Petrology and geochemistry of the Boolgeeda Iron Formation, Hamersley Basin, Western Australia

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ABSTRACT

The Boolgeeda Iron Formation and overlying Turee Creek Group, Hamersley Basin, Western Australia, represent a conformable succession of sediment deposited between 2.45 and 2.22 Ga. This interval of geologic history is of significant interest because it spans the Great Oxidation Event (GOE), when oxygen first accumulated in Earth’s atmosphere. Here we present geochemical and petrographic data from the uppermost 45 m of the Boolgeeda Iron Formation and an additional 30 m of the overlying Kungarra Formation mudstones, as sampled from the Turee Creek Drilling Project 1 drill core (TCDP1). This core captures the termination of BIF deposition in the Hamersley Basin and coincides with a global decline in BIF deposition in the Paleoproterozoic. We provide a continuous, high resolution chemostratigraphic dataset of major and trace element concentrations, as well as Fe speciation data, to assess the relationship between the rise of atmospheric oxygen and the subsequent decline in BIF deposition. We also highlight the interplay between local and global controls on the preservation of redox signatures, including the rise and fall of local base-level, input of weathered continental material, influx of reduced sulfur species associated with the continental weathering, and global increases in atmospheric oxygen. We interpret Boolgeeda deposition to have taken place under shallow water, oxic conditions overlying anoxic ferruginous deep water. Intermittent periods of oxidative weathering led to influxes of redox sensitive trace elements from land as continental sulfide minerals were weathered. This also led to the temporary disappearance of MIF-S, but O₂ remained below the threshold capable of completely eliminating S isotope signatures associated with the MIF-S recycling.

1. Introduction

Precambrian iron formations (IF) are marine sedimentary rocks composed of iron oxides, silica (most commonly chert), Fe-carbonates (siderite and ankerite), and Fe-silicates (Bekker et al., 2010, 2014; Konhauser et al., 2017). The presence of IF in the rock record is indicative of both high concentrations of dissolved ferrous iron (Fe²⁺) in seawater (Isley, 1995) and anoxic ocean conditions (e.g. Cloud, 1973; Konhauser et al., 2002; Klein, 2005). The combination of these two factors promoted the transport of Fe(II) from submarine hydrothermal sources to relatively shallow continental shelves where large Superior-type IF were deposited (e.g., Beukes and Klein, 1990; Morris, 1993). Although BIF were deposited throughout the Precambrian, perhaps as much as 60% of the global volume of BIF were deposited between 2.50 and 2.45 Ga (Isley and Abbott, 1999). Accordingly, peak BIF deposition may be related to either a major pulse of dissolved iron from hydrothermal input (e.g. Derry and Jacobsen, 1988, 1990; Klein and Beukes, 1993; Bühn and Stanistreet, 1997; Trompette et al., 1998; Walde and Hagemann, 2007) or a significant redox transition in the surface oceans that facilitated widespread Fe(II) oxidation into a ferric oxyhydroxide, such as ferric hydroxide, Fe(OH)₃; this iron phase may then have combined with amorphous silica to form a water-rich Fe(III)-Si gel (e.g., Percak-Dennett et al., 2011) or silica-rich Fe(III)-oxyhydroxide, likely precursor phases of IF (see Konhauser et al., 2017 for review).

The Hamersley Group in Western Australia hosts the world’s largest IF deposits by mass, and records over 150 million years of geological...
A number of studies have investigated the chemical composition, mineralogy, geochronology, and sedimentology of the major Hamersley Basin IF units, including the 2.60 Ga Marra Mamba Iron Formation (Blockley, 1979; Ewers and Morris, 1981; Blockley et al., 1993; Trendall et al., 1998; Lascelles, 2000), the Brockman Iron Formation, specifically the 2.48 Ga Dales Gorge Member (Ayres, 1972; Konhauser et al., 2002; Hamade et al., 2003; Pickard et al., 2004; Pecola et al., 2009; Steinhofel et al., 2010; Konhauser et al., 2015) and the 2.46 Ga Joffre Member (McConchie, 1984; Haugaard et al., 2016a), and the 2.45 Ga Weeli Wolli Formation (Trendall, 1973; Davy, 1992), or have compared and contrasted IF units in the context of the entire Hamersley Group (Trendall and Pepper, 1977; Morris and Horwitz, 1983; Baur et al., 1985; Alibert and McCulloch, 1993; Morris, 1993; Trendall et al., 2004; Partridge et al., 2008). In contrast, investigations of the youngest iron deposit and terminal unit of the Hamersley Group, the Boolgeeda Iron Formation, have been restricted to samples from sparse surface outcrops that appear in the hinges of large-scale folds along the southern part of the Hamersley (e.g. Swanner et al., 2013, Williford et al., 2011). Recently however, in order to obtain constraints on the rise of atmospheric oxygen and associated glacial events concomitant with the Paleoproterozoic Great Oxidation Event (GOE), the Turee Creek Drilling Project (TCDP) was undertaken to acquire three drill cores that capture representative portions of the Boolgeeda IF, different formations within the overlying Turee Creek group (TCG), and the stratigraphic boundaries between them. These cores, referred to as TCDP1, TCDP2, and TCDP3, provide a representative sample of over 4 km of conformable sediment that comprises the Boolgeeda IF and TCG (Philippot et al., 2018).

Deposition of the Boolgeeda Iron Formation and TCG occurred between 2.45 and 2.22 billion years ago, making them important units for the study of early Paleoproterozoic oxygen dynamics. Geochronological constraints on the deposition of these formations include a U-Pb zircon age of 2449 ± 3 Ma for the conformably underlying Woongarra Rhyolite (Barley et al., 1997), a U-Pb zircon age of 2209 ± 15 Ma for the unconformably overlying Cheela Springs Basalt of the Wyloo Group (Martin et al., 1998), and a U-Pb baddeleyite age of 2208 ± 10 Ma for a dolerite sill intruding the Turee Creek Group, interpreted to be coeval with the eruption of the Cheela Springs Basalt (Müller et al., 2005). Stratigraphically, the Cheela Springs Basalt lies unconformably above the Turee Creek Group and, therefore, the lower age constraint represents the minimum age of the Boolgeeda IF and Turee Creek package. Recently, Philippot et al. (2018) and Caquineau et al. (2018) reported a pyrite Re-Os age of 2309 ± 9.2 Ma and a detrital zircon U-Pb age of 2340 ± 22 Ma obtained from drill core samples at the base of the main glacial deposit of the Meteorite Bore Member of the Kungarra Formation (Hardey Syncline). In addition, a meter-scale layer of diamicrite identified within the Boolgeeda IF yielded a zircon U-Pb age of 2454 Ga ± 23 Ma (see Fig. 2; Philippot et al., 2018; Caquineau et al., 2018). The samples, sample depth scale, and sample IDs employed by Caquineau et al. (2018) are identical to those used in this study, and we direct the reader there for an in-depth discussion on the geochronology of the Boolgeeda IF.

Using a combination of the above age constraints and multiple sulphur isotope analyses performed throughout the three drill cores, Philippot et al (2018) showed the persistence of a monotonous small-magnitude mass-independent sulfur isotope (MIF-S) signal in sedimentsal sulphides from the base of the Boolgeeda IF to about 1000 m above the Meteorite Bore Member diamicite, which is punctuated by short episodes of sulphur isotope perturbations attributed to oxidative weathering of the Archaean continental surface. Given the age constraints and uninterrupted sequence of Boolgeeda IF and Turee Creek deposition, this is inconsistent with an abrupt, globally synchronous, atmospheric transition at about 2.32–2.33 Ga as previously advocated (Bekker et al., 2004; Guo et al., 2009; Luo et al., 2016). Rather, it is consistent with the view of the GOE as a transitional period (Reinhard et al., 2013), where an early (> 2.45 Ga) rise of atmospheric oxygen above the threshold value of 10^-5 Present Atmospheric Level (PAL) was followed by a long period of continued delivery of MIF-S anomalies to the oceans until their exhaustion from weathering catchments. In the case of the Boolgeeda-Turee Creek sedimentary basin, the source MIF-S rocks were not weathered out until after 2.25 Ma, thus indicating that the exhaustion process took at least 200 Myr. Asynchrony in the extinction of MIF-S signals between the Superior, Kaapvaal, and Pilbara cratons underline the need to better constrain the timing and dynamics of the GOE through the detailed study of sedimentary sequences deposited between 2.5 and 2.32 Ga.

In this study, we analyzed the uppermost 45 m of the Boolgeeda Iron Formation and an additional 30 m of the overlying Kungarra mudstones, as sampled in the Turee Creek Drilling Project 1 drill core (TCDP1). This interval captures the termination of IF deposition in the Hamersley basin and coincides with a decline in global IF deposition in the Paleoproterozoic. Using geochemical and mineralogical analyses, we provide a continuous, high resolution chemostratigraphic dataset of major and trace element concentrations and variations, as well as Fe speciation depth plots, in order to better understand the relationship between the rise of atmospheric oxygen and subsequent decline in IF deposition, and to further test the model for atmospheric oxygenation proposed by Philippot et al. (2018) based on S-isotopic systematics. The data presented here represents the highest resolution whole-rock geochemical dataset of a BIF produced to date.
prepared and examined using reflected and transmitted light microscopy. Detailed mineralogical analyses of these thin sections are presented in Section 3.1.

One hundred and twenty-eight TCDP1 rock chip samples were submitted to Actlabs for major and trace metal analyses, along with 12 pulp samples to monitor for contamination during the milling and/or analysis processes. Nickel, Zn, Cd, %s, Cu, Ag, and Pb measurements were made using the total digestion inductively coupled plasma mass spectrometry (TD-ICP-MS) method. Rock powder samples (~0.25 g/sample) were completely digested by first treating them in concentrated hydrofluoric acid, and subsequently treating them with a mixture of nitric and perchloric acids. Samples were then heated and dried using precise programmer-controlled heating in several ramping and holding cycles, and finally re-suspended in hydrochloric acid. Analyses were completed using a Varian Vista 735 ICP-MS. Standards used for TD-ICP-MS were GXR-4, SDC-1, GXR-6, SAR-M (U.S.G.S.), DNC-1a, and SBC-1. Detection limits for Ag, Cd, Cu, Ni, Pb, Zn, and S, as reported by Actlabs, are 0.3, 0.5, 1, 1, 5, 1 ppm, and 0.001%, respectively.

All other major and trace element values were obtained using a lithium metaborate/tetraborate fusion (FUS)-ICP-MS method. Samples were mixed with a flux of lithium metaborate and lithium tetraborate and fused in an induction furnace. The melt was immediately poured into a 5% nitric acid solution containing an internal standard, and then mixed continuously until completely dissolved (~30 min). The fused sample was diluted and analyzed using a Perkin Elmer Sciex ELAN 6000, 6100, or 9000 ICP-MS. Three blanks and five controls (three before the sample group and two following) were analyzed. Duplicate samples were analyzed every 15 samples and the instrument was re-calibrated every 40 samples. Following the reported Actlabs procedure, custom standard materials were prepared for the project and generally accepted results for these standards were those within three standard deviations on either side of the certified values. Standards used for FUS-ICP-MS were NIST 694, DNC-1, W-2a, SY-4, BIR-1a, LSKSD-3, TDB-1, NCS DC70009 (GBW07241), OREAS 100a (Fusion), OREAS 101a (Fusion), OREAS 101b (Fusion), and JR-1. Upper and lower limits of detection for each element analyzed are readily available on the Actlabs commercial website. Blank measurements for all analyses were below the detection limits. Raw data for all analyses are compiled in SI Table 1, and a quality control table is reported in SI Table 2. A summary of major and minor element analyses can be found below in Tables 1 and 2, respectively.

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.precamres.2018.07.015.

Fe speciation was evaluated for selected samples using the method of Poulton and Canfield (2005). Sequential extractions targeted 7 fractions: (1) exchangeable Fe (Fe_{Ex}), (2) carbonate associated Fe (Fe_{Carb}), (3) easily reducible oxides (Fe_{Ox1}, e.g. ferrihydrite, lepidocrite), (4) reducible oxides (Fe_{Ox2}, e.g. goethite, akaganéite, hematite), (5) magnetite (Fe_{Mag}), (6) poorly reactive sheet silicate Fe (Fe_{PRS}), and (7) pyrite Fe and unreactive silicate Fe (Fe_{Py} + U). Iodometric titrations to determine the exact fraction of pyrite bound Fe (Fe_{Py}) were not performed as robust silicates containing Fe unreactive with H_{2}S are relatively rare compared to pyrite in Boolgeeda sediments. This has been confirmed by the absence of robust Fe silicate phases in XRD diffraction patterns of samples analyzed (SI Fig. 1). Therefore, the Fe_{Py + U} fraction will here-on be treated as representative of the Fe_{Py}. All chemical standards used were ACS grade and obtained from Fisher Scientific (Toronto, Ontario, Canada). Procedures 1 through 5 were performed using 0.2 g of sample weighed into 50 mL polypropylene centrifuge tubes. The Fe_{Ex} fraction (1) was extracted using 1 M magnesium acetate solution at pH 5.8, and diluted at pH 7 for 2 h at room temperature. The Fe_{Carb} fraction (2) was extracted with 1 M sodium acetate at pH 4.5 and 50 °C for 24 h on a heating block. To adjust to pH 4.5, 8.6% v/v acetic acid was used. The Fe_{Ox1} fraction (3) was extracted over 48 h at room temperature using 1 M hydroxylamine hydrochloride in 25% v/v acetic acid. The Fe_{Ox2} fraction (4) was extracted with 50 g/L sodium

Fig. 2. Litholog for Turee Creek Drilling Project core 1 (TCDP1) after Philippot et al. (2018), displaying the stratigraphic position and relationship between different lithologies within the core.

2. Core, sampling, and analytical methods

The three drill cores (TCDP1, TCDP2, TCDP 3) retrieved as part of the Turee Creek Drilling Project (TCDP; Fig. 1) represent a combined 454 m of core recovered over 746 m of drilling. The core samples were split, and half is archived at Géosciences Montpellier. Samples discussed in this study were subsampled from TCDP1.

Samples were collected at regular intervals between 174.13 and 99.0 m depth. The Boolgeeda Iron Formation in this section of core is largely comprised of Fe-rich and silica-dominated IF (including jasper), with a distinct clastic package occurring around 152 m (see Section 3.1). The overlying Kungarra Formation is dominated by relatively homogeneous grey shales and siltstones. Forty thin sections representing drilling depths between 172.1 m and 130.39 m were

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**Table 1:**

<table>
<thead>
<tr>
<th>Element</th>
<th>Detection Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.001%</td>
</tr>
<tr>
<td>Pb</td>
<td>0.001%</td>
</tr>
<tr>
<td>Ni</td>
<td>0.001%</td>
</tr>
<tr>
<td>Zn</td>
<td>0.001%</td>
</tr>
<tr>
<td>AG</td>
<td>0.001%</td>
</tr>
</tbody>
</table>

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**Fig. 2:** Litholog for Turee Creek Drilling Project core 1 (TCDP1) after Philippot et al. (2018), displaying the stratigraphic position and relationship between different lithologies within the core.
Average, minimum, and maximum concentrations of major elements in the Boolgeeda Iron Formation and overlying Kungarra Formation sediments of TCDP1.

<table>
<thead>
<tr>
<th>Lithology</th>
<th>SiO₂ (%)</th>
<th>TiO₂ (%)</th>
<th>Al₂O₃ (%)</th>
<th>Fe₂O₃ (%)</th>
<th>MnO (%)</th>
<th>CaO (%)</th>
<th>Na₂O (%)</th>
<th>K₂O (%)</th>
<th>P₂O₅ (%)</th>
<th>S (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron Formation (n = 51)</td>
<td>50.35</td>
<td>0.09</td>
<td>2.14</td>
<td>41.71</td>
<td>0.07</td>
<td>1.79</td>
<td>0.14</td>
<td>0.18</td>
<td>0.22</td>
<td>341.79</td>
</tr>
<tr>
<td>Silica-dominated Iron Formation (n = 53)</td>
<td>52.79</td>
<td>0.09</td>
<td>2.25</td>
<td>35.06</td>
<td>0.16</td>
<td>1.64</td>
<td>0.27</td>
<td>0.18</td>
<td>0.22</td>
<td>706.53</td>
</tr>
<tr>
<td>Green Mudstone/Siltstone (n = 30)</td>
<td>55.02</td>
<td>0.03</td>
<td>0.16</td>
<td>11.11</td>
<td>0.40</td>
<td>1.21</td>
<td>0.24</td>
<td>0.24</td>
<td>0.24</td>
<td>706.53</td>
</tr>
<tr>
<td>Sandstone (n = 3)</td>
<td>56.72</td>
<td>0.03</td>
<td>0.16</td>
<td>13.06</td>
<td>0.36</td>
<td>1.79</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>706.53</td>
</tr>
<tr>
<td>Diamictite (n = 2)</td>
<td>57.29</td>
<td>0.03</td>
<td>0.16</td>
<td>28.06</td>
<td>0.36</td>
<td>1.79</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>706.53</td>
</tr>
<tr>
<td>Grey Siltstone/Argillite (n = 35)</td>
<td>58.25</td>
<td>0.03</td>
<td>0.16</td>
<td>16.97</td>
<td>0.36</td>
<td>1.79</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>706.53</td>
</tr>
</tbody>
</table>

To extract Fe₃O₅₅₅₆ (6), samples were transferred into Thermo Scientific Teflon FEP centrifuge tubes by rinsing with 18.2 Ω Milli-Q water. The water was then removed by centrifugation prior to the next extraction. This extraction was performed using boiling 37% hydrochloric acid. To do so, a heating block was preheated to 210 °C. Five mL of hot hydrochloric acid were added to the tubes, which were then placed in the preheated heating block, brought to a boil (3–5 min), and boiled for another 1 min. The boiling was stopped by removing the tubes from the heating block and adding 10 mL of cold ultrapure water. The tubes were centrifuged (15000g, 20 min), and 5 mL of the supernatant was discarded 3 times with 2% nitric acid and 0.5% hydrochloric acid for analysis. Another 5 mL were discarded, and the remaining 5 mL was left in the tubes for the final digestion step. The final digestion (7) was performed by adding 5 mL of 70% nitric acid and 3 mL of 48–51% hydrofluoric acid, and subsequently heating the mixtures at 155 °C until near dryness. One mL of 37% hydrochloric acid was added to the remaining solution and the mixture was heated again at 155 °C for 4 h. The remains were then diluted to 50 mL with 2% nitric acid and 0.5% hydrochloric acid.

All solutions were analyzed for Fe using an Agilent 8800 Triple Quadrupole ICP-MS in high matrix introduction mode, using Ar as carrier and dilution gas and He (5 mL/min) as collision gas to minimize polyatomic interferences (Sakai, 2015). Germanium and In were used as internal standards. Elemental recovery was verified using the certified standard STSD-3 (CANMET Mining and Mineral Sciences Laboratories, Natural Resources Canada), yielding an average total recovery of 107%.

3. Petrography and mineralogy

3.1. Lithologies in TCDP1

Based on mineralogy and grain size, Philippot et al. (2018) defined five major lithologies within TCDP1: (1) banded iron formation (BIF), (2) silica-dominated iron formation (3) green mudstone/siltstone, (4) diamictite associated with sandstone/siltstone, and (5) grey siltstone/argillite (Fig. 2). Lithologies 1 through 4 are the major components of the Boolgeeda IF, while lithology 5 comprises the overlying Kungarra Formation. Although in variable proportions, iron oxides (mostly magnetite, but also hematite), quartz, carbonate, chlorite, and pyrite, are present within the banded iron formation, silica-dominated iron formation, and green mudstone/siltstone. Rare occurrences of muscovite, plagioclase, apatite, and zircon are also present. These three lithologies are generally gradational, with subtle transitions and finescale (mm to cm) intercalations occurring within, and between, them. On the other hand, the diamictite and grey siltstone/argillite are defined within specific intervals of the core and represent distinct sediment packages separate from the other lithologies. Each lithology is discussed in more detail below.

3.1.1. Banded iron formation

The BIF is mainly composed of iron oxides (magnetite and hematite), quartz, and lesser amounts of carbonate, with minor chlorite and rare muscovite. Magnetite grains are typically large and euhedral relative to hematite grains (Fig. 3A), and in some instances, contain inclusions of elongated to rounded hematite and quartz (Fig. 3B). Macroscopic banding is well-to poorly-developed by alternating layers of...
Table 2

Average, minimum, and maximum trace element concentrations in the Boolgeeda Iron Formation and overlying Kungarra Formation sediments of TCDP1.

<table>
<thead>
<tr>
<th>Element</th>
<th>Iron Formation (n = 51)</th>
<th>Silica-dominated Iron Formation (n = 53)</th>
<th>Green Mudstone/Siltstone (n = 30)</th>
<th>Sandstone (n = 3)</th>
<th>Diamictite (n = 2)</th>
<th>Grey Siltstone/Argilite (n = 35)</th>
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<tbody>
<tr>
<td>Y</td>
<td>12.41</td>
<td>4.07</td>
<td>18.04</td>
<td>2.00</td>
<td>4.07</td>
<td>18.67</td>
</tr>
<tr>
<td>Zr</td>
<td>32.94</td>
<td>4.74</td>
<td>110.00</td>
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<tr>
<td>Ba</td>
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<td>389.00</td>
<td>4.00</td>
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<tr>
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<td>Dy</td>
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<td>3.20</td>
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<td>1.90</td>
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<td>53.16</td>
<td>5.10</td>
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<td>19.90</td>
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<tr>
<td>Cr</td>
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<td>43.11</td>
<td>1138.86</td>
<td>253.37</td>
<td>539.37</td>
<td>20.00</td>
</tr>
<tr>
<td>Cu</td>
<td>9.75</td>
<td>3.43</td>
<td>54.00</td>
<td>1.86</td>
<td>61.54</td>
<td>11.68</td>
</tr>
<tr>
<td>Pb</td>
<td>8.19</td>
<td>1.96</td>
<td>18.00</td>
<td>1.96</td>
<td>26.00</td>
<td>17.76</td>
</tr>
<tr>
<td>Zn</td>
<td>18.83</td>
<td>4.00</td>
<td>40.00</td>
<td>3.64</td>
<td>48.00</td>
<td>38.48</td>
</tr>
</tbody>
</table>
almost pure iron oxides (± quartz and occasionally chlorite) and quartz ± carbonate ± chlorite. Banding on the cm-scale is most clearly defined by alternating quartz and Fe-oxide rich layers. Thin mm-scale carbonate-rich bands typically occur at the transition between iron- and quartz-rich bands. Within the Fe-oxide-rich layers, slightly darker bands contain abundant microplaty hematite (Fig. 3A and B, SI Fig. 2). Notably, microplaty hematite grains in Fe-oxide-rich bands below 160 m depth are larger, more bladed, and more abundant than grains in A; hematite grains in B are larger and more euhedral than in A. C: Relationship of microplaty hematite bands (top) to silica dominated bands containing euhedral magnetite (bottom). D: Magnified image of microplaty hematite bands, displaying individual platy hematite grains and fine hematite dust yielding the red staining colour of the silica matrix. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. Typical textural relationships of iron minerals in the Boolgeeda Iron Formation under reflected light. A: General appearance of relatively large euhedral magnetite grains compared to smaller platy hematite grains. B: A large euhedral magnetite grain containing inclusions of hematite and quartz, suggesting magnetite crystals formed after quartz and hematite. C: Relationship of microplaty hematite bands (top) to silica dominated bands containing euhedral magnetite (bottom). D: Magnified image of microplaty hematite bands, displaying individual platy hematite grains and fine hematite dust yielding the red staining colour of the silica matrix. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 4. Typical textural associations of hematite and magnetite. A-B: Varying appearance of magnetite and hematite grains within closely spaced bands (< 3 cm apart) under reflected light; hematite grains in B are smaller, less bladed, and more abundant than grains in A; magnetite grains in B are larger and more euhedral than in A. C: Microbanding similar to Trendall’s (1973) type A under reflected light. D: Microbanding similar to Trendall’s (1973) type B under transmitted light.
crystals exist (SI Fig. 4). When green mudstone/siltstone is interbedded
with the BIF, layers of the latter are finer grained than usual and con-
tain pyrite, which is otherwise generally absent from the BIF lithology
aside from rare isolated euhedral grains (see Philippot et al., 2018 for
description and composition of pyrite).

Veins within the BIF are infilled by carbonate ± quartz ± chlorite.
Crosscutting relationships show quartz and carbonate veins disrupting
hematite, magnetite, and carbonate beds. In rare cases, flecks of mi-
croplaty hematite can be seen within both the quartz and carbonate
veins in sections where the veins disrupt beds containing these minerals
(SI Fig. 5). However, there is no visible gradation in microplaty he-
matite abundance moving away from the veins, and microplaty he-
matite distal to veins is restricted to thin beds, parallel to iron banding,
which typically contain what appear to be primary depositional struc-
tures.

3.1.2. Silica-dominated iron formation

The distinction between BIF and silica-dominated IF is centered on
variations in the Si content observed from bulk geochemistry data, with
the Si-dominated IF generally containing ~10% more Si by weight than the
BIF. Petrographic distinctions of this lithology from the BIF are
subtle, but most obvious in the chert content. Microcrystalline quartz
layers are largely present as two distinct varieties: (1) laminated red
chert (jasper) and (2) massive white chert. Individual layers range from
chert microbands (~1 mm) to thicker chert bands up to 15 cm thick.
White chert layers tend to be thicker, usually massive, and are composed of
almost pure quartz. Jasper layers tend to form microlayered units
composed of microcrystalline quartz with disseminated fine hematite
dust interbedded with carbonate- or chlorite-rich layers. Occasionally,
magnetite and carbonate crystals are dispersed in the quartz-rich layers,
and magnetite dispersed in the carbonate- or chlorite-rich layers. Jasper
underwent a less advanced stage of silicification than the white chert,
as indicated by the preserved original microlayering and partially
preserved original minerology. In jasper intervals that appear to have
been “bleached”, the red jasper colour has been removed from the
chert, hematite has recrystallized into semi-continuous wavy micro-
bands of “sutured” grains, and quartz has recrystallized into larger
grains. Notably, although white chert can be found throughout TCDP1,
it appears to be more common towards the contact between the
Booleggea IF and Kungarra Formation. Veins in the silica-dominated
iron formation are infilled by carbonate ± quartz ± chlorite.

3.1.3. Green mudstone/siltstone

The green mudstone/siltstone forms three distinct intervals. The
lower mudstone/siltstone around 160 m depth, ranging in color from
greenish to light grey, is mainly composed of quartz, carbonate, and
magnetite, with lesser amounts of muscovite and chlorite. Apatite is
also present as microscopic grains associated with iron oxides in green
mudstones; specifically, magnetite + apatite + carbonate microbands
alternate on the scale of 100s-of-µm to mm-scale with quartz + pyrite
microbands (see SI Fig. 6 of Philippot et al., 2018). Pyrite is present as
both small dispersed crystals, and several large idiomorphic crystals
with inclusions of quartz, carbonate, muscovite, and chlorite. Micro-
bands of pyrite can also be found within the shale, which intermingle
between large euhedral magnetite grains (Fig. 5). Texturally, pyrite can
be found as small, rounded inclusions within magnetite crystals closely
associated with the bands, in irregular contact with magnetite, and
overgrowing euhedral magnetite crystals (Fig. 5C), suggesting that
generations of pyrite pre-dated, co-precipitated, and post-dated the
large euhedral magnetite crystals. Veins infilled with carbonate ± iron
oxides ± quartz are also present.

The middle and upper green siltstones at ca. 148 m and 132 m
depths consist of chlorite, quartz, carbonate, magnetite, and lesser
amounts of pyrite. Lamination and bedding are marked by variable
proportions of carbonate and chlorite (Fig. 6A). Pyrite is present either as minute
crystals forming micro-layers parallel to bedding, or scarce, large
idiomorphic crystals, occasionally displaying pressure shadows and
hosting iron oxide inclusions. Veins are filled with chlorite ±
quartz ± carbonate ± iron oxides. Between 130 m and 128 m, a
transition is observed from green (chlorite-rich) siltstones to grey
(muscovite-rich) siltstones, corresponding with the transition from the
Booleggea Iron Formation to the Kungarra Formation. This transition
also coincides with a significant decrease in the iron oxide concentra-
tion from the chlorite-rich bands to the grey siltstone. Additionally, the
overall proportion of carbonate increases across transitions to the grey
siltstone.

Fig. 5. Typical pyrite textures found within the
TCDP1 under reflected light. A: Small euhedral pyrite
crystals intermingled between large euhedral mag-
netite grains; note the sharp boundary where mag-
netite grains become less prevalent and pyrite is ab-
sent. B: Thin microbands of pyrite grains that lie
parallel to primary bedding; presumably from in situ
sulphate reduction in shallow pore waters. C: Small
rounded inclusions of pyrite within euhedral mag-
netite crystals closely associated with pyrite micro-
bands; association suggests pyrite is more primary
than magnetite. D: Textural association of euhedral
magnetite and pyrite grains.
3.1.4. Clastic diamictite horizon

A ca. 2 m-thick layer of clastic diamictite sediment between 151.6 m and 153.4 m depth consists of white, rounded to angular mm- to cm-scale carbonate and quartz clasts embedded within a matrix of variably sized quartz grains and chlorite, with minor amounts of carbonate, apatite, ilmenite, and various sulfides. As shown by Philippot et al. (2018), this horizon is similar to the glacial diamictite described at the Duck Creek Syncline and Yerra Bluff locality (Martin, 1999; Martin et al., 2000). Generally, clasts are poorly sorted throughout the section with grains ranging in size from mm- to cm-scale, contained within a mudstone matrix. The presence of dropstones in this interval has previously been noted (SI Fig. 2 from Philippot et al., 2018).

3.1.5. Grey siltstone/argillite (Kungarra Formation)

The grey siltstone is mainly composed of muscovite and quartz, with subordinate amounts of carbonate. Scarce, but large, idiomorphic crystals of pyrite may also be present. Likewise, rare and minute crystals of pyrite and magnetite occur dispersed throughout the rock. Ripple-cross lamination is a common feature throughout this lithology and local veinlets are infilled by carbonate ± pyrite ± quartz. The presence of abundant muscovite typically imprints a clear cleavage to the siltstone beds. Small laminae and layers (< 5 cm) of calcareous mudrock, ranging in colour from light grey to greenish, can be found within the grey siltstone. These intercalations are typical in the upper part of TCDP1, the Kungarra Formation.

4. Bulk rock geochemistry

4.1. Major and trace elements

Chemostratigraphic depth profiles for selected major and trace elements are presented in Figs. 6 and 7, respectively (see also Tables 1 and 2). Two distinct intervals at 160 and 153 m depth show anomalous levels of major and redox sensitive trace elements. The interval at 160 m depth is associated with the S-rich lower green mudstone/siltstone, while the interval at 153 m depth represents the diamictite. Two smaller perturbations in trace element profiles are also found at 148 m and 132 m depth.

Iron concentrations generally decrease up-section, but anomalously low concentrations are found at 160 m, 148 m, and 132 m depth. A significant drop in Fe concentration occurs at the transition from the Boolgeeda Iron Formation to the overlying grey mudstones/argillite of the Kungarra Formation. Silica concentrations are relatively constant throughout the core, aside from the anomalous layers at 160, 148, and 132 m depth. Within these intervals, silica concentrations vary widely, comprising two distinct populations with either high SiO₂ (~80 wt%) or low SiO₂ (~20 wt%) contents. Generally, green mudstone/siltstone samples are included in the low Si population, while Si-dominated IF...
samples comprise the high Si-population.

Titanium, Al, and Mg depth plots (Fig. 6) are almost identical, aside from higher concentrations of Ti and Al in the diamictite. All three plots display an increase in concentration above 160 m depth, apart from depleted values in Si-rich samples at 160 m, 148 m, and 132 m depth. This increase is marked by the positive shift in concentration between the lower and upper sections of the BIF lithology, and further increases accompanying the transition to the overlying Kungarra Formation siltstone/argillite.

Calcium concentrations are relatively stable throughout the core and typically less than 3 wt%, aside from minor enrichments in the green mudstone/siltstone intervals. Concentrations of K, Na, and P are typically < 1 wt% throughout the core. Exceptions include a spike in K concentrations to 4–6 wt% in the diamictite interval and higher concentrations (~5 wt%) within the Kungarra Formation, Na enrichments leading up to the diamictite layer and at 132 m, and a P enrichment at 160 m. Loss on ignition (LOI) values are higher in the green mudstone/siltstone and grey siltstone/argillite intervals, as expected, given the prevalence of carbonate in these lithologies.

Sulfur concentrations are noticeably elevated within the lower green mudstone/siltstone at 160 m depth, and the diamictite at 153 m depth. Between these two intervals, concentrations increase up until the diamictite, and then progressively decrease up-section until 145 m depth. Sulfur values above 145 m in the upper BIF indicate a permanent increase in S concentrations, as S values shift from < 100 ppm in the lower BIF to > 400 ppm in the upper BIF. During the transition from the upper Boolgeeda Iron Formation to the Kungarra Formation, S values appear to be stable, aside from a slight increase at 130 m and a subtle decrease at 120 m depth.

Two intervals of Mn enrichment (up to 3 wt% MnO) are present at 150–151 m and 130 m depth. Aside from these thin intervals and a subtle increase in Mn leading up to the diamictite layer, Mn concentrations remain low and stable throughout the core.

To account for detrital contributions and reveal primary enrichments in the sediments, trace element profiles are normalized to Ti where appropriate (Fig. 7). Our decision to normalize to Ti opposed to other lithogenic elements (i.e. Al, Zr, Th, Sc) did not influence the depth profiles (SI Figs. 6–8). As stated above and congruent with major element patterns, generally, large perturbations are found at 160 m and 153 m depths, with smaller anomalies at 148 m and 132 m depths.

Barium concentrations decrease above 160 m, with an order of magnitude drop in abundance from the lower to upper BIF. This shift is maintained into the overlying Kungarra Formation. Aside from this general trend, anomalies in Ba abundance include a large spread of data between 160 m and 148 m depth, and low concentrations at the transition from the Boolgeeda Iron Formation to the Kungarra Formation mudstone/argillite at 130 m.

The V depth profile peaks at 160 m and 148 m depth. The Cu profile is almost identical to V, aside from more pronounced enrichments at 132 m and 148 m. Apart from three anomalous intervals at 160 m, 148 m, and 132 m, concentrations of V and Cu remain relatively unchanged throughout the core. Cobalt concentrations are relatively stable throughout the Boolgeeda Iron Formation aside from a slight depletion at 160 m and occasional spikes in concentration in samples of green mudstone/siltstone. Cobalt concentrations decrease slightly in the Kungarra Formation. The Zn profile appears to decrease slightly up section and displays a large positive spike at 160 m depth. Other discrepancies are relatively small or represented by a single data point. Uranium enrichments relative to Ti are pronounced at 160 m, 148 m, and 132 m, but otherwise stable throughout the core. Chromium enrichments occur at 172 m, 157 m, 148 m, and 132 m. They approach 400 ppm at 157 m depth, and Ti normalized enrichments breach 10,000. These values are comparable to those reported by Konhauser et al. (2011) for the 2.32 Ga Timeball Hill Formation (Fig. 8). Lead concentrations are highest at 160 m, 148 m, and 132 m depth, and generally decrease up-section with the Kungarra Formation containing the lowest concentrations.

It is interesting to note that Ba, V, Cu, Co, Zn, and U concentration...
plots that are not normalized to Ti (SI Fig. 9) exhibit near identical patterns, with peak concentrations of 1900 ppm, 200 ppm, 100 ppm, 25 ppm, 85 ppm, and 5 ppm, respectively, within the diamictite layer. All elemental concentrations increase towards the diamictite layer, and then gradually decrease moving stratigraphically up from it. Concentrations of all six elements again increase significantly in the Kungarra Formation, suggesting a predominantly clastic origin for these elements. Correlation plots of elemental concentrations vs TiO₂ (%) confirm a strong detrital component for V, Co, Zn, and U (SI Fig. 11). Barium and Cu have weaker, but still significant, correlations with TiO₂ (%), while Pb and Cr do not correlate at all. The non-normalized Cr abundance profile displays a similar trend, but the peak concentration occurs just below the diamictite layer at 157 m depth. Further, the ~400 ppm Cr concentration measured in this interval is greater than that found in any detrital lithology within the core, including the overlying Kungarra Formation. When not normalized to Ti, the Pb trend displays a large spike at 160 m (up to 100 ppm), and a smaller increase at 148 m. One sample within the diamictite also approaches 70 ppm. Notably, the Pb depth plot appears most similar to the S depth plot and concentrations of both elements display a linear correlation (r² = 0.6904; SI Fig. 10).

4.2. Rare earth element and yttrium features

The REE + Y patterns for samples containing less than 1 wt% Al₂O₃ are presented in Fig. 9. Elevated total REE + Y concentrations are apparent above 160 m depth, along with increased Al₂O₃ and TiO₂, especially between 150 and 160 m within the Boolgeeda Iron Formation (Fig. 10A). This interval coincides with a higher propensity for current structures and the observation that red jaspilite bands are clearly disrupted. Similar to the Al₂O₃ and TiO₂ depth plots, total REE + Y concentrations appear to undergo a permanent increase above 160 m, as demonstrated by the higher values recorded in the upper BIF compared to the lower BIF. A second increase in total REE concentrations occurs coincident to the transition from the Boolgeeda Iron Formation to the Kungarra Formation. Total REE + Y concentrations display a strong positive correlation with Al₂O₃ concentrations (Fig. 10C).

All non-clastic lithologies within the Boolgeeda Iron Formation display a La/Lu ratio < 1, which is indicative of HREE enrichment. The highest La/Lu values within the Boolgeeda Iron Formation occur at 160 m depth and within the diamictite layer, above which there appears to be a progressive decrease back to subdued values found in the BIF. Within the overlying Kungarra Formation, the REE + Y profile flattens, and La/Lu ratios often exceed 1 (Fig. 10A).

Y/Ho ratios vary widely throughout the core. Most igneous rocks and epiclastic sediments have a Y/Ho weight ratio of 28 and a molar ratio of 52, whereas large Y/Ho ratios are typical of aqueous and highly evolved magmatic systems (Bau, 1996; Bau and Dulski, 1999; and references therein). Aqueous fluids and their precipitates are commonly characterized by superchondritic Y/Ho ratios (values > 26.22 w/w as per Pack et al., 2007), with molar ratio values as high as 90 being reported in modern seawater (Zhang et al., 1994; Bau et al., 1997; Nozaki et al., 1997; Bau and Dulski, 1999). Elevated Y/Ho ratios are prevalent throughout the Boolgeeda Iron Formation, typically ranging between 35 and 50 (w/w). The Y/Ho ratio appears to decrease slightly up-section, with the lowest values found in the Kungarra Formation. Further, Y/Ho data appear to vary sinuosity-integrated throughout the core, with depressions possibly corresponding to periods of enhanced detrital input (Fig. 10A).

Post Archean Australian Shale normalized Eu anomalies (Eu/Eu°PAAS; Taylor and McLennan, 1985) were calculated using Eu/Eu°PAAS = Eu/(2/3)Sm + [1/3(Tb)] (Bau and Dulski, 1996). A positive Eu anomaly is prevalent throughout all lithologies of the TCDP1 core, but overall the Eu anomaly decreases up-section, with the lowest values found in the Kungarra Formation (Fig. 11A). Generally, samples with less Al₂O₃ have higher Eu anomalies (Fig. 11C).

Detecting the presence of Ce anomalies in seawater precipitates can be complicated by anomalous abundances of La. To avoid false negative Ce anomalies that may appear when using the equation Ce/Ce° = Ce/ (0.5La + 0.5Pr), we plotted Ce/Ce° versus Pr/Pr° to identify true negative Ce anomalies as prescribed by Bau and Dulski (1996), where (Pr/Pr°) = Pr/(0.5Ce + 0.5Nd) (Fig. 11B). Here it can be seen that while some true negative Ce anomalies (Ce/Ce° < 1.05 and Pr/Pr° > 1.05) and a few probable positive Ce anomalies (Pr/Pr° < 0.95) exist, most of the data show false negative Ce anomalies due to positive La anomalies (Ce/Ce° > 0.95, 0.95 < Pr/Pr° < 1.05). We thus focus on Pr/Pr° as an indicator of true Ce anomalies. The Pr anomaly shows significant variation throughout the core, with the most positive values (most negative true Ce anomalies) in upper iron formation interval, bracketed by rare negative Pr anomalies (positive Ce anomalies) (Fig. 11A). Similar to Eu/Eu°, true Ce anomalies indicated by Pr/Pr° appear progressively attenuated with increasing detrital input, approaching crustal values with increasing Al₂O₃ (Fig. 11C).

4.3. Chemical Index of Alteration (CIA) and intervals of anomalous enrichment

The Al₂O₃-(CaO°+Na₂O)-K₂O plot for detrital lithologies in the TCDP1 core is presented in Fig. 12, where CaO° represents the proportion of total Ca in the silicate fraction only. Data from the green mudstone/siltstone lithology plot close to the boundary of the ternary diagram defined by Al₂O₃ and CaO°+Na₂O, with K₂O proportions rarely exceeding 10%. The range of these values can be explained by the weathering of ultramafic to mafic source rocks (see discussion below). Conversely, data for the grey siltstone/argillite of the Kungarra Formation lies to the right of the boundary, and typically displays higher K₂O proportions, between 10 and 20%, reflecting the higher proportions of muscovite present in this section. This trend is typical of felsic source rock weathering, suggesting that a change in source material occurred during the transition from the Boolgeeda Iron Formation to the Kungarra Formation. The sandstone/siltstone and diamictite contain the highest proportion of K₂O (25–30%) (Fig. 12). These points fall within the average cluster of Fortescue shales, Jeerinah shales, and Mount McRae shales as plotted by Pecoits et al. (2009). As all shale
formations listed above were deposited before, and lie stratigraphically beneath the Boolgeeda Iron Formation, it is possible that the diamictite represents an average of the weathering products of these formations and their source-rocks. In general, the chemical index of alteration (CIA) values for shales in the TCDP1 core are relatively high, with some values approaching 90, suggesting intense chemical weathering of some source rocks.

4.4. Fe speciation

The concentration of Fe contained within each sequential extraction fraction, collected using the method of Poulton and Canfield (2005), is shown in Fig. 13A. Iron is dominantly contained in the FeMag and FePRS fractions, with lesser amounts present in the FePy, FeCarb, and FeOx1 fractions. Iron concentrations in the FeEx and FeOx2 fractions were negligible in all samples. Highly reactive Fe (FeHR) is defined as the sum of all fractions of Fe highly reactive towards H2S on short diagenetic time scales (i.e. FeHR = FeCarb + FeOx1 + FeOx2 + FeMag + FePy; Canfield et al., 1992; Raiswell and Canfield, 1998; Poulton et al., 2004). Total Fe (FeT) represents the sum of Fe in all sequential extraction fractions. The degree of pyritization is defined as the proportion of pyritized Fe within the highly reactive Fe pool (FePy/FeHR; Berner, 1970). Total Fe to Ti (Fe2O3/Ti) decreases up core, with particularly low ratios occurring within the diamictite and higher ratios present around 160 m, 148 m, and 132 m (Fig. 13B). Ratios of Fe3+Fe/FeT and FePy/FeHR increase up core, with clear increases in the ratios occurring
at 160 m depth (Fig. 13C). The Fe_IRR/Fe_T ratio exceeds 0.4 above 160 m depth, and remains above this value aside from a single point at 155.56 m. The Fe_PY/Fe_IRR ratio exceeds 0.7 at 109 m within the Kungarra Formation but remains below this threshold in all other samples. The Fe_OX/Fe_IRR and Fe_CARB/Fe_IRR ratios both display the highest values at ∼148 m. The Fe_CARB/Fe_IRR depth profile also displays a pronounced enrichment at 160 m whereas the Fe_OX/Fe_IRR depth profile does not.

5. Discussion

5.1. Boolgeeda iron formation composition and genesis

It is commonly held that IF sediments record contemporary ocean chemistry due to the high surface reactivity of primary precipitates (i.e. ferric oxyhydroxide particles or Fe(III)-Si gels) and their propensity to adsorb elements directly from seawater, as supported by the comparable rare-earth element (REE) signatures of IF and modern seawater (e.g. Bau and Dulski, 1996; Bau, 1999; Alexander et al., 2008). Therefore, IF geochemical analyses have been used to reconstruct temporal trends in marine trace element concentrations throughout Earth history (e.g. Konhauser et al., 2009). Minerals composing IF are not primary, but instead reflect diagenetic and metamorphic transformation of primary precipitates (Klein, 2005; Konhauser et al., 2017). However, if the system has remained closed, IF should preserve primary geochemical signatures of the water column. A detailed assessment of petrogenesis of the Boolgeeda Iron Formation is required in order to determine whether or not diagenesis, metamorphism, or secondary fluids have significantly altered sample composition at the whole-rock scale.

Hematite is interpreted to be an early diagenetic phase resulting from the dehydration and crystallization of a primary Fe(III)-Si gel (Fischer and Knoll, 2009; Percak-Dennett et al., 2011) or ferric oxyhydroxides precipitated from the water column (Konhauser et al., 2005). Three forms of hematite are prevalent in the Boolgeeda Iron Formation: (1) microplaty hematite, (2) fine disseminated hematite dust, and (3) thin continuous bands of “sutured” hematite grains. Microplaty hematite and disseminated hematite dust are interpreted to be the most primary Fe phases preserved in the Boolgeeda Iron Formation, supported by textural relationships with other minerals such as inclusions of microplaty hematite in large euhedral magnetite grains.
(Fig. 3A, B). This conclusion is consistent with the previous work of Spencer and Percival (1952), James (1954), Trendall (1973), Ahn and Buseck (1990), Beukes and Gutzmer (2008), Pecoits et al. (2009), Bekker et al. (2010), and Sun et al. (2015). However, Rasmussen et al. (2015, 2016, 2017) have recently proposed that hematite dust is neither primary nor an early diagenetic component of IF. Instead, they consider microplaty hematite to be an alteration product of earlier ferrous iron-silicate nanoparticles. If conclusions drawn by these authors hold true and hematite is a product of oxidizing fluids modifying the redox state and mineralogy of IF post deposition, then intervals containing hematite may be inappropriate for examining ancient redox conditions. We do, in rare cases, see flecks of microplaty hematite within quartz and carbonate veins in sections where the veins disrupt primary beds. With that said, as there is no visible gradation in microplaty hematite abundance moving away from the veins, we have no reason to believe that hydrothermal alteration led to the genesis of microplaty hematite. Further, microplaty hematite distal to veins is restricted to thin beds, parallel to iron banding, which typically contain primary depositional structures. If oxidizing fluids produced the microplaty hematite, we would expect grains to be present on a larger scale throughout the section, and not restricted to cm-scale beds. We, therefore, consider microplaty hematite grains and disseminated hematite dust to be relatively early diagenetic features, resulting from the dehydration and crystalization of primary ferric oxyhydroxide particles or Fe(III)-Si gel formed in the water column.

Microplaty hematite is more common in Fe-rich mesobands while disseminated hematite dust is prevalent in Si-rich mesobands (jasper). The microplaty hematite and disseminated hematite dust are interpreted to have formed from the same primary Fe(III)-Si gel phase, but to have undergone different diagenetic modifications as a result of their contrasting background matrices (i.e. Si dominated vs Fe dominated). These contrasting matrices on the mesoscale band are likely the result of temporal changes in seawater Fe and Si content during deposition (Trendall, 2002) as amorphous Si was carried to the ocean floor by precipitated ferric oxyhydroxides (Fischer and Knoll, 2009) in the form of an Fe(III)-Si gel. Silica rich bands resulted when hydrothermal Fe concentrations were depressed relative to Si, and Fe rich bands resulted when Fe(III) precipitation outpaced Si precipitation, perhaps with seawater Si drawdown due to extensive Fe precipitation.

Primary Fe(III) precipitates trapped in Si-rich layers were likely prevented from ripening into microplaty hematite as a result of insufficient space due to rapid lithification of chert bands during early diagenesis. It is possible that extensive burial and heating led to silica dissolution-precipitation creep (DPC) within some of the Si-rich mi-
formation of magnetite during metamorphism, likely the result of a reaction with reduced C compounds buried originally with the sediments. Similarly, the prevalence of large “bleded” microplaty hematite in iron oxide-rich mesobands below 160 m depth, and apparent absence above, may reflect a larger scale change in reduced C supply separating depositional conditions above and below 160 m.

Two varieties of chert exist in the Boolgeeda Iron Formation: (1) laminated red chert (jasper) and (2) massive white chert. Both varieties of chert are interpreted to be diagenetic; however, jasper is interpreted to have formed before the massive white chert. Quartz composing the massive white chert appears to have recrystallized into larger euhedral quartz grains lacking any trace of disseminated hematite thereby giving it a “bleached” appearance. Preserved reaction fronts captured in thin section highlight lateral mineralogical changes within microbands and mesobands of bleached and jasper zones; most notably, disseminated hematite has concentrated into sutured wavy microbands. As alluded to above, it is likely that “bleaching” occurred as an artifact of DPC during diagenesis and regional-scale deformation (Egglseder et al., 2016). The competency contrast between the Boolgeeda IF and Kungarra Formation may therefore explain the increased prevalence of white chert towards the contact between the two units.

The large euhedral magnetite within the Boolgeeda BIF lithology is clearly secondary, and likely metamorphic. Magnetic remanence and susceptibility analyses (Carlut et al., 2015) as well as sequential Fe extractions (Fig. 13) confirm the ubiquitous presence of magnetite throughout the Boolgeeda IF. Inclusions of hematite and quartz within magnetite (Fig 3B) and the even distribution of euhedral magnetite throughout the Boolgeeda BIF (i.e. little association with “primary” banding features) support the interpretation that this is a relatively late phase overprinted on sediments of earlier diagenetic origin. The bimodal size distribution of euhedral magnetite (SI Fig. 4) is likely the result of two separate regional scale metamorphic events that promoted the growth of euhedral magnetite from earlier sediments. The larger magnetite likely formed first while the smaller magnetite formed during a second event when BIF sediments were under higher pressures, resulting in their smaller size. Notably, Carlut et al. (2015) detected 2 Verwey transition temperatures in TCDP1 magnetite between 148 m and 146 m depth, and suggested localized Si-substitution into magnetite to explain this signature. It is possible a secondary silicification event affected this 2 m interval. However, the anomalous Verwey transition temperature is not found anywhere else in TCDP1, and therefore, there is no reason to believe alteration of the core in this manner was pervasive.

Chlorite within all lithologies, particularly prevalent in the green mudstone/siltstones, suggests low-grade metamorphism; the upper limit is prehnite-pumpellyte to lower greenschist facies. Notably, martite and geothite are absent from thin sections, suggesting microplaty hematite within the Boolgeeda Iron Formation is not a para-genetic product of alteration typically associated with the formation of high grade hematite ore. Further, minnesotaite and stilpnomelane appear absent from thin section, attesting to the pristine nature of the iron bands. The prevalence of chlorite in the green mudstone/siltstones is likely the result of metamorphic alteration of primary clay material that composed these intervals.

Philippot et al. (2018) documented the presence of multiple pyrite textures within TCDP1, including nodular pyrite aggregates, clusters of microcrystalline pyrite, inclusion free pyrite overgrowths around pyrite framboisids, finely disseminated euhedral to subhedral pyrite crystals, euhedral to subhedral pyrite crystals aligned with bedding and conforming to soft sediment deformation features, as well as bands of densely packed microcrystalline pyrite aggregates. The two most prevalent phases of pyrite in the Boolgeeda Iron Formation, primarily within the green mudstone/siltstone intervals, are: 1) large euhedral pyrites commonly found in thin horizontal layers parallel to primary bedding and 2) smaller euhedral crystals that cross-cut horizontal bedding and are brighter in reflected light. We suggest the large euhedral pyrites are a relatively primary phase formed early during diagenesis in shallow pore waters, and may represent the diagenetic product of primary mackinawite (Fe₃⁺₄S₈, Berner, 1970). Support for this exists in inclusions of this phase within large euhedral magnetite crystals. The brighter euhedral pyrite postdates and is systematically associated with primary pyrite. The systematic association of secondary pyrite with primary pyrite and lack of it elsewhere suggest that no additional input of sulfur or iron has occurred. Instead, secondary pyrite is likely the result of local remobilization or recrystallization of pre-existing pyrite. Trace element composition of pyrite acquired by LA-ICP-MS further supports the early diagenetic to syngeneric formation of pyrite layers (Philippot et al., 2018).

Carbonates within the Boolgeeda Iron Formation are primarily found in the green mudstone/siltstone intervals in thin bands, as reflected in the high LOI values found within these layers. The carbonates are typically dolomitized, supported by the high Mg concentrations in the green mudstones/siltstones. The P enrichment at 160 m is tied to the presence of apatite in this interval. Notably, microbands of Fe-oxide + apatite + carbonate can be found alternating with microbands of quartz + pyrite down to the 10s–100s of µm scale in the green mudstone/siltstone (SI Fig. 6 of Philippot et al., 2018). The Fe-oxide + apatite + carbonate bands are likely the diagenetic product of remnant P-rich organic debris deposited with the detrital sediments at 160 m depth. The influx of organic rich debris at 160 m depth may have occurred as a result of increased primary productivity in shallow marine settings. Inter-banded quartz + pyrite layers, on the other hand, may reflect remnants of microbial sulfate reduction spurred by increased organic carbon input. This conclusion is supported by strong δ^{34}S approaching -40‰ in the pyrites, suggesting microbial sulfate reduction under non-S-limiting conditions (Philippot et al., 2018). In short, pyrite layers reflect preserved interfaces where rising sulfide produced by SRB reacted with reduced iron in the water column to form pyrite. Apatite rich layers reflect intervals where organic carbon delivered to the sediment outpaced consumption by microbial metabolism, and thus excess C and P not used up in post depositional Fe reduction were diagenetically transformed into apatite.

5.2. Precipitated and detrital components in the Boolgeeda Iron Formation

A transition from precipitated sediments reflecting marine conditions to sediments increasingly dominated by continentally sourced detrital input is observed stratigraphically upward through the TCDP1 core. This progressive increase of clastic material up-section is also reported in surface expressions of the Boolgeeda Iron Formation (Morris, 1993), as the BIF grades into the overlying siltstones of the Kungarra Formation.

The BIF lithology marks the marine endmember of the TCDP1 core as reflected by its REE + Y composition. Shale normalized (PAAS) REE + Y patterns for samples that contain less than 1 wt% Al₂O₃ display consistent LREE depletions (La/Lu values < 1), high Y/Ho ratios (> 26), and positive La, Y, and Eu anomalies (Fig. 9). Notably, LREE depletion, positive La and Gd anomalies, and elevated Y/Ho ratios, have characterized seawater since the early Archean (Bau and Dulski, 1992; Nozaki et al., 1997; Bolhar et al., 2004; Alexander et al., 2008; Frei et al., 2016). Metal oxyhydroxides, the proposed precursor phases of IF, have long been known to play an important role in the removal of REE + Y from seawater (e.g., Bau, 1991; Koeppenkastrop and De Carlo, 1992; Bau, 1999; Ohla and Kawabe, 2001; Bau and Koschinsky, 2009), and thus chemically precipitated early Precambrian IFs (> 2.3 Ga) typically display Sm/Yb < 1 and Eu/Sm > 1, large positive Eu anomalies, and significant LREE depletion (Bau and Möller, 1993; Planavsky et al., 2010).

Sediments within the sandstone/siltstone and daniolitic layers, as well as the grey siltstone/argillite of the Kungarra Formation, display relatively flat PAAS normalized REE + Y patterns, and lack anomalies characteristic of seawater (SI Fig. 14). This departure from a seawater-
like REE + Y and elevated levels of lithogenic elements (i.e. Al, Ti) are characteristic of continentally-derived shales. These lithologies are strongly influenced by, or perhaps represent, the continental end-member of the depositional system at various periods in basin history.

Generally, total REE, La/Lu ratios, and concentrations of lithogenic elements increase up section, while Y/Ho ratios decrease. Decreasing Fe concentrations up-section further reflect the transition from deeper shelf conditions promoting IP deposition to shallow water conditions with high detrital input. This general pattern is interrupted by a more pronounced influx of detrital material between 160 and 148 m depth, as indicated by low Y/Ho ratios, high La/Lu ratios, and a spike in total REE, TiO$_2$, and Al$_2$O$_3$ concentrations (Fig. 10A). This interval coincides with the appearance of current generated structures, the loss of a positive La anomaly in sediments, and the appearance of abundant chlorite in thin section that likely resulted from low grade metamorphism of the original clay material. Collectively, these indicators are similar to the detrital contamination pattern observed by Viehmann et al. (2015). The variable Fe concentration data between 160 and 148 m depth is the result of sampling alternating Fe-rich and Fe-poor (Si-rich) bands within the BIF lithology, as well as the mixing of the BIF lithologies and detrital input containing moderate Fe concentrations.

Detrital input appears to subside above 148 m depth, and it remains low until deposition of the Kungarra Formation. A hiatus in detrital input is supported by a sharp drop in total REE, declining concentrations of TiO$_2$ and Al$_2$O$_3$, a progressive increase in the Y/Ho ratio, a progressive decrease in the La/Lu ratio, and a return to BIF lithologies at 148 m depth (Fig. 10A). Although indicators of detrital influx are subdued between 148 m and 132 m, they remain higher than levels within the BIF located below 160 m depth. This suggests a permanent change in the amount of clastic input, and perhaps a significant shift in the depositional environment leading up to deposition of the Kungarra Formation.

The periodic nature of detrital influx is interpreted to reflect changes in base level within the basin. As base level fell, detritus became an increasingly dominant component of the sediment. As base level rose, the depositional setting moved seaward and detritus-starved deposition resumed deeper on the shelf. The result is the sinusoidal pattern observed in all three plots – La/Lu, Y/Ho, and total REE (Fig. 10A).

The dichotomy in Si concentration at 160 m, 148 m, and 132 m depth is the result of interlaying between chert-rich sections of the BIF lithology and green mudstone/siltstone in these intervals. This is highlighted by plotting total Fe$_2$O$_3$ (wt. %) vs. SiO$_2$ (wt. %) (Fig. 10B). The log–log plot displays two curved trends that are distinguished by the lithologies that compose them. The high SiO$_2$ population follows the trend defined by the BIF and silica-dominated IF samples, while the low SiO$_2$ population represents a merger of the first trend and a second trend defined by detrital lithologies (i.e. sandstone, diamictite, grey siltstone/argillite, green mudstone/siltstone). Where the green mudstone/siltstone is interbedded with BIF, BIF bands become thinner and pyrite becomes more prevalent. The inter-banding in this interval represents deposition on the boundary of conditions promoting BIF conditions and those promoting the influx of detrital material. Pyrite formation may be the result of higher concentrations of S and organic C

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**Fig. 14.** Panel A: Schematic diagram of conditions leading to deposition of “pure” BIF intervals within the Boolgeeda Iron Formation. Upwelling hydrothermal Fe(II) is oxidized to Fe(III) in the persistently oxygenated shallow water column. Fe(III)-oxyhydr-oxides subsequently sorb dissolved Si to form an Fe (III)-Si gel, the primary phase of the Boolgeeda BIF. Europium anomalies from the hydrothermal source and the negative Ce anomaly prevalent in the oxygenated shallow water column are captured as the precipitated Fe(III)-Si gel phase sorbs REE + Y from the water column. Panel B: A fall in base level results in the deepening of the oxic-anoxic chemocline, and results in the weathering of sulfide minerals previously associated with submerged shelf sediments. The resulting dissolved sulfate is transported deeper into the basin (red line). Further, a decrease in base level leads to increased riverine incision and transport of terrestrially-sourced detrital sediments. These processes inhibited the precipitation of “pure” BIF intervals, and resulted in intervals of mixed detrital-BIF sediments. Panel C: A transgression leads to the resumption of BIF deposition as sulfate concentrations dissipate and detrital influx wanes. Note: the interval at 160 m represents a temporary coupling of the ocean-atmosphere system, resulting in the oxidation of reduced continental sulfides. This event can be viewed as an extreme case of panel B. Sulfate is generated and transported to the ocean, where it is then reduced to sulfide. Large amounts of detrital input also occurred as a result of changes in base level and increased local weathering. The combined effects led to the deposition of S-rich shale at 160 m depth. At 160 m depth, $\Delta^{34}$S goes to 0‰, and $\delta^{34}$S approaches -40‰ (Philippot et al., 2018). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
accompanying the influx of detrital material, as illustrated in Fig. 14. Higher sulfate in the water column and increased input of clastic and organic matter would intermittently prevent IF deposition and promote pyrite rich green mudstone/siltstone deposition. Further, higher S and reduced C delivery to sediments may have resulted in the microbanding of Fe-oxides + apatite + carbonate and quartz + pyrite down to the 10s-100s of μm scale within the green mudstone/siltstone, as discussed above.

The spike in K concentrations within the diamicite interval and the Kungarra Formation are attributed to a compositional change in source rock being weathered. Detrital input in these intervals was likely sourced from felsic source rocks containing higher proportions of K-rich minerals, which were subsequently broken down into K-rich clays during burial. Support for this theory is found in Fig. 12. Two weathering trends are defined by the green mudstone/siltstone samples and the diamicite and Kungarra Formation samples. Shales from the Kungarra Formation and diamicite appear to be sourced from more felsic lithologies in the Hamersley Basin, while the green mudstone/siltstone appears to be sourced from rocks with compositions similar to Pilbara, Fortescue, and Weeli Wolli basalt.

5.3. Redox proxies, oxidative weathering, and trace element enrichments during deposition of the Boolgeeda Iron Formation

The establishment of mildly oxidizing surface waters during deposition of the Boolgeeda Iron Formation are supported by true negative Ce anomalies (as indicated by positive Pr/Pr*) captured by the BIF lithology (Fig. 11). The presence of negative Ce anomalies is typical for Paleoproterozoic and Neoproterozoic IF (Laajoki, 1975; Fryer, 1977a,b; Graf, 1978; Barrett et al., 1988; Klein and Beukes, 1989; Viehmann et al., 2016), but is generally absent from IF older than 2.5 Ga, as oxygen levels were too low to oxidize Ce⁴⁺ to Ce⁴⁺. The presence of negative Ce anomalies in the Boolgeeda Iron Formation, which are not artifacts of positive La anomalies (Fig. 11B), confirms the conclusions of Philippot et al. (2018) that oxygen levels in shallow marine settings had reached appreciable levels by 2.45 Ga. The distribution of Ce anomalies in Boolgeeda Iron Formation sediments further suggests that elevated oxygen levels were pervasive within the shallow marine realm and stable above the threshold required to produce a negative Ce anomaly.

The largest negative Ce anomalies are found within the middle of the upper and lower BIF intervals (Fig. 11A). The sinuous nature of the Ce anomaly depth plot is interpreted to reflect background negative Ce anomalies captured by primary BIF precipitates being suppressed by detrital influxes. Support for this theory exists in the depression of negative Ce anomalies (as indicated by Pr/Pr*) with increasing Al₂O₃ concentrations (> 65% or < 40%).

Some Boolgeeda Iron Formation samples contain both a negative Ce anomaly and a positive Eu anomaly (Fig. 9). It may have been possible to preserve positive Eu anomalies from hydrothermal vent fluids emerging at depth and to also capture negative Ce anomalies from an overlyingoxic water column at the transition from anoxic to oxic conditions. Anoxic conditions would have promoted the long-distance transport of REE + Y in the deep ocean, as REE + Y removal from the water column by precipitating Fe(III) and Mn(IV) oxyhydroxides would have been limited to shallow oxic environments. As deep reducing ocean waters were upwelled onto the continental shelf, positive Eu anomalies could have been captured by Fe(III) oxyhydroxides precipitating at, or above, the chemocline.

Positive Eu anomalies disappear up section, best demonstrated by the moving average curve (black line) in Fig. 11A. This is attributed to waning hydrothermal influence as the depositional environment became shallower, approaching the onset of Kungarra Formation deposition. The loss of a positive Eu anomaly may have been compounded by detrital dilution of primary seawater signatures (Fig. 11C), similar to the Ce anomaly.

Amongst the large-scale transition from deep to shallow water deposition - corresponding to waning hydrothermal fluids and higher detrital input - there are periods of punctuated trace element influx into the sediments. Two major intervals occur at 160 m and 153 m depth, while two relatively minor intervals are found at 148 m and 132 m depth (Fig. 7). The interval at 153 m represents the clastic diamicite, while the intervals at 160 m, 148 m, and 132 m depth represent interlaying of green mudstone/siltstone and Si-dominated IF associated with variable TiO₂ and Al₂O₃ concentrations and dichotomous SiO₂ concentrations (> 65% or < 40%).

By comparing the TiO₂ normalized (Fig. 7) and un-normalized (SI Fig. 9) major and trace element depth plots, the role of detrital versus autochthonous controls on IF trace element profiles can be distinguished. In the un-normalized plots, Ba, V, Cu, Co, Zn, U, and Cr all display elevated concentrations between 160 m and 146 m depth, peaking within the diamicite layer. Concentrations are also relatively high within the green mudstone/siltstone intervals and the Kungarra Formation, suggesting a strong detrital component contributes to total elemental concentrations. In fact, correlation plots of V, Co, Zn, and U versus Ti concentrations suggest detrital material represents the largest proportion of these elements’ concentrations throughout the Boolgeeda Iron Formation (SI Fig. 11). Deposition of the diamicite likely occurred at the climax of base level fall within the basin; the progressive increase in trace element concentrations leading up to the diamicite and subsequent decreases moving stratigraphically up from it likely reflects a regressive-transgressive cycle. The onset of this cycle may have coincided with glaciation, as supported by dropstones previously identified within the diamicite interval (Philippot et al., 2018). The green mudstone/siltstone intervals inter-banded with the Si-dominated IF lie at the margins of the regressive-transgressive cycle. As discussed above, these represent periods when the depositional environment was on the boundary between depositional conditions promoting primary BIF deposition and conditions dominated by detrital influx.

When normalized to TiO₂, only thin intervals of trace element enrichment at 160 m, 148 m, and 132 m remain. This suggests that Ba, V, Cu, Co, Zn, U, and Cr are all enriched in continental material, but that autochthonous enrichments are also important at 160 m, 148 m, and 132 m depth. The largest autochthonous enrichment occurs at 160 m, as concentrations of all elements in the Ti normalized plots are highest at this depth. Notably, iron speciation suggests a major change in the redox state of the water column at 160 m, supported by an increase in the Fe₃O₄/Fe₂O₃ ratio (Fig. 13). This dramatic change in Fe speciation may be reflected in the disappearance of coarse grained microplaty hematite above 160 m depth, and is accompanied by a shift in S concentrations from < 100 ppm in the lower BIF to > 400 ppm in the upper BIF interval (Fig. 6), which may indicate an increase in the background
marine S reservoir. This transition is also reflected by the S-isotopic data from pyrites at 160 m depth, which show the disappearance of MIF-S (Δ34S = 0‰) and δ34S values approaching -40‰ (Philippot et al., 2018). This suggestsoxic atmospheric conditions capable of preventing MIF-S preservation and marine S concentrations high enough to sustain sulfate reduction under non-S-limiting conditions (see Philippot et al., 2018 for a discussion). Textural evidence for strong sulfate reduction near 160 m depth may be found in pyrite microbeds (Fig. 5), in which small euhedral grains of pyrite lie parallel to primary bedding and are interstitial between larger magnetite grains. Small rounded pyrite inclusions are also found in some of the larger euhedral magnetite grains, supporting the early diagenetic formation of pyrite in this interval. It is possible these beds were produced biogenically during in situ sulfate reduction in shallow pore waters.

Following Philippot et al. (2018), we suggest the oxidative weathering of continental sulfides can explain the observations listed above. Support for continental weathering of sulfides is found in the Cr/Ti ratios, which are comparable to elevated values within the Timeball Hill formation previously reported by Konhauer et al. (2011). Those authors attributed the elevated Cr concentrations to acid weathering events occurring as O2 began to increase in the lead up to the GOE. Values from the Boolgeeda Iron Formation, superimposed on the temporal Cr/Ti trend of Konhauer et al. (2011), correspond well with elevated Cr/Ti ratios observed around the GOE (Fig. 8). High S concentrations associated with pyrite grains in the diamictite suggest that a reduced continental S source was, at the very least, available for oxidation, transport, and precipitation in marine sediments (Philippot et al., 2018).

Although marine S concentrations appear to have increased between deposition of the upper and lower BIF intervals, euxinic conditions were not prevalent. The FePy/FeHR ratio approaches the threshold of euxinic conditions (0.7) at 160 m but does not breach this threshold from one sample at 109 m depth within the Kungarra Formation mudstone (Fig. 13). This is not unexpected, as euxinic conditions would prevent the deposition of the IF. It is possible that euxinic conditions occurred in shallower environments proximal to continental margins. Fed by the oxidative weathering of continental sulfides, sulfate generated by sulfate oxidation would have dissipated further into the basin. The Kungarra Formation data suggests that euxinic conditions are approached as the depositional setting shallows towards a more sulfate rich environment.

Aside from the diamictite layer and interval at 160 m depth, S concentrations do not exceed 1 wt%, and MIF-S does not disappear at any other depth in the core (Philippot et al., 2018). The lack of significant S enrichments within anomalous intervals at 148 m and 132 m depth indicates against oxidative weathering of continental sulfides as a driver for these trace element enrichments, at least to the extent of that observed at 160 m depth. We propose enrichments at 148 m and 132 m are mechanistically different; they are more likely the result of local base level dynamics transferring material across the chemocline separating anoxic and oxic settings and concentrating trace elements at the interface between IF deposition and clastic sedimentation. This interface represents a geochemical boundary separating input from shallow waters with a more active sulfur cycle from anoxic Fe(II)-rich deep waters, favouring iron precipitation and trace element enrichment at their intersection.

6. Summary and conclusion

The Boolgeeda Iron Formation and overlying sediments of the Kungarra Formation provide a snapshot of marine conditions around GOE time. Major and trace element concentrations coupled with Fe speciation suggest shallow marine conditions that were mildly oxic and anoxic ferruginous conditions in deep water. These background conditions appear to have been intermittently perturbed by interaction with shallow waters that were more trace-element and sulfur rich. We suggest that these events were driven by oxic weathering of sulfides and locally increased marine S concentrations, particularly in shallow marine environments proximal to the continental margin. Within the Boolgeeda IF, one such event is preserved at 160 m depth. This horizon is marked by a dramatic change in Fe speciation, a large increase in Ti normalized trace element concentrations, S isotope signatures characteristic of atmospheric oxygenation (Philippot et al., 2018), and perhaps an increase in reduced carbon input as reflected by the disappearance of coarse grained microplaty hematite above 160 m depth. Further, it separates two intervals of BIF with drastically different S concentrations. These events may mark significant changes in the balance between continental and marine S sources and sinks.

Traditional proxies for redox conditions may be masked by the influx of detrital materials. Shifts in detrital flux are most likely the result of baselevel fluctuation and may represent local changes rather than a global phenomenon. The TCDP1 core preserves a shallowing upward sequence associated with waning hydrothermal input, and a punctuated interval of detrital input between 160 m and 148 m depth. Iron speciation suggests that the shallower deposits may record coastal waters that approached euxinic conditions.

The transition from the Boolgeeda IF to the overlying Kungarra Formation marks a significant change in the local depositional environment. Yet, the termination of BIF deposition and eventual deposition of glacial sediments that comprise the Meteorite Bore Member of the Kungarra Formation indicate a significant global transition that overprints the local signatures preserved in TCDP1. The Boolgeeda IF and Kungarra Formation appears to mark the onset of these global changes, culminating in the GOE.

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