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Changes of Ge/Si, REE + Y and Sm—Nd isotopes in alternating Fe- and Si-rich mesobands reveal source heterogeneity of the ~2.54 Ga Sijiaying banded iron formation in Eastern Hebei, China

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ABSTRACT

The North China Craton (NCC) is one of the most important regions hosting abundant banded iron formations (BIFs). The ~2.54 Ga Sijiaying BIF, the best-preserved and most extensive deposit in Eastern Hebei, is intercalated and closely associated with meta-volcanic rocks of the Luanxian Group. In this context, major and trace element and Sm—Nd isotopic analyses of individual mesobands of a Sijiaying BIF specimen were conducted to characterize the source and depositional environment over a transient period.

Low Al_2O_3, TiO_2 and high field strength elements (HFSEs) concentrations show that the BIF is relatively detritus-free. Shale-normalized rare earth and yttrium distributions (REE + Y) of individual BIF mesobands exhibit positive La anomalies, enrichment in HREE relative to LREE and MREE and suprachondritic Y/Ho ratios, which are typical features of marine waters throughout the Archean and Proterozoic. The presence of consistently positive Eu anomalies indicates a significant high-T hydrothermal input, while the absence of true Ce anomalies suggests deposition from an anoxic water column. By comparison with other typical BIFs (e.g., the Isua BIF from Greenland; the Kuruman BIF from South Africa), the Sijiaying BIF is depleted in HREE, and appears to record variations in solute fluxes related to changing intensities of hydrothermal activity. These features, coupled with Sm—Nd isotopic relations and Ge/Si distributional patterns, point to two decoupled sources controlling the depositional environment of the BIF and thus reveal source heterogeneity for silica and iron of the Sijiaying BIF. High Fe fluxes were associated with seafloor-vented hydrothermal fluids, which received their Sm—Nd isotopic signature from alteration of depleted oceanic crust; whereas significant amounts of silica were associated with ambient seawater whose REE signature was controlled by solutes derived from weathering of nearby Mesoarchean continental landmasses. The old (up to ~3.0 Ga) Nd (T_{DM}) model ages of Si-rich mesobands of the BIF support such a scenario.
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1. Introduction

Banded iron formations (BIFs) are marine chemical sedimentary rocks (total iron (TFe) >15 wt.%) of alternating iron-rich (hematite, magnetite and siderite) and silica/carbonate-rich (e.g., chert, jasper, dolomite and ankerite) layers that are abundant in the Archean and Paleoproterozoic (James, 1954; Trendall, 2002; Bekker et al., 2010). The layers vary from the microscale (micrometers in thickness) to meter-thick units (Klein, 2005). These microbands were interpreted as annual depositional varves (Trendall and Blockley, 1970; Morris, 1993), alternating between deposition from an iron-rich water column followed by deposition from a silica-rich water column. This interpretation is accepted by some but also challenged by others (Krapež et al., 2003; Pickard et al., 2004; Rasmussen et al., 2013).

BIFs may serve as archives of proxies that provide clues about the composition and redox state of the ancient ocean and atmosphere (Holland, 1984; Bekker et al., 2010). Among the most robust proxies are the rare earth elements and yttrium (REE + Y) because of their coherent behavior in geochemical systems despite post-depositional overprint during diagenesis or metamorphism (e.g., Bau, 1993; Bau and Dulski, 1996; Bolhar et al., 2004). The similarity of certain REE signatures (e.g., positive Eu anomaly) between BIFs and modern mid-ocean ridge (MOR) hydrothermal fluids indicates that REE and iron in Paleoproterozoic and older BIFs had dominantly hydrothermal sources (Bau and Möller, 1993; Beukes and Gutzmer, 2008; Planavsky et al., 2010). Another viable proxy is the Sm—Nd isotope system which has also been shown to be highly valuable in tracing the continental vs. hydrothermal input to BIFs. For example, newly compiled $^{143}Nd/^{144}Nd$ data of Archean BIFs exhibit radiogenic Nd isotope compositions (i.e. positive εNd(t) values) (Alexander et al., 2009; Viehmann et al., 2015; Wang et al., 2015a), suggesting significant REE + Y contributions to

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seawater from black smoker-type high temperature hydrothermal fluids. However, deviation from this mantle Nd signal has been recorded in some BIFs where continental fluxes of Fe and REEs contributed greatly to seawater (Miller and O'Nions, 1985; Alexander et al., 2008; Wang et al., 2014a). Interpretations of Fe sources for BIFs using these proxies above are based on the assumption that REEs and Fe pathways were coupled during transport and deposition of materials for BIF (Bau et al., 1997; Li et al., 2015a, 2015b).

Much of the previous work on BIFs has focused on the source of iron and few studies were directed to the source of silica. Silica is regarded to have been derived either from continental sources (Hamade et al., 2003; Frei and Polat, 2007) or seafloor hydrothermal fluids (André et al., 2006; Steinhoefel et al., 2009). Ge/Si ratios are useful in this regard, as they could help to evaluate the relative proportion of hydrothermal vs. continental input of silica to the ocean. Hydrothermal vent fluids are characterized by Ge/Si values between 8 and 14 μmol/mol (Mortlock et al., 1993; Elderfield and Schultz, 1996), which are higher than the continental runoff defined at 0.54 μmol/mol (Froelich et al., 1992). Based on the covariation of Ge/Si ratios and silica content of the ~2.46 Ga Hamersley BIF mesobands, Hamade et al. (2003) proposed that silica was predominantly derived from weathering of a continental landmass, whereas iron was sourced from oceanic hydrothermal systems. Their proposal relies on the assumption that there is no fractionation of Ge relative to Si during silica precipitation and diagenesis.

In China, BIFs occur extensively throughout the Archean-Paleoproterozoic units of the North China Craton (NCC, Fig. 1a), among which Eastern Hebei in the north is considered to be the second largest iron metallogenic province (Li et al., 2014). Large amounts of BIFs are exposed in this area, such as Shuichang, Shirengou, Erma, Xingshan, Sijiaying, and Macheng BIFs (Fig. 1b), among which the Sijiaying BIF is the largest and laterally most extensive BIF in Eastern Hebei (Shen, 2012). Previous studies (e.g., Zhai and Windley, 1990; Shen, 1998; Zhang et al., 2011; Li et al., 2011; Zhang et al., 2012; Wu et al., 2015) on geological aspects suggested that the BIFs are Algoma-type (Gross, 1980) because they are closely associated with volcanic rocks, and likely formed in arc/back-arc basins. In addition, based on detailed geochronological studies of interbedded meta-volcanic rocks (e.g., Zhang et al., 2011; Han et al., 2014; Cui et al., 2014; Li et al., 2015a, 2015b), nearly all of BIFs are Neoarchean in age (2.55–2.50 Ga). In contrast, giant Algoma-type BIF deposition on other cratons were deposited mainly between 2.85 and 2.70 Ga, and can be found in most greenstone belts (Bekker et al., 2013).

Studies exist on the source of the major components of BIFs in Eastern Hebei (e.g., Li et al., 2010a, 2010b; Shen et al., 2011; Yao et al., 2014; Chen, 2014; Zheng et al., 2015). However, there is still only a nascent understanding of source characteristics of BIFs, given that most previous analyses were focused on major and trace element systematics of scattered bulk samples rather than individual micro- and mesobands. Therefore, we use a combination of major and trace element (including REE + Y) and Sm—Nd isotopic data from individual Fe- and Si-rich layers of a least altered BIF specimen from the ~2.54 Ga Sijiaying BIF (Fig. 1b) to elaborate on the origin and nature of source materials of the BIF and to investigate time-related changes of the relevant depositional environment.

2. Geological background

2.1. Regional geology

The NCC is the largest and oldest known cratonic block in China (e.g., Zhao et al., 2001; Zhai and Santosh, 2011). It has been widely accepted that the NCC is tectonically divisible into two major Archean to Paleoproterozoic blocks, named the Eastern and Western Blocks, separated by a Paleoproterozoic orogen, named the Trans-North China Orogen (TNCO) (Fig. 1a) (e.g., Zhao et al., 2005; Zhao and Zhai, 2013). Eastern Hebei is situated in the north of the Eastern Block and consists predominantly of early Archean to Paleoproterozoic metamorphic basement, partially overlain by Mesoproterozoic to Mesozoic platform cover

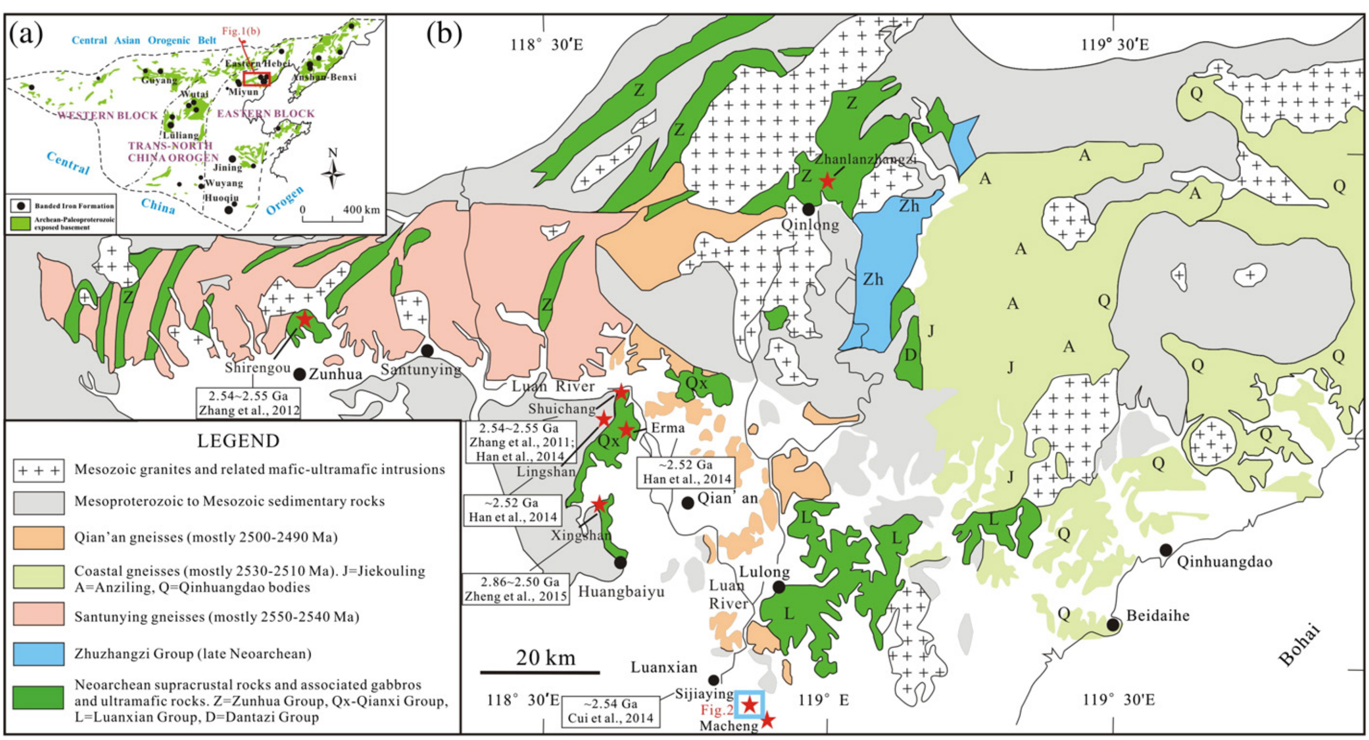

Fig. 1. (a) Subdivisions of the North China Craton (NCC) showing location of Eastern Hebei and distribution of major BIFs (after Zhao et al., 2005). (b) Geological sketch map of Eastern Hebei indicating study area (after Nutman et al., 2011). Stars represent typical BIFs.

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