

ZINCIAN AND MANGANOAN AMPHIBOLES
FROM FRANKLIN, NEW JERSEY¹

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ABSTRACT

Zincian and manganoan amphiboles occur locally as coarse-grained, irregular masses in the skarn zones of the Franklin orebody. These amphiboles are associated mainly with calcite, rhodochrosite, rhodonite, tephroite, andradite, willemite and franklinite. Chemical analyses, optical and X-ray parameters, and assemblage descriptions are given for three cummingtonites, nine members of the tremolite-actinolite series and one magnesioriebeckite. The cummingtonites show maximum ZnO and MnO contents of 10.8 and 13.79 weight percent respectively (1.22 and 1.83 atoms/half unit cell); members of the tremolite-actinolite series contain smaller amounts of ZnO and MnO, the maxima being 9.54 and 5.42 weight percent respectively (1.04 and 0.67 atoms/half unit cell); a magnesioriebeckite contains 7.84 weight percent ZnO and 4.16 weight percent MnO (0.86 and 0.81 atoms/half unit cell).

INTRODUCTION

In his study of Franklin minerals, Palache (1937) reported the analysis and optical parameters of a zinc-rich cummingtonite (see Table 1, no. 89365), but no other zinc-rich amphiboles are described in the literature. Manganoan amphiboles are much more common in nature and have been studied by various authors (Sundius, 1931; Yosimura, 1939; Bilgrami, 1955; Jaffe *et al.*, 1961; Segeler, 1961; Matkovskiy, 1962; and Klein, 1964 and 1966).

The amphiboles of this study are of interest because of the large and variable amounts of Zn and Mn²⁺ that are present in their structure. These amphiboles which include members of the cummingtonite-grunerite series, of the tremolite-actinolite series and one magnesioriebeckite, occur in the skarn zones of the orebodies at Franklin. They are part of Zn- and Mn-rich assemblages which consist of rhodonite, tephroite, franklinite, willemite, calcite, rhodochrosite and other minerals. The specific assemblage for each amphibole is given at the bottom of the chemical analytical tables (Tables 1, 3 and 5).

CHEMICAL ANALYSIS, OPTICAL, X-RAY AND SPECIFIC GRAVITY DETERMINATIONS

Four of the amphiboles, cummingtonite no. 90384, actinolites no. 2 and 3, and magnesioriebeckite no. 89407 were analyzed by Jun Ito using a combination of wet chemical

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TABLE 1. CHEMICAL ANALYSES OF CUMMINGTONITE

	90384	90391 ^a	89365
SiO ₂	53.6	51.5	49.74
Al ₂ O ₃	.51	0	1.72
Fe ₂ O ₃	.35	—	—
FeO	3.50	12.9	12.80
MnO	12.9	13.2	13.79
ZnO	6.95	10.8	10.46
MgO	16.9	11.1	8.31
CaO	1.66	.1	.49
Na ₂ O	.75	.1	.22
K ₂ O	.17	n.d.	n.d.
H ₂ O(+)	2.35	n.d.	} 2.16
H ₂ O(-)	.18	n.d.	
F	n.d. ^b	n.d.	n.d.
Total	99.82	99.7	99.69

	Number of ions on the basis of		
	24 (O,OH)	23 oxygens	24 (O,OH)
Si	7.87	7.92	7.82
Al	.09	—	.18
Al	—	—	.12
Fe ³⁺	.07	—	—
Fe ²⁺	.42	1.65	1.68
Mn	1.60	1.72	1.83
Zn	.75	1.22	1.21
Mg	3.70	2.54	1.95
Ca	.26	.02	.08
Na	.21	.04	.06
K	.02	—	—
OH	2.30	—	2.25
100 Mg/(Mg+Fe)	88.2	60.6	53.6
100Mg/(Mg+Fe+Mn+Zn)	56.5	35.6	29.2
100Mn/(Mg+Fe+Mn)	27.6	29.1	33.6
100Zn/(Mg+Fe+Zn)	15.2	22.5	25.0

Assemblage 90384: cummingtonite (light green, very coarse masses) -franklinite-calcite-tephroite-willemite (along cleavage planes in tephroite)-hendricksite. Cummingtonite analysis by J. Ito.

Assemblage 90391: large, anhedral, single crystal of willemite (6"×4"×2") with very fine grained, fibrous intergrowth of cummingtonite; trace of franklinite.

Assemblage 89365: cummingtonite (large masses)-rhodonite-schallerite-willemite-serpentine-hendricksite (trace). Specimen shows evidence of strong shearing and brecciation. Cummingtonite analysis by Bauer (Palache, 1937).

^a Electron probe analysis.^b n.d. = not determined.

and spectrophotometric techniques. Essentially monomineralic samples of these four amphiboles were crushed to between 50 and 120 mesh, and were subsequently purified by hand under a binocular microscope at $\times 30$ magnification. The grains were carefully scanned and those which showed inclusions or other adhering phases were removed with a needle. The resulting samples that were submitted for chemical analysis were estimated to have been 99.8 percent pure or better. Optical, X-ray and specific gravity measurements were made on a separate part of the analyzed sample.

All other analyses were made by C. Klein using an ARL-EMX (Applied Research Laboratories) electron microprobe. Handpicked grains were analyzed in carbon-coated polished sections, except for cummingtonite no. 90391 which was analyzed in polished thin-section. The analysis conditions were: 20 kilovolts accelerating potential, 0.03 microampere sample current, 3- to 5-micron beam size and ten seconds counting time. The four chemically analyzed amphiboles of this study and ten other chemically analyzed amphiboles were used for the construction of standard curves (see Klein 1968, for reference to standard samples and standard curves). Approximately ten data points were taken on each standard and each unknown, each data point was repeated once, and the count values were averaged. No chemical zonation or exsolution was detected in the samples. The *maximum* relative error in the weight percent values for SiO_2 , Al_2O_3 , FeO , CaO and MnO is estimated to be approximately ± 2 to 3 percent of the amount present. The *maximum* relative error in the MgO , Na_2O and ZnO values is probably ± 5 percent of the amount present.

X-ray diffractometer charts were obtained for all samples with filtered $\text{FeK}\alpha$ radiation (1.93728 Å) using high-purity silicon as an internal standard. The mixture was mounted as a very thin coating, approximately 1/10 mm thick, on a glass slide using a solution of collodion and isopentyl acetate as a binder. Two recordings were made, one in ascending and one in descending mode, with goniometer and chart speeds of $1/4^\circ$ per minute and $1/2$ inch per minute respectively. The peak positions were measured directly on the graph paper to $0.01^\circ 2\theta$ and were located with respect to the silicon peak positions. Whenever differences in peak positions were observed in the ascending and descending modes, the average of the two values was taken as the final 2θ value. The diffraction peaks were indexed by comparison with indexed patterns in the literature (Comeforo and Kohn, 1954; Ernst, 1960; and Klein and Waldbaum, 1967). Approximately fourteen unambiguously indexed diffraction lines were used in a least-squares refinement program (Burnham, 1962) for the calculation of the unit-cell parameters. The indexing and unit-cell parameter calculations were done on the basis of a $C2/m$ space group. Dr. Malcolm Ross of the U. S. Geological Survey, Washington, D. C. kindly verified the $C2/m$ symmetry for three of the samples (cummingtonite no. 89365, actinolite no. 2 and magnesioriebeckite no. 89407) with $(h0l)$ and $(0kl)$ precession photographs. The refined unit-cell parameters were used in calculating the density values.

Indices of refraction and extinction angles were determined by means of a spindle stage (Wilcox, 1959) using a sodium light source. The refractive indices are estimated to be accurate to ± 0.001 and the extinction angle measurements to $\pm 1^\circ$. Axial angles were calculated from the expression:

$$\tan^2 V_\gamma = \left(\frac{1}{\alpha^2} - \frac{1}{\beta^2} \right) / \left(\frac{1}{\beta^2} - \frac{1}{\gamma^2} \right).$$

Specific gravity determinations were made with the Berman Microbalance using 20 to 25 mg samples of minus 50- to 100-mesh grain size.

CUMMINGTONITE

The zincian and manganoan cummingtonites at Franklin are light to medium green in color and occur in irregular masses in the skarn zones.

Their green color is very similar to that of members of the tremolite-actinolite series and the manganoan cummingtonites described by Klein (1964).

The chemical analyses for three cummingtonites, arranged in decreasing Mg-content, are given in Table 1. The complete analyses for samples no. 90384 and no. 89365 are recalculated on the basis of 24 (O, OH), and the electron probe analysis for sample no. 90391 is recalculated on the basis of 23 oxygens because the H₂O content was not determined. A recalculation on the basis of 23 oxygens is possible because the Fe₂O₃ component in the cummingtonite-grunerite series is very small or non-existent. Although the Mg, Fe²⁺ and Zn contents vary considerably, the Mn content is similar in all three samples, and ranges from 1.60 to 1.83 Mn atoms/half unit cell. The Zn content is highest (10.8 weight percent ZnO) in sample no. 90391, in which the cummingtonite occurs in very intimate intergrowth with willemite, but willemite is present also in the other assemblages (for assemblage descriptions see the bottom of Table 1). The cummingtonite in sample 90391 occurs as numerous, very fine, slender needles within a large single-crystal of willemite. The *c*-crystallographic axis of the needles is parallel to the *c* axis of the enclosing willemite. Figure 1 illustrates this occurrence.

The relatively large Mn²⁺ ion (0.80 Å in sixfold coordination, Ahrens, 1952) probably substitutes mainly in the M(4) position in the amphiboles (corresponding to X in the general formula X₂Y₅Z₃O₂₂(OH)₂; for notation see Ghose, 1962). An approximate limit of 2 Mn²⁺ ions out of seven cations per formula was suggested by Klein (1964). The Zn-content in the cummingtonites varies from 0.75 to 1.22 Zn²⁺ ions/half unit cell. As the ionic size of Zn (0.74 Å) is the same as that of Fe²⁺ (0.74 Å) and fairly similar to that of Mg (0.66 Å), Zn is probably housed mainly in the M(1), M(2) and M(3) cation sites.

The unit-cell parameters (given in Table 2) of these cummingtonites are very similar to those of the manganoan, zinc-free cummingtonites given in Klein (1964). The *b* dimension of cummingtonite no. 90384 is considerably smaller than that of the more Fe-rich cummingtonite no. 89365.

The specific gravity of cummingtonite no. 90384 is similar to that of zinc-free manganoan cummingtonites (Klein, 1964), whereas that of cummingtonite no. 89365 is considerably higher and more in the range of that of Fe-Mg grunerites.

The optical properties, given in Table 2, are similar to those of zinc-free members of the cummingtonite-grunerite series. All three samples show multiple twinning parallel to (100).

Because of the similarity in the physical properties of these amphiboles with those of zinc-free members of the cummingtonite-grunerite series

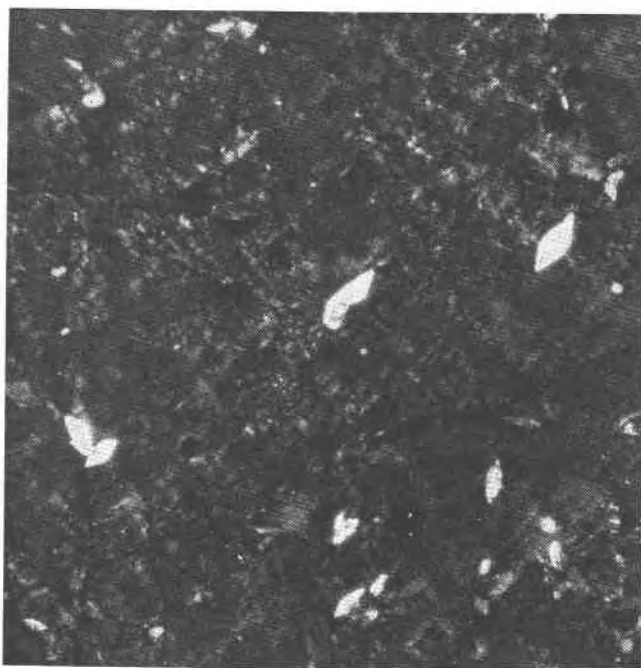


FIG. 1. Willemite-cummingtonite intergrowth (assemblage no. 90391) in thin section cut perpendicular to the willemite c axis. Cross polarized light. The willemite is dark (in extinction), the cummingtonite light colored. Although the c crystallographic axes of the willemite and cummingtonite are parallel, the a and b axes of the cummingtonite are randomly oriented with respect to the willemite. Magnification 100 \times .

TABLE 2. PHYSICAL PROPERTIES OF CUMMINGTONITE (SPACE GROUP $C2/m$)

	90384	90391	89365
$a, \text{\AA}$	$9.587 \pm .001$	$9.577 \pm .001$	$9.575 \pm .003$
$b, \text{\AA}$	$18.101 \pm .002$	$18.217 \pm .003$	$18.229 \pm .004$
$c, \text{\AA}$	$5.315 \pm .001$	$5.327 \pm .001$	$5.327 \pm .003$
β , deg.	$102.60 \pm .01$	$102.13 \pm .01$	$102.21 \pm .03$
$V (\text{\AA}^3)$	$900.16 \pm .25$	$908.71 \pm .28$	$908.74 \pm .63$
D (calc)	3.25	—	3.44
Sp. Gr. (meas.)	$3.24 \pm .02$	—	$3.44 \pm .02$
γ	1.660	1.682	1.685
β	1.647	1.670	1.674
α	1.634	1.654	1.657
$\gamma - \alpha$.026	.028	.028
$Z \wedge c$	20°	11°	15°
$2V_\gamma$ calc	$90^\circ 41'$	$98^\circ 56'$	$103^\circ 04'$
$2V_\gamma$ meas	—	—	$105^\circ \pm 2^\circ$
Colorless and non-pleochroic.			

and because of their likeness in color to members of the tremolite-actinolite series, the presence of manganese and zinc must be established chemically.

TREMOLITE-ACTINOLITE

Members of the tremolite-actinolite series vary from very light beige, for tremolite no. 4, to medium and dark green for the actinolites. These calcic amphiboles occur sporadically in irregular masses and stringers in the skarn zones of the orebody. Many of the assemblages show evidence of brecciation and shearing. The amphiboles are frequently bent and the associated franklinite and garnet crystals are sheared and broken, with the interstices filled with carbonate (see the bottom of Table 3 for specific associations). The assemblages in which the tremolite and actinolite occur are much more calcic and less zinc-rich than the cumingtonite-bearing samples. Calcite, rhodochrosite and rhodonite are present in large amounts in most of the assemblages, whereas willemite is found only in trace amounts in a few of them.

The analyses of nine members of the tremolite-actinolite series are given in Table 3. The complete, conventional analyses are recalculated on the basis of 24(O,OH) and the electron probe analyses on the basis of 23 oxygens. Although as much as 25 percent of the total Fe content of actinolite may be present as Fe^{3+} (Deer, Howie, and Zussman, 1963) the total iron contents of the analyses in Table 3 are so small (max. 5.4 wt. % FeO) that the error introduced by assuming all the iron to be present as FeO only, is negligible. The manganese and zinc contents are similar in all the analyses except for tremolite no. 4 which has a considerably lower Zn content than the actinolites. Yosimura (1939) described occurrences of manganoan tremolite (7.38 wt. % MnO) and manganoan actinolite (5.79 wt. % MnO) from the manganese deposits of the Kaso Mine in Japan. Zinc, however, was not reported to be present in the analyses.

In the majority of analyses in Table 3 the total number of (Ca+Na+K) atoms/half unit cell is considerably below 2.0 and ranges from 1.69 to 2.05. This apparent deficiency is not due to analytical error but is caused by the assignment of the atoms to the various cation positions in the structural formula. Undoubtedly the majority of the Mn^{2+} and probably some of the Fe^{2+} ions should be assigned to the $M(4)$ position to make the total number of ions 2.0. It should be noted, in this connection, that the total number of cations in the $M(1)$, $M(2)$, $M(3)$ and $M(4)$ positions calculates to close to 7 in all analyses.

The unit-cell parameters, specific gravity and optical data for the tremolite and actinolites are given in Table 4. The unit-cell parameters

TABLE 3. CHEMICAL ANALYSES OF TREMOLITE AND ACTINOLITE

	4 ^a	2	7	9C ^a	5 ^a
SiO ₂	55.7	53.5	54.4	54.2	53.9
Al ₂ O ₃	0	0.67	0.3	0.4	0.4
Fe ₂ O ₃	—	1.52	—	—	—
FeO	0.7	2.23	3.9	4.0	4.0
MnO	4.1	5.42	4.6	4.9	4.0
ZnO	4.3	8.99	8.4	8.5	8.8
MgO	21.2	14.6	15.4	14.6	14.6
CaO	10.7	9.88	9.7	10.7	10.6
Na ₂ O	0.9	0.45	1.4	0.6	1.3
K ₂ O	n.d. ^b	0.10	n.d.	n.d.	n.d.
H ₂ O(+)	n.d.	2.35	n.d.	n.d.	n.d.
H ₂ O(-)	n.d.	—	n.d.	n.d.	n.d.
F	n.d.	n.d.	n.d.	n.d.	n.d.
Total	97.6	99.71	98.1	97.9	97.6

	Number of ions on the basis of				
	23 oxygens	24 (O,OH)	23 oxygens	23 oxygens	23 oxygens
Si	7.88	7.86	7.96	7.97	7.95
Al	—	.11	.04	.03	.05
Al	—	—	—	.02	—
Fe ²⁺	—	.16	—	—	—
Fe ³⁺	.08	.27	.47	—	—
Mn	.48	.67	.56	.49	.49
Zn	.44	.97	.91	.61	.50
Mg	4.48	3.20	3.36	3.20	3.21
Ca	1.62	1.55	1.51	1.68	1.68
Na	.24	.12	.39	—	.37
K	—	.02	—	.18	—
OH	—	2.30	—	—	—

100Mg/(Mg+Fe)	98.3	88.1	87.6	86.8	86.8
100Mg/(Mg+Fe+Mn+Zn)	81.7	60.6	63.4	61.3	62.3
100Mn/(Mg+Fe+Zn)	9.6	15.6	12.8	14.2	11.8
100Zn/(Mg+Fe+Zn)	8.9	21.1	19.1	19.9	20.5

Assemblage no. 4: tremolite (light beige)-calcite-rhodochrosite band in host rock of franklinite and calcite. The tremolite is separated from the franklinite by the carbonates.

Assemblage no. 2: actinolite (green, very coarse grained)-calcite minor sphalerite and a trace of willemite. Actinolite analysis by J. Ito.

Assemblage no. 7: actinolite-calcite-quartz-rhodonite and a trace of sphalerite.

Assemblage no. 9C: actinolite-rhodochrosite-calcite-franklinite-manganooxide-andradite-quartz-microcline. The specimen shows evidence of brecciation.

Assemblage no. 5: actinolite-calcite-manganooxide-andradite. This specimen shows evidence of severe shearing and brecciation.

TABLE 3 (cont'd). Chemical Analyses of Tremolite and Actinolite

	8 ^a	1 ^a	6 ^a	3
SiO ₂	53.8	54.4	53.3	52.8
Al ₂ O ₃	0.5	0.4	1.6	0.90
Fe ₂ O ₃	—	—	—	2.92
FeO	4.2	4.3	5.4	3.56
MnO	4.7	4.3	4.6	4.24
ZnO	8.9	8.1	8.5	9.54
MgO	14.5	14.7	13.7	12.5
CaO	10.6	10.7	10.7	9.03
Na ₂ O	0.7	0.6	0.9	1.80
K ₂ O	n.d.	n.d.	n.d.	.30
H ₂ O(+)	n.d.	n.d.	n.d.	2.56
H ₂ O(-)	n.d.	n.d.	n.d.	n.d.
F	n.d.	n.d.	n.d.	n.d.
Total	97.9	97.5	98.7	100.15
	23 oxygens	Number of ions on the basis of: 23 oxygens 23 oxygens		24 (O,OH)
Si	7.93 } 8.00	8.00 } 8.00	7.83 } 8.00	7.79 } 7.93
Al	.07	—	.17	.14
Al	—	.05	.09	—
Fe ³⁺	—	—	—	.32
Fe ²⁺	.51	.52	.66	.43
	5.26	5.19	5.23	5.06
Mn	.58	.53	.56	.52
Zn	.97	.87	.92	1.04
Mg	3.20	3.22	3.00	2.75
Ca	1.67	1.68	1.68	1.43
Na	.19	.18	.25	.51
K	—	—	—	.05
OH	—	—	—	2.52
100Mg/(Mg+Fe)	86.1	86.0	81.9	78.5
100Mg/(Mg+Fe+Mn+Zn)	60.7	62.5	58.3	54.3
100Mn/(Mg+Fe+Mn)	13.6	12.4	13.4	13.0
100Zn/(Mg+Fe+Zn)	20.7	19.0	20.0	22.8

Assemblage no. 3: actinolite-serpentine-rhodonite-calcite-rhodochrosite.

Assemblage no. 1: actinolite-rhodonite-calcite, with traces of willemite and franklinite.

Assemblage no. 6: actinolite-franklinite-calcite-rhodonite and traces of willemite. The franklinite is highly brecciated.

Assemblage no. 3: actinolite-franklinite-calcite-manganooan andradite. Highly deformed and brecciated minerals. The actinolite analysis is by J. Ito.

^a electron probe analysis.

n.d.* = not determined.

TABLE 5. CHEMICAL ANALYSIS AND PHYSICAL PROPERTIES OF
MAGNESIORIEBECKITE No. 89407

wt %		Number of ions on basis of 24(O,OH)	
SiO ₂	53.0	Si	7.86
Al ₂ O ₃	.58	Al	.09
Fe ₂ O ₃	9.64	Al	—
FeO	3.18	Fe ³⁺	1.07
MnO	4.16	Fe ²⁺	.39
ZnO	7.84	Mn	.51
MgO	11.0	Zn	.86
CaO	2.63	Mg	2.43
Na ₂ O	5.30	Ca	.42
K ₂ O	.28	Na	1.51
			1.97
H ₂ O(+)	2.32	K	.04
H ₂ O(-)	.11	OH	2.28
F	n.d.*		
Total	100.04	100Mg/(Mg+Fe)	=62.5
		100Mg/(Mg+Fe+Mn+Zn)	=46.2
		100Mn/(Mg+Fe+Mn)	=11.7
		100Zn/(Mg+Fe+Zn)	=18.0
<i>a</i> , Å	9.760 ± .004	γ	1.670
<i>b</i> , Å	18.031 ± .012	β	1.669
<i>c</i> , Å	5.306 ± .004	α	1.666
β, deg	103.79 ± .05	γ-α	.004
<i>V</i> (Å ³)	906.85 ± .67	Z∧ <i>c</i>	40°
		2 <i>V</i> _γ calc.	101°37'
D (calc)	3.25	Z	dark green
Sp. Gr. (meas)	3.26 ± .02	Y	medium green
		X	brownish green

Assemblage: magnesioriebeckite (coarse-grained, dark green)-rhodonite-franklinite-calcite-serpentine.

are very similar for all samples, but the optical indices show a definite rise with increasing Fe-content.

MAGNESIORIEBECKITE

The chemical analysis and physical properties for magnesioriebeckite no. 89407 are given in Table 5. This sodium amphibole is very dark green, almost black, and occurs as coarsely crystalline masses closely intergrown with rhodonite, calcite and franklinite.

The MnO content (4.16 weight percent) of this magnesioriebeckite is less than that of the magnesioriebeckite (5.9 weight percent) coexisting

with a manganoan cummingtonite, reported by Klein (1966). The ZnO content of 7.84 weight percent is somewhat smaller than that found in the actinolites of Table 3. As in the actinolites, some of the Mn may well be present in the $M(4)$ position and the Zn probably substitutes for the Fe^{2+} and Mg in the $M(1)$, $M(2)$ and $M(3)$ sites.

The unit-cell parameters of this magnesioriebeckite are very similar to those reported by Borg (1967) for end-member magnesioriebeckite ($\text{Na}_2\text{Mg}_3\text{Fe}_2^{3+}\text{Si}_8\text{O}_{22}(\text{OH})_2$). The γ and β refractive indices are also similar to that of the end-member composition but the α index of the manganoan and zincian variety is higher than that for the pure Fe-Mg end-member. As in the case of the other zincian-manganoan amphiboles the assemblage makes one suspect a certain amount of Zn and Mn substitution in the amphibole; the physical properties, however, do not provide conclusive evidence.

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