

TIPTOPITE (Li,K,Na,Ca, \square)₈Be₆(PO₄)₆(OH)₄, A NEW MINERAL SPECIES FROM THE BLACK HILLS, SOUTH DAKOTA

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ABSTRACT

Tiptopite is a new mineral species from the Tip Top mine, near Custer, South Dakota. It occurs on massive beryl in a phosphate pegmatite as a secondary mineral associated with roschelite, fransoletite, montgomeryite and englishite. It forms clear, colorless, lustrous, radial aggregates of elongate hexagonal prisms up to $0.1 \times 0.1 \times 2.0$ mm. It is brittle with an uneven fracture. The measured density is $2.65(2)$ g/cm³. Optically it is uniaxial positive, ω 1.551(1) and ϵ 1.559(1). It is hexagonal, with possible space-group $P6_3/m$ or $P6_3$, a 11.655(5), c 4.692(2) Å, and $Z = 1$. The strongest ten X-ray-diffraction lines in the powder pattern [d in Å(hkl)] are: 3.81(40)(120), 3.65(40)(111), 3.36(50)(030), 2.966(100)(121), 2.525(90)(040), 2.348(70)(002), 2.223(60)(041), 2.077(50)(231), 1.943(40)(330) and 1.606(40)(142). The combined results of electron-microprobe, atomic absorption and thermal gravimetric analyses give: Li₂O, 4.5, Na₂O 6.1, K₂O 9.9, BeO 15.1, CaO 4.3, MnO 0.2, Al₂O₃ 0.3, P₂O₅ 55.1, H₂O 3.4, sum 98.9 wt. %, which yields the formula (Li_{2.68}K_{1.87}Na_{1.75}Ca_{0.68}Mn_{0.02})_{7.00}(Be_{5.38}P_{0.57}Al_{0.05})_{6.00}P_{6.00}O_{23.52}[(OH)_{3.37}(PO₄)_{0.35}]_{3.72} or, ideally, (Li,K,Na,Ca, \square)₈Be₆P₆O₂₄(OH)₄, based on the observed density.

Keywords: tiptopite, new mineral species, South Dakota, phosphate, pegmatite.

SOMMAIRE

La tiptopite, nouvelle espèce minérale, provient de la mine Tip Top, près de Custer (Dakota du Sud); elle cristallise sur le beryl massif comme minéral secondaire dans une pegmatite à phosphate. Elle est associée à: roschelite, fransoletite, montgomeryite et englishite. La tiptopite se présente en agrégats fibroradiés transparents, incolores et lustrés où les prismes hexagonaux peuvent atteindre $0.1 \times 0.1 \times 2.0$ mm. Elle est fragile, à fracture irrégulière. Sa densité mesurée est de $2.65(2)$. C'est un minéral optiquement uniaxe positif, ω 1.551(1), ϵ 1.559(1). Hexagonal, il appartient au groupe spatial $P6_3/m$ ou $P6_3$, avec a 11.655(5), c 4.692(2) Å, et $Z = 1$. Les dix raies de diffrac-

tion X les plus intenses (méthode des poudres) [d en Å(hkl)] sont: 3.81(40)(120), 3.65(40)(111), 3.36(50)(030), 2.966(100)(121), 2.525(90)(040), 2.348(70)(002), 2.223(60)(041), 2.077(50)(231), 1.943(40)(330) et 1.606(40)(142). Les analyses par microsonde électronique, absorption atomique et thermogravimétrie ont donné (en poids): Li₂O 4.5, Na₂O 6.1, K₂O 9.9, BeO 15.1, CaO 4.3, MnO 0.2, Al₂O₃ 0.3, P₂O₅ 55.1, H₂O 3.4, total 98.9. La formule peut s'écrire (Li_{2.68}K_{1.87}Na_{1.75}Ca_{0.68}Mn_{0.02})_{7.00}(Be_{5.38}P_{0.57}Al_{0.05})_{6.00}P_{6.00}O_{23.52}[(OH)_{3.37}(PO₄)_{0.35}]_{3.72} ou idéalement, d'après la densité observée, (Li,K,Na,Ca, \square)₈Be₆P₆O₂₄(OH)₄.

Mots-clés: tiptopite, nouvelle espèce minérale, Dakota du Sud, phosphate, pegmatite.

INTRODUCTION

The Tip Top mine occurs in one of many geologically related phosphate-rich pegmatites in the Black Hills of South Dakota. During mining operations for beryl during the winter of 1981-1982, fracture fillings of interesting and beautiful secondary phosphate minerals were encountered. The crystallized material was salvaged, and specimens were independently sent for identification to the National Museum of Natural Sciences, South Dakota School of Mines and Technology and the Smithsonian Institution. This unknowingly led to research by independent groups, which the authors discovered prior to publication, and which is reported in this synthesis. To date, 53 phosphate minerals have been identified from the Tip Top pegmatite. This includes eight new species: jahnsite, robertsite and segelerite (Moore & Ito 1974), fransoletite (Peacor *et al.* 1983), tinsleyite (Dunn *et al.* 1984), tiptopite (this study), and two other species. A description of some of these assemblages was given by Dunn *et al.* (1983). For variety in secondary phosphate minerals, this locality is certainly one of significance, along with the Palermo mine in New Hampshire and the Hagendorf pegmatites in Ger-

many. One of the authors (TJC) is presently studying the mineralogy of the Tip Top pegmatite in detail.

The new mineral *tiptopite* is named for the locality. Both the new mineral and name have been approved by the Commission on New Minerals and Mineral Names, IMA. Cotype specimens of tiptopite are in the collections of the National Museum of Natural Sciences, Ottawa (NMNS #48833), the Smithsonian Institution, Washington, D.C. (#149609), and the Museum of Geology, South Dakota School of Mines, Rapid City (SDSM & T #81-5102).

OCCURRENCE

Tiptopite is found at the Tip Top mine located just southwest of the centre of Sec. 8, T3S, R4E, about 8.5 km southwest of Custer, South Dakota. Tiptopite was discovered during mining operations in 1981 and 1982, in the recovery of beryl from the outer-intermediate zone. This zone consists of large crystals of microcline perthite, triphylite, quartz and muscovite, with minor amounts of beryl, albite, fluorapatite, elbaite and columbite-tantalite. Tiptopite was abundant at the mine, but subsequent mining activity has removed most, if not all, of the area where it was found. Tiptopite occurs predominantly along fracture surfaces in beryl, occasionally in quartz, and rarely in microcline perthite.

APPEARANCE AND PHYSICAL PROPERTIES

Tiptopite occurs as radial sprays and divergent fas-

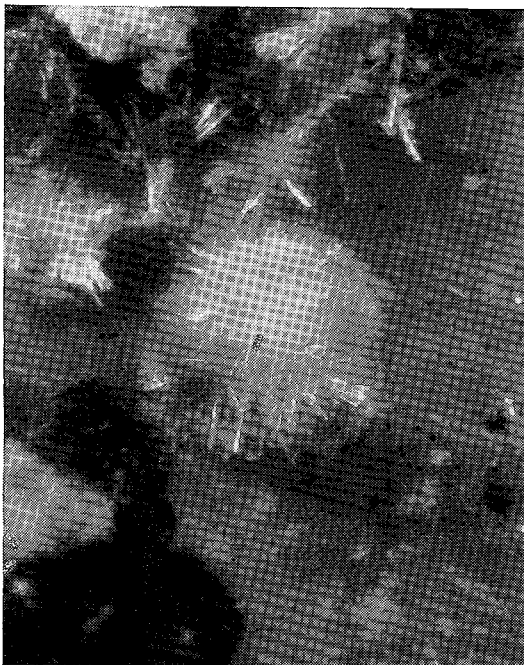


FIG. 1. Photomicrograph of radial aggregates of acicular tiptopite and white balls of englishhite. Central spray is 2.0 mm in diameter.

cicles of clear, colorless needles that have a vitreous lustre (Fig. 1). Individual crystals are prismatic and sometimes have cavernous tubes at the ends (Fig. 2). Prisms are generally 1 to 2.0 mm in length and less than 0.1 mm in width.

The mineral is brittle and has an uneven fracture with no apparent cleavage. The hardness could not be measured owing to the small size of the crystals. It does not fluoresce in ultraviolet radiation, and it is only slightly soluble in 30% HCl. The determination of density was difficult owing to the elongate habit of the crystals. Any turbulence in the heavy liquid caused the crystals to tumble erratically. The best experimental set-up proved to be a 15 mL rectangular glass cell, viewed through the side with a stereomicroscope and back illuminated with polarized light. Bromoform was diluted 1:1 with butyl alcohol, which has approximately the same vapor pressure as bromoform. This minimized evaporation of the diluent and reduced the "boiling" turbulence. The experiment was repeated four times using several crystals each time. The resulting average measured density is 2.65(2) g/cm³.

CRYSTALLOGRAPHY

Morphology

All observed crystals of tiptopite have the same simple morphology: an elongate hexagonal prism {100} and a basal pinacoid {001}.

Optical data

Optically, tiptopite is uniaxial positive (positive elongation) with indices of refraction ω 1.551(1) and ϵ 1.559(1), measured in sodium light (λ 589 nm).

X-ray-diffraction data

X-ray precession photographs show tiptopite to be hexagonal, with a choice of possible space-group $P6_3/m$, or $P6_3$. The unit-cell dimensions were refined using X-ray powder-diffraction data obtained using a 114.6-mm-diameter Debye-Scherrer camera with $\text{CuK}\alpha$ radiation (Table 1). The refined unit-cell parameters and volume are: a 11.655(5), c 4.692(2) Å and V 551.97(7.1) Å³.

The unit cell, space group and general conformation of the formula are similar to those of cancrinite. For example, Grundy & Hassan (1982) showed that a carbonate-rich cancrinite has cell parameters a 12.590(3) and c 5.117(1) Å and space group $P6_3$. These cell parameters are larger than those of tiptopite by an amount consistent with the differences in radius of the tetrahedrally co-ordinated cations. Precession photographs of cancrinite were directly compared with those of tiptopite, showing that there was similarity in the intensity values of equivalent reflections of each phase. With this strong implication of an isotypic relationship, three-dimensional intensity data have been measured for tiptopite and

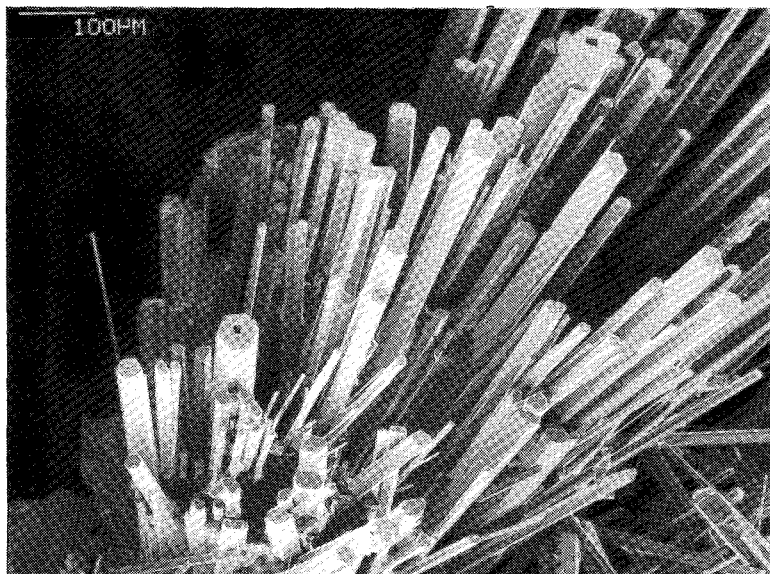


FIG. 2. Scanning-electron-microscope photograph of tiptopite.

an attempt is being made to determine the detailed crystal-structure.

CHEMICAL COMPOSITION

Owing to the particular elements present, it was necessary to employ several analytical means to determine the chemical composition of tiptopite. Ca, K, Na, Al, Mn and P were determined by wavelength-dispersion electron-microprobe analyses, using montgomeryite (Ca, Al, P), maričite (Na), hornblende (K) and manganite (Mn) as standards. An ARL-SEM-Q microprobe was used with operating conditions of 15 kV, sample current 0.025 μ A (standardized on brass) and a defocused beam to minimize volatilization of the lighter elements. The data were corrected using the MAGIC-4 computer program. Because of the significant content of light elements, possible variation in alkaline earths and lack of any suitable phases to use for comparison, a second microprobe analysis was carried out using different standards; this yielded virtually identical results. Except for trace amounts of Fe, Mg, Si and F, which were noted in both sets of analyses, no other element with atomic number greater than nine was detected.

Beryllium and lithium were analyzed by atomic-absorption spectrophotometry, and confirmed by ion probe. Water was determined by TGA with mass spectrographic analysis, and was evolved between 550–900°C, with a peak at 788°C. The presence of minor CO₂ and SO₂ was also noted.

The following is a composite of the results of the aforementioned analyses: Li₂O 4.5, Na₂O 6.1, K₂O

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

<i>hkl</i>	<i>d</i> calc	<i>d</i> obs	I	<i>hkl</i>	<i>d</i> calc	<i>d</i> obs	I
110	5.83	5.79	1	241	1.767	1.767	2
020	5.05	5.08	2	042	1.718	1.718	3
011	4.25	4.26	3	151	1.691	1.692	3
120	3.815	3.808	4	232	1.648	1.647	1
111	3.654	3.652	4	142	1.606	1.606	4
021	3.440	3.441	3	341	1.564	1.564	1
030	3.364	3.364	5	013	1.546	1.543	$\frac{1}{2}$
121	2.960	2.966	10	251	1.528	1.529	3
130	2.800	2.800	$\frac{1}{2}$	113	1.510	1.511	$\frac{1}{2}$
031	2.734	2.736	1	332	1.496		
040	2.523	2.525	9	023	1.494	1.495	2
131	2.404	2.403	1	161	1.462		
002	2.346	2.348	7	440	1.457	1.459	6
230	2.316	2.315	1	123	1.447	1.447	3
012	2.285	2.283	$\frac{1}{2}$	152	1.434	1.434	$\frac{1}{2}$
041	2.222	2.223	6	260	1.400	1.397	$\frac{1}{2}$
112	2.176	2.175	2	223	1.378	1.378	1
231	2.076	2.077	5	062	1.367	1.367	$\frac{1}{2}$
212	1.994	1.998	3	261	1.341	1.339	2
330	1.942	1.943	4	170	1.337		
051	1.854	1.851	$\frac{1}{2}$	252	1.331	1.330	3
222	1.827	1.827	2	043	1.329		
132	1.798	1.800	1	233	1.296	1.297	3

Plus additional weak lines : 1.288, 1.274, 1.260, 1.237, 1.228, 1.219, 1.209, 1.193, 1.184, 1.172 and 1.162 Å.

CuK α radiation, cell dimensions *a* 11.655(5), *c* 4.692(2) Å.

9.9, BeO 15.1, CaO 4.3, MnO 0.2, Al₂O₃ 0.3, P₂O₅ 55.1, H₂O 3.4, sum 98.9 weight %. Based on the observed density of 2.65 g/cm³, the empirical formula is (Li_{2.68}K_{1.87}Na_{1.75}Ca_{0.68}Mn_{0.02}) Σ 7.00(Be_{5.38}P_{0.57}Al_{0.05}) Σ 6.00P_{6.00}O_{23.52}[(OH)_{3.37}(PO₄)_{0.35}] Σ 3.72 or, ideally, (Li,K,Na,Ca, \square)₇Be₅P₆O₂₄(OH)₄.

The ideal formula for tiptopite is presented in a format consistent with that of the cancrinite group,

$A_{6-8}Al_6Si_6O_{24}[(SO_4)(CO_3)Cl_2(OH)]_{2-4} \cdot nH_2O$. Assuming that Be is tetrahedrally co-ordinated, the ratio (Be + P):(O + OH) requires that all or nearly all vertices of tetrahedra be shared between Be and P. Only if the OH is co-ordinated to Be can the structure be other than a framework structure, as consistent with the analogy with cancrinite. However, there are two significant problems with the empirical formula that concern tetrahedrally co-ordinated cations: (1) the number of Be atoms (5.38) is significantly less than the rank of the available equipoint (6). As the analysis also has an excess of P, some of this P has been assigned to the Be site, along with Al, to accommodate the requirements of the equipoint rank. However, if the structure is isostructural with that of cancrinite, this requires that some bridging oxygen atoms be shared between two P ions. This is unreasonable. A second explanation for the deficiency in Be may lie simply in analytical error. In either case, it is clear that the formula has six, or nearly six, Be atoms. (2) There is an excess of 0.92 P atoms above the 6 required by the available equipoint. Part of this excess was assigned to the Be site and part (0.35) as a phosphate radical to the columnar voids (assuming a cancrinite-like structure) containing OH. This radical could occupy a crystal-structure site in much the same way as sulfate in the cancrinite structure. There are numerous other possibilities for rearranging the formula; one of the most obvious is to fix the number of tetrahedrally co-ordinated cations (Be + Al + P) at 12 atoms. This, although sound in terms of crystal chemistry, gives a low calculated density of 2.58 g/cm³, compared to the observed density of 2.65 g/cm³. The problem of the formula will not be resolved until the crystal structure is known.

PARAGENESIS

The paragenesis of tiptopite is complex because it occurs in two similar, but distinct phosphate assemblages. The first phosphate paragenesis, discussed in detail by Peacor *et al.* (1983), is characterized by whitlockite, which is a dominant early phase, red and yellow montgomeryite, tiptopite, englishite, hurlbutite, red to orange roscherite, whiteite, robertsite or robertsite-mitridatite, fairfieldite and fransoletite. The second phosphate suite, discussed below, consists of mitridatite, light brown to colorless montgomeryite, tiptopite, eosphorite-childrenite, hurlbutite, englishite, dark olive-green roscherite, whiteite, fairfieldite, whitlockite and another new mineral. An obvious difference is the overall color of the assemblages, as exemplified by roscherite and montgomeryite. Another difference is that the second suite contains mitridatite and eosphorite-childrenite, lacks fransoletite, and does not have whitlockite as a dominant early phase.

Lamellar aggregates of dark red-brown mitrida-

tite form crusts on which montgomeryite and later phosphates are sometimes deposited; montgomeryite crystals also form directly on beryl along fracture surfaces. Subsequently, tiptopite began to form, and the two minerals are commonly intergrown. During and after the deposition of montgomeryite and tiptopite, eosphorite-childrenite crystals formed, followed by spherules of hurlbutite. Toward the end of hurlbutite crystallization, spherulitic aggregates of englishite, a moderately abundant mineral here (Dunn *et al.* 1984), began to form; these are commonly impaled on acicular tiptopite crystals. Roscherite formed contemporaneously with (and is sometimes partly covered by) englishite. Whiteite, where present, is then formed. Plates and parallel-stacked aggregates of fairfieldite were generally the last to form, and whitlockite, where present, deposited as a dusting on the other minerals.

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