

Origin of the Neoproterozoic BIFs at the southeastern margin of the Yangtze craton: implication for an

Hu Hao Chuan-Lin Zhang

College of Oceanography

Abstract The Neoproterozoic BIFs formed during the break-up of the supercontinent Nuna. The atmospheric anoxia (ca. 737 Ma) Baijiu Group dominated iron-formation. The concentrations of $\delta^{56}\text{Fe}$ in the BIFs are consistent with the $\delta^{56}\text{Fe}$ -Eu anomaly, which is slightly elevated, indicating hydrothermal

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Iron formation in sedimentary rocks is characterized by thin layered or laminated structures that are composed mainly of iron oxides (Holland, 1983). The oldest BIFs formed during the Archean (the Proterozoic eon). The Gaoligong billion-year history was related to the Cambrian (GOE), tectonic

and were usually such as passive margin (Gondwanic BIFs are even much less than those of Archean widely distributed worldwide, such as Banded Iron Formations in Egypt (Pasta et al., 2011), (Serra Pelada in Brazil (Freitas et al., 2011), and Wadi Auwana in the Arabian Shield (El-Rahman et al., 2020). They were discovered in the Cambrian massifs in Neoproterozoic orogenic belts of South China, such as the Jiang in Guangxi (Yan et al., 2010), Shuangfeng in the Central Transhan (Li et al., 2014; Shen et al., 2018; Zhang et al., 2014), and Dahongliutan BIF in the orogenic belt (Hu et al., 2017, 2020). Several

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models have been proposed for interpreting the formation of the Neoproterozoic BIFs: (1) During the break-up of Rodinia supercontinent

induced the addition of Fe flux from submarine exhalative (Basta et al., 2011; Cox et al., 2013); (2) The thick ice sheet formed by "Snowball Earth" event isolated the hydrosphere and oxidized atmosphere, which led to the reduction of ocean and the dissolution of a large amount of Fe element. After the ice cover melted, the Fe was oxidized and precipitated into BIF as a result of the contact between ocean and atmosphere (Hoffman et al., 1998; Hoffman and Schrag, 2002; Klein and Ladeira, 2004; Halverson et al., 2011) and (3) during the late Neoproterozoic, there was a reduced S-poor and Fe-rich environment, which was favorable for Fe element existing as divalent ions in seawater, and then to be oxidized and precipitated (Johnston et al., 2010).

In this study, we report a newly identified Neoproterozoic Baijianshan BIF at the southeastern margin of the Tarim Block in NW China. The precipitation mechanism and the oceanic redox condition of the Baijianshan BIF was investigated based on detailed field observations coupled with systematic elemental and isotopic compositions analysis. This study sheds a new light on our understanding of the possible coupling of the Cryogenian snowball Earth event and the formation of Neoproterozoic BIFs.

2 Regional Geology

The Tarim Craton in NW China, covering an area of more than 600,000 km², is one of the main three Precambrian nuclei in China (i.e., North China, South China and Tarim). It is surrounded by the Phanerozoic orogenic belts of Tianshan Mountains to the north, the western Kunlun Mountains to the south, and the Central-Southern Altyn Tagh Mountains to the southeast. Despite most of the Tarim Craton being covered by aeolian sands and difficulties in accessibility, previous work reveals that the craton is characterized by a typical double-layered structure consisting of a Pre-Cryogenian basement and Cryogenian-Cambrian cover sequences (Xinjiang BGMR, 1993; Zhang et al., 2013). Particularly, recent studies demonstrate that the craton docked at the northern fringe of the Rodinia slightly earlier than 760 Ma and then the Cryogenian-Cambrian sedimentary sequences deposited during the breakup of the Rodinia (Zhang et al., 2010, 2016; Xu et al., 2013).

These samples are dominated by magnetite and quartz with banded structures and main mesoband (mm- to cm-scale) and microband (sub-mm- to mm-scale), which are composed of magnetite, quartz, rare hematite, siderite, albite and biotite (Fig. 3e-f). Quartz and other minerals, such as chlorite (Fig. 3g) and sericite (Fig. 3h), occur occasionally as veinlets cutting the bedding.

The shallow gray tuffs under the four layers of Fe ore bodies have been altered into chlorite and albite. Nevertheless, the sub-euhedral or euhedral plagioclase and quartz crystal fragments, mostly less than 1 mm, can be seen under magnifier. The crystal fragments account for about 15-20% in the tuff. The sample was collected from the tuff to constrain the deposition age of the Baijianshan (Li et al., 2011; Li et al., 2017).

The blackish green basalt layer occurs at the bottom of the BIF layers, with the thickness of 1-2 m. The minerals in the basalt were intensively altered and needle-like albite, chlorite as well as hematite can be observed in thin sections, three samples were collected from the basalt for geochemical analysis (2702H1, 270H2 and 2702H3).

4 Analytical Methods

4.1 In situ zircon U-Pb isotope analysis

Conventional magnetic and density techniques were used to separate zircon grains from rock fractions and then zircon grains were hand-picked under a binocular microscope. The zircon grains were then polished to section the crystals in order to observe their internal structures. The polished zircon grains were analyzed with transmitted and reflected light micrographs as well as cathodoluminescence (CL) images to reveal their internal structures. Zircon U-Pb ages were analyzed using the Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) at the Tianjin Institute of Geology and Mineral Resources (China Geological Survey). The analytical procedures can be found in Li et al. (2009). Zircon standards 91500 and 437 were used to monitor the analysis. The U-Pb concentrations and data are reported in supplementary Table 2.

Seventeen BIF samples were collected from the Baijianshan area. The whole-rock geochemical location. Whole-rock major compositions were analyzed by X-ray fluorescence (XRF) on fused glass beads at the Nanjing Institute of Geology and Mineral Research (China Geological Survey), following the procedures similar to those described by Li et al., (2006a, b). Analytical uncertainties are between 1 and 5%. In addition, we used wet chemistry technique to measure Fe, Mn, Ni, and Co with the procedures described by Andrade et al. (2002). The measured data are reported in supplementary Table 2.

Trace elements were determined using a Perkin-Elmer Sciex ELAN DRC-e ICP-MS at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry (Chinese Academy of Sciences). The analytical accuracy better than 5%. Samples were digested with 1ml of HF and HNO₃ in Teflon-lined stainless steel bombs at 190 °C for 12h (Qi et al., 2000). The analytical accuracy was better than 1% with concentrations > 200 ppm, and 1-3% with concentrations < 200 ppm. The results are reported in supplementary Table 2.

Strontium and neodymium isotopes were analyzed using the Micromass Isoprobe Multi-collector MC-ICP-MS at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry (Chinese Academy of Sciences), with the analytical procedures described by Li et al. (2004). Measured ⁸⁷Sr/⁸⁶Sr and ¹⁴³Nd/¹⁴⁴Nd ratios were 0.71025 and 0.7219, respectively. The ⁸⁷Sr/⁸⁶Sr = 0.71025 and the Shin Etsu JNdi-1 standard were used to monitor the analysis. The ages of the BIF are calculated with a

5 Analytical Results

5.1 Zircon U-Pb age

Zircons from the tuff sample 2071 are variable in size with the length varying from 60 μm to 150 μm and the aspect ratios 1-2. In CL images most zircon exhibit oscillatory zoning, sharing the features of the zircons crystallized from silicic magma (Wu and Zheng, 2004). Thirty-two analyses were conducted on 32 zircon grains and the results are presented in supplementary Table 1 and illustrated in Fig. 4. Obviously, some analyses show variable radiogenetic lead lost. However, the results can be broadly divided into two sub-groups. Group 1, which is likely to be xenocrystal and generally have larger size, constructs a good Discordia with upper intercepted age of 1378 ± 44 Ma (MSWD=5.8). Group 2 mostly shows euhedral in form and smaller in size. Twenty-one analyses construct a good Discordia with an intercepted age of 736.2 ± 3.8 Ma (N=21, MSWD=1.08) (insert of Fig. 4). Excluded the significant discordant analyses, the left fifteen analyses of well concordance between $^{206}\text{Pb}/^{238}\text{U}$ age and $^{207}\text{Pb}/^{235}\text{U}$ age, yield a mean $^{206}\text{Pb}/^{238}\text{U}$ age of 737.0 ± 4.0 Ma (N=15, MSWD=0.20). This age is interpreted as the deposition time of the Baijianshan BIF.

5.2 Whole rock Geochemistry

5.2.1 Geochemistry of the basalts

Three basalt samples (2702H1, 270H2 and 2702H3) have low SiO_2 contents (39.93% to 44.55%). The incompatible elements for the rock type classification are used due to the high LOI. Their high Nb/Y ratios (1.05-1.09) define their alkaline signature and in the Nb/Y vs. Zr/TiO₂ diagram, they plot into the alkaline basalt field (Figure not shown). With respect to the trace elements, they have REE ranging from 186 ppm to 195 ppm and show variable LREE enriched Chondrite-normalized pattern (Fig. 5a) ($\text{La}_N/\text{Yb}_N = 9.8-11.0$). In line with their low Cr (214-306 ppm) and Ni contents (162-216.9 ppm), the basalts are evolved magma. However, the primitive mantle-normalized diagram shares most features of the OIB-like basalts with insignificant Nb-Ta trough (Nb/La = 1.0-1.1) (Figure not shown).

5.2.2 Geochemistry of the BIF

As shown in supplementary Table 2, the samples from Baijianshan BIF are rich in Fe_2O_3^T and SiO_2 . Fe_2O_3^T concentrations vary between 13.11% and 56.65% (38.44% on average), whereas SiO_2 varies between 26.81% and 55.06% (42.02% on average). They have low contents of Al_2O_3 (1.56%-7.58%, 3.66% on average), TiO_2 , MnO, P_2O_5 , CaO, Na_2O , K_2O and variable total rare earth elements and other incompatible elements (supplementary Table 2).

Their REE abundances vary from 38.1 ppm to 150.8 ppm. Normalized against Post Archean Average Shale (PAAS; McLennan, 1989), they are characterized by depletion of LREE relative to HREE with the La_N/Yb_N of 0.23-0.69 (Fig. 5b). The REY patterns exhibit no Ce and Pr anomalies (the combination of $\text{Ce}/\text{Ce}^* \sim 1$ and $\text{Pr}/\text{Pr}^* \sim 1$; Bau and Dulski, 1996) and insignificant Eu and Y anomaly ($\text{Eu}/\text{Eu}^* = 0.96-1.14$; Y/Ho ratios ranging from 23.3 to 31.8 with an averaged value of 26.39, Table 2).

5.2.3 Sr-Nd isotope compositions

Sr-Nd concentrations and isotopic ratios of the Baijianshan BIF and basalts are presented in supplementary Table 3. As for the basalts, the basalts exhibit high initial Sr isotope compositions with ($^{87}\text{Sr}/^{86}\text{Sr}$)_i ranging from 0.7061 to 0.7084 due to post-eruption hydrothermal alteration. In addition,

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Strontium and neodymium concentrations of Baijianshan BIF range from 20.3 ppm to 256 ppm and from 7.06 ppm to 59.8 ppm, respectively. The nine samples have a large range of measured $^{143}\text{Nd}/^{144}\text{Nd}$ (0.51231-0.51243) and $^{87}\text{Sr}/^{86}\text{Sr}$ (0.7179- (t = 737Ma) values range from -0.45 to 1.46, with an average of 0.37. However, the BIF samples exhibit a large range of the ($^{87}\text{Sr}/^{86}\text{Sr}$)_i values between 0.6412 and 0.7175, possibly due to the post-deposition hydrothermal alteration and the large range of Rb/Sr ratios varying from 0.02 to 3.47.

5.2.4 Fe isotope compositions

The Fe isotope compositions of the Baijianshan BIF samples are presented in supplementary Table 4. The six samples yield $^{56}\text{Fe}_{\text{IRMM-014}}$ values of 1.24- $^{57}\text{Fe}_{\text{IRMM-014}}$ values of 1.78- Their enrichment in heavy Fe isotopes shares the signatures of the Neoproterozoic BIFs (Halverson et al., 2011; Yan et al., 2011; Shen et al., 2018).

6 Discussions

6.1 Iron sources for the Baijianshan BIFs

Field and microscopic observations revealed that the Neoproterozoic Baijianshan BIF has not

experienced significant metamorphism (Fig. 3b, c and d), indicating the original geochemical characteristics were well retained and can be used to decipher the iron sources and the oceanic environments when it precipitated.

The Baijianshan BIF shows a modern seawater REE signature with significant LREE depletion relative to the HREE ($La_N/Yb_N = 0.41$) (Fig. 5b, Zhang and Nozaki, 1996; Alibo and Nozaki, 1999). A range of factors can affect the primary REY composition in terms of BIF depositional processes, including post-depositional metamorphism and/or syn-deposition clastic contamination (Alexander et al., 2008; Hu et al., 2020). Previous studies demonstrated that diagenetic and metamorphic events (such as weathering and/or fluid-rock interactions) have negligible effects on the REY of the chemical sediments (Bolhar et al., 2004). However, Rb is a relatively mobile element compared to highly immobile elements such as Th. In Fig. 6a, the well positive correlation between Rb and Th demonstrates insignificant mobility of the LILEs (Large Ion Lithophile Elements) and the absence of significant diagenetic or metamorphic alteration effects, this conclusion is also consistent with thin section observations (Fig. 3c, d, g, h). With respect to the syn-depositional processes, the contents of Al_2O_3 and TiO_2 are consistently low with averages of 3.66% and 0.41%. In addition, despite the positive correlations between Al_2O_3 and TiO_2 ($r = 0.93$), K_2O ($r = 0.79$), Rb ($r = 0.78$), V ($r = 0.45$), Sc REE ($r = 0.62$) (Fig. 6b-i) signify the incorporation of terrigenous contribution in the deposition processes, most correlation coefficients are much lower than those BIFs sourced from recycled crust (Basta et al., 2011; Cox et al., 2013; Hu et al., 2017, 2020). Besides, the Baijianshan BIF shares similar REE patterns with those BIFs from North China Craton but contains slightly higher contents of Al_2O_3 and TiO_2 (Li et al., 2014). Taken together, we suggest a little incorporation of terrigenous component in the Baijianshan BIF.

Positive Eu anomalies are generally interpreted as the precipitation of high-temperature hydrothermal fluids (Danielson et al., 1992; Bau and Dulski, 1999) while low-temperature hydrothermal fluids usually display weak or no Eu anomalies (Michard et al., 1993; Li et al., 2014). Most samples from the Baijianshan BIF show negligible Eu anomalies ($Eu/Eu^* = 0.96\sim 1.14$, averaging 1.07), which are indicative of low-temperature hydrothermal solutions (Danielson et al., 1992). The

(t) value can be used as a tracer to distinguish different sources and crustal contamination. As shown in Fig. 7, the Baijianshan BIF has slightly average (t) value (average of 0.37), much lower than those of Baijianshan basalt, indicating that the deposition of the Baijianshan BIF was controlled by a hydrothermal flux with mantle- (Jacobsen and Pimentel-Klose, 1988). However, the slightly negative correlation between (Ma) and Al_2O_3 contents (Fig. 8a) argues for the low proportion of detrital components inputting.

The Y/Ho ratios of BIFs can provide constraints of the material source and precipitation environment of BIFs (Hu et al., 2017). Modern seawaters have a Y/Ho ratio of 44-74 (Bau and Dulski, 1996). The terrestrial material has a Y/Ho ratio of ~26, any little terrestrial contamination could quickly descend seawater-like superchondritic Y/Ho ratios (>44) (Bolhar et al., 2004). The hydrothermal fluids have almost chondritic Y/Ho ratios (26-28, Douville et al., 1999; Bau and Dulski, 1999). The Baijianshan BIF has a range of Y/Ho ratios between 23 and 32, similar to the chondritic values (26-28, Bau and Dulski, 1999), possibly due to the mixture of high and/or low-T hydrothermal fluids (Hu et al., 2020). Y/Ho ratios of the Baijianshan BIF samples might inherit from the low-T hydrothermal fluids, but the influences of terrestrial materials can not be completely excluded. Compared with the BIFs in North China Craton, the Baijianshan BIF displays relatively low positive Eu anomalies, low Y/Ho ratios as well as a slightly depleted (Li et al., 2014; Wang et al., 2016), illustrating the input of low-temperature hydrothermal fluids during the deposition of the Baijianshan BIF.

Ce/Ce*_{PAAAS} values with variable Al₂O₃ contents of the Baijianshan BIF indicate that terrigenous detrital materials played little role in the geochemical budget of Ce. In oxidized seawater, Ce(III) transforms into Ce(IV), and then Ce(IV) is likely to be hydrolyzed and precipitated with Fe-Mn oxyhydroxides, organics and clay which lead to a significant negative Ce anomaly of seawater (Byrne and Sholkovitz, 1996). As shown in the Ce/Ce* vs. Pr/Pr* diagram (Fig. 10), all the Baijianshan BIF samples display no Ce anomalies, similar with most Neoproterozoic BIFs, unambiguously arguing for anoxic environment in the ancient ocean. Although the atmospheric and oceanic oxygen levels during the Neoproterozoic are still under debate, numerous studies revealed that Neoproterozoic oceans underwent a stepwise and protracted oxidation. Anoxic ferruginous deep seawater was a typical feature of the late Neoproterozoic, as inferred from geochemical proxies such as iron geochemistry (e.g., Canfield et al., 2008; Sperling et al., 2015), redox-sensitive elements (e.g., Schröder and Grotzinger, 2007; Rajabi et al., 2015), and framboidal pyrite (e.g., Rajabi et al., 2015). Stern et al. (2013) suggested that this scenario might be attributed to the seawater surfaces being covered by ice sheets, blocking the oxygen from atmosphere dissolving into the widespread anoxic ferruginous ocean. Despite no tillite was identified at the Baijianshan BIF, the coeval tillite sequences were documented in the Quruqtagh area (i.e., ca.740 Ma Beiyixi tillite) of NE Tarim (Xu et al., 2009), which argued for the possibility of ice sheets in the Cryogenian Baijianshan ocean.

In a Fe²⁺-rich marine settings, both abiotic and biotic action were demonstrated as oxidation pathways for the precipitation of iron oxyhydroxides (Fe(OH)₃) from dissolved Fe²⁺ (Konhauser et al., 2011). As an element of variable valency, the fractionation of Fe isotope is affected by the oxidation-reduction condition (Bullen et al., 2001; Zhu et al., 2002; Balci et al., 2006). Experimental studies demonstrated that oxidation of Fe²⁺ to Fe³⁺ in solution causes considerable Fe isotope fractionation, generating an enrichment of heavy Fe isotopes in Fe³⁺ (Bullen et al., 2001; Johnson et al., 2002; Balci et al., 2006; Hou et al., 2014). On the other hand, the fractionation caused by pyrite with light-Fe isotopes is considered to play a leading role in the enrichment of heavy Fe isotopes in the residual system relative to the original state (Rouxel et al., 2016), since the pyrite is easier to precipitation from plume. Nevertheless, there is no sulfide observed in the Baijianshan BIF, thus the potential influences of sulfides on the enrichment of heavy Fe isotopes can be excluded. Under oxidized environment, the enrichment of heavy Fe isotopes is shown in oxide or hydroxide of iron trivalent (Fe³⁺_{ppt}) and light Fe isotope is displayed in Ferrous solution (Fe²⁺_{aq}) (Johnson et al., 2002). The magnitude of Fe isotope fractionation is controlled by the degree of precipitation from Fe²⁺ to Fe³⁺, which is related to the degree of ocean oxidation (Yan et al., 2010). The Fe in the seawater can be completely precipitated and no fractionation of the Fe isotope occurs when the seawater is completely oxidized, thus the Fe isotope values in iron oxide precipitates (Fe³⁺) can represent the Fe isotope information of seawater. However, when the seawater is partially oxidized, the Fe in the seawater is partially precipitated and the Fe isotope fractionation will occur in iron oxide precipitates (Fe³⁺). Therefore, the Fe isotope value can be used as a proxy to decipher the redox state of seawater (Yan et al., 2010). Compared with some BIFs deposited during the Archean-Paleoproterozoic (Dauphas et al., 2004; Rouxel et al., 2005; Li et al., 2012; Johnson et al., 2003; Hou et al., 2014; Li et al., 2014), the Neoproterozoic Baijianshan Sanjiang (Yan et al., 2010) and Xinyu BIFs (Shen et al., 2008) have higher values ⁵⁷Fe (Fig. 11). Several studies demonstrated that the low ⁵⁷Fe values of BIFs could be due to the contributions from a continental component and the continental Fe source is best explained by Fe mobilization on the continental margin by microbial dissimilatory iron reduction (DIR) (Johnson et al., 2008; Li et al., 2015). As for the Fe isotope values of Archean-Paleoproterozoic BIFs we cited, the Fe source of SW Greenland BIF, Anshan-Benxi BIFs, Gongchangling BIFs and Yuanjiacun BIFs are unambiguously demonstrated to be hydrothermal type similar to the scenario of the Baijianshan BIF (Dauphas et al., 2004; Li et al., 2012; Li et al., 2014; Hou et al., 2014), while the Fe of Transvaal, Manjeri, Belingwe Belt and Zimbabwe BIFs are probably from multiple sources (abiologic and biologic processes) (Johnson et al., 2008; Grassineau et al., 2011). The comparison reveals that the environment in which they precipitated was more reduced. Both the iron isotope and elemental geochemistry thus demonstrate that the Neoproterozoic Baijianshan ocean might have the same reduced environment as Archean or Paleoproterozoic, or even more reduced.

6.3 A model of the Baijianshan BIF

During the late Neoproterozoic period (i.e., 750-550 Ma), the Earth experienced long-lived global glaciations, known as the Snowball Earth events (Hoffman et al., 1998). In view of the Neoproterozoic oxygenation event (NOE) at that time, the content of oxygen in atmosphere was much higher than before (Och et al., 2012). Recently, EI-Rahman et al. (2020) argued that some Neoproterozoic BIFs are not glaciogenic due to their significant depleted Nd isotope compositions. Under this scenario, the iron was most likely deriving from hydrothermal alteration of juvenile oceanic crust. The Chondritic-like Nd isotope compositions of the Baijianshan BIF (do not favor this model. Furthermore, the close temporally-spatially related tillite sequences in the Quruqtagh of NE Tarim (Xu et al., 2009), 765 Ma-735 Ma tillites in Namibia, suggested a local glaciation termed as Kaigas

at the Baijiashan BIF. The Fe²⁺-rich detritus and Fe²⁺ oxide in near-shore settings were the main Fe source during the precipitation of the BIF. Under the effect of the increased Fe fluxes and a small amount of terrestrial materials input, the Baijiashan BIF was formed.

The Baijiashan BIF was formed in glacially-influenced settings during the Neoproterozoic. The BIFs, accompanied with limited detritus input, were the dominant iron ore types in the Baijiashan BIF. The BIFs were initially covered by ice sheets, giving rise to the extreme Fe fluxes. Then it was oxidized into Fe³⁺ and precipitated as magnetite. In the early stage, local reduced ocean enhanced Fe fluxes generated by hydrothermal activities due to the existence of a reduced oxidized oceanic layer, favoring the formation of the BIF.

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Figure captions

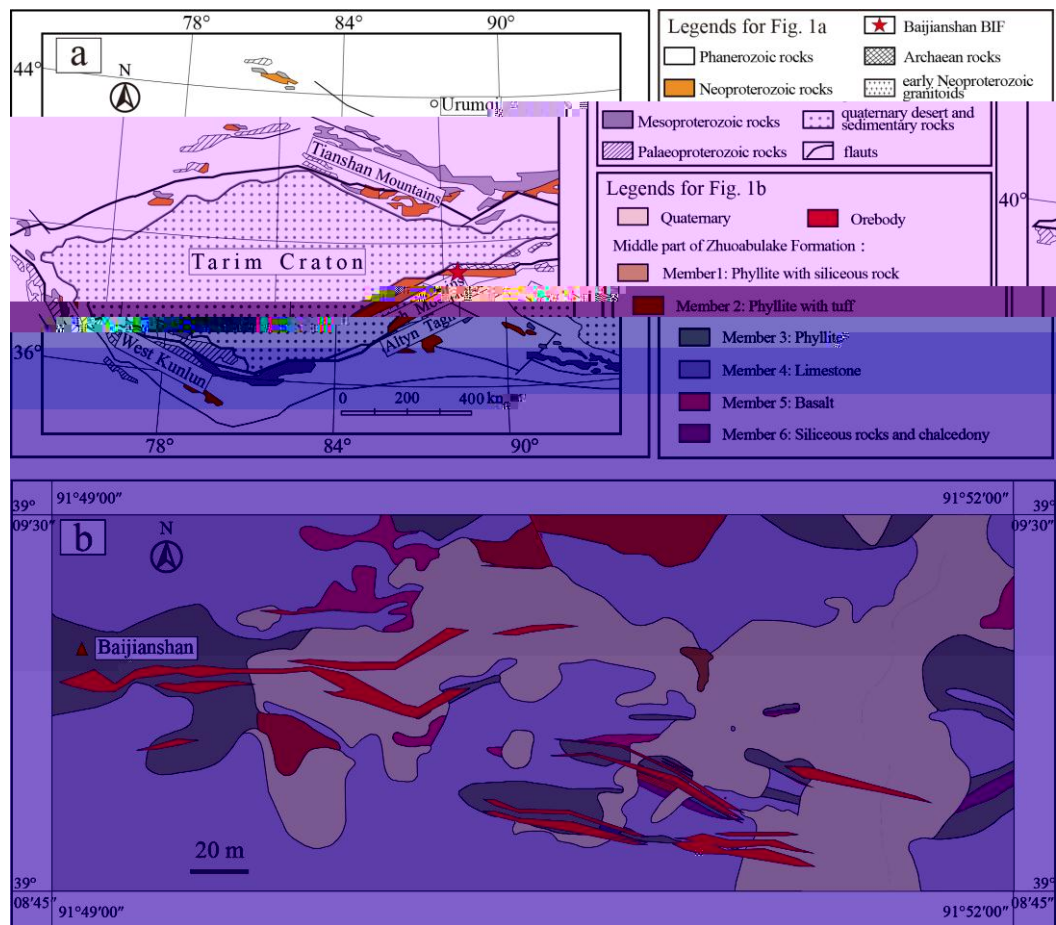


Fig. 1 (a) Sketch Precambrian geological map of Tarim Craton, showing the location of the Baijianshan BIF (modified after Lu et al., 2008). (b) Geological map of the Baijianshan Banded Iron Formation (Baijianshan BIF).

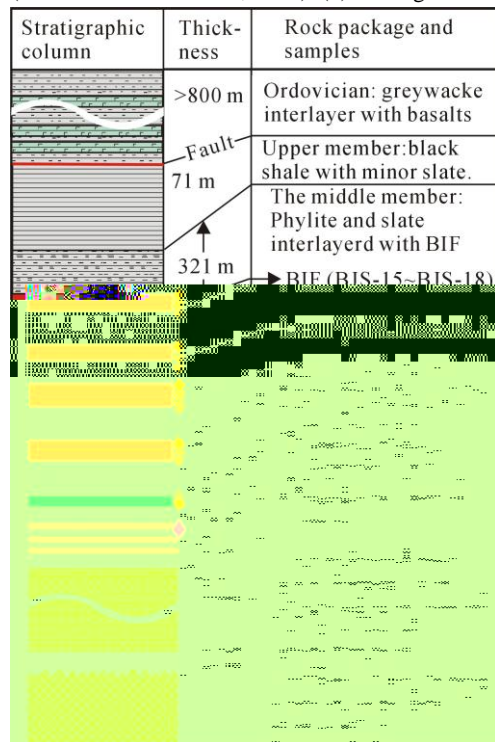


Fig. 2 Stratigraphical column of the Baijianshan BIF.

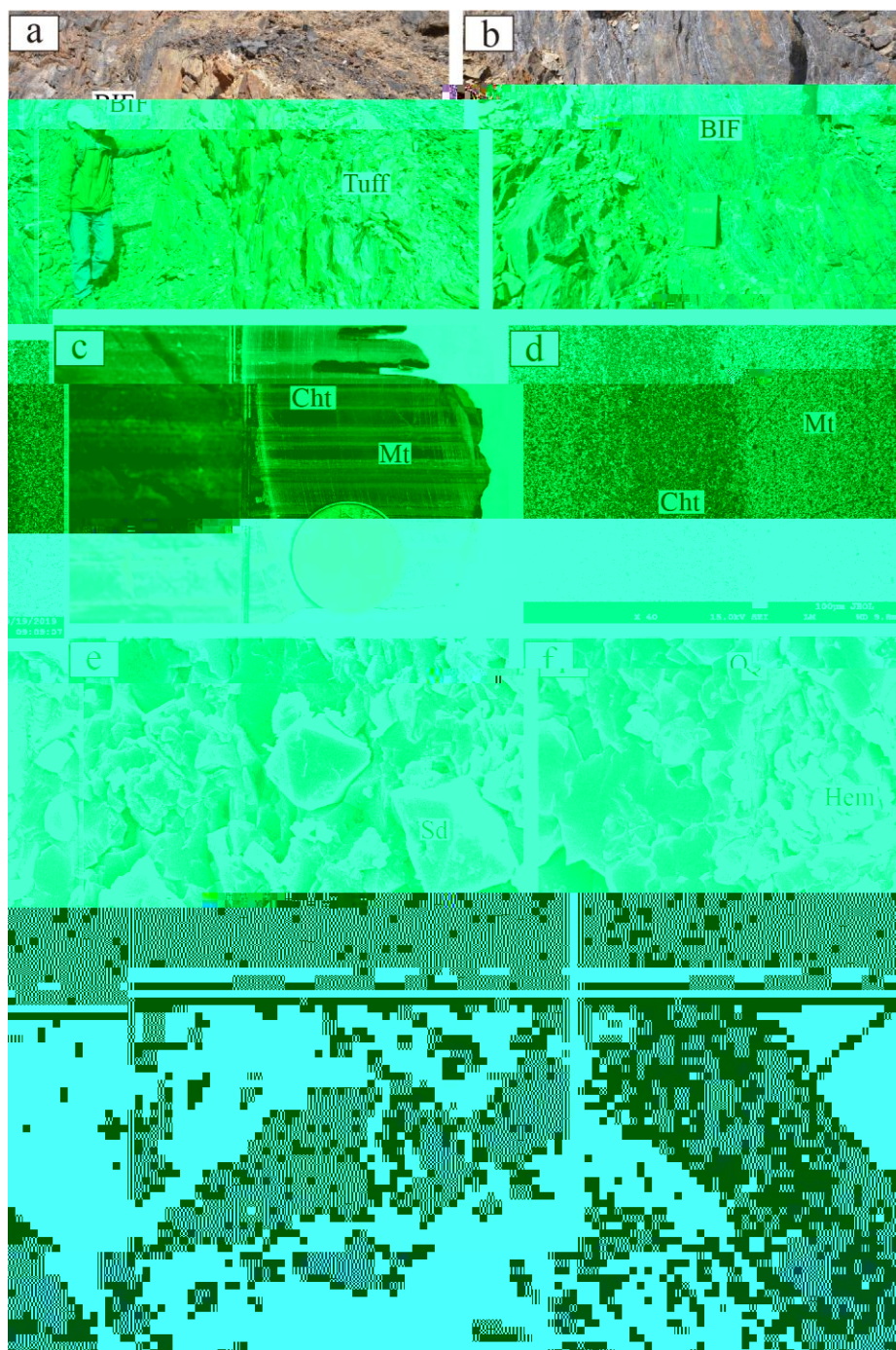


Fig. 3 Field photographs, hand specimen and mineral features of the Baijianshan BIF. (a) The tuff layers in the Baijianshan BIF. (b) Laminated Fe orebodies with local bend. (c) hand specimen. (d) Scanning electron microscopy (SEM) images. Detailed petrographic examination by SEM and transmitted light showing mineral assemblage: (e) Siderite. (f) Hematite. (g) Chlorite. (h) Sericite. Cht = Chert, Mt = Magnetite, Sd = Siderite, Q = Quartz, Hem = Hematite, Chl = Chlorite, Ser = Sericite.

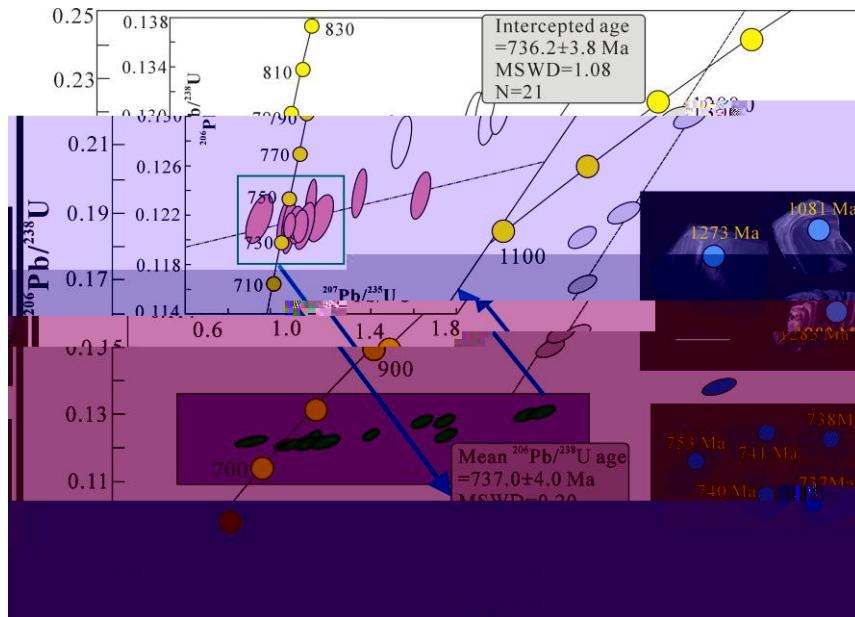


Fig. 4 Concordia diagram of the zircon U-Pb ages of the tuff at the Baijianshan BIF.

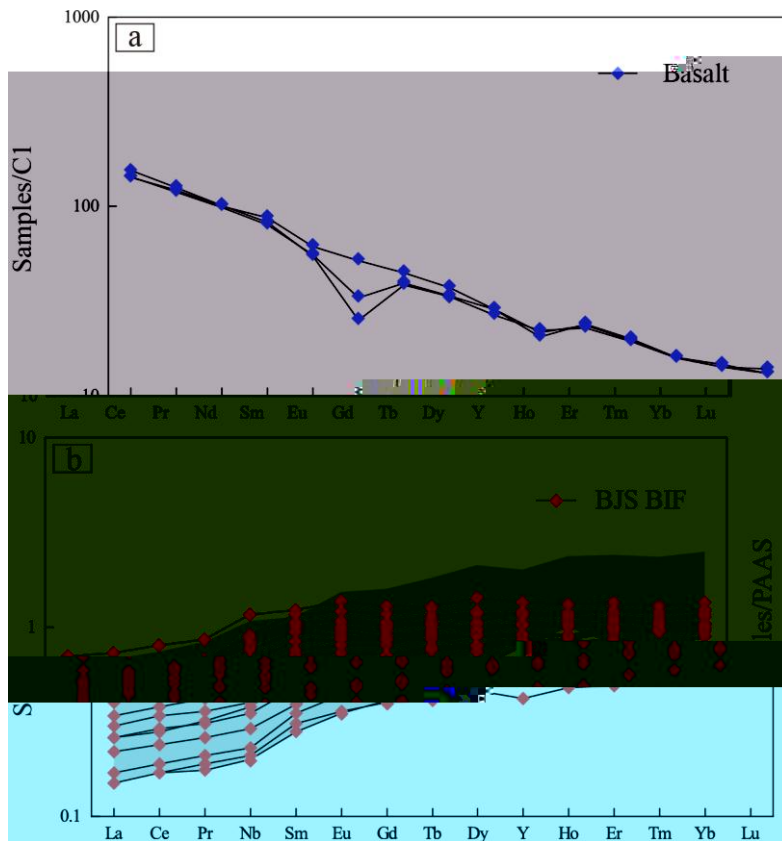


Fig. 5 (a) Chondrite-normalized REE pattern of the basalts. Chondrite-normalized values after Sun and McDonough (1989). (b) PAAS-normalized REE+Y diagrams of BIFs from the Baijianshan BIF. The grayish zone represents the REY data from the Xinyu BIF (Li et al., 2014). PAAS-normalized values after McLennan (1989).

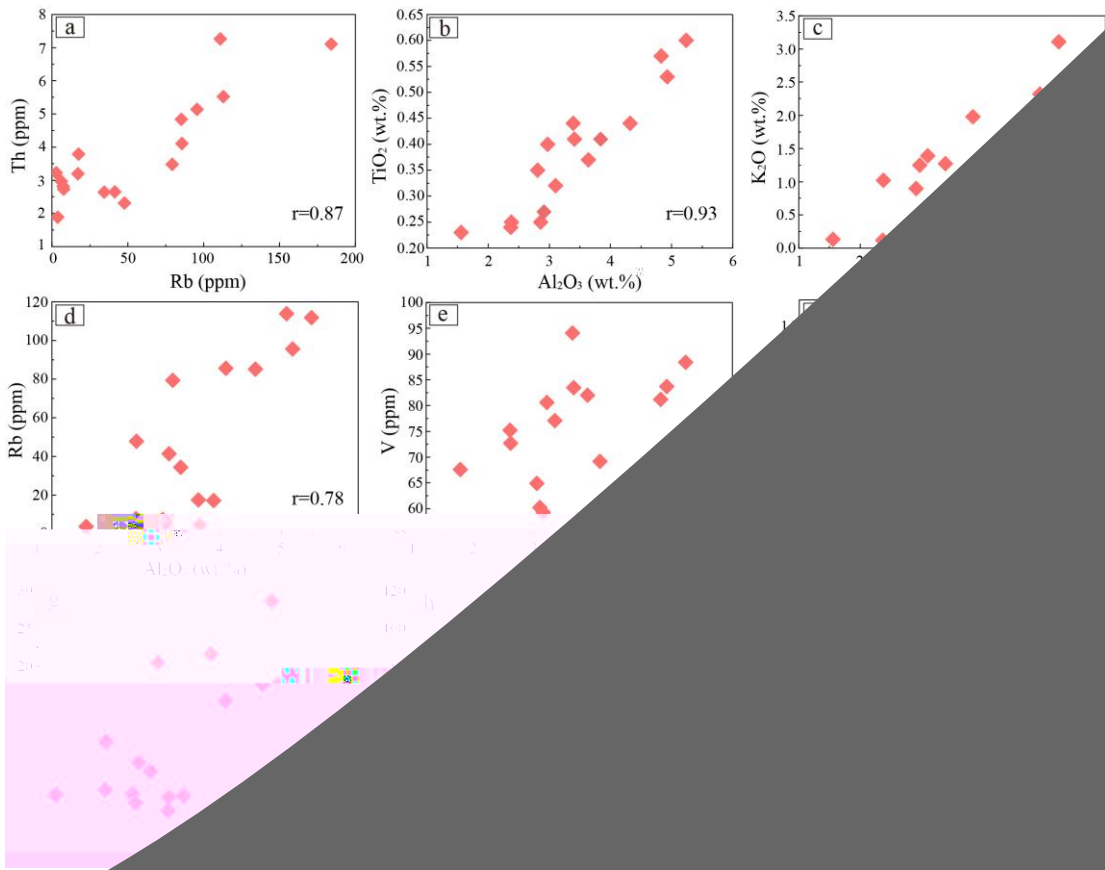


Fig.

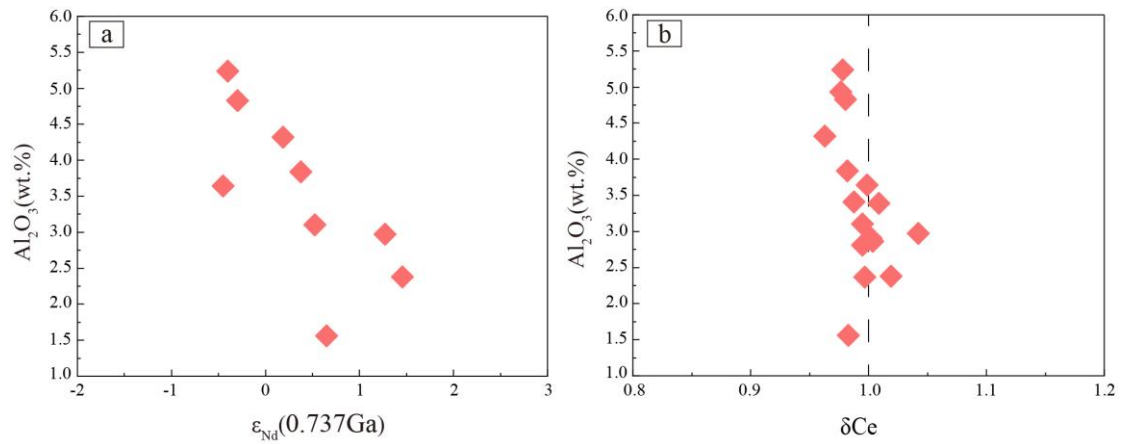


Fig. 8 (a) ϵ_{Nd} ($t = 0.737\text{Ga}$) vs. Al_2O_3 diagram of the Baijianshan BIF; (b) $\text{Ce}/\text{Ce}^*_{\text{PAAS}}$ vs. Al_2O_3 diagram of the Baijianshan BIF.

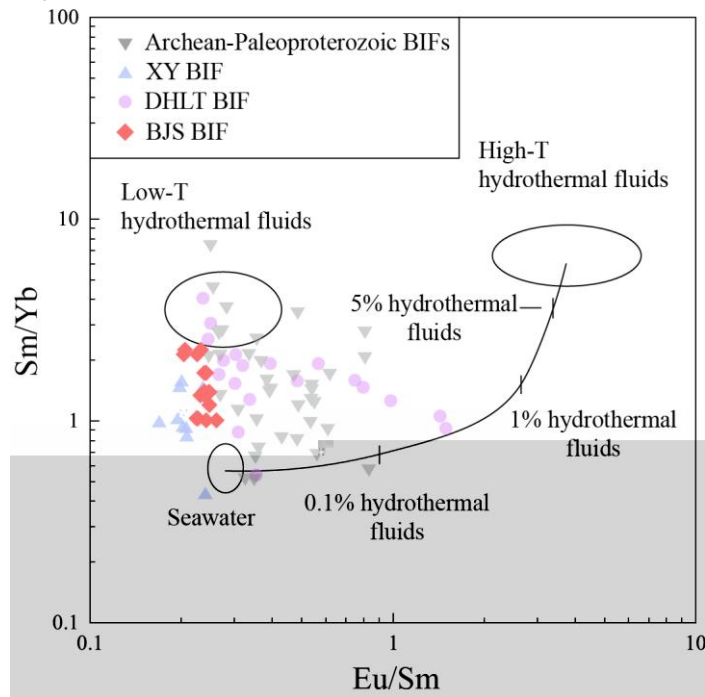


Fig. 9 Sm/Yb vs. Eu/Sm ratios illustrating two component mixing model of the hydrothermal fluid of the Baijianshan BIF (after Alexander et al., 2008). BJS-Baijianshan BIF; XY-Xinyu BIF (Li et al., 2014); DHLT-Dahongliutan BIF (Hu et al., 2017). Data sets of Archean-Paleoproterozoic BIFs are from Planavsky et al. (2010). Average compositions of high-T ($> 300\text{ }^\circ\text{C}$) hydrothermal fluids, low-T ($< 200\text{ }^\circ\text{C}$) hydrothermal solutions and Pacific seawaters were after Bau and Dulski (1999), Michard et al. (1983) and Alibo and Nozaki (1999), respectively.

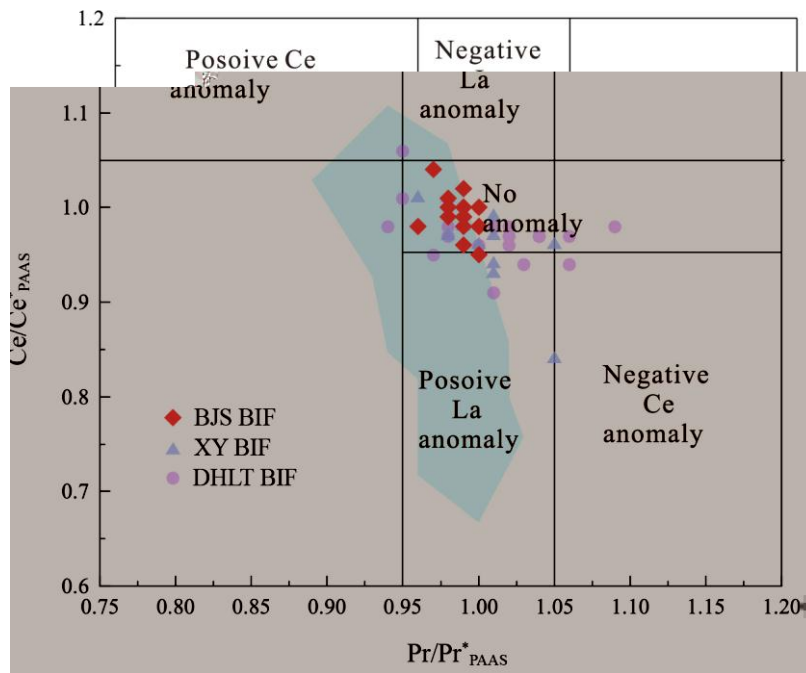


Fig. 10 Pr/Pr^*_{PAAS} vs. Ce/Ce^*_{PAAS} diagram for the BIF at Baijianshan (after Bau and Dulski, 1996). The light blue area represents the data of Archean-Paleoproterozoic BIFs. Data sets of other BIFs are same as those of Fig. 9.

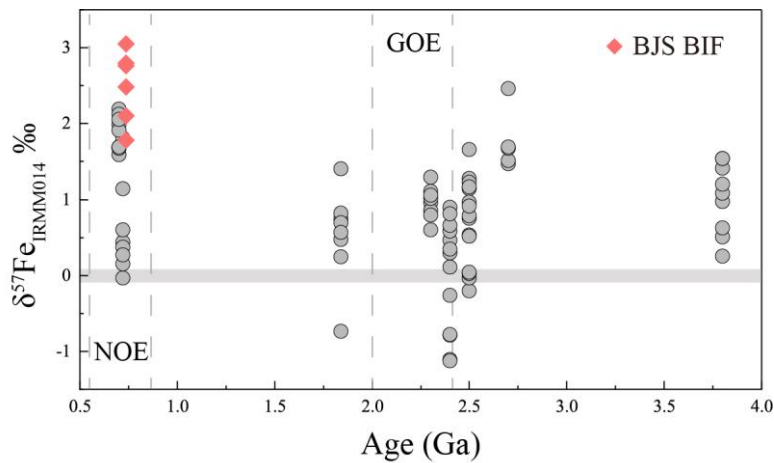


Fig. 11 $^{57}Fe_{IRMM-014}$ of various ages BIFs in the world (Data of SW Greenland BIFs are from Dauphas et al.(2004); Manjeri Formation, Belingwe Belt, Zimbabwe BIFs are from Rouxel et al. (2005); Anshan-Benxi BIFs are from Li et al. (2012); Transvaal BIFs are from Johnson et al. (2003); Yuanjiaocun BIFs are from Hou et al. (2014); Gongchangling BIFs from Li et al. (2014); Sanjiang BIF are from Yan et al. (2010) and Xinyu BIF are from Shen et al. (2008)).

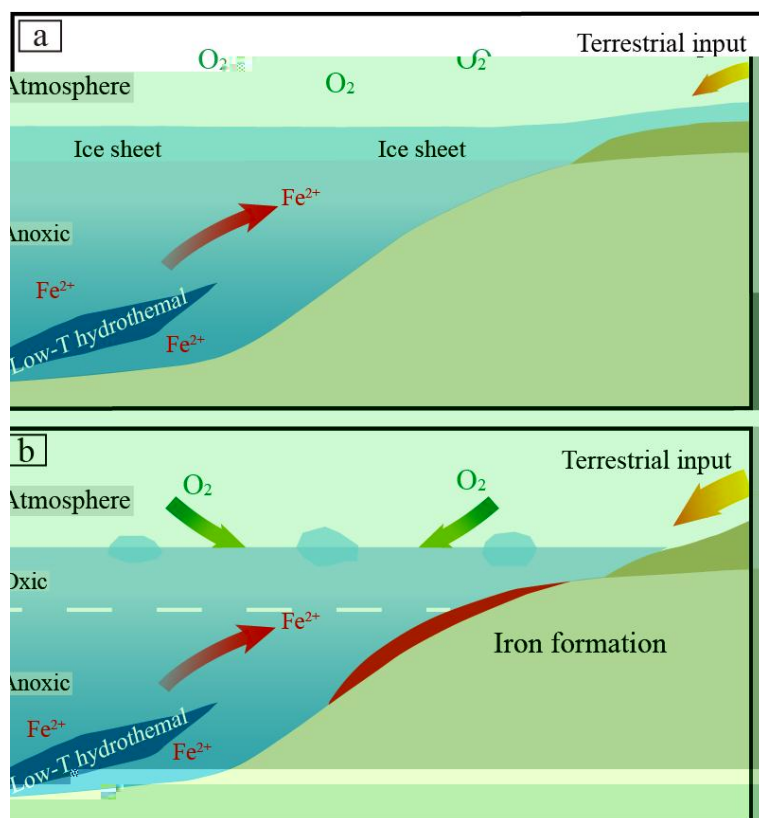


Fig. 12 Cartoon model of the formation of the Baijianshan BIF (see details in the text).

Appendix Table Captions

Appendix-Table 1 LA-ICP-MS U-Pb data for zircon from tuff in the first section of the Lapeiquan Formation

Appendix-Table 2 Geochemical compositions of the Baijianshan BIF

Appendix-Table 3 Sr-Nd isotopic data of the Baijianshan BIF

Appendix-Table 4 Fe isotopic data of the Baijianshan BIF

Supplementary Table 1 Zircon U-Pb age data of the tuff from the Baijianshan BIF

| Spot | U ppm | Th ppm | Th/U | ²⁰⁶ Pb/ ²³⁸ U Age | ²⁰⁷ Pb/ ²³⁵ U Age | ²⁰⁷ Pb/ ²⁰⁶ Pb | ²⁰⁷ Pb/ ²³⁵ U | ²⁰⁶ Pb/ ²³⁸ U |
|--------|-------|--------|------|---|---|--------------------------------------|-------------------------------------|-------------------------------------|
| 2071-1 | 3079 | 831 | 0.27 | 1335 | 14 | 1360 | 21 | 0.0887 |
| 2071-2 | 805 | 427 | 0.53 | 898 | 11 | 1154 | 20 | 0.1027 |
| 2071-3 | 529 | 381 | 0.72 | 776 | 8 | 1009 | 18 | 0.0965 |
| 2071-4 | 155 | 81 | 0.52 | 835 | 9 | 1350 | 22 | 0.1458 |
| 2071-5 | 184 | 101 | 0.55 | 751 | 8 | 1009 | 18 | 0.0999 |
| 2071-6 | 297 | 252 | 0.85 | 1273 | 14 | | | |

Supplementary Table 2 Geochemical compositions of Baijianshan BIF

| Sample | BJS-1 | BJS-2 | BJS-3 | BJS-4 | BJS-5 | BJS-6 | BJS-7 | BJS-8 | BJS-9 | BJS-10 |
|--------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------|
| Major elements (%) | | | | | | | | | | |
| Fe ₂ O ₃ | 53.60 | 41.52 | 56.64 | 52.26 | 30.01 | 36.85 | 41.01 | 45.22 | 39.78 | 48.55 |
| SiO ₂ | 29.91 | 38.96 | 26.81 | 31.20 | 40.92 | 40.79 | 36.97 | 41.77 | 43.66 | 37.59 |
| Al ₂ O ₃ | 1.56 | | | | | | | | | |

| | | | | | | | | | | |
|----------------------------------|--------|--------|--------|-------|--------|--------|--------|--------|--------|--------|
| TFe ₂ O ₃ | 21.79 | 28.86 | 44.82 | 42.63 | 26.98 | 13.11 | 40.45 | 11.61 | 11.70 | 11.98 |
| SiO ₂ | 55.06 | 49.87 | 41.24 | 43.65 | 53.64 | 59.90 | 42.80 | 39.94 | 40.91 | 44.55 |
| Al ₂ O ₃ | 5.24 | 4.93 | 2.81 | 2.86 | 4.83 | 7.58 | 3.84 | 11.36 | 11.45 | 10.76 |
| CaO | 0.81 | 1.02 | 0.75 | 0.75 | 0.76 | 0.84 | 0.65 | 9.77 | 9.31 | 7.45 |
| MgO | 1.57 | 1.51 | 0.74 | 0.86 | 1.36 | 2.32 | 1.31 | 8.40 | 8.54 | 10.38 |
| TiO ₂ | 0.60 | 0.53 | 0.35 | 0.25 | 0.59 | 0.86 | 0.41 | 3.66 | 3.80 | 3.60 |
| MnO | 0.03 | 0.04 | 0.05 | 0.03 | 0.03 | 0.02 | 0.03 | 0.24 | 0.25 | 0.23 |
| P ₂ O ₅ | 0.20 | 0.35 | 0.49 | 0.40 | 0.23 | 0.19 | 0.54 | 0.46 | 0.43 | 0.38 |
| K ₂ O | 3.11 | 2.32 | 0.26 | 0.17 | 1.86 | 3.78 | 1.98 | 1.35 | 1.27 | 0.36 |
| Na ₂ O | 0.94 | 1.25 | 0.14 | 0.19 | 0.63 | 0.77 | 0.88 | 0.94 | 0.98 | 0.59 |
| LOI | 2.06 | 1.97 | 4.57 | 2.89 | 2.9 | 3.19 | 1.92 | 12.02 | 11.39 | 9.60 |
| FeO | 7.97 | 7.26 | 3.89 | 5.29 | 6.06 | 6.57 | 5.31 | - | - | - |
| Total | 99.38 | 99.91 | 100.11 | 99.97 | 99.87 | 99.13 | 100.12 | 99.75 | 100.03 | 99.88 |
| Trace elements (ppm) | | | | | | | | | | |
| Cr | 118 | 81.0 | 59.7 | 10.5 | 86.2 | 112 | 50.9 | 214 | 214 | 306 |
| Ni | 15.6 | 14.5 | 12.1 | 11.0 | 15.6 | 12.3 | 12.6 | 162 | 166 | 217 |
| Co | 76.1 | 70.2 | 33.7 | 34.7 | 54.0 | 27.1 | 45.3 | 48.0 | 62.9 | 50.7 |
| Sc | 12.2 | 14.4 | 7.97 | 8.11 | 11.7 | 15.1 | 8.11 | 26.4 | 26.1 | 25.7 |
| Ba | 662 | 562 | 111 | 19.2 | 359 | 1219 | 385 | 877 | 864 | 296 |
| Sr | 45.0 | 53.3 | 45.8 | 26.1 | 32.6 | 37.0 | 48.9 | 205 | 209 | 150 |
| Rb | 111 | 95.6 | 7.36 | 6.13 | 113 | 184 | 85.6 | 34.4 | 32.2 | 12.3 |
| Zr | 101 | 93.4 | 60.0 | 87.9 | 79.9 | 116 | 79.7 | 259 | 251 | 228 |
| Hf | 2.63 | 2.37 | 1.23 | 1.50 | 2.11 | 2.99 | 1.92 | 5.35 | 5.74 | 6.00 |
| Ta | 0.88 | 0.75 | 0.37 | 0.36 | 0.64 | 0.84 | 0.53 | 2.24 | 2.33 | 2.14 |
| Ga | 7.95 | 7.63 | 4.39 | 4.63 | 7.12 | 10.3 | 5.97 | 18.3 | 17.2 | 18.8 |
| Cu | 27.6 | 21.6 | 8.12 | 3.56 | 21.4 | 36.0 | 12.4 | - | - | - |
| Zn | 62.1 | 40.0 | 26.0 | 23.8 | 35.3 | 37.0 | 29.6 | - | - | - |
| Pb | 7.80 | 8.24 | 3.54 | 5.32 | 7.64 | 15.4 | 5.75 | - | - | - |
| U | 0.47 | 0.69 | 0.39 | 0.40 | 0.72 | 0.82 | 0.37 | 1.45 | 1.09 | 0.92 |
| Th | 7.26 | 5.14 | 2.81 | 2.97 | 5.52 | 7.11 | 4.11 | 3.32 | 3.37 | 3.18 |
| Nb | 8.35 | 8.21 | 4.19 | 4.86 | 6.80 | 9.50 | 6.11 | 38.0 | 36.5 | 33.6 |
| La | 26.8 | 20.3 | 13.0 | 9.82 | 19.1 | 22.5 | 17.3 | 36.9 | 34.1 | 33.7 |
| Ce | 58.3 | 44.2 | 30.2 | 22.8 | 42.0 | 46.1 | 39.0 | 77.2 | 72.9 | 74.9 |
| Pr | 7.03 | 5.35 | 3.73 | 2.77 | 5.09 | 5.51 | 4.81 | 9.37 | 9.15 | 9.28 |
| Nd | 29.3 | 22.4 | 16.2 | 11.7 | 21.3 | 22.6 | 20.7 | 37.9 | 36.6 | 40.0 |
| Sm | 6.46 | 4.95 | 3.67 | 2.65 | 4.70 | 4.96 | 4.70 | 8.06 | 8.20 | 9.11 |
| Eu | 1.33 | 1.15 | 0.91 | 0.66 | 1.06 | 1.01 | 1.12 | 1.41 | 1.85 | 2.91 |
| Gd | 6.39 | 5.03 | 4.02 | 3.03 | 4.64 | 4.93 | 5.01 | 7.69 | 7.82 | 8.87 |
| Tb | 1.00 | 0.80 | 0.67 | 0.52 | 0.72 | 0.79 | 0.82 | 1.21 | 1.22 | 1.35 |
| Dy | 5.98 | 4.98 | 4.53 | 3.71 | 4.26 | 4.84 | 5.36 | 6.57 | 7.04 | 7.04 |
| Y | 28.5 | 24.9 | 27.9 | 22.0 | 20.1 | 26.1 | 31.9 | 34.8 | 34.0 | 32.1 |
| Ho | 1.20 | 1.04 | 1.02 | 0.85 | 0.86 | 1.01 | 1.17 | 1.25 | 1.29 | 1.31 |
| Er | 3.23 | 2.94 | 3.00 | 2.59 | 2.33 | 2.82 | 3.38 | 3.11 | 3.15 | 3.20 |
| Tm | 0.45 | 0.43 | 0.46 | 0.40 | 0.34 | 0.41 | 0.50 | 0.39 | 0.40 | 0.39 |
| Yb | 2.87 | 2.93 | 3.06 | 2.76 | 2.20 | 2.69 | 3.36 | 2.28 | 2.36 | 2.28 |
| Lu | 0.43 | 0.45 | 0.49 | 0.45 | 0.33 | 0.41 | 0.53 | 0.34 | 0.32 | 0.32 |
| | 150.77 | 116.95 | 84.95 | 64.71 | 108.93 | 120.58 | 107.75 | 193.68 | 186.4 | 194.67 |
| Y/Ho | 23.75 | 23.94 | 27.35 | 25.76 | 23.29 | 25.84 | 27.26 | 27.84 | 26.36 | 24.50 |
| La/La* | 1.06 | 1.07 | 1.09 | 1.02 | 1.06 | 1.09 | 1.10 | 1.14 | 1.06 | 1.14 |
| Ce/Ce* | 0.98 | 0.98 | 0.99 | 1.00 | 0.98 | 0.95 | 0.98 | 0.98 | 0.98 | 1.01 |
| Y/Y* | 0.85 | 0.88 | 1.04 | 0.99 | 0.84 | 0.95 | 1.02 | 0.89 | 0.83 | 0.78 |
| Pr/Pr* | 1.00 | 1.00 | 0.99 | 0.99 | 1.00 | 1.00 | 0.99 | 0.97 | 0.99 | 0.95 |
| Eu/Eu* | 0.97 | 1.08 | 1.10 | 1.08 | 1.07 | 0.96 | 1.08 | 0.54 | 0.69 | 0.97 |
| La _N /Yb _N | 0.69 | 0.51 | 0.31 | 0.26 | 0.64 | 0.62 | 0.38 | 10.99 | 9.82 | 10.04 |

Supplementary Table 3 Sr-Nd isotopic data of the Baijianshan BIF

| Sample | ⁸⁷ Rb/ ⁸⁶ Sr | ⁸⁷ Sr/ ⁸⁶ Sr | (⁸⁷ Sr/ ⁸⁶ Sr) _i | ¹⁴⁷ Sm/ ¹⁴⁴ Nd | ¹⁴³ Nd/ ¹⁴⁴ Nd | T _{DM} (Ga) | | | |
|--------|------------------------------------|------------------------------------|--|--------------------------------------|--------------------------------------|----------------------|----------|------|-------|
| BJS-1 | 0.0433 | 0.717927 | 0.000004 | 0.7175 | 0.1457 | 0.512425 | 0.000006 | 1.63 | 0.65 |
| BJS-4 | 4.2608 | 0.727751 | 0.000009 | 0.6829 | 0.1308 | 0.512394 | 0.000003 | 1.39 | 1.46 |
| BJS-5 | 1.4305 | 0.728893 | 0.000008 | 0.7138 | 0.1378 | 0.512363 | 0.000003 | 1.58 | 0.19 |
| BJS-7 | 2.4192 | 0.729423 | 0.000009 | 0.7040 | 0.1473 | 0.512376 | 0.000002 | 1.78 | -0.45 |
| BJS-8 | 2.8555 | 0.718681 | 0.000003 | 0.6886 | 0.1238 | 0.512351 | 0.000004 | 1.36 | 1.27 |
| BJS-10 | 2.6390 | 0.723954 | 0.000005 | 0.6962 | 0.1344 | 0.512364 | 0.000002 | 1.51 | 0.53 |
| BJS-12 | 7.0891 | 0.740795 | 0.000007 | 0.6662 | 0.1333 | 0.512311 | 0.000003 | 1.59 | -0.40 |
| BJS-16 | 9.9936 | 0.746329 | 0.000008 | 0.6412 | 0.1334 | 0.512317 | 0.000003 | 1.58 | -0.30 |
| BJS-18 | 5.0054 | 0.731954 | 0.000008 | 0.6793 | 0.1373 | 0.51237 | 0.000004 | 1.56 | 0.38 |
| 2702H1 | 0.4737 | 0.711034 | 0.000009 | 0.7061 | 0.1286 | 0.512662 | 0.000003 | 0.88 | 6.90 |
| 2702H2 | 0.4355 | 0.711156 | 0.000009 | 0.7066 | 0.1354 | 0.512694 | 0.000006 | 0.89 | 6.88 |
| 2702H3 | 0.2322 | 0.710822 | 0.000012 | 0.7084 | 0.1377 | 0.512644 | 0.000005 | 1.02 | 5.69 |

Supplementary Table 4 Fe isotopic data of the Baijianshan BIF

| Sample | ⁵⁷ Fe _{IRMM-014} | ⁵⁶ Fe _{IRMM-014} |
|--------|--------------------------------------|--------------------------------------|
|--------|--------------------------------------|--------------------------------------|

| | |
|--------|------|
| BJS-2 | 2.10 |
| BJS-5 | 1.78 |
| BJS-7 | 2.76 |
| BJS-9 | 2.49 |
| BJS-12 | 3.05 |
| BJS-17 | 2.80 |