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Anoxic to suboxic Mesoproterozoic ocean: Evidence from iron isotope and geochemistry of siderite in the Banded Iron Formations from North Qilian, NW China

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ABSTRACT

Banded Iron Formations (BIFs) provide important constraints on geochemical cycling of Fe and ancient marine environment. Globally, the formation of BIFs peaked during late Archean and early Paleoproterozoic, with limited reappearance during Neoproterozoic. Here we investigate a rare example of Mesoproterozoic (ca. 1.3 Ga) BIFs from Jingtieshan in the North Oilian region of NW China. We present rare earth element and yttrium (REE + Y) compositions together with iron isotope features of siderite from the BIFs, and integrate these with our published data on carbon isotope compositions from the siderite-rich BIFs (including carbonate facies BIFs and mixed carbonate-oxide facies BIFs). Siderite from the BIFs shows REE + Y characteristics that are consistent with submarine hydrothermal fluids mixed with seawater, including positive Eu/Eu* anomalies and high Y/Ho ratios. The siderite also displays homogeneous iron isotope compositions (δ^{56} Fe range from -0.71% to -0.41%, one sample down to -1.62%) and moderate negative carbon isotope compositions (δ^{13} C values = -8.40% to -3.0%). These findings argue against the traditional view that siderite associated with BIFs was formed through microbial dissimilatory iron reduction (DIR). Instead, siderite from Jingtieshan BIFs is in equilibrium with submarine hydrothermal fluids and seawater suggesting an inorganic origin, and was directly precipitated from the CO_2 and Fe oversaturated water column, with only insignificant role for DIR. These Mesoproterozoic BIFs are also characterized by Ce anomalies, and the siderite falls within the pe-log [S]_T and (P_{O_2}) - (P_{CO_2}) stability fields, suggesting that the BIFs were deposited in an anoxic to suboxic ocean. The results from our study suggest the presence of iron-rich Mesoproterozoic deep ocean in the North Qilian area.

1. Introduction

The cycling of iron is of major interest in the study of the Earth system because of the abundance of this metal in rock-forming minerals, sensitivity to redox, role in microbial metabolism, and its function as a micronutrient (e.g., Johnson et al., 2008; Halverson et al., 2011). Banded Iron Formations (BIFs) are sedimentary units, the deposition of which peaked mostly during Archean-Paleoproterozoic (3.8–1.8 Ga), and less commonly during Neoproterozoic (0.8–0.6 Ga) (e.g., Klein, 2005; Holland, 2005; Ilyin, 2009; Zhai and Santosh, 2013; Zhang et al., 2014; Li et al., 2014; Yang and Santosh, 2017, and references therein). Large–scale occurrence of BIFs deposits are rare during the age gap of 1.8–0.8 Ga, although several BIFs and iron-rich sedimentary rocks of this age have been documented (e.g., Slack et al.,

2009; Bekker et al., 2010; Lascelles, 2013; Yang et al., 2016a). Globally, BIFs have provide important insights into geochemical cycling of Fe and paleo-environment (Johnson et al., 2008).

However, the mechanisms responsible for the deposition of BIFs have been widely debated (e.g., Klein, 2005; Bekker et al., 2010; Cox et al., 2013). Early works suggested a continental source of the Fe in BIFs (James, 1954; Cloud, 1973). The discovery of modern ocean ridge (MOR) hydrothermal systems in the 1970s and the similarity of certain rare earth elements (REE) signatures (e.g., positive Eu anomalies) between BIFs and MOR hydrothermal fluids, led to that the understanding that iron was derived from submarine hydrothermal fluids (e.g., Holland, 1973; Manikyamba et al., 1993; Bau et al., 1997; Klein, 2005). However, recent studies that employed a combination of Nd, iron isotopes and REE, suggest that a significant component of BIFs is sourced

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from the continents (e.g., Viehmann et al., 2013; Li et al., 2015a), especially in the case of the Neoproterozoic BIFs (Cox et al., 2016). The iron pathways involved in BIFs genesis also remain equivocal. Some researchers argued that the iron-bearing minerals were inorganically precipitated from iron-rich ocean (e.g., Klein, 2005). However, several studies focusing on iron and carbon isotopes have emphasized the activity of microbial dissimilatory iron reduction (DIR) during diagenesis, which seems to have played an important role in the formation of BIFs (Johnson et al., 2003, 2008; Heimann et al., 2010; Bekker et al., 2010; Craddock and Dauphas, 2011).

Despite the apparent sudden disappearance of BIFs after 1.8 Ga and nearly one billion year hiatus in the sedimentary record (Klein, 2005; Bekker et al., 2010; Cox et al., 2013), minor Mesoproterozoic BIFs are preserved in some regions, although the origin and cycling of iron during this era remain poorly studied. Unlike the Archean and Paleoproterozoic BIFs that formed at a time of low atmospheric O2 and pervasively anoxic deep oceans (Bekker et al., 2004; Lyons et al., 2014; Wang et al., 2015), the relatively minor Mesoproterozoic BIFs and ironrich sedimentary rocks/sediments developed at a time when atmospheric O_2 should have been significantly higher (Bekker et al., 2010). It has been argued that the redox state of the ocean can vary widely both temporally and spatially (Poulton and Canfield, 2011), the source of iron, and the process of formation of BIFs remain enigmatic. The REE compositions of BIFs has been widely used as a tool to reconstruct the depositional environment (e.g., Planavsky et al., 2010; Mendes et al., 2017). Furthermore, iron isotopes provide one of the robust tools in gaining insights into iron cycling due to the large isotopic fractionations attending redox transformations in the near surface environment (e.g., Zhu et al., 2000; Johnson et al., 2003, 2008; Steinhoefel et al., 2010; Bekker et al., 2010; Hou et al., 2014; Li et al., 2015a; Cox et al., 2016). Iron isotopes allow us to trace Fe cycling and thus can improve our understanding of the mechanisms of BIFs deposition, e.g., the δ^{56} Fe values of BIFs have been interpreted to directly record those of ancient seawater (Rouxel et al., 2005), a mixture of seawater and diagenetic contributions (Steinhoefel et al., 2010), or microbial Fe cycling (Heimann et al., 2010; Johnson et al., 2013).

In the North Qilian region of NW China, several Mesoproterozoic BIFs units are well preserved, including the Jingtieshan BIFs (JBIF hereafter) which is composed of specularite (hematite) and siderite-rich BIFs. As siderite is often one of the earliest minerals to precipitate in sediments, and do not easily recrystallize during diagenesis which also serves as an important indicator of the depositional environment (Curtis and Coleman, 1986; Mozley, 1989; Mozley and Wersin, 1992). Therefore, siderite from the JBIF can be used as tool to understand the inventory of Fe in BIFs and Fe cycling in the ancient marine sedimentary rock record. In this study, we present the results from iron isotope and REE and yttrium (REE + Y) systematics of siderite from the JBIF. Integrated with the published carbon isotope data, we attempt to trace the Fe sources and pathways involved in BIFs genesis. Our results help to constrain the depositional conditions of this BIFs and also offer insights into the Mesoproterozoic oceanic environment.

2. Geological setting of the Jingtieshan BIFs

The NNW-trending North Qilian Orogenic Belt (NQOB) in NW China is located at the central part of the Qinling-Qilian-Kunlun composite orogenic belt, and lies between the North China Craton, Tarim Craton and Central Qianlian Blocks (Fig. 1; Song et al., 2013; Huang et al., 2015). The NQOB is considered to represent a typical oceanic suture zone and is composed of Precambrian basement, Neoproterozoic to Early Paleozoic ophiolite sequences, high-pressure metamorphic belts, island-arc volcanic rocks and granitoid plutons, Silurian flysch formations, Devonian molasse, and Carboniferous to Triassic sedimentary cover sequences (Song et al., 2013; Huang et al., 2015). The Archean-Paleoproterozoic basement of NQOB has been considered to have undergone continental rifting, initiated in the early Mesoproterozoic (e.g., Xu et al., 1996; Zhang et al., 1998), and continued until Neoproterozoic, accompanied by the emplacement of bimodal volcanic rocks. Imprints of strong magmatic activities are present in the area including alkaline, ultrabasic, basic, intermediate and felsic intrusions, among which intermediate–felsic and felsic groups dominate (Yang et al., 1991; Mao et al., 2003).

The JBIF is mainly hosted in the Jingtieshan Group, which comprises two successions. The upper succession is mainly dolomitic marble whereas in the lower succession BIFs is predominant. The stratigraphy is shown in Fig. 2, where the Jingtieshan Group belongs to clastic-carbonate sedimentary formation, metamorphosed to lower greenschist facies (Yang et al., 1991; Sun et al., 1998; Zhang et al., 2014). Yang and Zhao (1999) reported an Sm-Nd isochron age of 1309 Ma. Recently, Yang et al. (2016a) obtained the youngest concordant zircon U-Pb age of Jingtieshan Group as 1331.5 Ma, and also reported the emplacement age of diabase as 1234-1236 Ma. Furthermore, Re-Os dating of carbonaceous phyllite in Jingtieshan Group yielded an isochron age of ca. 1308 Ma which is interpreted as the depositional age (Yang et al., 2016b). These studies suggest that the Jingtieshan Group was deposited at ca.1300 Ma, and was later intruded by 1234-1236 Ga diabase (Yang et al., 2016a) and 421-476 Ma quartz diorite porphyrite (Zhao et al., 2003; Zhang et al., 2008).

The main minerals of JBIF are specularite/hematite, quartz, carbonate (siderite, ankerite and dolomite), and minor magnetite, barite, chlorite, albite, tourmaline, sericite, and pyrite. Three distinctive sedimentary facies are recognized in the BIFs on the basis of predominant iron minerals within the iron-rich layers: (1) oxide facies (Fig. 3a), mainly composed of specularite and jasper; (2) carbonate facies (Fig. 3b), in which the most prominent carbonate minerals are siderite and ankerite; and (3) mixed carbonate-oxide facies (Fig. 3c), containing varying specularite and carbonate minerals. The JBIF extends NW to SE with no significant sedimentary facies variation laterally. Vertically, the oxide facies BIFs is typically distributed at the upper middle parts. Carbonate facies BIFs is mainly distributed at the middle and lower parts. Mixed carbonate-oxide facies BIFs are the dominant sedimentary facies, and occur in the upper, middle and lower parts of the JBIF (Fig. 3). Based on the definition of the various scales of banding (Trendall and Blockley, 1970), microband is common in the Jingtieshan BIFs-related iron deposit, ranging from 1 to 10 mm. These microbands are defined by the alternation of specularite, jasper, siderite and barite laminae locally.

3. Sampling and analytical methods

3.1. Sampling

The samples analyzed in this study are exclusively from the sideriterich JBIF, including carbonate facies BIFs and mixed carbonate-oxide facies BIFs. The carbonate facies BIFs are buff and white banded rocks composed of distinctive mm-thick white chert and barite layers, which are interbedded with siderite layers (Fig. 3d). Their mineralogy consists of siderite (\sim 50%, with minor dolomite) and fine-grained jasper/ quartz (\sim 35%), barite, and specularite. Siderite is mainly fine–grained and globular with amorphous to anhedral quartz matrix, and sometimes anhedral (Fig. 4a). Banding and sedimentary textures of the mixed carbonate-oxide facies BIFs are similar to those of the carbonate facies BIFs, and contain specularite and siderite in varying proportions with specularite-rich, jasper/quartz-rich and siderite-rich bands/laminae (Fig. 3e; Fig. 4b).

The chemical compositions of the siderite is presented in Table 1 and plotted in Fig. 5. The siderite from carbonate facies BIFs contains 44.40-51.02 wt% FeO, 6.56-9.43 wt% MgO and 0.31-2.78 wt% MnO, consistent with 84-90 mol% FeCO₃ (average of 87 mol%), 9-14 mol% MgCO₃ (average of 11 mol%), 1-5 mol% MnCO₃ (average of 2 mol%). The siderite from mixed carbonate-oxide facies BIFs contain 44.11-60.57 wt% FeO, 0.03-9.19 wt% MgO and 0-1.92 wt% MnO,

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