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Petrochemical Features of Manganese Nodules in Madaka (Sheet 142) SE and Part of Kwana - Bala (Sheet 142) NE, Nigeria

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Abstract

Manganese nodule occurs in Madaka (Sheet 142) SE and part of Kwana - Bala (Sheet 142) NE, Nigeria. Four (4) samples of manganese nodules were analyzed petrochemical using X-ray diffractometry (XRD), reflected light microscopy, Electron probe micro analysis (EPMA), Atomic absorption spectrophotometer (AAS). XRD reveals sphalerite, manganates and ilmenite as major minerals in the nodules. Accessory minerals are siderite and rutile. Chemical study of the manganese nodules from Madaka and Kwana - Bala reveals that Mn-, Fe-, Co-, Ni-, and Cu-, minerals (including native elements and sulfides) commonly occur in the samples. Also, the results indicate that increased in Mn relative to the manganite content (10AO- plus 7AO), led to increase in Ni and Cu recovery. However, slightly greater amounts by weight of Ni and Cu were dissolved from the manganites than from Mn. This followed from the much higher Ni and Cu contents of manganites relative to Mn. The exploration for Ni and Cu from nodules on assay criterion was inadequate; the sphalerite Mn02 phase structure would also be a necessary criterion. It was suggested that nodules could be processed upon beneficiation for Ni and Cu contents for a future time relative to the original processing. It was thus proposed that Ni and Cu could be produced from manganese nodules in the study area.

Keywords: Manganese nodules; Ore; Madaka; Kwana-Bala; Beneficiation.

1. Introduction

Manganese ore play unique roles in metallurgical industries. Maganiferrous deposits is usually of economic values when the deposits proves to be profitable by considering factors such as composition, available tonnage, mining costs, timing of capital investment and revenue, location, magnitude and processing costs, etc. Manganese nodules have also been discovered in many parts of the world e.g. Atlantic Ocean, the Indian Ocean, Scottish lochs, British Columbia fiords, the Blake Plateau off the eastern coast of Florida, Madaka in Kushaka schist belt of Nigeria and amongst other locations depends on metal contents extracted from the manganese ores and nodules [1]. Presently, in Nigeria the local steel industries have continued to depend on imported source of manganese; this is because no test on local manganese deposits has been carried out. The ever increasing demand for steel products has continued to put pressure on federal government to complete the construction work at the nation's steel producing plant which, will result in the need for a local manganese concentrate [2]. No satisfactory substitute for manganese in steel production has been identified as at present globally in application as sulphur fixing through desulphurizing, reduce oxygen level through deoxidizing, and it enhances mechanical properties [2].

2. Previous Work

Few studies focused on gold, Banded Iron Formations (BIFs) and magnetite that are found alternating with manganese ores in the study area includes; Moneme, *et al.* [3]; Mucke and Okujeni [4]; Mucke, *et al.* [5]; Mucke and Annor [6]; Mucke [7, 8]. The study by Adekoya [9] used magnetic field data to unveiled hydrothermal fluids from the basic rocks where gold mineralization occurred by metasomatic ionic exchange. [8] revealed the association between BIFs and manganese in the study area. He recognized the presence of sedimentary cycles of BIFs and braunites, lutite in the area. He drew attention to the fact that the vast majority of manganese deposits are of sedimentary character and emphasized on the importance of additional processes like sea-floor, volcanic activity, sea level fluctuations, climate changes, biological productivity as critical in the development of large accumulation

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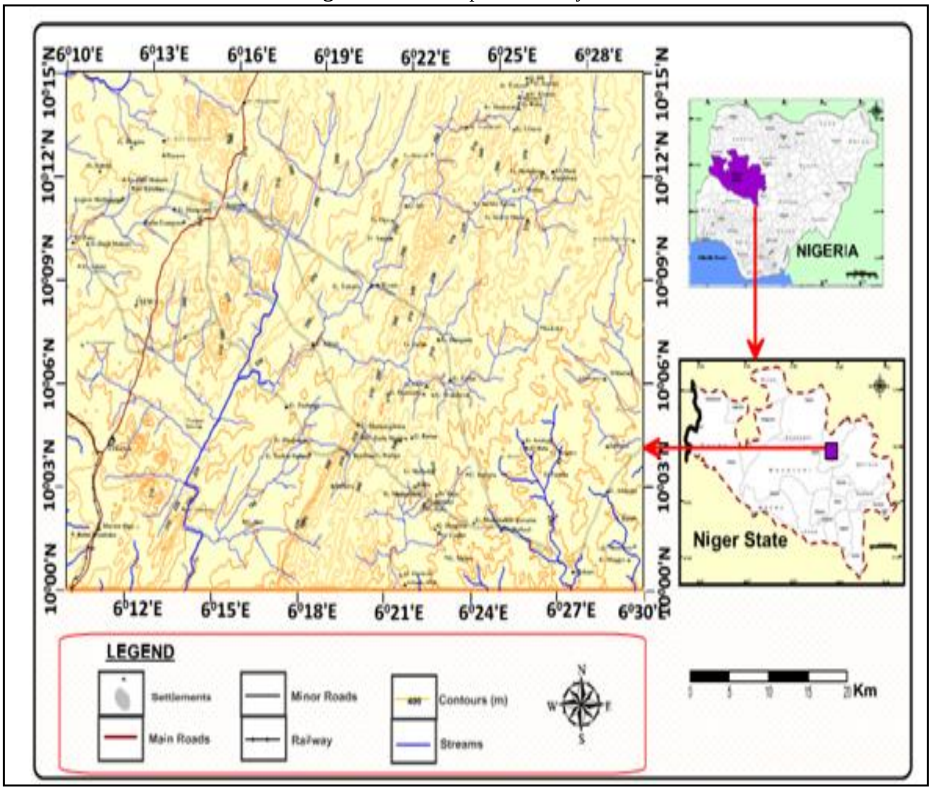
of magniferrous sediments in depositional environment. Other works done in the study area were related to beneficiation of manganese ores [10, 11]. The investigation carried out by Muriana, *et al.* [11] in Madaka focused on appraisal of manganese deposits in the study area with the emphasis on its metallurgical features. Muriana, *et al.* [11], produced crystals of manganese II sulphate having 97% purity after purification process using dilute sulphuric acid as solvent. Muriana [10], affirmed the hydrometallurgical extraction of manganese metal by thermal decomposition of the purified manganous nitrate (MnN_2O_6) crystals to synthesized the chemical manganese dioxide (CMD) from Madaka area. Ejepu, *et al.* [12] defined TiO_2 (rutile) and MnO_2 (pyrolusite) as gangue mineral as in gold within the oval shaped of high magnetic zones in the study area. However, apart from the aforementioned previous works in the study area, there are no documented studies on petrochemical and mineralogical assessment of manganese mineralization a major reason for this work figure 1 gives the location map of the study area.

Fig-1. Location map of the study area



3. Methodology

Four out of forty manganese nodules collected on the field were used. Colour determination was based on comparison with charts of Munsell Color Co [13]. The apparent wet bulk density and open porosity were determined by water absorption in void according to the UNE-EN 1936:1999 normative.

Real dry bulk density was obtained by helium pycnometer method. Two (2) selected samples consist of one (1) representative sample each of manganese nodules collected from Madaka and kwana Bala area and were analyzed for X-Ray Diffraction (XRD) at Nigerian Geological Survey Agency, Kaduna.

About 1 kg of each sample was broken into pieces with a hammer and crushed into smaller piece with a jaw crusher. The samples were thereafter pulverized in a disc mill for about two minutes. Each pulverized sample was thoroughly homogenized to obtain a representative portion. X-ray Diffraction analysis was performed on a Panalytical Pert Pro 29 diffractometer, equipped with a Cu X-ray source and an X'celerator detector, operating at the following X-ray settings: voltage: 40 kV; current: 40 mA; range: 5-70 deg 2θ; step size: 0.017 deg 2θ; time per step: 50.165 sec; divergence slit: fixed, angle 0.5°.

The crystalline mineral phases were identified in X'Pert High Score Plus using the PDF-4Minerals ICDD database.

Multi-elemental spot analyses and mapping profiles, in mineral phases and textural features, were carried out in the interesting areas determined by petrographic studies using electron probe micro analysis (EPMA) with aJEOL SuperprobeJXA-8900 M, operating at 15-20 kV and 50 mA, fitted with wavelength dispersive spectrometers (WDS).

Pulverized samples of manganese nodules were analyzed for elemental composition at the Activation Laboratories Limited (ACTLAB), Ancaster, Ontario, Canada using Atomic Absorption spectrophotometer.

The sample was dried by warming in an oven at 110°C for about 15 minutes and storing over silica gel for 24 hours. The sample was weighed accurately (about 1.5g), transferred to a 150m1 beaker, and water added to just cover the sample. 30m1 of HC1 was added and the sample was allowed to digest at 80°C for 4 hours;10m1 more of HC1 was added, and digestion continued for 1 more hour; the latter sequence was continued until dissolution of the Mn/Fe-oxides was complete. The solution was filtered, the residue washed and the filtrate diluted to 250m1. Dilutions were made from the filtrate for assay to the schedule: undiluted, x5, x10, x50, x100, x500, and x1000 dilutions. The samples were assayed for Mn, Fe, Co, Ni, and Cu using the atomic absorption spectrophotometer.

Standard solutions for each element were prepared to a concentration of 500ppm using sulfate salts and 0.1N H_2SO_4, Working standard solutions were prepared in 50m1 volumes by diluting the stock solutions. An appropriate set of standard solutions was 2, 5, 10, and 20ppm concentrations. Absorbance values were obtained for the various elements by spraying the solutions in the sequence of standards, unknowns, standards A 'working' curve was made by plotting the average absorbance values of the two sets of readings on the standard solutions versus the concentrations in ppm of the standards and The concentration of the unknown solutions was found by an appropriate comparison on the working curve of the absorbance values obtained on the unknown solutions.

4. Results and Discussion

4.1. Geology of the Study Area

The study area, (Fig. 2), contains migmatitic gneiss, banded gneiss, granitic gneiss, amphibolites, Kayanite–Silimanite schist, talcose rock, phyllite, granodiorite, porphyritic granite, fine-medium grained granite, and manganiferrous as major rock units. Migmatitic–gneisses are extensive in the area, intruded by the Older Granites at the northern part truncating its massive extension from the western part of the area to the eastern. It constitutes well over 52% of the rock types in the study area. The Older Granites in the study area are porphyritic and fine-medium grained granites. The porphyritic granites intruded the other rocks in the area especially in the southwestern axis and central part northwards, covering about 30% of the entire area while fine- medium grained granites covers 4% of the area notably in the northeast and toward the central part of the study area. The amphibolites and phyllites constitute about 8% 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.The talcose rocks constitute about 6% of the rocks in the study area and occur in the northwestern part close to Kagara in Tsaunin Agwaru area in a ridge surrounded by amphibolites and the Older Granites. Outcrop of the talc occurs as lensoid bodies of 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 massives 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 amphibolite bodies (Fig. 2). The talcose bodies are largely extensive in Kagara area with different grades, colours, sizes,and textures. There are metamorphosed Kayanite–Silimanite schist.Manganese hydrated-oxides are a common constituent of ocean sediments. They occur primarily as micro-nodules of diameters less than 0.5mm and nodules of diameters ranging from 0.5 to 25cm (average diameter of 3cm). A photograph of terrestrial nodules from Madaka and Kwana-Bala is presented in Plate 1. The figure shows a tabular to irregular big nodules as shown in images KB (1-4). The photographs M (1-4) show sub-spherical to spherical small nodules. The external layers are affected by alteration front discontinuity, especially visible in the pictures.

Plate-1. Photographs showing the morphology of the internal features of the nodules

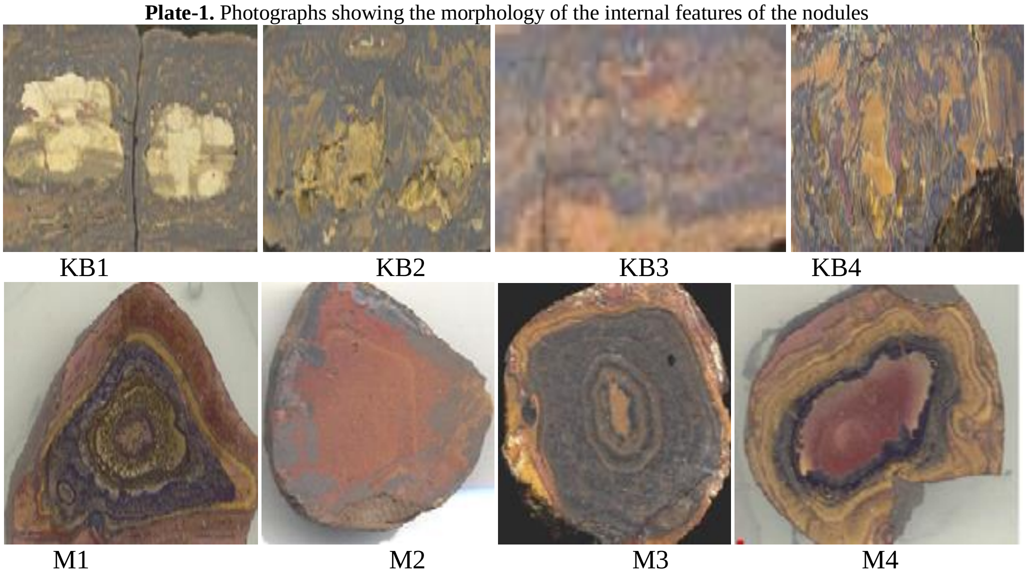
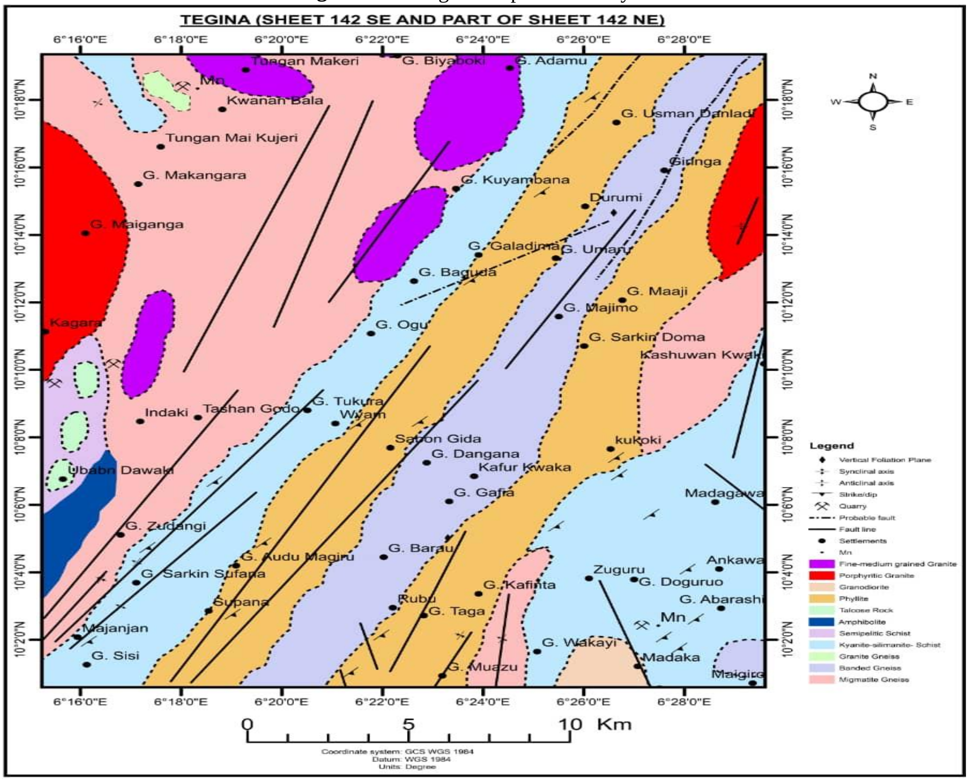


Table-1. Physical features of the nodules from the study araes

Sample	Kwana –Bala	Madaka
Colour (appearance)	irregular, black	rounded, brown
Apparent S.G	1.4	4.02
True S.G.	3.17	45
Total porosity	48	1.9
Average diameter (cm)	2.2	wide size

A geological map of the study area presented in Fig 2. shows marked location (Madaka) and Kwana Bala where most of the nodules have been found to date (Figure 2).

Figure-2. Geological map of the study area



4.2. X-RAY Diffraction Studies

Four representatives of manganese samples collected from Madaka and Kwana Bala were studied by X-ray diffraction to identify their mineralogical constituents in nodule materials. X-ray diffraction patterns were used to identify the mineralogical phases present in nodule materials. The X-ray diffraction patterns (Fig 2) indicate that the mineralogical composition of manganese nodules of the two areas are quiet similar. They are mainly composed of Mn oxides (7 A manganates and 10 A manganates) and spalerite, ilmenite, quartz, and phyllosilicates. Although, it is difficult to differentiate between the two magnaese nodules based on mineral composition. Accessory minerals are rutile, siderite, pyrite, chalcopyrite, potassium feldspar, zircon, and chlorite. The slight differences in X-ray diffraction pattern between Madaka and kwana bala nodules arise from structural changes brought about by additional processing, especially heating. Inspection shows that virtually all the diffraction lines in the patterns from the nodule samples are accounted for either as Mn-oxide lines or as insoluble material lines, and that the insoluble material is probably composed of quartz and plagioclase feldspar. Comparison of the X-ray intensities for Mn, Fe^{2+} Ni, and Cu as recorded by an area scan and given in Plates II (KB and M) shows that iron is less evenly distributed than Mn; both Ni and Cu concentrations increase relatively in the Fe-poor areas but the Ni concentration has a notice-able variation within these enriched areas. The correlation of high reflectivity material as iron-poor and the low reflectivity material as iron-rich is confirmed. It is also confirmed that the iron-poor areas are relatively en-riched in Ni and Cu compared to the iron-rich areas (Fig. 2).

Figure-3. (top): Powder XRD spectra for samples kwana Bala areas

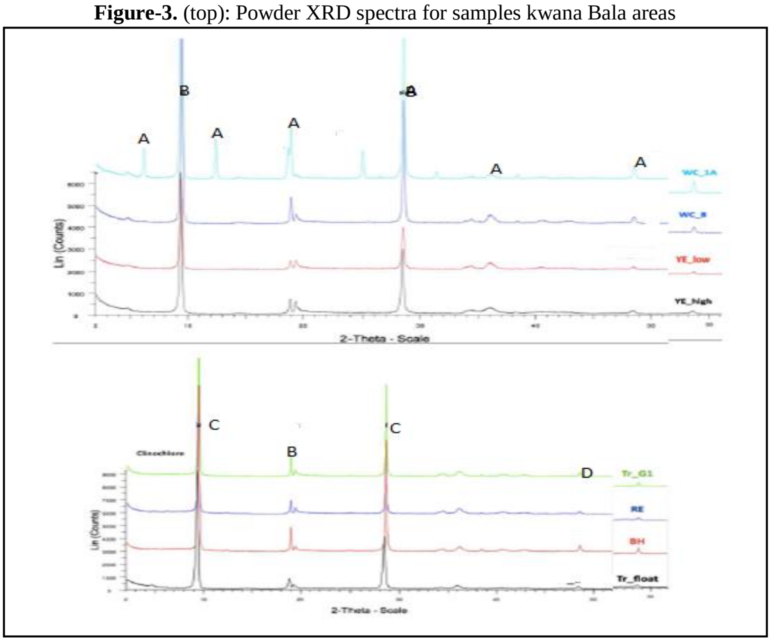


Fig-4. EPMA distribution for Mn, Fe Ni, Cu and Co

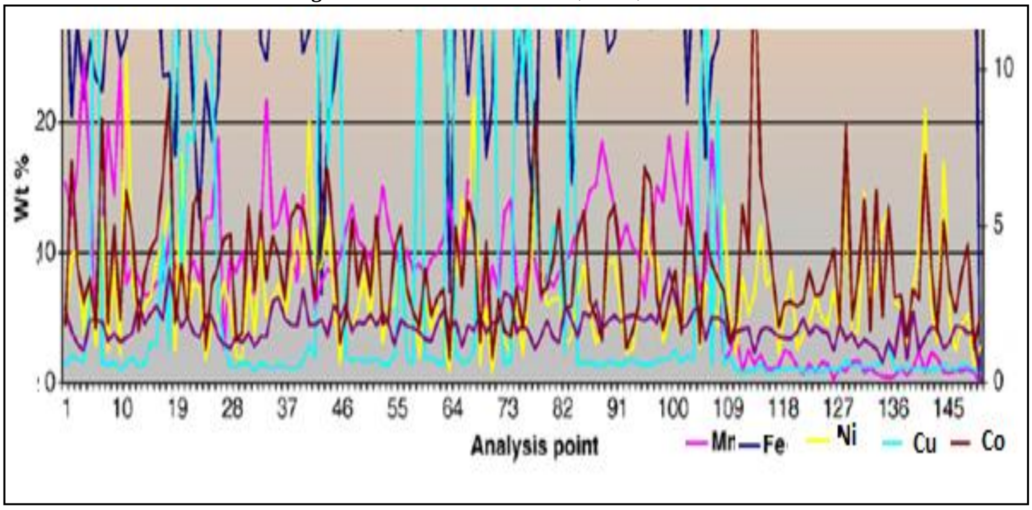
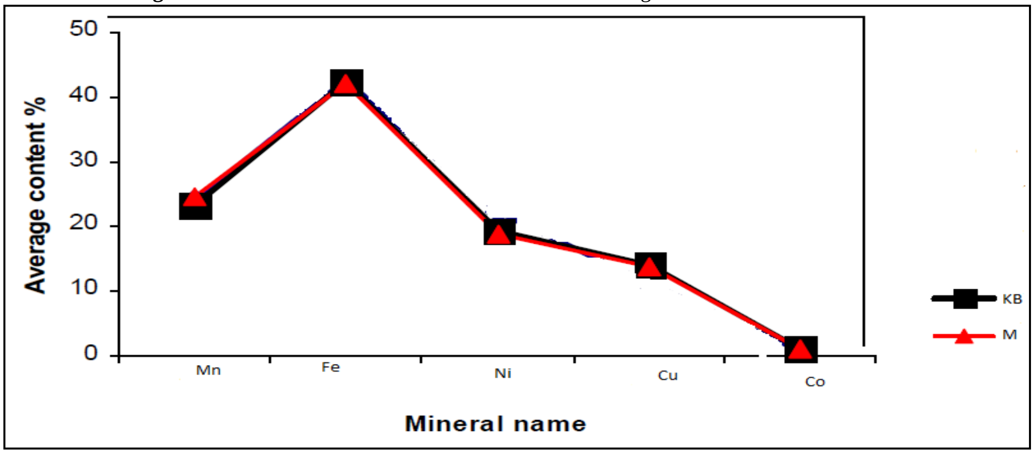


Table-2. Semi-quantitative percentage of manganese nodules in the study area All Values in (%)

Sample	Mn	Fe	Ni	Cu	Co
KB	20.9	6.24	0.77	2.04	1.8
M	17	5.6	0.34	1.99	1.99

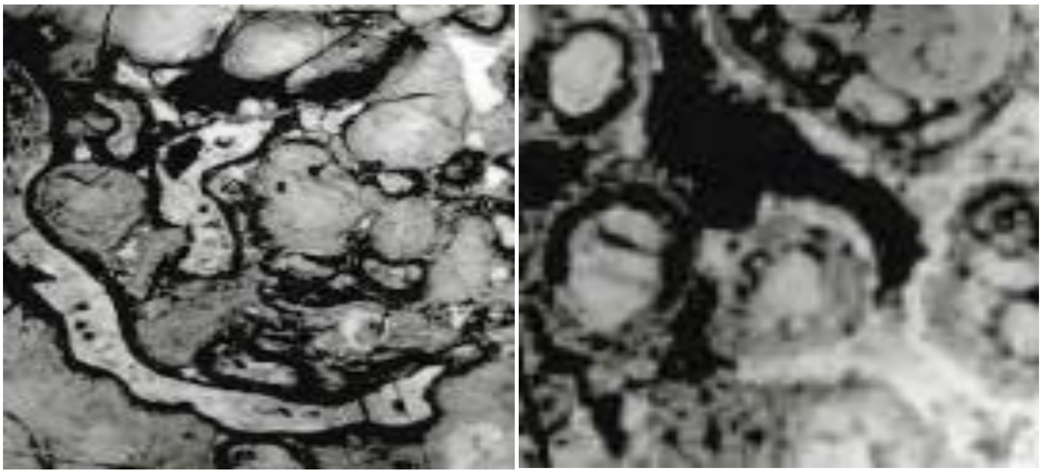
Fig-5. Distribution of the different minerals within the manganese nodules based on XRD



4.3. Polished Section Study

Study of nodule polished sections by reflected light give information concerning the phase identification, and phase growth habits, preliminary assessment of the size of liberation, and ontogenetic features, (morphological features) which evidence genetic mechanisms and sequences. A photomicrograph along a radius of a nodule from Kwana-Bala and Madaka samples were given in Plate 1. Major zones of different phase growth habits are noticed in Plate I (KB) as an inner zone and an outer zone. The inner zone shows micro-nodule development. The outer zone shows crenulation development.

Plate-1. Photomicrograph of nodules from Kwana-Bala and Madaka



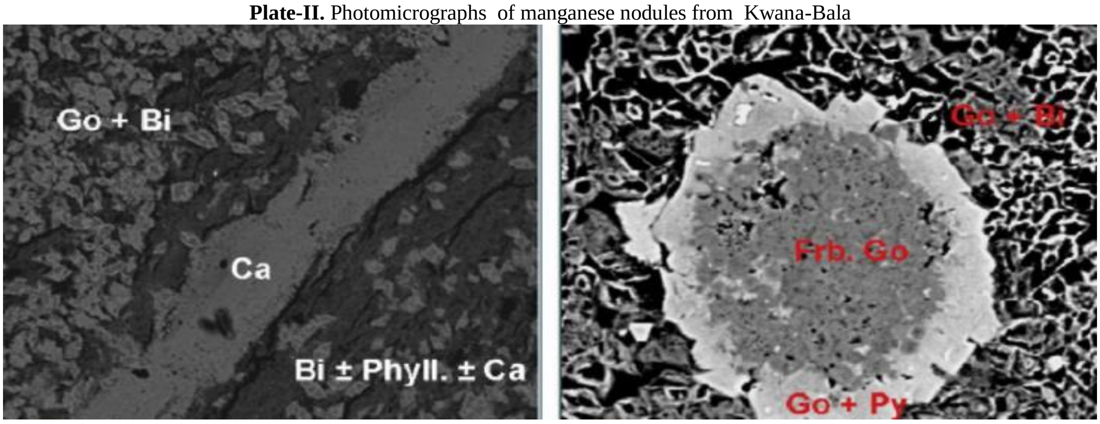
Kwana-Bala (KB) Madaka(M)

Crenulations structure is generally a better developed feature than is shown in Plate I (M). The differences in reflectivity shown by nodule material in Plate I (KB and M) could be due to the following causes: differences in mineralogy, different orientations of the same mineral differing and degrees of compactness, this is because of the very great range in reflectivities and the very fine nature of the growth patterns in large portions of the nodule, no identification of the mineralogical phases by reflected light techniques was attempted. Plate VII, though, showed a morphological feature of interest to this study. This is the development of micro-nodules, which are notable particularly as having a uniform reflectivity. Some of these structures were of diameters up to 150 microns.

5. Internal Microtextures of the Nodules

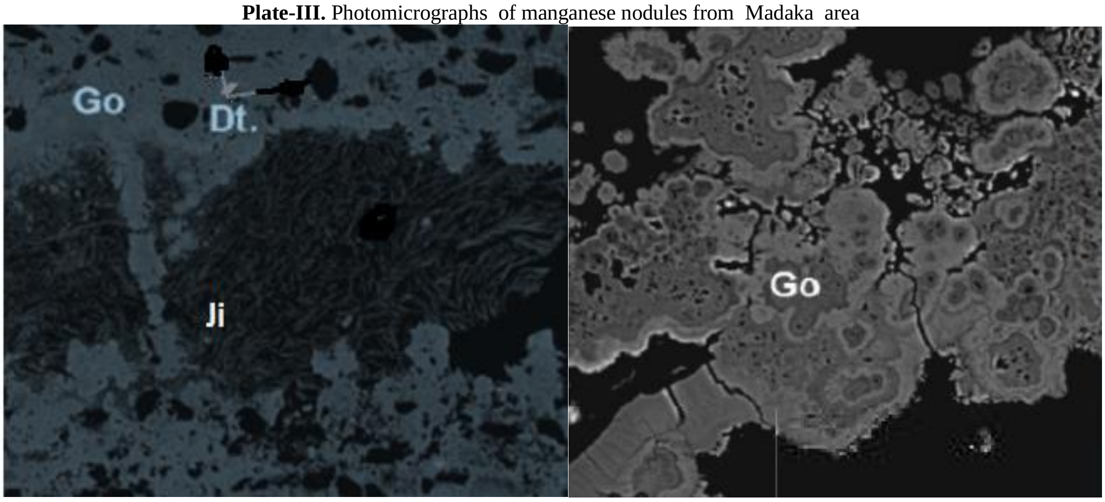
Photomicrographs plate II (KB) shows the Oxide layer showing spalerite-birnessite rhombic crystals (Go + Bi) surrounded by Mn oxides (Bi) and crosscut by a post-accretional crack filled with carbonates (Ca). (M) Pyrite aggregate formed by framboids (inside) and idiomorphic cubic crystals (outside), partially pseudomorphised by spalerite which is paragenetic with Fe-Mn rhombic crystals (Go + Bi), Jianshuite (Ji) filling up a void next to microcrystalline spalerite (Go) with scattered grains. spalerite(Go) filling a post-depositional crack in disperse or forming aggregates.

Plate-II. Photomicrographs of manganese nodules from Kwana-Bala



KB M

Plate-III. Photomicrographs of manganese nodules from Madaka area



KB M

5.1. Chemical Composition

The elemental compositions of manganese nodules from Madaka and Kwana-Bala is presented in Table 3.

Table-3. Elemental composition of the nodules from Kwana-Bala and Madaka (conc) in cm^3

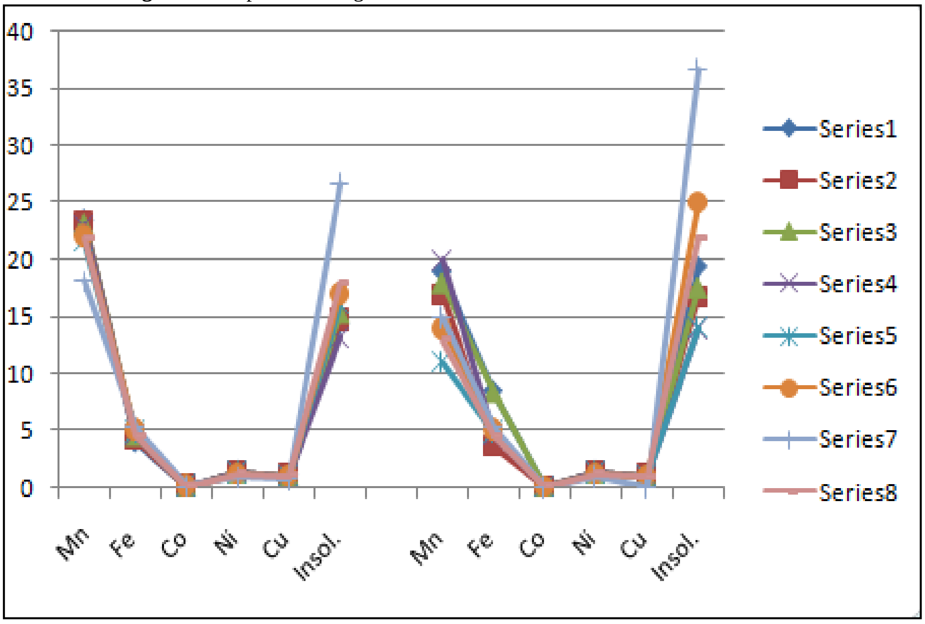
		Mad							**Kwa**	**Bala**		
Sp/conc	Mn	Fe	Co	Ni	Cu	Insol.	Mn	Fe	Co	Ni	Cu	Insol.
2*5	23.5	4	0.15	1.45	1.13	14.4	19	8.5	0.11	1.45	1.10	19.4
10	23.4	4.2	0.17	1.41	1.13	14.8	17	3.7	0.12	1.41	1.11	16.8
20	23.2	4.6	0.17	1.34	1.08	15.4	18	8.4	0.11	1.34	1.06	17.6
50	23	4.6	0.17	1.38	1.08	13.	20	4.6	0.11	1.38	1.05	14.
100	21.6	4.9	0.17	1.3	1.04	16.1	11	4.9	0.11	1.3	1.00	14.1
120	22.1	5.1	0.17	1.23	1.02	17	14	5.1	0.11	1.23	1.01	25
140	18.1	5.3	0.17	1.00	0.85	26.7	15	5.4	0.11	1.09	0.06	36.7
150	22	4.6	0.17	1.30	1.04	18	13	4.6	0.14	1.3	0.99	22
Ave	22.1	4.66	0.18	1.30	1.05	17.9	15.9	5.65	0.12	1.31	0.92	20.7

Total	177.	37.3	1.01	10.5	8.37	136.	127	45.2	0.92	10.8	7.38	166
Max	23.5	5.3	0.17	1.45	1.13	26.7	20	8.5	0.14	1.45	1.11	36.7
Min	18.1	4	0.15	1.00	0.85	13.2	11	3.7	0.11	1.06	0.06	14

Mn contents are the most abundant element in the nodules followed by Fe, Si and Ca Fig 6. The concentration of Mn- Fe nodules in the Madaka and Kwana-Bala area varies from 4.53 to 2.97 for Mn/Fe ratio for Madaka nodules and Kwana –Bala.

Combined Cu+Ni+Co concentrations are very low, ranging from 2.53% to 2.35%. In relation to average crustal abundance the elements are enriched in the nodules from Madaka by different order factors: (Mn (22.11), Fe (4.66), Ni (1.3), Cu (1.05) and Co (0.17).

Fig-6. The co-plots of manganese nodules from Kwana-Bala and Madaka area



Nodules have similar enrichment in elements as Mn, Fe, Co or Ni, regardless of their size. Only Ni shows a relative positive correlation with the sample size, and large nodules are more enriched in Ca than smaller nodules. These results show the inter-element correlations of samples from Kwana-Bala and Madaka exists in manganese and iron with e strong negative correlation and Nickel and copper characterized with positively correlated with manganese.

Since mining costs are probably not related to the different phase structures of nodules, economic assessment of the effect of $Mn0_2$ phase structure on a mining and metal-winning process for nodules can be made, in the first instance, on a comparison solely of the metal units extracted per unit of reagent consumption with a weighting for other considerations, particularly the selectivity of extraction achieved. In this respect it is seen from the foregoing discussion that processing nodules consisting of manganite $Mn0_2$ phase structures holds clear advantages through beneficiation.

6. Conclusion

In this work detailed of petrographical, textural, mineralogical and chemical characteristics of manganese nodules from Kwana-Bala and Madaka area reveals preponderance of sphalerite, and ilmenite as major minerals. Accessory minerals are siderite and rutile. preliminary assessment also indicates that metals like Mn, Fe, Co, Ni, and Cu would be sought for from composition, available tonnage, mining costs, timing of capital investment and revenue, location, magnitude and processing costs has indicated that exploitation of nodules could be profitable in Madaka area and Kwana- Bala. It follows from this conclusion that exploration for nodules on the basis solely of assay criterion is inadequate; composition by Mn phase structure must also be used as a criterion. It is also evident that the susceptibility of the nodule material to structural change, particularly by heating, and the effects that such a structural change can have must be considered in any evaluation of a nodule mining and metal-winning scheme through beneficiation. The findings of this work can be interpreted in a way which indicates profound effects on the philosophy of mining and processing of nodules, as the above analysis indicates. Mining operations on land normally require exclusive exploitation rights to an ore deposit as a pre-requisite to operations. This arises because the ore contains a higher concentration of the material desired than the surrounding earth structures. The profitable processing of the ore depends on this higher concentration of the material desired. In terms of a metal-winning process for nodules, it was shown to be somewhat more advantageous to process nodules containing a manganite rather than Mn02 phase structure. However, the advantage might be of secondary consideration in relation to other aspects of a total nodule exploitation operation in future. The physical and chemical characteristics of manganese nodules in Madaka and Kwana -Bala would be a vital factor to be consider when source for Ni and Cu in the study area.

Acknowledgements

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