

Kolicite, a new manganese zinc silicate arsenate from Sterling Hill, Ogdensburg, New Jersey

PETE J. DUNN

*Department of Mineral Sciences, Smithsonian Institution
Washington, D.C. 20560*

DONALD R. PEACOR

*Department of Geology and Mineralogy, University of Michigan
Ann Arbor, Michigan 48109*

AND B. DARKO STURMAN

*Department of Mineralogy and Geology
Royal Ontario Museum, 100 Queen's Park
Toronto, Ontario, Canada*

Abstract

Kolicite, $\text{Mn}_7\text{Zn}_4(\text{AsO}_4)_2(\text{SiO}_4)_2(\text{OH})_8$, is a new mineral found in the Sterling Hill mine, Ogdensburg, Sussex County, New Jersey. Kolicite is orthorhombic, space group *Cmca*, with $a = 18.59(3)$, $b = 8.789(5)$ and $c = 12.04(1)\text{\AA}$, $V = 1967.1\text{\AA}^3$, $Z = 4$. The six strongest lines in the X-ray diffraction pattern (d in \AA , intensity, hkl) are: 2.97 100 023, 512; 1.540 70 552, 517, 644, 842, 915; 3.58 60 113; 2.608 50 513, 132; 2.479 40 621, 024; 2.815 40 131, 114, 422, 223.

Kolicite is bright yellowish-orange with a light orange streak. There is no cleavage. The Mohs hardness is approximately 4½. Kolicite occurs as fractured grains with a vitreous luster which resemble fractured garnet. Optically, kolicite is biaxial negative, $2V_x = 78^\circ$, with refractive indices $\alpha = 1.779(2)$, $\beta = 1.786(2)$, and $\gamma = 1.790(2)$. Pleochroism is strong with Z light yellow, Y yellowish-orange, and X colorless or pale yellow. Absorption is $Z = Y > X$; dispersion is strong, $r < v$; orientation: $Z = a$, $Y = c$. D (meas) = 4.17(2), D (calc) = 4.20 g/cm³ for the ideal end-member composition.

The composition of kolicite, determined by electron microprobe, is: FeO 0.4, MgO 0.8, MnO 39.2, ZnO 26.0, As₂O₅ 18.9, SiO₂ 10.4 percent, which combined with 5.5 percent H₂O, determined by DTA/TGA, totals 101.2 percent, in good agreement with the theoretical composition.

Kolicite is found only in the Sterling Hill and Franklin mines and is associated with will-emite, franklinite, sonolite, friedelite, and calcite. There appears to be no direct structural relationship between kolicite and the platy silico-arsenates such as mcgovernite, dixenite, and kraisslite. Kolicite is named in honor of John Kolic of Rockaway, New Jersey, in recognition of his contributions to the advancement of knowledge about the mineralogy of Franklin and Sterling Hill, New Jersey.

Introduction

The new mineral kolicite was called to the authors' attention by Mr. John Kolic of Rockaway, New Jersey, and Mr. Ewald Gerstmann of Franklin, New Jersey, in the summer of 1978. The X-ray powder diffraction pattern and the physical characteristics of

the mineral did not match those of any known species, and we proceeded on the assumption that it was a new mineral. Subsequent analysis has proven it to be a new mineral.

We take pleasure in naming this new mineral kolicite in honor of John Kolic, who found the mineral and recognized it to be a unique and interesting

phase. The mineral and the name have been approved by the Commission on New Minerals and Mineral Names, IMA. Holotype material is preserved in the National Museum of Natural History, Smithsonian Institution, under catalog #143765. Additional holotype material is deposited in the American Museum of Natural History, New York, under catalog #AMNH #T45444; the Royal Ontario Museum, Toronto, under catalog #M-35863, and the Mineralogical Museum at Harvard University, Cambridge, Massachusetts. The pronunciation of the new mineral name is KO-LIK-AIT.

Physical and optical properties

Kolicite is orange in color, and the streak is very light orange. The hue is similar to that of most bright orange wulfenite with no tinges of red or brown. The Mohs hardness is approximately 4½. Kolicite is a brittle mineral and breaks with an even fracture. No cleavage was observed. This lack of cleavage is noteworthy in that some other minerals of similar composition, such as kraisslite and mcgovernite, do have one perfect cleavage, although holdenite does not. The density of kolicite, determined by heavy-liquid techniques, is 4.17(2) g/cm³, in excellent agreement with the calculated value of 4.20 g/cm³. Kolicite is neither fluorescent nor phosphorescent in ultraviolet radiation. Kolicite resembles a fractured garnet at first glance, but the anisotropy, pleochroism, and inferior hardness are diagnostic. Kolicite is easily soluble in cold 1:1 hydrochloric acid, and to a lesser degree it is also soluble in 1:1 nitric acid.

Optically, kolicite is biaxial (-), with $2V_x = 78(2)^\circ$ (meas), 74° (calc). The dispersion of the optic axes is strong, $r < v$. The refractive indices and the orientation of the indicatrix were determined with the spindle stage on a crystal previously oriented by X-ray methods. The refractive indices are: $\alpha = 1.779(2)$, $\beta = 1.786(2)$ and $\gamma = 1.790(2)$. The orientation is $Z = a$, $Y = c$. Kolicite is strongly pleochroic with Z light yellow, Y yellowish-orange, X colorless or pale yellow. Absorption is $Z = Y > X$. The Gladstone-Dale constant, K , calculated from the chemical analysis, is 0.191, in excellent agreement with the value of 0.188 obtained from the density and refractive indices. The constants of Mandarino (1976) were used in the calculations.

Chemistry

Kolicite was chemically analyzed using an ARL-SEMQ electron microprobe with an operating voltage

Table 1. Microprobe analysis of kolicite

	KOLICITE	Mn ₇ Zn ₄ (AsO ₄) ₂ (SiO ₄) ₂ (OH) ₈
MnO	39.2	39.91
FeO	0.4	
MgO	0.8	
ZnO	26.0	26.16
SiO ₂	10.4	9.66
As ₂ O ₅	18.9	18.48
H ₂ O*	5.5	5.79
Total	101.2	100.00

* H₂O determined by DTA/TGA

Accuracy of data: ± 4% for silica
± 3% for other elements

of 15 kV and a beam current of 0.15 μA. The standards used were: synthetic ZnO for zinc, synthetic olivenite for arsenic, manganite for manganese, and hornblende for silicon, iron, magnesium, and calcium. The data were corrected using the MAGIC-4 computer program. A spectrographic analysis indicated the absence of any light elements, and a

Table 2. X-ray powder diffraction data for kolicite

d(Obs)	d(Calc)	hkl	I/I ₀	d(Obs)	d(Calc)	hkl	I/I ₀
4.12	4.13	021*	10	1.969	1.970	515	2
3.97	3.97	220*	2	1.796	1.798	913	2
3.76	3.77	221*	2		1.792	640	
3.58	3.58	113*	60		1.791	226	
2.970	2.977	512	100				
	2.963	023		1.776	1.780	443	2
					1.777	10,0,2	
2.815	2.823	223	40		1.775	044	
	2.821	422			1.773	641	
	2.814	114		1.746	1.748	715	5
	2.814	131*			1.745	625*	
2.752	2.755	602*	2		1.743	244	
2.608	2.608	132*	50				
	2.605	513		1.731	1.732	151	5
					1.731	516*	
2.533	2.533	620	1	1.681	1.684	606	10
	2.526	404			1.681	117	
2.479	2.483	024	40		1.680	152*	
	2.478	621		1.577			10
2.342	2.347	113	40	1.550			5
	2.342	712					
	2.334	622					
					1.540		70
					1.506		10
2.304	2.304	115	5		1.478		5
2.263	2.261	514	10		1.454		10
	2.260	531*			1.423		5
2.194	2.197	040	1				
	2.190	424		1.378			5
2.147	2.150	532	5		1.318		2
	2.148	713			1.296		2
	2.142	623			1.196		2
					1.182		2
2.111	2.111	025*	10		1.168		1
2.067	2.064	042	1				
2.009	2.015	242	1				
	2.006	006					

¹Data obtained using a polycrystalline sample in a 114.6 mm diameter Gandolfi camera with CuK_α radiation and N.B.S. silicon as an internal standard. Intensities visually estimated.

* Indices which were used for least-squares refinement of lattice parameters.

Table 3. Unit-cell parameters for kolicite and related minerals

	a	b	c	Z	Space Group
KOLICITE ¹	18.59	8.789	12.04	4	<i>Cmca</i>
ARDENNITE ²	8.7126	5.8108	18.5214	2	<i>Pnmm</i>
HOLDENITE ³	11.99	31.46	8.697	8	<i>Abma</i>
GERSTMANNITE ⁴	8.185	18.65	6.256	8	<i>Bbcm</i>
MANGANOSTIBITE ⁵	8.727	18.847	6.062	4	<i>Ibmm</i>

¹Present study²Donnay and Allmann (1968)³Moore and Araki (1977b)⁴Moore and Araki (1977a)⁵Moore (1970)

wavelength-dispersive microprobe scan indicated that only the elements reported are essential to kolicite. Water was determined by DTA-TGA as a weight loss of 5.5% at 625°C. Analysis of several samples indicated very little variation in composition. The resultant analysis of the type sample is presented in Table 1. Calculation of the cell contents using these data, in part, yields 8.14 As per cell. Because the space-group equipoints have ranks 4, 8, and 16, and because solid solution between As and other elements is unlikely, we have normalized the cell contents to 8 As. This yields the following values of cations per cell: $Mn_{26.80}Fe_{0.26}Mg_{0.95}Zn_{15.49}Si_{8.40}As_{8.00}$. This can be interpreted to correspond ideally to $(Mn,Mg,Fe)_7Zn_4(AsO_4)_2(SiO_4)_2(OH)_8$ with $Z = 4$.

In a later section we show that kolicite is closely related both chemically and structurally to holdenite and gerstmannite. In the structures of these minerals Zn is tetrahedrally coordinated (Moore and Araki, 1977a, b), although the coordinating ions are OH and O in holdenite, and O in gerstmannite. The final form of the formula of kolicite should probably be consistent with tetrahedral coordination of Zn, but the results of a crystal-structure analysis, now in progress, will be necessary for an unambiguous definition.

X-ray crystallography

Irregular grains were studied by the precession and Weissenberg techniques. These showed that kolicite is orthorhombic, with extinction rules consistent with either space group *Aba2* or *Cmca* (the settings are different for these designations). Three-dimensional intensity data were measured using the Weissenberg-geometry, Supper-Pace automated system. After correcting for absorption and L_p factors, analysis of the data using the $N(Z)$ test indicated that kolicite is centrosymmetric. The space group is therefore *Cmca*.

X-ray powder diffraction data were obtained using

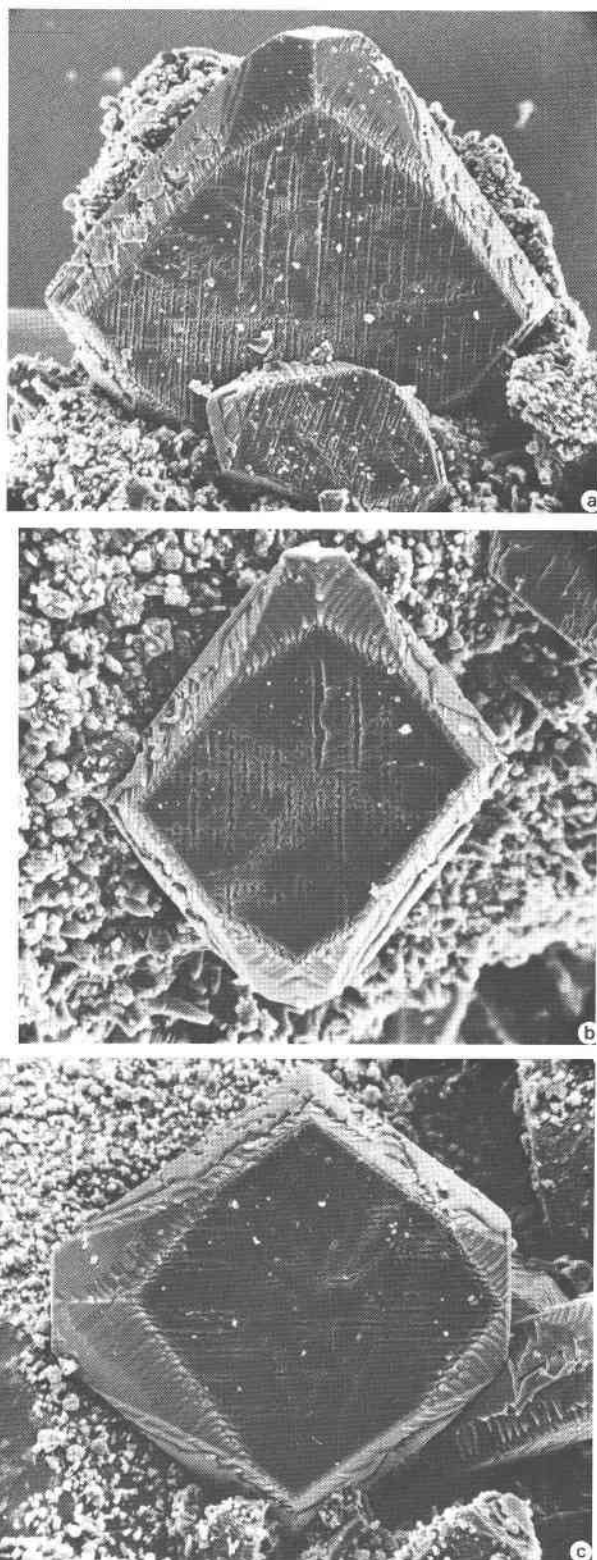


Fig. 1. Scanning electron photomicrographs of kolicite at (a) 125 \times , (b) 200 \times , (c) 160 \times .

a 114.6 mm diameter Gandolfi camera with a polycrystalline sample and NBS silicon as an internal standard. The data are listed in Table 2. The lattice parameters were refined by least-squares, utilizing indices chosen in part on the basis of intensity values from the single-crystal data set, where ambiguities existed. The refined unit-cell parameters are $a = 18.59(3)$, $b = 8.789(5)$ and $c = 12.04(1)$ Å.

The unit-cell parameters of kolicite are related to those of ardenite (Donnay and Allman, 1968), gerstmannite (Moore and Araki, 1977a), holdenite (Moore and Araki, 1977b), and manganostibite (Moore, 1970). These chemically related phases all have one translation of approximately 8.5 Å and two others which are multiples of approximately 6 Å (Table 3). Moore and Araki (1977a, b) showed that holdenite, $Mn_6Zn_3(OH)_8(AsO_4)_2(SiO_4)_4$, and gerstmannite, $(Mn,Mg)Mg(OH)_2[ZnSiO_4]$, both have structures based on cubic closest packing of oxygen ions. The lattice parameters are simple multiples of characteristic closest-packed parameters. These two phases have the same number of oxygen atoms per unit volume as kolicite. There is thus strong evidence that the structure of kolicite is also based on cubic closest packing of oxygen and hydroxyl ions.

Morphology

Crystals of kolicite were observed on only two specimens which were noted, after the characterization of the species, by Mr. Ewald Gerstmann who generously permitted us to borrow them. The largest crystals are 0.5 mm in diameter, but the crystal faces are so rounded as to preclude morphological description by goniometric techniques.

A small seam on one specimen yielded some very tiny crystals (about 0.05 mm). Through the generosity of Mr. Gerstmann, several of these were removed and studied by means of the scanning electron microscope. Representative photographs of kolicite are shown in Figure 1. Due to the roughness of crystal surfaces (perhaps caused by etching) and the extremely small crystal size, we cannot make precise statements about the morphological orientation of kolicite crystals or the precise indices for the faces observed. However, some general observations are possible. Kolicite crystals exhibit nearly identical morphological development on the one specimen studied. The crystals are pinacoidal in habit and predominantly tabular. The principal forms are pinacoids and dipramids. All crystals have a very irregular surface and curved crystal faces, perhaps as the

result of severe etching. The largest pinacoid is striated parallel to the long direction of the crystals, and the crystals appear to be centrosymmetric, as required by the space group.

Occurrence

Kolicite was found in April of 1977 by John Kolic, a miner at the Sterling Hill mine. According to Mr. Kolic, the mineral was found in the 1020 longitudinal stope, about 30 feet above the 1400 foot level, in the east branch of the west vein of the orebody in a shear zone with abundant slickensides. Kolicite encrusts ore comprised of red willemite and franklinite. The ore contains very little calcite. No other arsenate minerals were found in the immediate area of the kolicite occurrence. Given the fact that only about 15 specimens were recovered, kolicite must be regarded as a rare mineral at the type locality, and its occurrence adds one more species to the present list of 22 species known to occur only in the Franklin and Sterling Hill orebodies.

Kolicite occurs with the previously mentioned ore-sulfite and the following associated minerals: willemite, sonolite, friedelite, and also calcite, the last mineral to form in the assemblage. Kolicite is younger than sonolite and friedelite and contains colorless acicular crystals of secondary willemite which appear to have formed simultaneously with kolicite. No obvious epitaxy exists between the kolicite and the willemite or other associated species. One specimen of kolicite shows kolicite in contact with holdenite.

Note added in proof

The discovery by Mr. Kolic of a specimen in which kolicite was in contact with holdenite prompted an examination of the type holdenite from Franklin, New Jersey (NMNH 95434). Kolicite is present on the specimen as minute crystals imbedded in holdenite. Hence, kolicite was first found in the Franklin mine sometime prior to 1913 but was not noticed, and its characterization waited until the recent find in the Sterling Hill mine.

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