Age and potential for critical metals in the world-class regolith-hosted manganese deposits of the Franceville basin (Gabon).

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Abstract. The Franceville Basin hosts one of the world's largest Mn deposits, accounting for 16% of global reserves. Chemical weathering transformed a low-grade Paleoproterozoic carbonate-hosted ore into a high-grade supergene ore along several plateau levels. This study investigates regolith formation using cryptomelane $^{40}Ar/^{39}Ar$ dating and compare the mineralogy and geochemistry of different weathering profiles to assess their potential for critical metals. The results show that the Okouma-Bagombé plateaus in the NW are higher grade ores than elsewhere. This is related to longer exposure time (<14 Ma) to chemical agents, higher topography level (>550 m asl.) and consequently higher degree of hydrolysis, which led to important silica release. The low-lying Franceville-Biniomi profiles (<440 m asl.) to the SE are younger (<6Ma) and display medium ore grades. We also report important critical metal (Co, Ni, Zn, Cu, Li) accumulation at the base of the Mn ore in the Franceville area due to lithiophorite formation.

1 Introduction

Manganese has become increasingly in demand due to its critical role in steel and Li-ion batteries, leading many countries to classify it as a critical commodity. In natural environments, Mn can have three valences (+2, +3, +4) giving rise to more than 30 naturally occurring Mn oxides. These oxides are highly reactive, participating in oxidation-reduction and cation-exchange reactions (Post 1999). As strong metal scavengers, they significantly influence the composition and chemical behavior of mineral systems (Watanabe et al. 2012).

The Franceville basin (Gabon) is renowned for its substantial Mn resources (23%) and reserves (16%)(Fig. 1). The Mn protore is a Paleoproterozoic unmetamorphosed Mn-rich carbonate-bearing black shale (Franceville Fm, FB1c) that has undergone weathering, forming a Mn-rich regolith. These weathering profiles, found only atop plateau-like erosional highs, exhibit variable but generally low thicknesses (2 – 20 m). They display a regular structure (Leclerc and Weber 1980), with the following idealized units (from bottom to top): (i) unweathered black shale, (ii) transitional clayey zone, (iii) massive Mn ore, 0.1-0.5 m-thick, (iv) platy Mn ore, 0.5-9.0 m-thick, (v) transitional blocky zone, (vi) pisolith soil, and (vii) humic soil horizon (Fig.2).

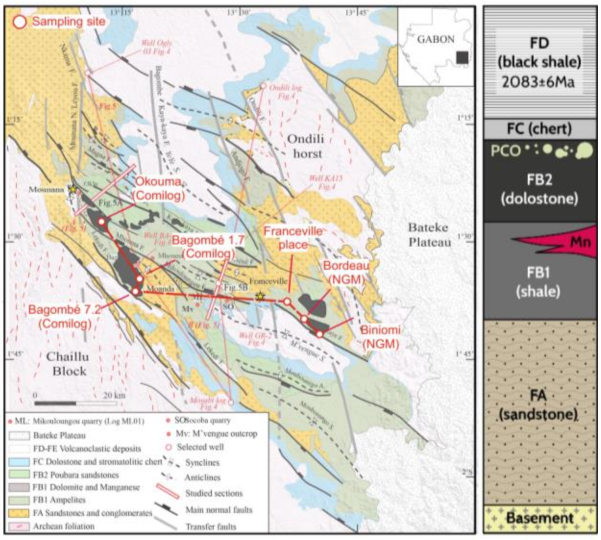

Figure 1. Geological map of the Franceville basin and location of the selected Mn-rich weathering profiles

Most previous studies have focused on the Bagombé plateau, the main mining area, but its future exhaustion highlights the need to assess other plateaus for future and sustainable extraction. No comparative mineralogical and geochemical investigations have been conducted across different regolith-hosted in the basin. In addition, no geochronological data exists to determine the age of the deposit and compare it with other regolith-hosted deposits of circum-Central Africa. These insights are essential for understanding the mineralization process during chemical weathering, identifying prospective areas, and evaluating the presence of critical elements within Mn oxides. This study aims to address these knowledge gaps.

2 Materials and methods

We targeted six cross-sections in mined (Biniomi, Bangombé, Okouma) and non-mined (Franceville) areas (Fig. 1). A total of 69 samples have been analyzed for their mineralogy using X-ray diffraction and Rietveld Refinement for quantification at University of Namur, University of Liège and University of Tartu. These samples have been analyzed for their major elements by ICP-OES at

ULB and by X-ray fluorescence at University of Tartu, and their trace elements by ICP-MS after total acid digestion at University of Tartu and Activation Laboratories ltd. (Canada). A SNE-4500 Plus Scanning Electron Microscope was used for imagery of the Mn ore.

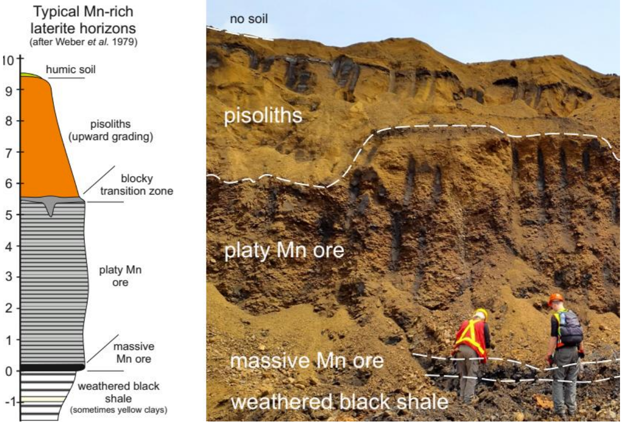

Figure 2. Typical structure of the Franceville Mn-rich regolith in the Kouma mine (Comilog-Eramet, 2023).

In addition, we have analysed 45 cryptomelane samples for $^{40}Ar/^{39}Ar$ geochronology from different horizons occurring in the sampling sites and complemented by samples from other locations in the basin. $^{40}Ar/^{39}Ar$ analyses were performed on single millimetre-scale fragments using a CO_2 laser probe coupled to a MAP215 mass spectrometer at the University of Rennes after irradiation at McMaster Nuclear Reactor (Canada).

3 Results

3.1 Structure of the Mn-rich regoliths

The total Mn-rich regolith thickness and individual horizon thickness vary significantly between sampling sites, even locally (i.e., Bagombé plateau) (Fig. 3), ranging from 2 to 15 meters. The platy Mn ore reaches a maximum thickness of 9 m at Bagombé and 1 m at Franceville. The pisolithic soil exceeds 3 m at Okouma, while the humic soil horizon reaches up to 4 m at Biniomi. The transition blocky horizon is absent in most sampling sites.

3.2 Mineralogy

Based on 37 analyses of the platy Mn ore, we established nsutite (46%), cryptomelane (20%), pyrolusite (10%) and lithiophorite (5%) as the main ore-forming minerals, with locally manganite and todorokite (Fig. 4). Gangue minerals are quartz (4%), kaolinite (4%), illite (avg. 4%), gibbsite (5%) and Fe oxides (2%), with local occurrence of halloysite. We also report extremely variable proportions between the sampling sites. At Okouma, cryptomelane is the main ore-forming mineral. We also observe the near-total absence of clays and very low content of quartz. Instead, gibbsite is the main gangue mineral. We draw similar observations for the Bagombé plateau, where quartz is very low and illite totally absent. Kaolinite is also absent except in interbedded clay lenses within the Mn ore. The Bordeau and Franceville regoliths exhibit opposite composition of gangue minerals, with high quartz and clay contents and low or absence of gibbsite. For these plateaus, we observe higher hematite instead of goethite. Lithiophorite is particularly concentrated at Franceville (12%). The Bagombé plateau has the highest content in nsutite (58%).

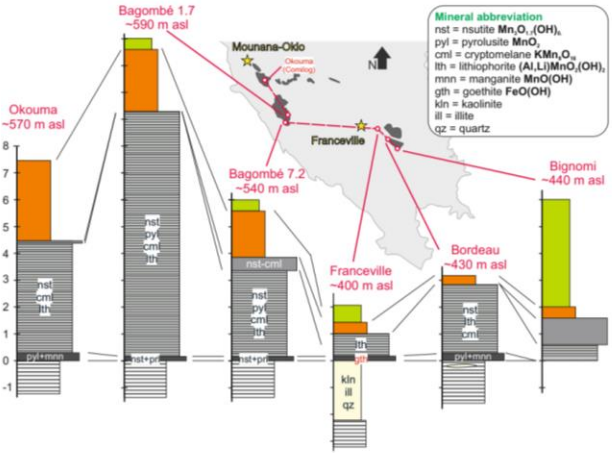

Figure 3. Structure of the Mn-rich weathering profiles showing the different typical horizons.

The composition of the underlying massive Mn ore varies consistently between the sampling sites with pyrolusite-manganite at Okouma, nsutite-pyrolusite-cryptomelane-lithiophorite at Bagombé, goethite-hematite at Franceville and todorokite-pyrolusite at Bordeau. The pisolith soil is predominantly composed of Al and Fe hydroxides with clays and quartz, and few Mn oxides. The weathered black shale and clays show similar compositions with quartz, kaolinite, illite and locally Fe oxides.

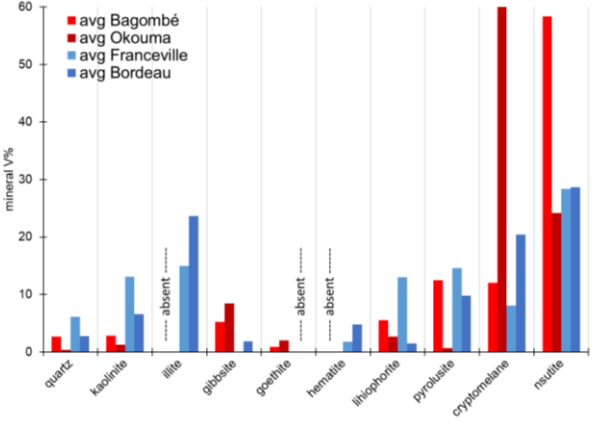

Figure 4. Average mineralogical composition of the platy ore (n=37).

3.3 Geochemistry

Mn ore horizons. The results show that the average Mn ore grade of the platy horizon across the different profiles is 44.5 wt.% Mn (n=37) with high concentrations of Al_2O_3 (10.0 wt.%) and SiO_2 (7.2 wt.%) and relatively low Fe_2O_3 (2.7 wt.%). The Bagombé (48.0 wt.% Mn) and Okouma deposits (46.6 wt.% Mn) display considerably higher average Mn grades than the Franceville (35.6 wt.% Mn) and Bordeau (38.2 wt.% Mn) deposits. These deposits contain proportionally more Al, Fe and Si. We do not observe significant upward/downward trends in Mn concentration in the platy ore.

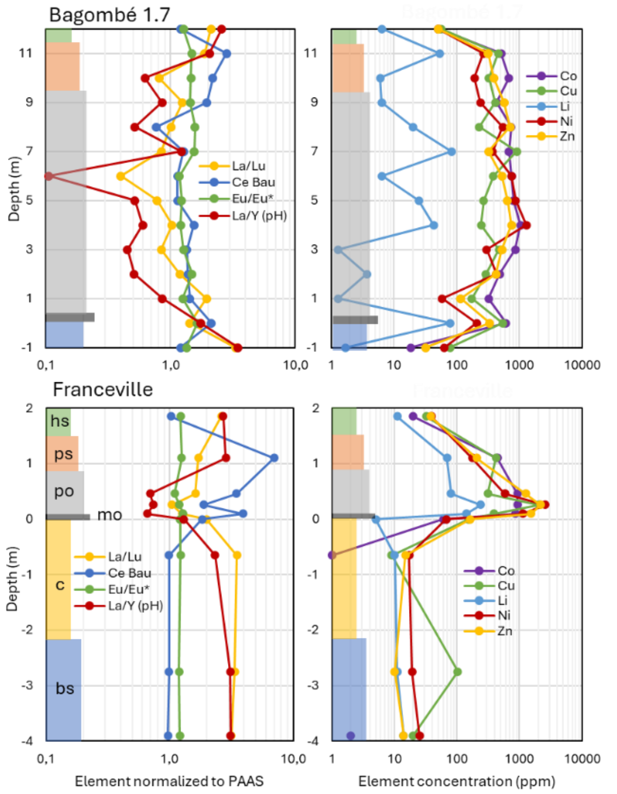

Figure 5. Geochemical variations along two Mn-rich regolith profiles of the Franceville basin.hs= humic soil, ps=pisolithic soil, po=platy ore, mo=massive ore, c=clays, bs=weathered black shale.

The platy Mn ore generally shows abnormally high average levels of strategic metals, such as Co (722 ppm), Cu (430 ppm), Ni (635 ppm) and Zn (631 ppm). Although these elements do not show any vertical trends within the platy ore at Bagombé and Okouma, they accumulate at the base of the platy ore horizon at Franceville and Biniomi. These metals can be up to 0.1 wt.% for Co, 0.2 wt.% for Cu and Zn and 0.3 wt.% for Ni above the massive Mn ore at Franceville. Lithium is particularly enriched at the base of this profile (> 150 ppm). We observe similar enrichments in interbedded clayey levels in the Bagombé deposits. Ba is also significantly enriched in all the studied areas (1708 ppm). We also observe that P is abnormally high (P > 590 ppm) in the Bagombé and Okouma deposits compared to the others (P < 330 ppm). The massive Mn ore shows comparable geochemical trends.

Other ore horizons. The pisolith soil horizon contains an average of 13.7 wt.% Mn (n=7), while the humic soil contains 3.4 wt.% Mn on average (n=3). The pisolith soil horizon displays high contents in Al (25.6 wt.% Al_2O_3), Fe (21.9 wt.% Fe_2O_3), Si (11.3 wt.% SiO_2) and Ti (1.0 wt.% TiO_2). Barium is particularly enriched (0.4 wt.%)

We generally observe increasing concentrations in immobile elements (Cr, Hf, P, Sc, Th, Ti, Zr) and some metals (Pb, Bi, Ga, In, Sb, U, V) in the soil horizons. Rare Earth Elements (REEs) also show fractionation of light REEs in the soil horizons with $(La/Yb)_{SN} > 2$ similar to the weathered black shales (Fig. 5). Accordingly, the Mn ore horizons tend to accumulate heavy REEs. We also observe distinctive Ce anomalies (>2) in the soil horizons compared to the underlying ore horizons. However, comparison of the Ce anomaly between the profiles shows different amplitudes, as for example the conspicuous positive Ce anomalies in the Mn ore horizons in the Franceville profile [$(Ce/Ce^*)_{SN} > 2$) which is generally lower in other Mn-rich regoliths (< 2), except for specific clayey levels. Eu anomalies are remarkably stable across the horizons (Fig. 5).

3.4 Geochronology

The $^{40}Ar/^{39}Ar$ results show important contaminations by inherited Paleoproterozoic material (i.e., illite) and additionally mixing between various generations of cryptomelane (Fig. 6), which accounts for inconsistent ages in most samples. Besides this material bias, we have identified pseudo- and plateau ages showing that weathering started at c. 14 Ma in the Okouma-Bagombé mining areas and later at c. 6 Ma in the Franceville area.

4 Discussion

The Franceville Basin Mn-rich regoliths exhibit significant variations in ore grades, with high-grade ores (>44 wt.% Mn) at Okouma and Bagombé, and medium-grade ores (30–40 wt.% Mn) at Franceville and Biniomi. These grades are three to four times higher than the Paleoproterozoic Mn carbonate protore (avg. 12 wt.% Mn; Dubois 2017). Despite differences in mineral composition and texture, both the protore and the pisolith horizon contain low-grade ore (10–30 wt.% Mn), though with distinct mineralogical characteristics. The pisolith horizon consists of Mn oxides, whereas the protore is composed of Mn carbonates.

New mineralogical and geochemical data allow to distinguish two types of Mn-rich regoliths. The high concentrations of gibbsite and goethite in the Bagombé-Okouma regolith, as opposed to the predominance of clays and hematite in the Franceville-Biniomi regolith (Fig. 3), suggest a more intense hydrolysis process in the former (Trolard et al. 1990). This process leads to the removal of SiO_2, which accounts for the higher Mn ore grades. Additionally, the greater maturity of the Okouma regolith likely explains the formation of cryptomelane instead of nsutite (Parc et al. 1989).

The gibbsite/kaolinite ratio generally increases with plateau altitude and laterite aging (Reatto et al. 2008). Our age data confirm two distinct weathering histories: the higher-elevation plateaus of Bagombé (~570 m asl) and Okouma (~590 m asl) have cryptomelane ages as old as 14 Ma, whereas the lower-elevation plateaus of Franceville (~400 m asl) and Biniomi (~440 m asl) have younger ages, under 6 Ma. The hydraulic gradient, defined as the elevation difference between the river and plateau levels, is approximately 180–200 m at Okouma-Bagombé and 100–130 m at Franceville-Biniomi. This gradient likely played a key role in the downward progression of the weathering front and the residence time of meteoric water, which likely influenced the thickness of the regolith horizons

(Fig. 3). This hydraulic gradient is crucial for sustaining chemical weathering of the organic matter-rich black shale, which acts as a strong reductant, inhibiting rapid oxidation of primary Mn-rich carbonates into Mn oxides. Additionally, the sub-horizontal stratification of the black shale further slows chemical reactions and progression of water.

The distinct weathering ages and hydrolysis processes likely influenced the (re)distribution of critical metals within the regolith profiles. For example, the peak concentration in Ni, Co, Cu, Zn and Li at the base of the Franceville and Biniomi deposits, whereas such enrichment is absent at Okouma and Bagombé (Fig. 5), is closely linked to the presence of lithiophorite (Fig. 3), which serves as a host for strategic metals.

The clear textural and chemical boundaries between the Mn-rich horizons of the regolith is likely related to variations in redox conditions. This is evidenced by increasing Ce anomalies in the pisolith soil horizon, attributed to the higher porosity and enhanced biological activity in this layer. The lower $(La/Y)_{SN}$ ratio in the platy ore horizon further suggests that pH played a role alongside redox processes. More acidic conditions in the Mn ore are indicated by $(La/Y)_{SN}$ ratios below 1 (Khosravi and Abedini 2025), a common characteristic of the Franceville regolith profiles (Fig. 5).

Weathering typically leads to the preferential release of HREE over LREE. Consequently, decreasing $(La/Lu)_{SN}$ ratios in the platy Mn ore indicate HREE mobilization from the soil horizons and their subsequent accumulation in Mn ores, likely due to the high cation-exchange capacity of Mn oxides (Post 1999). From a mineralization perspective, Mn was concentrated in situ through two mechanisms: (1) replacement of primary Mn-rich carbonates accompanied by progressive leaching of other cations, and (2) accumulation of Mn sourced from the overlying soil horizons. This is confirmed by microscopic observations, which reveal remnants of oxidized black shales replaced by nsutite, along with the precipitation of cryptomelane and lithiophorite within voids (Fig. 6).

5 Conclusion

Mn-rich regoliths developed the highest Mn ore grades in the higher-elevation and oldest plateaus (<14 Ma) at Okouma and Bagombé. Prolonged chemical weathering and a higher hydraulic gradient led to increased hydrolysis, as evidenced by the presence of gibbsite over clays (kaolinite and illite) and goethite over hematite, releasing most of the SiO_2. However, some younger (<6 Ma), medium-grade regoliths occurring in lower-elevation plateaus with lower hydraulic gradients accumulated Ni, Co, Cu, Zn, and Li at the base of the Mn ore due to conditions favouring precipitation of lithiophorite.

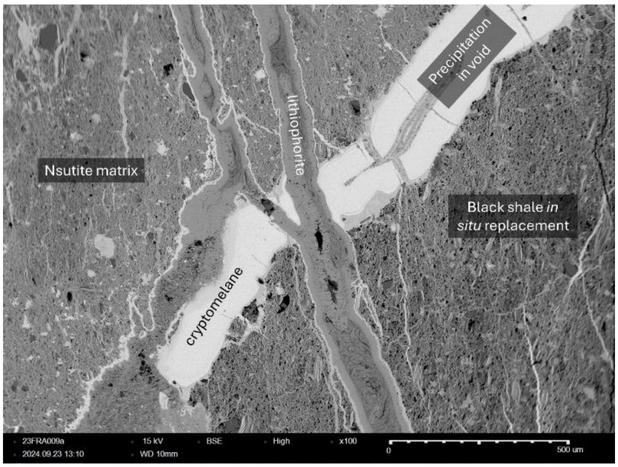

Figure 6. Petrogenetic relations in the platy Mn ore of the Franceville Mn-rich regolith (SEM view under BSE mode).

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