LENNILENAPEITE, THE Mg-ANALOGUE OF STILPNOMELANE, AND CHEMICAL DATA ON OTHER STILPNOMELANE SPECIES FROM FRANKLIN, NEW JERSEY

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ABSTRACT

Lennilenapeite, a new mineral species, is triclinic, with a = 21.9(1) Å and $d_{(001)} = 12.18(5)$ Å. The strongest reflections in the X-ray powder pattern are (d, I/Io) 12.11 100, 2.582 40, 1.578 30, 1.593 30, 2.365 30, 2.734 30. Two chemical analyses gave SiO₂ 44.5, 45.11; Al₂O₃ 5.4, 4.79; Fe₂O₃ 5.9, 7.15; FeO 6.4, 7.32;MgO 7.0, 11.39; CaO tr., 0.59; MnO 11.6, 6.22; ZnO 6.3, 4.92; K2O 3.0, 2.76; Na2O 0.2, 0.38; BaO 1.3, 0.91; H₂O 8.4, 8.46; sums = 100.0, 100.00 percent. These yield formulae in accordance with the Mg-dominant member of the stilpnomelane group, $K_{6-7}(Mg,Mn,Fe^{2+},Fe^{3+},Zn)_{48}(Si,Al)_{72}(O,OH)_{216} \cdot 16H_2O,$ Z = 1. Lennilenapeite occurs in two colors; the holotype is dark brown and the cotype is light green. Physical properties of the holotype include hardness (Mohs) \sim 3; lustre, vitreous; cleavage, perfect {001} and imperfect nearly perpendicular to (001); density is 2.72 g/cm³ (meas). Optically lennilenapeite is pseudo-uniaxial, 2V = 0, with indices of refraction $\alpha = 1.553(2)$, $\beta = \gamma = 1.594(4)$; pleochroism is strong; X faint brown to colorless, Y = Zdark brown; absorption Y = Z > X. Lennilenapeite is associated with nelenite, tirodite, franklinite, and willemite in the holotype assemblage and with sphalerite and dolomite in the cotype assemblage. Both are from the Franklin mine, Franklin, Sussex County, New Jersey. Lennilenapeite is named for the Lenni Lenape Indians, who were presumably the first inhabitants of the Franklin area and the first to see the deposits. Analytical, X-ray, and optical data are given for a Mn-dominant stilpnomelane from Franklin, tentatively assumed to be parsettensite. The composition of a ferristilpnomelane from Franklin is also presented.

Keywords: stilpnomelane group, lennilenapeite, new mineral species, Franklin, New Jersey, ferristilpnomelane, parsettensite.

Sommaire

La lennilenapéite, nouvelle espèce minérale, est triclinique, a 21.9(1) Å, d_{001} 12.18(5) Å. Les six raies les plus intenses du cliché de poudre [d(1)] sont: 12.11(100), 2.582(40), 1.578(30), 1.593(30), 2.365(30), 2.734(30). Données chimiques: SiO₂ 44.5, 45.11; Al₂O₃ 5.4, 4.79; Fe₂O₃ 5.9, 7.15; FeO 6.4, 7.32; MgO 7.0, 11.39; CaO traces, 0.59; MnO 11.6, 6.22; ZnO 6.3, 4.92; K₂O 3.0, 2.76; Na₂O 0.2, 0.38; BaO 1.3, 0.91; H₂O 8.4, 8.46; total 100.0%. Ces données indiquent que la lennilenapéite est une stilpnomélane magnésienne, K₆₋₇(Mg,Mn,Fe²⁺,Fe³⁺,Zn)₄₈(Si, Al)₇₂(O,OH)₂₁₆·16H₂O, Z = 1. L'échantillon holotype est brun foncé, et son cotype, vert pâle. L'holotype possède les caractères suivants: dureté (Mohs) ~3, éclat vitreux, clivage parfait suivant {001} et imparfait quasi perpendiculaire à (001); densité mesurée 2.72. Optiquement pseudouniaxe, avec 2V = 0 et indices de réfraction: $\alpha = 1.553(2)$, $\beta = \gamma = 1.594(4)$; pléochroïsme intense: X brun pâle à incolore, Y = Z brun foncé; absorption Y = Z > X. La lennilenapéite holotype est associée à: nélenite, tirodite, franklinite et willemite; le cotype se trouve dans un assemblage à sphalérite et dolomite. Ces deux échantillons proviennent de la mine Franklin à Franklin, comté de Sussex au New Jersey. Son nom rappelle les amérindiens de la tribu Lenni Lenape, qui furent vraisemblablement les premiers habitants de la région de Franklin et les premiers à examiner ces gisements. On présente des données chimiques, optiques et roentgenographiques sur un échantillon de stilpnomélane manganifère de Franklin, que l'on considère provisoirement comme exemple de parsettensite. On donne également la composition chimique d'une ferristilpnomélane, elle aussi de Franklin.

(Traduit par la Rédaction)

Mots-clés: groupe de la stilpnomélane, lennilenapéite, nouvelle espèce minérale, Franklin, New Jersey, ferristilpnomélane, parsettensite.

INTRODUCTION

During the process of characterization of the minerals associated with nelenite, a new manganese arsenosilicate member of the friedelite group (Dunn & Peacor 1984), we noted the occurrence of a closely associated black, lustrous mineral in small flattened aggregates that range up to 1 cm across. Although an X-ray powder-diffraction pattern of this mineral indicated that it is a stilpnomelane, the intimate association with tirodite, nelenite and rhodonite (all with Mn or Mg dominant) indicated that it should be chemically analyzed for Mn and Mg to determine the extent of solid solution of these elements in stilpnomelane. Stilpnomelane has Fe as the dominant cation; the limits of solid solution of other cations in this species are ill-defined. We therefore carried out analyses on a number of stilpnomelane-group minerals from Franklin because the dominant solid-solution there, in many silicate phases, involves Mn for Mg. The results of this study include new data on the solid solution of both Mn and Mg for Fe in stilpnomelane. The Mn-dominant phase at Franklin is shown to be similar to parsettensite, and the Mg-dominant species is described herein as the new mineral *lennilenapeite*.

Lennilenapeite is named in honor of the Lenni Lenape Indians, who inhabited the Franklin area and were presumably the first to find the deposits at Mine Hill and Sterling Hill, which cropped out in full view. The words "Lenni Lenape" mean "the original people" in the Algonquin language of the time. Holotype and cotype lennilenapeite are in the mineral collection at Harvard University, under catalog numbers H105542 and H108573, respectively. Both the species and the name were approved by the Commission on New Minerals and Mineral Names, I.M.A.

X-RAY CRYSTALLOGRAPHY

Study by precession methods indicated that lennilenapeite is isostructural with stilpnomelane. Single crystals of adequate quality to determine all the unitcell parameters could not be obtained. However, precession photographs parallel to the $\{001\}$ cleavage show well-defined pseudohexagonal periodicity with a 21.9 Å. Reflections normal to this plane (*i.e.*, parallel to c^*) are diffuse parallel to c^* and severely spread out owing to crystal imperfection. The true periodicity could therefore not be directly determined. However, these results are in concert

TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR LENNILENAPEITE

<u>d</u> (obs.)	<u>hk1</u>	I/Io
12.11 6.09	001 002	100 2
5.50 4.76		2 2 5 2
4.39		ž
4.07	003	20
3.67 3.04	004	5 20
2.734 2.582		30 40
2.439		2
2.365 2.204		30
2.125		2 10
1.965		1
1.695 1.593		1 30
1.593		30
1.542		10
1.413		1
1.373		1
	n, 114.6-mm-dfameter	
Si as internal estimated.	standard, intensitie	s visually

with those of Eggleton & Bailey (1965) for most crystals of stilpnomelane, such that nondiffuse reflections occur in only a small fraction of crystals. The X-ray powder-diffraction data are in good agreement with those for ferrostilpnomelane (see below) published by Eggleton (1972) and leave no doubt that this is a stilpnomelane-group mineral. Because of the pseudosymmetry, which causes nonsymmetrically equivalent d (calc.) values to be approximately equal, reflections can generally not be indexed, and unitcell parameters therefore have not been refined by least squares. Nevertheless, 00/ reflections can be indexed, and they lead to a value of $d_{001} = 12.18(5)$ Å, in good agreement with the value of 12.100 Å for ferrostilpnomelane as obtained by Eggleton (1972). The available data are fully consistent with a stilpnomelane-group mineral. The powderdiffraction data are given in Table 1.

Note that although the mineral names *fer*rostilpnomelane and *ferristilpnomelane*, used in this paper, have never been officially approved by the I.M.A.; they were proposed by Hutton (1938) before such approval was required. Their utility as names was affirmed by Eggleton (1972) in his comprehensive restudy of the stilpnomelane group, and they have been used extensively since then.

PHYSICAL AND OPTICAL PROPERTIES

The type lennilenapeite forms dense black lustrous aggregates of platy crystals. The brown color of these aggregates is not apparent in a hand specimen, but it is readily observed in thin chips under a binocular microscope. The streak is brown, and the mineral is brittle, unlike many samples of stilpnomelane. There are two directions of cleavage: $\{001\}$ is perfect and $\{hk0\}$ is imperfect. The hardness (Mohs) is approximately 3. The lustre is vitreous, inclining to resinous. The density, determined using heavy-liquid techniques, is 2.72 g/cm³. The poor quality of the crystals prevents the determination of unit-cell parameters, which in turn precludes the calculation of density for comparison.

Optically, lennilenapeite is sensibly uniaxial negative with 2V = 0. It has strong pleochroism: X faint brown to colorless, Y = Z dark brown; absorption Y = Z > X. The indices of refraction are $\alpha = 1.553(2)$ and $\beta = \gamma = 1.594(4)$. There is no discernible fluorescence in ultraviolet radiation. The above description applies to the holotype specimen, H105542. The more abundant material described by Frondel & Ito (1965) occurs as aggregates of platy yellowish green crystals with a distinctly bronze lustre. They found it to be optically negative, 2V = 0, with indices of refraction $\alpha = 1.539$ and $\beta = \gamma = 1.583$, and pleochroic with X pale yellow-brown and Y = Z dark olive brown.

PROCEDURES OF CHEMICAL ANALYSIS

Lennilenapeite and the Mn-dominant stilpnomelane discussed below were analyzed utilizing an ARL-SEMO electron microprobe with an operating voltage of 15 kV and a sample current of 0.025 μ A, standardized on brass. Wavelength-dispersion microprobe scans indicate the absence of other elements with atomic number greater than 8, except those reported herein. The following standards were used for analysis: barite (Ba), manganite (Mn), synthetic ZnO (Zn), and hornblende for all other elements. The data were corrected using both standard Bence-Albee and ZAF corrections. All specimens were checked for homogeneity on the microprobe with a small beam-spot, and then analvzed with a large (40 μ m) beam-spot to minimize volatilization. All specimens are chemically homogeneous for the elements detected, except for K, which varies by as much as $\pm 50\%$ of the amount present. This apparent inhomogeneity in K might be due to volatilization of K during microprobe

analysis. Similar effects were encountered by Plimer (1977) in microprobe analyses of the related mineral bannisterite. However, little is known of the interlayer cations in this group of minerals, such that the apparent inhomogeneity in K may be due to other substitutions. The compositions are presented in Table 2.

Several analytical procedures deserve special mention. The ratio Fe^{3+}/Fe^{2+} was obtained by titration on one specimen of the Mn-dominant stilpnomelane (analysis #6). Because this specimen (H-92791-b) is identical to the holotype lennilenapeite in every respect, and is an unusual specimen in textural aspects, and because Dunn & Peacor (1984) found the associated nelenite to be of nearly identical composition in both these specimens, we assume that the Fe^{3+}/Fe^{2+} ratio is likewise similar. This is further supported by the similar compositions of tirodite in these specimens. Accordingly, we have calculated the Fe^{3+}/Fe^{2+} ratio for lennilenapeite to agree with that determined experimentally for specimen H-92791-b. In addition, we have noted, in the

	Lennilenapeite				Ferristilpnomelane	Mn-dominant stilpnomelane				
Sample #	H105542 ^{°°}	H105542 ⁺	R582	140297	H108573 ^{§ §}	⁵ H114079 ⁵	Н92791-Ь	' H92791-b [†]	H89365	H899999
Analysis #	1	la	2	3	4	5	6	6a	7	8
S102	45.4	44.5	47.9	46.5	45.11	41.1	46.8	45.7	45.9	46.1
A1203	5.5	5.4	5.4	5.3	4.79	6.0	5.6	5.5	5.3	5.5
Fe203	6.0**	5.9	n.d.	n.d.	7.15	36.7	5.1*	5.0	n.d.	n.d.
FeÔ Š	6.6**	6.4	18.7	18.1	7.32	0.41	5.7*	5.5	12.3	11.4
1g0	7.1	7.0	10.9	10.2	11.39	1.77	5.6	5.4	6.1	6.9
CãO	tr.	tr.	0.0	0.0	0.59	0.50	0.0	0.0	0.2	0.0
¶nÓ	11.9	11.6	1.1	1.1	6.22	0.95	16.7	16.3	14.2	13.8
Zn0	6.4	6.3	7.8	7.1	4.92	n.g.	5.5	5.4	5.5	5.4
< ₂ 0	3.1	3.0	n.d.	n.d.	2.76	2.65	1.4	1.4	2.1	1.9
1a20	0.2	0.2	n.d.	n.d.	0.38	1.55	0.2	0.2	0.4	0.4
BaŌ,	1.3	1.3	n.d.	n.d.	0.91	0.1	1.2	1.2	0.8	0.9
l₂0 [™] l₂0 [™]		8.4++			8.46	6.32	8.4***	8.4***		
otal		100.0			100.00	100.17	102.2	100.0		
	Numbe	rs of ions	on the	e basis	of E(Si,Al	,Fe,Fe ³⁺ ,Mn,Mg,Zn)	= 120			
51		62.42	61.92	62.52	61 42	61.99		63.49	62.88	62.82
17		8.93	8.23	8.39	7.69	10.65		9.00	8.56	8.83
¹ e ³⁺		6.22			7.32	41.65		5.23		
Fe		7.50	20.21	20.35	8.33	0.52		6.39	14.08	12.98
1g		14.63	21.00	20.45	23.12	3.98		11.18	12.45	14.02
Ca		0.00	0.00	0.00	0.86	0.81		0.00	0.29	0.00
4n		13.78	1.20	1.25	7.17	1.21		19.18	16.47	15.92
Zn		6.52	7.44	7.04	4.95			5.53	5.56	5.43
ĸ		5.36			4.79	4.82		2.48	3.66	3.30
Na		0.54			1.01	4.53		0.53	1.06	1.06
Ba		0.71			0.48	0.05		0.65	0.43	0.47
Н		78.56			76.81	84.89		77.82		

TABLE 2. CHEMICAL COMPOSITION OF LENNILENAPEITE AND OTHER SPECIES OF STILPNOMELANE

∞ ---Analysis given "as-determined". §§---Analysis from Frondel & Ito (1965),

§ ----Unpublished analysis by Jun Ito.

+ ---Analysis normalized to sum to 100 % with 8.4% H20.

++---Water from sample H92791-b, as described in text.

***---Water determined by Penfield method.

n.g.--not given.

n.d.--not determined.

tr.--trace.

analytical data presented and in other data-sets not published here, that the sum of weight % oxides determined by microprobe on stilpnomelane-group minerals is consistently high, usually by approximately 2 weight %. We attribute this to a number of potential causes, including the loss of loosely bound H_2O (a) during sample preparation, (b) under vacuum in the microprobe chamber, or (c) by volatilization under bombardment by the microprobe beam. It has recently been shown (Dunn et al. 1981, 1983) that the related minerals bannisterite and ganophyllite can lose 3.9 and 5.3 weight % H₂O, respectively, in vacuum at 21°C. Hence, it is reasonable to presume that a stilpnomelane such as that described here, from the same deposit, could behave in a similar manner. We were not able to obtain a water determination for the holotype lennilenapeite owing to paucity of material, but we did measure H₂O on specimen H-92791-b, which is of the same paragenesis as noted above. The resultant analysis of the Mn-dominant specimen H-92791-b sums to 102.2 weight %, consistent with our observations noted above for the enhancement of determined weight % oxides by loss of water. Accordingly, we have normalized composition #6 to sum (with 8.4% H_2O) to 100.0 % (given as #6a). Because there was not adequate holotype lennilenapeite for direct determination of water, we have normalized it in the same manner (#1a). We note that the stated imprecision of K2O and H2O values does not affect the species status of these minerals: such status is wholly dependent upon the relative ratios of octahedrally co-ordinated cations Fe, Mg, Mn and Zn.

CHEMICAL FORMULAE

The chemical formula for lennilenapeite was calculated using a modification of the convention established by Eggleton (1972), in that we set the sum of octahedral and tetrahedral cations equal to 120 atoms, with 72 tetrahedral cations, 48 octahedral cations, and $\Sigma(O+OH) = 216$. The chemical formula for the yellowish-green cotype lennilenapeite analyzed by the late Jun Ito (Frondel & Ito 1965) and presented here as #4, yields: $(K_{4.79}Na_{1.01}Ca_{0.86}Ba_{0.48}) \sum_{7.14}(Mg_{23.12}Fe^{2+}_{8.33}Mn_{7.17}Zn_{4.95}Fe^{3+}_{4.43})\Sigma_{48.00}$ (Si_{61.42} Al_{7.69} Fe³⁺_{2.89}) $\sum_{72.00}(O_{170.33}OH_{45.67})\Sigma_{216}$. 15.57H₂O. The formula for the holotype lennilenapeite (H-105542, #1a) is: $(K_{5.36}B_{0.71}Na_{0.54})\Sigma_{6.61}$ (Mg_{14.63}Fe²⁺_{7.50}Mn_{13.78}Zn_{6.52}Fe³⁺_{5.57}) $\Sigma_{48.00}$ (Si_{62.42}Al_{8.93} Fe³⁺_{0.65}) $\Sigma_{72.00}(O_{171.29}OH_{44.71})\Sigma_{216}$. 16.94H₂O.

An average formula for lennilenapeite, reflecting the general composition of this mineral, is: $K_{6.7}(Mg,Mn,Fe^{2+},Zn,Fe^{3+})_{48}(Si,Al)_{72}(O,OH)_{216}$. 16H₂O. We provide, in Table 2, additional compositions (#2, 3) of the yellowish green lennilenapeite, which are partial in that they provide data only for octahedrally and tetrahedrally co-ordinated cations. Both partial compositions indicate that Mg is dominant in these specimens.

OCCURRENCE

Lennilenapeite occurs in two different assemblages from the Franklin mine, Franklin, Sussex County, New Jersey. One of these contains nelenite, tirodite, franklinite and willemite. These species occur as coarse-grained aggregates having a pegmatitic texture. Lennilenapeite occurs as small (5 mm) clusters of bladed crystals within tirodite, willemite and nelenite, but is concentrated at the contacts between these species. Another occurrence was noted by Frondel & Ito (1965). In this assemblage, lennilenapeite occurs as light green to light brownish green druses of platy crystals on sphalerite and dolomite. These druse coatings were referred to as "chlorite" in the older literature. These specimens are composed for the most part of morphologically interesting sphalerite crystals up to 1 cm across; they might be those referred to and illustrated by Palache (1935).

The occurrence of lennilenapeite in two such markedly different assemblages, the latter of which is low-temperature and hydrothermal, indicates that it might be a common phase at Franklin, but one that was overlooked in the past.

FRANKLIN FERRISTILPNOMELANE

In the course of examining several samples of stilpnomelane from Franklin, we encountered one that is dark red in color; it gives a strong reaction for Fe³⁺, and is intimately associated with green, prismatic hedenbergite of composition $(Ca_{0.93}Na_{0.08})(Fe_{0.80}Mg_{0.19}Mn_{0.04})(Si_{1.98}Al_{0.02})O_6$, based on $\Sigma(Si + Al) = 2$. Results of our microprobe analysis of this specimen are in excellent agreement with unpublished data for a ferric-iron stilpnomelane. The analysis was performed by Dr. Ito at Harvard University. Although not germane sensu stricto to the topic of this paper, we present the result of Dr. Ito's analysis in Table 2 for the record (#5).

A Mn-DOMINANT STILPNOMELANE

As mentioned previously, we found four samples of black stilpnomelane associated with nelenite, tirodite and rhodonite, but only one of these is Mgdominant. The other three were found to be Mndominant. These are crystallographically identical to the holotype lennilenapeite; no crystals suitable for full crystallographic characterization were found. An examination of imperfect crystals indicated that they are triclinic, with a = 21.9(1) Å; $a \simeq b$; they have $d_{001} = 12.15(5)$ Å.

Microprobe data for these grains of Mn-dominant stilpnomelane are presented in Table 2 (#6, 6a, 7 and 8). Calculation of a chemical formula, on the same basis as used for lennilenapeite, yields, for #6a: $(K_{2.48}Ba_{0.65}Na_{0.53})_{\Sigma 3.66}(Mn_{19.18}Fe^{2+}_{6.39}Mg_{11.18}Zn_{5.53}Fe^{3+}_{5.23}Al_{0.49})_{\Sigma 48.00}(Si_{63.49}Al_{8.51})_{\Sigma 72}(O_{169.52}OH_{46.48})_{\Sigma 216}$. 15.67H₂O.

The physical properties of this Mn-dominant stilpnomelane are similar to those of lennilenapeite from this assemblage. This phase is black; D (meas) = 2.75 g/cm³; {001} cleavage is good. Optically, this Mn-dominant stilpnomelane is sensibly uniaxial negative, with indices of refraction $\alpha = 1.556(2)$ and $\beta = \gamma = 1.600(4)$. Pleochroism is strong: Y = Z dark brown, X faint brown to colorless; absorption Y = Z > X

Parsettensite, first described by Jacob (1923), is commonly accepted as the Mn analogue of stilpnomelane. It is not our intention to analyze the status of parsettensite at this time. If indeed parsettensite is a member of the stilpnomelane group (definitive proof is still lacking), then the Mndominant phase we describe here can simply be considered as parsettensite that shows considerable solidsolution of other elements. Further studies are necessary to describe fully the limits of solid solution within the stilpnomelane group.

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