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1 **Origin of the Neoproterozoic VMS-BIF metallogenic association in the Qingyuan**
2 **greenstone belt, North China Craton: Constraints from geology, geochemistry,**
3 **and iron and multiple sulfur ($\delta^{33}\text{S}$, $\delta^{34}\text{S}$ and $\delta^{36}\text{S}$) isotopes**

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14
15 **Abstract**

16 The association of volcanogenic massive sulfide (VMS) deposits and Algoma-type banded iron
17 formations (BIFs) in many Precambrian terranes indicates a link between submarine hydrothermal
18 processes, seawater chemistry and chemical sedimentation. The Neoproterozoic (~2.55 Ga) Qingyuan
19 greenstone belt (QGB) VMS-BIF metallogenic association, located on the north margin of the North
20 China Craton, is a typical example of such association.

21 The stratigraphy of QGB includes three units (from the oldest to youngest): (1) the Shipengzi
22 Formation (SF) composed of tholeiitic-transitional arc basalts with negative Nb anomalies,
23 interlayered N-MORB-type basalts and FI-type dacites, and BIFs; (2) the Hongtoushan Formation
24 (HF) which consists of polycyclic bimodal suites of N-MORB-type basalts and FII-type dacites, as
25 well as VMS mineralization and minor BIFs; and (3) the Nantianmen Formation (NF) composed of
26 schist, quartzite and marble (amphibolite facies metamorphism), with minor basalts and BIFs.
27 Positive iron isotope compositions ($\delta^{56}\text{Fe}$ of 0.48‰ to 0.69‰) for magnetite in the silicate BIF of the
28 SF indicate partial oxidation of aqueous Fe(II). Using a dispersion-reaction model, the relatively high

29 $\delta^{56}\text{Fe}$ values (0.72‰ to 1.04‰) estimated for primary ferric (oxyhydr)oxides in this BIF constrain
30 local dissolved O_2 contents of the Neoproterozoic surface ocean to 10^{-4} - 10^{-3} $\mu\text{mol/L}$. By comparison,
31 negative $\delta^{56}\text{Fe}$ values for magnetite (-0.83‰ to -0.65‰) in silicate BIFs of the HF and NF suggest
32 deposition from a residual water column that was depleted in ^{56}Fe . Following the formation of the
33 bulk of the VMS deposits in the HF, a significant change to positive magnetite $\delta^{56}\text{Fe}$ values (0.79‰
34 to 1.04‰) occurs in the youngest sulfide-bearing BIF in the NF. This implies that the VMS-related
35 hydrothermal vents injected a large mass of unfractionated ferrous iron into the ocean. Negative $\Delta^{33}\text{S}$
36 anomalies in sedimentary pyrite of bedded VMS ores (average of $-0.08 \pm 0.007\%$, $n = 6$) and sulfide-
37 bearing BIFs (average of $-0.06 \pm 0.007\%$, $n = 3$) of the QGB, along with mass-independent
38 fractionations (with an average $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratio of -1.1 ± 0.3), are best explained by incorporation of
39 seawater sulfate of atmospheric photochemical origin during their formation. The systematic
40 differences in whole rock geochemistry and $\Delta^{33}\text{S}$ values for different types of VMS ores imply
41 variable seawater sulfate contributions to their mineralization. Our results are consistent with global
42 anoxic conditions during the Neoproterozoic to Paleoproterozoic transition (i.e., at 2.5 Ga), and confirm
43 that formation of the VMS-BIF metallogenic association took place in dominantly anoxic, ferruginous
44 basins at different depths, with the VMS-related hydrothermal system contributing significant iron to
45 the deposition of BIFs.

46

47 *Key words:* iron isotopes, multiple sulfur isotopes, VMS-BIF metallogenic association, Qingyuan
48 greenstone belt, Neoproterozoic

49

50

Introduction

51 Volcanogenic massive sulfide (VMS) deposits are stratiform or stratabound accumulations of
52 polymetallic sulfides that formed dominantly within extensional tectonic environments (i.e., rifting)
53 at or near the ancient seafloor (e.g., Franklin et al., 2005; Galley et al., 2007; Piercey, 2011). They
54 precipitated from metal-enriched fluids associated with seawater-derived hydrothermal convection,
55 and occurred episodically from the Neoproterozoic to the present (Franklin et al., 2005; Huston et al.,
56 2007; Mercier-Langevin et al., 2014). As a consequence, certain characteristics of VMS deposits are
57 markedly influenced by secular changes in tectonic, volcanic, hydrothermal and magmatic processes,
58 as well as atmosphere-hydrosphere conditions (Huston and Logan, 2004; Huston et al., 2010; Piercey,

59 2011; Jamieson et al., 2013).

60 By comparison, banded iron formations (BIFs) are iron-rich ($\text{Fe} > 15\%$) chemical sediments that
61 typically comprise of interbedded iron- and silica/carbonate-rich layers (e.g., Bekker et al., 2014).
62 Banded iron formations typify many Precambrian supracrustal successions and are potentially useful
63 chemical archives of contemporaneous seawater chemistry (e.g., Alexander et al., 2009; Planavsky et
64 al., 2010; Robbins et al., 2016). Given that BIFs periodically accumulated on the seafloor dominantly
65 from the Eoarchean to early Paleoproterozoic, changes in their chemical, mineralogical and isotopic
66 compositions also offer a unique glimpse into major environmental changes that took place on the
67 evolving Earth (Bekker et al., 2014; Konhauser et al., 2017). Furthermore, both VMS deposits and
68 BIFs have been, and continue to be, major contributors to the global supply of metals, such as Cu, Zn
69 and, to a lesser extent, Pb, Ag and Au from VMS deposits, and Fe from BIFs (e.g., Large, 1992; Isley,
70 1995; Tsikos et al., 2010).

71 Considering their scientific and economic significance, many studies have been conducted to
72 understand the depositional environment, source, genesis and tectonic setting of these two types of
73 deposits (e.g., Alexander et al., 2009; Huston et al., 2010; Piercey, 2011; Hannington, 2014; Wang et
74 al., 2017). A secular trend in Precambrian VMS and BIF deposits has been identified (e.g., Isley and
75 Abbott, 1999; Huston and Logan, 2004), with Algoma-type BIFs being coupled with VMS deposits
76 in greenstone belts (Bekker et al., 2010). Empirically, since iron in hydrothermal plumes was derived
77 by leaching of submarine volcanic rocks comprising the ocean crust to form Algoma-type BIFs (Gross,
78 1980; German and Von Damm, 2003), accompanying VMS deposits should have formed
79 contemporaneously near the volcanic sources (Slack et al., 2007; Bekker et al., 2010). In this regard,
80 there is a genetic relationship between VMS deposits and coeval Algoma-type BIFs, and together
81 these two types of deposits commonly comprise a metallogenic association. Although several papers
82 have described the close spatial and temporal association of VMS and BIFs and their depositional
83 mechanisms (e.g., Zaleski and Peterson, 1995; Peter, 2003; Angerer et al., 2013), an integrated
84 assessment of iron and sulfur sources and isotopes in the context of formational processes is lacking.
85 In addition, there is limited information on the paleoenvironmental implications of the VMS-BIF
86 association in Archean greenstone belts.

87 Large scale Algoma-type BIFs of Neoproterozoic age have been identified in greenstone belts of the
88 North China Craton (NCC), including in Anshan-Benxi, Wutai, Guyang, and Eastern Hebei (e.g., Li

89 et al., 2014; Liu et al., 2014; Wang et al., 2014; Tong et al., 2021). In particular, the Qingyuan
90 greenstone belt (QGB) on the northern margin of the NCC preserves both BIFs (e.g., Xiaolaihe,
91 Taiyanggou and Xiadianzi) and VMS deposits (e.g., Shujigou, Hongqishan and Hongtoushan) (Shen
92 et al., 1994; Yu, 2006; Gu et al., 2007; Peng et al., 2018a, b). Moreover, previous lithogeochemical
93 and geochronological studies on BIF- and VMS-related supracrustal sequences have revealed that
94 these deposits were consistently preserved within bimodal volcanic sequences of the QGB (Zhai et
95 al., 1985; Shen et al., 1994; Zhang, 2014), and formed simultaneously around 2.55 Ga (Qian et al.,
96 2014; Zhang, 2014; Peng et al., 2019). Therefore, the QGB may provide an ideal case study area for
97 elucidating the VMS-BIF relationship in the late Archean to early Proterozoic.

98 Herein, we present comprehensive geologic and petrographic data, together with the results of
99 whole rock geochemistry, iron isotope and multiple sulfur isotope ($\delta^{33}\text{S}$, $\delta^{34}\text{S}$ and $\delta^{36}\text{S}$) results of
100 pyrite and magnetite separates from the BIFs and VMS ores. Our aim is to (1) provide a detailed
101 geologic characterization of this typical Neoproterozoic VMS-BIF metallogenic association; (2) ascertain
102 its ancient depositional setting and sources of solutes (i.e., Fe and S); and (3) explore metallogenic
103 chemical processes and mechanisms in this system. These new data also allow us to consider the
104 operation of the iron and sulfur cycles in the early oceans, and provide valuable insight into the
105 geochemistry of the oceans and atmosphere before Earth's first rise of atmospheric oxygen.

106

Geological setting

Regional geology of the NCC and QGB

108 The NCC is one of the oldest cratonic blocks, and has witnessed multi-stage crustal growth and
109 secular changes in metallogenic epochs since ca. 3.8 Ga (e.g., Zhai and Zhu, 2016). The Precambrian
110 basement of the NCC consists of two Archean blocks, the Eastern and Western blocks, and the
111 intervening Trans-North China Orogen (e.g., Zhao et al., 2005; Liu et al., 2012; Zhao and Zhai, 2013;
112 Fig. 1A). The Eastern Block (EB) is distinguished by its widely distributed Archean basements, which
113 primarily contain Early to Late Archean tonalite-trondhjemite-granodiorite (TTG), granitoids, and
114 subordinate supracrustal rocks (including meta-mafic to -felsic volcanic rocks, metasedimentary
115 rocks and BIFs) preserved as pods, bands and enclaves (e.g., Liu et al., 1992; Zhao et al., 2001; Wan
116 et al., 2011). By comparison, the Western Block (WB) was formed by the ~1.95 Ga collision between
117 the Yinshan Block (YB) in the north and the Ordos Block (OB) in the south, with the E-W trending

118 Khondalite Belt that resulted from the collision between the YB and OB (Zhao et al., 2002; 2005).
119 The YB is a typical Neoproterozoic block dominated by TTG gneisses and minor supracrustal rocks (e.g.,
120 Zhao et al., 2005; Dong et al., 2012), while the OB is entirely covered by Mesozoic to Cenozoic
121 sedimentary rocks, with limited data to suggest the existence of granulite facies basement beneath the
122 overlying Ordos Basin (Wu et al., 1986).

123 The QGB is located on the north margin of the NCC (Fig. 1A), with its Archean basement separated
124 by the Cenozoic Hunhe fault zone into the Hunnan and Hunbei terranes (Fig. 1B; Shen et al., 1994).
125 The QGB consists of Neoproterozoic plutons (accounting for nearly 70% of this area) and supracrustal
126 rocks that are intruded by early Paleozoic plutons in places and unconformably overlain by Mesozoic
127 sedimentary rocks (Fig. 1B). The Neoproterozoic plutons (~2.56-2.49 Ga) are felsic in composition and
128 generally occur either as domes or as irregular shapes intruding into the supracrustal sequences (Wan
129 et al., 2005; Peng et al., 2015; Wang et al., 2016; Wang K. et al., 2017). By comparison, volcanic
130 rocks in both the Hunnan and Hunbei terranes were formed synchronously at 2.57-2.53 Ga and were
131 then subjected to regional amphibolite to granulite facies metamorphism around 2.50 Ga (Wan et al.,
132 2005; Qian et al., 2014; Li and Wei, 2017; Peng et al., 2019).

133 Lithologically, supracrustal rocks in the QGB can be divided into three volcano-sedimentary units
134 (Zhai et al. 1985; Mao et al., 1997; Yu, 2006; Fig. 1C). (1) The lowermost unit is the Shipengzi
135 Formation (SF), which can be further classified into two lithologic members. The lower member is
136 mainly composed of meta-basalts (plagioclase amphibolite and minor pyroxene hornblende), while
137 the upper member is dominated by interlayered meta-basalts and meta-dacites (biotite plagioclase
138 gneiss), with minor meta-sedimentary rocks (pyroxene-bearing hornblende gneiss) and BIFs. (2) The
139 overlying Hongtoushan Formation (HF) consists of three compositionally similar members.
140 Dominant rock types in these units include interbedded meta-basalts and meta-dacites, with
141 subordinate meta-sedimentary rocks (biotite schist) and BIFs. (3) The Nantianmen Formation (NF)
142 forms the stratigraphically youngest rock sequence. It consists mainly of meta-sedimentary rocks
143 (schist, quartzite and marble), with minor meta-basalts and BIFs at the base.

144 The tectonic setting of the QGB has long been controversial. Hypotheses included: (1) eruption of
145 a mantle plume in an intercontinental setting (Zhai et al., 1985); (2) formation due to ocean-ocean
146 plate collision, followed by subduction and latter arc-continental accretion (Wang et al., 2016); or (3)
147 formation related to subduction of the oceanic crust under a continental plate (Peng et al., 2015).

148 Nevertheless, the existence of old inherited zircon ages (>2.6 Ga) for TTG gneisses and metavolcanic
149 rocks of the QGB (e.g., Wan et al., 2005; Zhang, 2014; Peng et al., 2015; Wang K et al., 2017) seems
150 incompatible with the second model. Moreover, based on detailed field investigations and extensive
151 petrographic, whole-rock major and trace element geochemical data, and Sm-Nd isotopic analyses of
152 representative volcanic rocks from different stratigraphic sequences of the QGB, Peng et al. (2019)
153 concluded that basalts from the lower SF display geochemical features of arc-affinity. They also
154 suggested that both the bimodal volcanic sequences and related BIFs and/or VMS deposits in the
155 upper SF, HF and lower NF were genetically linked to extensional processes in a developing arc
156 assemblage around 2.55 Ga. Thus, an active continental margin (i.e., hypothesis 3) is favored for the
157 QGB.

158 In this setting, the VMS deposits would have formed at (or close to) the spreading center of an
159 intra-arc basin, where the rift-induced normal faults and grabens are conducive to the generation and
160 preservation of metal sulfides (e.g., Piercey, 2011; Huston et al., 2014; Tornos et al., 2015). By
161 comparison, the absence of ripple marks, cross lamination and ooids (Shen et al., 1994), as well as
162 the presence of shale and tuff layers (Peng et al., 2018b) in the QGB BIFs indicate that their deposition
163 occurred in a low energy marine environment, which in this case was likely to have been the shallow
164 part of the basin, closer to the continent than the rift.

165 *Geology of the QGB VMS deposit and BIFs*

166 A number of studies have addressed the geologic and tectonic settings of the VMS and BIF deposits
167 of the QGB (e.g., Zhai et al., 1985; Shen et al., 1994; Yu, 2006; Gu et al., 2007; Zhang et al., 2014;
168 Peng et al., 2019), together with their stratigraphy, ore textures, origins and nature of their country
169 rocks (e.g., Zhai et al., 1985; Shen et al., 1994; Yu, 2006; Gu et al., 2007; Zhang et al., 2014; Peng et
170 al., 2018b). The VMS deposits are constrained to a specific stratigraphic interval, termed the
171 ‘rhythmical member’ (~100 m in thickness) by local geologists. This interval belongs to the HF and
172 consists mainly of interlayered N-MORB-type basalts and FII-type dacite, as well as subordinate
173 garnet biotite schists (Zhang et al., 1984; Shen et al., 1994). Historically, tens of VMS deposits and
174 occurrences have been mined for Cu, Zn and S in the QGB, but most have now been shut down due
175 to resource exhaustion, with the exception of the Hongtoushan deposit.

176 By contrast, BIFs occur extensively in the bimodal volcanic sequences (N-MORB-type basalts and
177 FI- to FII-type dacites) of the upper SF and the entire HF, as well as the volcanic-sedimentary rocks

178 (N-MORB-type basalts, chlorite biotite schist and minor altered tuff layers) of the lower NF (Shen et
179 al., 1994; Yu et al., 2015; Peng et al., 2018b). Nevertheless, most of the BIFs are small occurrences,
180 and only the Xiaolaihe BIF in the upper SF, Taiyanggou BIF in the middle of the HF, and the Xiadianzi
181 BIF of the lower NF had economic value.

182 *VMS deposit:* The Hongtoushan VMS deposit is located in the Hunbei terrane of the QGB (Fig.
183 1B), with reserves of 0.5 Mt Cu at 1.5-1.8 %, 0.7 Mt Zn at 2.0-2.5 %, 20 t Au at 0.5-0.8 g/t, and 1000
184 t Ag at 20-60 g/t (Gu et al., 2007), and occurs within the Hongtoushan member of the middle HF (Fig.
185 1C). Host rocks for this deposit comprise ~2.55 Ga rhythmic interbeds of FII-type dacites and N-
186 MORB type basalts (Qian et al., 2014; Peng et al., 2019). Locally, there are also interlayers of
187 tuffaceous rocks, sandstones and mudstones (Zhai et al., 1985; Deng, 1994; Yu, 2006).

188 The above rocks were metamorphosed to amphibolite facies at around 2.50 Ga (Zhang et al., 1984),
189 and underwent multiple phases of deformation (Yang and Yu, 1984). Their foliations are roughly
190 parallel to lithological boundaries and dip towards the SE at 60-80°, defining an isoclinal fold. The
191 occurrence of the VMS deposit is essentially controlled by this fold, leading to the ore bodies having
192 a “Y” shape in map view (Fig. 2A). Minor, but regionally extensive BIF, composed of interbedded
193 magnetite- and quartz-rich layers, are well developed in the mineralization area (Yu et al., 2015; Fig.
194 2A). The BIF is preserved in the same belt (i.e., the Hongtoushan member) to the VMS deposit and
195 is stratigraphically higher than the later (Peng et al., 2018b). Similar situations where the VMS-
196 hosting rocks are overlain by BIFs have also been observed in the Dahuanggou and Zhanghugou
197 VMS deposits of the HF (Gu et al., 2007). Notably, the proximity of BIFs to VMS deposits has also
198 been reported in the Manitouwadge greenstone belt of Superior province (Zaleski and Peterson, 1995)
199 and the Koolyanobbing greenstone belt of Yilgarn Craton (Angerer et al., 2013). In this regard, it
200 seems likely that the BIFs were exhalative in source (i.e., same volcanic source as the VMS and
201 marking the most prospective VMS horizons, e.g., Peter, 2003) but they nonetheless represent
202 chemical sediments in that they precipitated in relatively deep seawater (Thurston et al., 2008) with
203 an oxidant required to convert dissolved Fe(II) into ferric (oxyhydr)oxide. In addition, granite
204 intrusions with strongly gneissic structures that intruded into the supracrustal sequences are also
205 locally observed in the mine area. Dikes of diabase, lamprophyre and olivine gabbro are observable
206 at the surface and underground, and crosscut all other units and the ore bodies (Fig. 2B), with no sign
207 of deformation or hydrothermal alteration (Gu et al., 2007).

208 Although the ore bodies in this deposit were intensely deformed and show a fold interference
209 pattern, most of them are still conformable with the host rocks (Fig. 2B). Moreover, most of the ores
210 are massive, but bedded structures comprising alternating and synchronously folded sulfide and
211 gneiss layers also appear locally. In addition, disseminated ores and moderate veinlets that cross-cut
212 the host-rocks are present adjacent to the main orebodies, but whether they represent a synchronous
213 subseafloor replacement type of mineralization (e.g., Doyle and Allen, 2003; Piercey et al., 2014) or
214 a pseudo-replacement-like texture is uncertain. Normally, most VMS deposits are characterized by
215 discordant stockwork vein systems that underline the massive sulfide lenses (Hannington et al., 1996;
216 Franklin et al., 2005). These systems, which form by interaction between rising hydrothermal fluids,
217 circulating seawater and sub-seafloor rocks, usually occur at the center of extensive alteration zones
218 (Galley et al., 2007). Due to complex deformation and metamorphism, alteration zones of various
219 orebodies in the Hongtoushan VMS deposit are largely obliterated and thus difficult to define. The
220 mineralogy of different types of ores is similar but their relative contents can be variable. Ore minerals
221 are dominated by pyrite, pyrrhotite, sphalerite and chalcopyrite, whereas gangue minerals are
222 composed mainly of quartz, biotite, plagioclase and hornblende, together with minor actinolite, garnet
223 and gahnite.

224 *BIF deposits:* BIFs from the QGB were interpreted to have been deposited contemporaneously
225 with VMS deposits between 2.57 and 2.50 Ga (Peng et al., 2018a, b). Details of their geological
226 setting have been reported previously (e.g., Shen et al., 1994; Zhang, 2014; Peng et al., 2018a, b) and
227 are summarized below according to their relative stratigraphic order.

228 The Xiaolaihe BIF is situated in the Hunnan terrane of the QGB (Fig. 1B), and exposed strata in
229 this area chiefly comprise the ~2.57 Ga bimodal volcanic-sedimentary sequences of the upper SF
230 (Peng et al., 2018b; Fig. 3). Both the BIF and associated rocks have undergone intense deformation
231 and regional metamorphism to granulite-facies, which is evidenced by the presence of minerals of
232 high metamorphic grade, such as pyroxene and fayalite that show distinct prograde textures (Shen et
233 al., 1994; Peng et al., 2018b). Five stratiform BIF-type iron orebodies ($43 \text{ wt}\% \leq \text{Fe}_{\text{total}} \leq 53 \text{ wt}\%$)
234 are distributed between the interbedded complex of FI-type dacite and N-MORB type basalt (Peng et
235 al., 2019). The BIFs strike NS and dip NEE or N at 30° - 60° , with an overall shape of a horizontal
236 "L". Locally, exposed single layers of BIF can be as long as 1.8 km, with thicknesses varying from
237 less than 2 m to tens of meters.

238 The Taiyanggou BIF is located near the Hongtoushan VMS deposit in the Hunbei terrane of the
239 QGB (Fig. 1B). It is also hosted by the ~2.55 Ga bimodal volcanic rocks of the Hongtoushan member,
240 and is stratigraphically higher than the Hongtoushan VMS deposit (Fig. 3; Peng et al., 2018b). The
241 BIF and associated rocks have been metamorphosed to amphibolite-facies. Four BIF-type iron
242 orebodies ($39 \text{ wt}\% \leq \text{Fe}_{\text{total}} \leq 57 \text{ wt}\%$), with thicknesses varying from 2 to 30 m, were recently
243 identified by a drilling project of the Fushun Ming Group Co., Ltd (Yu et al., 2015). These BIFs strike
244 NE and dip steeply E at 60° - 80° , and generally have a direct and comfortable contact with the dacites
245 (Peng et al., 2018b).

246 The Xiadianzi BIF is also situated in the Hunbei terrane (Fig. 1B). Exposed rocks in this area are
247 basalt and chlorite garnet biotite schist of the lower NF (Fig. 3). Both the rocks and BIF have been
248 metamorphosed to lower amphibolite-facies during the regional metamorphism (Zhang, 2014).
249 Previous zircon SIMS U-Pb dating has constrained the metamorphic age of the Xiadianzi BIF to ca.
250 2.50 Ga (Peng et al., 2018a). However, given its position relatively higher in the stratigraphic
251 sequence and the lower metamorphic grade compared to the Taiyanggou BIF, this BIF was likely
252 deposited between 2.55 and 2.50 Ga. The main BIF orebody (with Fe_{total} varying from 35 to 60 wt%)
253 is distributed in an N-S orientation and dips NNE to NE at 50° - 70° , with a length of 400 m and a
254 thickness of 40 to 50 m. Notably, in addition to the most common silicate BIFs occurring elsewhere
255 in the QGB, a sulfide-bearing BIF is also preserved in this area (Fig. 3F-G; see following sections for
256 a detailed description).

257 **Iron and multiple sulfur isotope systematics**

258 Iron isotope compositions are expressed as $^{56}\text{Fe}/^{54}\text{Fe}$ ratios ($\delta^{56}\text{Fe} = [({}^{56}\text{Fe}/{}^{54}\text{Fe}_{\text{sample}})/({}^{56}\text{Fe}/{}^{54}\text{Fe}_{\text{standard}})$
259 $- 1] \times 1000$) relative to the international standard IRMM-14 ($\delta^{56}\text{Fe} = -0.09\text{‰}$; Beard et al., 2003). It
260 is accepted that the most important controls on Fe isotope fractionations in natural, low-temperature
261 systems are oxidation state and bonding (Beard and Johnson, 2004; Anbar and Rouxel, 2007). At
262 equilibrium, ferrous dissolved iron species ($\text{Fe(II)}_{\text{aq}}$) and minerals have the lowest $\delta^{56}\text{Fe}$ values when
263 compared to minerals with either a mixed Fe(II)-Fe(III) or entirely Fe(III) composition (Johnson and
264 Beard, 2006; Anbar and Rouxel, 2007). Complete oxidation and precipitation of initial ferrous phases
265 produces ferric (oxyhydr)oxide minerals that have $\delta^{56}\text{Fe}$ values equal to those of the initial $\text{Fe(II)}_{\text{aq}}$
266 (Johnson et al., 2008).

267 The bulk silicate Earth is isotopically homogenous, with $\delta^{56}\text{Fe}$ close to zero (Schoenberg and
268 Blanckenburg, 2005; Dauphas et al., 2009), but the upper mantle has chondrite-like $\delta^{56}\text{Fe}$ values of
269 0.01-0.02‰ (Weyer and Ionov, 2007), while igneous rocks and bulk continental crust trend to have
270 slightly heavier $\delta^{56}\text{Fe}$ values of $\sim 0.11\%$ (Poitrasson et al., 2004; Heimann et al., 2008). By contrast,
271 significant Fe isotopic fractionation occurs within natural fluids (e.g., groundwater, river water and
272 hydrothermal fluids), with $\delta^{56}\text{Fe}$ values ranging between -2.55 and 0‰ (Johnson et al., 2008), and
273 chemical sedimentary rocks or sediments, with $\delta^{56}\text{Fe}$ values ranging from -4.00 to +2.00‰ (Anbar
274 and Rouxel, 2007; Johnson et al., 2008; Planavsky et al., 2012). For this reason, much research has
275 focused on Fe isotope variability in the sources of iron to seawater and associated fractionation
276 processes during mineral formation. Given that BIFs record a period of unprecedented authigenic
277 iron deposition in Earth's history (Bekker et al., 2010), their iron isotope compositions have proven
278 to be an invaluable tool for tracing Fe redox cycling in the early oceans (Rouxel et al., 2005;
279 Planavsky et al., 2012; Li et al., 2013), and in highlighting biotic (Johnson et al., 2004; Johnson and
280 Beard, 2006) or abiotic (Dauphas and Rouxel, 2006; Anbar and Rouxel, 2007) processes in BIF
281 genesis.

282 With a few exceptions, the enrichment or depletion of ^{33}S , ^{34}S and ^{36}S , relative to ^{32}S , is governed
283 by the relative mass differences of the isotopic species (i.e., mass-dependent fractionation, MDF)
284 (Hulston and Thode, 1965). Contrastingly, sulfur isotope mass-independent fractionation (S-MIF) is
285 defined as a departure from these theoretically-derived and empirically-observed mass laws. Such S-
286 MIF signals are commonly identified as non-zero $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values, which are denoted as $\Delta^{3x}\text{S} =$
287 $\delta^{3x}\text{S}_{\text{measured}} - 1,000 \times [(1 + \delta^{34}\text{S}_{\text{measured}}/1,000)^{3x\lambda} - 1]$ (in which $x = 3, 6$, $^{33}\lambda = 0.515$, $^{36}\lambda = 1.90$, $\delta^{3x}\text{S} =$
288 $1,000 \times [(^{3x}\text{S}/^{32}\text{S})_{\text{sample}} / (^{3x}\text{S}/^{32}\text{S})_{\text{standard}} - 1]$, and the standard is Vienna Cañon Diablo Troilite, VCDT)
289 (Hulston and Thode, 1965; Farquhar et al., 2001).

290 Sulfur isotope mass-independent fractionations have been measured in some of Earth's oldest rocks
291 (Farquhar et al., 2000; Ono et al., 2003), in modern sulfate aerosols (Romero and Thiemens, 2003),
292 and in volcanic horizons in ice cores (Savarino et al., 2003). On the basis of experimental surveys
293 and atmospheric chemistry models, the prevailing hypothesis to explain these observations concerns
294 UV-mediated gas-phase photolysis of SO_2 under anoxic conditions (e.g., Farquhar et al., 2001; Pavlov
295 and Kasting, 2002). Thus, the predominance of S-MIF signals in the Archean rock record, but its
296 disappearance after the 2.43-2.22 Ga Great Oxidation Event (GOE) (Poulton et al., 2021), is taken as

297 compelling evidence for low atmospheric and Earth surface oxygen levels ($<10^{-5}$ PAL, present-day
298 atmospheric level) before the GOE. This is a pre-requisite for the production, transfer and
299 preservation of S-MIF in surface sulfur pools (e.g., Farquhar et al., 2000; Pavlov and Kasting, 2002;
300 Ono et al., 2003). Moreover, given that mantle-derived sulfur has limited variability in $\Delta^{33}\text{S}$, with
301 Precambrian and modern mantle $\Delta^{33}\text{S}$ values well constrained to a narrow range of $0.00 \pm 0.03\text{‰}$
302 (e.g., Ueno et al. 2008; Labidi et al., 2012; Dottin III et al., 2020), this distinctive S-MIF signal has
303 proven to be very effective for differentiating Archean mantle and atmospheric sources of sulfur, and
304 for quantifying the role of atmospheric sulfur in producing economic VMS deposits (Jamieson et al.,
305 2013; Sharman et al., 2015, Chen et al., 2015).

306 **Samples and methods**

307 *Sampling methodology and petrography*

308 Samples collected and analyzed for this study include: (1) semi-massive to massive, disseminated-
309 stockwork and bedded sulfide ores from the Hongtoushan VMS deposit; (2) silicate BIFs from the
310 Xiaolaihe and Taiyanggou areas; and (3) both silicate and sulfide-bearing BIFs from the Xiadianzi
311 area (Table S1). Notably, some of the bedded VMS ores (i.e., HTB-1 to HTB-5) were collected from
312 the lower to upper parts of a 20m-length section to examine whether there is higher resolution
313 variability in iron and sulfur isotope values.

314 *VMS ore samples:* Generally, different types of VMS ores are distinguished by their distinct
315 textures and sulfide mineral abundances (Fig. 4A-D). The semi-massive to massive ores contain 70-
316 90 vol% sulfides, among which pyrite, pyrrhotite, sphalerite and chalcopyrite are the dominant
317 minerals, with approximate proportions of 4:4:1:1. Pyrite in these samples typically occurs as coarse-
318 grained subhedral aggregates and porphyroblasts in a matrix of chalcopyrite, sphalerite and pyrrhotite
319 (Fig. 4E). These pyrite aggregates contain inclusions of spherical quartz or plagioclase (Fig. 4E), and
320 have other sulfides (e.g., chalcopyrite and sphalerite) infilling fractures or rim grains (Fig. 4F).

321 By comparison, sulfides in the disseminated-stockwork samples only comprise 10 to 40 vol% of
322 the rocks, and are dominated by pyrite, pyrrhotite, sphalerite and chalcopyrite with approximate
323 proportions of 5:1:2:2. Pyrite in these ores usually occurs as subhedral to euhedral grains (0.1-0.5 mm
324 in diameter) that are intergrown in a matrix of chalcopyrite and sphalerite (Fig. 4G). The bedded ores
325 are composed of weakly deformed, sulfide-rich bands alternating with strongly foliated silicate-rich

326 layers (Fig. 4H). Pyrrhotite is the most common sulfide mineral in these ores and is usually present
327 as fine-grains (0.1-0.5 mm), anhedral grains or aggregates within the sulfide-rich bands (Fig. 4I).

328 Moreover, compared with other ore types, the bedded ores have extremely low chalcopyrite
329 contents, whereas pyrite also occurs as minor components of these samples and is preserved as
330 sporadic, anhedral grains among quartz, plagioclase and biotite (Fig. 4I). In addition, both
331 remobilization of sulfides (pyrrhotite, sphalerite and chalcopyrite), and sphalerite replacement by
332 chalcopyrite, are common in massive and disseminated-stockwork ores (Fig. 4E-G), but are absent
333 from the bedded samples (Fig. 4I).

334 *BIF samples:* Silicate BIF samples share some common features. For example, they all comprise
335 beds of thinly laminated silica- and iron-rich layers (Fig. 5A-B), and consist of combinations of
336 magnetite, quartz, silicates and occasionally carbonate. However, detailed textures and mineralogies
337 of different samples can be highly variable, likely due to the primary depositional environment and
338 subsequent metamorphism (Peng et al., 2018b). Samples from the Xiaolaihe BIF generally have
339 equigranular textures, and are composed of magnetite (~40%), silicates (25-35%), quartz (25-30%)
340 and minor calcite (< 5%) (Fig. 5D). Amongst the silicates, pyroxene is the most abundant mineral,
341 with ferrohedenbergite and eulite constituting ~70 vol% of the silicates. By comparison, BIFs from
342 the Taiyanggou area tend to show fine-grained banded structures and have actinolite (~60 vol% of
343 the silicates) being the most abundant silicate, although mineral components in both BIFs are quite
344 similar. Subordinate amounts of orthopyroxene grains are only observed alongside or within the iron-
345 rich layers of these samples and occasionally replace the actinolite (Fig. 5E). Silicate BIF samples
346 from the Xiadianzi area are very fine-grained and commonly composed of quartz (40-50%),
347 magnetite (40-50%) and ~10% of ferroactinolite. Magnetite grains in these samples are also finer than
348 those of the Xiaolaihe and Taiyanggou BIFs, while minor coarse-grained magnetite is only observed
349 within or along the silica-rich layers (Fig. 5F).

350 Sulfide-bearing BIFs are distinguished by their finely laminated alternating silica-, magnetite- and
351 pyrite-rich layers (Fig. 5C). Mineralogically, these BIFs consist of quartz (~40%), magnetite (~35%),
352 actinolite (10-15%), pyrite (5-10%) and minor calcite (< 5%), amongst which the pyrite grains are
353 coarser than the other constituents and tend to be euhedral (Fig. 5G-H). Detailed petrographic
354 analyses indicate that pyrite within these samples commonly shows textures indicative of a syngenetic
355 or early diagenetic origin. These include rounded or framboidal nodules, microcrystalline aggregates

356 intergrown with magnetite grains that formed during early diagenesis, finely isolated pyrite (< 0.05
357 mm) inclusions in coarse-grained magnetite, and subhedral to euhedral crystals (0.2-0.4 mm)
358 conformable to the original banding (Fig. 5H-I). Moreover, the presence of triple junction textures
359 (Fig. 5J) in some samples indicates recrystallization of smaller, earlier pyrite during metamorphism.

360 *Analytical methods*

361 *Whole rock geochemistry:* Twelve whole rock VMS ore samples (Table S1) were analyzed for major
362 and trace elements. All samples were crushed to a fine powder (< 200 mesh) using an agate puck mill
363 prior to geochemical analysis. Trace and major elements were initially determined by inductively
364 coupled plasma atomic emission spectrometry (ICP-AES, Varian VISTA) using a four-acid digestion
365 method, with a reproducibility of less than 5% for reported elements measured via this technique. Au
366 contents were also obtained by ICP-AES using a fire assay fusion followed by acid digestion, with a
367 reproducibility of less than 5%. Elements at low concentration (e.g., Cr, V, Co and Ni) were
368 determined by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7900), with a
369 reproducibility of 5-10%. The standards used in above analyses were provided in Table S1, with both
370 measured and reference values.

371 *Iron and multiple sulfur isotope analyses:* Magnetite and pyrite grains (handpicked using a
372 binocular microscope) separated from the BIFs and VMS ores were prepared for iron and multiple
373 sulfur isotope analyses by grinding to a fine powder (< 200 mesh) under methanol, using an agate
374 pestle and mortar. Thirteen magnetite and eighteen pyrite samples from the silicate BIF, sulfide-
375 bearing BIF and different types of VMS ores were prepared for iron isotope analysis, while eighteen
376 pyrite samples from both sulfide-bearing BIF and VMS ores were selected for multiple sulfur isotope
377 analysis (Table S1).

378 Iron isotope analyses were performed at the ALS Scandinavia Laboratory in Luleå, Sweden.
379 Samples were first dissolved in an HF-HNO₃-HCl acid mixture on a hot plate. Fe was then purified
380 with a Bio-Rad AG-MP1 anion exchange chromatographic resin. Iron isotope ratios were determined
381 on a Thermo Scientific Neptune multiple collector inductively coupled mass spectrometer (MC-ICP-
382 MS), following methods previously described by Rouxel et al. (2005). The precision for iron isotope
383 analysis was estimated to be better than ± 0.08‰ (2SD). Two georeference materials, including IF-G
384 and BHVO-2, were also measured, and results are provided in Table S2.

385 Sulfur extraction largely followed the method of Canfield et al. (1986). Powdered pyrite separates

386 were rinsed with Milli-Q water to remove water-soluble sulfate and possible sulfur oxidation products
387 arising during exposure. After rinsing, the residues were reacted with a heated solution of mixed HCl
388 (5 N, 10 ml) and acidic Cr(II) (0.3 M, 20 ml), while being flushed with nitrogen gas. The product H₂S
389 gas was cooled and then collected as Ag₂S in a slightly acidic AgNO₃ solution. After that, the Ag₂S
390 was dried and fluorinated overnight at ~250 °C in a nickel vessel under a tenfold stoichiometric excess
391 of F₂, to produce SF₆. The SF₆ gas was then purified cryogenically and chromatographically, and
392 analyzed on a Thermo-electron MAT 253 isotope ratio mass spectrometer for isotope ratios in dual-
393 inlet mode at the Laboratory of Stable Isotope Geobiology at Massachusetts Institute of Technology,
394 following the procedure outlined in Ono et al. (2012). The analytical uncertainties are estimated by
395 the long-term reproducibility of IAEA-S1, yielding $\delta^{34}\text{S} = -0.47 \pm 0.13\%$, $\Delta^{33}\text{S} = 0.118 \pm 0.007\%$
396 and $\Delta^{36}\text{S} = -0.81 \pm 0.10\%$, respectively (2SD, n = 37).

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Results

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Whole-rock geochemistry

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Although whole-rock chemical compositions of sulfide ores of the Hongtoushan VMS are highly variable, there are clear distinctions that reflect their mineralization types (Table 1). Generally, the semi-massive/massive ores have the highest contents of Fe₂O₃ (48.5-58.2 wt%) and S (> 10 wt%), but the lowest concentrations of Al₂O₃ (2.87-3.53 wt%). The disseminated-stockwork ores have Fe₂O₃, S and Al₂O₃ contents ranging from 18.4-25.9 wt%, 7.28-9.76 wt%, and 4.61-7.12 wt%, respectively. The bedded ores, however, tend to display much wider ranges in whole-rock compositions, with Fe₂O₃, S and Al₂O₃ concentrations of 10.4-26.5 wt%, 3.94-7.57 wt%, and 8.53-14.8 wt%, respectively. Other major oxides, such as TiO₂, MnO, MgO and P₂O₅ are consistently low (< 0.5 wt%) in all samples and show little variability amongst sample types.

The semi-massive/massive ores have the highest Cu (23,400-66,300 ppm) and Zn (19,200-49,760 ppm) contents; the disseminated-stockwork ores commonly have low and constant contents of Cu and Zn (11,000-16,500 and 4,300-8,500 ppm, respectively). Significantly, the bedded ores are distinguished by highly variable Cu (670-12,200 ppm) and Zn (6,090-34,000 ppm) concentrations, and by relatively low Cu/(Cu+Zn) values (0.10-0.36) when compared to semi-massive/massive (0.52-0.59) and disseminated-stockwork (0.66-0.75) ores. It is also noteworthy that both Ag and Au concentrations decrease systematically from semi-massive/massive ores, through disseminated-

415 stockwork ores, to bedded ores (Table 1).

416 *Iron and multiple sulfur isotope data*

417 *Iron isotope compositions:* Iron isotope compositions for magnetite and pyrite grains of the BIF and
418 VMS ore samples are listed in Table 2 and illustrated as a function of stratigraphic horizon in Fig. 6.
419 $\delta^{56}\text{Fe}$ values for pyrite grains from massive VMS ores vary across a limited range, from 0.00 ± 0.06
420 to $+0.08 \pm 0.06$ ‰ (n = 3), in comparison to bedded VMS samples, which show a larger variability
421 between -0.58 ± 0.06 to $+0.51 \pm 0.06$ ‰ (n = 5). For the latter, there is an obvious depositional control,
422 with negative values observed in pyrite from the lower sections and positive values are recorded in
423 higher layers.

424 By contrast, large variability in $\delta^{56}\text{Fe}$ values is observed for magnetite and pyrite grains from BIFs
425 of the QGB (Table 2). Amongst these samples, magnetite in the lowermost Xiaolaihe silicate BIF
426 shows a narrow range of positive $\delta^{56}\text{Fe}$ values varying between $+0.48 \pm 0.07$ and $+0.69 \pm 0.07$ ‰ (n
427 = 4), whereas those of the stratigraphically higher Taiyanggou and Xiadianzi silicate BIFs tend to
428 display consistently negative $\delta^{56}\text{Fe}$ values, ranging from -0.83 ± 0.07 to -0.65 ± 0.06 ‰ (n = 5). By
429 comparison, four magnetite samples of the Xiadianzi sulfide-bearing BIF show positive $\delta^{56}\text{Fe}$ values
430 of $+0.79 \pm 0.07$ to $+1.04 \pm 0.02$ ‰, while the co-existing pyrite has negative $\delta^{56}\text{Fe}$ values of $-1.29 \pm$
431 0.06 to -0.91 ± 0.05 ‰ (Fig. 6A).

432 *Multiple sulfur isotope compositions:* Pyrite grains from all types of VMS ores display relatively
433 uniform and positive $\delta^{34}\text{S}$ values from $+0.11$ to $+1.61$ ‰ (± 0.13 ‰, 2SD; n = 15), resembling the
434 mantle range of $\delta^{34}\text{S}$ values (0 ± 2 ‰; e.g., Chaussidon et al. 1989; Fig. 6B). By contrast, narrow but
435 significant variability in $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values is observed within some samples. Overall, massive and
436 disseminated VMS ores that are interpreted to have been formed below the seafloor have a small
437 range of $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values. The $\Delta^{33}\text{S}$ values are negative, with a narrow distribution characterized
438 by mean values of -0.05 ‰ (± 0.007 ‰, 2SD; n = 9), whereas $\Delta^{36}\text{S}$ values are positive, with mean
439 values of $+0.05$ ‰ (± 0.10 ‰, 2SD; n = 9; Table 2). This uniformity in both $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values
440 suggests a homogenous, well-mixed sulfur source for these ores, probably dominated by igneous
441 sulfide (e.g., Ueno et al., 2008). The bedded VMS ores that are interpreted as seafloor deposits are
442 distinguished by relatively large variability in both $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values (-0.06 to -0.13 and $+0.01$ to
443 $+0.15$ ‰, respectively; n = 6).

444 Pyrite from the Xiadianzi sulfide-bearing BIFs show a significant deviation from mantle sulfur

445 (Fig. 6B), with more negative $\delta^{34}\text{S}$ values varying between -3.36 to -1.31 ‰ ($\pm 0.13\%$, 2SD; $n = 3$)
446 (Table 2). Meanwhile, $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values for these samples also display small ranges, from -0.04
447 to -0.09 ‰ ($\pm 0.007\%$, 2SD; $n = 3$) and -0.11 to +0.06 ‰ ($\pm 0.10\%$, 2SD; $n = 3$), respectively (Table
448 2).

449 Discussion

450 *Iron and sulfur sources in the Neoproterozoic QGB intra-arc basin*

451 *Significant iron input from coeval VMS-related hydrothermal vents:* The accumulation of such large
452 masses of iron in the form of BIFs required the transport of dissolved Fe(II) in early oceans, because
453 Fe(III) has a very low solubility at circumneutral pH (Kendall et al., 2012). To explain this, early
454 studies invoked a continental source of iron, where Fe(II) would have been mobile during anoxic
455 weathering (e.g., Cloud, 1973; Holland, 1984). However, based on rare earth element and Nd isotope
456 data (e.g., Derry and Jacobsen, 1990; Bau and Dulski, 1996; Alexander et al., 2009), it is now apparent
457 that the iron was instead sourced from submarine, hydrothermally-influenced waters.

458 With the discovery of modern iron-rich seafloor hydrothermal systems (German et al., 2010; Saito
459 et al., 2013), the interpretation that the majority of the iron required for BIF formation originated from
460 deep ocean hydrothermal vents has become increasingly favoured (Bekker et al., 2010; Konhauser et
461 al., 2017). Furthermore, it has also been demonstrated that Archean oceans may have had their REE
462 (and other trace element) characteristics controlled dominantly, if not exclusively, by hydrothermal
463 input (Fryer et al., 1979). This assumption is supported by REE profiles of Archean marine sediments,
464 such as BIFs and shallow-water carbonates, which often carry pronounced Eu anomalies of
465 hydrothermal origin compared to modern seawater profiles (e.g., Kamber et al., 2014; Bolhar et al.,
466 2015).

467 Given such constraints, it is logical to invoke anoxic ferruginous conditions, with iron supplied by
468 submarine hydrothermal venting as the main source of iron in the Neoproterozoic QGB intra-arc basin.
469 Meanwhile, iron enrichments in the Xiadianzi shale layers (Total Fe_2O_3 of 20.6 to 22.3 %, $n = 3$; Peng
470 et al., 2018b), which were deposited between pulses of BIF formation, also provide further evidence
471 for persistent ferruginous conditions (e.g., Kendall et al., 2010) in the QGB seawater. Nevertheless,
472 it is noteworthy that the above interpretation does not allow us to further distinguish between iron
473 already accumulated in seawater by previous hydrothermal venting and those from coeval

474 hydrothermal input. In other words, if Archean seawater in the QGB basin contained sufficient Fe(II),
475 there is no reason why all BIFs in this area should be genetically linked to the extensional tectonic
476 processes (Peng et al., 2019). A similar situation has also been observed in the ~2.7 Ga Abitibi and
477 ~2.9-2.6 Ga Murchison greenstone belts, where BIFs are closely related to VMS mineralization that
478 post-date submarine volcanism (Zaleski and Peterson, 1995; Thurston et al., 2008; Hollis et al., 2015).
479 In light of these observations, it is highly plausible that the coeval VMS-related seafloor hydrothermal
480 vents could have contributed significant iron to BIF deposition.

481 Iron isotopic compositions of rocks and minerals are generally considered to be relatively
482 unaffected by post-mineralization processes and high-grade metamorphism, and thus are reflective of
483 their origin (e.g., Dauphas et al., 2004; Frost et al., 2007; Czaja et al., 2013). In this regard, variations
484 in $\delta^{56}\text{Fe}$ values for BIFs can be attributed to either primary oxidative or diagenetic mechanisms,
485 including both abiogenic and/or biogenic redox-controlled reactions (e.g., Czaja et al., 2013;
486 Planavsky et al., 2012; Li et al., 2015; Johnson et al., 2020). By contrast, magmatism and the related
487 seafloor hydrothermal circulation generally results in little iron isotope fractionation (e.g., Rouxel et
488 al., 2005; Johnson et al., 2008; Bekker et al., 2009). For these reasons, iron isotopic compositions of
489 magnetite and pyrite in the QGB BIFs present an opportunity to deduce possible effects of the VMS-
490 related hydrothermal vents on BIF formation.

491 As mentioned above, the most common mechanism proposed for the accumulation of iron in BIFs
492 is oxidation of hydrothermally-sourced $\text{Fe(II)}_{\text{aq}}$. Dissolved Fe(II) accumulated in the deep ocean
493 could then have been upwelled to shallow water, resulting in oxidation and formation of a precursor
494 ferric (oxyhydr)oxide phase, such as ferrihydrite (herein denoted as $[\text{Fe(OH)}_3]$), in the photic zone.
495 Subsequently, the poorly crystalline Fe(OH)_3 may have reacted with aqueous Fe(II) from
496 hydrothermal origin (e.g., Klein, 2005; Beukes and Gutzmer, 2008), may have transferred to green
497 rust as an intermediate phase (Zegeye et al., 2012; Halevy et al., 2017; Li et al., 2017), or may have
498 been partially reduced to Fe(II) via dissimilatory iron reduction (DIR) driven by heterotrophic
499 bacteria during sediment diagenesis (Johnson et al., 2008; Li et al., 2011), to ultimately form
500 magnetite (Konhauser et al., 2005; Li et al., 2013).

501 A prerequisite for producing $\text{Fe(II)}_{\text{aq}}$ in sediment porewaters by DIR lies in the assumption that
502 there is sufficient organic matter acting as an electron donor to reduce Fe(III) during BIF deposition.
503 However, both organic carbon and abundant carbonate minerals (siderite, ankerite and calcite) that

504 are believed to be by-products of the DIR process (e.g., Konhauser et al., 2005, 2017) are rarely
505 observed within our samples (Peng et al., 2018b; this study). Moreover, there is also a lack of evidence
506 for magnetite overgrowths on existing hematite within our BIF samples (Fig. 5I-J). Indeed, Li et al.
507 (2017) have experimentally demonstrated that the reaction of $\text{Fe(II)}_{\text{aq}}$ with biogenic ferrihydrite could
508 indirectly yield magnetite through a green rust precursor phase, but only when the solutions were
509 fully anoxic and at temperatures exceeding 50 °C, conditions fully consistent with a hydrothermal
510 fluid Fe(II) source. In light of these observations, it seems that the $\text{Fe(II)}_{\text{aq}}$ in the QGB basin might
511 instead be predominantly of hydrothermal origin. Although the $\delta^{56}\text{Fe}$ value of magnetite would likely
512 be altered by addition of $\text{Fe(II)}_{\text{aq}}$ that is commonly depleted in heavy Fe isotopes relative to the
513 primary ferric (oxyhydr)oxide, isotopic values would ultimately remain positive (Li et al., 2015).
514 Therefore, partial oxidation of hydrothermally sourced iron is one possible explanation for the
515 positive $\delta^{56}\text{Fe}$ values of magnetite in the Xiaolaihe silicate BIF (Fig. 6A), as quantitative oxidation
516 of $\text{Fe(II)}_{\text{aq}}$ in the water column would generate no Fe isotope fractionation.

517 Accordingly, magnetite with negative $\delta^{56}\text{Fe}$ values in the Taiyanggou and Xiadianzi silicate BIFs
518 (Fig. 6A) is best explained by quantitative oxidation of $\text{Fe(II)}_{\text{aq}}$ with a negative initial $\delta^{56}\text{Fe}$ value to
519 form the ^{56}Fe -depleted Fe(OH)_3 precursor. Such a process could be achieved by precipitation of Fe(III)
520 from the iron-rich water column that had previously undergone considerable oxidation, producing
521 very low $\delta^{56}\text{Fe}$ values in the residual $\text{Fe(II)}_{\text{aq}}$ (e.g., Rouxel et al., 2005; Anbar and Rouxel, 2007;
522 Tsikos et al., 2010). Significantly, values of $\delta^{56}\text{Fe}$ as low as -2.3‰ have been observed in iron-rich
523 groundwater springs that precipitate isotopically heavy ferrihydrite along a fluid-flow path, yielding
524 low $\delta^{56}\text{Fe}$ in the residual Fe(II) pool (Bullen et al., 2001). Collectively, in our model, $\text{Fe(II)}_{\text{aq}}$ with
525 $\delta^{56}\text{Fe}$ values around 0‰ was initially oxidized (partial) in a closed system, which in this case would
526 be the QGB intra-arc basin, to form the Xiaolaihe silicate BIF. This left the residual ^{56}Fe -depleted
527 Fe(II) pool to be continuously oxidized to deposit the Taiyanggou and Xiadianzi silicate BIFs.
528 Alternatively, the younger Taiyanggou and Xiaolaihe silicate BIFs could have been deposited from a
529 newly formed residual ^{56}Fe -depleted water column, given that there is a lack of evidence to support
530 such iron isotopic depletion occurring over a long time period of ~10 Ma (the time interval inferred
531 between the deposition of the Xiaolaihe and Taiyanggou BIFs).

532 Given the assumption that the QGB intra-arc basin was likely a restricted basin and thus had limited
533 iron supply from bulk global seawater, magnetite in the subsequently deposited Xiadianzi sulfide-

534 bearing BIF should also have inherited the negative $\delta^{56}\text{Fe}$ value. However, the consistently positive
535 $\delta^{56}\text{Fe}$ values for magnetite in the sulfide-bearing BIFs (Fig. 6A) are at odds with this assumption.
536 Meanwhile, coexisting pyrite in these samples, on the contrary, display negative $\delta^{56}\text{Fe}$ values. This
537 suggests that the isotopic compositions of both pyrite and magnetite were not re-equilibrated after
538 deposition, in which case pyrite is predicted to have higher $\delta^{56}\text{Fe}$ values (Polyakov et al., 2007), and
539 are reflective of primary features. In this respect, the positive $\delta^{56}\text{Fe}$ values for magnetite in these
540 sulfide-bearing BIFs, in combination with their elevated LREE abundances, more positive Eu
541 anomalies and mantle-like $\varepsilon\text{Nd}(t)$ values (Peng et al., 2018a, b), imply that the water column in the
542 QGB intra-arc basin was significantly overprinted by the coeval VMS-related hydrothermal vents
543 before the deposition of the Xiadianzi sulfide-bearing BIF. These hydrothermal vents must have
544 changed the chemical composition of the seawater (e.g., Nd isotope and REEs) by injecting
545 significant hydrothermally sourced iron (Fe(II)) with unfractionated Fe isotope values.

546 *Atmospheric sulfur in the Neoproterozoic QGB basin:* At first glance, the very limited range of $\delta^{34}\text{S}$
547 values (-3.36 to +1.61 ‰, Table 2) for pyrite in the QGB VMS and BIF ore samples, following
548 established genetic models (e.g., Franklin et al., 2005; Bekker et al., 2010), would indicate a purely
549 igneous source of sulfur for their formation. However, sulfate concentrations in Archean seawater
550 were very low (Canfield, 2001; Crowe et al., 2014), giving very limited sulfur isotope fractionations
551 during sulfate reduction (Canfield et al., 2000; Habicht et al., 2002; Farquhar et al., 2010). Thus, our
552 $\delta^{34}\text{S}$ data alone do not unambiguously constrain the sulfur source for our samples. It has been
553 proposed that additional information can be provided by also considering variability amongst minor
554 sulfur isotopes, particularly in terms of $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values, because of the mass-independent
555 fractionation (MIF) of sulfur isotopes that characterizes Archean sulfur reservoirs (e.g., Bekker et al.,
556 2009; Farquhar et al., 2010; Jamieson et al., 2013). Moreover, Archean MIF sulfur isotopic
557 compositions can be retained during metamorphism, subduction and arc magmatism (e.g., Muller et
558 al., 2017; Selvaraja et al., 2017). Data from diamond inclusions (Farquhar et al., 2002), modern
559 Pacific Ocean island basalts (Cabral et al., 2013) and Proterozoic orogenic gold deposits (Laflamme
560 et al., 2018) all indicate that Archean S-MIF signatures can be preserved in various environments and
561 even at extremely high temperatures (> 1300°C). In this respect, the S-MIF anomalies in our samples
562 are likely reflective of their primary geochemical features, rather than being the result of subsequent
563 processes.

564 Sulfur isotopic data for pyrite from the QGB BIF and VMS ores define a $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ slope of -1.1
565 ± 0.3 (Fig. 7A) at a 95% confidence level ($R^2 = 0.53$, $p < 0.01$). Although the uncertainty is relatively
566 large due to the small size of the measured $\Delta^{36}\text{S}$ values, the estimated slope of -1.1 is close to the
567 ratios measured in pre-2.3 Ga sedimentary rocks (approximately -0.9; Farquhar et al., 2000; Kaufman
568 et al., 2007) and those exhibited by laboratory experiments of SO_2 photolysis ($\Delta^{36}\text{S}/\Delta^{33}\text{S} = -1.1$ at
569 193 nm; Farquhar et al., 2001), but is statistically distinct from the canonical sulfur mass-dependent
570 fractionation (S-MDF) slope of approximately -7 (Ono et al., 2006; Johnston, 2011). Moreover, the
571 non-zero $\Delta^{33}\text{S}$ values measured here (~ 10 times larger than the external reproducibility) are associated
572 with relatively small $\delta^{34}\text{S}$ ranges (Fig. 6B). These combined characteristics cannot be explained by
573 MDF during either microbial sulfate reduction (Johnston et al., 2011) or mixing (Ono et al., 2006),
574 both of which require substantial changes in $\delta^{34}\text{S}$ to account for comparable changes in $\Delta^{33}\text{S}$ values.
575 In addition, similar cases of small S-MIF anomalies have been reported for Mesoarchean pyrite
576 samples (Farquhar et al., 2007) and modern subsurface fracture waters (Li et al., 2016). Consequently,
577 we conclude that the observed S-MIF signature in the QGB BIF and VMS ores are of atmospheric
578 photochemical origin, similar to ~ 2.7 Ga VMS deposits of Canada and Western Australia (e.g.,
579 Jamieson et al., 2013; Chen et al., 2015; Sharman et al., 2015). A detailed examination of the potential
580 mechanisms for this small S-MIF anomaly recorded in Neoproterozoic marine sediments is beyond the
581 scope of the current study, but should provide a critical target for future work.

582 Negative $\Delta^{33}\text{S}$ values measured in our samples (Table 2) are most likely indicative of the
583 incorporation of sulfur derived from the reduction of seawater sulfate via thermochemical (TSR)
584 and/or bacterial sulfate reduction (BSR) and the subsequent formation of sulfide minerals in the water
585 column and/or sediment porewaters. A negative $\Delta^{33}\text{S}$ signature is characteristic of oxidized species
586 (i.e., SO_4^{2-}) in the Neoproterozoic hydrosphere, as the elemental sulfur (i.e., S^0) of SO_2 photolysis
587 reactions would have positive $\Delta^{33}\text{S}$ values (Farquhar et al., 2000, 2001; Pavlov and Kasting, 2002).
588 By extension, the presence of non-zero $\Delta^{33}\text{S}$ values in our samples also suggests that the fractionated
589 sulfur isotopes were not significantly eliminated by dilution or re-mixing (e.g., Ono et al., 2003;
590 Zahnle et al., 2006) during transport from their production site in the atmosphere to the QGB intra-
591 arc basin. The reduction of seawater sulfate usually plays a major role in the formation of sulfides in
592 modern VMS deposits and sediments (e.g., Franklin et al., 2005; Seal, 2006; Shanks, 2014), thus it is
593 possible that sulfate in the Archean hydrosphere would be similarly incorporated into pyrite forming

594 within VMS and BIF deposits at that time, even though sulfate levels in the Archean ocean were much
595 lower than they are in the modern ocean (Habicht et al., 2002; Lyons and Gill, 2010).

596 *Paleoenvironmental conditions in the QGB depositional environment*

597 *Ocean redox chemistry at the end of the Neoarchean:* Rare earth element (REE) and yttrium (Y)
598 systematics in BIFs have long been used as tools to explore the evolution of marine geochemistry
599 (e.g., Bau and Dulski, 1996; Bolhar et al., 2005; Slack et al., 2007; Planavsky et al., 2010). Cerium
600 anomalies relative to average crustal sediments can reveal important insights into ocean redox
601 conditions (Byrne and Sholkovitz, 1996; Bau and Dulski, 1999), while ranges in Y/Ho and shale-
602 normalized light to heavy REE (LREE/HREE) ratios can provide further constraints on oceanic redox
603 conditions (Bau, 1991; Byrne and Sholkovitz, 1996). As documented in previous studies (Peng et al.,
604 2018a, b), the absence of Ce anomalies and monotonous LREE-depleted REE+Y (REY) patterns
605 recorded across the three BIF units of the QGB, suggest a chemically homogeneous water column
606 with minimal oxygen content during BIF genesis. However, considering that similar REY features
607 have been extensively identified within Archean BIFs worldwide (e.g., Frei and Polat, 2007;
608 Planavsky et al., 2010), the above conclusion, to a large extent, remains a qualitative description.

609 In this regard, experimental studies have modeled the amount of oxygen required to produce certain
610 degrees of Fe isotope fractionation between Fe(II)_{aq} and Fe(III) oxides during partial oxidation
611 processes in the photic zone (e.g., Czaja et al., 2012, 2013). Although previous studies suggested that
612 photoferrotrophic bacteria are possible oxidants for Fe(II) oxidation (Konhauser et al., 2002; Croal et
613 al., 2004; Kappler and Newman, 2004; Kappler et al., 2005) in Archean seawater, the possible
614 existence of cyanobacteria as early as ca. 3.0 Ga (Crowe et al., 2013; Planavsky et al., 2014) and the
615 widespread O₂-rich niches between 2.7 and 2.5 Ga (e.g., Wille et al., 2007; Reinhard et al., 2009;
616 Kendall et al., 2010; Czaja et al., 2012) make oxygenic photosynthesis another viable oxidative
617 mechanism for Fe(II) oxidation and isotope fractionation. Thus, the above approach has been used to
618 place quantitative constraints on O₂ concentrations in surface waters during BIF deposition (e.g., Li
619 et al., 2013; Busigny et al., 2017, 2018). Similarly, the Fe isotope signature of Fe oxides in the
620 Xiaolaihe silicate BIF may allow estimation of the O₂ content of QGB seawater.

621 The consistently positive $\delta^{56}\text{Fe}$ values (0.48‰ to 0.69‰) recorded in magnetite from the Xiaolaihe
622 silicate BIF are compatible with Fe(II)_{aq} oxidation under oxygen-limited conditions, assuming
623 deposition from an iron reservoir controlled by hydrothermal sources. However, as discussed above,

624 magnetite in the QGB BIFs was likely formed from reactions between $\text{Fe}(\text{OH})_3$ and $\text{Fe}(\text{II})_{\text{aq}}$ of
625 hydrothermal origin (i.e., $2\text{Fe}(\text{III}) + \text{Fe}(\text{II})_{\text{aq}} \rightarrow \text{Fe}_3\text{O}_4$ (1)). This means that the $\delta^{56}\text{Fe}$ value of
626 magnetite is not exactly equal to that for the primary $\text{Fe}(\text{OH})_3$ particle, although the similar $\delta^{56}\text{Fe}$
627 values for magnetite and hematite from the same samples have led researchers to conclude that both
628 minerals in BIFs tend to record the isotopic composition of the precursor ferric minerals (Johnson et
629 al., 2003). In this study we try to constrain the $\delta^{56}\text{Fe}$ values for the precursor $\text{Fe}(\text{OH})_3$ in the Xiaolaihe
630 silicate BIF by assuming the $\text{Fe}(\text{II})_{\text{aq}}$ needed in the formation of magnetite was derived entirely from
631 hydrothermal origin. The aim of this effort is on one hand to facilitate comparison with previous
632 studies, and on the other hand to provide a constraint on O_2 content in the QGB surface seawater.

633 The isotopic composition of hydrothermal $\text{Fe}(\text{II})$ has not varied significantly over Earth's history,
634 and in the Neoproterozoic was probably similar to modern seafloor hydrothermal vents, with $\delta^{56}\text{Fe}$ values
635 around 0‰ (e.g., Beard et al., 2003; Johnson et al., 2008). In this respect, taking $\delta^{56}\text{Fe}$ value of 0‰
636 for the hydrothermal member we can estimate (based on reaction (1)) that primary ferrihydrite in the
637 Xiaolaihe BIF had $\delta^{56}\text{Fe}$ values between 0.72‰ and 1.04‰. This result is within the range (as large
638 as 3‰) for observed and theoretically calculated isotope fractionations between coexisting $\text{Fe}(\text{III})$ and
639 $\text{Fe}(\text{II})_{\text{aq}}$ species during partial oxidation processes (e.g., Welch et al., 2003; Anbar et al., 2005).

640 Using the previously developed dispersion-reaction modes for $\text{Fe}(\text{II})$ oxidation (Czaja et al., 2012;
641 Li et al., 2013), we can estimate the concentration of dissolved oxygen in the surface ocean. This
642 model predicts that under relatively high O_2 levels in the photic zone ($> 1 \mu\text{M}$), $\text{Fe}(\text{II})_{\text{aq}}$ is completely
643 oxidized at the redox boundary and produces $\text{Fe}(\text{OH})_3$ precipitates with $\delta^{56}\text{Fe}$ values around 0‰ (Fig.
644 7B). By contrast, under low O_2 contents $\text{Fe}(\text{II})_{\text{aq}}$ is only partially oxidized, with the highest $\delta^{56}\text{Fe}$
645 values expected in ferrihydrite particles formed under the lowest O_2 content (Fig. 7B). According to
646 this model, the extremely positive $\delta^{56}\text{Fe}$ value of $\sim 2.2\%$ measured for ferruginous chert in the Mapepe
647 Formation, South Africa, suggests that the O_2 content of the 3.2 Ga surface ocean was lower than 10^{-4}
648 $\mu\text{mol/L}$ (Busigny et al., 2017), whereas the unfractionated $\delta^{56}\text{Fe}$ value of $\sim 0\%$ for hematite
649 precipitates in 2.3-1.7 Ga marine sediments (Planavsky et al., 2012) likely indicates that O_2
650 concentrations in the photic zone were higher than $10^{-2} \mu\text{mol/L}$ (Fig. 7B). The estimated $\delta^{56}\text{Fe}$ values
651 of 0.72-1.04 ‰ for primary ferrihydrite in the Xiaolaihe silicate BIF lie between the ranges for the
652 Mapepe ferruginous chert and the post-GOE hematite precipitates, and indicate that the O_2 content of
653 the ~ 2.57 Ga QGB surface ocean was between 10^{-4} and $10^{-3} \mu\text{mol/L}$ (Fig. 7B). This value is

654 particularly low and provides compelling evidence for widespread anoxic conditions at the end of the
655 Neoproterozoic, with low O₂ in shallow waters of the photic zone.

656 The documented anoxic, Fe(II)-rich seawater environment in the QGB basin is further supported
657 by the negative Fe isotope compositions of pyrite in the Xiadianzi sulfide-bearing BIF (Table 2),
658 whereby the most likely scenario to produce these $\delta^{56}\text{Fe}$ values is kinetic isotope fractionation
659 associated with pyrite formation in an iron-rich aqueous system. Experimental studies have shown
660 that a depletion of -2.2‰ in pyrite can be produced during kinetic isotope fraction associated with
661 pyrite formation in an anoxic, iron-rich aqueous system (Guilbaud et al., 2011). Alternatively, it is
662 possible that the negative pyrite $\delta^{56}\text{Fe}$ values were caused by DIR during diagenesis (e.g., Johnson et
663 al., 2008; Heimann et al., 2010). However, in this study two independent observations argue against
664 the latter hypothesis. First, in a closed system, which is similar to the case after very early diagenesis,
665 Fe isotope fraction during single-step bacterial reduction of Fe(III) (oxyhydr)oxides with an initial
666 $\delta^{56}\text{Fe}$ value of 0‰ is unlikely to produce Fe(II) with $\delta^{56}\text{Fe}$ less than -1.3‰ (Johnson et al., 2004;
667 Crosby et al., 2007), let alone situations for the Xiadianzi sulfide-bearing BIF where initial $\delta^{56}\text{Fe}$
668 values of the primary Fe(III) (oxyhydr)oxides are positive (the coexisting magnetite in the sulfide-
669 bearing BIFs have $\delta^{56}\text{Fe}$ values of 0.79-1.04 ‰, Table 2). Second, biological processes are expected
670 to produce pyrite with locally highly variable negative $\delta^{56}\text{Fe}$ values, depending on the extent of Fe(III)
671 reduction and Fe(II) reoxidation (Rouxel et al., 2005). Our analyses do not show large variability
672 between individual samples (Table 2) and suggest a common source of Fe(II).

673 *Localized sulfidic environment influenced by hydrothermal activity:* It is well established that some
674 primary seawater geochemical characteristics can be preserved in VMS ores, including sulfate
675 minerals, as well as sulfur and iron isotope compositions (e.g., Franklin et al., 2005; Huston et al.,
676 2010). The absence of sulfate minerals and limited $\delta^{34}\text{S}$ variability (0.11-1.61‰, Table 2) in all types
677 of sulfide ores of the Hongtoushan VMS deposit and its Archean counterparts (e.g., Huston et al.,
678 2010; Farquhar et al., 2010; Jamieson et al., 2012) are a strong indicator of low sulfate in coeval
679 seawater. This is in line with the anoxic, ferruginous environment proposed for the Neoproterozoic QGB
680 intra-arc basin. However, it is noteworthy that the near-zero $\delta^{56}\text{Fe}$ values (-0.58‰ to 0.51 ‰, Table
681 2) identified in our bedded VMS ores are markedly different from sedimentary pyrite formed in an
682 anoxic, Fe(II)-rich water column. In this respect, our new Fe isotope record may suggest that redox
683 conditions of the QGB bottom seawater were more complex, at least during the deposition of the

684 bedded VMS ores.

685 With a few exceptions, studies of Fe isotope compositions of sedimentary pyrite in both Proterozoic
686 and Phanerozoic black shales and/or organic-rich sediments have revealed near-zero or slightly
687 positive $\delta^{56}\text{Fe}$ values (e.g., Matthews et al., 2004; Rouxel et al., 2005; Johnson et al., 2008). It is
688 presumed that in such sediments, with either euxinic conditions in the water column, or abundant
689 sulfide production in sediment porewaters, most reactive Fe(II) is transformed to pyrite, minimizing
690 the extent of Fe isotope fractionation (Butler et al., 2004; Johnson et al., 2004). Accordingly, we
691 hypothesize that the limited Fe isotope variability in the QGB bedded VMS ores is linked to the
692 presence of sulfide, in which case complete precipitation of $\text{Fe(II)}_{\text{aq}}$ as pyrite near hydrothermal vents
693 limited Fe isotope fractionation. Nevertheless, the accumulation and subsequent deposition of a large
694 amount of iron in the relatively shallow part of the QGB intra-arc basin (i.e., the Taiyanggou and
695 Xiadianzi BIFs) indicates that this sulfidic environment was localized. In other words, QGB seawater
696 remained dominantly anoxic and ferruginous at ~ 2.55 Ga, although transient build-up of sulfide may
697 have occurred in relatively localized areas of the deep ocean due to hydrothermal activity.
698 Nevertheless, this short-lived sulfidic depositional environment could have been conducive to the
699 preservation of the sulfide ores (e.g., Rye et al., 1984).

700 In conclusion, anoxic and ferruginous conditions were pervasive in the Neoproterozoic QGB intra-arc
701 basin, with some localized areas experiencing transient or persistent sulfidic conditions depending on
702 the intensity of hydrothermal activity. Such conditions would have resulted in the continuous
703 accumulation of hydrothermally-sourced $\text{Fe(II)}_{\text{aq}}$ in seawater, but would also have led to the titration
704 of $\text{Fe(II)}_{\text{aq}}$ in local sulfidic water near seafloor hydrothermal vents, to form the bedded VMS ores.

705 *Depositional processes and mechanisms in the QGB VMS-BIF metallogenic association*

706 *Hydrothermal circulation in the VMS ore-forming system:* Systematic variations in the magnitude of
707 $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$ and $\delta^{56}\text{Fe}$ values for pyrite in different types of VMS ores enable the development of a
708 conceptual framework for hydrothermal circulation processes in the Hongtoushan VMS deposit.
709 Pyrite in the massive VMS ores exhibit near-zero $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ values (Table 2) and, therefore, are
710 considered to have a dominantly igneous sulfur source. Moreover, given that these ores have simple
711 mineral assemblages and lack sulfur isotope fractionations that accompany degassing of intrusions
712 and aluminous alteration common to assemblages associated with magmatic fluids (e.g., Rye et al.,
713 1992; Rye, 2005), the inferred igneous sulfur was more likely leached from volcanic rocks in the

714 underlying, deep reaction zone (e.g., Huston et al., 2010). This is generally consistent with the
715 situation for pyrite in the disseminated to stockwork ores, which also have $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ values close
716 to 0‰. Similarly, sulfides in stringers and massive lenses of Archean VMS deposits generally have
717 values for $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ near zero and are, therefore, interpreted to have formed with insignificant
718 sulfur contributions from seawater sulfate (e.g., Jamieson et al., 2013; Sharman et al., 2015; Chen et
719 al., 2015). In sum, the presence of chalcopyrite precipitated within sulfide pore spaces (Fig. 4F) and
720 sphalerite replacement by chalcopyrite (Fig. 4E and 4G) in both massive and disseminated
721 Hongtoushan VMS ores, in combination with their essentially magmatic sulfur isotope signature and
722 unfractionated Fe isotope composition (Fig. 6A), indicates they were likely formed during the high
723 temperature (>300 °C) stages (e.g., Large, 1992). In this case, the sulfides were precipitated from the
724 high temperature fluids below the seafloor, where the system was likely devoid of the entrapment of
725 seawater sulfate with a S-MIF signature.

726 By contrast, pyrite in some of the Hongtoushan bedded VMS ores that deposited on the seafloor
727 are distinguished by a S-MIF signature (Fig. 7A), indicating the influx of seawater-derived sulfur.
728 Therefore, there appears to have been a trend toward a more seawater-dominated sulfur source within
729 the hydrothermal system that formed these ores, when compared to the disseminated and/or massive
730 VMS sulfides. This is in line with the small positive and negative variability in $\delta^{56}\text{Fe}$ values for pyrite
731 in the bedded ores (Fig. 6A) that was interpreted to have been the result of quantitative scavenging
732 of $\text{Fe(II)}_{\text{aq}}$ discharged from hydrothermal fluid by reduced sulfur species (S^0 and HS^-) in localized
733 sulfidic seawater.

734 Collectively, the above observations are compatible with the mixing-cooling history of ore
735 solutions documented elsewhere in ancient VMS deposits and modern black smoker chimneys (e.g.,
736 Franklin et al., 2005; Huston et al., 2010; Hannington, 2014). As the hydrothermal system develops,
737 the ore solutions would have been dominated by deeper and hotter fluids with igneous sulfur and
738 other elements (e.g., Cu and Fe) sourced from deeply seated leaching. Near-zero $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$ and $\delta^{56}\text{Fe}$
739 values would most likely characterize sulfur and iron in ore-forming fluids initially trapped during
740 the formation of the Cu-rich stringer zone and sulfide mounds, as evidenced by the disseminated and
741 massive sulfides in the Hongtoushan VMS deposit. The bedded ores with more negative $\Delta^{33}\text{S}$ values
742 that typify seawater sulfate were interpreted to have been formed by the unfocused, shallow
743 circulation of heated seawater (e.g., Gemmill and Fulton, 2001) or by the mixing of the cooling

744 hydrothermal fluids with seawater in the shallow parts of the hydrothermal system (e.g., Gemmell
745 and Large, 1992; Large, 1992). In both cases, further scavenging of the $\text{Fe(II)}_{\text{aq}}$ in localized sulfidic
746 seawater would have finally eliminated the Fe isotope fractionation caused by pyrite deposition.

747 The above scenario, which readily explains the multiple sulfur and iron isotope data, is also
748 supported by the metal zoning in the Hongtoushan VMS deposit. Although multiple stages of
749 deformation have obscured the primary characteristics of the sulfide zones in Hongtoushan VMS
750 deposit, the massive and disseminated ores are characterized by relatively high Cu contents of 2.3-
751 6.6 % and 1.1-1.7 %, respectively, as well as elevated $\text{Cu}/(\text{Cu}+\text{Zn})$ ratios of 0.52-0.59 and 0.66-0.75,
752 respectively (Table 1). By comparison, the bedded ores tend to show variable and low concentrations
753 of Cu (0.07-1.2%, average of 0.7%) and consistently low $\text{Cu}/(\text{Cu}+\text{Zn})$ ratios (0.1-0.26). Generally,
754 most VMS deposits are compositionally zoned with Cu-rich sulfides being most abundant in the
755 interiors and in underlying stockwork zones of the deposits, and Zn- and Pb-rich sulfides being
756 deposited at the outer margins (e.g., Hannington, 2014). This is because the thermal regime exerts a
757 critical control on metal transport and deposition within the VMS deposits, due to a strong
758 temperature-solubility relationship for the major ore minerals (e.g., Large, 1992).

759 Accordingly, at the low temperature (<280 °C) stage (e.g., Campbell et al., 1984; Large, 1992),
760 hydrothermal fluids in the Hongtoushan deposit are expected to have been sourced from an unfocused,
761 shallow circulation hydrothermal system that carried significant Fe and Zn. Discharge of these fluids
762 onto the seafloor would have formed the early porous sulfide mound and bedded sulfides. However,
763 as observed in the Hongtoushan bedded VMS ores, significant Cu was not transported to the seafloor
764 at this stage due to its lower solubility. Continued input of high temperature (>300 °C) fluids from a
765 deep intensifying hydrothermal convection system (e.g., Gemmell and Fulton, 2001) would have
766 given rise to the precipitation of chalcopyrite in the stringer zone and in the basal part of the early
767 sulfide mound. Meanwhile, the replacement of sphalerite in the outer boundary of the mound by
768 chalcopyrite at this stage (i.e., the ‘zone refining’) might also have formed some of the Cu-rich ores.
769 As described above, the Cu-poor bedded ores could also be a late-stage product that precipitated
770 during the waning period of hydrothermal activity from the cooling (200-250 °C) fluids (e.g., Large,
771 1992). Thus, the metal zoning in the Hongtoushan VMS deposit is interpreted as the result of fluid
772 dynamic processes, with the massive and disseminated Cu-rich sulfides formed within a high
773 temperature hydrothermal system, and the bedded Zn-rich ores deposited at the low temperature

774 stages of ore formation. This interpretation is compatible with the model of formation of different
775 types of ores within the Hongtoushan VMS deposit described above, and suggests that multiple sulfur
776 and iron isotopes may be useful as proxies for reconstructing hydrothermal circulation in Archean
777 VMS ore-forming deposits.

778 *Formation mechanism of the Neoproterozoic VMS-BIF metallogenic association:* The coupling of the
779 previously documented tectonic evolution scenario (Peng et al., 2019) with new geological,
780 geochemical and isotopic systematics permits us to reconstruct a potential depositional model (Fig.
781 8) that provides new insight into the possible mechanism of formation of the Neoproterozoic QGB VMS-
782 BIF metallogenic association. The system tract for this association begins with the initial rift of a
783 continental arc and the subsequent accumulation of hydrothermally sourced Fe(II) within the rifted
784 intra-arc basin. Such a geodynamic process is supported by the secular change in lithologic sequences
785 in the QGB (Peng et al., 2019), which commences with the subduction-related basalts (tholeiitic and
786 transitional with negative Nb anomalies) in the lower SF, and grades upward into the polycyclic
787 bimodal suites (interlayered FI- to FII-type dacites and N-MORB-type basalts) that are indicative of
788 an extensional tectonic environment in the upper SF and the HF. Significantly, the dominance of FI-
789 type dacite (Peng et al., 2015, 2019) within the bimodal suite of the upper SF indicates a high pressure
790 (>0.75 Gpa) and low temperature (<750 °C) melting environment at deep crustal levels (~50 km)
791 (Hart et al., 2004) for the generation of this rock. This environment, in most cases (see Pilote and
792 Piercey, 2018 for a possible exception), is unsuitable for the development of high-temperature heat
793 sources and extensional faults that are necessary for VMS mineralization (e.g., Piercey, 2011, Huston
794 et al., 2014). It is, therefore, assumed that during this stage only diffuse, low temperature
795 hydrothermal vents enriched in Fe(II), Mn(II) and Si(IV) (e.g., Hein et al., 2008) developed at the
796 seafloor (Fig. 8A).

797 The anoxic and ferruginous feature of water column in the Neoproterozoic QGB intra-arc basin (Peng
798 et al., 2018a, b; this study) would then allow for dissolved Fe(II) to accumulate in the deep water and
799 periodically be moved (via upwelling) to shallower parts of the basin (Fig. 8A). Whether the Fe(II)
800 was directly oxidized by photoferrotrophs or indirectly via O₂ produced by cyanobacteria is unknown.
801 If the former, then the water column would have had exceedingly low dissolved O₂ concentration.
802 Yet, even assuming interaction with O₂ produced by oxygenic photosynthesis was the dominant
803 mechanism of Fe(II) oxidation in Neoproterozoic oceans (Cloud, 1973; Klein and Beukes, 1989), the Fe

804 isotope record supports the presence of low concentrations of dissolved O₂ (10⁻⁴-10⁻³ μmol/L) to form
805 primary ferrihydrite of the Xiaolaihe silicate BIF. Notably, the paradox between the proposed
806 biological Fe(II)_{aq} oxidation and the conspicuous absence of photosynthetic biomass produced during
807 iron oxidation (i.e., organic matter) from BIFs of the QGB might be reconciled by the high silica
808 content in Archean seawater (e.g., Jones et al., 2015). The laboratory experiments and modeling of
809 Thompson et al. (2019) has revealed that in the presence of silica, photoferrotroph cell surfaces repel
810 iron (oxyhydr)oxides. Accordingly, this repulsion would separate biomass from ferric iron and would
811 eventually lead to deposition of BIFs lean in organic matter (Thompson et al., 2019), similar to that
812 observed in BIFs of the QGB.

813 Subsequent rifting of the QGB intra-arc basin, as evidenced by the significant FII-type dacites in
814 bimodal volcanic suites of the overlying HF (~100 km², Zhai et al., 1985; Shen et al., 1994; Peng et
815 al., 2019), would have created the necessary conditions (e.g., Piercey, 2011; Huston et al., 2014) for
816 seafloor hydrothermal venting. The presence of chalcopyrite in the Hongtoushan VMS ores formed
817 at this stage implies that the temperature of the fluid flow was higher than 300 °C (e.g., Large, 1992).
818 Despite the formation of early seafloor sulfide accumulations, extensive submarine hydrothermal
819 processes in the deep part of the QGB basin would also inject considerable iron (δ⁵⁶Fe~0‰) and
820 sulfur (Δ³³S = 0‰) into the water column (Fig. 8B). Meanwhile, it is conceivable that a dynamic
821 chemocline (upper anoxic and ferruginous versus lower sulfidic) would have developed in some
822 restricted sub-basins (Fig. 8B), where the local sulfur fluxes were large enough to completely
823 scavenge aqueous Fe(II) within these basins (e.g., Tornos et al., 2015). Deposition of iron sulfide and
824 minor sphalerite at the early low temperature or the latter waning period of hydrothermal activity in
825 these sub-basins would have formed the bedded sulfide sediments (with δ⁵⁶Fe values of -0.58~0.51‰)
826 that represent the distal part of the Hongtoushan VMS deposit (Fig. 8B). By contrast, biological
827 oxidation of Fe(II)_{aq} in the residual water column in the shallow part of the QGB basin during volcanic
828 intervals was responsible for the formation of ⁵⁶Fe-depleted ferrihydrite in the Taiyanggou and
829 Xiadianzi silicate BIFs (Fig. 8B). Significantly, the very long residence time of iron inferred for
830 anoxic, ferruginous conditions (~10⁶ years, Johnson et al., 2003) would make it difficult to rapidly
831 change the iron isotope composition of the above ⁵⁶Fe-depleted residual water column. Therefore, the
832 positive δ⁵⁶Fe values recorded in magnetite of the Xiadianzi sulfide-bearing BIF is strong evidence
833 for the onset of partial oxidation of hydrothermal iron (δ⁵⁶Fe ~ 0‰) in the shallow part of the QGB

834 basin (Fig. 8C).

835 We discount hydrothermal sulfur for the formation of Xiadianzi sulfide-bearing BIF because it
836 would have precipitated proximal to deep-sea vents under the anoxic, ferruginous conditions (e.g.,
837 Jamieson et al., 2013) prevailing throughout the QGB basin. Accordingly, the occurrence of pyrite
838 with negative $\delta^{34}\text{S}$ values (-2.12 to -3.36 ‰) in the sulfide-bearing BIFs likely indicates that BSR or
839 TSR (e.g., Shen et al., 2001; Ueno et al., 2008) occurred under sulfate-limited conditions. In addition,
840 given the distinct S-MIF signal preserved therein, the deposition of sulfide-bearing BIF at this stage
841 was likely related to an increase in sulfur flux to the QGB seawater caused by the UV-mediated
842 photolysis of SO_2 from earlier subaerial volcanisms (Fig. 8C).

843 **Conclusions**

844 On the basis of petrographic, geochemical and isotopic lines of evidence, formation of the
845 Neoproterozoic QGB VMS-BIF metallogenic association is best explained by mineralization within a
846 rifted intra-arc basin characterized by anoxic, ferruginous seawater. Positive iron isotope signatures
847 for magnetite in the Xiaolaihe silicate BIF imply low oxygen levels in the surface water (10^{-4} to 10^{-3}
848 $\mu\text{mol/L}$), whereas the narrow range of $\delta^{56}\text{Fe}$ values for pyrite in the Hongtoushan bedded VMS ores
849 indicates that they were deposited in localized sulfidic sub-basins in deeper water. Significant change
850 in the QGB water column iron isotope composition supports the assumption that the VMS-related
851 hydrothermal system contributed significant $\text{Fe(II)}_{\text{aq}}$ to the seawater. S-MIF anomalies in pyrites of
852 the QGB VMS and BIF are a clear indication that seawater sulfur originating from SO_2 photochemical
853 reactions contributed to the formation of these deposits. Moreover, both multiple sulfur and whole-
854 rock geochemistry data support the published conceptual model for a relatively high proportion of
855 seawater sulfate during the deposition of Hongtoushan bedded VMS ores. It is anticipated that the
856 results of this study will place direct constraints on the origin of this typical VMS-BIF co-occurring
857 association.

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1400

1401 **Figure Captions**

1402 **Fig. 1.** A. Tectonic subdivision of the North China Craton (NCC), showing locations of the QGB and
1403 major Precambrian BIF and VMS deposits (modified from Zhao et al., 2005). Note the inset shows
1404 the location of the NCC. B. Geological sketch of the QGB (modified from Shenyang Institute of
1405 Mineral Geology, 2006; Peng et al., 2019), showing regional geological and Archean BIF and VMS
1406 deposits in this area. C. Stratigraphic column of the QGB (modified from Yu, 2006; Zhang, 2014;
1407 Peng et al., 2019), showing formation and member names of different rock assemblages; reported
1408 ages for meta-dacites from each group are provided.

1409

1410 **Fig. 2.** A. Geologic map of the Hongtoushan mining area (modified from Yu et al., 2015), showing
1411 locations of the Hongtoushan VMS deposit and Taiyanggou BIF, together with the No. 14 prospecting
1412 line for the former. B. Simplified cross section of the above No. 14 prospecting line (after Deng,
1413 1994), showing relationship between the orebody and associated rocks, as well as rough locations for
1414 VMS ores incorporated in this study.

1415

1416 **Fig. 3.** Studied stratigraphic sections of the QGB BIF-bearing volcanic-sedimentary sequences
1417 (modified from sketch profiles of Peng et al., 2018b), note the inset shows the relative relationship of
1418 the Taiyanggou BIF and Hongtoushan VMS deposit. A-B. Photographs of the Xiaolaihe BIF showing
1419 the distribution of main orebody (A) and the conformable contact between BIF and associated biotite
1420 plagioclase gneiss (B). C-D. Outcrop photograph taken along strike from the Taiyanggou BIF (C)
1421 together with its drill core photo showing interbedded Fe-rich and Si-rich bands within the BIF (D).
1422 E-G. Field photos of the Xiadianzi BIF showing its N-S distribution as well as the typical silicate (F)
1423 and sulfide-bearing (G) BIFs in this area. The length of the pen on (C), (D), and (F) is 12 cm, while
1424 the coin is 2 cm in diameter on (G).

1425

1426 **Fig. 4.** Representative photographs and photomicrographs of sulfide ores from the Hongtoushan VMS
1427 deposit. A. Massive sulfide lens that has been significantly recrystallized, containing coarse grained
1428 (> 1 mm; rarely medium- to fine-grained) pyrite intergrown with pyrrhotite, chalcopyrite and
1429 sphalerite. B-C. Disseminated-stockwork mineralization in chloritized and silicified dacitic volcanic-
1430 volcanoclastic rocks, fine grained (0.1-1 mm) pyrite is distributed as disseminated grain (B) or sparse
1431 stringer (C). D. Bedded ore sample in strongly foliated rocks, where the dark bands are quartz,
1432 plagioclase and biotite, while the lighter bands (1- to 10-mm-thick) are mainly disseminated very fine
1433 grained (0.1-0.5 mm) pyrrhotite. E. Photomicrograph of typical pyrite (Py) porphyroblast in a matrix
1434 of chalcopyrite (Ccp), sphalerite (Sp), and pyrrhotite (Po) within massive sulfide, note the Sp was
1435 normally replaced by Ccp, while subordinate quartz (Qz), biotite (Bi) and plagioclase (Pl) are
1436 preserved as globules (reflected light). F. Photomicrograph showing chalcopyrite and minor
1437 pyrrhotite filling the fractures of coarse grained pyrite within a massive sulfide ore (reflected light).
1438 G. Photomicrograph of typical disseminated-stockwork ores, showing pyrite porphyroblasts and
1439 porphyroclasts scattered in a veinlet of sphalerite and chalcopyrite (reflected light), note the Sp was
1440 replaced by Ccp to form chalcopyrite disease textures. H-I. Transmitted light (H) and reflected light
1441 (I) views showing oriented, anhedral pyrrhotite grains and aggregates within the bedded ores, note
1442 silicate-rich bands of this type of ore are typically composed of unaltered quartz, biotite and

1443 plagioclase. The coin is 2 cm in diameter on B-D.

1444

1445 **Fig. 5.** Representative photographs and photomicrographs for the QGB BIFs. A. Silicate BIF from
1446 the Xiaolaihe area, note the fading iron- and silica-rich bands. B. Silicate BIF from the Xiadianzi area
1447 showing finely laminated, well-defined, alternating iron- and silica-rich bands. C. Sulfide-bearing
1448 BIF from the Xiadianzi area is composed of interbedded silica-, magnetite- and pyrite-rich layers. D-
1449 F. Transmitted light views showing the most typical texture and mineralogy of the silicate BIFs from
1450 the Xiaolaihe (D), Taiyanggou (E) and Xiadianzi areas, respectively. Qz: quartz, Mag: magnetite, Cpx:
1451 clinopyroxene, Opx: orthopyroxene, FA: ferroactinolite, Act: actinolite. G-H. Transmitted light (G)
1452 and reflected light (H) views of the sulfide-bearing BIF, note microcrystalline pyrite aggregates and
1453 magnetite grains are intergrown with within the magnetite-rich band, while subhedral to euhedral
1454 pyrite crystals aligned with bedding along the magnetite-rich layer. Py: pyrite, Cal: calcite. I.
1455 Reflected light view of the sulfide-bearing BIF showing rounded pyrite nodule among fine-grained
1456 magnetite grains and pyrite inclusions within coarse-grained magnetite. J. Backscattered electron
1457 (BSE) image of pyrite aggregate and pyrite recrystallization showing pyrite and magnetite grains with
1458 straight boundaries. The coin is 2 cm in diameter on C.

1459

1460 **Fig. 6.** A. Variations in $\delta^{56}\text{Fe}$ values for magnetite and pyrite samples as a function of stratigraphic
1461 levels in the QGB. NF: Nantianmen Formation, HF: Hongtoushan Formation, SF: Shipengzi
1462 Formation, XDZ: Xiadianzi, TYG: Taiyanggou, HTS: Hongtoushan, XLH: Xiaolaihe, Mag:
1463 magnetite, Py: pyrite. B. Multiple sulfur isotope data for pyrite from the QGB sulfide-bearing BIF
1464 and VMS ores. The mantle range of $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ values reference from Bekker et al. (2016); note
1465 the inset in B shows the frequency distribution of $\Delta^{33}\text{S}$ values for pyrite from the QGB VMS and BIF
1466 deposits. Errors for $\delta^{56}\text{Fe}$, $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ values are not shown on the plot for clarity, but were 0.07‰,
1467 0.13‰ and 0.007‰ (2SD), respectively.

1468

1469 **Fig. 7.** A. Plot of $\Delta^{36}\text{S}$ versus $\Delta^{33}\text{S}$ for mass independent data for the QGB pyrite samples, sulfides
1470 data have a diagnostic $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ slope of -1.1, consist with previously documented Archean MIF
1471 reference line (solid line), and distinctly different from the classic MDF slop of -7 (dashed line).
1472 Errors for $\Delta^{33}\text{S}$ values are not shown on the plot for clarity. B. Comparison between the possible $\delta^{56}\text{Fe}$
1473 values of primary Fe oxides (0.72‰ to 1.04‰) recorded in the Xiaolaihe silicate BIF and results of
1474 a dispersion-reaction modeling of the Fe(II) oxidation developed in previous studies (Czaja et al.,
1475 2012, 2013; Li et al., 2013). To facilitate comparison with reported data, this model was also
1476 calculated for a 200m and a 500m basin, and a range of Fe isotope fractionation between Fe(II) and
1477 Fe(III), from 2.5 to 4‰ (Wu et al., 2011). $\delta^{56}\text{Fe}$ values of \sim 2.2‰ for the 3.2 Ga Mapepe ferruginous
1478 chert are reference from Busigny et al. (2017), while the maximum $\delta^{56}\text{Fe}$ value of 0.19‰ for hematite
1479 in the 2.3-1.7 Ga marine sediments comes from Planavsky et al. (2012).

1480

1481 **Fig. 8.** Conceptual model illustrating depositional environment and process for the Neoproterozoic QGB
1482 VMS-BIF metallogenic association during different stages (A-C) in the QGB intra-arc basin

1483 (modified from Bekker et al., 2009; Farquhar et al., 2011). The inset in Fig. 8A shows the relative
1484 location of this metallogenic association. A. Partial oxidation of hydrothermal iron ($\delta^{56}\text{Fe}\sim 0\%$) in the
1485 photic zone of the basin leads to the deposition of the Xiaolaihe silicate BIF. B. Formation of the
1486 VMS deposit and silicate BIFs at different depths of the ^{56}Fe -depleted residual water column, note
1487 the seawater was significantly influenced by MIF sulfur components. C. Partial oxidation of aqueous
1488 Fe(II) ($\delta^{56}\text{Fe} \leq 0\%$) that was previously overprinted by the VMS-related hydrothermal vents at
1489 shallow part of the QGB basin, possibly with increased sulfur flux from earlier subaerial volcanism,
1490 to deposit the Xiadianzi sulfide-bearing BIF. Significantly, water column in the QGB basin remains
1491 anoxic and ferruginous throughout the whole VMS-BIF metallogenic process, although activities of
1492 high temperature vents during stage (B) might induce the colonization of sulfidic environment in
1493 some localized, deep-water sub-basins to form the bedded VMS ores.

1494

1495 **Table Captions**

1496 **Table 1** Whole-rock major and trace elements compositions of sulfide ores in the Hongtoushan VMS
1497 deposit.

1498

1499 **Table 2** Iron and multiple sulfur isotopic compositions of pyrite and magnetite grains from the VMS
1500 and BIF ore samples.

1501

1502 **Supplemental Material**

1503 **Table S1** Location, type, associated rocks and analyses contents of VMS and BIF ore samples
1504 incorporated in this study.

1505

1506 **Table S2** Measured values for reference materials (standards) incorporated into this study.