Article:

Yang, X, Mao, J, Poulton, SW orcid.org/0000-0001-7621-189X et al. (4 more authors) (2021) The origin of early-Paleozoic banded iron formations in NW China. Gondwana Research, 93. pp. 218-226. ISSN 1342-937X

https://doi.org/10.1016/j.gr.2021.02.008

The origin of early-Paleozoic banded iron formations in NW China

Xiuqing Yang[a,*], Jingwen Mao[a, b], Simon W. Poulton[c], Aiguo Dong[d], Ting Liang[a], Dachuan Wang[e], Xusheng Zhang[a]

[a] MOE Key Laboratory of Western China's Mineral Resources and Geological Engineering, School of Earth Science and Recourses, Chang'an University, Xi'an 710054, China
[b] MLR Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing 100037, China
[c] School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK
[d] Institute of Earth Sciences, China University of Geosciences (Beijing), Beijing 100083, China
[e] Institute of Mineralogy, Leibniz University Hannover, Hannover 30167, Germany

* Corresponding author at: School of Earth Science and Recourses, Chang'an University, No. 126 Yanta Road, Xi'an 710054, China.
Email address: xiuqing2008@126.com (X. Yang)

Abstract

There is growing evidence that the earliest Paleozoic ocean experienced fluctuations in ocean redox chemistry, with anoxic ferruginous conditions being a prevalent feature at certain times. However, the general absence of early Paleozoic banded iron formations (BIFs) means that direct supporting evidence for ferruginous conditions inferred from geochemical proxy data is currently limited. Here, we describe an early-Paleozoic BIF (Tiande No.2) from the late Silurian Habahe Group in Altay, NW China. The BIF is hosted in meta-volcano-sedimentary rocks, and is characterized by alternating iron-rich and silica-rich laminae. In addition to abundant magnetite and quartz, Fe-silicates (garnet and amphibole) are dominant minerals in the BIF. Like most earlier Precambrian examples, the BIF horizons are dominated by high Si and Fe contents, but also contain significant Al, Ti and rare earth element concentrations, consistent with a dominant chemical origin, but with significant terrigenous contribution. We observe slightly positive Eu anomalies (1.17 to 1.57) and low $\varepsilon_{Nd}(t)$ values (-4.2 to -0.8) in BIF samples, indicating a mixed seawater and submarine hydrothermal source for the iron. The BIF also generally displays negative Ce anomalies, and homogeneous and slightly negative $\delta^{56}Fe$ values. This suggests near-quantitative oxidation of dissolved Fe(II) from the water column, likely following upwelling into oxygenated surface waters as sea level decreased, in a region where the terrigenous input was low relative to the dissolved Fe^{2+} flux. The Tiande No.2 BIF is conformably bedded within schist, which also has high concentrations of Fe (up to 12.67 wt%), generally elevated Fe/Al ratios (>1.0), and no Ce anomaly, while magnetite in the schist has heavy and variable $\delta^{56}Fe$ values. This suggests that the schist precursor, which likely comprised a significant contribution from deposited marine sediment, was also deposited from ferruginous waters, but with only partial oxygenation of dissolved Fe^{2+} in a dominantly anoxic water column. The occurrence of this late Silurian BIF and associated ferruginous rocks provides new constraints on the nature of ocean redox chemistry at this time, and supports continued dynamic Fe cycling and at least intermittent ferruginous deeper water conditions in this location during the late Silurian.

Keywords: band iron formations, early-Paleozoic, Fe isotopes, ferruginous conditions, Altay

1. Introduction

Banded iron formations (BIFs) are iron-rich and siliceous chemical sedimentary rocks that precipitated from seawater throughout extended parts of the Precambrian era (Klein, 2005; Bekker et al., 2010; Konhauser et al., 2017). BIFs commonly contain distinctive mineral layers of variable thickness, including magnetite, hematite, chert, siderite, ankerite and other related minerals. The large volume of BIFs deposited in Archean and Paleoproterozoic strata, as well as in association with the Cryogenian glaciations of the later Neoproterozoic, suggest a close relationship with contemporaneous seawater redox conditions (e.g., Bekker et al., 2010; Cox et al., 2016).

Iron formations are generally not prevalent in the Mesoproterozoic (but see Canfield et al., 2018) or the Phanerozoic (Song et al., 2017), but recently, Li et al. (2018) reported evidence for Earth's 'youngest' BIF in the early Cambrian of Western China, while early Paleozoic BIFs have also been reported from Altay, NW China (Zhou et al., 2014; Ren, 2017). As with Precambrian BIFs (e.g., Bekker et al., 2010; Poulton and Canfield, 2011), the early Cambrian BIF provides direct evidence in support of inferences from geochemical data for ferruginous (anoxic, containing Fe^{2+}) oceanic conditions (Li et al., 2018) at certain times and localities in the early Paleozoic (e.g., Sperling et al., 2015; Och et al., 2013; 2016). However, while the early Cambrian BIF was likely deposited in deeper waters in association with hydrothermal activity (Li et al., 2018), the paucity of detailed reports of early Paleozoic BIFs precludes a robust understanding of their depositional and environmental history, as well as controls on the dominant source of iron.

Rare earth elements (REEs), combined with Nd and Fe isotopes, have the potential to trace the source and depositional mechanism of Phanerozoic BIFs, as well as shedding light on contemporaneous seawater redox evolution (e.g., Bekker et al., 2010; Konhauser et al., 2017). In particular, REEs, Nd isotopes and Fe isotopes are relatively unaffected by post-hydrothermal and even high-grade metamorphism (e.g., Mloszewska et al., 2012; Li et al., 2015). For example, most Precambrian BIFs commonly have a significant positive Eu anomaly and no Ce anomaly, suggesting a dominant hydrothermal contribution to their origin under anoxic seawater conditions (e.g., Bekker et al., 2010; Planavsky et al., 2010). A strong hydrothermal contribution is further supported by positive $\varepsilon_{Nd}(t)$ values (where $\varepsilon_{Nd}(t)$ describes the deviation of the $^{143}Nd/^{144}Nd$ ratio measured in a sample relative to the $^{143}Nd/^{144}Nd$ ratio in a chondritic uniform reservoir at formation age) (e.g., Cox et al., 2016; Konhauser et al., 2017). In contrast to REEs and Nd isotopes, variability in Fe isotope compositions in BIFs is related to the ferrous oxidation process (Dauphas et al., 2004). Therefore, the combined study of these tracers has the potential to shed new insight into the origin of Phanerozoic BIFs.

Recent work provides additional support for at least periodic ocean anoxia during the early Phanerozoic up until ca. 400 Ma, after which a significant rise in atmospheric oxygen (the Paleozoic Oxygenation Event, POE) to near-modern levels apparently coincided with more pervasively oxygenated oceans (e.g., Lenton et al., 2016; Wallace et al., 2017; Krause et al., 2018). Thus, the aforementioned early Paleozoic BIFs provide a prime opportunity to examine potential links to the contemporaneous redox state of seawater prior to the POE. Here, we utilize REEs, and Nd and Fe isotopes, to trace the origin of the late Silurian Tiande No.2 BIF in the Habahe Group, Altay, NW China. Our data provide new insight into both the genesis of early Phanerozoic BIFs, and the nature of contemporaneous seawater redox conditions.

2. Geological setting

The Chinese Altay is located in the southeastern part of the Altay Orogen, which is an important component of the Central Asian Orogenic Belt in NW China (Fig. 1). It is divided into five NW–trending tectono-stratigraphic terranes (Windley et al., 2002; Broussolle et al., 2019), namely North Altaishan, Northwest Altaishan, Central Altai, Qiongkuer-Abagong, and the South Altaishan terranes (Fig. 1). The region mainly comprises early Paleozoic volcanic, pyroclastic and (meta-)sedimentary rocks. The regional stratigraphy includes the Habahe Group, and the overlying Dongxileke, Kangbutiebao and Kalaerqisi formations (Broussolle et al., 2019). Voluminous granites were emplaced in the above strata, which can be divided into two stages with peaks at 400 Ma and 290 Ma (Yu et al., 2019).

The BIFs in the region are found in the Habahe Group on the southeast side of the Chinese Altay, and include the Tiande No.2 (the focus of this study), Yegenbulake, Qianghan and Keketielieke BIFs (Fig. 1) (Zhou et al., 2014; Ren, 2017). All of these BIFs are relatively small-scale with moderate total Fe contents (<30%). The BIFs have distinct magnetite-rich and quartz-rich laminae with minor Fe-silicates (e.g., garnet, chlorite, amphibole and biotite). Some magnetite crystals are Ti-rich, particularly in the Yegenbulake and Tiande No.2 BIFs. In addition, pyrolusite has been observed in the Yegenbulake BIF. Some BIFs have been altered by post-hydrothermal activity, but this is not the case for the Tiande No.2 BIF (Zhou et al., 2014; Ren, 2017).

The Habahe group predominantly consists of clastic sedimentary rocks (sandstone, siltstone and shale), volcanic rock and local limestones that have been strongly deformed and generally metamorphosed to greenschist facies, with local metamorphism up to lower amphibolite facies (Long et al., 2007; Dong et al., 2018). Previous studies have shown that the group experienced regional metamorphism in the middle Devonian (383–384 Ma) (e.g., Long et al., 2007; Dong et al., 2018), and the BIFs are hosted by these greenschist–amphibolite facies metamorphic rocks (e.g., schist and gneiss). The Habahe Group is considered to have formed in an active continental margin arc tectonic setting due to oceanic subduction in the early-Paleozoic (e.g., Long et al., 2007; Dong et al., 2018).

The Habahe Group was once assumed to have formed in the Proterozoic era (e.g., Windley et al., 2002). However, Long et al. (2007) reported detrital zircon ages from clastic rocks and magmatic zircon ages from migmatites of the group, and concluded that the Habahe Group was deposited between 463 Ma and 384 Ma. Recently, Dong et al. (2018) determined a youngest detrital zircon U–Pb age of 427 ± 13 Ma for the Habahe Group in the Qinghe region, while zircons in tonalite that intruded the Habahe Group gave a U–Pb age of 405 ± 3 Ma, suggesting a depositional age of 427–405 Ma. Furthermore, Ren (2017) reported a zircon U–Pb age for the wall rock (meta-volcanic rock) of the Yegenbulake BIF of 423.7 ± 4.1 Ma. Taken together, these data indicate that BIFs hosted in Habahe Group in Altay were deposited in the late Silurian.

With a total iron ore resource of less than 10 Mt, the Tiande No.2 iron deposit located ~45 km southeast of Qinghe town (46°36′N, 90°42′E) (Fig. 1). The BIF has a NW-strike at an angle of 315°, and persists for ~1500 m with a width of ~7 m (Fig. 2a). The BIF is stratiform and stratiform-like, and is hosted in biotite-quartz schist and biotite-amphibole schist, with a conformable contact with the wall rocks (Fig. 2b). The BIF comprises alternating iron-rich (black) and silica-rich (white) laminae (Fig. 2c-f). The iron-rich layers are dominated by magnetite, whereas the silica-rich part is mainly composed of quartz, garnet and amphibole (Fig. 2g and h). Minor biotite, hematite, plagioclase, ilmenite, and apatite are also observed. With the exception of garnet, which has a euhedral and granular texture, most of the minerals show prolonged and oriented textures (Fig. 2h). In addition, some magnetite grains are observed in both biotite-quartz schist and biotite-amphibole schist (Fig. 2i). The garnet + amphibole + plagioclase mineral assemblage observed in the Tiande No. 2 BIF specifically suggests that this unit experienced amphibolite facies metamorphism.

3. Sampling and Methods

3.1 Samples

Representative BIF and schist outcrop samples were collected from the Tiande No.2 iron deposit (Fig. 2a). A total of 13 samples, including six from the BIF horizon as well as seven schists, were collected from both the footwall and hanging wall, and these samples did not show any visible hydrothermal alteration or weathering. Some BIF samples (TD-6) have low magnetite concentrations but are otherwise similar in composition to the other BIF samples, indicating that they represent silica-rich BIF. The schist samples are subdivided into biotite-quartz schist samples (TD-7, TD-8, TD-9 and TD-11) and biotite-amphibole schist samples (TD-10, TD-12 and TD-13). Detailed mineralogical and petrologic studies were initially performed, and then the samples were ground in an agate mortar to <74 μm for further geochemical analysis.

3.2 Mineral analyses

Electron microprobe analyses of magnetite, garnet and amphibole on three BIF samples (samples TD-2, TD-3 and TD-5) were performed using a JXA-8100 electron microprobe at the Mineralization and Dynamics Laboratory, Chang'an University, Xi'an, China. Compositions were obtained using the following operating conditions: an accelerating voltage of 15 kV, a beam diameter of 1 μm, beam current of 10 nA, a count time of 10 or 15 s, and background time of 5 s. The following standards were used: magnetite (Fe), forsterite (Mg), corundum (Al), quartz (Si), elemental Ni (Ni), picotite (Cr), V-P-K glass (V, P, and K), and pyrophanite (Mn and Ti). The analytical precision for most elements was better than 2%. The limit of detection was 0.01%.

3.3 Major and trace element analyses

Bulk-rock major and trace element (mainly REEs) analyses were conducted at the

Analytical Laboratory of Beijing Research Institute of Uranium Geology, Beijing, China. 700 mg of sample powder was mixed with 5.2 g of anhydrous lithium tetraborate, 0.4 g of lithium fluoride, and 0.3 g of ammonium nitrate in a platinum crucible. 1 mL of 15 g/L LiBr solution was then added to the platinum crucible and melted to form a glass bead at 1000ºC. Major element concentrations (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, and P) were then determined by x-ray fluorescence (XRF). The loss on ignition (LOI) was measured by placing 1 g of sample powder in the furnace at 1000°C for several hours before cooling in a desiccator and reweighing.

An inductively coupled plasma–mass spectrometer (ICP–MS, ELEMENT XR) was used for trace element analyses. Briefly, 50 mg of powder was dissolved in an equal mixture of sub-boiling distilled HF and HNO_3 in a Teflon digesting vessel over a hot-plate for 24 h, using high-pressure acid digestion bombs to ensure complete digestion. This procedure was repeated using 0.5 mL of 16 mol/mL HNO_3 for a further 12 h. Following digestion, each sample was evaporated to dryness and was then refluxed with HNO_3, followed by heating again to dryness. The sample was then dissolved in 2 ml of HNO_3 and diluted with Milli-Q water (18 MΩ) to a final dilution factor of 2000.

3.4 Isotope analyses

Sm and Nd isotope analyses were carried out using a PHOENIX-T thermal ionization mass spectrometer with an external precision of 0.00003 (2σ) at the Analytical Laboratory of Beijing Research Institute of Uranium Geology. Correction for Nd isotope fractionation was performed by normalizing the measured values to $^{146}Nd/^{144}Nd = 0.7219$.

Iron isotope ratios of BIF samples (n=6) were determined at the ALS Scandinavia Laboratory in Stockholm, Sweden. Samples were prepared by HNO_3+HF digestion and the analysis was carried out by MC-ICP-MS (NEPTUNE PLUS, ThermoScientific). The precision for Fe isotope analysis was ±0.08‰ (2σ, which was calculated from two independent consecutive measurements). Analyses of standard GSJ JB-2 gave a $^{56}Fe/^{54}Fe$ composition of 15.6990 ± 0.0035, relative to reference values of 15.6988-15.6991. For detailed analytical methods see (Rouxel et al., 2005).

In-situ iron isotope analyses of magnetite in BIF and schist samples were obtained using a UV femtosecond laser ablation device coupled to a Thermo Finnigan Neptune Plus multi-collector ICP-MS at the Leibnitz University of Hannover (Horn et al., 2006). The laser system is based on a 100-femtosecond Ti-sapphire regenerative amplifier system (Hurricane I, Spectra Physics, USA), as described in detail by Horn and Von Blanckenburg (2007). A spot diameter of 60 μm was used for the crystal size of our magnetite samples. A standard-bracketing sequence with the certified Fe metal standard IRMM-014 was used for sample and standard Fe-isotope measurements. All acquired data lie within 2σ uncertainty on the fractionation line and are expressed in delta notation (in ‰) relative to the IRMM-014 reference material. All iron isotope data (including whole rock and in-situ iron isotope analyses) are reported relative to IRMM-14 as $\delta^{56}Fe$ (‰) = $1000 \times [(^{56}Fe/^{54}Fe)_{sample} / (^{56}Fe/^{54}Fe)_{IRMM\text{-}14} - 1]$.

4. Results

4.1 EPMA Data

Magnetite: Magnetite is the main Fe-oxide mineral component of the Tiande No.2 BIF, occurring as a dominant constituent (<50 modal %). Magnetite occurs as subhedral and elongated grains typically between 100 and 400 μm in size (Fig. 2f-h). Some magnetite crystals were oxidized to hematite. Magnetite is characterized by a high and variable Fe content, ranging from 68.91 to 73.51 wt% (see Appendix Table 1). In addition, V and Mn are also enriched in BIF samples, with averages of 0.13 and 0.09 wt%, respectively. The concentrations of most other elements are lower than 0.10 wt%.

Garnet: Garnet (<10 modal %) is ubiquitous in both Fe-rich and silica-rich bands, and occurs as euhedral grains with a grain size of 50 to 150 μm (Fig. 2g and h). Major element analyses for garnet are in the range of 17.08–18.17 wt% for Si, 10.00–11.43 wt% for Al, 13.68–15.37 wt% for Fe, 11.78–13.69 wt% for Mn, 2.52–4.17 wt% for Ca, and 0.91–1.48 wt% for Mg (Appendix Table 2), consistent with a garnet composition of $Alm_{38\text{-}47}Sps_{34\text{-}41}Grs_{10\text{-}17}Prp_{6\text{-}10}$.

Amphibole: Most amphibole (5-10 modal %) occurs as platy and oriented crystals in Fe-rich bands (Fig. 2g and h), with some grains being replaced by biotite. Major element analyses for amphibole show a Si content ranging from 11.92 to 20.98 wt%, Al ranges from 6.13 to 6.50 wt%, Fe ranges from 11.44 to 11.77 wt%, Mg ranges from 6.51 to 6.92 wt%, Ca ranges from 7.79 to 8.37 wt%, and Na ranges from 0.86 to 1.04 wt%. According to the classification scheme of Leake et al. (1997), all amphibole grains in the Tiande No.2 BIF belong to magnesiohornblende–tschermakite (Appendix Table 3).

4.2 Total element geochemistry

Major and trace element data are reported in Appendix Table 4. The Tiande No.2 BIF primarily consists of Si (30.93 to 42.46 wt%) and Fe (2.78 to 18.92 wt%), and the SiO_2+FeO contents range from 87 to 97 wt%, with an average of 93 wt%. BIF samples also contain 0.52–2.03 wt% Al, 0.46–2.25 wt% Mn, 0.35–1.64 wt% Ca, 0.21–0.90 wt% Mg, 0.06–0.39 wt% Ti, and 0.02–0.16 wt% P, and show high Fe/Al ratios (between 2.48 and 28.40). BIF samples have relatively high ∑REE (total rare earth element) contents (28 to 124 ppm, average of 87 ppm). Relative to Post Archean Australian Shale (PAAS, McLennan, 1989), BIF samples show distinctly heavy REE enrichments relative to the light REEs, and the $(La/Yb)_{PAAS}$ ranges from 0.26 to 0.46 (average of 0.38). In addition, the samples have slightly positive Eu anomalies (Eu/Eu^* values ranging from 1.17 to 1.57, average of 1.35). The Ce/Ce^* values range from 0.75 to 0.96 (Fig. 3a).

Schist samples are dominated by Si (20.26–35.59 wt%), Al (5.69–10.15 wt%) and Fe (3.10–12.67 wt%) (Appendix Table 4). Mg, Ca and Ti concentrations are generally less than 6 wt%, and other major elements are lower. Most sample show high Fe/Al ratios (>1.00) (except for sample TD-12, where Fe/Al = 0.55). Nearly all the schist samples contain higher ∑REE contents (varying from 127 to 317 ppm) than BIF samples (Appendix Table 4), and the $(La/Yb)_{PAAS}$ are variable (ranging from 0.44 to 1.73, average of 0.76). The schist samples also show positive Eu anomalies (Eu/Eu^* values ranging from 1.18 to 2.03, average of 1.75) and Ce/Ce^* values vary from 0.88 to 0.97 (Fig. 3a).

4.3 Nd isotopes

Bulk-rock Sm–Nd isotope ratios are listed in Appendix Table 5. All of the initial $\varepsilon_{Nd}(t)$ values of the BIF and schist samples were calculated assuming an age of 424 Ma, which corresponds to the likely age of the nearby Yegenbulake BIF (see above; Fig. 1) (Ren, 2017). Most of the $\varepsilon_{Nd}(t)$ values for BIF samples are negative, ranging from -4.2 to -0.8, with an average of -2.8. Schist samples show variable $\varepsilon_{Nd}(t)$ values of -1.3–+5.6, with a mean of +3.2.

4.4 Fe isotopes

$\delta^{56}Fe$ values for bulk rock Tiande No.2 BIF samples are consistently negative, with an average of -0.24‰ and a range from -0.32‰ to -0.17‰ (Appendix Table 5). In-situ Fe isotope compositions are given in Appendix Table 6 and are displayed in Fig. 4. The $\delta^{56}Fe$ values of magnetite from BIF (sample TD-3) range between -0.46‰ and -0.17‰ (average of -0.31‰), which is broadly consistent with that of bulk rock BIF samples, although differences from laminae to laminae do exist (Fig. 4). However, the δ^{56}Fe values of magnetite from schist samples (sample TD-12 and TD-13) are isotopically heavier, ranging from -0.01‰ to 0.45‰ (Appendix Table 6).

5. Discussion

5.1 Terrigenous contributions

Most ancient BIFs are enriched in Fe and Si, with low concentrations of Al (<~0.5 wt%) and incompatible elements (Ti, Zr, Th, Hf, and Sc <20 ppm) (e.g., Klein, 2005; Konhauser et al., 2017). The Tiande No.2 BIF samples also have elevated Fe and Si contents, with Si+Fe contents of 45%–51% (Appendix Table 4), and magnetite crystals in the BIF are relatively pure (Appendix Table 1), indicating a strong chemical origin. However, the concentrations of Al, Ti and ΣREE in our samples are relatively high for BIF (Appendix Table 4), reflecting a significant detrital component (Cox et al., 2013; Konhauser et al., 2017). BIFs in the early-Paleozoic Habahe Group of Altay may have been deposited in a relatively restricted basin, such as a back-arc basin (Dong et al., 2018), which would potentially result in a higher terrigenous input. Subsequent diagenesis and metamorphism of these mixed chemical and terrigenous materials resulted in the mineral assemblage of magnetite + quartz ± Fe-silicates ($Alm_{38\text{-}47}Sps_{34\text{-}41}Grs_{10\text{-}17}Prp_{6\text{-}10}$, magnesiohornblende–tschermakite; Appendix Tables 2 and 3).

REEs are one of the most commonly used geochemical tools to understand the origin of BIFs (e.g., Planavsky et al., 2010). The ΣREE contents of BIF samples show a moderate correlation with Fe (Fig. 5a), which suggests that Fe, and particularly iron oxide minerals, controlled REE concentrations. Previous work has shown that high-temperature (>250°C) hydrothermal fluids have significant positive Eu anomalies (Michard et al., 1993), whereas low-temperature hydrothermal fluids have a weak or no Eu anomaly (Fig. 3b) (Michard et al., 1993). Unlike Archean BIFs that commonly display significant Eu anomalies (Eu/Eu* = 1.2−4.5, Konhauser et al., 2017), the Tiande No.2 BIF samples show only slight Eu anomalies (average of 1.35) (Fig. 3a and b). In addition, magnetite separates from the nearby contemporaneous Yegenbulake BIF also has only minor Eu anomalies (0.92−1.31 when normalized to PAAS; Ren, 2017). It is reasonable to infer that the slightly positive Eu anomalies in these early Paleozoic BIFs represent a low temperature hydrothermal source, or a hydrothermal signature that was diluted by seawater and terrigenous materials (Cox et al., 2013).

Neodymium isotope ratios provide further evidence for the depositional environment. Generally, continental crust displays significant negative $\varepsilon_{Nd}(t)$ values ($\varepsilon_{Nd}(t)$ values can be less than -10), whereas a hydrothermal component shows mantle-like signatures with positive $\varepsilon_{Nd}(t)$ values (Alexander et al., 2009; Li et al., 2015). Previous studies have shown that the $\varepsilon_{Nd}(t)$ values for Silurian seawater may be as low as -6.3 (Keto and Jacobsen, 1987). The $\varepsilon_{Nd}(t)$ values of our BIF samples range from -4.2 to -0.8 (average of -2.8), suggesting a mix between seawater and submarine hydrothermal fluids. In addition, both seawater and Precambrian BIF samples show distinctly heavy REE enrichments relative to the light REEs (Fig. 3b) (Bau et al., 1995, 1996), which is similar to our BIF samples and likely reflects interaction with seawater. Thus, when combined with slightly positive Eu anomalies, we infer that the BIFs were derived from mixed seawater and submarine hydrothermal fluids.

Given that the high Al contents (> 5.69 wt%) are observed in the schist, it is reasonable to infer that these schists were dominated by a terrigenous input. In addition, schist samples show positive $\varepsilon_{Nd}(t)$ values (average of 3.2) and Eu anomalies, both of which show a positive correlation with Fe (Fig. 5b and c), which suggests a significant Fe contribution from submarine hydrothermal fluids. Interestingly, Long et al. (2008) also reported mudrock and schist from the Habahe Goup with high Fe contents, and argued that the schist was derived from terrigenous materials. Taken together, these observations suggest that the dominant precursor to the schist was likely to have been a mudrock, dominated by terrigenous material with a contribution from submarine hydrothermal fluids. When the mudrocks were deposited, submarine hydrothermal fluids would have given a significant Eu and radiogenic Nd contribution to these mudrocks. Similarly, meta-mudrocks from the early Precambrian Yuanjiacun BIF also have consistently positive $\varepsilon_{Nd}(t)$ values and show a positive correlation with Fe, reflecting a significant hydrothermal fluid-sourced Fe component (Wang et al., 2016).

5.2 Source of iron and oxidation process

The main source of Fe in Precambrian BIFs is considered to be submarine hydrothermal fluids, continental weathering, or both (e.g., Klein, 2005; Bekker et al., 2010; Li et al., 2015). A continental Fe source for BIFs is best explained by Fe mobilization on the continental margin via microbial dissimilatory iron reduction (DIR) (Li et al., 2015). In this scenario, Fe isotope compositions of BIFs with a significant continental Fe source would likely display variable and negative δ^{56}Fe values. In the case of the Tiande No.2 BIF, $\delta^{56}Fe_{BIF}$ and $\delta^{56}Fe_{magnetite}$ values are homogeneous, and while compositions are negative, they are nevertheless close to zero (average of -0.24‰ and -0.31‰, respectively), strongly indicating that a dominant continental Fe source via DIR is an unlikely explanation.

Biotic and abiotic oxidation of Fe(II) to Fe(III) causes considerable Fe isotope fractionation, with Fe(III) becoming enriched in heavy Fe isotopes, and residual Fe(II) being enriched in the light Fe isotopes (Johnson et al., 2003). Therefore, limited precipitation of Fe(II) from seawater would be expected to lead to a greater degree of isotope fractionation, whereas near-quantitative precipitation would lead to a limited range of Fe isotope values (e.g., Busigny et al., 2018). Given that the δ^{56}Fe values of modern hydrothermal fluids range from -0.5 to 0‰ (e.g., Beard et al., 2003; Busigny et al., 2018), the relatively homogeneous

$\delta^{56}Fe_{BIF}$ and $\delta^{56}Fe_{magnetite}$ values (-0.32 to -0.17‰ and -0.46 to -0.17‰, respectively) likely reflect near-quantitative oxidation of hydrothermal Fe(II) (Fig. 4). In contrast to the BIF samples, the $\delta^{56}Fe_{magnetite}$ values of schist range from -0.01 to 0.45‰. Considering ferrous oxidation produces a significant Fe isotopic fractionation (with precipitated Fe(III)-(oxyhydr)oxides being enriched in ^{56}Fe; Johnson et al., 2003; Bekker et al., 2010), partial oxidation of Fe(II) is a likely explanation for the isotopic composition of the schist samples (Fig. 4).

In general, the oxidation of Ce(III) to Ce(IV) greatly reduces Ce concentrations in seawater, since Ce (IV) is largely insoluble (Bau and Dulski,1996), giving strong negative Ce anomalies in modern oxygenated seawater. Insoluble Ce(IV) may be adsorbed by Mn oxides, which is supported by positive Ce anomalies in modern ferromanganese crust (Nagender Nath et al., 1994). By contrast, suboxic and anoxic waters lack significant negative Ce anomalies due to reductive dissolution of settling Mn(IV)-Fe(III)-(oxyhydr)oxide particles (Byrne and Sholkovitz, 1996). Using a Ce/Ce^*-Pr/Pr^* cross-plot (Bau and Dulski, 1996), it is possible to identify true Ce anomalies (Fig. 6). On this basis, most of our BIF samples show a true negative Ce anomaly, which is also observed in the nearby Yegenbulake BIF (Fig. 6). Since the Yegenbulake BIF displays a more distinct Ce anomaly (Fig. 6) and contains pyrolusite (Ren, 2017), this suggests that it formed in more oxic seawater relative to the Tiande No.2 BIF. The REE features of the BIF samples could potentially be explained by a two end member mixing or Mn oxide reduction. Given that the Fe isotope data suggest a strong oxidation pathway for the BIF samples, the relatively small Ce anomalies we observe (Fig. 3a) may suggest mixing between oxic seawater with a negative Ce anomaly and hydrothermal fluids with no Ce anomaly. In terms of Mn oxide reduction, which may occur during diagenesis or as particles settle through deeper anoxic waters, associated Ce(IV) would be reduced to Ce(III) and re-dissolved, leading to a negative Ce anomaly in the BIF samples. Thus, it is not possible to confirm the precise process that produced the negative Ce anomalies in the BIF samples. However, our data clearly suggest that the magnetite (or primary precursor of the magnetite) in BIF samples was formed in oxygenated seawater, which is supported by a negative correlation between Ce/Ce^* and Fe concentration (Fig. 5d), suggesting that samples with high Fe content were accompanied by significant Ce(III) oxidation.

Nearly all the schist samples have Fe/Al ratios >1.0 (Appendix Table 4, except for sample TD-12), which are significantly above than the average value of 0.54 ± 0.11 for Phanerozoic siliciclastic rocks, suggesting deposition as a result of Fe(II) mobilization under ferruginous water column conditions (Clarkson et al., 2014). Schist samples also show a negative correlation between Ce/Ce^* and Fe concentration (Fig. 5d), again supporting a primary oxidative pathway for the magnetite precursor phases formed in the water column. However, our Fe isotope results support less extensive, partial oxidation of water column Fe(II), relative to BIF samples.

5.3 Depositional model and marine redox conditions

Several mechanisms have been proposed for the genesis of Precambrian BIFs (e.g., Klein, 2005; Bekker et al., 2010; Konhauser et al., 2017), but possible depositional models for more recently discovered Phanerozoic BIFs have received less attention. Unlike Precambrian BIFs forming at a time of low atmospheric O_2 and pervasively anoxic deep oceans (e.g., Bekker et al., 2010; Konhauser et al., 2017), early-Paleozoic BIFs deposited at a time when pO_2 was significantly higher (e.g., Lenton et al., 2016; Krause et al., 2018). Possible mechanisms for Fe^{2+} oxidation in Precambrian BIFs include direct oxidation by cyanobacterially-produced O_2, oxidation linked to anoxygenic photosynthesis, and ultraviolet (UV) photooxidation, while episodes of marine transgression may also have been particularly conducive to BIF deposition (e.g., Klein, 2005; Bekker et al., 2010). Here, we propose a depositional model for the early-Paleozoic BIFs of the Chinese Altay, whereby the setting was characterized by a stratified water column in a restricted basin, with oxic surface waters above ferruginous deeper waters (Fig. 7). The layering preserved in the BIF (Fig. 2c-g) indicates deposition below storm wave base. Oxidation of Fe(II) in oxic surface waters was near-quantitative, with continental weathering supplying a significant terrigenous flux. This process may have been related to a decrease in sea level and accompanying deepening of the oxycline. However, at times of further enhanced terrigenous input relative to the hydrothermal Fe flux, ferruginous mudrocks (the dominant precursor of the schist) were deposited.

Other recently reported Phanerozoic BIFs are considered to have deposited in isolated to semi-isolated basins, and indicate ferruginous deeper waters. Unlike these other Phanerozoic BIFs, which lacking Ce negative anomalies and have heterogeneous δ^{56}Fe values supporting deposition in an anoxic to low oxygen basin (Li et al., 2018; Chi Fru et al., 2018; Yang et al., 2021), precipitation of the late Silurian Tiande No.2 BIF was initiated by oxic surface waters, owing to a decrease in sea level, as discussed above.

When and how atmospheric O_2 first approached modern levels remains unresolved. However, most researchers argue that in the Paleozoic era, with the rise of land plants, atmospheric O_2 concentrations likely approached present-day concentrations (e.g., Lenton et al., 2016; Krause et al., 2018). With this rise to near-present atmospheric O_2 levels, the post-Devonian ocean is generally assumed to have been well-oxygenated (Lenton et al., 2016; Wallace et al., 2017). However, the redox state of late Silurian oceanic settings is currently poorly constrained. Our data suggest at least episodic ferruginous oceanic conditions in the Chinese Altay during the late Silurian, which further supports geochemical inferences of the major significance of ferruginous oceanic conditions well beyond that indicated by the extensive deposition of Precambrian BIFs (Poulton and Canfield, 2011).

6. Conclusions

We report here an early-Paleozoic BIF within the Habahe Group meta-volcano-sedimentary rocks of Altay, NW China. The BIF displays strong banding with distinct iron-rich and silica-rich lamina, consisting of magnetite, quartz and Fe-silicates (e.g., garnet and amphibole). The Tiande No.2 BIF comprises chemical sediments with a significant contribution from terrigenous material, and iron was mainly derived from mixed seawater and submarine hydrothermal fluids. Precipitation of Fe(III)-(oxyhydr)oxides was induced during near-complete oxidation of upwelling Fe(II) into oxic surface waters during a period of decreasing sea level. Schists that surround the BIF were likely originally mudrocks, but these rocks also record dominantly ferruginous water column conditions, accompanied by partial oxidation of dissolved Fe(II). Our study supports continued dynamic Fe cycling and at least intermittent ferruginous deeper water conditions in this location during the late Silurian.

Acknowledgements

This work was supported by the Natural Science Foundation of China (Nos. 41972075 and 41702063), Natural Science Basic Research Plan in Shaanxi Province of China (2020JM-213) and Fundamental Research Funds for the Central Universities, CHD (Nos. 300102279202 and 300102279401). SWP acknowledges support from a Royal Society Wolfson Research Merit Award. AD acknowledges support from the Fundamental Research funds for the Central Universities (2652017048). We thank two anonymous reviewers for constructive comments on an earlier version of this paper. We are grateful to Prof. Houmin Li, Jian Sun and Dr. Jialin Wu for their constructive discussions. We also thank Minwu Liu and Mu Liu for assisting with EPMA, geochemistry and isotope analyses.

References

Alexander, B.W., Bau, M., Andersson, P., 2009. Neodymium isotopes in Archean seawater and implications for the marine Nd cycle in Earth's early oceans. Earth Planet. Sci. Lett. 283(1-4), 144-155.

Bau, M., Dulski, P., 1996. Distribution of yttrium and rare earth elements in the Penge and Kuruman iron-formation, Transvaal Supergroup, South Africa. Precambrian Res. 79, 37-55.

Bau, M., Dulski, P., Möller, P., 1995. Yttrium and holmium in South Pacific seawater: vertical distribution and possible fractionation mechanisms. Chem. Erde 55, 1-15.

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

Bau, M., Koschinsky, A., Dulski, P., Hein, J.R., 1996. Comparison of partitioning behaviours of yttrium, rare earth elements, and titanium between hydrogenetic marine ferromanganese crusts and seawater. Geochim. Cosmochim. Acta 60, 1709-1725.

Beard, B.L., Johnson, C.M., VonDamm, K.L., Poulson, R.L., 2003. Iron isotope constraints on Fe cycling and mass balance in oxygenated Earth oceans. Geology 31, 629-632.

Bekker, A., Slack, J.F., Planavsky, A., Krapež, B., Hofmann, A., Konhauser, K.O., Rouxel, O.J., 2010. Iron formation: The sedimentary product of a complex interplay among mantle, tectonic, oceanic, and biospheric processes. Econ. Geol. 105, 467-508.

Broussolle, A., Sun, M., Schulmann, K., Guy, A., Aguilar, C., Štípská, P., Jiang, Y., Yu, Y., Xiao, W., 2019. Are the Chinese Altai "terranes" the result of juxtaposition of different crustal levels during Late Devonian and Permian orogenesis? Gondwana Res. 66, 183-

206.

Busigny V., Planavsky N.J., Goldbaum E., Lechte M.A., Feng L.J., Lyons T.M., 2018. Origin of the Neoproterozoic Fulu iron formation, South China: Insights from iron isotopes and rare earth element patterns. Geochim. Cosmochim. Acta 242, 123-142.

Byrne, R., Sholkovitz, E., 1996. Marine chemistry and geochemistry of the lanthanides. In Handbook on the Physics and Chemistry of the Rare Earths (eds. K. A. Gschneider Jr. and L. Eyring). Elsevier, Amsterdam.

Canfield, D.E., Zhang, S., Wang, H., Wang, X., Zhao, W., Su, J., Bjerrum, C.J., Haxen, E.R., Hammarlund, E.U., 2018. A Mesoproterozoic iron formation. Proc. Natl Acad. Sci. 115(17).

Chi Fru, E., Kilias, S., Ivarsson, M., Rattray, J.E., Gkika, K., McDonald, I., He, Q., Broman, C., 2018. Sedimentary mechanisms of a modern banded iron formation on Milos Island, Greece. Solid Earth 9, 573-598.

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

Cox, G.M., Halverson, G.P., Minarik, W.G., Le Heron, D.P., Macdonald, F.A., Bellefroid, E.J., Strauss, J.V., 2013. Neoproterozoic iron formation: An evaluation of its temporal, environmental and tectonic significance. Chem. Geol. 362, 232-249.

Cox, G.M., Halverson, G.P., Poirier, A., Heron, D.L., Strauss, J.V., Stevenson, R., 2016. A model for Cryogenian iron formation. Earth Planet. Sci. Lett. 433, 280-292.

Dauphas, N., van Zuilen, M., Wadhwa, M., Davis, A. M., Marty, B., Janney, P. E., 2004. Clues from Fe isotope variations on the origin of early Archean BIFs from Greenland. Science 306, 2077-2080.

Dong, Z., Han, Y., Zhao, G., Pan, F., Wang, K., Huang, B., Chen, J., 2018. Zircon U-Pb ages and Hf isotopes of Paleozoic metasedimentary rocks from the Habahe Group in the Qinghe area, Chinese Altai and their tectonic implications. Gondwana Res. 61, 100-114.

Douville, E., Bienvenu, P., Charlou, J. L., Donval, J. P., Fouquet, Y., Appriou, P., Gamo, T., 1999. Yttrium and rare earth elements in fluids from various deep-sea hydrothermal systems. Geochim. Cosmochim. Acta 63 (5), 627-643.

Halverson, G.P., Poitrasson, F., Hoffman, P. F., Nédélec, A., Montel, J.M., Kirby, J., 2011. Fe isotope and trace element geochemistry of the Neoproterozoic Syn-glacial Rapitan iron formation. Earth Planet. Sci. Lett. 309, 300-112.

Horn, I., Von Blanckenburg, F., 2007. Investigation on elemental and isotopic fractionation during 196 nm femtosecond laser ablation multiple collector inductively coupled plasma mass spectrometry. Spectrochim. Acta, Part B 62(4), 410-422.

Horn, I., von Blanckenburg, F., Schoenberg, R., Steinhoefel, G., Markl, G., 2006. In situ iron isotope ratio determination using UV-femtosecond laser ablation with application to hydrothermal ore formation processes. Geochim. Cosmochim. Acta 70(14), 3677-3688.

Johnson, C.M., Beard, B.L., Beukes, N.J., Klein, C., O'Leary, J.M., 2003. Ancient geochemical cycling in the Earth as inferred from Fe isotope studies of banded iron formations from the Transvaal Craton. Contrib. Mineral. Petrol. 144(5), 523-547.

Keto, L.S., Jacobsen, S.B. 1987. Nd and Sr isotopic variations of early paleozoic oceans. Earth Planet. Sci. Lett. 84(1), 27-41.

Klein, C., 2005. Some Precambrian banded iron-formations (BIFs) from around the world: Their age, geologic setting, mineralogy, metamorphism, geochemistry, and origin. Am. Mineral. 90, 1473-1499.

Konhauser, K.O., Planavsky, N.J., Hardisty, D.S., Robbins, L.J., Warchola, T.J., Haugaard, R., Lalonde, S.V., Partin, C.A., Oonk, P.B.H., Tsikos, H., Lyons, T.W., Bekker, A., Johnson, C.M., 2017. Iron formations: a global record of Neoarchaean to

Palaeoproterozoic environmental history. Earth Sci. Rev. 172, 140-177.

Krause, A.J., Mills B.J., Zhang S., Planavsky N.J., Lenton T.M., Poulton, S. W., 2018. Stepwise oxygenation of the Paleozoic atmosphere. Nat. Commun. 9, 4081.

Leake, B., Wooley, A.R., Arps, C.E.S., et al., 1997. The nomenclature of amphiboles: Report of the Subcommittee on Amphiboles of the International Mineralogical Association Commission on New Mineral Names. Can. Mineral. 82(9), 1019-1037.

Lenton, T.M., Dahl, T.W., Daines, S.J., Mills, B.J., Ozaki, K., Saltzman, M.R., Porada, P., 2016. Earliest land plants created modern levels of atmospheric oxygen. Proc. Natl Acad. Sci. 113(35), 9704-9709.

Li, W., Beard, B.L., Johnson, C.M., 2015. Biologically recycled continental iron is a major component in banded iron formations. Proc. Natl Acad. Sci. 112(27), 8193-8198.

Li, Z.Q., Zhang, L.C., Xue, C.J., Zhu, M.T., Robbins, L.J., Slack, J.F., Planavsky, N.J., Konhauser, K.O., 2018. Earth's youngest banded iron formation implies ferruginous conditions in the early Cambrian ocean. Sci. Rep. 8(1), 9970.

Long, X.P., Sun, M., Yuan, C., Xiao, W.J., Cai, K.D., 2008. Early Paleozoic sedimentary record of the Chinese Altai: implications for its tectonic evolution. Sediment. Geol. 208, 88-100.

Long, X.P., Sun, M., Yuan, C., Xiao, W.J., Lin, S.F., Wu, F.Y., Xia, X.P., Cai, K.D., 2007. U-Pb and Hf isotopic study of zircons from metasedimentary rocks in the Chinese Altai: implications for Early Paleozoic tectonic evolution. Tectonics 26, 1-20.

McLennan, S.B., 1989. Rare earth elements in sedimentary rocks: Influence of provenance and sedimentary processes. In: Lipin, B.R., McKay, G.A. (Eds.), Geochemistry and Mineralogy of the Rare Earth Elements. Mineralogical Society of America, 169-200.

Michard, A., Michard, G., Stuben, D., Stoffers, P., Cheminée, J.-L., Binard, N., 1993. Submarine thermal springs associated with young volcanoes: the Teahitia vents, Society islands Pacific Ocean. Geochim. Cosmochim. Acta 57, 4977-4986.

Mloszewska, A., Pecoits, E., Cates, N., Mojzsis, S.J., O'Neil, J., Robbins, L.J., Konhauser, K.O., 2012. The composition of Earth's oldest iron formations: the Nuvvuagittuq Supracrustal Belt (Québec, Canada). Earth Planet. Sci. Lett. 317-318, 331–342.

Nagender Nath, B., Roelandts, I., Sudhakar, M., Plger, W.L., Balaram, V., 1994. Cerium anomaly variations in ferromanganese nodules and crusts from the Indian Ocean. Mar. Geol. 120 (3-4), 385-400.

Och, L.M., Cremonese, L., Shieldszhou, G.A., Poulton, S.W., Struck, U., Ling, H., Zhu, M., 2016. Palaeoceanographic controls on spatial redox distribution over the Yangtze Platform during the Ediacaran–Cambrian transition. Sedimentology 63(2), 378-410.

Och, L.M., Shields-Zhou, G.A., Poulton, S.W., Manning, C., Thirlwall, M.F., Li, D., Chen, X., Ling, H.F., Osborn, T., Cremonese, L. 2013. Redox changes in Early Cambrian black shales at Xiaotan section, Yunnan Province, South China. Precambrian Res. 225, 166-189.

Planavsky, N., Bekker, A., Rouxel, O.J, Kamber, B., Hofmann, A., Knudsen, A., Lyons, T.W., 2010. Rare Earth Element and yttrium compositions of Archean and Paleoproterozoic Fe formations revisited: new perspectives on the significance and mechanisms of deposition. Geochim. Cosmochim. Acta 74(22), 6387-6405.

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

Ren, Y.C., 2017. Geological characteristics and genesis of Yegenbulake iron deposit in Altay, Xinjiang. M.Sc. thesis, China, Xinjiang University. 1-57p (in Chinese with English abstract).

Rouxel, O., Toner, B., Germain, Y., Glazer, B., 2018. Geochemical and iron isotopic insights into hydrothermal iron oxyhydroxide deposit formation at Loihi Seamount. Geochim.

Cosmochim. Acta 220, 449-482.

Rouxel, O.J., Bekker, A., Edwards, K.J., 2005. Iron isotope constraints on the Archean and Paleoproterozoic ocean redox state. Science 307 (5712), 1088-1091.

Song, H., Jiang, G., Poulton S. W., Wignall P. B., Wang, C., 2017. The onset of widespread marine red beds and the evolution of ferruginous oceans. Nat. Commun., 8(1), doi: 10.1038/s41467-017-00502-x.

Wallace, M.W., Hood, A.V., Shuster, A., Greig, A., Planavsky, N.J., Reed, C.P., 2017. Oxygenation history of the Neoproterozoic to early Phanerozoic and the rise of land plants. Earth Planet. Sci. Lett. 466, 12-19.

Wang, C.L., Konhauser, K.O., Zhang, L.C., Zhai, M.G., Li, W.J., 2016. Decoupled sources of the 2.3-2.2 Ga Yuanjiacun banded iron formation: implications for the Nd cycle in earth's early oceans. Precambrian Res. 280, 1-13.

Windley, B.F., Kroener, A., Guo, J., Qu, G., Li, Y., Zhang, C., 2002. Neoproterozoic to Paleozoic geology of the Altai Orogen, NW China: new zircon age data and tectonic evolution. J. Geol. 110, 719-737.

Yang, X.Q., Mao, J.W., Zhang, Z.H., Robbins, L.J., Planavsky, N.J., Jiang, Z.S., Duan, S.G., Chen, Z.W., 2021. Episodic ferruginous conditions associated with submarine volcanism led to the deposition of a Late Carboniferous iron formation. Geochim. Cosmochim. Acta 292, 1-23

Yu, Y., Sun, M., Yuan, C., Zhao, G.C., Huang, X.L., Rojas-Agramonte, Y., Chen, Q., 2019. Evolution of the middle Paleozoic magmatism in the Chinese Altai: Constraints on the crustal differentiation at shallow depth in the accretionary orogeny. J Asian Earth Sci 175, 230-246.

Zhou, G., Dong, L.H., Li., Y., He, L.X., Qin, J.H., Zhao, Z.H., 2014. Discovery and geological significance of BIF in the Altai Orogenic Belt, Xinjiang. Mineral Deposits 33(Supp), 165-

166 (in Chinese with English abstract).

Figures

Fig. 1. Generalized geological map of the Chinese Altay, NW China (modified after Broussolle et al. 2019).

Fig. 2. Photographs of BIF and schist from the Tiande No.2 iron deposit. a. Thin BIF layer housed within schist; b. BIF and surrounding schist; c-e. Typical BIF layers, showing alternations of iron-rich (black) and silica-rich (white) laminae. The laminae are straight, with thicknesses ranging from ~2 mm to ~2 cm; f-h. Microphotographs of BIF showing the banded structure, with magnetite, quartz, garnet and amphibole; i. Microphotographs of schist with a high magnetite content. Microphotographs of f, g and i were taken under plane-polarized light (transmitted), while h is a backscattered electron image. Am-amphibole; Bi-Biotite; Grt-Garnet; Mag-Magnetite; Qtz-Quartz.

Fig. 3. a. PAAS-normalize REE+Y compositions of BIF and schist from Tiande No.2 iron deposit; b. PAAS-normalized REE+Y patterns for average high-temperature hydrothermal fluids (red dashed line, Douville et al., 1999), low-temperature hydrothermal fluids (gray dashed line, Michard et al., 1993), modern hydrothermal Fe(III)-oxyhydroxides (purple dashed line, Rouxel et al., 2018), modern seawater (yellow dashed line, Bau et al., 1995, 1996), 3.8 Ga BIF (blue full line, Mloszewska et al., 2012), 2.5 Ga BIF (green full line, Bau et al., 1997), 0.7 Ga BIF (orange full line, Halverson et al., 2011), and the Tiande No.2 BIF (light-blue full line, this study).

Fig. 4. Iron isotope compositions of magnetite in the Tiande No.2 BIF and surrounding schist.

In-situ analyses were performed in samples TD-3 (BIF), and TD-12 and TD-13 (schist). Analysis spots for sample TD-3 are marked by yellow cycles (under plane-polarized light, transmitted).

Fig. 5. Variation diagram of Fe vs. $\sum$REE (a), Fe vs. ε_{Nd}(t) (b), Fe vs. Eu/Eu^* (c), and Fe vs. Ce/Ce^* (d).

Fig. 6. Ce/Ce^*_{PAAS} vs. Pr/Pr^*_{PAAS} diagram for the early-Paleozoic Altay BIFs (after Bau and Dulski, 1996). Data for magnetite separates from the Yegenbulake BIF from Ren (2017).

Fig. 7. Schematic diagram showing depositional model of Tiande No.2 BIF. Pink Fe circle expresses near-quantitative oxidation Fe(II); Darkgray Fe circle indicates partial oxidation of Fe(II); Light-gray Fe circle suggests submarine hydrothermal sourced-Fe.

Appendices

Figure A Classification of the calcic amphiboles (Leake et al., 1997)

Table 1 EPMA results for magnetite from BIF (wt%).

Table 2 EPMA results for garnet from BIF (wt%).

Table 3 EPMA results for amphibole from BIF (wt%).

Table 4 Major (wt%) and trace elements (ppm) of Tiande No.2 BIF and schist samples.

Table 5 Nd and Fe isotopic compositions of Tiande No.2 BIF and schist samples.

Table 6 In-situ Fe isotopic compositions of magnetite from Tiande No.2 BIF and schist samples.