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EHRLEITE, A NEW CALCIUM BERYLLIUM ZINC PHOSPHATE HYDRATE FROM THE TIP TOP PEGMATITE, CUSTER, SOUTH DAKOTA

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ABSTRACT

Ehrleite, a new mineral species from the Tip Top mine, Custer, South Dakota, occurs as vitreous, white to colorless, thick tabular crystals up to 2 × 2 × 0.1 mm on a matrix of beryl and quartz, with mitridatite, roscherite, hydroxyl-herderite and goyazite–crandallite. The crystals show three pinacoids {100}, {010} and {001} (assuming centrosymmetry), the habit form being chosen as {001}. Traces of parting are observed on (001); the fracture is uneven to subconchoidal. Precession photographs show ehrleite to be triclinic and twinned by reflection on {001}, with possible space-groups $P\bar{1}$ and $P1$. The cell parameters are a 7.32(7), b 7.54(1), c 12.42(4) Å, α 91.19(44), β 99.94 (82), γ 98.64(47)°, V 666.5 Å^3 and $Z = 1$. The strongest eleven X-ray powder-diffraction lines [d in Å (I) (*hkl*)] are 12.41(70)(001), 7.42(20)(010), 6.95(50)(100), 6.58(30)($\bar{1}$01,01$\bar{1}$), 5.10(20)($\bar{1}$02), 4.31(40)($\bar{1}$12), 3.86(20)($\bar{1}$03), 3.46(20)($\bar{1}$13), 3.43(20)($\bar{1}$21), 3.16(100)($\bar{2}$12,2$\bar{1}$1,1$\bar{1}$3) and 2.723(60)($\bar{1}$23,023). The density is 2.64(2) (meas.) and 2.62 g/cm^3 (calc.), with Mohs hardness 3½. Ehrleite is non-fluorescent in ultraviolet radiation and soluble in cold, 20% HCl. It is optically biaxial positive, with α 1.556(2), β 1.560(1) and γ 1.580(1) for λ = 589 nm; $2V$(meas) 62°, $2V$(calc) 49°; $X \| c^*$, $Y \Lambda b$ = 18° and $Z \Lambda a$ = 9°. Its composition, determined by electron and ion microprobes, gives BeO 7.9, CaO 20.9, ZnO 14.8, P_2O_5 40.5, [H_2O] 15.9, total 100.0 wt.%, and yields the empirical formula $Ca_{3.92}Be_{3.32}Zn_{1.91}P_6O_{24.15}\cdot 9.28H_2O$, based on six P atoms, or, ideally, $Ca_4Be_3Zn_2(PO_4)_6\cdot 9H_2O$. The name honors Mr. Howard Ehrle, who found the type specimen.

Keywords: ehrleite, new mineral species, South Dakota, phosphate, beryllium, pegmatite.

SOMMAIRE

L'ehrléite, nouvelle espèce minérale provenant de la mine Tip Top à Custer (Dakota du Sud), se trouve, sur béryl et quartz, en cristaux de facies tabulaire et d'éclat vitreux, blancs à incolores, atteignant 2 × 2 × 0.1 mm, associés à mitridatite, roschérite, hydroxyl-herdérite et goyasite–crandallite. Les cristaux, dans l'hypothèse d'une centrosymétrie, présentent trois parallélo èdres, {100}, {010} et {001} le plan d'aplatissement étant choisi comme (001), suivant lequel on observe aussi des plans de séparation. La fracture est irrégulière ou subconchoïdale. Les clichés de précession confirment la symétrie triclinique, groupe spatial $P\bar{1}$ ou $P1$, et un maclage par réflexion sur {001}. Les plans réticulaires sont a 7.32(7), b 7.54(1), c 12.42(4) Å, α 91.19(44), β 99.94 (82), γ 98.64(47)°, V 666.5 Å^3 et $Z = 1$. Les onze raies de diffraction X les plus intenses du cliché de poudre sont les suivantes [d en Å (I) (*hkl*)]: 12.41(70)(001), 7.42(20)(010), 6.95(50)(100), 6.58(30)($\bar{1}$01,01$\bar{1}$), 5.10(20)($\bar{1}$02), 4.31(40)($\bar{1}$12), 3.86(20)($\bar{1}$03), 3.46(20)($\bar{1}$13), 3.43(20)($\bar{1}$21), 3.16(100)($\bar{2}$12,2$\bar{1}$1,1$\bar{1}$3) et 2.723(60)($\bar{1}$23,023). La densité est de 2.64(2) (mesurée) et 2.62 (calculée), avec dureté Mohs ≃ 3½. L'ehrléite n'est pas fluorescente en lumière ultraviolette; elle est soluble dans HCl froid dilué à 20%. Optiquement, elle est biaxe positive, avec α 1.556(2), β 1.560(1) and γ 1.580(1) pour λ = 589 nm; $2V$(mesuré) 62°, 49° (calculé); $X \| c^*$, $Y \Lambda b$ = 18° et $Z \Lambda a$ = 9°. Les analyses par microsondes (électronique et ionique) ont donné BeO 7.9, CaO 20.9, ZnO 14.8, P_2O_5 40.5, [H_2O] 15.9, total 100% (poids), d'où la formule empirique (pour six atomes de phosphore) $Ca_{3.92}Be_{3.32}Zn_{1.91}P_6O_{24.15}\cdot 9.28H_2O$, soit idéalement $Ca_4Be_3Zn_2(PO_4)_6\cdot 9H_2O$. Le nom honore M. Howard Ehrle, qui a trouvé le spécimen type.

Mots-clés: ehrléite, nouvelle espèce minérale, Dakota du Sud, béryllium, pegmatite.

INTRODUCTION

The Tip Top mine, in the Black Hills of South Dakota, is famous for the wide variety of phosphate minerals it has produced. During the winter of 1981–1982, mining operations in the outer–intermediate zone resulted in the discovery of an unusual assemblage of secondary phosphate minerals. The subsequent collection and dispersal of specimens immediately roused the interest of both amateur and professional mineralogists, and has culminated in the discovery of five new mineral species: fransoletite (Peacor *et al.* 1983), tinsleyite (Dunn *et al.* 1984), tiptopite (Grice *et al.* 1985), ehrleite (this study) and an unnamed mineral presently under investigation. In addition, the specimens of the associated minerals montgomeryite, robertsite and englishite constitute some of the finest known of those species (Dunn *et al.* 1983, Campbell 1984).

Ehrleite $Ca_4Be_3Zn_2(PO_4)_6\cdot 9H_2O$ is a very rare species; to date, only two specimens are known. The name honors Mr. Howard Ehrle, of Miles City, Montana, who found the holotype specimen and submitted it to the National Museum of Natural Sciences for identification. Both the new mineral and the name have been approved by the Commission on New Minerals and Mineral Names, IMA. The holotype specimen is preserved in the collection of the National Museum of Natural Sciences, Ottawa

(NMNS #49289). A second specimen, the cotype, is in the Museum of Geology, South Dakota School of Mines and Technology, Rapid City (SDSM&T #2958).

Appearance, Physical and Optical Properties

Ehrleite occurs as individual tabular crystals up to 2 × 2 × 0.1 millimetres and as aggregates of randomly oriented crystals somewhat resembling clear, tabular barite. Upon magnification, however, their true morphology becomes evident (Figs. 1, 2). The

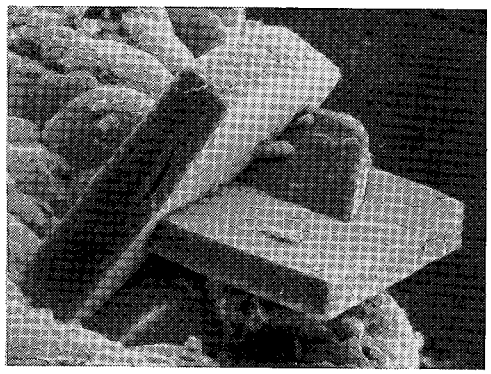

FIG. 1. Tabular crystals of ehrleite. SEM image; width of field of view is 130 μm.

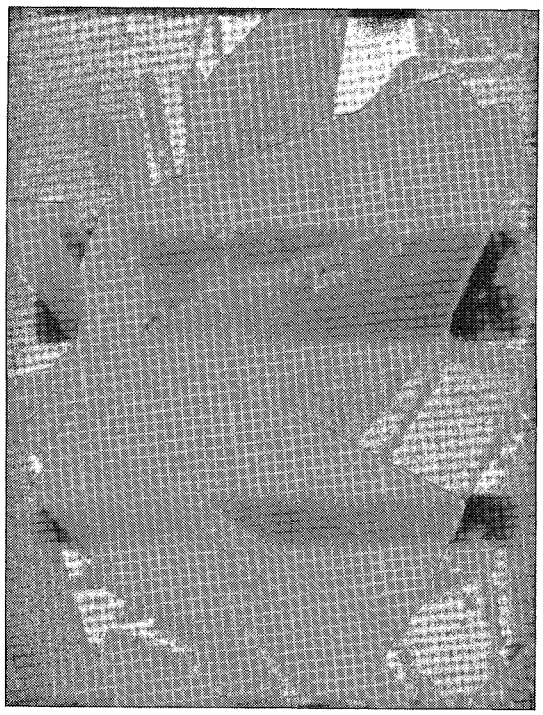

FIG. 2. Twinned tabular crystals of ehrleite. SEM image; width of field of view is 170 μm.

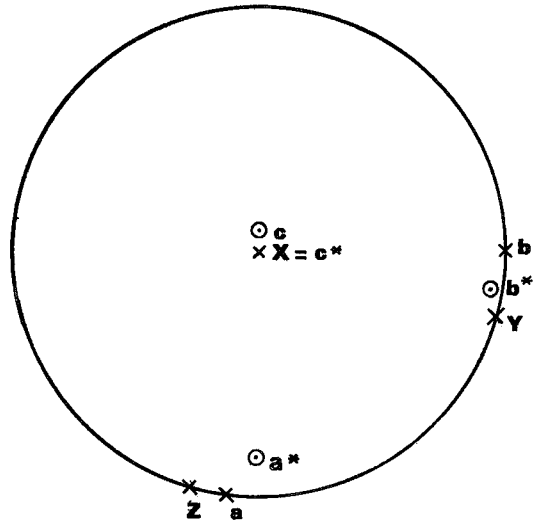

FIG. 3. Stereographic projection of optical and crystallographic elements of ehrleite.

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

hkl	*d*calc	*d*obs	I	*d*obs	I
001	12.22	12.41	7	2.441	1
010	7.44	7.42	2	2.323	1
100	7.12	6.95	5	2.305	1
$\bar{1}01$	6.69	6.58	3	2.287	1
$01\bar{1}$	6.50			2.223	½
011	6.22	6.18	2	2.191	1
002	6.11			2.130	2
$\bar{1}10$	5.60	5.61	1	2.086	1
$\bar{1}11$	5.30	5.33	2	2.044	½
$\bar{1}02$	5.11	5.10	2	2.034	1
$01\bar{2}$	4.84	4.82	½	1.981	½
012	4.61	4.59	½	1.932	½
$\bar{1}12$	4.36	4.31	4	1.903	2
111	4.24	4.16	2	1.878	1
$11\bar{2}$	4.08			1.835	2
$\bar{1}1\bar{2}$	3.93	3.98	1	1.817	½
$\bar{1}03$	3.84	3.86	2	1.793	2
020	3.71	3.72	1	1.767	1
$\bar{2}01$	3.60	3.59	2	1.730	3
200	3.56			1.668	1
$\bar{1}13$	3.47	3.46	2	1.648	1
$\bar{1}21$	3.43	3.43	2	1.620	1
$11\bar{3}$	3.361	3.351	½	1.595	1
$\bar{1}2\bar{1}$	3.355			1.569	1
201	3.267	3.286	½	1.540	½
$\bar{2}12$	3.200	3.161	10	1.525	1
$21\bar{1}$	3.179			1.502	1
$\bar{1}13$	3.143			1.479	1
004	3.055	3.014	3	1.451	½
210	3.033			1.431	½
$\bar{1}2\bar{2}$	3.003			1.412	1
$\bar{2}21$	2.793	2.783	½	1.395	1
014	2.779			1.366	½
$11\bar{4}$	2.770			1.348	2
$\bar{1}23$	2.727	2.723	6	1.322	2
$02\bar{3}$	2.683			1.301	½
$21\bar{3}$	2.660	2.662	2	1.284	½
$\bar{1}2\bar{3}$	2.614	2.613	½		
$\bar{2}04$	2.554	2.551	3		
212	2.549				
$03\bar{0}$	2.481	2.518	3		
$03\bar{1}$	2.454	2.459	1		

CuKα radiation, 1.54178Å. Cell Parameters: *a* 7.32(7), *b* 7.54(1), *c* 12.42(4)Å, α 91.2(4), β 99.9(8), γ 98.6(5)°.

crystals are triclinic and twinned on {001}, with observed forms {100}, {010} and {001}. Ehrleite is milky white to colorless and transparent, with a white streak. It has a vitreous lustre, a Mohs hardness of ~3½, an uneven to subconchoidal fracture and an apparent parting on (001). It is nonfluorescent in ultraviolet radiation. The average measured density, as determined by flotation in a bromoform–butyl alcohol solution, is 2.64(2) g/cm^3, which compares favorably to the calculated density of 2.62 g/cm^3 based on six phosphorus atoms. It is readily soluble in cold, 20% HCl.

All measurements of optical properties were made in sodium light ($\lambda = 589$ nm). Ehrleite is biaxial positive; its indices of refraction are α 1.556(2), β 1.560(1) and γ 1.580(1); $2V$ (measured) 62°, $2V$ (calculated) 49°. The optical orientation is shown in Figure 3, with $X \| c^*$, $Y \wedge b = 18°$ and $Z \wedge a = 9°$.

X-Ray Crystallography

Six crystals of ehrleite were chosen for precession studies, and all were found to be twinned by reflection on {001}. The zero- and upper-level a-axis precession photographs reveal the effect of this twinning on the reciprocal lattice; 1) there is a mirror plane perpendicular to c^*; 2) the observed periodicity along c^* yields a pseudocell with c ~74 Å and a twin index of six, and 3) the twin obliquity is zero, and there is no reciprocal-lattice row perpendicular to the c^* axis. Thus the twin lattice is close to, but not actually monoclinic. When the crystal is viewed with a polarizing microscope, it can be seen that the composition plane (001) centrally divides the crystal into two equal halves. This is also evident on the SEM photograph (Fig. 2).

The unit-cell dimensions were refined from X-ray powder-diffraction data obtained using a 114.6-mm-diameter Debye-Scherrer camera with Cu$K\alpha$ radiation (Table 1). The refined cell-parameters and volume are a 7.32(7), b 7.54(1), c 12.42(4) Å, α 91.19(44), β 99.94(82), γ 98.64(47)° and $V = 666.5$ Å^3, with $Z = 1$. The rather large standard deviations are a result of difficulties in indexing the powder pattern of a triclinic cell. Only 12 reflections could be indexed uniquely with the aid of precession photographs.

Chemical Composition

Because of the particular elements found in ehrleite and the small amount available for analysis, it was necessary to employ a combination of anlytical techniques to determine its composition. Analysis for Ca, P and Zn was done by an ARL – SEMQ electron microprobe using synthetic $Ca_2P_2O_7$ and sphalerite as standards. The microprobe was operated at 15 kV and a beam current of 100 × 10^{-9} amperes, standardized on copper. Wavelength-dispersion data were obtained and corrected by computer program (Tracor–Northern ZAF, version 11, 1981). Except for traces of Mg and Al, no other elements with atomic numbers greater than nine were found.

Beryllium was analyzed by ion probe, and water calculated by difference. It is regrettable that lack of sufficient sample precluded a water determination by any conventional means; the presence of hydrogen was confirmed by ion probe, though the amount could not be quantified.

The resulting composite analysis gave BeO 7.9(9), CaO 20.9(2), ZnO 14.8(7), P_2O_5 40.5(0), H_2O 15.9, total 100.0 wt.%. Based on six phosphorus atoms, the empirical formula is $Ca_{3.92}Be_{3.32}Zn_{1.91}P_{6.00}O_{24.15}$•9.28$H_2O$ or, ideally, $Ca_4Be_3Zn_2(PO_4)_6$•9H_2O. The observed excess Be is probably best explained by the relatively high range of error associated with the analytical technique employed.

Using the observed density and the constants of Mandarino (1981), the Gladstone–Dale calculations yield K_P 0.2141 and K_C 0.2136, with a compatibility index $1-(K_P/K_C)$ of 0.0023, indicating superior agreement between the physical and chemical data (Mandarino 1979).

Paragenesis and Occurrence

The Tip Top mine is located just southwest of the centre of Sec. 8, T3S, R4E, approximately 8.5 km southwest of Custer, South Dakota. As previously mentioned, mining activity at the time the two known ehrleite specimens were discovered was confined to the outer–intermediate zone of the pegmatite. This zone is characterized by large crystals of perthitic microcline, triphylite, quartz and muscovite. Accessory minerals include beryl, albite, fluorapatite, elbaite and columbite–tantalite (Grice *et al.* 1985). Secondary phosphate mineralization occurred along fractures in the beryl, quartz and perthite, but subsequent mining has removed virtually all of this area.

Neither of the ehrleite specimens were collected in place; therefore, their exact geological relationship to the pegmatite as a whole is unknown. Nevertheless, the paragenesis of species present on each specimen may be described. The associated species on each specimen is somewhat distinct. The matrix of specimen 1 (NMNS #49289) is intergrown beryl and quartz. The first phosphates to have formed are olive green mitridatite and orange-brown roscherite, followed by clear, botryoidal hydroxylherderite; white, micaceous goyazite–crandallite; and ehrleite. The matrix of specimen 2 (SDSM & T #2958) consists of beryl only. Rusty orange, botryoidal apatite appears to be the first phosphate to have formed, followed by black, globular, amorphous Mn oxide(s); beige-white, powdery roscherite; clear, radiating aggregates of paraścholzite; and ehrleite.

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