Geochemistry and Si–O–Fe isotope constraints on the origin of banded iron formations of the Yuanjiacun Formation, Lvliang Group, Shanxi, China

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1. Introduction

Banded iron formations (BIFs) are marine sedimentary rocks that formed in voluminous amounts during the Late Archean, with a peak of deposition at ~2.5 Ga (Klein, 2005). BIFs typically contain alternating maghemite (Fe2O3) or hematite (Fe2O3)-dominated iron-rich layers, and microbanded iron-oxide-bearing silica-rich and iron-poor layers. This layering is usually present in different scales within a given outcrop, from fine sub-millimeter scale laminations to meter-scale bands. The high grade and extensive distribution of BIFs make them currently the World’s dominant iron resource. In addition, the different layers within a BIF sequence record important information on the changing oxidation states of the ocean and atmosphere. Because BIFs provide information on the atmospheric evolution of the early Earth (e.g., Frei et al., 2013), the changing chemical composition of the ocean, and the changes and development of biota, understanding their formation is important in both economic and academic terms.

Major, trace, and rare earth element (REE) concentrations have been used extensively to evaluate the formation of BIFs (Bau and Dulski, 1996; Bau and Moller, 1993; Planavsky et al., 2010). Precambrian BIFs are dominated by quartz, maghemite, and hematite, and therefore quartz Si and O isotopes and iron oxide Fe isotopes have been used as powerful tracers that enable the identification of the processes that led to BIF formation. Jiang et al. (1993) reported the Si isotope compositions of the Gongchangling BIF deposit for the first time, which contains silicates...
that are highly depleted in $^{30}\text{Si}$, and have $\delta^{30}\text{Si}$ values of $-1.2\%_\text{o}$ to $-0.9\%_\text{o}$. André et al. (2006) used MC-ICP-MS to investigate the Si isotopes of the oldest (3.8 Ga) known BIFs in the Isua region of Greenland; these yielded $\delta^{30}\text{Si}$ values of $-2.80\%_\text{o}$ to $+0.68\%_\text{o}$, the majority of which were again highly depleted in $^{30}\text{Si}$. More recently, Li et al. (2010) reported the Si and O isotope compositions of BIFs within twenty-one ore deposits in the North China Craton; these BIFs have $\delta^{18}\text{O}$ values that lie between values for quartz within igneous rocks and quartz within marine siliceous rocks, and are similar to those of quartz in siliceous rocks formed during hydrothermal activity (Ding et al., 1996; Li and Jiang, 1995). These BIFs yielded $\delta^{30}\text{Si}$ values that are generally between $-2.0\%_\text{o}$ and $-0.3\%_\text{o}$, consistent with BIFs in other parts of the world. In comparison, Fe has significant variations in valence state, with oxidation of Fe$^{2+}$ to Fe$^{3+}$ in low-temperature solutions causing Fe$^{3+}$ to be enriched in heavy Fe, whereas Fe$^{2+}$ is enriched in light Fe isotopes (Anbar et al., 2005; Balci et al., 2006; Bullen et al., 2001; Croal et al., 2004; Johnson et al., 2002; Skulan et al., 2002; Wiesli et al., 2004). These studies indicate that iron isotope is an important tracer of oceanic redox process. Chemical sediments have Fe isotope signatures that are more variable than those of igneous rocks that typically have Fe isotope compositions close to 0 (Anbar and Rouxel, 2007; Beard et al., 2003; Zhu et al., 2002). This is exemplified by Precambrian BIFs, which have Fe isotope values of $-1.5\%_\text{o}$ to $2.7\%_\text{o}$ (Dauphas et al., 2004, 2007; Johnson et al., 2003, 2008; Li et al., 2012; Planavsky et al., 2012; Steinhoefel et al., 2009). Steinhoefel et al. (2009) undertook in situ analyses of Si and Fe isotopes within Zimbabwean Archean BIFs using femtosecond laser ablation-MC-ICP-MS. Their work indicated that magnetite within the BIF was $^{56}\text{Fe}$ enriched, chert within the BIF was highly depleted in $^{30}\text{Si}$, and $\delta^{30}\text{Si}$ and $\delta^{56}\text{Fe}$ values varied consistently, indicative of precipitation from submarine hydrothermal fluids. Previous study in this field of research has focused on BIFs formed before 2.5 or after 2.0 Ga, but the BIFs that formed during the GOE (Great Oxidation Event; e.g., Young, 2013) have not been studied in detail.

BIFs in China are mainly located in the North China Craton (Zhai and Santosh, 2011, 2013) including in the east of Hebei and Liaoning provinces and in the northern Shaxi Province (Fig. 1). The Yuanjiacun BIF deposit in Shaxi Province is the largest open-pit iron mine in Asia and is hosted by the Yuanjiacun Formation within the 2.3–2.1 Ga Lvliang Group (Geng et al., 2000; Wan et al., 2000; Yu et al., 1997). This deposit contains 1.25 billion tons of Fe and is considered to be similar to superior-type BIFs (Shen, 1998; Shen et al., 1982; Wang et al., 2012; Zhang et al., 2012; Zhu et al., 1988). BIFs in this area are composed of iron sulfides and oxides in a carbonate and silicate gangue, and formed in a sedimentary sequence that evolved from deep- to shallow-water sedimentation. The formation and sedimentary environment of the Yuanjiacun Formation BIFs are still controversial. Shen et al. (1982) suggested that these BIFs formed in shallow sea and lagoonal environments via the deposition of iron derived from terrigenous weathering, leaching, and subma-

FIG. 1. Distribution of banded iron formations in the North China Craton [after Shen, 1998]. 1—Upper Paleoproterozoic Erathem terrane; 2—Lower Paleoproterozoic Erathem terrane; 3—Proterozoic schist; 4—Archean Eonothem; 5—Fault; 6—Conjectural Fault; 7—the concentration area of BIFs; 8—the BIF deposits of this study.
Peijiazhuang, Jinzhouyu and Dujigou formations. The Yuanjiacun Formation is dominated by ferrosiliceous units such as BIFs, including the Yuanjiacun BIF Fe deposits (Fig. 2, Table 1). These BIFs have undergone low-grade greenschist facies metamorphism and outcrop over an 18-km-long belt between the northernmost Yuanjiacun deposit, through the central Hugushan deposit, and on to the southernmost Jianshan deposit near Luojiacha (Fig. 2). About 2 km south of the Jianshan deposit, the large south-dipping left-lateral Xichuanhe fault passes through east–west direction. Progressive metamorphic zonation from north to south has developed, and the Yuanjiacun deposit is located at the northern end of this belt. The weakly metamorphosed Precambrian strata show N–S strike and easterly dip at 60°–80°. Structurally, it is an overturned monocline. The middle part of the deposit hosts the iron ore horizons of the Yuanjiacun Formation. These are underlain by the Ningjiawan Formation to the east and are overlain by the Peijiazhuang Formation to the west. All these Proterozoic successions are unconformably covered by gently dipping Cambrian limestone (Shen et al., 1982; Zhu et al., 1988). The formation age of the Yuanjiacun BIF is still unclear, primarily as these units are not interlayered with any dateable igneous rocks. However, Geng et al. (2000) obtained a zircon U–Pb age of 2351 ± 95 Ma for an acidic tuff within the Jinzhouyu Formation, and Yu et al. (1997) reported a zircon U–Pb age of 2051 ± 48 Ma for basic volcanic rocks within the same formation. In addition, Wan et al. (2000) noted that the Jiehekou Group, which underlies the Lvliang Group, formed at 2.3–2.2 Ga, indicating that BIFs within the Yuanjiacun Formation formed between 2.3 and 2.1 Ga.

The total thickness of the BIF-bearing Yuanjiacun Formation is about 1500 m, and iron-bearing units within this formation can be subdivided into three series representing three discrete sedimentary–metallogenic cycles. These cycles have a lowermost medium- to coarse-grained clastic or quartz sandstones that are overlain by fine-grained sandstones, silty sericite schists, sericite schists, chlorite schists and iron-bearing schists to an uppermost magnetite- and hematite-bearing quartzite unit, indicating an upward change from detrital to chemical-dominated sedimentation (Fig. 3). Iron-bearing rocks within the Yuanjiacun Formation contain a diverse range of primary iron minerals; these are, from bottom to top, pyrite, Fe-carbonates, Fe-silicates, and Fe-oxides, with iron oxides dominating. Siderite and anchorite are generally present in carbonaceous chlorite schists within the southern Yuanjiacun deposit. The Yuanjiacun BIFs are divided into three ore zones based on the three sedimentary–metallogenic cycles described above; these zones are named I, II, and III. Zone II is the largest (thickness of 200–600 m) and most economically important of these zones, and is present within all the iron-bearing units of the Yuanjiacun Formation. This zone is generally weakly deformed, but contains localized areas of intense deformation (Shen et al., 1982; Zhu et al., 1988).

The Yuanjiacun BIF deposit is dominated by magnetite, rare hematite, siderite, specularite, limonite, and minor pyrite in a gangue of quartz and minor jasperite, chlorite, dolomite, and calcite. These minerals are euhedral to subhedral, and are distributed in both micro- and macroscale bands, with alternating silica- and iron-dominated bands typically having thicknesses of 0.1 mm to 2 cm (Fig. 4).

### Table 1

<table>
<thead>
<tr>
<th>Stratigraphic unit</th>
<th>Age</th>
<th>Thickness (m)</th>
<th>Lithology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lanhe group</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dujigou formation</td>
<td>2.2–2.1Ga</td>
<td>2560</td>
<td>Quartzite, sandstone, conglomerate, phylite, marble</td>
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<tr>
<td>Jinzhouyu formation</td>
<td></td>
<td>3545</td>
<td>Rhyolite, rhyolite-porphry, quartz-keratophyre</td>
</tr>
<tr>
<td>Peijiazhuang formation</td>
<td></td>
<td>2000–2500</td>
<td>Mafic volcanics with interbeds of submarine pelite</td>
</tr>
<tr>
<td>Yuanjiacun formation</td>
<td></td>
<td>880–2650</td>
<td>Phylite, quartz sandstone,</td>
</tr>
<tr>
<td>Ningjiawan formation</td>
<td></td>
<td>840–1200</td>
<td>Iron formation</td>
</tr>
<tr>
<td>Qingyanggu formation</td>
<td>2.2–2.1Ga</td>
<td>2000–5000</td>
<td>Intermediate-acidic volcanics, tuff, iron formation, marble, phylite</td>
</tr>
<tr>
<td></td>
<td>(Wan et al., 2000)</td>
<td>4000</td>
<td>Quartzite, lepiote, schist</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16700</td>
<td>Migmattite, gneiss, plagioclase-amphibolite, quartzite, marble</td>
</tr>
</tbody>
</table>

3. Sampling and analytical methods

BIF samples were collected from the Jianshan (JS), Hugushan (HGS), and Yuanjiacun (YJC) Fe deposits and a summary of these samples is given in Tables 1–3. Quartz from 12 BIF samples was analyzed for Si
and O isotopes, and magnetite, hematite, and siderite separates from 19 BIF samples were analyzed for Fe isotope compositions.

All geochemical analyses were undertaken at the National Research Center for Geoanalysis, Beijing, China. Major element concentrations were determined using ICP-AES; these analyses have RSD values of ~1%. Trace element concentrations were determined using a Thermo X-series ICP–MS instrument; these analyses have uncertainties that are better than ±5%.

Quartz grains were separated prior to Si and O isotope analysis, and analyses followed Ding et al. (1996) and Clayton and Mayeda (1963), respectively, with both isotopes analyzed in the same sample preparation unit. This approach used the following techniques, with heating to ~550 °C and reacting quartz with BrF5 to produce O2 and SiF4, with separation of SiF4 and BrF5 from O2 using liquid nitrogen. The O2 was reacted with kryptol at 700 °C and was converted into CO2, which was collected in a sample tube. The liquid nitrogen was then replaced by a

Fig. 3. Simplified geological section of the Yuanjiacun Deposit.
After Zhu et al., 1988

Fig. 4. Typical photomicrographs of the Yuanjiacun BIF.
### Table 3
Silicon and oxygen isotope compositions of the banded iron formations from Yuanjiacun Formation.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Sample description</th>
<th>Mineral</th>
<th>δ(^{30})Si NBS-28 (‰)</th>
<th>δ(^{18})O SMOW (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JS-1</td>
<td>Banded magnetite quartzite</td>
<td>Quartz</td>
<td>−0.5</td>
<td>11.0</td>
</tr>
<tr>
<td>JS-4</td>
<td>Banded magnetite quartzite</td>
<td>Quartz</td>
<td>−1.1</td>
<td>11.8</td>
</tr>
<tr>
<td>JS-5</td>
<td>Banded magnetite quartzite</td>
<td>Quartz</td>
<td>−0.4</td>
<td>11.6</td>
</tr>
<tr>
<td>JS-7</td>
<td>Banded magnetite quartzite</td>
<td>Quartz</td>
<td>−1.2</td>
<td>12.1</td>
</tr>
<tr>
<td>JS-9</td>
<td>Banded magnetite quartzite</td>
<td>Quartz</td>
<td>−1.3</td>
<td>11.9</td>
</tr>
<tr>
<td>JS-8</td>
<td>Banded magnetite quartzite</td>
<td>Quartz</td>
<td>−1.1</td>
<td>12.5</td>
</tr>
<tr>
<td>JS-13</td>
<td>Banded magnetite quartzite</td>
<td>Quartz</td>
<td>−1.0</td>
<td>11.8</td>
</tr>
<tr>
<td>JS-10-1</td>
<td>Banded magnetite quartzite</td>
<td>Quartz</td>
<td>−1.6</td>
<td>10.4</td>
</tr>
<tr>
<td>JS-10-2</td>
<td>Banded magnetite quartzite</td>
<td>Quartz</td>
<td>−1.5</td>
<td>11.3</td>
</tr>
<tr>
<td>HGS-2</td>
<td>Banded magnetite quartzite</td>
<td>Quartz</td>
<td>−0.6</td>
<td>10.7</td>
</tr>
<tr>
<td>YJC-16</td>
<td>Banded magnetite quartzite with a small amount of hematite</td>
<td>Quartz</td>
<td>−1.4</td>
<td>13.3</td>
</tr>
<tr>
<td>YJC-20</td>
<td>Banded magnetite quartzite with a small amount of hematite</td>
<td>Quartz</td>
<td>−1.7</td>
<td>12.2</td>
</tr>
</tbody>
</table>
drikold–acetone cooling liquid (−78 °C) to freeze impure gasses (e.g., BrF₅ and Br₂F₇) and to release SiF₄. The SiF₄ released at this stage was frozen using a liquid nitrogen cold trap before being distilled and purified using drikold–acetone cooling liquid at low temperatures; this stage was repeated three times, although it is possible that the distilled SiF₄ still contained trace amounts of BrF₅ and other active fluorides. If these impurities were present, they would react with sample tube glasses and with lipin on the piston used during analysis, producing interfering impurities (e.g., SiF₄ and CF₄) that could influence silicon isotope measurements. This problem was overcome by heating the SiF₄ gas that contained trace impurities to 70 °C and passing this heated gas through a tube filled with zinc granules, removing BrF₅ and any other active fluorides by reaction with the granules. The relatively high stability of SiF₄ meant that it did not react with the zinc granules, yielding a purified SiF₄. Oxygen and silicon isotope ratios were measured using a Thermo Finnigan MAT 253 mass spectrometer, and results are expressed in δ relative to V-SMOW and NBS-28 standards, as follows:

\[
\delta^{18}\text{O}_{\text{V-SMOW}} = \left( \frac{{^{18}\text{O}} / {^{16}\text{O}} \text{sample}} {^{18}\text{O} / {^{16}\text{O}} \text{V-SMOW}} - 1 \right) \times 1000
\]

\[
\delta^{30}\text{Si}_{\text{NBS-28}} = \left( \frac{{^{30}\text{Si}} / {^{28}\text{Si}} \text{sample}} {^{30}\text{Si} / {^{28}\text{Si}} \text{NBS-28}} - 1 \right) \times 1000
\]

The analytical precision of δ¹⁸O and δ³⁰Si measurements were 0.2‰ (1 SD) and 0.1‰ (1 SD), respectively, based on repeated measurements of standard samples.

Chemical separation and determination of magnetite, hematite, and siderite Fe isotope compositions were undertaken at the Key Laboratory of Mineralization and Resource Assessment of the Ministry of Land and Resources, Beijing, China, using the procedures described by Hou et al. (2012). Sample preparation was carried out in a clean room and all other critical work, including sample dissolution and purification, was completed in class 100 laminar flow hoods. The sub-boiling hydrochloric acid used during analysis was distilled twice; both hydrofluoric and nitric acids were distilled using Savillex DST-1000, and Milli-Q water (18.2 MΩ) was used throughout all procedures. Magnetite, hematite, and siderite separates were dissolved in 3 ml aqua regia, whereas BCR-2 and BIR-1 standards were dissolved in a mixed solution with 2.4 ml concentrated HF and 0.6 ml concentrated HNO₃ in a Teflon beaker for 72 h at 140 °C. All digested samples were left on a hot plate at 80 °C to evaporate to dryness; this procedure was sequentially repeated three times using 0.5 ml concentrated HCl in order to remove any remaining HNO₃ and HF. Each dry sample was then dissolved in 7 M HCl for chemical purification, with Fe and other elements separated using ion-exchange chromatography. Chemical purification was undertaken using procedures similar to those outlined by Maréchal et al. (1999), with anion-exchange chromatography using a Bio-Rad polypropylene column (diameter = 6.8 mm, height = 43.3 cm) filled with Bio-Rad AG MP-1 resin (100–200 mesh, chloride form). Prior to purification, the resin was cleaned using 2 ml of 0.5 M HNO₃ followed by 10 ml of 18.2 MΩ Milli-Q water; this cleaning was repeated three times, before 5 ml of Milli-Q water was used to remove any remaining HNO₃. The resin was then continuously preconditioned with 10 ml of 7 M HCl. Sample loading was followed by stripping of the matrix using 35 ml of 37 M HCl, with Fe elution using 20 ml of 2 M HCl; Fe eluates were evaporated to dryness on a hot plate at 80 °C. Finally, the purified Fe underwent three dissolutions using 0.5 ml of concentrated HNO₃, with each dissolution followed by evaporation to dryness to remove chloride ions. The final Fe eluate was dissolved in 1% HNO₃ to yield a concentration of 3 ppm for isotope analysis; Fe recoveries for all standard samples were 98%–101%. Procedural blanks, including digestion, column purification, and evaporation blanks, contained <0.3% of the total Fe extracted from the samples.

Fe isotope ratios were determined using MC-ICP-MS and a Thermo Neptune instrument operated in a high-resolution mode. Mass fractionation was calibrated using standard sample bracketing, and Fe isotope compositions are expressed as per mil deviations relative to the IRMM-014 standard:

\[
\delta^{56}\text{Fe}_{\text{IRMM-014}} = \left( \frac{{^{56}\text{Fe}} / {^{54}\text{Fe}} \text{sample}} {^{56}\text{Fe} / {^{54}\text{Fe}} \text{IRMM-014}} - 1 \right) \times 1000
\]

\[
\delta^{57}\text{Fe}_{\text{IRMM-014}} = \left( \frac{{^{57}\text{Fe}} / {^{54}\text{Fe}} \text{sample}} {^{57}\text{Fe} / {^{54}\text{Fe}} \text{IRMM-014}} - 1 \right) \times 1000
\]

The performance of the instrument was assessed by repeated measurements of an in-house standard (CAGS Fe) that yielded deviations relative to the IRMM-014 Fe isotope reference material. The average Fe isotope values for CAGS Fe are δ⁵⁶Fe = 1.22 ± 0.12‰ (2SD) and δ⁵⁷Fe = 0.78 ± 0.08‰ (2SD) for analysis undertaken in a high-resolution mode with optimized conditions, consistent with previously published values (Zhu et al., 2008). The long-term instrumental reproducibility determined from 5 months of replicate analyses is 0.14‰ for δ⁵⁷Fe, and 0.08‰ for δ⁵⁶Fe, with analysis of BCR-2 and BIR-1 this time yielding δ⁵⁶Fe values of 0.10 ± 0.07‰ and 0.03 ± 0.08‰, respectively, consistent with previously reported analyses (Craddock and Dauphas, 2000).

4. Analytical results

4.1. Whole rock geochemistry

The major and trace element compositions of nine BIF samples from the Yuanjiacun, Hugushan, and Jiashan deposits are listed in Table 2. The data show consistent major and trace element compositions that are dominated by Fe₂O₃ and SiO₂. SiO₂ concentrations vary between 34.97% and 51.61%, with an average of 43.50%, whereas Fe₂O₃ concentrations vary between 45.52% and 63.56%, with an average of 53.77%. All samples have low Al₂O₃ (0.12%–0.34%, with an average of 0.22%) and TiO₂ (<0.02%; Fig. 5A) concentrations, indicating that these BIFs contain small amounts of detrital material. These BIFs also have very low trace-element concentrations (generally <10 ppm), especially for incompatible elements such as Th, Hf, Zr and Sc, which usually have concentrations of <3 ppm.

The PAAS-normalized REE diagrams for the 9 BIF samples analyzed during this study are shown in Fig. 4B. We also discuss both Y and the REE together as these elements are geochemically similar. BIFs within the Yuanjiacun Formation contain low total rare earth element (REE) concentrations (6.89–15.3 ppm), with (Pr/Yb)PAAS values of 0.27–0.66, indicating light REE (LREE) depletion and heavy REE (HREE) enrichment. Ytrrium anomalies (Y/Y*) within these BIFs were determined using Y/Y* = YPAAS / (0.5DyPAAS + 0.5HoPAAS), yielding values of 1.29–1.47, suggesting the presence of positive Y anomalies. These samples have Y/ Ho ratios of 33.9–39.0 with an average value of 35.9. Europium anomalies were calculated using Eu/Eu* = EuPAAS / (0.65⁵⁷EuPAAS + 0.3⁵⁷⁷EuPAAS), which is a slightly modified version of the usual method of calculating these anomalies as seawater has a slight Gd anomaly. All samples have significant positive Eu anomalies with Eu/Eu* values of 1.48–2.81. Highly variable La concentrations suggest that the calculation of Ce anomalies using the normal method was complicated; consequently, a Ce/Ce* and Pr/Pr* >diagram (Bau and Dulski, 1996) was used to determine Ce anomaly values (Fig. 6), using Ce/Ce* = CePAAS / (0.5⁵⁷⁷CePAAS + 0.5⁵⁷⁷⁷CePAAS) and Pr/Pr* = PrPAAS / (0.5⁵⁷⁷PrPAAS + 0.5⁵⁷⁷⁷PrPAAS). The Yuanjiacun BIF samples analyzed during this study do not have significant Ce and Pr anomalies (Fig. 5B).
4.2. Quartz Si and O isotope compositions

The Si and O isotope compositions of quartz from twelve BIF samples analyzed during this study are given in Table 3; these quartz separates have low $\delta^{30}\text{Si}_{\text{NBS-28}}$ values ($-1.7$‰ to $-0.4$‰), with an average value of $-1.1$‰, similar to BIFs in other parts of the North China Craton and other global examples (André et al., 2006; Li et al., 2010; Steinhoefel et al., 2009). The quartz separates also have $\delta^{18}\text{O}_{\text{V-SMOW}}$ values of 10.4‰ to 13.2‰, with an average of 11.7‰, falling between values for quartz within igneous rocks and values for marine siliceous rocks, similar to siliceous rocks that formed during hydrothermal activity (Ding et al., 1996; Li and Jiang, 1995).

4.3. Fe isotope compositions

The Fe isotope compositions of magnetite, hematite, and siderite within nineteen BIF samples from the Yuanjiacun deposit are given in Table 4, and Fig. 7. Magnetite from fifteen of these samples yielded $\delta^{56}\text{Fe}_{\text{IRMM-014}}$ values of 0.24–1.27‰, with an average of 0.7‰, whereas hematite from 2 samples yielded $\delta^{56}\text{Fe}_{\text{IRMM-014}}$ values of 0.41‰ and 0.72‰, indicating that these iron oxides are all enriched in heavy Fe isotopes. The $\delta^{56}\text{Fe}_{\text{IRMM-014}}$ value of siderite from one sample yielded a value of $-0.12$‰, indicating enrichment in light Fe isotopes.

5. Discussion

5.1. Atmospheric and oceanic redox states during formation of the Yuanjiacun BIF

Precambrian BIFs formed during chemical precipitation from the ocean, and therefore their REE composition can be used to determine the geochemistry of seawater during BIF formation; this information can in turn be used to determine the redox state of the atmosphere and ocean at this time (Planavsky et al., 2010). Ce anomalies are considered to be indicative of an oxygenated hydrosphere (Kerrich et al., 2013). The BIFs within the Yuanjiacun Formation do not show negative Ce anomalies (Fig. 6), and some samples have positive La and Ce anomalies. The REE geochemistry of the Yuanjiacun BIF samples analyzed during this study is consistent with those reported in a previous study of these units (Wang et al., 2012), and with other Late Paleoproterozoic (~1.9 Ga) BIFs (Planavsky et al., 2010). Planavsky et al. (2010) suggested a link between the lack of Ce anomalies within Paleoproterozoic BIFs and the GOE, primarily as positive Ce anomalies within BIFs are a result of redox reactions in the ancient ocean. If an area of ocean is not totally oxidized, the Ce, LREE, and Ho in solution are oxidized and are preferentially adsorbed by Mn and Fe hydroxides within oxidized surface waters; in comparison, the reductive dissolution of these precipitates in oxidation-reduction transition zones or in deeper waters would release...
Ce, LREE, and Ho into the seawater column (Planavsky et al., 2010). The Yuanjiacun BIF formed at ~2.3–2.1 Ga, contemporaneous with the change in oxidation–reduction status of seawater during the GOE. These BIFs have an average Y/Ho ratio of 35.9, significantly lower than the Archean–Early Paleoproterozoic BIFs (average Y/Ho ratio of 39), but greater than the Late Paleoproterozoic BIFs (average Y/Ho ratio of 32; Planavsky et al., 2010). However, these samples are LREE-depleted and HREE-enriched, similar to the Archean and Early Paleoproterozoic BIFs.

Experimental analysis indicates that biotic or non-biotic oxidation of Fe²⁺ to Fe³⁺ in solution causes considerable Fe isotope fractionation, leading to an enrichment of heavy Fe isotopes in Fe³⁺ (Balki et al., 2006; Bullen et al., 2001; Croal et al., 2004; Johnson et al., 2002; Welch et al., 2003). The precipitation of Fe³⁺ and the formation of iron hydroxides or oxides do not cause a change in the valence state of Fe, meaning that only limited fractionation would occur, leading to an enrichment in lighter Fe isotopes in iron hydroxide or oxide precipitates (Dauphas and Rouxel, 2006; Skulan et al., 2002). In comparison, iron hydroxide or oxide precipitates are enriched in heavier Fe isotopes during incomplete oxidation and the precipitation of Fe in solution during Rayleigh fractionation (Li et al., 2012). The magnitude of Fe isotope fractionation depends on the proportion of precipitate oxidized from Fe²⁺ to Fe³⁺; a lower proportion of Fe precipitates within seawater leads to BIFs with heavier Fe isotope compositions, whereas increasing amounts of Fe precipitation should correspond to BIFs with lighter Fe isotope compositions. Complete precipitation would lead to the formation of BIFs with Fe isotope compositions identical to those of the paleoseawater during formation. Temporal variation in δ⁵⁶Fe for magnetite and hematite is shown in Fig. 7. Magnetite that has positive δ⁵⁶Fe values is interpreted to reflect inheritance from ferric oxide/hydroxide precursors produced by the incomplete oxidation of hydrothermal Fe²⁺aq, whereas magnetite that has negative δ⁵⁶Fe values is interpreted to have incorporated low-δ⁵⁶Fe Fe²⁺aq formed by DIR (Johnson et al., 2008). Magnetite and hematite within Yuanjiacun BIF samples show heavy Fe isotope enrichment which indicate that only part of the Fe within the paleoseawater was oxidized to Fe³⁺ and precipitated. The seawater was still reducing, meaning that not all Fe within the water column was oxidized and precipitated. The lighter Fe isotope composition of the siderite sample analyzed during this study is suggestive of precipitation of Fe²⁺ enriched in lighter Fe isotopes after binding to dissolved CO₂ within deeper, more reducing, parts of the seawater column. In turn, this suggests that the Fe isotope composition of this siderite may represent the composition of the paleoseawater during precipitation, although DIR process cannot be excluded.

Li et al. (2010) undertook multiple sulfur isotope analyses of two pyrites from the Yuanjiacun Fe deposit, and obtained Δ³⁴S (= δ³⁴S–0.52δ³⁴S) values of 0.81‰ and 0.89‰, indicating apparent mass-independent sulfur isotope fractionation. In addition, Farquhar et al. (2000a, 2000b) documented the first example of mass-independent sulfur isotope fractionation in ancient sedimentary rocks, with experimental observations indicating that this mass-independent fractionation could occur in SO₂ that was exposed to significant amounts of ultraviolet light (Farquhar et al., 2001). This type of naturally occurring gas-phase photochemical reaction and the preservation of these isotope signatures require an oxygen-deficient atmospheric environment (Pavlov and Kasting, 2002), with the increased oxygen fugacity conditions after 2.45 Ga meaning that mass-independent sulfur isotope fractionation was no longer being observed (Farquhar et al., 2007). The mass-independent sulfur isotope fractionation inferred from pyrite within Yuanjiacun Formation BIFs indicates that these sediments formed in an oxygen-deficient atmosphere, even though these BIFs formed after the start of the GOE.

5.2. Source of the Yuanjiacun BIF

The Fe- and Si-rich sediments in BIFs are thought to have been derived from a combination of weathering of continental crustal material and venting of submarine hydrothermal fluids (Belevtsev et al., 1982; Hamade et al., 2003). Yuanjiacun Formation BIFs have low ΣREE concentrations, with REE patterns characterized by LREE depletions and HREE enrichments, with positive Eu, Y, and La anomalies, consistent
with BIFs elsewhere in the world (Frei and Polat, 2007; Frei et al., 2008; Planavsky et al., 2010; Shen et al., 2009, 2011; Spier et al., 2007). Previous studies indicate that modern seawater REE patterns are also LREE-depleted and HREE-enriched, and modern seawater commonly has positive Y and La anomalies, and high Y/Ho ratios (Alibo and Nozaki, 1998; Bau and Dulski, 1995). Positive Eu anomalies are generally thought to indicate precipitation from high-temperature submarine hydrothermal fluids (Bau and Dulski, 1999; Danielson et al., 1992), although these fluids generally have elevated Cu, Co, and Ni concentrations (Klein and Ladeira, 2000) that contrast sharply with the low concentrations within the Yuanjiacun BIF, suggesting that these BIFs formed from submarine exhalation.

Quartz within Yuanjiacun Formation BIFs is highly depleted in 30Si, with δ30Si NBS-28 values similar to those of quartz in modern sinter and submarine black smoker environments, and within siliceous rocks formed during hydrothermal exhalative activity (Ding et al., 1996; Jiang et al., 1992, 1994, 2000; Li and Jiang, 1995). In comparison, the dissolved silicon that is generated by weathering and leaching, and then transported to the ocean is highly enriched in 30Si (Ding et al., 2004; Opfergelt et al., 2009; Ziegler et al., 2005). This indicates that the precipitation from seawater of a very small proportion of material with very high concentrations of dissolved silicon would lead to a kinetic isotope fractionation of Si that would cause significant δ30Si NBS-28 depletions within the precipitates. This suggests that this significant amount of silicon was formed during submarine hydrothermal eruptive activity. The silicon isotope composition is also among with the values of other global BIF samples (Fig. 7), the most negative δ30Si value of World’s BIF quartz reflects hydrothermally silicon source, although some higher δ30Si value may derived from continental weathering reflecting mixed sources. In addition, this quartz has δ18OVSMOW Values of 10.4±12.3‰, with an average of 11.7‰, similar to siliceous rocks formed by hydrothermal sedimentation (Ding et al., 1996; Li and Jiang, 1995). Although the Yuanjiacun BIF has undergone greenschist facies metamorphism, this metamorphism and hydrothermal fluid exchange are likely to have decreased rather than increased quartz δ18OVSMOW values (Knauth, 2005; Knauth and Lowe, 2003; Robert and Chauasson, 2006). This indicates that the original δ18OVSMOW value of quartz within the BIF is likely to have been higher than the values determined during this study. This is consistent with δ18OVSMOW Values (21.0‰–21.5‰) for quartz within the Zhuhangzi BIF in north China; this BIF has undergone very low-grade metamorphism, suggesting that the BIFs in the study area formed in a submarine exhalative environment.

5.3. Formation of the Yuanjiacun BIF

Previous studies suggested that the Yuanjiacun Formation was deposited in a N–S-trending, narrow, confined marine basin, with the eastern and western sides of the basin separated by the Archean Ningjiawan and Chijianling Formations, respectively. BIF deposition occurred in a shallow sea environment, and led to the formation of three iron-bearing members, each of which represents an individual sedimentary–metallogenic cycle. The sediments within the basin record an upward change from detrital to chemical deposition, possibly corresponding to transgression within three separate shallow-water basin environments (Shen et al., 1982). Rapid deposition of terrigenous detrital material formed sandstone and siltstone layers during this transgression, with subsequent submarine hydrothermal exhalative activity producing voluminous amounts of ore-forming materials, such as ferrosilicon and acidic, reducing gases. The 2.3–2.1 Ga Yuanjiacun BIF formed during the 2.4–2.0 Ga GOE and the period of formation of redox stratified oceans. The oxidation of Fe2+ to Fe3+ and subsequent precipitation from seawater occurred at the oxidation–reduction transition zone. These iron hydroxides would contain little or no Ce, LREE, or HREE relative to the abundance of Mn hydroxides within the pH range during precipitation (Bau and Dulski, 1999; De Carlo et al., 2000; Ohta and Kawabe, 2001), leading to BIFs without significant Ce anomalies. However, within oxidizing surface waters, these manganese oxides would preferentially adsorb Ho, the LREE, and Ce4+. Subsequent dissolution of these manganese oxides would increase the Ce, LREE, and Ho concentrations within the surrounding seawater, potentially leading to BIFs with positive Ce anomalies, and low Y/Ho and high LREE/HREE ratios (Planavsky et al., 2010). The formation of BIFs in the study area during the GOE suggests that the paleoseawater in the study area would have been only slightly oxidized, indicating in turn that surface seawater had only a limited effect on the fractionation of the REE in both seawater and BIFs, as demonstrated by the REE patterns of BIFs analyzed during this study.

Iron oxides that formed in oxidation and oxidation–reduction transition zones would have been enriched in heavier Fe isotopes, whereas deeper and more reducing seawater would have been enriched in lighter Fe isotopes, resulting in the precipitation of siderite enriched in light Fe isotopes. Vented hydrothermal fluids were mixed with seawater, causing a rapid decrease in temperature and the precipitation of silicon as a silica gel from a Si-oversaturated mixed fluid. However, the amount

### Table 4

Fe isotope compositions of the banded iron formations from Yuanjiacun formation.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Sample description</th>
<th>Mineral</th>
<th>δ30Si NBS-28(‰)</th>
<th>2σ</th>
<th>δ18OVSMOW(‰)</th>
<th>2σ</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>JS-10-1</td>
<td>Banded magnetite quartzite</td>
<td>Magnetite</td>
<td>0.44</td>
<td>0.06</td>
<td>0.65</td>
<td>0.12</td>
<td>2</td>
</tr>
<tr>
<td>JS-10-2</td>
<td>Banded magnetite quartzite</td>
<td>Magnetite</td>
<td>0.55</td>
<td>0.01</td>
<td>0.77</td>
<td>0.10</td>
<td>2</td>
</tr>
<tr>
<td>JS-13</td>
<td>Banded magnetite quartzite</td>
<td>Magnetite</td>
<td>0.74</td>
<td>0.04</td>
<td>1.15</td>
<td>0.09</td>
<td>2</td>
</tr>
<tr>
<td>JS-8</td>
<td>Banded magnetite quartzite</td>
<td>Magnetite</td>
<td>1.25</td>
<td>0.03</td>
<td>1.87</td>
<td>0.07</td>
<td>3</td>
</tr>
<tr>
<td>JS-9</td>
<td>Banded magnetite quartzite</td>
<td>Magnetite</td>
<td>1.27</td>
<td>0.07</td>
<td>1.89</td>
<td>0.13</td>
<td>2</td>
</tr>
<tr>
<td>Replicated</td>
<td></td>
<td></td>
<td>1.24</td>
<td>0.05</td>
<td>1.87</td>
<td>0.09</td>
<td>2</td>
</tr>
<tr>
<td>HGS-1</td>
<td>Banded magnetite quartzite</td>
<td>Magnetite</td>
<td>0.24</td>
<td>0.04</td>
<td>0.38</td>
<td>0.08</td>
<td>2</td>
</tr>
<tr>
<td>HGS-3</td>
<td>Banded magnetite quartzite</td>
<td>Magnetite</td>
<td>0.59</td>
<td>0.05</td>
<td>0.87</td>
<td>0.11</td>
<td>2</td>
</tr>
<tr>
<td>HGS-4</td>
<td>Banded magnetite quartzite</td>
<td>Magnetite</td>
<td>0.62</td>
<td>0.09</td>
<td>0.91</td>
<td>0.13</td>
<td>2</td>
</tr>
<tr>
<td>YJC-04</td>
<td>Banded magnetite quartzite</td>
<td>Magnetite</td>
<td>0.89</td>
<td>0.04</td>
<td>1.30</td>
<td>0.09</td>
<td>2</td>
</tr>
<tr>
<td>YJC-13</td>
<td>Banded magnetite quartzite</td>
<td>Magnetite</td>
<td>0.63</td>
<td>0.10</td>
<td>0.96</td>
<td>0.09</td>
<td>2</td>
</tr>
<tr>
<td>YJC-14</td>
<td>Banded magnetite quartzite</td>
<td>Magnetite</td>
<td>0.76</td>
<td>0.02</td>
<td>1.11</td>
<td>0.13</td>
<td>3</td>
</tr>
<tr>
<td>YJC-20</td>
<td>Banded magnetite quartzite with a small amount of hematite</td>
<td>Magnetite</td>
<td>0.58</td>
<td>0.02</td>
<td>0.86</td>
<td>0.10</td>
<td>2</td>
</tr>
<tr>
<td>YJC-21</td>
<td>Banded magnetite quartzite with a small amount of hematite</td>
<td>Magnetite</td>
<td>0.70</td>
<td>0.02</td>
<td>1.02</td>
<td>0.11</td>
<td>2</td>
</tr>
<tr>
<td>YJC-22</td>
<td>Banded magnetite quartzite with a small amount of hematite</td>
<td>Magnetite</td>
<td>0.68</td>
<td>0.05</td>
<td>1.02</td>
<td>0.09</td>
<td>2</td>
</tr>
<tr>
<td>YJC-23</td>
<td>Banded magnetite quartzite with a small amount of hematite</td>
<td>Magnetite</td>
<td>0.52</td>
<td>0.06</td>
<td>0.80</td>
<td>0.13</td>
<td>2</td>
</tr>
<tr>
<td>YJC-12</td>
<td>Banded magnetite quartzite with a small amount of hematite</td>
<td>Hematite</td>
<td>0.41</td>
<td>0.06</td>
<td>0.61</td>
<td>0.07</td>
<td>3</td>
</tr>
<tr>
<td>YJC-24</td>
<td>Banded magnetite quartzite with a small amount of hematite</td>
<td>Hematite</td>
<td>0.72</td>
<td>0.02</td>
<td>1.06</td>
<td>0.06</td>
<td>2</td>
</tr>
<tr>
<td>Replicated</td>
<td></td>
<td></td>
<td>0.70</td>
<td>0.05</td>
<td>1.04</td>
<td>0.07</td>
<td>2</td>
</tr>
<tr>
<td>YJC-19</td>
<td>Banded magnetite quartzite with a small amount of siderite</td>
<td>Siderite</td>
<td>–0.12</td>
<td>0.02</td>
<td>–0.17</td>
<td>0.12</td>
<td>3</td>
</tr>
<tr>
<td>BCR-2</td>
<td></td>
<td></td>
<td>0.10</td>
<td>0.07</td>
<td>0.14</td>
<td>0.09</td>
<td>3</td>
</tr>
<tr>
<td>BCR-1</td>
<td></td>
<td></td>
<td>0.03</td>
<td>0.08</td>
<td>0.05</td>
<td>0.11</td>
<td>3</td>
</tr>
</tbody>
</table>

* n: repeat times detected by MC-ICP-MS; replicated: means the sample matrices processed independently through the chemistry.
of silicon precipitated was only a small proportion of the total seawater Si budget, meaning that kinetic fractionation caused the precipitated silicon to have a very low $^{28}$Si/$^{29}$Si value.

6. Conclusions

This study leads us to the following conclusions:

(1) The BIFs within the Yuanjiacun Formation were deposited during the formation of a redox stratified oceanic coeval with the Great Oxidation Event, although both atmosphere and ocean were still evolving at this time.

(2) BIFs within the Yuanjiacun Formation formed in a shallow sea environment located far from any centers of volcanic activity, and the Fe deposits in the study area were derived from ferrosilicon material generated by venting of hydrothermal fluids. These geochemical characteristics indicate that the Yuanjiacun BIFs precipitated as a result of mixing between exhalative hydrothermal fluids and seawater.

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