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# Contrasting behavior of oxygen and iron isotopes in banded iron formations revealed by *in situ* isotopic analysis

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ABSTRACT

*In situ* O and Fe isotope measurements of magnetite and hematite in banded iron formations (BIFs) from the 2.5 Ga Dales Gorge member of the Brockman Iron Formation, Hamersley Group, Western Australia, document distinct fine-scale isotopic zonation. For hematite, $\delta^{18}O$ values (VSMOW) range from −7.1 to −0.6‰, and $\delta^{56}Fe$ values range from −0.50 to +1.53‰. Magnetite has a $\delta^{18}O$ range of −5.6 to +7.0‰ and a $\delta^{56}Fe$ range of −0.76 to +1.33‰. Notably, magnetite shows significant O isotope variability at a <100 μm scale in individual magnetite grains or layers, where up to 6‰ difference in $\delta^{18}O$ values exists between low-Si core and Si-rich overgrowth. Iron isotope compositions are homogeneous to ±0.2‰ in $\delta^{56}Fe$ values within individual grains or layers. Hematite is always isotopically heavier than co-existing magnetite by 0.1–0.4‰ in $\delta^{56}Fe$ within individual samples, and there is a large variation (>2‰) in $\delta^{56}Fe$ values between BIF samples at the > m-scale (e.g., between meso- or macro-bands of the Dales Gorge Member). *In situ* isotopic results highlight the distinct behavior of O and Fe isotopes during interaction with post-deposition diagenetic or metamorphic fluids. The large variations in $\delta^{18}O$ values of iron oxides likely reflect exchange with fluids during post-depositional events at temperatures up to ca. 280 °C, and the lower $\delta^{18}O$ values of Fe oxides are interpreted to reflect less isotopic modification and lower temperatures. $\delta^{18}O$ variations support a model where initial $Fe(OH)_3$ precipitates that formed in the photic zone were converted to hematite during very early diagenesis, followed by production of magnetite over a range of temperatures during later diagenesis/metamorphism. In contrast, magnetite and hematite seem to have preserved the initial $\delta^{56}Fe$ values of early $Fe(OH)_3$ precipitates, despite significant changes in O isotope compositions in magnetite. The consistency in apparent Fe isotope fractionation between co-existing hematite and magnetite suggests that they share a common precursor, where magnetite was formed in soft sediment through *in situ* reduction by microbial processes, and possibly including reaction with aqueous Fe(II). Combined *in situ* Fe–O isotope analyses allow distinctions to be made between near-primary and post-depositional signatures in BIFs, which bears on the use of BIFs as paleo-environmental proxies and recorders of microbial processes.

## 1. Introduction

Banded iron formations (BIFs) are marine chemical precipitates that contain >15 wt.% Fe that consist of iron- and silica-rich layers (James, 1954), and widely occur in Archean and Paleoproterozoic terranes (e.g., Klein, 2005; Trendall and Morris, 1983). BIFs record periods of Earth's geologic history when abundant, hydrothermally-sourced aqueous Fe(II) was removed from Archean and Proterozoic oceans through oxidation and precipitation as Fe(III) oxides and hydroxides (Holland, 1984). As such, BIFs have figured prominently in discussions on the paleo-environmental conditions of the early Earth, including the redox structure of Precambrian oceans, and recent reviews may be found in Klein (2005) and Bekker et al. (2010). The use of BIFs as a proxy for the ancient oceans may be complicated by the protracted diagenetic and metamorphic histories of BIFs. Fundamental to this issue is determining if BIF minerals formed in equilibrium with the oceans (Johnson et al., in press).

Stable isotope compositions of O in BIF minerals, including quartz, magnetite, and siderite, as well as C isotope compositions of Fe carbonates, have been used to infer paleo-environmental conditions, as well as post-depositional processes such as diagenesis and metamorphism that may later occur in BIFs (Baur et al., 1985; Becker and Clayton, 1972, 1976; Kaufman, 1996; Kaufman et al., 1990; Perry et al., 1973; Winter and Knauth, 1992). Specifically, O isotope compositions of BIFs have been used to infer paleotemperatures, but it also has been recognized that O isotopes

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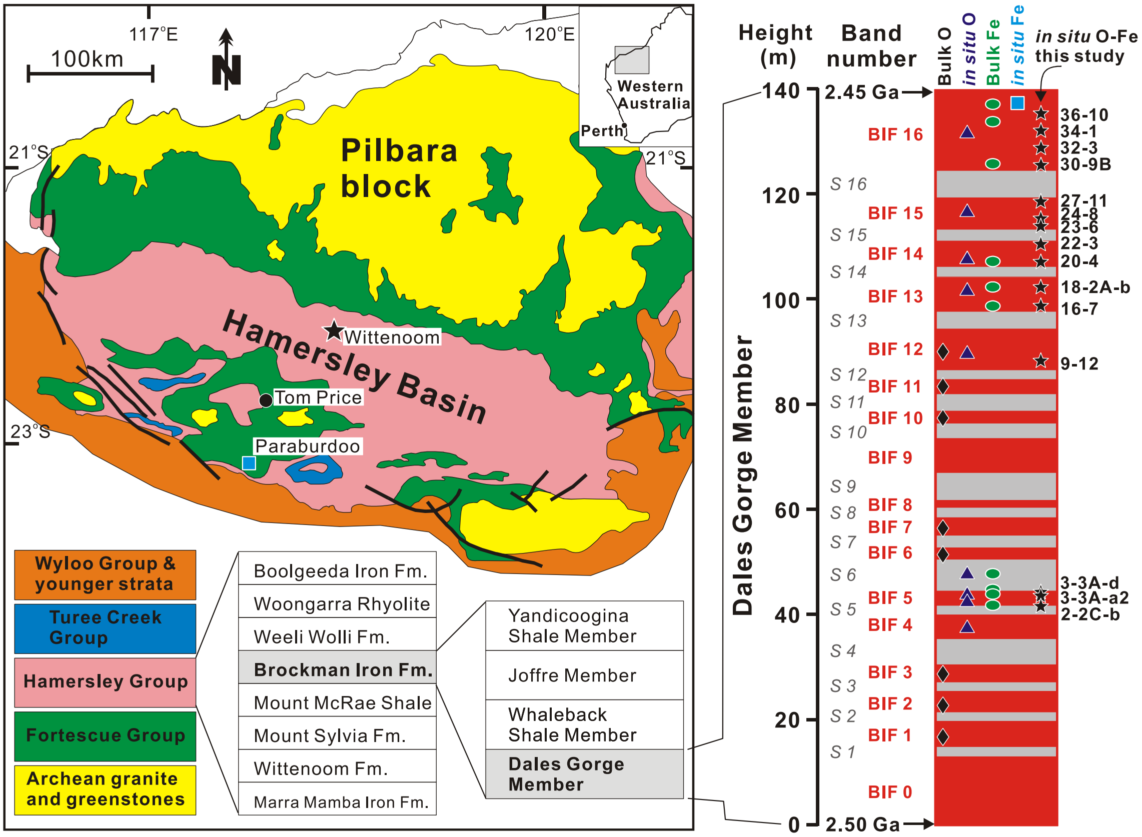

**Fig. 1.** Geological background of the Dales Gorge Member BIF of Hamersley Basin, Western Australia. Figure is modified after Trendall et al. (2004) and Johnson et al. (2008a). The 2.50–2.45 Ga age for the Dales Gorge Member BIF was based on zircon U–Pb geochronology constraints (Trendall et al., 2004). The Drill core DDH-47(A) was drilled ∼15 km south of Wittenoom (filled star). Prior to the present *in situ* Fe and O isotope study, samples from Drill core DDH-47(A) have been studied by analyzing O isotope composition of bulk mineral separates (black diamond; Becker and Clayton, 1976), O isotope composition of quartz using SIMS (blue triangle; Huberty et al., 2010a; Heck et al., 2011), Fe isotope composition of bulk mineral separates using solution-nebulization MC-ICP-MS (green oval; Johnson et al., 2008a). Another *in situ* Fe isotope study on the Dales Gorge Member BIF has been reported by Steinhoefel et al. (2010), and they investigated a sample from BIF band 16 from drill core DDH-44 at Paraburdoo (light blue square). Samples of Drill core DDH-47(A) that were analyzed in this study are marked with black stars. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

may provide information on fluid–mineral interactions and temperatures of equilibration or isotopic exchange (Gregory and Criss, 1986; Hyslop et al., 2008; Valley, 2001). Carbon isotope compositions have been used to infer the relative contributions of biologic and abiologic C sources. More recently, studies using Fe isotope geochemistry have investigated abiologic versus biologic pathways for BIF mineral formation (e.g., Craddock and Dauphas, 2011; Heimann et al., 2010; Johnson et al., 2003, 2008a, 2008b; Planavsky et al., 2012; Rouxel et al., 2005; Steinhoefel et al., 2010). In addition, Si isotope studies of BIFs have focused on distinguishing weathering and hydrothermal sources of silica (Heck et al., 2011; Steinhoefel et al., 2010).

The ubiquitous fine-scale variations in mineralogical and petrographic relations of BIFs, which may record primary depositional features or soft-sediment diagenesis (e.g., Ewers and Morris, 1981; Trendall and Morris, 1983), indicate that *in situ* analysis approaches are more likely to provide a full understanding of BIF genesis than bulk analysis methods. Recent developments in Secondary Ion Mass Spectrometry (SIMS) have enabled relatively high precision *in situ* O isotope ratio measurements of Fe oxides (Huberty et al., 2010b). *In situ* Fe isotope analyses of Fe oxides using femtosecond Laser Ablation (fs-LA) multi-collector ICP-MS have been reported, demonstrating great promise for widespread application of *in situ* isotopic analysis of Fe-bearing minerals (Czaja et al., 2013; Horn et al., 2006; Steinhoefel et al., 2009, 2010; Yoshiya et al., 2012). SIMS analyses of Fe isotopes in magnetite have also been reported (Marin-Carbonne et al., 2011; Whitehouse and Fedo, 2007), although Kita et al. (2011) show that an orientation effect exists for isotopic analysis of magnetite for both O and Fe isotopes, which may create spurious apparent variability. In this study, we present results of the first combined *in situ* O and Fe isotope investigation of BIF samples from the most voluminous interval of BIF deposition in Earth history, specifically, the 2.5 Ga Dales Gorge member of the Brockman Iron Formation, Hamersley Group, Western Australia. These new results demonstrate that O and Fe isotopes may record distinct processes during BIF mineral formation, early diagenesis, fluid–mineral interaction, and metamorphism. Combined, these two isotope systems, when measured on a mineral scale, provide new insights into the origin of BIFs and their use as tracers of paleo-environmental conditions, ancient ocean proxies, and the role of microbial processes.

## 2. Geological background and samples

The Hamersley Basin in Western Australia contains the world's most extensive Superior-type BIFs (Trendall and Blockley, 1970). The Paleoproterozoic Hamersley Group includes three major BIF units, which are, from older to younger, the Marra Mamba, Brockman, and Boolgeeda iron formations. The Dales Gorge member of the lowermost part of the Brockman Iron Formation (IF) is the subject of this study (Fig. 1). The depositional age of the Dales Gorge member lies between 2.50 Ga and 2.45 Ga (Trendall et al., 2004). The Dales Gorge member is approximately 160 m thick, consisting of 17 iron-rich, m-scale macro-bands and 16 shale macro-bands, named BIF0–BIF16 and S1–S16, respectively (Fig. 1). The