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**Mesoarchean banded iron-formation from the northern Yangtze Craton, South
China and its geological and paleoenvironmental implications**

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Abstract

Banded iron formations (BIFs) are important sedimentary rocks used for reconstructing the geochemical and environmental evolution of Precambrian Earth surface conditions. Here, we describe the oldest BIFs of Mesoarchean age in the Yemadong Formation, and their implications for paleo-environmental evolution of the Mesoarchean Ocean in the northern Yangtze Craton, South China. U-Pb dating of metamorphic zircons obtained from metavolcanic rocks interbedded within the Yemadong Complex, record two major tecto-thermal events at 2901 ± 8 Ma, in agreement with a Mesoarchean origin of the Dujiagou BIFs, and as recently as 775 Ma. A high SiO_2 +total Fe_2O_3 content of 90.95-94.62 wt.%, moderate 0.54-1.42 wt.% Al_2O_3 + TiO_2 , and broadly elevated levels of incompatible elements, point to a predominantly chemical origin of the BIF deposit, with a minor but influential terrigenous input. Rare Earth Element (REE) plus Yttrium patterns normalized against Post Archean Average Shale composition are characterized by the depletion of light REE relative to heavy REE. However, extremely weak Eu and Ce anomalies, together with low average chondrite Y/Ho ratios compared to average Mesoarchean BIF values, indicate that the primary REE composition of the BIF may have been diluted to some extent by terrigenous input, pointing to proximity or connection of the depositional setting to a continental margin environment. Despite potential terrigenous dilution of the syngenetic seawater-hydrothermal chemical composition, the preservation of an inherited hydrothermal REE signal in some samples, point to submarine hydrothermal provenance of the Dujiagou BIFs, as is the suggested case for most Precambrian BIFs. Positive $\delta^{56}\text{Fe}$ values, ranging from 0.25-0.45 ‰, characteristic of primary Archean BIFs, point to partial oxidation of reduced Fe(II) to divalent (Fe(II)/Fe(III)) magnetite-rich BIFs in a broadly reducing Archean Ocean lacking a persistent and pervasive redoxcline before the rise of atmospheric

oxygen.

Keywords: Banded iron-formation, Iron isotopes, Paleoenvironment, Mesoarchean, Yangtze Craton

1. Introduction

Banded iron formations (BIFs) are marine chemical sedimentary rocks of predominantly Precambrian origin. They consist mainly of iron-rich layers containing hematite and magnetite alternating with silica-rich bands, composed principally of chert and jasper. Deposition of BIFs in Earth's history is closely related to the secular changes in the atmosphere, hydrosphere, and lithosphere, and thus BIFs are excellent archives for reconstructing the composition and redox state of the ancient ocean-atmosphere system under which they formed ([Bolhar et al., 2004](#); [Klein, 2005](#); [Polat and Frei, 2005](#); [Bekker et al., 2010](#); [Basta et al., 2011](#); [Mloszewska et al., 2012](#); [Zhang et al., 2012](#); [Cui et al., 2014](#); [Brando Soares et al., 2017](#); [Ghosh and Baidya, 2017](#); [Huang et al., 2019](#)). Three principal types of BIFs are known, defined primarily by their depositional environment ([Bekker et al., 2010](#); [Li et al., 2014a](#); [Hagemann et al., 2016](#)). Algoma-type BIFs deposited in deep-sea island arc environments, and near subduction trenches. They are generally the most common BIFs found in Archean greenstone belts associated with old cratonic sequences ([Goodwin, 1973](#); [Klein, 2005](#))—are small in scale, with the oldest known deposit formed ~3.8 billion years ago (Ga) in the Isua greenstone belt, West Greenland ([Myers, 2001](#); [Bolhar et al., 2004](#); [Polat and Frei, 2005](#); [Czaja et al., 2013](#)). Superior-type BIFs are larger in scale, compared to Algoma-type BIFs. They formed mainly in oxidized environments lacking syn-depositional volcanic assemblages, and are found deposited with transgressive successions that formed on shallow continental shelves located in intra-cratonic Basins ([Klein, 2005](#); [Li et al., 2012a](#); [Li et al., 2014a](#)). The Neoproterozoic and early

Paleoproterozoic intervals witnessed prolific Superior-type BIF deposition, with examples found in the Hamersley Basin of Western Australia and the Transvaal Supergroup, South Africa ([Morris, 1993](#); [Johnson et al., 2003](#); [Bekker et al., 2010](#); [Smith, 2018](#)). Large-scale BIF deposition terminated at ~1.8 Ga, when they disappeared from the marine sedimentary rock record, before an abrupt but brief reappearance of Rapitan-type BIFs in conjunction with the Neoproterozoic snowball Earth glaciations, ~0.7-0.635 Ga ([Hoffman et al., 1998](#)). The long depositional history of BIFs, timing and coincidence with major redox, climatic and geochemical changes in the ocean-atmosphere system, has led to their wide use as reliable proxies for Earth oxygenation history and the evolution of the Precambrian crust ([Crowley et al., 2002](#); [Holland, 2006](#); [Jenner et al., 2009](#); [Poulton and Canfield, 2011](#); [Kasting, 2013](#); [Chi Fru et al., 2016](#); [Chi Fru et al., 2018](#)).

Although the timing and extent of Earth surface oxidation before the Paleoproterozoic Great Oxidation Event (GOE), ~2.4 -2.0 Ga remains debated ([Czaja et al., 2013](#)), most workers agree that atmospheric O₂ contents were low in the Archean (e.g., [Farquhar et al. \(2000\)](#); [Anbar et al. \(2007\)](#); [Guo et al. \(2009\)](#)). In line with this observation, the chemical composition of Archean BIFs often contain both reduced and oxidized iron reservoirs, with the deposition of BIFs 3.8–1.8 Ga taken as compelling evidence for the prevalence of anoxic iron rich waters that enabled high iron mobility in the marine realm ([Poulton and Canfield, 2011](#)). The Early Paleoproterozoic GOE and the Late Neoproterozoic Oxidation Event, NOE (e.g., [Och and Shields-Zhou \(2012\)](#); [Lyons et al. \(2014\)](#)), are proposed as the principal reason for the eventual disappearance of BIFs from the marine sedimentary rock record ([Poulton and Canfield, 2011](#)).

Because of their great antiquity, in many instances, the primary chemical composition of BIFs has been altered by post-depositional diagenetic and metamorphic processes. Nonetheless, a

substantial body of work suggests that Fe isotopes are particularly resistant to these secondary post-depositional changes in bulk BIF composition ([Dauphas and Rouxel, 2006](#); [Frost et al., 2006](#); [Dauphas et al., 2007a](#); [Czaja et al., 2013](#)). Consequently, iron isotopes often play an important role in the study of BIFs, and their distribution in BIFs used frequently to track global early Earth surface redox evolution and the workings of the early biogeochemical elemental cycles ([Johnson et al., 2003](#); [Dauphas et al., 2004](#); [Dauphas et al., 2007a](#); [Dauphas et al., 2007b](#); [Hyslop et al., 2008](#); [Johnson et al., 2008](#); [Li et al., 2012b](#); [Chi Fru et al., 2013](#); [Czaja et al., 2013](#); [Wang et al., 2017](#)).

In China, most Neoarchean-Paleoproterozoic BIFs are deposited in the North China Craton ([Li et al., 2012b](#); [Wang et al., 2014](#); [Wang et al., 2017](#); [Wu et al., 2020](#)), while the presence of BIFs in the older Mesoarchean South China Block, host to the Yangtze Craton, remains poorly explored. Consequently, there exists a considerable gap in our understanding of the redox and biogeochemical development of the iron-rich Mesoarchean oceans in the Yangtze Craton. This has major implications for the global evolution of the early ocean-atmosphere system, with respect to the independent development of the South China Mesoarchean Block. In this paper, we coupled new U–Pb LA-ICP-MS ages to elemental and iron isotope geochemistry, to constrain the depositional age and genesis of Dujiagou BIFs in the Mesoarchean Yangtze Craton of the South China Block, and the contemporaneous marine conditions in which they formed.

2. Regional geology

The South China Block is one of the largest cratonic blocks in East Asia and is generally divided into the Yangtze Craton in the northwest and the Cathaysia Block in the southeast, separated by the intervening Jiangnan orogenic belt ([Li et al., 2003](#); [Zhao and Guo, 2012](#); [Zhao and Cawood,](#)

110 [2012; Charvet, 2013; Zhai, 2013; Cawood et al., 2018](#)); **Figure 1a**). Located to west of the Qinghai
111 Tibet Plateau and south of the Qinling Dabie Sulu orogenic belt, the Yangtze Craton is composed
112 mainly of late Paleoproterozoic and Neoproterozoic rocks with sporadic outcrops of Archean rocks
113 ([Zhao and Cawood, 2012; Zhang and Zheng, 2013; Ji et al., 2014; Jiang et al., 2016; Han et al.,](#)
114 [2017; Wei et al., 2020](#)). The Huangling dome, located in the northern part of the Yangtze Craton, is
115 the only area where both Archean and Paleoproterozoic metamorphic rocks are exposed in the
116 region ([Gao et al., 1999; Qiu et al., 2000; Zheng et al., 2006; Gao et al., 2011; Chen et al., 2013;](#)
117 [Han et al., 2018](#)). They provide a natural laboratory for studying the extensive tecto-magmatic and
118 metamorphic processes that occurred during the tectonic evolution of the Yangtze Craton.

119 The Kongling terrane, a major Archean relic exposed in the center of the Huangling dome,
120 covers an area of ~ 360 km² ([Peng et al., 2009; Wei et al., 2019](#)). These Archean rocks were intruded
121 by the late Paleoproterozoic ~1.85 Ga Quanqitang A-type granites and the Neoproterozoic ~0.85
122 Ga Huangling granitoids in the north and south, respectively. The rocks are unconformably overlain
123 by a Neoproterozoic and Paleozoic sedimentary sequence that has experienced negligible
124 metamorphic alteration ([Li et al., 2003; Peng et al., 2009; Peng et al., 2012a; Peng et al., 2012b;](#)
125 [Zhao et al., 2013; Han et al., 2018](#)). Regionally, the Wuduhe Fault divides the the Kongling terrane
126 into the North and South Konling Terranes, abbreviated as NKT and SKT, respectively (**Figure 1b**).
127 The NKT is considered metamorphosed to amphibolite facies ([Jiang, 1986; Ling et al., 2001; Wei](#)
128 [and Jing, 2013; Wei et al., 2020](#)) and to be compose mainly of the Mesoarchean 2.9-3.0 Ga
129 Dongchonghe tonalitic-trondhjemitic-granodioritic (TTG) gneiss, granitic gneiss, and locally
130 preserved amphibolites. The protolith of most of the amphibolites is considered to be 3.2-3.0 Ga
131 ultramafic-mafic rocks—the oldest known lithologies in the Huangling basement, the maintain

constituent of the Huangling greenstone belt, HGB (Xiong et al., 2004; Wei et al., 2019; Wei et al., 2020; Wei, 2021). Based on chronological and petrological evidence, the Yemadong Complex is considered a relic of the HGB, named for its location near the Yemadong village (Figure 1c) (Wei et al., 2019; Zhou et al., 2019; Wei et al., 2020; Wei, 2021). Therefore, the lithological association of the Yemadong Complex inherits the HGB (Zhou et al., 2019). Their original igneous texture is almost obscured and their primary mineral composition replaced by secondary metamorphic minerals (Wei, 2021).

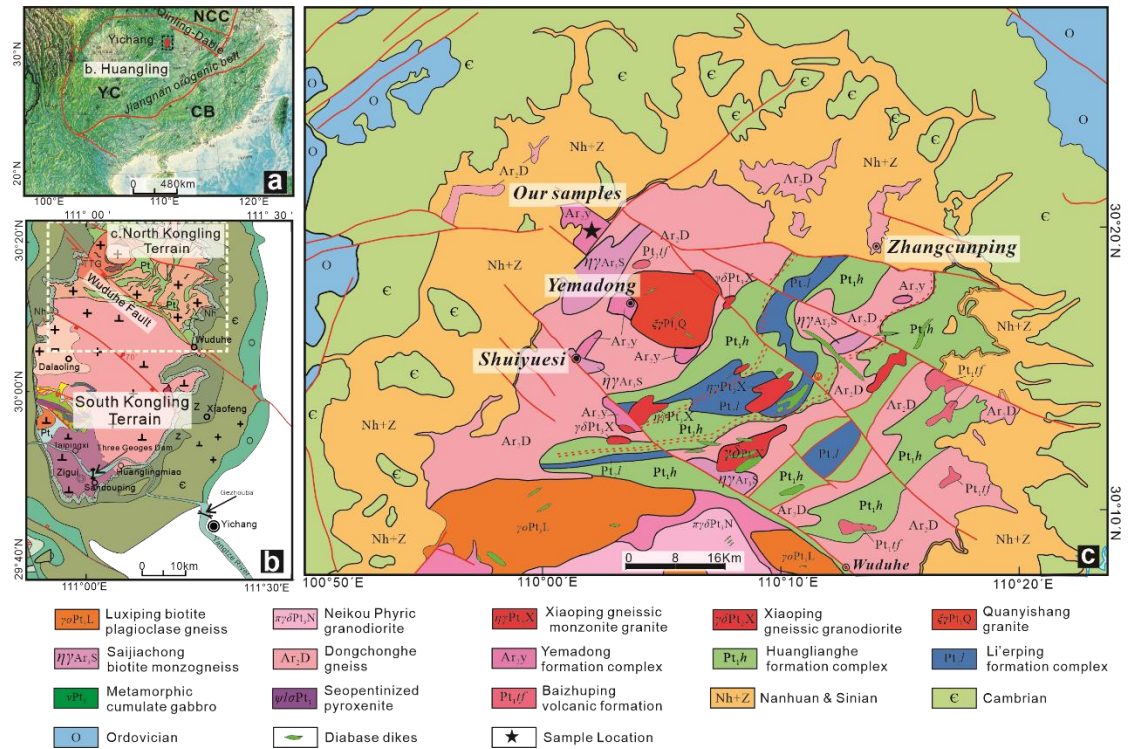


Figure 1. (a) Simplified tectonic map of major Precambrian blocks in South China, (b) Detailed tectonic map of the Kongling area on the northern margin of the Yangtze Craton, (c) Geological map showing the Huangling dome in Yichang City as well as the sampling locations, modified after Wei et al. (2019).

In the Huangling dome, the Yemadong Complex is divided into three portions based on lithology and structural position, the lowest part composed of biotite-tremolite and magnetite-bearing plagioclase-amphibole schist, considered to have originated from an ultrabasic-basic volcanic rock protolith. The middle portion is composed of biotite-plagioclase gneiss, feldspathic

quartzite, and the banded magnetite quartzite discussed in this paper. The upper section is comprised mainly of leptynite, leptyte metamorphic intermediate and acidic volcanic rocks ([Zhou et al., 2019](#)). The Dujiagou BIFs occur in the middle and upper part of the greenstone sequence of Yemadong Complex (HGB residue), consistent with the occurrence of most Precambrian BIFs in the greenstone belt sequence (e.g., [Ghosh and Baidya \(2017\)](#) and [Singh and Slabunov \(2015\)](#)).

In the field, they are exposed as four stratified BIF layers that are generally 20-50 cm thick, dominated by magnetite and quartzite with characteristic quartz and magnetite enrichment (**Figure 2a-c**). The magnetite and quartzite layers present a black and white stripe appearance, characterized by interbedded light-colored quartz and dark-colored magnetite stripes (**Figure 2d, e**). Magnetite is generally Subhedral or heteromorphic, with a grain size of 0.1-0.2 mm and a Fe content of 45-50%. In the magnetite-rich stripes, the grains are larger and interconnected, forming aggregates and irregular bedding planes, while magnetite is sparsely disseminated among quartz grains in the magnetite-poor stripes to form small, separate grains. Overall, the mineral assemblage in the sample is simple, consisting predominantly of quartz and magnetite with lesser amounts of actinolite and other accessory minerals (**Figure 2f, g**).

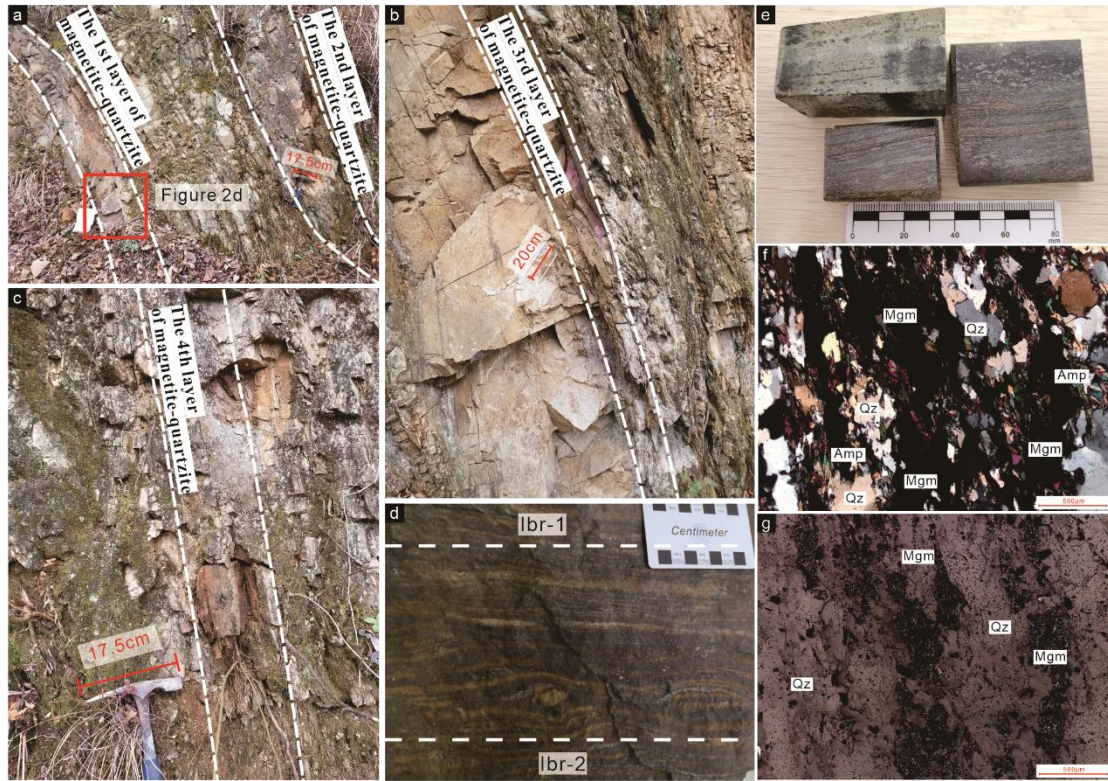


Figure 2. Representative photographs of the Dujiagou BIF. (a-c) Field photographs showing the outcrop of Dujiagou Algoma-type BIFs interbedded with felsic metavolcanic rocks, (d) Banded magnetite and quartzite layers composed of bands of dark color magnetite alternating with white color quartz layers. The Ibr-1 and Ibr-2 layers were sampled for iron isotope analysis, (e) An example of a fresh surface cut from the magnetite and quartzite layers in Figure 2d, (f-g) BIF mainly consisting of alternating magnetite Fe-oxide and quartz bands with other minor minerals (e- Polarized Light; f- Reflected Light), Qz stands for quartz, Mgm for magnetite and Amp for amphibole.

3. Analytical methods

In order to ensure the validity of the data and exclude the influence of weathering conditions on the analysis, exposed weathered surfaces of 13 representative magnetite and quartzite sample were cut and only the fresh portion (**Figure 2e**) used for the determination of major, trace and rare earth element contents.

3.1. Zircon U-Pb dating

U-Pb dating and trace element analysis of zircon were simultaneously conducted by LA-ICP-MS at Wuhan Sample Solution Analytical Technology Co., Ltd., Wuhan, China. Detailed operating conditions for the laser ablation system and the ICP-MS instrument and data reduction are the same as described by [Zong et al. \(2017\)](#). Laser sampling was performed using a GeolasPro laser ablation system consisting of a COMPexPro 102 ArF excimer laser with a wavelength of 193 nm, a maximum energy of 200 mJ, and a MicroLas optical system. A “wire” signal smoothing device was included with the laser ablation system ([Hu et al., 2015](#)). An Agilent 7700e ICP-MS instrument was used to acquire ion-signal intensities. The sample was delivered using the make-up gas argon, mixed with the carrier gas helium via a T-connector before entry into the ICP. The spot size and laser frequency were set to 32 μm and 5 Hz, respectively. Zircon 91500 and glass NIST610 were used as external standards for U-Pb dating and trace element calibration, respectively. Each analysis incorporated a background acquisition of approximately 20-30 s followed by 50 s of sample data acquisition. An Excel-based software ICPMSDataCal was used to perform off-line selection and integration of background and analyzed signals, time-drift correction and quantitative calibration for trace element analysis and U-Pb dating. Concordia diagrams and weighted mean calculations were made using Isoplot/Ex_ver4.15.

3.2. Bulk-rock major element

Bulk-rock major element analysis was conducted with an XRF Primus II, Rigaku (Japan) instrument at Wuhan Sample Solution Analytical Technology Co., Ltd., Wuhan, China. The detailed sample-digestion procedure was as follows: (1) Sample powder (200 mesh) were placed in an oven set at 105°C and dried for 12 hours; (2) ~1.0 g dried sample was accurately weighted and placed in

ceramic crucibles and heated in a muffle furnace at 1000°C for 2 hours. After cooling to 400°C, samples were placed in a drying vessel and weighed again in order to calculate the loss on ignition (LOI); (3) 0.6 g sample powder was mixed with 6.0 g $\text{Li}_2\text{B}_4\text{O}_7$: LiBO_2 : LiF = 9:2:1 cosolvent and 0.3 g NH_4NO_3 oxidant in a Pt crucible and heated in a furnace for 1150°C at 14 min. The melted samples were quenched with air for 1 min to produce flat discs on the fire brick for XRF analyses.

3.3. Bulk-rock trace element

Bulk-rock trace element analysis was conducted on an Agilent 7700e ICP-MS at Wuhan Sample Solution Analytical Technology Co., Ltd., Wuhan, China. Sample powders were prepared and dried in an oven at 105°C as described in section 3.2, after which 50 mg of the dried powder was accurately weighed and placed in Teflon bombs. This was followed by the slow addition of 1 ml HNO_3 and 1 ml HF. The Teflon bombs were then put in a stainless steel pressure jacket and heated to 190 °C in an oven for >24 hours. After cooling, the Teflon bombs were opened and placed on a hotplate at set at 140°C and evaporated, followed by the addition of 1 ml HNO_3 and another round of evaporation to dryness. To the dried sample was added 1 ml HNO_3 , 1ml MQ water and 1 ml 1 ppm internal standard solution. The Teflon bombs were resealed and placed in the oven at 190°C for >12 hours. The final solution was transferred to a polyethylene bottle and diluted to 100 g with 2% HNO_3 .

3.4. Bulk-rock Fe isotope

Iron isotopic measurements were performed on a Nu Plasma 1700 MC-ICP-MS (Nu Instruments, Wrexham, UK) at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan. Typically, ~1.0 g sample powders were weighed into individual Teflon beakers and dissolved in a mixture of HF- HNO_3 -HCl- HClO_4 . Iron

was purified using the AG1X-8 (200–400 mesh chloride form, Bio-Rad, Hercules, CA, USA) resin
 in HCl media. Matrix elements were removed by 8 ml 6 mol/L HCl, and Fe was then collected by
 9 ml 0.4 mol/L HCl. The same column procedure was repeated twice to ensure complete elimination
 of the matrices. The final Fe eluate was acidified with 100 µl of concentrated HNO₃. The dried
 sample was then dissolved in 3% HNO₃ for isotopic determination. Double distilled acids and
 Optima™ ultra pure HClO₄ were used. The whole procedure Fe blank was < 0.01% of the processed
 samples and therefore considered negligible. Samples were introduced into the Ar plasma using a
 Cetac ASX-100 auto sampler through a Thermo Scientific Stable Introduction System (SIS), which
 consists of quartz cyclonic and Scott-type spray chambers and a set of PFA Teflon self-aspirating
 micro-nebulisers with different uptake rates (45, 50, 100 µl min⁻¹). The instrument mass bias was
 routinely corrected by calibrator sample bracketing. Data were processed offline and reported in the
 δ notation ($\delta^x\text{Fe} (\text{‰}) = [({}^x\text{Fe}/{}^{54}\text{Fe})_{\text{sample}} / ({}^x\text{Fe}/{}^{54}\text{Fe})_{\text{calibrator}} - 1] \times 1000$, where x is 56 or 57 and
 (${}^x\text{Fe}/{}^{54}\text{Fe}$) calibrator is the average of the two bracketing calibrators). Most tests carried out in this
 study used GSB Fe (an ultrapure single elemental standard solution from the China Iron and Steel
 Research Institute) as an in-house reference solution ([He et al., 2015](#)).

Table 1. U-Pb age data of zircons from the metamorphic mafic rocks interbedded in Dujiagou BIFs

| Testing No. | Concentrations (ppm) | | | | Isotopic ratios | | | | | | | | ²⁰⁷ Pb/ ²⁰⁶ Pb | | ²⁰⁷ Pb/ ²³⁵ U | | ²⁰⁶ Pb/ ²³⁸ U | | ²⁰⁸ Pb/ ²³² Th | | Comments |
|-------------|----------------------|------|------|------|--------------------------------------|--------|-------------------------------------|--------|-------------------------------------|--------|--------------------------------------|--------|--------------------------------------|-----|-------------------------------------|----|-------------------------------------|----|--------------------------------------|-----|---------------|
| | Pb | Th | U | Th/U | ²⁰⁷ Pb/ ²⁰⁶ Pb | 1σ | ²⁰⁷ Pb/ ²³⁵ U | 1σ | ²⁰⁶ Pb/ ²³⁸ U | 1σ | ²⁰⁸ Pb/ ²³² Th | 1σ | Age (Ma) | 1σ | Age (Ma) | 1σ | Age (Ma) | 1σ | Age (Ma) | 1σ | |
| | | | | | | | | | | | | | | | | | | | | | |
| D5216-01 | 1825 | 64.1 | 484 | 0.13 | 0.2072 | 0.0035 | 16.0880 | 0.2833 | 0.5637 | 0.0131 | 0.1380 | 0.0041 | 2884 | 18 | 2882 | 17 | 2882 | 54 | 2613 | 72 | Concordant |
| D5216-02 | 2167 | 140 | 782 | 0.18 | 0.2078 | 0.0029 | 16.3513 | 0.2948 | 0.5681 | 0.0116 | 0.1465 | 0.0041 | 2888 | 15 | 2898 | 17 | 2900 | 48 | 2763 | 73 | Concordant |
| D5216-03 | 2068 | 105 | 790 | 0.13 | 0.1871 | 0.0029 | 10.5673 | 0.2509 | 0.4092 | 0.0110 | 0.1154 | 0.0039 | 2717 | 20 | 2486 | 22 | 2211 | 50 | 2207 | 71 | Disconcordant |
| D5216-04 | 374 | 82.6 | 714 | 0.12 | 0.1865 | 0.0032 | 9.8135 | 0.3361 | 0.3781 | 0.0116 | 0.1032 | 0.0035 | 2712 | 25 | 2417 | 32 | 2067 | 54 | 1985 | 63 | Disconcordant |
| D5216-05 | 192 | 166 | 1609 | 0.1 | 0.1075 | 0.0030 | 1.5302 | 0.0317 | 0.1033 | 0.0019 | 0.0299 | 0.0006 | 1757 | 52 | 943 | 13 | 634 | 11 | 596 | 11 | Positive Eu |
| D5216-06 | 633 | 117 | 993 | 0.12 | 0.1972 | 0.0035 | 13.1472 | 0.4356 | 0.4784 | 0.0138 | 0.1295 | 0.0054 | 2803 | 24 | 2690 | 31 | 2520 | 60 | 2460 | 97 | Disconcordant |
| D5216-07 | 900 | 73.4 | 580 | 0.13 | 0.2084 | 0.0039 | 16.3973 | 0.3808 | 0.5698 | 0.0133 | 0.1521 | 0.0059 | 2893 | 17 | 2900 | 22 | 2907 | 55 | 2861 | 104 | Concordance |
| D5216-08 | 638 | 83.7 | 798 | 0.1 | 0.2081 | 0.0033 | 16.0604 | 0.3027 | 0.5575 | 0.0108 | 0.1558 | 0.0051 | 2891 | 14 | 2880 | 18 | 2856 | 45 | 2927 | 89 | Concordance |
| D5216-09 | 639 | 89.6 | 754 | 0.12 | 0.2101 | 0.0034 | 16.3341 | 0.3041 | 0.5629 | 0.0117 | 0.1666 | 0.0051 | 2906 | 15 | 2897 | 18 | 2878 | 48 | 3114 | 88 | Concordance |
| D5216-10 | 675 | 90.4 | 751 | 0.12 | 0.2082 | 0.0028 | 16.0273 | 0.2622 | 0.5556 | 0.0108 | 0.1617 | 0.0044 | 2891 | 14 | 2878 | 16 | 2848 | 45 | 3029 | 76 | Concordance |
| D5216-11 | 531 | 75.3 | 634 | 0.12 | 0.2099 | 0.0032 | 16.3240 | 0.2665 | 0.5627 | 0.0119 | 0.1604 | 0.0046 | 2905 | 16 | 2896 | 16 | 2878 | 49 | 3007 | 80 | Concordance |
| D5216-12 | 2162 | 81 | 539 | 0.15 | 0.2096 | 0.0033 | 16.4806 | 0.2857 | 0.5686 | 0.0132 | 0.1666 | 0.0047 | 2903 | 18 | 2905 | 17 | 2902 | 54 | 3115 | 82 | Concordance |
| D5216-13 | 984 | 63.1 | 529 | 0.12 | 0.2117 | 0.0033 | 16.7031 | 0.3893 | 0.5701 | 0.0159 | 0.1666 | 0.0051 | 2919 | 20 | 2918 | 22 | 2908 | 65 | 3114 | 88 | Concordance |
| D5216-14 | 2173 | 130 | 1096 | 0.12 | 0.1485 | 0.0055 | 3.7124 | 0.1000 | 0.1814 | 0.0046 | 0.0509 | 0.0013 | 2328 | 65 | 1574 | 22 | 1074 | 25 | 1003 | 25 | Positive Eu |
| D5216-15 | 505 | 85.5 | 732 | 0.12 | 0.2001 | 0.0032 | 13.3950 | 0.2264 | 0.4855 | 0.0116 | 0.1320 | 0.0038 | 2827 | 19 | 2708 | 16 | 2551 | 50 | 2506 | 67 | Disconcordant |
| D5216-16 | 323 | 60.7 | 1068 | 0.06 | 0.1611 | 0.0053 | 6.3583 | 0.1352 | 0.2863 | 0.0071 | 0.0797 | 0.0020 | 2467 | 57 | 2027 | 19 | 1623 | 36 | 1550 | 38 | Positive Eu |
| D5216-17 | 474 | 138 | 1094 | 0.13 | 0.1708 | 0.0026 | 7.4467 | 0.1464 | 0.3154 | 0.0078 | 0.0913 | 0.0025 | 2566 | 19 | 2167 | 18 | 1767 | 38 | 1765 | 45 | Disconcordant |
| D5216-18 | 1981 | 195 | 1660 | 0.12 | 0.1218 | 0.0070 | 1.3469 | 0.0627 | 0.0802 | 0.0027 | 0.0230 | 0.0008 | 1983 | 105 | 866 | 27 | 497 | 16 | 459 | 15 | Positive Eu |
| D5216-19 | 1355 | 53.4 | 429 | 0.12 | 0.2065 | 0.0031 | 16.1155 | 0.3200 | 0.5642 | 0.0141 | 0.1460 | 0.0043 | 2879 | 19 | 2884 | 19 | 2884 | 58 | 2755 | 77 | Concordance |
| D5216-20 | 1152 | 69.8 | 629 | 0.11 | 0.2107 | 0.0034 | 16.3426 | 0.2878 | 0.5617 | 0.0132 | 0.1524 | 0.0047 | 2911 | 18 | 2897 | 17 | 2874 | 54 | 2866 | 82 | Concordance |
| D5216-21 | 453 | 92.8 | 739 | 0.13 | 0.1931 | 0.0037 | 11.4320 | 0.3174 | 0.4276 | 0.0123 | 0.1185 | 0.0035 | 2768 | 21 | 2559 | 26 | 2295 | 55 | 2264 | 63 | Disconcordant |
| D5216-22 | 460 | 165 | 1309 | 0.13 | 0.1778 | 0.0029 | 6.7369 | 0.3240 | 0.2717 | 0.0130 | 0.0797 | 0.0042 | 2632 | 36 | 2077 | 43 | 1549 | 66 | 1549 | 79 | High U |
| D5216-23 | 2614.9 | 41.9 | 1297 | 0.03 | 0.1104 | 0.0047 | 1.4999 | 0.0479 | 0.0985 | 0.0028 | 0.0285 | 0.0009 | 1806 | 80 | 930 | 19 | 606 | 16 | 568 | 18 | Positive Eu |
| D5216-24 | 2147 | 125 | 830 | 0.15 | 0.1843 | 0.0033 | 8.4064 | 0.2898 | 0.3281 | 0.0119 | 0.0926 | 0.0044 | 2692 | 27 | 2276 | 31 | 1829 | 58 | 1789 | 81 | Disconcordant |
| D5216-25 | 2301 | 73.2 | 570 | 0.13 | 0.1977 | 0.0032 | 12.9525 | 0.2619 | 0.4732 | 0.0123 | 0.1335 | 0.0048 | 2807 | 20 | 2676 | 19 | 2498 | 54 | 2533 | 85 | Disconcordant |
| D5216-26 | 922 | 196 | 1283 | 0.15 | 0.1661 | 0.0039 | 7.2453 | 0.1569 | 0.3034 | 0.0076 | 0.0907 | 0.0031 | 2518 | 19 | 2142 | 19 | 1708 | 37 | 1755 | 58 | Positive Eu |
| D5216-27 | 1673 | 67.2 | 539 | 0.12 | 0.2096 | 0.0069 | 14.9327 | 0.3300 | 0.5167 | 0.0127 | 0.1403 | 0.0035 | 2902 | 55 | 2811 | 21 | 2685 | 54 | 2654 | 63 | Disconcordant |
| D5216-28 | 1765 | 92 | 781 | 0.12 | 0.1776 | 0.0032 | 8.2399 | 0.3728 | 0.3299 | 0.0135 | 0.0979 | 0.0043 | 2630 | 34 | 2258 | 41 | 1838 | 66 | 1888 | 80 | Disconcordant |
| D5216-29 | 1977 | 38.1 | 323 | 0.12 | 0.2079 | 0.0039 | 16.4853 | 0.3260 | 0.5732 | 0.0152 | 0.1687 | 0.0054 | 2889 | 20 | 2905 | 19 | 2921 | 62 | 3151 | 94 | Concordance |
| D5216-30 | 3160 | 163 | 1253 | 0.13 | 0.1045 | 0.0052 | 1.3829 | 0.0548 | 0.0960 | 0.0029 | 0.0279 | 0.0008 | 1705 | 94 | 882 | 23 | 591 | 17 | 556 | 17 | Positive Eu |
| D5216-31 | 467 | 72.3 | 528 | 0.14 | 0.2101 | 0.0036 | 16.3015 | 0.3614 | 0.5588 | 0.0152 | 0.1649 | 0.0048 | 2907 | 20 | 2895 | 21 | 2862 | 63 | 3086 | 83 | Concordance |
| D5216-32 | 2653 | 50.1 | 444 | 0.11 | 0.2079 | 0.0037 | 16.2793 | 0.3365 | 0.5689 | 0.0172 | 0.1623 | 0.0046 | 2889 | 24 | 2893 | 20 | 2903 | 71 | 3040 | 79 | Concordance |
| D5216-33 | 298 | 313 | 1546 | 0.2 | 0.1256 | 0.0039 | 2.1096 | 0.0972 | 0.1151 | 0.0044 | 0.0359 | 0.0016 | 2037 | 37 | 1152 | 32 | 702 | 25 | 714 | 32 | High U |

| Testing No. | Concentrations (ppm) | | | | Isotopic ratios | | | | | | | | ²⁰⁷ Pb/ ²⁰⁶ Pb | | ²⁰⁷ Pb/ ²³⁵ U | | ²⁰⁶ Pb/ ²³⁸ U | | ²⁰⁸ Pb/ ²³² Th | | Comments |
|-------------|----------------------|------|------|------|--------------------------------------|--------|-------------------------------------|--------|-------------------------------------|--------|--------------------------------------|--------|--------------------------------------|-----|-------------------------------------|----|-------------------------------------|----|--------------------------------------|----|---------------|
| | Pb | Th | U | Th/U | ²⁰⁷ Pb/ ²⁰⁶ Pb | 1σ | ²⁰⁷ Pb/ ²³⁵ U | 1σ | ²⁰⁶ Pb/ ²³⁸ U | 1σ | ²⁰⁸ Pb/ ²³² Th | 1σ | Age (Ma) | 1σ | Age (Ma) | 1σ | Age (Ma) | 1σ | | | |
| | | | | | | | | | | | | | | | | | | | | | |
| D5216-34 | 1125 | 346 | 2521 | 0.14 | 0.0796 | 0.0046 | 0.6444 | 0.0296 | 0.0587 | 0.0021 | 0.0176 | 0.0006 | 1188 | 118 | 505 | 18 | 368 | 13 | 352 | 12 | Positive Eu |
| D5216-35 | 2004 | 219 | 1649 | 0.13 | 0.1155 | 0.0055 | 1.3622 | 0.0500 | 0.0855 | 0.0026 | 0.0246 | 0.0007 | 1888 | 88 | 873 | 21 | 529 | 15 | 491 | 15 | Positive Eu |
| D5216-36 | 1191 | 875 | 1362 | 0.64 | 0.1905 | 0.0034 | 6.6736 | 0.3390 | 0.2492 | 0.0115 | 0.0458 | 0.0024 | 2746 | 37 | 2069 | 45 | 1434 | 59 | 905 | 47 | Positive Eu |
| D5216-37 | 693 | 70.9 | 673 | 0.11 | 0.2142 | 0.0032 | 16.7282 | 0.2881 | 0.5650 | 0.0121 | 0.1579 | 0.0051 | 2937 | 16 | 2919 | 17 | 2887 | 50 | 2964 | 90 | Concordance |
| D5216-38 | 275 | 149 | 1816 | 0.08 | 0.1059 | 0.0039 | 1.3545 | 0.0355 | 0.0928 | 0.0024 | 0.0269 | 0.0007 | 1730 | 70 | 870 | 15 | 572 | 14 | 537 | 14 | High U |
| D5216-39 | 734 | 93.8 | 764 | 0.12 | 0.2112 | 0.0037 | 14.3764 | 0.3260 | 0.4926 | 0.0128 | 0.1423 | 0.0053 | 2915 | 19 | 2775 | 22 | 2582 | 55 | 2689 | 94 | Disconcordant |
| D5216-40 | 318 | 202 | 1704 | 0.12 | 0.1309 | 0.0135 | 1.9136 | 0.1589 | 0.1060 | 0.0065 | 0.0301 | 0.0018 | 2110 | 188 | 1086 | 55 | 650 | 38 | 600 | 36 | High U |
| D5216-41 | 618 | 92.5 | 991 | 0.09 | 0.1835 | 0.0036 | 9.9423 | 0.2736 | 0.3916 | 0.0116 | 0.1125 | 0.0051 | 2685 | 22 | 2429 | 25 | 2130 | 54 | 2154 | 92 | Concordance |
| D5216-42 | 436 | 65.4 | 634 | 0.1 | 0.1972 | 0.0052 | 10.5984 | 0.2424 | 0.3819 | 0.0103 | 0.1117 | 0.0051 | 2803 | 20 | 2489 | 21 | 2085 | 48 | 2139 | 93 | Concordance |
| D5216-43 | 462 | 44.1 | 495 | 0.09 | 0.2110 | 0.0038 | 16.4915 | 0.3976 | 0.5712 | 0.0182 | 0.1614 | 0.0056 | 2913 | 24 | 2906 | 23 | 2913 | 75 | 3025 | 97 | Concordance |
| D5216-44 | 789 | 95.1 | 700 | 0.14 | 0.2112 | 0.0030 | 16.7125 | 0.2901 | 0.5717 | 0.0123 | 0.1533 | 0.0046 | 2915 | 16 | 2918 | 17 | 2915 | 51 | 2883 | 80 | Concordance |
| D5216-45 | 701 | 106 | 1042 | 0.1 | 0.1896 | 0.0050 | 11.0389 | 0.3262 | 0.4051 | 0.0133 | 0.1151 | 0.0043 | 2739 | 24 | 2526 | 28 | 2193 | 61 | 2201 | 78 | Concordance |

The obtained concordia age (1063.6 ± 3.6 Ma, n = 20) and ²⁰⁷Pb/²³⁵U age (1063.5 ± 7.3 Ma, n = 20) of zircon standard 91500 agrees well with the preferred ID-TIMS ²⁰⁷Pb/²³⁵U age of 1065.4 ± 0.3 Ma ([Jackson et al., 2004](#)) within analytical uncertainty.

239 **Table 2.** major element (wt. %) and trace element (ppm) compositions of BIF from Dujiagou.

| Sample | 51-1 | 51-2 | 61-1 | 61-2 | 71-1 | 71-2 | 81-1 | 81-2 | 2018-1-1 | 2018-1-2 | 2018-2 | PM040-37-1 | D5216-2 | Sijiaying | Hamersley | Itilliarsuk | Um Anab | Nkout |
|---------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|----------|----------|--------|------------|---------|-----------|-----------|-------------|---------|-------|
| Magnetite quartzite | | | | | | | | | | | | | | Average | | | | |
| SiO ₂ | 56.00 | 54.56 | 55.95 | 54.55 | 56.12 | 54.39 | 63.47 | 63.42 | 55.90 | 54.70 | 63.67 | 39.75 | 55.04 | 55.88 | 50.35 | 47.37 | 54.62 | 46.93 |
| TiO ₂ | 0.09 | 0.03 | 0.08 | 0.03 | 0.09 | 0.04 | 0.12 | 0.12 | 0.08 | 0.03 | 0.11 | 0.04 | 0.09 | 0.01 | 0.09 | 0.18 | 0.20 | 0.11 |
| Al ₂ O ₃ | 0.89 | 0.82 | 0.88 | 0.83 | 0.87 | 0.82 | 1.28 | 1.28 | 0.93 | 0.87 | 1.31 | 0.50 | 0.88 | 0.47 | 2.14 | 3.78 | 3.60 | 3.38 |
| TFe ₂ O ₃ | 38.63 | 40.32 | 38.67 | 40.30 | 38.76 | 40.20 | 29.39 | 29.14 | 37.53 | 39.30 | 28.30 | 55.37 | 35.91 | 41.76 | 41.71 | 44.61 | 35.14 | 44.54 |
| MnO | 0.27 | 0.24 | 0.27 | 0.24 | 0.27 | 0.23 | 0.29 | 0.29 | 0.28 | 0.24 | 0.30 | 0.07 | 0.23 | 0.05 | 0.07 | 0.06 | 0.07 | 0.12 |
| MgO | 3.33 | 2.43 | 3.35 | 2.41 | 3.32 | 2.42 | 2.03 | 2.01 | 3.27 | 2.33 | 1.96 | 1.37 | 3.15 | 0.67 | 1.86 | 0.95 | 1.28 | 2.47 |
| CaO | 1.42 | 0.53 | 1.43 | 0.53 | 1.43 | 0.53 | 1.92 | 1.90 | 1.39 | 0.50 | 1.88 | 0.58 | 1.28 | 0.43 | 1.79 | 1.99 | 2.98 | 1.59 |
| Na ₂ O | 0.15 | 0.06 | 0.13 | 0.05 | 0.17 | 0.08 | 0.14 | 0.09 | 0.16 | 0.05 | 0.09 | 0.02 | 0.11 | 0.13 | 0.14 | 0.57 | 0.25 | 0.24 |
| K ₂ O | 0.13 | 0.12 | 0.12 | 0.13 | 0.12 | 0.12 | 0.14 | 0.13 | 0.16 | 0.05 | 0.09 | 0.03 | 0.09 | 0.06 | 0.18 | 0.25 | 0.12 | 0.96 |
| P ₂ O ₅ | 0.24 | 0.18 | 0.24 | 0.18 | 0.24 | 0.18 | 0.45 | 0.45 | 0.25 | 0.18 | 0.45 | 0.32 | 0.25 | 0.07 | 0.22 | 0.23 | 0.54 | 0.09 |
| LOI | -1.15 | 0.32 | -1.13 | 0.25 | -1.21 | 0.20 | 0.73 | 0.89 | -0.96 | 0.55 | 1.12 | 1.08 | 1.84 | 0.47 | 2.22 | - | 0.53 | -0.27 |
| FeO | 23.40 | 12.25 | 23.80 | 12.20 | 23.50 | 11.60 | 7.75 | 7.55 | 23.80 | 12.71 | 8.08 | 16.22 | 25.40 | 9.58 | - | - | - | - |
| Sc | 3.85 | 3.05 | 3.59 | 3.02 | 3.67 | 3.02 | 5.32 | 5.31 | 3.40 | 2.60 | 4.80 | 1.50 | 2.93 | 0.85 | 2.80 | 5.54 | 6.20 | - |
| V | 19.69 | 10.88 | 18.83 | 10.96 | 19.19 | 11.41 | 45.19 | 44.70 | 24.00 | 13.00 | 54.00 | 16.50 | 26.10 | 12.74 | 19.78 | - | 77.80 | 1.10 |
| Cr | 56.28 | 33.62 | 53.88 | 34.57 | 53.54 | 34.17 | 104.13 | 103.59 | 70.00 | 50.00 | 130.00 | 24.10 | 80.30 | 647.14 | 203.47 | 25.04 | 26.60 | 6.46 |
| Co | 118.76 | 110.74 | 111.75 | 112.65 | 111.01 | 112.29 | 144.17 | 142.72 | 115.00 | 112.50 | 143.50 | 2.45 | 9.89 | 4.78 | 4.49 | - | 95.50 | 0.25 |
| Ni | 36.98 | 49.25 | 35.58 | 50.51 | 35.15 | 50.83 | 102.63 | 101.90 | 40.50 | 53.50 | 103.50 | 14.40 | 42.00 | 21.74 | - | 17.36 | 10.67 | 1.01 |
| Ga | 4.58 | 2.45 | 4.44 | 2.52 | 4.53 | 2.52 | 11.07 | 10.64 | 4.70 | 2.70 | 11.50 | 4.46 | 4.15 | 1.81 | - | - | - | - |
| Rb | 3.18 | 8.59 | 3.27 | 8.80 | 3.15 | 8.65 | 7.61 | 7.49 | 3.40 | 9.00 | 8.20 | 4.70 | 4.20 | 5.68 | - | 3.09 | 3.60 | 8.06 |
| Sr | 11.41 | 5.36 | 11.16 | 5.66 | 11.06 | 5.43 | 10.66 | 10.71 | 11.90 | 5.80 | 11.40 | 8.80 | 7.08 | 29.59 | - | 85.27 | 147.80 | 1.28 |
| Y | 25.34 | 15.28 | 24.97 | 15.74 | 24.73 | 15.62 | 39.65 | 39.44 | 25.00 | 15.60 | 38.60 | 17.80 | 19.90 | 4.78 | 12.41 | 3.26 | 26.60 | 0.27 |
| Zr | 7.31 | 5.09 | 7.17 | 5.25 | 6.62 | 5.52 | 11.70 | 14.43 | 7.00 | 6.00 | 16.00 | 3.82 | 7.37 | 2.5 | 32.94 | 29.63 | 44.50 | 0.00 |
| Nb | 3.67 | 2.03 | 3.52 | 2.02 | 3.50 | 2.04 | 7.23 | 7.06 | 3.70 | 2.00 | 7.50 | 2.88 | 2.38 | 0.36 | - | - | 2.38 | 0.00 |
| Ba | 145.24 | 151.29 | 149.99 | 152.32 | 143.30 | 152.12 | 148.88 | 147.57 | 151.50 | 157.50 | 150.00 | 40.40 | 36.50 | 18.13 | 75.67 | - | 64.90 | 34.69 |
| La | 6.37 | 9.58 | 6.25 | 9.73 | 6.06 | 9.70 | 11.98 | 11.58 | 6.70 | 10.10 | 13.50 | 7.30 | 9.75 | 3.12 | 8.14 | 3.24 | 12.13 | 0.67 |
| Ce | 13.98 | 26.88 | 13.80 | 27.70 | 13.46 | 27.16 | 37.51 | 37.12 | 16.80 | 27.00 | 39.80 | 15.90 | 17.50 | 4.97 | 14.54 | 8.88 | 27.09 | 1.21 |

| | | | | | | | | | | | | | | | | | | |
|-------------------------------|-------|-------|-------|-------|-------|-------|--------|--------|-------|-------|--------|--------|-------|-------|-------|-------|--------|-------|
| Pr | 2.07 | 2.77 | 2.06 | 2.79 | 2.02 | 2.80 | 5.10 | 5.07 | 2.15 | 2.87 | 5.38 | 1.84 | 2.31 | 0.65 | 1.71 | 0.80 | 3.78 | 0.13 |
| Nd | 9.37 | 11.35 | 9.51 | 11.33 | 9.37 | 11.53 | 24.20 | 24.35 | 9.50 | 11.60 | 23.60 | 10.00 | 11.90 | 2.71 | 6.50 | 3.23 | 16.58 | 0.44 |
| Sm | 2.82 | 3.10 | 2.66 | 2.94 | 2.67 | 3.09 | 7.29 | 7.12 | 2.71 | 2.81 | 6.93 | 2.59 | 2.94 | 0.54 | 1.23 | 0.65 | 3.98 | 0.06 |
| Eu | 0.64 | 0.63 | 0.70 | 0.63 | 0.67 | 0.65 | 1.65 | 1.59 | 0.71 | 0.66 | 1.58 | 0.50 | 0.74 | 0.16 | 0.30 | 0.22 | 1.05 | 0.02 |
| Gd | 3.18 | 2.99 | 3.53 | 3.08 | 3.28 | 2.97 | 7.41 | 7.27 | 3.37 | 3.12 | 7.46 | 2.74 | 2.99 | 0.61 | 1.30 | 0.29 | 4.65 | 0.05 |
| Tb | 0.59 | 0.48 | 0.62 | 0.53 | 0.55 | 0.51 | 1.16 | 1.20 | 0.56 | 0.48 | 1.19 | 0.49 | 0.54 | 0.1 | 0.21 | 0.11 | 0.75 | 0.00 |
| Dy | 3.90 | 2.99 | 3.92 | 3.14 | 3.93 | 3.12 | 7.58 | 7.49 | 3.65 | 2.81 | 6.94 | 3.18 | 3.56 | 0.63 | 1.34 | 0.63 | 4.67 | 0.04 |
| Ho | 0.86 | 0.62 | 0.80 | 0.61 | 0.82 | 0.60 | 1.44 | 1.49 | 0.82 | 0.58 | 1.42 | 0.70 | 0.79 | 0.15 | 0.34 | 0.12 | 1.06 | 0.01 |
| Er | 2.36 | 1.63 | 2.39 | 1.68 | 2.35 | 1.63 | 3.91 | 3.91 | 2.36 | 1.59 | 3.77 | 1.90 | 2.22 | 0.43 | 1.05 | 0.35 | 3.19 | 0.02 |
| Tm | 0.35 | 0.25 | 0.36 | 0.26 | 0.36 | 0.24 | 0.56 | 0.55 | 0.36 | 0.25 | 0.59 | 0.30 | 0.37 | 0.06 | 0.16 | 0.05 | 0.47 | 0.00 |
| Yb | 2.30 | 1.68 | 2.35 | 1.71 | 2.34 | 1.70 | 3.63 | 3.51 | 2.36 | 1.63 | 3.71 | 1.90 | 2.54 | 0.42 | 1.13 | 0.31 | 3.19 | 0.02 |
| Lu | 0.36 | 0.27 | 0.39 | 0.27 | 0.37 | 0.27 | 0.57 | 0.55 | 0.38 | 0.27 | 0.59 | 0.26 | 0.36 | 0.07 | 0.19 | 0.05 | 0.50 | 0.00 |
| Hf | 0.26 | 0.18 | 0.33 | 0.17 | 0.26 | 0.19 | 0.52 | 0.58 | 0.20 | 0.20 | 0.50 | 0.18 | 0.34 | 0.09 | 0.85 | 0.82 | 0.68 | 0.00 |
| Ta | 0.23 | 0.14 | 0.25 | 0.15 | 0.25 | 0.14 | 0.64 | 0.62 | 0.21 | 0.12 | 0.54 | 0.07 | 0.12 | 0.05 | - | - | 1.38 | - |
| Pb | 1.18 | 8.27 | 1.33 | 8.29 | 1.19 | 7.91 | 7.87 | 7.96 | 1.10 | 6.70 | 7.30 | 42.60 | 14.30 | 3.55 | 8.91 | 2.69 | 7.00 | 0.18 |
| Th | 0.70 | 0.51 | 0.61 | 0.53 | 0.64 | 0.53 | 1.12 | 1.14 | 0.60 | 0.51 | 1.22 | 2.92 | 3.61 | 0.31 | 2.26 | 0.49 | 1.85 | 0.11 |
| U | 0.48 | 0.53 | 0.47 | 0.54 | 0.47 | 0.54 | 0.81 | 0.85 | 0.46 | 0.49 | 0.87 | 0.40 | 0.37 | 0.26 | 0.86 | 0.32 | 0.40 | 0.07 |
| ΣREE+Y | 74.49 | 80.52 | 74.31 | 82.15 | 72.98 | 81.59 | 153.62 | 152.24 | 77.43 | 81.37 | 155.06 | 67.40 | 78.41 | 19.4 | 50.55 | 22.19 | 109.69 | 3.12 |
| (La/Yb)_{PAAS} | 0.20 | 0.42 | 0.20 | 0.42 | 0.19 | 0.42 | 0.24 | 0.24 | 0.21 | 0.46 | 0.27 | 0.28 | 0.28 | 0.59 | 0.53 | - | 0.29 | 7.16 |
| La/La* | 1.48 | 1.11 | 1.67 | 1.11 | 1.65 | 1.14 | 1.52 | 1.63 | 1.35 | 1.10 | 1.05 | -40.23 | 7.35 | 1.34 | 1.11 | 1.33 | - | - |
| Pr/Pr* | 1.00 | 0.90 | 0.98 | 0.89 | 0.99 | 0.90 | 0.94 | 0.93 | 0.95 | 0.92 | 0.98 | 0.81 | 0.88 | 1.04 | 1.00 | - | 1.03 | 0.94 |
| Ce/Ce* | 0.87 | 1.19 | 0.87 | 1.22 | 0.87 | 1.19 | 1.06 | 1.06 | 1.01 | 1.15 | 1.04 | 1.00 | 0.85 | 0.8 | 0.89 | 1.63 | 0.91 | 0.93 |
| Eu/Eu* | 0.99 | 0.97 | 1.04 | 0.97 | 1.03 | 1.00 | 1.04 | 1.03 | 1.07 | 1.03 | 1.02 | 0.87 | 1.16 | 1.41 | 2.48 | 1.63 | 1.16 | 1.81 |
| Y/Ho | 29.59 | 24.55 | 31.25 | 25.64 | 30.21 | 25.90 | 27.55 | 26.51 | 30.49 | 26.90 | 27.18 | 25.43 | 25.19 | 31.64 | 36.50 | 26.86 | 25.10 | 34.04 |

240 La/La*=L_{PAAS}/(3Pr_{PAAS}-2Nd_{PAAS}); Ce/Ce*=2Ce_{PAAS}/(La_{PAAS}+Pr_{PAAS}); Eu/Eu*=2Eu_{PAAS}/(Sm_{PAAS}+Gd_{PAAS}); Pr/Pr*=2Pr_{PAAS}/(Ce_{PAAS}+Nd_{PAAS}) ([Bolhar et al., 2004](#)). BIF data of Sijiaying are from [Wang et](#)
241 [al. \(2017\)](#); BIF data of Hamersley are from [Warchola et al. \(2018\)](#); BIF data of Itilliarsuk are from [Haug Aa Rd et al. \(2013\)](#); BIF data of Um Anab are from [Basta et al. \(2011\)](#). BIF data of Nkout
242 West are from [Ndime et al. \(2019\)](#).

4. Results

4.1. Zircon U-Pb ages

The mostly sub-angular to sub-rounded zircon grains from the metamorphic mafic rock in the Yemadong Complex are 80-150 μm in length, with length/width ratios of 1-1.5 (**Figure 3**). Cathodoluminescence images show that the light gray, moderately rounded zircons commonly lack oscillating zonations, and that they possess core morphological characteristics suggestive of metamorphic zircons. The LA-ICP-MS ages for 45 zircon grains with single point analyses are displayed in **Table 1**. Ten with abnormally high Eu content and four with anomalously high U concentrations were omitted from the age calculation. Thirty-one of the forty-five grains were successfully dated and plotted on the concordia diagram shown in **Figure 3a**. Their U zircon concentrations varied from 323-1094 ppm and Th from 38.1-140 ppm, with Th/U ratios doubling from 0.09-0.18 (**Table 1**). Seventeen analyses formed a coherent group on the concordia line (**Figure 3b**), yielding a weighted $^{206}\text{Pb}/^{207}\text{Pb}$ mean age of 2901 ± 8 Ma (MSWD = 0.77, **Figure 3c**). Forteen points formed a discord stretched between the seventeen previously mentioned points, with an upper and lower $^{206}\text{Pb}/^{238}\text{U}$ age intercept of 2909 ± 14 Ma and 775 Ma (MSWD = 1.5), respectively (**Figure 3a**). The obtained 1063.6 ± 3.6 Ma concordia age for 20 samples, corresponded with the $^{207}\text{Pb}/^{235}\text{U}$ age of 1063.5 ± 7.3 Ma measured for the 91500 zircon standard, is within analytical uncertainty, and agrees well with the more robust ID-TIMS $^{207}\text{Pb}/^{235}\text{U}$ age of 1065.4 ± 0.3 Ma ([Jackson et al., 2004](#)).

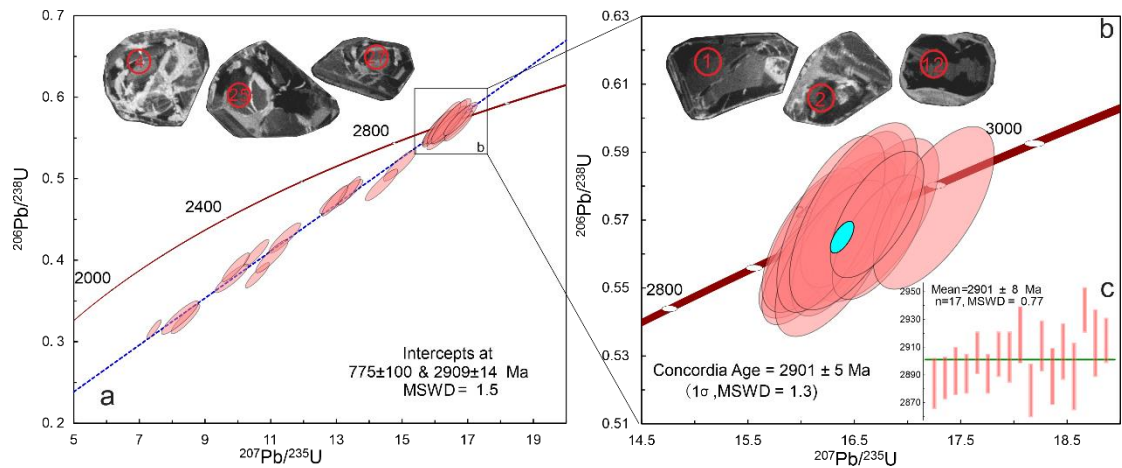


Figure 3. Zircon U-Pb concordia diagrams and their representative cathodoluminescence images from the Dujiagou BIF samples. Red circles indicate the location of the laser ablation spots. Each spot location is labeled by analysis number.

4.2. Bulk-rock geochemical compositions

The silicon-rich and iron-rich layers display typical characteristics typical of Archean BIF, composed mainly of 39.75-63.67 wt.% SiO_2 and 28.30-55.37 wt.% TFe_2O_3 . Al_2O_3 , MgO , TiO_2 and CaO contents range from 0.50-1.31 wt.%, 1.37-3.35 wt.%, 0.03-0.12 wt.% and 0.50-1.92 wt.%, respectively, suggest a degree of terrigenous detrital contamination (**Table 2**). The samples contain low K_2O , Na_2O , MnO and P_2O_5 concentrations averaging 0.11, 0.10, 0.25, and 0.28 wt.%, respectively concentrations, being generally compatible with the major element content of Early Precambrian BIF (**Table 2, Figure 4**).

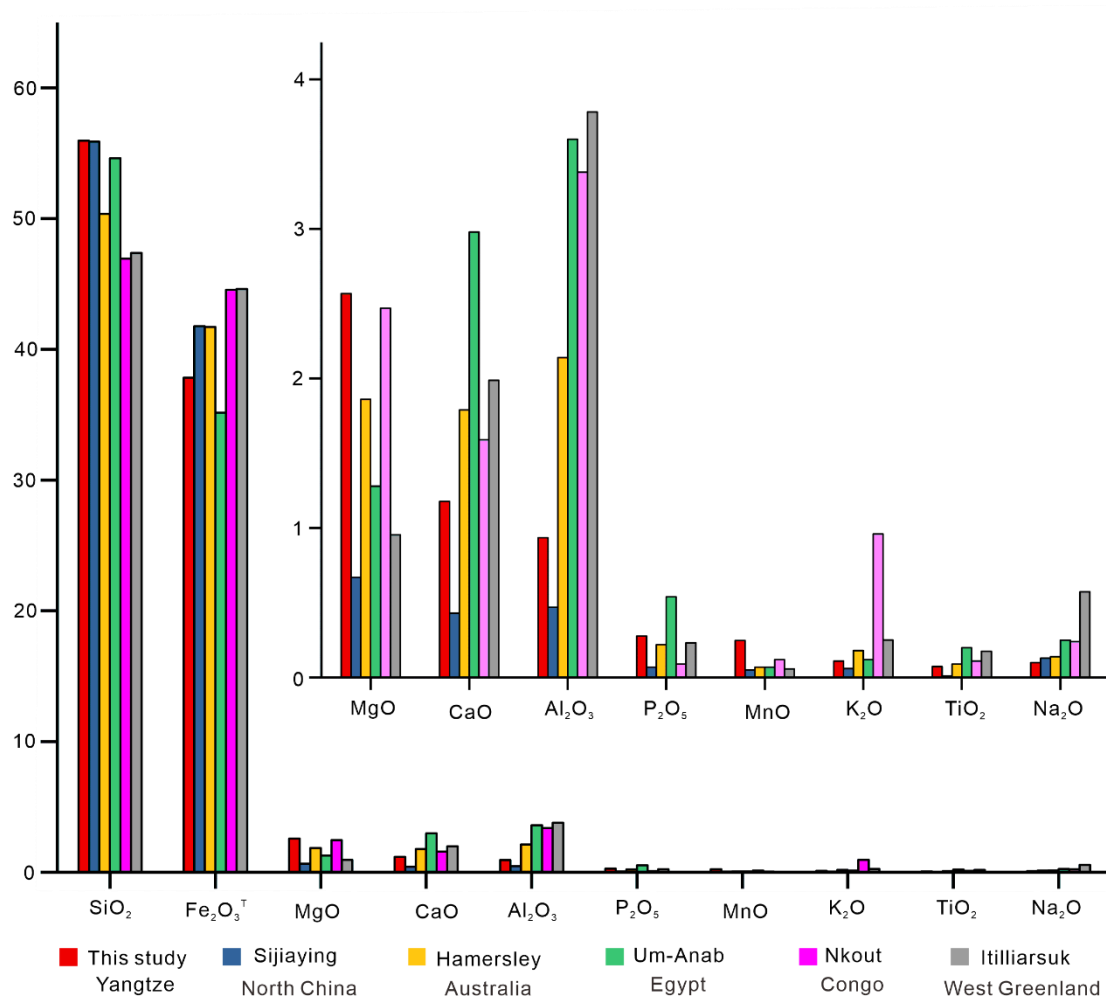


Figure 4. Mean values of major elements in the Dujiagou BIFs and early Precambrian BIFs from other areas. BIF data are from **Table 2**.

The samples display a wide range in incompatible element content, with Zr, Hf, Sc, and Th occurring in high concentrations of 3.82-16 ppm, 0.17-0.58 ppm, 1.5-5.32 ppm, and 0.51-3.61, respectively. Their high abundance not encountered in Archean and Paleoproterozoic detritus-free BIFs, support terrigenous contamination (e.g., [Li et al. \(2012b\)](#); [Wang et al. \(2017\)](#), **Table 2**). Total REE + Y average 94.74 ppm and range from 67.40-155.06 ppm (**Table 2**). Post Archean Average Shale (PAAS) normalized REY patterns are characterized by the depletion of light REE relative to heavy REE, $(La/Yb)^* = 0.19-0.46$, with an average of 0.30. Calculated Eu/Eu^* values varying from 0.87-1.12, point to positive and negative Eu anomalies across the sedimentary suite, while Ce/Ce^* values of 0.85-1.22 suggest Ce anomalies are muted across the sequence. The La/La^* values of 1.05-

7.35 and averaging 1.85, indicate a sample set characterized by moderate positive La anomalies (Table 2). Thirteen samples are significantly enriched in Y relative to Ho, yielding chondritic or suprachondritic Y/Ho ratios 24.55-31.25, with an average of 27.41. The Dujiagou BIFs show remarkably weaker positive or negative Eu* anomalies and higher Σ REY, which are significantly different from the average of most Archean BIFs (Table 2).

4.3. Fe isotopic composition

The $\delta^{56}\text{Fe}_{\text{IRMM-014}}$ of magnetite from seven samples are enriched in heavy Fe isotopes, with a range of 0.25-0.45 ‰ and an average 0.35 ‰. These values are similar to standard $\delta^{57}\text{Fe}_{\text{IRMM-014}}$ values of 0.37-0.68 ‰ that average 0.52 ‰ (Table 3). The $\delta^{56}\text{Fe}_{\text{IRMM014}}$ values of 0.110 ± 0.048 ‰ and $\delta^{57}\text{Fe}_{\text{IRMM014}}$ of 0.166 ± 0.080 ‰ (n=12) for AVG-2 measured here overlap with newly recommended Isoplot values (Ludwig, 2000) reported by ten independent laboratories ($\delta^{56}\text{Fe}_{\text{IRMM014}}=0.110 \pm 0.048$ ‰, $\delta^{57}\text{Fe}_{\text{IRMM014}}=0.141 \pm 0.005$ ‰ (He et al., 2015).

Table 3. Fe isotope compositions for BIFs representatives from the Dujiagou Formation

| Sample no. | Object (Whole rock) | $\delta^{56}\text{Fe}_{\text{IRMM-014}}$ (‰) | 2 σ | $\delta^{57}\text{Fe}_{\text{IRMM-014}}$ (‰) | 2 σ | $\delta^{57/56}\text{Fe}_{\text{IRMM-014}}$ (‰) | 2 σ |
|------------|---------------------|--|------------|--|------------|---|------------|
| Ibr 1-1a | BIF | 0.45 | 0.0252 | 0.65 | 0.0411 | 0.20 | 0.0349 |
| Ibr 1-1b | BIF | 0.45 | 0.0306 | 0.69 | 0.0371 | 0.22 | 0.0268 |
| Ibr 1-1c | BIF | 0.45 | 0.0281 | 0.65 | 0.0446 | 0.22 | 0.0332 |
| Ibr 2-2a | BIF | 0.27 | 0.0254 | 0.44 | 0.0372 | 0.17 | 0.0262 |
| Ibr 2-2b | BIF | 0.29 | 0.0262 | 0.44 | 0.0365 | 0.14 | 0.0327 |
| Ibr 2a | BIF | 0.27 | 0.0276 | 0.43 | 0.0390 | 0.14 | 0.0274 |
| Ibr 2b | BIF | 0.25 | 0.0227 | 0.37 | 0.0406 | 0.11 | 0.0360 |

5. Discussion

5.1. Metamorphic transformation and age of the Dujiagou BIFs

Previous compilations of zircon Th/U ratios led to the proposition of a general Th/U threshold value of 0.1 to differentiate between metamorphic and igneous zircon (Rubatto, 2017). Based on the

new compilation of zircon analyses from Western Australia, igneous zircons rarely possess Th/U ratios of <0.1 while those of metamorphic zircons range between <0.01 and >10 . Therefore, zircons with Th/U ratios <0.1 are more likely to be metamorphic, and those with Th/U ratios >0 of either igneous or metamorphic origin. However, it has been proposed that a Th/U ratio = 0.4 is more suitable for distinguishing metamorphic rocks from igneous rocks ([Yakymchuk et al., 2018](#)). Because Th^{4+} has a larger ionic radius than U^{4+} , it exhibits a weaker stability than U in the zircon lattice, and is easier to expel from the zircon lattice during metamorphic recrystallization, resulting in a relatively lower Th/U ratio in recrystallized metamorphic zircons ([Hoskin and Black, 2000](#)). Among the thirty-two zircons successfully dated in this study, six revealed $\text{Th/U} \leq 0.1$ and the remaining twenty-six had $0.1 < \text{Th/U} \leq 0.18$, which collectively suggests that the Th/U ratios of all the studied zircons fell within the expected metamorphic range. In addition, cathodoluminescence imaging, such as metamorphic accretion edge (**Figure 3a, b**), support the metamorphic genesis of the zircons.

Previous studies have shown that the TTG suites in the Kongling terrane were formed at ~ 3.0 – 2.90 Ga ([Qiu et al., 2000](#); [Zhang et al., 2006](#); [Zheng et al., 2006](#); [Gao et al., 2011](#); [Kang et al., 2013](#); [Qiu et al., 2018](#); [Wei et al., 2019](#); [Wei, 2021](#)). However, the xenoliths in the TTG of the Kongling terrane show an older age of 3.2 – 3.0 Ga (**Table 4**). Significant tecto-thermal activity between 3.2 and 3.0 Ga in the Yangtze Craton, formed the HGB (**Table 4**)—a typical Archean greenstone belt ([Wei and Wang, 2012](#); [Wei and Jing, 2013](#); [Wei et al., 2020](#); [Wei, 2021](#)). The 3.0 – 2.9 Ga TTG plutons intruded and split the greenstone belt into separate greenstone remnants or septa, leading to the cropping out of these HGB residues as enclaves of ~ 10 cm to 20 m thick within the younger TTG gneisses ([Gao and Zhang, 1990](#); [Xiong et al., 2004](#); [Li et al., 2014b](#); [Guo et al., 2015](#); [Wei et al.,](#)

[2020; Wei, 2021](#)). In the Kongling area, more than 96% of the HGB is invaded and covered by the Mesoarchean TTG gneiss, with a total sporadic exposure area of ~ 6 km² ([Wei, 2021](#)). In this study, we obtain an average weighted ²⁰⁶Pb/²⁰⁷Pb Mesoarchean age of 2901±8 Ma from the metamorphic zircons recovered from the metamorphosed mafic rocks interbedded with the thin Dujiagou BIFs. The layer thickness of these rocks is uniform, being regularly repetitive in the vertical section (**Figure 2a-c**), which may represent intermittent volcanic activity, and the BIFs moments quiescent volcanic activity. Therefore, the interlayered metavolcanic mafic rocks can be considered contemporaneous with the Dujiagou BIFs ([Zhang et al., 2012](#)), and the mafic volcanic rocks form the HGB ([Wei et al., 2019](#); [Wei et al., 2020](#); [Wei, 2021](#)). In this paper, since all the zircons underwent strong metamorphism, we interpret the ²⁰⁶Pb/²⁰⁷Pb age of 2901±8 Ma as the metamorphic age related to the same thermal tectonic event at ~2.95-2.90 Ga recorded by the aforementioned mafic volcanic rocks, while the deposition of the Dujiagou BIFs occurred prior to the inferred metamorphic event. Since it is difficult to observe the actual extent and full cross section of the HGB, the sampled outcrop probably represents only a limited exposure, true thickness and size of the Dujiagou BIFs. For example, in the Pitangui greenstone belt, exposed BIF outcrops consist of both thin and extremely thick layers with >10 times thickness difference along the cross section ([Brando Soares et al., 2017](#)). Regardless of actual size and thickness, the data suggest that the Dujiagou BIFs are the oldest known deposit in the Yangtze Craton.

Table 4. Compilation of isotopic ages of xenoliths in TTG suite of Kongling terrane in Huangling region

| Sample location | Lithology /xenoliths | Protolith | Sample number Rock/Zircon | Age (Ma) | Method |
|-----------------------|--------------------------|------------------------------|---------------------------|---------------------|-----------------------|
| Yemadong (this study) | metavolcanic mafic rocks | volcanic mafic rocks | 31 (zircon) | 2901±8 | Zircon U-Pb LA-ICP MS |
| ①Yemadong | Miotite–tremolite schist | Basic igneous rock | 41 (zircon) | 3011±27, 2933±13 | Zircon U-Pb LA-ICP MS |
| ②Yemadong | Massive amphibolite | Tholeiitic basalt | 15 (zircon) | 3000 ± 24 | Zircon U-Pb LA-ICP MS |
| ③Wangjiatai | Banded amphibolite | Tholeiitic basalt | 6 (zircon) | 3242 ± 140 | Zircon U-Pb LA-ICP MS |
| ④Hetaoyuan | Banded amphibolite | Komatiitic/Tholeiitic basalt | 4 (zircon) | 3013 ± 23 | Zircon U-Pb LA-ICP MS |
| ⑤Hetaoyuan | Amphibole schist | Komatiitic/Tholeiitic basalt | 7 (whole-rock) | 2998.9 | Sm-Nd isochronIsotope |
| ⑥Dongping | Banded amphibolite | Tholeiitic basalt | 13 (whole-rock) | 3290 ± 170 | Sm-Nd isochronIsotope |

The given ages are from ①Wei et al. (2019); ②Wei and Wang (2012); ③Wei et al. (2020); ④–⑤Wei and Jing (2013); ⑥Ma et al. (2002), respectively.

5.2. Elemental geochemistry

Clastic contamination, minor amounts of crustal material are sufficient to obscure original marine signatures if not carefully constrained (Bau, 1993; Bolhar et al., 2004). For instance, contamination with terrigenous detrital induces elevated and false correlated abundance of incompatible elements (Th, Hf, Zr, Sc, etc.) (Bolhar et al., 2004). BIF samples yielding high abundance of immobile trace elements (for example Sc > 2 ppm) should be excluded from a debris-free sample set (Bau, 1993) and high abundances of immobile trace elements such as 1.50–5.32 ppm Sc, 0.51–3.61 ppm Th, 3.82–16.0 ppm Zr, and 0.17–0.58 ppm Hf, confirm detrital incorporation. These values are about an order of magnitude higher than for the debris-free BIF samples (e.g., Li et al. (2012b) and Wang et al. (2017)). Crustal components are rich in Th (Zhao and Zhou, 2007), and therefore an $R^2=0.88$ supported positive correlation between Th and Zr (Figure 5a). This co-variation indicates that the Dujiagou BIFs were contaminated by detrital material. In addition, a

strong positive correlation between Al_2O_3 and TiO_2 is often interpreted to reflect the incorporation of detrital components in sedimentary rocks, and therefore widely used as a proxy for detrital contamination of chemical sediments (e.g., [Basta et al. \(2011\)](#)). The moderate positive correlation between Al_2O_3 and TiO_2 in the Dujigou BIFs with r value of 0.76 (**Figure 5b**) is therefore consistent with detrital input from the weathering of existing continental landmass. Although fairly low, the 0.54 -1.42 wt.% $\text{Al}_2\text{O}_3 + \text{TiO}_2$ content of the Dujigou BIFs, are largely higher than for pristine examples of Algoma-type BIFs (e.g., [Wang et al. \(2017\)](#)). The discovery of a small amount of amphibole and other accessory minerals in the Dujigou BIFs provide further strong evidence of terrigenous debris contamination (**Figure 2f**).

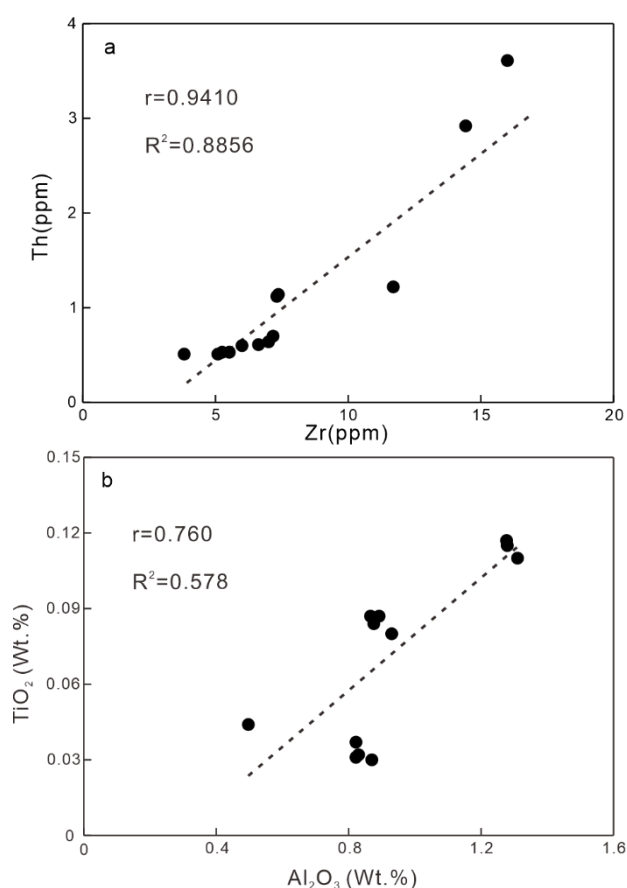


Figure 5 Discrimination diagrams for major and trace elements in the Dujigou BIF, Hangling region, Yangtze Craton, (a) Zr vs. Th and (b) Al_2O_3 vs. TiO_2 .

5.3. Sources of iron and silica

The sources of iron in BIFs is debated, with hydrothermal fluids ([Basta et al., 2011](#); [Wang et al., 2017](#)) or a mixture of both hydrothermal and terrigenous supply suggested ([Pecoits et al., 2009](#); [Li et al., 2015](#)). Also, as a remnant of HGB, the metamorphic amphibolite xenoliths believed to have originated from a tholeiitic protolith ([Wei, 2021](#)), show distinct positive correlation between Al_2O_3 and TFe_2O_3 ($R^2 = 0.84$). To the contrary, the strong negative correlation ($R^2 = 0.91$) between Al_2O_3 and TFe_2O_3 (**Figure 6a**), precludes the sourcing of Fe from the continent or derived by detrital contribution. Generally, diagenesis and various post-depositional processes, including hydrothermal alteration, could strongly affect the mobility of redox-sensitive elements, e.g., when Eu anomalies arise from the reduction of Eu (III) to Eu (II) ([Bau, 1993](#)). Previous studies have documented that REEs are largely immobile during low-grade metamorphism, e.g., in amphibolite facies ([Finger et al., 1998](#); [Huang et al., 2014](#)), and that the mineral reactions that occur during prograde metamorphism of BIF are essentially isochemical, except for decarbonation and dehydration ([Klein, 2005](#)). The amphibolite metamorphism experienced by the Dujiagou BIF may therefore be insignificant with respect to impact on the migration and enrichment of REEs.

The geochemical characteristics of ancient oceans and hydrothermal fluids are often inferred from the compositions of modern seawater and seafloor hydrothermal fluids ([Bolhar et al., 2004](#); [Bolhar and Vankranendonk, 2007](#)). Typically, when normalized to PAAS, REY patterns for the modern seawater are enriched in HREE relative to LREE. They are characterized by no Eu anomalies and a strong negative Ce anomaly typifies modern oxygenated seawater (**Figure 6b**). Further, high-temperature ($>250^\circ\text{C}$) hydrothermal fluids contain pronounced positive Eu anomalies, whereas a weak or no Eu anomaly characterizes low-temperature ($<250^\circ\text{C}$) hydrothermal fluids

(**Figure 6b**). Therefore, the Eu anomaly has become a mainstream proxy for identifying the material source of Precambrian BIFs. When normalized to PAAS, the Dujiagou BIFs $\Sigma\text{REY}_{\text{PAAS}}$ patterns are different from typical Precambrian debris-free IFs. For example, they are much higher, with several samples having element/PAAS ratios close to or above 1. Also, they contain extremely faint Eu and Ce positive anomalies, and the curves are much flatter than observed for pristine BIFs (**Figure 6c**). The lack of positive Eu anomalies in our samples is inconsistent with most Archean BIFs that tend to have strong positive Eu anomalies. Interestingly, the strong positive correlation ($R^2 = 0.83$) between Al_2O_3 and ΣREY (**Figure 6d**), suggest that the slightly positive Eu anomalies are indicative of the dilution of a high-temperature hydrothermal source of the BIFs by detrital material ([Yang et al., 2022](#)). Nonetheless, the positive Eu anomalies observed in the Dujiagou BIFs are consistent with those recorded for world-wide BIF deposits of the same age, attributed to a hydrothermal provenance. It is thus possible that terrigenous contamination did not completely erase the primary hydrothermal REE signal, in which case the observed positive Eu anomalies may in fact be pointing to the hydrothermal source of the Dujiagou BIFs. Moreover, the geochemical characteristics of biotite-tremolite schist enclaves from the Yemadong Complex are similar to those of island arc volcanic deposits ([Wei et al., 2019](#)), leading to the conclusion that the Dujiagou BIFs and their host volcanic rocks were developed in an island arc setting as opposed to a shelf environment, similar to Algoma-type BIFs. The Dujiagou BIFs are intimately associated with volcanic rocks, therefore, the hydrothermal activity that formed them is considered to be associated with volcanism, suggesting that the insignificant Eu anomalies are unlikely to be of low-temperature hydrothermal origin. Furthermore, BIFs of low-temperature hydrothermal origin appear to be mainly a feature of the Neoproterozoic (e.g., [Basta et al. \(2011\)](#); [Yang et al. \(2022\)](#)).

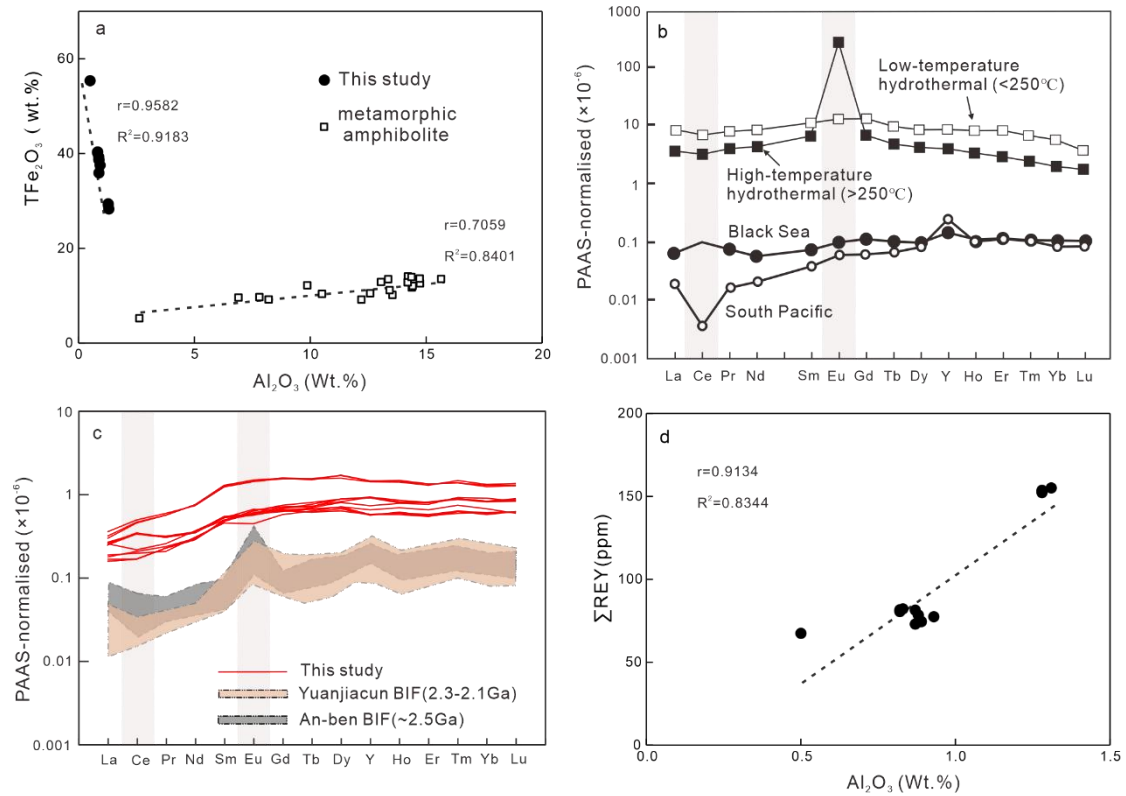


Figure 6. Discrimination diagrams for major and trace elements (a) Relationship between Al_2O_3 and TFe_2O_3 in the Dujiagou BIF and metamorphic amphibolite xenoliths (Wei, 2021), Hangling region, Yangtze Craton, (b) South Pacific ocean oxygenated modern seawater, the modern Black Sea anoxic seawater, and Eu anomaly of modern high and low-temperature marine hydrothermal fluids (Bolhar and Vankranendonk (2007) and references therein), (c) PAAS-normalized REE + Y diagrams of the relationships between REEs and different BIF types. Yuanjiacun Superior-type BIF data from Wang et al. (2014); An-ben Algoma-type BIF data from Li et al. (2012b), and (d) Relationship between Al_2O_3 and ΣREY in the Dujiagou BIF.

The Y/Ho ratio of BIFs are also widely used to interpret the source of ore-forming materials and sedimentary settings, e.g., Basta et al. (2011); Viehmann et al. (2014); Wang et al. (2017). The Blundy and Wood model (Blundy and Wood, 1994) suggests that in comparison to the degree of fractionation within the REE series, Y-Ho fractionation should be minor to negligible, and even more evolved melts do not readily fractionate Y from Ho (Bau and Dulski, 1996). Although Y and

436 Ho share similar geochemical properties they are fractionated differentially in seawater ([Nozaki et](#)
437 [al., 1997](#)). In the modern oxidized ocean, where hydrothermal fluids mix with seawater near vent
438 orifices, Y concentrations are conservative. On the contrary, REEs from the hydrothermal fluids are
439 partially adsorbed by precipitating Fe-oxyhydroxides when Fe^{2+} begins to rapidly oxidize to Fe^{3+}
440 immediately after release from the vents, producing a large decrease in sedimentary Y/Ho ratios
441 relative to seawater ([Bau and Dulski, 1999](#)). Chondritic Y/Ho ratios average ~28 ([Sun and](#)
442 [McDonough, 1989](#)), while seawater is characterized by superchondritic ratios of 44-47 ([Bau and](#)
443 [Dulski, 1999](#)). Although the Y/Ho ratio for rivers and estuaries fall between seawater and continental
444 rocks values, experiments have shown that fractionation in river and estuarine systems is negligible,
445 with little influence on the relative abundance of Y and Ho in the ocean ([Nozaki et al., 1997](#)). Y/Ho
446 ratios in the Dujiagou BIFs range from 24.6 to 31.3, with an average of ~27.4 being closer to
447 chondritic values, but far lower than modern seawater ratios. However, small admixtures of any
448 contaminant would depress seawater-like Y/Ho ratios ([Bau and Dulski, 1999](#)). The high Zr content
449 in BIFs samples has been confirmed as a source of terrigenous debris input, and the Y/Ho ratios
450 show a negative correlation with Zr ($R^2 = 0.18$, **Figure 7**). Therefore, the real Y/Ho ratio is
451 considered affected by terrigenous debris, thus presenting the illusion of a relatively low average
452 Y/Ho ratio. Although terrigenous debris reduces the Y/Ho ratio, four of the BIF samples contained
453 superchondritic ratios, consistent with a hydrothermal origin. In summary, the origin of the Dujiagou
454 BIFs is considered to be more closely related to a hydrothermal source rather than terrigenous debris.

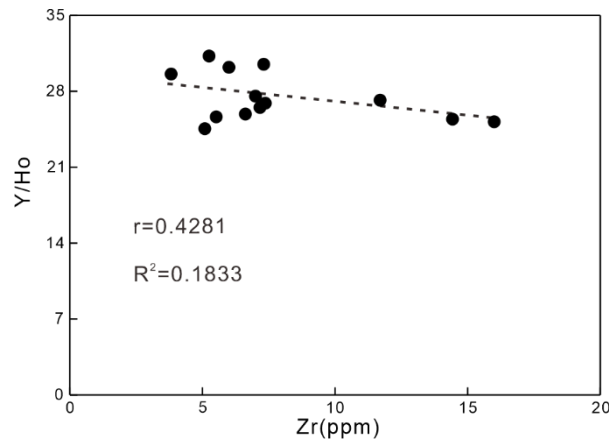


Figure 7. Plots of a Zr vs. Y/Ho in the Dujiagou BIF, Hangling region, Yangtze Craton.

5.4. Sedimentary environment

5.4.1. Rare Earth Elements (REE)

In general, anoxic and suboxic waters lack large negative Ce anomalies when normalized to PAAS, while oxygenated marine seawater displays a strong negative Ce anomaly (**Figure 6b**). In some cases, abnormal La enrichment may cause non-redox-dependent Ce depletion. As a consequence, [Bau and Dulski \(1996\)](#) proposed to use Ce/Ce* vs. Pr/Pr* cross plots to identify La and Ce anomalies in BIFs (**Figure 8a**). In **Figure 8a**, six BIF samples plot within positive Ce anomalies, which is generally not considered a predominant feature of chemical sediments precipitated from Archean seawater ([Bolhar et al., 2004](#)). The most likely cause is debris contamination, just as the Eu anomalies in the same batch of samples suggest. We are therefore inclined to consider the Ce anomalies as potentially unreliable tracers of the redox conditions in which they formed. Nonetheless, the lack of negative and true Ce anomalies is consistent with the expected anoxic waters of the Archean Ocean.

5.4.2. Iron isotopes

5.4.2.1. Iron isotopes and metamorphic influences

Given the fact that the Dujiagou BIFs have been metamorphosed, as shown by different lines of evidence, to amphibolite grade metamorphism, it is necessary to evaluate the influence of metamorphism on the studied iron isotopes before they are used for geochemical interpretative purposes. Based on studies on the Paleoproterozoic Biwabik iron formation, [Hyslop et al. \(2008\)](#) showed that metamorphism can alter the primary isotopic composition of O atoms in quartz and magnetite and iron in magnetite and iron silicate minerals. The self-diffusion coefficient of Fe in magnetite at a metamorphic temperature of 500 °C depends on the activity of O₂, but is greater than $\sim 10^{-16} \text{ cm}^2/\text{s}$ ([Atkinson et al., 1983](#)), with a corresponding diffusion length of $\sim 1 \text{ mm}$ ([Dauphas et al., 2007a](#)). In this case, $\sim 3 \text{ Ma}$ is required for complete diffusion of iron isotopes over an average length of 2 mm ([Czaja et al., 2013](#)). However, the diffusion of iron isotopes can only occur in individual iron layers, because magnetite bands are separated by quartz bands, which would be an effective barrier to iron diffusion. In the hand samples, it seems unlikely that large-scale transport of iron occurred during metamorphism and the overall average $\delta^{56}\text{Fe}_{\text{Mt}}$ values are likely to be reflective of those of the original BIF sediment ([Czaja et al., 2013](#)). The independent study of the $\sim 1.8 \text{ Ga}$ Biwabik BIFs shows that metamorphism could slightly reduce the $\delta^{56}\text{Fe}_{\text{Mt}}$ in BIFs, but that metamorphism cannot explain the positive $\delta^{56}\text{Fe}_{\text{Mt}}$ measured in BIFs, including Archean BIFs ([Hyslop et al., 2008](#)). Consequently, Fe isotopic composition of magnetite is much less affected by metamorphism compared to other mineral phases ([Dauphas et al., 2007a](#); [Hyslop et al., 2008](#)). Moreover, it has been proposed that the iron isotopic composition of BIFs are not involved in amphibolite facies metamorphism after formation ([Dauphas and Rouxel, 2006](#); [Frost et al., 2006](#);

[Dauphas et al., 2007a](#); [Czaja et al., 2013](#)). We therefore assume that the iron isotopic composition of the Dujiagou BIFs is likely representative of the original primary composition.

5.4.2.2. Iron isotopes and sedimentary environment

Recently, iron isotopes were proposed as a redox indicator of ancient oceans, resulting from the enrichment of heavy iron isotopes in Fe(III) minerals during the chemical oxidation of dissolved Fe (II) to Fe (III) precipitates ([Rouxel et al., 2005](#); [Anbar and Rouxel, 2007](#)). The enrichment of the heavy iron isotopes in the poorly mobile Fe (III)-rich minerals results in the transfer of the light isotopes to the highly mobile Fe (II) phase dissolved in anoxic waters ([Dauphas and Rouxel, 2006](#)). The seven whole rock $\delta^{56}\text{Fe}$ data from the Ibr 1 and Ibr 2 horizons (**Figure 2d**) are divided into $\sim 0.45\text{‰}$ for sample set Ibr 1 ($n = 3$) and $\sim 0.25\text{--}0.27\text{‰}$ for Ibr 2 ($n = 4$).

A study showed that the residual iron isotopic composition in magnetite and seawater gradually becomes lighter as the proportion of precipitate increases, implying early magnetite has heavier iron isotopes than late precipitates ([Li et al., 2012b](#)). Therefore, the variation of iron isotope composition of the Dujiagou BIFs can be explained by different precipitation stages. However, magnetite as a major BIF mineral, is not an authigenic phase but was probably formed diagenetically from ferrous ferric hydroxide precursors ([Ewers, 1983](#); [Klein, 2005](#); [Dauphas et al., 2007a](#)). For example, green rust was considered to be an important magnetite precursor in the Archean ocean ([Sumoondur et al., 2008](#); [Zegeye et al., 2012](#); [Sun et al., 2022](#)). Conversion to magnetite with inherited primary $\delta^{56}\text{Fe}$ values of precursor ferric oxide/hydroxide minerals, probably occur through interaction with hydrothermal Fe^{2+} in the deep marine environments of BIF deposition ([Johnson et al., 2008](#)). Hence, the iron isotopes in the BIF indicate changes in the ocean iron cycle as well as changes in

atmospheric redox, preserving a chemical record of Earth's most primitive oceans (Rouxel et al., 2005; Planavsky et al., 2012).

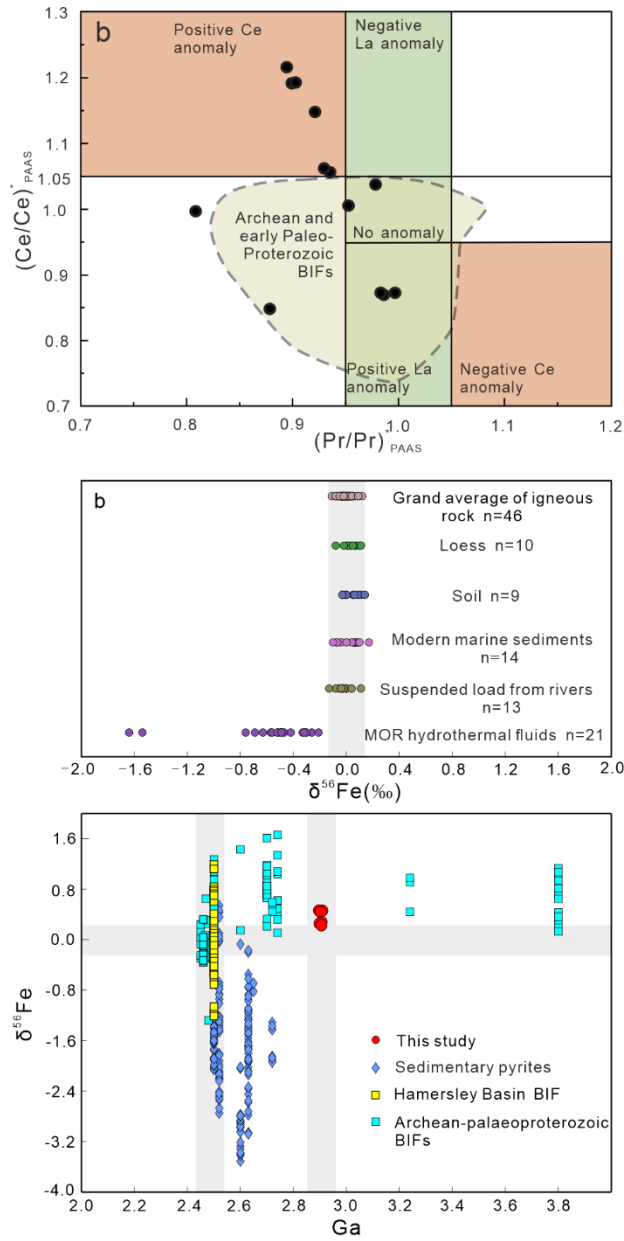


Figure 8. (a) Ce/Ce^* vs. (Pr/Pr^*) plot according to Bau and Dulski (1996), (b) Scatter plot of Fe isotopic composition of igneous rocks, clastic sedimentary rocks and chemically precipitated sedimentary rocks through Earth history. Igneous rock data from Beard et al. (2003b), other data from (Beard et al., 2003a), (c) whole-rock $\delta^{56}Fe$ values for iron formations from this study and literature (Dauphas et al., 2007b; Johnson et al.,

2008; Steinhofel et al., 2009; Li et al., 2012b; Planavsky et al., 2012; Ye et al., 2017), and $\delta^{56}\text{Fe}$ values for sedimentary pyrites from Rouxel et al. (2005) and references therein.

The heavy iron isotope compositions show the opposite behavior expected for modern weathered products and hydrothermal fluids (**Figure 8b**). They indicate that the valence state of iron changed from divalent to trivalent state during the deposition of magnetite. Precambrian BIFs generally exhibit a wide range of $\delta^{56}\text{Fe}$ values, spanning -1.6 to +1.5 ‰ (**Figure 8c**), with the >0 values consistent with partial oxidation of iron, while the <0 values are closer to those produced by dissimilatory Fe(III) reduction, DIR (Lovley et al., 2004). DIR can generate large iron isotope fractionation by reducing trivalent Fe(III) to highly soluble divalent Fe(II) (Beard et al., 1999; Crosby et al., 2007). Previous studies have shown that DIR may have evolved by 3.8 Ga (Craddock and Dauphas, 2011), but the broad absence of negative $\delta^{56}\text{Fe}$ values in the $>2.5\text{Ga}$ BIFs, has been taken to indicate that DIR may not have left a strong impact on the Archean iron sedimentary record (Johnson et al., 2008; Czaja et al., 2013). The variable negative $\delta^{56}\text{Fe}$ values in the Hamersley BIF in Western Australia may thus represent a record of the earliest period of expansive DIR expression in Earth history (**Figure 8c**) (Johnson et al., 2008). Therefore, the consistency of the data with numerous observations for various Archean BIFs, indicate that $\delta^{56}\text{Fe} > 0$ is a common characteristic of Archean BIFs, regardless of paleogeographical location (**Figure 8c**). This may be a reflection of the unique nature of biogeochemical cycling of iron during the Archean (Hyslop et al., 2008). Archean black shale pyrites are enriched with light Fe isotopes, with the most negative Fe isotope values being as low as -3.5‰ (**Figure 8c**). Because BIFs are a sink for isotopically heavy iron, black shale pyrite might therefore represent a corresponding reservoir for isotopically light iron in the

sedimentary record ([Planavsky et al., 2012](#)). Briefly, divalent Fe(II) is oxidized to trivalent Fe(III), enriching the heavy iron isotopes in the trivalent Fe(III) to form iron oxide-hydroxide. The residual dissolved divalent Fe(II) with its light iron isotopes would have been captured by the pyrite and enriched in pyrite-rich Archean sedimentary rocks. The rich iron oxide content of BIFs indicates the presence of significant Fe(II) oxidants in the Archean upper water column, much of which is debated, considering that the oceans are believed to have been strongly reducing for most of the Archean Eon ([Bekker et al., 2010](#)). The three processes most commonly advocated for iron oxidation in an anoxic atmosphere are; (1) oxidation with O₂ generated by oxygenic photosynthesis, (2) Oxidation by anoxic photosynthesis using Fe (II) as an electron donor rather than H₂O, and (3) Photooxidation ([Dauphas et al., 2007a](#)). Experimental results show that the enrichment of heavy isotopes of iron in Fe(III) minerals occurs during biotic and abiotic oxidation of Fe (II) to Fe(III) under varying redox conditions ([Bullen et al., 2001](#); [Johnson et al., 2002](#); [Welch et al., 2003](#); [Balci et al., 2006](#)), while the possibility of ultraviolet photooxidation in natural seawater compositions may be less likely than previously thought ([Konhauser et al., 2007](#)). The Great Oxidation Event (GOE) led saw the permanent rise of oxygen in the atmosphere, but there is increasing evidence that free oxygen may have predated the GOE ([Brocks et al., 1999](#); [Anbar et al., 2007](#); [Godfrey and Falkowski, 2009](#); [Ostrander et al., 2021](#)). We therefore interpret the prevalence of positive $\delta^{56}\text{Fe}$ values in the Dujiagou BIFs as representative of either abiotic and biotic partial oxidation of Fe(II) to Fe(III) minerals, or a combination of both processes. Thus, Archean marine shales and BIFs record iron isotopic composition different from those of modern marine sediments with typical $\delta^{56}\text{Fe}$ values of ~0‰ (**Figure 8b**). Collectively, these observations indicate that the Archean oceans were vastly anoxic/hypoxic before the rise of atmospheric oxygen, which as explained above would have

influenced the rates and quantitative abiotic and biotic oxidation of mobile Fe(II) in the Archean seawater column to particulate Fe oxide-oxyhydroxides, and therefore exerting a strong control on the $\delta^{56}\text{Fe}$ values of particulate and dissolved Fe.

6. Conclusions

The Dujiagou BIFs formed in an oceanic setting, probably near a subduction zone, similar to the suggested location where the Algoma-type BIFs that are generally prevalent in the Archean sedimentary rock record, deposited. With a predicted depositional age estimated at >2.90 Ga, the Dujiagou BIFs are likely the oldest BIFs in the Yangtze Craton. Their geochemical composition indicate that they are chemical sediments, marked by a minor detrital component that diluted and masked their primary REE composition. The data suggest that iron was sourced from submarine hydrothermal fluids, consistent with the origin of iron in most Precambrian BIFs. Moreover, their positive iron isotopic composition is characteristic of primary Archean BIF deposits, indicating that partial oxidation of iron led to the deposition of the divalent magnetite-rich BIFs in an Archean ocean that was broadly reducing.

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