

MacFallite and orientite: calcium manganese (III) silicates from upper Michigan

PAUL B. MOORE, JUN ITO,¹ AND IAN M. STEELE

Department of the Geophysical Sciences, The University of Chicago, Chicago, Illinois 60637, USA

SYNOPSIS

SUMMARY. MacFallite, $\text{Ca}_2(\text{Mn}^{3+}, \text{Al})_3(\text{OH})_3[\text{SiO}_4][\text{Si}_2\text{O}_7]$, is a new species occurring with manganite, braunite, orientite and pyrolusite blebs, stringers, and framboidal aggregates, which replace calcite in fissures and lenses in Keweenaw basalt near Manganese Lake, Copper Harbor, Keweenaw County, Michigan. It is rich reddish brown to maroon in coarse aggregates; compact massive material is brown to dull pink. The streak and powder are brown with a reddish tint. Lustre silky to subadamantine, specific gravity 3.43(2), hardness 5⁺, cleavage {001} perfect; twinning by reflection on {100} is universal. The mineral is monoclinic, space group $P2_1$ or $P2_1/m$, $Z = 2$, a 8.929(6), b 6.045(5), c 10.905(7) Å, β 119.10(3)°, α 1.773(5), β 1.795(5), γ 1.815(5), sign + or -, pleochroism α yellow, β light brown, γ dark brown, $\gamma \parallel b$. Orientite, $\text{Ca}_2\text{Mn}^{2+}\text{Mn}_2^{3+}(\text{OH})_4[\text{Si}_3\text{O}_{10}] \cdot \text{Ca}_2\text{Mn}_2^{3+}(\text{OH})_2[\text{Si}_3\text{O}_{10}] \cdot 2\text{H}_2\text{O}$, orthorhombic, space group $Cc2m$, $Ccm2_1$ or $Ccmm$, a 9.042(4), b 6.090(2), c 18.990(7) Å,

α 1.765(5), β 1.79(1), γ 1.81(1), sign + or -, α brownish yellow, β reddish brown, γ deep brownish red, $\alpha \parallel a$, $\gamma \parallel b$, also occurs in moderate abundance. It is turbid chocolate brown in platy masses but crystals are transparent rich reddish brown. Streak and powder brown. Observed forms are $m\{110\}$, $c\{001\}$, and poorly developed to absent $a\{100\}$, thin to thick tabular parallel to {001}, cleavage (or parting) {001} perfect, specific gravity 3.33.

A fumarolic origin is proposed for the assemblage, which in many respects is similar to the great manganese oxide deposits in Oriente Province, Cuba. Macfallite appears to be structurally related to pumpellyite while orientite is apparently related to ardennite.

[Manuscript received 1 September 1978]

¹ Died 6 June 1978.

MACFALLITE AND ORIENTITE: CALCIUM MANGANESE (III) SILICATES
FROM UPPER MICHIGAN

PAUL B. MOORE, JUN ITO[†], and IAN M. STEELE
Department of the Geophysical Sciences
The University of Chicago
Chicago, Illinois 60637, U.S.A.

Introduction and paragenesis. Small and local deposits of manganese oxides were known to Douglass Houghton in the 1840s during his early surveys of the mineralogy of Keweenaw Point in northern Michigan. These deposits occur to the east of Manganese Lake (Sec. 5, T58N, R28W) which is situated one mile south of the village of Copper Harbor, Keweenaw County, Michigan. They occur within large calcite fissure fillings and lenses which run east-west along the strike of fresh amygdaloidal basalts of the Greenstone flow adjacent to the Copper Harbor ("Great") conglomerate. Small copper mines in the vicinity produced but modest quantities of ore: the Star and Clark Mines were worked for fissure deposits of copper but by the end of the 1860s operations ceased since costs could not be covered. The manganese ores were mined about 3/4 mile east of Manganese Lake to a depth of 75 feet in 1881 by the Cambria Iron Company, a shaft later sunk, but only about 1200 tons were recovered by 1883 and the operation was abandoned. The ores ran 55.73% manganese and 1.36% copper (Cornwall, 1955; Clarke, 1974). Although numerous small prospects dot the area, our study focusses on two deposits: a small exposed calcite mass along the west wall of the outlet stream (Sec. 5, ctr. NE1/4) from Manganese Lake to Lake Fanny Hooe, and the larger deposit 3/4 mile to the east (Sec. 4, ctr. SW1/4 of NE1/4) in the vicinity of the Clark Mine. But little of the ores were visible in place and most samples were gathered from the long-abandoned stockpiles and tailings around the workings.

To our knowledge, the manganese minerals at these deposits--the assemblage of which is, in a sense, practically unique and which compares only to those of the Oriente Province, Cuba--never received earlier detailed study. Butler and Burbank (1929), in their classic treatise on the copper deposits of the Upper Peninsula, Michigan, mention manganite and pyrolusite occurring with "other manganese minerals as a 'vein', essentially coinciding with an amygdaloid a short distance below the Great conglomerate." These small manganese deposits appear to be disjoint to the sequence of basalts and conglomerates of the Keweenaw: manganese minerals in the copper-bearing deposits are unusual rarities and are largely confined to small and sporadic coatings and dendrites deposited upon other minerals in the vesicles of the amygdaloid and as rare thin films cementing conglomerates. Larger masses of manganese oxides and silicates, to our knowledge, have never been recorded from the various flows elsewhere in the copper deposits. Although manganese oxides and oxyhydroxides (psilomelane, pyrolusite, manganite, groutite, hausmannite) are known in minor quantities throughout the extensive sedimentary iron deposits to the east, the silicates which we discuss in this study have never been recorded from there.

We report herein on two curious species, both basic calcium manganese (III) silicates, which are not rare locally: one, macfallite, is new to scientific intelligence and the other, orientite, has hitherto been recorded only from the Oriente Province in Cuba where it occurs locally in minor amounts.

The manganese ores and associated silicates from Manganese Lake bear a striking resemblance, texturally and mineralogically, to those described

from the Oriente Province, Cuba, in the original study on orientite by Hewett and Shannon (1921). These deposits occur within an 8000 to 1000 foot deep trough of bedded volcanic breccias, tuffs with andesite and latite flows and limestones, all of Eocene age. The orientite occurred in a group of deposits--the Costa, Manuel and Vicente claims--6 miles south of Bueycito; and from the Santa Rosa prospect near Banes. The matrix is a glass which is altered near the ore bodies; the manganese oxides and silicates were deposited in the tuffs through replacement of the glassy matrix. The order of deposition was: ferruginous jasper ("bayate")--glauconite(?)--psilomelane-plumose manganite-barite-orientite-manganite (prisms)--quartz-zeolites-calcite. In order of decreasing abundance, the manganese minerals are psilomelane, manganite, pyrolusite, wad, neotocite, orientite. It was concluded that the minerals were deposited by warm hypogene waters.

Park (1942) noted that the jasper and manganese oxides deposited on the crests of arches and concluded that they were formed by ascending solutions during the last stage of the emplacement of the Eocene volcanics. Psilomelanes containing up to 5% barium were noted. Ore from the lucrecia prospect contained 0.25% Co. Piemontite was also found associated with manganese oxides from Sigua and from a deposit near the city of Camaguey. Braunite occurs as a minor constituent of the ores and rhodochrosite is very rare. Park and Cox (1944) also note the occurrence of rancifite as a minor constituent of some ores.

Simons and Straczek (1958), in an exhaustive account of the Oriente manganese deposits, note that the ores occur in the Cobre Formation of middle Eocene age. The presence of calcareous rocks (fossiliferous limestones) is an important factor in their distribution. The ores appeared to have formed shortly after deposition of matrix material and were probably introduced through volcanic vents. Psilomelane is the most common ore; pyrolusite, also abundant, was derived from the psilomelane. Other species mentioned as occurring in smaller amounts are the oxides hausmannite, rancifite, wad; and the silicates bementite, neotocite, braunite, inesite, orientite, piemontite. Their occurrences are sporadic and usually confined to only a few locations. Quartz is everywhere very rare. The most abundant of the psilomelanes is "delatorreite" (= todorokite).

The manganese silicates from Manganese Lake all contain minor (0.1-0.5%) copper, vanadium, and chromium, and trace amounts (<0.0%) of silver, titanium, and gallium. They and the oxides occur as blebs, plumose aggregates, fine-grained stringers and framboidal aggregates wholly within the calcite gangue. Free silica, either as amorphous material or as quartz, is exceptionally rare and is practically confined to small quartz grains occasionally occurring in tight masses of manganite. Of the silicates, the orientite appears to be the earliest mineral; it often occurs as millimetre-sized spheroidal-platy aggregates surrounded by braunite grains, forming dendritic to plumose aggregates in the calcite. Free crystals are rare and when they do occur, appear in small open cavities containing remnant calcite and wholly surrounded by the braunite. Figure 1 shows a typical example of the braunite which occurs adjacent to enclosing calcite. The grains form beads and stringers of tiny (<0.1 mm) lustrous crystals showing $e\{011\}$ which follow along cleavage planes and joints in the calcite.

The most abundant oxide is pyrolusite which occurs as steel-grey acicular crystals up to 1 cm in length. It characteristically occurs as radial aggregates and sprays, as islands of knot-like forms in fine-grained macfallite and as a bordering of clots of macfallite. Occasional crystals of macfallite are replaced by this mineral which in turn often projects into open cavities. The pyrolusite is soft and crushes into a deep grey powder. Manganite occurs as a hard, dense, black, fine-grained mineral.

[†]Died June 6, 1978.

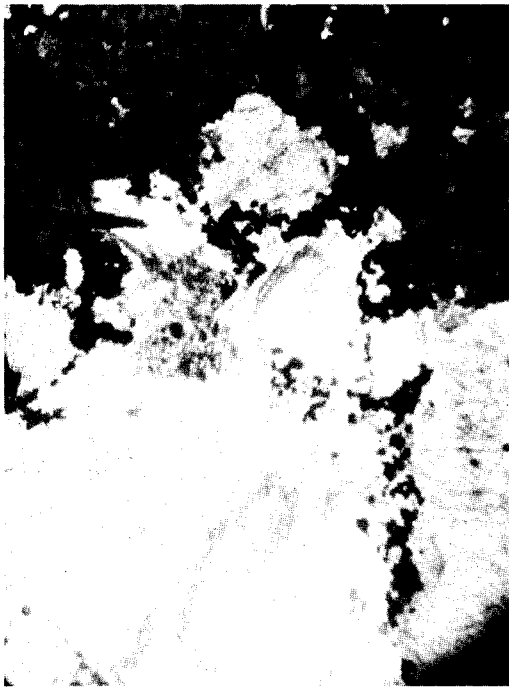


Fig. 1. -- Polished section in reflected light from Manganese Lake, Michigan. The white is fissure calcite. Black grains along joints and cleavage traces are braunite crystals. The greyish material toward the top is orientite and minor braunite.

The orientite occurs most frequently in association with the manganite and appears to be later than that oxide. The manganite crushes into a dark chocolate brown powder. Braunite much resembles the manganite in appearance. It occurs often as fine-grained coke-like masses and open cavities are frequently studded with the small pseudo-octahedral crystals of this mineral. The braunite crushes to a deep brownish-black powder, much darker than and easily distinguished from manganite. These, and other samples, were positively identified by X-ray powder diffractometry.

Macfallite is by far the most abundant silicate in the assemblage. It occurs as solid compact masses of chocolate brown color to thick fibrous aggregates of a dark reddish-brown color. The violet tint so characteristic of piemontite is entirely lacking. Single crystals, rare and invariably twinned, usually developed on a groundmass of compact macfallite and line open cavities. It is particularly abundant where the manganese oxide blebs are in contact with the calcite. Here, the mineral occurs as coarse fibrous masses projecting into open cavities which are usually filled with clear calcite or studded with simple rhombohedra of the carbonate, clearly of a later generation than the fissure calcite. Macfallite and pyrolusite often occur together as interlocking aggregates of fibrous-radial masses. Both appear to have crystallized about the same time.

Thin sections and hand specimens were studied in detail in order to establish the paragenetic sequence. There is clearly an overlap in the

sequence of crystallized phases suggesting that oxides and silicates crystallized at about the same time. The calcite gangue or fissure calcite (which individuals occur as coarse crystalline masses up to several centimeters across) appears to have been emplaced first and subsequently replaced by the manganese minerals. Particularly when the calcite masses come in contact with the manganese oxide and silicate blebs, an abundance of small open cavities appear. Unlike the Oriente occurrences, no equivalent to the ferruginous jasper could be found suggesting that introduced silica was consumed in the reaction of oxides -- particularly manganite -- to form silicates. The sequence is: (early) fissure calcite-manganite-orientite-braunite-macfallite, pyrolusite-calcite (clear rhombohedra). Psilomelane, todorokite, rancieite, marokite, bementite and neocite were sought but not found. Several unknown minerals have been recognized but they occur in trace quantities only and have so far resisted further investigation. The only exception is a very sporadic emerald green mineral which occasionally occurs in the cores of orientite-braunite framboids. The grains of the mineral rarely exceed 0.1 mm in dimension and appear to replace an earlier formed metallic material, the latter identified as native copper on the basis of a Gandolfi mount powder pattern. The green mineral was positively identified as conicalcalcite on the basis of powder and X-ray single crystal study.

Dr. L. L. Babcock has brought to our attention some observations which may shed light on the manganese oxide deposits. Fissure deposits which occur near the Great conglomerate-lava series contact, such as at Owl Creek and Copper Falls deposits (in the Ashbed lode), are noted for the unusual abundance of granular datolite, a mineral which also occurs in abundance in the East vein amygdaloid assemblage which includes the Clark and Star mines. The unusual abundance of this borosilicate, confined to fissure deposits along the Great conglomerate, suggests that late-stage fumarolic activity played a role in local mineralization of the flows. Dr. Babcock has also provided unpublished results on local occurrences of roscoelite containing 15-17% V_2O_5 and 1-3% Cr_2O_3 at Dan's Point west of Copper Harbor and fuchsite with 1.5-4.0% Cr_2O_3 and $1\frac{1}{2} \pm V_2O_5$ found northeast of Gay and Traverse Island in Keweenaw Bay. These micas occur within bleached joints in redbed sandstones. Dr. Babcock is of the opinion that these elements were concentrated during oxidation and alteration of the flow tops as Cr, V and Mn are concentrated (180-9000 ppm) in magnetites, ilmenites and augites associated with the flows (Cormwall and Rose, 1957). We cite these observations since these elements are all present in the manganese oxide-silicate deposits and it does not appear necessary to invoke an exotic source for them, although the mechanism for their concentration in the manganese deposits is not clear.

The dendritic to plumose textures of the manganese minerals in the calcite; the high purity of the calcite (confirmed by electron probe analysis); the presence of minor to trace Cu, V, Cr, Ag, and Ga; the impoverishment of Mg and Al; the apparent lack of reaction or exchange between the amygdaloidal basalt and the minerals in the calcite fissures; and the subordinate amount of Mn(II) all suggest that the manganese oxide and silicate pods and stringers were formed by replacement of the fissure calcite, from solutions, probably fumarolic in origin under conditions of high oxygen fugacity. In all likelihood, these small deposits may represent a late stage solution from which iron was earlier removed through hydrolysis. The relationship of the calcite-filled fissures to the basalts which they cut is not known, nor is it possible to assess when the event of manganese mineralization took place, except to conclude that it postdated the emplacement of the basalts and conglomerates.

Why are the minerals macfallite and orientite of restricted occurrence? It would appear that the conditions for their formation involve either low temperature or the lack of major alumina or both in the system.

Table 1. Crystal parameters of macfallite, orientite and related minerals with Mn³⁺.

	MacFallite	Pienontite	Orientite		Ardenite	Bermanite		Santafeite
	1	2	3	4	5	6	7	8
a(Å)	8.929(6)	8.859(3)	9.042(4)	9.04	8.71	5.446(3)	8.92	9.25(2)
b(Å)	6.045(5)	5.712(3)	6.090(2)	6.08	5.81	19.25(1)	6.21	50.00(2)
c(Å)	10.905(7)	10.200(4)	18.990(7)	19.14	18.52	5.428(3)	19.25(1)	6.33(2)
β(deg.)	119.10(3) ⁶	115.66(3)	90	90	90	110.29(4) ⁶	90.27(4)	90
Space Group	P2 ₁ /m, P2 ₁	P2 ₁ /m	Ccmm	Ccmm	Pnmm	P2 ₁	C222 ₁	B22 ₁ 2
Z	2	2	2	2	2	2	4	2
α	1.773(5)		1.765(5)	1.756(2)			1.690(1)	2.01
β	1.795(5)		1.79(1)	1.777(2)			1.729(1)	
γ	1.815(5)		1.81(1)	1.794(2)			1.750(1)	
2V	very large		large	68-83 ⁶			72 ⁶	
sign	+ or -		+ or -	-			-	
α	yellow	yellow-green	brownish-yellow	yellow			light red	deep red-brown
β	light brown	grey-violet	reddish-brown	yellow-brown			pale yellow	α = c
γ	dark brown	purple-red	deep brownish-red	red-brown			deep red	Absorption 2>β>γ
Orientation	γ b	β b	a a, γ b	a a, γ b			α = c, γ:b-2 ⁶	
Dispersion				r<v strong			r<v	distinct

¹This study. Lake Manganese, Michigan. Cell edges refined from powder data. ²Anastasiou and Langer (1977).

³This study. Lake Manganese, Michigan. ⁴Moore (1965). ⁵Allmann and Donnay (1971).

⁶Kampf and Moore (1976). The pseudo-orthorhombic cell to the right is converted from the primitive monoclinic cell. The optical data are from Hurlbut and Aristarain (1968), the orientation corresponding to the pseudo-orthorhombic cell.

⁷Sun and Weber (1958).

Anastasiou and Langer (1977) did not encounter them during synthesis of piemontites in the system CaO-Al₂O₃-(MnO·MnO₂)-6SiO₂-H₂O at P = 15 kb, T = 800°C, fO₂ = Mn₂O₃/MnO₂ buffer. Furthermore, they obtained as an upper limit of Mn³⁺ solution, Al_{1.1}Mn_{1.9}, in the piemontite. The usual presence of alumina in metamorphics, metasediments, skarns and volcanics which comprise the geological environments of piemontites may preclude the formation of macfallite and orientite, which appear to be phases occurring exclusively in alumina-poor assemblages.

Experimental Section

Physical properties. Macfallite is rich reddish-brown (fibrous aggregates) to maroon (needles) in color, lacking the violet tint characteristic of the piemontites. Compact massive material is chocolate brown to dull pink in extremely fine-grained material. The crystals, which are thin prismatic parallel to [010], range from 0.1 to 10 mm in length and 0.02 to 0.2 mm in thickness. The streak and powder are brown with a reddish tint. The hardness is 5*, cleavage {001} perfect. Crystals are invariably twinned by reflection on {100}, often repeatedly. The luster is silky (in fibrous masses) to subadamantine (crystals). Specific gravity, determined by sink-float in Clerici solution, is 3.43(2). The mineral is only slowly soluble in 1:1 HCl solution at room temperature and rather pure material can be cleansed of the manganese oxides by this method. Its typical appearance in hand specimens are radial aggregates of tightly packed thin prismatic crystals.

Orientite is turbid chocolate brown for platy material but free-standing crystals are transparent and rich reddish-brown in color, and range up to 0.55 mm in greatest dimension. The streak and powder are brown. The cleavage or parting is perfect {001}; observed forms are \bar{m} {110}, \bar{c} {001} and poorly developed to absent \bar{a} {100}. The crystals are thin to thick tabular parallel to {001}. Their appearance differ (owing to relative facial size) from the more prismatic development for crystals from the Oriente Province. The specific gravity is 3.33, measured in methylene iodide, and therefore crystals remain perfectly suspended in that liquid at 21.0°C. At first, the mineral was believed to be a new

species since the physical properties depart significantly from the type orientite and since the {001} cleavage or parting, well-developed and persistent in Michigan material but poorly produced in Cuban material, imparted preferred orientation effects on diffractometer traces which led to distinctly different patterns between samples from the two occurrences. Cuban orientite is typically prismatic parallel to [001] and presents a pseudohexagonal outline owing to equal development of \bar{a} {100} and \bar{m} {110}. In addition, the specific gravity for the Cuban material is distinctly lower although the originally reported value of 3.05 (Hewett and Shannon, 1921) may be low. Redetermination by sink-float in methylene iodide-toluene mixtures led to 3.15(4) for our material from Cuba.

Physical data for the two silicate minerals are summarized in Table 1. In addition data for related phases are also presented. These phases possess one 5.7-6.3Å axis which in the known structures is the direction of Mn³⁺-O edge-sharing distorted octahedral chains. It is also the direction of most intense optical absorption and usually the direction of highest refractive index (the indices for santafeite are stated only for α which is the most intensely absorbing direction). This phenomenon is akin to the ferric hydroxo-bridged sulfate corner-chain structures, the chain direction also being the most intensely coloured and with the greatest index of refraction (Wan et al., 1978).

X-ray crystallography

Macfallite crystals are invariably twinned by reflection on {100} but the two reciprocal lattices were resolved without difficulty. Single crystal rotation, Weissenberg, and Buerger precession photography established the crystal cell in Table 1. The final data were obtained from least-squares refinement of 41 unambiguously indexed powder reflections obtained from CuKα radiation with graphite monochromator, scan speed 1/2° min⁻¹ in 2θ. The powder data were corrected for absorption effects and are reported in Table 2. To correctly assign indices, precession photographs of the \bar{k} = 0- through 4-levels were used to match intensities. Preferred orientation enhances the {00k} reflections but since the structure is not accurately known, it is not presently possible to assess

Table 2. X-ray powder data for macfallite.

I(obs)	d(obs)	d(calc)	hkl	I(obs)	d(obs)	d(calc)	hkl
50	9.499*	9.528	001	30	2.227	2.224	402
20	8.346	8.346	101	20	2.214	2.216	014
25	7.803	7.802	100	70	2.181	2.181	205
30	5.598	5.598	102	10	2.102	2.102	105
10	4.961	4.967	101	30	2.091	2.089	321
90	4.763*	4.764	002	5	1.922	1.923	302
55	4.457	4.447	201	30	1.905*	1.906	005
10	4.175	4.173	202	5	1.870	1.871	024
80	3.904	3.901	200	5	1.812	1.814	415
15	3.616	3.620	103	10	1.754	1.757	502
70	3.400	3.403	203	10	1.701	1.701	033
		3.397	102	10	1.663	1.663	116
5	3.269	3.278	210	10	1.641	1.639	420
25	3.116	3.117	201	10	1.636	1.635	214
70	2.971	2.961	112	85	1.588*	1.588	006
25	2.895	2.891	301	10	1.560		
15	2.787	2.782	303	15	1.556		
100	2.699	2.699	204	5	1.540		
20	2.667	2.665	312	5	1.515		
10	2.633	2.637	122	10	1.483		
10	2.556	2.552	022	5	1.449		
10	2.485	2.484	202	5	1.394		
15	2.449	2.448	222	15	1.352		
15	2.443	2.442	114	5	1.356		
45	2.381	2.389	310	10	1.271		
5	2.269	2.268	314				

*Reflections enhanced by {001} cleavage. $\text{CuK}\alpha$ radiation, graphite monochromator, scan speed 1° min^{-1} . The sample was corrected for absorption.

the contribution by this effect.

The same experiment was repeated for orientite. Manganese Lake material has a persistent cleavage or parting on {001}, therefore the reflections of type {00 l }, are enhanced. Orientite from Buycito was also examined in this manner but since the parting is essentially absent, the intensities are quite different. Comparison of single crystal photographs of the two materials failed to reveal any major differences between them.

These data as well as previously published results are presented in Table 3.

Knowledge of the detailed atomic arrangements of macfallite and orientite will permit a more detailed assessment of the powder data and further discussion is deferred until the structures are formally known.

Chemical analyses

Both macfallite and orientite from Manganese Lake were chemically analyzed. Difficulty was encountered in securing enough orientite for the wet chemical study and we were forced to obtain electron probe analyses for this material. The macfallite was analyzed by wet chemical techniques (J. Ito) and by electron probe (R. Hervig). Utilizing a solid state detector and a detailed correction program SSOLID (developed by I. M. Steele), it was possible to obtain three independent determinations on orientite and six on macfallite. Standards included Gore Mountain garnet (Ca, Mg, Al, Fe, Si), a Mn-rich hortonolite (Mn), and a plagioclase glass (K, Na). In addition to these elements, minor Cu, V and S were detected. These were called from a file of minor elements and since standards were not employed during the present runs, uncertainties in their corrections lead to possible errors which we estimate to be as high as $\pm 10\%$ of the reported values. The analytical results are presented in Table 4.

Macfallite and orientite from Manganese Lake consistently show the presence of V and Cu which range up to 2.24% for V_2O_5 and 2.58% for CuO. We suspect that V substitutes for Si^{4+} as V^{5+} in tetrahedral coordination and Cu substitutes for Mn^{3+} as Cu^{2+} , the latter which exhibit the same kind of Jahn-Teller distortion (d^8 and d^9 configurations respectively). In addition, S was found, ranging up to 1.24% SO, which we believe substitutes for Si^{4+} . Iron is noteworthy in its relative absence in Manganese Lake samples. Although aluminum is virtually absent in Manganese Lake orientite, it ranges from 3.95% to 8.45% Al_2O_3 in macfallite. Furthermore, qualitative inspection of macfallite crystals from different samples shows a considerable range in the amount of this component. Unfortunately, since samples could

Table 3. X-ray powder data for orientites.

1				2		3		4	
I(obs)	d(obs)	d(calc)	hkl	I(obs)	d(obs)	I(obs)	d(obs)	I(obs)	d(obs)
100	9.448*	9.495	002	75	9.479	7	9.58	50	9.42
		?						25	5.89
10	5.059	5.051	110	100	5.042	9	5.06	50	5.05
		4.881	111	15	4.871	3	4.908		
100	4.740*	4.747	004	15	4.750	1	4.783	10	4.77
25	4.509	4.521	200	45	4.504	5	4.520		
15	4.388	4.398	201	75	4.383	9	4.394	60	4.40
35	4.070	4.082	202	60	4.070	5	4.080	30	4.07
2	3.927	3.948	113	15	3.950			10	3.95
		?		15	3.893				
5	3.669	3.679	203	15	3.680			10	3.69
		?		3	3.481				
		3.459	114	3	3.463			10	3.42
		?		3	3.598				
30	3.270	3.274	204	45	3.270	6	3.290	50	3.26
45	3.026	3.036	115	75	3.040	7	3.059	75	3.05
8	2.893	2.900	022	45	2.901	5	2.914	40	2.90
		?						10	2.78
15	2.696	2.701	310	75	2.688	10	2.704	100	2.68
15	2.673	2.682	116	45	2.666	5	2.679		
15	2.589	2.593	206	15	2.592	3	2.606		
10	2.559	2.563	024	30	2.567	4	2.578	50	2.58
5	2.521	2.526	220	100	2.523	2	2.537	50	2.51
5	2.437	2.441	222	30	2.440	4	2.452	20	2.44
		?				2	2.410		
10	2.372	2.389	117	15	2.347	6	2.357	50	2.34
		2.348	314						
		2.326	207						
10	2.239	2.230	224	15	2.232	3	2.244	30	2.23
		2.201	315					10	2.19
5	2.101	2.103	225			3	2.115	25	2.10
		2.102	208			2	2.068	20	2.05

¹Manganese Lake. $\text{CuK}\alpha$ (graphite monochromator), $1/2^\circ \text{ min}^{-1}$. Additional lines $> 10:1.584/45$ (the 00.12 reflection). Sample was not corrected for absorption. There exist 45 independent reflecting planes to $d(\text{calc}) = 2.102\text{\AA}$. The 19 not listed are all $I(\text{calc}) < 0.5$. All remaining lines $< 2.102\text{\AA}$ have $I(\text{calc}) < 7$. Reflections enhanced by {001} cleavage or parting are starred.

²Buycito, Oriente Province, Cuba. $\text{CuK}\alpha$ (graphite monochromator), $1/2^\circ \text{ min}^{-1}$.

³Moore (1965). Six additional lines were reported for $d(\text{obs}) < 2.0\text{\AA}$.

⁴Sejar (1961). Thirty-eight additional lines were reported for $d(\text{obs}) < 2.0\text{\AA}$.

*Reflections enhanced by perfect {001} parting in Manganese Lake material.

Table 4. Orientite and macfallite: chemical analyses

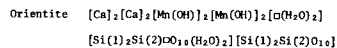
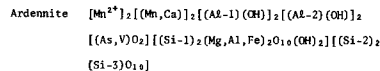
	1	2	3	4	5	6	7
K ₂ O	0.09(0.00-0.14)	-	-	-	0.12	0.08(0.00-0.14)	-
CaO	20.25(20.03-20.42)	22.47	20.13	22.24	19.75	20.04(19.92-20.50)	20.16
MgO	0.46(0.36-0.61)	-	-	-	0.39	nil	-
MnO	-	-	12.73	-	0.69	-	-
CuO	2.09(1.54-2.58)	-	-	-	1.13	1.54(1.19-1.94)	-
Al ₂ O ₃	nil	1.08	-	-	3.95	7.93(7.26-8.45)	-
V ₂ O ₅	0.96(0.37-1.54)	-	-	-	0.28	0.73(0.00-2.24)	-
Mn ₂ O ₃	33.64(33.48-33.88)	33.19	28.33	31.31	35.96	27.48(25.98-29.12)	42.57
Fe ₂ O ₃	nil	1.56	-	-	0.18	nil	-
SiO ₂	31.21(30.63-32.03)	32.48	32.35	35.74	32.04	31.83(31.14-32.55)	32.42
SO ₃	1.00(0.69-1.24)	-	-	-	-	0.47(0.36-0.60)	-
H ₂ O	[7.93]	7.93	6.46	10.71	5.39	[5.39]	4.85
Total	97.63	98.71	100.00	100.00	99.94	95.49	100.00

*Orientite:*¹Manganese Lake. R. Hervig, analyst. Average of three.²Oriente, Cuba, Hewett and Shannon (1921). E. V. Shannon, analyst. Average of three.³Computed from Ca₂Mn²⁺Mn³⁺(OH)₄[Si₃O₁₀]. The density is 3.54 g cm⁻³.⁴Computed from Ca₂Mn²⁺(OH)₂[Si₃O₁₀]·2H₂O. The density is 3.20 g cm⁻³.*MacFallite:*⁵Manganese Lake. J. Ito, analyst. Includes Na₂O 0.03%, Cr₂O₃ 0.03% and TiO₂ (trace).⁶Do. R. Hervig, analyst. Average of six.⁷Computed from Ca₂Mn³⁺(OH)₃[SiO₆]₂[Si₂O₇]. The density is 3.59 g cm⁻³.

not be recovered in place, we cannot offer further comments on its distribution with respect to the settings of the samples *in situ*. The results on our orientites from Manganese Lake are seen to be in good agreement with the earlier analysis of Hewett and Shannon (1921) on Oriente Province material.

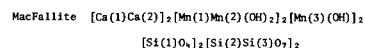
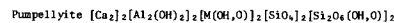
Chemical formulas: proposed structures. With the cells and chemical data at hand, we are now in a position to propose formula units for macfallite and orientite. Macfallite's cell and composition suggested that it may be isomorphic to the clinzoisite structure type. To test this, we isomorphically substituted the appropriate cations into the clinzoisite atomic positions (see Dollase, 1968, for the details of the clinzoisite structure), and calculated a powder pattern for the macfallite. The results clearly showed that the two are not isomorphic as hardly any agreement existed between the calculated and observed powder intensities. We therefore concluded that macfallite is based on a structure type different than clinzoisite.

Moore (1965) suggested that a structure relationship probably existed between orientite and ardenite. Indeed, ardenite's substructure shows affinities with the supergroup *Ccm* (the same space group as orientite) and the metrical properties of the cells for the two compounds are similar (see Table 1). Although ardenite possesses space group *Pnmm*, we examined its structure for further clues. Its structure was determined by Donnay and Allmann (1968) who showed in a subsequent study (Allmann and Donnay, 1971) that it is related to pumpellyite. They discerned a sheet of structure, the *ab*-plane, which is an isomorphic region between the two. We then placed this sheet and the loci of the screw axes over the space group of orientite. The result is a design which contains [Si₃O₁₀] trimeric units when one additional tetrahedron is added. The resulting structure is closely related to ardenite. Counting atoms in the formula unit for orientite, we obtain the following likely compositions (Z = 4): Ca₂Mn²⁺Mn³⁺(OH)₄(Si₃O₁₀) or Ca₂Mn²⁺(OH)₂[Si₃O₁₀](H₂O)₂, where □ is a vacancy. Note that both formulae conserve the same total oxygen contents as found in ardenite. Employing the ardenite formula in Donnay and Allmann (1968), the isomorphism is:



The major distinction between the ardenite and proposed orientite structure is the substitution of a tetrahedron plus vacancy (Si□) for 2(Mg, Al, Fe) octahedra. The trial coordinates for the proposed orientite structure were used toward a calculated powder pattern. The agreement is sufficiently good to warrant serious consideration of the model. It is not presently possible to select between the two proposed end-member compositions for orientite, nor does their comparison with the chemical analyses in Table 4 afford an obvious choice. The calculated density for Ca₂Mn²⁺(OH)₂[Si₃O₁₀](H₂O)₂ is closer to the observed specific gravities but the formula with partly filled vacancies gives a better fit with the chemical analyses. Clearly, a formal structure analysis will be necessary to resolve this matter.

Encouraged, we repeated the study for macfallite by placing the simple sheet unit and the loci of the screw axes on the space group of that compound. A plausible structure model immediately appeared. This model, also based on 14 oxygens, is closely related to the structure of pumpellyite and leads to the ideal end-member formula Ca₂Mn³⁺(OH)₃[SiO₆]₂[Si₂O₇]. The isomorphic regions in brackets are:



adopting the pumpellyite formula in Allmann and Donnay (1971). Trial coordinates from this model were used to calculate a powder pattern and the agreement is sufficiently good to warrant serious consideration of the model.

The chemical analyses in Table 4 were then recast into formula unit contents in Table 5 and were based on Σ oxygen = 14. Densities were then computed and it is gratifying to note that ρ = 3.36 g cm⁻³ for (1) is in

MACFALLITE AND ORIENTITE

Table 5. Unit formula contents for orientite and macfallite.

Orientite					
$\rho = 3.36 \text{ g cm}^{-3}$ (1)	Ca _{2.00}	Mn ²⁺ _{1.49} Mg _{0.06} Al _{0.45}	Mn ²⁺ _{1.85} Cu _{0.15}	Si _{2.66} So _{0.07} Vo _{0.07} O _{10.00} (OH) _{3.16} (H ₂ O) _{0.89}	
$\rho = 3.40 \text{ g cm}^{-3}$ (2)	Ca _{2.00}	Mn ²⁺ _{1.56} Ca _{0.23} Th _{0.21}	Mn ²⁺ _{1.77} Al _{0.12} Fe ³⁺ _{0.11}	Si _{3.00} O _{10.00}	(OH) _{3.56} (H ₂ O) _{0.42}
$\rho = 3.54 \text{ g cm}^{-3}$ (3)	Ca _{2.00}	Mn ²⁺ _{1.00}	Mn ²⁺ _{1.00}	Si _{3.00} O _{10.00}	(OH) _{4.00}
$\rho = 3.20 \text{ g cm}^{-3}$ (4)	Ca _{2.00}		Mn ²⁺ _{1.00}	Si _{3.00} O _{10.00}	(OH) _{2.00} (H ₂ O) _{2.00}
Macfallite					
$\rho = 3.51 \text{ g cm}^{-3}$ (5)	Ca _{1.93} Mn ²⁺ _{1.05}	Mn ²⁺ _{1.93} Al _{0.42} Cu _{0.08} Fe ³⁺ _{0.01}		Si _{2.92} Vo _{0.02} O _{11.00}	(OH) _{2.66} (H ₂ O) _{0.34}
$\rho = 3.41 \text{ g cm}^{-3}$ (6)	Ca _{1.98}	Mn ²⁺ _{1.93} Al _{0.06} Cu _{0.11}		Si _{2.93} Vo _{0.04} So _{0.03} O _{11.00} (OH) _{2.65} (H ₂ O) _{0.35}	
$\rho = 3.59 \text{ g cm}^{-3}$ (7)	Ca _{2.00}		Mn ²⁺ _{1.00}	Si _{3.00} O _{11.00}	(OH) _{3.00}

¹From average of probe analyses (R. Hervig) on Manganese Lake material. Densities computed from cell volume.

²From average in Hewett and Shannon (1921) on Oriente material.

^{3,4}Possible end-member compositions.

⁵From analysis of J. Ito on Manganese Lake material.

⁶From average of probe analyses (R. Hervig).

⁷Possible end-member composition.

satisfactory agreement with the determined specific gravity of 3.33 for Manganese Lake orientite; and $\rho = 3.41 \text{ g cm}^{-3}$ for (6) agrees well with 3.43 for macfallite. In addition, the calculated contents suggest that orientite may be a defect structure, with compositions lying along the join $\text{Ca}_2 \text{Mn}_2^+(\text{OH})_2[\text{Si}_3\text{O}_{10}](\text{H}_2\text{O})_2 - \text{Ca}_2\text{Mn}^{2+}\text{Mn}_2^+(\text{OH})_2[\text{Si}_3\text{O}_{10}](\text{H})_2$.

Of course, formal structure analysis, presently in progress, is the essential step in testing these models. Presently, we cannot offer any speculation why the space groups of orientite and macfallite are different than those of ardenite and pumpellyite respectively except to note that Mn³⁺ is absent in the latter compounds and the Jahn-Teller distortion induced by this cation may stabilize the related but distinct space groups of the former two.

Name. The new mineral honors Mr. Russell P. MacFall, a retired editor of the *Chicago Tribune* and dedicated amateur mineralogist who has written several popular books on mineral collecting, rocks and fossils. His long-lasting passion for the minerals of the Keweenaw Peninsula in upper Michigan makes a new species from that area most fitting to be named macfallite.

The name and the species received prior approval by the Commission on New Minerals and New Mineral Names, of the International Mineralogical Association. The type specimen is placed in the collection of types, the U.S. National Museum of Natural History and cotypes have been deposited in museums throughout the world. It is estimated that several tons of the new mineral and its associations probably exist on the waste heaps, of which about 100 kg were collected and preserved.

Acknowledgments. Dr. Larry Babcock of Hancock, and Mr. Carlton W. Gutman of Marquette, Michigan provided many fine samples for study in addition to guiding the senior author to the abandoned waste heaps of the manganese

mine. Assistance in aspects of this study by Mr. Rick Hervig and Dr. Takaharu Araki is appreciated.

We appreciate support of this study by the National Science Foundation grant EAR-19483 (Geochemistry).

REFERENCES

Allmann(R.) and Donnay(G.), 1971. *Acta Crystallogr.* **B27**, 1871-5.
 Anastasiou(P.) and Langer(K.), 1977. *Contrib. Mineral. Petrol.* **60**, 225-45.
 Butler(B. S.) and Burbank(W. S.), 1929. *U.S. Geol. Surv. Prof. Paper* **144**, p. 59.
 Clarke(D. H.), 1974. *Copper Mines of Keweenaw No. 3. Clark Mining Company.*
 Personal copy of copyrighted print by author, 21 pp.
 Cornwall(H. R.), 1955. *U.S. Geol. Surv. Map* **G074**.
 _____ and Rose(H.J., Jr.), 1957. *Geochim. Cosmochim. Acta* **12**, 209-24.
 Dollase(W. A.), 1968. *Am. Mineral.* **53**, 1882-98.
 Donnay(G.) and Allmann(R.), 1968. *Acta Crystallogr.* **B24**, 845-55.
 Hewett(D. F.) and Shannon(E.V.), 1921. *Am. Jour. Sci.* **5** Series, 491-506.
 Hurlbut(C. S., Jr.) and Aristarain(L. F.), 1968. *Am. Mineral.* **53**, 416-31.
 Kampf(A. R.) and Moore(P. B.), 1976. *Am. Mineral.* **61**, 1241-8.
 Moore(P. B.), 1965. *Can. Mineral.* **3**, 262-5.
 Park(C. F., Jr.), 1942. *U.S. Geol. Surv. Bull.* **935-B**.
 _____ and Cox(M. W.), 1944. *Ibid.* **935-F**.
 Sclar(C. B.), 1961. *Am. Mineral.* **46**, 226-34.
 Simons(F. S.) and Straczek(J. A.), 1958. *U.S. Geol. Surv. Bull.* **1057**.
 Sun(M.-S.) and Weber(R. H.), 1958. *Am. Mineral.* **43**, 677-87.
 Wan(C.), Ghose(S.) and Rossman(G. R.), 1978. *Am. Mineral.* **63**, 478-83.