THE AMERICAN MINERALOGIST, VOL. 47, MARCH-APRIL, 1962

# NSUTITE—A WIDESPREAD MANGANESE OXIDE MINERAL

W. K. ZWICKER, W. O. J. GROENEVELD MEIJER AND H. W. JAFFE,
*Union Carbide Ore Company, Division of Union*
*Carbide Corporation, Tuxedo, New York.*

## ABSTRACT

Nsutite is a widespread, hydrated, manganese oxide mineral of the composition: $Mn_{1-x}^{4+}Mn_x^{2+}O_{2-2x}(OH)_{2x}$; where $x=0.06$–$0.07$ for analyzed material from Ghana, Greece, and Mexico; and $x=0.16$ for a manganoan variety from Ghana. Nsutite occurs as opaque, dark gray to black, porous to dense aggregates; G is variable from 4.24–4.67; $H=8.5$ (Moh's scale) and 1150 (Vicker's scale). It shows a strong, diagnostic *x*-ray diffraction line at 1.64 Å. In reflected light, nsutite is anisotropic; reflectivity in air=40% (E), 38.5% (D), and 34.3% (C). Manganoan nsutite occurs in black, opaque masses; $G=3.86$; $H=6.5$–$7$ (Moh's scale) and 900 (Vicker's scale). It shows a strong, diagnostic *x*-ray diffraction line at 1.67 Å. It is anisotropic in reflected light; reflectivity in air=29.7% (E), 20.2% (D), and 16% (C).

Thermochemical and *x*-ray diffraction studies show that manganoan nsutite inverts to nsutite when heated to 150° C. in air; to a pyrolusite-type structure at 450° C. in oxygen; to bixbyite at 550–850° C; to hausmannite at 950°–1100° C.; and to a spinel form at temperatures above 1100° C. Manganoan nustite commonly forms from the oxidation of rhodochrosite or manganoan calcite. It is a relatively uncommon mineral probably because it is converted to nsutite by further oxidation.

## INTRODUCTION, HISTORY AND NOMENCLATURE

Gamma-$MnO_2$ is a collective name which is used to designate a group of slightly different synthetic phases of manganese dioxide, largely characterized by their *x*-ray diffraction patterns. Nsutite (ĕn.sōō′tīt) is the naturally-occurring equivalent of one specific form of gamma-$MnO_2$. It is named for the type locality at Nsuta, Ghana, where it occurs abundantly. The term gamma-$MnO_2$ was first used by Glemser (1939) for a specific, artificially prepared manganese dioxide. Later this term was applied to a group of materials with similar, or only slightly different, *x*-ray diffraction patterns, in papers published by Dubois (1936), McMurdie (1944), and Feitknecht and Marti (1945). Cole *et al.* (1947) summarized these data, including their own work, and suggested the terms I and II gamma-$MnO_2$ for additional distinct modifications. Several authors noted the abundance of nsutite ("gamma-$MnO_2$") in manganese ore from Nsuta in Ghana, West Africa: McMurdie (1944), (1948), Vinal (1950), Delano (1950), Skewes, Wadsley and Walkley (1952). Schossberger (1940) recognized differences in the diffraction patterns of nsutite ("gamma-$MnO_2$") and assumed that a natural series of transitions exist between gamma-$MnO_2$ and pyrolusite. Sorem and Cameron (1960) have also described nsutite ("Nsuta-$MnO_2$") from its type locality at Nsuta, Ghana. They suggest reserving the term gamma-

$MnO_2$ for artificial products only and trace the usage of the term gamma-$MnO_2$ from its inception by Glemser to the present. The reader is referred to their paper and later work performed by Brenet *et al.* (1959), de Wolff (1959), and Feitknecht, *et al.* (1960) for a detailed discussion of the implications of the term. Sorem and Cameron (1960) observed slight variations in the *x*-ray diffraction patterns of nsutite ("Nsuta-$MnO_2$") and differentiated between a "1.64, 1.65 and 1.67 type," on the basis of prominent d-spacings in diffraction patterns, but give no explanation for the shift of these diffraction lines.

Samples of the "1.64 and 1.67 types" of nsutite from Ghana have been chemically analyzed. The results show that the "1.64 type" from Nsuta contains 90.57% manganese determined as $MnO_2$ and 2.60% manganese determined as MnO. The "1.67 type," however, contains only 74.64% $MnO_2$ and as much as 11.02% MnO. This indicates that the observed shift in the *x*-ray diffraction lines is apparently due to an expansion of the unit cell caused by the presence of an increased amount of lower valent (larger) manganese ions. The two varieties, "types 1.64 and 1.67," may therefore be referred to as nsutite and manganoan nsutite, respectively.

Traore and Brenet (1959) describe how a mild cathodic reduction of synthetic gamma-$MnO_2$ in a Leclanché-type cell produces shifts in diffraction spacings due to the larger size of $Mn^{2+}$ ions which are formed during this process. Further, they describe how the expanded structures can be recollapsed by a mild thermal treatment at 120° C. in air. Feitknecht *et al.* (1960) were able to reduce partly some electrolytically prepared gamma-$MnO_2$ with hydrazine, without changing its lattice type. They state that the volume of the elementary cell increases approximately in a linear function with decreasing $Mn^{4+}$ content. One of our experiments was to heat a sample of manganoan nsutite for several hours at 150° C. The produced material gave a diffraction pattern identical to that of nsutite. The ratio $MnO/MnO_2$ changed during this heat treatment from 1:5 to 1:20, respectively.

The authors have observed that nsutite is far more abundant than manganoan nsutite. The latter was identified in only two of many samples studied over the past few years.

## CHEMICAL COMPOSITION

Three samples of nsutite and one of manganoan nsutite have been analyzed. Analyses are presented here (Table 1) on nsutite from Nsuta, Ghana; Tartana,[1] Greece; and the Molango Piedras Negras area,

---

[1] The "Tartana" mine, owned and operated by Dimitry Scalistiri, is located some 20 miles north of Drama, Macedonia, Greece. The authors are indebted to Mr. Sanford R. Knapp who kindly supplied the sample from his private collection.

TABLE 1.—ANALYTICAL RESULTS AND CALCULATIONS FOR NSUTITE AND MANGANOAN NSUTITE

| Analytical Results | | | | | Cations on the basis of 2.00 oxygens** $Mn^{4+}$ & $Mn^{2+}$ | | | | | | Cations on the basis of 2.00 oxygens** $Mn^{4+}$ & $Mn^{3+}$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | | 1 | 2 | 3 | 4 | | | 1 | 2 | 3 | 4 | |
| $MnO_2$ | 93.27 | 90.57 | 89.20 | 74.64 | $Mn^{4+}$ | .9144 | .9050 | .8773 | .8029 | | $Mn^{4+}$ | .8933 | .8731 | .8668 | .6578 | |
| $MnO$ | 1.76 | 2.60 | .87 | 11.01 | $Mn^{2+}$ | .0211 | .0319 | .0105 | .1451 | | $Mn^{3+}$ | .0422 | .0638 | .0210 | .2902 | |
| $ZnO$ | — | — | 2.88 | — | Zn | — | — | .0303 | — | | Zn | — | — | .0303 | — | |
| $CaO$ | .72 | .08 | .92 | .04 | Ca | .0109 | .0012 | .0140 | .0061 | | Ca | .0109 | .0012 | .0140 | .0061 | |
| $MgO$ | .22 | .12 | .17 | .12 | Mg | .0047 | .0025 | .0036 | .0027 | | Mg | .0047 | .0025 | .0036 | .0027 | |
| $NiO$ | — | .14 | — | — | Ni | — .0603 | .0016 .0579 | — .0666 | — .1632 | | Ni | — .0814 | .0016 .0898 | — .0771 | — .3083 | |
| $Fe_2O_3$ | .49 | 1.07 | .20 | .47 | $Fe^{3+}$ | .0053 | .0116 | .0021 | .0055 | | $Fe^{3+}$ | .0053 | .0116 | .0021 | .0055 | |
| $Al_2O_3$ | .50 | .22 | .04 | .20 | Al | .0084 | .0037 | .0007 | .0038 | | Al | .0084 | .0037 | .0007 | .0038 | |
| $SiO_2$ | .46 | 1.17 | .07 | 6.48 | Si | .0065 | —* | .0010 | —* | | Si | .0065 | —* | .0010 | —* | |
| $Na_2O$ | <.05 | .06 | .06 | <.05 | Na | — | .0015 | .0017 | — | | Na | — | .0015 | .0017 | — | |
| $K_2O$ | .19 | .22 | .15 | <.05 | K | .0034 | .0039 | .0027 | — | | K | .0034 | .0039 | .0027 | — | |
| $H_2O+$ | 2.10 | 2.64 | 3.76 | 4.36 | $H_+$ | .1986 | .2543 | .3569 | .4528 | | $H_+$ | .1986 | .2543 | .3569 | .4528 | |
| $H_2O-$ | .57 | .33 | 1.25 | .83 | | | | | | | | | | | | |
| C | — | .03 | — | — | | | | | | | | | | | | |
| Total | 100.28 | 99.25 | 99.57 | 98.15 | | | | | | | | | | | | |
| G | 4.67 | 4.55 | 4.24 | 3.86 | | | | | | | | | | | | |

—Not analyzed for

1. Nsutite, Molango Piedras Negras, Hidalgo, Mexico
2. Nsutite, Nsuta, Ghana
3. Nsutite, Tartana, Greece
4. Manganoan Nsutite, Nsuta, Ghana

1. Mexico $Mn^{4+}_{.91}(Mn^{2+}, \cdots)_{.06}O_{1.80}(OH)_{.20}$
2. Nsuta $Mn^{4+}_{.91}(Mn^{2+}, \cdots)_{.06}O_{1.75}(OH)_{.25}$
3. Greece $Mn^{4+}_{.88}(Mn^{2+}, \cdots)_{.07}O_{1.64}(OH)_{.36}$
4. Nsuta $Mn^{4+}_{.80}(Mn^{2+}, \cdots)_{.16}O_{1.55}(OH)_{.45}$

1. Mexico $Mn^{4+}_{.89}(Mn^{3+}, \cdots)_{.08}O_{1.80}(OH)_{.20}$
2. Nsuta $Mn^{4+}_{.87}(Mn^{3+}, \cdots)_{.09}O_{1.75}(OH)_{.25}$
3. Greece $Mn^{4+}_{.87}(Mn^{3+}, \cdots)_{.08}O_{1.64}(OH)_{.36}$
4. Nsuta $Mn^{4+}_{.66}(Mn^{3+}, \cdots)_{.31}O_{1.55}(OH)_{.45}$

---

* Visible quartz in specimen; analysis recast to total 100.00% after deduction of $SiO_2$.

** Neglecting $H_2O$—120° C.

Hidalgo State, Mexico; and also on manganoan nsutite from Nsuta, Ghana. Samples were prepared for analysis after exhaustive *x*-ray work had been done on the hand specimens and polished sections made therefrom in order to establish their purity. Nsutite from Nsuta has a porous structure and contains small amounts of fine-grained quartz. Nsutite from Greece is massive with very minor chalcophanite which occurs as violet platelets on one side of the specimen. Chalcophanite was removed from the sample used for the analysis. The Mexican nsutite sample is also porous and it has no visible impurities. The manganoan nsutite was obtained by hand picking of an "*x*-ray pure" specimen from Nsuta. It contains some fine-grained quartz which shows up in the *x*-ray diffraction patterns.

The chemical analyses, made by R. E. Dutton,[1] are given in Table 1, columns 1–4. Available oxygen, determined by titration (oxalate method) has been used to form $MnO_2$ from total Mn (not listed here) and remaining Mn is calculated as MnO. Alternatively, $Mn_2O_3$, containing trivalent manganese could be formed through use of the equation:

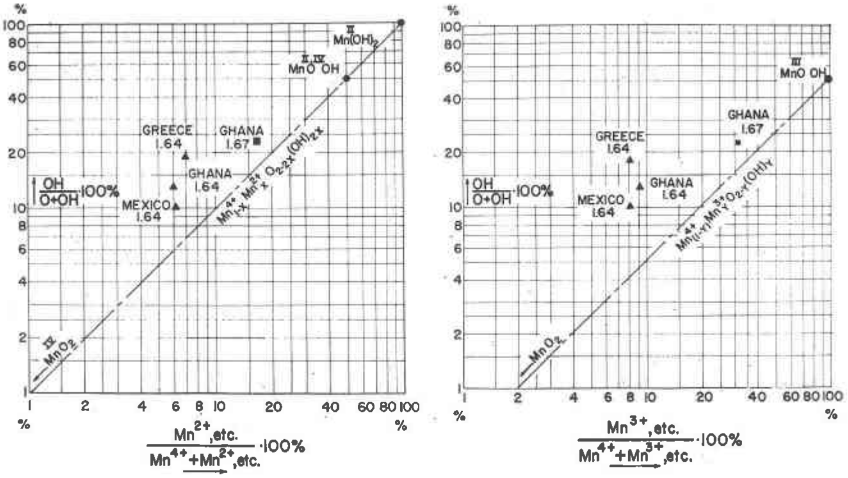
$$MnO + MnO_2 = Mn_2O_3$$

The atomic ratios and formulas obtained from the chemical analyses are presented in Table 1. In the case of both samples from Nsuta, $SiO_2$ was deducted from the analyses inasmuch as quartz was observed as an impurity. Analyses have not been corrected for $H_2O_{-120}$° C., but $H_2O_{-120}$° C. was not included in the formulas, not was its share of oxygen atoms brought into the totals. This was done since it was found that drying at 120° C. does not produce the collapse of manganoan nsutite to nsutite.

Two sets of formulas may be calculated depending on whether it is assumed that the deficiency of available oxygen to form stoichiometric $MnO_2$ is calculated as MnO or $Mn_2O_3$. It seems important to point out here that the very close stoichiometry of these formulas indicates that nsutite does not have a defective $MnO_2$ lattice. There is no agreement in the literature on the type of "lower valent" manganese in the structure of gamma-$MnO_2$ type compounds. Frondel (1953) prefers the use of trivalent manganese in the formula of hydrohausmannite; Traore and Brenet (1959) the use of divalent manganese, and Feitknecht *et al.* (1945) and (1960) the use of trivalent manganese in the formula of gamma-$MnO_2$. It is apparent that nsutite is richer in $Mn^{4+}$ and poorer in $H_2O+$ than the manganoan nsutite which has lower $Mn^{4+}$ and higher $H_2O+$ contents. This is the reason why substitutions of the type

---

[1] R. E. Dutton, Union Carbide Nuclear Company, Research Center, Tuxedo, New York.



FIGS. 1 (left) and 2 (right). Analyses of three nsutites (1.64) and one manganoan nsutite (1.67) plotted against idealized formula containing $Mn^{4+}$ and $Mn^{2+}$ or $Mn^{4+}$ and $Mn^{3+}$.

$$Mn^{4+}O^{2-} \rightarrow Mn^{+2}(OH)_2^{-1}$$

or

$$Mn^{4+}O^{2-} \rightarrow Mn^{+3}(OH)^{-1}$$

may be postulated (Feitknecht and Marti (1945)).

Such substitutions lead to the following generalized formulas:

$$\overset{4+}{Mn}_{1-x}\overset{2+}{Mn}_{x}O_{2-2x}(OH)_{2x}$$

and

$$\overset{4+}{Mn}_{1-y}\overset{3+}{Mn}_{y}O_{2-y}(OH)_{y} \text{ respectively}$$

End members of these series are:

$$MnO_2\ (x = 0),\ MnO(OH)\ (x = 1/2),\ \text{and}\ Mn(OH)_2\ (x = 1)$$

and

$$MnO_2\ (y = 0)\ \text{and}\ MnO\ (OH)\ (y = 1)$$

The generalized formulas with hypothetical end-members are plotted in Fig. 1 and 2 together with the analyses. A least squares treatment shows that the distribution of analytical points about the line representing the idealized formula is better for the case of divalent manganese. This is the only evidence which we can present for favoring the occurrence of divalent manganese in nsutite.

## *X*-RAY POWDER DIFFRACTION DATA

*X*-ray powder diffraction data obtained on the analyzed samples of manganoan nsutite and nsutite from Nsuta, synthetic gamma-$MnO_2$,[1] electrolytic gamma-$MnO_2$,[2] nsutite heated to 430° C., ramsdellite, and pyrolusite are given in Table 2a; Fig. 3 shows the *x*-ray diffraction photographs of these materials. These measurements are compared with data given by Sorem and Cameron (1960) for their "Nsuta $MnO_2$ types 1.64, 1.65, and 1.67," Cole, *et al.* (1947) for their synthetic and natural products, Glemser (1939), and the U. S. Army Signal Corps (1955) for rho-$MnO_2$, which are presented in Table 2b. Precision measurements of one and the same diffraction line on different samples of nsutite using a Norelco high angle diffractometer are presented in Table 2c.

It is clear that nsutite (Fig. 3C) is identical with one form of synthetic gamma-$MnO_2$ (Fig. 3D), probably rho $MnO_2$, and the gamma-$MnO_2$-I which Cole, *et al.* (1947) described as occurring in manganese ores from Ghana and other parts of the world. The general similarity between the nsutite patterns, and the patterns of ramsdellite (Fig. 3A), is apparent although important differences do exist (Glemser and Meisiek, 1957). It should be noted that ramsdellite shows much sharper diffraction lines than nsutite or pyrolusite (Fig. 3). Nsutite heated to 380° C. and electrolytic $MnO_2$ have much in common and these two patterns bear a certain resemblance to pyrolusite (Fig. 3G). This resemblance becomes even stronger if nsutite is heated to 430° C. (Fig. 3F). It is curious to note that heating of nsutite does not result in clearer, line-richer patterns, but the contrary.

Nsutite is thus somewhat similar to ramsdellite, whereas heated nsutite is similar to pyrolusite. It has been proposed by de Wolff (1959) that the transitory nature of gamma-$MnO_2$ patterns between those of ramsdellite and pyrolusite is due to the fact that structural units of both end-members are present in varying amounts in gamma-$MnO_2$. However, both ramsellite and pyrolusite are described as anhydrous polymorphs of $MnO_2$.

The chemical analyses suggest that variations in $Mn^{2+}$ content are responsible for the observed line shifts in the various types. This may be explained by considering the ionic radii of manganese in its various valency states. The ionic radii of manganese are: $Mn^{2+}=0.80$, $Mn^{3+}=0.66$ and $Mn^{4+}=0.60$ Å (Ahrens, 1952). Even though nsutite may not be a purely ionic compound, it is obvious that the introduction

---

[1] Prepared by oxidation of purified manganous sulfate solution with sodium chlorate. Experimental product of American Potash and Chemical Co., Henderson, Nevada.

[2] Prepared by electrolytic deposition from manganese sulfate solution. Commercial product of American Potash and Chemical Co., Henderson, Nevada.

TABLE 2A. *X*-RAY POWDER DATA FOR RAMSDELLITE, MANGANOAN NSUTITE, NSUTITE, CHEMICALLY AND ELECTROLYTICALLY PREPARED GAMMA-$MnO_2$, HEATED NSUTITE (430° C.) AND PYROLUSITE

| Ramsdellite[1] | | | Manganoan Nsutite from Nsuta | | Nsutite from Nsuta | | Synthetic Gamma-$MnO_2$[2] | | Electrolytic Gamma-$MnO_2$[3] | | Nsutite Heated to 430° C. | | Pyrolusite[4] | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| hkl | $I/I_0$ | d(A) | $I/I_0$ | d(A) | $I/I_0$ | d(A) | $I/I_0$ | d(A) | $I/I_0$ | d(A) | $I/I_0$ | d(A) | $I/I_0$ | d(A) |
| 020 | 20 | 4.64 | VW | 4.46 | VW | 4.36 | | | | | | | | |
| 110 | 100 | 4.07 | VS | 4.10 | VS | 3.96 | VS | 3.96 | S | 3.91 | VVW | 4.00 | | |
| | | | | | | | | | | | | | W | 3.43 |
| 120 | 20 | 3.24 | | | | | | | | | | | | |
| | | | | | | | | | | | M | 3.14 | VS | 3.13 |
| | | | M | 2.66 | Tr | 2.69 | | | | | | | | |
| 130 | 100 | 2.55 | | | VW | 2.59 | M | 2.60 | | | | | | |
| 021 | 70 | 2.44 | M | 2.45 | S | 2.43 | VS | 2.42 | VS | 2.41 | VS | 2.40 | S | 2.41 |
| | | | VW | 2.39 | | | | | | | | | | |
| 111 | 60 | 2.34 | M | 2.36 | M | 2.34 | | | | | | | | |
| 040 | 50 | 2.32 | | | | | S | 2.32 | | | | | | |
| 200 | 10 | 2.27 | | | | | | | | | | | | |
| | | | | | VVW | 2.22 | | | | | | | | |
| | | | | | | | | | | | | | W | 2.20 |
| 121 | 70 | 2.19 | S | 2.16 | | | | | | | | | | |
| | | | M | 2.13 | S | 2.13 | S | 2.12 | S | 2.12 | S | 2.12 | M | 2.12 |
| 140 | 40 | 2.06 | | | VW | 2.07 | W | 2.05 | | | | | | |
| | | | | | | | | | | | VW | 2.02 | M | 1.97 |
| | | | VW | 1.924 | | | | | | | | | | |
| 131 | 70 | 1.91 | VVW | 1.880 | VVW | 1.892 | | | | | | | | |
| 230 | 20 | 1.83 | | | Tr | 1.831 | | | | | | | | |
| 041 | 10 | 1.80 | | | | | | | | | | | | |
| 150 | 10 | 1.72 | | | | | | | | | | | | |
| | | | | | Tr | 1.706 | | | | | | | | |
| 221 | 80 | 1.66 | S | 1.667 | S | 1.638 | S | 1.637 | VS | 1.631 | | | | |
| 240 | 80 | 1.62 | | | | | | | | | VS | 1.620 | VS | 1.62 |

TABLE 2A.—(*continued*)

| Ramsdellite[1] | | | Manganoan Nsutite from Nsuta | | Nsutite from Nsuta | | Synthetic Gamma-$MnO_2$[2] | | Electrolytic Gamma-$MnO_2$[3] | | Nsutite Heated to 430° C | | Pyrolusite[4] | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| hkl | $I/I_0$ | d(A) | $I/I_0$ | d(A) | $I/I_0$ | d(A) | $I/I_0$ | d(A) | $I/I_0$ | d(A) | $I/I_0$ | d(A) | $I/I_0$ | d(A) |
| | | | | | W | 1.615 | M | 1.605 | | | | | | |
| | | | | | | | | | | | M | 1.570 | S | 1.56 |
| 231 | 30 | 1.54 | | | | | | | | | | | | |
| | | | W | 1.517 | | | | | | | | | | |
| | | | | | VVW | 1.488 | VVW | 1.486 | | | | | | |
| 151 | 80 | 1.47 | | | | | | | | | | | W | 1.44 |
| 002 | 50 | 1.43 | W | 1.426 | W | 1.425 | M | 1.422 | | | W | 1.427 | | |
| | | | M | 1.394 | | | | | M | 1.395 | | | W | 1.39 |
| 061 | 80 | 1.36 | VW | 1.372 | VW | 1.362 | W | 1.362 | | | | | | |
| 112 | 40 | 1.35 | | | | | | | | | | | | |
| 301 | 10 | 1.34 | | | | | | | | | | | | |
| 311 | 50 | 1.32 | W | 1.330 | | | | | | | | | | |
| | | | VVW | 1.292 | VVW | 1.306 | VVW | 1.306 | | | VW | 1.304 | S | 1.31 |
| 170 | 60 | 1.27 | | | | | | | | | | | | |
| 132 | 60 | 1.25 | VW | 1.257 | Tr | 1.250 | VVW | 1.250 | | | | | VW | 1.25 |
| 042 | 30 | 1.22 | VVW | 1.225 | Tr | 1.212 | Tr | 1.211 | | | | | | |
| | | | | | | | | | | | | | VW | 1.20 |
| | | | VW | 1.187 | | | | | | | | | | |
| | | | | | Tr | 1.165 | Tr | 1.169 | | | | | VW | 1.16 |
| | | | VVW | 1.136 | | | | | VVW | 1.130 | | | VW | 1.12 |
| | | | Tr | 1.107 | Tr | 1.116 | Tr | 1.104 | | | | | VW | 1.10 |
| | | | W | 1.082 | VW | 1.067 | W | 1.066 | VW | 1.061 | M | 1.057 | M | 1.05 |
| | | | | | | | | | | | | | W | 1.04 |
| | | | | | | | | | | | VW | 0.999 | W | 1.00 |

[1] ASTM Card No. 7-222 (Bystrom, 1949).

[2] Experimental chemical product of American Potash and Chemical Co., Henderson, Nevada.

[3] Commercial electrolytic product of American Potash and Chemical Co., Henderson, Nevada.

[4] Ramdohr (1956).

Symbols are: VS—very strong, S—strong, MS—medium strong, M—medium, W—weak, VW—very weak, VVW—very, very weak.

TABLE 2B. X-RAY POWDER DATA FOR GAMMA-MnO$_2$, NSUTA-MnO$_2$ AND RHO-MnO$_2$

| Glemser (1939) | | Cole, Wadsley and Walkley (1947) | | | | | | Sorem and Cameron (1960) | | | | Signal Corps U.S. Army[2] 1955 | | Sorem and Cameron 1960[1] | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Gamma-MnO$_2$ | | Gamma-MnO$_2$ | | Gamma-MnO$_2^{I}$ | | Gamma-MnO$^{II}$ | | Nsuta MnO$_2$[1] (type 1.64) | | Nsuta-MnO$_2$[1] (type 1.65) | | Rho-MnO$_2$[1] | | Nsuta-MnO$_2$ (type 1.67) | |
| I/I$_0$ | d(Å) | I/I$_0$ | d(Å) | I/I$_0$ | d(Å) | I/I$_0$ | d(Å) | I/I$_0$ | d(Å) | I/I$_0$ | d(Å) | I/I$_0$ | d(Å) | I/I$_0$ | d(Å) |
| | | | | | | M | 4.38 | VVW | 4.4 | VW | 4.45 | | | W | 4.58 |
| M | 3.89 | S(d) | 4.02 | S | 3.94 | MS | 3.82 | VS | 3.96 | VS(s) | 4.00 | 10(d) | 4.0 | VW | 4.11 |
| | | | | | | | | VVW | 3.75 | | | | | | |
| | | | | | | W | 2.68 | | | | | | | M | 2.66 |
| | | VVW | 2.53 | W | 2.57 | | | VW | 2.60 | W | 2.59 | 2(vb) | 2.60 | | |
| | | | | | | | | | | | | | | M | 2.46 |
| M | 2.42 | | | | | MS | 2.42 | M(s) | 2.43 | M(s) | 2.43 | 9(s) | 2.43 | | |
| | | M | 2.41 | M | 2.41 | | | | | | | | | W(s) | 2.41 |
| | | | | VW | 2.33 | W | 2.34 | M | 2.34 | M | 2.35 | 4 | 2.35 | M | 2.36 |
| | | | | | | | | VVW | 2.21 | Tr | 2.25 | | | VW | 2.29 |
| | | | | | | | | | | | | | | S(s) | 2.17 |
| M | 2.09 | MS | 2.10 | MS | 2.11 | S | 2.12 | S(s) | 2.13 | M(s) | 2.13 | 10 | 2.12 | M | 2.14 |
| | | | | | | W | 2.05 | VW | 2.07 | VW(s) | 2.07 | | | | |
| | | | | | | | | | | | | | | W | 1.93 |
| | | | | | | | | Tr | 1.90 | VVW | 1.89 | | | VW | 1.88 |
| | | | | | | | | | | Tr | 1.82 | | | Tr | 1.85 |
| ? | 1.80 | | | | | | | | | | | | | | |
| VW | 1.614 | VS | 1.62 | VS | 1.62 | S | 1.63 | S | 1.64 | S(s) | 1.65 | 8 | 1.65 | S | 1.67 |
| | | | | | | W | 1.59 | W(s) | 1.60 | W | 1.61 | | | | |
| | | | | | | | | VVW | 1.50 | VVW | 1.51 | | | W | 1.52 |
| VW | 1.416 | | | VW | 1.41 | VW | 1.43 | VW(s) | 1.42 | VVW(s) | 1.44 | 8(s) | 1.43 | W(s) | 1.43 |
| | | | | | | | | | | | | | | M | 1.40 |
| | | W | 1.38 | VW | 1.37 | | | Tr | 1.37 | VVW | 1.37 | 2 | 1.36 | VW | 1.36 |
| VW | 1.349 | | | | | VW | 1.35 | | | VW | 1.35 | | | | |
| | | | | | | | | | | | | | | W | 1.33 |
| VW | 1.305 | | | | | VW | 1.31 | Tr | 1.30 | Tr | 1.31 | 2(vb) | 1.30 | VVW | 1.29 |
| | | | | | | | | Tr | 1.27 | | | | | VW | 1.26 |
| | | VVW | 1.25 | | | | | | | Tr | 1.25 | vw | 1.25 | | |
| | | | | | | | | Tr | 1.21 | ? | 1.21 | vw | 1.21 | Tr | 1.22 |
| | | | | | | | | Tr | 1.17 | Tr | 1.17 | | | Tr | 1.19 |
| | | | | | | | | | | | | | | Tr | 1.14 |
| | | | | | | | | | | | | | | Tr | 1.11 |
| | | | | | | | | VVW | 1.06 | VVW | 1.07 | 2(vb) | 1.07 | W | 1.08 |

[1] Lines are broad unless designated sharp by letter s or very broad by letters vb.
[2] See Sorem and Cameron (1960).
Symbols are: VS—very strong, S—strong, MS—medium strong, M—medium, W—weak, VW—very weak, VVW—very, very weak, (d)—diffuse.

TABLE 2c. PRECISION MEASUREMENTS OF A PROMINENT *X*-RAY POWDER DIFFRACTION LINE OF NSUTITE AND MANGANOAN NSUTITE FROM DIFFERENT LOCALITIES

| Location | Mineral | *d*(Å) |
|---|---|---|
| Mexico | nsutite | $1.635^5 \pm .0004$ |
| Nsuta | nsutite | $1.638^2 \pm .0004$ |
| Tartana | nsutite | $1.639^4 \pm .0007$ |
| Nsuta[1] | nsutite | $1.644^5 \pm .0004$ |
| Nsuta | manganoan nsutite | $1.666^9 \pm .0010$ |

[1] Not chemically analyzed.

of $Mn^{2+}$ in lieu of $Mn^{4+}$ does expand the structure. Incidentally, this reasoning cannot solve the problem of whether $Mn^{3+}$ or $Mn^{2+}$, substitutes for $Mn^{4+}$. The deficit in available oxygen to form $MnO_2$ can be calculated as being due to the presence of $Mn^{3+}$ or one-half as much $Mn^{2+}$ and an expansion would result in both cases. On the basis of chemical data, however, the authors believe that $Mn^{2+}$ substitutes for $Mn^{4+}$. The introduction of $OH^-$ for $O^{2-}$ would not produce any significant changes as the ionic radii are very similar: $O^{2-} = 1.32$ Å and $OH^- = 1.33$ Å (Goldschmidt, 1954). The Greek sample contains considerable zinc and, although chalcophanite occurs locally in the hand specimen, most of the zinc reported in the analysis must be substituting as $Zn^{2+}$ for $Mn^{2+}$. The ionic radius of zinc is 0.74 Å, intermediate between the radii of $Mn^{2+}$ and $Mn^{3+}$.

Feitknecht, *et al.* (1960) found that the volume of the elementary cell of synthetic gamma-$MnO_2$ increases approximately linearly with decreasing $Mn^{4+}$ content. Nsutite and manganoan nsutite may therefore be considered as members of a series in which $Mn^{2+}$ or $Mn^{3+}$ replaces $Mn^{4+}$. Nsutite is by far the most common member of this series. The diffraction data for nsutite from Nsuta presented in Table 2a represent values for an average type of nsutite. Measured diffraction lines of other nsutite samples showed a maximum shift of $\pm 0.006$ Å for the $\sim 1.64$ Å line. Manganoan nsutite was found only in two samples from Nsuta. "Nsuta $MnO_2$-type 1.65," described by Sorem and Cameron (1960), as strongly resembling rho-$MnO_2$, may be an intermediate member of the series between nsutite and manganoan nsutite.

## THERMOCHEMICAL STUDIES

Manganoan nsutite (Fig. 3B) when heated to 150° C. for 16 hours in air reverts to nsutite (Fig. 3C). Synthetic reduced gamma-$MnO_2$ ap-

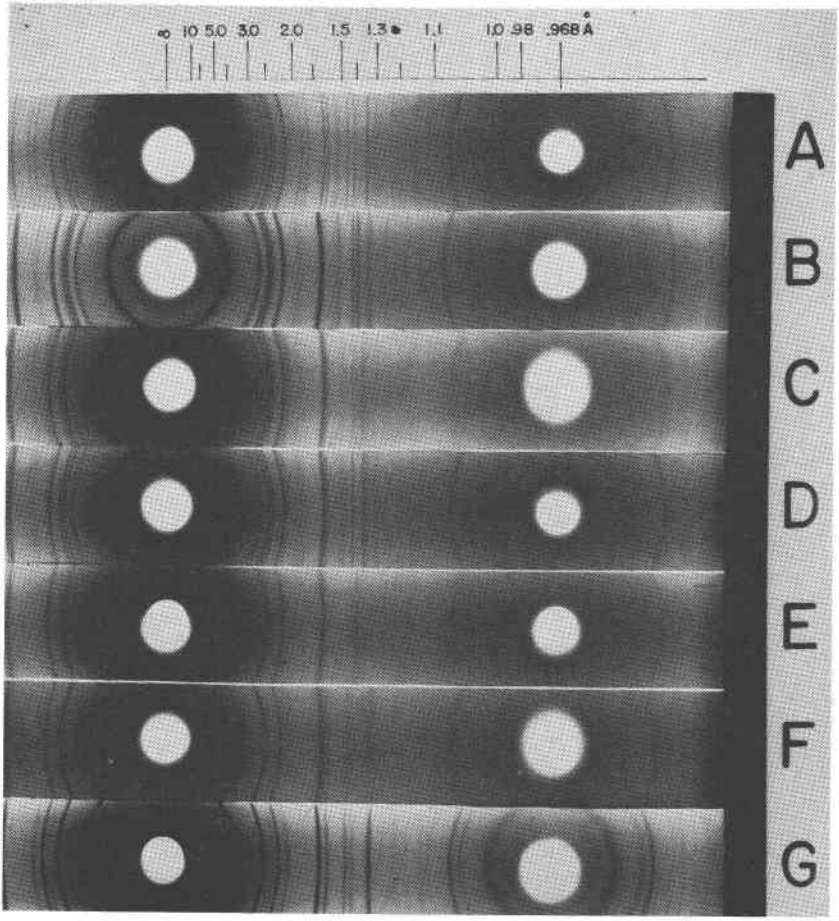


FIG. 3. $X$-ray powder diffraction patterns of: A—Ramsdellite (Durango, Mexico); B—Manganoan nsutite (Nsuta, Ghana); C—Nsutite (Nsuta, Ghana); D—Synthetic gamma-$MnO_2$ (chemically precipitated) (American Potash and Chemical Company); E—Electrolytic gamma-$MnO_2$, (American Potash and Chemical Company); F—Nsutite heated to 430° C.; and G—Pyrolusite (Nsuta, Ghana), using filtered iron radiation.

parently reverts at 120° C. (Traore and Brenet, 1959). The $MnO:MnO_2$ ratio changes during this heat treatment from 1:5 to 1:20, which means that nearly 70% of the MnO in the manganoan nsutite is oxidized to $MnO_2$. No structural changes were noted when this converted material was heated for 16 hours at 170° C. and 190° C., respectively. Upon heating to 380° C. the nsutite pattern degrades into a pattern containing only a few lines. After heating to 430° C. in air, the patterns (Fig. 3F) resemble that of pyrolusite (Fig. 3G). When nsutite is heated in pure dry oxygen at atmospheric pressure for 15 minutes at 450–500° C., the *x*-ray diffraction pattern obtained is identical to that of pyrolusite except for a slightly diffuse (110) reflection at 3.1 Å. A chemical analysis of this pyrolusite showed no notable difference in the $MnO_2$ and MnO content to that of the original nsutite, which indicates that the $Mn^{2+}$, originally present in nsutite, cannot be oxidized under these conditions once it occurs in a pyrolusite structure. The deficiency in oxygen should give rise to distorted oxygen octahedra in the structure. The fact that these more distinct pyrolusite patterns are obtained at higher temperatures (below the transition to bixbyite) indicates that some type of ordering takes place with increased temperature. When the same nsutite is heated under identical conditions in oxygen-free, dry nitrogen, considerable oxygen is evolved and bixbyite is formed.

Thermogravimetric curves were obtained with an automatically recording thermobalance having a heating rate of $7\frac{1}{2}$° C. per minute. Figure 4 shows the curves for nsutite and manganoan nsutite from Nsuta run in air. Several runs of other samples of nsutite from Nsuta showed good reproducibility of these curves. Since the temperature limit of the thermobalance was about 1000° C., the rest of the curve (1000–1200° C.) was constructed from data obtained from weight losses determined after heat treatments in a high temperature furnace. This part of the curve is dotted in Fig. 4A. Figure 4B shows the inverse of the first derivative of the thermogravimetric curves, versus the change in temperature. This method permits selection of the transformation point for reactions connected with weight loss because each acceleration in weight loss appears as a minimum in this curve. The position of each of these minima corresponds to an inflection point on the thermogravimetric curve in Fig. 4A. Temperature ranges in which the weight stays constant lead to infinity which means an interruption of the curve for these temperatures in the upper part of Fig. 4B.

Differential thermal analysis curves were obtained from an automatic, photographically recording unit with a standard heating rate of 10° C. per minute. Calcined alumina was used as inert reference material and only $\frac{1}{10}$ of the full sensitivity of the apparatus was applied during these runs. The curves, obtained from samples of the same specimens which were used for the thermobalance studies, have been plotted in Fig. 4C.

The materials used for all thermochemical studies were crushed in identical manner to minus 400 mesh size. Each sample was examined afterwards by *x*-ray diffraction for its purity.

The transformation of the manganoan nsutite to nsutite between 120° and 150° C. is described above. It is evident that between 100° and

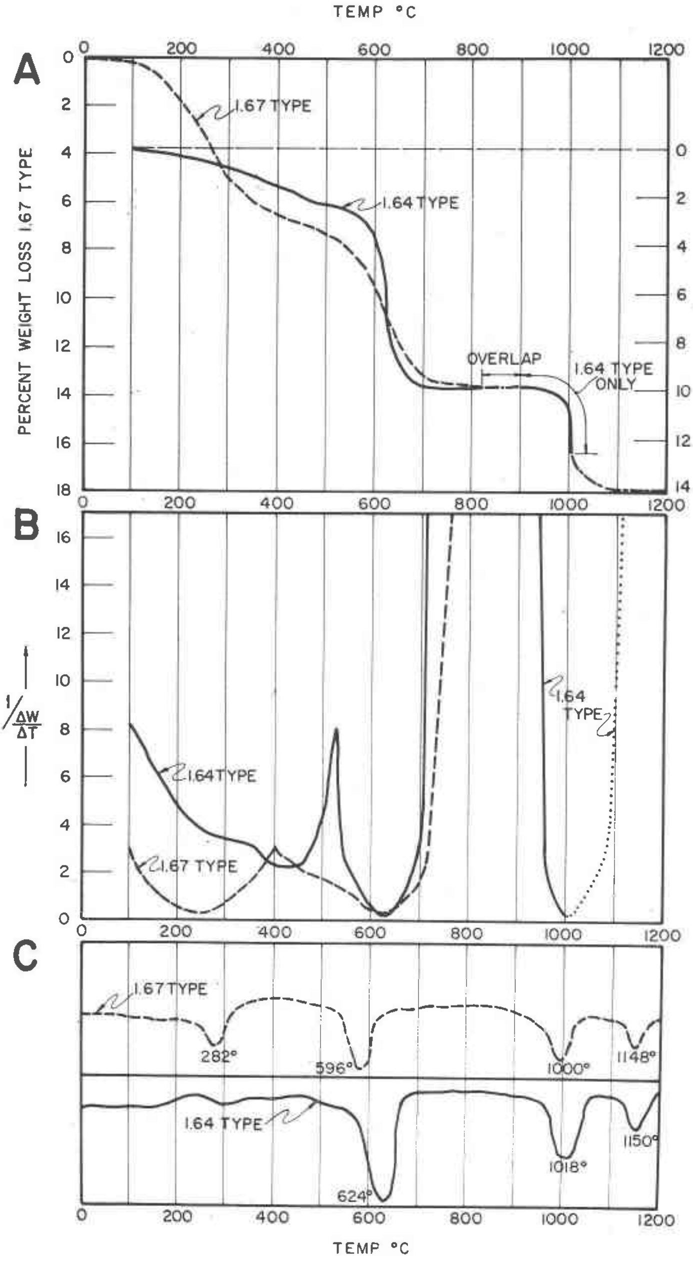


FIG. 4. A—Thermobalance curve of nsutite (1.64) and manganoan nsutite (1.67) from Nsuta, Ghana; B—First derivative curves of the thermobalance curves; C—DTA curves of the same two samples.

450° C. manganoan nsutite loses more weight than nsutite, although the thermobalance curves for the two show a slightly different course. The net weight losses in this area are due to the loss of adsorbed water and hydroxyl as exemplified by the following reaction:

$$\mathrm{Mn}_{1-x}^{4+}\mathrm{Mn}_x^{2+}\mathrm{O}_{2x}^{2-}(\mathrm{OH})_{2x} + \mathrm{y\,H_2O} \rightarrow \mathrm{MnO}_{2-\mathrm{x}} + (\mathrm{x}+\mathrm{y})\mathrm{H_2O}.$$

The point where the dehydration and formation of $MnO_{2-x}$ is completed and the reduction to $Mn_2O_3$ is just starting shows up as a minimum in the weight loss curve. Figure 4B shows that this point lies for the manganoan nsutite at 400° C. and for nsutite at around 530° C., for samples heated on the thermobalance in air. Samples heated to this temperature showed *x*-ray diffraction patterns very similar to pyrolusite. The net weight losses at these points were about 2.3% and 6.4% for nsutite and manganoan nsutite, respectively. Figure 4B shows also that the greatest rate of weight loss occurs at 240° C. and 440° C. for manganoan nsutite and nsutite, respectively.

The transformation to bixbyite causes the greatest weight loss according to the thermobalance curves. This transformation is complete at about 850° C. and the thermobalance curves of nsutite and manganoan nsutite have been united at this point in Fig. 4A. Figure 4B shows that the maximum rate of weight loss is at about 620° C. for both nsutite as well as manganoan nsutite. A further 4% weight loss is incurred during the transformation of bixbyite ($Mn_2O_3$) to hausmannite ($Mn_3O_4$), between 950° and 1100° C. The maximum rate of weight loss during the bixbyite-hausmannite transformation occurs at about 1010° C.

The chemical analyses of nsutite and manganoan nsutite from Nsuta, listed in Table I, may be used to calculate the weight lost in the transition from nsutite, through $MnO_{2-x}$ and $Mn_2O_3$, to $Mn_3O_4$. The respective weight loss percentages for nsutite are: 3.0%, 11.1% and 14.0%. In Fig. 4A the thermobalance curve is continued for nsutite beyond 1000° C. to a net weight loss of 14.15%, the value observed by heating a sample at 1100° and 1200° C. The calculated weight losses for manganoan nsutite are 5.3%, 11.0% and 13.8%, respectively. When comparing these figures with the thermal balance curves it is apparent that the figures check fairly well for nsutite but that the correspondence is poor for manganoan nsutite. This lack in correspondence is probably due to different moisture contents as the chemical analysis was performed on a different material than that used for the thermobalance experiments.

The differential thermal analysis curves for nsutite and manganoan nsutite, shown in Fig. 4C, agree well with the thermobalance curves. The curve of manganoan nsutite exhibits four endothermic peaks. The weak endothermic reaction at 282° C. is apparently caused by the dehydration and oxidation of the manganoan nsutite. The transformation to bixbyite is indicated by a peak at 596° C. and the transformation of bixbyite to hausmannite by a peak at 1000° C. Nsutite shows no definite dehydration reaction. The formation of bixbyite is indicated at 624° C. and the transformation of bixbyite to hausmannite at 1018° C.

Both nsutite and manganoan nsutite show a reversible endothermic peak at about 1150° C. According to McMurdie and Golovato (1948, p. 598), this reversible effect is due to the transition of the tetragonal beta form of $Mn_3O_4$ to the cubic gamma-form of $Mn_3O_4$. This spinel form of $Mn_3O_4$ has also been observed during heat treatments of cryptomelane by Faulring *et al.* (1960).

Differential thermal analysis curves of natural "gamma-$MnO_2$" obtained by McMurdie and Golovato (1948) and Sreenivas (1947) appear very similar to the curves for nsutite presented in Fig. 4C.

Ukai, Nishimura and Mayeda (1946, p. 212) found that "natural gamma-$MnO_2$" shows an endothermic peak slightly below 200° C., attributable to dehydration, and further peaks between 500 and 700° C. and 950° and 1000° C., attributable to the formation of bixbyite and hausmannite, respectively. The imprecise location of these endothermic peaks with respect to temperature was noted on D.T.A. curves of different samples. This is probably due to such factors as particle and crystallite sizes and lattice imperfection. The beta-gamma $Mn_3O_4$ inversion, however, is spontaneous and similar in character to the alpha-beta quartz inversion.

## OCCURRENCE

Nsutite has been found as a major constituent in manganese ores from Nsuta but it has also been found in samples from Tartana, Greece, and the Molango Piedras Negras area, State of Hidalgo, Mexico. It was further observed in a sample from the Morro da Mina mine, Lefaiete District, Minas Gerais, Brazil. Sorem and Cameron (1960) have observed material, which yielded *x*-ray patterns closely resembling those of nsutite, in specimens from Busuanga Island, Philippines and the Quadrilatero Ferrifero, Brazil. Sreenivas (1947) reports natural "gamma-manganese dioxide" from Mysore, India. McMurdie and Golovato (1948) describe natural "gamma manganese dioxide" from Ghana, California, Papua and Hunan, China; and Cole, Wadsley and Walkley (1947) from Mt. Martin and Mossman, Queensland; Barabba, New South Wales; Auckland, New Zealand; and Phillipsburg, Montana. The *x*-ray diffraction pattern of nsutite is also similar to that of "Mineral V" from several additional localities in U. S. Geological Survey *x*-ray files.

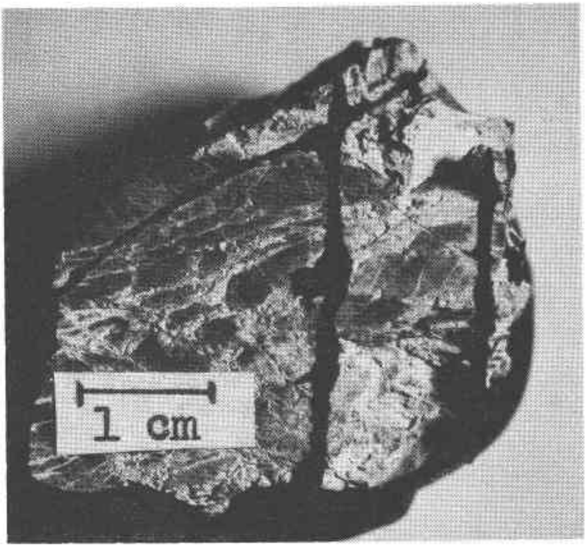


FIG. 5. Manganoan nsutite forming replacement veinlets in manganese carbonate from Nsuta, Ghana.

There is little doubt that nsutite will eventually be detected in manganese deposits throughout the world, and that it is much more abundant then ramsdellite.

It is doubtful whether nsutite can be identified from a megascopic examination alone. Shrinkage cracks, however, which are somewhat diagnostic for nsutite in polished sections, give massive specimens, such as that from Tartana, a strongly developed columnar jointing (Fig. 6). The Morro da Mina material is a soft, brown, earthy mass, whereas numerous samples from the Nsuta mine are fairly hard, metallic gray, porous aggregates.

Characteristic of many occurrences of nsutite is its proximity to manganese caronbate. In some occurrences manganoan nsutite forms replacement veinlets in manganese carbonate rock (Fig. 5). It then appears to be among the first oxides forming from the oxidation of manganese carbonate along with birnessite. In other specimens from Nsuta, described by Sorem and Cameron (1960) as "cavity filling ore," nsutite replaces other manganese minerals along fractures, along colloform banding, or diffusely. Nsutite thus appears to form at ambient temperatures in a slightly alkaline environment such as that afforded by carbonate minerals in contact with oxygen-rich waters. It has never been found in typical hydrothermal assemblages.

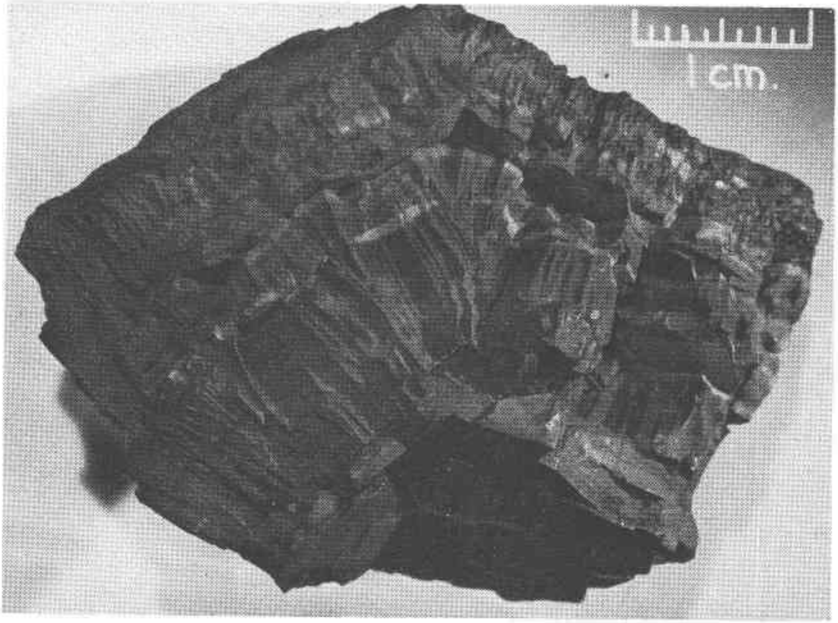


FIG. 6. Massive specimen of nsutite from Tartana, Greece, with columnar jointings.

Nsutite frequently shows shrinkage cracks in fine-grained colloform aggregates (Fig. 7). These have also been described by Sorem and Cameron (1960). Fine-grained manganoan nsutite has not been observed with this development. It is felt that the cracks might be due to the volume reduction which would occur in the transition from manganoan nsutite to nsutite. As described before, this collapse can be achieved by heating in air somewhere between 120° and 150° C. It thus appears that the transition might take place at lower temperatures in nature, possibly under the influence of different chemical environments of $E_h$ and pH, as it is unlikely that any specimens have ever been subjected to such high temperatures.

## PHYSICAL PROPERTIES

In polished sections nsutite has a high reflectivity. The results of measurements on very fine-grained nsutite aggregates are shown in Table 3. These results were obtained with a photometer ocular using monochromatic filters having maximum transmission for red (C), orange (D) and green (E) light. The reflectivity was also measured with a photoelectric lightmeter according to the method described by Folinsbee (1959). Reflectivity, as measured by these methods, is dependent on the

TABLE 3. REFLECTIVITY MEASUREMENTS ON NSUTITE

| NSUTITE | *In air* | *In oil* |
|---|---|---|
| Photometerocular | | |
| green (E) | 40% | 29.4% |
| orange (D) | 38.5% | 28.5% |
| red (C) | 34.3% | 27.2% |
| photo-electric cell | 33.4% | |
| MANGANOAN NSUTITE | | |
| Photometerocular | | |
| green (E) | 29.7% | 22.1% |
| orange (D) | 20.2% | 16% |
| red (C) | 16% | 14.2% |
| photo-electric cell | 30% | |

degree of weathering that the sample has undergone. The measurements listed in Table 3 were obtained on the freshest material available and indications are that nsutite has a higher reflectivity than manganoan nsutite.

Fine-grained nsutite is white with a slight creamy hue. It is very much like pyrolusite but slightly grayer. In coarser grained aggregates a weak but clearly visible bi-reflectance is discernible with colors which vary from grayish white with a creamy tint to bluish gray white. Cryptocrystalline aggregates of nsutite are, of course, isotropic under crossed nicols; however, under strong magnification or when one views coarser aggregates (Fig. 8), the anisotropic character of individual crystals is very distinct. The anisotropic effects range between light and dark gray without the development of colors. An uncommon fibrous form of nsutite (Fig. 9) dramatically shows the anisotropism where aggregates of fan-like oriented fibers show a radial and simulated undulatory extinction.

Nsutite and manganoan nsutite are hard minerals; with Moh's hardness of about 8.5 and 6.5–7, respectively. Sapphire tipped needles are, therefore, necessary to extract powder from polished sections for *x*-ray powder analysis. A Vicker's microhardness tester using a 300 g load gave the following Vicker's hardness numbers: nsutite 1,150 ± 50, manganoan nsutite 900 ± 50. All hardness values reported here were obtained using the freshest material available. Hardness of manganese oxides is often dependent on the state of aggregation and is therefore

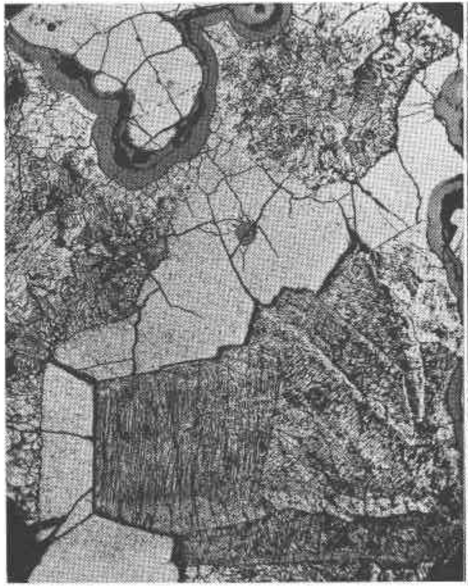


FIG. 7

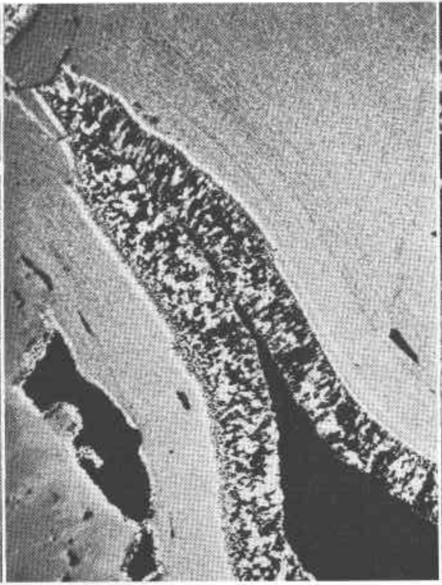


FIG. 8

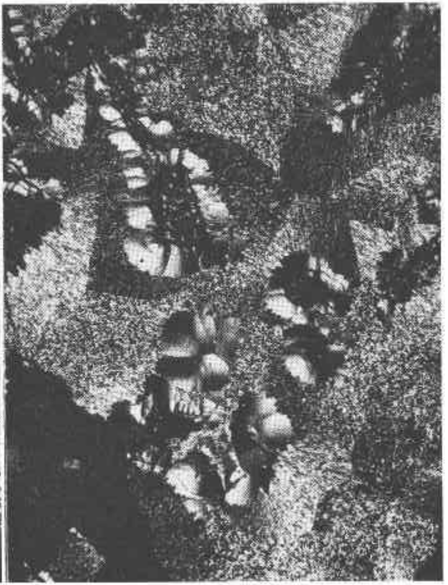


FIG. 9

FIG. 7. Polished surface of oxide ore from Nsuta, Ghana, plain light, 40×. Veinlet in center and upper left part of picture consists of an extremely fine-grained aggregate of nsutite crystals (white). In top and lower right part of picture aggregates of large, often well-developed, pyrolusite crystals. In upper left corner a veinlet of goethite (gray) surrounds nsutite.

FIG. 8. Polished surface of oxide ore from Piedras Negras area, Mexico, polarized light, 40×. Cavity lined by aggregate of nsutite crystals. The surrounding medium is very fine-grained nsutite.

FIG. 9. Polished surface of oxide ore from Nsuta, Ghana, polarized light, 40×. Groundmass consists of fibrous aggregates of fan-like oriented nsutite crystals. In center spherulitic aggregates of extremely fine fibrous nsutite, revealing undulatory extinction.

one of the most variable properties. In polished section nsutite and pyrolusite are often very similar in hardness, color and reflectivity. It would, therefore, be difficult to distinguish nsutite from very fine-grained pyrolusite without recourse to $x$-ray diffraction patterns. Coarse-grained pyrolusite is usually easy to recognize due to twinning and its well-developed cleavage.

The size of nsutite crystals varies from less than 0.1 micron up to 50 microns. Figure 7 shows a cavity filled with an extremely fine-grained aggregate of nsutite. The shape of individual nsutite crystals varies from platy to wedge-like. The latter are less common and occasionally show spherulitic arrangements which also have been observed by Sorem and Cameron (1960). Relatively well-developed crystals of nsutite, lining a cavity in fine-grained nsutite are shown in Fig. 8. The unusual fibrous modification of nsutite is shown in Fig. 9 where fine fibers, up to 2 mm in length, form radiating aggregates.

Density measurements were made on selected fragments of nsutite and manganoan nsutite using the Berman microbalance and toluene. Values of 4.24, 4.55, and 4.67 were obtained on three different nsutites, and 3.86 on manganoan nsutite, after correction for moisture and quartz impurities. The density values vary inversely with the $H_2O+$ content, as would be expected.

## ACKNOWLEDGMENT

The authors wish to express their appreciation to Mr. H. R. Spedden, Director of Research, Union Carbide Ore Company, for collecting the samples from Nsuta described herein, for encouraging the study, and for technical suggestions. Thanks are also due to Prof. E. N. Cameron of the University of Wisconsin, to Dr. Michael Fleischer of the U. S. Geological Survey and to Mr. R. A. Specker of Union Carbide Consumer Products Company for reading of the manuscript and for helpful suggestions regarding this work.

We are also indebted to Mr. J. A. Straczek of Union Carbide Ore Company for collecting the sample from Mexico and to Mr. R. E. Dutton of Union Carbide Nuclear Company for the chemical analyses of the nsutite samples.

## REFERENCES

AHRENS, L. H. (1952), Use of ionization potentials I. *Geochim. Cosmochim. Acta.*, **2,** 155–169.

BYSTRÖM, A. M. (1949), The crystal structure of ramsdellite, an orthorhombic modification of $MnO_2$. *Acta Chem. Scand.*, **3,** 163–173.

COLE, W. F., A. D. WADSLEY AND A. WALKLEY, (1947), An $x$-ray diffraction study of manganese dioxide. *Electrochem. Soc. Trans.*, **92,** 133–158.

DELANO, P. H. (1950), Classification of manganese dioxide. *Indus. Eng. Chem.*, **42,** 523–527.

Dubois, P. (1936), Contribution to the study of oxides of manganese. *Ann. Chim.* **5,** 411–482.

Faulring, G. M., W. K. Zwicker, and W. D. Forgeng, (1960), Thermal transformations and properties of cryptomelane. *Am. Mineral.,* **45,** 946–959.

Feitknecht, W. and W. Marti, (1945), Manganite and artificial manganese dioxide. *Helv. Chim. Acta,* **28,** 149–156.

———, H. R. Oswald and U. Feitknecht-Steinmann, (1960), Ueber die topochemische einphasige Reduktion von Gamma-$MnO_2$. *Helv. Chim. Acta.,* **43,** 1947–1950.

Folinsbee, R. E., (1959), Determination of reflectivity of ore minerals. *Econ. Geol.* **44,** 425–435.

Frondel, C. (1953), New manganese oxides. Hydrohausmannite and woodruffite. *Am. Mineral.,* **38,** 761–769.

Glemser, O. (1939), A new modification of manganese dioxide. *Ber. Deut. Chem. Ges.,* **72B,** 1879–1881.

——— and H. Meissiek, (1957), Reine synthetische Braunsteine. *Naturw.,* **44,** 614.

Goldschmidt, V. M. (1948), Geochemistry. Oxford at the Clarendon Press, London, p. 88–89.

McMurdie, H. F. (1944), Microscopic and diffraction studies on dry cells and their raw materials. *Trans. Electrochem. Soc.,* **86,** 313–326.

——— and E. Golovato, (1948), A study of the modifications of manganese dioxide. *Jour. Res. Nat. Bur. Stand.,* **41,** 589–600.

Nye, W. F., S. B. Levin, and H. H. Kedesdy, (1959), Structure and morphology of manganese dioxide. *Proc. 13th Ann. Power Sources Conf.,* p. 125–129.

Ramdohr, P. (1955), Die Erzmineralien und ihre Verwachsungen. Akad. Verlag, Berlin, p. 770.

Schossberger, F. (1940), *X*-ray examination of natural and synthetic manganese dioxide. *Batterien,* **9,** 17–20, 33–35.

Skewes, H. R., A. D. Wadsley and A. Walkley, (1952), The behavior of manganese oxides in Leclanché-type dry cells. *Austral. Jour. Appl. Sci.,* **3,** 368–383.

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.

Sreenivas, B. L. (1957), Gamma-manganese dioxide from Mysore, India. *Mineral. Mag.,* **31,** 605–606.

Traore, K. De and J. P. Brenet, (1959), Effects de faibles reduction cathodique de gamma-$MnO_2$ sur leur dissociation thermique. *Zeit. Elektrochem. Ber. Bunsenges. Physik. Chem.,* **63,** 563–565.

Ukai, Y., S. Nishimura, and Mayeda, R., (1956), Mineralogical study on manganese dioxide minerals: *Mem. College Sci. Univ. Kyoto, Ser. B.,* **23,** 203–222.

Vinal, G. W. (1951), Primary Batteries. John Wiley and Sons, Inc., New York.

Wolff, P. M. De, (1959), Interpretation of some gamma-$MnO_2$ diffraction patterns. *Acta Cryst.,* **12,** 341–345.

*Manuscript received, May 17, 1961.*