Origin of the Neoproterozoic Baijianshan banded iron formation at the southeastern margin of the Tarim Block in NW China: implication for an extremely reducing ocean

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Abstract: The Neoproterozoic Banded iron formations (BIFs) were closely associated with the K = during the breakup of the Rodinia, thus they played an important role in our understanding of the atmospheric and oceanic oxygen levels during this period. In this contribution, the Neoproterozoic (ca. 737 Ma) Baijianshan BIF at Southeast Tarim, northwestern China was identified. Magnetite is the dominated iron-species, which occurs as the lamina interbedded with chert. The BIF contains low concentrations of trace elements, and is depleted in light rare earth elements (LREEs) based on comparison with the Post Archean Australian Shale (PAAS). In addition, the BIF exhibits slightly positive La-Eu anomalies, negligible Ce anomalies, insignificant Y anomalies, chondritic Y/Ho ratios (23-32), and slightly chondritic initial F 5 /+/ E ! -0.45 to 1.46, averaging 0.37). All these features indicate that the precipitation of Baijianshan BIF was closely related to the submarine low-T hydrothermal fluids with little detrital contribution. Moreover, the Baijianshan BIF is > $^{57}Fe_{IRMM-014}$ values ranging) / 0 +(- revealing the partial oxidation of Fe^{2+} into Fe^{3+} during the precipitation of this BIF. Our data suggest that the formation of Baijianshan BIF was closely associated with a significantly reducing ocean, which most likely was isolated from the oxidized atmosphere by a local ice sheet. This Neoproterozoic Baijianshan ocean has the initial oxygen levels as low as, or even lower than that of Archean and Paleoproterozoic oceans.

Key words: Neoproterozoic, banded iron formations (BIFs), Sr-Nd isotope, Fe isotope, Tarim block

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1 Introduction

Banded iron formations (BIFs), one of the most important iron sources in the world, are typical marine sedimentary rocks mainly precipitated during the Precambrian. BIF was firstly defined as a type of sedimentary rock containing more than 15% iron (James, 1954, 1966), which was later revised as thinly layered or laminated rock in which chert (or its metamorphic equivalent) alternating with layers that are composed mainly of iron minerals with the iron content ranging from 20% to 35% (James, 1983). The oldest BIFs precipitated at 3.8 Ga (Isua, Greenland), and then a large number of BIFs formed during the Archean-Paleoproterozoic (3.5-1.8 Ga), with a peak at ca. 2.5 Ga (Klein, 2005 and the references therein). They disappeared at ca. 1.8 Ga, and reoccurred in the Neoproterozoic (0.8-0.6 Ga) after a billion-year hiatus (Klein, 2005). It is commonly accepted that the precipitations of BIFs were closely related to fundamental changes in atmospheric and/or oceanic oxygen levels (i.e., Great Oxidation Event, GOE), although some key issues, including the source of the hydrothermal fluids, oxygen level and tectonic settings, are still under debate (Holland, 2002). In line with tectonic backgrounds, the BIFs can be subdivided into Algoma- and Superior-type (Gross, 1980), the Algoma-type generally precipitated nearby the volcano craters, in the sequences mainly composed of volcanic rocks, greywackes and turbidites (Klein and Beukes, 1992; Li et al., 2014; Sial et al., 2015), while the Superior-type were usually formed with sedimentary rock in shallow marine environment, such as passive continental margin (Gross and Mcleod, 1980).

Although the resources of Neoproterozoic BIFs are even much less than those of Archean and Paleoproterozoic, they are widely distributed worldwide, such as Rapitan BIF in Canada (Halverson et al., 2011), Wadi Karim and Um Anab BIF in Egypt (Basta et al., 2011), Sawawin BIF in Saudi Arabia (Stern et al., 2013), Jacadigo in Brazil (Freitas et al., 2011), Holowilena and Oraparinna in South Australia (Cox et al., 2016), the Kingston Peak Formation in California (Lechte et al., 2018) and Wadi Hamama in the Arabian Nubian Shield (El-Rahman et al., 2020). They were also discovered in the Precambrian massifs in Phanerozoic orogenic belts of South China, such as Sanjiang in Guangxi Province (Yan et al., 2010), Shilu in Hainan Province (Xu et al., 2014), Xinyu in Jiangxi Province (Li et al., 2014; Shen et al., 2018; Zhu et al., 2019), the Shalong in the Central Tianshan (Lei et al., 2016, 2018) and Dahongliutan BIF in the Western Kunlun 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 km^2, 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).

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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 $^{206}Pb/^{238}U$ age and $^{207}Pb/^{235}U$ age, yield a mean $^{206}Pb/^{238}U$ 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/TiO_2 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 Chrondrite-normalized pattern (Fig. 5a) (La_N/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 Ce/Ce^* ~ 1 and Pr/Pr^* ~ 1; Bau and Dulski, 1996) and insignificant Eu and Y anomaly (Eu/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 ($^{87}Sr/^{86}Sr)_i$ ranging from 0.7061 to 0.7084 due to post-eruption hydrothermal alteration. In addition, F F 5 /+/ E ! - / 6.9.

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 $^{143}Nd/^{144}Nd$ (0.51231-0.51243) and $^{87}Sr/^{86}Sr$ (0.7179-(/, . +! L F (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 ($^{87}Sr/^{86}Sr)_i$ 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 $^{56}Fe_{IRMM-014}$ values of 1.24-*)/ $^{57}Fe_{IRMM-014}$ 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

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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 5 (//! ; 5 (. .! ; 5 (/*! 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^* = 0.96~1.14, averaging 1.07), which are indicative of low-temperature hydrothermal solutions (Danielson et al., 1992). The F (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 F (t) value (average of F ! 5 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- F ! (Jacobsen and Pimentel-Klose, 1988). However, the slightly negative correlation between F /+/ 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 superchondretic 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 slighly depleted F ! 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^*_{PAAS} values with variable Al_2O_3 contents of the Baijianshan BIF indicate that terrigenous detrital materials played little role in the geochemical budget of Ce. In oxidized seawater, Ce( ) transforms into Ce( ), and then Ce( ) 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 Fe^{2+}-rich marine settings, both abiotic and biotic action were demonstrated as oxidation pathways for the precipitation of iron oxyhydroxides ($Fe(OH)_3$) from dissolved Fe^{2+} (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 Fe^{2+} to Fe^{3+} in solution causes considerable Fe isotope fraction, generating an enrichment of heavy Fe isotopes in Fe^{3+} (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 (Fe^{3+}_{ppt}) and light Fe isotope is displayed in Ferrous solution (Fe^{2+}_{aq}) (Johnson et al., 2002). The magnitude of Fe isotope fractionation is controlled by the degree of precipitation from Fe^{2+} to Fe^{3+}, 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 (Fe^{3+}) 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 (Fe^{3+}). 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 ^{57}Fe (Fig. 11). Several studies demonstrated that the low ^{57}Fe 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 dissimilatiry 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 (F ! 5 (+/! 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

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glaciation (Kay et al., 2001; Cailteux et al., 2005; Hoffmann et al., 2006). Considering the high latitude position of the Tarim in the Rodinia configuration (Li et al., 2008), the Kaigas glaciation (corresponding to the Beiyixi tillite in Tarim) most possibly occurred in Tarim. In combination with previous studies on other BIFs with the data presented in this study, we construct a cartoon model showing the formation mechanism of the Baijianshan BIF (Fig. 12).

Stage 1, the seawater was covered by ice sheet which led to the insulation between atmosphere and oceans with the in K = And then it induced the emergence of a reductive ocean. The iron supplied by low-temperature hydrothermal fluids could exist as the ferrous form, forming a relatively stable anoxic ferruginous reservoir in the ocean.

Stage 2, at interglacial period, the partial melting of the ice sheet caused some oxygen from the atmosphere into the ocean, which emerged a stratified seawater. There were mainly anoxic and Fe^{2+}-rich deeper seawater, whereas the Fe^{2+} was gradually oxidized into Fe^{3+} and precipitated into iron oxide in near-shore oxic shallow seawaters. The low-temperature hydrothermal was the dominant source during the precipitation process to interpret the slight positive Eu anomalies and positive values F !. Under the effect of the melting ice-sheet, the increasing weathering then contributed to a small amount of terrestrial materials into the shallow seawater, resulting the precipitation of the Baijianshan BIF.

7 Conclusions

The Baijianshan BIF precipitated in glacially-influenced settings during the Neoproterozoic (737 Ma). Low-T hydrothermal fluids, accompanied with limited detritus input, were the dominated iron sources for the formation of Baijianshan BIF.

The Baijianshan ocean was initially covered by ice sheets, giving rise to the extremely reduced environment favored by Fe^{2+}. Then it was oxidized into Fe^{3+} and precipitated as magnetite due to the thawing of ice sheets. At the early stage, local reduced ocean enhanced Fe fluxes genetically related to the intensive marine magmatism and hydrothermal activities due to the existence of ice sheets. Thawing of ice sheets induced oxidized oceanic layer, favoring the formation of the Neoproterozoic BIF at the later stage.

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Figure captions

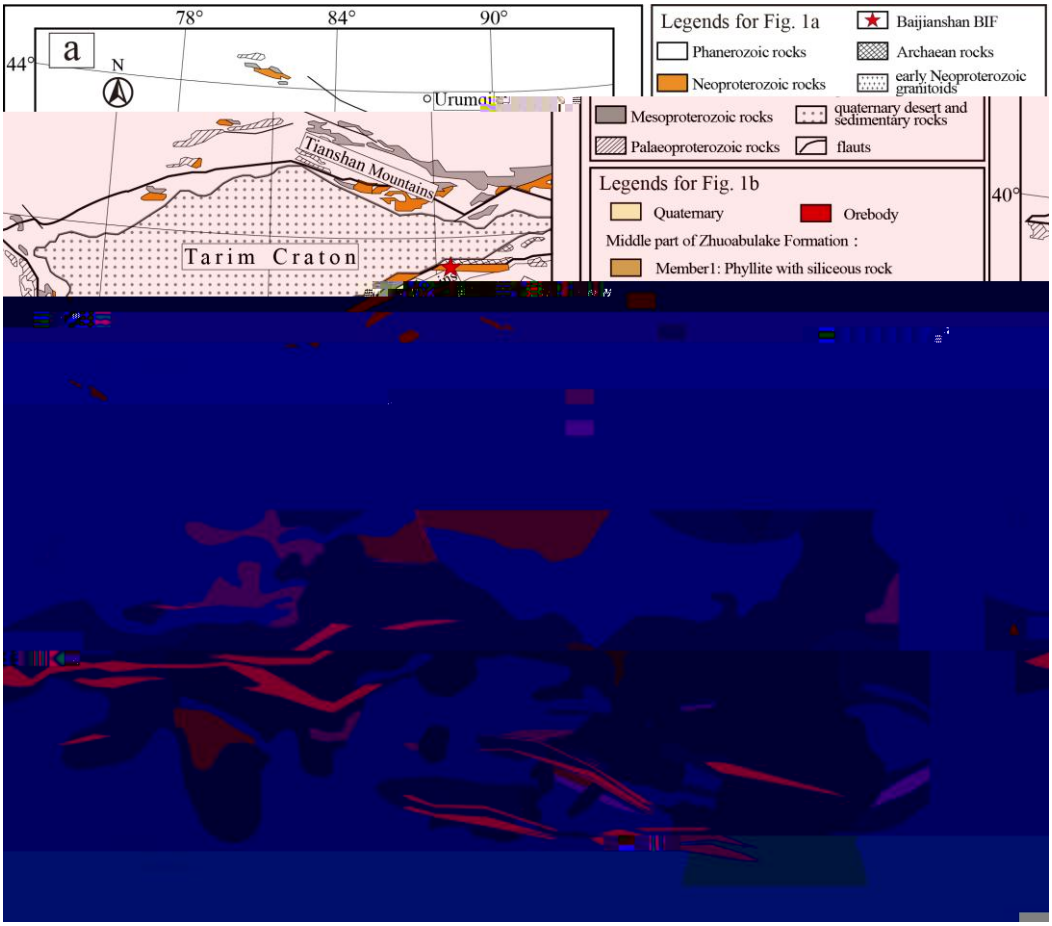

Fig. 1 (a) Sketch Precambrian geological map of Tarim Craton, showing the location of the Baijianshan BIF (modified after Lu et al., 2008). (b) Geological map of the Baijianshan Banded Iron Formation (Baijianshan BIF).

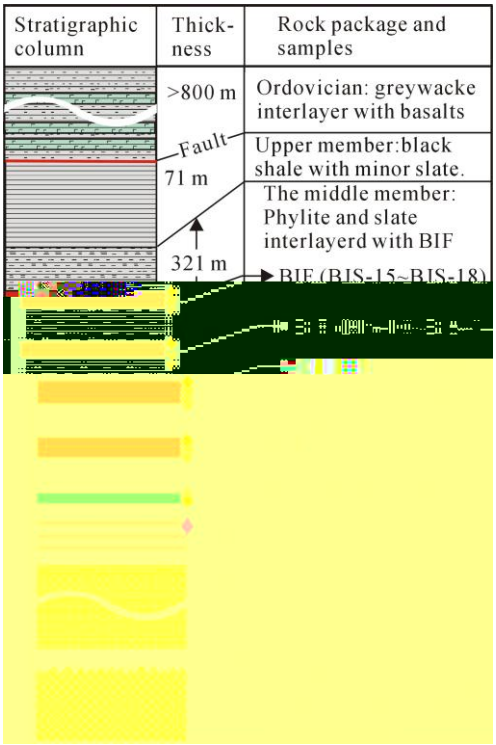

Fig. 2 Stratigraphical column of the Baijianshan BIF.

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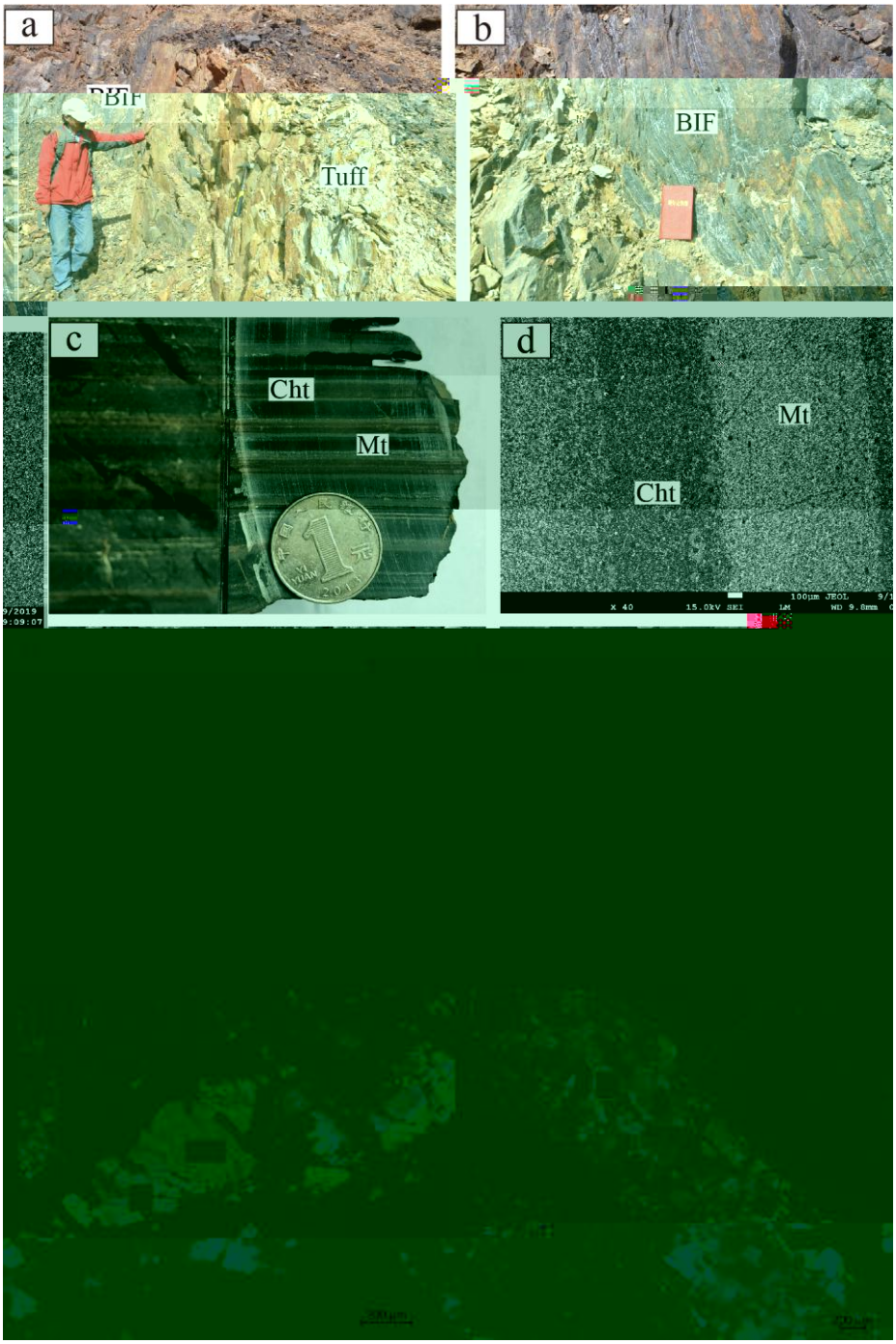

Fig. 3 Field photographs, hand specimen and mineral features of the Baijianshan BIF. (a) The tuff layers in the Baijianshan BIF. (b) Laminated Fe orebodies with local bend. (c) hand specimen. (d) Scanning electron microscopy (SEM) images. Detailed petrographic examination by SEM and transmitted light 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.

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

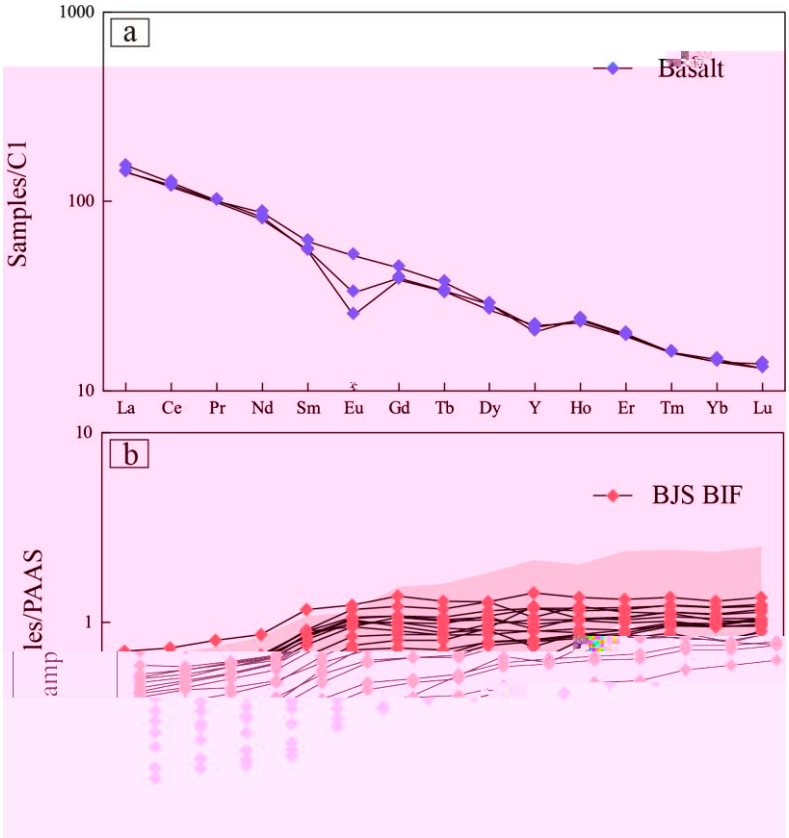

Fig. 5 (a) Chondrite-normalized REE parttern of the basalts. Chondrite-normalized values after Sun and McDonough (1989). (b) PAAS-normalized REE+Y diagrams of BIFs from the Baijianshan BIF. The grayish zone represents the REY data from the Xinyu BIF (Li et al., 2014). PAAS-normalized values after McLennan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

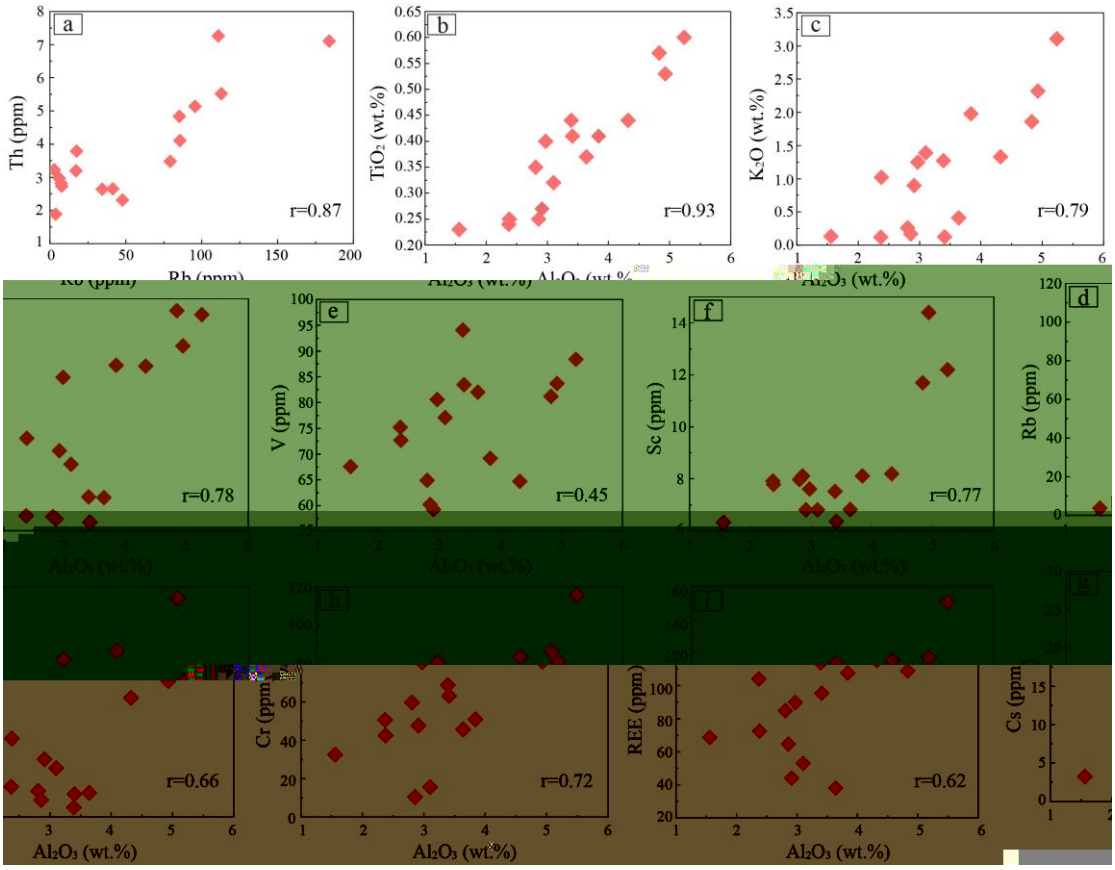

Fig. 6 (a) Bi-variation n between Rb and Th of Baijianshan BIF samples; (b-i) Bi-variation between Al_2O_3 and TiO_2 (b), K_2O (c), Rb (d), V (e), Sc (f), Cs (g), Cr (h) and REE (i) of the Baijianshan BIF. Data for bulk-rock BIF samples are listed in supplementary Table 2.

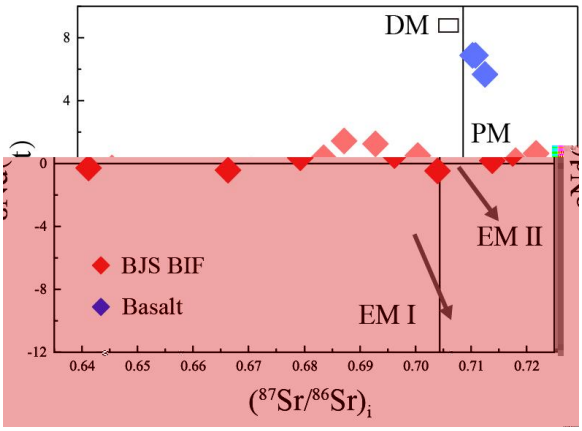

Fig. 7 F ! $^{87}Sr/^{86}Sr)_i$ diagram of BIF and basalt samples in Baijianshan.

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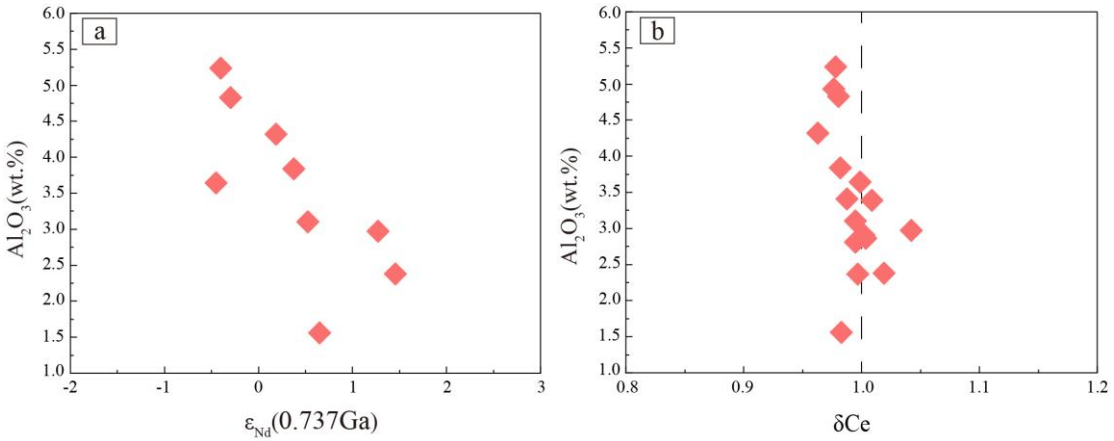

Fig. 8 ! F (t = 0.737Ga) vs. Al_2O_3 diagram of the Baijianshan BIF; (b) Ce/Ce^*_{PAAS} vs. Al_2O_3 diagram of the Baijianshan BIF.

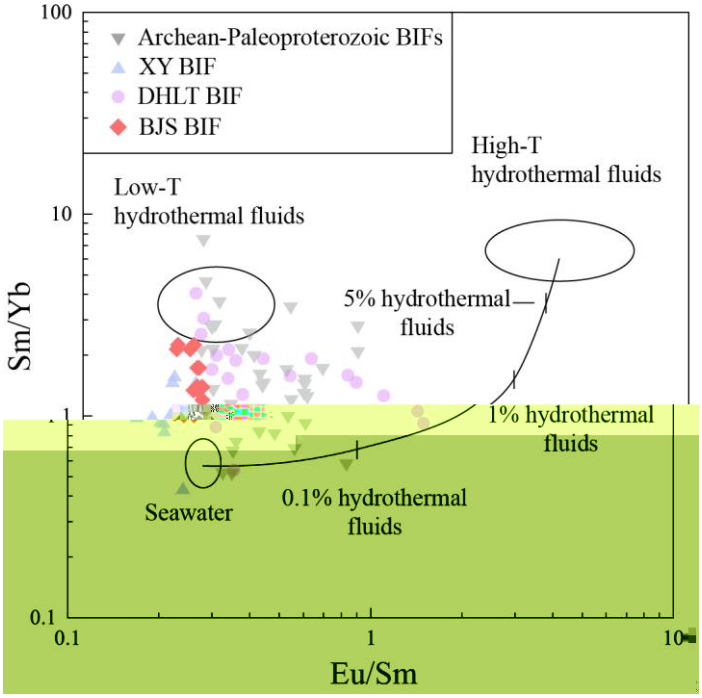

Fig. 9 Sm/Yb vs. Eu/Sm ratios illustrating two component mixing model of the hydrothermal fluid of the Baijianshan BIF (after Alexander et al., 2008). BJS-Baijianshan BIF; XY-Xinyu BIF (Li et al., 2014); DHLT-Dahongliutan BIF (Hu et al., 2017). Data sets of Archean-Paleoproterozoic BIFs are from Planavsky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

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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.

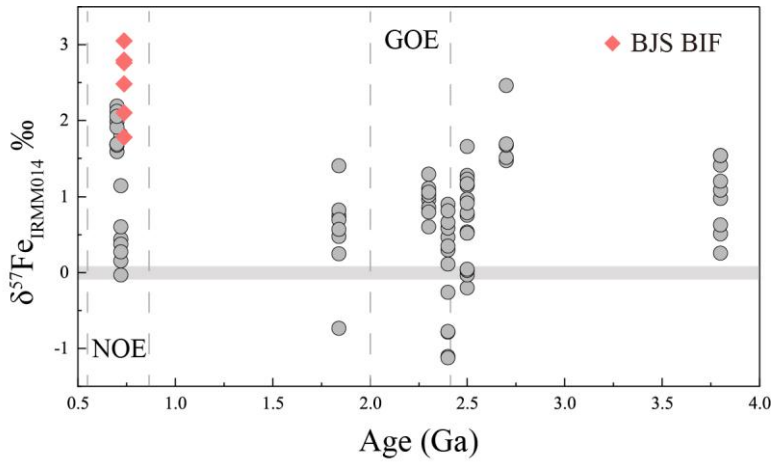

Fig. 11 L $^{57}Fe_{IRMM-014}$ of various ages BIFs in the world (Data of SW Greenland BIFs are from Dauphas et al.(2004); Manjeri Formation, Belingwe Belt, Zimbabwe BIFs are from Rouxel et al. (2005); Anshan-Benxi BIFs are from Li et al. (2012); Transvaal BIFs are from Johnson et al. (2003); Yuanjiacun 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)).

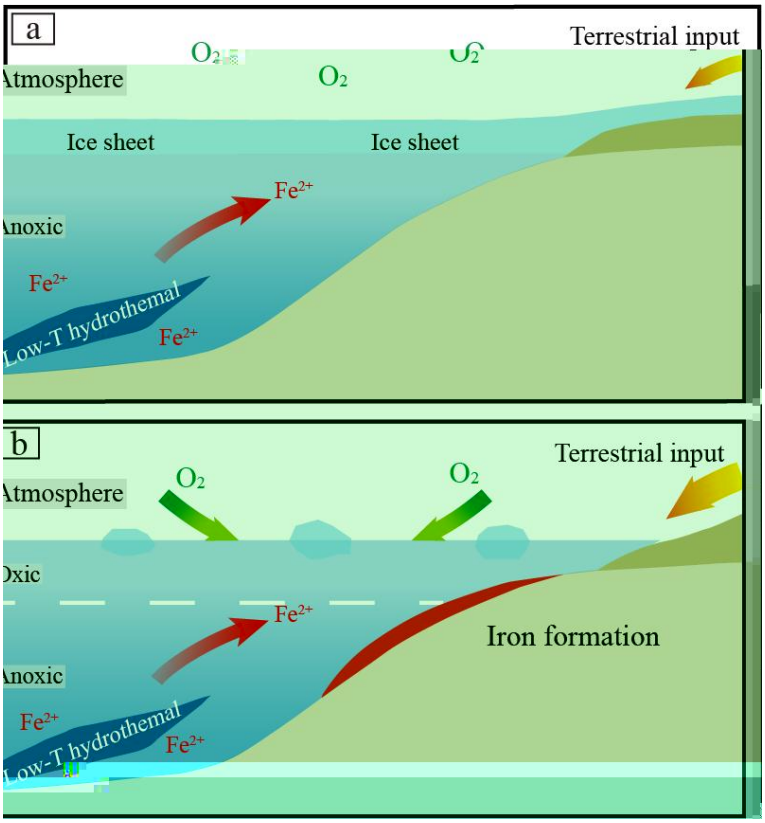

Fig. 12 Cartoon model of the formation of the Baijianshan BIF (see details in the text).

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	0.0012	2.8156	0.0427	0.2301	0.0025
[redacted]			0.53	898	11	1154	20	0.1027	0.0014	2.1169	0.0369	0.1495	0.0018
2071-3	529	381	0.72	776	8	1009	18	0.0965	0.0016	1.7019	0.0307	0.1279	0.0014
2071-4	155	81	0.52	835	9	1350	22	0.1458	0.0022	2.778	0.0462	0.1382	0.0015
2071-5	184	101	0.55	751	8	1009	18	0.0999	0.0016	1.7022	0.0304	0.1236	0.0013
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_2O_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_2O_3	1.56									

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TFe_2O_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_2O_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_2O_5	0.20	0.35	0.49	0.40	0.23	0.19	0.54	0.46	0.43	0.38
K_2O	3.11	2.32	0.26	0.17	1.86	3.78	1.98	1.35	1.27	0.36
Na_2O	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
J ==	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	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$	*	$(^{87}Sr/^{86}Sr)_i$	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$	*	$T_{DM}(Ga)$	F !
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	$^{57}Fe_{IRMM-014}$	*	$^{56}Fe_{IRMM-014}$	*