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WHITEITE-(CaMnMg), A NEW MINERAL SPECIES FROM THE TIP TOP PEGMATITE, CUSTER, SOUTH DAKOTA

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Abstract

Whiteite-(CaMnMg), a new mineral species found in a granitic pegmatite in the Tip Top mine, near Custer, South Dakota, occurs as dull or etched, yellowish bipyramidal crystals or blebs up to 1.5×0.5×0.5 mm. It occurs as a secondary mineral on massive beryl associated with montgomeryite, tiptopite, roscherite and englishite. The mineral has a Mohs hardness of about 3½ and a poor cleavage on (001). The density is 2.63(2) (meas.) and 2.64 g/cm³ (calc.). Optically, it is biaxial positive with α 1.580(1), β 1.584(1), γ 1.591(1), $2V$ (meas.) 81(5)° and $2V$ (calc.) 74°. It is monoclinic, with possible space-groups $P2/a$ or Pa, a 14.842(9), b 6.976(1), c 10.109(4) Å, β 112.59(5)°, and $Z = 2$. The strongest ten X-ray-diffraction lines in the powder pattern [d in Å (I) (hkl)] are: 9.31(10)(001), 5.60(3)($\bar{1}11$,011), 4.85(5) ($\bar{2}11$,210,$\bar{2}02$), 4.64(3)(002), 3.51(5)($\bar{3}12$,020), 3.256(4)(021), 2.953(5)($\bar{4}03$), 2.867(4)(401), 2.790(8)(022) and 2.547(4) (510,$\bar{4}21$). The combined results of electron microprobe and thermal gravimetric analyses give: Al_2O_3 12.9, MgO 9.4, CaO 5.6, MnO 12.0, FeO 1.6, P_2O_5 38.2, H_2O 20.8, sum 100.5 wt.%, which yields the chemical formula $(Ca_{0.76}Mn_{0.24})_{\Sigma 1.00}Mn_{1.00}(Mg_{1.78}Fe_{0.17}Mn_{0.05})_{\Sigma 2.00}Al_{1.93}(PO_4)_{4.11}(OH)_{1.46}\cdot 8.1H_2O$ (based on 26 oxygen atoms) or, ideally, $CaMnMg_2Al_2(PO_4)_4(OH)_2\cdot 8H_2O$.

Keywords: whiteite-(CaMnMg), new mineral species, South Dakota, phosphate, granitic pegmatite.

Sommaire

La whitéite-(CaMnMg), nouvelle espèce minérale provenant d'une pegmatite granitique qu'exploite la mine Tip Top, près de Custer au Dakota du Sud, forme des cristaux jaunâtres bipyramidaux, mats ou corrodés, ainsi que des cristaux xénomorphes atteignant 1.5 × 0.5 × 0.5 mm. C'est un minéral secondaire précipité sur le béryl massif, en association avec montgomeryite, tiptopite, roscherite et englishite. Dureté de Mohs: 3½; clivage (001) de piètre qualité. Densité: 2.63(2) (mesurée), 2.64 (calculée). Biaxe positive, α 1.580 (1), β 1.584(1), γ 1.591(1), $2V$ 81(5)° (mesuré), 74° (calculé). La whitéite-(CaMnMg) est monoclinique; elle cristallise dans le groupe spatial $P2/a$ ou Pa. Les paramètres réticulaires sont: a 14.842(9), b 6.976(1), c 10.109(4) Å, β 112.59(5)°, $Z = 2$. Les dix raies les plus intenses du cliché de diffraction [d en Å(I) (hkl)]: sont 9.31(10)(001), 5.60(3)($\bar{1}11$,011), 4.85(5)($\bar{2}11$,210,$\bar{2}02$), 4.64(3)(002), 3.51(5)($\bar{3}12$,020), 3.256(4)(021), 2.953(5)($\bar{4}03$), 2.867(4)(401), 2.790(8)(022) et 2.547(4) (510,$\bar{4}21$). Les résultats d'analyses à la microsonde électronique et par thermogravimétrie ont donné: Al_2O_3 12.9, MgO 9.4, CaO 5.6, MnO 12.0, FeO 1.6, P_2O_5 38.2, H_2O = 20.8, total 100.5% par poids, ce qui mène à la formule $(Ca_{0.76}Mn_{0.24})_{\Sigma 1.00}Mn_{1.00}(Mg_{1.78}Fe_{0.17}Mn_{0.05})_{\Sigma 2.00}Al_{1.93}(PO_4)_{4.11}(OH)_{1.46}\cdot 8.1H_2O$ (base de 26 atomes d'oxygène). La formule idéale est $CaMnMg_2Al_2(PO_4)_4(OH)_2\cdot 8H_2O$.

(Traduit par la Rédaction)

Mots-clés: whitéite-(CaMnMg), nouvelle espèce minérale, Dakota du Sud, phosphate, pegmatite granitique.

Introduction

The study of specimens collected from the 1981–1982 mining operations in the Tip Top pegmatite has resulted in the discovery of five new phosphate mineral species: fransoletite (Peacor *et al.* 1983), tinsleyite (Dunn *et al.* 1984), tiptopite (Grice *et al.* 1985), ehrleite (Robinson *et al.* 1985) and whiteite-(CaMnMg) (this study). Even though the X-ray powder-diffraction pattern of the latter phase closely resembles that of whiteite-(CaFeMg), $CaFeMg_2Al_2(PO_4)_4(OH)_2\cdot 8H_2O$, a detailed study was initiated because many phosphate minerals in this particular geological environment are notably low in iron. An electron-microprobe analysis verified the occurrence of a new species, resulting in the present description of a low-iron, high-calcium member of the whiteite group.

The nomenclature is in keeping with that proposed by Moore & Ito (1978) for the whiteite group. In the general formula $XM(1)M(2)M(3)^{3+}_2(PO_4)_4(OH)_2\cdot 8H_2O$, the $M(3)$ site is dominantly populated by Al^{3+} for the whiteite series and Fe^{3+} for the jahnsite series. Of the large number of possible species in this group, only six have been described to date: whiteite-(CaFeMg), whiteite-(MnFeMg), whiteite-(CaMnMg), jahnsite-(CaMnMg), keckite, and rittmannite. Both the new mineral and the name have been approved by the IMA Commission on New Minerals and Mineral Names (CNMMN). In our submission to this commission concerning this new species, and another soon to be described, we attempted to have the nomenclature of the whiteite group simplified and made consistent by eliminating the 'extended Levinson system' (Levinson 1966), in which species names have one or several suffixes that are not rare-earth elements. We proposed the use of unique names which, in some cases, had chemical prefixes. This proposal was defeated by the CNMMN in favor of the 'extended Levinson system' in spite of the fact that the contemporaneous submission for rittmannite (Marzoni Fecia Di Cossato *et al.* 1989) was accepted. Unfortunately, like the pumpellyite group, the whiteite group now has a mixture of both trivial and suffixed names in contrast to most other mineral groups (approximately 90 groups), in which suffixes appear only for rare-earth elements, as originally prescribed by Levinson (1966) and modified by Bayliss & Levinson (1988).

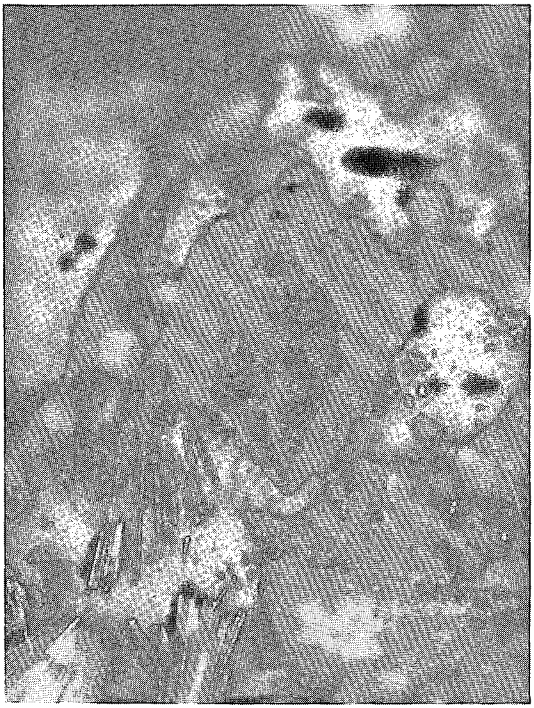

FIG. 1. A pale lavender crystal of whiteite-(CaMnMg), 1 mm in length, associated with sprays of slender, prismatic tiptopite crystals and dark red, rounded aggregates of roscherite.

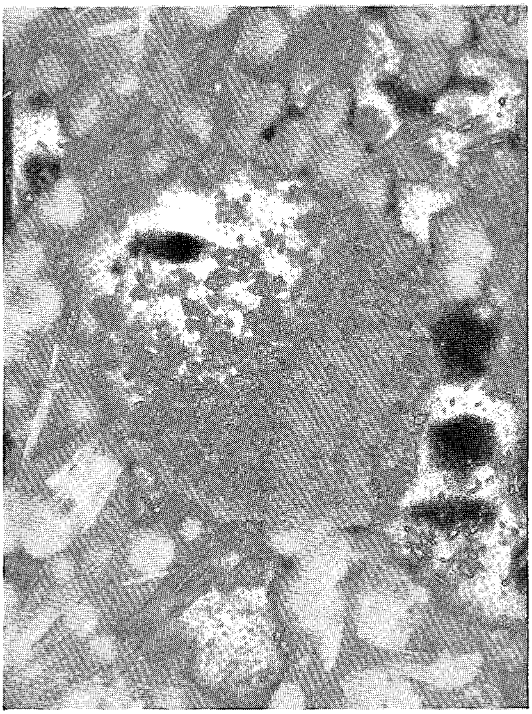

FIG. 2. A dark, yellow-green, etched crystal of whiteite-(CaMnMg), 2 mm across.

Cotype specimens of whiteite-(CaMnMg) are preserved in the National Museum of Natural Sciences, Ottawa (NMNS #49712 and 49707) and the Smithsonian Institution, Washinton, D.C. (NMNH #163775, part of NMNS #49712).

APPEARANCE, PHYSICAL AND OPTICAL PROPERTIES

Whiteite-(CaMnMg) occurs as individual, dull bipyramidal crystals up to 1.5 × 0.5 × 0.5 mm (Fig.1) or anhedral, etched, millimetric blebs (Fig.2). It is yellow, greenish yellow or occasionally pink or pale lavender in color, with a white streak. It is transparent, nonfluorescent in ultraviolet radiation, and has a Mohs hardness of about 3½. The mineral is brittle and has a poor cleavage parallel to (001). The average measured density, as determined by flotation in a bromoform - butyl alcohol solution, is 2.63(2) g/cm^3, which agrees well with the calculated density of 2.64 g/cm^3.

The optical properties of whiteite-(CaMnMg) were measured in sodium light (λ = 589 nm). The mineral is biaxial positive, with indices of refraction α 1.580(1), β 1.584(1) and γ 1.591(1); $2V$(meas.) 81(5)°, $2V$(calc.) 74°. The optical orientation is $Y \parallel b$ and $Z{:}c = +15°$ in the obtuse angle of β. Dispersion was not observed, but there is a slight pleochroism, with

X mauve, *Y* light mauve and *Z* colorless, which indicates that the absorption is $X > Y > Z$. These optical properties do not differ significantly from those of whiteite-(CaFeMg), but there are slight differences in the orientation matrix and pleochroism.

X-RAY CRYSTALLOGRAPHY

X-ray precession photographs show whiteite-(CaMnMg) to be monoclinic, with *P2/a* or *Pa* as possible choices for the space group. Diffraction spots on the precession photographs show a considerable mosaic spread. The unit-cell dimensions were refined from X-ray powder-diffraction data obtained using a 114.6-mm-diameter Debye–Scherrer camera with Cu*Kα* radiation (Table 1). The refined cell-parameters and volume are *a* 14.842(9), *b* 6.976(1), *c* 10.109(4) Å, *β* 112.59(5)°, and *V* 966.3 Å³, with $Z = 2$.

CHEMICAL COMPOSITION

The chemical analysis for elements with atomic number greater than nine was carried out using an ARL–SEMQ electron microprobe with an operating voltage of 15 kV and a sample current of 0.025 mA, measured on brass. A 70-μm beam spot was utilized to minimize the loss of volatiles after first checking for homogeneity with a small spot. The following standards were used: montgomeryite (Al,Ca,P), manganite (Mn), and hornblende (Fe,Mg). The data were corrected using a modified version of the MAGIC–4 program. The resultant composition for the cotype material (NMNS #49712) is given in Table 2, along with that of two other Smithsonian Institution specimens. Specimen #R18801 consists of light yellow crystals, whereas specimen #150085 consists of bright pink, etched, euhedral crystals.

TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR WHITEITE-(CaMnMg)

hkl	*d*calc	*d*obs	*I* est	*d*obs	*I* est
001	9.33	9.31	10	2.203	½
110	6.22	6.23	½	2.138	½
$\bar{1}11$	5.65	5.60	3	2.102	½
011	5.59			2.079	1
$\bar{2}11$	4.92	4.85	5	2.049	½
210	4.89			2.020	½
$\bar{2}02$	4.81			2.007	1
002	4.67	4.65	3	1.989	½
$\bar{1}12$	4.09	4.04	2	1.951	3
$\bar{3}11$	4.02			1.935	3
012	3.88	3.88	2	1.908	1
$\bar{4}01$	3.71	3.73	½	1.865	4
$\bar{3}12$	3.57	3.51	5	1.798	1
020	3.49			1.744	2
400	3.43	3.43	3	1.715	½
021	3.267	3.256	4	1.702	½
003	3.111	3.107	2	1.686	½
220	3.108			1.643	1
$\bar{2}13$	3.027	3.029	½	1.599	½
$\bar{4}03$	2.931	2.953	5	1.584	½
401	2.878	2.867	4	1.564	3
022	2.794	2.790	8	1.554	2
411	2.661	2.664	½	1.539	2
122	2.622	2.610	½	1.518	2
113	2.606	2.590	1	1.491	3
510	2.551	2.547	4		
$\bar{4}21$	2.541				
$\bar{4}22$	2.460	2.468	½		
$\bar{6}02$	2.458				
$\bar{2}23$	2.420	2.417	½		
222	2.401	2.388	½		
213	2.349	2.350	½		
004	2.333	2.328	1		
030	2.325				

CuKα radiation. Cell parameters: *a* 14.842(9), *b* 6.976(1), *c* 10.109(4)Å, β 112.59(5)°.

TABLE 2. CHEMICAL COMPOSITION OF WHITEITE-(CaMnMg) FROM THE TIP TOP PEGMATITE

	49172* yellow	R18801 yellow	150085 pink
Al_2O_3	12.9	13.4	13.6
MgO	9.4	10.1	11.7
CaO	5.6	4.6	6.3
MnO	12.0	12.6	8.8
FeO	1.6	0.9	0.1
P_2O_5	38.2	37.5	37.7
H_2O	20.8**	20.9***	21.8***
Total	100.5	100.0	100.0

* Cotype specimen: $Ca_{0\cdot76}Mn_{1\cdot29}Mg_{1\cdot78}Fe_{0\cdot17}(PO_4)_{4\cdot11}(OH)_{1\cdot46}\cdot 8.1\ H_2O$

** TG-EGA, specimen #49707, yellow

*** H_2O by difference

Water was determined by TG–EGA on a 12.7-mg sample *in vacuo* (specimen NMNS #49707). Between 22 and 950°C, the sample lost a total of 20.8 wt.% H_2O. The three major peaks of evolved gas, at 195, 360 and 500°C, correspond to weight losses of approximately $5H_2O$, $3H_2O$ and $1H_2O$ (probably as OH in the crystal structure), respectively.

For the cotype material the empirical formula (based on 26 oxygen ions) is $(Ca_{0.76}Mn_{0.24})_{\Sigma 1.00}Mn_{1.00}(Mg_{1.78}Fe_{0.17}Mn_{0.05})_{\Sigma 2.00}Al_{1.93}(PO_4)_{4.11}(OH)_{1.46}\cdot 8.1H_2O$, which corresponds to the ideal formula $CaMnMg_2Al_2(PO_4)_4(OH)_2\cdot 8H_2O$.

OCCURRENCE

Whiteite-(CaMnMg) occurs in the Tip Top pegmatite, located in the Black Hills just southwest of the center of Sec. 8, T3S, R4E, approximately 8.5 km southwest of Custer, South Dakota. It was discovered in the outer-intermediate zone of the pegmatite, which consists of large crystals of microcline perthite, triphylite, quartz and muscovite, with minor amounts of beryl, albite, fluorapatite, elbaite and columbite–tantalite. Whiteite-(CaMnMg) is commonly associated with several other secondary phosphate minerals found along fracture surfaces in beryl and quartz. Grice *et al.* (1985) described the paragenesis of these minerals and refer to this new species as "whiteite". On early formed crusts of whitlockite and carbonate–apatite, montgomeryite crystals are deposited, locally with tiptopite. Following these, roscherite, englishite, whiteite-(CaMnMg) and mitridatite formed. Fairfieldite, where present, is the last to crystallize.

To date, whiteite-(CaMnMg) is the only member of the whiteite group found in this portion of the pegmatite. Jahnsite-(CaMnMg), another important member of this group, was described by Moore & Ito (1974) from a different portion of the Tip Top pegmatite, where it occurs as a late-stage product in corroded triphylite–heterosite–ferrisicklerite–rockbridgeite masses.

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