



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

Hou Kejun<sup>a,\*</sup>, Li Yanhe<sup>a,\*</sup>, Gao Jianfeng<sup>b</sup>, Liu Feng<sup>a</sup>, Qin Yan<sup>a</sup>

<sup>a</sup> MLR Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing, China

<sup>b</sup> Geological Survey of Canada, Ottawa, Canada

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## ABSTRACT

Banded iron formations (BIFs) within the Lvliang region of Shanxi Province, China, are hosted by sediments of the Yuanjiacun Formation, part of the Paleoproterozoic Lvliang Group. These BIFs are located in a zone where sedimentation changed from clastic to chemical deposition, indicating that these are Superior-type BIFs. Here, we present new major, trace, and rare earth element (REE) data, along with Fe, Si, and O isotope data for the BIFs in the Yuanjiacun within the Fe deposits at Yuanjiacun, Jianshan, and Hugushan. When compared with Post Archean Australian Shale (PAAS), these BIFs are dominated by iron oxides and quartz, contain low concentrations of  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , trace elements, and the REE, and are light rare earth element (LREE) depleted and heavy rare earth element (HREE) enriched. The BIFs also display positive La, Y, and Eu anomalies, high Y/Ho ratios, and contain  $^{30}\text{Si}$  depleted quartz, with high  $\delta^{18}\text{O}$  values that are similar to quartz within siliceous units formed during hydrothermal activity. These data indicate that the BIFs within the Yuanjiacun Formation were precipitated from submarine hydrothermal fluids, with only negligible detrital contribution. None of the BIF samples analyzed during this study have negative Ce anomalies, although a few have a positive Ce anomaly that may indicate that the BIFs within the Yuanjiacun Formation formed during the Great Oxidation Event (GOE) within a redox stratified ocean. The positive Ce anomalies associated with some of these BIFs are a consequence of oxidization and the formation of surficial manganese oxide that have preferentially adsorbed Ho, LREE, and  $\text{Ce}^{4+}$ ; these deposits formed during reductive dissolution at the oxidation–reduction transition zone or in deeper-level reducing seawater. The loss of Ce, LREE, and Ho to seawater and the deposition of these elements with iron hydroxides caused the positive Ce anomalies observed in some of the BIF samples, although the limited oxidizing ability of surface seawater at this time meant that Y/Ho and LREE/HREE ratios were not substantially modified, unlike similar situations within stratified ocean water during the Late Paleoproterozoic. Magnetite and hematite within the BIFs in the study area contain heavy Fe isotopes ( $^{56}\text{Fe}$  values of 0.24–1.27‰) resulting from the partial oxidation and precipitation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  in seawater. In addition, mass-independent fractionation of sulfur isotopes within pyrite indicates that these BIFs were deposited within an oxygen-deficient ocean associated with a similarly oxygen-deficient atmosphere, even though the BIFs within the Yuanjiacun Formation formed after initiation of the GOE.

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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 magnetite ( $\text{Fe}_3\text{O}_4$ )- or hematite ( $\text{Fe}_2\text{O}_3$ )-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, magnetite, 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

\* Corresponding authors. Tel.: +86 10 68999644; fax: +86 10 68999096.  
E-mail addresses: [kejinhou@126.com](mailto:kejinhou@126.com) (K. Hou), [lyh@mx.cei.gov.cn](mailto:lyh@mx.cei.gov.cn) (Y. Li).

that are highly depleted in  $^{30}\text{Si}$ , and have  $\delta^{30}\text{Si}$  values of  $-1.2\%$  to  $-0.9\%$ . André et al. (2006) used MC-ICP-MS analysis 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  $-2.80\%$  to  $+0.68\%$ , 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  $-2.0\%$  and  $-0.3\%$ , consistent with BIFs in other parts of the world. In comparison, Fe has significant variations in valence state, with oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  in low-temperature solutions causing  $\text{Fe}^{3+}$  to be enriched in heavy Fe, whereas  $\text{Fe}^{2+}$  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  $-1.5\%$  to  $2.7\%$  (Dauphas et al., 2004, 2007; Johnson et al., 2003, 2008; Li et al., 2012; Planavsky et al., 2012; Steinhöfel et al., 2009). Steinhöfel 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  $\delta^{56}\text{Fe}$  and  $\delta^{30}\text{Si}$  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 Shanxi Province (Fig. 1). The Yuanjiaocun BIF deposit in Shanxi Province is the largest open-pit iron mine in Asia and is hosted by the Yuanjiaocun 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 Yuanjiaocun 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 submarine volcanism, whereas Zhu et al. (1988) suggested that these BIFs formed from a colloidal chemical material present in seawater.

Here we present a systematic study of the variations in Fe, Si, and O isotopes, and major, trace, and REE compositions of the BIFs that form the Yuanjiaocun Fe deposit. These data enable us to constrain the formation and depositional environment of the Yuanjiaocun Formation BIFs.

## 2. Geological setting

The majority of large Chinese BIF deposits are located in the North China Craton including the Yuanjiaocun BIF Fe deposit (Fig. 1). The BIFs in the Yuanjiaocun Formation form part of the Lvliang Group, a 15,000-m-thick sequence of spilitic keratophyre, terrigenous detrital sedimentary, ferruginous silica, and shallow-sea carbonate units that are overlain and underlain by volcanic units of the Jiehekou and Yejishan groups, respectively. The Lvliang Group is subdivided from bottom to top into the Qingyanggou, Ningjiawan, Yuanjiaocun,

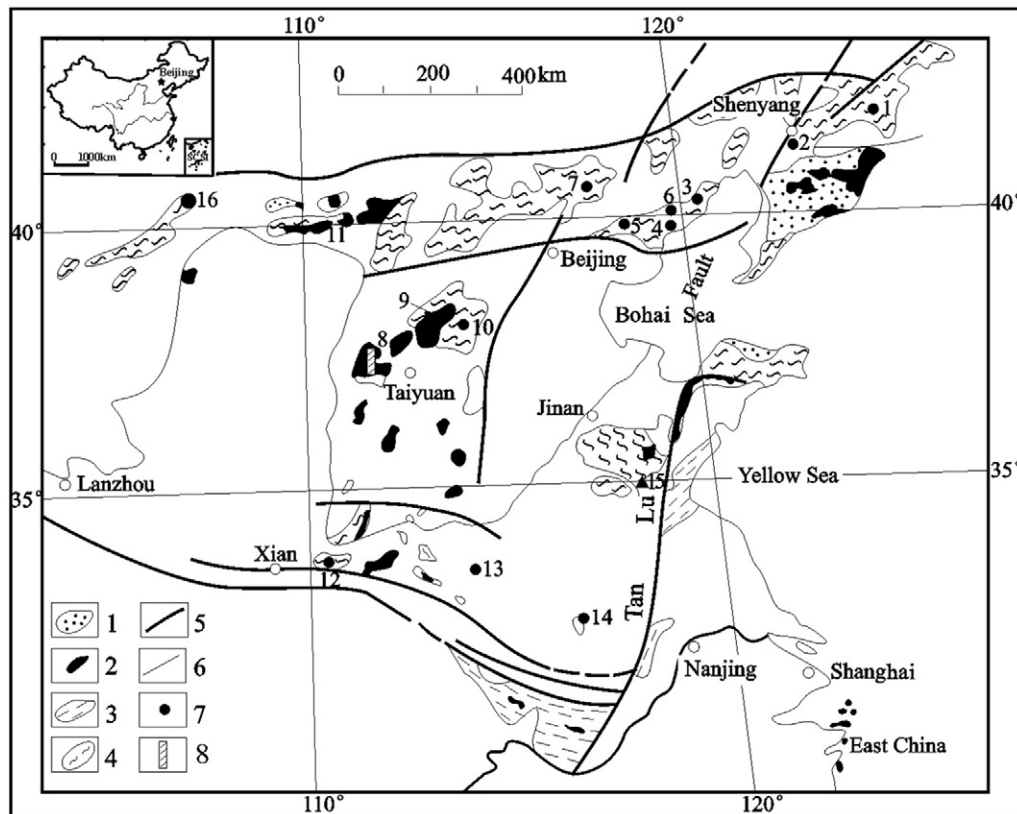


Fig. 1. Distribution of banded iron formations in the North China Craton (after Shen, 1998). 1—Upper Paleoproterozoic Erathem terrane; 2—Lower Paleoproterozoic Erathem terrane; 3—Proterozoic schist; 4—Archean Eonothem; 5—Fault; 6—Conjectural Fault; 7—the concentration area of BIFs; 8—the BIF deposits of this study.

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