# Manganese Enrichments in Matthews Ridge, Guyana

# Master Thesis Project, Earth Life and Climate Master's Program.

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# Abstract

The Matthews Ridge manganese Mineralisation is part of the Barama Mazaruni Trans-Amazonian Greenschist Belt in the Guyana Shield, northern South America. The Matthews Ridge Formation is composed of two major units. The lower unit is made up of mafic volcanic and metavolcanic rocks and the upper rock unit consists of clastic metasediments and intermediate metavolcanics that are intercalated with chemical sediments. The deposit was accumulated in the Early Proterozoic when the ocean and atmosphere had a substantial amount of oxygen, up to 10% of presentday levels. Manganese was deposited at this time in significant amounts. in contrast to the Archean where Fe deposition dominated. The Fe redox cycle has been studied extensively throughout Earth's history while the Mn redox cycle has received less attention. Little is known about the processes that led to Mn enrichment in the Matthews Ridge Formation and most of the knowledge about the mineralization comes from an unpublished mining report. In contrast to this mineralization, other Mn deposits of similar, Early Proterozoic age have been studied thoroughly, e.g. Nsuta (West Africa) and Serra do Navio Brazil. These deposits are places where Fe-rich minerals are found in minimal proportions and as secondary minerals, thus making it a unique location to study the Mn redox behaviour and deposition mechanisms. For this study, the major oxide and REE components of the sediments were explored using XRF and ICP-MS data and focusing on the similar redox properties of Manganese and Cerium to identify the conditions under which the sediments were accumulated. By combining the data with petrographic observations and Micro Probe data the Mathews Ridge sediments were deposited in a shallow marine environment under oxidative conditions following the weathering of the mafic and ultramafic rocks. The sediments were later metamorphosed to greenschist facies and subjugated to tectonic overprinting and tropical weathering resulting in lateritism.

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# <span id="page-6-0"></span>1 Introduction

# <span id="page-6-1"></span>1.1 Mn Geochemical behaviour in the Marine Environment and Mineralization types.

In the marine environment, manganese enrichments are typically supplied by either an endogenic hydrothermal source or related to exogenic processes that lead to concentration in coastal and continental areas (Roy,2006a). From observations in modern marine basins (e.g. Black Sea, Baltic Sea), coupled with thermodynamic calculations that mimic natural conditions, it has been proven that the main factor that drives the Mn deposition is Eh-ph variations in the inorganic aqueous system (Krauskopf, 1957). In addition, the presence of organic matter  $HCO^{3-}$ ,  $SO_4^{2-}$  and  $HPO_4^{2-}$  also affects the behaviour of manganese in exogenic conditions (Hem, 1972, 1978; W. Stumm und J. J. Morgan, 1973). The initial precipitation of Mn oxyhydroxides by oxidation of aqueous  $Mn^{2+}$  leads to a metastable state that undergoes fast changes into stable species. Mn<sub>3</sub>O<sub>4</sub> and  $\gamma$ -MnOOH were shown as the solid phases in equilibrium with seawater (Grill, 1982; Landing & Bruland, 1980). Experimental oxidation of Mn<sup>2+</sup> has been shown to produce Mn<sub>3</sub>O<sub>4</sub> and β-MnOOH (Stumm W & Giovanoli R, 1976), Mn<sub>3</sub>O<sub>4</sub> (Murray et al., 1985), and  $\gamma$ -MnOOH (manganite) (Hem, 1978; Hem & Lind, 1983). Manganite is considered as the most stable species to be derived from  $Mn_3O_4 \beta$ -MnOOH by aging and in all these phases the oxidation number does not exceed  $+3$ . By contrast, the primary phases (todorokite, δ-MnOOH, birnessite) in modern Fe-Mn nodules the crusts approach the +4 oxidation number (Murray et al., 1984; Piper et al., 1984). This anomaly was explained by attributing kinematically controlled disproportionation reactions involving γ-MnOOH producing thermodynamically stable  $Mn^{4+}$  oxides (Hem, 1978; Hem & Lind, 1983; Lind, 1987) Owing to the transient nature of the  $Mn^{3+}$  phases in sedimentary conditions, the  $Mn^{2+}/Mn^{4+}$ redox couple effectively controls the precipitation of dissolved  $Mn^{2+}$  from solution (Roy, 2006) (Figure 1a).

The precipitation of Mn carbonate is controlled almost exclusively by high-level dissolved  $Mn^{2+}$  precipitation in pore waters, which in combination with dissolved bicarbonate, could exceed the solubility of Mn carbonate. (Roy,2006a). Such an extensive supply of dissolved  $Mn^{2+}$  is considered possible only in oxygen-stratified basins where Mn oxyhydroxides precipitated from overlying oxygenated seawater into the reduced zone below where they were buried and the dissolved  $Mn^{2+}$  could be in stable conditions ('manganese pump'; Calvert & Pedersen, 1993, 1996). Mn carbonates (rhodochrosite, kutnohorite), which are hosted in black shales and carbonates-rich organic matter, are typically formed by the

diagenetic reaction of dissolved  $Mn^{2+}$  with organically derived dissolved  $HCO^{3-}$  in the anoxic zone. Such diagenetic Mn carbonates are depleted in  $^{13}$ C indicating that the carbon originated, at least in part, from the organic matter. (Okita et al., 1988; P. M. Okita & Shanks III, 1992; Polgári et al., 1991). This high organic carbon flux to the anoxic zone of the stratified ocean can explained by enhanced plankton productivity in the continental margin setting, during transgression and followed by their decomposition and  $O<sub>2</sub>$  consumption during and after settling. (Roy, 2006). (Figure 1b).



Figure 1: (a) Stability of Mn oxides and carbonate deposits in natural water. The dashed bold lines represent 10-4 and 10-6  $Mn^{2+}$ . The dotted lines represent the boundary of natural water (Krauskopf, 1957). (b) Mn deposition schematic related to sea level changes (Roy, 2006).

The processes regarding Mn deposition can be divided between those that are hydrothermal and those that occur at ambient temperature in a sedimentary environment. Both sets of processes can take place in a variety of tectonic and geochemical systems. Hydrothermal Mn deposits are found in smaller sizes in contrast to sedimentary ones. Sedimentary ones can be divided into two types, volcanogenic (or exhalative) and nonvolcanogenic (terrigenous), and are based on the presence or absence of volcanic rocks and their proximity in the sequence. Modern settings of sediment-hosted hydrothermal Mn deposits crusts, mounds, etc, are found in either spreading centres or island arc types of environments, but they can be often confused with volcanogenic sedimentary deposits due to their similar attributes. Furthermore, the spatial association of volcanic rocks further induces uncertainty between the nature of Mn, hydrothermal or volcanic source, and only in certain locations, such as freshwater lakes and shallow seas can the terrigenous source of manganese be detected. In large open ocean basins, the Mn flux and the occurring deposits can have multiple sources. (Roy, 1992)

# <span id="page-8-0"></span>1.2 Sedimentary Manganese deposition during the Early Proterozoic Earth.

The Paleoproterozoic main characteristic was the ongoing evolution of large shallow sinking basins that acted as suitable repositories of sediments on a large scale intercalated with volcanic rocks (Roy,1988). In combination with the substantial free oxygen that was produced by photosynthetic prokaryotes plus the sufficiently oxygenated hydrosphere (and atmosphere) that could support significant biota, resulted in the deposition of both iron and manganese, in much greater amounts than was possible before this time. Iron formations peaked at the time of the Early Proterozoic while at the same time, Mn deposits started to develop on a substantially larger scale (Roy, 1988).

The oxygen production by cyanobacteria commenced at least ca. 2.75 Ga ago and no extensive rise in the  $O_2$  content of the atmosphere-hydrosphere system was detectable until oxygen sinks (mainly reduced gases, organic matter, and  $Fe<sup>2+</sup>$  in dissolved form) were overcome or removed. Organic matter burial was increased during periods of increased mountain building and could result in an increase in positive  $\delta^{13}C$  values in certain pulses during ca. 2.4 Ga and ca.2.06 Ga (A. Karhu & Heinrich D. Holland, 1996; Buick et al., 1993; Melezhik et al., 1999; Melezhik & Fallick, 1994). The escape of hydrogen (reductant) to space following the photolysis of CH<sup>4</sup> might also have contributed to atmospheric oxygenation (Catling D.C. et al., 2001). This increase of oxygen in the atmosphere and interacting hydrosphere occurred at the same time as the deposition of large Mn deposits at the very early Proterozoic (Roy, 2006).

At the same time, the Late Archean supercontinents (Vaalbara/Zimvaalbara, Kenorland) were tectonically elevated and attenuated by the upwelling of the mantle, which could cause a geoid high before ultimate breakup (Michael Gurnis, 1988; Worsley et al., 1984). The continental areas were expanded and with the decrease of sea level, continental weathering at high rates was promoted, and as a result, massive areas of platform carbonates were formed (e.g. Campbellrad subgroup, Postmasburg Supergroup) (Altermann & Nelson, 1998; Eriksson et al., 1998).

Some examples of Mn deposits during the Early Proterozoic include Mn deposition in the Transval Supergroup of the Kaapval craton, South Africa (ca. 2.5-2.4 Ga) where Mn beds of 1 m thickness are found intercalated with the Banded Iron Formation sequence (BIF). Mn deposition was linked with the transgression of Mn-rich deep anoxic waters of a stratified ocean (Beukes, 1993). The Kalahari manganese field in the ca. 2.4 Ga-old Hotatzel Formation consists of interbedded BIF (four distinct units) and three interlayered Mn ores that correspond to repeat transgression-regression cycles (Tsikos & Moone, 1997). The Paleoproterozoic greenstone of the Birimian unit in the West African craton (Ghana, Ivory Coast, Burkina Faso, Mali, eastern Liberia, Guinea) shows distinct settings and hosts significant Mn deposits hosted inside the Birimian greenstone sequence, which includes isoclinally folded volcanic rocks (mainly MORB-type basalts with a low amount of andesite, dacite, and minor rhyolite) underlay a package of chemical sediments, volcanoclastics, argillites and turbidites (Leube et al., 1990.; Roy, 1988). In the Guiana Shield (which is a continuation of the Birimian greenstone belt) in South America, manganese silicate-oxide ore and silicate carbonate protores are interstratified with metamorphic rocks that consist of low to medium-grade carbonaceous black shales, pelitic rocks and quartzites in the time equivalent Yuruari Series (Venezuela), the Barama series (Guyana) the Lower Paramaka series (French Guiana and Suriname) (Roy, 2006).

# <span id="page-9-0"></span>1.2.1 Serra do Navio deposit (Brazil)

The Serra do Navio Mn deposit is located in the Amazonian rainforest 235 km northwest of the regional capital of Macapá in the Amapa province of northwestern Brazil. The Mn deposit was exploited from 1957 to 1997 and during the early years of production it was one of the most important high-grade manganese ores for the North American market (Chisonga et al., 2012).

The deposit is hosted by metamorphosed and strongly deformed rocks of the Paleoproterozoic age forming part of the Guiana shield of the Amazonian craton and belongs to the Guianese Paleoproterozoic greenstone belts and more specifically to the Villa Nova Group (Kroonenberg et al., 2019). The rocks were metamorphosed during the Trans-Amazonian tectonothermal event that resulted in the rework of both the Archean basement, (lower rock unit of the Guiana shield) and the volcanic and volcano-sedimentary successions that have been dated at 2.11 Ga (Voicu et al., 2001). The sedimentary sequence that hosts the Mn deposit constitutes part of such a Paleoproterozoic sequence that is exposed in the southwestern part of the Amapa Province. It forms a poorly exposed NW-SE striking fold belt that is composed of the Vila Nova Group and surrounded by granitic gneiss domes (Scarpelli, 1970).

The lithotypes of the Serra do Navio group include biotite and graphite schists, Mnsilicate rock, Mn-calcite, and rhodochrosite marble (Figure 2). The main Mn-bearing minerals identified are spessartine, tephroite, rhodonite, Mn-calcite, and Mn-amphiboles (Chisonga et al., 2012).



Figure 2: Schematic profile of the three drill cores at the Sera do Navio deposit.(Chisonga et al., 2012).

The mineralization was deposited in a marine environment and the siliciclastic/ volcanoclastic sediments were accumulated proximal to an active volcanic arc. Possibly  $Mn^{4+}$ oxyhydroxides precipitants were accumulated proximal to organic-rich matter sediments in deeper waters to account for the apparent abundance of organic matter and their transformation into diagenetic Mn carbonates. The carbonaceous pelites accumulated in a shallower marine environment under suboxic to anoxic conditions. (Chisonga et al., 2012).

# <span id="page-11-0"></span>1.2.2 Nsuta deposit (Ghana)

The Nsuta Manganese deposit is hosted in the Paleoproterozoic Birimian supergroup which is located on the eastern side of the West African craton (Nyame, 2008) and was deposited at ~2.2 Ga (Albani et al., 2010; El Albani et al., 2014). The Nsuta deposit's stratigraphy is composed of a basal greenstone unit followed successively upwards by argillaceous rocks and tuffs and greenstone (Kesse, 1976). The rocks that underlie and overlie the Mn carbonate proto-ore are grey to dark grey, fine to medium-grained, and variably bedded to laminated phyllite (Nyame, 1998). Other sedimentary structures identified include graded bedding, thin or localized slump structures, and various flame structures and intraclasts. (Nyame, 2001).



Figure 3: (a) Birimian Supergroup map (b,c) The Nsuta deposit(Goto et al., 2021)

The Mn-bearing rocks that have been reported in the Nsuta deposit include carbonates (rhodochrosite), silicate (gondite), and oxide (cryptomelane and pyrolusite) rocks. Mncarbonate rocks are considered the least altered while in contrast Mn-silicate and Mn-oxide rocks are considered the products of local metamorphism and oxidative weathering respectively (Dixon, 1979; Nyame, 1998).

The Nsuta Mn deposit was deposited in a reduced marine environment in the outer margin where carbonate could be chemically precipitated resulting in a Mn carbonate-mud

marine sedimentation. Subsequent slumping, sliding and other gravity flows may have led to the formation of breccia, and the reworking of carbonate deposition by storms in the depositional environment (Nyame, 2008).

# <span id="page-12-0"></span>1.3 Purpose of Research

Although most of the Proterozoic Banded Manganese Formation (BMF) deposits have been studied thoroughly, little is known about the Mn deposition at Mathews Ridge in Guyana. This deposit is part of the Paleoproterozoic Greenstone Belt of the Guiana Shield in northern South America. Most of our knowledge about mineralization comes from an unpublished mining report from the Reunion gold company. A unique feature of this mineralization is that almost no iron can be found inside the mineralization as a primary metal. Thus, the purpose of this research is to understand the geochemical mechanisms that resulted in the deposition and preservation of Mn enrichments at this locality. More specifically, the main geochemical features of the basal rock unit will be analysed to understand the geochemistry of the rock unit, and its petrographical features and a first assessment of a deposition model will be introduced to explain the Mn deposition and preservation. The above results will be compared with the Paleoproterozoic Manganese deposits of Serra do Navio (Brazi) and Nsuta (Ghana) to recreate the redox environment of the Early Proterozoic Ocean.

# <span id="page-13-0"></span>2 Geological Setting

# <span id="page-13-1"></span>2.1 Guyana Shield and Greenschist belts

Matthews Ridge is a region located in the northwest of Guyana, on the northern coast of South America. Rocks in this area belong to the Barama group, part of the Barama-Mazaruni supergroup. This group encompasses multiple greenstone belts across the central-western part of the Guyana Shield (Guyana, 2013). The geological strata of the Guiana Shield are characterized by two primary lithological sequences. The more ancient geological units compromise the orogenic Archean and Paleoproterozoic sequences, exemplified by the Imataca Complex in Venezuela and the Trans-Amazonian granitoid-greenstone belts (Voicu et al., 2001).

The Guianese belts (2.26-2.09 Ga) (Kroonenberg et al., 2019) are usually divided into two lithological units (Gibbs, 1987; Gibbs, 1983). The stratigraphy of the lower rock unit indicates a classical succession with a tholeiitic mid-ocean ridge or back-arc basin basalts at the base, often with pillow structures, followed by sequences of more evolved island-arc-type andesites, dacites, rhyolites, and intercalated chemical sediments that were deformed and metamorphosed before the deposition of the upper unit. In contrast, the upper unit is composed of clastic meta-sediment rocks, that include greywackes and shales deposited as turbites, in combination with intermediate to felsic meta-volcanic rocks and mafic and ultra-mafic metavolcanic rocks in smaller amounts. On top of the sequence, they are typically overlain unconformably by a sequence of epicontinental fluvial deposits (Capdevila, 1999; Choudhuri, 1980; Kroonenberg et al., 2019). The belts were shaped at the time of the Trans-Amazonian Orogeny, between 2.26 and 1.98 Ga, as a consequence of seafloor spreading, with southward subduction and finally the continental collision, between the ancestral Guyana Shield and the West-African craton, where they continue into the Birimian of West-Africa (Figure 2) (Delor, 2003; Gibbs and Gabbon, 1993). The entirety of the rocks have been metamorphosed to greenschist facies conditions that can locally reach up to amphibolite facies, near the boundaries of tonalite-trondhjemite-granodiorite (TTG) intrusions (2.18-2.11 Ga) (Figure 4) (Kroonenberg et al., 2019).

The Barama-Mazaruni supergroup follows a similar greenstone belt stratigraphy and is composed of tholeiitic basalts and associated mafic to ultramafic dykes and sills, that are overlain by intermediate-felsic volcanic rocks, interlayered with thick sedimentary and volcanic-sedimentary rocks. The syn-to late-tectonic calc-alkaline Trans-Amazonian

'granitoids' are intruded into the supergroup, ranging from felsic to intermediate composition (Vanderhaeghe et al., 1998).



Figure 4: Modified, Guyana shield map, from Kroonenberg et al., 2019. The box in yellow highlights the Barama- Mazaruni Supergroup and the Matthews Ridge area.



Figure 5: Modified, Paleogeographic reconstruction map at 2.0 Ga, suggested by, Ledru et al., 1994, Cratonic areas in mid grey: GS-Guyana Shield; SLC-São Luiz Craton; WAC-West African Craton. Darker grey areas, schematic representation of areas of the greenstone-granite belts in the Guyana Shield, V-Venezuela, G-Guyana, S-Surinam, FG-French Guiana, B-Brazil; W and E-western and eastern belts in the West African Craton.

# <span id="page-14-0"></span>2.2 Matthews Ridge Regional Geology

The Matthews Ridge Mn deposit is part of the Mathews Ridge Formation (MRF), which belongs to the Barama group of the Barama-Mazaruni supergroup. Little is currently published about the area and the Mathews Ridge Formation in general. Most of our knowledge currently comes from the unpublished Reunion Gold Corporation mining report.

The Barama group rocks were deposited in a basin environment. They can be divided into three formations which are from top to bottom, the Arakaka Formation contains a coarser sedimentary series and rudites, intercalated with volcanic piles and intrusives of mafic to acidic affinity, followed by the Matthews Ridge Formation (MRF) and overlain the Tenapu Formation. The rocks are all of low metamorphic grade and make up a predominately sedimentary sequence of very-fined clastic (pelitic) and chemical sediments that were most likely deposited in a marine environment. (Guyana, 2013).

The MRF sedimentary sequence is composed of a thick basal lower phyllitic unit (LPHY) that contains, thin and very local manganiferous and occasional chert beds, which appear to be over 75m thick. As the series progresses upwards, it progressively grades into a manganiferous phyllitic unit (MPH), which is constituted of phyllites intercalated with very thin manganese-rich beds. This unit is approximately 10 meters thick and overlain by a Banded Manganese Formation (BMF), which is described by well-stratified intercalations of phyllites and Mn-rich beds, that sequentially lead into a thick Massive Manganese unit (MMF). The BMF thickness varies from 10 to 15 meters, as the MMF unit is estimated to be around 1 to 3 meters thick. On top of the sequence, the Upper Phyllites unit (UPHY) appears. The contact between the two beds is sharp, while there are no manganiferous beds inside the UPHY and the thickness of the unit is more than 100 meters. The whole sedimentary sequence is crosscut by late dioritic intrusions, forming dikes, sills, and dome-like structures (Figure 3) (Goulet, 2012).

The sedimentary sequence has been tectonically deformed creating folds that are characterized by thickening in the hinge zone and thinning in the flanks. This is considered the product of the first deformation, which had a considerable impact on the mineralization as it is repeated several times in the same manganese beds by anticline and syncline fold structures with axial plans dipping south 40 degrees, trending east-northeast. While also subject to lateritic weathering, creating a typical laterite profile at the top of the sequence. (Guyana, 2013).

# Manganese Enrichments in Matthews Ridge, Guyana



Figure 6: MRF stratigraphic sequence(Goulet, 2012)



Figure 7:Banded Manganese Unit (BMF) Affected by Typical Anticline and Syncline Structure (Guyana, 2013)

# <span id="page-17-0"></span>3 Methods

# <span id="page-17-1"></span>3.1 Sampling

For this research, 23 phyllite samples were retrieved from four drill cores, part of the Reunion- Gold Corporation geological exploration program. The samples include nine samples from drill core 11MR1001 (74.7m-87.6m) from hill 7, eight samples from core 11MR1091 (85m-106.6m) from hill 9c, two samples from drill core 11MR1094 (64.4m-73.5m) and three samples from drill core 11MR2014 (69.9m-75.4m) of an unknown location. All samples were retrieved right below the CSR zone (saprolite zone) as they were the only ones available from the targeted drill holes retrieved from the geological model documented in the NI-43-101 technical report. Drill cores of the upper stratigraphy units (MMF and BMF) were not documented well at that time and were mostly of saprolitic material. Therefore, the least samples, of the basal phyllitic unit were selected which likely preserved primary geochemical signatures even though the deposit has been affected by multiple tectonic phases and metasomatism. The cross-sections and the sampling depths of the cores 11MR1001 and 11MR1091 are seen in Figures 5-7.



Figure 8: Sampling of Corres 11MR1001 and 11MR1091.



Figure 9: Cutting of cores during sampling.





Figure 10: Cross sections of the Mathews mineralization. With red are highlighted the two cores that were sampled (Guyana, 2013).

# <span id="page-19-1"></span><span id="page-19-0"></span>3.2 Microscopy

Polished thin sections were prepared at Utrecht University for the samples of drill core 11MR1001 (nine samples). All thin sections were digitalized using ZEISS Axioscan. Petrological and mineralogical characteristics were determined through optical microscopy using an Axio Scope with a colour 305 Axiocam. Mineral compositional analyses of three samples of 11MR1001 were acquired on an electron microprobe (JEOL JXA-8530F) at Utrecht University equipped with 5 tuneable wavelength dispersive spectrometers. Operating conditions were 40 degrees take-off angle, and a beam energy of 15 keV, for all measurements. The beam current was 20 nA, and the beam diameter was 10 microns for most spots, except for a few measurements that used a more focused beam of 1 micron. Both peak and background counting times were 20 seconds. The Teph and Diops house standards were used to calibrate the instrument. For the electron microprobe, a thin carbon coating was applied on the surface of the thin sections to induce conductivity and prevent the build-up of electric charge.

### <span id="page-20-0"></span>3.3 Whole Rock Chemistry

After measurement by XRF, the glass beads were broken into small pieces, and the fragments were used to measure the trace elements by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). The analysis was performed with a Lambda Physik 193 nm wavelength COMPex 102 ArF excimer laser ablation system, connected to a Thermo Fisher Scientific-X Series 2 ICP-MS at Utrecht University. The mass- spectrometer was operated at low resolution. A 10 Hz laser repetition frequency was used with a fluence of 2-12 J cm2. Each measurement included a 50-second background interval, followed by 70 seconds of ablation. The data was acquired and calibrated against the standard NIST SRM 612 glass using Glitter software and accuracy was assessed by the USGS basalt standard BCR2-G.

For the reproducibility and precision of the data, three spots were measured in each sample that created craters of 120 μm diameter on the fusion beads After the homogeny of each sample was determined, the average of the three measurements was measured as a result, and presented with the standard division in Appendix 1.REE+Y anomalies calculations.

Due to the distinguishing behaviour of the rare earth elements and yttrium (REY) in seawater, they are often used to provide information about the depositional environment of the sediments (Bolhar & Vankranendonk, 2007; Kamber & Webb, 2001). When normalized to PAAS (post Archean Australian Shale, Pourmand et al., 2012) it produces smooth distribution patterns. Normalizing REY with PAAS is a common practice to remove natural variation in the absolute concentration of REY and allows the comparison with the upper continental crust for which shale is a proxy (Tostevin et al., 2016).

Usually, anomalous REE abundance spikes are expressed as the ratio, of the observed element divided by the value, interpolated from immediately neighbouring trace elements. The general expression is  $[REE_n/REE_n^*] = 2REE_n/(REE_{n-1} +REE_{n+1})$ , where REE is the shalenormalized abundance and  $n=1, 2, 3,...$  is the REE in the order of the lanthanide series (e.g. La=1). This simple principle was initially used for the calculation of the Ce and Eu enrichment in igneous rocks. Due to the complexity of the marine REE systematics, this principle is not strictly applicable to seawater (and precipitants) (Bolhar et al., 2004). The calculation of the anomalies presented in this study are as follows:

I. Ce anomaly: Ce is unique among the REY since it can exist in both  $+3$  and  $+4$  oxidation states. In the presence of oxygen, Ce (III) is partially oxidized to Ce (IV)on the surface of Mn (oxyhydr)oxides, where it no longer participates in solid-solution exchange reactions, leaving residual seawater depleted in Ce relative to other trivalent REE (German & Elderfield, 1990). This fractionation occurs only under oxic conditions (German et al., 1991). Traditionally the anomaly is calculated by comparing the normalized concentrations of Ce with the neighbouring REE (La and Pr) by using the formula proposed by Bau and Dulksi,1996:

$$
Ce_{sn}/Ce_{sn} * = \frac{Ce_{sn}}{0.5 * La_{sn} + 0.5 * Pr_{sn}}
$$

The anomalous behaviour La can artificially exaggerate the Ce anomaly. That is why a more appropriate way to calculate the Ce anomaly avoiding the comparison with La (Lawrence et al., 2006):

$$
Ce_{sn}/Ce_{sn}^* = \frac{Ce_{sn}}{(Pr_{sn})^2/Nd_{sn}}
$$

II. Eu anomaly: On a similar note, Eu anomaly was calculated by comparing the normalized concentrations of Eu with the neighbouring REE (Sm and Gd). BaO can cause significant spectral interference with Eu (Jarvis et al., 1989; Smirnova et al., 2006). However, no correlation was noted between Ba and Eu anomalies ( $r^2$ =0.0358) (Figure 8). Although, because of the anomalous abundances of Gd, Eusn anomalies have been quantified as (Bau & Dulski, 1996):





III. Y anomaly: Y is inserted between Dy and Ho according to its ionic radius. The closest similarity exists between Y and Ho, hence the anomalous behaviour of Y concerning the REEs will be evaluated by considering Y/Ho ratios (Bau & Dulski, 1996).

# <span id="page-21-0"></span>3.4 Chemical Alteration Indexes Calculations.

To understand the chemical weathering trends of the LPHY rock unit, several chemical alteration indexes were calculated. The indexes are the chemical index of alteration (CIA) proposed by Nesbitt & Young (1982), the mafic index of alteration (MIA), and the index of lateralization (IOL) proposed by Babechuk et al. (2014). For their calculations, the molar fractions of the major oxides were used for the CIA and MIA indexes, and the % values for the IOL index and presented as % below.

$$
CIA = 100 * (\frac{Al_2O_3}{Al_2O_3 + CaO + Na_2O + K_2O})
$$
  

$$
MIA = 100 * (\frac{Al_2O_3}{Al_2O_3 + Fe_2O_3 + CaO + MgO + Na_2O + K_2O})}
$$
  

$$
IOL = 100 * (\frac{Al_2O_3 + Fe_2O_3}{SiO_2 + Al_2O_3 + Fe_2O_3})
$$

# <span id="page-22-0"></span>4 Results

# <span id="page-22-1"></span>4.1 Petrographic features of core 11MR1001.

### <span id="page-22-2"></span>4.1.1 Petrography of core samples

All the phyllite core samples of 11MR1001 appear to have yellow, orange, and grey colours. The phyllites are composed of a typical phyllite rock paragenesis that includes micas (muscovite/illite/Al-illite hydromica/chlorite), quartz, and feldspars, alongside Fe-oxides (hematite, magnetite, ilmenite) and Mn-oxides (cryptomelane, todorokite, lithiophorite). The preferred orientation of micas and chlorite defines the well-developed schistosity planes. Elongated grains of quartz of quartz and feldspar run parallel to the schistosity planes.

Two varieties of muscovite have been identified based on the grain size and grain relationship to other minerals. Muscovite type I has a small grain size that shows preferred orientation marking the schistosity along with illite and chlorite grains. Muscovite type II appears with bigger developed crystals showing angular relationship with quartz crystals and in some cases, it is developed on top of deformed quartz crystal, or with a smaller grain size in between microcrystalline quartz as a matrix alongside illite. Chlorite shows a yellowish green to light green pleochroism with first-order interference colours. It shows the preferred orientation marking the schistosity along with mica minerals. The mica bends round or is pushed aside slightly by quartz grains which indicate quartz formation before or during the matrix development.

Quartz appears fined grained in most cases alongside a small number of feldspars parallel to the schistosity plane. Recrystallized quartz shows a wavy extinction, and inclusions of muscovite were observed. Also, quartz veins occur parallel to the schistosity plains, along with small amounts of micas and well-formed hematite crystals (as opaque minerals).

Iron oxides include well-formed hematite crystals and microcrystalline hematite parallel to the schistosity planes, either in between quartz as a matrix or on top of quartz and mica crystals. Magnetite and hematite crystals occur alongside secondary manganese minerals such as cryptomelane, todorokite, and lithiophorite in sample 11MR1001(76.6m) that has been developed parallel to the schistosity planes. Lastly, ilmenite crystals appear as opaque minerals.

# <span id="page-23-0"></span>4.1.2 Tectonic Features

Post-tectonic features and mylonite zones are frequently observed in the majority of samples. The mylonites are characterized by a homogeneous planar fabric defined collectively and aligned phyllosilicate minerals (including muscovite, chlorite, and illite) polycrystalline quartz, or heavily deformed quartz and a fine-graded mylonitic " paste" rich in quartz, micas, and Fe-oxides (Figure a,b,e,f).

Other post-tectonic features include the kinking of micas, and the deformation of quartz crystals, shattered quartz crystals, surrounded by mica crystals. (Figure 9g).



Figure 12: Thin sections images (a)11MR1001(81.3m), (b) 11MR1001(79.8m),(c)11MR1001(83.4m), (d and g) 11MR1001(76.6m) (e) 11MR1001(87.6m), (f)11MR1001(79.8m), (h) 11MR1001(74.4m).

#### <span id="page-24-0"></span>4.1.3 TT-SEM and Microprobe Findings.

Through the TT-SEM and microprobe analysis, the identification of different phyllosilicate minerals is established while also the identification of the different oxides based on their chemistry is presented in Appendix X. The phyllosilicate minerals include micas: muscovite, illite, chlorite, and kaolinite and are identified by using microprobe analysis. All micas have a low percentage of potassium (K) and it was able to identify Al-illite hydromica a variety of muscovite low in  $K_2O$  wt.% and high  $H_2O$  wt.%. A lot of micas appear to be enriched in either Fe or Mn. Chlorite minerals are Fe-rich and Mg-poor. Kaolinite is identified using SEM analysis and is only found in core samples 11MR1001(74.7m), 11MR1001(76.6m), and 11MR1001(89.7m). The Fe-oxides include hematite, magnetite, and ilmenite, while the Mnoxides include cryptomelane and lithiophorite. Other minerals that were identified using SEM analysis are small monazite crystals on top of Fe and Mn oxides.



Figure 13:SEM pictures, a-c SEM pictures of thin section 11MR1001(76.6m) focused on the secondary Mn mineralization, d-f SEM images of thin section 11MR1001(81.3m).

# <span id="page-24-1"></span>4.2 Major element oxides.

The whole rock and trace element chemical data of the 23 analysed samples is shown in Appendix 1. The lower phyllite unit (LPHY) is characterized by low to moderate silica  $(SiO<sub>2</sub>)$  concentrations ranging from 48.17 wt.% to 74.42 wt.%. Aluminum  $(A<sub>12</sub>O<sub>3</sub>)$  content is also high ranging from low to high values from 3.86 wt.%. up to 23.97 wt.%. The iron content of the phyllites (total Fe as  $Fe<sub>2</sub>O<sub>3</sub>$ ) is characterized as low to moderate ranging from 3.28 wt.% to 10.85 wt.%. The manganese content (total Mn as MnO) is less than 1 wt.% in most of the samples in contrast to two samples  $11MR1001(7.6.6m)$  and  $11MR1001(87.6m)$  that display Mn values of 24.94 wt.% and 16.63 wt.%, respectively. Other major element oxide contents include, K<sub>2</sub>O (-0.21 wt.%-2.97 wt.%.), MgO (0.05 wt.%-2.97 wt, %), Na<sub>2</sub>O (0 wt.%-1.77 wt, %),  $P_2O_5$  (0.01 wt.%-0.17 wt.%) and TiO<sub>2</sub> (0.16 wt.%-1 wt.%).

The lower phyllite unit is mainly composed of quartz and phyllosilicate minerals (white micas). For this reason,  $Al_2O_3$  was chosen as a fractionation index for creating Harker variation diagrams that are presented in Figure 8. In most diagrams, the entire dataset has a similar behaviour by comparing the major oxides with the aluminium content, although in some cases cores 11MR1001 and 11MR1091 follow opposite trends. A strongly positive trend is observed between  $TiO_2$ -Al<sub>2</sub>O<sub>3</sub> and a weaker positive correlation between  $Fe_2O_3$ -Al<sub>2</sub>O<sub>3</sub>. A negative correlation is observed between  $SiO_2$ -Al<sub>2</sub>O<sub>3</sub>, and no correlation is observed between MnO, MgO, and  $P_2O_5-AI_2O_3$ . By comparing the cores 11MR1001 and 11MR1091, it is apparent of the variability in the geochemical content of the samples since a difference was observed in the CaO-Al<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub> variation diagrams. In 11MR1001 a strong negative correlation can be observed for CaO-Al<sub>2</sub>O<sub>3</sub> while in contrast a strong positive correlation between K<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub> is observed. Vise-versa in 11MR1091 core samples, a positive correlation between  $CaO-Al<sub>2</sub>O<sub>3</sub>$ is noticed and a none to a weak correlation between  $K_2O-Al_2O_3$ . The same trend is also noted for the Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub> variation diagram (Figure 14).







Figure 14:Harker variation diagrams of major oxides. (major oxides are presented as %).

#### <span id="page-26-0"></span>4.3 REE+Y patterns.

The PAAS normalized patterns of the 23 analysed samples are presented by core in Figure 9. Again, the variability of the geochemical content between the samples is clear, and different patterns of REE+Y distribution can be detected, although there are features that remain in all samples. All samples appear to have positive Eu anomalies, with their values ranging from 1.19 to 1.77. Also, all samples present positive Y anomalies with weak to absent Y/Ho anomaly values that range from 24.65 to 32.88, while the Ce anomalies are variable from strongly negative (0.24) to strongly positive (4.42). All samples show a negative to zero correlation between  $Al_2O_3$  indicating zero terrestrial REE influence (Figure 15).

#### Manganese Enrichments in Matthews Ridge, Guyana



Figure 15:  $\Sigma$ REE+Y and Al<sub>2</sub>O<sub>3</sub> harker variation diagram.

Most of the samples from core 11MR1091 have a positive slope (LREEs<HREEs), in their REE pattern, similar to seawater patterns, except samples 97.5m and 101.4m which have a slightly negative slope (LREEs>HREEs). Only some samples show Y anomalies, while Ce anomalies vary from sample to sample. Samples from the depth of 106.6m to 97.5m have a weak to strong negative Ce anomaly, and samples from the depth of 94m to 85m have a strong positive Ce anomaly. A similar positive slope pattern is observed in core 11MR1094 samples, with solid positive Ce anomalies, and weakly positive Eu and Y anomalies.

In contrast to these two cores samples, samples from cores 11MR1001 and 11MR2014, have a relatively flat REE pattern (LREEs=HREEs), similar to the UCC pattern, to a very weak positive one except for sample 11MR1001(81.3m) which has a positive slope. The samples have weak positive Eu anomalies and very weak positive to no Y anomalies. Most samples have a weak or absent Ce anomaly except for sample 11MR1001(83m) which appears to have a strong negative Ce anomaly. 11MR2014 samples have even more flat patterns with strongly positive Eu anomalies and less strong positive Y, while Ce anomalies are very weak, and they vary from flat (74.5m) to negative (73m) to positive (69.9m) (Figure 16).

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Figure 16: REE+Y (PAAS normalized) patterns of the 23 samples.

# <span id="page-28-0"></span>4.4 Chemostratigraphy of cores 11MR1091 and 11MR1001.

To understand the distribution of the major and trace components inside the two cores and their changes, chemostratigraphic diagrams of  $iO_2$ ,  $A<sub>2</sub>O<sub>3</sub>$ ,  $M<sub>n</sub>O$ ,  $Fe<sub>2</sub>O<sub>3</sub>$ ,  $K<sub>2</sub>O$ , Ba, MgO, and CaO were created and presented in Figures 17 and 18. The major oxides are in wt.% and Ba is in ppm.

Samples in core 11MR1001 contain a relatively higher amount of  $SiO<sub>2</sub>$  (56.72-74.72) wt.%) in contrast with the samples in core 11MR1091(55.19-67.49 wt.%) with the values fluctuating with depth. In core 11MR1001 the peak can be found at the depth of 74.7m and drops sharply to the lowest value observed at 56.72 to the depth of 76.6m, afterward the values rise with depth with minor fluctuations and reach the value of 74.42 at the depth of 86.5m and again it drops very suddenly at 57.57 at the depth of 88m. In contrast, in core 11MR1091, at the top of the core the drops strongly from 64.14 at the depth of 85m to 55.19 at the depth of 89.7m. From there the value increases steadily to the value of 67.49 at the depth of 97.5m and falls to the value of 59.72 at the depth of 99.4m. Then, the value remains relatively steady with minor fluctuations until the depth of 106.6m reaches 60.63.

By contrast to Silica content,  $Al_2O_3$  presents higher values in core 11MR1091 rather than core 11MR1001, with the values ranging from 15.91 to 20.90 and 3.86 to 20.16, respectively. In core 11MR1001, at the top of the core at a depth of 74.5m, the value is at 9.34 and drops slightly at 3.86 at the depth of 76.6m, similar to  $SiO<sub>2</sub>$ . From there the values greatly increase to the value of 18.6 at the depth of 79.8m and continue to grow until it reaches 20.16 at the depth of 81.3m and then drops steadily until it reaches 10.95 at the depth of 87.6m. In core 11MR1091, Al<sub>2</sub>O<sub>3</sub> increases from 16.51 at 85 depth and increases to 19.28 at the depth of 89.7m, then drops steadily to 15.91 at the depth of 97.5m. Then the value remains relatively steady with a minor increase to 20.90 at the depth of 105.5m and again a minor drop to 19.28 at the depth of 106.6m.

Iron content behaves similarly in the two cores and increases steadily with depth with major fluctuations in core 11MR1001 (from 6.20 at the depth of 74.7 to 8.78 at the depth of 87.6m) with the lowest peak being at the depth of 76.6m at 4.13, and the highest peak at the depth of 81.3m at 9.53. In contrast in core  $11MR1001$ , Fe<sub>2</sub>O<sub>3</sub> values fluctuate slightly from 8.57 at the depth of 85m to 9.66 at the depth of 106.6m, with the lowest peak being at the depth of 89.7m at 89.7m and the highest peak at the depth of 105.5m at 10.85m.

In contrast to iron, Manganese shows different behaviour in two cores. In core 11MR1001 MnO is below 0.1 in the entire core except for the depths of 76.6m and 87.6m where it reaches the values of 24.94 and 16.63 respectively. In core 11MR1091 MnO decreases steadily with depth, except for two sharp drops, with the values being 0.19 and 0.02 at the depths of 89.7m and 99.4m.

Potassium and Barium content follows a similar trend in both cores. In 11MR1001 at the depths, of 74.7m and 76.6m K<sub>2</sub>O slightly decreases from 0.73 to 0 while Ba slightly increases from 252.62 to 302. At the depth of 79.8m, both values increase sharply at 3.6 and 1072, and then both values decrease steadily until the depth of 86.5m and then there is a sudden drop at the depth of 87.6m with the values being 0.03 and 283. On a similar note, in core 11MR1091, K2O and Ba have a sudden increase from 1.36 and 808 at the depth of 85m to 3.71 and 5454.51 at the depth of 89.7. In deeper depths, the values of  $K_2O$  drop at a steady rate, to the value of the depth of 101.40m reaching the value of 1.69. Then the value increases to the value of 2.33 at the depth of 105.5m and then drops a little to 2.08 at the depth of 106.6m. Ba values drop suddenly to the value of 898.69 at the depth of 94. The values continue to drop at a steady rate to the value of 606.08 at the depth of 97.5m and they remain steady with minor fluctuations until the bottom of the core, where Ba reaches 584.15.

Magnesium and Calcium content both decrease with depth in core 11MR1001. The highest values of MgO are observed at the top of the core at a depth of 74.7m at 0.94 while the value of CaO, at the same depth, is at 0.08. At the depth of 76.6m, there is a sudden increase of CaO reaching the value 0.11, and a sudden decrease of MgO at 0.08. MgO increases at 0.36 at the depth of 79.8m and then it decreases at a steady pace until the depth of 87.6m at 0.05. In

contrast in core 11MR1091 CaO increases with depth. From the depth of 85m to the depth of 97.5m, the values increase from 0.05 to 0.07 while at the depth of 99.4m, the values increase to 0.11 and then remain steady with minor fluctuations until the depth of 106.6m at 0.10.



#### Figure 17: Chemostratigraphic diagrams of core 11MR1091.



Figure 18:Chemostratigraphic diagrams of core 11MR1001.

# <span id="page-31-0"></span>4.5 Cesn/Cesn anomaly.

By plotting the  $Ce_{sn}/Ce_{sn}$ <sup>\*</sup> to  $Pr_{sn}/Pr_{sn}$ <sup>\*</sup> variation diagram proposed by (Bau & Dulski, 1996), in Figure 19b it is clear that the majority of the Ce anomalies are real and not affected by the anomalous behaviour of La except samples 11MR1001(74,7m) 11MR1001(83m) 11MR1001(83.4m) that present negative La anomaly and sample 11MR1001(87.6m) that presents positive La.anomaly. The rest of the core samples, present either positive, negative, or no Ce anomaly, while no La anomaly was detected in the rest of the samples. Positive Ce anomalies are considered at values above 1.10, as negative ones were considered anomalies with values below 0.90, while the values between 0.90 and 1.1 were considered to be without a Ce anomaly.

Ce behaves differently in each core and Ce anomaly presented different patterns with depth. In core 11MR1091, Ce decreases with increasing depth. In the upper parts of the core depths 85m, 89.7m, and 94m Ce anomaly appear positive with the values being 2.21, 1.73, and 2.53. In the lower part of the core, from the depth of 94m to 106.6m the Ce anomaly drops sharply, and negative values are found. The values minorly fluctuate from 0.56 to 0.65 with the lowest peak at 0.30 at the depth of 99.4m and the highest peak at 0.89 at the depth of 105.5m.

In contrast, on the whole in core 11MR1001 Ce anomaly appears as negative or nonexistent and decreases with increasing depth, except in one sample at the depth of 81.3m, where Ce appears to be positive with the value being at 1.21. From the depth of 74.7m to 76.6m Ce anomaly decreases from 0.97 to 0.78 and remains steady until the depth of 79.8m. From the depth of 83m to 83.4m, the values are 0.94 and 0.98. At the depth of 84.2m the value suddenly dropped to 0.24 increased steadily to 0.57 at the depth of 86.5m and finally at 1.08 at the depth of 87.6m.

In core 11MR2014 Ce anomaly shows variation. At the top of the core at 69.9m the value is detected at 1.16, it drops sharply at 0.86 at 73m and it increases at 1.02 at 75.4. In core 11MR1094 the values are positive with the values being 4.42 at 64.4m and 1.75 at 73.5m (Figure 19a).

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Figure 19: (a) Chemostratigraphy of Ce anomaly of cores 11MR1091, 11MR2014, 11MR1094, and 11MR1001 (b) Ce/Ce\* and Pr/Pr\* variation diagram *(Bau & Dulski, 1996).*

# <span id="page-32-1"></span><span id="page-32-0"></span>5 Discussion

5.1 Paleoweathering conditions.

# <span id="page-32-2"></span>5.1.1 Alteration indexes: Chemical Index of Alteration (CIA), Mafic Index of Alteration (MIA), and Index of Lateralization (IOL)

All the values present values that range from intermediate weathering to strong weathering for both CIA and MIA indexes, with the values being 68.93-98.65 and 77.43-99.06 respectively, indicating the strong present paedogenetic minerals and kaolinite inside the rock samples. The CIA index tracks the dissolution of feldspar and release of Ca, Na, and K in contrast to Al (H. W. Nesbitt et al., 1996). MIA index is an extension of CIA that includes Mg and Fe and tracks the loss of Mg in mafic minerals.(Babechuk et al., 2014).

In core 11MR1001, the samples appear to be mostly intermediate weathered except samples in the depths 74.7m, 76.6m, and 87.6m with the values being 89.13, 86.94, and 99.06. In the rest of the core, the values fluctuate minorly with the values being from 79.63 to 81.31 at the depths from 81.3m to 84.2, and the lowest value being recorded at the depth of 83 at 77.43. The MIA follows a very similar trend to the CIA, with the values recorded being lower. The strongly weathered values are reported at the depths of 76.6m and 86.7m at 89.38 and 98.65. In the rest of the core, the value increases with the depth with fluctuations from 79.03 to 83.18 at the depths from 74.7 to 86.7 (Figure 20a)

At core 11MR1091, CIA and MIA indexes follow again a similar trend with each other. CIA shows that all samples are intermediate weathered while MIA shows the same except sample 99.4m which is reported as strongly weathered. From depths 85m to 97.5m both increase from 78.8 and 82.01 to 81.29 and 83.84m respectively, with a small fluctuation at the depth of 94m where the CIA value increased to 82.22 and MIA value dropped at 82.25. At the of 99.4m, both values have their highest peaks, CIA at 84.7 and MIA at 86.10. Then the values drop steadily until the depth of 106.6m at 80.4 and 83.6m (Figure 20a).

MIA and CIA show a very good correlation with each other  $(r^2=0.6245)$  confirming the similar bulk behaviour of Ca, Na, and Mg (Figure 20b).

The IOL for samples is below 40 and ranges from 12.35 to 38.45, indicating that none of the samples were subjected to the lateritic profile that is recorded in the upper parts of the Mathews Ridge mineralization (Figure 20b).



Figure 20: (a) MIA and CIA indexes stratigraphy of cores 11MR1001 and 11MR1091, (b) CIA MIA variation diagram.

#### <span id="page-33-0"></span>5.1.2 A-CN-K, S-A-F, AF-CNK-M, A-L-F diagrams.

The SAF diagram is created with a mass fraction of  $SiO<sub>2</sub>$ ,  $Al<sub>2</sub>O<sub>3</sub>$ , and Fe<sub>2</sub>O<sub>3</sub>, while also the Index on lateralization is plotted to highlight the degree of lateralization, due to later tropical weathering that the samples had gone under. None of the samples appear to be lateralized, although samples from cores 11MR1001, 11MR2014, and 11MR1091 appear to be on the kaolinized part of the diagram (Figure 21a). The A-CN-K diagram is created with the molar fractions of  $A<sub>12</sub>O<sub>3</sub>$ , CaO Na<sub>2</sub>O, and K<sub>2</sub>O and it showed the chemical weathering and removal of CaO+Na<sub>2</sub>O with increasing  $Al_2O_3$  content while also K<sub>2</sub>O in enriched inside the rock samples. All the samples are plotted between the Kaolinite-Illite/Muscovite line of the diagram, and one sample is plotted on the smectite/ Kaolinite line of the diagram (Figure 21b).

The ALF diagram studies the weathering trends in an oxidative environment and shows that Ca, Na K, and Mg weathering have similar behaviour, while the samples are being enriched in Al and then they are shifted towards the Fe end as the iron content increases (Figure 22b).



Figure 21: (a) Molar Al2O3-CaO+Na2O-K2O (A-CN-K) and (b) mass SiO2-Al2O3-Fe2O<sup>3</sup> (SAF) ternary plots illustrating the different degrees of alteration as seen between the 11MR core samples. The chemical index of alteration (CIA) and index of lateralization can both be included in the A-CN-K and SAF plots ternary as shown.



Figure 22: Molar ternary plots in Al-Fe-Ca-Na-K. The A-CNKM-F (ALF) *(Babechuk et al., 2014; H., & Y. G. M. Nesbitt, 1982)* diagram exposes the contribution of the mafic and felsic mineral components to rock weathering. The integration of the new mafic index of alteration (MIA) is illustrated; while the A–L–F and AF–CNK–M plot is integrated with the MIA for studying oxidative weathering trends.

# <span id="page-35-0"></span>5.2 Preservation state of weathering and tectonics.

The Phyllite rocks of the lower phyllite unit of the Matthews Ridge deposit were deposited at around 2097±39 Ma-2238±81 Ma (Carvalo & Cousens, 2022). The Serra do Navio Mn deposit (2.11 Ga; Voicu et al., 2001) and the Nsuta deposit (2.2 Ga Albani et al., 2010; El Albani et al., 2014) were also deposited during this period. Mn deposition occurred during the event of the Trans-Amazonian orogeny. The rocks in these areas were metamorphosed up to greenschist facies(Kroonenberg et al., 2016). The metapelitic rocks in these areas include the phyllite rocks of Matthews Ridge (Goulet, 2012), the biotitic and graphite schists of the Serra do Navio deposit (Chisonga et al., 2012), and the Mn-phyllites of the Nsuta deposit (Nyame, 2008).



Figure 23: Recreation of the tectonical setting between the Guyana Shield and West African Craton. In the schematic the proximity between the Mathews Ridge, Nsuta and Serra do Navio deposits are highlighted (modified from Leube et al., 1990).

The Matthews Ridge has been subjected to intense tectonic activity. This tectonic activity according to (Westerman,1969) is controlled by regional block faulting. Relative movement between the basement blocks gave the effect of a recumbent fold, considered to be related to the main folding stresses, southwest of Matthews Ridge. This is folded by compression tectonics that have resulted due to the southward tilting of the Barima river basin block. Gravitational compression was directed into a funnel-shaped area followed by basement scraps. This resulted in domal structures in the Matthews Ridge area and a consequent rare type of major drag faulting. Regarding the regional tectonic activity, Matthews Ridge has also been subjected to local smaller-scale tectonic activity as seen in the petrographical observations, which makes the distinction between the tectonic activities very hard.
The tectonic impact of the area is also seen in the nature of the phyllites and the presence of certain minerals. The strongest weathered samples are correlated with the presence of kaolinite and in core 11MR1001 secondary Mn-oxide mineralization is observed, parallel to the plain schistosity of the phyllites. In addition, the strongly weathered samples also show fault presence and correlate with the presence. of mylonites All the samples of core 11MR1001, are affected by tectonic activity indicated by petrographic observations of mylonite structures in the samples. The activity could be characterized as microtectonic activity since in all thin sections small faults are found indicated by the presence of a mylonitic pattern. The least weathered samples are characterized by the presence of muscovite +chlorite+ quartz. Illite crystals are always found in thin sections affected by tectonism and most of the samples are part of the mylonite mix. Illite formed by later weathering of muscovite reflected by the low K2O, CaO, MgO, and Na2O content Subsequently, kaolinite in faults was formed by leaching of K<sub>2</sub>O. Also, the Al-illite-hydromica occurs which is a low K<sub>2</sub>O variety of muscovite with high H<sub>2</sub>O, suggesting a higher degree of depletion of K<sub>2</sub>O (Figure 21). The CIA and MIA indexes suggest that mobile elements have been leached out of the system due to weathering. A-CN-K indicates the removal of  $CaO + Na<sub>2</sub>O + K<sub>2</sub>O$  while being enriched in Al<sub>2</sub>O<sub>3</sub>MgO is leached out of the system, while being enriched in  $Al_2O_3$  and  $Fe_2O_3$ , proven by the presence of Fe-rich chlorites.

During the time of the Trans-Amazonian orogeny (2.26-1.98 Ga), the West African craton was southwardly subducted below the Guyana Shield (Leube et al., 1990). By using the Th-Sc-Zr/10 and La-Th-Sc triangular diagrams provided by Bhatia & Keith AW Crook (1986) can be used as indicators that the LPHY was accumulated in continental arc/ocean island arc environment (Figure 25a, b). This is aligned with the tectonic depositional setting of the area. In contrast to the Matthews Ridge deposit, the Serra do Navio deposit was deposited in an active continental margin (Chisonga et al., 2012).



Figure 24: Tectonic features of the depositional environment of Matthews Ridge.

The low mobility of a few REEs and major elements of sediments create useful indicators to trace the sedimentary provenance (Taylor & McLennan 1985). Felsic rocks are richer in both La and Th and poorer in Sc, Cr, and Co in contrast to mafic rocks, the La/Sc, Th/Co, Th/Sc, and Cr/Th ratios are good indicators of uncovering the source rock of the sediments (Condie, 1993; Cullers, 1994; Matthew W. Totten et al., 2000). By comparing these ratios, the Matthews Ridge metasediments appear to show a mafic and ultramafic source rock. The mafic nature of the volcanic rocks of the Mazaruni Group (Kroonenberg et al., 2016) area suitable source rock for the basal phylltic unit of the Matthews Ridge deposit (Figure 25a-c).



Figure 25: Source rock diagrams of the metapiletic sediments of the LPHY unit (a) (Cullers, 1994), (b) (Condie, 1993), (c)(Matthew W. Totten et al., 2000).

By comparing the data of the Nsuta and Serra do Navio deposit it can also be seen that the Serra do Navio graphite and biotite schist contain a similar mafic mixed with felsic volcanic source rock originating from the Jornal Formation (Chisonga et al., 2012). This highlights the similar compositions of the greenschist belts of the Guyana Shield and the exogenetic influences that resulted in the weathering of the mafic volcanic rocks of the Barama-Mazaruni and Villa Nova Supergroups. In contrast to the Guyana deposit, the Mn-phyllites of the Nsuta deposit have a felsic rock source signature.





By using the Pb/Zn and Co+ Ni/As+ Pb+ Zn+ Ni+ Cu diagrams provided by Nicholson, (1992), it appears that the mafic weathered terrigenous metasediments of the LPHY unit were deposited in a freshwater shallow marine environment (Figure 27a-b) in contrast to the Nsuta and Serra do Navios deposits that were accumulated in a marine environment (Figure 28a-b).



Figure 27: Depositional environment of the LPHY(Nicholson, 1992).



Figure 28a) Depositional environment of Serra do Navio deposit (Chisonga et al., 2012), (b) Depositional environment of the Nsuta deposit.

There are similarities between their major elements oxide. The trend of the silica, titanium, aluminum, and iron content of the rocks is similar for the phyllitic rocks of the Matthews Ridge deposit, the Nsuta deposit and Serra do Navio. Matthews-Ridge and Serra do Navio have similar  $SiO_2$  content that ranges from 48 wt.% to 77 wt.% and from 43 wt.% to 79 wt.%, respectively. Nsuta records the lowest  $SiO_2$  values at 24.4-47.2 wt.%. TiO<sub>2</sub> is also similar for both reaching up to 1 wt.% and for the Nsuta reaching up to 0.41 wt.%. Al<sub>2</sub>O<sub>3</sub> varies between the three rock units. The Matthews Ridge records the highest one with 3.86-23.97 wt.%  $Al_2O_3$ , followed by the Serra do Navio at 4.617.9 wt.%  $Al_2O_3$  and the Nsuta at 8.8-11.8 wt.%  $Al_2O_3$ . Matthews Ridge and Nsuta phyllites have similar Fe<sub>2</sub>O<sub>3</sub> content of 3.28-10.85 wt.% while Serra do Navio has a higher iron content of 2.6-19.2 wt.%. The changing trend of MnO, MgO, and CaO reflects the abundance of carbonate minerals inside the rock units. The Nsuta phyllites have the highest values of MnO, MgO, and CaO of respectively 1.5618.6 wt.%, 2-18 wt.%, and 0.939.65 wt.%. Both Mathews Ridge phyllites and Serra do Navio schists are depleted in these components, with the values being 0%-3.11% for MnO, 0.05-2.97% for MgO, and 0.03%-0.11% for CaO and 0.08%-4.37% for MnO, 0.7-4.5% MgO and 0.7%-4.2% CaO respectively. K<sub>2</sub>O content is low in all rock units. e. in Serra Do Navio and Matthews Ridge it is less than 4.9 wt, %, and in Nsuta it reaches up to 1.18 wt.%. Serra do Navio appears to have the highest amount of Na2O with values up to 4 wt.%, while for Mathews Ridge the values reach up to 1.18 wt.%, and for the Nsuta 2.2 wt.%. Lastly, for all rock units the  $P_2O_5$  content is almost negligible with the value being less than 0.1 wt.% for both Mathews Ridge and Serra do Navio, and less than 0.42 wt.% for Nsuta. The major components of the rock units are presented in Figure 29.

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Figure 29: Major oxide plot of Mathews Ridge, Serra do Navio, and Nsuta metapelitic rock units.

The similarities between the host rocks of the deposits can also be seen when comparing the REE+Y patterns (Figure 24). All phyllitic rocks present positive Eu and Y anomalies and relatively flat REE+Y patterns similar to the UCC, where the LREE has a similar concentration relative to the HREE. The Serra do Navio schists and Matthews Ridge phyllites present a very similar REY pattern with approximately similar concentrations. In contrast, the Nsuta Mnphyllites are enriched in the LREE relative to HREE.



Figure 30:REE+Y patterns of Mathews Ridge, Nsuta and Serra do Navio.

Another difference that is observed in the REE+Y patterns is the negative Ce anomaly of the Matthews Ridge LPHY unit in contrast to the positive Ce anomaly in the Nsuta Mnphyllites, and Serra do Navio graphite and biotite schists.

### 5.3 Redox state of the oxidative environment.

Both negative and positive Ce anomalies are closely associated with the oxidation of  $Mn^{2+}$  given their similar reduction potentials (Ederfield H., 1988). The oxidation of soluble  $Ce^{3+}$  to  $Ce^{4+}$  is catalyzed on top of Mn oxyhydroxides/oxides and immobilization of  $Ce^{4+}$  occurs on top of particulate Mn oxides. (Takahashi et al., 2002). Cerium oxidation can also happen on the surface of Fe<sup>3+</sup> oxyhydroxide/oxides (Bau, 1999; Bau & Koschinsky, 2009), but evidence for this phenomenon is less consistent than the adsorption on Mn oxyhydroxides/oxides surfaces. (Loges et al., 2012). Negative Ce anomalies are generated when the amount of available oxygen in the system is enough to drive the oxidation of  $Ce^{3+}$  to  $Ce^{4+}$ . Positive Ce anomalies in seawater occur when the  $O_2$  concentration is enough to facilitate the oxidation Ce from the trivalent to the tetravalent state in surface waters, but due to the oxygen stratification of the water column, the lower part of the water column is  $O_2$  limited (Tostevin, Shields, et al., 2016b; Tostevin, Wood, et al., 2016) Sinking oxidized Ce particles in the anoxic/suboxic zone results in the reduction of the now unstable  $Ce^{4+}$  and Mn and Fe oxides oxyhydroxides/ hydroxides (Ostrander et al., 2019; Tostevin, Shields, et al., 2016b).

The LPHY unit of the Matthews ridge contains both negative and positive Ce anomalies, with the average Ce anomaly being negative. Core 11MR1091 presents negative anomalies at the lower and deeper part of the core while the upper parts of the core present positive Ce values. This indicates a relatively oxidizing and reducing depositional environment.

The LPHY unit is characterized by a low percentage of MnO with local impure Mn beds and cherts (Goulet, 2012). The two core samples have different percentages of Mn available. In core 11MR1001 MnO is below 0.1 wt.% except for two samples that present secondary Mn-oxides mineralization. The MnO in core 11MR1091 is lower but still higher than the core 11MR1001 ranging from 0.02-0.76 wt.%. Thus, core 11MR1091 is more suitable for investigating the controls of Ce anomaly. In addition, core 11 MR1001 is heavily impacted by intense tectonic activity and weathering, since every sample has mylonite inside, in contrast to core 11MR1091, which is less tectonically impacted and less samples present strong weathering features. By removing samples 11MR1091(94m) and 11MR1091(99.4m) and comparing the Ce/Ce\* with MnO% and Mn/Fe ratio, it can be seen that the MnO% shows a weak correlation with the Ce anomaly  $(r^2=0.32)$  (Figure 31a) and a stronger correlation with Mn/Fe ratio ( $r^2$ =0.61) (Figure 31b). This reflects the oxidative scavenging of Ce on Mn-Fe oxides. This is further proven from mineral data where small monazite crystals can be identified on top of both Mn and Fe oxides.

The above observations must be used with attention. The tectonic nature of core 11MR1091 has not been thoroughly studied. Even though none of the samples have been subjected to lateritic weathering the Mn and Ce recycling due to tectonic activity and tropical weathering is still a possibility that needs to be studied. Thus, the assumption that the Ce anomalies that are reflected in the results reflect the true depositional environment must be made.



Figure 31: Ce anomaly variation diagrams (a) Correlation MnO (b) Correlation with Mn/Fe.

In Serra do Navio, the metaplectic rocks do not show a correlation with the MnO concentration but the Mn-carbonate rock samples fit well with the MnO proportion inside the carbonate rocks (Chisonga et al., 2012), and overall positive Ce/Ce\* values supporting the presence of a oxic-anoxic environment. Similar to the Nsuta deposit positive Ce anomalies are detected in the Mn-ore samples whereas such anomalies are rarely observed in the Mn-phyllites (Goto et al., 2021). While Nyame (2008), reports negative or no Ce anomalies in the Nsuta Mn-carbonate.

## 5.4 Depositional model of the MPHY unit and the state of the Early-Paleoproterozoic Ocean.

By combining all the above results and comparing the metallogenic models of the Nsuta deposit (Nyame, 2008), the Serra do Navio deposit (Chisonga et al., 2012) and the Manganese stromatolites in Koegas Group, South Africa (Warke et al., 2020) a first assessment about the depositional model of Matthews Ridge can be made.

The Matthews Ridge metasediments are composed of terrestrial sediments that are more enriched in HREEs than LREEs, sediments with mafic/ultra-mafic signatures that probably originate from the mafic volcanic rocks of the Mazaruni group. By accepting the assumption that the Mn/Fe variability is controlled by variations that occurred in the depositional environment it is suggested that the sediments have been deposited in an oxygen

and redox stratified ocean in a continental /ocean island arc environment. The upper part of the ocean was oxygen efficient to facilitate the oxidation of soluble  $Mn^{2+}$ , above the  $Mn^{4+}/Mn^{2+}$ redoxcline, to insoluble  $Mn^{4+}$  oxides that catalyze the oxidation of  $Ce^{3+}$  (Bau, 1999) resulting in negative Ce anomalies. As the ocean basin was deepening due to the ocean stretching because of the Trans-Amazonian orogeny processes the sediments started to be deposited below the Mn<sup>4+</sup>/Mn<sup>2+</sup> where the amount of  $O_2$  was insufficient, resulting in anoxic/suboxic conditions. The particulate oxides sink through the redox stratified waters, resulting in the reduction of Mn<sup>4+</sup> oxides to Mn<sup>2+</sup> oxides and consequentially resulting in the reduction of Ce<sup>4+</sup> to  $Ce^{3+}$  and generating positive Ce anomalies (Tostevin, Shields, et al., 2016b). Even though MnO is low, it is still non-negligible because the Ce anomalies are positively correlated to Mn/Fe. This suggests redox cycling of these elements by the rise of oxygen in the atmosphere. In this model, the lower phyllitic unit has been deposited deeper in the basin just where the environment became reducing again, resulting in the transformation of Mn oxides into  $Mn^{2+}$ before reaching the sediment profile. Subsequently, the mobile  $Mn^{2+}$  is transported to shallower oxygenated water depths where conditions are favourable for Mn to be stored in sediments together with the scavenged Ce (need some references). If such is the case, we should find positive Ce anomalies in the Mn-enriched rocks higher up in the stratigraphy, which supports the hypothesis of the barren basal LPHY. With the Mn/Fe controlling the oxidation of  $Ce^{3+}$  it is suggested that the formation of  $Fe<sup>3+</sup>$  oxyhydroxides along Mn redoxcline is related to the upward diffusion of Fe<sup>2+</sup> due to  $O_2$  consumption by  $Mn^{2+}$  oxidations and the following replacement of  $Mn^{4+}$  by Fe<sup>3+</sup> in particulate  $Mn^{4+}$  oxides (Dellwig et al., 2010; Kurzweil et al., 2016).

The origin of Mn is still a mystery in most Early-Paleoproterozoic Mn deposits, most authors support that Mn originates from a subthermal volcanic activity supported by the high positive Eu anomalies and the enrichment of the Early Paleproterozoic ocean in Eu due to volcanic activity (Bau & Dulski, 1996) or a terrestrial source that was eroded and resulted to the Mn enrichment (Roy, 2006).



*Figure 32: Depositional model of the LPHY unit (modified by* Warke et al., 2020).

# 6 Conclusions

Summarizing, the Lower Phyllite Unit of the Matthews Ridge Unit is composed of moderately to strongly weathered terrestrial sediments with mafic signatures. It suggested that the sediments accumulated in a freshwater shallow-marine environment and an oxygen/redox stratified ocean, above the Mn4+/Mn2+ redoxcline, and, as the ocean basin was deepening the sediments were continuously deposited in a reduced environment below the Mn2+/Mn4+redoxcline. The sediments were later metamorphosed to greenschist facies because of the event of the Trans-Amazonian orogeny. Later tectonic activity and dioritic intrusions resulted in the creation of major fault units and folds in the entire stromatographic column, while due to tropical weathering, it was subjugated to lateritic weathering.

### 7 Reference

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#### **APPENDIX 2 (ICP-MS data)**


















































































