Texture and Compositional Evidence for Epigenetic Alteration in Mn Carbonate Protore at the Palaeo-proterozoic Nsuta Manganese Deposit, Western Ghana*

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Abstract

This communication is the first to report the presence of significant epigenetic alteration in protore manganese carbonate at the Palaeo-proterozoicNsuta manganese deposit in the Birimian of Ghana. The alteration is recognisable macroscopically by strong veining of quartz and/or pink rhodochrosite and, in some cases, in slightly sheared or deformed carbonate rock. Under the ore microscope, the alteration assemblage commonly consists of micro-granular rhodochrosite, occasionally coexisting with one or more of alabandite, mangano-cummingtonite, alleganyite andjacobsite. The compositions of carbonate minerals also demonstrably show an increase in the $MnCO_3$ end-member in the altered compared to the least altered carbonate protore. These textural and compositional features sharply contrast with low regionally metamorphosed protore that shows remarkable preservation of primary sedimentary features including lamination and is, in addition, dominated by micro-concretionary to microcrystalline rhodochrosite ± kutnahorite ± mixed Ca-Mg carbonates ± spessartine garnet. The alteration is not only suggested to be post-metamorphic (low-metamorphosed) and pre-supergene but may also, contrary to the interpretations of some previous workers, have introduced unusual manganese-bearing minerals (e.g. alabandite and mangano-cummingtonite) as well as possibly enriched the protore carbonate.

1 Introduction

The Nsuta deposit in Ghana is at present the most important carbonate manganese mineralisation in the Palaeo-proterozoicBirimian of the West African craton. The deposit has had a continuous history of exploitation for nearly a century, initially due to the extensive occurrence of battery grade nsutite-rich manganese oxide ore and, at present, comparatively low grade but economically important manganese carbonate ore. Many studies such as Service (1943), Jaffe *et al*. (1961), Sorem and Cameron (1960), Mücke *et al*. (1999), Nyame (1998; 2001), Nyame *et al*. (2002), Nyame and Beukes (2006) and Nyame (2008) have been conducted over the years on various aspects of the mineralisation. Kleinschrot *et al*. (1994) suggested that the entire package of metavolcanic and metasedimentary rocks (including protore carbonate) at the Nsuta deposit record peak greenschistfacies metamorphism of about 500ºC and 5 kb followed by retrograde conditions such as documented by breakdown of kutnahorite to form submicroscopic domains of calcite, rhodochrosite and ankerite. Nyame *et al*. (2002) suggest, however, that much of the primary sedimentary features including microscopic textures of the carbonate rocks may have been remarkably preserved. Apart from very brief mention of alteration in the protore carbonate by Nyame (1998), not much is known and/or has been documented of alteration in the protore carbonate other than the widespread supergene modifica-

tion of the carbonate into manganese oxide ores. Jaffe *et al*. (1961) reported on the occurrence of the manganese amphibole mangano-cummingtonite in localized shears within carbonate ore but did not provide much linkage with alteration in the protore carbonate. Mücke *et al*. (1999) also interpreted alabandite as a diagenetic product formed within the manganese-rich sediment after deposition. These two minerals, it would seem, are only observed in altered protore carbonates in a paragenetic relationship that suggests their late formation or derivation. The textural and compositional data from Mn carbonate minerals presented in this study, the first to report on the significant alteration, contribute new information which may be useful in genetic interpretations on, and/or evolution of, this very important Palaeo-proterozoic manganese deposit.

2 Geological Setting

The Nsuta manganese deposit occurs in Palaeo-proterozoic Birimian Supergroup at the eastern portion of the West African craton. Workers such as Junner (1935), Attoh (1982), Milesi *et al*. (1989; 1992), Leube *et al*. (1990), Boher *et al*. (1992), Abouchami *et al*. (1990), and John *et al*. (1999) have reported on aspects of the geology, structure and stratigraphy, tectonics, mineralisation and metamorphism of the mainly volcano-sedimentary Birimian rocks. The stratigraphic subdivision of the Birimian, in particular, has still not been adequately resolved.

The Birimian sequence is unconformably overlain by fluvio-deltaic, in part auriferous formations known as the Tarkwaian in Ghana (Milesi *et al.* 1992) which, in some respects, is similar to the Witwatersrand basin of Southern Africa. Many workers have presented evidence to suggest that Birimian and, in some cases Tarkwaian rocks were deformed, metamorphosed and tectonically stabilised during the ~2.0-19 GaEburnian event (Milesi *et al.* 1991; Wright *et al.* 1985).

Well known studies that have reported on the Nsuta deposit include Service (1943), Kesse (1976), Kleinschrot *et al.* (1994), Nyame (1998), Mücke *et al.* (1999) and Yeh*et al.* (1995), Nyame *et al.* (2002), Nyame and Beukes (2006). According to Kesse (1976), the general stratigraphy of the Nsuta deposit consists of a basal greenstone unit followed successively upwards by argillaceous rocks and tuffs, manganese carbonates, argillaceous rocks and tuffs which, in turn, is overlain by greenstone. The manganese-rich rocks strike approximately N15°E, dip about 55-90°E and are demonstrably conformable within the thick sequence of argillaceous rocks. Disagreements still persist in literature on some aspects of the mineralisation such as the metamorphic evolution (e.g. Kleinschrot *et al.*, 1994; John *et al.*, 1999; Nyame *et al.*, 2002), nature and processes of Mn deposition (e.g. Kleinschrot *et al.*, 1994; Yeh *et al.*, 1995; Nyame *et al.*, 2002; Mücke *et al.*, 1999). According to John *et al.* (1999), Birimian rocks including the Nsuta deposit appear to record a P-T path from amphibolite facies to retrograde greenschistfacies. Many other workers, however, hold contrary opinion and suggest instead that the Nsuta rocks were metamorphosed to greenschistfacies conditions (e.g. Service 1943; Ntiamoah-Agyakwa 1979; Nyame 2001; Nyame *et al.* 2002). Nyame (2001) also suggested that rocks or ore from the northern part of the deposit could have been affected by post-metamorphic, pre-supergene alteration or modification distinctly different from the "relatively unaltered" and/or least deformed manganese-carbonate bearing protore present in most parts of the deposit.

3 Methodology

Samples of manganese carbonate-bearing rocks were collected from drill cores and outcrops throughout the deposit, carefully examined and suitable ones selected for thin and polished thin sections. Petrographic work involved optical microscopy, x-ray powder diffraction (XRD), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). Detailed textural and mineralogical studies using a combination of microscopic and SEM methods were conducted at Okayama University, Japan and Rand Afrikaans University (now university of Johannesburg), South Africa. Microscopic work in

transmitted and reflected light was done on a Leica DMLP microscope. Chips from selected samples were removed and ground to fine powder for XRD analysis on graphite-monochromisedRigakudiffractometer with a Cu target at operating conditions of 30kV, 15mA and scan speed 4° per minute. Polished thin sections for SEM determinations were first coated with carbon to ensure good conductivity. SEM was undertaken on a Jeol JSM-5600 with an energy dispersive (EDS) link at operating conditions of 30kV and 15mA on cobalt standard. Qualitative mineral compositions were initially obtained on the SEM using both the backscatter and secondary electron modes. X-ray element maps of various mineral phases were also obtained on the SEM. Electron probe microanalysis (EPMA) was used for both qualitative and quantitative composition of mineras. This was conducted on a CAMEBAX 355 with a 3-mm beam diameter at 15kV accelerating voltage and 10 nA specimen current measured on brass. All the microprobe results were ZAF corrected.

4 Petrography and Microprobe Chemistry of Nsuta Mn Carbonate Protore

Petrographic studies on samples of Mn bearing rocks taken throughout the deposit suggest that two main types of manganese carbonate protore could be distinguished. In outcrop and in hand specimen, the first type, hereinafter described as "least altered" carbonate protore, varies from massive to bedded or laminated, the latter usually in contact with and/or in the proximity of host rock Mn bearing phyllite. Microscopically, the least altered protore is dominantly micro-crystalline to concretionary in texture, typical concretions varying in size from about 60 to 120 μm in diameter (Nyame, 1998; Nyame *et al.*, 2002). Spessartine garnet crystals are commonly observed in this type of protore carbonate. SEM investigations of concretions revealed they are not only commonly cemented by quartz and mixed or two-phase carbonate minerals but also compositionally composed mainly of rhodochrosite and kutnahorite. Figs. 1a-f show megascopic and microscopic features in least altered carbonate protore.

The second type, hereafter referred to as "altered" carbonate protore, frequently exhibits strong veining or shearing and bedding or lamination, where present, may be characteristically affected. Under the ore microscope, carbonate minerals are coarse to granular in texture and some crystals display twinned or bent cleavages suggesting they may have been affected by deformation. Typical sections consist of mono-mineralicrhodochrosite, occasionally associated with long, prismatic manganocummingtonite and other Mn mineral phases uncommon in least altered protore. Diagnostic microscopic
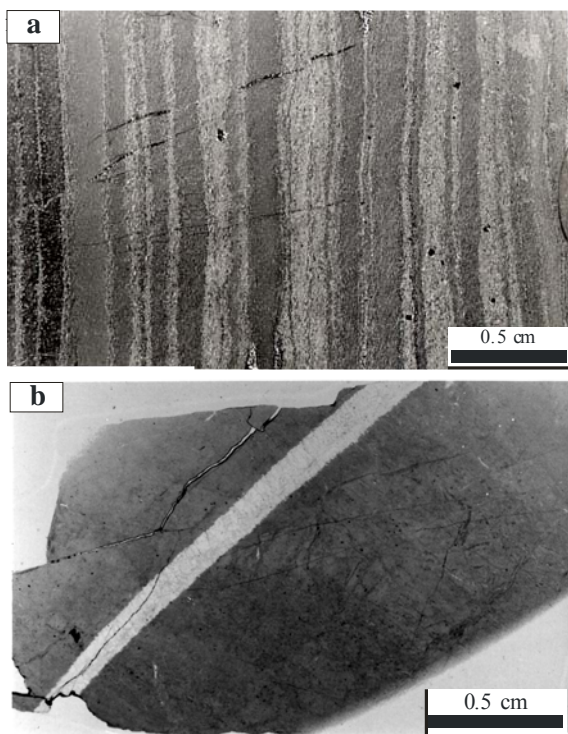
Fig. 1 Polished Surface, Microscope and Scanning Electron Microscope (SEM) Images. (a) commonly present in the Proximity of host Rock Mn bearing phyllite, Nsuta; (b) Massive, Structureless Mn Carbonate Protore from the central part of the Orebody. Quartz vein (light) cuts across the Rock;
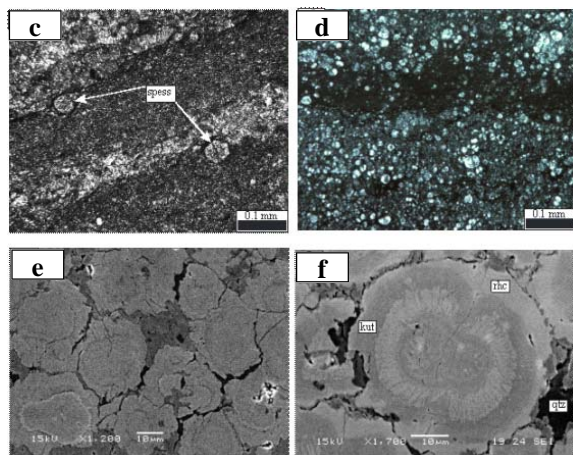
Fig. 1 (c) Photomicrograph of Microcrystalline Protore Carbonate with accessory Spessartine (spess) partially cutting across sedimentary lamination; (d) Carbonate Microconcretions in least altered Protore Carbonate; (e) Scanned Electron Microscope (SEM) photo of Carbonate Concretions with mixed Carbonates (grey) and Quartz or Silica (dark) Cement; (f) Zoning in some Carbonate Microconcretions.
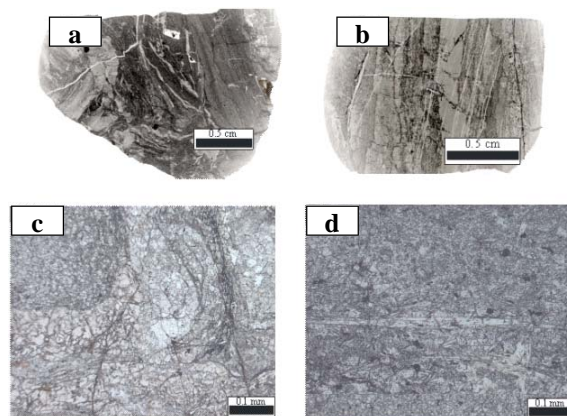
Fig. 2 Polished Surface, Microscope and SEM Images in altered Protore Carbonate; (a), shows Micro-folding (left of photo) and Sedimentary Lamination (right of photo); (b) Displacement of Original Laminae; (c) and (d) are Photomicrographs showing Micro-folding and Mangano-cummingtonite (long prismatic crystals) in altered Protore Carbonate

microprobe investigations revealed that rhodo-chrosite in some cases coexist with one or more of mangano-cummingtonite, alabandite, alleghanyite, jacobsite and a host of suphide minerals (Nyame, 1998; Nyame *et al*., in prep.). Some of these minerals replace rhodochrositepseudomorphously, along deformation zones and crystal boundaries or have inclusions of carbonates and quartz, suggesting their late derivation. Some macro- and microscopic features in altered protore carbonate are provided in Figs. 2 a-h. Microprobe compositions of representative carbonate minerals in the two carbonate protore types are presented in Table 1 and Fig. 3.

It is seen that the least altered carbonates (Table 1a) exhibit greater variability in chemistry with the possible presence of phases such as kutnahorite, mixed or complex Mg, Mn, Ca carbonates and Mg rhodochrosite. The altered carbonates, on the other hand, are enriched in Mn relative to Ca, Mg and Fe (Table 1b) to such an extent that in some grains, very little of the latter three components occur. The comparatively high Mn and correspondingly low Ca, Mg and Fe contents in carbonate minerals (see Fig. 3) suggest the altered carbonates are dominantly composed of rhodochrosite, an observation which corroborates microscopic determinations. Whole rock compositions of two samples each of the Mn carbonate ores are given in Table 2. Even though limited, the whole rock chemistry does suggest fairly high contents of Si, Al, Ca, Na and K in the least altered compared to the altered carbonate protore. The Mn content of the latter is, however, also comparatively higher.

Table 1a Selected Electron Microprobe Compositions of Carbonate Minerals in least altered (low metamorphosed) Manganese Carbonate Ore, Nsuta, Ghana

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
MgO(wt.%)	2.94	2.84	5.64	8.48	6.79	1.60	5.96	7.48	5.29	2.82	6.00	3.32	2.77	5.93	3.34	5.33	3.68	1.77	5.18	9.19
CaO	4.85	6.42	27.45	3.07	2.30	26.00	2.99	3.10	26.79	5.31	27.54	2.99	6.38	25.94	4.13	27.21	3.82	5.32	26.24	3.77
MnO	52.35	50.48	20.55	41.63	49.33	30.00	49.42	47.36	25.12	51.68	19.93	53.04	50.73	24.33	52.25	21.51	51.62	52.64	24.69	39.70
FeO	0.49	0.47	3.40	5.62	1.03	0.34	1.06	1.06	0.35	0.48	3.89	0.85	0.45	0.75	0.80	3.86	0.75	0.51	0.93	5.51
*CO₂	39.79	39.74	42.53	40.94	40.45	40.97	40.16	40.62	42.60	39.60	42.91	39.40	39.78	42.39	39.79	42.88	39.49	39.07	42.13	41.00
Total	**100.42**	**99.94**	**99.57**	**99.75**	**99.90**	**98.92**	**99.59**	**99.6 n1**	**100.16**	**99.89**	**100.28**	**99.60**	**100.12**	**99.35**	**100.32**	**100.79**	**99.36**	**99.30**	**99.18**	**99.18**
Mol.%																				
MgCO₃	8.1	7.8	14.5	22.6	18.3	4.3	16.2	20.1	13.6	7.8	15.3	9.2	7.6	15.3	9.2	13.6	10.2	4.9	13.4	24.5
CaCO₃	9.6	12.7	50.6	5.9	4.5	49.8	5.8	6.0	49.4	10.5	50.4	6.0	12.6	48.0	8.1	49.8	7.6	10.7	48.9	7.2
MnCO₃	81.6	78.8	30.0	63.1	75.7	45.5	76.4	72.3	36.6	81.0	28.8	83.5	79.1	35.6	81.5	31.1	81.1	83.6	36.4	60.1
FeCO₃	0.8	0.7	4.9	8.4	1.6	0.5	1.6	1.6	0.5	0.7	5.6	1.3	0.7	1.1	1.2	5.5	1.2	0.8	1.4	8.2

Table 1b Selected Electron Microprobe Compositions of Carbonate Minerals in "altered" Manganese Carbonate Ore, Nsuta, Ghana

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
MgO(wt.%)	2.29	4.94	7.59	5.69	0.09	3.73	0.36	2.97	3.41	2.31	3.18	0.36	1.03	1.89	4.18	3.97	0.74	1.14	0.78	5.25
CaO	1.44	1.46	1.18	1.35	0.04	2.29	0.42	2.20	1.95	1.95	1.99	0.42	0.83	1.44	2.01	2.14	0.47	0.30	2.01	3.56
MnO	57.05	53.84	49.28	52.22	61.69	54.34	60.62	55.51	54.02	55.84	55.48	60.62	59.43	57.46	55.01	54.98	60.25	59.74	58.75	51.02
FeO	0.31	0.34	1.40	0.74	0.09	0.06	0.33	0.33	0.55	0.42	0.12	0.33	0.26	0.46	0.11	0.10	0.12	0.09	0.11	0.44
*CO₂	39.21	40.15	40.64	40.12	38.46	39.62	38.54	39.60	39.10	38.95	39.53	38.54	38.80	39.12	40.34	40.19	38.63	38.59	38.93	40.45
Total	**100.30**	**100.73**	**100.08**	**100.11**	**100.37**	**100.04**	**100.28**	**100.61**	**99.03**	**99.47**	**100.30**	**100.28**	**100.36**	**100.37**	**101.66**	**101.38**	**100.21**	**99.85**	**100.57**	**100.73**
Mol.%																				
MgCO₃	6.4	13.4	20.4	15.5	0.3	10.3	1.0	8.2	9.5	6.5	8.8	1.0	2.9	5.3	11.3	10.8	2.1	3.2	2.2	14.2
CaCO₃	2.9	2.9	2.3	2.6	0.1	4.5	0.9	4.4	3.9	3.9	4.0	0.9	1.7	2.9	3.9	4.2	1.0	0.6	4.1	6.9
MnCO₃	90.3	83.2	75.2	80.8	99.5	85.1	97.6	87.0	85.7	88.9	87.1	97.6	95.0	91.1	84.6	84.9	96.8	96.0	93.6	78.3
FeCO₃	0.5	0.5	2.1	1.1	0.1	0.1	0.6	0.5	0.9	0.7	0.2	0.6	0.4	0.7	0.2	0.2	0.2	0.1	0.2	0.7
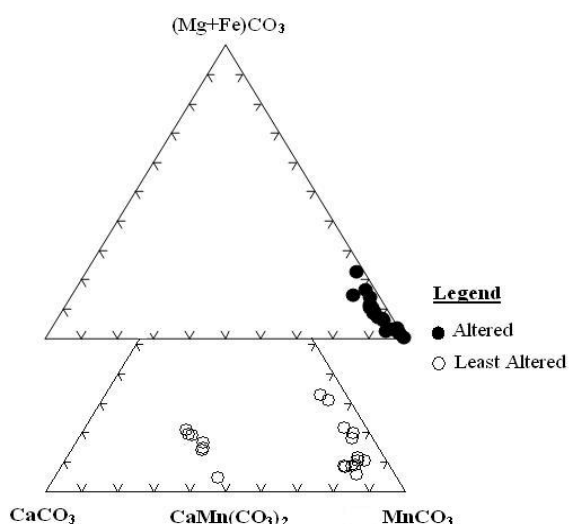
Fig. 3 Electron Microprobe Compositions of altered versus least altered Protore Carbonate, Nsuta, Plotted on the $(Mg+Fe)CO_3$-$CaCO_3$-$MnCO_3$ Ternary Diagram. The altered Protore Carbonates are highly enriched in the $MnCO_3$ component compared to least altered Protore which not only has Carbonates of Kutnahorite composition present but may also have high contents of $MgCO_3$ (see Tables 1 a and b)

Table 2 Whole Rock Chemistry of least Altered Versusaltered Manganese Carbonate Ores, Nsuta

Ore type	Least altered		altered	
Sample	HA 11	HCSC 03	HDSC C2	HDSC 05B*
SiO_2(wt.%)	4.52	4.00	1.10	3.94
TiO_2	0.04	0.03	0.04	0.04
Al_2O_3	1.43	1.59	0.99	0.73
FeO**	0.68	0.92	0.39	0.92
MnO	48.68	48.43	55.64	55.62
MgO	2.36	3.97	2.77	3.61
CaO	5.06	4.43	0.74	0.63
Na_2O	0.11	0.28	0.03	0.04
K_2O	0.39	0.17	0.06	0.07
P_2O_5	0.16	0.07	0.08	0.16
Co(ppm)	50	10	20	50
Ni	180	150	300	360
Cu	30	20	10	20
Zn	190	70	460	230
Ba	270	50	40	20
V	290	110	220	450
B	40	10	30	11650
Cr	100	80	90	110

Si was determined by conventional gravimetry as SiO_2, Na and K by flame photometry on a Hitachi 208 spectrophotometer and all other elements by ICP-MS on a Seiko SPS 7000 plasma spectrometer.

*SiO_2 is present in sample as minute quartz veinlets.

**Total Fe as FeO

5 Discussion

5.1 Origin and Post-formational Modification of the Nsutaprotore

Even though the source of manganese responsible for the enrichment at the Nsuta deposit is still debatable, there appears to be little doubt, as demonstrated in previous investigations, on a sedimentary origin of the Mn carbonate protore via primary or early diagenetic precipitation, subsequent (regional) metamorphism of the entire sequence (i.e. manganese bearing and host rocks) and eventual supergene modification of the manganiferous horizon into battery grade, nsutite-rich manganese oxide ores (e.g. Kleinschrot *et al.*, 1994; Mücke *et al*; 1999). Both

Table 3 Comparison of Petrographic and Geochemical Features in Least Altered (Low Metamorphosed) and Altered (Post-metamorphic?) Manganese Carbonate ores, Nsuta, Ghana

	Least Altered Ore	Altered Ore
Location (orebody)*	Hills A, B, E	Hills C, D
Colour (dominant)	Grey to dark grey	Light grey to grey
Texture (including microscopic)	Fine grained, micritic, micro-crystalline, microconcretionary	medium grained, coarsely crystalline to granoblastic. Twin and cleavage planes common in large crystals
Structure	Massive. Occasional laminae. Graded, flame, load and other sedimentary structures in the proximity of host rocks	Streaky appearance. Sedimentary structures rare to absent or evidently deformed. Abundant veins and veinlets of quartz and/or quartz-carbonate. Shearing and brecciation in some specimens
Major minerals (microscopy)**	Rhodochrosite, kutnahorite, mixed carbonates, quartz, chert (?)	Rhodochrosite
Accessory minerals**	Pyrite, spessartine, muscovite, sphalerite, chalcopyrite	Mangano-cummingtonite, sphalerite, alleghanyite, alabandite, chlorite molybdenite, millerite, jacobsite, rutile
Mineral association**	rhc-qtz; rhc-kut; rhc-qtz-mus; rhc-Py; Py-Sph-Cpy; rhc-qtz-spess	rhc-Mn cum; rhc-alg-chl; rhc-alg; rhc-alab-mill; rhc-molyb; alg-jb; rhc-alg-alab; rhc-Sph-alab-alg
Mn Carbonate chemistry	$Mn_{0.8-0.5}(Mg+Ca+Fe)_{0.2-0.5}CO_3$, $Ca_{0.5}(Mn+Mg+Fe)_{0.5}(CO_3)_2$, $Mn_{0.5}Mg_{0.4}(Ca+Fe)_{0.1}CO_3$	$Mn_{0.6-0.9}(Ca+Mg+Fe)_{0.1-0.4}CO_3$
Bulk chemistry	Higher SiO_2, Al_2O_3, CaO, Na_2O, K_2O. Low Mn to Ca, Si and Al ratios	Lower SiO_2, Al_2O_3, CaO, Na_2O, K_2O. Comparatively high Mn to Ca, Si and Al ratios
C, O isotopes	$\delta^{13}C_{PDB}$ from $-3.7‰$ to $-8.4‰$ and $\delta^{18}O_{PDB}$ from $-16.5‰$ to $-17.8‰$	$\delta^{13}C_{PDB}$ from $-6.7‰$ to $-20.8‰$ and $\delta^{18}O_{PDB}$ from $-10.9‰$ to $-16.4‰$

*Minor alteration occurs at all the Hills but is much more pronounced around Hill D.
Abbreviations: rhc rhodochrosite; qtz quartz; kut kutnahorite; mus muscovite; Py = pyrite;
Sph = sphalerite; Cpy = chalcopyrite; spess = spessartine; Mn cumm = mangano cummingtonite;
Alg = alleghanyite; chl = chlorite; alab = alabandite; mill = millerite; molyb = molybdenite; jb = jacobsite
**Mineral identifications and chemistry taken from Nyame (1998), Nyame (2001), Nyame *et al*. (2002) and Nyame (in prep.)

at the deposit scale and in microscopic investigations, protore carbonate and host Mn bearing phyllite distinctly display features such as graded bedding, lamination, flame and load structures, all typical of sedimentary deposition (Nyame, 1998). Mücke *et al*. (1999) suggested that two diagenetic processes, referred to by the authors as diagenesis I and II, were present in the rocks. The current study, however, could not petrographically distinguish between any such two distinct diagenetic processes in many specimens of carbonate protore or host rocks examined.

The metamorphic evolution of the deposit has attracted varied interpretations. Kleinschrot *et al*. (1994) and, to some extent John *et al*. (1999), suggest peak greenschistfacies metamorphism of about 500ºC and 5kb followed by retrograde conditions resulting in breakdown of kutnahorite to form submicroscopic domains of calcite, rhodochrosite and ankerite. Such prograde-retrograde metamorphic path was, however, disputed by Nyame *et al*. (2002) who presented evidence on the remarkable preservation of carbonate mineral texture, composition and assemblages. Dominant petrographic features present in the carbonate rocks, therefore, strongly suggest formation of kutnahorite and other carbonate phases not through retrograde metamorphism but

most likely as a result of primary sedimentary or early diagenetic deposition (see Figs. 2b, c, d).

This notwithstanding, the overall effect of regional metamorphism is, in most cases, clearly manifested not only in hand samples but also under the ore microscope. Many specimens of manganese carbonate rocks taken from the margins of the orebody depict interbedding of spessartine-rich and poor layers with retention of primary sedimentary features (Nyame, 1998; 2001; Nyame *et al*., 2002). Micro-textural features generally reveal the low grade nature of metamorphism in the rocks. For example, spessartine crystals not only cut across primary or early diagenetic (sedimentary) bands but also abundantly include matrix carbonate crystals, concretions and quartz, overall features which clearly suggest greater retention of primary sedimentary features during regional metamorphism (see Fig. 2a). Foliation in thin section is also recognizable by aligned muscovite grains which, together with the appearance of spessartine and dravite (Nyame, 1998), suggest metamorphism of originally impure manganese carbonate sediments in the depositional environment. Furthermore, carbonate mineral compositions and, in particular, coexisting carbonate phases of kutnahorite and rhodochrosite appear consistent with low temperature regional metamorphism of manganese-rich sediments (Nyame, 2001). As demonstrated by Nyame *et al*. (2002), textural evidence suggesting metastability and equilibrium can be inferred, respectively, from concretionary and microcrystalline carbonates in host Mnphyllite and protore carbonate. In general, mineral textures, compositions and assemblages (see Figs. 1 and 3) appear to be consistent with low temperature sedimentary deposition of carbonates (Goldsmith and Graf, 1957; Calvert and Price, 1970; de Capitani and Peters, 1981; Goldsmith, 1983; Hem and Lind, 1994; Huckriede and Meischner, 1996; Sternbeck and Sohlenius, 1997).

5.2 Effect and Significance of the Epigenetic Alteration

Effect of alteration in the protore carbonate is manifested in both mega- and micro-fabrics that appear to clearly overprint regional foliation (see Figs. 2a, b, c and f) and are especially dominant in protore from economically the most important part of the deposit. Many protore samples affected by the alteration show strong veining by quartz and quartz-carbonates of variable thickness and orientation, "tectonised" bedding and lamination, shearing, micro-folding and fracturing. In some cases, primary sedimentary structures have both been disaggregated and preserved in different parts of the same rock (see Fig. 2a). In addition, microscopic texture, assemblages and composition of Mn carbonate phases appear quite different in the altered protore. Carbonate minerals are frequently coarse to granular, recrystallized
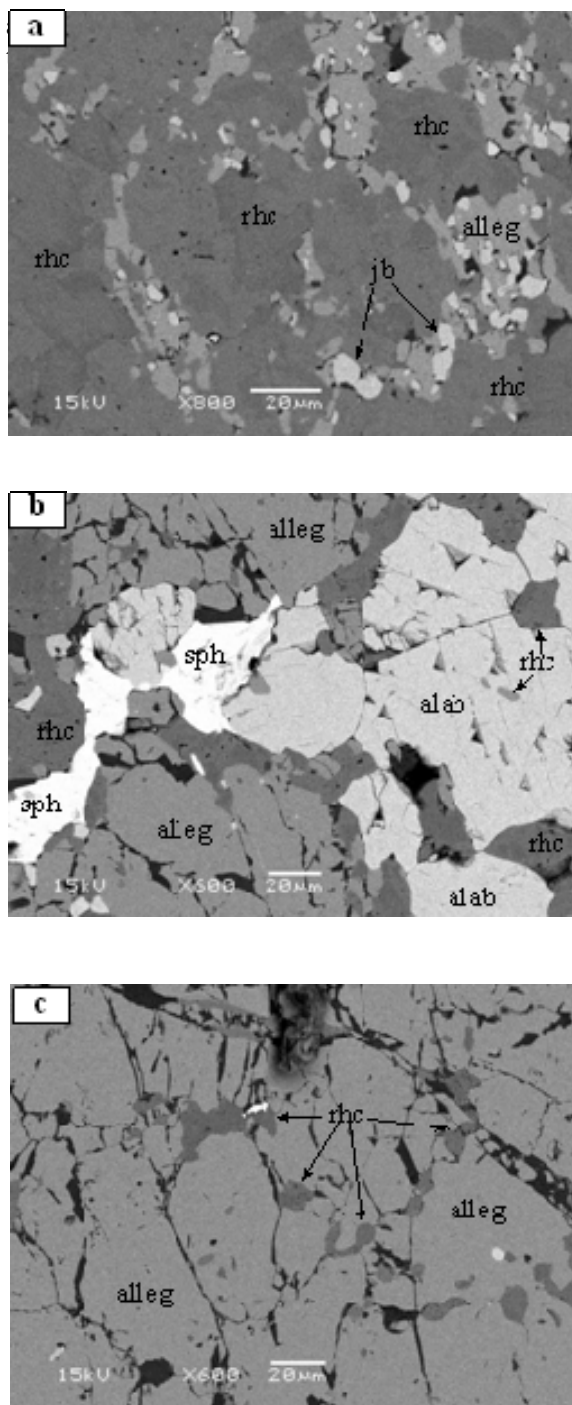
Fig. 4 Replacement of Rhodochrosite (rhc) in altered Protore by Alleghanyite (alleg) and jacobsite (jb) in (a), Alleghanyite, sphalerite (sph) and alabandite (alab) in (b), and alleghanyite in (c). In a, replacement appears to be preferentially along crystal boundaries in rhodochrosite whereas in b and c, nearly complete replacement is suggested by pseudomorphs of the minerals after rhodochrosite. Note relict rhodochrosite in some cases (b and c)

microcrystalline and microconcretionary nature of carbonates present in least altered ore. Typical mineral assemblages include "granoblastic" rhodochrosite occasionally coexisting with manganese bearing phases which, as indicated above, were identified as mangano-cummingtonite, alabandite, alleghanyite and jacobsite (Nyame, 1998; Nyame *et al.*, in prep.). Some of these minerals show clear pseudomorphous replacements for, or appear to have formed mainly in the interstices of, rhodochrosite grains in protore carbonate (Fig. 4).

Many of these textures and compositions are distinctly different from those encountered in the least altered protore and are interpreted to represent post-metamorphic alteration of the rhodochrosite-bearing protore carbonate, partly though indirectly, confirming the observations of Jaffe *et al.* (1961) especially on the formation of manganoancummingtonite in localised shear zones within carbonate rock.

Another interesting observation concerns the mineral alabandite. According to Mücke *et al.* (1999), alabandite is a diagenetic product formed within the manganese-rich sediment after deposition. In this study, however, the mineral was not observed in many samples of least altered or low metamorphosed carbonate protore but instead seems to be present mainly in granular or altered carbonates in a paragenetic relationship that suggests late formation or derivation (see Fig. 4b). The pre-supergene nature of the alteration is also manifestly clear. Supergene altered protore samples exhibit a number of features including presence of solution cavities and variably shaped "enclaves" or pockets of dark manganese oxide compared to the often massive, veined carbonate ore. In addition, specimens of carbonate ore taken from within transition zones between protore and supergene oxides clearly demonstrate, in hand specimen and under the microscope, mineralogical transformation of Mn carbonate into oxide ore (see Nyame, 1998).

The microprobe compositions of carbonate minerals and bulk rock chemistry of two samples each of the rocks further appear to corroborate petrographic observations. The least altered, low metamorphosed protore shows far less MnO contents than the altered counterpart, one sample of which returned very high B contents (see Table 2). Records available from the Nsuta mine (GMC, mine records) indicate that portions of the deposit which show both mega- and micro-features of significant alteration have not only produced by far the richest manganese oxide (mainly nsutite) and carbonate ore but also, especially in the latter, host increased contents of deleterious boron which invariably affects the quality or market price of the manganese carbonate ore.

A brief comparison of the two protore types, provided in Table 3, suggest that the texture, structure, mineral assemblages and Mn carbonate chemistry

may be different in the two protore types. Analyses of whole rock samples appear to show significant differences, as are their carbon and oxygen isotopic compositions (Nyame, 1998; Nyame and Beukes, 2006). Isotopically, least altered carbonate protore varies in $\delta^{13}C_{PDB}$ from –3.7‰ to –8.4‰ and $\delta^{18}O_{PDB}$ from –16.5‰ to –17.8‰ whereas altered protore carbonates vary in $\delta^{13}C_{PDB}$ from –6.7‰ to –20.8‰ and $\delta^{18}O_{PDB}$ from –10.9‰ to –16.4‰, suggesting much greater variation in both C and O isotopes in the altered compared to the least altered protore carbonates. In combination with petrographic observations on the texture, lithology and carbonate microfacies, Nyame and Beukes (2006) interpreted isotope values in the former, i.e. fine grained carbonate rocks (or least altered protore carbonates in this study) as primary and the latter (i.e. coarse grained or altered protore carbonates) as secondary in origin, most likely the result of post-metamorphic overprinting on primary carbon and oxygen isotope signatures.

The observations made above have important implications on the genesis of the Nsuta manganese deposit in so far as the hitherto unrecognized and/or unreported alteration of protore carbonate may have affected the mineralisation pattern at the deposit. The petrographic and geochemical evidence suggest that the alteration which formed the subject of this study could be distinctly different from any that had been previously described. In many respects, the alteration appears to have resulted in a distinctive suite of textural and compositional features typified by the introduction of new and apparently unusual manganese phases but also possibly enriched the Mn content of protore carbonate.

Not surprisingly, therefore, areas with evidence of intense alteration in the protore appear to have coincided, at the deposit scale, with comparatively richer manganese carbonate and battery-grade nsutite ores throughout the mine's history. Recognition of such an alteration process could, it would seem, have important implications on the genesis and/or evolution of this deposit whichis, by far, the most famous manganese mineralisation in the West African craton.

It is further argued that after sedimentation and/or diagenesis (or submarine halmyrolysis) and regional metamorphism of the manganese rich sediments, the alteration affected at least some portions of the manganese carbonate protore and/or Mn rich rocks before the well-known transformation in the supergene environment to produce nsutite-rich manganese oxide ores. Such a transformation path appears consistent with observed petrographic and geochemical features in the protore carbonate.

The possible existence of different manganese protore types, with differing petrographic and geochemical characteristics such as presented in this study, may not be limited to the Nsuta deposit. A number of authors (Kleyenstuber, 1984; 1985; Nel et al., 1986; Miyano and Beukes, 1987) established the presence of two distinctly different ore types in the World's largest Kalahari manganese field in South Africa. According to these authors, the low-grade, sedimentary Mamatwan-type ore and high-grade hydrothermally altered Wessels-type ore (the latter apparently derived from the former) display major differences in chemistry, mineralogy, petrography and regional distribution. Subsequent work by Gutzmer and Beukes (1995) indicated that hydrothermal alteration of the primary sedimentary Mamatwan-type ore to high-grade Wessels-type ore took place along a system of normal faults in the northwestern part of the Kalahari manganese field. Even though Cornell and Schutte (1995) have suggested a volcanic-exhalative origin for this giant manganese deposit, Beukes and Gutzmer (1996) argued further that a sedimentary origin appears to be much more consistent with the geologic, petrographic and geochemical features abundant in the rocks. Similar sedimentary and epigenetically altered Mn protore types, with distinct differences in petrographic and geochemical features, may be present at the Nsuta deposit except that, in this case, detailed work on the nature, process and overall effect of the suggested alteration still await further study.

6. Conclusion and Recommendations

The texture and compositional features of Mn carbonate bearing minerals at the Nsuta deposit strongly suggest that an epigenetic alteration process affected the protore, at least before onset of the ubiquitous supergene enrichment into manganese oxide ores. Whereas low-grade regional metamorphism did not appear to obliterate primary textures and/or mineral compositions, the suggested post-metamorphic alteration significantly affected carbonate mineral texture and composition, possibly enriched the Mn content of protore carbonate and also likely resulted in appearance of new Mn bearing phases such as mangano-cummingtonite, alabandite and alleganyite, minerals rarely present in least altered protore. Recognition of such an alteration could have important implications on the evolution of this very important Palaeo-proterozoic manganese deposit. More detailed studies on the nature, effect and extent of the alteration process could, if undertaken, help provide useful insights into various aspects of the mineralisation which are as yet not fully understood.

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