Occurrence and composition of manganese oxide minerals from the Nsuta manganese deposit, Western Ghana

Frank K. NYAME, Katsuo KASE, and Masahiro YAMAMOTO

Department of Earth Sciences, Faculty of Science,

Okayama University

X-ray diffraction, ore microscopy, and electron microprobe studies have been done on ore samples obtained from the mine site at Nsuta, Ghana. Manganese ore minerals identified include nsutite, cryptomelane, pyrolusite, and lithiophorite. Except for pyrolusite, all these minerals are poorly crystalline. Chemical compositions of the minerals indicate little contamination by other elements. Quartz, muscovite, and clay minerals feature prominently as gangue in most samples. Textures are varied, and modes of occurrence are principally by replacements, cavity or fracture fills, leaching and precipitation. Mineral associations seem rather complex, as a result of which definitive paragenetic relations could not be established.

Supergene formation of the manganese oxide ore is shown by the abundance of manganese minerals in solution channels such as fractures and cavities within silicate gangue. Much of the ore, however, appears to have been enriched by leaching of gangue minerals and the later addition of manganese.

Keywords: Nsuta, nsutite, cryptomelane, pyrolusite, lithiophorite

I. Introduction

The Nsuta manganese deposit has been an important mineral resource for Ghana ever since its discovery by A. E. Kitson (then Director of the Geological Survey) in the early part of the century. It is located about 6 km SE of Tarkwa and 60 km NW of Takoradi (Fig.1). Two main types of ore, manganese oxides and carbonates, are being mined. The oxide ores are generally subdivided into detrital and bedded types. The former are described as rounded and nodular masses, from pellets to boulders, usually embedded in soft lateritic soil or clay.

The lenticular, bedded ore bodies show evidence of contemporaneous deposition with host rocks and are also said to exhibit extensive modification by lateritization and weathering (Service, 1943). Very little information, however, exists on the carbonate ore body, presumably due to its exposure only a few decades ago.

A section through the ore bodies consists of stratigraphically higher detrital ore followed downwards by bedded, lenticular manganese oxide ore. Underlying these oxide ores is a persistent zone of manganese carbonates (Kesse, 1976). The oxide ores, grading over 50% Mn, have furnished several million tons of ore over the years. High grade, battery-active, manganese oxide minerals have been exploited for quite a long time. One such abundantly occurring mineral, nsutite, derives its name from this very locality.

Detailed description of the geology of the deposit was done by Service (1943). However, apart from Sorem and Cameron (1960) who undertook a mineralogical study of the manganese oxides, published descriptions on the deposit, mainly by the Geological Survey of Ghana, have commonly been directed towards evaluation of ore reserves (Kesse, 1976). Details on the chemical compositions of ore minerals in both the manganese oxide and carbonate ores may thus be entirely lacking, not to mention similar data for the associated minerals and/or rocks.
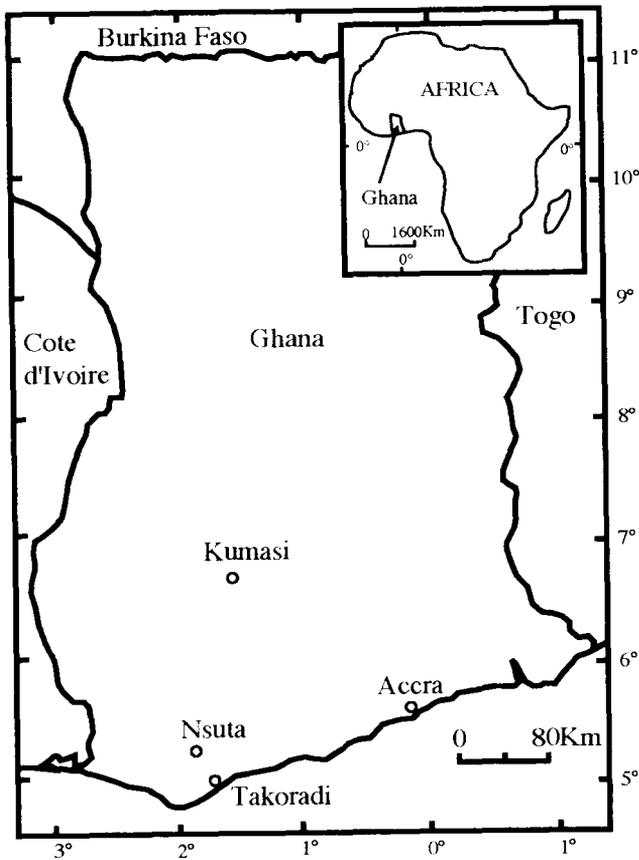
Fig.1 Location of Nsuta. Inset is map of Africa showing Ghana.

This paper may therefore be the first in a series of investigations aimed at elucidating the mineralogical and chemical characteristics of the mineralization as a prelude to the deduction of genetic processes.

II. Geologic setting

The deposit forms part of a volcano-sedimentary rock unit of the Proterozoic Birimian System (Leube et al., 1990). The manganiferous zone is known to lie conformably within Upper Birimian rocks. The manganese deposit occupies five NNE-trending ridges, designated Hills A, B, C, D and E, respectively (Fig.2). The hills consist of a series of interbedded tuffs and thin argillaceous horizons. In the mine area, manganese occurs within this series in a definite horizon. The manganiferous zone lies sandwiched between argillaceous metatuff units. The latter are themselves under- and overlain by greenstone rocks. Lithologic units are frequently described as metamorphosed (Service, 1943). A summary of the geology and stratigraphy (Table 1)

serves to provide an overview of the main lithologic associations.

Table 1. Geology and stratigraphy of Nsuta mine (After Wilking and Doe, quoted in Kesse, 1976)*

Unit	Thickness (m)	Description
Upper greenstones	450-600	Metamorphosed lavas and pyroclastics
Upper argillaceous metatuffs	150	Bedded sequence of sediments, lavas, and tuffs
Manganiferous horizon	45-60	Detrital Oxide ore Bedded Oxide ore Carbonate ore
Lower argillaceous metatuffs	45-90	Bedded sequence of sediments, lavas, and tuffs
Basal greenstones	450-600	Metamorphosed lavas and pyroclastics

* Age relations are not necessarily implied, especially for the detrital ores within the stratigraphic sequence.

III. Sample descriptions

The oxide ore samples generally range from hard, dark coloured to relatively soft, greyish-white pulverulent masses. The latter easily stains the fingers when touched. The hard oxide ore is usually massive and compact. Both ore types are, however, highly cavernous and are often characterized by the presence of abundant shiny crystals (pyrolusite?) in cavities. Examination of cut surfaces revealed that such cavities are prominent, even within massive, apparently compact ore. Some cavities are partially filled with yellowish-brown earthy material. Thin bands of manganese oxides and siliceous material (probably quartz) form distinct layers in some specimens. Quartz occurs mostly as grains and veinlets, often showing various degrees of dissolution and replacement by manganese oxide minerals.

IV. Procedure and methods of investigation

Ore samples from various localities of the manganiferous zone at Nsuta were obtained from the mine. Data acquisition for this paper consisted of X-ray diffraction, ore microscopy, and electron probe microanalysis (EPMA). Compositions of ore minerals were determined on a JEOL JXA-733 three-channel microanalyzer. Operating conditions

LEGEND

Late or post-Birimian intrusives
- Meta-basaltic intrusion
- Meta-andesitic intrusion
- Meta-microgranodioritic intrusion

Upper Birimian series
- Manganiferous zone
  - Upper greenstone
  - Upper argillaceous tuffs
  - Manganese carbonate/oxide
  - Lower argillaceous tuffs
  - Basal greenstone

N/C   North crest
S/C   South crest

scale

0   200   400 metres
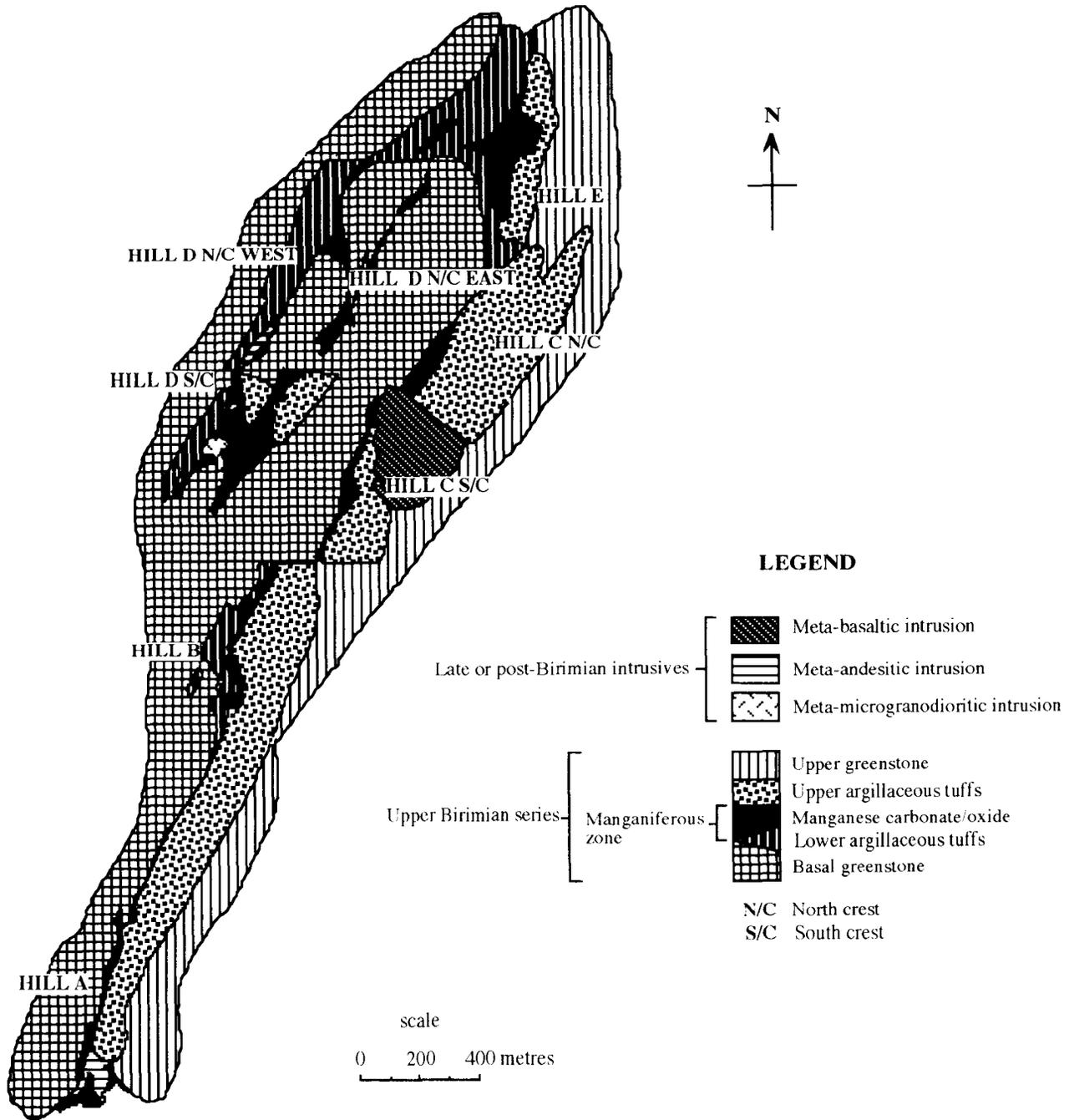
Fig. 2   Geological map of Nsuta mine area. (modified from Service, 1943)

were 15kV accelerating voltage and 2×10^{-8} A specimen current measured on Cu metal. Relative X-ray intensities were corrected using the ZAF data reduction programme of Yui (1992).

V. Petrography
1. Nsutite

Under reflected light, nsutite is white to light grey and anisotropic in finely crystalline varieties. Crystals are, however, rare and the mineral is usually present as cryptocrystalline masses. Polished

surfaces of oxide ore specimens indicate that variations in texture may be typical. Textures such as dense or massive (Fig.3A), botryoidal, mammillary (Fig.3B), and colloform occur frequently. In some cases, dense crosscutting veins of nsutite traversing earlier massive ones occur. Contraction cracks, transverse or polygonal, are prominent. Transverse cracks are mainly found in dense, vein or fracture-filling types whereas polygons are common in massive but fine-grained aggregates. Colloform aggregates do not usually exhibit these textural

features.

Replacements by, and intimate intergrowths with, cryptomelane and pyrolusite are common. Nsutite also either replaces these two minerals (Fig.3C) or forms concentric alternating layers with them. Its association with lithiophorite, however, is such that the latter is almost always observed either as rims to (see Fig.3A) or in cavities enclosed by veinlets of nsutite. Many optically homogeneous specimens of nsutite were apparently found to be heterogeneous under back-scattered electron image (BEI) of EPMA. The mineral is intimately associated with an Fe-rich phase in a few sections of oxide ore.

2. Pyrolusite

Except for the detrital ore in which it is evidently the most abundant constituent, its presence in the manganese oxide ore as a whole may be limited. The colour is white to light grey, with distinct metallic luster. In polished sections it is pleochroic and strongly anisotropic, the latter with shades of yellow to steel grey. Pyrolusite typically occurs in polycrystalline aggregates with diverse morphology, often evident in a single specimen. In particular, textural types include mosaic, accicular, tabular or bladed, radiating (Fig.3D), massive, and euhedral or blocky. Well-developed cleavage traces occur in coarse crystals (Fig.3E). Aggregates of fine grained, prismatic crystals lining cavities are sometimes observed to pass outwards into spherulitic, radiating mass of bladed forms.

Replacement by nsutite is suggested by pyrolusite 'islands' often seen in massive nsutite. The mineral also replaces nsutite. Association with cryptomelane is common, probably with the latter replacing pyrolusite (Fig.3F). Locally, pyrolusite veinlets are also observed traversing colloform nsutite, cryptomelane, and earlier formed pyrolusite (Fig.3G). Its most common mode of occurrence is as cavity fills and in replacement textures.

3. Cryptomelane

Cryptomelane in the oxide ores is light to dark grey and is almost always cryptocrystalline, except in pseudomorphous relationships notably with

pyrolusite. Texture is massive to colloform. Colloform varieties are distinctly darker. Anisotropic effects are less to indistinct. Cryptomelane frequently occurs as massive structureless replacement products containing shrinkage cracks and abundant inclusions of silicate gangue (Fig.3H). It is also found as dense crosscutting veinlets in nsutite. Colloform varieties are nearly always associated with nsutite.

In some specimens, colloform layers concentric or alternating with nsutite are seen, often with cryptomelane in contact with crystalline pyrolusite (Fig.3I). Intergrowths with nsutite are quite common. Its replacement relations with pyrolusite (Fig.3J) are such that it replaces the latter much more than it is replaced by pyrolusite. In one section, veinlets are observed in which radiating clusters of fibrous cryptomelane form a botryoidal aggregate. Some veinlets also exhibit frost flower textures.

4. Lithiophorite

This mineral has been observed in a few specimens of oxide ore. It is grey to dark grey and strongly anisotropic with bluish-grey colours. Under crossed nicols, aggregates of discrete black and white tints are seen. As noted by Sorem and Cameron (1960), its reaction to the sensitive plate enables it to be easily identified.

In its most usual form of occurrence, it is found as rims to veinlets of nsutite, even though its presence in replacement textures in preexisting manganese oxide phases or silicate gangue is equally not uncommon, especially where relict mica flakes are abundant (Fig.3K). It is also observed filling cavities in nsutite.

5. Unknown mineral

An unidentified mineral has been recognized in a few specimens of oxide ore. It is dark grey, massive to colloform, and isotropic. Extensive distributions of the mineral occur near cavities, often closely intergrown with (and possibly formed by alteration of) nsutite (Fig.3L).

6. Silicates

Most polished surfaces contain quartz, mica,
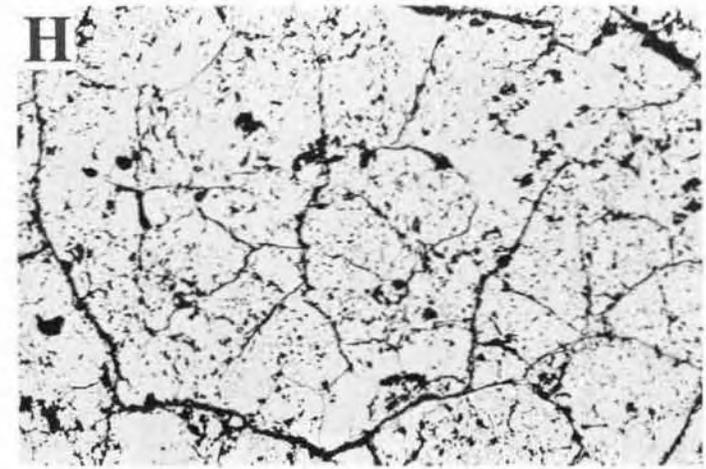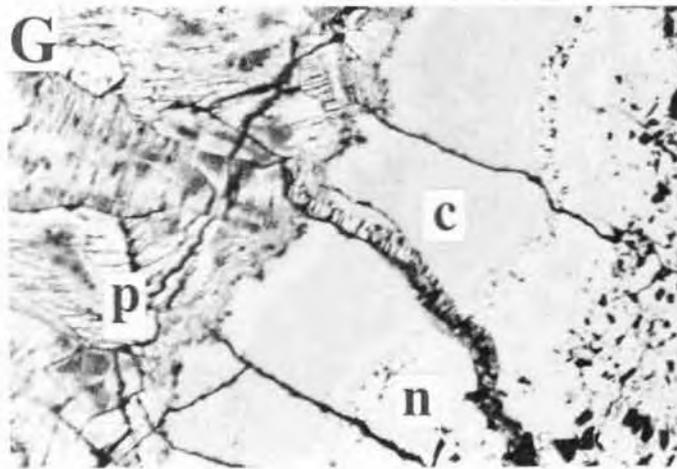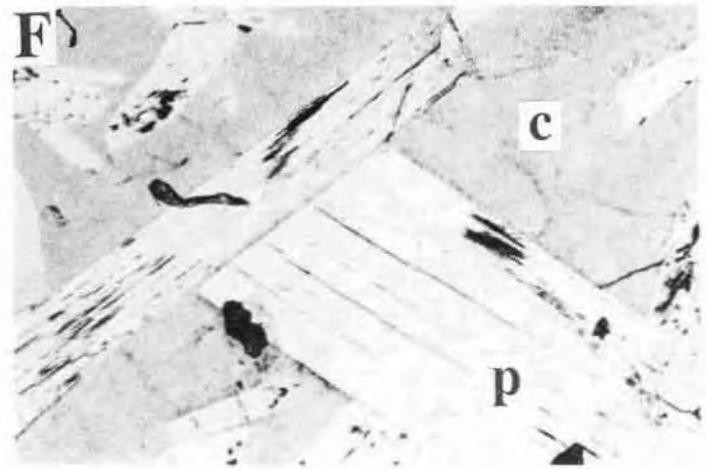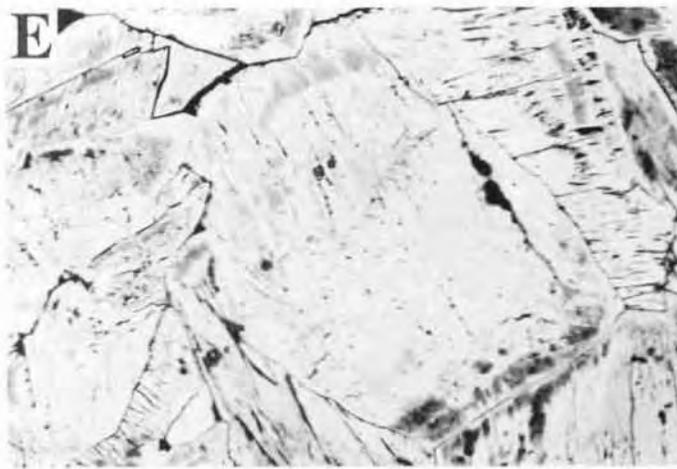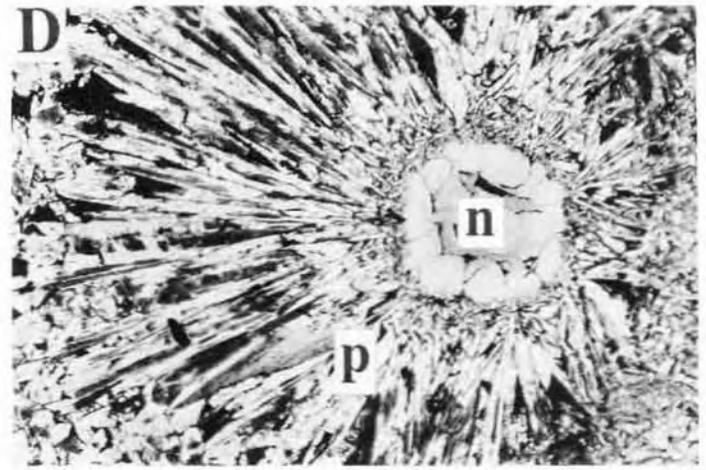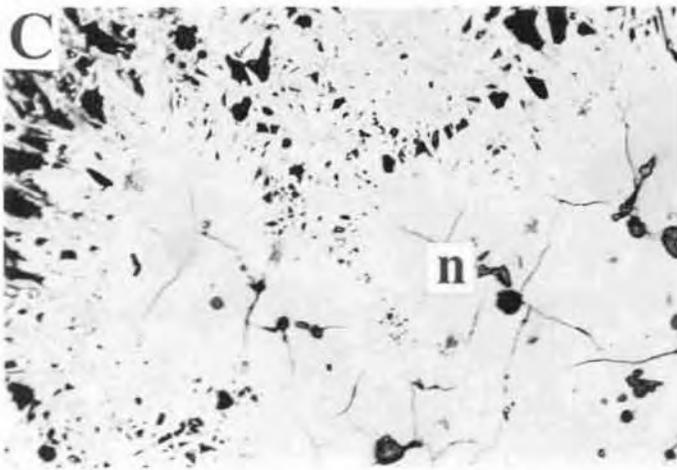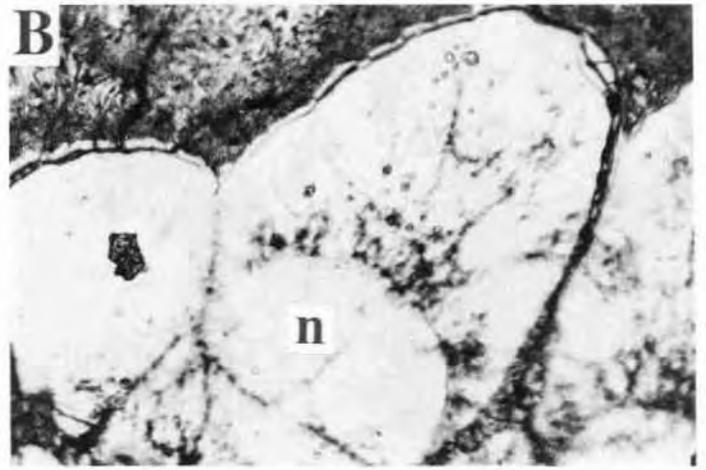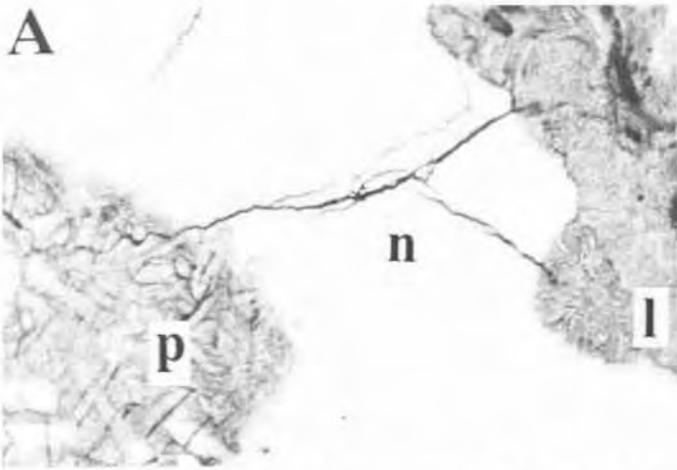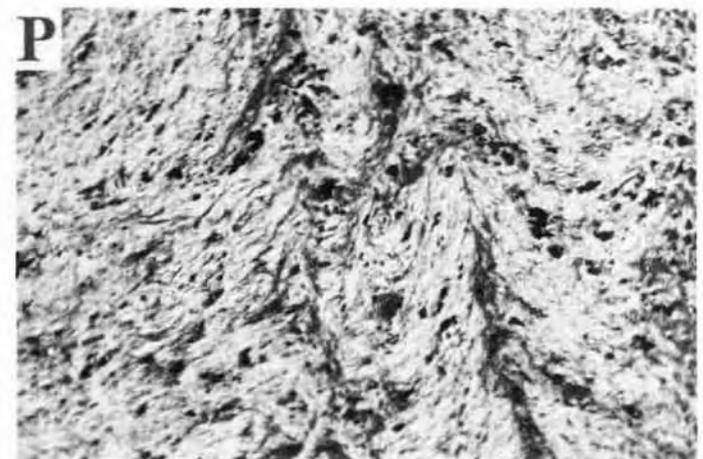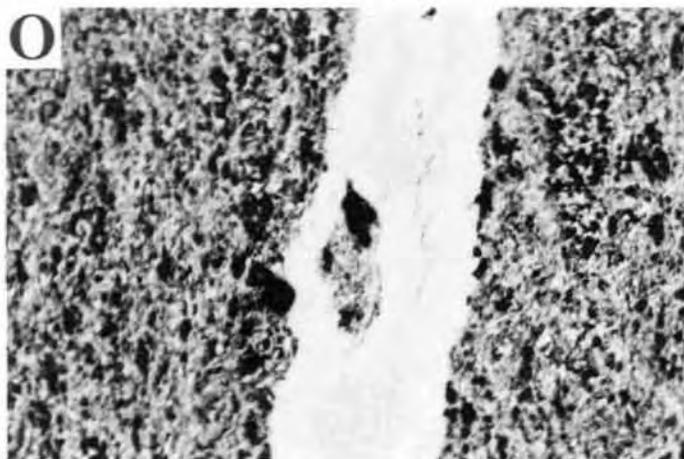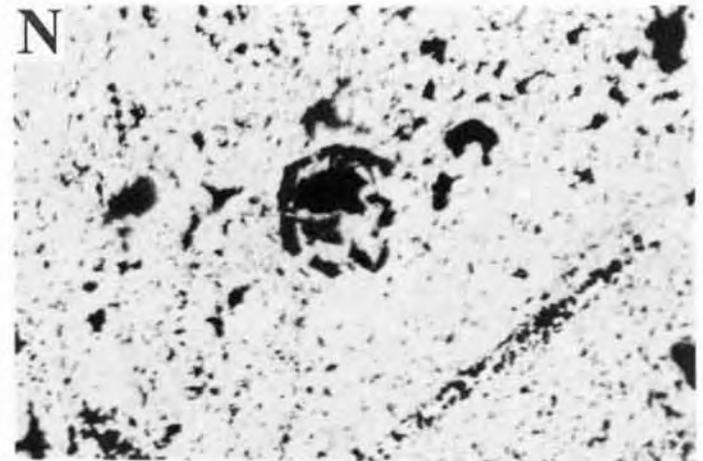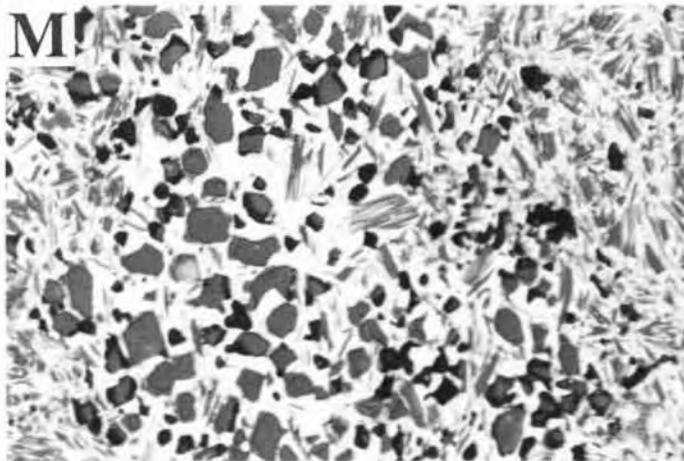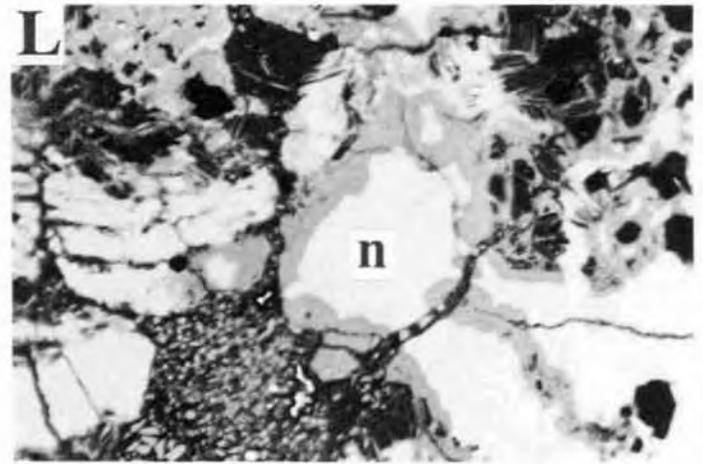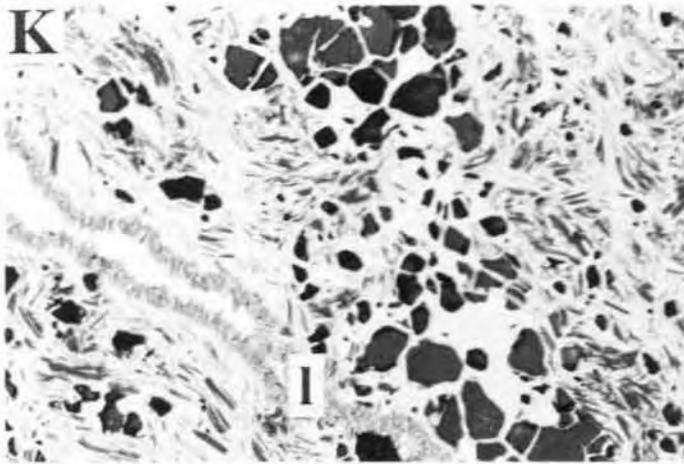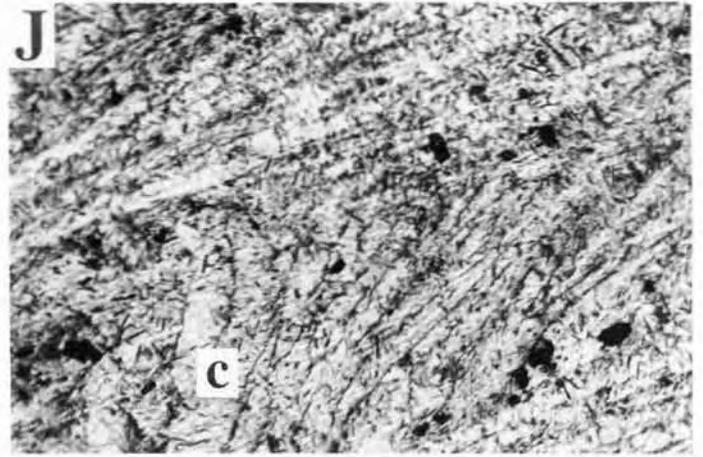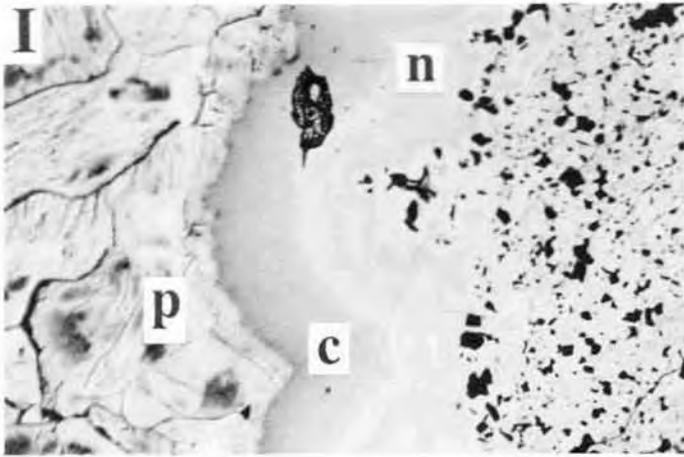
and clay minerals. These commonly form the matrix material within which many manganese oxide ore minerals, in various textures and modes of occurrence, are found (Fig.3M). Partially or completely replaced moulds and solution cavities of spessartine (Fig.3N) also occur. In one polished surface, nicely layered, parallel-oriented minerals, in association with quartz and other non-opaques, are transected mainly along fractures by manganese oxide minerals (Fig.3O). Replacement of matrix material by manganese oxide minerals is well shown, in some cases with retention of original schistose structures and microfolds (Fig.3P). Microscopic relations suggest that the original rock might have been phyllitic.

VI. Chemical compositions of minerals
1. Nsutite

EPMA analyses of nsutite are given in Table 2. It is essentially an MnO_2 mineral with traces of Si, Na, K, Al, P, Mg, Ca, Fe. In all cases, MnO_2 is around 98%; Fe_2O_3 up to 0.9%; SiO_2, CaO, Na_2O, MgO, P_2O_5 up to 0.2%; Al_2O_3 up to 0.8%; K_2O up to 0.4%.

2. Pyrolusite

Table 2 gives the results of EPMA analyses of pyrolusite. It is seen that except for phosphorus and, to some extent the Si content, the mineral is almost devoid of other elements. MnO_2 was found to be around 98 %; Fe_2O_3 up to 0.3%; CaO, Na_2O, MgO, K_2O always less than 0.1%; SiO_2, Al_2O_3 up to 0.6%; P_2O_5 up to 1.3%.

3. Cryptomelane

Analyses of optically homogeneous layers are shown in Table 2. These are from colloform cryptomelane associated with nsutite. Other textural types were mostly found, under back-scattered electron image, to be heterogeneous. It is seen that the K contents are exceptionally low when compared to cryptomelane from some other localities (Frenzel, 1980; Ostwald, 1988). Impurities are essentially the same as in nsutite and pyrolusite.

Chemical composition of the mineral is as follows : MnO_2 around 95%; Fe_2O_3 about 2%; SiO_2, MgO, P_2O_5 up to 0.2%; CaO, Al_2O_3 up to 0.5%; Na_2O roughly 0.8%; K_2O up to 2.1%.

4. Lithiophorite

In EPMA determinations (qualitative only),

Fig. 3. Photomicrographs of polished sections showing some textures in the manganese oxide ore samples. All photographs in reflected plane polarized light; width of sections = 0.6mm. A. Massive nsutite vein (n) rimmed by lithiophorite (l). Occupying a cavity on the left (p) is pyrolusite. B. Clusters of mammillary nsutite (n) in manganese oxide ore. C. Nsutite (n, with cracks) developing from an intimate intergrowth of pyrolusite and cryptomelane. Dark grey areas are cryptomelane; non-opaque minerals and voids are black. D. Accicular and radiating crystals of pyrolusite (p) growing respectively outwards from cavity-filling nsutite (n). E. Pyrolusite crystals, with distinct cleavage traces, showing replacement by cryptomelane. Cryptomelane areas appear dark grey. F. Selective replacement of tabular pyrolusite crystals (p) by cryptomelane (c). G. A veinlet of pyrolusite (p), cuts across colloform alternations of nsutite (n) and cryptomelane (c). At the right end of the section, a siliceous rock is replaced by manganese oxide minerals. H. Massive cryptomelane, with shrinkage cracks. Abundant dark, spotty areas are mainly non-opaque minerals. I. Cryptomelane (c) in rhythmic alternation with nsutite (n). Immediately bordering cryptomelane (left) is pyrolusite (p). On the right of section, manganese oxide minerals have replaced preexisting rock. Dark areas are non-opaque minerals. J. Cryptomelane (c) pseudomorphous after pyrolusite. Crystalline outline of pyrolusite still preserved. K. Lithiophorite (l) and other manganese oxides developing in a silicate rock. Fibrous mineral mainly muscovite. Dark, subhedral grains are quartz. L. Colloform mineral (dark grey) associated with nsutite (n) in some specimens of manganese oxide ore. Dark areas are voids and non-opaque minerals. M. Muscovite-quartz rich rock showing extensive replacement by manganese oxide minerals (high reflectivity). N. Leached and partly replaced crystal of spessartine, with retention of original cubic outline, in manganese oxide ore. Dark areas within spessartine mould are voids. O. Manganese oxide minerals filling a fracture in a phyllitic rock. Note fracture approximately in direction of schistosity. Bright areas on both sides of fracture (within rock) are manganese oxide minerals replacing original rock. P. Replacement of original rock by manganese oxides. Note the presence of microfolds suggestive of pre-ore deformation.

Table 2. Electron probe microanalysis of pyrolusite, nsutite, and cryptomelane (wt %)*

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
MnO$_2$'	98.82	98.06	98.40	97.31	99.94	97.80	98.78	96.97	97.30	98.04	99.13	99.91	93.60	94.45	96.47	96.18
CaO	0.17	0.19	0.18	0.20	0.12	0.22	0.08	0.07	0.06	0.04	0.04	0.06	0.50	0.35	0.38	0.25
MgO	0.13	0.14	0.14	0.20	0.03	0.06	0.01	-	0.02	-	0.03	0.02	0.10	0.04	0.02	0.01
Fe$_2$O$_3$'	0.24	0.93	0.24	0.89	0.16	0.16	0.22	0.18	0.27	0.20	0.29	0.18	0.22	0.16	0.22	0.18
Al$_2$O$_3$	0.28	0.22	0.71	0.76	0.30	0.60	0.16	0.50	0.14	0.01	0.21	0.13	0.48	0.39	0.38	0.33
SiO2	0.06	0.14	0.17	0.13	0.12	0.13	0.56	0.40	0.22	0.18	0.15	0.32	0.07	0.22	0.07	0.09
Na$_2$O	0.16	0.10	0.15	0.12	0.11	0.19	0.02	0.02	0.09	0.01	0.06	0.02	0.75	0.72	0.75	0.78
K$_2$O	0.32	0.19	0.32	0.26	0.16	0.43	0.02	0.04	0.04	0.03	0.05	0.04	1.74	2.13	1.70	1.83
P$_2$O$_5$	0.16	0.19	0.23	0.20	0.17	0.18	0.13	0.78	1.26	1.02	0.51	0.96	0.11	0.10	0.08	0.07
Total	100.34	100.16	100.54	100.07	101.11	99.77	99.98	98.60	99.40	99.13	100.47	101.64	97.57	98.56	100.07	99.72

*Analysis 1-6, nsutite; 7-12, pyrolusite; 13-16, cryptomelane.
- Not detected.
'Mn, Fe as MnO$_2$ and Fe$_2$O$_3$, respectively.

the mineral is found to be composed of manganese and aluminium, with traces of Co, Ni, Zn, and probably undetectable Li and H$_2$O.

5. Unknown mineral

Microprobe analyses (Table 3) reveal that the mineral is an iron oxide phase rich in manganese and phosphorus. Al and Si contents are similarly higher in comparison with the manganese oxide minerals nsutite, pyrolusite, and cryptomelane.

VII. Discussion

Service (1943), in a discussion on the Nsuta manganese oxide ores, noted that a representative profile through the ore (then only manganese oxides) revealed a downward sequence from a mass of lateritized or detrital ores through leached and porous types to a more compact ore, the latter often

Table 3. Electron probe microanalysis of unknown mineral (wt%)

	1	2	3	4
MnO$_2$'	14.50	14.50	16.58	10.75
Fe$_2$O$_3$'	67.69	67.56	65.39	71.89
Al$_2$O$_3$	2.88	2.25	1.83	1.76
SiO$_2$	0.67	0.72	0.65	1.03
P$_2$O$_5$	15.26	15.81	16.42	16.50
Total	101.00	100.84	100.87	101.93

'Mn, Fe as MnO$_2$ and Fe$_2$O$_3$, respectively.

showing relict sedimentary features. He further indicated that structures reminiscent of the effects of weathering and lateritization were prominent. According to Sorem and Cameron (1960), the mineral assemblage, paragenetic sequence, and the structures and textures of the ores were consistent with supergene deposition of the manganese oxides. It may be of interest to note that several workers have emphasized the apparent difficulty in identifications of manganese oxide minerals, especially in many of their concentrations in weathering environments (Potter and Rossman, 1979; Parc et al., 1989; Ostwald, 1988). This difficulty has usually been attributed to the often poorly crystallized, finely particulate and disordered nature of manganese oxide concentrations in such environments.

Powder diffraction patterns obtained from ore samples in the present study are generally broad and diffuse. Some patterns are characterized by quite prominent peaks, but most could not be assigned to either nsutite, cryptomelane, or pyrolusite due to similarities in d-values. In spite of these apparent setbacks, textural characteristics, where prominent, facilitated identification amongst the manganese oxide minerals, notably according to the identification procedures of Sorem and Cameron (1960). Pyrolusite in the ores is almost always crystalline. Cleavage is distinct, and anisotropism

well shown. The reaction to the sensitive plate for lithiophorite as well as its association with nsutite enabled the former to be easily identified. The major obstacle was between cryptomelane and nsutite, especially in their cryptocrystalline and colloform varieties. However, in dense or massive types, texture, anisotropic character, and mode of occurrence of the minerals served to distinguish between them.

Some authors assert the importance of parent rock composition and mineral assemblage as controls on ultimate mineralogy in weathered or supergene derived manganese oxide deposits (Parc et al, 1989; Roy, 1968). Bricker (1965) has, on the contrary, noted the apparent similarity in oxide mineralogy regardless of protore type. The latter has indicated that the physico-chemical environment of formation and availability of ions in the weathering profile might be influential in ultimate oxide mineralogy. It seems clear, therefore, that the mineralogy as well as mineral associations at any particular deposit could be dependent on several factors and could therefore be varied and complex. This situation may hold true for the Nsuta ores, given the complexities of mineral relationships as outlined above.

Vertical columnar crystals of pyrolusite replaced by cryptomelane; pyrolusite veinlets traversing colloform nsutite, cryptomelane, and earlier pyrolusite; relict pyrolusite cores in nsutite; cryptomelane veinlets traversing nsutite; and massive cryptomelane being replaced by nsutite, all exemplify the complexity of mineral relationships. As observed microscopically, therefore, sequences of replacements and crosscutting relationships do not permit any meaningful deduction of which mineral or minerals could have been early or late in the sequence. Indications of processes responsible for ore formation are, however, observed. Cavities and moulds of spessartine garnet, in some cases partially or completely replaced by manganese oxide minerals; the presence of abundant relict silicate gangue (commonly quartz and micaceous minerals) within manganese oxides; relict layering or banding, some showing microfolds; and the preponderance of manganese oxide minerals in cavities and in

fractures, all attest to probable secondary derivation of the manganese oxide ore. These observations seem to confirm those of Service (1943) and Sorem and Cameron (1960) on the weathered or supergene origin of the ores.

The complete absence of carbonate minerals in the samples studied may be quite intriguing, more especially so when other relict silicate minerals are observed. It is suggested that in cases where carbonate protores might have been involved in manganese oxide mineralization, processes responsible for ore formation may have proceeded to such an extent that no vestiges of carbonate minerals remained. The fact that some polished surfaces consisted almost exclusively of nsutite and/or cryptomelane, with little or no indications of other minerals or their relict equivalent, may be consistent with such a supposition.

Chemical compositions of nsutite, cryptomelane, and pyrolusite indicate very little contamination from other elements. A comparison of the elemental compositions of pyrolusite and nsutite (Table 2) shows that apart from Si and P, pyrolusite seems to have less affinity for other elements. It is therefore seen that the Na, K, Ca, and Mg contents are almost negligible in pyrolusite compared with quite significant traces in nsutite. The Fe and Al contents are also slightly higher in nsutite than pyrolusite. Although P contents are higher in pyrolusite than nsutite, much variability is shown in pyrolusite, suggesting that nsutite may be relatively uniform in its uptake of phosphorus. Cryptomelane, on the other hand, seems to be associated with Na and Ca more than either nsutite or pyrolusite. The rather low content of potassium in the cryptomelane analyses may be quite interesting. Analyses of the mineral from Sandur, India (quoted in Frenzel, 1980; p61) similarly contained almost no K.

The relatively high Si content in pyrolusite may indicate the element's presence in cleavage planes (Ostwald, 1988), whereas the increased P content may be reminiscent of selective incorporation into the crystal lattice of pyrolusite (Pracejus and Bolton, 1992). Concentration of the trace elements

Ni, Co, and Zn in lithiophorite may be consistent with observations of some other workers (Larson, 1970; Ostwald, 1988).

The unidentified Fe mineral associated with nsutite could presumably be an alteration product of the latter by Fe-rich solutions. Some manganese oxide ores are associated with high phosphorus goethite or hematite (Slee, 1980). It could thus be possible that the unknown Fe phase may be similar in mineralogy to one of these Fe minerals.

VIII. Conclusions

Nsutite and/or cryptomelane may be the most abundantly occurring mineral (s) in the manganese oxide ore samples studied. Lithiophorite is also mostly observed in the marginal areas of fractures and cavities in-filled by nsutite. Pyrolusite is found mainly in the detrital ore. Due to complexities in crosscutting and replacement textures, no definite paragenetic relationships could be established. Chemical compositions of the minerals indicate high manganese contents, with very little contamination from other elements. The mineralogical characteristics of the samples may be consistent with their formation in weathered environments.

References

Bricker, O.B. (1965), Some stability relations in the system Mn-O$_2$-H$_2$O at 25° and one atmosphere total Pressure. *Am. Mineralogist*, **50**, 1296-1354.

Frenzel, G. (1980), The manganese ore minerals. In Geology and geochemistry of manganese, vol. 1 (Varentsov, I.M. and Grassely, G., Eds.), 25-158, Akademiai Kiado, Budapest.

Kesse, G.O. (1976), The manganese ore deposits of Ghana. Ghana Geological Survey Bulletin, No. **44**, pp.97.

Larson, L.T. (1970), Cobalt and nickel-bearing manganese oxides from the Fort Payne Formation, Tennessee. *Econ. Geol.*, **65**, 952-962.

Leube, A., Hirdes, W., Mauer, R. and Kesse, G.O. (1990), The early Proterozoic Birimian Supergroup of Ghana and some aspects of its associated gold mineralization. *Precambrian Res.*, **46**, 139-165.

Ostwald, J. (1988), Mineralogy of the Groote Eylandt manganese oxides: A review. *Ore Geology Rev.*, **4**, 3-45.

Parc, S., Nahon, D., Tardy, Y. and Vieillard, P. (1989), Estimated solubility products and fields of stability for cryptomelane, nsutite, birnessite, and lithiophorite based on natural lateritic weathering sequences. *Am. Mineralogist*, **74**, 466-475.

Potter, R.M. and Rossman, G.R. (1979), The tetravalent manganese oxides: Identification, hydration, and structural relationships by infrared spectroscopy. *Am. Mineralogist*, **64**, 1199-1218.

Pracejus, B. and Bolton, B. R. (1992), Geochemistry of supergene manganese oxide deposits, Groote Eylandt, Australia. *Econ. Geol.*, **87**, 1310-1335.

Roy, S. (1968), Mineralogy of the different genetic types of manganese deposits. *Econ. Geol.*, **63**, 760-786.

Service, H. (1943), The geology of the Nsuta manganese ore deposits. *Gold Coast Geological Survey Memoir*, No. **5**, pp.32.

Slee, K.J. (1980), Geology and origin of the Groote Eylandt manganese oxide deposits, Australia. In *Geology and geochemistry of manganese*, vol. 2 (Varentsov, I.M. and Grassely, G., eds.), 125-148, Akademiai Kiado, Budapest.

Sorem, R.K. and Cameron, E.N. (1960), Manganese oxides and associated minerals of the Nsuta manganese deposits, Ghana, West Africa. *Econ. Geol.*, **55**, 278-310.

Yui, S. (1992), A system of EPMA data reduction programs using BASIC for personal computers in 1992. *Jour. Fac. Sci., Hokkaido Univ., Ser. IV*, **23**, 147-158.