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Petrography and Mineralogy of Manganese Nodules around Madaka, Sheet 143, 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. The study area is underlain by rocks of the Nigerian Basement Complex. Some of the rocks in the area show metamorphic imprints, indicative of various degree of deformation they have suffered. These rocks comprise of gneisses (migmatitic gneiss, banded gneiss and granitic gneiss), the metasediments (kyanite-sillimanite schist, semi-pelitic schist; amphibolites, talcose rock, quartzite, and phyllite) and the granitic rocks (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 silimanite schist. Two importance varieties of Mn nodules (red and brown) occur in the study area. The ore microscopy of manganese nodules 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. The mn nodules from Madaka are apparently controlled by physico-chemical factors (environment, heat and water) in the area. 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.

Keywords: Petrography; Mineralogy; Manganese nodules; Madaka; Redox reaction

Introduction

Manganese with symbol (Mn) is a naturally occurring element that is found in rock, soil and water (Howe et al., 2004). It is the tenth most abundant element in the Earth^{1}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 source from which economically mineral from which Manganse (Mn) and iron (Fe) is being extracted (International Seabed Authority -ISA, 2010; Wilburn, 2012). 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 [2]. Other sources comes from its ore and mineral oxides such as braunite (Mn2Mn6SiO12), haussmannite (Mn3O4), pyrolusite (MnO2), spessartine (Mn2+3Al2(SiO4)3 psilomelane (BaMn9O16(OH)4), manganite (Mn2O3H2O) and Wad birnessite (Na,Ca,K)(MnO2)4 (H2O)3 [3]. 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 Tegina Sheet 143 SE, located on Latitude 10° 3^1 33^{11}N and Longitude 6° 27^1 33^{11}E (Figure 1). 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 occurs 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 Supana, Kagara, kwoi, Durumi, and Godo area.

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.

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 [4]. Each worker erected a sequence of events based on the field relations [5]. 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 [6].

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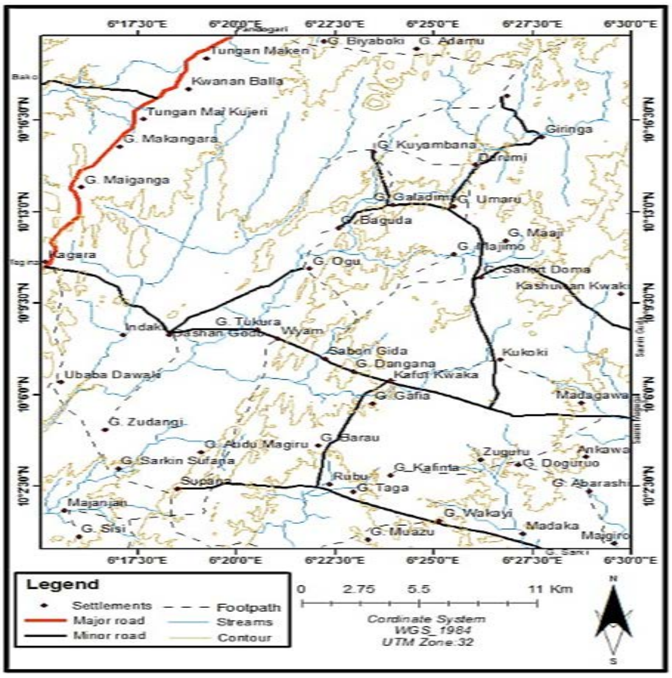

Figure 1: Location, accessibility, drainage and relief map of Madaka area.

Occurrences of manganese deposits have been reported in northwestern Nigeria schist belts [7] (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 (Gross, 1983, 1986), manganese deposits within this age are found in several parts of the world and exhibit remarkable petrographic and geochemical similarities [8]. Many classification schemes have been proposed for the vast number of manganese – iron formation occurrences of the Precambrian [9].

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. The co-genetic links between manganese and iron - formation differ in many in many respects, particularly in terms of geotectonic setting and origin. In the Kushaka schist belt the work of (Grant, 1978) provides insight into the geotectonic evolution of the area. The tectonic fabric and igneous reactivation zones of this suite area attributed to the Pan-African age (-600 Ma) (Ball, 1980). The geochronology evidence and structures preserved in this crystalline complex, show that the rocks belong to Archaen- Early Proterozoic succession (Dada, 1998). 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.

Methodology

The methodology adopted in the execution of this work consists field mapping and laboratory analyses includes ore microscopy, and differential thermal analysis. The detailed of surface sample preparation and ore microscopy was done according to Fuerstenau and Hau, (1977). The principle of employed for the X-ray Diffraction was in accordance with the Warsaw, (1996) at Nigerian Geological Survey Agency –(NGSA) Kaduna, Nigeria.

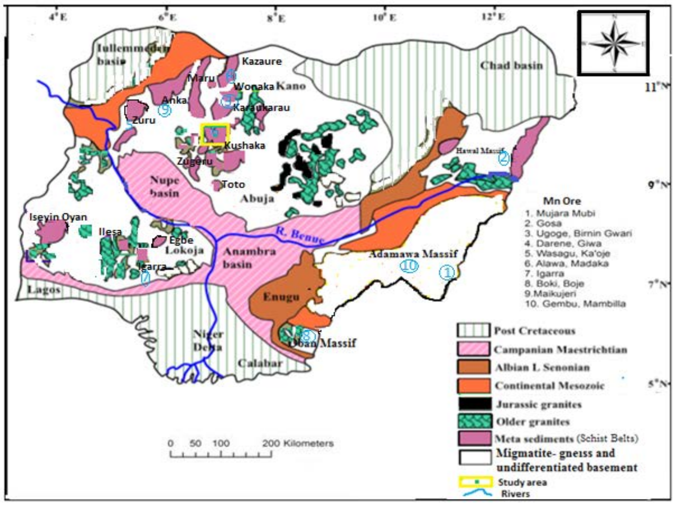

Figure 2: Schist belt localities within the context of geology of Nigeria and occurrence of manganese deposits (Modified after Woake et al., 1987, Mucke, 2005 and Akintola, 2019).

Results

The study area is underlain by rocks that are typical of the Nigerian basement complex Figure 3. Some of these rocks show metamorphic imprints in the area, indicative of various degree of deformation they have suffered. These rocks comprise of gneisses (migmatitic gneiss, banded gneiss and granitic gneiss), the metasediments (kyanite-sillimanite schist, semi-pelitic schist; amphibolites, talcose rock, quartzite, and phyllite) and the granitic rocks (granodiorite, fine-medium-grained granites and porphyritic granite) as shown on the geological map of the study area in Figure 3 except the minor rocks (the pegmatite and quartzite). The migmatitic–gneisses are extensive in the area, the rocks intruded by the Older Granites at the northern part truncating its massive extension from the western part of the study area to the eastern. It constitutes well over 45% of the rock types in the study area. In the southern part of the Madaka a well banded, somewhat micaceous quartzite with a minimum thickness of about 5 metres was observed. It is overlain here by kyanite- silimanite-bearing metasedimentary rocks which occupy a major synform and at one place displays cross-bedding indicating younger beds southwards towards indaki within the talcose rocks (Figure 3). The Older Granites in the study area are porphyritic granites, fine-medium grained granites and granodiorites. The porphyritic granites intruded the other rocks in the area especially in the southwestern axis and eastern part northwards, covering about 15% of the entire area while fine- medium grained granites covers 20% of the area notably in the northwestern and toward the southern part of the study area. The granodiorites are less abundant than the granites. They are characterized by gentle slopes, blocky and bouldery appearance and show exfoliation weathering. These rocks are characterized by jointing and exfoliation. They are usually sheared with fractures filled by veinlets of quartz. The amphibolites and phyllites constitute about 10% of the rock types in the area. Outcrops of the amphibolites in are lenticular, texturally distinctive and well oriented sub- parallel to the N-S foliated trend. In the extreme Northeast of the Gidan Usman domain, running up to Gidan Ogu, the phyllites dominates. It continues into the west of Gidian Sisi where the same rocks and relationships can be observed on several kilometres of river channels. The talcose rocks constitute about 2% of the rocks in the study area and occur in the southwestern part close to Kagara in Tsaunin Agwaru area in a ridge surrounded by amphiobolites, schists and the Older Granites. Outcrop of the talcose rock occurs as lensoid bodies of

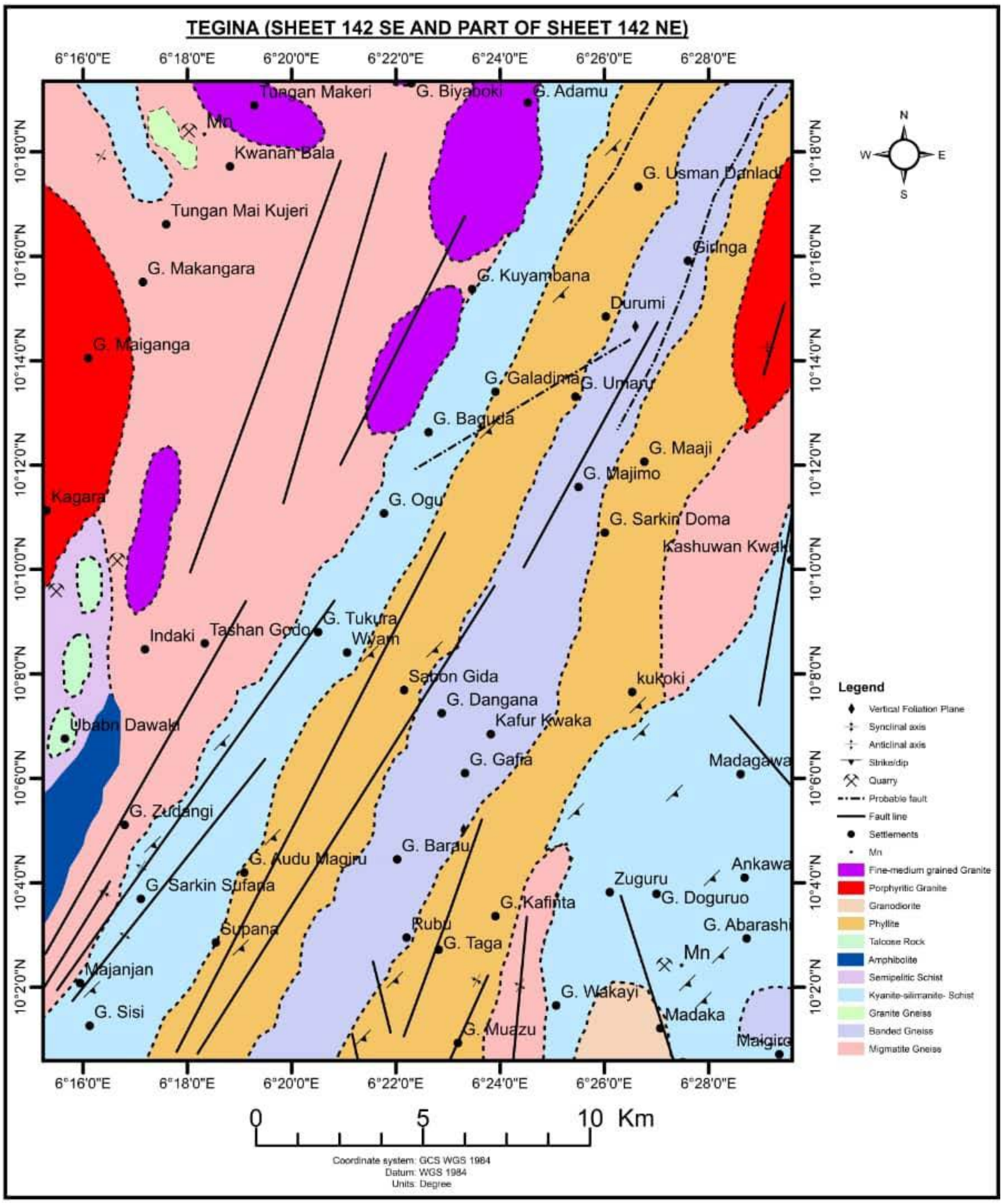

Figure 3: Geological map of the study area.

moderate size and length. It extends to the southwestern part having contacts with the migmatitic–gneisses and the Older Granites in an oval shaped outcrops of about 15 m above the surrounding ground surface. In the southern part of Kumunu, talcose rocks occurs as large inselbergs and massive exposures, and are bounded by the Older Granites and migmatitic gneiss in the western and eastern sides. The talcose rock truncate the linearly elongated north - south by quartzites. The talcose rocks are largely extensive in Kagara area with different grade, colours, sizes, and textures. The colour of talcose rock varies from grey, white to pale brown colour with a soapy feel when handled. In this area, the greatest thicknesses of quartzitic rocks are to be found southwest of Kagara. Around Kumunu area, several thick units make up the NW of a major antiformal structure (the Dome) and have been commercially exploited for many years (Figure 2). A similar large quarrying operation was located in a thick quartzite unit on Kagara 1.5 km east of Tegina. In both areas, recrystallization is extreme and no sedimentary structures have yet been reported. Circular to elongated intrusive bodies of granodiorites, fine –medium grained granite and semi-pelitic schists occur within the Madaka area. Granodiorites intrusions sometimes contain small (20 cm) xenoliths of the sequence and shows narrow zones (50 meters) of contact metamorphism with sillimanite. A large area occupied by metasedimentary rocks including quartzites and kyanite-sillimanite schist occurs in the Southeastern part of the study area, more specifically around Madaka. The metamorphosed kyanite-sillimanite rock overlies the manganese ore deposits in the study area. This unit runs in N-S direction in the southeastern part of the study area around Madaka and also occurs in the north towards the west around Kwana- Bala though not as massive as in southeastern part of

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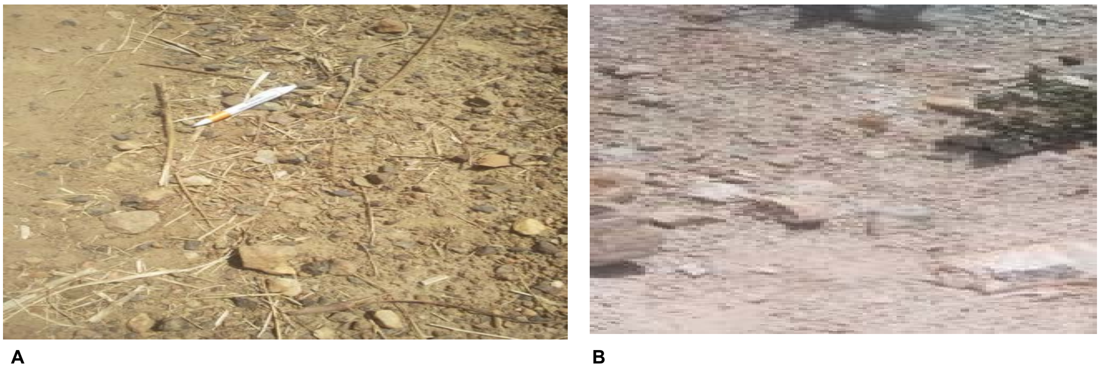

Figure 4: Field occurrence of manganese nodules within the lateritic materials (A) yellow- brown (Latitude 10° 3¹ 44¹¹N and Longitude 6° 28¹ 23¹¹E (B) red-brown (Latitude 10° 3¹ 44¹¹N and Longitude 6° 28¹ 55¹¹E).

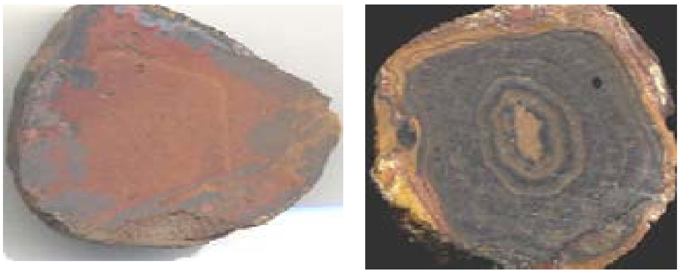

Figure 5: Milankovitch cycle with special emphasis on (a) eccentricity and tilt and also Earth precession ((a) and (b)).

the study area. The dominant rock units which hosts the manganese ores in both Madaka and Kwana-Bala is the quartzite. The quartzites are invariably steep dipping and are commonly associated with fracture and shear zones. The manganese nodules in Madaka characterized with an irregular distribution and varying in thickness. The diameter of the concretions varies from 0.1 to 1.45m being most commonly of fist. The nodules have concentric structures and are impregnated with silica. Cavities are common in the centres of the concretions of the walls of which are covered with crystals of quartz and pyrolusite. The most important tectonic feature in the mapped area is the Ogu fault, situated in the western part which forms the contact between two quite different sequences of rocks. The sequence occurring to the east of the fault has a general strike of NE-SW, dips westward and consists of semi- pelitic schists, and talcose rock, amphibolites which have been subjected to greenschist facies metamorphism. It is strongly folded and the main foliation of the schists strikes between N08E and N20W, and dips 15-30W. All the rocks observed on the field show the evidence of regional metamorphism and ductile deformation. The laterite hills behind Gidan Bana and laterite boulders which are chemical weathering products contains of manganese nodules, a widespread clay soil cover the area form a thick overburden, in a wide gentle undulating plane. Within the Madaka area, two generations of laterites were recognized; the red- brown and the yellow-brown varieties (Plate iv).

The red- brown variety is relatively free of impurities. It is porous with iron-rich concretionary materials. They occur mainly at the hill tops. The yellow-brown variety on the other hand is a secondary laterite and occurs locally on the clay particles, along the stream and break of slopes. They are less porous and less cellular with higher proportions of impurities than the primary laterites (Plate v).

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 vi) The manganese nodules in the study area contain the following minerals: spalerite 45%, birnessite 22%, jianshuite 12% and pyrolusite 13% (Mn oxides). The gauge 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 vii).

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 (Figure 5). 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, together 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 IIa-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 (Hayes *et al.* 1992; Hein *et al.* 2000). 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- A1 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 [10]. 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 [11].

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 manganeferrous quartz veins underneath the kyanite sillimanite schist which served to be alteration zones around metalliferrous 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, porpyhritic 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 depend 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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