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1 **Fluctuating oxygenation and dynamic iron cycling in the late Paleoproterozoic ocean**

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Abstract

The mid-Proterozoic (1.8–0.8 billion years ago, Ga) is generally considered to have been an interval of relative stasis in terms of environmental and biological evolution. Indeed, in terms of ocean redox chemistry, deeper ocean waters are considered to have dominantly remained anoxic and ferruginous throughout this interval. Despite the persistence of ferruginous conditions, the mid-Proterozoic has long been considered notable for a general absence of iron formations (IFs), in stark contrast to the major intervals of IF deposition that occurred in the ferruginous oceans of the earlier Precambrian. In recent years, however, sporadic IFs have been found in the mid-Proterozoic, but controls on the genesis of these IFs, as well as implications for the evolution of ocean chemistry, remain poorly understood. Here, we present major and trace element data, iron speciation systematics, and organic carbon and iron isotope data for the ~1.64 Ga Chuanlinggou Formation, which hosts a sudden reappearance of substantial IF deposition on the North China Craton. The Chuanlinggou IF has low Y/Ho ratios (24–26), slightly positive Eu anomalies ($\text{Eu}/\text{Eu}^* = 1.14\text{--}1.47$), no Ce anomalies, slightly positive $\delta^{56}\text{Fe}$ values (0.05 to 0.35‰), and high $\delta^{13}\text{C}_{\text{org}}$ values (-29‰) relative to deeper water facies (down to -33.4‰). These observations provide support for a redox-stratified ocean with oxic surface waters overlying ferruginous deeper waters, and further suggest that IF deposition occurred in a stratified ocean with a shallow redoxcline during an interval of elevated Fe concentrations. Specifically, we suggest that the development of relatively intense ferruginous conditions was likely a consequence of hydrothermal activity during the breakup of the Columbia supercontinent. Microaerophilic iron-oxidizing bacteria and/or anoxygenic photosynthesizers likely played a key role in the generation of the Chuanlinggou IF. Importantly, however, data for shales that overly the Chuanlinggou IF suggest episodic intervals of deeper water oxygenation. Thus, similar to recent studies of the later Mesoproterozoic ocean, our data indicate that ocean chemistry during the latest Paleoproterozoic may have been more dynamic than previously considered, with fluctuating oxygen and iron levels likely exerting a limiting constraint on both the evolution of eukaryotes and the deposition of IFs across the immense interval of time encapsulated by the mid-Proterozoic.

Keywords: iron formations; Proterozoic; ocean oxygenation; iron isotopes; Chuanlinggou iron formation

64 1. Introduction

65 It is generally accepted that the Archean atmosphere and oceans were largely
66 anoxic, with the exception of ‘oxygen oases’, representing regions of relatively shallow
67 water oxygenation that became progressively more widespread during the Neoproterozoic
68 (e.g., [Ostrander et al., 2019](#); [Ossa Ossa et al., 2019](#)). However, shallow water
69 oxygenation became particularly expansive following Earth’s first major rise in
70 atmospheric oxygen, which occurred during the Great Oxidation Event (GOE) around
71 2.4 to 2.1 billion years (Ga) ago (e.g., [Holland, 1984](#); [Poulton et al., 2021](#)). During the
72 GOE, atmospheric O₂ rose in a fluctuating manner ([Gumsley et al., 2018](#); [Poulton et al.,](#)
73 [2021](#)) to levels above 10⁻⁶ of the present atmospheric level (PAL; [Zahnle et al., 2006](#)).
74 Subsequently, the Paleoproterozoic ocean is widely considered to have been redox-
75 stratified (e.g., [Planavsky et al., 2011](#); [Poulton and Canfield, 2011](#)), with a possible
76 decrease in atmospheric O₂ levels after peak concentrations towards the end of the GOE
77 (e.g., [Ossa Ossa et al., 2022](#)). A second interval of highly fluctuating atmospheric
78 oxygen levels (between ~10-50% PAL) occurred during the Neoproterozoic
79 Oxygenation Event (NOE) between ~900 and 540 million years (Ma) ago ([Krause et](#)
80 [al., 2022](#)), before atmospheric oxygen levels rose to near modern levels during the
81 Paleozoic Oxygenation Event (POE; e.g., [Krause et al., 2018](#)).

82 The mid-Proterozoic (1.8–0.8 Ga) encapsulates a major proportion of time
83 between the GOE and the NOE, and is considered to have been a prolonged interval of
84 relative stasis in terms of both Earth surface oxygenation and the evolution of
85 eukaryotic organisms (e.g., [Zhang et al., 2016, 2018](#)). However, oxygen levels in the
86 atmosphere and surface ocean, as well as the chemical composition of the deeper ocean,
87 remain topics of considerable debate. A general view of a mid-Proterozoic ocean
88 characterized by oxygenated surface waters, with anoxic and sulfidic waters in mid-
89 depths along productive continental margins, and anoxic ferruginous deeper waters has
90 emerged (e.g., [Poulton and Canfield, 2011](#); [Planavsky et al., 2011](#)). However, recent
91 evidence has documented more dynamic redox conditions, with pulses of water column
92 oxygenation at 1.57–1.56 Ga (e.g., [Zhang et al., 2018](#); [Luo et al., 2021](#)), ~1.4 Ga (e.g.,
93 [Zhang et al., 2016](#)) and ~1.33 Ga ([Canfield et al., 2018a](#)), and significant spatial
94 heterogeneity driven by global climatic variability (e.g., [Song et al., 2023](#)).

95 The deposition of iron formations (IFs) represents a major line of evidence for
96 ferruginous oceanic conditions through the Archean and earlier Paleoproterozoic (up
97 until ~1.88 Ga) (e.g., [Bekker et al., 2010](#)). Deposition of IFs requires the oceans to have

98 been sufficiently reducing to allow transport and storage of large quantities of aqueous
99 Fe(II). During IF deposition Fe(II) was oxidized, commonly in the photic zone by local
100 cyanobacterial O₂ production or via direct metabolic Fe(II) oxidation (e.g., by
101 chemolithoautotrophic iron-oxidizing bacteria (FeOB) or anoxygenic
102 photosynthesizers; Bekker et al., 2010; Konhauser et al., 2017). However, despite
103 evidence for persistent anoxia and ferruginous deeper waters, substantial deposition of
104 IFs is commonly considered not to have occurred during the mid-Proterozoic (e.g.,
105 Bekker et al., 2010). Recent reports have, however, documented the occurrence of
106 major IFs at ~1.64 Ga (Lin et al., 2019 and references therein) and ~1.4 Ga (Canfield
107 et al., 2018b), thereby questioning this paradigm. Nevertheless, IF deposition during
108 the mid-Proterozoic appears to have been rare relative to earlier in Earth's history, and
109 controls on the genesis of mid-Proterozoic IFs, as well as detailed implications for the
110 evolution of ocean redox conditions, have received little attention.

111 Here, we focus on the ~1.64 Ga Chuanlinggou Formation (CF) in the Yanliao
112 Basin, North China Craton (NCC) (Fig. 1a), where ~4700 million tons of IF-type
113 hematite ore occurs (Lin et al., 2019), representing the first large IF deposit after their
114 apparent demise at ~1.88 Ga (Bekker et al., 2010). We utilize major and trace element
115 data, Fe speciation systematics, and Fe and organic C isotope data to assess the
116 evolution of water column redox conditions and controls on IF genesis. In doing so, our
117 data provide a direct assessment of marine redox conditions and iron cycling towards
118 the end of the Paleoproterozoic era (~1.64 Ga), with broader scale implications for the
119 IF record and eukaryotic evolution across the mid-Proterozoic.

120

121 **2. Geological setting**

122 The Yanliao Basin formed via a continental rift that developed on the northern
123 margin of the NCC beginning at ~1.7 Ga, possibly linked to the early break-up of the
124 Columbia Supercontinent (Fig. 1b; Kusky and Li, 2003). Sedimentary rocks in the
125 Yanliao Basin contain the 1.8–1.6 Ga Changcheng Group, the 1.6–1.4 Ga Jixian Group,
126 the 1.4–1.0 Ga Huailai group, and 1.0–0.8 Ga Qingbaikou Group (Fig. 1c; Zhu et al.,
127 2016; Lin et al., 2019).

128 The 1.8–1.6 Ga Changcheng Group was deposited on Archean-early
129 Paleoproterozoic crystalline basement, and in stratigraphic order consists of the
130 Changzhougou, Chuanlinggou, Tuanshanzi and Dahongyu formations. During the
131 latest Paleoproterozoic, the Yanliao Basin was likely connected to the open ocean in the

132 north, and the transgression of seawater into the basin was from the northwest or
133 northeast (Lin et al., 2019). The Changzhougou Formation is dominated by fluvial
134 coarse sandstones and conglomerates in its lower portion, and by littoral-intertidal
135 siltstones and sandstones in its upper portion, representing the initial development of
136 the Yanliao Basin. IFs, dolostones, black shales and interbedded sandstones of the CF
137 record a transition from a shallow marine environment to a subtidal low-energy
138 environment (e.g., Li et al., 2015; Lin et al., 2019) (Figs. 2a and b). Volcanic rocks in
139 the Tuanshanzi and Dahongyu formations mark the peak development of the basin.

140 The 1.6–1.4 Ga Jixian Group, including the Gaoyuzhuang, Yangzhuang,
141 Wumishan, Hongshuizhuang and Tieling Formations, is dominated by carbonate rocks,
142 including laminated and stromatolitic dolostone, limestone, muddy dolostone and chert
143 bands. The younger ~1.4 Ga Xiamaling Formation consists of black shale, muddy
144 dolostone, mudstone and IFs (Zhang et al., 2016; Canfield et al., 2018b). The 1.0–0.8
145 Ga Qingbaikou Group, which mainly consists of sandstone and shale, marks the return
146 of dominantly siliciclastic deposition prior to regional uplift of the Yanliao Basin (Fig.
147 1c; Luo et al., 2014; Li et al., 2015; Zhang et al., 2018).

148 The CF documents a basin-scale water depth gradient running from north to south,
149 with deeper water facies deposited in the south along a narrow belt bounded by two sets
150 of NE- to SW-trending rift faults (Beijing–Lingyuan and Luanxian–Jianchang; Li et al.,
151 2015). The CF is widely distributed on the NCC and can be divided into three
152 depositional areas. The eastern area, including Jixian, Zunhua, Xinglong and
153 Kuancheng, is characterized by the development of thick black shales. The middle area
154 is located in the northern part of Miyun–Huairou and comprises thick stromatolitic
155 dolostones and lagoonal facies deposition. The western area is located in the Xuanhua–
156 Zhangjiakou area, where the CF is significantly thinner and characterized by the
157 development of IFs. Regionally the IFs extend for ~154 km in a NS direction and ~130
158 km in a WE direction, and cover an area of ~3900 km². The western area, with an
159 estimated total iron ore resource of ~4700 Mt, is characterized by a thin depositional
160 thickness (<50 m) and multiple layers of IF in its lower part (Fig. 2c). The CF is
161 interpreted as a passive-margin sequence, suggesting a strong connection to the open
162 ocean (Lin et al., 2019), and the depositional age of the CF can be constrained to ~1.64
163 Ga (see Supplementary Information Appendix A; Fig. 1c).

164

165 3. Materials and methods

166 **3.1 Materials**

167 Chuanlinggou Formation drill core samples were collected from the western area
168 (Xuanhua-Chicheng-Longguan; hereon abbreviated to Xuan-Long), Hebei province.
169 Samples comprise sandstone (n = 1) (Fig. 2d), IF (n = 12) (Fig. 2e), black shale
170 (including two siderite-rich shales) (n = 87) (Fig. 2f), and dolostone (n = 32) (Fig. 2g),
171 deposited under marine conditions ranging from a shallow subtidal/intertidal zone to a
172 deeper subtidal setting (Fig. 2h; Supplementary Information Appendix A). Prior to
173 analysis, samples were fragmented using a jaw crusher, followed by crushing to a fine
174 powder in a Tema mill with a tungsten carbide barrel.

175

176 **3.2 Carbon concentration analyses**

177 Total organic carbon (TOC) and total carbon (TC) contents were obtained for all
178 samples using a LECO C/S Analyzer in the Cohen Geochemistry Laboratory,
179 University of Leeds. For TOC content, sample powders were first treated with 10% HCl
180 to remove carbonate phases. Replicate analyses of certified standards (Soil 502–309,
181 Soil 502–062, Calcium carbonate 501–034 and Coal 502–671) gave RSDs of < 2% for
182 TC and < 2% for TOC, with close to 100% recovery in all cases. Total inorganic carbon
183 (TIC) contents were calculated as $TIC = TC - TOC$, and replicates of TIC analyses gave
184 a RSD of < 2%.

185

186 **3.3 Organic carbon isotope analyses**

187 Organic carbon isotope ($\delta^{13}C_{org}$) compositions were measured in the Analytical
188 Laboratory of the Beijing Research Institute of Uranium Geology, Beijing, China.
189 Powdered samples were first oven dried at 40°C and then dissolved with 0.5 N HCl to
190 remove carbonate minerals, with residuals combusted at 900°C for 1 h to collect the
191 CO₂ derived from organic matter. The resulting CO₂ was then dehydrated and purified
192 before analysis via a Finnigan MAT-253 isotope mass spectrometer. Analyses of
193 standard IAEA-600 (Caffeine, $\delta^{13}C_{org} = -27.771\text{‰}$) gave an analytical precision of
194 better than 0.1‰. Standards were measured every six samples to monitor and correct
195 for potential drift. $\delta^{13}C_{org}$ values are reported in per mil (‰) notation relative to the
196 Vienna Pee Dee Belemnite (V-PDB) standard.

197

198 **3.4 Major and trace element analyses**

199 Total element concentrations (Fe, Mn and Al) were determined on samples via an

200 HF-HClO₄-HNO₃ extraction, with HBO₃ used to ensure full solubilisation of Al,
201 followed by analysis using a ThermoFisher iCAP 7400 radial inductively coupled
202 plasma optical emission spectrometer (ICP-OES). Trace elements (Mo, U and V) were
203 analysed on the same solutions using a ThermoFisher iCAP Qc inductively coupled
204 plasma mass spectrometer (ICP-MS) in the Cohen Geochemistry Laboratory,
205 University of Leeds. Accuracy was monitored relative to reference material USGS
206 Eocene Green River Shale (SGR-1), with all elements being within 93 ± 6% of certified
207 values. Repeat measurements of samples yielded RSDs for all elements of better than
208 3%.

209 Rare earth element (REEs), Y and Ba concentrations were obtained by an Agilent
210 7700x ICP-MS at the ALS Chemex, Guangzhou, China. Briefly, 50 mg of sample
211 powder was melted in LiBO₂/Li₂B₄O₇ solvent and heated at 1025°C. The sample was
212 then dissolved using a HClO₄, HNO₃ and HF mixture, then evaporated to near dryness
213 and dissolved in dilute HCl to 100 mL. Certified standards MRGeo08 (granite),
214 GBM908-10 (oxide copper gold ore), OREAS 25 (mature soil) and OREAS 25 (a blend
215 of mineralized ferruginous soil and barren mature soil) were used as standards during
216 the analyses. Analytical uncertainties are ± 5% for REEs, and ± 5–10% for other trace
217 elements.

218

219 **3.5 Iron isotope analyses**

220 Bulk-rock Fe isotope compositions were analyzed at the Key Laboratory of Crust-
221 Mantle Materials and Environments, University of Science and Technology of China,
222 Hefei, China. Fe was purified using anion resin (Bio-Rad AG1-X8) conditioned with 8
223 N HCl, and matrix elements were removed by washing with 8 N HCl. Fe was eluted
224 using 0.5 N HCl and H₂O followed by 8 N HNO₃ and H₂O. A pure Fe solution with
225 high yield was obtained by two passes through the column for all samples. Standard
226 bracketing methods were followed ([Huang et al., 2011](#)), and analyses were performed
227 on a Neptune Plus MC-ICP-MS. Iron solutions were diluted to 1.5 ppm for analysis and
228 bracketed with IRMM-14 at the same concentration. ⁵⁴Fe, ⁵⁶Fe and ⁵⁷Fe (along with
229 ⁵³Cr for correcting any ⁵⁴Cr interference) were measured in static mode on L3, H4 and
230 H6 Faraday cups, respectively. Contributions from isobaric interferences (⁴⁰Ar¹⁴N on
231 ⁵⁴Fe and ⁴⁰Ar¹⁶O on ⁵⁶Fe) were eliminated by measuring in pseudo-high resolution
232 mode with M/ΔM of ~8000. Iron isotope results are reported as ‰ in the standard delta
233 notation:

234
$$\delta^{56}\text{Fe} (\text{‰}) = 1000 \times [({}^{56}\text{Fe}/{}^{54}\text{Fe})_{\text{sample}} / ({}^{56}\text{Fe}/{}^{54}\text{Fe})_{\text{IRMM-14}} - 1]$$

235 The international geological reference standards BHVO-2 = $0.11 \pm 0.01\text{‰}$, BIR-1 =
236 $0.05 \pm 0.01\text{‰}$, RGM-1 = $0.21 \pm 0.05\text{‰}$, were analyzed repeatedly to monitor the
237 external reproducibility, were within the error of certified values (Huang et al., 2011
238 and references therein).

239

240 **3.6 Iron speciation analyses**

241 Iron speciation analyses were conducted following the sequential extraction
242 procedure of Poulton and Canfield (2005) in the Cohen Geochemistry Laboratory,
243 University of Leeds. Extractions were performed according to the calibrated procedure,
244 whereby carbonate-associated Fe (e.g., siderite, ankerite; Fe_{carb}) was targeted with Na-
245 acetate at pH 4.5 and 50°C for 48 h, ferric (oxyhydr)oxides (e.g., goethite, hematite;
246 Fe_{ox}) were targeted using Na-dithionite at pH 4.8 for 2 h, and magnetite (Fe_{mag}) was
247 targeted by an ammonium oxalate extraction for 6 h. Sulfide-bound Fe was determined
248 via the two-step chromous chloride distillation procedure of Canfield et al. (1986). Acid
249 volatile sulfide (Fe_{AVS} ; below detection in all cases) was extracted with boiling 6 N HCl,
250 and pyrite (Fe_{py}) was extracted with boiling chromous chloride. The liberated sulfide
251 was trapped as Ag_2S , and Fe_{py} was determined gravimetrically. Accuracy was ensured
252 by repeat analyses of international sediment standard WHIT, with RSDs of <5% for all
253 stages.

254

255 **4. Interpretational framework**

256 **4.1 Redox reconstruction**

257 We use four independent approaches to assess water column redox conditions:
258 REE+Y, Fe speciation, Fe_T/Al (where Fe_T represents total Fe) ratios and redox-sensitive
259 trace element (RSE) systematics. The capture and preservation of aqueous REE+Y
260 patterns in IFs provide a window into ancient ocean chemistry and redox state. In
261 general, modern oxygenated seawater is characterized by a strong negative Ce anomaly
262 when normalized to Post-Archean Average Shale (PAAS, Supplementary Information
263 Appendix A; Byrne and Sholkovitz, 1996). This is because the oxidation of Ce(III)
264 greatly reduces Ce solubility, resulting in preferential removal of Ce by Fe- and Mn-
265 (oxyhydr)oxides, organic matter and clay particles. By contrast, dysoxic and anoxic
266 waters lack true negative Ce anomalies (e.g., Planavsky et al., 2010). Yttrium and Ho
267 act as a twin pair due to their similar charge and radius. Modern seawater is

268 characterized by super-chondritic Y/Ho ratios of 44 to 74, significantly greater than
269 both upper crustal rocks and chondritic Y/Ho ratios of 26–28 with no apparent
270 fractionation of Y from Ho (Bau et al., 1996), which result from faster scavenging of
271 Ho over Y by Fe- and Mn-(oxyhydr)oxides. When Fe- and Mn-(oxyhydr)oxide particles
272 settle into dysoxic/anoxic deeper waters in a redox stratified ocean, a decrease in
273 dissolved seawater Y/Ho ratios develops due to reductive dissolution (Bau et al., 1996;
274 Planavsky et al., 2010).

275 Iron speciation data potentially allow oxic water column conditions to be
276 distinguished from ferruginous (anoxic, Fe(II)-containing) and euxinic conditions
277 (Poulton and Canfield, 2011; Poulton, 2021), whereby the biogeochemically highly
278 reactive Fe pool (Fe_{HR}), including Fe_{carb} , Fe_{ox} , Fe_{mag} and Fe_{py} , is quantified relative to
279 Fe_T . Iron speciation has been extensively calibrated in modern and ancient settings, and
280 ancient oxic marine sediments commonly have $Fe_{HR}/Fe_T < 0.22$, whereas water column
281 enrichments under anoxic conditions typically result in $Fe_{HR}/Fe_T > 0.38$ (Poulton and
282 Canfield, 2011). Ratios between 0.22–0.38 are considered equivocal, and may represent
283 either oxic or anoxic depositional conditions. For anoxic samples, ferruginous
284 conditions are distinguished from euxinic conditions by quantifying the extent of
285 pyritization of the highly reactive iron pool (Fe_{py}/Fe_{HR}). $Fe_{py}/Fe_{HR} > 0.8$ is characteristic
286 of euxinic deposition, whereas $Fe_{py}/Fe_{HR} < 0.6$ indicates deposition under ferruginous
287 conditions. Ratios between 0.6–0.8 are considered equivocal, and may represent either
288 euxinic or ferruginous conditions (Poulton and Canfield, 2011; Poulton, 2021). Fe_T/Al
289 ratios can also distinguish anoxic and oxic depositional environments, particularly in
290 IF samples where enrichments in Fe_T/Al can be extreme, resulting in ratios that are
291 highly elevated relative to the wide range of regional compositions that can occur due
292 to the geochemical composition of the source material. Fe_T/Al ratios $> 0.55 \pm 0.11$ are
293 commonly taken to indicate anoxic conditions (Clarkson et al., 2014).

294 We utilize the redox-dependent behaviour of Mo, U and V to provide further
295 independent insight into redox conditions (e.g., Tribovillard et al., 2006). In oxygenated
296 modern oceans, the conservative elements Mo and U mainly occur as soluble molybdate
297 (MoO_4^{2-}) and uranyl carbonate complexes ($UO_2(CO_3)_3^{4-}$). High sediment Mo
298 accumulation tends to occur through the formation of particle-reactive thiomolybdates
299 when water-column concentrations of sulfide are high (e.g., Helz et al., 1996). By
300 contrast, U may be fixed in the sediment under anoxic porewater conditions, without
301 the requirement for free H_2S (e.g., Anderson et al., 1989). Such conditions also explain

302 enrichments in vanadium, as the vanadate ion $[\text{VO}_2(\text{OH})_3]^{2-}$, V(V)] is reduced to
303 immobile V(IV) and V(III) phases under reducing conditions (e.g., [Emerson and](#)
304 [Huested, 1991](#)).

305

306 **4.2 Fe cycling**

307 Ferrous iron oxidation in reducing environments can be driven by local
308 cyanobacterial O_2 production or by direct metabolic Fe(II) oxidation (e.g., by
309 microaerophilic FeOB and anoxygenic photosynthesizers; [Bekker et al., 2010](#);
310 [Konhauser et al., 2017](#)). UV photo-oxidation has also been considered as a possible
311 mechanism, but the efficiency of UV-dependent oxidation in complex seawater
312 solutions has been questioned in recent experimental studies ([Konhauser et al., 2017](#)).
313 Submarine hydrothermal-sourced Fe has a characteristic $\delta^{56}\text{Fe}$ value of -0.5 to 0.0‰,
314 while seawater has a relatively homogeneous Fe isotope composition of close to 0‰
315 ([Johnson et al., 2008](#)). Biotic and abiotic partial oxidation of Fe(II) to Fe(III) in solution
316 can cause large Fe isotope fractionations, typically in the region of 1.5 to >2.5‰
317 ([Johnson et al., 2008](#); [Planavsky et al., 2012](#)). By contrast, complete oxidation and
318 precipitation produces Fe-(oxyhydr)oxide $\delta^{56}\text{Fe}$ values equal to those of the initial Fe(II)
319 ([Johnson et al., 2008](#)).

320 Whole rock $\delta^{56}\text{Fe}$ compositions reflect the net Fe isotopic composition of a
321 mixture of different iron-bearing minerals, whose contents and isotopic compositions
322 vary between samples. In this study, we use a simple mixing model to calculate $\delta^{56}\text{Fe}$
323 values of Fe_{HR} : $\delta^{56}\text{Fe} = (\text{Fe}_{\text{HR}} \times \delta^{56}\text{Fe}_{\text{HR}} + \text{Fe}_{\text{U}} \times \delta^{56}\text{Fe}_{\text{U}}) / (\text{Fe}_{\text{HR}} + \text{Fe}_{\text{U}})$, where $\delta^{56}\text{Fe}$ is
324 the measured whole rock value, $\delta^{56}\text{Fe}_{\text{HR}}$ is the isotopic composition of highly reactive
325 iron, and $\delta^{56}\text{Fe}_{\text{U}}$ is the isotopic composition of unreactive iron, which we assume to
326 have crustal values (i.e., 0.1‰; [Planavsky et al., 2012](#)).

327

328 **5. Results**

329 All data are listed in Supplementary Information [Appendix B](#). In the lower CF, the
330 4 black shale samples have varying TOC contents (from 0.57 to 1.34 wt.%), with TIC
331 contents of 0.13 to 0.99 wt.%, and $\delta^{13}\text{C}_{\text{org}}$ values of -31.8 to -30.8‰ ([Fig. 3](#)). The twelve
332 IF samples from the lower CF have lower TOC (0.08 to 0.14 wt.%) and higher TIC
333 (1.42 to 3.19 wt.%) contents, with $\delta^{13}\text{C}_{\text{org}}$ values that range from -29.9 to -28.1‰. The
334 single sandstone sample from the top of the lower CF has a low TOC content (0.08

335 wt.%) with no detectable TIC, and a $\delta^{13}\text{C}_{\text{org}}$ value of -28.8‰. The black shale samples
336 from the upper CF have TOC contents that range from 0.11 to 4.84 wt.%, with relatively
337 low TIC values of 0 to 7.82 wt.%, and $\delta^{13}\text{C}_{\text{org}}$ values that range from -33.4 to -29.3‰
338 (Fig. 3). The dolostone samples in the upper CF have relatively low TOC contents of
339 0.03 to 0.61 wt.%, with expected higher TIC values of 8.38 to 12.80 wt.%, and $\delta^{13}\text{C}_{\text{org}}$
340 values that range from -33.4 to -29.7‰.

341 All IF samples have low Y/Ho ratios, ranging from 23.50 to 26.05 (Fig. 3). When
342 normalized to PAAS, the IF samples show depletions in light REEs (LREEs) and
343 enrichments in heavy REEs (HREEs; exemplified by PAAS-normalized ratios of Pr to
344 Yb, where $\text{Pr}_{\text{PAAS}}/\text{Yb}_{\text{PAAS}}$ ratios range from 0.35–0.76; Appendix B; Bau et al., 1996;
345 Planavsky et al., 2010). Slight positive Eu anomalies ($\text{Eu}/\text{Eu}^* = 1.14\text{--}1.47$; where
346 $\text{Eu}/\text{Eu}^* = \text{Eu}_{\text{PAAS}}/(0.67 \times \text{Sm}_{\text{PAAS}} + 0.33 \times \text{Tb}_{\text{PAAS}})$) and no true Ce anomalies (based on a
347 Ce/Ce* versus Pr/Pr* plot) are evident (Appendix A; Fig. 3). Dolostone also lack true
348 Ce anomalies (Appendix A). The black shale and dolostone samples throughout the CF
349 have weakly positive Eu anomalies ($\text{Eu}/\text{Eu}^* = 1.00\text{--}1.31$, with the exception of one
350 dolostone sample towards the top of the CF, which has a slightly negative Eu/Eu*
351 anomaly of 0.96).

352 The IF samples have high Fe_T concentrations, ranging from 45.6 to 59.9 wt.%
353 (Appendix B), with very high Fe_T/Al ratios of 27.6–61.4 (Fig. 4). The shale samples
354 have variable Fe_T concentrations and Fe_T/Al ratios of 1.06–36.1 wt.% and 0.11–44.4,
355 respectively. Dolostone samples have low Fe_T concentrations of 1.16–3.22 wt.%, and
356 Fe_T/Al ratios ranging from 0.76 to 10.9. Most of our samples have high $\text{Fe}_{\text{HR}}/\text{Fe}_T$ ratios
357 (> 0.38 ; $n = 98$; Fig. 4). However, 4 samples have low $\text{Fe}_{\text{HR}}/\text{Fe}_T$ ratios (< 0.22), and 30
358 samples have $\text{Fe}_{\text{HR}}/\text{Fe}_T$ ratios ranging from 0.22 to 0.38, and these samples tend to
359 cluster around depth intervals 381.1–401.9 m and 420.5–484.8 m. All of the samples
360 have very low $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$ ratios (< 0.11 ; Fig. 4). IFs have consistently elevated RSE (U,
361 Mo and V) concentrations when normalized to Al (Fig. 4). By contrast, other samples
362 (particularly the shales) have variable U/Al, Mo/Al and V/Al ratios (Fig. 4).

363 In the lower CF, all IF samples have slightly positive $\delta^{56}\text{Fe}$ values (0.05 to 0.35‰,
364 average = $0.19 \pm 0.09\%$; Fig. 4). The $\delta^{56}\text{Fe}$ value of the single sandstone sample is -
365 0.44‰. The 4 black shale samples have $\delta^{56}\text{Fe}$ values ranging from -0.10 to 0.32‰
366 (average = $0.15 \pm 0.14\%$). In the upper CF, the $\delta^{56}\text{Fe}$ values of black shales spread
367 across a large range, from -0.60 to 0.54‰ ($0.08\% \pm 0.29\%$, $n = 13$), and the dolostones
368 have slightly negative $\delta^{56}\text{Fe}$ values, ranging from -0.42 to -0.06‰ ($-0.26 \pm 0.11\%$, $n =$

369 9; Fig. 4).

370

371 6. Discussion

372 6.1 Evaluating ocean redox chemistry

373 Our samples, which include sandstone, IF, black shale (including siderite-rich
374 shale) and dolostone, span a significant range in water depth (from shallow through to
375 deeper environments on the outer shelf; Fig. 2h), thus allowing a detailed reconstruction
376 of oceanic redox structure. The IF is hosted in the lower CF, which reflects deposition
377 in shallow intertidal to subtidal environments above fair-weather wave base (Li et al.,
378 2015; Lin et al., 2019) (Fig. 2h). The IF samples are dominated by hematite with minor
379 detrital phases (Figs. 2c and e), and the observed LREE depletion over HREE
380 enrichment is similar to ancient IFs and modern seawater (Planavsky et al., 2010 and
381 references therein). In addition, no obvious covariation is observed between Al vs.
382 Y/Ho or Ce/Ce* ratios, suggesting that the IFs preserve primary seawater REE+Y
383 signals without significant detrital influence (Supplementary Information Appendix A).

384 The absence of true negative Ce anomalies suggests that the CF IF was deposited
385 under anoxic or dysoxic conditions. The CF IF has homogeneous low Y/Ho ratios (24–
386 26; lower than that of upper crustal rocks and chondrite; Fig. 3), which are consistent
387 with CF IFs from other sites in the NCC (e.g., Lin et al., 2019), and similar REE+Y
388 features are recorded by other late Paleoproterozoic IFs (e.g., Planavsky et al., 2010;
389 Qiu et al., 2022). Redox-induced changes in REE+Y patterns in some modern redox-
390 stratified basins can be linked directly to Mn cycling, giving decreased Y/Ho ratios
391 below the Mn chemocline (Planavsky et al., 2010). Oxidation of Mn(II) to Mn(IV)
392 requires a higher redox potential compared to Fe(II) and takes place above the Fe
393 chemocline (e.g., Tebo et al., 2004; Ossa Ossa et al., 2018). Therefore, like some late
394 Paleoproterozoic IFs, the low Y/Ho ratios provide evidence for a shallow Mn
395 chemocline above the Fe chemocline, where IF deposition and Mn-(oxyhydr)oxide
396 reduction occurred. The high Fe_T/Al and Fe_{HR}/Fe_T ratios for the CF IF (Fig. 4) thus
397 support upwelling of deeper anoxic ferruginous waters to the Fe chemocline. The
398 enrichments in U, Mo and V (see discussion below for the evaluation of local redox
399 thresholds) in IF samples either reflects anoxic water column conditions, at least around
400 the sediment-water interface, or uptake and draw down in association with Fe minerals
401 that precipitated at the Fe chemocline (see below).

402 The non-IF samples with elevated Fe_{HR}/Fe_T (>0.38) and Fe_T/Al ratios (>0.55 ±

403 0.11), as well as low Fe_{py}/Fe_{HR} ratios (Fig. 4), suggest that anoxic and ferruginous water
404 column conditions were a prevalent feature during deposition of the CF. However, the
405 low Fe_T/Al and Fe_{HR}/Fe_T ratios for non-IF samples in the lower CF, as well as groupings
406 of samples in the upper CF, suggest oxic or equivocal deposition (Fig. 4). In terms of
407 the upper CF, these samples occur from 381.1–401.9 m and 420.5–484.8 m, and are
408 interspersed with samples that have elevated Fe_T/Al and Fe_{HR}/Fe_T ratios, suggesting
409 that the water column likely fluctuated between oxic and anoxic-ferruginous conditions
410 through these zones. However, to provide a more robust redox evaluation, we consider
411 these Fe speciation data alongside our redox sensitive trace element data.

412 Uranium is particularly useful in this context because U and Fe have similar redox
413 potentials, and both require only water column anoxia (i.e., not sulfide) to generate
414 significant enrichments (e.g., Anderson et al., 1989; Poulton, 2021). Here, recognising
415 that redox proxy thresholds should be characterised for the local environment wherever
416 possible (e.g., Poulton, 2021) we take the approach of recent studies (e.g., Li et al., 2023)
417 and consider U and Fe systematics together (Fig. 5a). This approach demonstrates that
418 U/Al ratios only start to increase when Fe_{HR}/Fe_T ratios approach ~ 0.45 , suggesting that
419 samples below this value were likely deposited under oxic conditions. Some of the
420 samples with Fe_{HR}/Fe_T ratios >0.45 also have relatively low U/Al ratios, but we note
421 here that elevated U/Al ratios coincident with high Fe_{HR}/Fe_T ratios is also a
422 characteristic of anoxic ferruginous waters upwelling into oxic shallower waters, and
423 thus these sporadic samples likely represent deeper water anoxia. Thus, taking these
424 considerations together, we utilise samples with Fe_{HR}/Fe_T ratios of <0.45 to provide
425 oxic baseline ranges for U/Al (0.22 ± 0.41), Mo/Al (0.19 ± 0.48) and V/Al (9.52 ± 2.49),
426 and we use this redox calibration to distinguish dominantly oxic and ferruginous
427 samples on the trace element plots (Fig. 4).

428 Our local redox calibration supports fluctuating water column redox conditions,
429 from oxic to anoxic, on a variety of timescales through the CF (Fig. 4). Intervals of
430 anoxic deposition are supported by elevated U/Al and V/Al ratios, alongside high
431 Fe_T/Al and Fe_{HR}/Fe_T ratios, while the very low Fe_{py}/Fe_{HR} ratios in these well-preserved
432 drill core samples suggests ferruginous anoxia. Given this interpretation, the moderate
433 enrichments that occur in Mo/Al ratios in dominantly ferruginous intervals likely reflect
434 Mo draw down via uptake to Fe minerals formed in the ferruginous water column (the
435 ‘particle shuttle’ mechanism; Tribouillard et al., 2006). We note here that anoxic
436 intervals occur in both black shale and dolostone intervals (Fig. 4), and dolostones also

437 lack Ce anomalies, suggesting that there is no specific lithological control on the redox
438 interpretation. Indeed, since the dolostones likely formed in shallower waters relative
439 to the black shale, a major deepening of the oxycline at certain intervals appears likely.
440 Thus, in contrast to the shallow oxycline invoked for the lower CF (above fair weather
441 wave base, which is usually <20 m in modern settings), redox fluctuations in the upper
442 CF resulted in the periodic oxygenation of deeper waters (likely below storm wave base,
443 which may be up to 200 m). Previous studies of the CF at other sites also show highly
444 variable Fe speciation characteristics (Fig. 5b; Planavsky et al., 2011; Li et al., 2015),
445 providing support for fluctuations in the depth of water column oxygenation at the end
446 of Paleoproterozoic era.

447

448 **6.2 Iron cycling and generation of the Chuanlinggou IF**

449 Iron formations are rare between 1.8 and 0.8 Ga (e.g., Bekker et al., 2010), and
450 therefore, the formation of the Chuanlinggou IF at ~1.64 Ga likely required a source of
451 Fe(II) well in excess of the normal mid-Proterozoic marine flux. Recent studies have
452 provided support for a strong hydrothermal flux at this time (Lin et al., 2019), and since
453 the CF coincides with the breakup of Columbia (Kusky and Li, 2003; Lin et al., 2019),
454 increased hydrothermal activity would be expected. Indeed, both the CF IF samples and
455 the overlying sediments of the upper CF have positive Eu anomalies (Fig. 3), which are
456 widely considered to define hydrothermal inputs to the depositional setting (e.g., Bau
457 et al., 1996). These Eu anomalies are, however, relatively small ($\text{Eu}/\text{Eu}^* = 1.14\text{--}1.47$;
458 Fig. 3), and follow a general trend of reduced Eu anomalies through time, from IFs
459 deposited in the Archean Eon ($\text{Eu}/\text{Eu}^* = 1.2\text{--}4.5$) to the Neoproterozoic era ($\text{Eu}/\text{Eu}^* =$
460 $1\text{--}1.4$) (Konhauser et al., 2017). Nevertheless, the presence of positive Eu anomalies in
461 almost all of the CF samples strongly points to a hydrothermal signature. Since
462 submarine hydrothermal activity commonly supplies Fe(II) to the marine environment,
463 elevated Fe concentrations linked to enhanced hydrothermal activity likely played a
464 major role in the genesis of the Chuanlinggou IF (Lin et al., 2019), although we stress
465 that this would likely have been in addition to Fe(II) supplied via release from sediment
466 porewaters under widespread ferruginous conditions (Poulton and Canfield, 2011;
467 Poulton, 2021).

468 The continuation of small positive Eu anomalies in the upper CF also has
469 implications for the continued persistence of deeper ferruginous waters after deposition
470 of the IF. Previous studies have argued that the flux of organic matter was a major

471 control on the redox landscape of the mid-Proterozoic ocean, with productivity and the
472 organic flux limiting the extent of euxinia (Planavsky et al., 2011). Generally low TOC
473 contents in the CF (average = 0.66 ± 0.77 wt.%) might be consistent with this view.
474 However, some samples have higher TOC contents (up to 4.8 wt.%; Fig. 3), and yet do
475 not show evidence for enhanced sulfide production, even during diagenesis (as
476 indicated by very low pyrite concentrations). Relative changes in the oceanic influx of
477 Fe_{HR} and sulfate have also been proposed as a first-order control on the chemical nature
478 of water column anoxia in the mid-Proterozoic (Poulton and Canfield, 2011). An
479 enhanced hydrothermally-derived supply of dissolved Fe(II) would provide a specific
480 mechanism to increase the upwelling flux of dissolved Fe(II), thereby ultimately
481 increasing the flux of Fe_{HR} (after precipitation in the water column) relative to sulfate.
482 We therefore suggest that a significant supply of hydrothermally-derived Fe(II)
483 provided a source for the Chuanlinggou IF, as well as subsequently helping to maintain
484 ferruginous deeper water column conditions through the upper CF.

485 The IF samples in the CF have positive $\delta^{56}\text{Fe}_{\text{HR}}$ values (0.04–0.42‰, average =
486 0.21 ± 0.12 ‰) which is higher than expected for the hydrothermal flux (-0.5 to 0.0‰;
487 Johnson et al., 2008; Planavsky et al., 2012), and also higher than values expected
488 during the reductive dissolution of Fe (oxyhydr)oxides during diagenesis (-2.5 to -0.5‰;
489 Johnson et al., 2008; Ossa Ossa et al., 2018). Hence, partial oxidation of Fe(II) is a
490 likely explanation for the Fe isotopic composition of our IF samples (e.g., Bekker et al.,
491 2010). Importantly, there is a weak negative correlation between $\delta^{56}\text{Fe}$ and $\text{Fe}_{\text{T}}/\text{Al}$ (R^2
492 = 0.33) and a strong negative correlation between $\delta^{56}\text{Fe}_{\text{HR}}$ and Mn/Fe ($R^2 = 0.82$) (Figs.
493 6a and b), which suggests that the Fe isotopic compositions of the IFs may be influenced
494 by the formation of Fe carbonate phases (e.g., siderite and ankerite; Fe_{carb}) and limited
495 detrital minerals, consistent with petrological observations and Fe speciation results
496 (Appendix A). The oxidizing mechanism involved in this partial oxidation is difficult
497 to define based on Fe isotopes. Previous studies have suggested microbial oxidation of
498 Fe(II) by microaerophilic FeOB (Lin et al., 2019; and references therein), which thrive
499 under dysoxic conditions. However, anoxygenic photosynthesizers may also have
500 oxidized the Fe(II) (Bekker et al., 2010). The average $\delta^{13}\text{C}_{\text{org}}$ values for the IFs (about
501 -29‰), likely reflect photoautotrophic CO_2 fixation as the dominant primary producers
502 (e.g., Ossa Ossa et al., 2019; Rego et al., 2021). Overall, our results suggest that
503 microaerophilic FeOB and/or anoxygenic photosynthesizers exerted the main control
504 on the deposition of the CF IFs (Fig. 7a).

505 The dolostones have slightly negative $\delta^{56}\text{Fe}_{\text{HR}}$ values, ranging from -0.53 to -0.11‰
506 (average of $-0.34 \pm 0.15\%$), and $\delta^{56}\text{Fe}$ values exhibit a weak negative correlation with
507 $\text{Fe}_{\text{T}}/\text{Al}$ ($R^2 = 0.33$, Fig. 6a). Since Fe isotope fractionations between Fe-carbonate
508 phases and $\text{Fe}(\text{II})_{\text{aq}}$ range between -0.2 and -0.7‰ (e.g., Wiesli et al., 2004; Rego et al.,
509 2021), this suggests that the dolostone may have formed in equilibrium with seawater
510 ($\delta^{56}\text{Fe}=0\%$, Johnson et al., 2008), although the presence of minor detrital minerals may
511 have resulted in increased $\delta^{56}\text{Fe}_{\text{HR}}$ values in some dolostone samples.

512 The DIR process would have created an isotopically light Fe pool in porewaters,
513 relative to the initial Fe-(oxyhydr)oxide minerals (Planavsky et al., 2012; Ossa Ossa et
514 al., 2018). However, complete Fe reduction would produce early diagenetic minerals
515 with a similar Fe isotope composition to the precursor Fe-(oxyhydr)oxides (Johnson et
516 al., 2008). For the black shales, the Fe isotope values of the Fe_{HR} fraction range from -
517 2.57 to 1.09‰. These shale samples can be divided into three groups. Firstly, two
518 samples have $\delta^{56}\text{Fe}_{\text{HR}}$ -2.57 and -1.31‰, and these samples are dominated Fe_{carb} .
519 Combined with negative $\delta^{13}\text{C}_{\text{carb}}$ values ($-3.4 \pm 1.4\%$) in the CF black shales, this
520 supports diagenetic carbonate precipitation (Li et al., 2015) following DIR. Secondly,
521 8 black shale samples (which is dominated by Fe_{carb} , with minor Fe_{mag}) have $\delta^{56}\text{Fe}_{\text{HR}}$
522 values ranging from -0.66 to -0.16‰, and one siderite-rich shale sample has a $\delta^{56}\text{Fe}_{\text{HR}}$
523 value of -0.60‰. These values can be explained by a balance between the formation of
524 Fe carbonate minerals and magnetite. For the third group, the $\delta^{56}\text{Fe}_{\text{HR}}$ values of black
525 shales range from 0.53 to 1.43‰ ($n = 6$), and is dominated by Fe carbonate phases and
526 magnetite. In addition, the $\delta^{56}\text{Fe}$ values show a positive correlation with $\text{Fe}_{\text{T}}/\text{Al}$ ($R^2 =$
527 0.46, Fig. 6c), but no correlation between $\delta^{56}\text{Fe}_{\text{HR}}$ and Mn/Fe (Fig. 6d). These data can
528 be attributed to mixing between Fe(II) formed from near complete DIR, which would
529 inherit the initial positive $\delta^{56}\text{Fe}$ values of Fe-(oxyhydr)oxides, and an overprint from
530 detrital materials. For example, sample 6-78 has a $\delta^{56}\text{Fe}$ value of 0.15, which is close
531 to crustal values, and also has a low $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$ ratio of 0.18, supporting a dominant
532 signature from detrital minerals. Therefore, we conclude that mixing between different
533 Fe mineral phases can explain the $\delta^{56}\text{Fe}$ variability (Fig. 7b).

534 The $\delta^{13}\text{C}_{\text{org}}$ composition ranges from -33.4 to -28.1‰, dependent on sedimentary
535 facies (Luo et al., 2014), where the $\delta^{13}\text{C}_{\text{org}}$ composition of shallower water sediments is
536 generally ^{13}C -enriched relative to deeper water sediments. Average $\delta^{13}\text{C}_{\text{org}}$ values of
537 about -29‰ for shallow water sediments (IFs and sandstone) likely reflect a kinetic
538 isotope fractionation produced by autotrophic organisms (Schidlowski, 2001), which

539 initiated deposition of the CF IF. By contrast, the deeper-water $\delta^{13}\text{C}_{\text{org}}$ values may
540 reflect biological carbon cycling (e.g., [Ossa Ossa et al., 2019](#)), potentially with a
541 significant contribution from dissimilatory Fe reducers, as Fe in carbonate phases (i.e.,
542 Fe_{carb}) is common in these sediments. Hence, the water column appears to have been
543 both redox and ecologically stratified, with autotrophic organisms (microaerophilic
544 FeOB and/or anoxygenic photosynthesizers) in shallower waters, and dissimilatory Fe
545 reducers driving Fe reduction in deeper waters ([Figs. 7a and b](#)).

546

547 **6.3 Implications for biological evolution during the mid-Proterozoic**

548 As discussed above, the deeper ocean was dominated by anoxic and ferruginous
549 conditions, with pulses of water column oxygenation at 1.57–1.56 Ga (e.g., [Zhang et](#)
550 [al., 2018](#); [Luo et al., 2021](#)), ~1.4 Ga ([Zhang et al., 2016](#)) and ~1.33 Ga ([Canfield et al.,](#)
551 [2018a](#)) ([Fig. 8a](#)). Our data extend these fluctuations back to the late Proterozoic,
552 suggesting that episodic deeper water oxygenation (likely extending to outer shelf
553 settings) was a common phenomenon between the GOE and NOE. The oxygen levels
554 required for early animal respiration were lower than those needed to sustain large
555 motile animals ([Canfield et al., 2018a](#)). For example, an oxygen requirement of around
556 0.1–0.2% PAL is typical for a choanoflagellate with a diameter of 5–10 μm , and 0.36%
557 PAL has been calculated as the requirement for small bilaterian animals ([Canfield et al.,](#)
558 [2018a](#)). Eukaryotic life had likely evolved at least by the late Paleoproterozoic era (e.g.,
559 [Zhu et al., 2016](#)), and our data reinforce the suggestion that sufficient levels of oxygen
560 for animal evolution were episodically available. Thus, it appears that highly fluctuating
561 redox conditions likely constrained the radiation of eukaryotes, and by extension the
562 ultimate rise of animals (e.g., [Luo et al., 2021](#)).

563

564 **7. Conclusions**

565 Our new geochemical data for the ~1.64 Ga Chuanlinggou Formation provides
566 support for a redox-stratified ocean with oxic surface waters overlying ferruginous
567 deeper waters. However, the data also provide insight into the intensity and dynamics
568 of ferruginous conditions during the Late Paleoproterozoic. In this context, the general
569 lack of IFs between ~1.88 Ga and the Cryogenian is commonly considered to represent
570 decreased dissolved Fe(II) concentrations relative to the Archean and earlier intervals
571 of the Paleoproterozoic (e.g., [Song et al., 2018](#)). The Chuanlinggou IF contrasts with
572 this broader scale outlook, representing an extensive deposit that formed in a shallow

573 ocean setting during an interval of particularly elevated Fe concentrations. This interval
574 of more intense ferruginous conditions was likely a consequence of hydrothermal
575 activity during the breakup of the Columbia supercontinent, and autotrophic Fe-
576 oxidizers likely played a key role in the precipitation of the Fe minerals that comprise
577 the IF.

578 The Chuanlinggou IF adds to a growing database of mid-Proterozoic IFs from
579 different locations, including central Arizona in the USA, the Xiamaling and
580 Yunmenshan IFs of the NCC, and the Jingtieshan IF in North Qilian, northwestern
581 China (Fig. 8b; Bekker et al., 2010; Yang et al., 2015; Canfield et al., 2018b; Qiu et al.,
582 2022). Most of these IFs have significant hydrothermal signals (e.g., Yang et al., 2015;
583 Canfield et al., 2018b), suggesting that intervals of enhanced hydrothermal activity
584 played an important role in their genesis. Thus, dissolved Fe(II) concentrations were
585 likely highly dynamic across the mid-Proterozoic, and in large part this appears to have
586 been a consequence of tectonic activity (Fig. 8c). Data for shales that overly the
587 Chuanlinggou IF additionally suggest episodic intervals of deeper water oxygenation.
588 Thus, similar to recent studies of the later Mesoproterozoic ocean, our data indicate that
589 ocean oxygenation during the latest Paleoproterozoic may have been more dynamic
590 than previously considered. These fluctuating levels of oxygenation may have served
591 as a constraint on the early evolution of eukaryotes.

592

593 **CRedit authorship contribution statement**

594 **Xiuqing Yang:** Data collection, Investigation, Visualization, Writing – original draft.

595 **Jingwen Mao:** Supervision, Writing – review & editing. **Rongxi Li:** Supervision,

596 Writing-review & editing. **Fang Huang:** Data analysis, Writing – review & editing.

597 **Chong He:** Resources, Data analysis. **Chao Zhao:** Visualization, Writing – review &

598 editing. **Wei Wei:** Data analysis, Writing – review & editing. **Guowei Yang:**

599 Investigation. **Yijun Xiong:** Data analysis. **Simon W. Poulton:** Conceptualization,

600 Writing – review & editing.

601

602 **Declaration of competing interest**

603 The authors declare that they have no competing financial interests or personal

604 relationships that could have appeared to influence the work reported in this paper.

605

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616

617 **References**

- 618 Alcott, L.J, Mills, B.J.W., Poulton, S.M., 2019. Stepwise Earth oxygenation is an
619 inherent property of global biogeochemical cycling. *Science* 366, 1333–1337.
- 620 Anderson, R.F., Lehuray, A.P., Fleisher, M.Q., Murray, J.W., 1989. Uranium deposition
621 in Saanich Inlet sediments, Vancouver Island. *Geochim. Cosmochim. Acta* 53,
622 2205–2213.
- 623 Bau, M., Koschinsky, A., Dulski P., Hein, J.R., 1996. Comparison of the partitioning
624 behaviours of yttrium, rare earth elements, and titanium between hydrogenetic
625 marine ferromanganese crusts and seawater. *Geochim. Cosmochim. Acta* 60(10),
626 1709–1725.
- 627 Bekker, A., Slack, J.F., Planavsky, A., Krapež, B., Hofmann, A., Konhauser, K.O.,
628 Rouxel, O.J., 2010. Iron formation: The sedimentary product of a complex
629 interplay among mantle, tectonic, oceanic, and biospheric processes. *Econ. Geol.*,
630 105, 467–508.
- 631 Byrne, R., Sholkovitz, E., 1996. Marine chemistry and geochemistry of the lanthanides.
632 In *Handbook on the Physics and Chemistry of the Rare Earths* (eds. K. A.
633 Gschneider Jr. and L. Eyring). Elsevier, Amsterdam.
- 634 Canfield, D.E., Raiswell, R., Westrich, J.T., Reaves, C.M., Berner, R.A., 1986. The use
635 of chromium reduction in the analysis of reduced inorganic sulfur in sediments
636 and shales. *Chem. Geol.* 54, 149–155.
- 637 Canfield, D.E, Zhang, S., Frank, A.B., Wang, X., Wang, H., Su, J., Ye, Y., Frei, R.,
638 2018a. Highly fractionated chromium isotopes in Mesoproterozoic-aged shales
639 and atmospheric oxygen. *Nat. Comms.* 9, 2871.
- 640 Canfield, D.E., Zhang, S., Wang, H., Wang, X., Zhao, W., Su, J., Bjerrum, C.J., Haxen,

641 E.R., Hammarlund, E., 2018b. A Mesoproterozoic iron formation. *Proc. Natl. Acad.*
642 *Sci. USA* 115(17), 3895–3904.

643 Clarkson, M.O., Poulton, S.W., Guilbaud, R., Wood, R.A., 2014. Assessing the utility
644 of Fe/Al and Fe-speciation to record water column redox conditions in carbonate-
645 rich sediments. *Chem. Geol.* 382, 111–122.

646 Emerson, S.R., Huested, S.S., 1991. Ocean anoxia and the concentrations of
647 molybdenum and vanadium in seawater. *Mar. Chem.* 34, 177–196.

648 Gumsley, A.P., Chamberlain, K.R., Bleeker, W., Söderlund, U., de Kock, M.O., Larsson,
649 E. M., Bekker, A., 2017. Timing and tempo of the Great Oxidation Event. *Proc.*
650 *Natl Acad. Sci. USA* 114, 1811–1816.

651 Helz, G.R., Miller, C. V., Charnock, J.M., Mosselmans, J.F.W., Patrick, R.A.D., Garner,
652 C.D., Vaughan, D.J., 1996. Mechanism of molybdenum removal from the sea and
653 its concentration in black shales: EXAFS evidence. *Geochim. Cosmochim. Acta*
654 60, 3631–3642.

655 Holland, H., 1984. *The chemical evolution of the atmosphere and oceans*. New York,
656 Princeton University Press, 582 p.

657 Huang, F., Zhang, Z., Lundstrom, C.C., Zhi X., 2011. Iron and magnesium isotopic
658 compositions of peridotite xenoliths from Eastern China. *Geochim. Cosmochim.*
659 *Acta*, 75(12), 3318–3334.

660 Johnson, C.M., Beard, B.L., Klein, C., Beukes, N.J., Roden, E.E., 2008. Iron isotopes
661 constrain biologic and abiologic processes in banded iron formation genesis.
662 *Geochim. Cosmochim. Acta* 72, 151–169.

663 Konhauser, K.O., Planavsky, N.J., Hardisty, D.S., Robbins, L.J., Warchola, T.J.,
664 Haugaard, R., Lalonde, S.V., Partin, C.A., Oonk, P.B.H., Tsikos, H., Lyons, T.W.,
665 Bekker, A., Johnson, C.M., 2017. Iron formations: a global record of Neoproterozoic
666 to Palaeoproterozoic environmental history. *Earth-Sci. Rev.* 172, 140–177.

667 Krause AJ, Mills BJW, Zhang S, Planavsky NJ, Lenton TM, Poulton SW. 2018.
668 Stepwise oxygenation of the Paleozoic atmosphere. *Nature Comms.* 9, 4081.

669 Krause, A.J., Mills, B.J.W., Merdith, A.S., Lenton, T.M., Poulton, S.W., 2022. Extreme
670 variability in atmospheric oxygen levels in the late Precambrian. *Sci. Adv.*, 8,
671 eabm8191.

672 Kusky, T.M., Li, J., 2003. Paleoproterozoic tectonic evolution of the North China
673 Craton. *J. Asian Earth Sci.* 22(4), 383–397.

674 Li, C., Planavsky, N.J., Love, G.D., Reinhard, C.T., Hardisty, D., Feng, L., Bates, S.M.,

675 Huang, J., Zhang, Q., Chu, X., 2015. Marine redox conditions in the middle
676 Proterozoic ocean and isotopic constraints on authigenic carbonate formation:
677 Insights from the Chuanlinggou Formation, Yanshan Basin, North China.
678 *Geochim. Cosmochim. Acta* 150, 90–105.

679 Li, S., Wignall, P.B., Xiong, Y.J., Poulton, S.W., 2023. Calibration of redox thresholds
680 in black shale: Insight from a stratified Mississippian basin with warm saline
681 bottom waters. *Geol. Soc. Am. Bull.* 21, 10.1130/B36915.1.

682 Lin, Y., Tang, D., Shi, X., Zhou, X., Huang, K., 2019. Shallow-marine ironstones
683 formed by microaerophilic iron-oxidizing bacteria in terminal Paleoproterozoic.
684 *Gondwana Res.* 76, 1–18.

685 Luo, G.M., Junium, C.K., Kump, L.R., Huang, J.H., Li, C., Feng, Q.L., Shi, X.Y., Bai,
686 X., Xie, S.C., 2014. Shallow stratification prevailed for 1700 to 1300 Ma ocean:
687 evidence from organic carbon isotopes in the North China Craton. *Earth Planet.*
688 *Sci. Lett.* 400, 219–232.

689 Luo, J., Long, X., Bowyer, F.T., Mills, B., Li, J., Xiong, Y.K., Zhu, X.K., Zhang, K.,
690 Poulton, S.W., 2021. Pulsed oxygenation events drove progressive oxygenation of
691 the early Mesoproterozoic ocean. *Earth Planet. Sci. Lett.* 559, 116754.

692 Lyons, T.W., Reinhard, C.T., Planavsky, N.J., 2014. The rise of oxygen in earth's early
693 ocean and atmosphere. *Nature* 506, 307-315.

694 Ossa Ossa, F., Hofmann, A., Wille, M., Spangenberg, J.E., Bekker, A., Poulton, S. W.,
695 Schoenberg, R., 2018. Aerobic iron and manganese cycling in a redox-stratified
696 Mesoarchean epicontinental sea. *Earth Planet. Sci. Lett.* 500, 28–40.

697 Ossa Ossa, F., Hofmann, A., Spangenberg, J.E., Poulton, S.W., Stüeken, E.E.,
698 Schoenberg, R., Eickman, B., Wille, M., Bekker, A., 2019. Limited oxygen
699 production in the Mesoarchean ocean. *Proc. Nat. Acad. Sci.* 116, 6647-6652.

700 Ossa Ossa, F., Spangenberg, J.E., Bekker, A., König, S., Stüeken, E. E., Hofmann, A.,
701 Poulton, S.W., Yierpan, A., Varas-Reus, M.I., Eickmann, B., Andersen, M.B.,
702 Schoenberg, R., 2022. Moderate levels of oxygenation during the late stage of
703 Earth's Great Oxidation Event. *Earth Planet. Sci. Lett.* 594, 117716.

704 Ostrander, C.M., Nielsen, S.G., Owens, J.D., Kendall, B., Gordon, G.W., Romaniello,
705 G. R., Anbar, A.D., 2019. Fully oxygenated water columns over continental
706 shelves before the Great Oxidation Event. *Nat. Geosci.* 12, 186–91.

707 Planavsky, N., Rouxel, O.J., Bekker, A., Hofmann, A., Little, C.T.S., Lyons, T.W., 2012,
708 Iron isotope composition of some Archean and Proterozoic iron formations.

709 Geochim. Cosmochim. Acta 80, 158–169.

710 Planavsky, N.J., Bekker, A., Rouxel, O.J., Kamber, B., Hofmann, A., Knudsen, A.,
711 Lyons, T.W., 2010. Rare Earth Element and yttrium compositions of Archean and
712 Paleoproterozoic Fe formations revisited: new perspectives on the significance and
713 mechanisms of deposition. *Geochim. Cosmochim. Acta* 74, 6387–6405.

714 Planavsky, N.J., McGoldrick, P., Scott, C.T., Li, C., Reinhard, C.T., Kelly, A.E., Chu,
715 X.L., Bekker, A., Love, G.D., Lyons, T.W., 2011. Widespread iron-rich conditions
716 in the mid-Proterozoic ocean. *Nature* 477, 448–495.

717 Poulton, S.W., 2021. *The Iron Speciation Paleoredox Proxy: Elements in Geochemical*
718 *Tracers in Earth System Science*. Cambridge University Press.

719 Poulton, S.W., Bekker, A., Cumming, V.M., Zerkle, A.L., Canfield, D.E., Johnston, D.T.,
720 2021. A 200-million-year delay in permanent atmospheric oxygenation. *Nature*
721 592, 232–236.

722 Poulton, S.W., Canfield, D.E., 2005. Development of a sequential extraction procedure
723 for iron: implications for iron partitioning in continentally derived particulates.
724 *Chem. Geol.* 214, 209–221.

725 Poulton, S.W., Canfield, D.E., 2011. Ferruginous conditions: a dominant feature of the
726 ocean through Earth’s history. *Elements* 7, 107–112.

727 Qiu, Y., Qin, L., Huang, F., Zhao, T., Li, Y., 2022. Early prosperity of iron bacteria at
728 the end of the Paleoproterozoic era. *Geophys. Res. Lett.* 49, e2022GL097877.

729 Rego, E.S., Busigny, V., Lalonde, S.V., Philippot, P., Bouyon, A., Rossignol, C.,
730 Babinski, M., Zapparoli, A.C., 2021. Anoxygenic photosynthesis linked to
731 neoproterozoic iron formations in Carajás (Brazil). *Geobiology* 19, 326–341.

732 Schidlowski, M., 2001. Carbon isotopes as biogeochemical recorders of life over 3.8
733 Ga of earth history: Evolution of a concept. *Precambrian Res.* 106, 117–134.

734 Song, H., Jiang, G., Poulton S.W., Wignall P.B., Wang, C., 2017. The onset of
735 widespread marine red beds and the evolution of ferruginous oceans. *Nat. Comms.*
736 8, 399.

737 Song Y., Bowyer F.T., Mills B.J.W., Merdith A.S., Wignall P.B., Peakall J., Zhang S.,
738 Wang X., Wang H., Canfield D.E., Shields G.A., Poulton S.W. (2023) Dynamic
739 redox and nutrient cycling response to climate forcing in the Mesoproterozoic
740 ocean. *Nature Comms.* 14, 6640.

741 Tebo, B.M., Bargar, J.R., Clement, B.G., Dick, G.J., Murray, K.J., Parker, D., Verity, R.,
742 Webb, S.M., 2004. Biogenic manganese oxides: properties and mechanisms of

743 formation. *Annu. Rev. Earth Planet. Sci.* 32, 287–328.

744 Tribovillard, N., Algeo, T.J., Lyons, T., Riboulleau, A., 2006. Trace metals as
745 paleoredox and paleoproductivity proxies: an update. *Chem. Geol.* 232, 12–32.

746 Wiesli, R.A., Beard, B.L., Johnson, C.M., 2004. Experimental determination of Fe
747 isotope fractionation between aqueous Fe(II), siderite and “green rust” in abiotic
748 systems. *Chem. Geol.* 211, 343–362.

749 Yang, X.Q., Zhang, Z.H., Duan, S.G., Zhao, X.M., 2015. Petrological and geochemical
750 features of the Jingtieshan banded iron formation (BIF): a unique type of BIF from
751 the Northern Qilian Orogenic Belt, NW China. *J. Asian Earth Sci.* 113, 1218–1234.

752 Zahnle, K., Claire, M.W., Catling, D., 2006. The loss of mass-independent fractionation
753 in sulfur due to a Palaeoproterozoic collapse of atmospheric methane. *Geobiology*
754 4, 271–283.

755 Zhang, K., Zhu, X., Wood, R.A., Shi, Y., Gao, Z., Poulton, S.W., 2018. Oxygenation of
756 the Mesoproterozoic ocean and the evolution of complex eukaryotes. *Nat. Geosci.*
757 11, 345–350.

758 Zhang, S., Wang, X., Wang, H., Bjerrum, C.J., Hammarlund, E.U., Costa, M.M.,
759 Connelly, J.N., Zhang, B., Su, J., Canfield, D.E., 2016. Sufficient oxygen for
760 animal respiration 1,400 million years ago. *Proc. Nat. Acad. Sci.* 113, 1731–1736.

761 Zhao, G.C., Wilde, S.A., Cawood, P.A., Sun, M., 2001. Archean blocks and their
762 boundaries in the North China Craton: lithological, geochemical, structural and P–
763 T path constraints and tectonic evolution. *Precambrian Res.* 107, 45–73.

764 Zhu, S., Zhu, M., Knoll, A.H., Yin, Z., Zhao, F., Sun, S., Qu, Y., Shi, M., Liu, H., 2016.
765 Decimetre-scale multicellular eukaryotes from the 1.56-billion-year-old
766 Gaoyuzhuang Formation in North China. *Nat. Comms.* 7, 11500.

767 **Figures**

768 Fig. 1. a. Major tectonic units in China, with the position of the North China Craton
769 (Zhao et al., 2001); b. Geological map of the North China Craton (Canfield et al.,
770 2018b); c. Mid-Proterozoic stratigraphic profile of the Yanliao Basin (modified after
771 Zhu et al., 2016, with age data from references therein).

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773 Fig. 2. a. Black shale from the upper Chuanlinggou Formation in the Xuan-Long area.
774 b. Boundary between the upper Chuanlinggou Formation (black shale and siderite-rich
775 shale) and the lower Chuanlinggou Formation (sandstone). c. Ooidal IF. d. Sandstone
776 with rounded quartz clasts. e. The IF consists of iron ooids and minor rounded quartz
777 clasts. f. Black shale. g. Dolostone. h. Schematic diagram showing facies subdivisions.
778 d and e are backscattered electron (BSE) images; f and g were taken under transmitted
779 light and plane-polarized light, respectively. Qtz-Quartz.

780

781 Fig. 3. Geochemical profiles for TOC, TIC, $\delta^{13}\text{C}$, Y/Ho and Eu/Eu^* through the CF in
782 Xuan-Long area. The yellow circles represent the siderite-rich shale, and grey
783 horizontal shading represents the fluctuating zones between oxic and anoxic-
784 ferruginous conditions (see text for details).

785

786 Fig. 4. Geochemical profiles for $\text{Fe}_\text{T}/\text{Al}$, Fe speciation, $\delta^{56}\text{Fe}$ and redox sensitive
787 elements through the CF in the Xuan-Long area. $\delta^{56}\text{Fe}_\text{WR}$ and $\delta^{56}\text{Fe}_\text{HR}$ represent the
788 $\delta^{56}\text{Fe}$ values of whole rock and the highly reactive Fe pool, respectively. In the $\text{Fe}_\text{T}/\text{Al}$,
789 U/Al , Mo/Al and V/Al plots, the vertical shading indicates the calibrated redox
790 thresholds (see text). The yellow circles represent the siderite-rich shale, and grey
791 horizontal shading represents the fluctuating zones between oxic and anoxic-
792 ferruginous conditions (see text for details).

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796 for the Chuanlinggou Formation, with previous data from Planavsky et al. (2011) and
797 Li et al. (2015).

798

799 Fig. 6. a. Plot of $\delta^{56}\text{Fe}$ versus $\text{Fe}_\text{T}/\text{Al}$ for ironstone and dolostone samples. b. Plot of
800 $\delta^{56}\text{Fe}_\text{HR}$ versus $\text{Mn}/\text{Fe}_\text{T}$ for ironstone and dolostone samples. c. Plot of $\delta^{56}\text{Fe}$ versus

801 Fe_T/Al for black shale samples. d. Plot of $\delta^{56}Fe_{HR}$ versus Mn/Fe_T for black shale
802 samples.

803

804 Fig. 7. Seawater redox conditions and Fe cycling during deposition of the CF. a. During
805 deposition of the lower CF, deeper waters were anoxic and ferruginous with a very
806 shallow chemocline. Periods of enhanced upwelling caused partial oxidation of iron
807 below the Mn chemocline, via microaerophilic FeOB and/or anoxygenic
808 photosynthesizers. This process led to the deposition of IFs with positive $\delta^{56}Fe$ values
809 and low Y/Ho ratios. b. During deposition of the upper CF, the position of the oxycline
810 fluctuated, likely to below storm wave base. Dolostone formed under anoxic conditions
811 and in equilibrium with seawater. However, partial and complete DIR of Fe-
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813 resulted in a wide range of $\delta^{56}Fe$ values for black shale samples.

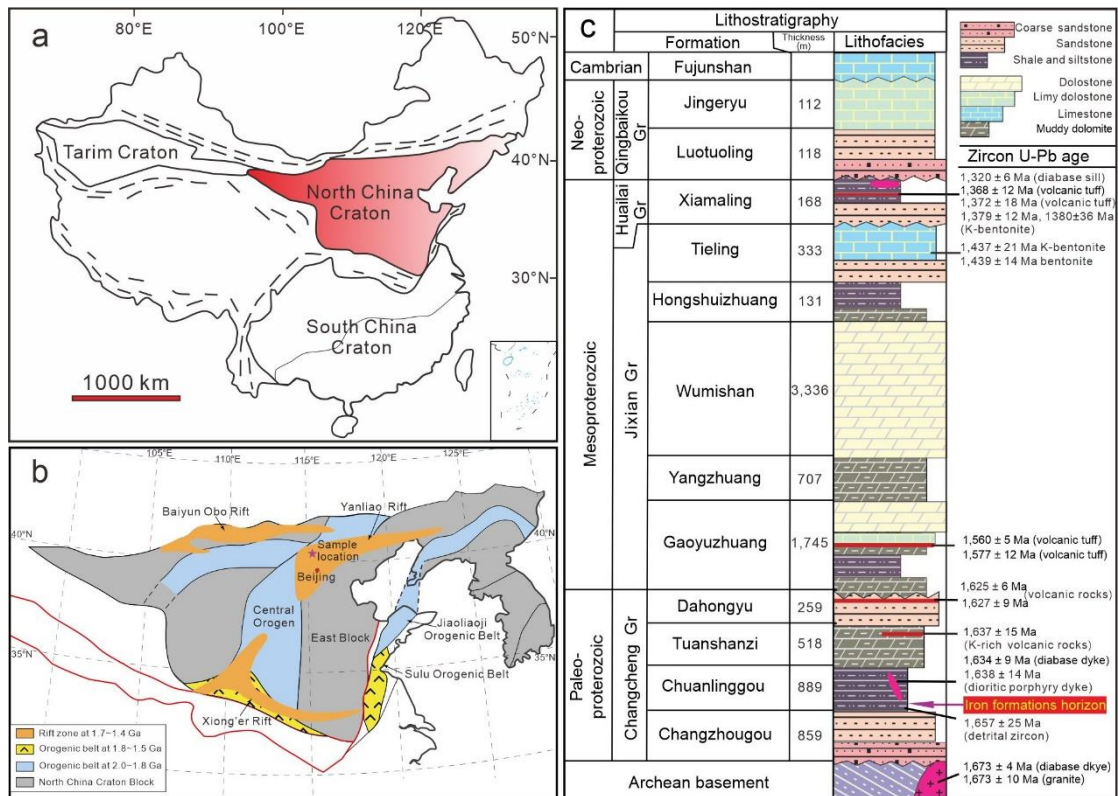
814

815 Fig. 8. Distribution of IFs and the redox history of the Earth. a. Evolution of
816 atmospheric oxygen concentrations through time. The purple curve shows the classical,
817 two-step view of atmospheric evolution, while the blue curve shows the emerging
818 model (after [Lyons et al., 2014](#)). Blue arrows represent intervals with apparent enhanced
819 oxygenation levels. b. Secular trend in the distribution of IFs (modified after [Bekker et](#)
820 [al., 2010, with the addition of the CF IF and others](#)). c. Evolution of marine conditions
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822 green shading represent moderate/high and low Fe concentrations, respectively.

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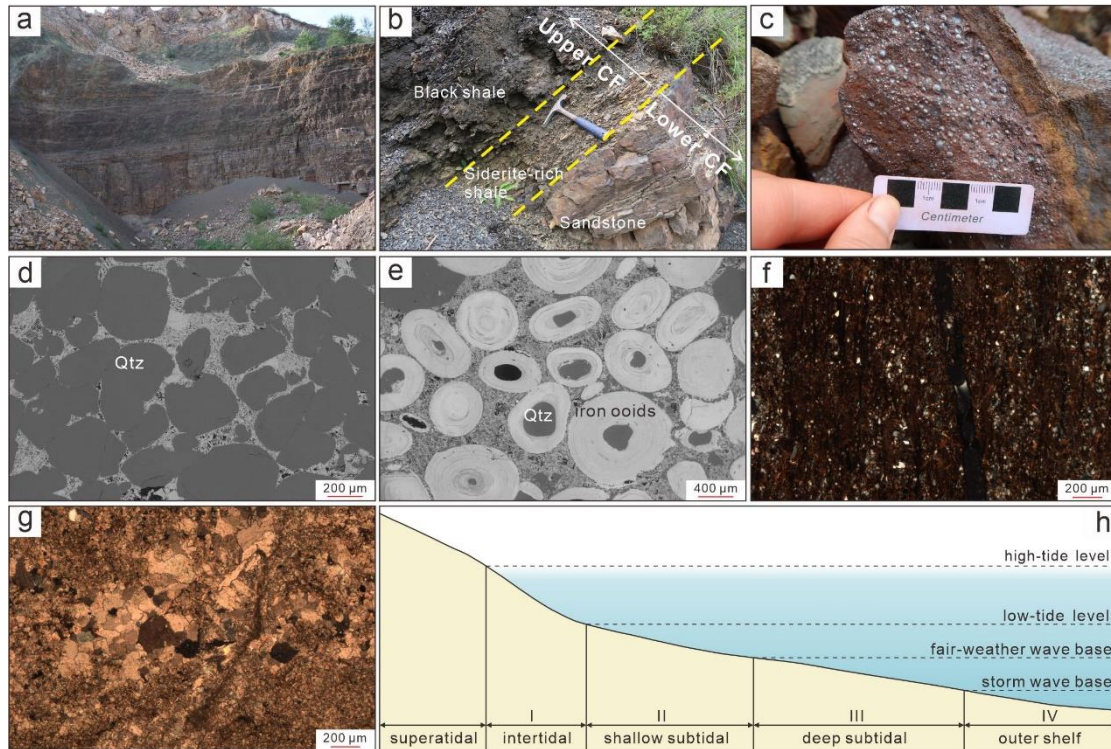
824 **Appendix A. Supplementary material**

825 **Appendix B. Supplementary data**



826

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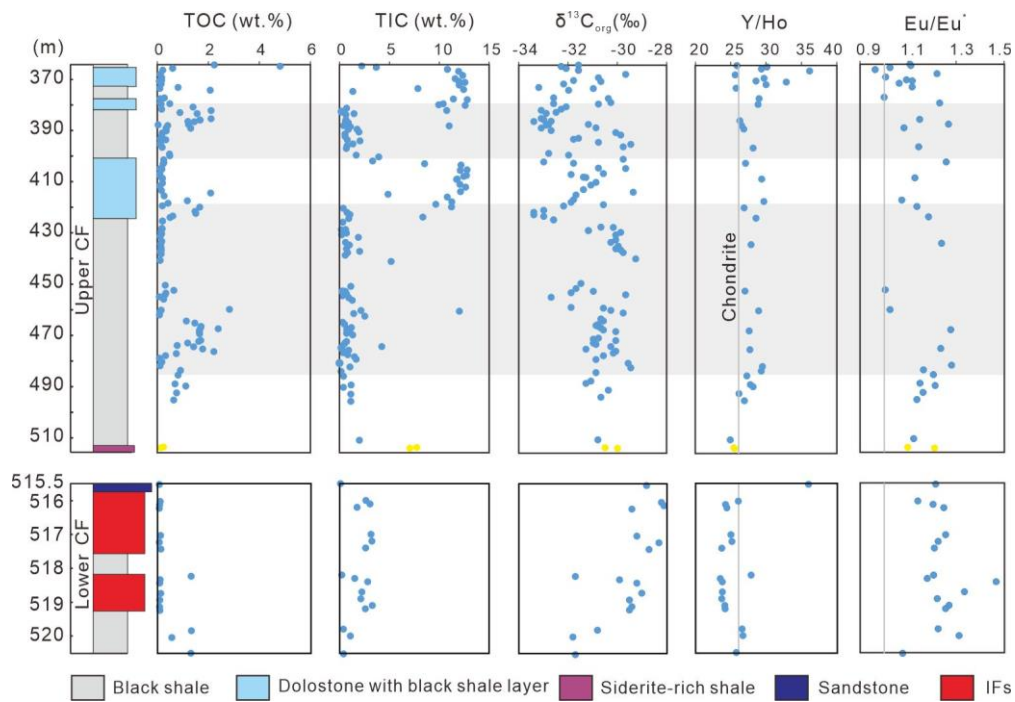
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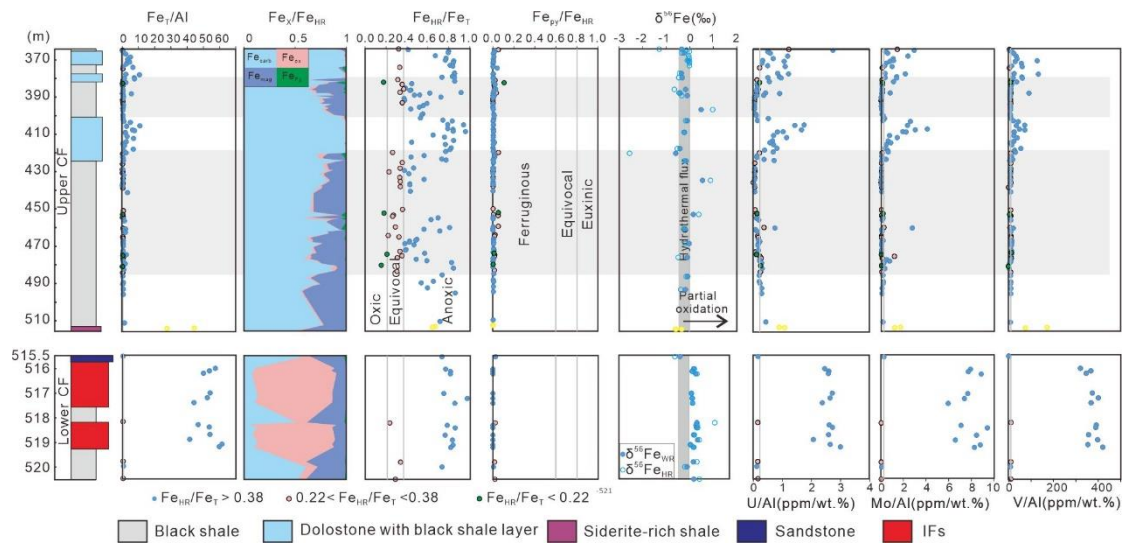
838 light and plane-polarized light, respectively. Qtz-Quartz.

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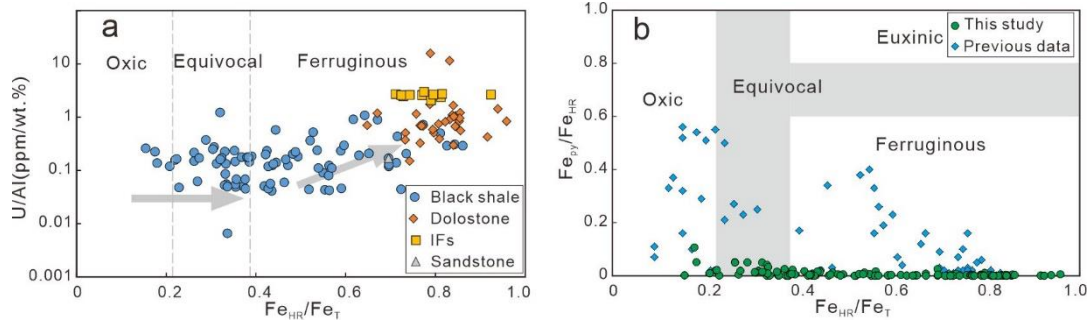
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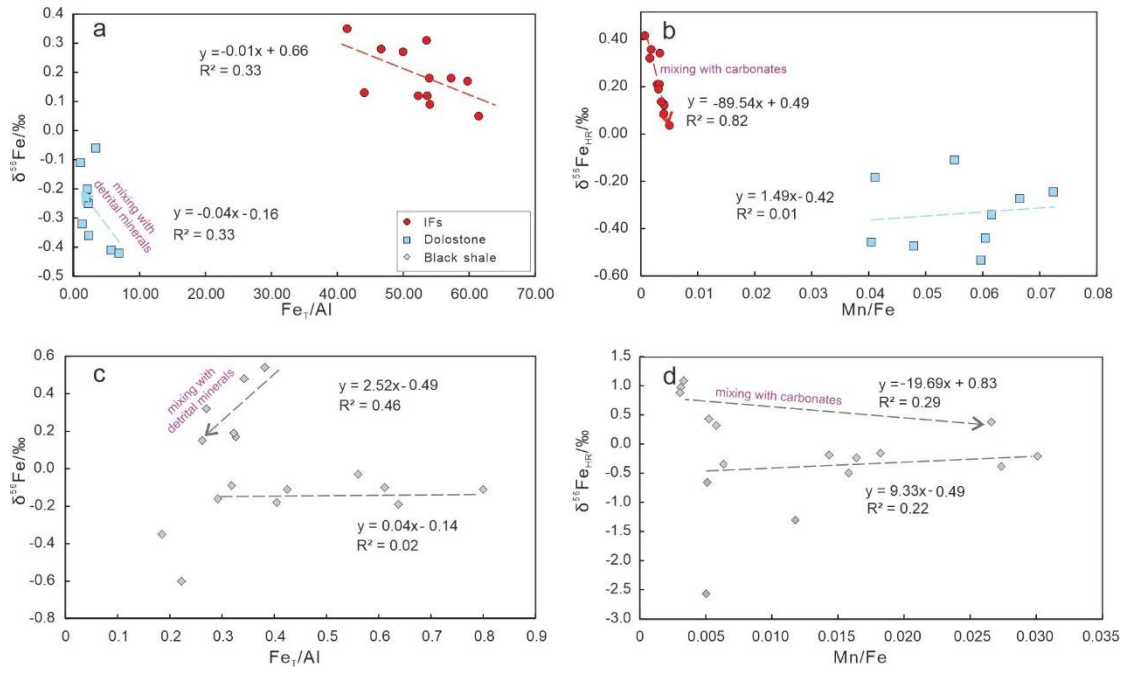


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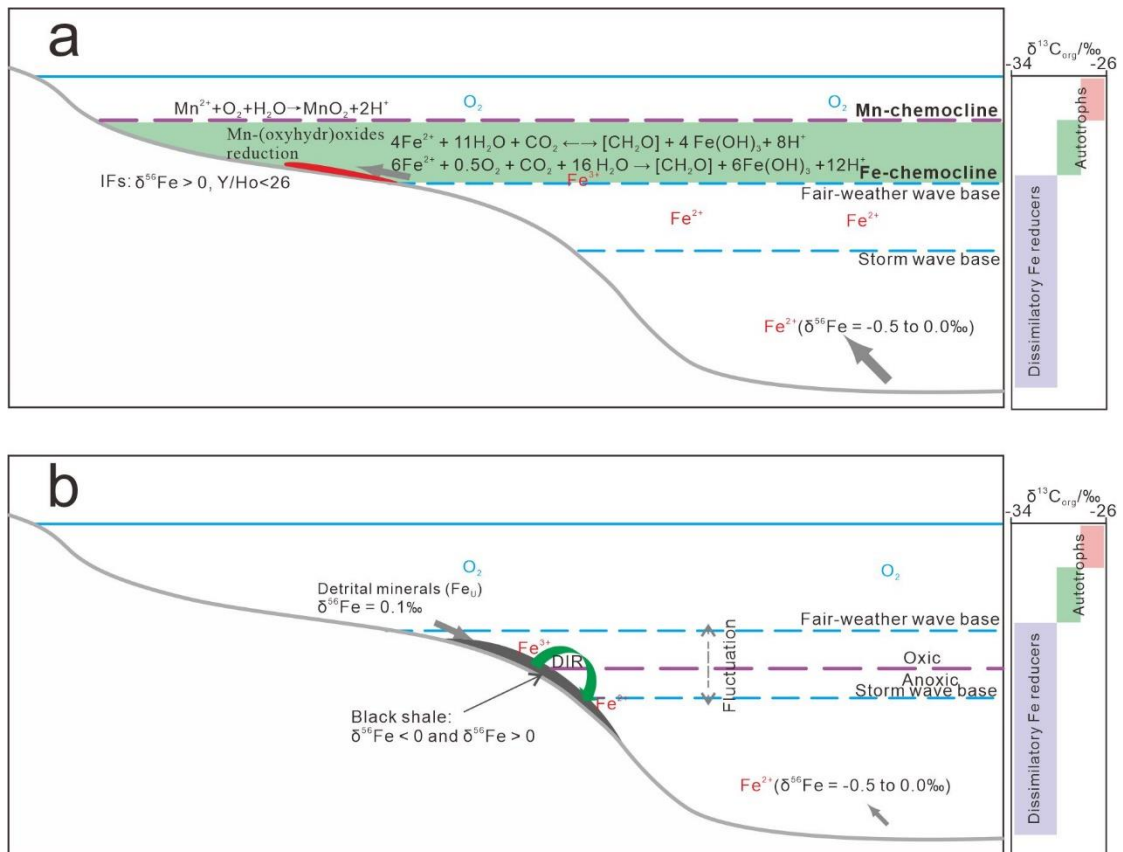
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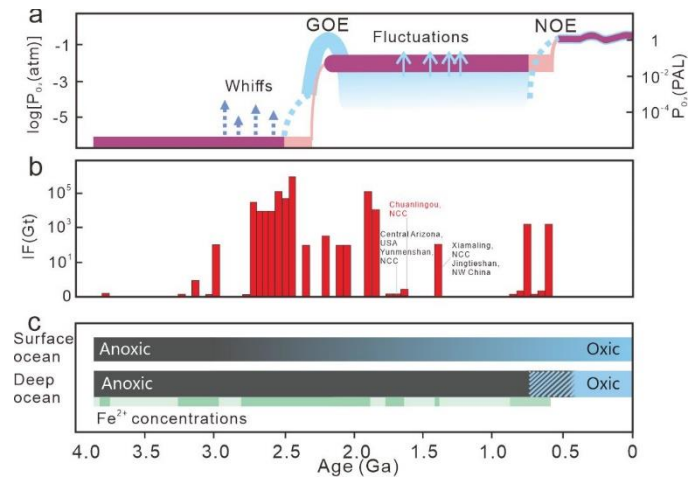
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 860 $\delta^{56}\text{Fe}_{\text{HR}}$ versus Mn/Fe_T for ironstone and dolostone samples. c. Plot of $\delta^{56}\text{Fe}$ versus
 861 Fe_T/Al for black shale samples. d. Plot of $\delta^{56}\text{Fe}_{\text{HR}}$ versus Mn/Fe_T for black shale
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 865 deposition of the lower CF, deeper waters were anoxic and ferruginous with a very
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 882 green shading represent moderate/high and low Fe concentrations, respectively.

Supplementary Information

883

884

885 1. Geochronology

886 A high-precision chronological framework has been established for the
887 Chuanlinggou Formation exposed in North China Craton (NCC) in recent years.
888 Diagenetic xenotime from fine-grained sandstones of the Chuanlinggou Formation
889 yielded the oldest SIMS U–Pb age of 1716 ± 3 Ma, which has been suggested as a
890 minimum age for the formation (Zhang et al., 2015). The youngest U–Pb age of 1657
891 ± 25 Ma comes from detrital zircons in the Jiangjiazhai and Pangjiabu regions (Duan
892 et al., 2018). Gao et al. (2009) obtained a SHRIMP U–Pb zircon age of 1638 ± 14 Ma
893 from a diabase, whereas Zhang et al. (2013) obtained a SHRIMP U–Pb zircon age of
894 1634 ± 9 Ma from a dioritic porphyrite dyke. Both the diabase and dioritic porphyrite
895 dyke were emplaced into the Chuanlinggou Formation. Sun et al. (2013) discovered a
896 volcanic tuff bed in the upper Chuanlinggou Formation and obtained a SHRIMP zircon
897 U–Pb age of 1621 ± 12 Ma. In addition, Li et al. (2013) obtained granite-porphyry dike
898 ages of 1673 ± 10 Ma and 1669 ± 20 Ma by LA-MC-ICP-MS and SHRIMP U–Pb
899 dating methods, and these dykes are unconformably overlain by the Changzhougou
900 Formation. Furthermore, TIMS zircon U–Pb ages of 1625 ± 6 Ma (Lu and Li, 1991)
901 and SHRIMP U–Pb ages of 1625.9 ± 8.9 Ma (Gao et al., 2008) from the Dahongyu
902 volcanic rocks in the Jixian area have been reported. These geochronological ages
903 constrain Chuanlinggou Formation deposition to ~ 1640 Ma (Tang et al., 2015; Lin et
904 al., 2019).

905

906 2. Materials

907 All samples analyzed in this paper were obtained from fresh drill core (ZK 83-6 in
908 the Zengjiakou iron deposit, Chicheng City, Hebei Province). The Chuanlinggou
909 Formation in the drill core is about 174 m in thickness without dip correction (from -
910 346.5 to -520.5 m), with comfortable contacts with the underlying Changzhougou
911 Formation and the overlying Tuanshanzi Formation. A total of 132 samples were
912 collected, including the lower Chuanlinggou Formation interval comprising sandstone,
913 IF and black shale, and the upper Chuanlinggou Formation comprising black shale and
914 dolostone. The lower Chuanlinggou Formation consists mainly of silty shales with
915 interbedded sandstones and is characterized by sedimentary structures, such as cross
916 bedding, indicative of a shallow subtidal to intertidal origin. The upper Chuanlinggou

917 Formation is mainly composed of black illitic shales with clear planar bedding,
918 suggesting a subtidal low-energy environment during deposition (below storm wave
919 base). Some dolostone and silty beds and lenses with relatively high-energy
920 sedimentary structures have been found locally in the top of upper Chuanlinggou
921 Formation, suggesting episodic shoaling into an intertidal environment (Li et al., 2015;
922 Lin et al., 2019).

923 The IF mainly has an ooidal texture, and iron ooids varying from 0.1 mm to 0.5
924 mm in diameter. The ooids are mainly spherical to ellipsoidal in shape, with some
925 having squashed ellipsoidal and irregular dumbbell shapes. In addition, IF samples also
926 contain rounded quartz grains (0.02 to 0.1 mm) and minor hematite, carbonate minerals
927 and clay mineral cements in the quartz matrix. Sandstone is mainly composed of a
928 rounded quartz matrix and hematite cement, with minor clay minerals. Black shale
929 mainly contains clay minerals, quartz and minor carbonate minerals. Dolostone is
930 mainly composed of dolomite with minor clay minerals.

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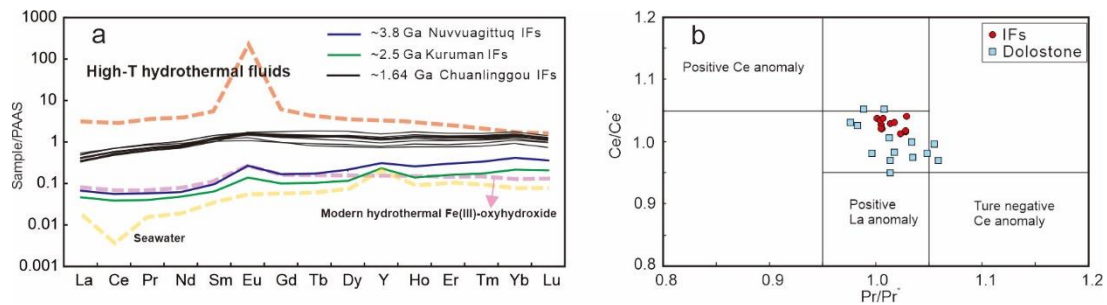
932 **3. Preservation of primary geochemical and isotopic signals**

933 The ZK 83-6 drill core provides a unique opportunity to examine shallow to deeper
934 water sedimentary facies in the Yanliao Basin. All of the samples were collected from
935 drill core, avoiding any influence from weathering. The mid-Proterozoic strata of the
936 NCC are well preserved and have a metamorphic grade below prehnite–pumpellyite
937 facies (e.g., Chu et al., 2007; Luo et al., 2014). Thus, metamorphic alteration of the
938 geochemical data is likely insignificant. Previous studies have indicated that these
939 strata show primary iron speciation signatures (e.g., Planavsky et al., 2011; Li et al.,
940 2015; Zhang et al., 2018). Furthermore, the Fe isotope composition of minerals is also
941 relatively unaffected by secondary processes, including hydrothermal and high-grade
942 metamorphism (Dauphas et al., 2017).

943 Although the IF samples contain quartz debris and ~1.0 wt.% Al concentrations
944 (as a proxy for the detrital fraction), they show LREE depletion and HREE enrichment,
945 similar to that of ancient IFs and modern seawater (Supplementary Fig. 1a) (Bau et al.,
946 1996). Furthermore, the IF shows no correlation between Al and Y/Ho (Supplementary
947 Fig. 2a) and Ce/Ce* (Supplementary Fig. 2b). These suggest that the IF captures the
948 seawater signature of REE+Y, as suggest by previous studies (Li and Zhu, 2012; Lin
949 et al., 2019). Analytical interference with barium (Ba) can create artificial positive Eu
950 anomalies (Dulski, 1994), but there is no correlation between either Eu and Ba, or

951 Eu/Eu* vs Ba/Nd in this study (Supplementary Figs. 2c and d), suggesting that the
 952 positive Eu anomalies are true attributes. In addition, all analyzed samples show no
 953 correlation between Al and Eu/Eu* (Supplementary Fig. 2e), which also implies that
 954 Eu anomalies represent authigenic signatures that were not significantly influenced by
 955 detrital material. Using a Ce/Ce*-Pr/Pr* cross-plot (Bau and Dulski, 1996), it is
 956 possible to identify true negative Ce anomalies (Supplementary Fig. 1b). On this basis,
 957 all IF and dolostone samples lack true negative Ce anomalies.

958

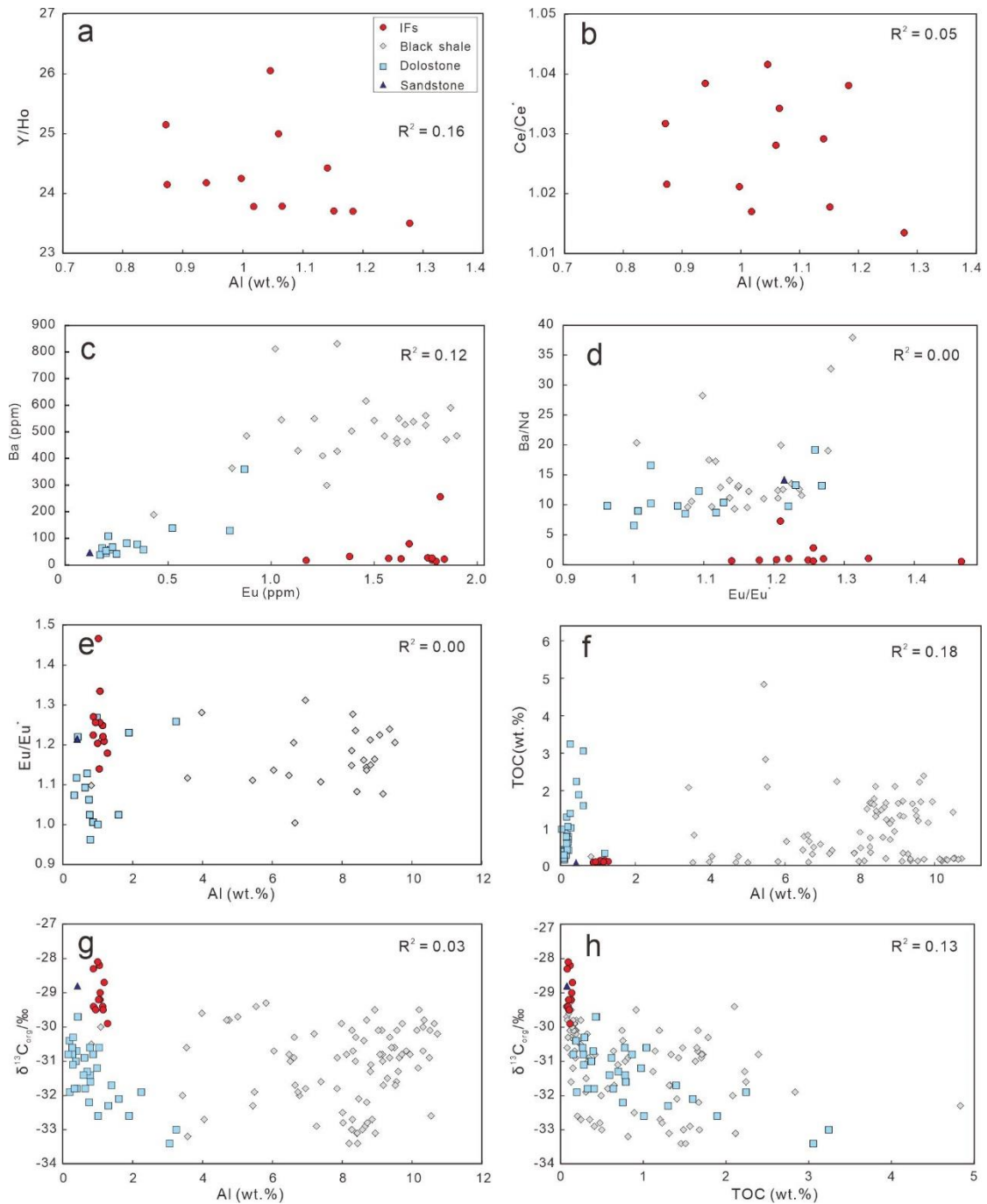


959

960 Supplementary Fig. 1. a. PAAS (Post-Archean Average Shale)-normalized REE+Y patterns
 961 for the Chuanlinggou IF. PAAS data from McLennan, 1989, average high-temperature
 962 hydrothermal fluids from Douville et al., 1999, average modern seawater from Bau et al., 1995,
 963 3.8 Ga Nuvvuagittuq IFs from Mloszewska et al., 2012, 2.5 Ga Krumman IFs from
 964 Bau et al., 1997. b. Ce/Ce* vs. Pr/Pr* diagram for the IF and dolostone samples (after Bau and
 965 Dulski, 1996). $Ce/Ce^* = 2 \times Ce_{PAAS} / (La_{PAAS} + Pr_{PAAS})$; $Pr/Pr^* = 2 \times Pr_{PAAS} / (Ce_{PAAS} + Nd_{PAAS})$.

966

967 In this study, the samples with the lowest organic contents were principally located
 968 in the IF and sandstone, where detrital organic matter, if any, might be present in a
 969 higher proportion, thereby potentially influencing $\delta^{13}C_{org}$ values (Johnston et al., 2012).
 970 For example, if detrital organic matter was ^{13}C -enriched relative to coeval marine
 971 organic matter, a higher ratio of detrital organic matter in the shallow water samples
 972 would induce much higher $\delta^{13}C_{org}$ values. However, we observe no relationship
 973 between Al content and TOC, and no positive relationship between Al content and
 974 $\delta^{13}C_{org}$ (Supplementary Figs. 2f and g), suggesting detrital organic matter is unlikely to
 975 influence $\delta^{13}C_{org}$ values. The $\delta^{13}C_{org}$ data from the studied samples fall within the typical
 976 range of early mid-Proterozoic strata in the central NCC (e.g., Guo et al., 2013; Luo et
 977 al., 2014). In addition, the absence of significant correlation between $\delta^{13}C_{org}$ and TOC
 978 (Supplementary Figs. 2h) in our samples suggests that the degradation of organic matter
 979 during metamorphic processes had limited effect on $\delta^{13}C_{org}$ values.



980

981 Supplementary Fig. 2. Binary variation diagrams for samples from the Chuanlinggou Formation.

982 a. Al vs. Y/Ho. b. Al vs. Ce/Ce*. c. Ba vs. Eu. d. Eu/Eu* vs. Ba/Nd. e. Al vs. Eu/Eu*. f. Al vs.

983 TOC. g. Al vs. $\delta^{13}\text{C}_{\text{org}}$. h. TOC vs. $\delta^{13}\text{C}_{\text{org}}$. One outlier is not shown in parts c and d.

984

985 References

986 Bau, M., Dulski, P., Möller, P., 1995. Yttrium and holmium in South Pacific seawater:
 987 vertical distribution and possible fractionation mechanisms. *Chem. Dere-*
 988 *Geochem.* 55, 1–15.

989 Bau, M., Dulski, P., 1996. Distribution of yttrium and rare earth elements in the Penge

990 and Kuruman iron-formation, Transvaal Supergroup, South Africa. *Precambrian*
991 *Res.* 79, 37–55.

992 Bau, M., Höhndorf, A., Dulski, P., Beukes, N.J., 1997. Sources of rare-earth elements
993 and iron in Paleoproterozoic iron-formations from the Transvaal Supergroup,
994 South Africa: evidence from neodymium isotopes. *J. Geol.* 105, 121–129.

995 Bau, M., Koschinsky A., Dulski, P., Hein, J.R., 1996. Comparison of the partitioning
996 behaviours of yttrium, rare earth elements, and titanium between hydrogenetic
997 marine ferromanganese crusts and seawater. *Geochim. Cosmochim. Acta.* 60(10),
998 1709–1725.

999 Chu, X.L., Zhang, T.G., Zhang, Q.R., Lyons, T.W., 2007. Sulfur and carbon isotope
1000 records from 1700 to 800 Ma carbonates of the Jixian section, northern China:
1001 implications for secular isotope variations in Proterozoic seawater and
1002 relationships to global supercontinental events. *Geochim. Cosmochim. Acta.* 71,
1003 4668–4692.

1004 Dauphas, N., John, S.G., Rouxel, O., 2017. Iron isotope systematics. *Rev. Mineral.*
1005 *Geochem.* 82, 415–510.

1006 Douville, E., Bienvenu, P., Charlou, J. L., Donval, J. P., Fouquet, Y., Appriou, P., Gamo,
1007 T., 1999. Yttrium and rare earth elements in fluids from various deep-sea
1008 hydrothermal systems. *Geochim. Cosmochim. Acta.* 63, 627–643.

1009 Duan, C., Li, Y., Yang, Y., Liang, Y., Wei, M., Hou, H., 2018. U-Pb Ages and Hf Isotopes
1010 of Detrital Zircon Grains from the Mesoproterozoic Chuanlinggou Formation in
1011 North China Craton: Implications for the Geochronology of Sedimentary Iron
1012 Deposits and Crustal Evolution. *Minerals* 8, 547.

1013 Dulski, P., 1994. Interferences of oxide, hydroxide and chloride analyte species in the
1014 determination of rare earth elements in geological samples by inductively coupled
1015 plasma-mass spectrometry. *J. Anal. Chem.* 350, 194–203.

1016 Gao, L.Z., Zhang, C.H., Liu, P.J., Ding, X.Z., Wang, Z.Q., Zhang, Y.J., 2009.
1017 Recognition of Meso- and Neoproterozoic stratigraphic framework in North and
1018 South China. *Acta Geosci. Sin.* 30, 433–446 (in Chinese with English abstract).

1019 Gao, L.Z., Zhang, C.H., Yin, C.Y., Shi, X.Y., Wang, Z.Q., Liu, Y.M., Liu, P.J., Tang, F.,
1020 Song, B., 2008. SHRIMP zircon ages: basis for refining the chronostratigraphic
1021 classification of the Meso- and Neoproterozoic strata in North China Old Land.
1022 *Acta Geosci. Sin.* 29, 366–376 (in Chinese with English abstract).

1023 Guo, H., Du, Y., Kah, L. C., Huang, J., Hu, C., Huang, H., Yu, W., 2013. Isotopic

1024 composition of organic and inorganic carbon from the Mesoproterozoic Jixian
1025 Group, North China: Implications for biological and oceanic evolution.
1026 *Precambrian Res.* 224, 169–183.

1027 Johnston, D.T., Macdonald, F.A., Gill, B.C., Hoffman, P.F., Schrag, D.P., 2012.
1028 Uncovering the Neoproterozoic carbon cycle. *Nature* 483, 320–323.

1029 Kendall, B., Reinhard, C.T., Lyons, T.W., Kaufman, A.J., Poulton, S.W., Anbar, A.D.,
1030 2010. Pervasive oxygenation along late Archaean ocean margins. *Nat. Geosci.* 3,
1031 647–652.

1032 Li, C., Planavsky, N.J., Love, G.D., Reinhard, C.T., Hardisty, D., Feng, L., Bates, S.M.,
1033 Huang, J., Zhang, Q., Chu, X., 2015. Marine redox conditions in the middle
1034 Proterozoic ocean and isotopic constraints on authigenic carbonate formation:
1035 Insights from the Chuanlinggou Formation, Yanshan Basin, North China.
1036 *Geochim. Cosmochim. Acta.* 150, 90–105.

1037 Li, H.K., Lu, S.N., Su, W.B., Xiang, Z.Q., Zhou, H.Y., Zhang, Y.Q., 2013. Recent
1038 advances in the study of the Mesoproterozoic geochronology in the North China
1039 Craton. *J. Asian Earth Sci.* 72, 216–227.

1040 Li, Z.H., Zhu, X.K., 2012. Geochemical features of Xuanlong type iron ore deposit in
1041 Hebei Province and their geological significances. *Acta Petrol. Sinica* 28(9), 2903–
1042 2911.

1043 Lin, Y., Tang, D., Shi, X., Zhou, X., Huang, K., 2019. Shallow-marine ironstones
1044 formed by microaerophilic iron-oxidizing bacteria in terminal Paleoproterozoic.
1045 *Gondwana Res.* 76, 1–18.

1046 Lu, S.N., Li, H.M., 1991. A precise U-Pb single zircon age determination for the
1047 volcanics of Dahongyu Formation, Changcheng system in Jixian. *Acta Geosci. Sin.*
1048 22, 137–145 (in Chinese with English abstract).

1049 Luo, G.M., Junium, C.K., Kump, L.R., Huang, J.H., Li, C., Feng, Q.L., Shi, X.Y., Bai,
1050 X., Xie, S.C., 2014. Shallow stratification prevailed for 1700 to 1300 Ma ocean:
1051 evidence from organic carbon isotopes in the North China Craton. *Earth Planet.*
1052 *Sci. Lett.* 400, 219–232.

1053 McLennan, S.B., 1989, Rare earth elements in sedimentary rocks: Influence of
1054 provenance and sedimentary processes. In: Lipin B. R., McKay G. A. (Eds.),
1055 *Geochemistry and Mineralogy of the Rare Earth Elements.* Mineral. Soc. Am.,
1056 *Spec. Pap.*, 169–200.

1057 Mloszewska, A.M., Pecoits, E., Cates, N.L., Mojzsis, S.J., O'Neil, J., Robbins, L.J., and

1058 Konhauser, K.O., 2012, The composition of Earth's oldest iron formations: The
1059 Nuvvuagittuq Supracrustal Belt (Québec, Canada). *Earth Planet. Sci. Lett.* 317–
1060 318, 331–342.

1061 Planavsky, N.J., McGoldrick, P., Scott, C.T., Li, C., Reinhard, C.T., Kelly, A.E., Chu,
1062 X.L., Bekker, A., Love, G.D., Lyons, T.W., 2011. Widespread iron-rich conditions
1063 in the mid-Proterozoic ocean. *Nature* 477, 448–495.

1064 Sun, H.Y., Gao, L.Z., Bao, C., Chen, Y.L., Liu, D.Y., 2013. SHRIMP zircon U-Pb of
1065 Mesoproterozoic Chuanlinggou Formation from Kuancheng County in Hebei
1066 Province and its geological implications. *Acta Geol. Sin.* 87, 591–596 (in Chinese
1067 with English abstract).

1068 Tang, D.J., Shi, X.Y., Liu, D.B., Lin, Y.T., Zhang, C.H., Song, G.Y., Wu, J.J., 2015.
1069 Terminal Paleoproterozoic ooidal ironstone from North China: a sedimentary
1070 response to the initial breakup of Columbia Supercontinent. *Earth Sci. - J. China*
1071 *Univ. Geosci.* 40, 290–304 (in Chinese with English abstract).

1072 Zhang, K., Zhu, X., Wood, R.A., Shi, Y., Gao, Z., Poulton, S.W., 2018. Oxygenation of
1073 the Mesoproterozoic ocean and the evolution of complex eukaryotes. *Nat. Geosci.*
1074 11, 345–350.

1075 Zhang, S.H., Zhao, Y., Ye, H., Hu, J.M., Wu, F., 2013. New constraints on ages of the
1076 Chuanlinggou and Tuanshanzi formations of the Changcheng System in the Yan-
1077 Liao area in the northern North China Craton. *Acta Petrol. Sin.* 29, 2481–2490 (in
1078 Chinese with English abstract).

1079 Zhang, Y.B., Li, Q.L., Lan, Z.W., Wu, F.Y., Li, X.H., Yang, J.H., Zhai, M.G., 2015.
1080 Diagenetic xenotime dating to constrain the initial depositional time of the Yan-
1081 Liao Rift. *Precambrian Res.* 271, 20–32.