MANGANOAN CUMMINGTONITE FROM NSUTA, GHANA

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Abstract

Manganoan cummingtonite (Mg:Mn:Ca:Fe=60:35:3:2) from a manganese carbonate rock, Nsuta, Ghana, contains more manganese and less iron than any cummingtonite previously described. The unit cell dimensions are: $a_0 = 9.531$ Å, $b_0 = 18.10$ Å, $c_0 = 5.326$ Å, $\beta = 102° 15'$. Crystals are pale greenish white, acicular-prismatic, non pleochroic and colorless in transmitted light; $\alpha = 1.628$, $\beta = 1.642$, $\gamma = 1.650$, 2V = 74°, biaxial negative, $Z \wedge c = 22°$. G. = 3.12 (obs.), 3.19 (cacl. from x-ray data), 3.12 (calc. from $(n-1)/d = K$). A revision in nomenclature of the series is suggested whereby cummingtonite, grunerite, and $Mn_7(Si_4O_{11})_{12}(OH)_2$ represent the Mg, Fe^{+2}, and Mn^{+2} end members of an essentially three-component system.

Introduction

Manganese-bearing amphiboles of the cummingtonite group, described by Sundius (1931) and Bauer and Berman (1930), are all rich in iron. Manganoan cummingtonite from Nsuta, Ghana, is unique in that it contains more manganese (19.2% MnO) and far less iron (1.2% FeO) than any amphibole of this group previously described. It occurs as slender acicular prisms (0.5×0.1 mm.) in a metamorphosed manganese carbonate rock (Fig. 1). The mineral is often intimately associated with a calcian, magnesian rhodochrosite ($n_\omega = 1.786$), pure spessartite ($n = 1.800$), rhodonite, talc, and minor quartz. At Nsuta, spessartite is a frequent product of low-grade metamorphism of sedimentary manganese carbonate and argillaceous and tuffaceous sediments, whereas rhodonite and cummingtonite are relatively uncommon. The latter minerals appear to have formed in localized shears in carbonate rock.

The cummingtonite group of amphiboles has the formula $X_7(Si_4O_{11})_2$ $(OH)_2$, where X is predominantly Mg, Fe^{+2}, and Mn^{+2}. Manganoan cummingtonite from Nsuta has an X cation ratio of Mg:Mn equal to approximately 60:40. It has lower indices of refraction and specific gravity than its ferroan analogue, Mg:Fe = 60:40, and is optically negative, whereas the latter is optically positive. Both manganoan and ferroan cummingtonites have virtually identical x-ray powder diffraction patterns which can be readily distinguished from those of the calcium- and sodium-rich amphiboles: tremolite, richterite, edenite, hornblende and others. This distinction results from the presence or absence of the relatively large Ca and Na ions which require eight-fold coordination. These may also occupy some of the normally vacant twelve-fold lattice positions. Warren (1930) has shown that Fe^{+2} and

Mg have six nearest oxygen neighbors closely approaching octahedral coordination in cummingtonite, whereas Ca is eight-fold coordinated in tremolite.

MINERALOGY

Separation and purification

The sample was ground in stages to minus 60 mesh and sieved on 100, 200, and 325 mesh screens. Microscopic examination indicated that the optimum mesh of liberation of cummingtonite occurred in the 200–325
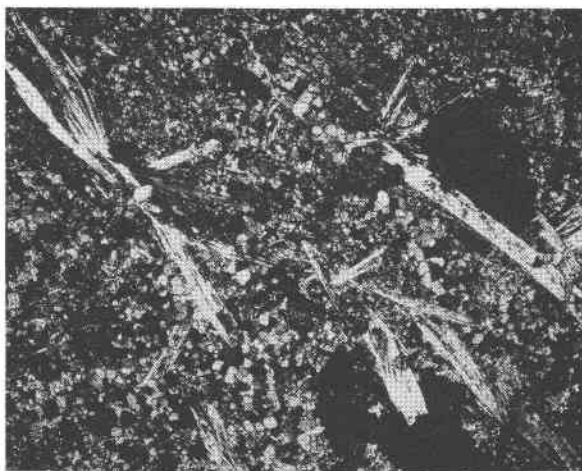

FIG. 1. Metamorphosed manganese carbonate rock from Nsuta, Ghana, showing acicular-prismatic manganoan cummingtonite in a matrix of granular calcian, magnesian rhodochrosite, quartz, and spessartite. Crossed nicols ×30.

mesh fraction. This fraction was separated in fresh methylene iodide (density = 3.3) to remove the spessartite garnet, rhodonite, and rhodochrosite. The float fraction, containing the cummingtonite was then separated in bromoform (density = 2.86) to remove quartz. The bromoform sink, composed essentially of cummingtonite (density = 3.12), was then leached in a dilute hydrochloric acid to remove adhering particles of carbonate. The concentrate was then shake-sifted in stages on glossy paper to remove any remaining granular minerals. Microscopic examination and a grain count of the concentrate indicated a purity of $> 99\%$ cummingtonite prisms containing an estimated 5% of inclusions of spessartite garnet (Fig. 2). This was verified by analysis which yielded 1.1% Al_2O_3 equivalent to a maximum of 5.4% spessartite.
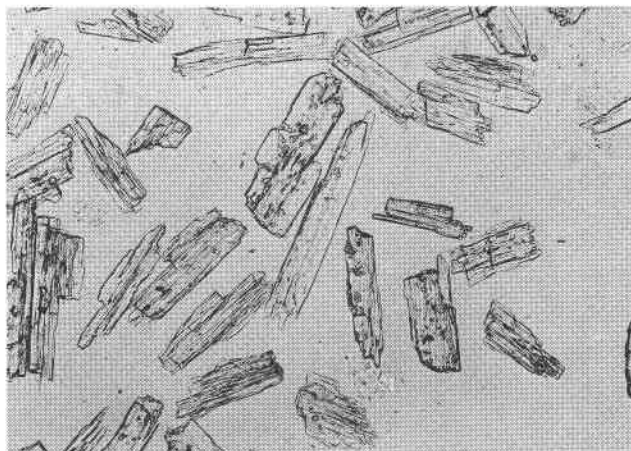
FIG. 2. Manganoan cummingtonite concentrate from carbonate rock. Many of the prisms contain small inclusions of spessartite. Plane polarized light ×45.

Unit Cell

Two small prismatic grains were studied with a single crystal x-ray goniometer by R. P. Dodge who obtained the value $b_0 = 18.10$ Å. Three spacings on the x-ray powder diffraction pattern at 3.06 Å, 2.61 Å, and 2.51 Å could be identified as the (310), (061), and ($\bar{2}$02) reflections, respectively, by analogy with other monoclinic amphiboles. From these data it was possible to calculate $a_0 \sin \beta$, $c_0 \sin \beta$, $\cos \beta$, β, $\sin \beta$, a_0 and c_0. Warren (1930), who analyzed the structures of the monoclinic amphiboles, noted that tremolite and the cummingtonites have the same space group, (C_2/m), and similar unit cell dimensions. The unit cell dimensions of manganoan cummingtonite from Nsuta, Ghana, are given in Table 1.

TABLE 1. MONOCLINIC UNIT CELL DATA FOR MANGANOAN
CUMMINGTONITE FROM NSUTA, GHANA

$a_0 = 9.531$ Å	Cell volume $= 897.9$ Å³
$b_0 = 18.10$ Å	Cell weight $= 1725.4$
$c_0 = 5.326$ Å	Cell formula $= (Mg, Mn, Ca, Fe)_{14}Si_{16}O_{44}(OH)_4$
$\beta = 102°15'$	$Mg:Mn:Ca:Fe = 60:35:3:2$

Density $= 3.19$ (calculated from x-ray data)
       3.12 (observed)
       3.12 (calculated from the law of Gladstone and Dale, $(n-1)/d = K$[1]

[1] $(\alpha + \beta + \gamma)/3 = 1.640$. K $= 0.205148$.

X-ray powder diffraction data

An *x*-ray powder diffraction pattern of manganoan cummingtonite was obtained with a 57.3 mm. camera using FeK_α radiation ($\lambda = 1.93597$ Å) and a Mn filter. All of the lines measured, down to 1.163 Å, were indexed on the basis of the unit cell data given in Table 1. The *x*-ray powder diffraction data for manganoan cummingtonite from Ghana and ferroan cummingtonite from Sweden (Johansson, 1930) are compared in Table 2. Cummingtonites may be distinguished from all other monoclinic amphiboles by measurement of the (310) and the ($\bar{6}61$) and ($\bar{6}42$) spacings. These *d* values and a_0 increase directly with the Ca+Na content going from cummingtonite to edenite (Table 3). Figure 3 compares *x*-ray powder diffraction patterns of manganoan cummingtonite from Nsuta, Ghana with those of pure white tremolite from Fowler, New York, and dark greenish-black hornblende from a mafic shonkinite from Mountain Pass, California. Both the tremolite and hornblende, which contain essential amounts of the large cations Ca and Ca+Na, respectively, give very similar patterns. The cummingtonite, however, which does not contain significant amounts of either Ca or Na, yields an *x*-ray pattern that can be readily distinguished from that of either hornblende or tremolite. Noteworthy is the position of a strong line at 1.405 Å on this and other cummingtonite patterns compared with 1.43–1.44 Å in tremolites and hornblendes. This line indexes closer to ($\bar{6}42$) than to ($\bar{6}61$) for manganoan cummingtonite (this paper) and for ferroan cummingtonite of Johansson (1930). In the patterns of natural tremolite, hornblende and synthetic fluor-tremolite, fluor-richterite, and fluoredenite, the corresponding line indexes much closer to ($\bar{6}61$) than ($\bar{6}42$). Whether a transposition or a true line shift, the position of this strong line serves to distinguish members of the cummingtonite group from all other calcium- and sodium-rich monoclinic amphiboles.

Optical properties

Manganoan cummingtonite from Nsuta, Ghana, occurs as pale greenish white, long prismatic to acicular crystals. It is colorless and non-pleochroic in transmitted light. Multiple twinning on (100) was observed on several crystals. In thin-section, the mineral cannot readily be distinguished from tremolite although the latter has a smaller extinction angle. The indices of refraction of Nsuta cummingtonite are, however, significantly higher than those of tremolite so that the two can be distinguished in immersion media. A manganoan cummingtonite with a lower Mn content than the Nsuta mineral could not be distinguished from tremolite by optical properties alone. Ferroan cummingtonite with

TABLE 2. X-RAY POWDER DIFFRACTION DATA FOR CUMMINGTONITES FROM NSUTA, GHANA AND UTTERSVIK, SWEDEN (FeK$_\alpha$ RADIATION, $\lambda = 1.9359$ Å, Mn FILTER)

Nsuta, Ghana			hkl	Uttersvik, Sweden	
I (obs.)	d(obs.)	d(calc.)		d(obs.)*	I
20	9.0	9.05	020	—	
80	8.25	8.28	110	8.32	50
20	4.83	4.84	$\bar{1}11$	—	
40	4.52	4.52	040	4.55	10
20	4.14	4.14	220	4.16	10
40	3.86	3.86	$\bar{1}31$	3.87	20
	—	3.59	$\bar{2}21$	3.60	10
30	3.42	3.44	131	3.46	40
		3.41	041		
40	3.24	3.24	240	3.26	50
100	3.06	3.06	310	3.07	40
30	2.96	2.98	221	2.99	10
		2.94	$\bar{1}51$	—	
10	2.75	2.76	330	2.76	100
90	2.73	2.74	151		
40	2.61	2.61	061	2.63	60
80	2.51	2.51	$\bar{2}02$	2.51	60
5	2.37	2.38	$\bar{2}61$	—	
		2.36	350	—	
20	2.29	2.29	$\bar{3}51$	2.30	50
10	2.24	2.24	421	—	
		2.22	$\bar{3}12$	2.23	10
60	2.17	2.18	261	2.19	70
20	2.08	2.09	202	2.10	20
		2.07	440	—	
		2.07	081	—	
10	2.03	2.03	351	2.04	20
10	1.954	1.954	$\bar{4}02$	1.957	20
10B	1.860	1.867	$\bar{1}91$	1.871	
		1.853	510	—	10
10	1.799	1.799	$\bar{5}31$	—	
40B	1.693	1.693	390	—	
	—	1.687	$\bar{5}12$	1.693	10
40	1.651	1.652	461	1.663	60
10	1.620	1.621	480	1.633	40
		1.620	$1 \cdot 11 \cdot 0$		
		1.620	043		
	—	1.594	$\bar{1}53$	1.600	20
40	1.588	1.588	531	—	
	—	1.553	600	1.561	10
	—	1.515	263	1.521	60
50	1.508	1.508	$0 \cdot 12 \cdot 0$		
5	1.486	1.486	$0 \cdot 10 \cdot 2$	—	

TABLE 2. (continued)

Nsuta, Ghana			hkl	Uttersvik, Sweden	
I (obs.)	d(obs.)	d(calc.)		d(obs.)*	I
5	1.455	1.454	3·11·0	1.465	10
80	1.405	1.405	$\bar{6}42$	1.409	90
	—	1.402	$\bar{6}61$		
5	1.376	1.378	512	1.386	20
		1.377	1·13·0	—	
	—	1.327	710	1.335	40
	—	1.301	004	1.305	10
60B	1.292	1.292	2·12·2	1.291	70
			751	1.280	40
			$\bar{4}04$	1.257	
			602	1.231	
			5·11·2	1.187	
60	1.182	1.183	770	—	
		1.181	642	—	
5	1.163	1.164	800	1.171	
40B	1.113			—	
40	1.056			—	
60	1.037			1.041	
30	1.030			—	
40	1.020			—	
40	1.011			—	
30	1.003			—	
40	0.991			—	
30	0.983			—	
20	0.976			—	
20	0.974			—	

* The ASTM card No. 2-0865 for this mineral contains several errors.

The d values cited here were recalculated from the original $\sin^2 \theta$ values published by Johansson (1930).

B = broad.

Mg:Fe = 60:40 is optically positive (Sundius, 1931), whereas manganoan cummingtonite from Nsuta, with Mg:Mn = 60:40 is optically negative. The indices of refraction of the manganoan cummingtonite are significantly lower than the ferroan analogue as could have been predicted. The optical properties of manganoan cummingtonite from Nsuta and those of its ferroan analogue from Persberg are compared in Table 4.

CHEMISTRY

Analysis and composition

When it became apparent that the pure material that could be obtained was insufficient for a conventional wet chemical analysis, a

TABLE 3. VARIATION OF a_0, d_{310}, AND $d_{\bar{6}42-\bar{6}61}$ WITH THE Ca+Na CONTENT OF SEVERAL MONOCLINIC AMPHIBOLES

	1 Manganoan cummingtonite	2 "Cummingtonite"*	3 Fluortremolite	4 Fluorrichterite	5 Fluoredenite
a_0	9.53 Å	9.58 Å	9.78 Å	9.82 Å	9.85 Å
d_{310}	3.06 Å	3.07 Å	3.11 Å	3.12 Å	3.12 Å
$d_{\bar{6}42}$	1.405 Å	1.409 Å			
$\bar{6}61$			1.430 Å	1.432 Å	1.435 Å
Ca+Na†	0.45	0.80	3.88	5.86	5.98

* According to the nomenclature proposed in this paper, this mineral is a magnesian grunerite as Fe>Mg or Mn (See Figure 4).

† Cations per 48 oxygens.

1. Nsuta, Ghana, new data.

2. Uttersvik, Sweden, Johansson (1930).

3. Synthetic, Comeforo and Kohn (1954).

4. and 5. Synthetic, Kohn and Comeforo (1955).

quantitative emission spectrographic method was developed by Mr. A. L. Hallowell. SiO_2, Al_2O_3, MgO, MnO, FeO, and CaO were determined by internal standardization with cobalt using the following line pairs: Si 2438.8/Co 2989, Al 3082/Co 2989, Mn 2705.7/Co 2989, Mg 2790.8/Co 2989, Fe 2947.8/Co 2989, and Ca 3179/Co 2989. Siliceous manganese ores previously analyzed at the Research Center were used
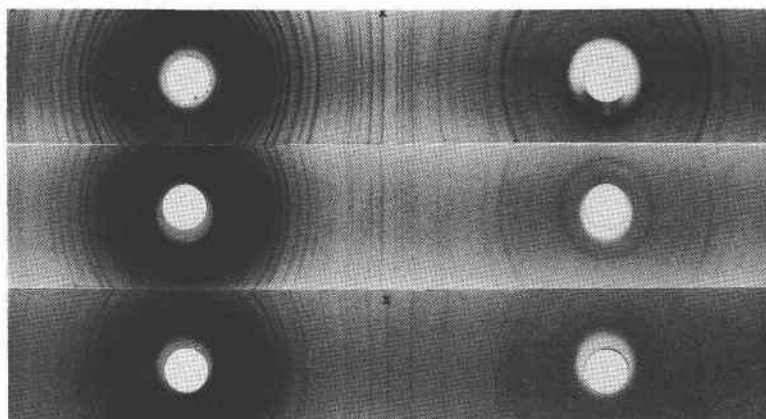

FIG. 3. X-ray powder diffraction patterns. (top) Hornblende, Mountain Pass, Calif. X indicates the $\bar{6}61$ line. (middle) Tremolite, Fowler, N. Y. (bottom) Manganoan cummingtonite, Nsuta, Ghana. X indicates $\bar{6}42$ and $\bar{6}61$ lines. (Fe K_α radiation, $\lambda = 1.93597$ Å, Mn filter).

as standards for obtaining the necessary working curves. Water was not determined and is given by difference. Fluorine was determined to be absent. In order to further check some of the spectrographic determinations, MnO and MgO+CaO were determined by wet chemical methods on very small amounts of material. The agreement is satisfactory as indicated in the tabulation of the analytical data (Table 5).

The formula for amphiboles of the cummingtonite-grunerite group may be written as $X_7(Si_4O_{11})_2(OH)_2$ where X is occupied predominantly by divalent Mg, Fe, and Mn in six-fold coordination (Warren, 1930). Divalent Zn may occupy X positions as in the Franklin Furnace, New Jersey, occurrence (Bauer and Berman, 1930), but this is uncommon.

TABLE 4. OPTICAL PROPERTIES OF MANGANOAN AND FERROAN CUMMINGTONITE

	1 Manganoan cummingtonite Mg:Mn=60:40	2 Ferroan cummingtonite Mg:Fe=60:40
α	1.628 ± 0.002	1.640
β	1.642 ± 0.002	1.647
γ	1.650 ± 0.002	1.665
$\gamma - \alpha$	0.022	0.025
$Z \wedge c$	22°	20°
2V	74° (calc.)	65°
Optic sign	negative	positive

1. Nsuta, Ghana, new data.
2. Persberg, Sweden, Sundius (1930).

One of the characteristics of the cummingtonite-grunerite group is the absence of essential amounts of the larger cations Ca and Na in X positions and the similar absence of Al in tetrahedral positions occupied by Si. Both Ca and Na are coordinated by eight or more oxygens in tremolite and the alkalic amphiboles, depending on the degree of occupancy of the vacant 12-fold sites known to exist in tremolite (Warren, 1930 and Kohn and Comeforo, 1955).

The formula calculated from the analysis of manganoan cummingtonite from Nsuta is as follows:

$$\underbrace{(Mg_{4.0}Mn_{2.3}Fe_{0.1}Ca_{0.2})}_{6.6}Si_{8.0}O_{21.8}(OH)_{1.8}$$
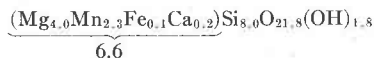
This represents one-half of the unit cell formula of cummingtonite. In Table 5, the ratios obtained on a basis of anions and cations per unit cell (Hey, 1939) are compared with those obtained on a basis of cations per

48 oxygens. Either calculation shows reasonably good agreement with the accepted unit cell formula of cummingtonite:

$$X_{14}(Si_4O_{11})_4(OH)_4$$

Relation between density, index of refraction and chemical composition.

The density of manganoan cummingtonite from Nsuta was measured by suspension of grains in acetone-diluted methylene iodide. The meas-

TABLE 5. SPECTROCHEMICAL ANALYSIS OF MANGANOAN CUMMINGTONITE
FROM NSUTA, GHANA

(A. L. Hallowell, analyst)

Oxide	Determined[2]	Recalculated[3]	Anions per Unit Cell		Cations per Unit Cell		Cations on a basis of 48 oxygens
SiO_2	56.0	57.1	32.08	Si	16.04	16.04	16.32
Al_2O_3	1.1						
MnO	20.5*	19.2	4.57	Mn^{+2}	4.57		
MgO	18.1*	19.1	7.99	Mg	7.99	13.29	13.52
FeO	1.1	1.2	0.28	Fe^{+2}	0.28		
CaO	1.4*	1.5	0.45	Ca	0.45		
H_2O[1]	1.8	1.9	1.78	H	3.56	3.56	3.62
	100	100	47.15		32.89		

[1] H_2O by difference.

[2] SiO_2, Al_2O_3, MnO, MgO, FeO, and CaO were determined by internal standardization with cobalt using the following line pairs: Si 2438.8/Co 2989, Al 3082/Co 2989, Mn 2705.7/Co 2989, Mg 2790.8/Co 2989, Fe 2947.8 Co 2989, and Ca 3179/Co 2989.

[3] After deduction of 1.1% Al_2O_3, 2.0% SiO_2, and 2.3% MnO equivalent to 5.4% of spessartite garnet included in cummingtonite.

* Wet chemical determinations made on small samples as a check on the spectrographic results gave: MnO = 19.4 and MgO + CaO = 20.2.

Unit Cell Formula: (from analysis) $(Mg, Mn, Ca, Fe)_{13.3}Si_{16.0}O_{43.6}(OH)_{3.6}$
Mg : Mn : Ca : Fe = 60 : 35 : 3 : 2

ured value, 3.18, was then corrected for the presence of 5.4% spessartite occurring as inclusions in cummingtonite. A density of 4.185 (Yoder, 1959, Fleischer, 1937, Skinner, 1956) was assumed for spessartite as it has a measured index of refraction of 1.800 and no calcium, indicating it to be an end member. The corrected value for the density of the manganoan cummingtonite is 3.12. The density calculated from the x-ray data (Table 1) and the chemical composition is 3.19 for Mg : Mn : Ca : Fe = 60 : 35 : 3 : 2.

The density was also calculated from the law of Gladstone and Dale,

$(n-1)/d = K$ using the optical data (Table 4), the chemical composition (Table 5), and the specific refractive energy values (k) of Larsen and Berman (1934). These are $k_{MgO} = 0.200$, $k_{MnO} = 0.191$, $k_{CaO} = 0.225$, $k_{FeO} = 0.187$, $k_{SiO_2} = 0.207$, and $k_{H_2O} = 0.34$. The calculated density is 3.12, the same as that measured. Agreement between the measured density and that calculated from the law of Gladstone and Dale consistently is excellent for all amphiboles of very diverse composition (Jaffe, 1956).

Nomenclature

The present nomenclature of the cummingtonite-grunerite series is confused and inadequate. Sundius (1931) suggested that the name cummingtonite be reserved for the mineral containing 50–70 mol per cent of the magnesium component and that varieties richer in iron be named grunerite. Mason (1953) has noted that "this proposal would have the curious effect of requiring the original cummingtonite from Cummington, Massachusetts, to be called grunerite." The work of Sundius (1931) and others indicates that this group of minerals may be considered a three component system, with the end members represented by $Mg_7(Si_4O_{11})_2(OH)_2$, "kupfferite," $Fe_7(S_4O_{11})_2(OH)_2$, grunerite, and $Mn_7(Si_4O_{11})_2(OH)_2$, unnamed. Of these only the Fe end member, grunerite, is known to occur naturally. The fluorine analogue of the Mg end member, has however been synthesized by Bowen and Schairer (1935). Inasmuch as the name cummingtonite has priority over all others, the writers suggest that it be assigned to the Mg-dominant member of the series in place of "kupfferite," and that grunerite be retained for the Fe^{+2}-dominant member. The Mn^{+2}-dominant member has not been found or synthesized and a new name is deemed inappropriate. This classification would be more in keeping with the nomenclature of other isomorphous series. The proposed revision in nomenclature is as follows:

cummingtonite—$Mg_7(Si_4O_{11})_2(OH)_2$ with Mg > Fe or Mn
grunerite— $Fe_7(Si_4O_{11})_2(OH)_2$ with Fe > Mg or Mn
$Mn_7(Si_4O_{11})_2(OH)_2$ with Mn > Mg or Fe

The names, cummingtonite and grunerite, could be further qualified by prefixing the terms manganoan, ferroan or magnesian. This classification is illustrated in Fig. 4 on a ternary diagram showing the compositions of the natural cummingtonites and grunerites previously described by Sundius (1931), Winchell (1938), Bowen and Schairer (1935), and Mason (1953). Manganoan cummingtonite from Nsuta (Fig. 4) contains far less iron and more manganese than any of the other cummingtonites described in the literature. Inasmuch as this mineral al-
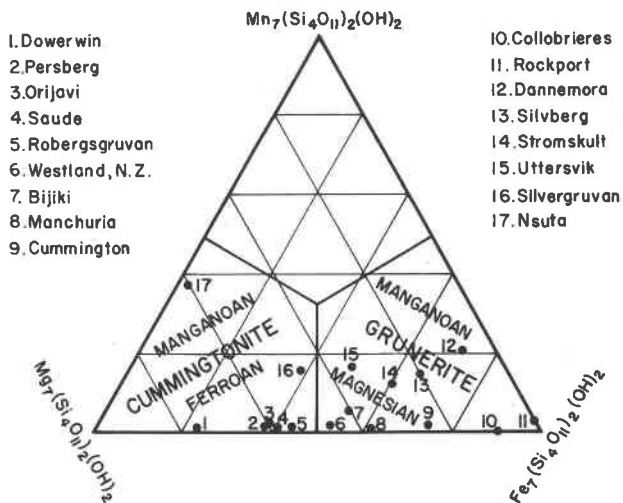
FIG. 4. Composition of cummingtonites and grunerites, and suggested nomenclature.

ready contains almost 40 mol per cent of the Mn component, and the ionic radius of Mn^{+2} is only 7 per cent larger than that of Fe^{+2}, the mineral should be capable of accepting a much larger amount of manganese. No attempt has been made by the authors to synthesize the end member.

Acknowledgments

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Manuscript received June 14, 1960.