American Mineralogist, Volume 68, pages 951–959, 1983

Mn-humites from Bald Knob, North Carolina: mineralogy and phase equilibria[1]

G. A. WINTER

Tennessee Valley Authority
P.O. Box 2957, Casper, Wyoming 82606

E. J. ESSENE AND D. R. PEACOR

Department of Geological Sciences
The University of Michigan, Ann Arbor, Michigan 48109

Abstract

Alleghanyite, manganhumite and sonolite have been found in the Bald Knob manganese deposit of North Carolina. These minerals are the manganese analogues of chondrodite, humite and clinohumite respectively. They are close to end-member Mn minerals in terms of cations but have about 25–30% of hydroxyl replaced by fluorine. The observed partitioning of minor elements among coexisting alleghanyite–manganhumite and manganhumite–sonolite suggests that minor element substitution does not stabilize one manganese humite relative to another. The Bald Knob humites coexist with rhodonites and manganese carbonates. Qualitative phase equilibria suggest that these assemblages require water-rich conditions to form in silica-undersaturated rocks during regional metamorphism and that variations in $XH_2O/(XH_2O+XCO_2)$ may account for their formation.

Introduction

The Bald Knob manganese deposit in Alleghany County, North Carolina has been shown by Simmons *et al.* (1981) to have originally been a manganiferous sediment metamorphosed to the mid-amphibolite facies. Winter *et al.* (1981) estimated conditions of peak metamorphism of $T = 575 \pm 40$°C, $P = 5 \pm 1$ kbar, $XH_2O = 0.5$, and fO_2/fS_2 located between $10^{-19}/10^{-3}$ and $10^{-16}/10^{0}$ based on analyses of coexisting phases, experimental data and thermodynamic calculations. The deposit is characterized by both silica-rich and carbonate-rich bulk compositions and is host to a wide variety of unusual manganese silicates, carbonates, titanates, sulfides, and spinel group minerals; three of these (galaxite, alleghanyite, and kellyite) were first described from this locality (Ross and Kerr, 1932; Peacor *et al.*, 1974). Of much interest is the occurrence of three manganese members of the humite group (alleghanyite, manganhumite and sonolite, the respective analogues of the magnesium humites chondrodite, humite and clinohumite) as well as tephroite, the manganese olivine. Although *P–T–X* relations between olivine and the various humites at other localities are not clear-cut, well-defined equilibrium relationships are found at Bald Knob which permit a simple interpretation of olivine-humite relations.

The humite minerals comprise a homologous series of nesosilicates having the general formula $nMg_2SiO_4 \cdot Mg(OH,F)_2$ where n = 1, 2, 3, and 4 for norbergite, chondrodite, humite and clinohumite, respectively. Ribbe (1980) gives examples of the previously confusing and variable space group nomenclature for the humite minerals and recommends adoption of the conventions used by Jones (1969) which we follow here.

Sonolite, $Mn_9(OH)_2(SiO_4)_4$, is isostructural with clinohumite and is abundant at Bald Knob. Manganhumite, $Mn_7(OH)_2(SiO_4)_3$, is isostructural with humite. It is relatively uncommon at Bald Knob and is generally identified only in thin section and by microprobe analysis. Alleghanyite, $Mn_5(OH)_2(SiO_4)_2$, is isostructural with chondrodite. Momoi (1980) reports the synthesis of fluor-alleghanyite, fluor-sonolite, and fluor-norbergite; Francis and Ribbe (1978) also synthesized the manganese analogue of norbergite (MAN), although it has not yet been found in nature.

Two additional, closely-related manganese end-member phases, leucophoenicite (a dimorph of manganhumite) and jerrygibbsite (a dimorph of sonolite), are only known from the Franklin area of New Jersey. They have no known equivalents in Mg endmembers, and although we have carefully searched for them, neither has been found at Bald Knob. Moore (1978) determined the structure of leucophoenicite and showed that it is characterized by an unusual kinked and serrated octahedral chain arrangement which is unlike that of the humites. White

---

[1] Contribution No. 386 from the Mineralogical Laboratory, The University of Michigan.

0003–004X/83/0910–0951$02.00

and Hyde (1983, ms.) have further described this structure and its relation to other phases. Jerrygibbsite has been described recently as a new mineral by Dunn *et al.* (1984). It is orthorhombic and either is derived by unit-cell twinning of monoclinic sonolite or, more likely, is a member of the leucophoenicite group. The equilibrium relations of leucophoenicite group minerals with the Mn-humites remain unknown.

Some occurrences of humites and olivines are enigmatic in that apparently incompatible phases are reported to coexist. Since most humites lie on a binary join between $R^{2+}(OH,F)_2$ and $R_2^{2+}SiO_4$, only two contiguous phases should coexist unless additional components complicate the phase relations. However, many exceptions are known in reported occurrences of humites and olivines. Smith *et al.* (1944) reported parallel intergrowths of tephroite and alleghanyite from the Benallt manganese mine in Wales without observing intervening manganhumite, leucophoenicite or sonolite. Tilley (1951) described parallel intergrowths of humites and olivines from a contact skarn in Skye, Scotland, in the sequence forsterite–chondrodite–humite–clinohumite–monticellite, where forsterite should be found adjacent to clinohumite rather than chondrodite. Bourne (1974) found no humite in a variety of assemblages among forsterite, clinohumite, chondrodite and norbergite from the Canadian Grenville terrane. Duffy and Greenwood (1979) and Rice (1980) concluded from Bourne's observations and from Duffy's (1977) experiments in the system $MgO–MgF_2–SiO_2–H_2O$ that humite may be metastable relative to chondrodite and clinohumite at moderate to high temperatures. If so it is difficult to reconcile occurrences of humite unless it is always a late, low-temperature replacement of other humites. It should be noted, however, that humite can only be demonstrated to be unstable if it can be made to decompose to clinohumite and chondrodite, and that its lack of growth in the laboratory indicates nothing about its stability. Yoshinaga (1963), Chopin (1978), and Fukuoka (1981) report alleghanyite with sonolite without finding intervening manganhumite, and it is possible that under some *P–T* conditions manganhumite is less stable than alleghanyite and sonolite, analogous to the relation inferred by Bourne (1974), Duffy and Greenwood (1979) and Rice (1980) for humite. White and Hyde (1982) observe tephroite–alleghanyite intergrowths from Hokkeyino, Kyoto Prefecture, Japan using transmission electron microscopy. The Bald Knob assemblages involving sonolite, manganhumite and alleghanyite exhibit none of these apparent inconsistencies. The detailed chemistries of these phases, especially where two coexist, therefore hold implications for equilibrium associations among humites and olivines.

Observations

All samples were collected from the waste dumps at Bald Knob and therefore we have no direct knowledge of

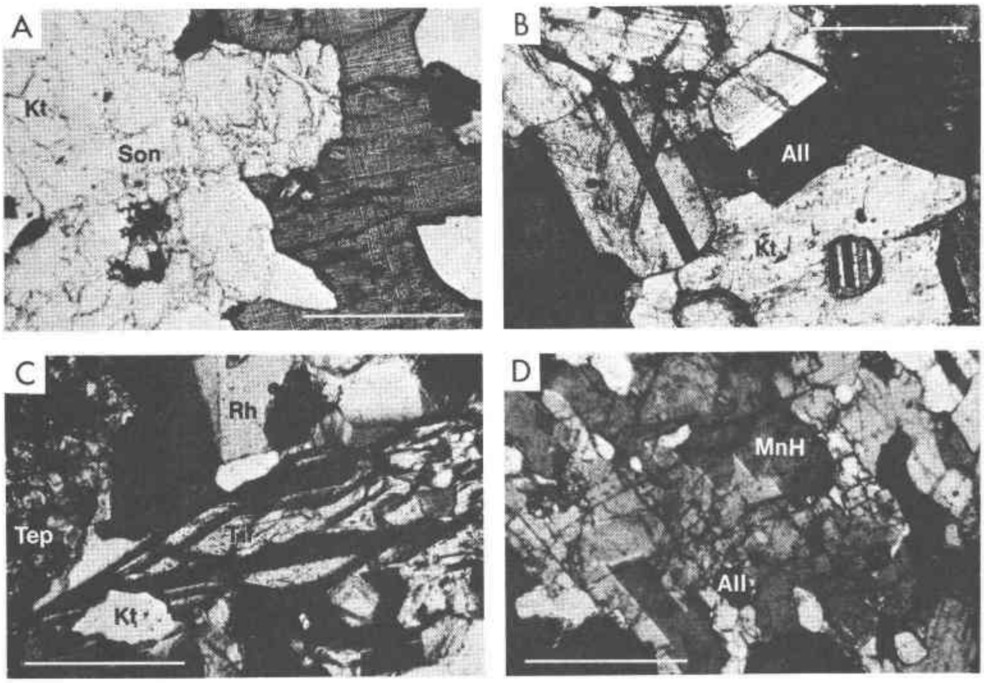

Fig. 1. Photomicrographs of Bald Knob Mn–humites, scale bar = 0.30 mm. Figure 1A, sonolite (Son) porphyroblasts in a kutnohorite (Kt) matrix with a large alabandite (Abd) grain (uncrossed polars, sample BK14). Figure 1B, twinned alleghanyite (All) in a kutnohorite (Kt) matrix. (crossed polars, sample 635). Figure 1C, tephroite (Tep) grains in a tirodite (Tir)–rhodonite (Rh) gneiss (crossed polars, sample BK4). Figure 1D, manganhumite (MH) intergrowths with alleghanyite (All) (crossed polars, sample BK22).

their original relative positions. Ross and Kerr (1932) described the ore body, however, so that inferences can be made about relative specimen position by reference to their descriptions. Seventeen samples were chosen for detailed characterization as being representative of the range of bulk composition, mineralogy and texture. These were studied using qualitative and quantitative electron microprobe analysis (EMPA) and standard optical methods

Table 1. X-ray powder diffractometer data for Bald Knob Mn–humites

Alleghanyite				Manganhumite				Sonolite			
I/I_o	d_{obs}	d_{calc}	hkl	I/I_o	d_{obs}	d_{calc}	hkl	I/I_o	d_{obs}	d_{calc}	hkl
								8	**7.08**	7.04	002
13	**5.06**	5.07	020					7	**5.27**	5.26	020
				4	**4.78**	4.79	022	4	**4.63**	4.63	022
						4.76	101				
9	**4.38**	4.37	110					8	**4.44**	4.43	110
8	**4.13**	4.13	101	5	**4.05**	4.05	103	7	**4.01**	4.01	102
7	**3.90**	3.91	002					13	**3.88**	3.89	211
										3.89	112
5	**3.74**	3.74	021	21	**3.78**	3.79	113	5	**3.78**	Manganhumite	
		3.73	022	6	3.61	3.63	006				
76	**3.63**	3.62	111			3.60	120	49	**3.63**	3.63	112
				8	**3.56**	3.55	121	8	**3.57**	3.58	120
										3.58	121
22	**3.51**	3.51	120								
				58	**3.43**	3.44	411	12	**3.45**	Manganhumite	
										3.37	121
								32	**3.35**	3.36	122
										3.35	113
85	**3.15**	3.14	112	6	**3.14**	Alleghanyite					
				9	**3.11**	3.11	115	3	**3.11**	3.11	311
				1	**3.00**	3.00	124	5	**3.04**	3.04	312
						3.00	026			3.03	212
100	**2.868**	2.865	131	51	**2.872**	2.874	130	100	**2.869**	2.876	131
										2.864	114
				75	**2.849**	2.849	131				
				50	**2.811**	2.810	116	17	**2.815**	Manganhumite	
52	**2.777**	2.776	130	18	**2.779**	2.779	132	4	**2.783**	Manganhumite	
						2.776	125				
71	**2.739**	2.736	112	16	**2.725**	2.723	008	7	**2.727**	Manganhumite	
53	**2.701**	2.704	022	25	**2.689**	2.688	027	68	**2.704**	2.707	024
				50	2.672	2.672	133	68	**2.658**	2.659	114
						2.667	040				
93	**2.615**	2.615	131	9	**2.602**	2.614	107	28	**2.613**	2.609	133
		2.613	003			2.591	042				
23	**2.533**	2.535	040	86	**2.545**	2.548	117	21	**2.549**	Manganhumite	
						2.542	134				
								23	**2.517**	2.515	132
				16	**2.505**	2.504	043	25	**2.508**	2.505	041
								44	**2.464**	2.463	115
53	**2.428**	2.433	200	9	**2.433**	2.440	200	13	**2.443**		
		2.422	131			2.426	028				
63	**2.393**	2.392	113	14	**2.393**	2.399	135	51	**2.362**		
						2.396	044				
64	**2.350**	2.346	141	33	**2.355**	2.355	127				
				20	**2.343**	2.341	140		**2.342**		
								8	**2.287**		
12	**2.217**	2.219	211	3	**2.217**			4	**2.259**		
22	**2.209**	2.212	041								
		2.206	043								
10	**2.122**	2.116	113	5	**2.152**			11	**2.128**		
10	**2.046**	2.039	121	1	**2.053**						
6	**1.924**			8	**1.955**						
4	**1.901**										
9	**1.885**			8	**1.888**			13	**1.887**		
4	**1.873**			3	**1.864**			3	**1.866**		
				5	**1.840**			5	**1.839**		
100	**1.807**			100	**1.803**			87	**1.808**		
10	**1.781**							13	**1.777**		
23	**1.757**			14	**1.747**			20	**1.744**		
14	**1.711**			8	**1.727**						
15	**1.700**										
27	**1.691**			13	**1.690**			25	**1.691**		
10	**1.652**			9	**1.657**			4	**1.659**		
22	**1.638**			5	**1.631**			8	**1.631**		
23	**1.611**			8	**1.601**			30	**1.606**		
13	**1.588**			14	**1.590**						
32	**1.564**			9	**1.569**			24	**1.563**		
53	**1.551**			36	**1.556**						
38	**1.544**			44	**1.544**			43	**1.546**		

on polished thin sections cut normal to the obvious 1–5 cm banding. Single-crystal and powder X-ray diffraction, as well as universal-stage optics, were used to characterize specific grains which were chosen on the basis of EMPA and optical characteristics.

Alleghanyite is easily identified in thin-section at Bald Knob due to its striking polysynthetic twinning (Fig. 1B) and its occurrence as small (0.05–1 mm) rounded grains in manganese carbonate matrix. Its X-ray powder diffraction data (Table 1) are in good agreement with the data of Lee (1955) and Yoshinaga (1963). The unit cell parameters obtained from these data (Table 2) agree well with the calculations of Yoshinaga (1963), Rentzeperis (1970), and Momoi (1980). Cook (1969) reports X-ray data for alleghanyite from Franklin, New Jersey (which is that listed by JCPDS) with extra lines at 5.20, 4.32 and 3.26Å which cannot be indexed with our unit cell data for alleghanyite, indicating contamination with other phase(s). The X-ray powder data of Lee (1955), Yoshinaga (1963), or that in Table 1 should be used in place of Cook's data.

Manganhumite is found intimately intergrown with either sonolite or alleghanyite at Bald Knob, although in sample DS10 it forms large porphyroblasts with only very minor intergrowths of alleghanyite. It was initially identified due to its different extinction position in intergrowths (Fig. 1D). Its 2*V* and indices of refraction are both much higher than the type material of Moore (1978), as would be expected considering its much greater Mn content. Manganhumite is very difficult to distinguish from the other humites in thin-section, and even microprobe analysis is insufficient to resolve the dimorphs manganhumite from leucophoenicite and jerrygibbsite from sonolite. Single-crystal X-ray work was necessary to unequivocally demonstrate the presence of manganhumite at Bald Knob. Its unit cell and space group are compared with type materials (Table 2) and powder diffractometer data are given (Table 1).

Sonolite occurs as centimeter-sized, irregular porphyroblasts at Bald Knob (Fig. 1A) intergrown with other phases, especially manganhumite, which makes it difficult to obtain sufficiently pure material for powder X-ray diffraction (Table 1). This sample contained a small quantity of manganhumite, as noted. Lattice parameters, obtained by least-squares refinement of the diffractometer data, are also given (Table 3). These data agree well with those of Yoshinaga (1963), Cook (1969), and Momoi (1980).

Although originally reported by Ross and Kerr (1932), tephroite is not a common mineral at Bald Knob. It is difficult to distinguish from the humites both optically and chemically. Many powder X-ray diffraction patterns were obtained on possible tephroites in humite rocks without positive results and we believe that some sonolite was mistaken as tephroite by Ross and Kerr (1932). Where identified (Fig. 1C), it occurs as 0.2 mm anhedral grains in clusters with abundant carbonates in spessartine–rhodonite/pyroxmangite–tirodite assemblages and is impossible to identify except in thin section. We have not yet found tephroite coexisting with sonolite although such a relation should occur. The Bald Knob tephroites, carbonates and pyroxenoids are often enriched in iron and magnesium relative to the humites (see Winter *et al.*, 1981, for analyses of carbonates and pyroxenoids).

Table 2. X-ray unit cell and optical data for Bald Knob Mn–humites

Mineral Locality Sample Number •	Manganhumite Brattfors Mine	Manganhumite Bald Knob DS10	Sonolite Bald Knob 635	Alleghanyite Bald Knob BK-2
Space Group	Pbnm	Pbnm	$P2_1/b$	$P2_1/b$
a(Å)	4.822(9)Å	4.879(5)	4.884(9)	4.866(6)
b(Å)	10.54(1)	10.670(6)	10.700(11)	10.708(19)
c(Å)	21.45(2)	21.787(13)	14.314(19)	8.260(16)
(°)	--	--	100.44(17)	108.77(19)
V(Å)	1090.2(27)	1134.3(9)	735.6(14)	407.5(17)
	1.707(3)	1.761(calc)	--	--
	1.712(3)	1.772(2)	--	--
	1.732(3)	1.781(2)	--	--
$2V_z$	37(5)°	84(5)°	--	--
dispersion	r v	r v	--	--
density	3.83(5)	4.053(calc)	4.023(calc)	4.000(calc)
OH/(F+OH)	1.0	0.73	0.71	(0.7)
Mn/(Mn+Mg+Fe)	0.68	0.97	0.97	(0.95)

The settings recommended by Jones *et al*. (1969) are used. The settings for monoclinic sonolite and alleghanyite have alpha as the unique angle.

These values were obtained by Moore (1978) for type manganhumite. We have modified his axial setting from space group setting Pnma to Pbnm.

Values estimated by comparison with analyzed specimens from Bald Knob (Table 2).

Assemblages involving Bald Knob humites and tephroite are listed in Table 3. Although tephroite and quartz are both found in BK-4 they are located in different bands with no indication of having equilibrated. Common accessories are kellyite (Peacor *et al.,* 1974) and galaxite with less common jacobsite and pyrophanite (Essene and Peacor, 1983), fluorapatite and nickeloan cattierite.

Characterization of the humites by powder X-ray diffraction often leads to ambiguous results due to the similarity in the patterns. This is in part caused by the difficulty in obtaining samples which comprise only a single species. Isolation and characterization of individual samples is even more difficult when studying Mn-humites from Franklin, New Jersey, because leucophoenicite and jerrygibbsite also occur and their diffraction patterns are similar to those of the Mn-humites. Indeed, patterns of all five minerals have principal peaks in common, and have similar distributions of weak and intense peaks so as to appear equivalent at first sight. We have therefore taken great care to obtain high quality diffractometer patterns of single-phase materials to serve as a guide for other investigators (Table 1). These patterns were obtained using a 1°/minute scan rate and were standardized using quartz as an internal standard. The final criteria for yielding pattern accuracy were: (1) the data were indexible using lattice parameters obtained by

Table 3. Mineral assemblages in Bald Knob rocks containing Mn–humite or tephroite

Sample	Alleghanyite	Manganhumite	Sonolite	Tephroite	Rhodonite	Pyroxmangite	Kutnahorite	Galaxite	Jacobsite	Kellyite	Alabandite	Cattierite	Pyrophanite	Spessartine	Apatite	Quartz	Cobaltite	Tirodite	Stilpnomelane	Caryopilite
BK 2	X						X	X		X	X		X							
BK 4				X	X		X	X					X	X					X	
BK 6	X						X	X	X	X	X	X	X		X				X	
BK 8				X	X	X	X	X					X	X	X	X				
BK 11	X						X	X	X	X	X	X	X							X
BK 13			X				X	X	X	X		X	X							
BK 14		X	X				X	X	X	X	X				X					
BK 18				X	X	X	X	X	X	X			X	X					X	X
BK 19			X				X	X							X			X		
BK 22	X	X			X		X	X	X	X	X	X		X	X		X			
BK 25			X				X	X		X										
BK 26	X	X	X				X	X	X	X		X					X			
BK 28			X				X	X						X			X	X		
BK 50	X						X	X		X						X				
BK 2B			X				X													
DS5	X						X	X			X									
DS10		X					X	X												
635		X	X				X	X		X				X	X					

least-squares refinement (Table 2); and (2) a direct comparison of patterns verified a minimum number of interferences by characteristic peaks of other phases. Only unambiguously indexed X-ray lines were used in the unit-cell refinements. The alleghanyite pattern was of single-phase material, that of sonolite contained significant manganhumite and that of manganhumite contained a trace of alleghanyite as cited in Table 1.

Reference to the *d*-values listed in Table 1 shows that it is possible to unambiguously characterize patterns using peak *d*-values between 3.78 and 3.15Å. Alleghanyite has an intense peak at $d = 3.15$Å which has no equivalent in either sonolite or manganhumite (and one at $d = 3.63$Å which overlaps a peak in sonolite but not in manganhumite). Sonolite has a unique and intense peak at $d = 3.35$Å (and a more intense peak at $d = 3.63$Å overlapping one of alleghanyite). Manganhumite has two characteristic peaks having $d = 3.78$ and 3.43Å. We emphasize that even having reasonably well-characterized patterns with which unknowns could be directly compared, we experienced difficulty until these characteristic peaks were identified in samples previously well characterized by single-crystal and/or electron microprobe techniques.

White and Hyde (1982) report on TEM observations of Bald Knob Mn-humites. They found alleghanyite, manganhumite and sonolite to occur as relatively perfect crystals with no intergrowths and few faults. The Bald Knob materials may be relatively perfect crystals because of the long annealing times attendant with regional metamorphism. This is in contrast with a sonolite sample from Hokkeyino, Kyoto, Japan which contained tephroite, manganhumite and alleghanyite with many faults, inhomogeneities and intergrowths. Another sonolite sample from Längban, Sweden in part contained an ordered intergrowth of manganhumite and sonolite. These observations imply that microprobe analyses of some Mn-humites may yield intermediate stoichiometries (as has been reported by Fukuoka, 1981) even where X-ray diffraction apparently shows the presence of a single phase.

Electron microprobe analyses

The electron microprobe procedures for analyzing Mn–humites were essentially the same as those described by Winter *et al.* (1981) for pyroxenoids. The resultant analyses (Table 4) permit the unambiguous identification of each specific Mn–humite, but we note that in general, any two such phases have very similar compositions and care must be taken in the identification of specific Mn–humites using analytical data alone. All of the analyses show near end-member compositions in terms of cations, having $Mn/(Mn + Mg + Fe^{2+}) = 95\%$ (Fig. 2). The elements Ti and Ca are present only as minor elements in the Bald Knob humites and presumably do not have a significant effect on the phase relations. Dal Piaz *et al.* (1979) report a calcian alleghanyite from the western Alps of Italy but our powder X-ray diffraction data on their sample shows that it is leucophoenicite. The lack of titanium in the manganese humites at Bald Knob may be caused by the fact that pyrophanite scavenged much of the Ti present in the protolith. The low values for Al given in Table 4 may not represent amounts that actually exceed background values; Jones *et al.* (1969) conclude that Al is probably not present in humite structures. Boron has been shown

Table 4. Microprobe analyses of Mn–humites and tephroites. Son = Sonolite, MH = Manganhumite, All = Alleghanyite, Tep = Tephroite.

Sample wt%	BK2 Son	BK4 Tep	BK8 Tep	BK14a Son	BK14b MH	BK22a All	BK22b MH
SiO_2	27.38	30.39	28.69	27.25	26.19	24.65	26.21
TiO_2	0.09	0.01	n.a.	0.42	0.41	0.14	0.17
Al_2O_3	0.09	0.07	0.08	0.19	0.21	0.00	0.00
[1]FeO	1.28	9.19	5.63	1.69	1.30	0.84	0.94
MnO	68.84	57.13	64.39	67.84	68.87	70.15	69.47
MgO	1.08	2.06	0.45	1.23	0.81	0.78	0.73
CaO	0.09	0.06	0.02	0.14	0.06	0.11	0.13
[2]H_2O	1.57	----	----	1.37	1.84	2.60	1.89
F_2	0.91	n.a.	n.a.	1.13	1.41	2.20	1.46
[3]sum	100.95	99.91	99.26	100.78	100.51	100.54	100.39
[4]mole ratios							
Si	4.02	1.02	0.97	4.00	2.99	2.00	3.01
Ti	0.01	0.00	n.a.	0.05	0.03	0.01	0.01
Al	0.02	0.00	0.00	0.03	0.03	0.00	0.00
[1]Fe^{2+}	0.16	0.26	0.16	0.21	0.12	0.06	0.09
Mn	8.56	1.64	1.82	8.42	6.67	4.82	6.76
Mg	0.24	0.10	0.02	0.27	0.14	0.10	0.12
Ca	0.01	0.00	0.00	0.02	0.01	0.01	0.02
[2]OH	1.54	0.00	----	1.44	1.40	1.41	1.45
F	0.42	n.a.	n.a.	0.53	0.51	0.57	0.53
O	16.08	4.04	3.94	16.13	12.07	8.02	12.04
Sample BK wt.%	BK22c MH	BK22d All	BK22e All	BK22f MH	BK22g All	635-a MH	635-b Son
SiO_2	26.21	24.29	23.96	25.73	24.10	26.18	27.13
TiO_2	n.a.	n.a.	n.a.	n.a.	n.a.	0.04	0.03
Al_2O_3	0.10	0.10	0.11	0.10	0.11	0.08	0.09
[1]FeO	1.13	0.82	0.77	0.93	0.82	0.91	0.89
MnO	69.75	69.27	69.41	68.62	68.90	71.17	69.79
MgO	0.78	0.86	0.82	0.76	0.80	0.48	0.47
CaO	0.13	0.11	0.13	0.09	0.17	0.09	0.11
[2]H_2O	2.00	2.73	2.71	1.87	2.70	1.52	1.41
F_2	1.30	1.89	1.93	1.47	1.91	1.88	1.24
[3]sum	100.86	99.27	99.03	98.95	98.71	101.56	100.64
[4]mole ratios							
Si	2.99	2.00	1.98	2.99	1.99	2.96	4.01
Ti	n.a.	n.a.	n.a.	n.a.	n.a.	0.00	0.00
Al	0.01	0.01	0.01	0.01	0.01	0.01	0.02
[1]Fe^{2+}	0.11	0.06	0.05	0.09	0.06	0.09	0.11
Mn	6.73	4.81	4.83	6.76	4.83	6.83	8.75
Mg	0.13	0.11	0.11	0.13	0.10	0.07	0.10
Ca	0.02	0.01	0.01	0.01	0.01	0.01	0.02
[2]OH	1.52	1.50	1.49	1.45	1.49	1.44	1.40
F	0.47	0.49	0.50	0.54	0.50	0.55	0.58
O	11.98	8.01	7.98	11.99	8.00	11.93	16.04

[1] n.a. = not analyzed; all Fe assumed to be Fe^{2+}

[2] H_2O is calculated: mole OH = 2-F-2Ti-Al.

[3] Sum adjusted for F = 0

[4] Normalized to Mn + Mg + Fe + Ca + Ti + Al = 9 for sonolite; 7 for manganhumite; 5 for alleghanyite; 2 for tephroite.

to substitute for Si in some humites (Hinthorne and Ribbe, 1974), but we were unable to analyze for it; however, the normalized analyses are consistent with its absence at Bald Knob. Compared with most previously published analyses of Mn–humites (Smith *et al.*, 1944; Yoshinaga, 1963; Moore, 1978), those at Bald Knob are enriched in F substituting for OH, with up to a third of the anion site occupied by F (Fig. 3). The F/(F + OH) ratio is remarkably constant (0.21–0.32), considering the variety of specimens analyzed.

The analytical data for the Bald Knob manganese humites can be said to show simplicity in both solid solution in all phases and in constancy of ratios of trace to minor elements where they do occur, suggesting that such variables do not complicate the phase relations. The Bald Knob manganese humites present an ideal situation for

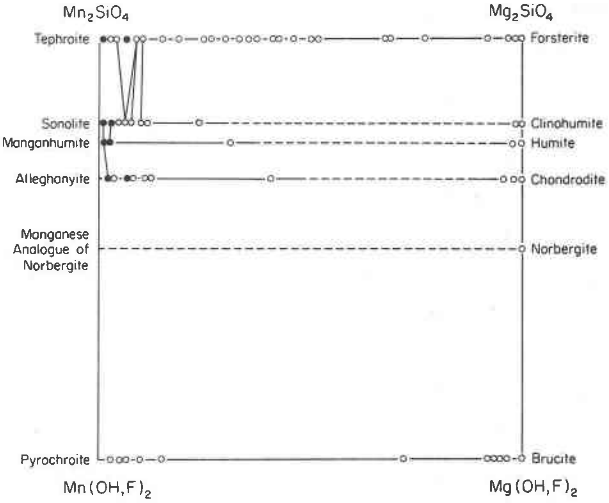

Fig. 2. Humite, olivine, and brucite-group minerals projected onto the plane Mg_2SiO_4–Mn_2SiO_4–$Mg(OH,F)_2$–$Mn(OH,F)_2$. Only analyses with (Fe+Ti)/(Fe+Ti+Mg+Mn) < 5% are plotted. Data are taken from Dana (1892), Hintze (1915), Rogers (1935), Palache *et al.* (1944), Lee (1955), Hurlbut (1961), Deer *et al.* (1962), Yoshinaga (1963), Peters *et al.* (1977), Moore (1978), Chopin (1978), Francis (1980), Ribbe (1980), Nambu *et al.* (1980) and Fukuoka (1981). Solid dots from Bald Knob, open circles from other localities. Fukuoka (1981) has a plethora of analytical data on Japanese alleghanyites, sonolites, and tephroites, and only a few representative points are shown here.

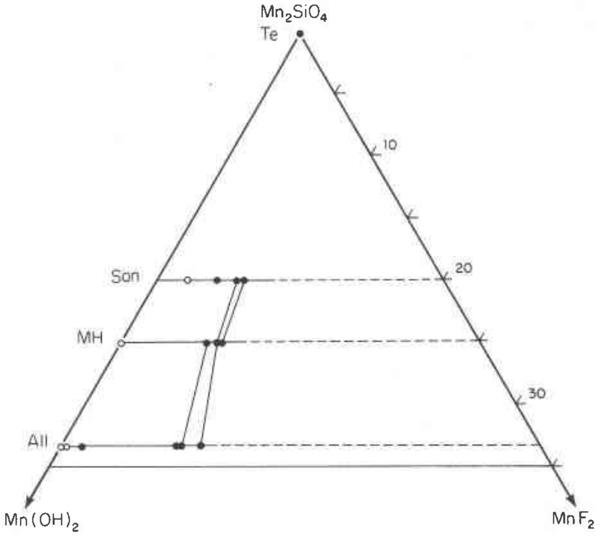

Fig. 3. Manganese humites projected onto the plane Mn_2SiO_4–$Mn(OH)_2$–MnF_2. Only minerals with Mn > Mg and with (Fe+Ti)/(Fe+Ti+Mg+Mn) < 5% are shown. References and symbols are given in Fig. 5. The data of Chopin (1978), Francis (1980) and Fukuoka (1981) could not be plotted because they did not analyze their humite group minerals for fluorine.

the evaluation of humite group phase relations in a chemically simple system.

Solid solutions and phase equilibria

There are no experimental or thermodynamic data on the stability of manganese humites so any inferred phase equilibria must be schematic and based solely on the assemblages and mineral formulae. The phase equilibria inferred by Duffy and Greenwood (1979) and Rice (1980) for magnesium humites provide an imperfect analogue for manganese humites for two reasons: (1) norbergite is inferred to be stable in the magnesium system, but a manganese equivalent is not yet known at Bald Knob or elsewhere; (2) manganhumite occurs at Bald Knob, but humite is inferred to be unstable at high temperatures in the magnesium system.

The cell volumes of the humite and leucophoenicite group minerals offer some clue to their relative stabilities. Using the cell volumes in Table 3 for the humites and the data of Dunn *et al.* (1984) for Franklin leucophoenicite and jerrygibbsite, one can calculate that Bald Knob manganhumite is 2.1% denser than Franklin leucophoenicite, while Franklin jerrygibbsite is 0.7% denser than Bald Knob sonolite. Therefore, manganhumite and jerrygibbsite are apparently the high pressure polymorphs. The Bald Knob humite group minerals contain significant fluorine and the Franklin leucophoenicites contain some calcium and zinc, and these elements may stabilize the respective phases. However, analyses of coexisting Franklin jerrygibbsite and sonolite show little partitioning of Zn and Ca between the two phases (P. J. Dunn, pers. comm., 1982). It is judged that these solid solutions will not change the relative volumes for reactions between the polymorphs leucophoenicite *vs.* manganhumite and jerrygibbsite *vs.* sonolite. The reaction manganhumite = alleghanyite + sonolite may also be considered. Since manganhumite is 0.8% denser than an equimolar mixture of alleghanyite + sonolite, it should be favored at high pressures. Thermal expansion and compressibility data are needed to quantify volume changes at high pressures and temperatures, but the sign of the calculated volume changes is not expected to change for crustal conditions.

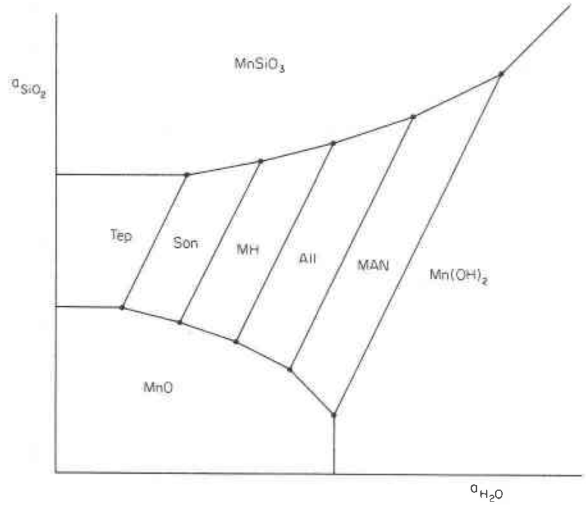

Fig. 4. Phase equilibria for manganese humites in the space $a(SiO_2)$–$a(H_2O)$. All humites are assumed to decompose regularly to the chemically adjacent phase.

Major element chemical variations for the humites may be shown on two graphs, one for Mg_2SiO_4–Mn_2SiO_4–$Mg(OH,F)_2$–$Mn(OH,F)_2$, and one for Mn_2SiO_4–$Mn(OH)_2$–MnF_2 (Figs. 2–3). The Bald Knob minerals show regular variation in Mn:Mg and F:OH with no evidence of one humite systematically partitioning these elements relative to other humites. When data from other occurrences are also plotted, evidence can be seen for significant solid solution along the binaries for pyrochroite–brucite, manganhumite–humite, alleghanyite–chondrodite, sonolite–clinohumite and tephroite–forsterite, but only insignificant solution of manganese in norbergites (see also Francis, 1980). Fukuoka (1981) reports analyses of coexisting tephroite and sonolite which are shown in Figure 2. He also gives data for coexisting alleghanyite and sonolite which have been excluded from Figure 2 for clarity and because some of Fukuoka's analyses appear to represent manganhumite rather than alleghanyite or sonolite.

If one considers the Bald Knob assemblages it is clear that the activities of SiO_2 and H_2O are likely to be of importance in controlling the specific manganese silicate assemblage. Humites are more undersaturated than olivines because they have $R^{2+}/Si > 2$, but substitution of the excess R^{2+} is paired to OH+F. We have chosen to plot the activities of SiO_2 *vs.* H_2O to further examine silicate reactions (Fig. 4) because OH is greater than F in Bald Knob humites. The effect of F could be considered as a diluent in the humites, extending their stability somewhat with respect to pyroxenoids and olivines. A sample reaction in Figure 4 is:

$$\text{Manganhumite} + H_2O = \text{Alleghanyite} + SiO_2$$
$$5Mn_7(OH)_2(SiO_4)_3 + 2H_2O = 7Mn_5(OH)_2(SiO_4)_2 + SiO_2$$

This reaction separates the manganhumite field from the alleghanyite field. The other field boundaries are generated by similar reactions. This figure shows the five relevant two-phase manganese silicate assemblages at Bald Knob: rhodonite–tephroite, rhodonite–manganhumite, rhodonite–alleghanyite, manganhumite–alleghanyite, and manganhumite–sonolite (Table 3). The lack of manganese hydroxides and oxides at Bald Knob is apparently explained by a lack of extreme variations in $a(SiO_2)/a(H_2O)$ or because their place is taken by manganese carbonates due to the availability of CO_2, suggesting that equilibria among manganese carbonates and silicates should also be considered.

The inferred T–$XCO_2/(XCO_2+XH_2O)$ equilibria for manganese silicates in the system MnO–SiO_2–H_2O–CO_2 have been constructed to be consistent with observed

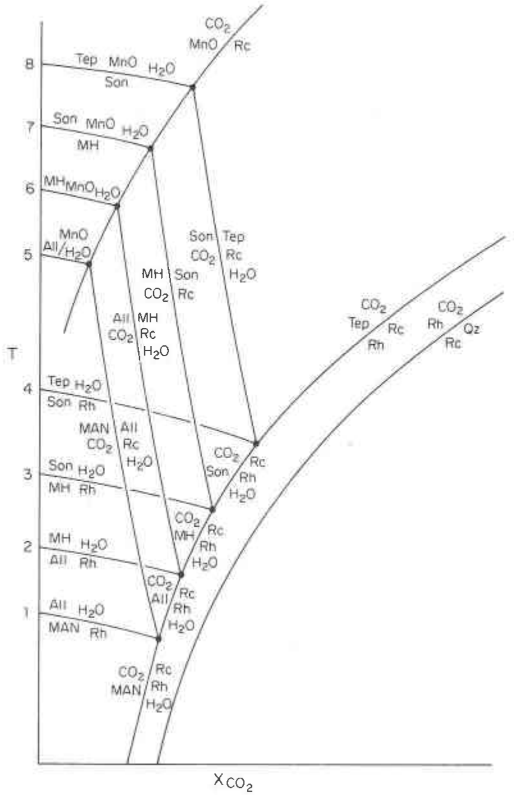

Fig. 5. Phase equilibria for manganese humites in the space T–$XCO_2/(XCO_2+XH_2O)$. All humites are assumed to be stable with rhodochrosite (Rc) and/or rhodonite (Rh) and/or the chemically adjacent manganese silicate as suggested by observations at Bald Knob. MAN = Manganese Analogue of Norbergite, Alleghanyite (All), Manganhumite (MH), Sonolite (Son), Tephroite (Tep).

Bald Knob assemblages (Fig. 5). By extension, the stability of a hypothetical manganese analogue of norbergite has been derived although it may always be less stable than alleghanyite + $Mn(OH,F)_2$. Any three coexisting manganese silicates, or two manganese silicates coexisting with rhodochrosite define a univariant equilibrium, *e.g.*,

$$\text{Manganhumite} + \text{Rhodochrosite} + H_2O = \text{Alleghanyite} + CO_2$$

$$2Mn_7(OH)_2(SiO_4)_3 + MnCO_3 + H_2O = 3Mn_5(OH)_2(SiO_4)_2 + CO_2.$$

Similar reactions for other assemblages of manganese silicates, carbonates and oxides can be balanced and placed on a T-X diagram relative to simple decarbonation reactions for rhodochrosite (Fig. 5). If it is assumed that this diagram applies directly to Bald Knob assemblages, variations in CO_2/H_2O alone may explain most of the observed associations. The lack of a known manganese analogue of norbergite may be explained either by a certain minimum level of CO_2, by restricted values of $a SiO_2/a H_2O$ (Fig. 4), or possibly by its intrinsic instability. The apparent temperature difference implied in Figure 5 for tephroite *vs.* alleghanyite + rhodonite may be minimized if the dehydration equilibria (1)–(4) are close together or if additional solid solutions shift the curves. The significant solid solutions in Bald Knob minerals of 25–30% F/(F + OH) in humites, 10–30% (Ca + Mg + Fe)/(Ca + Mg + Fe + Mn) in pyroxenoids, and 10–70% (Ca + Mg + Fe)/(Ca + Mg + Fe + Mn) in carbonates (this paper and data in Winter *et al.*, 1981) clearly cannot be disregarded. A complete analysis of phase equilibria at Bald Knob would require the evaluation of these solid solutions after the simple phase diagram (Fig. 4) is calibrated. Nevertheless, it seems clear that water-rich conditions are required for manganese humites, and that local variations in $X(H_2O/X(CO_2)$ and $a(SiO_2)$ will ultimately prove to account for the various assemblages found at Bald Knob.

Acknowledgments

We thank Prof. W. C. Bigelow and his staff of The University of Michigan Microbeam Laboratory for providing the facilities for microprobe analyses. We also thank Prof. W. B. Simmons, Jr. for introducing us to the interesting Bald Knob deposit and for conducting preliminary optical, X-ray and microprobe work on Bald Knob minerals. We are grateful for the helpful reviews provided by P. J. Dunn, C. A. Francis and P. H. Ribbe.

References

Bourne, J. H. (1974) The petrogenesis of the humite group minerals in regionally metamorphosed marbles of the Grenville supergroup. Ph.D. thesis, Queen's University.

Chopin, C. (1978) Les paragenèses reduites ou oxydées de concentrations manganesifères des schistes lustrés de Haute-Maurienne (Alpes françaises). Bulletin de Minéralogie, 101, 514–531.

Cook, D. (1969) Sonolite, alleghanyite and leucophoenicite from New Jersey. American Mineralogist, 54, 1392–1398.

Dal Piaz, G. V., Battistini, G. di, Kienast, J. R., Venturelli, G. (1979) Manganiferous quartzitic schists of the piemonte ophiolite nappe. Memorie degli Instituti di Geologia e Mineralogia dell'Universita di Padova, 32, 1–24.

Dana, E. S. (1892) The System of Mineralogy, 6th Ed. John Wiley and Sons, New York.

Deer, W. A., Howie, R. A., and Zussman, J. (1962) Rock-forming Minerals. Volume 1. Ortho- and ring-silicates. Longmans, Green and Company, Limited, London.

Duffy, C. J. (1977) Phase equilibria in the system MgO–MgF_2–SiO_2–H_2O. Ph.D. thesis, University of British Columbia.

Duffy, C. J., and Greenwood, H. J. (1979) Phase equilibria in the system MgO–MgF_2–SiO_2–H_2O. American Mineralogist, 64, 1156–1174.

Dunn, P. J., Peacor, D. R., Simmons, W. B., Jr. and Essene, E. J. (1984) Jerrygibbsite, a new polymorph of sonolite and member of the humite–leucophoenicite groups, from Franklin, New Jersey. American Mineralogist, in press.

Essene, E. J. and Peacor, D. R. (1983) Crystal chemistry and petrology of coexisting galaxite and jacobsite from near Bald Knob, N. C. American Mineralogist, 68, 449–455.

Francis, C. A. and Ribbe, P. H. (1978) Crystal structures of the humite minerals: V. Magnesian manganhumite. American Mineralogist, 63, 874–877.

Francis, C. A. (1980) Magnesium–manganese solid solution in the olivine and humite groups. Ph.D. thesis, Virginia Polytechnic Institute and State University, Blacksburg, Virginia.

Fukuoka, M. (1981) Mineralogical and genetical study on alabandite from the manganese deposits of Japan. Memoirs of the Faculty of Science, Kyushu University, Series D, Geology, 24, 207–251.

Hinthorne, J. R. and Ribbe, P. H. (1974) Determination of boron in chondrodite by ion microprobe mass analysis. American Mineralogist, 59, 1123–1126.

Hintze, C. (1915) Handbuch der Mineralogie. I(2). Leipzig, Verlag Von Veit.

Hurlbut, C. S, Jr. (1961) Tephroite from Franklin, New Jersey. American Mineralogist, 46, 549–559.

Jones, N. W., Ribbe, P. H. and Gibbs, G. V. (1969) Crystal chemistry of the humite minerals. American Mineralogist, 54, 391–411.

Lee, D. E. (1955) Mineralogy of some Japanese manganese ores. Stanford University Publications, Geological Sciences, 5, 1–64.

Momoi, H. (1980) Notes on hydrothermal syntheses of alleghanyite group. Mineralogical Society of Japan Bulletin, 14, 179–187.

Moore, P. B. (1970) Edge-sharing silicate tetrahedra in the crystal structure of leucophoenicite. American Mineralogist, 55, 1146–1166.

Moore, P. B. (1978) Manganhumite, a new species. Mineralogical Magazine, 42, 133–136.

Mossman, D. J. and Pawson, D. J. (1976) X-ray and optical characterization of the forsterite–fayalite–tephroite series with comments on knebelite from Bluebell mine, British Columbia. Canadian Mineralogist, 14, 479–486.

Nambu, M., Tanida, K., and Kitamura, T. (1980) Alleghanyite from Hanawa Mine, Iwate Prefecture. Research Institute of Mineral Dressing and Metallurgy, Tohobu University, 36, 43–54.

Palache, C., Berman, H. and Frondel, C. (1944) The System of Mineralogy. Volume I. John Wiley and Sons, Inc., New York.

Palache, C. (1937) The minerals of Franklin and Sterling Hill, Sussex, New Jersey. United States Geological Survey Professional Paper 180.

Peacor, D. R., Essene, E. J., Simmons, W. B. Jr., and Bigelow, W. C. (1974) Kellyite, a new Mn–Al member of the serpentine group from Bald Knob, North Carolina and new data on grovesite. American Mineralogist, 59, 1153–1156.

Peters, Tj., Valarelli, J. V., Coutinho, J. M. V., Sommerauer, J. and von Raumer, J. (1977) The manganese deposits of Buritirama (Para, Brazil). Schweizerische Mineralogische und Petrographische Mitteilungen, 57, 313–327.

Rentzeperis, P. J. (1970) The crystal structure of alleghanyite, $Mn_5(OH)_2/(SiO_4)_2$. Zeitschrift für Kristallographie, 132, 1–18.

Ribbe, P. H. (1980) The humite series and Mn–analogs. In Paul H. Ribbe, Ed., Reviews in Mineralogy, Volume 5, Orthosilicates, p. 231–274. Mineralogical Society of America, Washington, D. C.

Rogers, A. F. (1935) The chemical formula and crystal system of alleghanyite. American Mineralogist, 20, 25–35.

Ross, C. S. and Kerr, P. F. (1932) The manganese minerals of a vein near Bald Knob, North Carolina. American Mineralogist, 17, 1–18.

Simmons, W. B. Jr., Peacor, D. R., Essene, E. J. and Winter, G. A. (1981) Manganese minerals of Bald Knob, North Carolina. Mineralogical Record, 12, 167–171.

Smith, W. C., Bannister, F. A., and Hey, M. H. (1944) Banalsite, a new barium-felspar from Wales. Mineralogical Magazine, 27, 33–46.

Tilley, C. E. (1951) The zoned contact–skarns of the Broadford area, Skye: a study of boron–fluorine metasomatism in dolomites. Mineralogical Magazine, 29, 621–666.

White, T. J. and Hyde, B. G. (1982) Electron microscope studies of humite (chondrodite) series of minerals. II. Natural manganese-rich specimens. Physics and Chemistry of Minerals, 8, 167–174.

White, T. J. and Hyde, B. G. (1983) A description of the leucophoenicite family of structures and its relation to the humite family. Acta Crystallographica, in press.

Winter, G. A., Essene, E. J. and Peacor, D. R. (1981) Carbonates and pyroxenoids from the manganese deposit near Bald Knob, North Carolina. American Mineralogist, 66, 278–289.

Yoshinaga, M. (1963) Sonolite, a new manganese mineral. Memoir of the Faculty of Sciences, Kyushu University, Series D, Geology, 14, 1–21.

Manuscript received, August 23, 1982;
accepted for publication, March 18, 1983.