

Manganhumite, a new species

PAUL BRIAN MOORE

Department of the Geophysical Sciences, The University of Chicago,
Chicago, Illinois 60637, U.S.A.

SUMMARY. Manganhumite, orthorhombic, a 10.54(1), b 21.45(2), c 4.822(9) Å, space group $Pnma$, $Z = 4$, $(Mn_{0.68}Mg_{0.30}Fe_{0.01}Ca_{0.01})_7(OH)_2(SiO_4)_3$, is the manganese analogue of humite whose type locality is the Brattfors mine, Nordmark, Province of Värmland, Sweden. It is a skarn assemblage mineral and occurs with katoptrite, manganostibite, magnussonite, galaxite, etc., which replace manganosite grains in magnetite-manganosite ore.

The mineral is biaxial (+), $\alpha = 1.707(3)$, $\beta = 1.712(3)$, $\gamma = 1.732(3)$, $2V_1(\text{obs.}) = 37(4)^\circ$, $r > v$ perceptible, cleavage {010} perfect, hardness = 4, specific gravity = 3.83(5). The five strongest powder lines are 1.777(10), 2.500(7), 3.371(6), 2.628(6), and 1.525(6).

MANGANHUMITE is one of several mineral species that were identified in the course of examining a small suite of skarn and fissure minerals from the abandoned Brattfors mine, Nordmarks Odalfält, in the Province of Värmland, Sweden (Moore, 1970). This deposit, like several in the region of which Långban is the most famous, consists of iron oxide ores (hematite and magnetite) and subsidiary manganese oxide ores (braunite and hausmannite), which occur as well-separated lenses in dolomitic marbles. The curious Brattfors deposit, the neighbouring Moss mine, and the other deposits in the region have been discussed in considerable detail by Geijer and Magnusson (1944). At a depth of about 140 m, mining activity at Brattfors encountered small local pods and lenses of hausmannite-manganosite-pyrochroite ore. The pyrochroite ore, a retrograde product derived from the manganosite, yielded along fractures pockets studded with ruby-red crystals of basic manganese arsenites and arsenates (synadelphite, hematolite, allactite, etc., see Sjögren, 1885, who describes their occurrence from the near-by Moss mine). The primary ores and associated skarns, however, did not receive the same attention by the earlier mineralogists and only a little material was preserved. What follows is the result of the limited evidence at hand, found in but a score of specimens preserved in the collections of the Swedish Natural History Museum. Documentary evidence indicates that all these specimens were col-

lected by one Mr. Backelin in 1910 during which time the Brattfors mine was still active.

Manganhumite occurs as a rather rare constituent of a curious fine-grained skarn assemblage that appears in intimate association with the ore minerals magnetite and manganosite. The ground mass is recrystallized calcite and the ore minerals and skarns occur as sparse to tight bands of grains with a distinctly layered appearance in the calcite. The skarns include katoptrite as up to 1 cm long lustrous reddish-black prismatic crystals, manganostibiite as black rounded grains, magnussonite as pale-greenish to orange grains, tephroite as reddish-grey rounded crystals, and galaxite as bright-orange rounded octahedra. Manganhumite is distinctly later in the sequence and frequently includes grains of katoptrite and magnetite. Specimens that show only skarn bands in calcite reveal magnesian sonolite as the major skarn mineral. The system is clearly complex and involves the components $CaO-MgO-MnO-FeO-Al_2O_3-Fe_2O_3-CO_2-SiO_2-As_2O_3-As_2O_5-Sb_2O_5-H_2O$. Table I lists the species encountered in this study. The Brattfors paragenesis appears to resemble closely that from Långban and probably has the same mode of evolution (Moore, 1970). It is interpreted as a gross recrystallization of hydrated Mn-Fe oxide proto-ores, which locally contained subsidiary amounts of coprecipitated antimony and arsenic oxides. Magnesium was provided by the dolomitic matrix and silicon and aluminium from the presence of quartz and clays. The temperature crest of recrystallization probably occurred contemporaneously with the appearance of katoptrite, manganostibite, tephroite, and galaxite, with the basic manganese humites forming in succession under somewhat retrograde conditions. Manganhumite appears to have formed in close contact with the ores while the sonolite appears as bands in the marble, which is lean in primary ore. The manganosite appears to have been extensively replaced by the unusual skarn minerals while the magnetite hardly reacted at all and contributed but little to their succession. The existence of subsilicic oxides of manganese

TABLE I. *The Brattfors mine assemblage**

<i>Gangue</i>		
Calcite	CaCO ₃	Ubiquitous (cm)
<i>Ore minerals</i>		
Magnetite	Fe ²⁺ Fe ₃ ³⁺ O ₄	Black fine-grained (mm)
Hausmannite	Mn ²⁺ Mn ₃ ³⁺ O ₄	Black fine-grained (mm)
Manganosite	MnO	Deep-green coarse-grained (cm)
<i>Skarn minerals</i>		
<i>Early</i>		
Katoprite	(Mn, Mg) ₁₃ ²⁺ Sb ₂ ⁵⁺ (Al, Fe) ₃ ³⁺ Si ₂ O ₂₈	Red-black, perfect cleavage (cm)
Manganostibite	(Mn, Mg) ₇ ²⁺ Sb ₅ ⁵⁺ As ₅ ⁵⁺ O ₁₂	Black rounded grains (mm)
Tephroite	(Mn, Mg) ₂ SiO ₄	Reddish-grey granular (cm)
Galaxite	Mn ²⁺ Al ₂ O ₄	Bright-orange small octahedra (mm)
<i>Late</i>		
Manganhumite	(Mn, Mg) ₇ ²⁺ (OH) ₂ (SiO ₄) ₃	Orange grains, perfect cleavage (mm)
Sonolite	(Mn, Mg) ₉ (OH) ₂ (SiO ₄) ₄	Orange grains, poor cleavage (mm)
Magnussonite	(Mn, Mg) ₅ (OH)(AsO ₃) ₃	Greenish to orange grains (mm)
<i>Basic vein minerals</i>		
Pyrochroite	Mn(OH) ₂	Pink to brown platy (cm)
Baryte	BaSO ₄	Snow-white crystals (mm-cm)
Hematolite	(Mn, Mg) ₁₃ ²⁺ Al ₂ (OH) ₂₃ (AsO ₃)(AsO ₄) ₂	Garnet-red tabular crystals (mm)
Synadelphite	(Mn, Mg) ₉ ²⁺ (OH) ₉ (AsO ₃)(AsO ₄) ₂	Reddish-black prismatic (mm)
Retzian	Mn ₂ ²⁺ Y(OH) ₄ (AsO ₄)	Deep-brown thick prismatic (mm)
Allactite	Mn ₇ (OH) ₈ (AsO ₄) ₂	Greenish-brown thin tabular (mm)

* The descending list roughly corresponds to the paragenesis *early* → *late*. Phases were determined by X-ray techniques.

that contain essential amounts of antimony and arsenic is not peculiar to Brattfors, but is generally observed in all deposits of the Långban type (Moore, 1970) and differs from deposit to deposit only in the relative abundances of the phases present. At Långban and the Sjö mine, långbanite and berzeliite predominate but are evidently absent at the Brattfors mine with the compositionally related katoprite and manganostibite occurring instead. At Långban, magnesian sonolite is not rare and much of the reddish 'tephroite' is this mineral; it also occurs as a fissure mineral, where complex brown crystals are found in association with the arsenate adelite (Moore, unpublished results); despite an extensive search, however, manganhumite has not yet been positively identified from this locality.

Studies on the Brattfors mine assemblage have failed to uncover any other manganese-bearing humite with the manganhumite, nor is manganhumite found with the sonolite bands. The sonolite, as with the other minerals, was identified by X-ray diffraction techniques. Its specific gravity is 3.59 (Berman torsion balance) and in combination with major Mn, Mg, and Si found in a qualitative electron probe scan, the material is therefore highly magnesian. One specimen showing sonolite bands presented a fracture which, when further examined,

revealed baryte, pyrochroite, synadelphite, hematolite, allactite, and retzian, species that belong to a late stage basic vein assemblage. These specimens afford a tolerably complete inventory of the Brattfors paragenesis, which is summarized in Table I.

X-ray crystallography. No euhedral crystals of manganhumite were found and it was necessary to obtain axial ratios from the X-ray study. Preliminary axial dimensions were obtained from rotation and Weissenberg photographs. Owing to the presence of inclusions, pure grains were carefully selected, crushed, and the powder rolled into a cylinder. The X-ray powder results are given in Table II and obtain from a calibrated film, utilizing Mn-filtered Fe-K α radiation and a 114.6 mm camera diameter. To correctly index the powder lines, a calculated powder pattern was obtained by isomorphically replacing the cations found in the chemical analysis for those atomic positions in the detailed crystal structure analysis of humite (Ribbe and Gibbs, 1971). We note that differences between observed and calculated intensities may arise from preferred orientation owing to the perfect {010} cleavage and from likely partial ordering of the octahedral cations over the four non-equivalent sites in the structure type, since our calculated pattern is based on a random distribution of Mn,

TABLE II. *Manganhumite. X-ray powder data**

<i>I/I₀</i>	<i>I_{calc}</i>	<i>d_{obs}</i>	<i>d_{calc}</i>	<i>hkl</i>	<i>I/I₀</i>	<i>d_{obs}</i>
4	2	10.65	10.726	020†	1	1.454
1	1	5.315	5.363	040†	2	1.436
1	8	5.092	5.116	210	1	1.426
3	7	4.705	4.729	220	2	1.408
2	7	3.957	3.998	031	4	1.371
5	33	3.719	3.738	131	1	1.358
2	4	3.549	3.575	060†	2	1.346
2	9	3.492	3.509	211	1	1.313
6	76	3.371	3.395	141	1	1.290
1	2	3.182	3.205	051	2	1.276
2	8	3.043	3.067	151	1	1.254
1	4	2.949	2.964	241	1	1.238
5b	41	2.813	2.839	301	1	1.231
—	55	—	2.814	311	3	1.203
5	59	2.752	2.771	161	2	1.179
6	53	2.628	2.639	331	1	1.168
—	34	—	2.649	270	3	1.160
7	57	2.500	2.512	171	1	1.153
—	46	—	2.509	341	1	1.143
1	15	2.464	2.472	430	2	1.122
1	7	2.363	2.368	351	3	1.098
5	35	2.310	2.322	271	2	1.096
1	17	2.277	2.288	181	3	1.086
2	2	2.219	2.245	450	3	1.069
—	4	—	2.233	132	1	1.056
—	7	—	2.223	361	3	1.050
1	4	2.142	2.153	142	2	1.042
1	2	2.024	2.029	242	2	1.037
2	7	1.921	1.927	1.10.1	2	1.029
1	1	1.863	1.865	172	3	1.022
1	3	1.829	1.837	2.10.1	2	1.015
10	100	1.777	1.783	272	3	0.996
2	13	1.723	1.726	432	3	0.987
2	8	1.706	1.712	3.10.1	3	0.978
3	13	1.669	1.669	640		
2	9	1.631	1.634	571		
2	12	1.604	1.607	3.11.1		
3	8	1.566	1.567	4.11.0		
2	1	1.547	1.549	532		
—	2	—	1.544	1.13.1		
6	29	1.525	1.532	0.14.0†		

* Mn-filtered Fe-K_α radiation, 114.6 mm camera diameter. The calculated data were obtained from the humite structure (by isomorphous substitution) and by least-squares refinement of the indexed lines.

† Reflections of the type (0k0) whose intensities are enhanced by preferred orientation.

Mg, Fe, and Ca over these sites. The indexed lines were then used towards least-squares refinement of the axial dimensions, care being taken to provide an absorption correction to the observed *d*-spacings. The results are *a* = 10.54(1), *b* = 21.45(2), *c* = 4.822(9) Å, space group *Pnma*. The space group conforms to the extinction criteria observed on the X-ray films and to the humite structure type. The axial ratio is 0.4914:1:0.2248, which compares

favourably with 0.4919:1:0.2273 found for humite by Ribbe and Gibbs (1971).

Physical properties. Manganhumite occurs as anhedral grains up to 1 mm in greatest dimension, which exhibit perfect {010} cleavage. The lustre is subadamantine, hardness 4. The colour is pale to deep brownish-orange and grains, although transparent, often show small inclusions of katoptrite and magnetite. For specific gravity determination, grains without inclusions were hand-picked until 6 mg were accumulated. The specific gravity, determined on a Berman torsion balance (toluene: 21.0 °C), is 3.83(5), in excellent agreement with 3.84 g cm⁻³ calculated from the cell volume and formula unit. The species dissolves easily in warm diluted HCl solution.

Optical properties. Biaxial +, birefringence moderate, $\alpha = 1.707(3)$, $\beta = 1.712(3)$, $\gamma = 1.732(3)$, $2V(\text{obs}) = 37(4)^\circ$, $r > v$ perceptible $\alpha = c$. The mineral is weakly absorbing and not noticeably pleochroic. It is palest orange in transmitted light. The calculated average $n = 1.77$ by the method of Gladstone and Dale.

Chemical analysis. Owing to the frequent presence of katoptrite and magnetite inclusions, it was not possible to select sufficient pure material for wet chemical analysis. Dr. C. E. Nehru performed the analysis on the ARL electron microprobe facility at the University of Chicago. The elements detected include Si, Al, Ca, Mg, Mn, and P but it was not possible to ascertain the presence of elements lower in atomic number than Na. The standards applied were tephroite and a magnesian fayalite and, owing to similar matrices, structures, backgrounds, and compositions of standards and unknown, corrections were not applied. The results are given in Table III. To derive the final composition, the general formula was assumed to be

TABLE III. *Manganhumite. Chemical analysis*

	1	2
SiO ₂	29.8	28.62
Al ₂ O ₃	tr.	—
CaO	0.34	0.62
MgO	14.2	13.44
MnO	57.1	53.66
FeO	0.98	0.80
P ₂ O ₅	tr.	—
H ₂ O	—	2.86
Total	102.42	100.00

¹ C. E. Nehru, analyst. Electron microprobe, average of five grains.

² Calculated for (Mn_{0.68}Mg_{0.30}Fe_{0.01}Ca_{0.01})₇(OH)₂(SiO₄)₃.

$R_7(\text{OH})_2(\text{SiO}_4)_3$ and the ratios of the octahedral cations were obtained to assess the average populations at the R-sites. The formula thus derived is $(\text{Mn}_{0.68}\text{Mg}_{0.30}\text{Fe}_{0.01}\text{Ca}_{0.01})_7(\text{OH})_2(\text{SiO}_4)_3$. Thus, the type material is a magnesian manganhumite.

Unfortunately, it was not possible to determine fluorine by this technique but the paragenetic setting and associated minerals would indicate that this element, if present, would be minor.¹

Name and disposition of the type material. The species and name were approved by the International Commission on New Minerals and New Mineral Names prior to submission for publication. The name applies to the humite structure type where $\text{Mn}^{2+} > \text{Mg}^{2+}$. The type specimen was split in two; half is preserved in the collection of types,

¹ After this paper had gone to press, Dr. E. J. Essene (University of Michigan) informed me that F is less than c. 0.1 wt.% based on an electron-probe analysis of the cotype. Therefore, Brattfors material is nearly a pure hydroxyl end-member.

the U.S. National Museum of Natural History (Smithsonian Institution) and the other half in the collection of the Swedish Museum of Natural History (Mineralogical Section).

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