert et al., 2008). If weakly euxinic waters were widespread throughout the late Ediacaran  
484 oceans and such environments were typically characterized by a Mo isotope fractionation of  
485  $\sim 3\text{‰}$  between seawater and ORM, then the seawater  $\delta^{98}\text{Mo}$  could have been driven to high  
486 values. However, this scenario is challenged by the well-known observation that Mo burial  
487 fluxes to sediments are  $\sim 2\text{-}3$  orders of magnitude higher in the presence of  $\text{H}_2\text{S}$  relative to  $\text{O}_2$ ,  
488 even when dissolved  $\text{H}_2\text{S}$  in bottom waters is low (because sulfide is also present in sediment  
489 pore waters; Scott et al., 2008; Poulson Brucker et al., 2009). The consequence of these high  
490 burial rates is that the oceanic Mo inventory is sensitive to small changes in the extent of seafloor  
491 covered by euxinic waters (Arnold et al., 2004). Recent modeling of the oceanic Mo inventory  
492 and isotope mass balance demonstrates that if euxinia expanded to cover only 1% of the ocean  
493 floor (compared to  $< 0.1\%$  today), then the seawater Mo concentration would be less than one-  
494 third the modern value, and the Mo abundances and Mo/TOC ratios of euxinic ORM would be  
495 low (Scott et al., 2008; Dahl et al., 2011; Sahoo et al., 2012; Reinhard et al., 2013). Hence,  
496 widespread weakly euxinic oceans will not generate both high Mo/TOC and high  $\delta^{98}\text{Mo}$  in  
497 ORM.

498         Interpretation of the Mo isotope data from the stratigraphically underlying and overlying  
499 ORM in Member IV is less straightforward. At face value, the low  $\delta^{98}\text{Mo}$  (typically  $< 0.8\text{‰}$ ) of  
500 these ORM suggests that seawater was isotopically light and hence that extensive Mo removal



501 occurred beneath anoxic (and especially euxinic) water masses. However, this interpretation  
502 conflicts with the high  $\delta^{238}\text{U}$  and high Mo/TOC that point to extensive oxygenation (this study;  
503 Scott et al., 2008). Furthermore, some of these  $\delta^{98}\text{Mo}$  values are appreciably lower than the  
504 modern oceanic input ( $\sim 0.7\text{‰}$ ). There is no known sink that can preferentially remove heavy Mo  
505 isotopes from seawater, so seawater  $\delta^{98}\text{Mo}$  is unlikely to be lower than the oceanic input.

506 On this basis, we infer that the low  $\delta^{98}\text{Mo}$  values are fractionated from coeval seawater.  
507 Sedimentary Fe speciation data point to persistently euxinic waters at the studied localities but do  
508 not reveal if bottom water sulfide concentrations were high enough for quantitative  $\text{MoS}_4^{2-}$   
509 formation and the capture of seawater-like  $\delta^{98}\text{Mo}$  in sediments. Following the Black Sea and  
510 Mediterranean examples (Neubert et al., 2008; Arnold et al., 2012; Azrieli-Tal et al., 2014), the  
511 lower  $\delta^{98}\text{Mo}$  in Member IV ORM may record local deposition from weakly sulfidic waters and  
512 the associated expression of Mo isotope fractionation during formation of intermediate  
513 thiomolybdate complexes. In contrast, the higher  $\delta^{98}\text{Mo}$  points to more intensely sulfidic local  
514 conditions. The high Mo/U ratios of Member IV ORM consistently exceed the modern seawater  
515 value, indicating that Mo was more efficiently transferred to the sediments compared to U (cf.  
516 Algeo and Tribovillard, 2009). Hence, it is possible that the prevalence of lower  $\delta^{98}\text{Mo}$  reflects  
517 the operation of a particulate Fe-Mn oxyhydroxide shuttle analogous to that observed in the  
518 weakly euxinic Cariaco Basin (Algeo and Tribovillard, 2009). The Fe-Mn oxyhydroxide  
519 particles form at the chemocline where upwelling  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  comes into contact with  
520 oxygenated waters. These particles will preferentially adsorb the lighter isotopes of Mo while  
521 sinking through the water column. Reductive dissolution of Fe-Mn oxyhydroxide particles below  
522 the sediment-water interface releases Mo, which can then be sequestered by Fe sulfide minerals  
523 and organic particles, thus preserving a low  $\delta^{98}\text{Mo}$  signature in sulfidic sediments (Herrmann et

524 al., 2012; Scholz et al., 2013). In both sections, the samples with highest  $\delta^{98}\text{Mo}$  have among the  
525 lowest Mo/U ratios (see Fig. 3a), suggesting a decreased shuttle effect, along with increased  
526 bottom water sulfide concentrations, enabled better capture of seawater  $\delta^{98}\text{Mo}$  in these samples.

527

### 528 **5.3 Temporal trends in ocean oxygenation: the molybdenum isotope perspective**

529 To explore the relevance of our data within a broader temporal context, we compiled  
530  $\delta^{98}\text{Mo}$  and associated Mo/TOC data from ORM deposited since the end of the Great Oxidation  
531 Event (Fig. 4; inadequate U isotope data exist for this purpose). We have recalculated the  
532 literature  $\delta^{98}\text{Mo}$  values relative to NIST SRM 3134 as  $\delta^{98}\text{Mo} = [(\frac{^{98}\text{Mo}_{\text{sample}}}{^{98}\text{Mo}_{\text{standard}}} * 0.99975) - 1] \times 1000$ , following Nägler et al. (2014) by using the conversion values in Goldberg  
533 et al. (2013). Our compilation, updated from Dahl et al. (2010b), includes our new data from  
534 Member IV plus new data from the  $640.7 \pm 4.7$  Ma Black River Dolomite (Kendall et al., 2009b;  
535 the Black River Dolomite is described in Appendix A and the data are reported in Table A.1).  
536 The compilation specifically targeted ORM deposited beneath euxinic bottom waters as defined  
537 by sedimentary Fe speciation (including degree-of-pyritization; Lyons and Severmann, 2006;  
538 Scott et al., 2008) and included intervals containing ORM with Mo contents that are sufficiently  
539 high to suggest euxinic conditions (Scott and Lyons, 2012). Although ORM deposited from  
540 strongly euxinic bottom waters are most likely to capture a seawater-like  $\delta^{98}\text{Mo}$  signature,  
541 straightforward interpretation of the record is complicated by the likelihood that the  $\delta^{98}\text{Mo}$  of  
542 ORM deposited from weakly euxinic waters will be offset significantly to values lower than  
543 those of seawater (as was observed for most Member IV samples). Hence, we use the highest  
544  $\delta^{98}\text{Mo}$  from each interval as the most conservative estimate of coeval seawater because the  
545

546 highest  $\delta^{98}\text{Mo}$  in an interval could still be fractionated from seawater (Dahl et al., 2010b;  
547 Dickson et al., 2014).

548 An interval of low  $\delta^{98}\text{Mo}$  and moderate Mo/TOC between 2050 Ma and 640 Ma points to  
549 a generally moderate-sized oceanic Mo reservoir that reflects a combination of pervasive  
550 oxidative weathering and redox-stratified oceans (oxic surface waters, euxinic waters at mid-  
551 depths along productive ocean margins, and ferruginous deep waters; Arnold et al., 2004; Scott  
552 et al., 2008; Kendall et al., 2009a, 2011; Dahl et al., 2010b, 2011; Planavsky et al., 2011; Poulton  
553 and Canfield, 2011; Lyons et al., 2014). Elemental and isotopic mass balance models indicate  
554 that the oceanic Mo reservoir probably stayed below 20% of modern levels because of  
555 pronounced Mo burial in sulfidic marine environments (Scott et al., 2008; Dahl et al., 2011;  
556 Reinhard et al., 2013). Our new Mo data from the Black River Dolomite suggests that a similar  
557 redox character prevailed at ca. 640 Ma, consistent with moderate Mo/TOC in ca. 660 Ma  
558 euxinic ORM from the lower part of the Datangpo Formation, South China (Li et al., 2012).

559 In contrast, Baldwin et al. (2013) infer a higher  $\delta^{98}\text{Mo}$  of  $\sim 1.8$  ‰ for middle Cryogenian  
560 seawater based on analyses of jasper beds from the dropstone-bearing (syn-glacial) Rapitan iron  
561 formation (NW Canada). This value was calculated assuming Mo isotope fractionation during  
562 adsorption to hematite. An alternative to this local-scale interpretation is that high seawater  
563  $\delta^{98}\text{Mo}$  was generated globally by preferential removal of isotopically light Mo from a small  
564 oceanic Mo reservoir to abundant Fe oxyhydr(oxides). Under icehouse conditions where the  
565 oceans are stagnant and predominantly anoxic (thus Mo-poor) beneath widespread ice cover  
566 (with low sulfur inputs), Fe oxyhydr(oxides) would likely precipitate as a result of  $\text{Fe}^{2+}$  oxidation  
567 via oxygenic photosynthesis beneath thin ice cover or via photoferrotrophy (Kirschvink, 1992;  
568 Canfield and Raiswell, 1999; Hoffman and Schrag, 2002). As another (non-glacial) example

569 involving extensive ocean anoxia, preferential removal of isotopically light Mo from a small  
570 oceanic Mo inventory to Fe oxyhydr(oxides) was suggested to account for high  $\delta^{98}\text{Mo}$  in late  
571 Archean euxinic ORM deposited before the Great Oxidation Event (Duan et al., 2010; Czaja et  
572 al., 2012).

573 High Mo/TOC ratios from ORM of lower Member II near the base of the Doushantuo  
574 Formation indicate extensive ocean oxygenation at ca. 632 Ma (Sahoo et al., 2012). Otherwise,  
575 geochemical data from early and middle Ediacaran sedimentary successions are consistent with  
576 less oxygenated conditions, except following the ca. 580 Ma Gaskiers glaciation and at ca. 560-  
577 551 Ma (Canfield et al., 2007, 2008; McFadden et al., 2008; Li et al., 2010; Johnston et al., 2012;  
578 Och and Shields-Zhou, 2012). Future work is required to determine if additional episodes of  
579 extensive ocean oxygenation also took place during early and middle Neoproterozoic time.

580 Late Ediacaran ocean oxygenation is roughly coincident with key steps in the radiation of  
581 animals. Weakly calcified tubular metazoans (e.g., *Cloudina*) and their predators appeared before  
582  $548.8 \pm 1$  Ma (Bengston and Zhao, 1992; Grotzinger et al., 1995; Warren et al., 2012).  
583 Macroscopic motile bilaterians (e.g., *Kimberella*) and their trace fossils appear in the rock record  
584 by  $555.3 \pm 0.3$  Ma and  $585 \pm 3$  Ma, respectively (Martin et al., 2000; Fedonkin et al., 2007; Liu  
585 et al., 2010; Pecoits et al., 2012; Rogov et al., 2012). Regionally stable ocean oxygenation  
586 following the Gaskiers glaciation is temporally associated with the appearance of soft-bodied  
587 Ediacaran macroscopic fauna (Canfield et al., 2007; Narbonne et al., 2009; Xiao and Laflamme,  
588 2009; Wilby et al., 2011; Johnston et al., 2012). However, surface ocean oxygen levels during  
589 earlier Neoproterozoic time were not necessarily low enough to preclude the existence of small  
590 bilaterians (Sperling et al., 2013a; Planavsky et al., 2014). Furthermore, ecological and genetic  
591 factors were likely important driving forces for metazoan evolution (e.g., Butterfield, 2009;

592 Erwin et al., 2011; Penny et al., 2014). Disentangling the relative importance of environmental,  
593 ecological, and genetic factors is difficult given the current resolution of geochemical and  
594 paleontological datasets. However, it is likely that the initial episodes of extensive ocean  
595 oxygenation helped accelerate the radiation of Ediacaran metazoans in tandem with ecological  
596 triggers, because more complex food webs and larger metazoans would be supported by higher  
597 oxygen levels (Sperling et al., 2013b). High  $\delta^{98}\text{Mo}$  and high Mo/TOC from early Cambrian  
598 ORM (Wille et al., 2008) and high  $\delta^{98}\text{Mo}$  from phosphorites (Wen et al., 2011) suggest at least  
599 transient occurrences of widespread ocean oxygenation around the time of the Cambrian  
600 Explosion.

601 A return to generally less oxygenated deep oceans with expanded sulfidic marine  
602 environments (possibly triggered by a significant increase in bioturbation; Boyle et al., 2014) is  
603 marked by lower  $\delta^{98}\text{Mo}$  and lower Mo/TOC at 520-440 Ma, except for one example of high  
604  $\delta^{98}\text{Mo}$  in the late Ordovician (Dahl et al., 2010b; Zhou et al., 2012). This time interval includes  
605 an episode of extreme  $\text{O}_2$  deficiency during the ca. 500 Ma Steptoean Positive Carbon Isotope  
606 Excursion (SPICE) (Gill et al., 2011). Because the  $\delta^{98}\text{Mo}$  and Mo/TOC proxies are highly  
607 sensitive to changes in the extent of water column euxinia over a small percentage of the  
608 seafloor, it is difficult to infer the redox state of early Paleozoic deep oceans using Mo alone. A  
609 return to Proterozoic-style ferruginous deep ocean conditions (Planavsky et al., 2011; Poulton  
610 and Canfield, 2011) is not strictly required to explain the low  $\delta^{98}\text{Mo}$  and moderate Mo/TOC at  
611 520-440 Ma despite the similarities in Mo data with the ca. 2050-640 Ma interval. Compilations  
612 of Cr and U concentrations in ORM suggest a first-order increase in the seawater inventory of  
613 these metals in the early Paleozoic compared to the Precambrian (Reinhard et al., 2013; Partin et  
614 al., 2013). The oceanic mass balances of Cr and U are less sensitive to water column euxinia

615 compared to Mo. Taking this into account, the Mo data at 520-440 Ma can be interpreted as  
616 reflecting mid-depth euxinic waters along productive ocean margins and weakly oxygenated  
617 deep waters (cf. Dahl et al., 2010b).

618 High  $\delta^{98}\text{Mo}$  and generally high Mo/TOC in later Phanerozoic ORM indicates that  
619 widespread and persistent ocean oxygenation was probably established by 390 Ma, possibly  
620 coincident with the diversification of vascular land plants (Dahl et al., 2010b). Widespread ocean  
621 oxygenation during younger Phanerozoic time may have been interrupted only by sporadic, brief  
622 intervals of expanded oceanic anoxia during which the oceanic Mo inventory and seawater  
623  $\delta^{98}\text{Mo}$  became temporarily smaller and lower, respectively (e.g., the Mesozoic examples in Fig.  
624 4; Pearce et al., 2008, 2010; Westermann et al., 2014). The picture that emerges is an Ediacaran  
625 to early Paleozoic interval of fluctuating ocean redox conditions that bridges the transition from  
626  $\text{O}_2$ -deficient Proterozoic oceans to widely oxygenated later Phanerozoic oceans.

627

## 628 **6. CONCLUSIONS**

629

630 New U and Mo isotope data from Member IV ORM of the Doushantuo Formation point  
631 to extensively oxygenated oceans during ca. 560-551 Ma, consistent with the previous  
632 conclusion reached by Scott et al. (2008) on the basis of high Mo concentrations in Member IV.  
633 The consistently high  $\delta^{238}\text{U}$  values throughout Member IV, when corrected for isotope  
634 fractionation accompanying U burial in ORM, point to high seawater  $\delta^{238}\text{U}$  at 560-551 Ma and  
635 hence a broadly similar oceanic redox character and oceanic U isotope mass balance as today.  
636 Most of the Mo isotope data in Member IV are probably fractionated from seawater, consistent  
637 with deposition from local bottom waters that were weakly sulfidic ( $[\text{H}_2\text{S}]_{\text{aq}} < 11 \mu\text{M}$ ). High

638 Mo/U ratios also suggest the efficient transfer of isotopically light Mo to sediments by a local  
639 particulate Fe-Mn oxyhydroxide shuttle. However, an instance of high seawater  $\delta^{98}\text{Mo}$  paired  
640 with high Mo/TOC occurs in the upper part of Member IV, again pointing to widespread ocean  
641 oxygenation. A temporal compilation of  $\delta^{98}\text{Mo}$  and associated Mo/TOC reveals that ocean  
642 oxygenation was probably not a linear process. It is likely that the late Neoproterozoic rise in  
643 atmospheric  $\text{O}_2$  led to an Ediacaran-to-early-Phanerozoic interval of dynamic ocean redox  
644 changes, which bridged the transition from predominantly  $\text{O}_2$ -deficient Proterozoic oceans to  
645 widely oxygenated later Phanerozoic oceans.

646

647

## ACKNOWLEDGEMENTS

648

649 This study was financially supported by the National Science Foundation, the NASA  
650 Astrobiology Institute, and the Agouron Institute. Support was provided to TWL by NSF-EAR  
651 and the NASA Exobiology and Astrobiology programs. BK is supported by a NSERC Discovery  
652 Grant (RGPIN-435930). Constructive comments by three anonymous reviewers improved the  
653 manuscript.

654

655

## APPENDIX A

656

### A.1. Black River Dolomite samples

658

659 The Western Tasmania Terrane is suggested to have formed part of the East Antarctic  
660 margin of the Australia-East Antarctica continental block during the Neoproterozoic before

661 rifting away at ca. 580 Ma (Direen and Crawford, 2003; Meffre et al., 2004; Berry et al., 2008).  
662 In northwestern Tasmania, the ca. 740-542 Ma Togari Group begins locally with the coarse-  
663 grained Forest Conglomerate, which in turn is overlain by 600 m of stromatolitic dolostones,  
664 organic-rich chert and mudrock, and diamictite of the Black River Dolomite (Calver, 1998;  
665 Calver and Walter, 2000). These lithologies record continental shelf deposition, with the organic-  
666 rich units representing sedimentation in deeper-water environments. Overlying the Black River  
667 Dolomite are fine-grained mudrocks, volcanoclastic arenites, rhyodacite, diamictite, and tholeiitic  
668 basalt of the 1 km thick Kannunah Subgroup, deposited in a rift setting (Calver et al., 2004). In  
669 the Forest-1 core, the top of the Black River Dolomite is represented by 40 m of pyritic ORM  
670 with subordinate carbonate (Calver and Walter, 2000). Samples of finely laminated pyritic ORM  
671 were obtained from the lower part of this interval at ca. 828 m and 836 m depth in Forest-1. A  
672 precise Re-Os depositional age of  $640.7 \pm 4.7$  Ma (MSWD = 0.91) was obtained from the ORM  
673 at 836 m (Kendall et al., 2009b). Molybdenum concentration and isotope data, sedimentary Fe  
674 speciation analyses, and TOC data were obtained using the same methods described in section 3  
675 (Analytical Methods). Data are presented in Table A.1.

676

677

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1121

## 1122 **FIGURE CAPTIONS**

1123

1124 Fig. 1. (a) Paleogeographic map of the Yangtze platform at ~600 Ma showing the location of the  
1125 Three Gorges region. (b) Geological map of the Yangtze Gorges area, showing the location of  
1126 the Jiulongwan outcrop section. The enclosed region is expanded in (c) to show the location of  
1127 the drill core section (Site 1), which is ~5 km away from the Jiulongwan section in the Three  
1128 Gorges region. (d) Cross-section along line A-B in (c) showing the Neoproterozoic stratigraphy  
1129 and location of the Site #1 core. Modified from Sawaki et al. (2010) and Tahata et al. (2013).

1130

1131 Fig. 2. Geochemical profiles through Member IV, Doushantuo Formation. Stratigraphic columns  
1132 of the Jiulongwan outcrop section and the Site 1 drill core section are modified from McFadden  
1133 et al. (2008) and Sawaki et al. (2010), respectively (NF = glaciogenic Nantuo Formation; DF =  
1134 Dengying Formation). The ovals within the black shale in the Jiulongwan section represent  
1135 dolomite nodules. The error bars in the isotope profiles denote the long-term reproducibility of  
1136 our secondary standards ( $\sim 0.15\%$  for Mo and  $\sim 0.07\%$  for U; 2SD). For clarity, individual  
1137 sample error bars are not shown. Total organic carbon, total Fe, highly reactive Fe and pyrite Fe  
1138 are denoted by TOC,  $Fe_T$ ,  $Fe_{HR}$ , and  $Fe_{PY}$ , respectively. Sediments deposited from anoxic bottom  
1139 waters typically have  $Fe_{HR}/Fe_T > 0.38$ , and  $Fe_{PY}/Fe_{HR}$  distinguishes between euxinic ( $> 0.7$ ) and  
1140 ferruginous ( $< 0.7$ ) conditions.

1141  
1142 Fig. 3. (a) Mo EF versus U EF for the Member IV ORM. The dashed lines are equivalent to the  
1143 molar Mo/U ratio for modern seawater ( $1\times$  SW) and for a fraction of modern seawater ( $0.3\times$   
1144 SW), following Algeo and Tribovillard (2009). Green squares = Jiulongwan outcrop section. Red  
1145 triangles = Site 1 drill core section. Large filled symbols = samples with highest  $\delta^{98}\text{Mo}$  from  
1146 each section. (b)  $\delta^{98}\text{Mo}$  versus  $\delta^{238}\text{U}$  for the Member IV ORM, showing no correlation between  
1147 the two isotope systems ( $R^2 < 0.3$  for both sections). Symbols are the same as in (a).

1148  
1149 Fig. 4. Temporal record of  $\delta^{98}\text{Mo}$  and associated Mo/TOC data from euxinic ORM, since the end  
1150 of the Great Oxidation Event. Large squares represent the highest  $\delta^{98}\text{Mo}$  for that time, with other  
1151 data represented by small circles (red: 2050-640 Ma; orange: 555-530 Ma; blue: 520-440 Ma;  
1152 green: 390-0 Ma). (a) Mo isotope record over the past 2050 Ma, with the 800-0 Ma interval  
1153 expanded in (b) (Dsh IV = Doushantuo Formation, Member IV). (c) Cross plot of average

1154 Mo/TOC ratio versus highest  $\delta^{98}\text{Mo}$  (Mo/TOC data is not available for all intervals). Black Sea  
1155 euxinic sediments have low Mo/TOC because of basin restriction (Algeo and Lyons, 2006).  
1156 Three Mesozoic intervals also have low Mo/TOC because of a transient expansion of ocean  
1157 anoxia (the highest  $\delta^{98}\text{Mo}$  from the Jurassic sections mark a return to widespread ocean  
1158 oxygenation; Pearce et al., 2008, 2010; Westermann et al., 2014). (d) Temporal comparison of  
1159 known episodes of extensive ocean oxygenation (green bars), the Shuram-Wonoka carbon  
1160 isotope anomaly, and the appearance of complex macroscopic metazoans (modified from Sawaki  
1161 et al., 2010). The extent of ocean oxygenation at the start of the Shuram excursion is not known  
1162 (see text for discussion). Data sources:  $\delta^{98}\text{Mo}$  (Barling et al., 2001; Arnold et al., 2004; Lehmann  
1163 et al., 2007; Wille et al., 2008; Neubert et al., 2008; Pearce et al., 2008; 2010; Gordon et al.,  
1164 2009; Kendall et al., 2009a, 2011; Dahl et al., 2010b, 2011; Dickson and Cohen, 2012; Dickson  
1165 et al., 2012; Herrmann et al., 2012; Zhou et al., 2012; Asael et al., 2013; Proemse et al., 2013;  
1166 Westermann et al., 2014; this study), Shuram-Wonoka anomaly (McFadden et al., 2008; Sawaki  
1167 et al., 2010; Tahata et al., 2013), acanthomorph acritarchs (Yin et al., 2007; McFadden et al.,  
1168 2008), animal embryos (Yin et al., 2007), Ediacara fossils (Narbonne and Gehling, 2003), motile  
1169 metazoans (Liu et al., 2010; Pecoits et al., 2012), macroscopic motile bilaterians (Martin et al.,  
1170 2000), and weakly calcified metazoans (Grotzinger et al., 1995).

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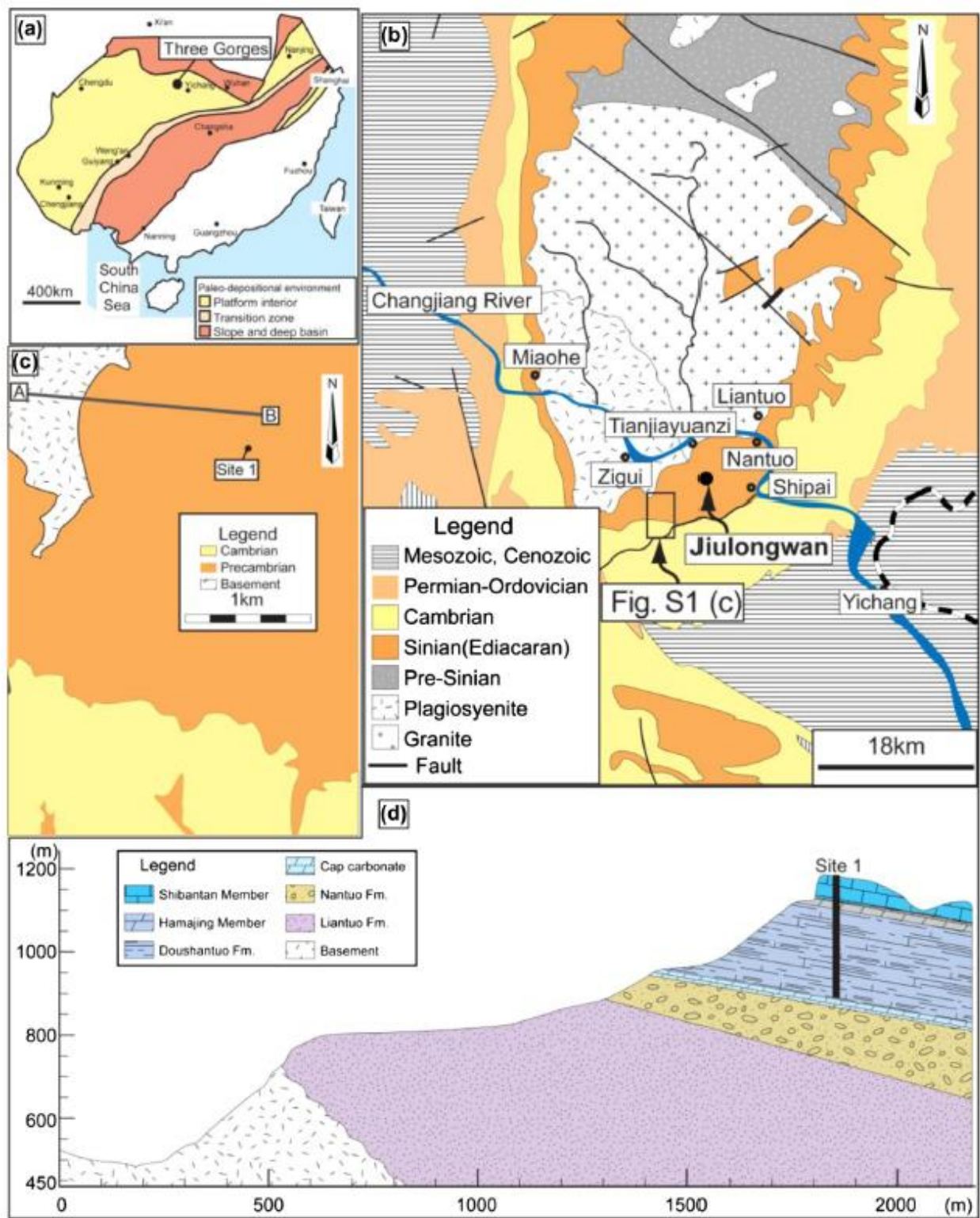
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1177 **Figure 1**

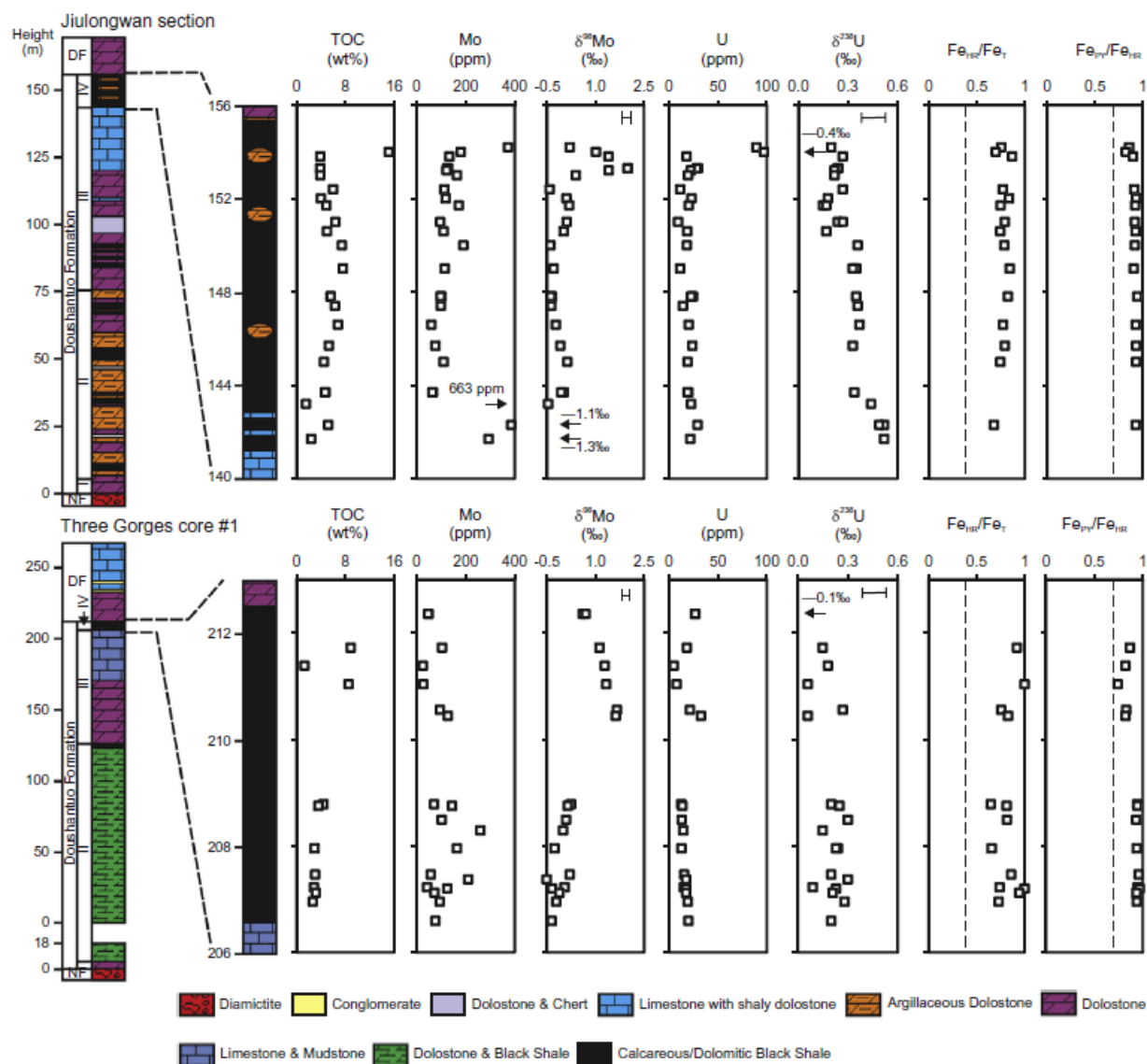
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1180 **Figure 2**

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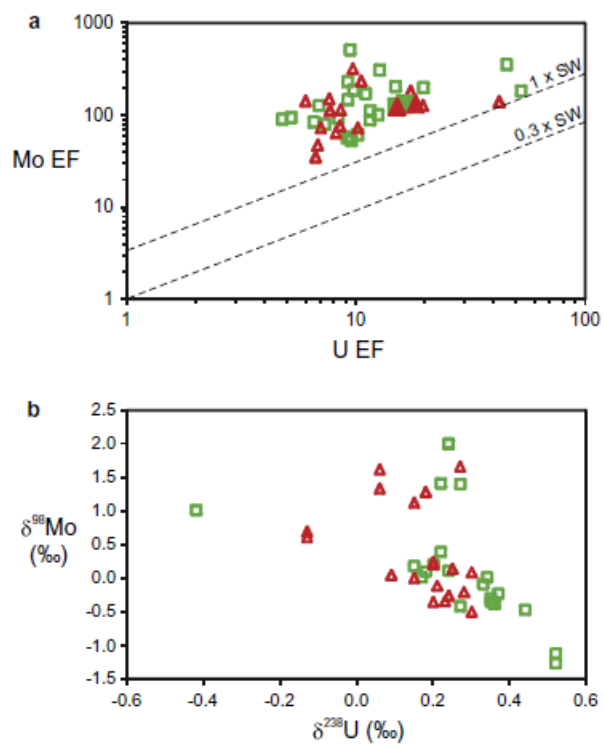
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1188 **Figure 3**

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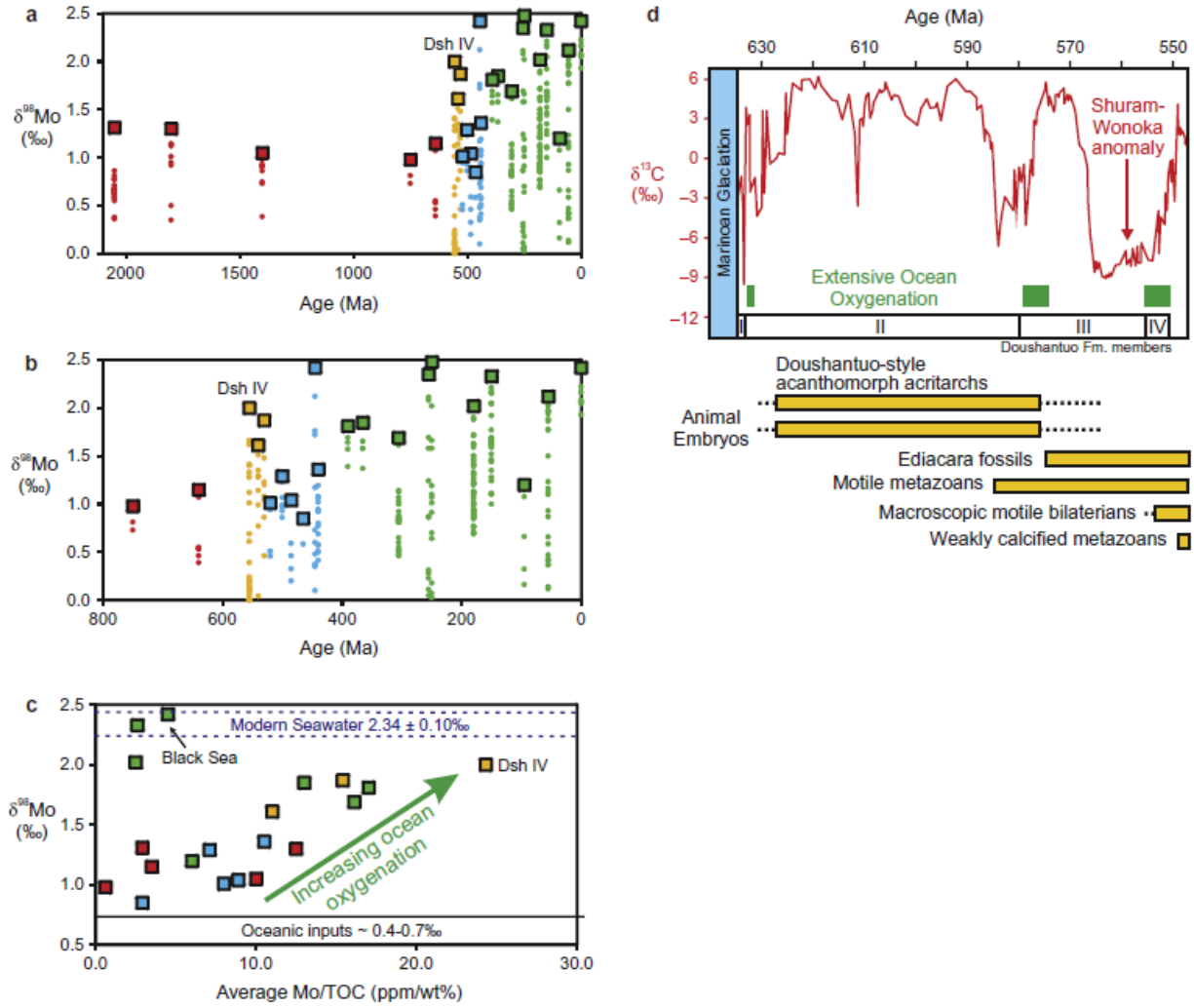
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1202 **Figure 4**

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1217 **Table A.1**

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Table A.1  
Geochemical data for the Black River Dolomite, Tasmania.

Sample	Depth (m)	TOC <sup>a</sup> (wt%)	Al (wt%)	Mo (ppm)	Mo EF	Mo/TOC (ppm/wt%)	$\delta^{98}\text{Mo}^b$ (‰)	$\delta^{98}\text{Mo}^c$ (‰)	2SD Measured	2SD <sup>d</sup> Reported	<i>n</i> <sup>e</sup>	Fe <sub>Carb</sub> (wt%)	Fe <sub>Ox</sub> (wt%)	Fe <sub>Mag</sub> (wt%)	Fe <sub>Py</sub> (wt%)	Fe <sub>HR</sub> <sup>f</sup> (wt%)	Fe <sub>T</sub> <sup>g</sup> (wt%)	Fe <sub>HR</sub> /Fe <sub>T</sub>	Fe <sub>Py</sub> /Fe <sub>HR</sub>
RC06- FOR01-A	835.84– 835.87	5.1	4.8	14	15	2.7	1.15	1.07	0.06	0.15	3	0.1	0.1	0.0	2.7	2.9	2.8	1.00	0.94
RC06- FOR01-B	835.77– 835.79	5.6	4.7	14	16	2.5	1.20	1.12	0.10	0.15	3	0.1	0.1	0.0	2.5	2.6	2.6	0.99	0.95
RC06- FOR01-C	835.70– 835.72	5.3	5.4	14	14	2.6	1.23	1.15	0.10	0.15	3	0.1	0.1	0.0	3.1	3.3	2.9	1.00	0.96
RC06- FOR01-D	835.65– 835.68	5.6	5.1	12	13	2.2	1.18	1.10	0.13	0.15	3	0.1	0.1	0.0	2.6	2.8	2.8	0.98	0.95
RC06- FOR01-E	835.58– 835.62	5.3	5.1	12	13	2.3	1.17	1.09	0.06	0.15	3	0.1	0.1	0.0	2.5	2.7	2.6	1.00	0.95
RC06- FOR02-B	828.11– 828.15	6.5	7.0	29	22	4.5	0.61	0.53	0.10	0.15	3	0.1	0.1	0.0	3.0	3.3	4.1	0.79	0.93
RC06- FOR02-D	828.23– 828.27	6.6	5.7	29	27	4.4	0.63	0.55	0.18	0.18	6	0.1	0.1	0.0	3.0	3.3	4.1	0.80	0.93
RC06- FOR02-G	828.37– 828.40	6.5	7.4	33	24	5.1	0.54	0.46	0.21	0.21	6	0.1	0.1	0.0	3.4	3.6	4.5	0.80	0.93
RC06- FOR02-H	828.48– 828.50	6.4	5.6	30	29	4.7	0.47	0.39	0.10	0.15	3	0.1	0.1	0.0	3.3	3.6	4.0	0.90	0.93
RC06- FOR02-I	828.55– 828.58	6.8	7.3	29	21	4.2	0.62	0.54	0.12	0.15	4	0.1	0.2	0.0	2.9	3.3	4.0	0.81	0.90

<sup>a</sup> TOC = total organic carbon.

<sup>b</sup> Mo isotope data reported relative to RochMo2.

<sup>c</sup> Mo isotope data reported relative to NIST SRM 3134 = 0.25‰.

<sup>d</sup> Uncertainty is the 2SD of replicate measurements or 0.15‰, whichever is greater.

<sup>e</sup> Number of replicate analyses of the same sample solution.

<sup>f</sup> Fe<sub>HR</sub> = Highly reactive Fe abundance = Fe<sub>Carbonate</sub> (Fe<sub>Carb</sub>) + Fe<sub>Ferri-Oxide</sub> (Fe<sub>Ox</sub>) + Fe<sub>Magnetite</sub> (Fe<sub>Mag</sub>) + Fe<sub>Pyrite</sub> (Fe<sub>Py</sub>).

<sup>g</sup> Fe<sub>T</sub> = Total Fe abundance.

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