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PARAROBERTSITE, $Ca_2Mn_3^{3+}(PO_4)_3O_2{\cdot}3H_2O$, A NEW MINERAL SPECIES FROM THE TIP TOP PEGMATITE, CUSTER COUNTY, SOUTH DAKOTA, AND ITS RELATIONSHIP TO ROBERTSITE[1]

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ABSTRACT

Pararobertsite is rare, occurring as thin red transparent single plates, or clusters of plates, on whitlockite at the Tip Top pegmatite, Custer County, South Dakota. Associated minerals are carbonate–apatite and quartz. Individual crystals are tabular on {100}, up to 0.2 mm long and are less than 0.02 mm in thickness. The streak is brownish red; luster vitreous; brittle; cleavage on {100} perfect; indiscernible fluorescence under long- or short-wave ultraviolet light; hardness could not be determined, but the mineral apparently is very soft; D (meas.) 3.22 (4), D (calc.) 3.22 (for the empirical formula) or 3.21 g/cm³ (for the idealized formula). Pararobertsite is biaxial negative, α 1.79(1), β 1.81(1), γ 1.83(1), $2V_x$ (meas.) 84 (2)°, $2V_x$ (calc.) 85°, $Y = b$ and $Z \wedge c = 4$ (2)° in the acute β angle. The pleochroism is weak; $Z = Y$ reddish brown, X yellowish brown. Absorption: $Z = Y > X$. Microprobe analyses give Fe_2O_3 0.1, Mn_2O_3 38.0, CaO 18.3, P_2O_5 35.2, H_2O [8.4], sum 100.0 wt.%, which yield the empirical formula $Ca_{8.05}(Mn^{3+}_{11.87}Fe^{3+}_{0.03})_{\Sigma 11.90}(PO_4)_{12.24}O_{7.54}{\cdot}11.5H_2O$ on the basis of O = 68 or, ideally, $Ca_2Mn_3^{3+}(PO_4)_3O_2{\cdot}3\,H_2O$, with $Z = 4$. The symmetry is monoclinic, space-group $P2_1/c$, with a 8.825(3), b 13.258(4), c 11.087(3) Å, β 101.19(4)°, V 1273 (1) Å³, $a{:}b{:}c$ 0.6656:1:0.8363. A pronounced A-centered subcell has $b' = ½\,b$. The unit-cell data are given with the unconventional cell setting $a < c$ in order to facilitate a crystallographic and chemical comparison between it and robertsite. The strongest nine reflections of the X-ray powder-diffraction pattern [d in Å (I) (hkl)] are: 8.69(100)(100), 5.66(60)(021), 5.44(50)(002), 3.179(50)(023), 2.884(60)(300), 2.834(50)(123,042), 2.772(70)($\bar{1}42$), 2.611(60)(142), 2.163(60)(400). The mineral is named for its close relationship to robertsite.

Keywords: new mineral species, pararobertsite, calcium manganese phosphate oxide hydrate, Tip Top pegmatite, Custer County, South Dakota, X-ray data, chemical composition, robertsite.

SOMMAIRE

La pararobertsite, espèce rare, se présente sous forme de plaquettes isolées minces et rouge transparent, ou en agrégats de telles plaquettes, situées sur la whitlockite dans la pegmatite de Tip Top, comté de Custer, Dakota du Sud. Lui sont associés apatite carbonatée et quartz. Les plaquettes, tabulaires sur {100}, atteignent une longueur de 0.2 mm et moins de 0.02 mm en épaisseur. La rayure est rouge brunâtre, et l'éclat, vitreux; cassante; clivage {100} parfait; fluorescence non-discernable en lumière ultra-violette (onde courte ou longue); la dureté, quoique indéterminée, semble très faible; D_{mes} 3.22(4), D_{calc} 3.22 (formule empirique) ou 3.21 (formule idéale). La pararobertsite est biaxe négative, α 1.79(1), β 1.81(1), γ 1.83(1), $2V_x$ (mesuré) 84(2)°, $2V_x$ (calculé) 85°, $Y = b$, $Z \wedge c = 4$ (2)° dans l'angle aigu β. Le pléochroïsme est faible, $Z = Y$ brun rougeâtre, X brun jaunâtre. Absorption: $Z = Y > X$. Les analyses à la microsonde électronique ont donné Fe_2O_3 0.1, Mn_2O_3 38.0, CaO 18.3, P_2O_5 35.2, H_2O [8.4], total 100.0% en poids, ce qui mène à la formule $Ca_{8.05}(Mn^{3+}_{11.87}Fe^{3+}_{0.03})_{\Sigma 11.90}(PO_4)_{12.24}O_{7.54}{\cdot}11.5\,H_2O$ sur un base de 68 atomes d'oxygène ou, idéalement, $Ca_2Mn_3^{3+}(PO_4)_3O_2{\cdot}3H_2O$, avec $Z = 4$. La symétrie est monoclinique, groupe spatial $P2_1/c$, a 8.825(3), b 13.258(4), c 11.087(3) Å, β 101.19(4)°, V 1273(1) Å³, $a{:}b{:}c$ 0.6656:1:0.8363. Une sous-maille centrée sur A évidente possède $b' = ½\,b$. Les paramètres réticulaires sont exprimés en termes d'axes non-conventionnels, $a < c$, afin de faciliter la comparaison cristallographique et chimique avec la robertsite. Les neuf raies les plus intenses du cliché de poudre [d en Å(I)(hkl)] sont: 8.69 (100)(100), 5.66(60)(021), 5.44(50)(002), 3.179(50)(023), 2.884(60)(300), 2.834(50)(123, 042), 2.772(70)($\bar{1}42$), 2.611 (60)(142), 2.163 (60)(400). Le choix du nom souligne le lien étroit qui existe avec la robertsite.

(Traduit par la Rédaction)

Mots-clés: nouvelle espèce minérale, pararobertsite, phosphate et oxyde de calcium et de manganèse hydraté, pegmatite de Tip Top, comté de Custer, Dakota du Sud, données de diffraction X, composition chimique, robertsite.

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*Deceased March, 1987.

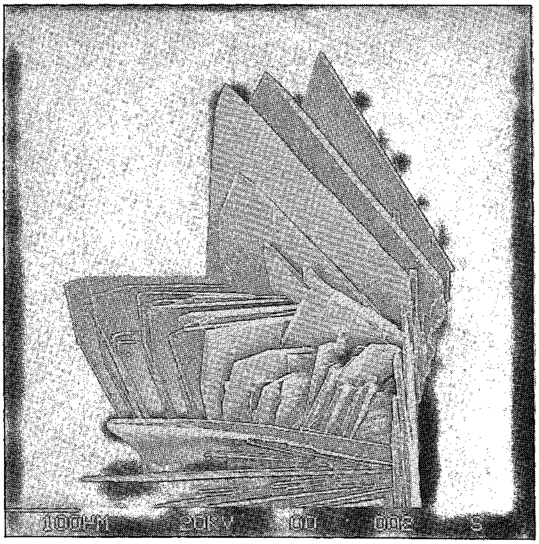

FIG. 1. Scanning electron photomicrograph of a group of pararobertsite crystals, illustrating the typical habit.

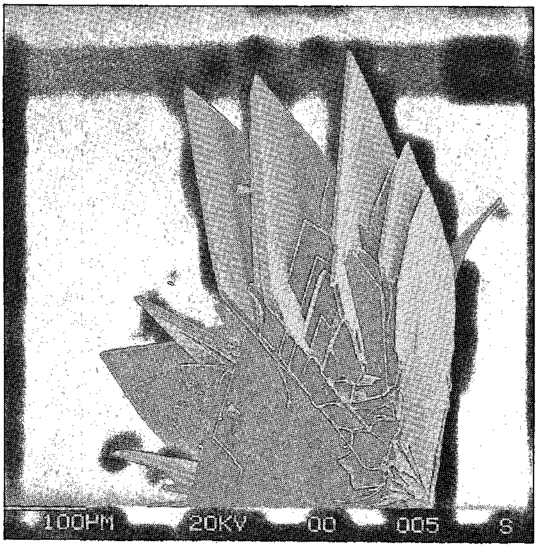

FIG. 2. Scanning electron photomicrograph of the same group of pararobertsite crystals shown in Fig. 1, rotated by 90°.

INTRODUCTION

As part of a continuing investigation of rare minerals found at the Tip Top pegmatite in South Dakota, one of the authors, the late Willard L. Roberts, for whom robertsite was named (Moore & Ito 1974), noticed the occurrence of tiny red crystals. A preliminary investigation showed them to be closely related to robertsite, yet to be different, and they were set aside for several years in the hope of finding additional material. None has been found, despite an assiduous search, and we therefore present the description of the mineral here. The mineral has been named *pararobertsite* for its close chemical and crystallographic relationship to robertsite. The mineral and name have been approved by the Commission on New Minerals and Mineral Names, IMA. Holotype specimens are deposited in the Smithsonian Institution, Washington, D.C. (NMNH #149606) and in the Royal Ontario Museum (M43771).

OCCURRENCE

Pararobertsite occurs in secondary seams at the Tip Top pegmatite, near Custer, Custer County, South Dakota, as single platy crystals 0.02 mm thick and up to 0.2 mm long and in clusters (Figs. 1,2). These crystals occur on whitlockite that encrusts several generations of carbonate–apatite, which itself encrusts quartz. The exact position within the pegmatite is unknown. The mineral is rare at this, the type and only known locality.

PHYSICAL AND OPTICAL PROPERTIES

Pararobertsite is found as red vitreous transparent plates, up to 0.2 mm in longest dimension, that do not exceed 0.02 mm in thickness. The crystals are tabular on {100}. Other forms evident in Figure 1 are too small to measure on an optical goniometer. The mineral possesses a brownish red streak and a perfect cleavage on {100}. The fluorescence is indiscernible under both long- and short-wave ultraviolet light. The crystals are brittle; the hardness could not be determined owing to the small size of the individual crystals and to the lack of sufficient material, but apparently is very soft. The crystals scratched rather easily when touched with a needle. The measured specific gravity, determined using heavy liquid techniques, is 3.22 (4); the calculated density for the empirical formula is 3.22 g/cm^3 and, for the idealized formula, 3.21 g/cm^3.

Optical properties were determined with a spindle stage and white light on crystals previously studied and oriented by X-ray precession single-crystal methods. White light was used for measurement in order to enhance the Becke line (which for this red-colored mineral is virtually invisible in the reddish, high-index-of-refraction oils). In addition, the mineral reacts with immersion oils of index greater than 1.80; the Becke line is visible for only a short duration after the crystal is immersed in the oil. Pararobertsite is biaxial negative, with α 1.79(1), β 1.81(1), γ 1.83(1), $2V_x$ (meas.) 84(2)°, $2V_x$ (calc.) 85°, $Y = b$ and $Z \wedge c = 4(2)°$ in the acute β angle.

In immersion oils the mineral appears dark brown, and only thin plates are transparent. Pleochroism is weak, $Z = Y$ reddish brown, X yellowish brown. The absorption is $Z = Y > X$. Dispersion of the optic axis angle could not be observed because the individual grains are too small to provide a conoscopic figure.

CHEMICAL COMPOSITION

Owing to the paucity of material, pararobertsite was chemically analyzed by means of an electron microprobe, utilizing an operating voltage of 15 kV and a sample current of 0.025 μA, measured on brass. A wavelength-dispersion scan on the microprobe confirmed the absence of any elements with atomic number greater than nine other than those reported herein. The following standards were used for analysis: arrojadite (Fe, P), manganite (Mn), and fluorapatite (Ca, P). Duplicate analyses with other standards confirmed the composition given below. Water could not be determined directly owing to the small amount of material; it was therefore calculated by difference. The resultant analyses yielded Fe_2O_3 0.1, Mn_2O_3 38.0, CaO 18.3, P_2O_5 35.2, H_2O [8.4], sum 100.0 wt.%. The empirical formula, calculated on the basis of 68 oxygen atoms, is: $Ca_{8.05}(Mn^{3+}_{11.87}Fe^{3+}_{0.03})_{\Sigma 11.90}(PO_4)_{12.24}O_{7.54} \cdot 11.5H_2O$, idealized as $Ca_2Mn^{3+}_3(PO_4)_3O_2 \cdot 3H_2O$, with $Z = 4$. This idealized formula requires Mn_2O_3 38.45, CaO 18.21, P_2O_5 34.58, H_2O 8.76, sum 100.00 wt.%.

Calculations using the Gladstone–Dale relationship yield a K_P of 0.252 and a K_C of 0.247 for the idealized formula and measured specific gravity using constants reported by Mandarino (1981); hence $1 - (K_P/K_C)$ is -0.018, indicating superior compatibility (Mandarino 1979). An excellent compatibility of -0.024 is obtained if the empirical formula is used to calculate the chemical molar refractivity.

X-RAY DATA

Single-crystal precession studies of pararobertsite, employing Zr-filtered Mo radiation, were undertaken at both the Geological Survey of Canada and the Royal Ontario Museum. The mineral displays monoclinic symmetry, with measured and calculated unit-cell parameters: a 8.79, b 13.18, c 11.00 Å, β 101.3° derived from zero-level precession photographs. The space-group extinction conditions (hkl all orders, $h0l$ with $l \neq 2n$, and $0k0$ with $k \neq 2n$) dictate that the unique space-group is $P2_1/c$. This cell is in its reduced form, as indicated by a cell-reduction program. There is a very pronounced A-centered monoclinic subcell with $a' = a$, $b' = \frac{1}{2}b$, $c' = c$ and hkl with $k + l \neq 2n$. Single-crystal reflections with $k \neq 2n$ are very weak or absent on both zero- and upper-level precession films. A fully indexed X-ray powder-diffraction pattern is given in Table 1. Unit-cell refinement, based on 23 unambiguously indexed reflections between 3.76 and 1.534 Å, gave: a 8.825(3), b 13.258(4), c 11.087(3) Å, β101.19 (4)°, V 1273(1) Å^3, and a:b:c 0.6656:1:0.8363. The intensities of all indexed reflections were checked on single-crystal precession films. The majority of the X-ray powder lines can be indexed on the pseudocell with $b' = \frac{1}{2}b$. Only a few

TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR PARAROBERTSITE, COMPARED WITH DATA FOR ROBERTSITE

PARAROBERTSITE (This Study)				ROBERTSITE (Moore & Ito 1974)		
Iest.	dÅmeas.	dÅcalc.	hkl	Iest.	dÅmeas.	hkl
100	8.69	8.66	100	100	8.63	200
60	5.66	5.66	021	50	5.61	031
50	5.44	5.44	002			
3	4.97	4.97	$\bar{1}21$			
10	4.53	4.53	121			
20	4.33	4.33	200	20	4.32	500
5	4.11	4.11	210	10	4.14	$\bar{3}31$
20	3.76	3.76	$\bar{2}02$			
3	3.62	3.62	$\bar{2}21$	20	3.48	$\bar{4}31$
40	3.315	3.315	040	20	3.27	033, $\bar{1}33$
50	3.179	3.181	023	40	3.17	160
10	3.095	3.095	140			
5	3.053	3.051	113	10	3.03	260
3	3.013	3.024	212			
		3.010	$\bar{2}13$	10	2.937	233
60	2.884	2.886	300	30	2.876	600
50	2.834	2.834	123			
		2.830	042			
10	2.802	2.801	$\bar{2}23$	10	2.807	004, $\bar{1}62$
70	2.772	2.774	$\bar{1}42$			
15	2.750	2.751	$\bar{1}04$	60	2.749	$\bar{2}04$, 162
40	2.718	2.719	004			
10	2.630	2.632	240			
60	2.611	2.613	142	40	2.590	$\bar{3}62$
10	2.534	2.535	$\bar{2}04$			
20	2.466	2.472	321	20	2.465	602
		2.464	$\bar{3}13$			
3	2.346	2.345	$\bar{3}23$			
3	2.254	2.266	242			
		2.249	152	20	2.223	404
5	2.179	2.183	$\bar{1}15$			
		2.176	340			
60	2.163	2.164	400	30	2.160	800
5b	2.133	2.136	410			
		2.131	$\bar{3}42$			
15	2.101	2.102	044	20	2.112	
		2.100	$\bar{1}25$			
3	2.083	2.082	161			
5	2.065	2.067	025	20	2.048	
5	1.979	1.979	$\bar{1}35$			
10	1.957	1.957	421			
15	1.925	1.926	342			
20	1.884	1.887	063	30	1.899	
		1.881	$\bar{4}04$			
5	1.812	1.813	006			
		1.812	440			
10	1.795	1.797	$\bar{2}63$			
3	1.766	1.765	$\bar{3}61$	20	1.745	
3	1.734	1.732	500			
20	1.704	1.709	106			
		1.705	$\bar{5}21$			
		1.701	361			
		1.699	$\bar{1}55$			
3	1.678	1.679	073			
		1.677	036			
25	1.657	1.657	080			
10	1.642	1.641	442			
5b	1.628	1.628	180	50	1.623	
40	1.614	1.614	$\bar{1}46$			
10	1.591	1.590	046			
5	1.581	1.583	$\bar{2}46$	10	1.585	
3	1.562	1.564	502			
		1.553	404			
30	1.549	1.548	$\bar{5}42$	30	1.542	
		1.548	280			
10	1.534	1.535	540			
				10	1.464	
				20	1.412	
				20	1.375	

- 114.6 mm Gandolfi camera, Fe radiation Mn filter (λFe$K\alpha$ = 1.9373Å)
- b = broad line
- indexed with a 8.825, b 13.258, c 11.087Å, β 101.19°
- intensities estimated visually

TABLE 2. CRYSTALLOGRAPHIC AND OPTICAL DATA FOR PARAROBERTSITE AND ROBERTSITE

	PARAROBERTSITE (this study)	ROBERTSITE (Moore & Araki 1977)
a Å	8.825 (3)	17.36 (2)
b Å	13.258 (4)	19.53 (5)
c Å	11.087 (3)	11.30 (3)
β	101.19 (4)°	96.0°
V Å^3	1273 (1)	3810.2
Space group	$P2_1/c$	Aa
Z	4	8
d (meas.) g/cm^3	3.22	3.13, 3.17
d (calc.) g/cm^3	3.21	3.22*
α	1.79 (1)	1.775 (5)
β	1.81 (1)	1.82 (1)
γ	1.83 (1)	1.82 (1)
2 V (obs.)	$2V_x = 84(2)°$	$2V_x = 8°$
2 V (calc.)	$2V_x = 85°$	–
absorption	$Y = Z > X$	$Y, Z \gg X$
pleochroism	Y, Z reddish brown X yellowish brown	Y, Z deep reddish brown X pale reddish pink
orientation	$b \parallel Y$ $c \wedge Z = 4(2)°$ in acute β	X nearly ⊥ {100}

* calculated for the theoretical formula of end-member robertsite (pers. comm. from P.B. Moore)

weak reflections are indexable on the true cell. We have chosen to present the crystallographic data as described above, and in Tables 1 and 2, using the unconventional setting $a < c$ in order to facilitate comparison with the data for robertsite (see section below). With the conventional setting of $c < a$, the refined unit-cell parameters are: a 11.087(3), b 13.258(4), c 8.825(3) Å, β 101.19(4)°, V 1273(1) Å^3, a:b:c 0.8363:1:0.6656, with space group $P2_1/a$.

DISCUSSION: PARAROBERTSITE COMPARED TO ROBERTSITE

Chemical composition

Robertsite was originally given the formula $Ca_3Mn_4^{3+}(OH)_6(PO_4)_4{\cdot}3H_2O$, with $Z = 8$ (Moore & Ito 1974). More recently, Moore & Araki (1977) reported another formula for robertsite based on detailed crystal-structure analysis, $Ca_6(H_2O)_6Mn_9^{3+}(PO_4)_9O_6{\cdot}3H_2O$, which requires CaO 18.21, Mn_2O_3 38.45, P_2O_5 34.56, H_2O 8.78, sum 100.00 wt.%. We re-analyzed the type robertsite (NMNH #127151), using the same procedures as outlined above for pararobertsite, and obtained CaO 17.9, Fe_2O_3 0.9, Mn_2O_3 38.1, P_2O_5 35.6, and H_2O (determined on another sample, not the type material, by means of the Penfield method) 8.1, sum 100.6 wt.%. Using the Moore & Ito (1974) value of density (3.17 g/cm^3) and a cell volume of 3810.2 Å^3, we obtained unit-cell contents of $Ca_{23.18}Fe_{0.82}^{3+}Mn_{35.05}^{3+}P_{36.43}H_{65.28}O_{200.70}$. These are reasonably close to those required by the formula of Moore & Araki (1977), except for a shortfall in determined H (8.1 wt.% measured H_2O instead of 8.78 wt.% theoretical H_2O). Accepting the crystal structure of mitridatite, and thus the robertsite formula derived from it (Moore & Araki 1977), and assuming a shortfall of 0.68% in our H_2O determination, the formula of Moore & Araki (1977), $Ca_6(H_2O)_6Mn_9^{3+}(PO_4)_9O_6{\cdot}3H_2O$ with $Z = 4$, is substantiated. This gives full cell contents $Ca_{24}(H_2O)_{24}Mn_{36}^{3+}(PO_4)_{36}O_{24}{\cdot}12H_2O$ for robertsite.

The crystallographic data for robertsite and pararobertsite (Table 2) demonstrate a close relationship between these two species. Full cell contents for pararobertsite, $Ca_8Mn_{12}^{3+}(PO_4)_{12}O_8{\cdot}12H_2O$, or $Ca_8(H_2O)_8Mn_{12}^{3+}(PO_4)_{12}O_8{\cdot}4H_2O$, are ⅓ of the full cell contents of robertsite, suggesting a possible relation, and, as well, indirectly supporting our calculation of H_2O by difference. Although we have no direct information as to whether oxygen should be O_8 or $(OH)_{16}$ in our pararobertsite formula, we tentatively adopt O_8 because of the close crystallographic relation to robertsite, which is isostructural with mitridatite, $Ca_6(H_2O)_6Fe_9^{3+}(PO_4)_9O_6{\cdot}3H_2O$ (Moore & Araki 1977). The precise chemical formula for pararobertsite must await a determination of its crystal structure.

Crystallography

The X-ray powder-diffraction patterns of robertsite and pararobertsite (Table 1), although similar, show distinct differences. The most prominent of these, especially in the lower 2θ region, are the splitting of the 5.61 Å reflection of robertsite into 5.66 and 5.44 Å reflections for pararobertsite, and the splitting of the 2.876 Å reflection of robertsite into 2.884 and 2.834 Å reflections for pararobertsite. Other differences are present and clearly evident in Table 1.

Single-crystal precession films obtained from type robertsite (NMNH #127151) and from pararobertsite display many similarities but, like their powder patterns, show distinct differences. The $h0l$ precession single-crystal films of both minerals are similar and give an almost identical value of a^*. Both the c^* of pararobertsite and the c^* of robertsite are present as strongly diffracting rows on both sets of films. However, the presence and position of other reflections on these zero-level films and on upper-level films clearly indicate that a different c^* and, consequently, a different β angle must be chosen for each mineral. Both minerals also show pseudohexagonal symmetry in the $0kl$ plane. In robertsite, the angle between the directions [010] and [011] is 60°00 (5)′, with identical values of d along both rows. A similar relationship exists between directions [001] and [031], where the corresponding d values [5.59 for (002) and 5.61 Å for (031)] are virtually identical. In pararobertsite, this pseudosymmetry is not as well expressed; the angle between the directions [001] and [021] is 58°40 (5)′, and the d values along each row are slightly different. These differences are clearly evident in the X-ray powder-diffraction data, as shown in the d values of the diffraction maxima (021)(d = 5.66) and (002)(d = 5.44 Å). Crystallographic and optical data for both robertsite and pararobertsite are compared in Table 2.

The unit-cell relationships between robertsite and pararobertsite may be summarized as follows: $a^*_{\text{robertsite}} \simeq \frac{1}{2} a^*_{\text{pararobertsite}}$, $b_{\text{robertsite}} \simeq 3/2\, b_{\text{pararobertsite}}$, $c^*_{\text{robertsite}} \simeq c^*_{\text{pararobertsite}}$, $[001]_{\text{robertsite}} \simeq [\bar{1}04]_{\text{pararobertsite}}$, $V_{\text{robertsite}} \simeq 3V_{\text{pararobertsite}}$.

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