A reappraisal of the origin of the Hotazel Fe-Mn Formation in an evolving early Earth system through the application of mineral-specific geochemistry, speciation techniques and stable isotope systematics

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By

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"There is no greater agony than bearing an untold story inside you." -Maya Angelou

## Synopsis

Marine chemical sediments such as Banded Iron Formations deposited during the Archean-Palaeoproterozoic are studied extensively because they represent a period in the development of the Earth's early history where the atmospheric  $O_2$  content was below the present levels (PAL) of 21%. Prior to the Great Oxidation Event (GOE) at *ca*. 2.4 Ga, highly ferruginous and anoxic marine environments were dominated by extensive BIF deposition such as that of the Griqualand West Basin of the Transvaal Supergroup in South Africa. This basin is also thought to record the transition into the first rise of atmospheric  $O_2$  in our planet, from the Koegas Subgroup to the Hotazel Formation dated at *ca*. 2.43 Ga (Gumsley *et al.*, 2017). Two drill cores from the north eastern part of the Kalahari Manganese Field characterized by a well-preserved and complete intersection of the cyclic Mn-Fe Hotazel Formation were studied at a high resolution (sampled at approximately one-meter interval). Such high-resolution approach is being employed for the first time in this project, capturing in detail the three manganese rich layers intercalated with BIF and the transitions between these lithofacies.

The micro-banded BIF is made up of three major phases, namely Fe-Ca-Mg carbonates (ankerite, siderite & calcite), magnetite, and silicates (chert and minor Fe-silicates); laminated transitional lutite consist of mainly hematite, chert and Mn-carbonates, whereas the manganese ore layers are made up of mostly calcic carbonates (Mn-calcite and Ca-kutnahorite) in the form of laminations and ovoids, while Mn-silicates include dominant braunite and lesser friedelite. All three lithofacies are very fine grained (sub-mm scale) and so petrographic and mineralogical observations were obtained mostly through scanning electron microscope analysis for detailed textural relationships with focus on the carbonate fraction. Bulk geochemical studies of the entire stratigraphy of the Hotazel Formation have previously provided great insights into the cyclic nature of the deposit but have not adequately considered the potential of the carbonate fraction of the rocks as a valuable proxy for understanding the chemistry of the primary depositional environment and insights into the redox processes that were at play. This is because these carbonates have always been attributed to diagenetic processes below the sediment-water interface such as microbially-mediated

dissimilatory iron/manganese reduction (DIR/DMR) where the precursor/primary Fe-Mn oxyhydroxides have been reduced to result in the minerals observed today.

The carbonate fraction of the BIF is made up of ankerite and siderite which co-exist in a chert matrix as anhedral to subhedral grains with no apparent replacement textures. This suggests coprecipitation of the two species which is at apparent odds with classic diagenetic models. Similarly, Mn-carbonates in the hematite lutite and manganese ore (Mn-calcite, kutnahorite, and minor rhodocrosite) co-exist in laminae and ovoids with no textures observed that would suggest an obvious sequential mode of formation during diagenesis. In this light, a carbonate-specific geochemical analysis based on the sequential Fe extraction technique of Poulton and Canfield (2005) was employed to decipher further the cyclic nature of the Hotazel Formation and its primary *versus* diagenetic controls. Results from the carbonate fraction analysis of the three lithofacies show a clear fractionation of iron and manganese during primary – rather than diagenetic - carbonate precipitation, suggesting a decoupling between DIR and DMR which is ultimately interpreted to have taken place in the water column.

Bulk-rock concentration results for minor and trace elements such as Zr, Ti, Sc and Al have been used for the determination of either siliciclastic or volcanic detrital inputs as they are generally immobile in most natural aqueous solutions. These elements are in very low concentrations in all three lithofacies suggesting that the depositional environment had vanishingly small contributions from terrigenous or volcanic detritus. In terms of redox-sensitive transition metals, only Mo and Co appear to show an affinity for high Mn facies in the Hotazel sequence. Cobalt in particular attains a very low abundance in the Hotazel BIF layers at an average of ~ 4 ppm. This is similar to average pre-GOE BIF in South Africa and worldwide. Maxima in Co abundance are associated with transitional hematite lutite and Mn ore layers, but maxima over 100ppm are seen in within the hematite lutite and direct association with the hematite fraction in the rocks, which is modally much higher in the lutites but drops substantially in the Mn layers themselves.

The similarities of bulk-rock BIF and modern-day seawater REE patterns has been used as a key argument for primary controls in REE behaviour and minimal diagenetic modification. Likewise, the three lithofacies of the Hotazel Formation analysed in this study all share similar characteristics with a clear seawater signal through gentle positive slopes in the normalised abundance of LREE

*versus* HREE. Negative Ce anomalies prevail in the entire sample set analysed, which has been interpreted before as a proxy for oxic seawater conditions. However, positive Ce anomalies that are traditionally linked to scavenging and deposition of primary tetravalent Mn oxyhydroxides (e.g., as observed in modern day ferromanganese nodules) are completely absent from the current dataset. The lack of a positive Ce anomaly in the manganese ore and peak Co association with ferric oxides and not with peak Mn, suggests that primary deposition must have occurred within an environment that was not fully oxidizing with respect to manganese.

The use of stable isotopes (i.e., C and Fe) was employed to gain insights into redox processes, whether these are thought to have happened below the sediment-water interface or in contemporaneous seawater. At a small scale, all lithofacies of the Hotazel Formation record bulkrock  $\delta^{13}$ C values that are low and essentially invariant about the average value of -9.5 per mil. This is independent of sharp variations in overall modal mineralogy, relative carbonate abundance and carbonate chemistry, which is clearly difficult to reconcile with in-situ diagenetic processes that predict highly variable  $\delta^{13}$ C signals in response to complex combinations of precursor sediment mineralogy, pore-fluid chemistry, organic carbon supply and open vs closed system diagenesis. At a stratigraphic scale, the carbonate  $\delta^{13}$ C (-5 to -13‰) variations between the different lithologies could instead represent temporal changes in water-column chemistry against well-developed physico-chemical gradients, depth of deposition and biological processes. The low iron isotope values recorded in the hematite lutite and manganese ore samples can be attributed to fractionation effects of initial oxidation of ferrous iron to form Fe-oxyhydroxides in the shallow parts of the basin, from an already isotopically highly depleted aqueous Fe-pool as proposed previously. The slightly higher but still negative bulk-rock  $\delta^{56}$ Fe values of the host BIF can be attributed to watercolumn Fe isotopic effects at deeper levels between primary Fe oxyhydroxides and an isotopically heavier Fe(II) pool, which was subsequently preserved during diagenetic recrystallization.

All above findings were combined into a conceptual model of deposition for the three different lithologies of the Hotazel Formation. The model predicts that free molecular oxygen must have been present within the shallow oceanic environment and implicates both Mn and Fe as active redox "players" compared to classic models that apply to the origin of worldwide BIF prior to the GOE. The deposition of the Hotazel strata is interpreted to have occurred through the following three stages: (1) BIF deposition occurred in a relatively deep oceanic environment above the

Ongeluk lavas during marine transgression, where a redoxcline and seawater stratification separated hydrothermally sourced iron and manganese, in response to an active Mn-shuttle mechanism linked to Mn redox cycling. Abundant ferrous iron must have been oxidized by available oxygen but also by oxidised Mn species (MnOOH) and possibly even some soluble Mn(III) complexes. Through this process, Mn(III) was being effectively reduced back into solution along with cobalt(III), as Mn(II) and Co(II) respectively, thus creating maxima in their concentrations. A drawdown of Fe(OH)<sub>3</sub> particles was therefore the only net precipitation mechanism at this stage. Carbonate species of Fe and the abundant magnetite would possibly have formed by reaction between the ferric hydroxides and the deeper Fe(II) pool, while organic matter would also have reacted in the water-column via DIR, accounting for the low  $\delta^{13}$ C signature of Fe carbonate minerals. (2) Hematite lutite formation would have occurred at a relatively shallower environment during marine regression. At this stage, reductive cycling of Fe was minimal in the absence of a deeper Fe(II) reservoir reacting with the ferric primary precipitates. Therefore, DIR progressively gave way to manganese reduction and organic carbon oxidation (DMR), which reduced MnOOH to form Mn(II)-rich carbonates in the form of kutnahorite and Mn-calcite. Cobearing Fe(OH)<sub>3</sub> would have precipitated and was ultimately preserved as Co-bearing hematite during diagenesis. (3) Deposition of manganese-rich sediment occurred at even shallower oceanic depths (maximum regression) where aerobic organic carbon oxidation replaced DMR, resulting in Ca-rich carbonates such as Mn-bearing calcite and Ca-kutnahorite, yet with a low carbon isotope signature recording aerobic conditions of organic carbon cycling. Mn(III) reduction at this stage was curtailed, leading to massive precipitation of MnOOH which was diagenetically transformed into braunite and friedelite. Simultaneous precipitation of Co-bearing Fe(OH)<sub>3</sub> would have continued but at much more subdued rates.

Repeated transgressive-regressive cycles resulted in the cyclic BIF-hematite lutite- manganese ore nature of the Hotazel Formation in an oxidized oceanic environment at the onset of the Great Oxidation Event, which was nonetheless never oxic enough to drive Mn(II) oxidation fully to its tetravalent state. The mineralogy and species-specific geochemistry of the Hotazel strata, and more specifically the carbonate fraction thereof, appear to faithfully capture the chemistry of the primary depositional environment in a progressively evolving Earth System. This project opens the door for more studies focusing on better constraining primary *versus* diagenetic depositional

mechanisms of iron and manganese during the period leading up to the GOE, and possibly redefining the significance of Fe and Mn as invaluable redox proxies in a rapidly changing planet.

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"Education is the passport to the future, for tomorrow belongs to those who prepare for it today." – Malcom X

# 1. Introduction

### 1.1 Early Earth evolution and major geochemical signals

One of the pieces of geological evidence most frequently cited in the literature as being amongst the strongest indications for the Earth's first major oxygenation event (GOE) at *ca*. 2.4 Ga (Figure 1.1), is the first occurrence of large manganese deposits of marine sedimentary origin (e.g., Anbar & Knoll, 2002; Holland, 2002; Lyons *et al.*, 2014). This is an important stage in the evolution of the Earth as it is thought to represent a period of the earliest development of multicellular life (Schirrmeister *et al.*, 2013) delivering oxygen to the atmosphere and oceans. Most of what is known about these significant changes at around that time is through the study of well-preserved chemical sedimentary rocks which are studied to derive proxies used to predict oceanic and atmospheric conditions at the time of primary deposition (Pufahl and Hiatt, 2012).



Figure 1.1: (**Top**) Atmospheric oxygen content as log-function of present-day atmospheric levels (PAL); (**Bottom**) Summary of  $\delta^{13}$ C excursions and  $\Delta^{33}$ S values indicating the loss of mass independent sulfur fractionation (MIF-S), over the Earth's history. (Lyons, *et al.*, 2014).

There is probably no more striking an example of such deposits in the Precambrian geological record than the Kalahari Manganese Field (hereafter referred to as KMF), a giant manganese deposit in the Hotazel Formation at the uppermost part of the Archean to Paleoproterozoic (2.6-2.0 Ga) Transvaal Supergroup, as the latter develops in the Griqualand West Basin of the Northern Cape Province of South Africa (Tsikos & Moore, 1997; Tsikos et al., 2003; 2010). The association of three manganese rich layers within BIFs in the Hotazel Formation has been attributed to an oxygenated atmosphere-ocean post-GOE environment, where Mn(II) in solution was fully oxidized to Mn(IV)-oxyhydroxides prior to precipitation. The lithological separation of these manganese layers with BIFs has been attributed to repeated transgressive-regressive cycles during deposition (Beukes, 1983; Tsikos and Moore, 1997), while other prevailing models suggest pulses of plumes supplying hydrothermal Mn(II) into the system thus resulting in the layering of this Formation. These plumes would have ejected Fe(II) and Mn(II) periodically in a dynamic circulating ocean which is not permanently stratified, thus resulting in Mn(IV)-oxyhydroxide precipitation alternating with Fe(III)-oxyhydroxide precipitation (Beukes, 1983). Another model of formation of the Hotazel suggest a metasomatic source of manganese in which Mn rich fluids would have percolated through bacterial mats and deposited Mn, Fe and Si into primary sediments (Kuleshov, 2012). Diagenetic transformations would have led to the present configuration of the unique interlayering between BIF and Mn ore.

The occurrence of oxygenic photosynthesis in the early Earth has been a widely-debated topic in literature, with little or no consensus on when this metabolic mechanism and hence free  $O_2$  as a by-product first became available in the atmosphere. Evidence for the evolution of oxygenic photosynthesis has been reported to be from as early as ~3.7 Ga based on Rosing and Frei (2004) who suggested that organic matter preserved in pelagic shales were derived from planktonic organisms. A variety of trace metal isotope proxies have been used in recent years in support of a late Archaean onset of oxygenic photosynthesis, including U (Wang *et al.*, 2018), Mo (Planavsky *et al.*, 2014) and Cr (Crowe *et al.*, 2013). Other evidence for the first occurrence of oxygenic photosynthesis has been linked to the global snowball Earth event at *ca.* 2.43 Ga (Kirschvink and Kopp, 2008; Gumsley *et al.*, 2017). Global glaciation is thought to have been triggered by large igneous provinces on extensive, low latitudinal continental masses. Enhanced chemical weathering of such aerially extensive, continental flood basalts would have caused extensive carbon dioxide drawdown and increased flux of nutrients such as phosphorus into intra-cratonic basins and

continental margins (Gumsley *et al.*, 2017 and references therein). This flux of nutrients would have led to increasing photosynthetic activity and hence increase in oxygen delivery. Large igneous provinces such as the Ongeluk lavas of the Transvaal Supergroup are thought to have also played a role in the termination of the first snowball Earth state of the early Paleoproterozoic, by contributing carbon dioxide that would have led to the increase in greenhouse gas concentrations in the atmosphere (Gumsley *et al.*, 2017). Konhauser *et al.*, (2009) further suggest that oxygenation of the atmosphere occurred due to the rise in photosynthetic bacteria, facilitated by a loss of methanogens due to a decline in volcanic Ni-input in seawater.

Other indications of the rise of oxygen in the atmosphere include the disappearance of redoxsensitive detrital uraninite and pyrite grains from the sedimentary record after the GOE (Johnson *et al.*, 2014). However, the most robust indication for the oxygenation of the atmosphere during the Archean is the loss of mass-independent fractionation of sulfur isotopes (MIF-S) (Farquhar and Wing, 2003; Lyons *et al.*, 2014). Farquhar and Wing (2003) suggest that in an anoxic atmosphere with  $O_2 < 10^{-5}$  PAL such as that prior to 2.33 Ga (Luo *et al.*, 2016) in the Archean, gasphase photolytic reactions led to anomalous variability in the <sup>33</sup>S and <sup>36</sup>S isotopes recorded in sulphur rich minerals such as barite and pyrite in sedimentary rocks. At around 2.33 Ga, the disappearance of MIF-S in the geological record indicates that *p*O<sub>2</sub>-levels must have risen above 0.001% of PAL (Farquhar and Wing, 2003). Once atmospheric oxygen levels reached such levels, ozone and to a lesser extent oxygen started to adsorb ultraviolet radiation at wavelengths of 300 nm. The ozone shield restricted the penetration of ultraviolet radiation in the atmosphere and so prevented the mass independent fractionation of volcanically sourced sulfur gases.

#### 1.2 Banded Iron Formations (BIFs) and their models of deposition

Banded Iron Formations are described as laminated/banded iron-rich (~20-50% iron) chemical sedimentary rocks which formed as early as 3.9-3.8Ga (e.g Isua) (Klein., 2005; Koehler *et al.*, 2010). Though undoubtedly sedimentary in origin, BIFs also record diagenetic or metamorphic overprint in terms of mineralogy, textures and geochemical signals (Koehler *et al.*, 2010), which often obscure signals of primary deposition.

Gross (1983) divided BIFs into two groups based on their sedimentary-tectonic environments. The first group, termed "Superior-type", were deposited over lengthy periods of time (~500 Ma) along the margins of cratons or continental platforms where tectonic conditions were very stable and minimal volcanic activity occurred. The second group, namely "Algoma-type" BIF, were deposited in tectonically and volcanically more dynamic systems, along with siliciclastic sediments and volcanic rocks. It is suggested that biogenic factors and atmospheric conditions had far less impact on the precipitation of Algoma-type BIF as opposed to their Superior-type counterparts (Gross, 1983). The biggest arguments in most early BIF depositional models are the exact pathways of primary iron deposition and diagenesis (e.g., Beukes, 1983; Konhauser *et al.*, 2005; Johnson *et al.*, 2003,2008; Anbar *et al.*, 2007); the source of iron, silica and carbon (Lovley and Phillips, 1988; Klein, 2005; Konhauser *et al.*, 2005; Heimann *et al.*, 2010); and whether deposition occurred in a restricted or open ocean environment.

Previous research suggests a hydrothermal source of Fe(II) (e.g., Morris and Horwitz., 1983; Klein and Beukes., 1989; Isley, 1995) where Fe-enriched and O<sub>2</sub>-depleted plumes from mid-oceanic ridges were a more important source of Fe(II) in the ancient ocean compared to today. Others have emphasized the importance of continental sources for iron (Canfield, 1998). Planavsky et al., (2011) further suggest that persistent ferruginous conditions in the deep ocean during BIF formation, in combination with low sulphide availability and high rates of hydrothermal Fe(II) supply, resulted in conditions conducive to precipitation of oxide-rich BIF. The oxidation of Fe(II) to Fe(III) is necessary for the formation of Fe-oxyhydroxides (e.g., Fe<sup>3+</sup>OOH), as likely sedimentary precursors to BIF. The oxidation of ferrous to ferric iron invariably requires the presence of an electron acceptor such as O<sub>2</sub> in the shallow ocean, and the upwelling of hydrothermally sourced Fe(II) from deeper parts of the ocean. Proposed theories vary widely: Konhauser et al., (2002) suggest that microorganisms using ferrous iron for energy and produce ferric iron as a by-product could have been a major, if not the sole contributor to Fe(III) precipitation during Precambrian BIF deposition, while others suggest that Fe(II) oxidation was a function of photochemical processes or inorganic reactions (Braterman and Cairnssmith, 1987). It has been suggested, however, that even though ultraviolet light has the potential to oxidize ferrous iron (Cairns Smith, 1978; Braterman et al., 1983), experimental work has proven this to be infeasible in complex environments such as those in which BIF formed.

As discussed earlier in this chapter, it remains uncertain exactly when photosynthetic oxygen emerged in the oceanic system. Dauphas *et al.*, (2004), for example, propose an origin as early as 3.7 Ga based on evidence from the Isua BIF in Greenland. However, with reference to the abundant BIF that formed at the Archaean-Paleoproterozoic transition (see examples in Figure 1.2) the major arguments pertaining to the deposition of BIF revolve around the issue of biogenicity. Specifically, there are long-standing debates whether Fe(II) in solution in the depositional environment was oxidized to Fe(III) by photosynthetic  $O_2$  produced by cyanobacteria or by anoxygenic photoautotrophic/photolithoautotrophic bacteria (Cloud, 1973; Winter and Knauth, 1992; Konhauser *et al.*, 2002; Kappler *et al.*, 2005; Crowe *et al.*, 2008; Sun *et al.*, 2015; Chan *et al.*, 2016). Clearly, the few BIFs deposited at post-GOE times (e.g., Biwabik IF, USA) could well have been the result of  $O_2$  oxidation of Fe in an oxygenated oceanic and atmospheric environment.

The mineralogy of un-metamorphosed to low-grade metamorphic BIF is dominated by mixedvalence to reduced iron species (Klein *et al.*, 2005). These mineralogical assemblages require diagenetic reconstitution of primary ferric iron-rich sediments in the presence of an electron donor. With respect to BIF, reductive diagenesis is thought to have been controlled by organic carbon that settled onto the ocean floor along with primary iron oxyhydroxides (Fe<sup>3+</sup>OOH) (e.g., Heimann *et al.*, 2010). Coupled reduction of iron and oxidation of organic carbon *via* iron reducing microorganisms (Dissimilatory Iron Reduction, DIR) forms mineral species of reduced Fe(II) such as siderite (Walker, 1984; Pecoits *et al.*, 2009; Heimann *et al.*, 2010; Posth *et al.*, 2013). Direct evidence for organic C involvement in BIF diagenesis is supported by the typically low  $\delta^{13}$ C values in iron carbonate minerals such as siderite and ankerite. These are thought to reflect variable contributions of organic carbon ( $\delta^{13}$ C -28‰) and marine bicarbonate ( $\delta^{13}$ C ~0‰) to the formation of carbonate minerals, to produce the intermediate ( $\delta^{13}$ C: -13 to -5‰; see Figure 4.1 later) carbonate-carbon isotope signal as observed in BIF deposits globally (Walker, 1984; Kaufman *et al.*, 1990).

The stable isotope fractionations of iron and carbon have been widely used as tools to understand redox cycling in BIF depositional and diagenetic environments. Planavsky *et al.*, (2010) explain the large positive iron isotope fractionation in BIF in direct association with partial initial iron oxidation, either abiotically or microbially. In a closed system, where removal of iron from the water-column dominates supply, Welch *et al.*, (2003) and Johnson *et al.*, (2008), among others,

suggest that a Rayleigh fractionation model can explain isotopic fractionation effects. The maximum iron fractionation factor of Fe(II) oxidation to Fe (III) [Fe(III)<sub>solid</sub>-Fe(II)<sub>aqueous</sub>] is thought to be around 1% - 3% at 25°C, with kinetic isotope fractionation resulting in a ~1‰ decline as Fe(OH)<sub>3</sub> is precipitated (Welch *et al.*, 2003).



Figure 1.2: Global distribution of Banded Iron Formations (BIFs) from the Mesoarchean to the Neoproterozoic (Bekker, *et al.*, 2014)

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Contrary to Fe(II) oxidation pathways, DIR during diagenesis is thought to fractionate the light iron isotope resulting in high  $\delta^{56}$ Fe values in the residual dissolved iron pool. Heimann *et al.*, (2010) suggest that both  $\delta^{13}$ C and  $\delta^{56}$ Fe values in BIF carbonates are affected differently in response to partial and complete DIR (Figure 1.3). During diagenesis below the sediment-water interface, organic matter oxidation (simplistically expressed herein as CH<sub>2</sub>O) and microbial Fe(OH)<sub>3</sub> reduction initially results in light aqueous Fe<sup>2+</sup> ( $\delta^{56}$ Fe ~-1‰) delivery in solution and  $\delta^{13}$ C ~-30‰ in the HCO<sub>3</sub><sup>-</sup> derived from organic remineralization (Figure 1.3, Stage 1). These would be remobilized elsewhere within the sediment to react with near-0‰ marine HCO<sub>3</sub><sup>-</sup> (DIC) to form siderite with an isotopic signature of  $\delta^{56}$ Fe ~1‰ and  $\delta^{13}$ C ~-7.5‰. Residual Fe(OH)<sub>3</sub> with an isotopic composition of  $\delta^{56}$ Fe ~+1‰ could also react with organic matter through nearcomplete DIR to form siderite with an iron isotope signature similar to the residual Fe(OH)<sub>3</sub>. Partial DIR (Figure 1.3, Stage 2) is bound to produce secondary (diagenetic) carbonates such as siderite, that have lower  $\delta^{56}$ Fe values by 2 to 3‰ compared to the initial Fe(OH)<sub>3</sub>.



Figure 1.3: A schematic diagram showing the origin of iron rich carbonates in BIFs, based on mineralogical, chemical and stable isotope data (i.e Fe, C, O) (Heimann *et al.*, 2010).

#### 1.3 Manganese in the context of BIF and the early Earth

Manganese is the ninth or tenth most abundant element in the Earth's crust depending on the crustal composition model used (Maynard, 2003). This transition metal exists in three oxidation states,

with Mn(II) being dominant under anoxic conditions in aqueous form. Mn(II) is readily oxidized in the presence of O<sub>2</sub>, leading to the formation of Mn (III,IV)-oxyhydroxides (Wariishi *et al.*, 1992; Rincón-Tomás *et al.*,2016). Extensive manganese ore deposits globally (Table 1.1) are the result of accumulation of such manganese oxides. In a review paper, Johnson *et al.*, (2016) state that the redox state between ancient manganese deposits differs from their modern counterparts: the latter tend to be more manganese oxide-rich either through primary oxidative precipitation or through oxidation of pre-existing reduced manganese deposits under aerobic conditions; whereas the former, are dominated by reduced manganese assemblages such as manganese carbonates.

Ore Name/Location	Valume	Estimated	Reference
	(million	Age	
Nikopol, Ukraine, Georgia	1000	28	Varentsov and Grasselly, 1976
Groote Eylandt, Australia	400	123	Pracejus and Bolton, 1992
Molango, Mexico	200	155	Martino, 1986
Xialei, China + Atasu,	200	370	Varentsov and Grasselly, 1976; Fan
Kazakhstan			and Yang, 1999
Usinsk, Siberia + others	150	520	Varentsov and Grasselly, 1976
Corumba', Brazil + small Baltic	686	625	Urban <i>et al.</i> , 1992
deposits			
Woodie-Woodie, East Pilbara,	65	110-950	Jones <i>et al.</i> , 2013
Australia			
Wafangzi, China	38	1200	Rodionov et al., 2004
			, ,
Sausar Group, India + Postmasburg	115	2000	Dasgupta <i>et al.</i> , 1991; Gutzmer and
Group			Beukes, 1996a;
1			Cairneross and Beukes, 2013
Moanda, Gabon	400	2150	National Materials Advisory Board.
			1981: Gauthier-
			Lafave <i>et al</i> 1996
Birimian Supergroup West Africa	49	2200	National Materials Advisory Board
Diminan Supergroup, west Amea	Т <b>)</b>	2200	1081: Davis et al
			1901, Davis et ut., 1004
Hotozal Formation/Valabari	1250	2220/2420	Gutzmar and Daukas 1006h
Ma field	1330	2220/2430	Taliaardt 1082: Cumalax at al. 2017
Mines Camia Drazil	20	2400	Maurul 1072 Dahinaki et al. 1005
Winas Gerais, Brazil	20	2400	Maxwell, 1972; Babinski <i>et al.</i> , 1995
Koegas subgroup, South Africa	200	2420	Cairneross and Beukes, 2013

Table 1.1: The location, age and volume of major manganese ore deposits around the globe. Modified from Johnson, J.E. *et al.*, (2016).

The association of manganese with BIF is manifested in bulk-rock abundances generally below 0.5 wt. % (Klein, 2005). Oonk *et al.*, (2017), conducted species-specific analyses of a large

population of BIF samples in South Africa and concluded that Mn is almost exclusively contained in iron-rich carbonate minerals such as ankerite and siderite. Such contents can range from less than 1 wt.% up to 8 wt.% of the carbonate structure. This translates to bulk-rock Mn contents as high as 5 wt.% or higher in bulk-rock analyses of carbonate dominated samples. In the same samples, no preservation of any Mn oxide was observed as a possible precursor.

The importance of Mn-oxyhydroxide complexes as possible precursors to manganese contained in BIF has been previously evaluated through the use of redox-sensitive transition metals, such as molybdenum, chromium and thalium (e.g., Crowe *et al.*, 2013; Planavsky *et al.*, 2014). Mo isotopes in particular have been used extensively to constrain the oxidation state of BIF depositional environments: low  $\delta^{98}$ Mo values in manganese-enriched BIF have been interpreted to reflect high pre-diagenetic Mn (IV) oxide concentrations in the sediment, which would have preferentially adsorbed the light Mo isotopes (Kurzweil *et al.*, 2016). The inference made from the above interpretation is that high manganese in BIF represents a proxy for transient oxygenation events in the pre-GOE world; some of these events are thought to be dating back to the Neoarchean and have been aptly termed oxygen "whiffs" (Anbar *et al.*, 2007).

In terms of speciation of primary manganese oxides in a BIF environment, the lack of preservation does not constrain whether these oxides were dominantly Mn (IV)-rich or Mn(III)-rich. Murray *et al.* (1984) state that the most preferred Mn oxyhydroxide species to form from the oxidation of Mn(II) at a pH of 9 at 25°C, would be a Mn(III) species such as  $\gamma$ -MnOOH (manganite). This means that the behavior of trace metals such as Mo must be assessed and interpreted against the exact possible precursor. For example, Ce is a redox-sensitive REE which in oxidizing seawater conditions tends to partition into Mn(IV) oxyhydroxides in the form of Ce(IV) (Bau *et al.*, 1996). A classic manifestation of this is in the form of the widespread ferromanganese nodules in the modern ocean, which show a pronounced positive Ce anomaly whilst modern seawater is relatively depleted in Ce compared to the other REE (Hein *et al.*, 2015). On these grounds, a positive Ce anomaly within the Mn layers in the Hotazel could be used as evidence for oxidizing conditions during precipitation leading to the formation of tetravalent Mn oxide precursors. As will be shown later in this thesis, knowledge of the exact speciation of the Hotazel Mn oxide precursors has obvious and profound implications with regard to correctly interpreting the behavior of a number of redox sensitive elements in the primary depositional environment.

### 1.4 The South African record: background

The Transvaal Supergroup of South Africa (Figures 1.5 and 1.6) was deposited on the Kaapvaal Craton during the end of the Archean and early Proterozoic i.e., the period between 2.65- 2.05 Ga (Moore *et al.*, 2001). According to Cheney, 1996 the Kaapvaal craton is one of three lithospheric fragments along with the Pilbara Province of northern Western Australia and the Grunehogra Province of Antarctica; these together formed the ~3.05-1.5 Ga *Vaalbara* Province. The Transvaal Supergroup is preserved in the Transvaal and Griqualand West basins which are geographically disconnected: the Transvaal basin occurs on the eastern part of the Vryburg arch and consists of two major groups, namely the Chuneispoort and Pretoria Groups. The Griqualand West basins and their stratigraphic correlation have been a major discussion topic in previous studies (e.g Moore *et al.*, 2001, 2012). This study does not include any discussion on these correlations but rather focuses on the Griqualand West basin and more specifically the Hotazel Formation of the Postmasburg Group which is the central theme of this thesis. For the purposes of this thesis therefore, only detailed reference to the stratigraphy of the Griqualand West Supergroup will be made.

At the lower part of the Griqualand West Supergroup, the Ghaap group is made up of four major stratigraphic sub-entities, namely the Schmidtsdrif Subgroup with basal shale, quartzite, carbonate and volcanic rocks; the Campbellrand Subgroup containing dolomite and minor shale; the Asbestos Hills Subgroup which contain the Kuruman and Griquatown BIFs; and the Koegas Subgroup, dominated by siliciclastic sediments, BIF and lesser carbonate rock (Beukes and Smit, 1987). The Postmasburg Group overlies the Ghaap Group and is made up of a sequence of diverse lithologies. At the base occurs a glacial diamictite of the Makganyene Formation (Polteau *et al.,* 2006), which is overlain by the Ongeluk Formation comprising almost entirely massive andesitic flows and volcanic rocks. Above the Ongeluk volcanic sequence rests the Hotazel Formation, the central theme of this thesis, which contains BIF and intercalations of manganese rich layers. The Hotazel Formation is conformably overlain by carbonate rocks of the Moodraai Formation (Tsikos and Moore, 2001). Together, the Hotazel and Moodraai Formations make up the Voëlwater Subgroup. The Griqualand West sequence is unconformably overlain by a sequence of siliciclastic rocks and minor volcanic rocks, regionally belonging to the Olifantshoek Supergroup.



Figure 1.4: A) Regional geological map of the Griqualand West and Transvaal Basins of the Transvaal Supergroup, the neighboring Kanye Basin, Ventersdorp Supergroup, and Granite-Greenstone basement. B) East-West cross-sectional profile with a 10x vertical exaggeration going through the Griqualand West and Transvaal Basins on the A-B transect on the Map, above. (Moore *et al.*, 2012)



Figure 1.5: Age and stratigraphic correlations between the Griqualand West and Transvaal Basins with unconformities represented by shading. Ages from Cornell *et al.*, (1996), Sumner and Bowing, (1996), and Bau *et al.*, (1999). *From Moore et al.*, (2001).

#### The Hotazel Formation

The Hotazel Formation is described as cyclic units of BIF and three stratiform manganese ore bodies (Figure 1.7 & 1.8) (Tsikos *et al.*, 2010). The transitions between the two major lithofacies is in the form of strikingly reddish, hematite-rich lutite facies. The mineralogy of the iron formation consists of bands of variable thickness, consisting of combinations of oxides (mainly magnetite), silicates (greenalite, quartz, stipnomelane, minnesotaite) and carbonates (ankerite, siderite and calcite); The transitional hematite lutite lithologies are made up of hematite and manganese bearing carbonates, whilst the quartz free, laminated manganese ore bodies are composed of mainly braunite, manganese-bearing carbonates such as kutnahorite and manganoan calcite, and lesser friedelite (Tsikos *et al.*, 2003).

The age of the Hotazel Formation has remained contentious for many years. Indirect age constraints derived previously from overlying and underlying rocks (the Mooidraai and Ongeluk Formations respectively) place the Hotazel age between ~2.39 Ga and ~2.22 Ga (U-Pb & Pb-Pb respectively) (Cornell *et al.*, 1996; Bau *et al.*, 1999; Fairey *et al.*, 2013). Recent radiometric U-Pb dating of the Ongeluk Formation at  $2424 \pm 32$  Ma (Gumsley *et al.*, 2017, Figure 1.6) has put an end to the above age controversy and has arguably placed the overlying Hotazel Formation at the heart of the GOE.

In terms of economic significance, the Mn deposits in the Hotazel Formation constitute one of the largest on land manganese resources in the world, with around 13.6 billion tons of ore estimated to be hosted within the KMF (Cairncross *et al.*, 1997, Roy, 2006). Different ore types are currently preserved in the KMF: the dominant type in terms of volume is the so called "Mamatwan type" ore. This ore type is made up of braunite, hematite and manganese-rich carbonates in the form of mm-scale laminae and ovoids and runs at a maximum of 40 wt. % Mn. The Mamatwan type ore corresponds to the primary manganese precipitates in the Hotazel Formation, overprinted by diagenesis and burial (Gutzmer and Beukes, 1996; Preston, 2001; Tsikos *et al.*, 2003).

The north-western part of the KMF has been subjected to major structural deformation in the form of North to South and East to West striking faults (Figure 1.8b). This area consists of hydrothermally altered and manganese-enriched ores, which are currently being exploited extensively. These have been termed in the literature under the collective name "Wessels type" ore from the homonymous mine (Gutzmer and Beukes, 1996). The enrichment process has been attributed to fluid-flow along the abundant faults, which upgraded the primary braunite-rich ore through the leaching and redistribution of calcium, silica, magnesium, and CO<sub>2</sub>. These processes resulted in the development of oxide rich ores (e.g., hausmannite) at bulk manganese metal grades as high as 55 wt.%. Gutzmer and Beukes (1996) further propose that the effects of alteration are more pronounced proximally to the faults and appear to have had less effect further away from them. Tsikos *et al.* (2003) have challenged the role of the faults in hydrothermally enriching the ores and highlighted instead the Transvaal-Olifantshoek unconformity as an alternative major fluid conduit.



Figure 1.6: Stratigraphic synthesis of the Transvaal Supergroup as preserved in its two main basins: (A) Griqualand West and (B) Transvaal sub-basin (Eastern Transvaal). (Gumsley *et al.*, 2017)

#### 1.5 Research rationale

The Hotazel Formation has been previously considered a post-GOE deposit based on the assumption that the precursor precipitates of the preserved manganese species were in the form of high valence Mn (IV) oxides (e.g., Kirschvink *et al.*, 2000). This was supported on the previously determined *ca.* 2.22 Ga radiometric Pb-Pb age of the Ongeluk lavas which consequently placed the deposition of the Hotazel Formation well after the postulated rise of oceanic and atmospheric  $O_2$  (Cornell *et al.*, 1996). The key findings from Gumsley *et al.*, (2017) suggest that the earliest onset of the GOE must have been after the Paleoproterozoic Snowball Earth event that is recorded by the Makganyene Formation, which was followed by the deposition of the manganese-rich Hotazel Formation. Support for oxygenation during this period is thought to be the consistently

negative Ce anomalies in the Hotazel rocks in conjunction with the assumption of tetravalent precursors to the abundant Mn (Figure 1.6). Gumsley *et al.*, (2017) also stated that the period of oxygenation ceased after deposition of the Hotazel Formation culminating into carbonate deposition of the Mooidraai Formation. Again, the evidence used for this is a lack of a Ce anomaly at post-Hotazel times, suggesting atmospheric oxygen oscillations after the onset of the GOE. As such, the presence of Mn mineralization in the Hotazel Formation tied to the postulate of primary high-valence Mn oxides, and by extension, their assumed requirement for an O<sub>2</sub> enriched oceanic environment, carries important weight in debates on the actual timing of the GOE, generally placed between 2.3 and 2.4 Ga (Bekker *et al.*, 2004).

A number of questions arise from the aforementioned which previous research on the Hotazel Formation appears to have so far overlooked, such as: was the Hotazel Formation deposited prior to the GOE or right at the very onset of it? Could extensive Mn deposition in cycles during Hotazel times be interpreted as the result of episodic whiffs of oxygen, as precursors to the GOE? Were these coincident with sharp unprecedented increases in O<sub>2</sub> in the early atmosphere thus signaling the GOE? Are precursor Mn precipitates in the form of tetravalent Mn oxides imperative for the changes in redox associated with the GOE? How much of the primary marine signal is preserved in the whole Hotazel sequence, and if so, which proxies meaningfully inform its redox history? Is it possible to constrain further the exact primary speciation of the Hotazel Mn? Does the Hotazel Formation ultimately inform, or even potentially define the GOE? All these questions ultimately feed into the objectives of this thesis as presented in the next section.

#### Approach and objectives

The evidence of primary iron and manganese precipitation in the marine environment of the Neoarchean and Palaeoproterozoic has been the driver for extensive research in deep time paleoceanography and biogeochemistry. Such research invariably focuses on deposits of these metals as proxies for the oxidation state of the planet through geological time and thus major evolutionary changes, such as the oxygenation of the Earth's oceans and atmosphere during the GOE. BIFs are a major sink of iron with different Fe-rich phases preserved, which allows for a plethora of possibilities for different geochemical techniques that can be used to investigate the primary depositional and burial environments. These techniques include the use of bulk-rock

geochemical signatures such as bulk carbonate carbon isotope ratios, to infer diagenetic microbial dissimilatory iron reduction pathways of precursor Fe oxyhydroxide species to form reduced mineral such as Fe(II) carbonates or silicates (e.g., greenalite) or mixed valence oxides such as magnetite (e.g., Konhauser, 2007; Heimann *et al.*, 2010). Whole-rock iron isotope signatures have been used to constrain redox dependent biogeochemical processes and, by extension, the oxidation state of the Earth's early atmosphere and shallow oceans (Planavsky *et al.*, 2012). Extensive research has also utilised other geochemical signals in BIFs to infer redox conditions during time of deposition, such as the abundance and isotope compositions of Mo, Cr, Co, and U (e.g., Crowe *et al.*, 2013; Wang *et al.*, 2017).

As the Hotazel Formation contains significant quantities of manganese mineralization, the aforementioned techniques (and more) can be applied with added element of interest that Mn would be a central candidate in redox interpretations. For example, oxidizing conditions have been linked to initial manganese oxidation, through the use of Mo abundances and its stable isotope variations (Planavsky *et al.*, 2014). Other metals used to fingerprint oxidizing conditions during manganese deposition include the use of Co as a proxy for the oxidation state of manganese and iron (Swanner *et al.*, 2014). The work of Oonk (2017) applied a fraction-specific approach to understanding primary *versus* diagenetic depositional controls in and oceanic environment of the BIFs of the Asbestos Hills Subgroup (Kuruman and Griquatown). The said study investigated at depth the influence of mineralogy on classic, bulk-rock major and trace element and stable isotope geochemistry. The results and interpretations of that work was based on fine-tuning existing sequential extraction protocols such as that of Poulton and Canfield (2005), adapted on rocks with very high Fe content such as BIFs. One of the major findings of the work of Oonk (2017), was that the carbonate fraction of BIF recorded clear seawater geochemical signatures (e.g., in REE; Oonk *et al.*, 2018) during deposition of the pre-GOE Asbestos Hills BIFs.

The above findings were central in prompting the interrogation of the species-specific geochemistry of the Hotazel Formation with particular emphasis of the carbonate fraction. This thesis therefore revisits the Hotazel Formation rocks through the deployment of bulk but also species-specific geochemical techniques as used by Oonk *et al.*, (2017), namely detailed mineralogy with emphasis on the carbonate fraction of the rocks; bulk-rock major, trace and stable isotope geochemistry; and lastly, for the first time, carbonate fraction-specific analysis of the entire
Hotazel Formation. The overarching aim of all these applications is to elucidate the primary *versus* diagenetic processes that occurred during the deposition of the unique Hotazel Formation and the implications of these results in the context of atmosphere-ocean redox evolution around the GOE. The principal questions this thesis will try to address are whether: 1) the observed mineral phases and particularly the carbonate species in the Hotazel strata record purely diagenetic reactions against fully oxidized metal precursors: 2) diagenetic effects can be unraveled to infer and reconstruct the exact precursor mineralogy; 3) preservation of primary seawater chemical and potentially biological signals can be reliably extracted; and ultimately, how these signals can be potentially utilized as potential proxies for the initiation of oceanic and atmospheric oxygenation relating to the GOE. This will be achieved through the following corresponding steps:

- Chapter 2 Documentation and re-assessment of the Fe- and Mn-rich carbonate mineralogy and bulk-rock geochemistry of the entire Hotazel Formation at unprecedented stratigraphic resolution;
- Chapter 3 A first-time account of the carbonate fraction geochemistry and carbonate mineral chemistry at similarly high resolution, to shed light on the observed lithological cyclicity of the Hotazel Fe-Mn succession;
- Chapter 4 A small-scale examination of carbon and iron isotope variations between the three main lithofacies of the Hotazel Formation, and the implications on classic diagenetic models *versus* reconstructions of seawater chemistry during deposition; and,
- Chapter 5 Merging of all major findings from the three previous chapters into an interpreted depositional environment of the Hotazel Formation at the onset of the GOE.

Each of the aforementioned chapters (chapter 2-4) will contain a rationale, specific sampling and analytical techniques applied, results and interpretations, and a discussion/summary. All of these will be synthesized in chapter 5 which will present a conceptual model for the deposition of the three lithofacies of the Hotazel Formation, in direct connection to increased oxidation potential in line with the GOE. Chapter 1 will naturally play the role of the introductory chapter to the main body of this thesis.

### Sample selection and analytical approach

Sample collection for this study was carried out from drill core intersections of the Hotazel Formation preserved in the Gloria mine area. The drillcores GL137 and GL136 represent a complete stratigraphy of unmetamorphosed BIF-manganese ore layers of the Hotazel Formation, where hydrothermal alteration appears to have had no effect whatsoever on the rocks. These drill core interceptions are located ~500 meters apart, at the North-Western part of Gloria mine were manganese grade is 36-42 wt. % Mn (Figure 1.8) These cores were drilled by the company ASSMANG Ltd as part of their mining operations, grade control and exploration; sampling for this study was carried out with kind permission of, and support by the company.



Figure 1.7: A) The three lithofacies of the Hotazel Formation, namely: BIF, Hematite lutite, and Mn ore. B) Sharp contact of BIF and hematite lutite. C) Gradational contact between BIF and Mn hematite lutite. D & E) Gradational contacts between hematite lutite and Mn ore.

A total of 95 samples from drill core GL137, 89 from GL136, and a total of 32 subsamples from drillcore GL136 (Figure 1.9) were selected for this project. All analytical techniques applied for the various objectives of this project will be outlined in the chapters of this thesis that follow. All samples from both cores were selected at approximately one-meter intervals where possible, and extreme care was taken to avoid secondary/late stage fractures where carbonate/quartz veins dominated. Secondary veins were further avoided during subsequent sample preparation to obtain the most pristine BIF, Mn ore and hematite lutite material possible. The samples were selected to represent the Hotazel stratigraphy in its entirety, with special emphasis placed on capturing the lithologic transitions at a high resolution.



Figure 1.8: A. Locality of the Griqualand West Basin of the Transvaal Supergroup in the northwestern part of South Africa. B. The delineated extent of the Kalahari Manganese Field (KMF), showing the major subdivision between low (Mamatwan type) and high (Wessels type) grade manganese distribution and locality of Gloria mine. C. GL136 and GL137 sampled for this project within the geographical boundaries of Gloria mine.



Figure 1.9: The two drill cores GL137 and GL136 of the Hotazel Formation from Gloria mine as sampled for this thesis. The log indicates also part of the uppermost Ongeluk lavas and basal Moodraai carbonate rocks enveloping the Hotazel succession.

"If you're walking down the right path and you're willing to keep walking, eventually you'll make progress." – Barack Obama 2. Mineralogy and bulk-rock geochemistry of the Hotazel Formation

# 2.1 Rationale

The mineralogy and geochemistry of the Hotazel Formation has been extensively reported in literature (Gutzmer and Beukes, 1996; Tsikos and Moore, 1997; Tsikos et al., 2003; Schneiderhahn et al., 2006), with emphasis on the variations between different localities within the KMF and stratigraphic changes between the different lithologies. According to Tsikos and Moore (1997), the BIF of the Hotazel Formation is made up of 3 major mineralogical subdivisions, namely: the silicate group, comprising minerals such as stipnomelane, greenalite, minnesotaite, riebeckite, Ferich mica and abundant quartz; the oxide-sulfide group, consisting of mainly magnetite, hematite and usually minor pyrite; and lastly, the carbonate group, which is essentially made up of siderite, calcite, and the dolomite-ankerite series of carbonate minerals. These phases occur either as monomineralic mm-thick laminae, mainly for magnetite, or as mm- to cm-thick bands containing variable proportions of the above minerals (Tsikos and Moore, 1997). The transitional hematite lutite is made up of mostly hematite and carbonate laminae and ovoids of Mn-rich carbonates such as manganese rich calcite, kutnahorite and rhodocrosite (Beukes, 1987; Tsikos and Moore, 1997). The carbonate mineralogy of the lutite is similar to that of the manganese ore but, in addition to the Mn-carbonates, braunite is a dominant Mn-species in the ore layers while hematite becomes a minor component. No free quartz is present in the manganese-rich facies.

This chapter provides a comprehensive account of the bulk mineralogy and bulk-rock geochemical composition of the entire Hotazel succession at the highest resolution conducted to date. Mineralogical and analytical results are assessed in light of previously published studies, mainly from the southern KMF. Geochemical results include major oxide constituents (Mn, Fe, Ca, Mg & Si), trace elements and rare earth elements. Relationships are explored between these chemical signatures and BIFs of the older Kuruman and Griquatown formations; modern manganese deposits (nodules) and seawater; the possible implications of these relationships are highlighted towards reconstructions of the paleo-depositional environment. The abundances of trace elements (Sc, Ti, V, Cr, Co, Ni, Cu, Zn, Zr, Mo and U) are reported and evaluated mainly as proxies for detrital/volcanic input or as tracers of redox processes during deposition and diagenesis (e.g., Bau, 1993; Pecoits *et al.*, 2009; Planavsky *et al.*, 2014; Swanner *et al.*, 2014). Although emphasis has been placed on the carbonate mineralogy of the Hotazel Formation as a previously underutilized mineral fraction, the mineralogical context of the rocks is presented in full.

# 2.2 Sample Selection and Analytical Techniques

Samples from both drill cores (GL137 and GL136) selected for this study were analyzed for and are reported in this chapter. A total of 51 samples were cut into sections and polished for petrographic analysis using primarily a scanning electron microscope. The entire suite of 89 samples from drill core GL136 was analyzed for bulk-rock geochemistry. A selection of 8 representative samples were also analyzed for bulk mineralogy using X-ray diffraction analyses.

## 2.2.1 X-ray diffraction analysis and SEM imaging

The eight selected samples (Table 2.1) were analyzed on a Brucker X-ray diffractometer at the chemistry department of Rhodes University. Spectra were obtained at  $2\theta$  angles between 5° and 65° which should include most rock forming minerals. The data extracted were then analyzed using the mineral identification software *Crystal Sleuth*, where sample spectra were compared with published spectra of the expected mineral phases in each instance (Laetsch and Downs, 2006; Anthony *et al.*, 1990). Backscattered electron (BSE) images were obtained using various EPMA instruments at different universities alongside mineral chemistry analyses, as will be seen in the next chapter.

Sample Number	Depth	Lithology
GL137-91	237.63	BIF
GL137-75	259.64	Hematite lutite
GL137-61	276.19	Mn-ore
GL137-54	282.58	Hematite lutite
GL137-18	310.06	BIF
GL137-15	312.05	Mn-ore
GL137-8	322.44	Mn-ore
GL137-3	329.41	BIF

Table 2.1: List	of samples	selected for XRD	analyses for	this study.
			2	2

## 2.2.2 Bulk geochemical analysis

Glass disks were prepared for XRF analysis using 7.3 g of ultra-high purity trace element and Rare Earth Element-free flux (LiBO<sub>2</sub>=49.75%, Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>=49.75% LiI=0.50%) mixed with 0.4g of the pulverized sample. Whole-rock major element compositions were determined by XRF spectrometry on a PANalytical Axios Wavelength Dispersive spectrometer at the Central of Analytical Facilities, Stellenbosch University, South Africa. The spectrometer is fitted with a Rhodium tube and with the following analytical crystals: LIF200, LIF220, PE002, GE111 and PX1. The instrument is also fitted with a gas-flow proportional counter and a scintillation detector. The gas flow-flow proportional counter uses a 90% Ar to 10% methane gas mixture. Major element analysis was carried out using a fused glass disk, using a 2.4kW Rhodium tube. The matrix effects in the samples were corrected for by applying theoretical alpha factors and measured line overlap factors to the raw intensities measured with the SuperQ PANalytical software. The concentration of the control standards (see appendix II) that were used in the calibration procedures for major element analysis, fit the range of concentration of the samples.

# 2.3 Mineralogy and mineral textures

### 2.3.1 BIF mineralogy & textures

The BIF mineralogy of the Hotazel Formation displays little variability up stratigraphy, except were the BIF transitions into other, Mn-rich lithofacies. The main mineral species making up the bulk of the BIF as identified from petrographic observations and XRD results where appropriate, include quartz, magnetite, and carbonates (mainly ankerite, siderite, and lesser calcite) (Figures 2.1 (A, D & H), 2.2, & 2.3; Table 2.1). Very minor occurrences of iron silicate minerals (mainly greenalite and minnesotaite) were also occasionally seen under the microscope. Hematite only occurs at the basal part of the Hotazel succession and at transitions between BIF and hematite lutite. Typical texture of the BIF is microband alternations between dominantly magnetite-rich laminae and chert bands containing variable magnetite and carbonate abundances.

## 2.3.1.1 Ankerite-dominated BIF

The most common carbonate mineral in the BIF throughout the entire Hotazel Formation is ankerite which co-exists with various other minerals in either oxide- or chert-dominated bands. In chert-dominated bands, ankerite occurs as mainly disseminated subhedral to euhedral grains or as end-member massive clusters of subhedral grains. Individual grains develop in the form of rhombohedral shaped crystals with chert inclusions (Figure 2.2 A), or with both chert and occasional magnetite inclusions (Figure 2.2 B). In magnetite-dominated bands, ankerite similarly occurs as subhedral to euhedral disseminations and masses (Figure 2.2 C-F). The main inclusion type in ankerite in these bands is magnetite, with the latter also occurring along ankerite grain boundaries (Figure 2.2 G & H). Although ankerite and magnetite grains are generally clear and discrete in space, complex intergrowths between the two are also variously seen (Figure 2.2 C). Figure 2.2 B also shows an apparent compositional zonation in individual ankerite grains represented by brighter cores and darker rims. This feature is not prevalent in all ankerite grains observed in the Hotazel Formation.

Table 2.2: List of minerals in the Hotazel Formation and their chemical formulae as identified through a combination of x-ray diffraction, petrography, scanning electron microscopy and microprobe analysis.

Mineral	Formula
Kutnahorite	$Ca(Mn^{2+},Mg, Fe^{2+})(CO_3)_2$
Rhodocrosite	MnCO <sub>3</sub>
Calcite	CaCO <sub>3</sub>
Ankerite	Ca(Fe <sup>2+</sup> , Mg, Mn <sup>2+</sup> )(CO <sub>3</sub> ) <sub>2</sub>
Siderite	FeCO <sub>3</sub>
Hematite	Fe <sub>2</sub> O <sub>3</sub>
Magnetite	$Fe^{2+}Fe^{3+}{}_2O_4$
Braunite	$Mn^{2+}Mn^{3+}_{6} SiO_{12}$
Friedelite	Mn2+8 Si6O15(OH;Cl)10
Quartz (Chert)	SiO <sub>2</sub>

## 2.3.1.2 Siderite-dominated BIF

Siderite is the other iron rich carbonate present in the BIF of the Hotazel Formation. It is not modally as common as ankerite but rather occurs in increased abundance only at the top BIF layer above the uppermost manganese ore layer. Similar to ankerite, siderite occurs in both chert- and magnetite-dominated bands (Figure 2.3 A-D). It develops exclusively as subhedral to anhedral grains with chert and magnetite inclusions in chert-dominated bands (Figure 2.3 A), and magnetite grains scattered around the grain edges.



Figure 2.1: X-ray diffraction spectra (5-65° 2-theta) from the three representative lithofacies BIFs (A, D, and H), Mn-ore (B, C and F), and Hematite lutite (E and G) throughout the entire stratigraphy from drill core GL137. Abbreviations: Ank (ankerite); Mt (magnetite); Cc (calcite); Kut (kutnahorite); Hem (hematite); Br (braunite); Frd (Friedelite). GL137 samples selected- 3(A), 8(B), 15(C), 18(D), 54(E), 61(F) 75(G), 91(H).



Figure 2.2: SEM-BSE photomicrographs of ankerite-dominated BIF from drillcore GL137 sample- 47(A), 43(B), 77(C & H), 79 (D & E), 90(F), and 45(G), indicating textural relationships between oxide, silicate and carbonate minerals. Abbreviations: Cc (calcite); Ank (ankerite); Mt (magnetite); Qz (quartz); Kut (kutnahorite); Hem (hematite); Br (braunite).

Both ankerite and siderite appear to texturally co-exist, with no apparent textures observed that would indicate a sequential mode of formation (Figure 2.3 B & C). They both occur as sub- to anhedral grains, with no apparent inclusions in a random distribution where they appear to "float" in a chert-dominated matrix. The only observable differences between the two iron carbonates in BSE imagery are their established chemical signatures as observed through their relative brightness, and their dissimilar grain sizes with the ankerite grains being generally larger than siderite grains. Siderite in magnetite-dominated bands is less common and occurs as anhedral grains with no observable mineral inclusions.



Figure 2.3: Backscatter electron images of siderite textural relationships in BIF from drillcore GL137, sample-38(A) and 90(B-D). Abbreviations: Cc (calcite); Ank (ankerite); Sid (siderite) Mt (magnetite); Qz (quartz); Kut (kutnahorite); Hem (hematite); Br (braunite).

## 2.3.2 Transitional hematite lutite: mineralogy & textures

The mineralogy of the transitional hematite lutite is dominated by hematite as the main oxide species, kutnahorite and manganese-calcite  $\pm$  rhodocrosite as the main carbonate species, and braunite as the main silicate species. Free quartz is only observed at transitions between the lutite and BIF (Figure 2.1 G) and declines in abundance towards the Mn ore itself. Mineral textures within the hematite lutite varies quite significantly throughout the entire Hotazel succession as observed in the selection of samples displayed in Figure 2.4 A-H.

Hematite forms the matrix of the lutite as microscopic grains which develop as either anhedral or needle-like crystals (Figure 2.4 D). Braunite also forms part of the matrix in proximity to carbonate laminae and ovoids. Manganese-rich calcite occurs almost exclusively as microcrystalline laminae and ovoids, or as anhedral grains in a hematite and braunite dominated matrix. Within a groundmass of Mn-calcite, irregular blobs of kutnahorite commonly occur with well-defined grain boundaries and no apparent reaction textures along these boundaries (Figure 2.4 A-D, G-H).

Kutnahorite is the most prevalent manganese carbonate within the lutite, which is characterized by almost entirely anhedral grain shapes or masses in the form of laminae and ovoids (Figure 2.4 A-D, G-H). Disseminated kutnahorite grains are also observed within the hematite and braunite matrix (Figure 2.4 F). An observable chemical zonation in kutnahorite as seen in Figure 2.4 C, G & H, indicates higher manganese content in the rim (light grey) compared to the core (darker grey) as confirmed from the backscatter imagery and microprobe analysis.

An interesting textural observation is that of the successive occurrence of different mineral species across individual carbonate laminae or ovoids towards the surrounding carbonate poor hematitic groundmass. The following sequence is observed:

#### Mn-calcite – kutnahorite – braunite – hematite

where braunite essentially forms a border zone between the carbonate- and oxide-dominated domains within the hematite lutite (Figure 2.4 A & E). Figure 2.4 E shows a kutnahorite-dominated ovoid being enveloped by such a braunite-rich zone. This feature is not observed throughout all selected samples; in some cases, such as seen in Figure 2.4 C, G & H, the observed sequence is somewhat different, by following the pattern:



Figure 2.4: SEM-BSE photomicrographs of textural relationships between carbonates and oxides in transitional hematite lutite from drillcore GL137, sample-25(A), 10(B), 34(C), 35(D), 54(E), 22(F), and 36 (G & H). Abbreviations: Cc (calcite); Ank (ankerite); Mt (magnetite); Qz (quartz); Kut (kutnahorite); Hem (hematite); Br (braunite).

#### Mn-calcite – kutnahorite – hematite

that is, with no intermediate braunite zone observed. The above mineralogical associations are also observed in the manganese ore lithologies as will be shown later, with the required adjustments for the specific mineral assemblage that occur therein.

### 2.3.3 Manganese ore mineralogy & textures

The manganese ore mineralogy is in many ways similar to the transitional hematite lutite with the main difference being the dominance of braunite as compared to hematite. Contrary to the hematite lutite, the most dominant carbonate phase in the manganese ore is Mn-calcite and, to a lesser extent, kutnahorite and rhodocrosite. The manganese calcite in the ore also appears to be strikingly lighter in color compared to the equivalent in the hematite lutite. This is an indication of a higher Ca/Mn ratio in the ore calcite, which will be confirmed through corresponding geochemical data in the chapters that follow. Another major mineralogical difference between the hematite lutite and manganese ore is the common occurrence of friedelite in the latter (Figure 2.1).

The mineral textures of Mn-calcite in the manganese ore are very similar to those of adjacent hematite lutite: they occur mainly as anhedral masses within carbonate laminae and ovoids, and as anhedral grains within braunite-dominated matrix/groundmass as seen in Figure 2.5 B-H. Similarly, calcic kutnahorite occurs as anhedral grains dispersed within laminae and ovoids which are composed by manganese-poor calcite. Compared to the hematite lutite, chemical zonation of kutnahorite in the manganese ore is less prevalent and so is its abundance, as both carbonate laminae and ovoids are dominated by Mn-poor calcite.

#### Ovoid/laminae to matrix boundaries

Ovoids occur mainly as lenticular or circular features (Figure 2.5 A), which are dominated by both manganese carbonates. The hosting matrix is dominated by braunite and to a lesser extent hematite. Arguably the most striking feature observed in both the lutite and manganese ore is that of the mineralogical sequence from carbonate laminae/ovoids to the matrix; in the case of the manganese ore, the mineralogical sequence plays out as:



Figure 2.5: SEM-BSE photomicrographs of mineral textures in manganese ore from drill core GL137, samples 13(A & B), 63(C, E & G), 10(D), and 15(F & H), showing relationships between manganese rich carbonates, silicates and hematite. Abbreviations: Cc (calcite); Ank (ankerite); Mt (magnetite); Qz (quartz); Kut (kutnahorite); Hem (hematite); Br (braunite); Frd (friedelite).

#### Mn-calcite – kutnahorite – friedelite – braunite – hematite

which is seen in Figure 2.5 B and E - H. In an analogous fashion with braunite in the hematite lutite, friedelite appears to be enveloping the carbonate laminae/ovoid (Figure 2.5 F & H) thus forming a boundary between the carbonate and silicate/oxide-dominated zones.

## 2.4 Bulk geochemical chemo-stratigraphic relationships

#### 2.4.1 Major element oxides

The bulk geochemistry of the Hotazel Formation comprises mainly iron, manganese, calcium, magnesium and silica with minor to trace amounts of titanium, phosphorus, sodium, potassium and aluminum as seen from Figure 2.6-2.8 below, and appendix II. The concentrations of titanium, potassium and sodium are in fact below detection limit in most samples and will not be discussed further in this section.

The average bulk BIF composition within the Hotazel Formation from drill core GL136 is  $45.3\pm7.8$  wt. % Fe<sub>2</sub>O<sub>3</sub>,  $35.5\pm6.8$  wt. % SiO<sub>2</sub>, and low MnO<sub>2</sub>, CaO and MgO at  $0.6\pm0.7$  wt. %,  $7.8\pm4.6$  wt. %, and  $1.6\pm0.6$  wt. %, respectively. The transitional hematite lutite is comprised of relatively lower SiO<sub>2</sub> concentrations, at an average of  $15.5\pm4.2$  wt. %, with MnO<sub>2</sub> and MgO at  $14.9\pm7.2$  wt. % and  $4.6\pm2.1$  wt. % respectively. Fe<sub>2</sub>O<sub>3</sub> concentrations are similar to BIF at  $34.5\pm9.4$  wt. %, whereas CaO concentrations average at  $11.5\pm7.7$  wt. %. The manganese ore layers consist of very high average MnO<sub>2</sub> at  $36.2\pm9.2$  wt. % and very low bulk SiO<sub>2</sub> at  $8.5\pm3.8$  wt. %. Bulk-rock CaO ( $15.5\pm6.2$  wt. %) and MgO ( $4.0\pm1.4$  wt. %) concentrations are higher compared to average BIF and hematite lutite, whilst Fe<sub>2</sub>O<sub>3</sub> concentrations average at  $16.2\pm9.4$  wt. %.

As expected, the major oxide constituents in the Hotazel succession show the largest variations in concentrations across lithologic transitions. The BIF contains essentially little manganese at bulk oxide contents generally below 0.5 wt. %, whereas with respect to bulk iron oxide, a gradual decline in concentration is registered from BIF (as high as 57.9 wt.%) to Mn ore (as low as 4.8 wt. %). Stratigraphically, silica behaves similarly to iron in that it peaks in the BIF layers and drops to a few weight percent within the manganese rich layers (Figure 2.6). In order to elucidate the geochemical signatures of these lithological transitions and inform the modelling and

interpretations of these transitions with respect to the primary environment of the Hotazel Formation, it was deemed essential to treat each one of these 3 cycles separately. This is presented in the sections that follow.

#### Lower BIF-Mn transition (LBMT)

This is the lowermost cycle of the Hotazel Formation which, in drill core GL136 occupies the depth from 389.5 to 368.3 meters. It comprises the lowermost BIF-hematite lutite-lower Mn ore layer-hematite lutite-BIF. Compared to average Hotazel BIF, the 5.4-meter thick (389.5-384.1 m) lowermost BIF layer has a higher bulk average Fe<sub>2</sub>O<sub>3</sub> concentration at 53.6 $\pm$ 3.4 wt. % and lower average SiO<sub>2</sub> at 32.9 $\pm$ 4.9 wt. %. With respect to MnO<sub>2</sub> and MgO, average values are higher compared to average Hotazel BIF at 2.2 $\pm$ 1.1 wt. and 2.7 $\pm$ 0.7 wt. %, whereas CaO is lower at 2.7 $\pm$ 1.5 wt. %. The above concentration averages in combination with low LOI at an average of 4.3 $\pm$ 2.7 wt. % indicate that this lowermost BIF is carbonate-lean and oxide-rich.

The overlying transitional hematite lutite straddles the depths 384.1-381.3 meters and is characterized by rising MnO<sub>2</sub> and declining Fe<sub>2</sub>O<sub>3</sub> average contents ( $17.3\pm6.1$  wt. % and  $39.2\pm7.9$  wt. % respectively). Bulk-rock average SiO<sub>2</sub> concentration within the hematite lutite appears lower than the underlying BIF at  $16.8\pm19$  wt. %, whereas CaO and MgO average abundances increase to  $3.4\pm0.9$  and  $8.5\pm0.9$  wt. % respectively. Above the hematite lutite lies the lowermost Mn ore layer (381.3-368.3 meters), which expectedly contains high average content of MnO<sub>2</sub> ( $39.7\pm8.9$  wt. %), that increase towards the middle part of the ore layer. This is where the relative ratio of braunite to carbonate is the highest in the ore. Bulk-rock average CaO also increases markedly ( $18.0 \pm 4.3$  wt. %) compared to the underlying lithologies, whereas bulk Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> drop to averages of  $11.6\pm7.9$  wt. % and  $5.4\pm1.8$  wt. % respectively. Average MgO concentrations are at  $4.1\pm1.6$  wt. %; this, in-conjunction with CaO at a similar average and high LOI at 20.6 wt. %, indicate large modal abundance of calcic carbonate (Mn calcite and calcic kutnahorite) in the ore.

Overlying the Mn ore is a thin (0.8-meters) transitional hematite lutite at depths of 368.3-367.5 meters. The single sample analyzed is characterized by very high CaO and LOI values at 23.4 wt. % and 24.7 wt. %; MnO<sub>2</sub> at 19.9 wt. %, Fe<sub>2</sub>O<sub>3</sub> at 12.6 wt. %, SiO<sub>2</sub> at 12.0 wt. % and MgO at 6.1

wt. %. This lutite is overlain by a BIF layer at depths between 367.5-363.4 meters with bulk average Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> concentrations of 45.7 $\pm$ 9.8 wt. % and 42.7 $\pm$ 5.8 wt. % respectively. The concentrations of MnO<sub>2</sub>, CaO and MgO are very low at values of 0.8 $\pm$ 0.6 wt. %, 4.2 $\pm$ 2.9, and 1.4 $\pm$ 1.0 wt. % respectively, with correspondingly low and variable LOI at 3.5 $\pm$ 4.0 wt. %.

#### Manganese marker sub-cycle (MMSC)

Overlying the LBMT cycle, is a manganese sub-cycle at depths between 363.4-353.9 meters. This cycle is characterized by arguably the most transitional and thus geochemically variable lithologic signature. The lithologic sequence of this sub-cycle comprises hematite lutite-Mn ore-hematite lutite-BIF-hematite lutite. Based on a single sample analysis, the lower hematite lutite layer (363.4-362.1 meters depth) is characterized by a bulk Fe<sub>2</sub>O<sub>3</sub> value of 42.1 wt. %, MnO<sub>2</sub> at 12.8 wt. %, SiO<sub>2</sub> at 18.2 wt. % and CaO and MgO values of 6.4 wt. % and 4.9 wt. % respectively. The lutite is overlain by a thin Mn ore layer widely referred to in mining jargon as "the marker" (362.1-359.5 meters, depth) with higher average Fe<sub>2</sub>O<sub>3</sub> ( $26.0\pm7.0$  wt. %) and lower average MnO<sub>2</sub> ( $26.7\pm4.5$  wt. %) concentrations compared to the lowermost manganese ore layer. Bulk SiO<sub>2</sub> concentrations are at 14.6±0.9 wt. %, with CaO, MgO, and LOI values at 10.3±4.4 wt. %,  $5.0\pm1.9$  wt. %, and  $17.4\pm2.8$  wt. % respectively. These values collectively reflect the high modal abundance of hematite and carbonate relative to braunite, and hence the overall subdued bulk MnO<sub>2</sub> concentrations.

The bulk-rock analysis of the hematite lutite overlying the Mn marker, registers Fe<sub>2</sub>O<sub>3</sub> of 37.0 wt. %, MnO<sub>2</sub> at 5.2 wt. %, SiO<sub>2</sub> at 16.8 wt. %, CaO and MgO at 18.9 wt. % and 4.3 wt. % respectively, and LOI at 15.4 wt. %. This composition reflects a high modal abundance of carbonate which, as will be shown later accounts for the high manganese content as well. The lutite layer transitions upward into hematite-free BIF with average bulk Fe<sub>2</sub>O<sub>3</sub> concentration of  $48.2\pm10.8$  wt. %. The average MnO<sub>2</sub> content is higher compared to the Hotazel BIF, at  $1.8\pm0.4$  wt. % and in that respect compares well with the stratigraphically lowermost BIF in cycle LBMT above. The average bulk SiO<sub>2</sub> of 24.6±7.0 wt. % and CaO and MgO of  $11.9\pm9.6$  wt. % and  $1.6\pm0.1$  wt. %, respectively, reflect a carbonate-rich assemblage, supported by the LOI of  $10.4\pm8.3$  wt. %. Finally, the BIF layer is overlain by another hematite lutite at depths of 356.4-353.9 meters. Geochemically, this lutite is characterized by average bulk Fe<sub>2</sub>O<sub>3</sub> concentration of  $25.5\pm8.9$  wt. %, MnO<sub>2</sub> content of

 $10.0\pm1.0$  wt. %, a high CaO average concentration at  $22.9\pm5.8$  wt. %, low average MgO ( $2.8\pm0.7$  wt. %), SiO<sub>2</sub> at  $13.5\pm9.1$ , and high LOI ( $22.9\pm3.7$  wt. %). This hematite lutite facies is therefore particularly carbonate-rich, dominated by manganiferous calcite and hematite.

#### Middle BIF-Top Mn cycle (MBTMC)

The uppermost manganese ore layer and enveloping lithologies (hematite lutite, BIF) straddles the depths of 353.9-316.1 and represents probably the least intricate cycle of the Hotazel Formation with respect to geochemical variability on a fine scale. It comprises a sequence of BIF-hematite lutite-uppermost Mn ore-hematite lutite-BIF. The lower BIF from this cycle, at depths of 353.9-339.5 meters is characterized by average bulk Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> concentrations of 45.9 $\pm$ 6.5 wt. % and 32.6 $\pm$ 5.5 wt. %, respectively. The average MnO<sub>2</sub> value here is the lowest recorded in the entire Hotazel sequence (0.4 $\pm$ 0.2 wt. %), whereas average MgO (1.3 $\pm$ 0.3 wt. %), CaO (9.6 $\pm$ 4.7 wt. %) and LOI (8.8 $\pm$ 3.8 wt. %) concentrations reflect the dominance of modal ankerite in the rock.

The hematite lutite overlying the above BIF (339.5-335.9), is characterized by high bulk-rock average MnO<sub>2</sub> (22.3±13.9 wt. %), Fe<sub>2</sub>O<sub>3</sub> at 31.4±9.5 wt. %, CaO at 9.9±2.3 wt. %, MgO at 3.7±0.8 wt. %, and LOI at 18.5±7.5 wt. %.One sample from this lutite layer is characterized by a high concentration of Na<sub>2</sub>O at 3.5 wt. %; this is due to the presence of riebeckite in this sample as the latter has also been occasionally reported from hematite lutite in the southern KMF (Tsikos, 1999). The uppermost manganese ore layer overlies this hematite lutite and attains a thickness of 9.8 meters (335.9-326.1 depth). The bulk average MnO<sub>2</sub> concentration here is at 34.9±8.6 wt. %, with an average Fe<sub>2</sub>O<sub>3</sub> content of 18.3±9.2 wt. %. Similar to the lowermost manganese layer, the uppermost counterpart shows peak manganese content at the center with correspondingly lowest Fe<sub>2</sub>O<sub>3</sub> concentration. With regard to the carbonate-specific oxides, the average CaO and MgO values of 14.1±7.3 wt. % and 3.6±0.8 wt. %, respectively, combined with the LOI average values of 18.7±3.7 wt. %, point to lower modal carbonate (and relatively higher modal hematite) in the uppermost managanese layer. Moreover, the higher SiO<sub>2</sub> concentration at 10.3±2.3 wt. % indicates a higher modal abundance of friedelite *versus* braunite in this ore. All these attributes contribute to the lower economic viability of the uppermost manganese layer compared to the lowermost one.



Figure 2.6: High-resolution major oxide composition chemo-stratigraphic relationships from drill core GL136. Note that the subdivisions of the major transitions are labeled on the right edge of the figure

Between the depths of 326.1- and 316.2-meters and overlying the uppermost Mn layer, lies the stratigraphically uppermost hematite lutite layer with a thickness of 9.9 meters. This hematite lutite records average bulk MnO<sub>2</sub> concentration of  $13.8\pm3.6$  wt. %, Fe<sub>2</sub>O<sub>3</sub> at  $39.5\pm2.7$  wt. %, SiO<sub>2</sub> at  $17.0\pm2.7$  wt. %, CaO and MgO of  $8.6\pm4.5$  wt. % and  $3.7\pm1.2$  wt. %, respectively, and LOI at  $15.0\pm2.5$  wt. %. Collectively, these data reflect a mineral assemblage dominated by hematite and manganese-rich carbonates.

### Top BIF-Mooidraai Cycle (TBMC)

The uppermost cycle is in fact a 24.2 meters thick transition between the uppermost BIF layer (316.2-292.0 m depth) that gradually and conformably grades into the overlying Mooidraai Formation. The bulk geochemical composition of this BIF layer comprises average  $Fe_2O_3$  concentration of 43.4±8.1 wt. %, average SiO<sub>2</sub> concentration of 37.4±6.2 wt. %; very low average MnO<sub>2</sub> concentration of 0.3±0.2 wt. %; average LOI at 8.2±4.2 wt. %; and CaO and MgO average concentrations of 8.0±3.7 wt. % and 1.5±0.4 wt. %, respectively. The mineralogy corresponding to the above geochemical signatures is made up of quartz, magnetite, and the iron carbonates ankerite and siderite. The transition to the overlying Moodraai Formation is marked by a gradual decline in the bulk SiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> concentrations and corresponding increase in carbonate specific oxides (mainly CaO).

# 2.5 Trace element relationships

# 2.5.1 Alkali and alkali earth metals (including P<sub>2</sub>O<sub>5</sub>)

The alkali and alkali earth metals (Rb, Sr, Cs, Ba) and  $P_2O_5$  analyzed for this study show considerably diverse behavior throughout the Hotazel succession, most probably related to equally diverse mineralogical controls. Figure 2.8 illustrates the chemo-stratigraphic behavior and relationships between all five chemical species.



Figure 2.7: High-resolution, alkali and alkali earth elemental and P<sub>2</sub>O<sub>5</sub> abundance chemostratigraphic relationships from drill core GL136.

Rubidium (Rb) concentrations range between 0.12-35.25 ppm, with the highest and most variable values recorded in the uppermost hematite lutite, with an average concentration of 9.58±10.57 ppm. The high standard deviation reflects the characteristic peak in Rb that defines that hematite lutite zone. Similarly, high values are seen in the lowermost BIF and also the hematite lutite underlying the uppermost manganese layer. In all of these stratigraphic zones, petrographic examination has shown increased concentrations of stipnomelane and riebeckite, which are minerals thought to control the behavior of Rb. Strontium (Sr) concentrations are highest within

the uppermost manganese ore and reach the value of 1026 ppm, with an average value of 259.08±285.52 ppm. Similarly, high average Sr values (203.87±226.14 ppm) are registered in the hematite lutite above the manganese marker. The high bulk CaO content in these parts of the Hotazel stratigraphy suggest that Sr substitutes for Ca in the structure of calcite.

With regard to cesium (Cs) there is no notable variability, at average concentrations of  $0.48\pm0.55$  ppm in manganese ore and  $0.59\pm0.61$  ppm in BIF. The highest average Cs value is recorded in hematite lutite at  $1.03\pm0.82$  ppm. Both barium and phosphorus show considerable variability up stratigraphy with distinct spikes of concentration maxima for both elements occasionally seen. The average Ba concentration in hematite lutite is at  $383.18\pm528.40$  ppm; this drops to  $245.19\pm351$  ppm in the manganese ore, and ultimately to  $63.51\pm75.02$  ppm in the BIF. Phosphorus (P<sub>2</sub>O<sub>5</sub>) concentrations have an average of  $0.10\pm0.04$  wt.% in BIF,  $0.06\pm0.01$  wt.% in hematite lutite, and  $0.04\pm0.01$  wt% in manganese ore. It is expected that the stratigraphic variability observed in both Ba and P correspond to variability in trace barite and/or Ba carbonate, and in apatite, respectively.

## 2.5.2 Transition metals, actinides and lanthanides

The transition metals (Zn, Ni, Cu, Cr, V, Mo, Co) analyzed, display concentrations at or below 100 ppm. Zn, Cu, Cr, and V exhibit no clear variability against the lithostratigraphy of the Hotazel Formation and show occasional spikes in concentration that cannot be attributed to any specific mineralogical signal. It is anticipated that these elements are controlled by the very low detrital component in the Hotazel Formation as this will be further illustrated in the behavior of high field strength elements (HFSE) later. Therefore, there will be no further discussion here on these four elements.

With regard to Ni and Mo, there appears to be a statistically clear increase in average concentration between BIF and manganese ore. Average Ni concentrations appear to be similar between BIF and hematite lutite at values of  $12.84\pm4.30$  ppm and  $13.40\pm3.90$  ppm, respectively. Relatively higher average concentration is however seen in the Mn ore layers at  $19.81\pm2.79$  ppm. Stratigraphically, this is shown by a slight positive trend from hematite lutite to the ore (Figure 2.8). Similarly, Mo is very low with the lowest average observed in the BIF at  $1.79\pm0.40$  ppm. The manganese layers have the highest Mo concentration at a grand average of  $2.86\pm0.68$  ppm, whilst the hematite lutites show an average value that is comparable to BIF at  $1.85\pm0.52$  ppm. The inference therefore that can be made for those two elements is that they must be controlled by the manganese component of the sequence (Figure 2.8).



Figure 2.8: High resolution, transition metal (Zn, Cu, Ni, Cr, V, Mo, Co) abundance and chemostratigraphic relationships from drill core GL136.

Average Co concentration is very low in the BIFs at  $3.79\pm3.42$  ppm, with values increasing significantly towards the manganese rich assemblages. However, unlike with Ni and Mo, peak Co concentrations appear to be developed in the hematite lutite transitions and not in the manganese ore layers themselves. Specifically, the hematite lutites exhibit the highest average Co concentrations at a value of  $50.29\pm18.77$  ppm, whereas the manganese layers record a lower average at  $40.78\pm14.30$  ppm. By contrast, the concentration in the BIF layers is strikingly lower at an average of  $3.87\pm3.41$  ppm. It becomes apparent that Co behavior across the Hotazel stratigraphy is controlled neither by peak manganese nor by peak iron but rather by the increased

Zr ppm Y ppm Sc ppm Nb ppm **U** ppm **EREE** ppm 0.2 0.4 36. 

abundance of hematite as only seen in the hematite lutite. This feature will be dealt with in more detail later in this thesis.

Figure 2.9: High-resolution, HFSE (Zr, Sc, Nb) U, Y and ∑REE abundances and chemo-stratigraphic relationships from drill core GL136.

With regard to the HFSE (Zr, Sc, Nb), U, Y and the sum of REE ( $\sum$ REE), absolute concentration and stratigraphic variability appear to be low and erratic across the entire Hotazel Formation. Average concentration for Y is at 8.80±2.33 ppm for BIF, 8.01±2.57 ppm for hematite lutite and 5.75±1.19 ppm for the manganese ore. Uranium (U) content is extremely low at average values of 0.09±0.05 ppm for BIF, 0.12±0.07 ppm for hematite lutite and 0.10±0.02 ppm for manganese ore. The correspondence of the stratigraphic variability for both above elements and the  $\sum$ REE suggests a common mineralogical control by a mineral phase (e.g., phosphate) enriched in these species.

Average Zr values also appear to be low throughout the Hotazel Formation at  $5.18\pm1.68$  ppm for BIF,  $5.28\pm2.68$  ppm for hematite lutite and  $4.25\pm1.61$  ppm for the manganese ore. Average Nb concentrations are extremely low (<1.2 ppm) across all three lithofacies, with a value of  $0.42\pm0.15$  recorded in BIF,  $0.46\pm0.20$  in hematite lutite, and  $0.44\pm0.14$  in the manganese ore. Finally, average Scandium (Sc) concentrations are also low and invariant in all three lithofacies, at  $2.91\pm0.85$  ppm for BIF,  $2.20\pm1.06$  ppm for hematite lutite, and  $1.63\pm0.36$  for manganese ore.

# 2.6 Rare earth element patterns

Rare earth elements (REE) spidergrams for the entire analyzed sample set of drill core GL136 have been produced and are displayed in Figure 2.10. Normalization of the data was done against the post Archean Average Shale (PAAS; Pourmand *et al.*, 2012) and results are shown separately for each major lithofacies, namely BIF, hematite lutite and manganese ore. All three lithofacies exhibit characteristic positive slope reflecting relative depletion in LREE compared to HREE. In terms of absolute normalized values, all samples are clearly depleted in REE abundance with respect to PAAS. Specifically, ratioed values for the LREE (La to Gd) range between 0.04 to 0.13 for all three lithofacies; for the HREE (Tb to Lu) the corresponding ratioed values range between 0.11 to 0.29. With respect to Y/Ho ratios, the BIF, hematite lutite and manganese ore have very similar average values of  $48.80\pm5.45$ ,  $47.71\pm6.51$ , and  $47.74\pm7.82$ , respectively.

There are several first order observations that can be gleaned from the diagrams of Figure 2.10: firstly, there appears to be little variability in the slope of the REE spidergrams between the three sample populations, namely BIF, hematite lutite and manganese ore. Secondly, all samples are characterized by an apparent positive La anomaly, which is a feature that has been reported widely before in BIFs of the Neoarchean and Paleoproterozoic (Barrett *et al.*, 1988; Bau and Dulski, 1996; Planavsky *et al.*, 2010). This La anomaly renders difficult the definition and determination of negative Ce anomalies in the same samples, an issue which will be discussed further in the concluding parts of this chapter. The third observation relates to the behavior of Eu and specifically

the erratic development of weak to distinct positive Eu anomaly across different sample populations or within a given population.



Figure 2.10: Bulk-rock REE/PAAS patterns from selected samples from: A) the Hotazel BIF (n=43); B) transitional hematite lutite (n=19); and C) manganese ore (n=27)

# 2.7 Summary and conclusions

#### Carbonate mineralogy

The carbonate mineralogy of chemical sediments has been attributed to either diagenetic processes, where precursor Fe and Mn oxyhydroxides precipitated from the water column were reduced through bacterially-mediated dissimilatory iron/manganese reduction (i.e., DIR/DMR) within the sediment pile (Klein, 1983; Lovley, 1991) or precipitated directly from the seawater-column (Webb et al., 2003; Ohmoto, et al., 2004 Pecoits et al., 2009). The diagenetic pathway is mainly based on the crystalline neomorphic textures they commonly exhibit. In the BIF layers of the Hotazel Formation, the main carbonate mineral phases are ankerite and siderite, with ankerite occurring as either anhedral or subhedral grains in both oxide and chert dominated bands, and siderite occurring mainly in the uppermost part of the BIF stratigraphy (to be dealt with more in chapter 3). Similarly, siderite occurs as subhedral to anhedral fine grains and typically occurs in coexistence with ankerite. This is at apparent odds with widely accepted diagenetic processes: these predict that carbonates formed through processes such as DIR will depend on the availability of pore fluid cations (Ca<sup>2+</sup> Mg<sup>2+</sup>) and marine bicarbonate, in addition to water column-sourced organic carbon reacting with ferric oxyhydroxides within the sediment pile. This assumption implies that, in theory at least, only one carbonate phase should form at any given time in response to local equilibria unless one replaces the other through fluid rock interactions during burial processes sensu lato (Kappler, 2005). Other ideas (Klein and Beukes, 1989; Webb et al., 2003; Ohmoto, et al., 2004 Pecoits et al., 2009) suggest that siderite, due to its fine grained and anhedral nature, could record direct precipitation from seawater, which then gets recrystallized below the sediment water interface via early diagenesis, whilst ankerite is a more clear diagenetic candidate due to its rhombohedral habit and replacement textures wherever visible. As stated above, this is not observable within the samples analyzed, and textures exhibited suggest co-genesis.

The carbonate mineralogy of the hematite lutite and manganese ore consists mainly of Mn-calcite, kutnahorite, and some rhodochrosite. These minerals, like their Fe counterparts in BIF, seem to exhibit co-genetic precipitation features, as they occur as anhedral grains and coexist within carbonate rich laminae with no diagenetic replacement textures observed. This suggests possible

primary precipitation of these mineral phases from a stratified oceanic water column. Further discussion on this point will be made in chapter 5.

#### Implications of major and trace element geochemistry in the Hotazel Formation

The Hotazel Formation records typical major oxide concentration for BIF as reported before (Tsikos *et al.*, 1997; 2003; 2010). The average Fe<sub>2</sub>O<sub>3</sub> concentration is 45.5±7.8 throughout the succession, with high values recorded mainly within the BIF layer from the bottom cycle (LBMT). The latter points to a period of high initial iron oxide deposition, whilst the subsequent cycles may signify a more diluted iron oxide precipitation by increased silica. An increase in carbonate deposition is also indicated by an increase in calcium concentrations towards the upper BIF layers, especially the MBTMC and TBMC. The middle "marker" sub-cycle is highly transitional, and possibly represents a period of a relatively transient, fast-changing depositional environment. Evidence for this would be the highly gradational geochemical and lithological boundaries between BIF and manganese rich assemblages. Periods of manganese deposition were clearly silica impoverished, as represented by very low SiO<sub>2</sub> concentrations and high modal carbonate.

Elements such as Zr, Ti, and Al have been used for the determination of allochthonous material input (either detrital or volcanic ash) in chemical sedimentary rocks such as BIF, due to their general immobility in aqueous solution (Bau *et al.*, 1993; Pecoits *et al.*, 2009). The low concentrations of the aforementioned trace elements are indicative of insignificant detrital input during deposition.

Transition metals such as Cu, V, Ni and Cu, generally show no appreciable concentrations or variability between the different lithologies, with only Ni and Mo showing higher concentration in manganese ore. These metals are classically adsorbed onto Mn and Fe oxyhydroxide complexes, hence their concentrations and stable isotopes are widely used as indirect proxies for such precursors transferring the signals from seawater to the sediment (e.g., Tribovillard *et al.*, 2006). Cu and Ni are also thought to be good proxies for organic carbon fluxes/productivity in anoxic conditions (Tribovillard *et al.*, 2006; Piper and Perkins, 2004) either forming complexes with organic matter or adsorbing onto Fe-Mn-oxyhydroxides. This is thought to accelerate scavenging

and sediment enrichment (Nameroff *et al.*, 2004), and subsequent release into the pore waters upon reduction of oxyhydroxides and/or organic matter decay.

Cr isotopes have been used in BIF as proxy of the rise of atmospheric oxygen around 2.45 - 2.2 Ga (e.g., Frei *et al.*, 2009). This is based on the premise that oxidative weathering produces more oxidized and aqueously mobile Cr(VI) which prefers the heavier Cr isotope. Reinhard *et al.*, (2014) state that due to the efficiency of reduction of Cr(IV) by Fe(II) in solution, co-precipitation of ferric oxide and Cr(OH)<sub>3</sub> would be expected, resulting in elevated Cr concentrations in BIFs. The data analyzed here show comparatively very low concentrations between the three lithofacies of the Hotazel with hardly any variance, suggesting no clear control by Fe or Mn, low redox proxy value and thus a likely detrital provenance. With regard to Mo, extensive studies have been made on its utility as redox proxy and have linked its behavior and isotope fractionation directly to the formation of sulphides versus Fe/Mn oxide species (e.g., Kohler *et al.*, 2010' Kurzweil *et al.*, 2016). Although the Hotazel Formation records very low Mo concentrations in all three lithofacies (<4 ppm) similar to the older Asbestos Hills (Figure 5.3), the slightly higher abundances in the Mn-rich layers suggest a high potential for application of isotope analyses. This kind of work was, however, beyond the scope of this thesis.

In experimental work on the behavior of cobalt in marine environments performed by Swanner *et al.*, (2014), it is suggested that Co does not form carbonate compounds, but rather at very high EhpH conditions it will precipitate as Co(OH)<sub>3</sub> precipitates through oxidation of Co(II) to Co(III) at the same Eh-pH space where Mn(II) oxidation to Mn(IV) occurs. This suggests that Co(III) will likely be adsorbed by Fe(III) and/or Mn(III,IV) oxyhydroxides which is deemed to be an important pathway for Co scavenging under anoxic conditions (Swanner *et al.*, 2014). The data from this study show high concentrations of Co in the manganese rich assemblages, with the hematite lutite recording the highest concentrations. The BIF on the other hand shows very low Co contents, indistinguishable to those of the Kuruman and Griquatown BIFs as will be seen later in chapter 5. This suggests that if Mn (IV) oxyhydroxides were the precursor precipitates, Co concentrations would likely be expected to be higher within the manganese ore compared to the hematite lutite, which is not the case (see Figure 2.7 for MnO<sub>2</sub>, then 2.9 for Co). This hints to another sink for Co in the Hotazel Formation, namely Fe(III) oxyhydroxides, the implications of which will be discussed further in chapter 5.

### Rare earth elements in the Hotazel Formation

It is known that the distribution of REE in chemical sedimentary rocks can be influenced by syndepositional (e.g., clastic contamination) and post-depositional processes alike (e.g., hydrothermal alteration (Bau, 1993). Bulk-rock REE patterns in BIF have been used extensively in research to constrain direct primary chemical precipitation of BIF minerals from seawater (e.g., Bau and Dulski, 1996). In BIFs with little detrital influence such as seen in the Hotazel Formation and most classic pre-GOE BIFs, the observed REE patterns are most likely due to their scavenging during precipitation of either primary Fe-oxyhydroxides or carbonates (Bau, 1993). This effect can be assumed for both the hematite lutite and manganese ore samples as well, since similar patterns and concentrations are recorded in both of these facies as well. The average REE pattern of Hotazel BIF is similar to that of the older Asbestos Hills (Figure 2.12) in which the study of Oonk *et al.*, (2017) suggest that they record a seawater pattern similar to modern-day. Diagenetic processes appear to have had a negligible effect on the REE pattern of Hotazel rocks due either to the demonstrable low mobility and concentration of REE in pore water solutions (Elderfield and Sholkovitz, 1987), and/or evidence of closed system diagenetic conditions for REEs due to impermeability imparted by Fe-oxyhydroxide layers (Bau, 1993).

Apart from the concentration and fractionation of REE in BIFs, the presence of a Ce anomaly is regarded as a direct proxy of the redox state of seawater (Ling *et al.*, 2013), whereby negative Ce anomalies are observed in oxygenated seawater (see Figure 2.12), whilst suboxic and anoxic waters would exhibit no Ce anomalies. Bau *et al.*, (1996) also suggest that positive Ce anomalies ought to be recorded by Fe-Mn oxyhydroxide-rich deposits, as they are known to adsorb tetravalent cerium (e.g., see Cook Islands ferromanganese nodules, Figure 2.11 B). As mentioned in preceding sections (section 1.2 and 1.3), these oxyhydroxides have been thought to be the precursor precipitates of the Hotazel Formation assemblages, but Figure 2.11 D shows the complete absence of a positive Ce anomaly in all samples analyzed and considered here. The manganese ore samples in fact record a similar REE pattern to the BIF and lutite of the Hotazel Formation in showing no positive Ce anomaly. Finally, the ratio of yttrium over holmium (Y/Ho) is also used to distinguish between marine carbonates which have values between 44 and 74 (super-chondritic) (Bau *et al.*, 1996), while freshwater ones range between 26 and 28 (chondritic) (Taylor



and McLennan, 1985). The Y/Ho ratios of all three lithofacies studied here from the Hotazel Formation range between 47 and 49, consistent with a marine origin.

Figure 2.11: Bulk-rock REE/PAAS ranges and mean (colored line) for selected samples from the Hotazel Formation, Kuruman and Griquatown averages, and seawater averages (A); Hotazel hematite lutite and seawater averages (B); Manganese ore, Cook Island nodules averages, and seawater averages (C). The Kuruman and Griquatown average BIF values are from Oonk, 2017. The present-day seawater average curve (\*10<sup>6</sup>) is from the North Pacific Deep Water (NPDW) at 2500 meters deep, data from Alibo and Nozaki, 1999. Cook Island nodules (EEZ) average curve is from Hein *et al.*, 2015. D) La and Ce anomalies of all Hotazel lithofacies from selected samples, calculated from (Ce/Ce\*)<sub>SN</sub> vs (Pr/Pr\*)SN as by Bau and Dulski (1996).

The all-encompassing conclusions from the mineralogy, bulk-rock major and trace elements, and REE relationships in the Hotazel Formation are as follows:

- There is clear evidence for the co-existence of end-member carbonate pairs, such as ankerite and siderite within BIF and Mn-calcite and kutnahorite within the Mn ore and hematite lutite.
- These carbonate assemblages and their mineral textures seem to be at odds with microbial diagenesis and suggest a possible primary control in all lithofacies studied (BIF, hematite lutite and manganese ore);
- Ovoids in manganese-rich assemblages seem to represent nucleation sites for the development of envelopes of Mn(II/III) silicate species such as friedelite and braunite.
- There is no preservation whatsoever of Mn(IV) species within manganese rich lithofacies at the petrographic scale. This is an important observation as it raises questions over the nature of the initial primary precipitates during deposition of the Hotazel sediments (implications of this will be discussed in chapter 5).
- The bulk-rock major oxide composition of the entire stratigraphy records continuous iron precipitation at various rates between the three lithofacies during the deposition of the Hotazel Formation.
- Detrital inputs during the deposition of the Hotazel Formation must have been minimal at best, as recorded by very low concentrations in elements such as Ti, Al and Zr. Similarly, low Cr concentrations support little to no oxidative weathering during BIF deposition.
- Co was not precipitated with primary Mn(III/IV) oxyhydroxides, as supported by relatively low Co concentrations in the manganese ore layers. Maximum Co concentrations in hematite lutite suggest Co(III) adsorption by Fe(III) oxyhydroxides. Lack of hematite in BIF would thus explain its very low Co contents.
- The REE patterns of the three lithofacies of the Hotazel Formation record sea-water patterns. The lack of a positive Ce anomaly in the Mn-rich facies suggests a primary environment that was never oxic enough to oxidise Ce and Mn to their tetravalent states and therefore fractionate them out of contemporaneous seawater.

"Universal education is not only a moral imperative but an economic necessity, to pave the way toward making many more nations self-sufficient and selfsustaining." –Desmond Tutu
# 3. High resolution carbonate stratigraphy and mineral chemistry (cyclicity and lithologic transitions)

# 3.1 Rationale

The bulk-rock geochemistry of the Hotazel Formation has been well studied (Gutzmer and Beukes, 1996; Tsikos and Moore, 1997; Tsikos *et al.*, 2003, 2010; Schneiderhahn *et al.*, 2006) in an effort to understand primary *versus* diagenetic processes (Tsikos *et al.*, 2003), and to elucidate and model the unique cyclicity of iron and manganese rich assemblages preserved (Beukes, 1983). The application of sequential extraction procedures (Poulton and Canfield, 2005, Oonk *et al.*, 2017) has never been applied at a high resolution in iron and manganese rich rocks of the Hotazel Formation, with only the unpublished work of Fryer (2015) attempting to elucidate the speciation of Fe and Mn (i.e., carbonate, oxide, and silicate fractions) across the manganese "marker" zone from a drill core intersection at Gloria mine (GL81). The key findings from that study was that this procedure can be applied in both BIF and the manganese rich assemblages (hematite lutite and manganese ore) of the Hotazel Formation, shown by the reproducibility between the bulk-rock and species-specific data obtained.

Application of speciation methodology cannot be devoid of limitations and complexities related to the intrinsic mineral chemical variability of rocks such as BIF. As seen in section 2.3, the three main lithofacies of the Hotazel Formation host different iron and manganese-rich carbonate phases with variable chemistries. Through the combined use of sequential extraction procedures targeting the bulk carbonate fraction and mineral chemical data from individual carbonate minerals, one can fully and rigorously elucidate the controls for the variability in mineral chemistry and ultimately bulk geochemistry of the different Hotazel lithofacies, especially over the transitions between them.

This study therefore aims to shed light on the lithologic transitions of the entire Hotazel succession from drill core GL137 in terms of primary depositional *versus* diagenetic processes that would have resulted in the presently observed geochemical signatures. The findings will then be used to constrain the precursor precipitate constituents in the primary depositional environment of the Hotazel Formation and ultimately derive the chemical and physical processes which apparently controlled the deposition of this cyclic iron and manganese succession.

# 3.2 Sample selection, preparation and analytical techniques

# 3.2.1 Drill core and sample selection

The drill core intersection used in this chapter is GL137 containing a complete unaltered succession of the Hotazel Formation in the Gloria mine area (See Chapter 2). The entire total of 95 samples was used from this intersection, at a resolution of one sample per meter. Such resolution allows for every lithological transition to be studied at a scale which has not been previously performed on these rocks. Each sample varied in thickness, between 2 and 10 cm, to provide a sufficiently homogenous sample against variable band thickness variations in both BIF and Mn rich assemblages.

All samples were pulverized into fine powder using a tungsten-carbide Zibb mill and crusher. Powdered samples were stored in glass vials, and for sequential Fe-extraction and total digestion, analysis was carried out at the University of California, Riverside and specifically the NAI (NASA Astrobiology Institute) geochemical laboratories under Professor Timothy Lyons. The data integrity and reproducibility were attested by the author on the complete sample set from drill core GL136 during a 3 month visit at UCR (See data in appendix II). In this chapter, only the dataset from drill core GL137 will be presented and evaluated.

With respect to electron microprobe analysis, these were carried out by the author using three different instruments at different universities. This allowed for the delivery of a comprehensive record of the chemical composition of the various carbonate minerals found in the Hotazel Formation at Gloria mine.

# 3.2.2 Sequential Fe and Mn-extraction (acetate soluble fraction)

In iron speciation studies, highly reactive iron (FeHR) is the sum of Fe bound in amorphous and crystalline Fe-(oxy)hydroxides, magnetite, siderite, and pyrite. In principle, sequential Fe extraction procedures consider the amount of Fe available in minerals that react with hydrogen sulfide on short diagenetic time scales to form pyrite - namely FeHR - versus the amount of pyritic Fe (Fe<sub>py</sub>) in the sediments (Canfield *et al.*, 1992; Raiswell and Canfield 1998; Poulton and Canfield

2005). In the Hotazel Formation, as in BIF in general, sulphides minerals are extremely rare. Therefore, in order to characterize the speciation of the carbonate fraction of the studied rocks, the elements Mn, Mg, Ca, Al and Fe, bound to that fraction were extracted using 1 M sodium acetate buffered with acetic acid to pH 4.5. These extracts were then analyzed by inductively coupled plasma-mass spectrometry (ICP-MS; Agilent 7500ce) using H<sub>2</sub> and He in the collision cell after 100-fold dilution in trace-metal grade 2% HNO<sub>3</sub>. That way, the carbonate specific geochemistry of the studied samples was determined, and the speciation of the non-carbonate fraction of the rocks was derived by difference from the corresponding bulk-rock analyses.

#### 3.2.3 Total digest (bulk-rock)

Total bulk-rock solid-phase major and trace element concentrations were determined on ashed samples (580 °C) using a three-step digestion method (HNO<sub>3</sub>/HCl/HF at 140°C). Final concentrations were determined on an Agilent 7900 ICP-MS with100-fold dilution in trace-metal grade 2% HNO<sub>3</sub>. Reference standards SDO-1 (Devonian Ohio Shale) and Hawaiian Basalt (BHVO-1) were digested and analyzed in parallel with the sample extractions and yielded errors of less than <3%.

#### 3.2.4 Microprobe analysis

#### Rhodes University and University of Cape Town

Quantitative mineral chemical analyses were obtained by using four wavelength dispersive spectrometers on a JEOL JXA-8230 electron probe micro-analyzer (Rhodes)/ JEOL Superprobe JXA-8100 electron probe micro-analyzer (UCT). The beam was generated by a Tungsten cathode; 15 kV accelerating potential, 5 nA current, and 1  $\mu$ m beam size was applied. All elements were measured on K $\alpha$  peaks. Counting times were 10 seconds on the peak, and 10 totals on the background, for all elements. Commercial "SPI" standards were used for intensity calibration. The standards were Si (Quartz), Ca (Plagioclase), Mg (Diopside), Fe (Hematite), Mn (Rhodonite). Calibration acquisitions were peaked on the standards, while unknown acquisitions were peaked on the samples before each point analysis. The data was collected with JEOL software. An

automated PRZ(Armstrong) matrix algorithm was applied to correct for differential matrix effects. Oxygen was calculated by stoichiometry.

#### University of Johannesburg

Quantitative mineral chemical analyses were obtained by using four wavelength dispersive spectrometers on a Cameca SX-100 microprobe. A carbonate probe set-up at 15 kV accelerating voltage and 6 nA beam current was used, with a defocused 1  $\mu$ m beam size. Mg, Al, Si, Ca, Mn, Fe and Zn were measured on their K $\alpha$  lines; Sr and Ba, on their L $\alpha$  lines. Mg was calibrated on Periclase, Al on almandine, Si on diopside, Sr on Celestine, Ca on calcite, Ba on Baryte, Mn on Rhodonite, Fe on hematite and Zn on Sphalerite. The MgO and ZnS RMs were synthetic, the other RMs were natural materials.

# 3.3 High resolution, fraction-specific geochemistry

The MnO and FeO contents of the carbonate fraction in the Hotazel Formation varies throughout the entire sequence in a cyclic nature, with sharp chemical changes naturally occurring across lithologic transitions. Based on bulk geochemical results of chapter 2, the BIF layers stratigraphically distal to lithologic contacts do not contain appreciable Mn, while both the transitional hematite lutite and manganese ore layers record bulk-rock MnO<sub>2</sub> values up to 50 wt. % or higher. Therefore, the expectation is that the carbonate fraction in the latter two facies will yield highest carbonate hosted Mn content. Conversely, the carbonate hosted FeO is expected to be highest in the BIF and its transitions into hematite lutite zones.

One of the central objectives of the speciation work is to precisely elucidate changes in the FeO/MnO ratio of the carbonate fraction across such transitions. The reason for this is because carbonate minerals in BIF are widely thought to be purely diagenetic in origin and therefore changes in the partitioning of iron and manganese in the carbonate fraction has clear potential to reveal insights into changing redox conditions during primary deposition, as well as diagenesis. It should be noted that the results reported in the following sections are weight percent values against the total mass of sample processed in each instance.

#### 3.3.1 Lower BIF-Mn transition (LBMT)

The lower BIF to Mn ore transition in drill core GL137 (334.2-307.8 me) comprises the cycle lowermost BIF-hematite lutite-Mn ore-hematite lutite-BIF cycle of the Hotazel Formation. The geochemical nature of the lowermost BIF layer (334.2-329.4 m), exhibits low carbonate hosted MnO with an average of  $0.6\pm0.7$  wt %; similarly, the FeO content in the carbonate fraction is  $0.9\pm0.2$  wt. %, whilst the average MgO values are at  $0.4\pm0.1$  wt. %. Given that the carbonate hosted average CaO concentration in this BIF layer shows a value of  $3.5\pm3.5$  wt. %, allows the conclusion to be made that the dominant carbonate here is calcite. The non-carbonate fraction of the same BIF layer comprises, as expected, an average FeO concentration with a value of  $43.1\pm4.3$ wt. %. Average CaO and MgO concentrations are at  $1.8\pm2.1$ wt.% and  $1.7\pm1.3$  wt. %, respectively, while non-carbonate hosted MnO content is very low with a value of  $0.2\pm0.2$  wt%. The noncarbonate fraction is therefore dominated by bulk iron oxides and the manganese content is controlled largely by the carbonate fraction.

The carbonate fraction of the hematite lutite layer overlying the basal BIF comprises average CaO content of  $2.0\pm0.7$  wt. %; MgO of  $0.9\pm0.1$  wt. %; and FeO at  $0.5\pm0.3$  wt. %. Here the carbonate hosted MnO content is much higher with a value of  $7.8\pm4.8$  wt. % compared to the underlying BIF. The non-carbonate fraction is low in average CaO value at  $0.7\pm0.04$  wt. % but has high average MgO ( $5.4\pm3.2$  wt. %), MnO ( $3.2\pm2.0$  wt. %) and FeO at  $48.2\pm6.0$  wt. %. Clearly, this hematite lutite is dominated by iron oxide (hematite) and subordinate Fe-Mg silicates, whereas its carbonate fraction is definitely more manganese rich, evidently approximating compositions between Mg-calcite and rhodocrosite

Overlying the hematite lutite (322.85-312.05 m) lies the lowermost manganese ore layer through a relatively sharp lithologic contact. It shows a comparable average carbonate hosted MnO content compared to the lower hematite lutite, with a value of  $8.5\pm3.0$  wt. %. Average carbonate hosted FeO concentration is negligible ( $0.1\pm0.02$  wt. %) whereas average MgO and CaO contents are  $2.2\pm0.5$  wt. % and  $13.8\pm3.8$  wt. %, respectively. This signals a change to a far more calcic carbonate-dominated mineralogy in the manganese ore. As expected, the non-carbonate hosted average MnO within the manganese layer is very high at  $35.0\pm16.0$  wt. % with a maximum of 58.0 wt. %. The non-carbonate hosted average FeO content is also very low at  $8.4\pm4.3$  wt. % compared to the underlying hematite lutite. The average non-carbonate MgO and CaO contents are slightly lower compared to the hematite lutite (respectively3.0±1.3 wt. % and 2.9±2.3 wt. %).

The manganese layer is overlain by another, 1.5-meter thick transitional hematite lutite layer. Here, a sharp decline in the concentration of non-carbonate hosted average MnO occurs  $(4.6\pm1.2 \text{ wt. }\%)$  compared to the underlying manganese layer, whereas average FeO content increases  $(14.3\pm5.5 \text{ wt. }\%)$  as modal hematite increases. The average CaO concentration is at  $5.8\pm3.1 \text{ wt. }\%$ , whilst MgO values remain similar to the underlying manganese layer at an average of  $3.1\pm1.8 \text{ wt. }\%$ . The carbonate fraction of this hematite lutite records high average MnO  $(12.0\pm1.9 \text{ wt. }\%)$ , CaO  $(18.3\pm4.7 \text{ wt. }\%)$  and MgO  $(1.2\pm0.5 \text{ wt. }\%)$ , which signify the dominance of more manganiferous carbonate mineralogy compared to the underlying manganese layer. Carbonate-hosted FeO remains low at  $0.3\pm0.4 \text{ wt. }\%$ .

The BIF layer overlying the transitional hematite lutite above, records similar average carbonate hosted geochemistry, with FeO at  $0.7\pm0.0$  wt. %, MnO at  $3.5\pm0.6$  wt. %, CaO at  $6.1\pm3.1$  wt. % and MgO values at  $0.9\pm0.2$  wt. %. The non-carbonate fraction of this layer contains an average FeO content of  $41.4\pm2.2$  wt. %, with MgO at  $3.7\pm0.6$  wt. %, low CaO ( $1.5\pm$  wt. %) and MnO ( $0.8\pm0.5$  wt. %), suggesting a dominance of iron oxide in this fraction.

#### 3.3.2 Manganese marker sub-cycle (MMSC)

The middle manganese marker sub-cycle records highly transitional bulk-rock geochemistry as seen in chapter 2. The carbonate-fraction geochemical signal similarly replicates the same trends. The hematite lutite layer at the base of this cycle is characterized by very low carbonate-hosted average FeO concentration  $(0.2\pm0.1 \text{ wt. \%})$ ; high MnO concentration at an average of  $10.0\pm5.6 \text{ wt. \%}$ ; and average MgO and CaO contents at  $0.8\pm0.2 \text{ wt.\%}$  and  $5.1\pm1.2 \text{ wt.\%}$  respectively. The non-carbonate fraction is made up of a variable average MnO ( $5.7\pm5.3 \text{ wt.\%}$ ), and a high concentration of FeO with an average at  $37.0\pm13.9 \text{ wt.\%}$ . This is a reflection of high modal carbonate abundance. The average non-carbonate concentrations of CaO and MgO in this layer are  $1.5\pm0.7 \text{ wt.\%}$  and  $5.2\pm2.0 \text{ wt.\%}$ , respectively.



Figure 3.1: High resolution chemo-stratigraphy of the Hotazel Formation from drill core GL137 indicating the variations in carbonate (acetate fraction) and non-carbonate (bulk-rock minus acetate fraction) MnO, FeO, CaO, and MgO oxide contents throughout the major lithological transitions (BIF, Mn ore and transitional hematite lutite), and the relationships between the two fractions.\*Oxide values calculated from elemental ICPMS data (see data tables in Appendix) using the following formula (example for Mn): MnO\*= (Mn<sub>ICPMS</sub>\*MnO<sub>molecular weight</sub>)/Mn<sub>molecular weight</sub>

Overlying this lutite (305.2-303.0 m) lies the manganese ore "marker" with a geochemical composition similar to that of the lowermost manganese layer. The carbonate fraction of this layer comprises average MnO of  $11.6\pm3.9$  wt. %; very low average FeO values of  $0.1\pm0.01$  wt. %; and low average MgO concentration at  $0.8\pm0.2$  wt. %. By contrast, the average CaO concentration is high with a value of  $12.7\pm8.5$  wt. %. Again, like with the lowermost manganese layer, Ca-Mn carbonate species prevail in the marker. The non-carbonate fraction has high average MnO values at  $20.2\pm7.9$  wt. %; low FeO at  $9.8\pm2.0$  wt. %; and MgO and CaO contents averaging at  $1.8\pm0.8$  wt. % and  $2.9\pm1.8$  wt. % respectively.

The manganese marker transitions upwards into a BIF facies at a depth of 303.0 - 300.1 meters. The said BIF is characterized by elevated average carbonate hosted MnO and FeO concentrations  $(2.6\pm1.3 \text{ and } 1.0\pm0.6 \text{ wt. }\%$ , respectively). Average CaO concentration in the carbonate fraction has a value of  $7.7\pm2.9$  wt. % while MgO is low at  $0.5\pm0.2$  wt. %. The non-carbonate fraction shows average FeO concentration at  $40.5\pm5.4$  wt %, low average MnO at  $0.9\pm0.5$  wt. %, while MgO and CaO average at  $2.3\pm1.4$  wt. % and  $1.1\pm0.3$  wt. %, respectively. This transitional BIF is therefore characterized by carbonate phases rich in both manganese and iron as will be also seen in section 3.5.2.

Overlying the transitional BIF above (300.08 -298.2 meters), is a *ca*. 2-meter-thick hematite lutite layer characterized by very high carbonate-hosted CaO concentrations at a mean value of 21.4 $\pm$ 5.9 wt. %. This is comparatively high against the other hematite lutite layers throughout the Hotazel succession. The average concentration of MnO in the same carbonate fraction is higher than that of the immediately underlying BIF with a value of 8.5 $\pm$ 2.4 wt. %, whilst FeO remains low at 0.6 $\pm$ 0.7 wt. %. Similar to the other two hematite lutite layers in this cycle, the average concentration of carbonate hosted MgO is very low at 0.9 $\pm$ 0.2 wt. %. Chemically, the noncarbonate fraction of this layer comprises average FeO value of 19.5 $\pm$ 7.9 wt. % and average MnO at 2.3 $\pm$ 1.7 wt. % which is the generally expected composition of hematite lutite in the Hotazel Formation. The non-carbonate hosted MgO and CaO concentrations are similar to the underlying BIF facies with values at 2.4 $\pm$ 1.0 wt. % and 1.2 $\pm$ 1.9 wt. % respectively.

#### 3.3.3 Middle BIF-top Mn cycle (MBTMC)

The middle BIF to Mn ore cycle at depths of 298.2–259.5 meters has sharper lithologic transitions with relatively simpler geochemical manifestation compared to the middle marker sub-cycle. The middle BIF (298.2-284.2 m) comprises a carbonate fraction characterized by high and variable average CaO concentration with a value of 10.5±7.8 wt. %. This BIF also contains average MgO with a value of 0.5±0.3 wt. % hosted in the carbonate fraction. Average carbonate-hosted FeO content is high compared to the underlying BIF already described in the foregoing sections, at 2.6±09 wt. %. These data support mineralogical results from this BIF which point to a high modal abundance of ankerite as evident from petrographic analyses (Chapter 2). The average carbonate hosted MnO concentration is very low at a value of 0.3±0.1 wt. %, with the highest values recorded at the top and bottom margins of this layer in contact with adjacent hematite lutites. This is indicative of the gradual change from iron- to manganese-rich carbonates. The average noncarbonate hosted FeO concentration is lower compared to underlying oxide rich BIF layers reported earlier, with a value of 34.0±9.4 wt. %. Similarly, this layer is characterized by low average MgO and CaO concentrations at 0.9±0.2 wt. % and 1.0±1.0 wt. %, respectively. Finally, average MnO content in the non-carbonate fraction is low with a value of 0.5±0.1 wt. %, which agrees with the typical Mn-poor character of the Hotazel BIF.

Overlying this BIF layer is a transitional hematite lutite through a relatively sharp lithological contact (284.2- 279.3 m). This hematite lutite contains a carbonate fraction high in CaO content with an average value of  $11.1\pm5.2$  wt. %, and a high average MnO concentration at  $8.4\pm6.4$  wt. %. The high standard deviations are indicative of the wide-ranging values from the contact with the underlying BIF, which gradually increase upwards and peak towards the upper margin of this layer in proximity to the overlying manganese layer. This is also evident from the corresponding decline in FeO content which records an average value of  $0.3\pm0.2$  wt. %. Similar to hematite lutite layers lower in the stratigraphy, average carbonate-hosted MgO content is low with a value of  $0.6\pm0.4$  wt. %. With regard to the non-carbonate fraction, average MnO concentration (ave.  $5.0\pm7.2$  wt.%) also increases upwards and peaks at the transition into the overlying manganese layer. This is supported by the gradual increase in modal braunite and friedelite as revealed from basic petrography. In the same fraction, average FeO concentration (29.1\pm9.8 wt. %) is also accompanied by high deviation as a result of the increasing modal hematite content

stratigraphically upwards. Finally, average non-carbonate hosted MgO and CaO concentrations are similar to other hematite lutite layers in the Hotazel succession with values of  $2.1\pm1.3$  wt.% and  $1.0\pm1.6$  wt.%, respectively.

Overlying the hematite lutite, is the uppermost manganese layer (8.3-meters thick) of the Hotazel Formation straddling the depth range of 279.3-271.0 m. This layer has the highest carbonate hosted average CaO concentration compared to the other manganese layers in this succession with a value of  $16.6\pm6.2$  wt. %. By contrast, the average carbonate hosted MnO concentration is the comparatively lowest with a value of  $8.4\pm1.6$  wt. %, indicative of a relatively low manganese, Cadominated carbonate mineralogy. Like all the manganese assemblages in the Hotazel Formation, the average carbonate-hosted FeO and MgO concentrations are low with values of  $0.2\pm0.03$  wt. % and  $0.9\pm0.2$  wt. %, respectively.

As also seen in the lowermost manganese layer, carbonate-hosted MnO content plateaus when the non-carbonate hosted MnO content peaks. The MnO content in the non-carbonate fraction ranges between 8.2 and 28.7 wt. %, symmetrically peaking at the center of the layer and with lowest values at the transitional contacts with adjacent hematite lutites. The non-carbonate hosted FeO concentration ranges from 4.3 to 26.0 wt. % and displays broadly antithetic geometry to that of MnO (see Figure 3.1 and appendix III). Average MgO and CaO hosted in the non-carbonate fraction of the manganese layer record values of  $2.5\pm0.9$  wt. % and  $1.4\pm1.5$ wt. %, respectively.

Overlying the uppermost manganese ore layer is the thickest transitional hematite lutite (11.5meters), with a higher average carbonate-hosted MnO concentration compared to the underlying manganese layer, at a value of  $10.4\pm3.0$  wt. %. Conversely, the average CaO concentration in the carbonate fraction declines to the value of  $7.1\pm3.2$  wt. %. Average carbonate hosted MgO concentration is low, at  $1.1\pm0.3$  wt. %. This clearly signifies a switch to a mineralogy dominated by more manganiferous carbonates in the hematite lutite. The average FeO content ( $0.8\pm1.1$  wt. %) in the same carbonate fraction is invariably low and apparently independent of the MnO/CaO ratio, although its concentration shows a subtle gradual increase towards the contact with the uppermost BIF layer. Finally, the average FeO content ( $29.0\pm3.9$  wt.%) in the non-carbonate fraction increases in the hematite lutite layer broadly in concert with an upward increase in modal hematite. The corresponding average MnO concentration ( $6.2\pm4.5$  wt. %) decrease upwards as modal braunite and friedelite decline in abundance.

#### 3.3.4 Top BIF-Mooidraai carbonate (TBMC)

The MBTMC cycle sharply transitions into the top BIF to Moodraai carbonate sequence at 259.5-235.0 meters depth, which effectively marks the top of the Hotazel Formation in this specific drill core (GL137). This section is characterized by a 24.5-meter-thick BIF with variable geochemistry. The lower part of this BIF (259.5-252.3 meters) is characterized by a carbonate fraction high in CaO (7.4 $\pm$ 6.3 wt. %), high FeO (4.1 $\pm$ 1.8 wt. %), and average MnO at 0.6 $\pm$ 0.2 wt. % with higher values at the contact with the underlying hematite lutite. This BIF layer is also characterized by high carbonate-hosted MgO compared to underlying BIF with an average value at 2.2 $\pm$ 0.4 wt. %. The non-carbonate fraction is low in average MnO (0.1 $\pm$ 0.06 wt. %), MgO (0.7 $\pm$ 0.2 wt. %), CaO (0.9 $\pm$ 0.8 wt.%) and is expectedly dominated by FeO (94.2 $\pm$ 8.3 wt. %). An apparent transition develops between relatively higher CaO and MgO composition of the carbonate fraction to a relatively more FeO rich one across the interval 252.3-236.5 m, which reflects a corresponding decline in the modal ankerite to siderite ratio. The carbonate fraction here is nevertheless characterized by very low MnO content at 0.2 $\pm$ 0.16 wt. %. In the non-carbonate fraction, FeO content is very high, at 39.8 $\pm$ 6.9 wt. %, with low MgO (0.5 $\pm$ 0.2 wt. %), CaO (0.8 $\pm$ 0.6 wt. %), and MnO at 0.1 $\pm$ 0.04 wt. %.

At 236.5-235 meters depth, the gradational transition between the Hotazel Formation and Moodraai Formation occurs. The carbonate and non-carbonate hosted FeO abundance across this transition drops drastically to  $2.7\pm0.7$  wt. % and  $19.9\pm2.8$ wt. % respectively, with a simultaneous increase in average carbonate hosted CaO at  $25.1\pm0.9$  wt. %. The remainder of the carbonate fraction is made up of low MgO ( $0.7\pm0.1$  wt. %) and MnO ( $0.7\pm0.2$  wt. %) whereas the non-carbonate fraction also contains very low MgO ( $0.3\pm0.2$  wt. %) and MnO ( $0.2\pm0.2$  wt. %).

# 3.4 Carbonate mineral chemistry and its variations

The speciation analyses presented above provides insights into the bulk carbonate fraction and its geochemical characteristics, but it does not offer any information with respect to variability in the composition of individual carbonate phases in each lithofacies examined. The following sections fill this gap through the employment of mineral chemical analyses using the EPMA technique.

#### 3.4.1 Mn calcite & kutnahorite

As stated in chapter 2, Mn-calcite and kutnahorite in both the hematite lutite and manganese ore, appear to coexist along carbonate-rich laminae and ovoids. EMPA analysis of these two manganese carbonates show varying MnO/CaO ratios throughout the Hotazel stratigraphy. Microanalysis of these carbonates from different laminae from a single manganese ore sample (GL137-63) was carried out to document and understand small-scale variability. Figure 3.2 (II) shows the MnO/CaO ratios of both manganese-rich carbonates and their various textures within different laminae (L1-7). The Mn-calcite show a MnO/CaO ratio of up to 0.5, with the kutnahorite ranging between 0.6 and 2.1 across the single sample. The lack of variation between the two carbonates across the laminae at a microscale, is supported by the largely invariant carbonate-fraction MnO/CaO ratios in the center of the manganese ore layers as seen in the above section and sections 3.5.1-3 below.

Figure 3.3 below shows variable average major oxide compositions of Mn-calcite across the manganese-rich assemblages, with CaO ranging between  $29.24\pm0.89$  wt. % and  $48.87\pm5.29$  wt. %. Average MnO contents range between 6.32 wt. % and 19.90 wt. %. The Mn-calcite accommodates a small amount of Fe within its structure as shown by FeO contents varying between 0.27 wt. % and 2.83 wt. %. The MgO concentrations in these carbonates range between values of 0.13 wt. % and 12.24 wt. %, with the higher values suggesting a more dolomitic variant.

Kutnahorite is known to accommodate approximately a 1:1 MnO to CaO ratio (Anthony *et al.*, 1990). The average major oxide compositions of kutnahorite presented in Figure 3.4 exhibit similar ratios across the different samples from the Hotazel stratigraphy, with the exception of Fe and Mg rich kutnahorite found in the BIF layer above the lowermost manganese layer, and the contact between BIF and hematite lutite layers where FeO and/or MgO seem to substitute for MnO. Typical kutnahorite MnO concentrations show a range in concentration of 20.20 wt. % and 33.48 wt. %, whilst CaO concentrations range between 20.60 wt. % and 32.55 wt. %. These specific phases also exhibit low FeO ranges between the values of 0.35 wt. % and 3.73 wt. %





Figure 3.3: Averaged major-element compositions of Mn-calcite from manganese rich assemblages (hematite lutite and Mn ore) of the Hotazel Formation. Note: only data with 8 (n=8) or more analyses per samples are reported here; see appendix IV for full data tables. SD=standard deviation; n=number of analyses.



Figure 3.4: Averaged major-element compositions of kutnahorite minerals from Hotazel manganese rich assemblages (hematite lutite and Mn ore). Note: only data with 8 (n=8) or more analyses per samples reported, See appendix IV for full table of analysis.SD (standard deviation).

A variety of FeO-rich kutnahorite is seen in samples from the lowermost BIF layers, and from hematite lutite close to a lithological contact with BIF, record average FeO values of between 5.22 wt. % and 9.74 wt. %. More Mg-rich kutnahorite varieties are seen in samples from the BIF layers above the lowermost manganese rich layer with an average MgO value of 6.16±2.81 wt. % which is the highest throughout the entire Hotazel succession. The high MgO content is reproduced in carbonate-specific analyses in section 3.3 above. The kutnahorite samples in the same layer show MnO concentrations of 16.78±3.05 wt. %.

#### 3.4.2 Rhodocrosite

Rhodocrosite is an end-member Mn carbonate (MnCO<sub>3</sub>) which in its purest form accommodates only traces of Mg and Fe (Anthony *et al.*, 1990). The rhodocrosite analyzed within the manganese lithofacies of the Hotazel Formation appear to have a variable composition with FeO, MgO, CaO content being accommodated within its structure. All samples analyzed record appreciable average CaO concentration with values of up to  $17.34\pm3.40$  wt. % (Figure 3.5). The high CaO content is observed in the uppermost manganese layer, specifically at the top and bottom contacts with hematite lutite, with MnO values ranging between 36.70 wt. % and 48.97 wt. %. Average MgO concentrations from all samples range between 1.25 wt. % and 3.34 wt. %. per sample from the BIF layer above the manganese marker record high average FeO concentrations in rhodocrosite, with an average value of 7.67 $\pm$ 0.49 wt. %.

#### 3.4.3 Ankerite & Siderite

Figure 3.6 below shows average major oxide compositions of ankerite and siderite from different samples in the carbonate rich BIF layers of the Hotazel stratigraphy. Typical average FeO concentrations range between 13.25 wt. % and 23.15 wt. %, whilst average CaO content ranges between 26.09 wt. % and 28.86 wt. %. The CaO concentration in individual ankerite grains appear to increase with stratigraphic height, with higher values observed in the uppermost BIF layer. The ankerite analyzed in this study accommodates variable MgO within their structure with concentrations ranging between 4.82 wt. % to 10.10 wt. %. Samples with the highest MgO content

are observed at the uppermost BIF layer. Most of the samples analyzed record low MnO concentrations between 0.88 wt. % and 3.3 wt. %, with the exception of a Mn-rich variant at the lithologic contact between the uppermost hematite lutite and BIF layers, which has an average MnO concentration of  $6.48\pm1.14$  wt. %. The average MnO content of ankerite from this specific sample seems to substitute for FeO ( $13.25\pm2.81$  wt. %) which tracks an upward gradual transition from hematite lutite to BIF. There appear to be no other systematic variations in major oxide compositions across the BIF stratigraphy, except for the high MnO in samples in transitional contacts with hematite lutite.



Figure 3.5: Averaged major-element compositions of rhodocrosite minerals from Hotazel manganese rich assemblages (hematite lutite and Mn ore) and transitional BIF. note the occurrence of rhodocrosite only on the manganese ore- hematite lutite contact where bulk MnO is low. Note: only data with 6 (n=6) or more analyses per samples reported See appendix IV for full table of analysis. SD (standard deviation)



Figure 3.6:Selected averaged major-element compositions of ankerite (light green) and siderite (dark green) from Hotazel BIF. Note: only data with 5 (n=5) or more analyses per samples reported See appendix IV for full table of analysis.SD (standard deviation)

Siderite, which is an end-member Fe carbonate (FeCO<sub>3</sub>), occurs within the uppermost BIF of the Hotazel Formation (see section 3.5). The average major oxide compositions from measurements in two BIF samples shown in Figure 3.6, register FeO contents between 49.67 wt. % and 53.62 wt. %, with low average CaO concentration at an average of of  $3.26\pm1.27$  wt. %. These samples record average MgO concentration ranges between the values of 2.71 wt. % and 4.57 wt. %. The siderite samples analyzed show low average MnO concentration of  $0.97\pm0.07$  wt. %, with the exception of a single sample close to the lithologic contact between the uppermost BIF and underlying hematite lutite with an average value of  $2.61\pm4.01$  wt. %.

#### 3.4.4 Calcite

The manganese-rich assemblages (i.e., hematite lutite and manganese ore) host Mn rich calcite (section 3.4.1). The BIF across the stratigraphy is characterized by Mn-poor calcite with MnO concentrations of less than 1 wt. %, except for a single sample (Table 3.1) with an average MnO value of 3.74 wt. %. This sample is from the BIF layer above the middle manganese marker which, as seen in previous sections in this chapter, contains a large modal abundance of manganese rich Ca-carbonates. These calcite analyses also show low MgO concentrations below the value of 0.26 wt. %, and maximum FeO concentrations at 2.68 wt. %.

Table 3.1: Averaged major-element compositions of calcite from Hotazel BIF in wt. %; see appendix IV for full table of analyses

Rock type	Mineral	Sample #s	Depth M	MgO	MnO	CaO	FeO	Total	n
BIF	Calcite	94	235.11	0.25	0.56	48.86	2.42	52.50	12
BIF	Calcite	93	235.68	0.19	0.59	56.29	1.05	58.28	6
BIF	Calcite	43	294.58	0.23	0.57	48.82	2.46	53.22	1
BIF	Calcite	30	301.90	0.26	3.74	51.27	2.68	58.75	5
BIF	Calcite	3	329.41	0.00	0.14	54.80	0.63	55.78	1

# 3.5 Carbonate fraction vs Fe & Mn carbonate mineral chemistry

The acetate extraction performed as a key analytical approach in this study, shows the geochemistry of the carbonate fraction of the entire Hotazel Formation which naturally incorporates mixtures of the carbonate minerals present and their chemical variabilities. In summarizing, these include kutnahorite, Mn-calcite, rhodocrosite in the manganese rich assemblages (Mn-ore and hematite lutite) and calcite, ankerite and siderite in the BIF (see chapter 2, & appendix III for data). This section aims to ground-truth the acetate extraction procedure applied to understand the carbonate fraction variability across the Hotazel Formation while informing and elucidating the lithological and geochemical trends and underlying controls for it. All the presented Fe/Ca and Mn/Ca ratios from mineral chemical data are averages from section 3.4 above. Raw EMPA data tables are included in the appendices (appendix IV).

#### 3.5.1 Lower BIF-Mn transition (LBMT)

In this cycle, carbonate minerals identified in the lowermost BIF layer are calcite and ankerite (see section 2.3). The average carbonate fraction Fe/Ca and Mn/Ca ratios of this BIF layer are  $0.49\pm0.34$ , and  $0.29\pm0.37$ , respectively (Figure 3.7). At the transition towards the overlying hematite lutite, calcite was measured that revealed undetectable Mn and Fe contents. This layer also contains Fe-rich kutnahorite with average Mn/Ca and Fe/Ca ratios of 0.67 and 0.38, respectively. The overlying hematite lutite records an average carbonate fraction Mn/Ca ratio of  $4.39\pm2.49$  and a Fe/Ca ratio of  $0.28\pm0.16$ . Fe-rich kutnahorite at the base of this layer records Mn/Ca and Fe/Ca ratios of 1.13 and 0.23, respectively. Ca-rhodochrosite was also measured with Mn/Ca and Fe/Ca ratios of 8.59 and 0.29, while coexisting Mn-calcite averages 0.69 Mn/Ca and 0.21 Fe/Ca.

By comparison, the overlying manganese ore has a substantially lower average carbonate fraction ratio for Mn/Ca ( $0.70\pm0.31$ ), reflecting the dominance of Mn-calcite and kutnahorite. The former has a mineral-specific Mn/Ca ratio of 0.30, while the latter has a corresponding ratio of 0.85. The overlying hematite lutite records similar Mn/Ca and Fe/Ca ratios to the manganese ore at  $0.75\pm0.30$  and  $0.02\pm0.03$ . Although no samples were selected for EPMA analysis from this layer, an

assumption can be made that the dominant mineral phases were Mn-calcite and kutnahorite based on the carbonate fraction Mn/Ca and Fe/Ca ratios. Overlying this lutite layer, lies a BIF with Mn/Ca and Fe/Ca ratios of  $0.70\pm0.25$  and  $0.14\pm0.06$ , respectively. As seen from section 3.4 above, the observed mineral phases here are mainly compositional variants of kutnahorite, with average Mn/Ca ratios between 0.93 and 0.57.



Figure 3.7: Carbonate-fraction and carbonate mineral-chemical chemo-stratigraphic relationships for Mn/Ca and Fe/Ca ratios across the lower BIF to Mn transition.

#### 3.5.2 Manganese marker sub-cycle (MMSC)

As stated in section 3.3.2, this cycle is characterized by highly transitional lithologic and hence geochemical contacts. This is also shown by the highly variable carbonate-fraction geochemical signatures. The carbonate fraction Mn/Ca and Fe/Ca ratios of the lower hematite lutite records values of 1.99±0.91 and 0.05±0.04, with the Fe/Ca ratio gradually increasing towards the manganese ore marker (Figure 3.8). One selected sample from this layer was dominated by kutnahorite with a Mn/Ca ratio of 1.31.

The overlying manganese ore "marker" records a variable Mn/Ca ratio of  $1.58\pm1.56$  and a very low Fe/Ca ratio. Kutnahorite, Mn calcite and Ca-rhodocrosite on the margins of the marker are all dominant carbonate phases with corresponding Mn/Ca ratios of 5.35, 1.04, and 0.57, respectively. Overlying this marker is a BIF layer with carbonate fraction Fe/Ca and Mn/Ca ratios of  $0.14\pm0.05$  and  $0.45\pm0.33$ . Mineral phases in this layer include Ca-rich rhodocrosite, Mn-rich and Mn-poor varieties of calcite, and kutnahorite. The Ca-rich rhodocrosite records average Fe/Ca and Mn/Ca ratios of 1.27 and 7.42; Mn-calcite at 0.05 and 0.14; and kutnahorite at 0.06 and 0.86.

The overlying hematite lutite to the Mn marker has average Mn/Ca and Fe/Ca ratios of  $0.44\pm0.12$  and  $0.04\pm0.07$  respectively. The only two carbonate phases analyzed by EPMA include Mn-calcite with average Mn/Ca and Fe/Ca ratios of 0.26 and 0.01, respectively, and kutnahorite with respective ratios of 1.18 and 0.03. Within this layer, the Mn/Ca ratios of the two carbonates faithfully bracket that of the bulk carbonate fraction.

#### 3.5.3 Middle BIF-Top Mn cycle (MBTMC)

This middle BIF to uppermost manganese ore cycle is characterized by a well-defined separation of mineral phases (Figure 3.9) in concert with lithologic and geochemical contacts (see section 3.3.3). The carbonate fraction of the BIF layer records a variable average Fe/Ca ratio of  $0.44\pm0.35$  and low Mn/Ca ratio of  $0.06\pm0.05$ . The lower part of this BIF is more Ca-rich (i.e., has a low carbonate fraction Fe/Ca ratio); it is specifically dominated by ankerite with mineral-specific Fe/Ca and Mn/Ca ratios of 0.65 and 0.10 respectively. Co-existing calcite in this layer records an average Fe/Ca ratio of 0.05 and a Mn/Ca ratio of 0.01.



Figure 3.8: Carbonate-fraction and carbonate mineral-chemical chemo-stratigraphic relationships for Mn/Ca and Fe/Ca ratios across the manganese "marker" sub-cycle.

The overlying hematite lutite has a variable average carbonate fraction Mn/Ca ratio of  $1.31\pm1.35$ , increasing towards the uppermost manganese ore, with correspondingly low Fe/Ca ratio of  $0.04\pm0.07$ . The carbonate fraction Mn/Ca is faithfully tracked by the similarly increasing ratio of kutnahorite (0.98 -1.39) at an average of 1.18, and Ca-rhodocrosite with a Mn/Ca ratio of 2.12. Mn-calcite is observed in the lower margin of the hematite lutite layer with a Mn/Ca ratio of 0.22. The overlying uppermost manganese ore layer displays a carbonate fraction Mn/Ca ratio of 0.66 $\pm$ 0.37 which is lower than that of the underlying hematite lutite and faithfully tracked by the carbonate mineral chemistry of the individual carbonate phases present. These include Mn-calcite with a Mn/Ca ratio of 0.21, kutnahorite with a ratio of 1.08, while Ca-rhodocrosite with a ratio of

2.21 is spotted at the upper margin of the layer in contact with the uppermost hematite lutite. This hematite lutite layer has also a highly variable carbonate fraction Mn/Ca  $(1.99\pm1.03)$ , similar to the underlying hematite lutite to the Mn layer, which decreases towards the uppermost BIF. The low and variable carbonate fraction average Fe/Ca ratio  $(0.10\pm0.10)$  increases towards the aforementioned transition. This is tracked consistently by the carbonate phases: kutnahorite at the upper margin of this layer records an average Fe/Ca ratio of 0.14, wand an average Mn/Ca ratio of 0.77, while the average Mn/Ca and Fe/Ca kutnahorite ratios within this layer are 1.15 and 0.05, respectively. Mn-calcite and Ca-rhodocrosite are the other carbonate phases within this layer, with Mn/Ca ratios of 0.26 and 2.48, respectively.



Figure 3.9: Carbonate-fraction and carbonate mineral-chemical chemo-stratigraphic relationships for Mn/Ca and Fe/Ca ratios for the middle BIF to uppermost manganese ore cycle.

## 3.5.4 Top BIF-Mooidraai cycle (TBMC)

Samples from the uppermost BIF to Mooidraai transition is dominated by either ankerite only, or ankerite and siderite (see section 2.3.1). The lower part of this BIF is ankerite-rich with a carbonate fraction Fe/Ca ratio of  $0.62\pm0.72$  and a Mn/Ca ratio of  $0.10\pm0.02$  (Figure 3.10). The samples at proximity to the contact between the uppermost hematite lutite and BIF contain a manganese-rich ankerite variant with an average Mn/Ca ratio of 0.22 and Fe/Ca ratio of 0.46, which faithfully replicates the bulk carbonate fraction trend. Moving up the stratigraphy, a decrease in the carbonate fraction Mn/Ca ratio is observed; the average ankerite ratio is also lower (0.06) with a high Fe/Ca ratio of 0.65. Siderite within this ankerite dominated BIF records Fe/Ca and Mn/Ca ratios of 15.24 and 0.80, respectively.



Figure 3.10: Carbonate-fraction and carbonate mineral-chemical chemo-stratigraphic relationships for Mn/Ca and Fe/Ca ratios for the top BIF to Mooidraai cycle.

The part of the upper BIF containing ankerite and siderite has a bulk carbonate fraction with Fe/Ca and Mn/Ca ratios of  $1.84\pm0.56$  and  $0.09\pm0.02$  respectively. The ankerite specifically records an average Fe/Ca ratio of 0.67, and a low Mn/Ca ratio of 0.05. The siderite here has naturally a very high Fe/Ca ratios of 50.88 and a Mn/Ca ratio of 0.83. The last two samples measured at the top margin of this BIF represent a very gradual transition into the Mooidraai carbonates with a low Fe/Ca ratio of  $0.12\pm0.03$ , and a Mn/Ca ratio of  $0.03\pm0.01$ . The dominant carbonate mineral phase in the Mooidraai Formation is calcite, with an average Fe/Ca ratio of 0.03 and Mn/Ca ratio of 0.01.

# 3.6 Summary and conclusion

The results shown in the foregoing sections have significant implications on deciphering and interpreting the cyclicity of the Hotazel Formation, in view of the carbonate-specific geochemical signals obtained at both bulk and mineral-specific level. Below is an executive summary and implications of these results and findings.

# 3.6.1 Fe and Mn acetate extraction procedure

One of the most important findings is that the application of the Poulton and Canfield, (2005) acetate extraction protocol works very well in both iron and manganese rich chemical sediments of the Hotazel Formation. The carbonate fraction and carbonate mineral chemistry Mn/Ca and Fe/Ca ratios are in excellent agreement, as shown for example in ankerite dominated BIF with a Fe/Ca of around 0.6 (see section 3.5.3) against the expected Fe/Ca ratio of ankerite of 0.64 based on literature (Anthony *et al.*, 1990), and analyzed ankerite grains from this study with an average ratio of  $0.65\pm 0.064$ . This suggests, in that specific instance, that the bulk carbonate-fraction data represent essentially that of pure and complete ankerite dissolution. Similarly, the manganese ore and hematite lutite facies which, although characterized by a more complex mixture of carbonate minerals (Mn-calcite, kutnahorite and rhodocrosite) still return a carbonate fraction Mn/Ca ratio that falls between the averaged ratios of these minerals at approximately the average compositional range of modal carbonate mineralogy, as also seen in section 3.4. It is to be noted though that,

variable carbonate mineral modal abundances per sample result in slight deviations of the carbonate fraction data and mineral chemical data in some instances.

#### 3.6.2 Carbonate fraction cyclicity

Bulk carbonate fraction- and mineral-specific analysis of BIFs of the lower Asbestos Hills were studied to understand the primary *versus* diagenetic processes resulting in the deposition of extensive Fe rich chemical sediments prior to the GOE (Rafuza, 2015; Oonk, 2017). The results show that the Kuruman and Griquatown Formations host Mn exclusively in Fe carbonates with an increase in bulk-rock Mn content towards the upper Griquatown Formation. The Hotazel Formation at the uppermost part of the Transvaal Supergroup, presents a unique case were manganese is not exclusively hosted as substitutions in Fe rich carbonates, but as three discrete, world class Mn ore layers intercalated by BIF.

As stated in section 2.7, there is evidence for continuous iron precipitation in the Hotazel Formation across both Fe and Mn rich lithofacies, whereas appreciable manganese precipitation occurred during the deposition of the three manganese ore layers and transitional hematite lutite. Therefore, bulk-rock Fe and Mn concentrations alone do not record the lithological boundaries of the three lithofacies most effectively. The carbonate fraction, however, reveals mineral-chemical and corresponding carbonate fraction-specific trends that succeed in mapping out very eloquently the different mineralogical and compositional facies and particularly the transitions thereof.

#### Lithologic transitions

A summary of the most salient results of this chapter with respect to the three key lithofacies and their lithologic transitions include:

In general, the carbonate fraction of BIF across the Hotazel stratigraphy shows a first-order transition from very low iron content in the lower third (including both the lowermost BIF to manganese transition and manganese marker sub-cycle) with values less than 3 wt.% FeO (section 3.3.1 and 3.3.2), to values as high as 8 wt.% FeO in the middle and uppermost BIF.

- The transition into the Mooidraai Formation record a gradual decline in carbonate hosted iron and increase in calcic carbonate as low-Mg calcite.
- The carbonate fraction of the manganese rich lithofacies up stratigraphy, show MnO values of up to 18 wt.% within hematite lutite, and much lower MnO values within the manganese ore layers at a maximum of 4.9 wt.%. This means that maximum carbonate fraction Mn is recorded within hematite lutite layers, where bulk-rock manganese concentrations are significantly lower compared to the manganese ore layers themselves.
- During manganese deposition, practically no Fe is incorporated into carbonate minerals except for the margins of hematite lutite in contact with BIF.
- The lower parts of the stratigraphy appear to be highly transitional, in terms of the cyclic nature of Fe to Mn deposition which suggests highly transient chemical and physical conditions within the primary oceanic environment.
- By contrast, the upper parts of the stratigraphy record clearer stratification of Fe and Mn as recorded by the carbonate fraction, suggesting relatively more stable physiochemical conditions within the ambient depositional environment.

# 3.6.3 Carbonate mineral chemical variations

The combined use of carbonate fraction and carbonate mineral chemical data has also provided some interesting insights in terms of mineral, geochemical and lithologic variations across the Hotazel succession which are listed below.

#### Manganese rich lithofacies

- The main carbonate minerals found within both hematite lutite and manganese ore are kutnahorite, Mn-calcite and rhodocrosite.
- There is a complete paucity in the presence of Fe carbonates (ankerite and/or siderite) within both manganese rich lithofacies throughout the entire succession. This includes the highly transitional lower parts (i.e., LBMT and MMSC), which are both characterized by high bulk-rock Fe concentrations, with iron almost entirely present as hematite.

- The manganese layers are modally dominated by low-Mn calcite and Ca-kutnahorite compared to the high-Mn kutnahorite-calcite dominance in hematite lutite.
- There is consistently reproducible chemical composition between co-existing Mn-calcite and kutnahorite on small scales, i.e., between successive mm-scale laminae in the manganese ore layers.
- On a stratigraphic scale, major oxide compositions of all three manganese rich assemblages form a compositional continuum along the Ca-Mn tie line from end-member calcite (CaCO<sub>3</sub>) to rhodocrosite (MnCO<sub>3</sub>) end-member (Figure 3.11 below). Departures towards high Mg are recorded mainly by Mn calcite



Figure 3.11: Major-element compositions of calcitic and Mn rich carbonate minerals from Hotazel manganese rich assemblages (hematite lutite and Mn ore), obtained from election microprobe analysis and expressed in mol% rhodocrosite, calcite, and magnesite end-members.

#### Banded Iron Formation

- Ankerite and siderite and alcite are the main carbonate minerals in the BIF of the Hotazel Formation.
- The oxide rich BIF layers from the lower parts of the stratigraphy (i.e., LBMT and MMSC) contain occasionally Fe-rich manganese carbonates such as kutnahorite and rhodocrosite.
- Manganese-rich ankerite variants are hosted at the margins of BIF layers in gradational contact with transitional hematite lutite.
- Siderite only occurs at the uppermost BIF layers which is consequently characterized by higher carbonate fraction Fe/Ca ratios.
- The major oxide composition of calcite, ankerite, and siderite in BIF record typical, discrete end-member compositional clusters (Figure 3.12, below)



Figure 3.12: Major-element compositions of calcitic and Fe rich carbonate minerals from Hotazel BIFs, obtained from election microprobe analysis and expressed in mol% siderite, calcite, and magnesite end-members.

"Science is an enterprise that should be cherished as an activity of the free human mind. Because it transforms who we are, how we live, and it gives us an understanding of our place in the universe." — Neil deGrasse Tyson

# 4. Small-scale and stratigraphic-wide geochemical and stable isotope variations

## 4.1 Rationale

The utility of chemical sedimentary rocks such as Banded Iron Formations (BIFs) as proxies for ancient seawater chemical and biological conditions has been a well-documented and discussed topic in research (e.g., Anbar *et al.*, 2007; Raisewell *et al.*, 2011; Bekker *et al.*, 2012). As stated in chapters 1.2 and 1.3, previous studies propose the primary precipitation of organic matter along with high valence Fe(III) and Mn(IV) oxyhydroxides as drivers for the secondary (diagenetic) formation of iron and manganese-rich carbonate assemblages in sediments beneath Archean-Paleoproterozoic oceans (Walker, 1984; Pecoits *et al.*, 2009; Heimann *et al.*, 2010; Kohler *et al.*, 2013; Posth *et al.*, 2013; Kurzweil *et al.* 2016). In this context, a leading argument would be whether variations in carbon and iron isotopes in BIFs and similar ancient chemical sedimentary rocks containing Fe/Mn-rich carbonates solely record microbially mediated redox processes occurring exclusively below the sediment-water interface prior to lithification or – at least under certain circumstances – may also be used as proxies for ancient oceanic chemistry and biology.

The most widely supported notion is that low and variable  $\delta^{13}$ C in BIF carbonates reflects the initial presence in the sediment of bicarbonate produced locally, in the pore fluids, *via* microbial oxidation of organic carbon (low  $\delta^{13}$ C -28 ‰) along with bicarbonate derived from the overlying seawater (i.e.,,  $\delta^{13}$ C near 0 ‰) (Baur *et al.*, 1985; Kaufman *et al.*, 1990; Klein, 2005; Heimann *et al.*, 2010). The assumed low  $\delta^{13}$ C value of organic carbon (-28 ‰) and heavier marine bicarbonate (~0 ‰), through microbially mediated dissimilatory iron reduction (DIR) will result in the diagenetic formation of carbonates with an isotopic range between -13 to -5 ‰ as seen in Figure 4.1 below. Variations in the iron isotope ( $\delta^{56}$ Fe) values (from -1 to 1 ‰) in BIF iron carbonates such as siderite have also been attributed to authigenic pathways of DIR (Johnson *et al.*, 2003, 2008; Heimann *et al.*, 2010; Craddock and Dauphas, 2011). Magnetite in BIF is likewise thought to form as a result of DIR, with variability in its  $\delta^{56}$ Fe values attributed to a combination of fractionation of ferric hydroxide, and ferrous iron generated by DIR within the sediment and incorporated into the magnetite structure (Planavsky *et al.*, 2012).



Figure 4.1: Ranges of bulk carbonate-carbon isotopes from various Archean-Palaeoproterozoic deposits around the globe. a) Hotazel BIF; and b) Hotazel Mn-rich layers (Tsikos *et al.*, 2003; Schneiderhan *et al.*, 2006; this study); c) Kuruman & Griquatown BIFs (Rafuza 2015; Oonk 2017; Beukes and Klein 1990); d) Koegas Subgroup BIFs (Johnson *et al.*, 2013); e) Hamersley BIFs (Becker and Clayton 1972; Baur *et al.*, 1985; Kaufman *et al.*, 1990). Note: age of deposits listed in Figure 1.2 and Table 1.1. All deposits are of low metamorphic grade with maximum burial temperatures ~300°C for the Western Australian deposits and ~150°C for the Transvaal basin deposits (Klein and Gole 1981a; Miyano and Klein 1983a; Klein 2005)

The distinctiveness of the Hotazel Formation in terms of hosting both iron and manganese rich assemblages affords a special opportunity to interrogate further the dynamics and processes of BIF genetic models and their relationships to organic carbon oxidation. The inclusion of manganese opens a particularly opportune door. Manganese oxide is the thermodynamically preferred electron acceptor relative to iron oxide during the remineralization of organic carbon-based observations in modern very low O<sub>2</sub> (suboxic) marine diagenetic environments and in the laboratory (Balzer, 1982; Lovley, 1991; Canfield *et al.*, 1992; Nealson and Staffarini, 1994; Kappler et al., 2005; Posth *et al.*, 2013). BIF is known to be generally depleted in Mn compared to average crust, yet the Hotazel strata constitute arguably the most notable exception to that norm (Roy, 2005; Tsikos *et al.*, 2010). In this chapter, a re-examination of the Hotazel BIF-Mn Formation will be performed, with a primary focus of elucidating the role of primary iron and manganese oxides in the diagenetic history of these deposits and the overall mechanisms of their formation.

In this context, of particular interest is the precarious geochronological placement of the Hotazel Formation at the Great Oxidation Event (GOE; Gumsley *et al.*, 2017, but see also Cornell *et al.*, 1996). This demands thorough exploration of the exact nature of the precursor Fe and Mn species because the assumed presence of primary Mn oxides carries with it an additional assumption – namely the presence of adequately high  $O_2$  levels within the local environment. In fact, the presence of the pronounced Mn enrichments in the Hotazel Formation has in itself often been used as a fingerprint of the GOE, without any in-depth discussion of the full merits of such an interpretation. To explore the full utility of the Hotazel Fe-Mn mineralization, a combination was adopted of high-resolution mineralogy and whole-rock geochemistry, coupled with carbonate-carbon and iron isotope analysis of all three main iron- and manganese-rich Hotazel lithofacies.

In this analytical work, a continuous cm-scale approach was employed with main emphasis on small-scale variations in the examined geochemical parameters and their possible controls. This was used as an essential backdrop for stratigraphic variation of both  $\delta^{13}$ C and  $\delta^{56}$ Fe throughout the Hotazel Formation at a relatively high resolution. These results are evaluated in light of existing diagenetic models, highlight disparities between the latter and these data where necessary and provide alternative interpretations for the origin and related chemical and isotopic signatures of the Hotazel sequence. The results have the potential to impact models for the origin of BIF and signatures of the GOE – and Fe/Mn carbonate-rich marine sedimentary deposits in general.
# 4.2 Geology, Sampling and analytical techniques

As stated in chapter 1, the typical stratigraphy of the Hotazel Formation consists of microbanded BIF interlayered with three manganese-rich beds (Figure 4.2a). The transition between these two first-order lithofacies is represented by a very fine- grained hematite-rich sedimentary rock, referred to as hematite lutite (Beukes, 1983; Beukes & Gutzmer, 1996, 2008).

## Cm-scale sampling and analysis

Figure 4.4 shows the log of the selected drill core and key lithostratigraphic relationships. The three samples selected for the cm-scale analysis represent the end-member lithofacies described above. Original half-cores were halved into two mirroring quarter cores; one quarter was used for subsampling, whereas the other was crushed as a single bulk sample. Subsampling of the microbanded Hotazel BIF was most challenging due to its heterogeneity at a sub-mm scale, coupled with the often highly gradational contacts between individual chert/carbonate- and magnetite-rich microbands. Individual band thicknesses also vary across the entire section from <1 mm to >1 cm, which results in large modal mineralogical variations on a sample-per-sample basis.

A total of 13 successive banding-parallel slices of BIF were cut from a 35-cm-thick section at individual thicknesses that ranged from 18-51 mm. This was done in an attempt to capture as faithfully as possible the observed band-to-band modal mineralogical variability. Texturally, the hematite lutite and manganese-rich layers are relatively more homogeneous on a cm-scale, comprising sub-mm-scale carbonate laminations and ovoids in a very fine-grained oxide/silicate matrix. A total of ten subsamples parallel to carbonate lamination were selected from a 26.5-cm-thick section of hematite lutite with thicknesses varying between 26 and 32 mm per slice. Similarly, eight lamination-parallel subsamples were selected from a 23-cm-thick manganese-rich (ore) section, ranging from 25 to 31 mm thickness per slice.

Representative samples were made into thin sections for basic petrographic and SEM examination. All samples were pulverized in a steel ring-mill and analyzed for their bulk mineralogy via XRD and for their major/minor element composition using high-resolution inductively plasma mass spectrometry (ICP-MS) Element XR operated at the French Research Institute for Exploitation of the Sea (IFREMER, Brest). About 100 mg of powder was dissolved in PTFE beakers on a hot plate using an acid mixture of HCl, HNO<sub>3</sub> and HF. Samples were further diluted with 0.28M HNO<sub>3</sub>, and the resulting solutions were introduced into the plasma torch using a quartz spray chamber system equipped with a micro-concentric PFA nebulizer operating at a flow rate of about 100  $\mu$ L/min. Indium solution was mixed on-line at a final concentration of 5 ppb to correct for instrument sensitivity changes due to matrix effects. For each element, ICPMS sensitivity was calibrated using matrix-matched standard solutions corresponding to seawater matrices. Note that only major elements (Fe, Mg, Ca, Mn) are reported in this study, with an overall precision of about 5 % (2 rsd). Aliquots of the same solutions were subsequently purified for Fe isotope geochemistry and analyzed by Multi-collector ICP-MS at IFREMER following established protocols (Rouxel *et al.*, 2005; 2008; 2016).

All analyses are reported in delta notation relative to the IRMM-014 standard, expressed as  $\delta^{56}$ Fe, which represents the deviation in per mil relative to the reference material. As  $\delta^{56}$ Fe and  $\delta^{57}$ Fe are on a single mass fractionation line, only  $\delta^{56}$ Fe values are reported in this study.

$$\delta^{56}$$
Fe = [(<sup>56</sup>Fe/<sup>54</sup>Fe) sample/(<sup>56</sup>Fe/<sup>54</sup>Fe) standard - 1] X 1000

An external precision of 0.05 to 0.06 ‰ (2 SD) for  $\delta$  <sup>56</sup>Fe values has been calculated based on duplicated measurements of standard solutions and geo-reference materials performed during the same analytical session.

Fractions of all sample powders were also analyzed for bulk carbonate-carbon isotope ratios through CO<sub>2</sub> extraction using 100% phosphoric acid at 50°C. Carbon isotope determinations were carried out on a Delta XP dual inlet gas-source mass spectrometer at the University of Cape Town. Finally, the three bulk powdered quarter cores corresponding to the ones selected for high-resolution analysis, were analyzed for their total carbonate-specific element chemistry (Mg, Ca, Fe, Mn) at the University of California at Riverside, using ICP-MS instrumentation following established extraction protocols (Poulton & Canfield, 2005). All analytical results are included in appendix V.

#### Stratigraphic sampling and analysis

For stratigraphic analysis, all samples used in chapters 2 and 3 from both drill core intersections GL137 and GL136 were selected for carbon isotope and total carbon analysis. Selected samples from the top half of the Hotazel stratigraphy were used for iron isotope analysis from drill core GL137 and were combined with existing data from the lower half as published previously (Tsikos *et al.*, 2010). Bulk carbonate  $\delta^{13}$ C values were obtained after reaction with phosphoric acid at 50°C; this was done on the basis that the Hotazel rocks have been reported to contain almost exclusively calcite and carbonates of the dolomite group, chiefly ankerite in BIF and kutnahorite in the manganese-rich intervals (Tsikos *et al.*, 2003; 2010). Moreover, calcite and coexisting dolomite-type carbonates have been previously shown to have comparable  $\delta^{13}$ C values within 1-2 per mil from each-other in any given sample (Tsikos *et al.*, 2003).

Therefore, it is expected that bulk  $\delta^{13}$ C data would fall within the narrow range between the endmember values for each coexisting carbonate, irrespective of their relative modal abundance. It should be stressed though that, in a few selected samples, minor siderite or rhodocrosite (see sections 3.4.2 and 3.4.3) were also detected which are not expected to dissolve in 50°C. These samples were consequently also reacted at 70°C over three days to test whether the said carbonates had any significant effect on the bulk  $\delta^{13}$ C value measured in the same sample powders after reaction at 50°C (see appendix V). The results demonstrated that this was not the case, and therefore that the possibility of non-reaction of siderite or rhodocrosite in samples that contain these minerals would have no measurable effect on the bulk  $\delta^{13}$ C value as determined at 50°C. All carbon isotope values are reported as Standard Delta ( $\delta$ ) notation relative to Vienna Pee Dee Belemnite (VPDB)

Bulk  $\delta^{56}$ Fe values of selected samples from drill core GL137 were obtained from a similar procedure outlined above and values from drill core GL26 were obtained from Tsikos *et al.*, (2010), with stratigraphic adjustments made to account for varying vertical lithological differences of the Hotazel Formation across space. These analyses were carried out at SUERC in Glasgow, Scotland. Total carbon analysis is carried out using a combustion method: powdered samples were weighed at masses of around 100±10 grams each in a ceramic crucible. The sample and crucible were steadily inserted into a furnace with care to prevent atmospheric CO<sub>2</sub> contamination. Here, induction heats up the sample and releases CO<sub>2</sub> from carbonate minerals, which is transported to

an infrared detector where quantitative measurement of  $CO_2$  is carried out. The reference materials AR4016, AR4007, and AR4024 were used to calibrate the instrument in between sample analysis. These analyses were carried out at the University of California, Riverside.

# 4.3 Results

# 4.3.1 High resolution cm-scale variations.

Petrographic observations (Figure 4.2) and XRD analyses (Figure 4.3) reveal a simple mineralogy for all three rock sections selected for this study. Subsamples of BIF show mixtures of quartz, magnetite, ankerite, calcite and very low abundances of Fe silicate minerals. Quartz-rich bands contain variable concentrations of all major mineral phases and are the key carbonate hosts (Figure 4.2b), while mm-scale oxide laminae comprise essentially mono-mineralic magnetite with very minor silicates and carbonates. The hematite lutite is made up of a groundmass of very fine-grained quartz (chert) with abundant "dusty" hematite and minor braunite inclusion. Within this matrix, mixtures of Mn-rich calcite and kutnahorite occur in characteristic mm-scale laminae (Figure 4.2c) and less so as fine disseminations in the matrix itself. Similarly, Mn-calcite and kutnahorite in the Mn ore occur as discrete laminae and as disseminations in a braunite matrix containing minor hematite (Figure 4.2d).

Profiles for bulk carbonate-carbon, bulk Fe isotopes and Fe/Ca and Mn/Ca ratios for the three selected rock sections are illustrated in Figure 4.4. The bulk Fe/Ca and Mn/Ca ratios serve as faithful geochemical records of variations in modal carbonate versus oxide/silicate mineralogy in all three samples, as Ca is hosted exclusively in carbonate minerals. Bulk carbonate  $\delta^{13}$ C values of the BIF samples average -10.4±0.7‰, whereas the corresponding average Fe/Ca ratio is 6.9±3.5. The hematite lutite has an average  $\delta^{13}$ C value of -12.3±0.2 ‰ and average Fe/Ca and Mn/Ca ratios of 8.2±1.2 and 4.8±0.4, respectively, while the manganese ore sample has an average value  $\delta^{13}$ C of -10.5±0.4‰ and an average Mn/Ca ratio of 3.2±0.5. Overall, the three samples exhibit remarkably small variability in their bulk carbonate-carbon isotope signatures, despite the fact that the relative modal abundance of carbonate fluctuates significantly, particularly in the case of the BIF section.



Figure 4.2: a) Image of a typical drillcore of the Hotazel Formation illustrating a succession of BIF, hematite lutite and Mn ore. Representative back-scattered electron images: b) Subhedral to anhedral grains of magnetite, ankerite and calcite set in a matrix of microcrystalline quartz in BIF; c) Hematite lutite, showing anhedral grains of apparently zoned kutnahorite contained in a lamina of Mn-rich calcite. Surrounding matrix is dominated by very fine quartz (dark domains) and microcrystalline, "dusty" hematite (bright domains); d) Mn ore containing intergrowths of anhedral kutnahorite, braunite, Mn-rich calcite and minor hematite. Abbreviations: Cc (calcite); Ank (ankerite); Mt (magnetite); Qz (quartz); Kut (kutnahorite); Hem (hematite); Br (braunite).



Figure 4.3: Partial X-ray diffraction spectra (from 20-40° 2-theta) from the three different lithofacies showing relative intensities in the base peaks of the main minerals present: a) BIF section, sub-samples HRB-4 (bottom) and -12 (top). b) Hematite lutite, sub-samples HRH-5 (bottom) and -10 (top); and, c) Mn-ore, subsamples HRM-3 (bottom) and -7 (top). Note the slight offset in the two Mn carbonate peaks for Mn ore and hematite lutite, which reflect the substantially lower Mn/Ca carbonate ratio in the former as also revealed by speciation geochemistry (see Table 2). Abbreviations: Ank (ankerite); Mt (magnetite); Cc (calcite); Kut (kutnahorite); Hem (hematite); Br (braunite).

With respect to the bulk iron isotope data (Figure 4.4.), all three samples display curiously low variability across the three examined high-resolution profiles. The BIF sample has an average  $\delta^{56}$ Fe value of -1.85±0.05 ‰ (1SD, n=13), with iron hosted in variable modal combinations of magnetite and ankerite. The hematite lutite yielded the lowest values out of the selected three samples, with bulk a  $\delta^{56}$ Fe average value of -2.1±0.04 ‰ (1SD, n=10); almost all the Fe is in hematite. The same mineral host Hematite also, accounts for the bulk of the iron in the Mn ore sample, albeit in much smaller modal abundances, with an average  $\delta^{56}$ Fe value of -1.7±0.09 ‰ (1SD, n=8).

# 4.3.2 Stratigraphic carbon and iron isotope variations

#### Carbon isotope and total carbon variations

The  $\delta^{13}$ C profiles of both drill core intersections, illustrated in Figure 5.1 is the first expression to date of the carbon isotope stratigraphy of the Hotazel Formation at such high stratigraphic resolution. These profiles illustrate a smooth pattern of generally low variability in  $\delta^{13}$ C around the grand average value of -9.7 ±2.9‰ for drillcore GL137 and -10.1±2.7‰ for drillcore GL136, over most part of the examined sections. There is also very close similarity of this entire dataset to previously published data for the Hotazel Formation and other BIF occurrences elsewhere, both in terms of the average  $\delta^{13}$ C value and the range and frequency of  $\delta^{13}$ C values displayed (Figure 4.1).

Excursions (positive and negative) in  $\delta^{13}$ C of a magnitude generally 2-4‰ about the above average are recorded across the Hotazel stratigraphy, mostly over intervals of sharp lithologic change (e.g., BIF to hematite lutite). Arguably the sharpest excursion is observed within the uppermost part of the section where the Hotazel BIF progressively grades into the Mooidraai carbonates. By contrast, the lowest  $\delta^{13}$ C values are recorded at the basal BIF layer below the lowermost manganese ore-layer, consistent with previous studies (Tsikos *et al.*, 2003; Schneiderhahn *et al.*, 2006).



Figure 4.4: High-resolution profiles of bulk carbonate  $\delta^{13}$ C, bulk  $\delta^{56}$ Fe, bulk Fe/Ca and Mn/Ca from the uppermost hematite lutite, middle BIF and lower Mn-rich layer, Hotazel Formation, drillcore GL136.

Carbonate Fraction					
Sample	Mg (wt. %)	Ca (wt. %)	Fe (wt. %)	Mn (wt. %)	C <sub>org</sub> %
Hematite lutite	0.32	2.87	0.09	7.30	0.02
BIF	0.31	3.24	1.57	0.19	0.05
Mn Ore	1.50	8.29	0.05	4.34	0.08

Table 4.1: Acetate-soluble (carbonate) fraction analyses and bulk organic carbon data from composite hematite lutite, BIF and manganese ore samples.

Similar to Chapter 2 and 3, a high-resolution account of the variations of the entire succession will be described and interpreted with regards to the isotope signals of the different lithofacies and transitions between them. As stated in the two previous chapters, the lower BIF to Mn ore cycle comprises of the basal BIF-hematite lutite-low manganese ore layer-hematite lutite-BIF. The  $\delta^{13}$ C values of the basal BIF are almost identical in both intersections at values of  $-16.0\pm1.2\%$  and  $-16.5\pm1.5\%$  for GL137 and GL136, respectively. Low values are also recorded at the overlying hematite lutite layer with  $\delta^{13}$ C values of  $-15.4\pm1.0\%$  and  $-16\pm0.3\%$ , respectively. The overlying manganese ore layer records  $\delta^{13}$ C values of  $-9.5\pm1.5\%$  and  $-9.9\pm1.7\%$  between the two intersections, with a general increase in values towards the overlying hematite lutite to as high as -7.9% and -6.8% in GL137 and GL136, respectively. The hematite lutite overlying the ore is characterized by slightly higher  $\delta^{13}$ C values of  $-8.5\pm2.0\%$  from GL137 and a single sample value of -6.4% from GL136. The BIF at the uppermost part of this cycle records  $\delta^{13}$ C values of  $-10.8\pm0.9\%$  from GL137 and  $-11.5\pm2.6\%$  from GL136.

The middle manganese marker sub cycle comprises the highly transitional succession: hematite lutite-middle manganese "marker"-transitional BIF-hematite lutite, as comprehensively described in chapters 2 and 3. The  $\delta^{13}$ C record of the lower hematite lutite layer records values at -11.1±0.5‰ from GL137 and -12.5‰ from a single sample from GL136. The manganese "marker" layer above the hematite lutite, records  $\delta^{13}$ C values similar to that of the lower ore body at -9.3±2.0‰ and -9.8±0.8‰ from GL137 and GL136, respectively. Overlying the ore "marker" is a very thin hematite lutite layer (not sampled from GL137) that records a  $\delta^{13}$ C value of -7.5 from a single sample in core GL136. Above this hematite lutite is a BIF layer with a  $\delta^{13}$ C record of -7.6±1.2‰

and -6.9 $\pm$ 3.7‰ from GL137 and GL136, respectively. The BIF is overlain by a hematite lutite layer recording the heaviest  $\delta^{13}$ C values throughout the entire succession with an average value of -4.6 $\pm$ 2.6‰ from GL137 and -4.8 $\pm$ 2.4‰ from GL136.

The BIF to uppermost manganese ore cycle is represented, as stated previously (chapter 3), by a more well-defined lithologic sequence of BIF-hematite lutite-Mn-ore layer-hematite lutite-BIF. The BIF records average  $\delta^{13}$ C values of -9.8±2.3 and -10.5±1.2 from GL137 and GL136, respectively. The overlying hematite lutite exhibits slightly lower and comparable  $\delta^{13}$ C values forboth drillcores at averages of -10.8±1.0‰ for GL137 and -10.8±1.1‰ for GL136. The uppermost manganese ore layer is characterized by a  $\delta^{13}$ C record similar to the of the lower manganese layers with values of -9.4±1.4 and -9.6±2.1 from GL137 and GL136, respectively. The hematite lutite records very similar  $\delta^{13}$ C averages to the lutite below the manganese layer with values of -10.3±2.3 from GL137 and GL136, respectively.

Based on carbonate specific (Fe/Ca ratio) and mineralogical observations and interpretations in Chapter 3 (Figure 3.8), the top BIF to Mooidraai cycle is divided into ankerite rich and ankerite+siderite rich BIF from drill core GL137. The lower part of this cycle is characterized by an ankerite-rich BIF with an average  $\delta^{13}$ C record of -10.2±0.6. The overlying, ankerite + siderite rich BIF records slightly higher average  $\delta^{13}$ C value of -9.8±1.5. The top part of this cycle is a gradational transition into the Moodraai Formation which records high  $\delta^{13}$ C values of -2.5±1.0. This gradual increase in the  $\delta^{13}$ C signal towards heavy values is observed in both G137 and GL136, signalling the near-0‰ average isotopic signature of the Mooidraai carbonates as reported previously (Tsikos *et al.*, 2001).

#### Iron isotope variations

The Fe isotope results, together with bulk-rock Fe analysis from selected samples from the three lithofacies (BIF, hematite lutite, and manganese ore) up stratigraphy are shown in Figure 4.6 below. There is a first-order the co-variation between bulk-rock Fe and  $\delta^{56}$ Fe values up stratigraphy with high values in BIFs and a decline across manganese rich assemblages. The highest  $\delta^{56}$ Fe values in BIFs are recorded by the lower part of the Hotazel stratigraphy, with the basal BIF from the LBMT cycle registering a single  $\delta^{56}$ Fe value of -0.20 ‰ from a sample from drillcore GL26 of Tsikos *et al.* 2010. The lowermost manganese ore layer records an average  $\delta^{56}$ Fe value of -



2.08±0.21‰, whereas the BIF layer overlying the lowermost manganese ore layer registers higher  $\delta^{56}$ Fe at 0.19‰, while a value of -1.50‰ is recorded by the overlying hematite lutite.

Figure 4.5: High resolution bulk-rock stratigraphic  $\delta^{13}$ C and total carbon (TC) relationships from drill cores GL137 and GL136 showing reproducibility between the two intersections. Note the co-variance between TC and  $\delta^{13}$ C across the entire stratigraphy and within the three lithofacies.

Arguably the most striking drop in  $\delta^{56}$ Fe values is recorded within the BIF layer overlying the middle manganese ore "marker" at -2.2±0.07 ‰. Overlying the BIF layer lies a hematite lutite with a low  $\delta^{56}$ Fe average value of -2.1±0.26‰. This is followed by another shift to higher  $\delta^{56}$ Fe values within the overlying BIF, at an average of -0.74±0.45‰. A single sample from the hematite lutite layer underlying the uppermost manganese ore layer registers low  $\delta^{56}$ Fe of -2.5‰. This

signal is retained in the Mn ore layer itself with  $\delta^{56}$ Fe values remaining low at -1.9±0.12‰, and ultimately in the overlying hematite lutite with average  $\delta^{56}$ Fe at -2.1±0.07‰.

As stated in section 3.5.4, the uppermost BIF of the Hotazel Formation (TBMC), is divided into ankerite and ankerite+siderite facies. The former records an average  $\delta^{56}$ Fe value of -1.3±0.09‰, whereas the latter has a slightly lower average  $\delta^{56}$ Fe of -1.5±0.40‰. The two uppermost BIF samples transitioning to the Mooidraai Formation, have a similarly low average  $\delta^{56}$ Fe value of -1.8±0.15‰. In summarizing, across the entire Hotazel stratigraphy, abrupt major shifts in  $\delta^{56}$ Fe signatures are seen from BIF to manganese rich assemblages and back, with slight variations in  $\delta^{56}$ Fe within individual lithofacies. In concert with previous reports (Tsikos *et al.*, 2010), the Hotazel BIF consistently returns highest  $\delta^{56}$ Fe values, with the lowest ones recorded in the manganese ore layers and the hematite lutite transitions.

# 4.4 Discussion

## 4.4.1 Basic principles of suboxic Fe and Mn diagenesis

Previous researchers focusing on the diagenetic re-constitution of BIF (Beukes, 1983; Konhauser *et al.*, 2005; Johnson *et al.*, 2003,2008; Anbar *et al.*, 2007; Tsikos *et al.*, 2010; Raisewell *et al.*, 2011; Posth *et al.*, 2013; Kurzweil *et al.* 2016) have reiterated the requirement for precursor Fe(III) oxy-hydroxides such as ferrihydrite to have been the overwhelming primary iron precipitate. This is then reduced in the presence of co-precipitated organic matter to form ferrous iron species such as iron-rich carbonates as observed in the mineral assemblages today. Similar diagenetic models for sedimentary manganese-rich deposits of the Phanerozoic, implicate primary precipitation of Mn(IV) oxides as electron acceptors for organic matter re-mineralization (Lovley and Phillips, 1988; Okita *et al.*, 1988; Polgari *et al.*, 1991; Okita and Shanks, 1992; Nealson and Myers, 1992; Maynard, 2010). Herndon *et al.*, (2018), however provides evidence for manganese carbonate precipitation in a redox stratified basin below the chemocline which does not require reductive dissolution of Mn(IV) oxides to occur in the sediments.



Figure 4.6: Bulk-rock stratigraphic Fe concentrations and  $\delta^{56}$ Fe from drill core GL137 ( $\delta^{56}$ Fe in red dots) with  $\delta^{56}$ Fe data for the lower Hotazel sequence sourced from Tsikos *et al.*, 2010 (blue dots). Note the slight offset in overlapping absolute  $\delta^{56}$ Fe values from the two drill cores which may be related to the fact that the two datasets were obtained by two different laboratories.

By analogy to iron, diagenetic products of organic carbon oxidation with Mn(IV) as the electron acceptor will be manganese carbonates or mixed-valence mineral species, depending mainly on the degree to which the coupled redox reactions will progress. Clearly, the latter will be a function of the relative availability of organic carbon *versus* primary reactive oxy-hydroxides of Mn and/or Fe respectively (Lovley and Phillips, 1988; Konhauser *et al.*, 2005; Heimann *et al.*, 2010). The fact that BIF has an average bulk iron oxidation state of approximately 2.5 and is also known to be universally impoverished in preserved organic carbon (Klein, 2005), suggests that its diagenetic modification must have been limited by primary organic carbon supply.

In the unique case of the Hotazel Formation being a mixed BIF-Mn sequence, the need emerges to make an inference regarding the alternate nature of electron acceptors for the diagenesis of organic matter. Bacteria responsible for the diagenetic process could have utilized either iron and/or manganese as electron acceptors, depending on the relative availability of the latter in each instance. Therefore, results from this study will be assessed on the premise that both DIR and Dissimilatory Manganese Reduction (hereafter referred to as DMR) would have been operative by the same consortium of chemoautotrophic bacteria (Lovley and Phillips, 1988). To this end, it is important to emphasize the relative thermodynamic advantage that tetravalent Mn oxides offer towards biological organic carbon cycling by comparison to their ferric counterparts (Lovley, 1991; Canfield, 1993; Canfield *et al.*, 1993). This implies that primary manganese oxides ought to have been the preferred electron acceptor and therefore the resultant diagenetic mineralogy would be expected to record the prevalence of primary manganese- versus iron oxy-hydroxides in the initial sediment, provided that organic carbon was the predominant electron donor.

Support for the diagenetic origin of iron and manganese carbonate minerals in BIF and sedimentary Mn carbonate deposits alike, is commonly provided by their low  $\delta^{13}$ C values (Figure 4.1). Compilation of previously reported carbon isotope data on BIFs in the Hamersley Basin and Transvaal Supergroup as well as from the Hotazel Mn ores themselves, show a consistent depletion in isotopically heavy carbon, with >95% of  $\delta^{13}$ C values reported ranging between -5 and -13 ‰ (Baur *et al.*, 1985; Kaufmann *et al.*, 1990; Tsikos *et al.*, 2003; Johnson J.E *et al.*, 2013). Similarly, low iron isotope compositions in BIF carbonates have been used as a proxy for diagenetic iron reduction via DIR (Yamaguchi, 2005; Johnson *et al.* 2008; Heimann *et al.*, 2010; Czaja *et al.*, 2010). High  $\delta^{56}$ Fe values of BIF-associated carbonates have also been interpreted to represent

either partial or complete reduction in an open or closed suboxic diagenetic system (Heimann *et al.*, 2010; Craddock and Dauphas, 2011).

Notwithstanding the diagenetic control on iron isotopes, several studies argue that bulk iron isotope compositions of oxide-facies BIFs may ultimately be used as records of water-column processes and oceanic evolution across the Neoarchaean and Palaeoproterozoic (Planavsky *et al.*, 2012; Rouxel *et al.*, 2005; Busigny *et al.*, 2014; Kurzweil *et al.*, 2016). Bulk samples of IF show large ranges of  $\delta^{56}$ Fe values, from -2.5 to 2.7 ‰ (Dauphas *et al.*, 2017) which provide insights into iron enrichment mechanisms and sources.

The two most commonly proposed iron sources, hydrothermal and benthic/diagenetic, have both negative (sub-crustal)  $\delta^{56}$ Fe values (Rouxel *et al.*, 2008; Severmann *et al.*, 2008; Homoky *et al.*, 2013; Chever *et al.*, 2015). The largest equilibrium Fe isotope fractionations reported so far were observed and theoretically calculated for coexisting Fe(III) and Fe(II) aqueous species, with  $\delta^{56}$ Fe Fe(III)aq–Fe(II)aq = 3 ‰ at 20°C (Johnson *et al.*, 2003; Welch *et al.*, 2003; Anbar *et al.*, 2005). Hence, the presence of high  $\delta^{56}$ Fe values in oxide-facies BIF indicate that partial Fe(II) oxidation and Fe(III) precipitation was the main process driving the deposition of BIF.

Following the same mechanism, negative  $\delta^{56}$ Fe values in BIFs have been explained by the progressive oxidation of hydrothermal fluids following a Rayleigh fractionation-type model (Rouxel *et al.*, 2005; von Blanckenburg *et al.*, 2008; Steinhoefel *et al.*, 2009; Tsikos *et al.*, 2010; Planavsky *et al.*, 2012; Busigny *et al.*, 2014). In this scenario, anoxygenic phototrophic oxidation could have established significant water-column Fe concentration gradients – and therefore Fe isotope gradients – through ferric Fe removal during upwelling. An alternative hypothesis leading to isotopically light BIF involves the mobilization and release of isotopically light Fe in the water column from continental shelf environments (Li *et al.*, 2015). Low  $\delta^{56}$ Fe values of BIF-hosted carbonate are expected regardless of biotic *versus* abiotic origins, given the isotopic fractionation during siderite precipitation and expected light Fe isotope values for seawater.

# 4.4.2 Predicted diagenetic pathways

Possible diagenetic mineral-forming pathways will be considered in this section, that are expected to have been involved in the primary Hotazel sediment pile, based on the observed carbonate

mineralogy of the three different rock types and standard principles of carbon cycling *via* DIR/DMR (Lovley and Phillips, 1988; Okita *et al.*, 1988; Lovley, 1991; Konhauser *et al.*, 2005). These simplistic diagenetic reactions are constructed in order to infer the reactants from the observed products, as revealed from bulk mineralogy against the average carbonate speciation analyses of each bulk sample. Ideally, the diagenetic assemblages should contain direct evidence of at least a fraction of preserved precursor Fe(III)/Mn(IV) hydroxides or organic matter, either interstitially and/or as inclusions in diagenetic minerals. Curiously, in the case of the Hotazel Formation, whereas organic matter contents are extremely low (Table 4.1), there is also no direct evidence whatsoever of preservation of primary Mn (IV) oxides anywhere in the succession. On the other hand, ferric iron is the solitary Fe species in the hematite lutite and manganese ore in the form of very fine-grained hematite, whereas in the BIF sample it is contained entirely in the structure of magnetite.

Simplified reaction (1) below provides the predicted diagenetic pathway expected to have produced the carbonate fraction contained in the hematite lutite sample, based on the Mn/Ca/Mg ratio of 45:18:2 as revealed from the corresponding bulk carbonate speciation analysis of Table 4.1:

primary precipitate pore-fluid  $45CH_2O + 90MnO_2 + 36Ca_{aq}^{2+} + 4Mg_{aq}^{2+} + 85HCO_3^{-} \rightarrow$ 

 $90MnCO_3 + 36CaCO_3 + 4MgCO_3 + 85H_2O + 5OH^-$  (1)

#### *kutnahorite* +*Mn*-*calcite*

The first notable point in the above reaction is that due to the very low amount of Fe in the carbonate fraction (<0.1wt %, Table 4.1), complete organic carbon oxidation must have been effectively achieved through DMR alone, resulting in the formation of a mixture of kutnahorite and Mn-rich calcite. The fact that some XRD-detectable braunite (a predominantly Mn(III) mineral) is present in the bulk sample, also suggests that Mn(II) produced diagenetically was not quantitatively captured in the carbonate fraction and may have been available for reaction with residual Mn(IV) to produce intermediate-valence Mn species.

With respect to iron, the lack of carbonate-hosted Fe and exclusive occurrence of hematite in the rock suggests that DIR has either not occurred in favor of DMR – as expected on thermodynamic grounds, experimental results and examples from modern natural environments (Lovley and Phillips, 1988; Lovley, 1991; Nealson and Myers, 1992; Nealson and Saffarini, 1994; Mucci, 2004) – or any ferrous iron produced by DIR was subsequently oxidized into hematite through a late-stage burial diagenetic/alteration pathway. The latter appears unlikely, considering that BIF directly overlying the hematite lutite is itself entirely hematite-free (see also Figure 4.2a).

Similar with reaction (1), reaction (2) below presents the pathway that would have produced the average carbonate fraction of the BIF assemblage, based on the Ca/Fe/Mg/Mn ratio relationship of 20:10:2:1 as recorded in the corresponding bulk carbonate speciation results of Table 4.1:

#### primary precipitate

pore-fluid

 $3CH_2O + 10Fe(OH)_3 + MnO_2 + 20Ca_{aq}^{2+} + 2Mg_{aq}^{2+} + 30HCO_3 \rightarrow$ 

$$20CaCO_3 + 10FeCO_3 + 2MgCO_3 + MnCO_3 + 26H_2O + 14H^+$$
(2)

#### *ankerite* $\pm$ *calcite*

In marked contrast to the hematite lutite sample, the very low Mn concentration in the bulk carbonate fraction of the BIF suggests that DIR would effectively be the sole diagenetic pathway in this instance. The abundance of magnetite contained in the same rock section also suggests that DIR must have produced excess Fe(II) for reaction with available precursor Fe(III); therefore, the relative abundances of organic matter and iron hydroxide indicated in reaction (2) can only be minimum ones, should magnetite be interpreted solely as a product of DIR.

Finally, reaction (3) shows the pathway for carbonate formation in the Mn ore sample, based on the Ca/Mn/Mg ratio of 12:6:3 as derived from the corresponding bulk carbonate speciation results of Table 4.1:

#### primary precipitate pore-fluid

 $3CH_{2}O + 6MnO_{2} + 12Ca_{aq}^{2+} + 3Mg_{aq}^{2+} + 18HCO_{3}^{-} \rightarrow 12CaCO_{3} + 6MnCO_{3} + 3MgCO_{3} + 6H_{2}O$ + 12H<sup>+</sup>  $Mn-calcite + kutnahorite \qquad (3)$  In a directly comparable fashion to reaction (1) earlier and in light of the very low Fe content of the carbonate fraction, DMR would clearly be the solitary diagenetic pathway here as well. Moreover, the abundance of braunite associated with Mn carbonate in the ores suggests a larger initial availability of both organic matter and  $MnO_2$  than that indicated in reaction (3) in order for surplus Mn(II) to be available for braunite-forming reactions, on the proviso that braunite is also a product of DMR.

## 4.4.3 Evidence from carbon and iron isotopes

Diagenesis is expected, in principle, to produce highly variable stable isotope signals in compositionally heterogeneous chemical sedimentary rocks such as BIFs and laminated manganese-rich assemblages, as both seen in the Hotazel Formation. This variability would be a function of a multitude of intertwined factors involved in the diagenetic cycle, such as primary organic carbon supply and its isotopic signature; dissolved inorganic carbon concentrations and potential isotopic variations with water depth; pore-fluid chemistry and its evolving isotopic characteristics; fluctuations through time in the type, relative abundance and depositional fluxes of primary electron acceptor species; and closed *versus* open system diagenetic effects.

The diagenetic reactions inferred in the foregoing section encapsulate much of that potential variability, particularly in the case where the generation of mixed-valence species other than carbonates (i.e., magnetite, braunite) is interpreted as a result of DIR/DMR. With specific reference to equations (1), (2) and (3), and assuming average end-member  $\delta^{13}$ C values for bulk organic matter at -28 ‰ and marine/pore-fluid bicarbonate at 0 ‰, quantitative sequestration of organic carbon into diagenetic carbonate would result in bulk carbonate carbon isotope signatures of approximately -9.7, -4 and -2.5 ‰ for hematite lutite, Mn ore and BIF respectively. These inferred values are several per mil higher than the respectively measured average  $\delta^{13}$ C ones, implying that delivery of Fe(II) and Mn(II) *via* diagenetic organic carbon re-mineralization must have progressed well beyond that required for the formation of the carbonate fraction in the rocks as observed in the present assemblages. Consequently, variability of bulk carbonate  $\delta^{13}$ C should be expected to be large and dependent – among several other factors – on the modal Fe and Mn mineralogy of individual sub-samples, and specifically on the relative abundance of other partly

or wholly reduced mineral species, such as magnetite in BIF or braunite in the Mn ore and hematite lutite.

The carbonate-carbon isotope analyses of the 13 successive sub-sections of the BIF sample exhibit the largest range of  $\delta^{13}$ C values from -11.7 to -9.4‰ (Figure 4.7a). This variation appears to be a direct function of the proportion of ankerite *versus* calcite in the individual sub-samples, as illustrated in the corresponding positive statistical relationship between  $\delta^{13}$ C and carbonatespecific ratio of Ca/(Ca+Mg) of Figure 4.7b. The hematite lutite sub-samples display a much narrower range of comparatively lower  $\delta^{13}$ C values that show essentially no correlation between carbon isotopes and the ratio of Ca/(Ca+Mg), whereas the manganese ore sub-samples display an obvious antithetic relationship between the same two parameters, in spite of the very narrow range of *ca*. 1‰ in the  $\delta^{13}$ C values.

Collectively, the above relationships are intriguing and do not seem to conform directly to the isotopic effects that both DIR and DMR would predict. The first point of note is that the high-resolution  $\delta^{13}$ C data obtained in this study are *bulk* values, i.e., they represent mixtures of at least two co-existing carbonate phases with correspondingly contrasting mineral chemistries. The fact that the  $\delta^{13}$ C data are essentially invariant irrespective of relative modal mineralogical variation – particularly for the Mn-rich samples – points to a common origin of the carbonates in each instance against an isotopically homogeneous reservoir of dissolved bicarbonate. This is difficult to reconcile with classic diagenetic processes that involve *in-situ* reaction of particulate organic matter with a suitable electron acceptor in the presence of a pore-fluid, unless the mass balance between marine bicarbonate and organic-derived carbon input to carbonate formation is maintained curiously constant through large volumes of precursor sediment.

A further emerging question concerns the origin of the CaCO<sub>3</sub> molar fraction of bulk carbonate, i.e., whether it derives from a direct water-column precipitate or is an indirect product of reaction of DIR/DMR-sourced bicarbonate with pore-fluid Ca(II)<sub>aq</sub>. In the case of the BIF dataset, extrapolation of the regression line of Figure 4.7b predicts an isotopic value of pure end-member calcite close to -9 per mil. Such a low isotopic signature is unlikely to represent a seawater bicarbonate value if no organic carbon cycling during BIF deposition was operative in the ambient water-column, as has been argued elsewhere (e.g., Fisher *et al.*, 2009). Therefore, diagenetic formation of calcic carbonate (as calcite and ankerite) involving respired organic carbon would

become a requirement. To this end, whereas DIR may have been the main pathway for organic carbon remineralization, it remains intriguing why the optimum diagenetic carbonate in the BIF is Ca-rich carbonate and not end-member iron carbonate as siderite, considering that DIR must have produced substantial excess Fe for the generation of abundant coexisting magnetite.





By direct contrast to the BIF, the Mn ore sample shows a relationship of progressively lower  $\delta^{13}$ C with increasing Ca content of the carbonate fraction (Figure 4.7b). This is at clear odds with a diagenetic model involving DMR, which would predict relatively lower  $\delta^{13}$ C values with increasing incorporation of Mn(II) in the structure of carbonates. In fact, the very dominance of CaCO<sub>3</sub> in the contained carbonate fraction is itself an unexpected feature in a DMR-dominated diagenetic environment: the Mn ore sample represents the lithified product of postulated maximum initial MnO<sub>2</sub> deposition, and thus the delivery of abundant Mn(II) during diagenesis would be expected to promote manganese-rich carbonate formation potentially as far as end-member rhodocrosite, with concomitant inhibition of Ca(II) uptake (Mucci,1988; 2004; Böttcher, 1998). The fact that low-Ca, Mn-rich carbonates developed in the relatively more Mn-depleted hematite lutite, highlights further this apparent disparity in manganese carbonate chemistry and isotopic signature.

The iron isotope results provide further important constraints: bulk  $\delta^{56}$ Fe data from the hematite lutite show a remarkable constancy of very low values between -2.0 and -2.2 ‰ (Figure 4.7a), which conform very well to other current and previously reported data from the Hotazel rocks (Tsikos *et al.*, 2010). By comparison, the Mn ore sample is relatively enriched in the heavy iron isotopes, with bulk  $\delta^{56}$ Fe values between -1.5 and -1.8 ‰. In both cases, the hematite is thought to represent the de-hydration product of primary ferric oxy-hydroxide that was not implicated in DIR or other reductive diagenetic reactions. Previous interpretations for the origin of these light values argue for a depleted water-column reservoir of Fe(II)<sub>aq</sub> with respect to the heavy iron isotopes, due to long-term prior deposition of high- $\delta^{56}$ Fe BIF (Tsikos *et al.*, 2010). If that was indeed the case, the *ca*. 0.5‰ difference between hematite lutite and Mn ore remains difficult to account for: partial Fe oxidation and primary Fe(OH)<sub>3</sub> precipitation would still result in  $\delta^{56}$ Fe signatures of the ferric precipitates being higher than those of the dissolved Fe(II) inventory.

In the case of the hematite lutite and Mn ore, it is assumed that maximum initial Mn precipitation as MnO<sub>2</sub> would have occurred in an environment which was oxidizing enough to cause minimum iron isotope fractionation during Fe oxidation against the dissolved Fe(II)<sub>aq</sub> reservoir (i.e., nearquantitative Fe(II) oxidation). Therefore, the Mn ore sample ought to have recorded a relatively lower and not higher average  $\delta^{56}$ Fe value by comparison to the more manganese-impoverished hematite lutite sample. A plausible explanation may be sought in the possibility that the two manganese-bearing lithofacies record different parcels of a stratified water column with respect to Fe isotopes, possibly as a result of additional redox cycling involving  $Fe(II)_{aq}$  and primary high-valence manganese species in seawater, or the contribution of additional (i.e., benthic) Fe sources.

The remarkably invariant iron isotope signature of the BIF sample is equally insightful. Bulk  $\delta^{56}$ Fe data across all BIF sub-samples exhibit a narrow range between -1.8 and -2.0 ‰. This is despite the variable modal iron mineralogy of the individual sub-samples, each of which comprises a different relative mixture of magnetite and co-existing ankerite. Both minerals are widely thought to have formed as a consequence of DIR (Heimann et al., 2010; Johnson et al., 2003, 2008, 2013), with ankerite representing a likely direct product of Fe reduction whilst magnetite could have conceivably formed through reaction between DIR-generated Fe(II) and primary ferric iron precipitates. Since equilibrium iron isotope fractionation between magnetite and Fe carbonate ought to be around 1.8 ‰ (Wiesli et al., 2004; Johnson et al., 2008a), fluctuations in modal magnetite versus ankerite would be expected to result in significant variations in measured bulk  $\delta^{56}$ Fe. The fact that the data for the 13 BIF sub-samples display such small variability, suggests that ankerite and magnetite must record closely comparable  $\delta^{56}$ Fe values. The latter is variously used as evidence for quantitative DIR in an essentially closed diagenetic system with respect to Fe (Johnson et al., 2008a; Heimann et al., 2010; Planavsky et al., 2012), implying that the bulk iron isotope value should represent closely that of the original ferric precursor material. In that case, it becomes puzzling why the average iron isotope signature of the BIF is intermediate and hence not directly comparable to that of either the hematite lutite or the Mn ore sample, unless a primary water-column stratification control in iron isotopes is again invoked.

# 4.5 Summary

Three diverse Fe- and Mn-rich lithologies of the Hotazel Formation, namely BIF, Mn ore and transitional hematite lutite, were sub-sampled at high resolution and examined mineralogically, geochemically and isotopically, in an attempt to interrogate the diagenetic origin of the observed assemblages and the predicted pathways for their formation. For each of these three end-member rock types, a number of notable chemical and isotopic signatures are recorded, many of which

appear to be at obvious variance with classic diagenetic models with isotope data from the entire stratigraphy supporting deposition in a stratified water-column, specifically:

- Should carbonate chemistry have been controlled entirely by DIR and DMR, then both processes are clearly decoupled between BIF and the Mn-rich portions of the Hotazel Formation (Mn ore and hematite lutite): namely, BIF carbonates are essentially Mn-free while Mn carbonates are, in turn, Fe-free. Although this can be expected on the basis of experimental data and natural observations of bacterial Mn *versus* Fe reduction, the evident lack of ferric iron reduction even in the Fe-dominated hematite lutite section reinforces the notion of the strong decoupling between DIR and DMR.
- The chemistry of the observed iron and manganese carbonates is also noteworthy: the carbonate fraction of the BIF is characterized by a high molar fraction of CaCO<sub>3</sub> as discrete calcite grains and as component in the chemistry of ankerite. Siderite is curiously absent from the examined assemblage (see section 3.4.3.) even though the preponderance of co-existing magnetite would have required abundant excess ferrous iron produced during anaerobic, microbially-mediated diagenesis. In the hematite lutite sample, the carbonate fraction is strongly manganiferous with Mn-calcite and kutnahorite having an average, combined Mn/Ca ratio just below 3 (Table 4.1 and Appendix III). By sharp contrast, the Mn-calcite and kutnahorite pair in the much more Mn-enriched ore sample is comparatively far more Ca-rich and Mn impoverished, at a combined average Mn/Ca ratio of around 0.5. This is despite the obvious requirement for much excess Mn(II) to have become available diagenetically for co-existing braunite to have also formed via DMR.
- Isotopically, all samples show remarkably low small-scale variation in both bulk carbonate  $\delta^{13}$ C and bulk-rock  $\delta^{56}$ Fe records. This is, in itself, a highly irregular occurrence in the context of diagenetic mineral assemblages which are known to vary widely in response to forming under open system conditions through a complex confluence of sources and processes. The only high-resolution record that shows appreciable enough variation is the BIF  $\delta^{13}$ C record: here, the degree of heavy carbon isotope depletion is directly proportional to the relative modal abundance of ankerite *versus* calcite. Curiously, the opposite appears to be the case in the Mn ore whereby the richer the carbonate fraction is in molar calcite, the lower its  $\delta^{13}$ C appears to be. In both cases, however (i.e., BIF and Mn ore), estimated end-member  $\delta^{13}$ C of pure calcite is very low, i.e., respectively around -9 and -12‰. If primary, such an isotopic composition

for calcite is hard to reconcile through DIR and requires a pool of isotopically light – with respect to carbon – marine bicarbonate as its source. Finally, the iron isotope records are in all instances remarkably homogeneous; the difference in average  $\delta^{56}$ Fe values between BIF (-1.85‰), hematite lutite (-2.1‰) and Mn ore (-1.7‰), however, cannot be readily attributed to DIR *sensu stricto*, and also points to the possibility of an iron isotope gradient for aqueous Fe(II) having existed in the ambient water column.

At a stratigraphic scale, the lower part of the stratigraphy and especially the basal BIF layer records the lowest δ<sup>13</sup>C values and this is replicated across space between the two drill cores (Figure 4.5). The middle marker sub-cycle exhibit highly transitional bulk-rock geochemistry and carbonate mineralogy as seen in chapters 2 and 3, yet the corresponding δ<sup>13</sup>C data remain similar up stratigraphy, with only exception the hematite lutite layer above the ore marker itself. Both drillcores record extremely similar δ<sup>13</sup>C values irrespective of lithological or even slight thickness variations between each sub-facies, suggesting a possible seawater control in terms of iron and manganese stratification and isotopic DIC gradient, with lower values recorded during Mn precipitation.

The slight isotope variations between BIF, hematite lutite, and manganese ore suggest a likely separation of redox processes within the water-column, possibly due to variations in depths of precipitation and hence water-column DMR/DIR. This will be explored and discussed further in chapter 5 later. Within the BIF, bulk carbon content ranges between 0% and 6% yet  $\delta^{13}$ C values range between ~-11 to -8‰; this would be in disagreement with quantitative diagenetic DIR whereby large variation in carbonate modal abundance would reflect in a far more erratic carbon isotope signal. Figure 4.7 above suggests that at a cm-scale, the more calcitic the BIF, the heavier the  $\delta^{13}$ C signature, whilst the opposite is true within the manganese ore samples. In a collective sense, Figure 4.8 illustrates no obvious relationship between the above parameters in both BIF and manganese ore, while extrapolation of regression trajectories suggests  $\delta^{13}$ C values for pure end-member calcite well below 0‰. Similarly, Figure 4.9 illustrates no relationship between manganese content and  $\delta^{13}$ C values in which a negative correlation is thought to strongly suggest a diagenetic origin for such samples (Preston, 2001).



Figure 4.8: Bulk-rock  $\delta^{13}$ C values against carbonate-specific Ca/(Ca+Mg) data for BIF, hematite lutite, and manganese ore samples from both drill cores analyzed in this thesis (i.e., GL137 & GL136). Note the low isotopic value for pure end-member calcite derived from extrapolation of the correlation trajectories.

The overarching conclusion garnered from this specific part of the work is that the examined assemblages do not exclusively register chemical and isotopic variations produced diagenetically in a closed system, but rather ambient water-column variability in response to well-developed physico-chemical depth gradients. This study has therefore reinforced the potential that BIF mineralogy, and particularly the carbonate fraction thereof, may faithfully record oceanic biogeochemistry and not merely diagenesis. To this end, the use of carbon and iron isotope stratigraphy across BIF sequences would hold exciting untapped potential to provide clues into Precambrian chemical and biological ocean evolution, especially with respect to the carbon, iron and manganese redox cycles and the history of oxygen in the earliest atmosphere-ocean system. The following synthesis chapter will bring together findings from this and previous chapters to

further understand the implications for the water-column structure, redox evolution, oceanic conditions and probable precursor minerals that led to the deposition of the Hotazel Formation.



Figure 4.9: Bulk-rock  $\delta^{13}$ C values against MnO<sub>2</sub> content from BIF, hematite lutite and manganese ore samples form drill core GL136.

"Education is the most powerful weapon which you can use to change the world." – Nelson Mandela

2020

# 5. Synthesis

# 5.1 Primary mineral precipitation in the Hotazel Formation

One of the key arguments regarding the modelling of the deposition of BIFs (Siderian) during the Paleoproterozoic has been the requirement of primary oxidation of iron in a marine reservoir saturated with hydrothermally sourced iron, in an environment where free atmospheric  $O_2$  was absent (e.g., Sun *et al.*, 2015). It should be noted here though, that there is an emerging school of thought which proposes that primary iron precipitation need not have been through iron oxidation but rather as reduced iron silicate species, such as greenalite (e.g., Rasmussen *et al.*, 2019). A number of oxidative mechanisms discussed in the relevant literature have been deemed responsible for the conversion of ferrous iron to the primary ferric particulates that settled through the water column to result in extensive BIF deposition. These are:

- Photochemical oxidation by UV radiation (Cairns Smith, 1978; Braterman et al., 1983). The basic premise of this model is that in the absence of free dissolved O<sub>2</sub>, Fe oxidation would have occurred through the absorption of radiation by dissolved Fe(II) in the water-column; through hydrolysis, Fe(III)-oxyhydroxides would thus have formed in widespread fashion. This model has recently been refuted as recent studies have shown that the rate of iron oxidation is slower than that of the precipitation of ferrous carbonate and silicate species (Konhausser et al., 2007).
- 2. Oxidation of dissolved ferrous Fe by phototrophic Fe(II) oxidizing bacteria (Heising et al., 1999; Konhausser et al., 2005). This mechanism suggests that prokaryotic microorganisms called photoferrotrophs, thrived in BIF environments by utilizing Fe(II) as a preferred electron donor to the reduction of CO<sub>2</sub>, and produced Fe(III) solids as a bi-product without the production of O<sub>2</sub>. This model has garnered extensive support in literature (e.g., Kappler et al., 2005; Kappler and Pasquero, 2005), and is seen as a far more viable alternative pathway to photochemical oxidation.
- 3. Oxidation of dissolved ferrous Fe via cyanobacterially-produced O<sub>2</sub> (e.g., Koehler *et al.*, 2010). This mechanism, as its name intuitively suggests, requires the presence of O<sub>2</sub> producing microorganisms via photosynthesis, namely by cyanobacteria. The general premise of this model is that, in a well-stratified shallow oceanic basin, O<sub>2</sub> would have been essentially produced in the photic zone (uppermost layer of the ocean, exposed to direct sunlight) by photosynthetic bacteria (Koehler *et al.*, 2010). Hydrothermally sourced

Fe(II) would have been periodically upwelled from the deeper anoxic water-column to the photic zone where dissolved  $O_2$  abiotically produced precursor Fe(III) oxyhydroxides, which then settled onto the ocean floor to ultimately form BIFs.

The most obvious requirement for the photosynthetic  $O_2$  model, is that during the Archean to Paleoproterozoic,  $O_2$ -producing photosynthesis was occurring. Evidence for this has been reported to be as early as ~3.7 Ga (Rosing and Frei 2004), when organic matter from planktonic organisms is thought to have been preserved in pelagic shales of the time. A large body of literature presents a diverse set of geochemical evidence in support of the onset of oxygenic photosynthesis in the mid to late Archean (e.g., Crowe *et al.*, 2003; Kirschvink and Kopp, 2008; Planavsky *et al* 2014; Gumsley *et al.*, 2017; Wang *et al.*, 2018). Kirschvink and Kopp (2008) have linked the  $O_2$ producing photosynthesis to the global Huronian Snowball Earth Event at *ca*. 2.4 Ga. As stated previously, the most direct evidence for the first appearance of oxygen in the atmosphere globally has been suggested to be the disappearance of mass independent fractionation of sulfur isotopes (MIF-S) in the geological record at or around 2.33 Ga where  $pO_2$ -levels increased to around 0.001% of PAL, in causal response to the GOE (Farquhar *et al.*, 2000; Farquhar and Wing, 2003; Luo et al., 2016).

Sumner (1997) has interpreted the presence of stromatolites on the Campbellrand carbonate platform as evidence for a localized production of O<sub>2</sub> in the Transvaal Basin at the end of the Archean. In this light, oxidation of ferrous Fe by biologically produced O<sub>2</sub> could have driven the precipitation of precursor Fe(III) oxyhydroxides leading to the deposition of the extensive BIFs of the Asbestos Hills Subgroup. This further suggests that the same mechanism could, in principle, have led to the deposition of the younger Hotazel Formation at ca. 2.43 Ga (Gumsley *et al.*, 2017). However, what distinguishes the Hotazel Formation from the older BIFs is that it hosts a world class sedimentary manganese ore deposit in the form of three Mn-rich layers (Laznicka, 1992). Sedimentary-hosted manganese enrichments are commonly associated with oxidizing conditions, suggesting that O<sub>2</sub> must be present in the depositional environment for Mn(IV) oxyhydroxides to form. Partial diagenetic reduction of manganese would have resulted in Mn(II)-rich carbonates and mixed valence (II/III) species such as braunite and friedelite as seen in the Hotazel Formation (Chapter 2).

If the above scenario is correct, then Mn can be used as an indicator for the first appearance of appreciable  $pO_2$ -levels which, if holds true, would place the Fe-Mn Hotazel Formation at the heart of the GOE. The study of Oonk *et al* (2017) has indicated that the upper part of the Asbestos Hills (Kuruman and Griquatown) BIFs is manganese enriched in the form of manganese bearing iron carbonates. This could be taken as a strong precursor signal for the extraordinary manganese deposition in the Hotazel Formation, and possibly for increasing redox conditions in the ocean and atmosphere around 2.4 Ga.

It should be noted that the presence of increased manganese in pre-GOE BIF has been widely interpreted as the result of transient oxygenation events termed "whiffs" (Anbar *et al.*, 2007). The dominance of manganese in carbonates however (Oonk *et al.*, 2017), does not readily support primary Mn(IV) deposition episodically in BIF. At the same time, the Hotazel Formation contains enormous volumes of Mn(II)/Mn(III) assemblages which are not seen in the earlier BIF record. The author maintains that the change in manganese speciation between pre-GOE BIF and the Hotazel Formation is a strong indication for the GOE itself, on the assumption that Mn(II) incorporation into ankerite and siderite need not necessarily implicate process of primary Mn(IV) reduction. In the following sections, evidence for the above contentions leading to a syn-GOE model for the formation of the Hotazel deposit will be presented and discussed.

#### Evidence from mineral associations

Biologically mediated diagenetic processes such as DIR and DMR below the sediment-water interface are considered as prime mechanisms for the reduction of precursor Fe(III) and Mn(IV) oxyhydroxides to form reduced carbonate species in anoxic environments, similar to those recorded in BIFs and Mn rich assemblages of the Hotazel Formation (Klein, 1983; Lovely. 1991). In section 2.3 of this thesis were presented the mineralogy and mineral textures of the Hotazel Formation with emphasis on carbonate minerals from the three lithofacies. Within the BIF, the main carbonate minerals documented are calcite, ankerite and lesser siderite, which together with chert and magnetite, make up >95 % of the bulk modal composition. Classic diagenetic models predict that the iron carbonate minerals in BIF will have formed through organic carbon oxidation and reduction of ferric iron precursors. Against a homogenous pore fluid, such reactions would be expected to deliver secondary (diagenetic) carbonate minerals of comparable compositions from

band to band scales. The coexistence, therefore, of siderite and ankerite within a single band appears to be in direct odds with a microbial diagenetic origin (Figure 5.1).



Figure 5.1: SEM-BSE photomicrographs of textural relationships between carbonates in (a) BIF,(b) transitional hematite lutite and (c) manganese ore. Abbreviations: Cc (calcite); Ank (ankerite);Mt (magnetite); Qz (quartz); Kut (kutnahorite); Hem (hematite); Br (braunite).

Similar findings from the carbonate mineralogy of the hematite lutite and manganese ore (i.e., Mncalcite, kutnahorite and rhodocrosite) (sections 2.3 and 3.4) suggests a similar mode of formation as carbonate minerals in the BIF, except for the required switch from Fe to Mn-dominated precipitation pathways. Both Mn-calcite and kutnahorite occur in discrete carbonate laminae which suggest that they possibly formed against a primary carbonate precursor. This possibility is perhaps consistent with pathways of other Fe(II) and Mn (II) species that are thought to have formed as primary precipitates in the BIF environment. For example, greenalite, a ferrous silicate, has been experimentally found to represent a direct primary precipitate from an alkaline anoxic water-column (Rasmussen *et al.*, 2015, 2017). Similarly, the primary precipitation of magnetite from the water-column could have been possible through the reaction of ferrihydrite and dissolved Fe(II) at pH 7 in the deeper parts of the basin, as suggested by Li *et al.*, (2017) and Lovley and Phillips (1988).

## Evidence from carbonate specific geochemistry and mineral chemistry

In chapter 3, carbonate specific stratigraphic signals were reported in conjunction with carbonate mineral chemistry; combination of these two approaches was necessary due to the variety of carbonate minerals present within the three different lithofacies. The major findings from the data presented can be summarized in the following points:

- Similar to reports from BIF of the older Asbestos Hills Subgroup (Oonk *et al.*, 2017), manganese in the Hotazel BIF is exclusively hosted in Fe-rich carbonate minerals. The MnO content varies between as low as 1 wt% to a high as 6 wt.% in parts of the BIF close to transitions with hematite lutite. Classic diagenetic models involving DIR would explain this manganese contents as resulting from DMR accompanying DIR. It is expected, on thermodynamic grounds that in fact DMR would precede DIR and that the same consortium of bacteria would be mediating both reactions.
- The hematite lutite zones represent primary precursors with iron abundances comparably as high as those in BIF. Despite such high primary iron contents, the contained carbonate mineralogy is almost exclusively manganese rich. Diagenetic models involving bacterially mediated reduction would implicate only DMR in this instance. This is curious if one considers similar oxide-rich primary precursor sediment for both BIF and hematite lutite. The only explanation for such different carbonate mineralogy can only be found in primary controls of carbonate precipitation, rather than expecting diagenesis to produce such disparate carbonate mineralogy in compositionally similar sedimentary precursors. Any other explanation involving fluctuating primary organic carbon contents limiting DIR and DMR reactions, is not readily supported from carbon isotope results that will be presented later in this chapter.

The manganese ore layers contain carbonate mineralogy which is predominantly calcic and substantially lower in manganese than adjacent hematite lutite. Again, the same carbonate minerals (Mn-calcite and kutnahorite) are essentially iron free, pointing to DMR only as a diagenetic carbonate-forming process. However, the dominance of high-Ca Mn-carbonates is peculiar in a sediment saturated with respect to manganese, as the latter would be expected to result in Ca inhibition during carbonate formation (Mucci, 1988, 2004; Böttcher, 1998). After all, adjacent hematite lutite with much lower manganese contents contain more manganese-enriched carbonate species, and carbon isotope data (discussed further later) suggest that organic carbon fluxes would have remained high enough for maximum manganese reduction and incorporation into carbonates.

The above observations and findings appear to be at variance with classic diagenetic models of DIR and DMR against an oxide dominated sedimentary precursor. It is thought instead that the transition: BIF-hematite lutite-manganese ore encloses primary mineralogical variability in terms of both the carbonate and the oxide fraction of the original sediments. Specifically, the aforementioned transition reflects a progressive change from an Fe(II) dominated system (BIF) to a Fe(III)/Mn(II) dominated one (hematite lutite) and ultimately a Mn(II/III) dominated one (manganese ore). This will be further discussed in a proposed depositional model at the end of this chapter.

#### Evidence from redox-sensitive elements (Co, Ce)

Changes in the concentrations of trace elements over time as recorded by ancient chemical sediments, can serve as proxies for changing redox conditions in primary depositional oceanic environments and atmosphere (Anbar, 2008; Scott *et al.*, 2008; 2012; Swanner *et al.*, 2014). From the Hotazel trace element data reported in chapter 2, a first order inference that can be made is that there was very minimal detrital input as suggested by the very low concentrations of elements such as Zr, Ti, Nb and Al. An important set of elements that have the potential to provide insights into the primary environment of deposition of the Hotazel rocks, is that of the so-called redox sensitive elements. For the purpose of this discussion two such elements appear to contain valuable new information for the depositional conditions of the Hotazel strata, namely cobalt and cerium.

Average cobalt concentrations in BIF are known to be very low, and in that sense the Kuruman and Griquatown Formations are compositionally typical, with an average value of  $\sim$ 4 ppm. In terms of speciation, the cobalt is almost entirely hosted in the silicate fraction of the rocks (Oonk *et al.*, 2017). The low cobalt concentrations in these and other BIFs suggest that either conditions were not oxidizing enough to form Co(OH)<sub>3</sub> particulates co-precipitating with ferric oxides, or that diagenetic transformation of such oxides led to recycling of soluble Co(II) back to the water-column. Figure 5.2 illustrates how Co(OH)<sub>3</sub> precipitates are stable at high Eh-pH conditions conducive to the stability of ferric oxyhydroxides. Therefore, if the latter species were dominant precursors to BIF, then Co concentrations in BIF ought to have been correspondingly high.



Figure 5.2: **a**. Speciation diagram of Co (white) and Fe in varying Eh–pH conditions.  $Co^{2+}$  is stable under marine Eh and pH conditions (i.e., 7–8) inferred for the Precambrian ocean. In the absence of carbonate,  $Fe^{2+}$  is soluble. **b**. Speciation diagram of Co (white) and Mn, showing the similar redox potential for Mn(II) and Co(II) oxidation, which are both higher than that of Fe(II) oxidation (caption and Figure from Swanner *et al.*, 2014).

The occasional presence of Mn(IV) oxides in BIF would also have contributed to increased Co fluxes to the sediment (Figure 5.2). Polymetallic nodules represent modern marine chemical precipitates dominated by high valence oxides of manganese precipitating from an oxidized water-column. Nodules from the Cook Islands contain very high Co concentrations with an average value

of 5000ppm (Hein *et al.*, 2015) (Figure 5.2). Such values are indicative of the very high capacity of tetravalent manganese oxides in scavenging a variety of transition metals from seawater (Figure 5.3)



Figure 5.3: Bulk-rock average patterns of trace elements (V,Cr,Co,Ni,Cu,Zn,Mo)/upper continental crust from selected samples from the Hotel BIF (n=43), lutite (n=19) and Manganese ore (n=27), Griquatown and Kuruman BIFs (from Oonk *et al.*, 2017) and Cook Island Nodules representing modern oceanic deposits (Hein *et al.*, 2015).

As seen in Figure 2.6 and 2.8 (Chapter 2), cobalt concentrations show a very interesting stratigraphic pattern in the Hotazel Formation, whereby concentrations are very low within BIF layers, peak at hematite lutite zones, and decline to lower values in the manganese ore layers, which are nonetheless much higher than those of BIF. It becomes apparent therefore, that Co tracks ferric iron and specifically the abundance of hematite in the Hotazel sequence. Hrischeva and Scott (2007), amongst others, have suggested that Fe-Mn oxyhydroxides are an important carrier of transition metals such as Co in near vent hydrothermal sediments, with a correlation co-efficient of 0.763; this is a very similar correlation co-efficient to that displayed in Figure 5.4 below, between bulk rock iron oxide (as FeO) and Co.


Figure 5.4: Co-precipitation of Co and  $Fe(OH)_3$  (primary oxyhydroxide) inferred from the positive correlation of FeO *versus* Co with an R<sup>2</sup>-value of 0.7543. The samples defining this relationship are all magnetite-free and represent the uppermost manganese ore and adjacent hematite lutite from drill core GL137.

The co-variance between FeO and Co of Figure 5.4 utilizes a group of selected samples from the uppermost manganese ore and hematite lutite, that contain little to no ferrous iron as magnetite or iron silicate species. The relationship provides possible evidence for primary co-precipitation control for Fe(III) and cobalt, or scavenging of the latter by primary Fe-oxyhydroxide (Musić *et al.,* 1979); at the same time, it does not constitute any evidence for an association of Co with primary Mn(IV/III) oxides. Therefore the behavior of Co in the Hotazel rocks appears to constrain the primary speciation of manganese and specifically the dearth of Mn(IV) oxides which would otherwise have been very strong scavengers of Co by comparison to Fe(III).

The behavior of Ce in the Hotazel Formation seems to corroborate the evidence from Co. One of the key arguments for primary chemical precipitation of BIF has been the strong similarity of modern-day seawater REE patterns and that of bulk-rock BIF (Bau and Dulski, 1996; Frei *et al.*, 2008; Planavsky *et al.*, 2010). The REE patterns of the three lithofacies analyzed in this thesis

(chapter 2), all share similar characteristics with modern day seawater, therefore they are considered here to be faithful records of seawater signals during primary deposition.

It has been widely reported that Mn (IV) oxyhydroxides scavenge Ce as Ce(IV). This results in a positive Ce anomaly in manganese rich nodules, thus indicating the fully oxidizing oceanic environment of present (Hein *et al.*, 2015). None of the samples analyzed in this study (Figure 2.11) from the Hotazel Formation – including the manganese rich lithofacies – records a positive Ce anomaly that would support a primary Mn(IV) precipitate controlling Ce behavior . This suggests that the primary depositional environment was not fully oxidizing with respect to both Mn and Ce, and therefore, tetravalent Mn oxyhydroxides are unlikely to have been the precursor precipitates. This theory is supported by the lack of evidence for preserved Mn(IV) oxides within the manganese rich lithofacies (chapter 2). Instead, the possibility emerges that Mn(III) precursors were possibly most dominant. This is also supported by the experimental work of Murray *et al.*, (1984), which deals with initial solid phase products formed during the oxidation aqueous of Mn(II) at 25°C over time. The study suggests that the Mn(III) species manganite ( $\gamma$ -MnOOH) was the more stable phase after initial oxidation product of Mn(II), and remains so after a few months of reaction as compared to minerals such as hausmannite.

#### Evidence from Fe isotope variations

The oxidation of hydrothermally sourced aqueous Fe(II) in marine systems to iron oxyhydroxides such as ferrihydrite, involve a positive fractionation effect towards the ferric oxyhydroxides and is therefore expected to result in lower  $\delta^{56}$ Fe values for the remaining dissolved Fe(II) (Johnson *et al.*, 2008a). It follows that the aqueous Fe pool associated with marine chemical sedimentary deposits such as those in the Transvaal Supergroup, may have evolved to produce isotopically lighter BIF through time (Rouxel *et al* 2005). Planavsky *et al* (2012) suggest that whereas BIFs are a sink for isotopically heavy iron, a sink for the light iron isotopes will have to be identified in the global sedimentary record of the time. This is thought to be pyritic black shales deposited at shallow shelves, which would have received light iron through shuttling from deeper parts of the ocean.

The low bulk-rock  $\delta^{56}$ Fe values of the Hotazel Formation as reported in chapter 4 are interpreted to represent a chemically evolved marine basin, whereby stratigraphically older BOF of the Asbestos Hills Subgroup (Oonk *et al.*, 2017) would be isotopically heavier sinks of iron (Planavsky *et al.*, 2012). This would have progressively resulted in the development of a lighter aqueous Fe isotope pool in a commonly evolving marine setting. In the absence of any other sedimentary sinks for isotopically light iron, Tsikos *et al.*, 2010 propose that the Hotazel Formation itself is the effective low  $\delta^{56}$ Fe sink.

If the precursor precipitate for the observed assemblages in the Hotazel Formation was Fe(III)oxyhydroxide (e.g.,, ferrihydrite), then the initial oxidation of ferrous iron would have involved a fractionation factor of ~+1 ‰ through a combination of isotopic exchange between Fe(III)aq and Fe(II)aq (+3 ‰) (Johnson *et al.*, 2003; Welch *et al.*, 2003; Anbar *et al.*, 2005) and a kinetic exchange effect from dissolved iron (II) to precipitation of ferrihydrite (~-2.0 ‰) (Bullen *et al.*, 2001; Beard and Johnson, 2004; Johnson *et al.*, 2008a). It is believed that the abundant hematite within the hematite lutite and manganese ore layers is a simple dehydration product of primary ferrihydrite (Vu *et al.*, 2008) and would thus record such a fractionation effect. Therefore, the very low  $\delta^{56}$ Fe values for these lithofacies would be a direct proxy of an isotopically very light shallow iron pool.

Slight differences between the bulk  $\delta^{56}$ Fe values of the hematite lutite and the manganese ore could be attributed to effects of variable degrees of ferrous iron oxidation (e.g., Croal *et al.*, 2005; Rouxel *et al.*, 2005; Jang *et al.*, 2008; Beard *et al.*, 2010; Wu *et al.*, 2011; Busigny *et al.*, 2014). However, the higher  $\delta^{56}$ Fe values in the BIF cannot be explained purely through an oxidative pathway. The BIF is hematite free and dominated by magnetite which is a mixed valence iron oxide. It is therefore possible that the magnetite that dominates the BIF facies, is produced from the reaction of initial, isotopically low ferrihydrite with a heavier aqueous Fe(II) pool. It is envisaged that such reaction would have taken place either in the benthic marine environment or during diagenesis in the presence of an Fe(II) pore fluid. So in essence, the palaeodepositional environment of the Hotazel Formation would have been stratified with respect to iron isotopes, with the shallow parts of the water-column being the relatively most depleted in heavy iron. Finally, it is possible that the slightly higher but still negative  $\delta^{56}$ Fe values observed in the BIF, may signify a gradual depletion in  $\delta^{56}$ Fe values in the primary aqueous iron pool of the Hotazel Formation, possibly supporting an ongoing reservoir effect through time.

#### Evidence from C isotope variations

The key arguments against diagenetic organic carbon re-mineralization and precursor oxyhydroxide reduction to form the preserved mineral assemblages in the Hotazel Formation, were made in chapter 4 of this thesis. It was argued that the largely invariant  $\delta^{13}$ C data against highly variable bulk geochemistry, is not fully consistent with predicted diagenetic pathways of DIR and DMR (i.e., Beukes, 1983; Lovley and Phillips, 1988; Konhauser *et al.*, 2005 etc.). It is, for example, difficult to explain why major isotopic variability does not reflect the major changes in carbonate chemistry across all lithofacies examined. It is believed instead that, at a stratigraphic scale, the observed subtle variations in  $\delta^{13}$ C values could represent depth-related variations in water-column chemistry and carbonate formation in response to well-developed physico-chemical gradients.

Processes of microbially mediated organic carbon and metal oxide cycling are omnipresent an extremely important in modern anerobic diagenetic environments (Canfield *et al.*, 1993). For the very same reason, similar processes are thought to have dominated in early marine environments on Earth. In the case of BIF depositional environments, DIR is thought to have been a central process of redox cycling during diagenesis (Kappler, 2005). However, there has been very little discussion in the literature as to whether processes like DIR may have controlled redox cycling in the oceanic water-column and not exclusively in the sedimentary pile of ancient BIF environments. Havig *et al.*, (2018), for example, have suggested extensive organic carbon cycling within the water column of an extant lake, which evidently results in an increasingly isotopically depleted DIC (dissolved inorganic carbon) pool driving water-column low  $\delta^{13}$ C carbonate formation. The main difference between these two sub environments has to do with the ways in which the carbon isotope signatures in the sediment pile and within the water-column, are interpreted.

Fundamentally, carbonates minerals that form as a result of DIR and DMR should be end-member carbonate mineral species like siderite and rhodocrosite. Furthermore, the availability of CO<sub>2</sub> through DIR and DMR would be directly associated with the balance of electron acceptors (metal oxides) *versus* organic carbon. In other words, DIR and DMR do not make provision for the formation of calcic and magnesium carbonates (e.g., magnesian calcite). The abundance of such carbonate species in the Hotazel rocks namely ankerite, kutnahorite and a variety of calcite compositions (see Chapters 3 and 4) is therefore not fully compatible with classic reactions related to DIR and DMR. The largely homogenous  $\delta^{13}$ C signature of the Hotazel succession is far more easily explained as a result of organic carbon remineralization in seawater and resultant development of a gradient in the  $\delta^{13}$ C of dissolved inorganic carbon. That way, carbon isotope records could be interpreted in similar light to the iron isotope record earlier. This and other elements of interpretation of the Hotazel record are collectively modelled in the next section.

#### 5.2 Hotazel depositional model

In this section, a conceptual model is presented for the deposition of the three main lithofacies of the Hotazel Formation, namely BIF, hematite lutite and manganese ore. The model is based on findings and interpretations from this thesis and relevant information from previous research on BIF in general, and the stratigraphically older Kuruman and Griquatown Iron formations in particular. At the center of the model is the characteristically cyclic nature of the Hotazel Formation hosting three manganese layers interlayered with transitional hematite lutite and BIF (Beukes, 1983, Tsikos and Moore, 1997). The cyclic nature of this unique Fe-Mn succession has been attributed to either marine transgressive and regressive cycles in a well-stratified basin during deposition (Beukes, 1983; Tsikos and Moore, 1997), or by periodic hydrothermal plumes ejecting Mn(II) and Fe(II) in discrete pulses in a dynamic circulating ocean (Beukes, 1983).

The transgression-regression model above seems to be far more applicable in light of predicted models for the Paleoproterozoic oceans which are thought to have been well-stratified, with a clear separation of anoxic, suboxic, oxic and sulphidic layers (e.g., Anbar and Knoll, 2002; Planavsky *et al.*, 2009; Kendall *et al.*, 2012). As indicated in earlier parts of this chapter, the notion of oxygen production as early as the Neoarchean is regarded as a fundamental precondition for modelling the Hotazel paleoenvironment (e.g., Klein and Beukes, 1989; Sumner, 1997). The source of Fe(II) and Mn(II) would have been from hydrothermal plume activity (Beukes, 1983; Isley, 1995; Isley and Abbott, 1999) which saturated the anoxic ocean of the time; the source of silica can likewise be

attributed to a hydrothermal source (Fischer and Knoll, 2009). A detrital influx of these three species cannot be discounted; however as seen in chapter two, concentrations of bulk-rock trace elements of a common detrital origin – such as Zr, Al, and Ti – are very low, suggesting minimal detrital input. Both Fe(II) and Mn(II) would have been oxidized within the shallow parts (partially oxic) of the seawater column through reaction with cyanobacterially produced  $O_2$ .

The strikingly interlayered nature of the Hotazel Formation is indicative of processes of primary deposition of iron and manganese in a very well fractionated fashion. For that reason, stratification of the water-column with respect to both metals is an element of paramount importance in terms of modelling. The deposition of manganese poor BIF at pre-Hotazel times is likely to have led to the relative enrichment of the ocean in manganese *versus* iron. Nevertheless, that enrichment is not in itself sufficient to explain every element of the genesis of the Hotazel Formation. The second requirement for the present model is that of the oxidation of manganese to a trivalent oxyhydroxide precursor such as  $\gamma$ -MnOOH. As explained earlier, there is no preservation of any high valence species of manganese in global BIF and the Hotazel Formation is the only sequence where Mn in an oxidized form is so abundant. Therefore, the proposed model below requires an oxidative pathway for Mn(II) to Mn(III) which is assumed to be *via* photosynthetic O<sub>2</sub>. The generation of Mn(III) would have introduced a powerful new redox player in the marine environment of the Neoarchean and Paleoproterozoic thus resulting in the development of redox shuttles (Canfield *et al., 2005*) driving processes of iron, organic carbon and ultimately managanese of processes of a well.

The model is subdivided into three parts: each part accounts for the deposition of each major lithofacies present in the Hotazel succession, and collectively all three parts can be merged to account for the cyclic deposition of the Hotazel strata in a temporal sense. The model incorporates only the salient mineralogical and geochemical information and attributes that were highlighted earlier in this chapter, but it is hoped that it can be adapted in future when new information on the Hotazel rocks becomes available.

#### 5.2.1 BIF Deposition (DIR-dominated)

The first stage of the model accounts for BIF deposition; this would represent a relatively deeper during (transgressive) stage in terms of sea level, where primary precipitation is taking place at the



Figure 5.5: A conceptual model for the deposition of BIF in the Hotazel Formation. Gradients of  $\delta^{13}C_{(DIC)}$ , Fe<sup>2+</sup><sub>(aq)</sub>,  $\delta^{56}$ Fe, Mn<sup>2+</sup><sub>(aq)</sub>, Co<sup>2+</sup><sub>(aq)</sub>, and O<sub>2(aq)</sub> characterizes ambient seawater. An active Mn-Fe shuttle recycles manganese back into solution while primary ferric oxyhydroxide particles are partially reduced *via* **DIR** below the redoxcline forming carbonates, and possibly magnetite and silicates as they "rain down" to the seafloor. High Fe/Ca in solution results in occasional highest Fe carbonate saturation as primary siderite. Carbonate minerals record seawater chemical signatures and recrystallize below the sediment-water interface through early and late stage diagenesis.

redoxcline under anoxic conditions (Figure 5.5). The seawater column must have been well stratified in terms of Fe<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup> and O<sub>2</sub> in solution, with well-developed vertical gradients of  $\delta^{13}C_{(DIC)}$  and  $\delta^{56}$ Fe. Oxidation of Mn(II) to  $\gamma$ -MnOOH is thought to have driven effective oxidation of Fe(II) to Fe(OH)<sub>3</sub> and recycling of manganese back into the water-column as Mn(II). These would have resulted in the development of a zone of Mn(II) maximum concentration and Fe(II) minimum concentration. It is thought that Co(II) would have behaved in a similar way to Mn(II).

Below the redoxcline of maximum Mn(III) reduction and Fe(II) oxidation (Mn-shuttle), primary delivery of Fe(OH)<sub>3</sub> would have been taking place. Oxidation of sinking C<sub>org</sub> by Fe(OH)<sub>3</sub> would have acted as a water-column DIR mechanism and would have produced primary carbonate precursors to ankerite and siderite. At times of diminished DIR (e.g., during low organic carbon production at surface waters) carbonate formation would be curtailed and magnetite formation may have been promoted instead through reaction of Fe(OH)<sub>3</sub> with aqueous Fe(II). The resultant mineralogy of the BIF facies would therefore record chemical and isotopic signals of this specific part of the water-column where primary mineral nucleation occurred. Textural manifestation of the minerals in the rocks is thus mainly in the form of recrystallisation and neomorphism, without necessarily changing the primary chemical signals in general.

#### 5.2.2 Hematite lutite deposition (DMR-dominated)

The second stage represents the deposition of the transitional hematite lutite at a shallower depth i.e., during marine regression (Figure 5.6). The main change in this stage compared to the BIF stage (deep water conditions) is the progressive elimination of the deep aqueous Fe(II) reservoir. In this instance, oxidized manganese supply in the form of  $\gamma$ -MnOOH would outcompete its reduction to Mn(II) by the dwindling availability of aqueous Fe(II). At this stage, Mn(III) would become the main electron acceptor for organic carbon oxidation and recycling and thus a switch from DIR to DMR would occur. Unlike Mn, oxidized Co as Co(III) would not be reduced by organic matter and would co-precipitate with Fe(III) in the form of Co-bearing Fe(OH)<sub>3</sub>.



Figure 5.6: A conceptual model for the deposition of hematite lutite in the Hotazel Formation. Gradients of  $\delta^{13}C_{(DIC)}$ , Fe<sup>2+</sup><sub>(aq)</sub>,  $\delta^{56}$ Fe , Mn<sup>2+</sup><sub>(aq)</sub>, Co<sup>2+</sup><sub>(aq)</sub>, and O<sub>2(aq)</sub> characterizes ambient seawater. Mn oxidation just below the redoxcline, leads to formation of  $\gamma$ -MnOOH particulates and possibly soluble Mn(III) species. Here, reduction of manganese(III) overwhelms redox cycling through **DMR**, leading to primary Mn carbonate saturation and nucleation. Highest Mn carbonate as rhodochrosite would be expected to be precipitated from zones of high Mn/Ca in solution.

Manganese carbonate precursors in the form of Mn-calcite and kutnahorite – would have precipitated from zones of DMR, in a similar manner to Mn carbonates from the water-column in the redox-stratified Fayetteville lke in Canada (Herndon *et al.*, 2018). Unreduced Mn(III) would have reacted with silica to form braunite probably during early diagenesis. The complete lack of iron reduction during hematite lutite formation can be explained by the thermodynamic preference that Mn(III) oxides offer to mediating bacteria compared to Fe(III). With regard to isotopic values, the  $\delta^{13}$ C data for manganese carbonates would be comparatively low to those for iron carbonates whereas  $\delta^{56}$ Fe values for hematite would be low and reflective of the highly depleted nature of Fe(II) at the shallow levels of the water-column where these processes took place.

#### 5.2.3 Manganese ore deposition (aerobic OC oxidation)

The third stage involves the precipitation of the manganese ore layers at even shallower depths (maximum regression) where conditions were arguably the most oxic (Figure 5.7). In this environment, the overwhelming redox pathway would have been oxidation of manganese by  $O_2$ , accompanied by far more subdued iron oxidation. Co(III) deposition would have continued to be controlled by Fe(OH)<sub>3</sub> deposition and subsequent conversion to Co-bearing hematite during diagenesis. Unlike with the situation in the hematite lutite stage, the overwhelming electron acceptor for organic carbon oxidation would now have been molecular  $O_2$  itself. Aerobic oxidation of organic carbon would have produced isotopically low  $CO_2$  which, upon reaction with Ca(II) and Mg(II) ions would have produced the predominantly calcic and magnesium bearing carbonate mineralogy. At the same time, the oxidation of Mn(II) to  $\gamma$ -MnOOH would have prevented significant availability of Mn(II) for carbonate formation. That way, the assemblage of braunite and Mn poor calcic carbonates with minor hematite, would have formed.

The model presented in the foregoing sections encloses, possibly for the first time in Earth history, lithological and geochemical transitions that mimic a so-called 'redox ladder'. Specifically, the three stages described in the said model portray a transition from redox processes driven by iron oxyhydroxide as the main electron acceptor (stage 1, Figure 5.5) to those where a manganese oxyhydroxide (stage 2, Figure 5.7) and ultimately molecular oxygen (stage 3, Figure 5.6) were the preferred electron acceptors. Repeated transgressive-regressive cycles would have resulted in the.



Figure 5.7: A conceptual model for the deposition of Mn ore in the Hotazel Formation. Gradients of  $\delta^{13}C_{(DIC)}$ ,  $Fe^{2+}_{(aq)}$ ,  $\delta^{56}Fe$ ,  $Mn^{2+}_{(aq)}$ ,  $Co^{2+}_{(aq)}$ , and  $O_{2(aq)}$  characterize ambient seawater. A Mn-Fe shuttle is non-operative at the shallowest parts of the water column above the redoxcline. **Aerobic C**<sub>org</sub> oxidation is the dominant pathway here, resulting in Ca-rich, manganese carbonate formation (Mn calcite and Ca-kutnahorite), and unidirectional Mn(III) precipitation as  $\gamma$ -MnOOH which transformed into braunite during diagenesis. Contemporaneous Fe(OH)<sub>3</sub> precipitation (eventually preserved as hematite) was ongoing throughout but very subdued by comparison.

three intercalations of manganese ore layers with BIF as so strikingly seen in the Hotazel Formation. Changes in relative vertical thicknesses of the different lithofacies across space as seen to some degree between the two drill cores analyzed in this study and particularly as it seen in the southern KMF (Tsikos *et al.*, 1997) suggests that at times, simultaneous deposition of BIF, manganese ore, or hematite lutite could have been occurring due to irregularities in basin paleotopography and resultant depth variability. This could also account for the highly transitional middle manganese ore sub-cycle (MMSC) and its occurrence at different stratigraphic depths within the Hotazel Formation across space, namely proximal to the lowermost manganese ore layer in the southern KMF

#### 5.3 Future work

This work forms part of a larger research initiative undertaken by the research unit PRIMOR at Rhodes University (www.ru.ac.za/primor) that focuses on the Griqualand West Supergroup of South Africa and its spectacular deposits of Fe and Mn. The recent (Fryer, 2015; Rafuza, 2015; Oonk, 2017) and current activities of this unit have had two overarching aims: the first was to research and understand primary and post-depositional processes during sedimentary Fe and Mn deposition in the marine realm of the Neoarchaean and Paleoproterozoic, and the implications for paleoenvironmental reconstructions and early Earth redox evolution. The second objective concerns the genesis of commercial Fe and Mn deposits associated with these rocks and processes, and beyond. This study presents a relatively novel research approach to the world-famous Mn-rich Hotazel Formation, focusing on the mineralogy and geochemistry of the carbonate fraction with less emphasis given to the silicate and oxide fractions. Therefore, it is considered paramount by the author that future projects should aim at furthering understanding of the silicate and oxide precursors to the observed mineralogy and their implications. Speciation techniques, which have been recently optimized for BIF studies (Oonk et al., 2017), can potentially be expanded further to explore Mn-rich facies in these deposits, with prime aim to constrain the geochemical controls that Mn-rich mineralogy exerts in terms of trace element behaviors and distributions.

This study involved only two drill cores through the Hotazel Formation which are located approximately 500 m apart. The rocks were analyzed for, among others, high resolution carbonate-

carbon isotope variations. The said cores show small but distinct lithological thickness variations among individual subfacies (see Figure 1.9), with the  $\delta^{13}$ C record seemingly tracking these changes across the stratigraphy. However, the total thickness of the Hotazel Formation from evidence in both cores is around 100 meters whereas in some localities elsewhere in the KMF, the total thickness preserved can be as high as 200 meters or more (Tsikos *et al.*, 2003), with the lowermost manganese ore layer alone attaining a thickness of over 40 meters. A high-resolution carbonate-carbon isotope study across larger expanses of the Kalahari Manganese Field has therefore clear potential to provide much better insights into stratigraphic correlation, further understanding of controls on carbonate formation in the primary depositional setting and illuminate possible seawater  $\delta^{13}C_{DIC}$  gradients and processes of primary iron and manganese carbonate precipitation at the dawn of the GOE. "Remember to celebrate milestones as you prepare for the road ahead." – Nelson Mandela

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## 7. Appendices

# TO ACCESS APPENDICES, DOUBLE CLICK ON PAPER CLIP SIGNS **BELOW** OR **VIEW** ON ATTACHMENT TAB ON YOUR ADOBE READER (ALL FILES ARE EMBEDDED WITHIN PDF)

#### APPENDIX I: STRATIGRAPHIC OBSERVATIONS AND DESCRIPTIONS

## 0

#### APPENDIX II: BULK-ROCK DATA FOR DRILL CORE AND GL136 STANDARDS

The following excel spreadsheet contain tables of bulk-rock major and trace element analyses from drill core GL136. Erroneous data highlighted in red. Duplicate data was averaged.

### 0

#### **APPENDIX III**: ICP-MS ACETATE AND TOTAL DIGEST DATA FOR DRILL CORES GL137 AND GL136

The tables in the excel spreadsheet contain elemental concentrations (wt.%) of the carbonate fraction and HF (total digest) fractions from the two drill cores analyzed for this project. Erroneous data highlighted in red. Duplicate data was averaged.

## 0

# **APPENDIX IV**: ELECTRON MICROPROBE DATA OF SELECTED SAMPLES FROM DRILL CORE GL137

The following excel spreadsheet contain mineral chemical data for the different Fe and Mn carbonates from selected samples.  $SiO_2$  analyses was included to control cross analytical errors

due to the very fine-grained nature of the different assemblages of the Hotazel Formation. erroneous data was filtered out based on high  $SiO_2$  (>1 wt.%) and not included in presented tables.

## 0

**Appendix V**: Carbon and iron isotope analysis from drill cores GL137, GL136

The tables in the following spreadsheet contain C isotope averaged and raw data tables for both drill cores and Fe isotope data for selected samples from GL137. I have included  $\delta^{18}$ O data not used in this study. Duplicate sample analyses were averaged for use in this study.

## 0

**APPENDIX VI**: ICP-MS TOTAL DIGEST, C AND FE ISOTOPE ANALYSIS FOR SMALL SCALE VARIATION SUB-SAMPLES FROM GL136

The following spreadsheet contains tables of C and Fe isotope data including total digest major and trace element data for subsamples of the three Hotazel lithofacies and acetate (carbonate) fraction data for the composite samples selected.

### 0