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Decoupling of Neoarchean sulfur sources recorded in Algoma-type banded iron formation

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ABSTRACT

Neoarchean Algoma-type banded iron formations (BIFs) are widely viewed as direct chemical precipitates from proximal volcanic–hydrothermal vents. However, a systematic multiple sulfur isotope study of oxide-facies BIF from a type locality in the ca. 2.74 Ga Temagami greenstone belt reveals mainly bacterial turnover of atmospheric elemental sulfur in the host basin rather than deposition of hydrothermally cycled seawater sulfate or sulfur from direct volcanic input. Trace amounts of chromium reducible sulfur that were extracted for quadruple sulfur isotope (^{32}S–^{33}S–^{34}S–^{36}S) analysis record the previously known mass-independent fractionation of volcanic SO_2 in the Archean atmosphere (S-MIF) and biological sulfur cycling but only minor contributions from juvenile sulfur, despite the proximity of volcanic sources. We show that the dominant bacterial metabolisms were iron reduction and sulfur disproportionation, and not sulfate reduction, consistent with limited availability of organic matter and the abundant ferric iron deposited as $Fe(OH)_3$. That sulfur contained in the BIF was not a direct volcanic–hydrothermal input, as expected, changes the view of an important archive of the Neoarchean sulfur cycle in which the available sulfur pools were strongly decoupled and only species produced photochemically under anoxic atmospheric conditions were deposited in the BIF-forming environment.

1. Introduction

Precambrian banded iron formation (BIF) provides an important record of ancient marine paleoenvironments, atmospheric conditions, and bacterial metabolisms involved in its formation (Kappler and Newman, 2004; Konhauser et al., 2005; Viehmann et al., 2014). Trace elements and a range of different isotopic systems in BIF track the evolution of the oceans and atmosphere as far back as 3.8 Ga (Ohmoto et al., 2006; Bau and Alexander, 2009; Konhauser et al., 2009; Bekker et al., 2010). Studies of sulfur systematics have focused mainly on Superior-type BIF, ranging in age from 2.7 to 1.8 Ga, that formed in shallow, continental-shelf settings with uncertain but distal sources of iron (Johnston et al., 2006; Partridge et al., 2008; Mishima et al., 2017). Those studies showed the predominance of bacterial sulfate reduction promoted by abundant organic carbon available in Superior-type BIF. Algoma-type BIF, which formed in deep, semi-enclosed Neoarchean volcanic basins, derived its iron mainly from local volcanic–hydrothermal sources (Bekker et al., 2010). This type of BIF is useful for gauging hydrothermal input into the basins, but it is not the type of BIF normally studied to understand atmospheric conditions. In particular, sulfur systematics in Algoma-type BIF are expected to reflect the proximal volcanic input. However, data presented in this paper suggest that other sources (i.e., atmospheric deposition) were more important, even where major hydrothermal activity was underway.

Algoma-type BIF is a ubiquitous feature of Archean greenstone terranes, such as in the Southern Superior Province of Canada, with more than 150 mapped occurrences (Fig. 1). They are typically small in comparison to Superior-type BIF, generally <100 m thick and <100 km^2 in area, and are closely associated with submarine volcanic rocks, especially felsic volcanic centers that also host volcanogenic massive sulfide deposits (e.g., Gross, 1965; Franklin et al., 2005). Individual occurrences contain tens to hundreds of millions of tonnes of iron ore precipitated from the nearby seafloor hydrothermal vents. The flux of Fe to these local basins was comparable to that of the largest volcanic–hydrothermal systems in today's oceans (Ohmoto et al., 2006). The ∼2.74 Ga Temagami BIF in Ontario (Fig. 1; Ayer et al., 2006) is widely recognized as a type locality for Archean greenstone-hosted BIF (Gross, 1980) and has provided important benchmarks in understanding their formation (Ohmoto et al., 2006; Bau and Alexander, 2009). In this study, we analyzed multiple sulfur isotopes (^{32}S–^{33}S–^{34}S–^{36}S) in trace amounts of chromium reducible sulfur (CRS) extracted from

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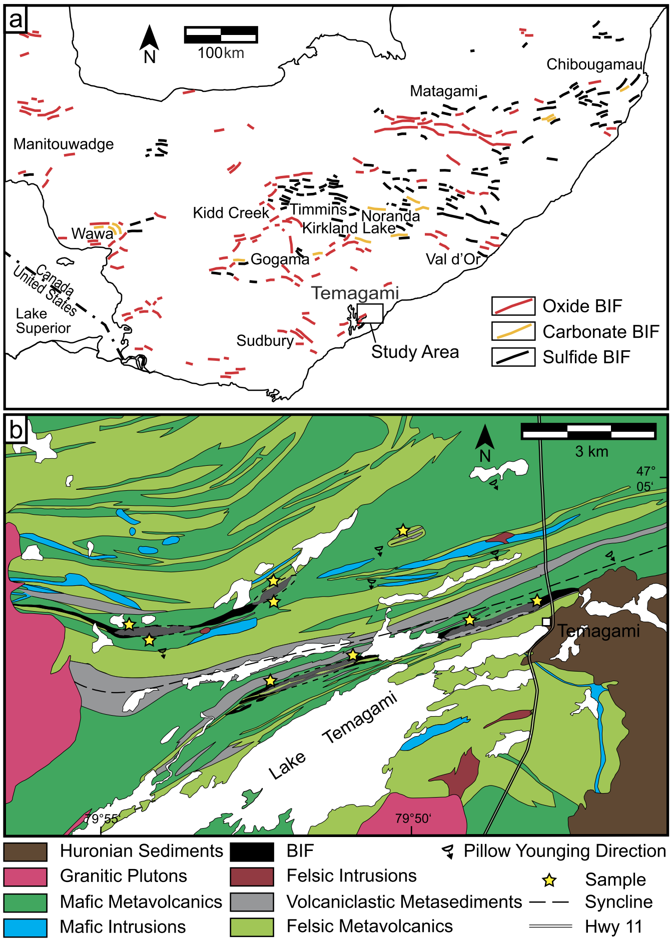

Fig. 1. a) Distribution of Algoma-type BIF in the Southern Superior Province, Canada (modified from Ohmoto et al., 2006). b) Geological map of the Temagami area showing the location of the Hwy 11 outcrop depicted in Fig. 2 and surface sample locations (see Supplementary Material for details) (modified after Bennett, 1978).

52 samples of the oxide-facies and contemporaneous sediments to constrain the sources of reduced sulfur.

Archean sediments deposited before ~2.3 Ga record mass-independent fractionation of sulfur species (S-MIF) produced photochemically from atmospheric SO_2 (Farquhar et al., 2000; Guo et al., 2009). Two dominant sulfur species entered the marine environment from the atmosphere: SO_4 and zero- or near-zero valent sulfur (expressed here as S_8 for simplicity). The sulfate had a $\Delta^{33}S_{SO_4} < 0‰$; S_8 had a $\Delta^{33}S_{S8} > 0‰$ (e.g., Ono et al., 2003). Both sulfur species were transferred to Archean sediments via a number of different biotic and abiotic pathways, including bacterial sulfate reduction (BSR) and disproportionation of elemental sulfur (BSD) (Farquhar et al., 2000; Philippot et al., 2007; Lyons, 2009; Jamieson et al., 2013). These different pathways have been investigated in marine black shales, volcanogenic massive sulfide deposits, sandstones, rare barite deposits, and in carbonates using the S-MIF signal (Bao et al., 2007; Bekker et al., 2009; Guo et al., 2009; Wacey et al., 2010; Philippot et al., 2012; Roerdink et al., 2012; Montinaro et al., 2015). Recent studies of Eoarchean (>3.8 Ga) lithologies from the Nuvvuagittuq greenstone belt (Ungava Peninsula) used the S-MIF signal to show the supracrustal character of these enigmatic units (Thomassot et al., 2015). Another study of highly metamorphosed rocks of similar age in China, interpreted to be Algoma-type oxide-facies BIF, also reported S-MIF (Hou et al., 2007). The two studies showed a typical array for Archean metasediments of positive $\Delta^{33}S$ and positive $\delta^{34}S$, indicating atmospheric sulfur sources but no biological activity (Thomassot et al., 2015), and negative $\Delta^{33}S$ with variable $\delta^{34}S$, indicating bacterial sulfate reduction (Hou et al., 2007). Similar results were obtained in a small study of samples from the Abitibi greenstone belt (three samples of pyritic argillite and one sample of sulfide facies iron formation: Thurston et al., 2012). Our samples from the Temagami BIF reveal more diverse microbial metabolisms and present a different story of metal and sulfur sources.

2. Samples and methods

2.1. Samples

The sampled BIF occurs in two units (up to 160 m in thickness each) belonging to a 4-km thick bimodal volcanic succession of the Temagami greenstone belt (Fig. 1). From 1964 to 1990, the north and south BIF units were exploited in the former Sherman iron mine (Donaldson and Garrett, 1991; Gross, 1980), and a classic exposure of the mined BIF, corresponding to the strike extension of the South Pit of the Sherman Mine, is still accessible in outcrop along Highway 11 (Figs. 1 and 2). All units now dip subvertically, exposing continuous sections of the BIF and adjacent lithologies. Contemporaneous volcaniclastic metasediments and sulfidic cherts occur along strike from the southern BIF units within 5 km. The host volcanic succession comprises subaqueous mafic volcanic rocks with south-facing pillows, indicating younging directions, intercalated with felsic flow units, abundant felsic volcaniclastic rocks and shale. Mapping and sampling of the volcanic host rocks previously identified rhyolitic feeder dykes, interpreted to be volcanic vents, in the stratigraphic footwall of the BIF horizons in the central part of the mine (Bennett, 1978; Fyon and Crocket, 1986). Widespread chloritization and sericitization of the volcanic rocks is evident, as well as Na loss and variable Eu anomalies, typical of synvolcanic hydrothermal alteration (Fyon and Crocket, 1986; Schwartz, 1995). The BIF units are dominated by jasper–magnetite layering, mainly in the open pits, and a larger volcaniclastic component with chert and lesser magnetite and jasper in the Hwy 11 outcrop. The different layers are interpreted to be products of precipitation from silica- and iron-enriched bottom waters; the primary precipitate most likely a Si-Fe(oxy)hydroxide gel from which the present mineral assemblage crystallized during burial and diagenesis (Gross, 1980; Bekker et al., 2010). Locally abundant sulfidic chert occurred at the transition from the volcaniclastic footwall to the BIF, in particular near the western end of the south pit (sample location 5: Supplementary Fig. 1). The relative abundance of volcaniclastic material increases with distance from the mine as dilution by chemical precipitates decreases. Regional metamorphism of the entire succession did not exceed greenschist facies conditions (Bennett, 1978; Bowins and Heaman, 1991).

Samples were collected for this study from the Highway 11 outcrop, from surface outcrops within the mine, and from a collection taken in the open pits by G.A. Gross and I.R. Jonasson (Geological Survey of Canada) when the mine was in operation. Samples of sulfidic chert, volcaniclastic sediment, minor massive sulfide and mafic intrusive (dikes) and extrusive rock were also collected from within the BIF-hosting section. The BIF samples consist of cm-scale oxide and silicate layers (Fig. 3a, b) that were cut into separate jasper (hematitic) bands, chert bands, magnetite bands, and chlorite-rich bands. Many of the original depositional textures were preserved through the regional lower greenschist metamorphism, and only limited recrystallization occurred since burial. Common accessory minerals include apatite, monazite, (Fe-rich) dolomite, ankerite, pyrite, and pyrrhotite. Pyrite, which is the dominant sulfide (>95%), occurs mainly as very fine disseminations of sub- to euhedral grains, 5–20 µm in size, commonly as inclusions in other phases. Trace sulfides occurring as inclusions