HENDRICKSITE, A NEW SPECIES OF MICA

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Abstract

Hendricksite is a new species of trioctahedral mica, representing the Zn member of the group. It occurs abundantly at Franklin, N. J., where it has earlier been called biotite or manganophyllite, as rough crystals and anhedral plates up to a foot in size.

Two complete and seven partial analyses are given. The studied material represents a solid solution extending from slightly zincian and manganoan varieties of phlogopite up to material in which the octahedral positions are occupied by Zn 50 and Mn 40 in atomic per cent with the balance Mg, Fe^{2+} and Fe^{3+}. Ba is generally present in the interlayer positions to the extent of 0.6 to 1.6 weight per cent BaO. Synthetic micas of the end-compositions $KZn_3(Si_3Al)O_{10}(OH)_2$ and $KMn_3(Si_3Al)O_{10}(OH)_2$ were prepared by the hydrothermal crystallization of stoichiometric gels at 350° and 2000 bars to 650° and 3000 bars.

Hendricksite varies in color from coppery red to reddish black. The indices of refraction and the specific gravity are very high for a mica, with γ up to 1.697 and specific gravity to 3.4. The interplanar spacings also are relatively large as compared to those of biotite. The gamma refractive index and d (060) decrease in a roughly linear manner with decreasing content of Zn or (Zn+Mn) in the octahedral positions. The intensity ratio, I(004)/I(005), decreases with increasing content of Mg.

Most of the material represents the 1M polytype. A few examples of the $2M_1$ and 3T polytypes and of unidentified polytypes and interstratifications, in part random, were recognized. The optic plane usually has the normal position parallel (010) in the 1M polytypes, but in a few instances it is perpendicular (010). In the $2M_1$ polytypes the orientation also is abnormal, parallel (010).

Hendricksite occurs in the skarn zones at Franklin associated chiefly with andradite, rhodonite, bustamite, barium feldspars, axinite, vesuvianite, hancockite, hardystonite, members of the aegirine-augite to augite series, members of the diopside-hedenbergite-johannsenite series, and cummingtonite. Most of the skarn silicates contain both Zn and Mn in solid solution and the crystallochemical distribution of these elements is described.

The name hendricksite is proposed in honor of Dr. Sterling B. Hendricks, American crystallographer and chemist, who with M. E. Jefferson in 1938 first recognized and described polymorphism in the micas. With regard to nomenclature, it is suggested that all trioctahedral micas in which more than two-thirds of the occupied octahedral positions are Mg be called phlogopite. When the Mg content falls below this limit, the nomenclature is to be determined by the divalent cation other than Mg that is dominant in atomic per cent.

Introduction

The so-called skarn zones found locally in the orebody at Franklin, New Jersey, were characterized by the development of large amounts of rhodonite, andradite, and a dark coppery brown to bronzy black mica that looks like biotite. The mica has not been analyzed hitherto, but tests reported by Chester (1894) and by Palache (1937) indicated that it contained a considerable amount of manganese. It has been generally re-

ferred to in the literature and by collectors of Franklin minerals as manganophyllite, in the sense of a manganoan variety of biotite or phlogopite, or as biotite. A semi-quantitative examination by x-ray fluorescence of numerous specimens, selected from the Harvard collection on the basis of variation in color and in indices of refraction, revealed that they contain variable and often quite large amounts not only of manganese but also of zinc. This material is described beyond.

CHEMICAL COMPOSITION

Of the nine specimens which by preliminary examination showed a large range in composition, two were analyzed completely and seven for the chief trioctrahedral cations only (Table 1). Zn was found to range up to 22.97 weight per cent ZnO, and in six specimens was the dominant divalent cation. The number of ions calculated on the basis of 12 (O, OH, F) are listed in Table 2, together with measurements of the gamma index of refraction, the specific gravity and the d-spacings of certain planes.

The analyzed material represents a solid solution extending from phlogopite of essentially the end-composition to material containing Zn and Mn as the dominant trioctahedral cations. The bulk of the mica in the skarn zones at Franklin falls in the range of analyses 1 to 4, as indi-

TABLE 1. CHEMICAL ANALYSES OF HENDRICKSITE

	1	2	3	4	5	6	7	8	9
SiO_2			31.58	31.68					
Al_2O_3			13.72	12.48					
TiO_2			0.32	0.12					
Fe_2O_3			2.25	4.85	4.8				
FeO	0.3	0.3	0.34	0.69	1.2	0.2	3.7	5.10	1.27
ZnO	21.6	22.1	22.97	21.40	23.2	16.8	12.2	12.0	0.27
MnO	15.3	13.6	12.28	13.38	11.9	11.0	4.8	5.3	0.02
MgO	1.8	3.3	3.69	1.76	3.5	6.7	13.4	13.6	27.3
BaO		1.4	0.65	0.91		1.3	1.5		
Na_2O			0.24	0.23					
K_2O			7.91	8.37					
H_2O+			3.65	3.45					
H_2O-			—	—					
F			0.45	0.10					
Total			99.76	99.88					
$F=0$			0.19	0.04					
Total			99.57	99.84					

Analyses by Jun Ito, 1965.

TABLE 2. COMPOSITION AND PROPERTIES OF HENDRICKSITE

	1	2	3	4	5	6	7	8	9
Si			2.664	2.727					
Al			1.336	1.266					
			4.000	3.993					
Al			.019	—					
Ti⁴⁺			.041	.008					
Fe^{3+}	n.d.	n.d.	.143	.314	.30	n.d.	n.d.	n.d.	n.d.
Fe^{2+}	.03	.02	.024	.050	.08	.02	.25	.34	.08
Mg	.25	.45	.464	.226	.42	.94	1.66	1.60	2.91
Mn	1.22	1.05	.878	1.012	.81	.88	.34	.36	.001
Zn	1.50	1.48	1.431	1.360	1.39	1.17	.75	.70	.01
	3.00	3.00	3.000	2.970	3.00	3.00	3.00	3.00	3.00
K			.852	.920					
Na			.040	.038					
Ba			.021	.031					
			.913	.989					
O			10	10					
OH			1.98	1.99					
F			.02	.01					
Zn/Mn	1.23	1.41	1.63	1.34	1.72	1.33	2.20	1.94	
n(Na)	1.697	1.692	1.686	1.686	1.682	1.674	1.644	1.625	1.583
d(060)	1.5564	1.5546	1.5540	1.554	1.5554	1.5502	1.5428	1.537	1.530
d(004)	2.544	2.542	2.541	2.546		2.536	2.519	2.504	2.488
d(005)	2.036	2.034	2.033	2.034	2.036	2.030	2.015	2.006	1.989
I(004)/I(005)	4.3	4.3	3.7	4.0	6.2	2.8	1.3	1.2	.36
d(200)	2.651	2.648	2.640	2.652	2.651	2.638	2.627	2.623	2.602
S.G.		3.41	3.43	3.40		3.28	3.14	3.17	2.86
Polytype	2M	1M	2M	1M	1M	3T	1M	1M	1M

cated by the optical properties, and contains from 45 to 50 atomic per cent Zn in the octahedral positions. The remaining octahedral positions are mostly occupied by Mn^{2+}, with the balance Mg, Fe^{2+}, and Fe^{3+}. In all samples Zn predominates over Mn, with the Zn/Mn atomic ratio varing from 1.23 to 2.2. The range of composition is shown graphically in Fig. 1. The arbitrary calculation of these partial analyses to a total of three cations involves a small error. The partial analyses reported are for the divalent trioctahedral cations only, and do not include Fe^{3+} (with one exception) or octahedrally coordinated Al. The possibility that the octahedral positions are not wholly occupied, as is often the case in trioctahedral micas, also is excluded.

The amount of Fe^{3+} present is comparable to that commonly found in biotite and phlogopite. Ba is present, however, in relatively large amounts in the interlayer psitions. Muscovite containing 9.89 per cent BaO has been already described from Franklin (Bauer and Berman, 1933). Both it and hendricksite occur in association with barium feldspar.

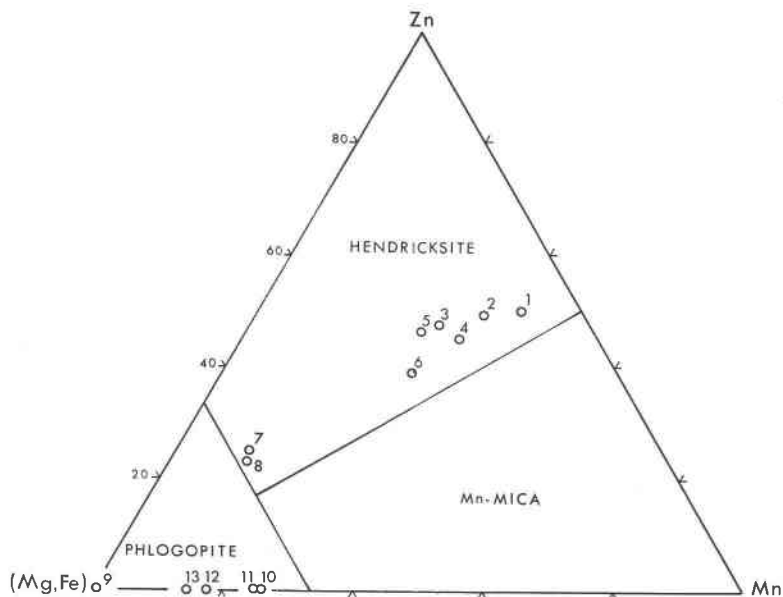The high content of Zn and of Mn place this material in a new field

FIG. 1. Composition of hendricksite and of manganoan phlogopite (manganophyllite). Numbers 1–9 correspond to analyses 1–9 in Tables 1 and 2. 10. Kaso mine, Japan. Recalculated from mixture. Yoshimura (1939). 11. Harstig mine, Sweden. Mn^3 in part assigned to (Si, Al). Jakob (1925). 12. Langban, Sweden. Mn^3 in part assigned to (Si, Al). Jakob (1925). 13. Chikla, Bhandara district, India. Bilgrami (1956).

of composition for the micas in general. The largest amount of Zn hitherto reported in any mica is 1.84 per cent, in the barian muscovite mentioned above. A ferroan lepidolite (cryophyllite) from pegmatite contains about 0.4 per cent ZnO (Foster and Evans, 1962). The most closely related zinc mineral is sauconite, the Zn analogue of saponite in the montmorillonite group (Ross, 1946). Trioctahedral micas containing considerable amounts of Mn^{2+} are already known and have been termed manganophyllite. The reported analyses, excluding the the apparently erroneous original analysis of Igelstrom (1872), are of manganoan phlogopite and range up to a maximum of approximately 26 atomic per cent Mn^{2+} in the octahedral position (Fig. 1). The mica described here contains much more Mn^{2+} than this (with 40 atomic per cent Mn^{2+} in the material of analysis 1) but as noted, Zn always is in excess of Mn. A search was made for Franklin specimens with Mn > Zn but without success.

NOMENCLATURE

The natural trioctahedral micas hitherto known compose a chemical system in which the dominant divalent ions in the octahedral layer are
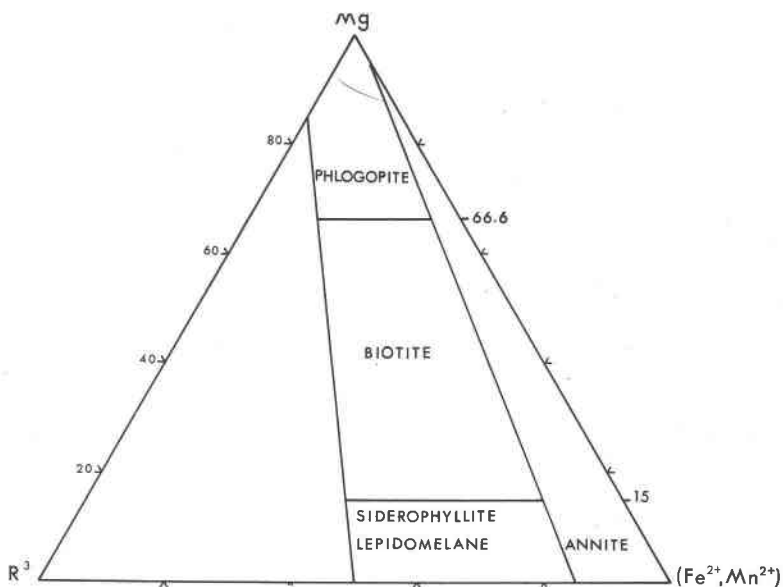
FIG. 2. Nomenclature of the (Mg, Fe³⁺, Fe³⁺, Al) trioctahedral micas, modified from Foster (1960).

either Mg or Fe^{2+}. The observed range of composition and the nomenclature is indicated in Fig. 2, derived from a critical survey of the reported analyses by Foster (1960). The nomenclature is based primarily on the ratio of Mg to divalent Fe. The boundary between phlogopite and biotite is placed at 66.6 atomic per cent Mg, following the suggestion originally of Heinrich *et al.* (1953). The boundary between biotite and the high-iron micas siderophyllite and lepidomelane is placed at 15 atomic per cent Mg, as given by Foster (1960). The names siderophyllite and lepidomelane as redefined by Foster apply to compositions with less than 15 atomic per cent Mg and in which the dominant trivalent cation in the octahedral layer is Al or Fe^{3+}, respectively. No natural material has been found in this region that contains little or no (Al, Fe^{3+}); the name annite, in the sense of Winchell (1925), would be appropriate for it.

No general rules have been proposed to guide the nomenclature of trioctahedral micas containing ions other than Mg or Fe as major constituents. It is suggested that all trioctahedral micas in which more than 66.6 atomic per cent of the occupied 6-coordinated positions are Mg be called phlogopite. When the Mg content falls below this limit, the nomenclature is to be determined by the divalent cation, other than Mg, that is dominant in atomic per cent. The region of composition in which Mg is dominant but below the 66.6 per cent limit could be indicated, if

desired, either by the symbol Mg before the name in question, such as Mg biotite, as used by Foster (1960) for this situation, or preferably by the adjectival modifier magnesian. Compositions with a relatively large content of trivalent ions in the octahedral layer can be designated ferrian or aluminian. The name hendricksite is proposed for the region of composition in which Zn is the dominant trioctahedral cation, as here defined, including the end-composition. The name is given in honor of Dr. Sterling B. Hendricks (1902–   ), American crystallographer and chemist, who with M. E. Jefferson first recognized polymorphism in the micas. It has the approval of the Commission on New Mineral Names of the International Mineralogical Association.

Trioctahedral micas containing significant amounts of Mn^{2+} are already known but in no instance do the rules suggested above permit the definition of a new species of Mn mica. In the present material, although the content of Mg is quite low, Zn dominates over Mn. It is suggested that the term manganophyllite be restricted to a variety of phlogopite or, better, be discarded in favor of the modifier manganoan.

Physical Properties

The color of hendricksite varies from coppery brown and bronze brown to dark reddish brown and reddish black. Toward the phlogopite end of the series, with diminished content of Mn and Zn, the color becomes lighter and passes into brown and yellowish brown. Fresh hendricksite gives the impression on direct comparison with ordinary biotite and phlogopite, and especially with muscovite, of being somewhat more plastic and less elastic than these micas.

Many specimens of hendricksite show the familiar rulings on basal cleavage surfaces that are associated with mechanical deformation. In some specimens the fractures inclined to (001) are so well developed that the crystals can be separated into small polyhedral fragments. The inclined surfaces often are smooth and permit measurement by optical goniometry; the planes ($\bar{1}04$), ($\bar{2}05$) and (135) (in Dana's orientation and unit) were identified on crystals oriented by Laue photographs. These and other inclined fracture planes were first described by Tschermak (1878) in biotite, both in natural crystals and in the artificially obtained pressure-figure, and were ascribed to (translation-) gliding. The present examples, especially when the surfaces are examined under high magnification, are more suggestive of cleavages but they could not be produced experimentally.

The measured density of hendricksite in the range of composition from 40 to 50 atomic per cent Zn in the octahedral position is much higher than that of ordinary biotite. The values cited in Table 2 were ob-

tained pycnometrically. Hendricksite does not fluoresce in either short or long-wave ultraviolet radiation. The mineral is readily soluble in acid, much more rapidly than biotite or phlogopite.

X-RAY CRYSTALLOGRAPHY

The interplanar spacings for (200), (060), (004) and (005), obtained in Cu radiation on a diffractometer from viscous smear mounts of powdered samples, are given in Table 2. The spacings are relatively large as compared to phlogopite and ordinary biotite. They decrease in roughly linear manner with decreasing content of Zn or $(Zn+Mn)$. The higher ob-

TABLE 3. X-RAY POWDER DATA FOR HENDRICKSITE

Cu radiation, Ni filter, Si internal standard, in Angstrom units. Data on the material of analysis 4, Tables 1 and 2. 1M polytype. Relative intensities in arbitrary chart units. Approximate cell dimensions: a 5.37A, b 9.32, c 10.30, β 99°.

I	d, meas.	hkl	I	d, meas.	hkl
100	10.20	001	17	1.696	006
36	5.094	002	10	1.554	060
60	3.398	003	3	1.495	205
7	2.682	130,20$\bar{1}$	6	1.454	007
13	2.652	13$\bar{1}$,200	6	1.378	027,136
35	2.546	004	3	1.327	117,206
9	2.462	201,13$\bar{2}$	5	1.272	008
8	2.202	202,13$\bar{3}$	5	1.002	
9	2.034	005	5	0.974	
5	2.016	20$\bar{4}$,133			

served values of (060), for material with very little Mg, are roughly comparable to that of synthetic annite, $KFe_3(Si_3Al)O_{10}(OH)_2$. The ratio of intensity (004)/(005) in general decreases with increasing content of Mg, analogous to the variation in the phlogopite-biotite series as shown by Gower (1957). X-ray powder data for the material of analysis 4 are given in Table 3.

POLYTYPES

The analyzed specimens and a number of additional specimens were examined variously by x-ray Weissenberg, Laue and powder methods to identify the polytypes present. All of the manganoan and zincian phlogopites and most of the hendricksite specimens proved to be the 1M polytype. A few hendricksites were the $2M_1$ polytype, although with some peculiar features, and one trigonal polytpe, apparently 3T, was recognized. The (001) reflections appearing on sharp Weissenberg 0-level

photographs of the 2M polytypes include a few very faint and diffuse reflections that are irrationally related to the main reflections with $1 = 2, 4$ etc. The 2M polytypes closely approach trigonal symmetry, a feature also noted by Levinson and Heinrich (1954) for some Swedish 2M manganophyllites with small 2V. Semi-continuous diffuse x-ray scattering parallel to c^* representing random stacking sequences was frequently observed, together with evidence of interstratification of different polytypes.

OPTICAL PROPERTIES

The indices of refraction of hendricksite are relatively high and are comparable to those of biotite very high in Fe. The highest observed
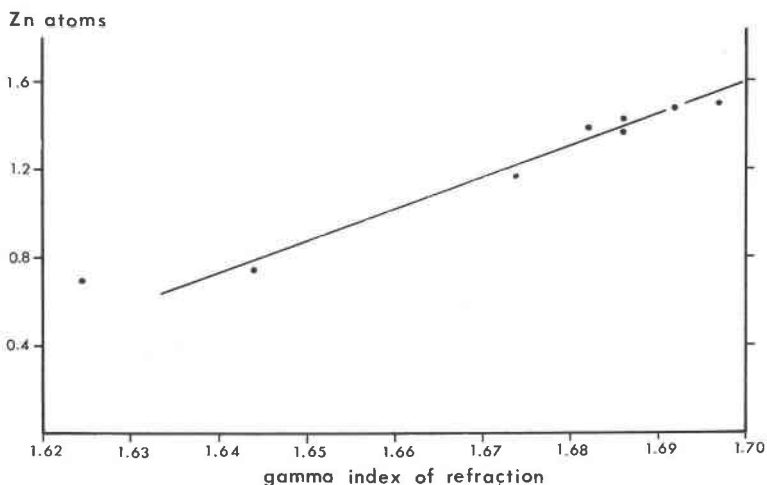

FIG. 3. Variation of the gamma index of refraction with composition. Material of analyses 1–8, Tables 1 and 2.

value of gamma, 1.697 in material containing about 50 atomic per cent Zn in the octahedral positions, is approximately the value observed in synthetic annite, $KFe^{3+}(Si_3Al)O_{10}(OH)_2$ (Wones, 1963). The relatively high refractivity of hendricksite is associated with the Zn. Heinrich (1946) has shown that the refractivity of Mn^{2+} is less than that of Fe^{2+} in the phlogopite-biotite series. The gamma index of refraction of hendricksite varies roughly linearly with the number of Zn or $(Zn + Mn)$ ions in the octahedral layer (Fig. 3). The indices of refraction also are affected by the content of Fe^{3+} and of Ba, not determined in all specimens.

The optical orientation and axial angle were determined for the analyzed specimens and for a number of additional specimens whose

composition was approximately determined from Fig. 3. 2V is very small and varies erratically in the range of 2° to 5° for hendricksite; it increases up to 10°–15° for the phlogopite part of the series with a low content of Zn and Mn. One specimen, that of analysis 6 in Table 2, was uniaxial. The value 2V 14° was measured by Benjamin Silliman Jr. (1850) on phlogopite from Franklin. He also noted the occurrence of deep reddish copper-colored and nearly uniaxial mica at this locality that presumably is the present hendricksite.

The crystallographic orientation of the optic plane was established with the aid of Laue photographs. It is parallel (010) in the 1M polytypes, following the general rule in biotite and phlogopite, with one exception in which it was perpendicular (010). The latter orientation also has been found by Levinson and Heinrich (1954) for a few of the 1M manganoan phlogopites (manganophyllite) from Sweden analyzed by Jakob (1925). In the 2M polytypes the optical orientation also departed from the general rule and was parallel (010). This feature was first noted by Levinson and Heinrich (1954) in an unanalyzed "manganophyllite" from Franklin. We have re-examined this specimen, originally borrowed from the Harvard collection, and have confirmed their finding. Chemical and optical examination established that this specimen was hendricksite.

OCCURRENCE

Hendricksite did not occur in the normal ore of the Franklin mine (now entirely worked out), but was restricted to the skarn zones found locally in the orebody. The skarn formed irregular lens or sheet-like bodies, intercalated with essentially normal ore, that were confined to the orebody and were conformable to its synclinal structure. The skarn zones were especially abundant in the northern part of the orebody, where they constituted up to about one-fourth of the whole.

The skarns contained andradite, rhodonite and calcite chiefly, with hendricksite, barium feldspars, and zincian and manganoan varieties of both the diopside-hedenbergite-johannsenite series and the aegirine-augite to augite series as typical but subordinate constituents. Franklinite and willemite also were present, although in amounts much less than in the normal ore. Zincite is generally lacking. A variety of other minerals occurred sporadically in smaller amounts. Among them were vesuvianite, cummingtonite, wollastonite, bustamite, axinite, hancockite, hardystonite, ganophyllite, members of the friedelite group, apatite, barite and fluorite. Quartz, an extremely rare mineral at Franklin, occurred sparingly as anhedral masses in relatively highly feldspathic areas. Certain skarn zones, notably in the vicinity of the Parker shaft, locally yielded small amounts of unusual minerals variously containing Pb, Ba, B, Be,

As, Sb, S, Cl and F, including over a dozen new species, mostly lead silicates, that have been the subject of numerous investigations. The older literature on these minerals has been summarized by Palache (1937).

Hendricksite occurred abundantly throughout the skarn, as massive interlocking aggregates and as anhedral plates ranging to over 1 foot across. Specimens undoubtedly can be found in most collections of Franklin minerals. Well defined crystals are uncommon; one euhedral crystal, bounded by (110), (010) and (001), measured 4 inches along the a-axis, $5\frac{1}{2}$ inches along the b-axis and was almost 2 inches thick (analysis 7). Much of the mica is bent, crinkled or shows other signs of mechanical deformation.

Hendricksite occurred associated with virtually all of the skarn minerals mentioned above. Andradite, calcite and franklinite, the latter sometimes as rounded crystals embedded in the mica, are almost invariable immediate associates. The feldspar in the skarn in general contains Ba, and includes hyalophane, barian varieties of microcline and anorthoclase, and celsian. It is often immediately associated with hendricksite. The unusual silicates containing lead, among them nasonite, margarosanite, barysilite, roeblingite, esperite and larsenite, together with hedyphane and other arsenates and various minerals containing boron, are of a late stage of mineralization in the skarn and in general follow hendricksite. They occur filling the interstices of brecciated masses of skarn, as veinlets, and in some instances as small, irregular replacement patches. Pectolite, prehnite, xonotlite and minerals of the serpentine-bementite complex also belong to this late, hydrothermal stage.

Distribution of Zn in Skarn Minerals

The average bulk mineral composition and corresponding average chemical composition of the normal ore of the Franklin mine is given in column 1 of Table 4. The data are based on a composite sample of crude ore representing mill feed over a five year period, on analyses of mill concentrates averaged over a ten year period, and on averaged analyses of individual ore minerals. The data as supplied by the New Jersey Zinc Company are subject to somewhat divergent interpretations and can be regarded as only a close approximation.

The average mineral composition and chemical composition of the skarn is less well known. The available quantitative data are based on mineral separations made of a composite sample of mill feed containing a mixture of skarn and normal ore. The averaged mineralogical and chemical data of column 2 in Table 4 represent only the relative amounts of the skarn silicates, and do not include calcite, franklinite and other constit-

TABLE 4. AVERAGE CHEMICAL COMPOSITION OF NORMAL ORE AND OF SKARN

	1 Normal ore	2 Skarn
SiO_2	7.5	40.6
Al_2O_3	0.1	4.9
Fe_2O_3	25.8	11.2
FeO		1.2
ZnO	24.5	4.4
MnO	10.0	13.3
MgO	0.4	1.2
CaO	14.4	17.6
BaO	—	0.7
Na_2O	—	0.22
K_2O	—	1.75
Rem.	17.3	2.93
	100.0	100.0

1. Normal ore. Rem is CO_2 and 5 per cent miscellaneous minerals. Total Fe and Mn arbitrarily calculated to trivalent and divalent states, respectively; the bulk of the Fe is trivalent and that of Mn divalent, but accurate analytical data are lacking. Mineral composition: franklinite 39 (weight per cent), willemite 24, zincite 1, tephroite 1, andradite 1, rhodonite 1, calcite 28, miscellaneous 5.
2. Skarn. Calcite and other components of the normal ore, usually present in more or less amount, have been excluded. Rem. is H_2O, Sr, Pb, F, SO_4 and various rare minerals in part containing B, Be, As, etc. Mineral composition: andradite 42 (weight per cent), rhodonite 28, feldspars 13, hendricksite 4, pyroxenes and amphiboles 4, hardystonite 5, fluorite 1, hancockite 1, miscellaneous 2.

uents of the normal ore that are present in more or less amount in the skarn. The skarns also are not wholly uniform in mineral composition, but locally show an increase in andradite in particular or rhodonite, and sometimes in feldspar or pyroxene.

The skarn zones are enriched in Si, Al and alkalies, with K in excess of Na. The total and relative amounts of Mn and Zn vary with assumptions as to the proportion and composition of the normal-ore components, but in general the skarn is higher in Mn and much lower in Zn than the normal ore. The Zn/Mn atomic ratios of the normal ore and the skarn silicates are 2.1 and 0.29, respectively. The ratios of Fe^{2+} to Fe^{3+} and of Mn^{2+} to Mn^{3+} in the normal ore and in the skarn are not known precisely, but, as earlier noted by Ridge (1952), Fe^{3+} and Mn^{2+} greatly predominate. The skarn contains certain minor elements not present in the normal ore, particularly Ba, which is present chiefly in substitution for K in feldspar and in hendricksite, and also Sr, Pb, B, Be, As, F, and Cl. The latter elements are chiefly contained in various rare minerals that

TABLE 5. DISTRIBUTION OF Zn AND Mn IN ORE AND SKARN MINERALS

Name	Atomic per cent occupancy of site		Atomic ratio in site,	Coord. no. of site	Ions normally in site
	Zn	Mn	Zn/Mn		
Ore minerals					
Zincite	94	6	15.7	4	Zn
Willemite	90	10	9	4	Zn
Franklinite	60	Note 1	—	4	Zn
Tephroite	14	83	.17	6	Mn
Skarn minerals					
Hendricksite	48	35	1.37	6	Mg, Fe
Aegirine-augite	27	25	1.0	6	Mg, Fe
Augite	23	24	1.0	6	Mg, Fe
Idocrase	19	22	.96	6	Mg, Fe
Cummingtonite	18	27	.66	6	Mg, Fe
Schefferite	9	21	.4	6	Mg, Fe
Rhodonite	12	62	.2	6+	Mn
Pectolite	1	5	.2	6	Ca
Ganophyllite	11	62	.18	?	Mn
Axinite	9	91	.1	6	Mn, Fe
Glaucochroite	6	82	.07	6	Mn, Ca
Bustamite	1	47		6+	Mn, Ca
Friedelite group	2	98		?	Mn
Andradite	0	17		8	Ca
Bementite	low	high		?	Mn

Note: Remainder of the A position and all of the B position is filled with Mn and/or Fe but the distribution is not known.

have attracted much attention, but, other than Pb and Sr, the total amount present in the skarn is minute.

Many of the skarn silicates contain both Zn and Mn in solid solution, or, in a few instances, as essential constituents. The bulk content of Zn and the Zn/Mn atomic ratio in these silicates varies widely (Table 5). The highest content of Zn and the highest Zn/Mn ratio, as referred to actual structural sites, is found in silicates in which the Zn occurs in 6-coordinated positions that are normally occupied by relatively small ions, either Mg, Fe^{2+} or Fe^{3+}. Hendricksite stands first in this regard. In these minerals the Zn/Mn atomic ratio is considerably greater than the Zn/Mn ratio, approximately 0.29, in the idealized bulk skarn.

A low content of Zn and a low Zn/Mn ratio is found in silicates in which the Zn occupies sites normally occupied by larger ions, such as Mn^{2+} or Ca, that are in distorted or expanded 6-coordination, in part with unbonded more distant neighbors in the first coordination sphere,

or that are in higher coordination than 6. In these minerals the Zn/Mn ratio is lower than the Zn/Mn ratio in the idealized skarn. The main mechanism of compositional variation in them involves the mutual substitution of Ca and Mn.

The Zn in the skarn silicates is present wholly in 6-coordination with the exception of hardystonite and esperite, isostructural with melilite and beryllonite, respectively, in which it is 4-coordinated. In the normal ore, on the other hand, the Zn is almost entirely present in 4-coordination. Here it occurs in the A position of the normal spinel franklinite; in the Be_2SiO_4-type structure of willemite, Zn_2SiO_4; and in the BeO-type structure of zincite, ZnO. It is present in 6-coordination to a small extent in the manganese-olivine tephroite, a minor constituent of the normal ore, from which it has in part exsolved as willemite (Hurlbut, 1961). In these species, with the exception of tephroite, Zn is an essential constituent and the choice of structure-type and coordination number primarily expresses the general tendency of Zn to form a tetrahedrally directed, largely covalent bond. The crystallochemical aspects of this matter have been discussed by Neumann (1949), Fyfe (1951) and Wells (1962). The skarn constitutes a different chemical environment, in which the choice of structure-type is primarily determined by Si-O linkages and by cations other than Zn. The distribution of Zn as a vicarious constituent of these silicates, in which the bond is relatively strongly ionic, is primarily a function of ionic size, with Zn closer to Mg, Fe^{2+} and Fe^{3+} than to Mn^{2+} and Ca.

Caswellite

Hendricksite has a marked tendency to be replaced by andradite. This is observed both as the development of garnet reaction rims around aggregated masses and by the common occurrence of pseudomorphs of very fine-grained andradite after crystals of the mica. The pseudomorphs vary in color from brown to yellowish brown and pale buff, with a dull luster, and have a distinct parting inherited from the basal mica cleavage. All stages of the alteration can be followed from the original mica through cloudy, brownish, altered mica crowded with minute inclusions to the complete pseudomorphs. Books of mica with a peripheral altered zone are common. The name caswellite was originally applied to the more or less altered mica by Chester (1894). His analysis (SiO_2 38.74, Fe_2O_3 6.85, Mn_2O_3 15.95, Al_2O_3 6.58, CaO 22.30, MgO 5.52, ign. loss 4.64, total 100.58) represents an advanced stage of alteration of the mica in which much manganoan andradite was present. He noted that this material was associated with a very dark red mica containing K, Mn and little or no Ca. This is the fresh parent material. Later,

TABLE 6. SYNTHETIC Zn-MICA AND Mn-MICA

Run	Temperature	Pressure	Duration	Phases
1.	650°	3000 bars	24 hours	Zn-mica, sanidine, willemite
2.	450°	1000	40	Zn-mica, sanidine, willemite
3.	250°	2000	40	Zn-mica, sanidine, willemite
4.	650°	3000	40	Mn-mica, tephroite
5.	450°	2000	40	Mn-mica, tephroite, sanidine

Chester (1896) said that caswellite was "An altered biotite from Franklin Furnace, N. J., resembling clintonite, and containing much manganese." The later identification of the reddish mica at Franklin as manganophyllite stems primarily from these observations. The name caswellite has since been applied more specifically by local collectors and mineral dealers to the garnet pseudomorphs themselves. Specimens are common. The name caswellite lacks species or varietal significance and should be abandoned.

SYNTHESIS OF Zn-MICA AND Mn-MICA

Synthetic micas of the ideal end-compositions $KZn_3(Si_3Al)O_{10}(OH)_2$ and $KMn_3(Si_3Al)O_{10}(OH)_2$ were made by the hydrothermal crystallization of stoichiometric gels (Table 6). The starting gels were prepared by the precipitation of solutions containing aluminum nitrate and zinc acetate or manganous chloride by the addition of KOH solution to a final pH of 8. The solution was stirred vigorously during reaction, and the resulting precipitate was centrifuged and washed in distilled water. Appropriate amounts of concentrated K_2SiO_3 solution were then added. After drying in vacuum at 110° the material was placed into gold tubes and heated in cold-seal rod bombs at the stated temperatures and pressures. Measured amounts of H_2O were added to control pressure.

The reaction products were identified by x-ray and optical techniques. The particle size of the mica was too small for satisfactory optical study; the gamma index of the Zn-mica was over 1.72 and that of the Mn-mica near 1.70. X-ray powder spacing data for the two micas, obtained in filtered Cu radiation on a diffractometer, are given in Table 7. A trioctahedral mica containing Ni as the octahedral cation has been synthesized by Klingsberg and Roy (1957), and synthetic Mg and (Fe^{2+}, Fe^{3+}) micas are well known.

TABLE 7. X-RAY POWDER DATA FOR SYNTHETIC Zn-MICA AND Mn-MICA

Cu radiation, Ni filter, Si internal standard, in Angstrom units. Relative intensities in arbitrary chart units. Approximate cell dimensions: a 5.41, b 9.37, c 10.23Å, beta 99° (Mn-mica); a 5.38, b 9.32, c 10.3Å, beta 99° (Zn-mica).

hkl	Mn-mica		Zn-mica	
	d	I	d	I
001	10.13	100	10.18	100
002	5.06	5	5.08	5
110	4.62	3		
11$\bar{1}$	4.35	2		
021	4.23	3		
111	4.03	5		
11$\bar{2}$	3.627	100	3.62	25
022	3.463	8		
003	3.371	15	3.38	30
121	3.229	3	3.27	25
11$\bar{3}$	2.886	8	2.90	20
023	2.764	3		
10$\bar{3}$	2.696	10		
103, 20$\bar{1}$	2.696	10		
200, 13$\bar{1}$	2.657	50	2.67	5
113	2.603	50		
004	2.559	30	2.55	5
13$\bar{2}$	2.453	20		
040	2.354	10		
132	2.328	5		
114	2.308	3		
203	2.179	15		
221, 12$\bar{4}$	2.173	10	2.172	40
141	2.113	5		
005	2.039	20	2.032	5
10$\bar{5}$	2.007	10		
13$\bar{4}$	1.878	8		
300	1.776	3	1.774	10
006	1.699	10	1.697	5
135	1.685	10		
144	1.608	3		
060	1.562	30		
330	1.536	10	1.535	20

David R. Wones for a manuscript copy of a study on the systematic description and identification of mica polytypes.

REFERENCES

BAUER, L. H. AND H. BERMAN (1933) Barium-muscovite from Franklin, N. J. *Am. Mineral.* **18,** 30.

BILGRAMI, S. A. (1956) Manganese silicate minerals from Chikla, Bhandara district, India. *Mineral. Mag.* **31,** 236.

CHESTER, A. H. (1894) On caswellite, an altered biotite from Franklin Furnace, N. J. *Trans. New York Acad. Sci.* **13,** 181.

———— (1896) A dictionary of the names of minerals. New York, 49, 166.

DEVRIES, R. C. AND R. ROY (1958) Influence of ionic substitution on the stability of micas and chlorites. *Econ. Geol.* **53,** 958.

EUGSTER, H. P. AND D. R. WONES (1958). *Ann. Rpt. Geophys. Lab., Carnegie Inst.* **57,** 194 (1957–58).

FOSTER, M. D. (1960) Interpretation of the composition of the trioctahedral micas. *U. S. Geol. Surv. Prof. Paper* **354-B,** 11.

———— AND H. T. EVANS (1962). New study of cryophyllite. *Am. Mineral* **47,** 344.

FYFE, W. S. (1951). Isomorphism and bond type. *Am. Mineral* **36,** 538.

GOWER, J. A. (1957). X-ray measurement of the iron-magnesium ratio in biotites. *Am. Jour. Sci.* **244,** 836.

HEINRICH, E. WM., A. A. LEVINSON, D. W. LEVANDOWSKI AND C. H. HEWITT (1953) Studies in the natural history of the micas. *Univ. Michigan Eng. Res. Inst. Project M978, Final Rept.*

HENDRICKS, S. B. AND M. JEFFERSON (1939) Polymorphism of the micas, with optical measurements. *Am. Mineral.* **24,** 729.

HURLBUT, C. S. (1961) Tephroite from Franklin, N. J. *Am. Mineral.* **46,** 549.

IGELSTROM, L. J. (1872) Ueber Manganophyll, eine neue Glimmerart. *Jb. Mineral.* 296.

JAKOB, J. (1925) Beitrage zur chemischen Konstitution der Glimmer. I. Mittheilung: Die Schwedischen Manganophylle. *Zeit. Krist.* **61,** 155.

KLINGSBERG, C. AND R. ROY, (1957) Synthesis, stability and polytypism of nickel and gallium phlogopite. *Am. Mineral.* **42,** 629.

LEVINSON, A. A. AND E. WM. HEINRICH (1954) Studies in the mica group: single-crystal data on phlogopites, biotites and manganophyllites. *Am. Mineral.* **39,** 937.

NEUMANN, H. (1949) Notes on the mineralogy and geochemistry of zinc. *Mineral. Mag.* **28,** 575.

PALACHE, C. (1937) The minerals of Franklin and Sterling Hill, Sussex County, N. J. *U. S. Geol. Survey Prof. Paper* **180.**

RIDGE, J. D. (1952) The geochemistry of the ores of Franklin, New Jersey. *Econ. Geol.* **47,** 180.

ROSS, C. (1946) Sauconite, a clay mineral of the montmorillonite group. *Am. Mineral.* **31,** 411.

ROSS, M., H. TAKEDA AND D. R. WONES, (1965). Systematic description and identification of mica polytypes. *Science* (in press).

SILLIMAN, B., JR. (1850) Optical examination of several American micas. *Am. Jour. Sci.* **10,** 372.

SMITH, J. V. AND H. S. YODER (1956). Experimental and theoretical studies of the mica polymorphs. *Mineral. Mag.* **31,** 209.

TSCHERMAK, G. (1878) Die Glimmergruppe. *Zeit. Krist.* **2,** 26.

WELLS, A. F. (1962) *Structural Inorganic Chemistry.* Oxford, 3rd Ed., 506.

WINCHELL, A. N. (1925) Studies in the mica group. *Am. Jour. Sci.* **9**, 309.

WONES, D. R. (1963) Physical properties of synthetic biotites on the join phlogopite-annite. *Am. Mineral.* **49**, 1300.

YOSHIMURA, T. (1939) Studies on the minerals from the manganese deposit of the Kaso mine, Japan. *Jour. Facu. Sci. Hokkaido Univ.* **4**, 430.