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Petrography and Mineralogy of Manganese Nodules Around Madaka, Tegna Sheet 143 SE, North Central Nigeria

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ABSTRACT

Petrographical and mineralogical characterization of manganese nodules around Madaka, north central Nigeria has been examined using ore microscopy and X-ray Diffraction for the clay in the study area. These rocks comprise of (migmatitic gneiss, banded gneiss and granitic gneiss, kyanite-sillimanite schist, semi-pelitic schist; amphibolites, talcose rock, quartzite, and phyllite, granodiorite, fine-medium-grained granites and porphyritic granite. Manganese nodules were found as concretions of different size dispersed in a variegated clay as hosted by kyanite sillimanite schist. The ore microscopy of manganese nodules reveals spessartine, cryptomelane / birnessite, jianshuite, and pyrolusite as major minerals. The gauges in the studied nodules constitute calcite, hematite, a trace of quartz and pyrite. The X-ray Diffraction of the clay indicates the presences of Illite/mica, smectites and kaolinite/halloysite as major minerals. Traces of mn and quartz were observed as gauge in the clay. The mn nodules in Madaka area are apparently controlled by physico-chemical factors (environment, heat and water). The appearance of pyrolusite and cryptomelane at an intermediate stage of oxidation rather than end product is considered the result of the acidic environment and the high potassium content of the host rocks. The source of the manganese nodules around Madaka area is at a considerable distance and consisted probably of a moderately basic igneous or metamorphic rock, which underwent disintegration, leaching and, the manganese nodules being transported in solution to its present state under influence of redox reaction through hydrothermal process.

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Introduction

Manganese with symbol (Mn) is a naturally occurring element that is found in rock, soil and water [1]. It is the tenth most abundant element in the Earth's crust (Webb, 2008). Manganese rarely exists in its pure, elemental state but instead combines with other elements in nearly 300 different minerals [1]. Manganese nodule is one of the major sources from which economically mineral from which Manganese (Mn) and iron (Fe) is being extracted [2,3]. The metals of greatest economic interest, however, are manganese, nickel, copper, and cobalt. In addition, there are traces of other valuable metals-such as lithium, rare-earth elements, and molybdenum-that have industrial importance in many high-tech and green-tech applications and can be recovered as by-products from the manganese nodules [4,5]. Other sources come from its ore and mineral oxides such as braunite ($\text{Mn}_2\text{Mn}_6\text{SiO}_{12}$), haussmannite (Mn_3O_4), pyrolusite (MnO_2), spessartine ($\text{Mn}^{2+3}\text{Al}_2(\text{SiO}_4)_3$), psilomelane ($\text{BaMn}_9\text{O}_{16}(\text{OH})_4$), manganite ($\text{Mn}_2\text{O}_3\cdot\text{H}_2\text{O}$) and Wad birnessite (Na, Ca, K) (MnO_2)₄ (H_2O)₃ [6]. In Nigeria, the ever increase for Mn and Fe in metallurgical industries calls for an

alternative mean of bridge the gaps between the sources and the routes for beneficiations. The Manganese nodules from Madaka lie in the southern part of the Tegna Sheet 143 SE, located on Latitude 10° 3' 33"N and Longitude 6° 27' 33"E. The area was an ancient massif that was uplifted gradually and exposed after a long period of erosion. The elevation of the Madaka the nodules occur range from 150 to 450m above the sea level. Madaka area appears to be inclined gently to the north, at the elevation of 400m high. The relief over the Madaka area is not pronounced with the exception to the granodiorite 2km away to Madaka. Gently sloping hills were also presents around Spina, Kagara, kwai, Durumi, and Godo area. The principal valley in the study area follows the trend of the faults, which is NE-SW, whereas the minor once strike NW-SE (Figure 1). This structure controlled the rivers system in the study area. At the north west, River Luga with many tributaries flow north west area and River Durumi from the north central have many tributaries from the north east which later joined River Luga, the tributaries from Supana, Wayan and Kunukunu also joined the main River Luga which flow southwest ward. The aim of this study is to summarize the petrographic and mineralogy of manganese nodules around Madaka area.

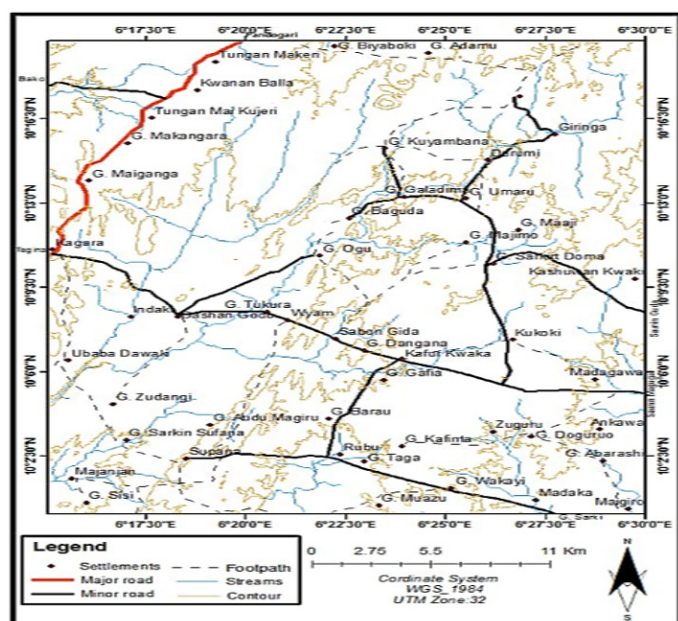


Figure 1: Location, accessibility, drainage and relief map of Madaka area

Figure 2: Schist belt localities within the context of geology of Nigeria and occurrence of manganese deposits Modified after [25-27].

Previous Works

Early workers on the Nigerian basement complex observed that the terrain has undergone a complex and long history of deposition, deformation, metamorphism and igneous activity [7-11]. Each worker erected a sequence of events based on the field relations [12,13]. The younger metasediment or schist belts occurs along north-south trending troughs which are infolded within the Migmatite- Gneiss Complex (MGC) down to the western half of Nigeria are [7,13-22]. Occurrences of manganese deposits have been reported in northwestern Nigeria schist belts [23-28] (Figure 2). The very well- constrained distribution of manganese formation in space and time is a characteristic of great scientific interest. It is well-documented that the vast majority of manganese formation was deposited during the late Archaean-palaeoproterozoic manganese deposits within this age are found in several parts of the world and exhibit remarkable petrographic and geochemical similarities [26,29-31]. Many classification schemes have been proposed for the vast number of manganese-iron formations occurrences of the Precambrian [31-33].

However, most authors agreed that, besides the superior-type occurrences, the majority of the remaining manganese – iron – formations are found in Archaean greenstone-terranes and Neoproterozoic glacio-marine sedimentary successions [31,34]. The co-genetic links between manganese and iron – formation differ in many in many respects, particularly in terms of geotectonic setting and origin [26,35]. In the Kushaka schist belt the work of provides insight into the geotectonic evolution of the area [36]. The tectonic fabric and igneous reactivation zones of this suite area attributed to the Pan-African age (-600 Ma) [37]. The geochronology evidence and structures preserved in this crystalline complex, show that the rocks belong to Archaen-Early Proterozoic succession [38]. All-important Phanerozoic manganese deposits were formed during transgression - regression cycles triggered by greenhouse conditions followed by oxygenation. However, all such cycles did not necessarily produce manganese deposits of economic value during the early Palaeozoic (Akintola 2022 in press).

The observable features of the under a reflected microscope were the zones of different phase, growth habits were observed within the radius of the mn nodule from Madaka sample (Plate 1) The manganese nodules in the study area contain the following minerals: spalerite 45%, birnessite 22%, jianshuite 12% and pyrolusite 13% (Mn oxides). The gauges in the studied nodules constitutes calcite 4%, hematite 2%, a trace of 1% of quartz and an opaque mineral (pyrite)2%. The radius of a nodule from Madaka in a reflected light microscope was presented in (Plate 1).

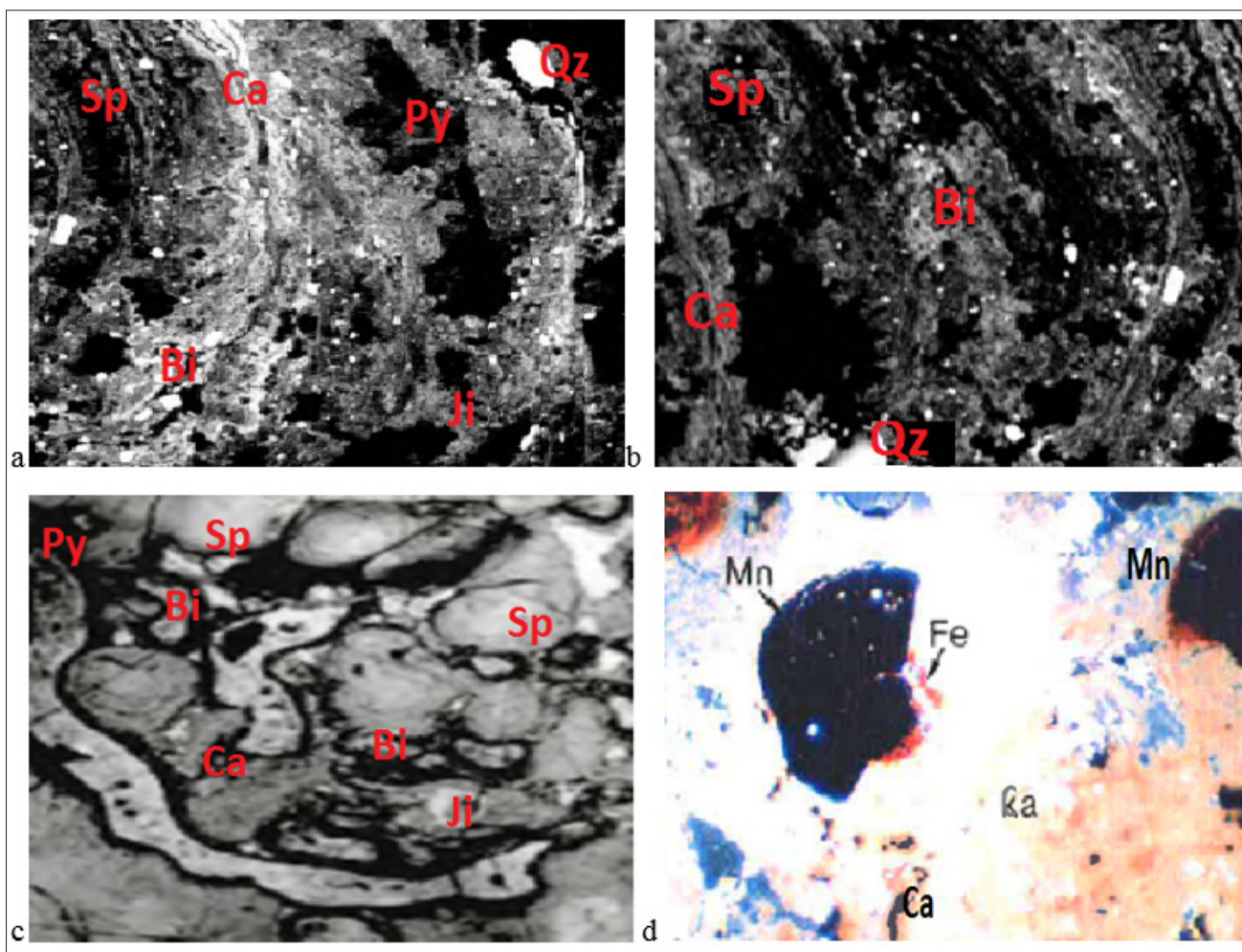


Plate II: Reflected light microscope of nodules from Madaka (a) a crystal of spalerite-birnessite surrounded by pyrolusite (Py), (b) Spalerite (Sp) filling a post-depositional crack in disperse or forming aggregates (C) partially pseudomorphed by spalerite which is paragenetic with Fe-Mn rhombic crystals (Sp + Bi) and (d) Rhombic crystal of iron and manganese within the nodule with the calcite filling the void space.

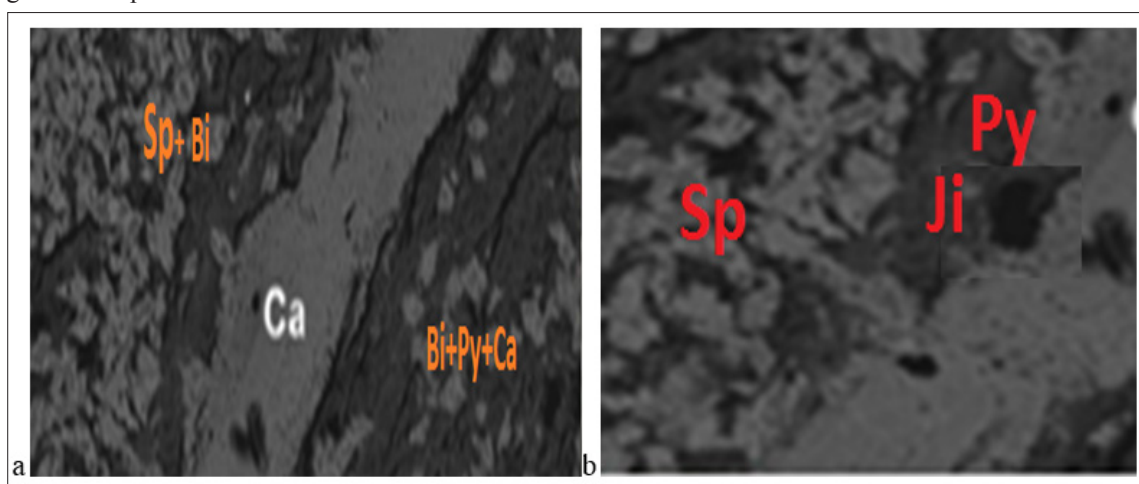


Plate III: Reflected light microscope of manganese nodules from Madaka quarry area (a) spalerite-birnessite in a rhombic crystals (Sp + Bi) surrounded by pyrolusite (Py) and crosscut by a post-accretional crack filled with calcite (Ca) and (b) Spalerite (Sp) grains scattered within the nodule.

The mineral phases of the clay were identified with the xrd pattern (Figure 4) in accordance with the mineral phases. Quartz is the most abundant non clay mineral while calcite and feldspars are accessory minerals.

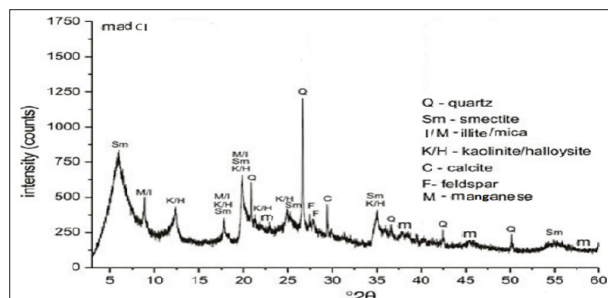


Figure 4: XRD spectra for clay from Madaka area

Clay: Illite.....>Smectites> kaolinite Equation (i)



Plate IV: Exposure of Kyanite – sillimanite schist around Madaka (Latitude 10° 5' 47" N and Longitude 6° 25' 34" E)

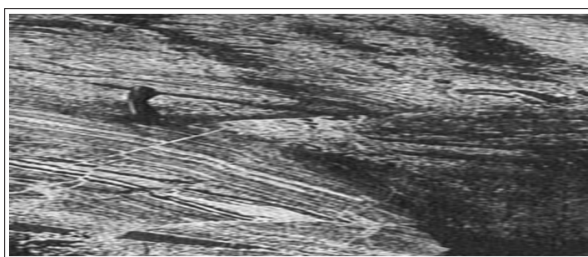


Plate V: Photograph of banded gneiss around Gidan Sisi the darker layers showing extension of pre-tectonic dykes at a low angle to banding (Latitude 10° 5' 47" N and Longitude 6° 14' 23" E).



Plate VI: Photograph of semi-pelitic schist around Gidan Sisi, the (Latitude 10° 6' 41" N and Longitude 6° 21' 22" E)



Plate VII: Highly deformed siliceous phyllite around Gidian Kafinta (Latitude 10° 22' 47" N and Longitude 6° 16' 23" E)



Plate VIII: The granodiorite around Madaka (Latitude 10° 00' 52" N and Longitude 6° 27' 39" E)



Plate IX: Fine –medium grained granite showing crystals of K-feldspar, quartz, tourmaline and muscovite around Giriga (Latitude 10° 13' 42" N and Longitude 6° 17' 23" E)

Discussion

The internal structure of manganese nodules from Madaka is characterized with concentric banding which is developed to a greater or lesser extent in most of them (Plate 1). They are thought to possibly represent varying growth conditions during its formation. The low detrital content of the mn nodules themselves suggest that erosions was not vigorous at the time. It is noteworthy that although the amount of iron in the mn nodules is low, the patterns of Fe and Mn distributions, where investigated are similar. This, thogether with the remarkably localized high concentration of Mn suggests the operation of two or more influences it its formation. Most manganese deposition within the intracratonic and rifted continental margin basins derived their source from terrestrial weathering, diagenetic-hydrogenetic processes and hydrothermal effluent respectively. The photomicrograph of mn nodules shows the layer of spalerite-birnessite in rhombic crystals (Sp + Bi) surrounded by pyrolusite (Py) and crosscut by a post-accretional crack filled with calcite (Ca) Plate Ila-b). The pyrite aggregate formed by framboids (inside) and idiomorphic cubic crystals (outside), partially pseudomorphised by spalerite which is paragenetic with Fe-Mn rhombic crystals (Sp + Bi), Jianshuite (Ji) filling up a void next to microcrystalline spalerite (Sp) with scattered grains. Spalerite (Sp) filling a post-depositional crack in disperse or forming aggregates (Plate Iic-d). The southern part of Madaka area, is covered up with clay of different types. The host or wall rock in the district is the variegated clay overlaying the kyanite sillimanite. The grain size of the manganese nodules, for the most part, is colloidal and its mineralogy is rather uniform. Factors such as the size of the nodules, sediment on the surface of the nodules, and how often the nodules are turned influenced the formation and source of manganese nodules in the study area. Diagenetic nodules tend to be rougher. Hydrogenetic nodules, in their most pure form, have a botryoidal surface (shaped like a bunch of grapes) that can be smooth or rough, but usually falls somewhere between those two extremes. If the surface is very smooth, it was likely worn down by bottom currents, hydrothermal process [39-41]. The leaching of manganese and

iron may take place together or one in preference to the other. Selective leaching of manganese with respect to iron can occur by enzymatic microbial reduction. In the Mn -Fe- Al triad, the solubility of manganese is maximum (as is its mobility) and hence, during downward movement of iron and manganese in solution, a change in Eh-pH may lead to precipitation of iron in preference to manganese and an effective separation between the two may take place. Where the weathered profile attains sufficient thickness, the upper zone is depleted in manganese which travels deeper and is re-precipitated in the lower zone [28]. Most manganese deposition took place in intracratonic and rifted continental margin basins and the source of manganese was inferred to be terrestrial weathering in one hand and hydrothermal effluent on other side [28].

According to XRD pattern in the mineral phases, the principal clay mineral is smectites with lesser quantities of illite, and kaolinite figure (3) equation (i). Calcite, feldspars, and manganese oxides are also present. The color of the clay layers or bands is controlled by the proportion mineralogical form, the acid–basic character (pH and ionic strength) and the Iron-manganese ratio of the manganese minerals present the rock and gray colours alternate with each other. The compact, hard layers of nodules are separated from each other by thin laminae of red and brown clay. The layered of the nodules consists of an intergrowth of fine aggregates and acicular crystals of pyrolusite. Its grain size, for the most part, is colloidal. In adjourned area, clay is present in various parts of the Maikuri, locally in the form of a flat, elongated discontinuous body, or as a thin layer between the black manganiferous clay layers. Because of its soft disintegrating nature, it is not suitable for mineralogical examination, and its mineralogical composition is not known, though the principal minerals of the very soft and plastic clays belong to the montmorillonite group. In the study area, the common of the clay minerals are those of illite and kaolinite groups. The illites of the sediments were deposited as such after their formation by weathering of silicates, principally feldspars as evidenced from the granodiorite, pelitic schist and other associated rocks, but in phyllites, its occurrences of clay minerals are deprived by alteration of other during diagenesis. The illites formed from hydrothermal process as manganeseiferous quartz veins underneath the kyanite sillimanite schist which served to be alteration zones around metalliferous veins. The kaolinite groups are formed principally by the hydrothermal alteration (accompanied by quartz, muscovite, pyrite and other clay minerals) or weathering of feldspars, and other silicates. Field observation and mineralogical evidenced in the study area indicates that the rocks which altered to kaolinite are usually the more acid types (fine-medium granite, porphyritic granite and granodiorite) while the montmorillonite results sodium-rich and calcium rocks. The kaolinite that produced this alteration sometimes occurs in situ be product of weathering and transportation.

Variation in the composition (and colour) of biotities with different grade of metamorphism also occurs around Madaka rocks and in many cases decrease in Fe^{2+} , Mn and Fe^{3+} and increase in Ti and Mg can be correlated with increasing grade of metamorphism in most of the associated rocks in the study area.

Smectites/Montmorillonite results from the weathering of basic rocks mainly in conditions of poor drainage when magnesium is not removed. In good drainage conditions magnesium is leached and kaolinite results others factors favour the formation of smectites are the alkaline environment, availability of calcium, and paucity of potassium. Alteration of basic igneous rocks yields Smectites/ Montmorillonite, and acid rocks tends to yields illites unless Mg and Ca are high and K low in concentration: The textural relations

in many pelitic and semi pelitic sediments do not suggest that the biotite forms at the expense of any specific pre-existing materials; but the increase in the biotite in the biotite zone is coincident with a decrease in chlorite and especially in muscovite.

Conclusion

Petrographical and mineralogical characterization of manganese nodules from Madaka area reveals spalerite, birnessite, jianshuite, and pyrolusite (Mn oxides) as major minerals. The gauges in the studied nodules constitute calcite, hematite, a trace of quartz and an opaque mineral (pyrite). The X-ray Diffraction of the clay indicates the presences of Illite/mica, smectites and kaolinite/halloysite as major minerals. Traces of mn and quartz were observed as gauge in the clay. Manganese and iron are the principal metals in manganese nodules. The surface texture of nodules depends partly on the dominant mechanism of formation. Other factors that influence texture include the size of the nodules, the strength of bottom currents, sediment on the surface of the nodules, and how often the nodules are turned. The mineralogy of clay in the study area reveals that Illites results from the alteration of mica and feldspars, high Al and K concentration favoured from associated rocks in the study area. The alteration of basic rocks, volcanic materials, alkaline conditions with high Mg and Ca but low K concentration favoured the formation of Smectites/Montmorillonite: Kaolinite/halloysite results from the alteration of biotite flakes or volcanic materials, chlorites and hornblendes.

The manganese nodules from Madaka is apparently controlled by physico-chemical factors such as the acid–basic character (pH and ionic strength), and thermodynamic conditions (pressure and temperature) of the surrounding medium (environment).

The source of the manganese nodules around Madaka area is at a considerable distance and consisted probably of a moderately basic igneous or metamorphic rock, which underwent disintegration, leaching and, the manganese nodules being transported in solution to its present state under influence of redox reaction. Based on the data on obtained, the manganese nodule occurrence in madaka area formed through hydrothermal process.

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