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Research paper



# Petrography and geochemistry of iron-bearing units from Mingo'o area (Ntem complex, southern Cameroon)

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# Abstract

The banded iron formation (BIF) of the Mingo'o region is located on the northern edge of the Congo Craton. They constitute a significant component of the southern Cameroonian Archean to Paleoproterozoic. Petrographic description indicates that the most characteristic facies of the Mingo'o BIFs are quartz-magnetite BIFs (QMB), which are mostly composed of magnetite and quartz. Geochemistry analyses show that the major elements of this BIF are very simple, with SiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> representing 95.25 wt. % of the bulk rock on average. The low concentrations of Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and HFSE reveal that these chemical sediments are detritus-free. According to Paerson's major element correlation matrix, there is a slight contribution of detrital material to chemical sediment, as confirmed by the strong positive correlation (r = 0.72) of Al and Ti, also by the binary diagrams Al vs.  $\Sigma(Y + Nb + Zr)$  with a weak positive correlation ( $r^2 = 0.31$ ) and Al vs.  $\Sigma REE$  with a zero correlation ( $r^2 = 0.08$ ), indicating that the detrital input was insignificant. The transition metals Zn, Cr, Sr, and V are among the trace elements with low enrichments. This suggests the direction of the volcanogenic hydrothermal input in chemical precipitates. The mean  $\sum$ REE concentration of the studied BIF is 26.74 ppm, with a range of 8.82 to 36.74 ppm. Pure chemical sediments are comparable to that. The shale-normalized patterns display minor positive europium anomalies, a sharp decrease in heavy REE, and enrichment in light REE. These geochemical characteristics suggest that the hydrothermal activity in the deep ocean, coupled with seawater, was the source of the Fe and Si. Low-temperature hydrothermal solutions play a key role in the studied BIF, as shown by the absence of a notable positive Eu anomaly. Ce anomalies are seen in the chrondrite-normalized REE patterns, which are characterized by LREE-enriched (mean Lacn/Ybcn = 5.28) and HREE depletion (mean  $Tb_{CN}/Yb_{CN} = 1.04$ ) patterns. This may indicate that the BIF within the Mingo'o region was formed in place of the basin towards redoxcline, alternating at different times and under various influences from the influx of seawater that has been oxidized.

Keywords: Banded Iron Formations; Congo Craton; Hydrothermal Fluids; Seawater.

# 1. Introduction

Sedimentary rocks with a Fe content of 15% or above compose the majority of the stratigraphic units identified as the Iron Formations (IFs) [1,2]. Due to interpreted depositional circumstances [3,4], IFs have historically been divided into two types: superior type and algoma type. Superior-type of IFs are commonly found interbedded with carbonates, quartz arenite, and black shale; it is assumed that they were deposited in nearshore continental shelf environments. Algoma-type of IFs can occur in graywacke but are more frequently seen in volcanic rocks. It is believed that exhalative-hydrothermal processes produced them close to volcanic centers [4]. Based on their textural features, two groups of iron formations (IFs) can be identified: banded iron formations (BIFs) and granular iron formations (GIFs) [5–7].

Despite the importance of iron's everyday use in meeting human requirements, iron production continues to attract attention on a global scale [8]. Moreover, significant advancements in iron exploration have been achieved by mining countries such as Australia, Brazil, and South Africa [9–12]. In South Africa, [9] show the origin and palaeoenvironmental significance of major iron formations at the Archean-Paleoproterozoic boundary. Very little progress has been achieved in Cameroon's iron mineralization research, despite several studies and discoveries by academics and mining companies. This is occurring in southern Cameroon, especially in the areas of Mbalam, Mamelles, Nkout, Ngovayang, Meyongo, and Mayo-Binka in the Ntem Complex, on the northern edge of the Congo Craton [13–22]. But because the origin of iron mineralization still has to be determined, there are still some places where the search for iron mineralization has not yet advanced. This is currently the case under investigation at the northern edge of the Congo Craton, in the Mingo'o region of southern Cameroon. Therefore, in order to expand iron exploration both globally and in Cameroon specifically, the objective of this study is to determine the origin of Mingo'o's iron mineralization using petrographic and geochemical data.



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# 2. Geological setting

# 2.1. Regional geology

The northern edge of the Congo Craton in Cameroon constitutes the Ntem complex [23], [24] (Fig. 1a). The Pan-African orogenic belt, which is a relatively stable block of Archean and Palaeoproterozoic rocks, covers this complex from the north [25], [26]. Over a distance of more than 500 kilometers, the Ntem complex is separated into three main units: the eastward-facing Ayna unit, the central Ntem unit, and the westward-facing Nyong unit (Fig. 1b).

Greenstone belts, a banded series, and an intrusive series are formations that define the Ntem unit (Fig. 1b). The bulk of the intrusive series is located in the northern area and is composed of the magmatic Charnockitic suite and the Tonalite-Trondjemite-Granodiorite (TTG) suite [23], [27]. Among the significantly deformed granulitic gneisses that comprise the banded series are leptynites, enderbergites, granitic gneisses, and charnockitic gneisses, which are distributed across the southern part of the Ntem unit [23], [28]. The fractured bands and xenoliths of greenstones from the Ntem unit are discovered in the intrusive series, indicating that they formed earlier BIFs. These supracrustal rocks are composed of metagraywackes, paragneisses containing sillimanite, amphibolites having garnet, and pyroxenites [29]. They experienced granulite-facies metamorphism with estimated peak temperatures of  $750 \pm 50$  °C at 5–6 kbar [26]. The location of the greenstone belts in the Ntem unit has been dated to about 3.1 Ga using the zircon Pb-Pb evaporation process [30]. Greenstone belts are seriously fragmented by late syenitic plutons and doleritic veins that crosscut them [26].

The rocks of the Ayna unit (Fig. 1b) are the same as those of the Ntem unit. This unit is associated with a Paleoproterozoic trench composed of the volcano-sedimentary Mbalam series. Granodiorites are also present in this region. The volcano-sedimentary sequence gneissified between 2 and 2.1 Ga, forming Eburnian granodiorites. Liberian N130°E foliation continued after massive senestial N40°E blastomylonite gullies and posterior N50°E folds ascribed to the Eburnian orogeny [23].

The Nyong unit, which involves Mingo'o iron mineralization (Fig. 1b), was reworked as part of the northern edge of the Congo Craton in Cameroon during the Eburnian-Transamazonian orogeny [24], [31], [32]. It is composed of iron-rich formations, mafic and ultramafic metavolcanics, migmatitic grey gneisses of TTG composition, syn to late tectonic charnockites, augenic metadiorites, orthopyroxene gneiss, amphibolo-pyroxenites, garnet-rich gneisses, and granites [31], [32]. In the polycyclic metamorphic of the high-grade gneisses of the Nyong unit, Pan-African high-grade recrystallization overprints the Paleoproterozoic granulite assemblage [31], [33]. Recent examples of eclogite facies metamorphic rocks include garnet-clinopyroxenites and garnet-clinopyroxene amphibolites found in the high-grade supracrustal gneisses of the Nyong Range [34], [35]. These rocks belong to the Nyong unit greenstone formation. According to [36], their pressure-temperature conditions of around 25 kbar and 850 °C suggest that they were buried at a depth of more than 90 km and with a lower geothermal gradient of roughly 10 °C/km. The metamorphism of the eclogite facies is limited to 2.09 Ga by eclogite samples from SHRIMP U-Pb analysis [35]. Massive local open folds generally connected to N-S sinister sliding faults, a shallow to moderately dipping S1/S2 regional trough, and a variably oriented stretching lineation are the components that define the Nyong unit. The highest depositional age for the Nyong unit, as determined by SHRIMP U-Pb studies, is  $2423 \pm 4$  Ma [31].



Fig. 1: (A) - Craton Map in Africa. (B) - Geological Map Of South West Cameroon Modified From [23]: 1. Faults, 2. Supposed Faults, 3. Overlaps, 4. Study Area, 5. Quaternary Fluvial and Coastal Deposits, 6. Itabirites Quartzites from the Neoarchean to the Paleoproterozoic, 7. Ultrabasites, Veins Rocks, 8. Dolerites, Veins Rocks, 9. Gabbros, Veins Rocks, 10. Archean Noritic Gneiss, 11. Paleoproterozoic Neoarchean Garnetiferous Amphibolitic Gneiss, 12. Amphibolites, Garnetites, Eclogitoids from the Neoarchean to the Paleoproterozoic, 13. Archean Granulitic Gneisses, Leptynites, Enderbites, 14. Archean Charnockitic Grainy Core, 15. Archean Syenite Charnockites, 16. Porphyroid Biotite-Amphibole Granites, 17. Micaceous Quartzites of the Yaounde Group, 18. Neoarchean To Paleoproterozoic Tonalites, 19. Neoarchean to Paleoproterozoic Nepheline Syenites, 20. Undifferentiated Neoarchean To Paleoproterozoic Granites. 21. Neoarchean to Paleoproterozoic Repatines, 22. Archean Leucocratic, Biotite and Alaskitic Granites, 23. Neoarchean to Paleoproterozoic Nepheline Syenites, 24. Sedimentary Pile of the Post Panafrican Cover, 25. Schist, Limestone of the Neoproterozoic, 26. Two-Mica Gneiss, Anatectites of Yaounde Group, 27. Muscovite-Chlorite Quartzitic Epischists of Yaounde Group.

# 2.2. Local geology

Paleoproterozoic Neoarchean garnetiferous amphibolitic rocks constitute the Mingo'o region [23]. In addition, we discover banded iron formations, amphibolites, and amphibole garnet gneiss (Fig. 2). Their outcrops frequently take the shape of stable domes, massively stuctured slabs and blocks, and microlithic textures with granular or semi-granular textures. BIFs are composed of 0.5 to 1.5 cm-long mesobands of Fe-oxide and recrystallized quartz that alternate in a dynamic pattern and change from greenschist to amphibolite facies. But transposition and metamorphic differentiation have destroyed it, resulting in the formation of tectonometamorphic layers of iron oxides and quartz. Itabirite's layered structure is usually inherited from the parent sediment, which is rich in iron. The principal directions in the area are similar to NE-SW and NE-SSW, according to an analysis of remote sensing data.

# 3. Sampling and analysis methods

Eight representative BIF samples were chosen for petrographic and geochemical analysis in this study. In Figure 2, the sample sites are represented. The Institut for Geological and Mining Research (Cameroon) Ore Processing Laboratory generated polished thin sections. Polarizing microscopy was used in the Laboratory of the School of Geology and Mining Engineering, University of Ngaoundere (Cameroon), to carry out petrographic studies of these thin sections. Geochemical analysis was done using the pulp. Whole-rock analyses were done by Inductively Coupled Plasma-Atomic Emission (ICP-AES) for major elements and by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for trace elements at ALS Global, Brisbane (Australia). The samples were pulverized to obtain a homogeneous sample, out of which 50–60 g were obtained for the analyses. 0.1 g of rock powder was fused with 1.5 g of LiBO<sub>2</sub> and then dissolved in 100 mm<sup>3</sup> of 5% HNO<sub>3</sub>. Loss on ignition (LOI) was determined by the weight difference after ignition at 1025 °C. Various standards were used, and data quality assurance was verified by running these standards between samples as unknowns.



Fig. 2: Geological Map of the Mingo'o Area.

# 4. Results

#### 4.1. Petrography

The banded iron formations observed are represented by one type of facies, which is quartz-magnetite BIFs (QMB). This facies is the most representative.

#### 4.1.1. Quartz-magnetite BIFs

It is dispersed throughout the soil in the form of blocks (Figs 3a and b). They are available in two different color varieties: Fig. 3c shows a reddish-grey color with good compositional bedding, and Fig. 3d illustrates a gray color with fine bedding that alternates between light and dark levels. The light and dark minerals alternate continuously throughout this rubbing. The light minerals have a millimeter thickness and a quartzo-feldspathic composition. Magnetite makes up the majority of the dark minerals (Figs 3e and f).

The rock has a granolepidoblastic texture in thin sections (Figs 3e and f). Its main constituents are quartz (30-35 vol.%), potassium feldspar (5-10 vol.%), and magnetite (50-55 vol.%).

The most common iron mineral is magnetite, which may be found in bands that are Si-rich at percentages under 30 vol. % and Fe-rich at percentages over 50 vol. %. Black magnetite crystals in both bands range in size from 0.1 to 2 mm and have subhedral to anhedral shapes (Figs 3e and f). Magnetite crystals can occur alone in quartz grains or in clusters to create asymmetric aggregates (Figs 3e and f). There are quartz and feldspar inclusions in some magnetite grains (Figs 3e and f).

In the Si-rich bands, quartz predominates as subhedral to anhedral crystals with diameters ranging from 0.1 to 2 mm. Within the Fe-rich bands, quartz crystals often occur as amorphous aggregates rather than as discrete grains. In general, quartz combines with feldspar to create elongated polycrystalline bands, which are transparent beds that match the light beds of the rock. It is also xenomorphic (Figs 3e and f).

K-feldspar crystals range in size from 0.1 to 0.5 mm and appear in xenomorphic crystal forms. There are spots on these crystals where weathering has occurred (Figs 3e and f).



Fig. 3: (A), (B), (C), (D), (E), And (F) - Macroscopic and Microscopic Views of the Iron Fomations of the Studied Locality: Quartz-Magnetite Bifs (QMB).

# 4.2. Geochemistry

#### 4.2.1. Major elements

Table 1 displays the major elements of the overall geochemical composition of eight representative samples from the Mingo'o banded iron formations. These iron formations have basic element chemistry, with SiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> as the main components (all Fe being expressed as Fe<sup>3+</sup>). This is evident from the petrography and the general mineralogy of the rocks under study, which are mostly composed of quartz and iron oxide/hydroxyl minerals. The table shows that Fe<sub>2</sub>O<sub>3</sub> is the most abundant major oxide in all samples, with values ranging from 49.5 to 73.7 wt. % (mean: 60.95 wt. %), resulting in a percentage of native iron that varies from 34.62 to 51.54 wt. %. The second is SiO<sub>2</sub>, with values ranging from 15.25 to 44.3 wt. % (mean: 34.29 wt. %). SiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> make up an average of 95.25 wt. % of the mass of the banded iron formations. Samples MIN3 and MIN21 are marked by high concentrations of Fe<sub>2</sub>O<sub>3</sub> (73.7 wt. %, respectively) and low concentrations of SiO<sub>2</sub> (15.25 and 16.95 wt. %, respectively), showing, compared with the other samples, high signs of weathering of SiO<sub>2</sub> in favor of Fe<sub>2</sub>O<sub>3</sub>.

In the respective binary diagrams (Fig. 4):  $SiO_2/Fe_2O_3$  ( $r^2 = 0.888$ ),  $K_2O/Fe_2O_3$  ( $r^2 = 0.431$ ),  $TiO_2/Fe_2O_3$  ( $r^2 = 0.006$ ),  $CaO/Fe_2O_3$  ( $r^2 = 0.006$ ),  $MnO/Fe_2O_3$  ( $r^2 = 0.46$ ),  $MgO/Fe_2O_3$  ( $r^2 = 0.603$ ), and  $Na_2O/Fe_2O_3$  ( $r^2 = 0.509$ ), we observe negative correlations (Figs 4a, b, d, e, f, g and i), which show progressive decreases of  $SiO_2$ ,  $K_2O$ ,  $TiO_2$ , CaO, MnO, MgO, and  $Na_2O$ , while  $Fe_2O_3$  increases. A positive correlation is observed in the binary diagrams  $Al_2O_3/Fe_2O_3$  ( $r^2 = 0.579$ ) and  $P_2O_5/Fe_2O_3$  ( $r^2 = 0.555$ ), showing the progressive increase of  $Al_2O_3$  and  $P_2O_5$  with  $Fe_2O_3$  (Figs 4c and h). The Pearson correlation matrix (Table 2) confirms the binary diagrams obtained. It shows that there is a strong negative correlation (r = -0.94) between  $Fe_2O_3$  and  $SiO_2$  in different mineral phases.  $Al_2O_3$  shows a negative correlation with  $SiO_2$  (r = -0.49) and a positive correlation with  $Fe_2O_3$  (r = -0.25). CaO, MgO, Na<sub>2</sub>O, K<sub>2</sub>O, TiO<sub>2</sub>, and MnO show negative correlations with  $Fe_2O_3$  (r = -0.76, r = -0.78, r = -0.71, r = -0.66, r = -0.08, and r = -0.68, respectively), while  $P_2O_5$  shows a positive correlation with  $Fe_2O_3$  (r = 0.75).



Fig. 4: Binary Diagrams of Major Element Variations as A Function of  $Fe_2O_3$ : (A) -  $Sio_2/Fe_2O_3$ ; (B) -  $K_2O/Fe_2O_3$ ; (C) -  $Al_2O_3/Fe_2O_3$ ; (D) -  $Tio_2/Fe_2O_3$ ; (E) -  $Cao/Fe_2O_3$ ; (F) -  $Mno/Fe_2O_3$ ; (G) -  $Mno/Fe_2O_3$ ; (H) -  $P_2O_5/Fe_2O_3$ ; (I) -  $Na_2O/Fe_2O_3$ .

Table 1: Major Element Composition (Wt. %) and Element Ratios of the Mingo'o BIF										
Sample	MIN3		MIN4	MIN7	MIN10	MIN12	MIN17	MIN18	MIN21	Mean
Weight percent (wt %)										
SiO <sub>2</sub>	15.25		38.90	35.00	39.50	43.70	44.30	40.70	16.95	34.29
$Al_2O_3$	1.52		1.24	0.47	1.54	1.79	1.03	0.23	2.42	1.28
Fe <sub>2</sub> O <sub>3</sub>	73.70	57.50		66.60	57.40	49.50	51.10	58.10	73.70	60.95
CaO	0.01		0.05	0.01	0.01	1.27	1.02	0.46	0.01	0.36
MgO	0.02	0.15		0.03	0.08	1.94	1.38	0.78	0.03	0.55
Na <sub>2</sub> O	0.01	0.02		0.02	0.01	0.20	0.22	0.02	0.01	0.06
$K_2O$	0.01	0.01		0.02	0.19	0.42	0.18	0.02	0.07	0.12
TiO <sub>2</sub>	0.08		0.03	0.01	0.12	0.09	0.06	0.01	0.07	0.06
MnO	0.03		0.02	0.02	0.03	0.05	0.04	0.03	0.02	0.03
$P_2O_5$	0.96		0.10	0.07	0.20	0.10	0.11	0.08	0.49	0.26
LOI	6.04		0.31	-0.81	1.06	-0.40	-1.48	-0.36	5.87	1.28
Total	97.63		98.33	101.44	100.14	98.66	97.96	100.07	99.64	99.23
Fe	51.54		40.21	46.58	40.14	34.62	35.73	40.63	51.54	42.62
Si/Al	8.90		27.97	68.13	22.79	21.72	38.33	158.50	6.19	44.07
Fe/Al	64.07		61.28	187.28	49.25	36.55	65.55	333.81	40.24	104.75
Al/Ti	20.00		65.00	48.00	11.57	18.80	18.00	24.00	32.00	29.67
Fe/Ti	1288.50		4021.00	9316.00	573.43	692.40	1191.00	8126.00	1288.50	3312.10
Table 2: Pearson's Correlation Matrix for Major Element Oxides										
	SiO <sub>2</sub>	$Al_2O_3$	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	MnO P <sub>2</sub> O <sub>5</sub>	LOI
SiO <sub>2</sub>	1.00									
$Al_2O_3$	-0.49	1.00								
Fe <sub>2</sub> O <sub>3</sub>	-0.94	0.25	1.00							
CaO	0.60	-0.03	-0.76	1.00						
MgO	0.62	-0.04	-0.78	1.00	1.00					
Na <sub>2</sub> O	0.55	0.06	-0.71	0.94	0.91	1.00				
$K_2O$	0.47	0.37	-0.66	0.78	0.79	0.75	1.00			
TiO <sub>2</sub>	-0.14	0.72	-0.08	0.12	0.12	0.20	0.60	1.00		
MnO	0.47	0.09	-0.68	0.90	0.91	0.84	0.85	0.44	1.00	

#### 4.2.2. Trace elements

 $P_2O_5$ 

LOI

-0.89

-0.96

0.46

0.65

The trace element contents of the whole rock in the Mingo'o BIF samples are displayed in Table 3. When compared to the composition of the upper continental crust, the concentrations of trace elements, such as high-field elements (HFSE), transition trace metals, and rare earth elements, are relatively low (Fig. 5; [37], [38]). It should be noted that trace element concentrations are frequently low, as is the case with other BIFs across the world [9,39]. Transition metals such as Zn (20–101 ppm), Cr (7–91 ppm), Sr (1.4–8.3 ppm), and V (10–39 ppm) are examples of trace elements with low enrichment. These elements (Zn, Cr, Sr, and V) are commonly used as indicators of direct hydrothermal input from volcanoes in chemical precipitates, according to [40], [41]. [42], [43] reveal that whereas Zr, Hf, Rb, Y, and Sr are frequently generated from the alteration of felsic rocks in the Earth's crust, Cr, Ni, Co, V, and Sc have a mafic source. When compared to the upper continental crust, incompatible elements such as Th (0.500 ppm), Hf (0.227 ppm), Sc (5.875 ppm), and Zr (8.000 ppm) are discovered in very low concentrations. This suggests that there is little to no detrial origin for the silicates [44].

-0.42

-0.54

-0.35

-0.50

-0.30

-0.32

0.36

0.36

1.00

0.91

1.00

-0.15

-0.34

-0.40

-0.53

0.75

0.83



Fig. 5: Trace Elemental Patterns of the Mingo'o Iron Formations.

#### 4.2.3. Rare earth elements

All of the BIF samples had a total REE concentration ranging from 8.82 to 66.54 ppm. When comparing nearly flat or slightly fractionated HREE ((Tb/Yb)<sub>CN</sub> = 0.61-1.65 ppm) to REE profiles normalized with the chrondrite (CN index, [37,38]), enrichment in LREE ((La/Yb)<sub>CN</sub> = 1.11-10.92 ppm) is evident, just like the negative to positive anomalies in Eu ( $(Eu/Eu^*)_{CN} = 0.46-1.87$  ppm) (Table 3 and Fig. 6a). This suggests a low-rare earth fractionation. In comparison to HREE ((Tb/Yb)<sub>SN</sub> = 0.52-1.41 ppm), the REE profiles normalized to the post-Archean Australian shales (PAAS, SN index, [37], [38]) similarly demonstrate enrichment in LREE ((La/Yb)<sub>SN</sub> = 1.64-16.15 ppm), but with positive Eu anomalies ( $(Eu/Eu^*)_{SN} = 1.27-2.61$  ppm) and negative to positive anomalies in Ce ( $(Ce/Ce^*)_{SN} = 0.63-2.17$  ppm) (Table 3 and Fig. 6b). The Figure 7 displays the (Ce/Ce\*)<sub>SN</sub> vs. (Pr/Pr\*)<sub>SN</sub> diagram introduced by [45]. This diagram allows us to differentiate between real and false Ce anomalies in iron formations that may be caused by anomalous La abundances. In this diagram (Fig. 7), only one sample is in field I (no Ce or La anomaly), while three samples are in field IIa (positive La anomaly) and two others are in field IIIb (true negative Ce anomaly).



Fig. 6: (A) - Chondrite-Normalized; (B) - PAAS-REE Patterns of Mingo'o BIF. Normalization Value of PAAS and Chondrite After [37], [38].





# 5. Discussion

#### 5.1. Source of the chemical component

It was initially proposed by [5], [46] that the primary constituents of BIFs, silica and iron, originated from seawater. The origins of Fe and Si, according to [39], [47], are considered to be deep ocean hydrothermal activity combined with seawater. This theory explains why nearly all BIFs' REE profiles have positive Eu anomalies [48]. The Mingo'o BIFs' chemical composition shows that SiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> constitute the majority of the composition, with lower proportions of Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, MnO, MgO, and CaO following (Table 1). The purity of the chemical precipitates is shown by the high concentrations of SiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> found in the banded iron formations studied. Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> are regularly used as indicators of clastic input, whereas Fe and Mn operate as partial hydrothermal proxies [40,49]. Terrigenous clastic materials were involved in the deposition of the Mingo'o BIFs, as shown by the strong positive correlation of Al with Ti and K (Table 3, [50], [51]). Nonetheless, the samples studied reveal a heterogeneous distribution (nugget effect) in the binary diagrams Al vs.  $\Sigma$ (Y + Nb + Zr) and Al vs.  $\Sigma$ REE (Figs 8a and b), indicating that the detrital input was insignificant. Furthermore, there is a low detrital input during the precipitation of BIFs, illustrated by the concentrations of HFSE (such as Nb, Zr, Hf, U, Th, and Pb) that are normally enriched in chemically developed crusts [41]. The foregoing signatures all suggest the insignificant contribution of crustal materials to the chemical precipitation of the BIFs studied.

Table 3: Trace and Rare Earth Element Compositions (Ppm) and Element Ratios of BIF From Mingo'o Area Sample MIN3 MIN4 MIN7 MIN10 MIN12 MIN17 MIN18 MIN21 Mean Parts per million (ppm) 101.000 66.000 42.000 54.000 53.000 57.000 20.000 48.00055.125 Zn 12.000 13.000 Cu 23.000 17.000 17.000 3.000 3.000 2.000 27.000 45,000 9.000 8,000 13,000 6.000 10.125 Ni <d1 <d1 <d1 Co 9.000 6.000 6.000 8.000 9.000 4.000 4.0007.000 6.625 91.000 32.000 54.000 23.000 42.000 21.000 7.000 30.000 37.500 Cr V 37.000 15.000 26.000 24.000 39.000 17.000 10.000 39.000 25.875 0.980 0.804 Nh 0.950 1.040 0.290 0.7400.460 0.1701.800 Cs 0.100 0.020 0.010 0.160 0.110 0.220 0.040 0.190 0.106 Hf 0.310 0.210 0.130 0.240 0.270 0.180 0.080 0.390 0.227 5.000 11.000 4.000 4.000 5.000 1.000 17.000 5.875 <dl Sc Rb 0.800 0.400 0.400 7.300 12.800 11.400 0.900 6.600 5.075 2.400 1.400 1.400 2.000 8.200 13.600 8.300 1.900 4.900 Sr U 0.610 0.490 0.320 0.220 0.140 0.090 0.080 2.720 0.584 0.290 0.250 0.500 Th 0.350 0.270 0.360 0.220 0.250 2.010Pb 14.000 12.0008.000 10.000 9.000 9.000 10.000 22,000 11.750 7.000 5.000 8.000 5.000 13.000 8.000 Zr 17.000 6.000 3.000 Y 0.700 2.300 1.900 20.600 4.600 5.300 10.500 9.325 28.700 w 0.700 0.700 0.500 0.500 0.300 <d1 <d1 <d1 <d1 La 4.8002.1001.900 1.500 12.600 2.7008.300 5.400 4.913 Ce 6.300 8.200 2.800 3.300 26.500 5.900 14.800 7.400 9.400 0.930 0.310 0.440 0.360 2,630 0.720 1.550 1.083 Pr 1.720 Nd 4.400 0.900 1.900 1.400 11.100 3.200 6.800 5.900 4.450 0.180 0.570 0.380 0.790 1.040 1.800 1.043 Sm 1.220 2.360 0.690 0.050 0.160 0.130 1.060 0.320 0.560 0.500 0.434 Eu Gd 2.260 0.190 0.580 0.4002,960 0.770 0.980 1.720 1.233 Tb 0.420 0.030 0.120 0.070 0.430 0.120 0.130 0.310 0.204 1.410 Dy 3.350 0.160 0.670 0.460 2.830 0.720 0.900 2.190 0.880 0.030 0.150 0.100 0.580 0.319 Ho 0.140 0.190 0.480 0.080 0.480 0.300 1.860 1.011 Er 2.910 0.480 0.580 1.400 0.440 0.020 0.070 0.030 0.210 0.060 0.080 0.230 0.143 Tm Yb 2.910 0.130 0.560 0.350 1.220 0.310 0.570 1.580 0.954 0.040 0.040 0.090 0.490 0.020 0.090 0.200 0.220 0.149 Lu  $Y/P_2O_5$ 29.896 7.000 32.857 9.500 206.000 41.818 66.250 21.429 51.844 0.089 0.091 0.143 0.148 0.170 0.070 0.146 0.132 Co/Zn 0.200 Eu/Sm 0.566 0.278 0.281 0.342 0.449 0.405 0.538 0.278 0.392 19.000 35.517 26.053 Y/Ho 32.614 23.333 15.333 32.857 27.895 21.875 (La/Yb)<sub>SN</sub> 1.649 16.154 3.393 4.286 10.328 8.710 14.561 3.418 7.812 (Tb/Yb)<sub>SN</sub> 0.526 0.841 0.781 0.729 1.284 1.410 0.831 0.715 0.890 6.979 (La/Yb)<sub>CN</sub> 10.920 2.293 2.897 5.886 9.842 5.280 1.115 2.3100.916 (Tb/Yb)<sub>CN</sub> 0.617 0.987 0.855 1.507 1.655 0.975 0.839 1.044 1.871 0.462 0.892 0.822 0.751 0.657 0.613 0.849 0.865 (Eu/Eu\*)<sub>CN</sub> (Eu/Eu\*)<sub>SN</sub> 1.957 1.273 1.310 1.570 1.889 1.932 2.612 1.338 1.735 (Pr/Pr\*)<sub>SN</sub> 0.985 0.902 0.975 1.010 1.039 0.671 1.122 1.009 1.380 (Ce/Ce\*)<sub>SN</sub> 0.638 2.173 0.655 0.960 0.984 0.905 0.837 0.547 0.962 32.000 ∑REE 12.400 10.490 8.820 66.540 16.270 36.740 30.680 26.743

dl: detection limits.  $(Ce/Ce^*)_{SN} = (Ce \operatorname{rock/Ce PAAS})/[(La \operatorname{rock/La PAAS})0.5(Pr \operatorname{rock/Pr PAAS})0.5]; (Eu/Eu^*)_{SN} = (Eu \operatorname{rock/Eu PAAS})/[(Sm \operatorname{rock/Sm PAAS})0.5(Gd \operatorname{rock/Gd PAAS})0.5]; (La/Yb)_{SN} = (La \operatorname{rock/La PASS})/(Yb \operatorname{rock/Yb PASS}); (Tb/Yb)_{SN} = (Tb \operatorname{rock/Yb PASS})/(Yb \operatorname{rock/Yb PASS}); (Pr/Pr^*)_{SN} = (Pr \operatorname{rock/Pr PAAS})/[(Ce \operatorname{rock/Ce PAAS})0.5(Nd \operatorname{rock/Nd PAAS})0.5].$ 



**Fig. 8:** (A) - Detrital Trace Elements (Nb, Y, And Zr) vs. Al<sub>2</sub>O<sub>3</sub> Showing Relatively Low Positive Correlations Between Al<sub>2</sub>O<sub>3</sub> and These Elements; (B) - Null Correlations Between Al<sub>2</sub>O<sub>3</sub> and the  $\sum$ REE in the Bulk Samples of the Studied BIF.

#### 5.2. Origin of Mingo'o BIF

The degassing of submarine hydrothermal fluids and the weathering of continental crustal materials combine to produce Fe- and Si-rich BIFs [52]. The approaches that have been put out to make the distinction between seawater sources that are hydrothermal, biogenic, and detrital depend on variations in the composition of minerals, chemicals, and isotopes. For instance,  $Al^{3+}$  and  $Ti^{4+}$  are considered to be very insoluble in seawater and resistant to hydrothermal alteration [53], [54]. Hydrothermal fluids present high ratios of Fe/Ti, Fe/Al, and Si/Al (Table 1) as a consequence. The Mingo'o BIFs have high ratios of Fe/Ti (3312.10), Fe/Al (104.75), and Si/Al (44.07) that are indicative of sediments that have significant levels of hydrothermal process [54] or that originated from oceanic crust or Fe- and Si-rich submarine weathered shales where Ti and Al form a solid solution in a mineral phase.

The depiction in the hydrothermal field of [55] Si-Al discrimination diagram (Fig. 9a) confirms that the origin of the BIFs studied is mostly hydrothermal. High Al/Ti ratios and low Al content are characteristics of pure hydrothermal deposits [56]. Deep-sea pelagic and terrigenous sediments contaminate these deposits, enriching them with elements like Ti and Al. This causes a sharp decrease in the Fe/Ti ratios and an increase in the Al/(Al + Fe + Mn) ratio. When considering the potential hydrothermal input in hydrogenated sediments and their dilution with clastic or volcanic material, the Fe/Ti vs. Al/(Al + Fe + Mn) diagram is helpful [57–59]. According to [60], the diagram illustrates that clastic or volcanic material is defined by Al and Ti, whereas pure hydrothermal chemical sediments are rich in Fe and Mn. As can be observed in the diagram, all of the samples studied were centered on the hydrothermal deposits of the Red Sea and the East Pacific Rise (13°N and 21°N), which are situated far from the contemporary pelagic-terrigenous sediments (Fig. 9b). This implies that the majority of the Mingo'o BIF's constituents (>90%) are primarily hydrothermally derived. A low average Y/P<sub>2</sub>O<sub>5</sub> ratio of 51.84, which is less than the >100 found in pelagic and hydrogenated deposits but comparable to ratios indicated in pure hydrothermal deposits, is likewise compatible with a mostly hydrothermal origin (Table 3; [56]). With the exception of sample MIN12, which indicates a hydrogenated origin with a Y/P<sub>2</sub>O<sub>5</sub> ratio of 206, which is greater than 100 (Table 3). The prior conclusion that the BIFs studied are purely chemical sediments with little or no detrital input is confirmed by the low levels of detrital elements like Y, Nb, and Zr in the Mingo'o BIF and the low positive correlations between Al<sub>2</sub>O<sub>3</sub> and these elements (Fig. 8a). This conclusion was based on the major oxide distributions. Furthermore, there appears to be no detrital contribution to the  $\Sigma REE$  contents, as indicated by the zero correlations (r<sup>2</sup> = 0.08) between the  $\Sigma REE$  contents and the Al<sub>2</sub>O<sub>3</sub> contents (Fig. 8b).

[61] suggested using the Co/Zn ratio as a hydrothermal input tracer. This author affirms that hydrothermal deposits have a low Co/Zn ratio (0.15), while hydrogen deposits have a high Co/Zn ratio (2.5). The iron mineralization samples studied had an average Co/Zn ratio of 0.13, which is in line with trace metals coming mostly from hydrothermal sources with a little proportion of hydrogen impact (Table 3; [61]). Therefore, hydrothermal solutions, which could have originated from hydrothermal vents in marine environments, added the materials that form the mineralization to the seafloor.



**Fig. 9:** (A) - Si Vs. Al Discrimination Diagram Indicating the Hydrothermal Affinity of the Studied BIF; (B) - Fe/Ti Vs. Al/(Al + Fe + Mn) Diagram of Mingo'o BIF. the Curve Represents Mixing of East Pacific Rise Deposits (EPR) with Pelagic Sediments (PC) Whereas the Numbers Indicate the Approximate Percentage of EPR in the Mixture (Adopted From [57]). Also Indicated Are Compositions for Mean Upper Continental Crust (UC, [38]), Red Sea Hydrothermal Deposits (RS, [56]) And The Cyprus Umber (CU).

#### 5.3. Petrography and geochemistry in comparison

According to [39], [62-64], the mineral assemblages presented in the petrographic section are similar to oxidized facies banded iron formations found all over the world. The majority of BIFs in Cameroon are oxide facies, with magnetite or hematite predominating. The Mingo'o BIFs are mostly magnetite-rich, similar to the Ngoa and Elom iron ore deposits, when compared to other BIF occurrences in the same Precambrian iron ore belt in southern Cameroon [15]. The iron ore deposits in Metzimevin, Njweng (Mballam), and Nkout are not the same as these iron mineralizations in Mingo'o; the former are mostly made of hematite and martite, with minor phases of monazite, apatite, and pyrite [21], [65]. Furthermore, the silicate facies BIF in the Njweng prospect of the Mballam iron ore deposit was characterized by [65]. The Mingo'o region has not seen any of these BIF varieties. When compared to the average chemical compositions of other banded iron formations found in the Proterozoic and Archean supracrustal belts, the Mingo'o banded iron formations have slightly elevated Fe<sub>2</sub>O<sub>3</sub> values and depressed SiO<sub>2</sub>, TiO<sub>2</sub>, MgO, MnO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, and P<sub>2</sub>O<sub>5</sub> values in bulk rock geochemistry (Fig. 10a). The proportions of MnO, which are extremely low in the BIF of the study area, vary significantly, as seen in this Figure, although the proportions of  $Fe_2O_3$ are slightly higher. The average P2O5 concentration (0.3 wt. %) in the BIFs studied is greater than the one in Isua (0.2 wt. %), Hamersley (0.15 wt. %), Hotazel (0.12 wt. %), Orissa (0.06 wt. %), and Superior (0.04 wt. %) types, but it is similar to that of the Algoma oxidized facies [63]. According to [66], the Al<sub>2</sub>O<sub>3</sub> concentrations of the Mingo'o BIF (1.5 wt. %) are high in comparison to the Al<sub>2</sub>O<sub>3</sub> contents of the Orissa BIF (0.8 wt. %), which are close to the Al<sub>2</sub>O<sub>3</sub> concentrations of the Isua and Superior BIF (1.6 wt. %). There are various concentrations of iron-rich silicate minerals found inside the different banded iron formations, as shown by the slight variations in Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, and Na<sub>2</sub>O<sub>3</sub>. The metal concentrations of the Algoma, Superior, Isua, Hamersley, and Hotazel types are similar to the Zn Cu, Ni Co, and V contents of the BIFs studied, with values >2 ppm (Fig. 10b). With a mean REE concentration ( $\Sigma REE = 26.74$  ppm) comparable to other Archean to Proterozoic oxide-facies BIFs around the world, the REE depletion of the Mingo'o BIFs is compatible with REE data from Archean iron formations elsewhere [39], [67]. Similar to REE profiles from other Archean BIFs [15,20,50,68], PASS-normalized REE profiles from the study area show slightly positive Eu anomalies (Eu/Eu\* = 1.73) relative to HREE (Tb<sub>SN</sub>/Yb<sub>SN</sub> = 0.89) with slightly negative Ce anomalies (Ce/Ce\* = 0.96). Archean, early (> 2.4 Ga) and late (< 2.0 Ga) Palaeoproterozoic banded iron formations are characterized by negative Ce anomalies [20], [67]. Due to their low positive Eu anomalies, which are comparable to those of late Palaeoproterozoic BIFs, we consequently suggest that the Mingo'o BIFs were most likely deposited between the early and late Palaeoproterozoic [67]. Moreover, [68] proposed that Archean (0.40-1.22) and Proterozoic (0.24-0.40) BIF may be distinguished using the Eu/Sm ratio. Between 0.27 and 0.56 is the Eu/Sm ratio of the BIFs studied, which includes both Archean and Proterozoic BIFs.



Fig. 10: Plot of Average Major Elements Concentrations (A) and Transition Metal Values (B) of Mingo'o BIF (N = 8) and Other Well Studied Banded Iron-Formations Around the World.

# 6. Conclusion

To understand the origins of the Fe formations, representative samples of BIFs from the Mingo'o region in the Ntem complex (southern Cameroon) were analyzed for their major, trace, and rare earth elements. The BIFs studied are mostly oxide facies comprised of potassic felspar, microcrystalline quartz, and magnetite. The majority of the BIF samples have low concentrations of Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Y, Nb, Zr, and Th, indicating chemical sediments lacking detritus. The BIFs studied have an average Si/Al ratio (mean 44.07), which points to a hydro-thermal origin. This hypothesis is confirmed by the Fe/Ti vs. Al/(Al + Fe + Mn) binary diagram, which plots all the data in the Red Sea and East Pacific Rise hydrothermal deposit fields (Fig. 9b). Conversely, the low  $\sum$ REE concentrations, the Y/Ho ratio nearby chondrules, and the HREE profiles for the BIFs studied reveal the signs of seawater and hydrothermal solutions. A positive Eu anomaly is an indicator obtained from bottom water carrying a hydrothermal signature, whereas HREE enrichment is a signature inherited from seawater. Low-temperature hydrothermal solutions play a key role in the BIF studied, as evidenced by the lack of a strong positive Eu anomaly. It is possible that the Mingo'o BIFs were precipitated in suboxic to anoxic seawater since negative Ce anomalies were found in the samples studied. According to [67], this suggests that the redox conditions in the Mingo'o basin were variable, possibly in a stratified basin with a redoxcline dividing the deeper anoxic to suboxic waters from the upper oxic water column. Deposition possibly occurred in places of the basin towards redoxcline, alternating at different times and under various influences from the influx of seawater that has been oxidized.

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