Oncoidal granular iron formation in the Mesoarchaean Pongola Supergroup, southern Africa: Textural and geochemical evidence for biological activity during iron deposition

A. J. B. Smith¹,²,³ | N. J. Beukes¹,²,³ | J. Gutzmer¹,⁴,⁵ | A. D. Czaja⁶,⁷,⁸ | C. M. Johnson⁷,⁸ | N. Nhleko¹,⁹

¹Paleoproterozoic Mineralization Research Group, Department of Geology, University of Johannesburg, Johannesburg, South Africa
²Department of Science and Technology – National Research Foundation Centre of Excellence for Integrated Mineral and Energy Resource Analysis, University of Johannesburg, Johannesburg, South Africa
³Department of Geology, University of Johannesburg, Johannesburg, South Africa
⁴Helmholtz Zentrum Dresden-Rossendorf, Helmholtz Institute Freiberg for Resource Technology, Freiberg, Germany
⁵Department of Mineralogy, TU Bergakademie Freiberg, Freiberg, Germany
⁶Department of Geology, University of Cincinnati, Cincinnati, OH, USA
⁷Department of Geoscience, University of Wisconsin, Madison, WI, USA
⁸NASA Astrobiology Institute, University of Wisconsin, Madison, WI, USA
⁹Geological Survey and Mines Department, Mbabane, Swaziland

Abstract

We document the discovery of the first granular iron formation (GIF) of Archaean age and present textural and geochemical results that suggest these formed through microbial iron oxidation. The GIF occurs in the Nconga Formation of the ca. 3.0–2.8 Ga Pongola Supergroup in South Africa and Swaziland. It is interbedded with oxide and silicate facies micritic iron formation (MIF). There is a strong textural control on iron mineralization in the GIF not observed in the associated MIF. The GIF is marked by oncoids with chert cores surrounded by magnetite and calcite rims. These rims show laminated domal textures, similar in appearance to microstromatolites. The GIF is enriched in silica and depleted in Fe relative to the interbedded MIF. Very low Al and trace element contents in the GIF indicate that chemically precipitated chert was reworked above wave base into granules in an environment devoid of siliciclastic input. Microbially mediated iron precipitation resulted in the formation of irregular, domal rims around the chert granules. During storm surges, oncoids were transported and deposited in deeper water environments. Textural features, along with positive δ⁵⁶Fe values in magnetite, suggest that iron precipitation occurred through incomplete oxidation of hydrothermal Fe²⁺ by iron-oxidizing bacteria. The initial Fe³⁺-oxyhydroxide precipitates were then post-depositionally transformed to magnetite. Comparison of the Fe isotope compositions of the oncoidal GIF with those reported for the interbedded deeper water iron formation (IF) illustrates that the Fe²⁺ pathways and sources for these units were distinct. It is suggested that the deeper water IF was deposited from the evolved margin of a buoyant Fe²⁺ rich hydrothermal plume distal to its source. In contrast, oncolitic magnetite rims of chert granules were sourced from ambient Fe²⁺-depleted shallow ocean water beyond the plume.
1 | INTRODUCTION

The importance of biological activity in the deposition of Precambrian iron formations (IFs) has been the subject of protracted debate (e.g., Bekker et al., 2010; Beukes & Gutzmer, 2008; Kappler, Pasquero, Konhauser, & Newman, 2005; Klein, 2005; Konhauser et al., 2002). Commonly three models are proposed for biological activity relevant to iron oxidation and precipitation in producing IFs: indirect oxidation via free O$_2$ produced by oxygen-producing photosynthetic microbes (e.g., Cloud, 1973; Klein & Beukes, 1993); direct oxidation via chemolithoautotrophic iron-oxidizing bacteria (e.g., Konhauser et al., 2002); or direct oxidation via anoxygenic photoautotrophic iron-oxidizing bacteria (e.g., Kappler et al., 2005). Oxidation of Fe(II) may also occur using other electron acceptors such as nitrate (e.g., Kappler, Johnson, Crosby, Beard, & Newman, 2010). Despite these possibilities, all arguments in favour of biological activity during IF genesis suffer from the general lack of direct (i.e., textual) evidence for biological activity. Such textual evidence is provided by the occurrence of oncoids in the Sokoman and Animikie basin IFs (Knoll & Simonson, 1981; Planavsky et al., 2009) and microfossils and stromatolites in the Gunflint and Biwabik IFs (Barghoorn & Tyler, 1965; Planavsky et al., 2009), all approximately 1.9 Ga in age, on the Superior Craton.

Oncoids are a subtype of coated grains and are defined as biogenically encrusted grains (Peryt, 1983a,b). Except for the older examples noted above, modern examples of oncoids have been recorded in the shallow marine environment (e.g., Alshuaibi, Duane, & Mahmoud, 2012; Nguetchoua & Giresse, 2010). The term "oncoidal" or "globoidal" is also applied by Hofmann (2000) to a type of lamina shape for stromatolites that occur around grains, with the author also including oncoids in the classification of Archaean stromatolites. The occurrence of oncoids containing iron minerals in its biogenically formed coatings may thus be taken as evidence for the significance of microbial processes for the deposition of IFs in ancient sedimentary successions.

Older coated grains in ironstones have been reported in the Palaeoproterozoic Timeball Hill Formation of the Transvaal Supergroup of South Africa (Dorland, 1999). However, it is important to note that these grains are concentric and lack irregular rims and can therefore be classified as ooids similar to what is commonly seen in Phanerozoic ironstones (e.g., Garzanti, Haas, & Jadoul, 1989; Gehring, 1989; Kearsley, 1989), which do not necessarily require biological activity for its formation (Richter, 1983). In addition, such oolitic ironstones form in proximal marine to deltaic environments which is in contrast to more distal marine settings in which most micritic iron formations (MIFs) formed during the Palaeoproterozoic.

This study documents the discovery of a granular iron formation (GIF) from the Mesoarchaean Mozaan Group of the Pongola Supergroup of southern Africa, which was first reported briefly by Smith, Beukes, Gutzmer, Johnson, and Czaja (2012) at the Goldschmidt Conference in Montreal, Canada, during June 2012. The irregular topology of the granules’ coatings is similar to domal microstromatolitic textures and suggests a biogenic origin, defining the granules as oncoids. This suggests that microbial activity played a role during iron deposition in a shallow marine environment that took place penecontemporaneously to the deposition of MIF at greater water depth. A comparison of the iron isotopes of the GIF and associated deeper water IF is also presented and indicates distinct sources and pathways for Fe$^{2+}$ in the shallow and deep water depositional environments in the Mozaan Group.

2 | GEOLOGICAL AND STRATIGRAPHIC SETTING

The Mesoarchaean Pongola Supergroup on the Kaapvaal Craton of southern Africa (Figure 1a) is one of the oldest well-preserved laterally extensive supracratonic successions in the world (Beukes & Cairncross, 1991; Wronkiewicz & Condie, 1989). It consists of the essentially volcanic lower (~3.0–2.97 Ga) Nsuze Group and the dominantly siliciclastic upper (~2.96–2.84 Ga) Mozaan Group (Gutzmer, Beukes, Pickard, & Barley, 1999; Hegner, Kröner, & Hunt, 1994; Mukasa, Wilson, & Young, 2013; Wilson, Groenewald, & Palmer, 2013). The GIF that is the focus of this contribution is hosted by the Nconga Formation of the Odwaleni Subgroup of the Mozaan Group (Figure 1b). It is closely associated with massive and banded (for textural classification details see Beukes & Gutzmer, 2008) MIF (Figure 1c).

The Nconga Formation is a laterally extensive argillaceous unit of some 100 m thick in the Mozaan Group wedged between quartzite and shale of the Delfkom Formation below and mafic lava of the Tobolsk Formation above (Figure 1a). It is mainly composed of siltstone and shale, capped by a thin sharp-based quartzite, and contains two distinct magnetic mudstone units, one towards the base and another near the top. These units are similar in character to several others present in the Mozaan Group and the correlative Witwatersrand Supergroup that in some cases contain interbeds of MIF (Beukes & Cairncross, 1991; Smith, 2007; Smith, Beukes, & Gutzmer, 2013). The upper magnetic mudstone of the Nconga formation, however, differs from all others in the sense that it hosts the rather unique GIF described in this contribution.

Currently the GIF unit is known from two localities. Most details and samples for this contribution were obtained from an exploration drill core (PNG-4), drilled by Anglogold-Ashanti 20–25 km north northeast of Nongoma in the KwaZulu-Natal Province of South Africa in which the magnetic mudstone with two interbeds of GIF was intersected at depth of around 1,295 m (Figure 1a,c). The second locality is from outcrop on a ridge in the Kubuta-Mooihoek area of Swaziland (Nhleko, 2003), located approximately 90 km north northwest from the location of drill core PNG-4 (Figures 1a and 2). The stratigraphic position of the GIF in the outcrop is exactly similar to that in the drill core indicating that it is developed over an area of at least hundred or more km$^2$. However, in another well known outcrop area of the Nconga Formation in the Hartland area (Figure 1a), the GIF is not developed, although the host magnetic mudstone unit is present. This suggests that the GIF was only deposited in a rather small localized area of the original Witwatersrand-Mozaan depository (Figure 1a).

In the Kubuta-Mooihoek area, the GIF outcrops as two continuous, well-defined beds separated by a thin mudstone layer over an exposed strike length of some 300 m along a ridge (Figure 2a). The GIF beds and
mudstone interlayer have an average combined thickness of 0.8–1.0 m. Top surfaces of both the GIF beds display hummocky wave ripple marks. These are especially well developed along the top surface of the lower GIF bed (Figure 2a). The lower GIF bed also contains good examples of combined hummocky and linear wave ripple marks (Figure 2c). The GIF beds typically display poorly defined flat bedding but some cross-bedding is present (Figure 2d). The top of the upper GIF bed shows reworked granule surfaces in places that are sharply overlain by MIF with abundant angular flat mud sherd or chips in places (Figure 2e). Along strike the MIF also contain interlaminated granule lenticles composed of granules similar to those in the immediately underlying GIF (Figure 2f). The GIF contains mud laminae, which in some places are highly silicified and in others Fe-rich. In places the mud laminae have a broken up appearance with rip-ups occurring above them (Figure 2g). The GIF beds occur as stacked upward fining graded granule layers (i.e., graded beds; Figures 2h and 3a–c). The layers that are in the order of 5–10 cm thick display poorly defined flat to wavy bedding with some low angle discontinuities that could represent part of hummocky cross-stratification (Figure 3a,c). The bases of the upward fining granule layers are marked by load casts and the top by mud drapes (Figures 2h and 3a). Subangular chert intraclasts occur throughout (Figures 2h and 3a).

In the studied drill core (Figure 1c), the Nconga Formation consists of 40 m of upward coarsening shale-siltstone followed by 50 m of upward fining siltstone-shale that becomes slightly magnetic towards the top before it is overlain with sharp gradational contact by a 20-cm-thick silicate facies feluinite (terminology after Beukes & Gutzmer, 2008). The feluinite is overlain with sharp contact by 50 cm of GIF. The GIF unit comprises three stacked graded beds of granular magnetite in chert (Figure 3b). A brown, massive silicate facies IF, also termed silicate facies feluinite, sharply overlies the GIF. The feluinite, which is 2.6 m thick, is again overlain with sharp basal contact by 50 cm of three stacked beds of GIF (Figure 3c). Lenses of GIF, representing starved ripples, occur in the feluinite immediately below the GIF (Figure 1c). The GIF is overlain by 1 m of mixed facies micro-banded IF, also termed mixed facies ferhythmitite (terminology after Beukes & Gutzmer, 2008) that contains green chert bands. The ferhythmitite grades upwards into brown feluinite (typical magnetic mudstone reported by Smith et al., 2013) that is overlain by a quartzite with a sharp erosive contact.

The depositional age of the Nconga IFs is constrained by the deposition of the Pongola Supergroup that has been placed at a maximum of 2,985 ± 1 Ma (U-Pb zircon age) by the felsic volcanic rocks of the Nsuze Group (Hegner et al., 1994) and a minimum of 2,954 ± 9 Ma (U-Pb zircon age) by the Tobolsk volcanics in the upper part of the Mozaan Group (Mukasa et al., 2013).

3 METHODOLOGY

Five samples of IF and two samples of GIF (Table 1) were taken from the drill core (PNG-4) for this study, as the drill core is fairly pristine and has only been affected by lower greenschist facies regional metamorphism which would have had a minimal effect on the depositional and diagenetic minerals, which are dominated by non-hydrous phases (i.e., chert, oxides and carbonates) that have not been recrystallized. Surface samples were not used for this study, as they have been affected by supergene alteration, where, for example, oxidation of all magnetite to haematite may occur.
3.1 Petrography and mineralogy

X-ray powder diffraction (XRD) was conducted on milled powders of the studied units to identify major minerals present. Measurements were carried out using a Panalytical X'Pert diffractometer with an X'Celerator detector housed at Spectrum, the central analytical facility of the Science Faculty at the University of Johannesburg. Analyses of the measured XRD patterns were carried out on X'Pert HighScore Plus software. Further diffractometer settings are reported in Smith (2007). This was complemented by petrographic studies on seven polished thin sections of GIF and MIF using light and scanning electron microscopy (SEM). SEM studies were conducted on a set of carbon-coated polished thin sections with a Jeol 5600 SEM equipped with a Noran Si(Li) energy dispersive X-ray spectrometry (EDS) detector, with an ultra-thin beryllium window, at Spectrum. The samples were examined under high vacuum with a 15 kV, 15 mA electron beam by means of secondary (SEI) and backscattered electron (BSE) imaging. Minerals were identified by semi-quantitative EDS-spot analyses. Additional BSE imaging and EDS analyses were performed on polished blocks prepared from both the lower and upper GIF beds in the drill core at the University of Wisconsin, Madison using a Hitachi S-3400 variable pressure scanning electron microscope equipped with a Si(Li) EDS detector. Analyses were performed at high vacuum and with 15 kV accelerating voltage.

FIGURE 2 Field photographs of the Nconga Formation GIF and MIF outcrop in the Kubuta-Moolhoek area of Swaziland. (a) The general outcrop illustrating two steeply dipping GIF beds separated by an Fe-rich mud bed draping the hummocky top surface of the lower GIF bed. (b) Close up photograph of the hummocky wave ripple marks on the lower GIF bed (plan view). (c) Example of a hummocky and linear wave rippled surface in the lower GIF bed (plan view). (d) Cross-bedding in the GIF. (e) Reworked granule surface at top contact of upper GIF bed with overlying MIF. MIF contains reworked mud shads. (f) Bedding parallel granule lenticles in MIF overlying the upper GIF bed. (g) Silicified mud rip-ups above a partially broken up silicified mud lamina in GIF. (h) Sedimentary features in the GIF which include graded bedding, chert intraclasts, mud intraclasts and mud drapes.
3.2 | Geochemistry

A set of seven samples of the IF and GIF was analysed for major element composition (Table 1) using X-ray fluorescence spectrometry at Spectrum using fusion beads. In addition, a set of four samples of the IFs was sent to ACME laboratories in Vancouver, Canada for rare earth element (REE) analysis by ICP-MS (Table 1). For the samples analysed at ACME laboratories, concentrations above 10 times the detection limit have a precision of 15%. Analytical quality was checked using certified standard reference materials. Two samples of GIF were analysed for REE at the Geochemistry Laboratory at Jacobs University, Bremen using ICP-MS (Table 1). All data produced at Jacobs University have been interference-corrected (e.g., BaO on Eu) and analytical quality was frequently checked by analysing internal and external reference materials such as IF reference standards IF-G (Isua BIF, Greenland; e.g., Viehmann, Bau, Hoffmann, & Münker, 2015) and FeR-3 and FeR-4 (Temagami BIF, Canada; e.g., Bau & Alexander, 2009).

Calcite-bearing whole rock samples of the GIF and ferhythmite were analysed for their carbon and oxygen stable isotope composition (Table 1) at the Stable Isotope Laboratory in the Department of Earth Sciences, University of Cape Town. Analyses were carried out by selectively dissolving the carbonate minerals in phosphoric acid at 50°C, extracting the produced carbon dioxide gas and analysing it on a DeltaXP mass spectrometer in dual inlet mode. The internal standard used for the carbonate measurement was the NM (Namaqualand Marble) standard. Measured values were corrected by applying fractionation values for calcite (α = 1.009; Al-Aasm, Taylor, & South, 1990).

The Fe isotope compositions of one specimen of each of the three distinct lithologies (felutite, ferhythmite and GIF) were measured. Multiple ~3 mm by 3 mm regions within each specimen were sampled using a tungsten-carbide hand scribe. These samples included two from the ferhythmite (two each of the silicate facies, magnetite facies and mixed facies) and four from the GIF (three from granule-rich areas and one from a minnesotaite-bearing chert devoid of granules). The minnesotaite-bearing chert sample from the GIF contained a small amount of magnetite. In order to measure the Fe isotope composition of the minnesotaite alone, a strong magnet was used to remove as much of the residual magnetite as possible.

The resulting powders from all of the samples were dissolved in heated Savillex beakers using ultrapure, concentrated HF and HNO₃ for 24 hr. The samples were dried and re-suspended in ultrapure 8 M HCl until complete dissolution was achieved. The iron was separated from the rest of the matrix by anion exchange chromatography (Beard & Johnson, 1999; Beard, Johnson, Von Damm & Poulsen, 2003). All samples were measured for total Fe contents by the Ferrozine method (Stookey, 1970) before and after chromatographic separation to ensure that there was no loss of Fe. Yields through the columns were all >90% and most were ≥98%. Isotopic analyses of the purified Fe were performed using a Micromass Isoprobe MC-ICP-MS and an Aridus desolvating nebulizer following the methods of Albarède and Beard (2004) and Beard et al. (2003).

Iron isotope data are reported here in standard delta notation as both δ⁵⁶Fe and δ⁵⁷Fe, in units of per mil (‰):

$$\delta^{56}\text{Fe} = \left( \frac{^{56}\text{Fe}^{54}\text{Fe}}{^{54}\text{Fe}^{54}\text{Fe}} \right)_{\text{sample}} - 1 \times 10^3$$

(1)

$$\delta^{57}\text{Fe} = \left( \frac{^{57}\text{Fe}^{54}\text{Fe}}{^{54}\text{Fe}^{54}\text{Fe}} \right)_{\text{sample}} - 1 \times 10^3$$

(2)

The reference ratio for these values is the average of igneous rocks (Beard et al., 2003). The IRMM-014 standard has a δ⁵⁶Fe value from the ferhythmite (two each of the silicate facies, magnetite facies and mixed facies) and four from the GIF (three from granule-rich areas and one from a minnesotaite-bearing chert devoid of granules).
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of −0.09‰ on this scale (Beard & Johnson, 2004). Analytical precision and accuracy were determined by multiple analyses of samples, including multiple analyses of the same solution, as well as test solutions made of laboratory standards of known Fe isotopic composition, namely IRMM-014, J-M and HPS Fe. Repeat analyses of individual sample solutions yield a 2-σ error in δ^{56}Fe values of ±0.07‰ (n = 14).

4 | RESULTS

4.1 | Petrography and mineralogy

The GIF can be described as a massive grey chert rock that contains abundant black round and oval-shaped magnetite-coated granules (Figures 3b,c and 4a) of 0.2–2 mm in size. The coated grains are irregular in outline and do not have a concentric internal texture (Figure 4a,c,d). The coated granules are thus very distinct from chemically precipitated free-rolling ooids (Richter, 1983). Many of the granule rims display internal domal structures as well as irregular laminations of various sizes that are similar in appearance to stromatolitic microtextures (Figure 4c–f). The stromatolite-shaped domes are visible in cross section (Figure 4c,d) and plan view (Figure 4e), depending whether the thin section intersects the granules through their cores or rims, respectively. The cores of granules are composed of microcrystalline quartz (chert) that in turn is overgrown by rather poorly defined zones of calcite intergrown with microcrystalline quartz. The rims of the granules are then coated by magnetite with subordinate calcite. These coatings have variable thicknesses (<10–100 μm; Figure 4d,f). Where well developed, the magnetite ± calcite coatings

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FIGURE 4  Transmitted light optical photomicrographs (a,b) and SEM images (c–f) illustrating the important petrographic features of the GIF occurring in the Nconga Formation. (a) General texture illustrating magnetite (Mag) and calcite (Cal) coated chert (Qz) granules in a chert matrix. Red blocks indicate magnetite and calcite rim fragments occurring in the chert matrix. (b) Minnesotaite (Mns) needles in the chert matrix. (c, d) Cross section view of domal features, similar in appearance to microstromatolites, in magnetite rims of granules. (e) Plan view of domal features in magnetite rims of granules with minor minnesotaite in the chert matrix. (f) Irregular lamination in domal rims of granules.
display internal, irregular to very fine wrinkly laminations (Figure 4f). Fragments of the coatings are also visible in the chert matrix between the granules (Figure 4a). Fe-bearing carbonates are notably absent (Figure 5). The magnetite crystals in the coatings are euhedral and very fine, 2–20 μm in size. In surface outcrop samples, the magnetite has been replaced by haematite due to supergene alteration. However, no haematite is present in any of the drill core samples of the GIF. The oval shape and bedding-parallel orientation of many of the grains suggest they were affected by compaction, although it could also be due to a sorting effect.

The granules define graded beds that are 4–5 cm thick, with the number and size of the coated grains decreasing from the bottom to the top of the individual beds (Figure 3b,c). Granules are enclosed in a microcrystalline quartz (chert) cement or matrix, with traces of minnesotaite occurring (Figure 4b). Crosscutting veins are filled with calcite.

The felutite that occurs between the GIF units and above the ferhythrite is best described as a massively textured silicate facies IF with stilpnomelane as the dominant mineral phase (Figure 6a,b). The stilpnomelane occurs as fine (10–30 μm) needle-shaped crystals surrounded by microcrystalline quartz. Magnetite is present as isolated, sub- to anhedral crystals in a wide range of sizes (<10–100 μm) that overgrow and replace stilpnomelane (Figure 6b). Traces of fine crystalline pyrite occur.

The ferhythrite that immediately overlies the upper GIF unit is a mixed oxide and silicate facies microbanded IF (Figure 6c). The microbands comprise magnetite, quartz, Fe-silicates (stilpnomelane and minnesotaite) and calcite in variable proportions (Figure 6c,d). The magnetite-bearing microbands contain small (≈10 μm), subhedral magnetite aggregates associated with quartz and minor stilpnomelane and calcite. The calcite, where present, appears to crosscut magnetite microbands (Figure 6d). Large (≈200 μm), slightly compacted spheroids of stilpnomelane and calcite occur locally in the magnetite microbands. The silicate microbands consist of fine stilpnomelane and minnesotaite needles enclosed in quartz. The mixed silicate-calcite microbands are similar to the silicate microbands except that calcite occurs as anhedral, isolated crystals. Contacts between microbands are generally sharp (Figure 6c), but can occasionally be gradational. Just as in the felutite, traces of fine crystalline pyrite also occur in the ferhythrite (Figure 6d).

4.2 | Geochemistry

The SiO₂ content of the GIF varies between 55.6 and 79.4 wt % (Figure 7a; Table 1). The other two major constituents are Fe₂O₃ (17.3–24.0 wt %) and CaO (2.34–13.1 wt %). These compositions reflect the major mineral constituents, which are quartz, magnetite and calcite. All other major elements show concentrations of <0.5 wt %. Trace elements show extremely low contents that are generally close to or below detection limits (Table 1). Only Ti and Sr concentrations exceed 50 ppm.

Compared to the GIF, the felutite has significantly higher concentrations of Fe₂O₃ (44.8–49.0 wt %) and lower contents of SiO₂ (39.5–45.2 wt%). Concentrations of Al₂O₃ (1.59–3.33 wt %) and MgO (2.36–4.10 wt %) are also higher in the felutite (Figure 7a; Table 1), as are concentrations of trace elements. The ferhythrite, in turn, contains similar SiO₂ concentrations (41.5–74.1 wt %) to the GIF and rather variable Fe₂O₃ (17.4–45.6 wt %) contents, with Al₂O₃ and MgO
contents intermediate to that of felutite and GIF (Figure 7a). CaO contents (4.34–7.16 wt %) in the ferhythmite are in the same range as in the GIF. As with the GIF, only Ti and Sr show contents in excess of 50 ppm in the ferhythmite.

Rare earth element concentrations in the GIF are exceptionally low with a total (ΣREE) of only 2.1–3.7 ppm. ΣREE is somewhat higher in the ferhythmite (8.1–10.8 ppm) and highest in the felutite samples (29.4–38.4 ppm). Post-Archaean Australian Shale (PAAS) normalized plots of the REEs and Y (inserted between Dy and Ho after Bau & Dulski, 1996) for the studied samples (Figure 7b) show slight heavy REE (HREE) enrichment over light REE (LREE) in the GIF. The stratigraphically upper GIF unit shows lower REE contents and prominent positive Eu and Y anomalies when compared to the lower GIF unit. The ferhythmite samples show positive Eu and Y anomalies, and one sample shows a true positive Ce anomaly (Bau & Dulski, 1996). HREE enrichment is also observed. The felutite samples show flat normalized REY patterns with no prominent anomalies.

Stable isotope analyses of calcite in the GIF and ferhythmite show δ¹⁸O₁𝑃D ranges between −22.0 and −21.5‰ relative to PeeDee Belemnite (PDB). The δ¹³C₁PDB ranges between −15.7 and −11.6‰ (Figure 7c; Table 1).

The δ⁵⁶Fe values of magnetite in felutite (sample PNG4-1294) range from −0.18 to −0.02‰ (average = −0.10 ± 0.23‰ 2-SD, n = 2; Table 2 and Figure 8). In the ferhythmite (sample PNG4-1297.15), magnetite-rich microbands have δ⁵⁶Fe values that range from −0.01 to +0.04‰ (average = +0.01 ± 0.07‰ 2-SD, n = 2), silicate facies microbands have δ⁵⁶Fe values that range from −0.12 to +0.04‰ (average = +0.01 ± 0.07‰ 2-SD, n = 2), and the mixed facies microbands have δ⁵⁶Fe values that range from −0.31 to −0.12‰ (average = −0.21 ± 0.27‰ 2-SD, n = 2) (Table 2 and Figure 8). For the GIF (sample PNG4-1298), magnetites have δ⁵⁶Fe values that range from +0.39 to +0.48‰ (average = 0.44 ± 0.09‰ 2-SD, n = 3). Minnesotaite in chert cement of coated granules has a δ⁵⁶Fe value of +0.04‰ (n = 1; Table 2 and Figure 8).

5 | DISCUSSION

The petrography and isotope geochemistry provide insight into the mineral paragenesis of the GIF and the associated iron-rich units, whereas the field observations, lithostratigraphy and geochemistry provide insight into the depositional environment of all iron-rich units. These characteristics are discussed with the aim of providing a depositional model for this iron-rich succession as well as a model for the origin of the structures in the granule coatings of the GIF.

5.1 | Mineral paragenesis

Microcrystalline quartz (chert) is the most common mineral in the felutite, ferhythmite and GIF. All the iron-bearing minerals occur closely associated and intergrown with chert, except in the GIF where the magnetite and calcite only occur as rims around chert nuclei (Figure 4) that are suspended in a chert matrix (Figure 3). These relations, as well as the consistently high SiO₂ contents of all samples, would suggest continuous precipitation and deposition of silica in the background in all IF units of the Nconga Formation. The microcrystalline nature of the quartz suggests that it was derived from recrystallization of an amorphous precursor (Clout & Simonson, 2005; Maliva, Knoll, & Simonson, 2005). Recent studies of mixed Fe-Si gels indicate that this was the most likely primary precipitate for Si and Fe in the Archaean oceans, and later burial diagenesis, dewatering and recrystallization of such materials would produce a mixture of Fe minerals and quartz (Rasmussen, Krapež, Muhling, & Suvorova, 2015; Wu, Percak-Dennett, Beard, Roden, & Johnson, 2012; Zheng, Beard, Reddy, Roden, & Johnson, 2016). The bulk Fe:Si ratios of the samples analysed in this study span the range of Fe-Si gels studied in experiment.

Stilpnomelane and minnesotaite are common in both the ferhythmite and felutite and are common silicates in diagenetic to low-grade IF mineral assemblages (Klein, 2005). Amorphous Fe²⁺-rich silica gel
is commonly regarded as precursor to such silicates (Klein, 2005) and could have been precipitated in a non-redox process. Alternatively, Fe$^{2+}$-silicates may also form as the product of diagenetic reactions where Fe(III)-Si gels were reduced in situ (Percak-Dennett et al., 2011), or interacted with porewater aqueous Fe(II) (Zheng et al., 2016). Another possibility is that the Fe$^{2+}$-silicates formed from the diagenesis of Fe$^{2+}$-rich gels.
<table>
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$^a$Repl. = replicates. Repeated letters refer to multiple analyses of the same sample aliquot. Different letters refer to distinct sample aliquots processed separately.

$^b$Based on petrographic analyses.

$^c$Averages of mean values for multiple samples of the same mineral type within a core.
of precipitated green rust, a ferrous-ferric hydroxyl salt (Halevy, Alesker, Schuster, Popvitz-Biro, & Feldman, 2017). Indeed, the only mild effect of compaction on the shape of stilpnomelane spheres suggests a diagenetic rather than synsedimentary origin of stilpnomelane.

Two texturally distinct types of magnetite are recognized. Larger euhedral and isolated magnetite crystals occur in the felutite (Figure 6b), whereas minute (~2–20 μm in size) euhedral to subhedral magnetite crystals form aggregates or massive monomineralic microbands in the ferhythmite (Figure 6c,d) and rims around granules in the GIF (Figure 4f). Based on textural relations, the larger euhedral magnetite crystals in the felutite may well replace stilpnomelane, indicating that they are late in the paragenetic sequence. This euhedral magnetite is thus interpreted as forming by low-grade metamorphic decomposition of stilpnomelane to magnetite and quartz.

In contrast, minute magnetite crystals appear to be finely intergrown with microquartz and calcite and appear to be very early in the mineral paragenesis. This magnetite is thus considered to be early diagenetic in origin. This is consistent with in situ O isotope studies of magnetite in IFs that show fine-grained pure magnetite commonly has relatively low δ18O values, indicating an early, low-temperature formation (Li et al., 2013). The minute magnetite in the ferhythmite and GIF are inferred to have formed at the expense of an initial Fe3+-oxyhydroxide-silica precipitate. Possible origins for the initial precipitate include oxidation of Fe2+-aq by free molecular oxygen generated by photosynthesis (Klein & Beukes, 1993), chemolithoautotrophs (Konhauser, 2007; Konhauser et al., 2002) or anoxygenic phototrophic iron-oxidizing bacteria (Kappler et al., 2005; Posth, Hegler, Konhauser & Kappler, 2008). The stable Fe isotope data place constraints on these
possible models as discussed below in the section titled, Constraints on Iron Source and Deposition. It is unlikely that the fine-grained magnetite was produced by metamorphic breakdown of Fe carbonates (e.g., McCollom, 2003), which would produce abundant hydrocarbons and likely retain residual siderite, neither of which is observed in our samples.

There are several possible pathways for the diagenetic formation of magnetite. Diagenetic reduction in Fe$^{3+}$ through the oxidation of organic matter is a possible origin of magnetite in the GIF and the ferhythmite, and magnetite is a common product of microbial dis-similatory iron reduction (e.g., Roden & Lovley, 1993). Carbonates in both the GIF and ferhythmite are Ca-rich, however, and contain very little to no Fe (Figure 5), as might be expected if associated with microbial iron reduction. Iron-rich carbonates are common in other Mesoarchaean BIFs in the Witwatersrand and Pongola Supergroups as well as in Neoarchaean BIFs of the Transvaal Supergroup, consisting of predominantly ankerite and siderite that have very negative $\delta^{13}C$ values that indicate inheritance through oxidation of organic matter (Heimann et al., 2010; Smith, 2007; Smith et al., 2013). The Fe-poor nature of the carbonates in the GIF and ferhythmite units studied here suggests another pathway for carbonate formation that is not related to magnetite formation. Alternatively, the fine-grained magnetite in the GIF and ferhythmite could be related to a non-redox reaction of Fe$^{3+}$ oxyhydroxides with Fe$^{2+}$-rich fluids in the water column and in the sediments (Ohmoto, 2003) and is a possible formation pathway for fine-grained magnetite in the Nconga Formation. Recent experimental studies of Fe-Si gels, however, indicate that only limited conversion of Fe$^{3+}$ hydroxides occurs in the presence of aqueous Fe$^{2+}$ (Zheng et al., 2016), insufficient to produce magnetite stoichiometry for Fe$^{2+}$, even using aqueous Fe$^{2+}$ contents of ~1 mm, which greatly exceeds most estimates for Archaean seawater (e.g., Czaja et al., 2012; Holland, 1984). It is therefore possible that if the Fe$^{3+}$ precursor sediment was an Fe$^{3+}$-Si gel and not Fe$^{3+}$ hydroxide, conversion to a mixed Fe$^{2+}$-Fe$^{3+}$-Si gel that, upon dewatering, produced magnetite and quartz, may in fact require microbial iron reduction despite the absence of Fe-bearing carbonates.

The light $\delta^{13}C$ signature of the calcite (Figure 5c) in the rims of the granules in the GIF indicates that carbonate was likely derived through oxidation of organic carbon. It is unclear, however, what the electron acceptor may have been. Sulphate (SO$_4^{2-}$) was unlikely to have been the oxidant, as this would have formed sulphide, and pyrite is all but absent from the studied samples (only trace amounts occur in the IF and none in the GIF). In addition, ferric iron (Fe$^{3+}$) would not be thought to have been the oxidant, as Fe-bearing carbonates (ankerite or siderite) are absent in the studied samples, as noted above. In their detailed study of the Kuruman IF, Heimann et al. (2010) noted that clear evidence for microbial Fe$^{3+}$ reduction was supplied by the occurrence of haematite inclusions in Fe-bearing carbonates (ankerite and siderite) that simultaneously had negative $\delta^{13}C$ and positive $\delta^{56}Fe$ values. The absence in our samples of Fe-bearing carbonates, as well as haematite, makes it difficult to argue for Fe$^{3+}$ as the electron donor that was coupled to organic carbon oxidation to produce the low $\delta^{13}C$ calcite. A metamorphic origin for the calcite is also considered unlikely, as it has no exclusive mineral association and therefore shows no petrographic evidence for being part of a metamorphic mineral assemblage, for example an exclusive association with magnetite if it would have been derived from precursor siderite. The calcite texture reported here is also very different from contact metamorphic calcite associated with grunerite formed from the breakdown of iron-rich carbonates documented in the Scotts Hill Member IF which occurs stratigraphically below the Nconga Formation in the Mozaan Group (Smith, 2007).

We speculate that, in the absence of a clear mineralogical record for sulphate or Fe$^{3+}$ reduction, that oxidation of organic carbon might
have occurred via an oxidant that did not leave a mineralogical byproduct, and hence may have been a mobile or volatile phase. One possibility is that the oxidant was nitrate \( \text{NO}_3^- \), which could have participated via the microbially mediated reaction (Castanier, Le Métayer-Levrel, & Perthuisor, 2000; Konhauser, 2007):

\[
2(\text{CH}_2\text{O}) + \text{NO}_3^- + \text{Ca}^{2+} \rightarrow \text{CaCO}_3 + \text{CO}_2 + \text{NH}_4^+ \tag{3}
\]

We suggest that nitrate may have existed in the water column at 2.9 Ga, based on the increasing evidence for incipient oxygen contents, including in shallow marine settings, as far back as 3.2 Ga based on Cr and Mo stable isotopes, as well as the combination of Fe and U-Th-Pb isotopes (Crowe et al., 2013; Planavsky et al., 2014; Satkoski, Beukes, Li, Beard, & Johnson, 2015). Although equilibrium thermodynamic relations suggest that nitrate is unlikely to coexist with aqueous \( \text{Fe}^{2+} \), significant quantities of aqueous \( \text{Fe}^{2+} \) and nitrate is found in pore fluids in modern marine settings, dependent upon diagenetic and authigenic microbial cycling (e.g., Laufet al., 2016).

Direct evidence for nitrate in the environment in the late Archaean comes from N isotopes, where positive \( \delta^{15}\text{N} \) values in Neoarchaean rocks have been interpreted to reflect nitrate cycling (Godfrey & Falkowski, 2009; Thomazo & Papineau, 2013), although interpretation of N isotope data in Archaean rocks can be difficult (e.g., Ader et al., 2016; Stüeken, Kipp, Koehler, & Buick, 2016). To our knowledge, however, there are no N isotope data from Mesoarchaean rocks similar to those studied here that provide direct evidence for nitrate cycling.

### 5.2 Depositional setting

The Nconga Formation is marked by a very close and genocetic association of microbanded IF (ferrythmite), massively textured IF (felutite) and GIF. The textural difference between GIF and the IF can at least partly be attributed to different hydrodynamic conditions in the depositional environment (Simonson & Goode, 1989). Ferrythmite and felutite are generally associated with deep water, below wave base environments (Figure 9). The GIF, in contrast, is marked by the occurrence of coarse-coated grains that require formation on a shallow submerged shelf with constant wave action that was locally able to rework chert precipitates (Figure 9). As thin interbeds of GIF are sandwiched between deeper water IF deposits (Figure 1c), it may be assumed that granules were washed in from the shallow submerged shelf by storm wave surges into deeper water environments (Figure 9). This interpretation is supported by the recognition of the following features: cross-bedding (Figure 2d); internal low angle cross-lamination (Figure 3a,c); graded bedding (Figures 2h and 3a–c); load casts and mud drapes at the base and top of graded beds, respectively (Figures 2h and 3a); subangular chert intraclasts (Figures 2h and 3a); reworked granule surfaces at the top of GIF beds (Figure 2e); granule lenticles within MIF overlying the GIF (Figure 2f); partially broken mud laminae with overlying rip-ups of the mud laminae (Figure 2g); hummocky and linear wave ripple marks (Figure 2b,c); and fragments of the magnetite-calcite coatings in the chert matrix (Figure 4a). The felutite below the upper GIF unit contains some starved ripples of GIF (Figure 1c), illustrating that some of the coated grains were transported as traction load into the depositional environment of the MIF (Figure 9). The quartzite unit that caps the deep water iron-rich unit does so with an erosive contact (Figure 1c), most likely marking a forced regression (Posamentier, Allen, James, and Tesson (1992) that occurred after the deposition of the iron-rich units. In sequence stratigraphic terms, the IFs in the Mozaan Group are considered to have been deposited in starved shelf settings developed during periods of maximum rates of relative sea-level rise in the basin, that is along maximum flooding surfaces (Beukes & Caimcros, 1991).

As is typical for IFs, felutite, ferrihydrite and GIF of the Nconga Formation are all marked by very low concentrations of constituents reflecting detrital influx (\( \text{Al}_2\text{O}_3, \text{TiO}_2, \text{Zr} \); Table 1). Concentrations in the GIF, however, are exceptionally low and significantly lower than in felutite and ferrihydrite. This may suggest that the depositional environment of the GIF was well shielded from detrital input from the continent. Here, we suggest this sheltered shallow environment to have been a submerged palaeo-high in the Mozaan Basin in the form of a shelf bank isolated from land (Figure 9). Such a setting would also explain the rather restricted distribution of the GIF, surrounded by magnetic mudstone, in the Ngocna Formation and the larger original Witwatersrand-Mozaan basin (Figure 1a).

The deep water IFs in the Nconga Formation comprise only mixed oxide and silicate facies ferrihydrite and silicate facies felutite. Other IFs in the Mozaan Group and the correlative West Rand Group of the Witwatersrand Supergroup show more complete stratigraphic sequences (Smith et al., 2013). From a distal to proximal depositional setting, oxide facies is found to grade into mixed oxide-carbonate-facies grading into silicate facies and finally into iron-rich mudstone and iron-poor shale and quartzite in the most proximal settings (Smith et al., 2013). The abundance of silicate facies IF, lack of pure oxide facies IF and the top erosive contact with quartzite in the studied sequence of the Nconga Formation suggest that only the more proximal environments are preserved in the studied drill core. The original lateral facies distribution in the depositional environment of the Nconga Formation can only be assumed to have been a complete mineralogical facies sequence (Figure 9).

### 5.3 Origin of structures in granule rims

The presence of stratiform and conical stromatolites in partly silicified dolostone has been established in the lower Nsue Group by Beukes and Lowe (1989) and evidence for sediment-stabilizing bacterial mats has been documented in the quartzites of the Ntombe (Noffke, Hazen, & Nhleko, 2003) and Sinqeni Formations (Noffke, Beukes, Bower, Hazen, & Swift, 2008) of the Mozaan Group. These occurrences illustrate that biological activity in the form of filamentous bacteria was likely present at earlier times during the deposition of the Pongola Supergroup than the Nconga Formation.

The minute domal textures and irregular layering observed around the granules that resemble stromatolites (Figure 4c–f) along with the carbon isotope composition of the calcite in the rim (Figure 7c)
strongly suggest a biological influence on the precipitation of the iron-rich rims. These rims are therefore interpreted to be microstromatolites that grew around the granules. The round and oval-shaped chert cores of the granules would suggest that precipitation of an iron-rich phase occurred on the rims of chert peloids that were being shaped by episodic reworking, most likely by wave action. Becausestromatolites grow upwards towards sunlight, the rolling of these peloids on the seafloor due to wave reworking also explains the multi-directional nature observed in the microstromatolites coating the granules (Figure 4c,d). Further evidence for a direct role by biological activity is provided by marked negative values for δ13C in calcite intimately associated with magnetite (Figure 7c). Such negative δ13C values indicate carbon that was sourced from the oxidation of organic carbon and strongly suggests that organic matter contributed as the source of carbon for carbonate mineralization (Des Marais, 2001; Schidlowski, 1995). Furthermore, the likely biological origin of the granule coatings indicate that they can be classified as oncoids, which are defined as biogenically encrusted grains (Peryt, 1983a) and are also classified as a stromatolite subtype (Hofmann, 2000). The Nconga GIF can therefore be classified as an oncoidal GIF.

Iron precipitates responsible for oncoidal textures could have been deposited by either chemolithoautotrophic (Konhauser, 2007; Konhauser et al., 2002) or anoxygenic phototrophic iron-oxidizing bacteria (Kappler et al., 2005; Posth et al., 2008) forming strong microbial films or mats (Emerson & Revsbech, 1994) around chert peloid nuclei to survive in the wave-dominated shallow marine environment. Such microbial films are well-known to trap detrital particles (Kearsley, 1989), but in the absence of such detritus in case of the Ncongo oncoidal GIF the films formed around consolidated nuclei of chert and acted as chemical traps for iron (Fortin, Ferris, & Beveridge, 1997). The bacterial films then grew in the shape of domal microstromatolites. Successive microbial films around the grains created the irregular layering (Figure 4f) and caused chert and organic material to be trapped.

It has been suggested that bacterial surfaces could have served as nucleation sites for iron mineralization in IFs (Konhauser, 1998; Konhauser & Ferris, 1996; Warren & Ferris, 1998). In microbial mats from Icelandic hot springs many contemporary examples have been studied of bacterial cells being completely encrusted by iron-rich precipitates, potentially enhancing their preservation potential (Ferris, 2000; Konhauser & Ferris, 1996). These encrusted cells show morphology and layering rather similar to that of the microstructures in the Ncongo oncoids, even though the contemporary examples are smaller in size.

It should be noted that Dodd et al. (2017), who documented haematite filaments, carbonate rosettes and magnetite-rimmed granules in the Palaeoarchaean Nuvvuagittuq supracrustal belt (NSB) jaspers of Quebec, Canada, state that the latter granules are comparable to the ones in the Ncongo GIF as briefly presented by Smith et al. (2012). Furthermore they interpret the granules in the NSB jaspers to be diagenetic and that biomass oxidation played a major part in their growth. The implication is that a diagenetic origin for the granules in the Ncongo GIF could be considered. However, although there are some similarities such as granule sizes and the presence of magnetite and chert, there are several marked differences between the Ncongo granules and the NSB jasper granules: the magnetite rim morphologies are drastically different, with the coarser, angular and euahedral magnetite in the NSB jasper granule rims not completely encapsulating the granules and lacking any domal structures; where calcite is a major constituent in the Ncongo granules, it is mostly absent from the NSB jasper granules;apatite and haematite are common constituents of the NSB jasper granules and are completely absent from the Ncongo granules; and the complex internal mineralogy and what could be interpreted as internal growth structures in the NSB jasper granules, are completely absent in the Ncongo granules. Therefore, it is not accurate to call the Ncongo granules and the NSB jasper granules comparable. Although diagenesis and organic carbon oxidation did play a role in the mineralogy currently observed in the Ncongo GIF, a diagenetic growth origin for the granules as a whole is not supported by the data for the following reasons: abundant evidence of wave transport and reworking (Figures 2 and 3); no observed intergrowth of granules and their rims, but rather a stacked and graded nature to the granules beds (Figures 3 and 4); and a complete lack of internal growth structures in the granules (Figure 4a,c,d). The sedimentological evidence does show that the granules were formed at a different setting from where they were finally deposited. However, if they were initially grown diagenetically and only then reworked by storm surges, the GIF would have had a more clastic and broken up texture rather than the mostly intact coated granules observed (Figure 3). Reworked rock fragments with an internal granular texture should also be present and that is not the case. This is because if the granules initially grew diagenetically in the sediment at conditions that require significant burial, as opposed to granules forming and being coated in a silica gel-rich environment as proposed here, it would be a lithified rock unit being reworked.

5.4 | Constraints on iron pathways, sources and deposition

Rare Earth Elements and Y abundances ("REY") are an important geochemical tool in understanding the origin of IFs (e.g., Bau & Dulski, 1996; Bekker et al., 2010; Klein & Beukes, 1992). The PAAS-normalized REY patterns of the ferhythmite show a typical Precambrian IF signature with HREE enrichment and positive Eu and Y anomalies (Klein, 2005; Planavsky et al., 2010). LREE depletion and HREE enrichment is typical for ocean water precipitates (Brookins, 1989; Fryer, 1983). The positive Eu anomaly is consistent with hydrothermal input into the depositional setting (Bau & Dulski, 1996; Dymek & Klein, 1988; Klein & Beukes, 1993) and suggests that the iron in the deeper water IF was introduced by hydrothermal fluids, which would be expected to be reduced (e.g., Slack, Grenne, Bekker, Rouxel, & Lindberg, 2007; Bekker et al., 2010; Figure 9).

The oncoidal GIF units show some but not all of the REY characteristics seen in the ferhythmite, with the lower unit showing HREE enrichment, but no Eu or Y anomalies, and the upper unit showing positive Eu and Y anomalies but less HREE enrichment (Figure 7b). The flat PAAS-normalized patterns observed in the felutite are most likely due to REEs from detrital material that would have dominated the REE
signature of the chemical precipitates. This conclusion is supported by elevated concentrations of constituents reflecting detrital influx (e.g., AlO$_2$, TiO$_2$, and Zr) in this lithology (Table 1).

Iron isotope geochemistry provides further insight into iron cycling and therefore the mechanism of iron deposition (Czaja et al., 2012, 2013; Johnson, Beard, Beukes, Klein, & O’Leary, 2003; Johnson, Beard, Klein, Beukes, & Roden, 2008a; Planavsky et al., 2012). The largest iron isotope fractionations occur with redox processes (Johnson, Beard, & Roden, 2008b), wherein partial oxidation of ferrous iron produces a ferric iron precipitate that has relatively high $\delta^{56}$Fe values, and a residual ferrous iron pool has relatively low $\delta^{56}$Fe values relative to the original source (Bullen, White, Childs, Vivit, & Schulz, 2001; Croal, Johnson, Beard, & Newman, 2004; Planavsky et al., 2012). This observation applies to pure Fe$^{3+}$ precipitates, as well as Fe$^{3+}$-Si gels (Wu et al., 2012). In general, it is not possible to use stable Fe isotope compositions to distinguish between biological and abiological oxidation paths (Bullen et al., 2001; Croal et al., 2004), but the magnitude of the increase in $\delta^{56}$Fe values for the Fe$^{3+}$ precipitates do constrain the extent of oxidation and hence can be used to estimate ambient oxygen levels (e.g., Czaja et al., 2013). This will be further explored below.

A hydrothermal source of iron located in deep water environments of the Archaean Ocean would most likely have had a $\delta^{56}$Fe value of about 0‰ (Johnson et al., 2008a) (Figure 9). Oxidation and precipitation of a portion of this ferrous iron in distal (pelagic or outer shelf) settings as oxide facies IF would have rendered the precipitated iron enriched with positive $\delta^{56}$Fe values, and the remaining dissolved ferrous iron would have somewhat negative $\delta^{56}$Fe values. This process would have been ultimately expressed in more elevated $\delta^{56}$Fe values in distal IFs and lower $\delta^{56}$Fe values in more proximal lithotypes. This process might explain the distribution of Fe isotope data in the IFs of the N Congo Formation (Table 2 and Figures 8 and 9).

The dominance of Fe-silicates in the ferrihydrite and the fetulite suggests that they were deposited in a more proximal closer to shore environment with higher input of terrestrial detritus. The hydrothermal Fe$^{2+}$$_{aq}$ if sourced from the open ocean, would be expected to have negative $\delta^{56}$Fe values in these proximal Fe-silicates if it represents the residue from extensive deposition of oxide facies IF in a more distal setting (Figure 9). Precipitation of ferric oxyhydroxides in the more proximal settings, if formed from low-$\delta^{56}$Fe Fe$^{2+}$$_{aq}$, might have near-zero $\delta^{56}$Fe values, given the $^{56}$Fe/$^{54}$Fe fractionations between Fe$^{3+}$-bearing minerals and Fe$^{2+}$$_{aq}$ as discussed above (Table 2 and Figure 8). The ferrous silicate precursor to minnesotaite and stilpnomelane, most likely precipitated through a non-redox process, would be expected to inherit the negative $\delta^{56}$Fe values of the hydrothermal Fe$^{2+}$$_{aq}$, as seen in the silicate-rich bands and zones in the ferrihydrite and fetulite (Figure 8); this is based on the anticipation that Fe$^{2+}$ silicates will have little isotopic fractionation relative to Fe$^{2+}$$_{aq}$ (Polyakov & Mineev, 2000).

An important finding in this study is the distinct Fe isotope compositions of the oncoidal GIF (Table 2 and Figure 8), which was formed in the shallowest setting of the units studied. The positive $\delta^{56}$Fe values of the oncoids suggest that the Fe which precipitated in shallow, wave agitated conditions, had a different source or pathway than the fetulite and ferrihydrite. If the iron in the oncoidal GIF was sourced from the same hydrothermal plume as the deeper water ferrihydrite, continued distillation of Fe$^{2+}$$_{aq}$ in the plume as it spread from the deep to shallow shelf should have resulted in $\delta^{56}$Fe values that were more negative than in the ferrihydrite. In contrast to the ferrihydrite and fetulite, however, the magnetite in the oncoidal GIF has significantly positive $\delta^{56}$Fe values and the coexisting minnesotaite $\delta^{56}$Fe values are close to zero. This suggests that the Fe$^{2+}$$_{aq}$ source from which the iron in the oncoid rims precipitated had $\delta^{56}$Fe values close to zero (Figure 9). The iron in the oncoidal GIF is thus interpreted to be most likely sourced from a shallow ocean pool that had a lower concentration of Fe$^{2+}$$_{aq}$ and not from the deep water hydrothermal plume. We favour this model over the possibility that intense upwelling, resulting in partial oxidation of Fe$^{2+}$, and offshore flow of the evolved water mass produced the Fe isotope variations measured. The latter model would most likely result in the opposite trend for Fe-silicate Fe isotope values measured.

It is important to also note that the magnetite $\delta^{56}$Fe values for GIF are likely to be minimum values because the initial precipitate would have been an iron oxyhydroxide. Later interaction with Fe$^{2+}$$_{aq}$, likely having a $\delta^{56}$Fe value of around 0‰, would have tended to decrease the $\delta^{56}$Fe value from the initial iron oxyhydroxide, and a simple mixing calculation indicates that the original Fe oxyhydroxide precipitates likely had an average initial $\delta^{56}$Fe value of about 0.66‰ (Czaja et al., 2013). The near-zero $\delta^{56}$Fe value of the minnesotaite-bearing chert between the oncoids, however, suggests that the pure magnetite component in the oncoid rims probably has slightly higher $\delta^{56}$Fe values than analysed for the small bulk samples.

A lack of abundant Fe$^{2+}$$_{aq}$ in the shallow part of this depositional basin, interpreted to have been an isolated submerged shelf bank (Figure 9), is supported by the lower Fe content in the oncoidal GIF when compared to the deeper water IF (Table 1), as well as the stronger textural control on magnetite in the GIF, which only occurs in microstromatolitic rims of oncoids (Figure 4). Consistent with the textural and other geochemical data, partial oxidation of a low concentration of Fe$^{2+}$$_{aq}$ on the isolated bank, as indicated by significantly positive $\delta^{56}$Fe values in the oncoidal GIF Fe oxides, also suggests oxidation in a low oxygen environment, possibly by chemolithoautotrophs or microaerobic anoxygenic photosynthetic iron oxidizers (APIO) rather than by reaction with free oxygen. (Czaja et al., 2013) modelled Fe isotope fractionation during oxidation by free oxygen and by APIO and argued that low amounts of iron that has significantly positive $\delta^{56}$Fe values are best explained by APIO rather than reaction with molecular oxygen. It is important to note, however, that the possible presence of nitrate, as inferred for the formation of calcite in the mineral paragenesis section above, could indicate that there may have been some free oxygen in the environment (i.e., microaerobic conditions). In addition, the environment in which the granules formed must have been highly depleted in iron as essentially only chert was precipitated and the Fe-rich minerals are essentially confined to the oncoid rims (Figure 4), which is in stark contrast to pervasive Fe mineralization in the deeper water MIF (Figure 6). In the IFs of the Witswatersrand Supergroup, which is correlatable to those of the Moaian Group, there is also a notable absence of Fe in units deposited above wave base and the inferred base of the photic zone (Smith et al., 2013). This implies the removal of hydrothermal Fe$^{2+}$
in deeper water facies by chemolithoautotrophs under micro-oxic conditions (Figure 9). Chemolithoautotrophy instead of APIO could therefore have been responsible for the precipitation of Fe in the GIF.

6 | CONCLUSION

We describe the oldest known well-preserved oncoidal GIF, which textural and compositional data indicate likely formed through biological activity in the shallow water environments of the Pongola Supergroup as early as 3.0–2.8 Ga. Initial iron oxides are proposed to have formed by iron-oxidizing bacteria as part of layered microbial films that were developed in a shallow water wave-dominated environment. Evolution of these films continued into shapes similar to domal microstromatolites. The lower iron content, strong textural control on iron mineralization and the stable Fe isotope systematics of the oncoidal GIF, when compared to the deeper water IFs, illustrate that there were different pathways sources for the iron in the deeper and shallower ocean. Oxidation of \( \text{Fe}^{2+}_{\text{aq}} \) in the deep water evidently took place in the presence of abundant iron, as suggested by the wealth of iron-bearing mineral throughout the IFs. Microbes living in the shallow water had a much more limited source of iron, and the iron was only precipitated in the bacterial filaments that grew around chert granules that were formed by wave reworking of chert beds on an isolated shallow submerged shelf bank, developed locally on a palaeo-high, in the original very extensive Witwatersrand-Mozaan depository.

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