

MCAUSLANITE, A SUPERGENE HYDRATED IRON ALUMINUM FLUOROPHOSPHATE FROM THE EAST KEMPTVILLE TIN MINE, YARMOUTH COUNTY, NOVA SCOTIA*

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ABSTRACT

The new mineral species mcauslanite, $\text{HFe}_2\text{Al}_2(\text{PO}_4)_4\text{F}\cdot 18\text{H}_2\text{O}$, occurs as clusters of radiating crystals on fracture surfaces in leucomonzogranite at the East Kemptville greisen-hosted tin mine, Yarmouth County, Nova Scotia. These clusters, up to 4 mm across, of clear, radiating, tabular to acicular yellowish white fibers and bladed crystals have a silky to vitreous luster, white streak and $H = 3.5$. Cleavage is good parallel to [001]. $D_{\text{meas}} 2.22(2)$, $D_{\text{calc}} 2.17 \text{ g/cm}^3$. Mcauslanite is nonpleochroic, biaxial negative, $\alpha 1.522(1)$, $\beta 1.531(1)$, $\gamma 1.534(1)$, $2V_{\text{meas}} 55(5)^\circ$, $2V_{\text{calc}} 59.7^\circ$. Indicatrix orientation is $X:b = 17^\circ$ in β obtuse, $Y:c = 18^\circ$ in α obtuse and $Z:a = 14^\circ$ in γ obtuse, absorption and dispersion not observed. The symmetry is triclinic, space group $P1$ or $\bar{P}1$, with $a 10.055(5)$, $b 11.568(5)$, $c 6.888(5) \text{ \AA}$, $\alpha 105.84(6)^\circ$, $\beta 93.66(6)^\circ$, $\gamma 106.47(5)^\circ$, $Z = 1$, $V = 730.43(1.81) \text{ \AA}^3$ and $a:b:c = 0.8692:1:0.5954$. Twinning occurs as a 180° rotation about a^* . The (010) face has a twin suture. The strongest eight lines in the X-ray powder-diffraction pattern [d in $\text{Å}(hkl)$] are: 10.6(90)(010), 9.53(85)(100), 6.55(70)(001), 5.41(25)($\bar{1}20$), 4.96(100)(011,02 $\bar{1}$), 3.436(35)(012), 2.812(55)(310), 2.785(45)($\bar{1}40$). The preferred formula, derived from electron-microprobe and TG-EGA analyses, is $\text{H}_{1.02}(\text{Fe}^{2+}_{2.40}\text{Mn}_{0.67})_{\Sigma 3.07}\text{Al}_{2.08}(\text{PO}_4)_{4.10}\text{F}_{1.10}\cdot 17.49\text{H}_2\text{O}$, based on 35 (O+F) anions per unit cell. Fluorapatite, triplite, vivianite, phosphophyllite and childrenite-eosphorite are associated phosphate minerals. The mineral name honors Dr. David A. McAuslan, who coordinated the discovery of the deposit.

Keywords: mcauslanite, new mineral species, hydrated iron aluminum fluorophosphate, greisen, East Kemptville tin mine, Nova Scotia, electron-microprobe data, X-ray-diffraction data, optical data, thermal analysis.

SOMMAIRE

La mcauslanite, dont la formule idéale est $\text{HFe}_2\text{Al}_2(\text{PO}_4)_4\text{F}\cdot 18\text{H}_2\text{O}$, est une nouvelle espèce minérale qui se présente en agrégats le long de fractures et de diaclases exposées dans le leucomonzogranite altéré de la mine d'étain de East Kemptville, comté de Yarmouth, en Nouvelle-Écosse. Ces agrégats fibroradiés atteignent 4 mm, et sont constitués de fibres et de lames incolores à blanc jaunâtre, tabulaires à aciculaires, entre 1 et 4 mm de long et un maximum de 0.2 mm de large. La mcauslanite possède un éclat soyeux à vitreux; sa rayure est blanche, et sa dureté, 3.5. Elle n'est pas fluorescente. Le minéral présente un bon clivage parallèle à [001]. Densité mesurée est de 2.22(2), et calculée est de 2.17. La mcauslanite n'est pas pléochroïque; elle est biaxiale négative, $\alpha 1.522(1)$, $\beta 1.531(1)$, $\gamma 1.534(1)$, $2V$ (mesuré) $55(5)^\circ$, $2V$ (calculé) 59.7° . L'orientation de l'indicatrice est: $X:b = 17^\circ$ dans l'angle obtus de β , $Y:c = 18^\circ$ dans l'angle obtus de α , et $Z:a = 14^\circ$ dans l'angle obtus de γ . Il n'y a ni absorption, ni dispersion. La symétrie est triclinique; son groupe spatial $P1$ ou $\bar{P}1$ (aspect de diffraction P^*), $a 10.055(5)$, $b 11.568(5)$, $c 6.888(5) \text{ \AA}$, $\alpha 105.84(6)^\circ$, $\beta 93.66(6)^\circ$, $\gamma 106.47(5)^\circ$, $Z = 1$, $V = 730.43(1.81) \text{ \AA}^3$, $a:b:c = 0.8692:1:0.5954$. Les cristaux sont maclés par rotation de 180° sur a^* . Il y a une suture de maclé sur (010). Les huit raies les plus intenses du cliché de poudre [d en $\text{Å}(hkl)$] sont: 10.6(90)(010), 9.53(85)(100), 6.55(70)(001), 5.41(25)($\bar{1}20$), 4.96(100)(011,02 $\bar{1}$), 3.436(35)(012), 2.812(55)(310), 2.785(45)($\bar{1}40$). La formule déterminée par l'analyse à la microsonde électronique, l'analyse thermogravimétrique et l'analyse des gaz émis est $\text{H}_{1.02}(\text{Fe}^{2+}_{2.40}\text{Mn}_{0.67})_{\Sigma 3.07}\text{Al}_{2.08}(\text{PO}_4)_{4.10}\text{F}_{1.10}\cdot 17.49\text{H}_2\text{O}$, en supposant 35 anions de O et F par maille. Les minéraux phosphatés associés sont: fluorapatite, triplite, vivianite, phosphophyllite et childrenite-eosphorite. Le nom du minéral honore M. David A. McAuslan, géologue en chef de l'exploration pour l'Est du Canada, Shell Canada Resources Limited.

Mots-clés: mcauslanite, nouvelle espèce minérale, fluorophosphate de fer et d'aluminium hydraté, greisen, mine d'étain, East Kemptville, Nouvelle-Écosse, données à la microsonde électronique, données aux rayons X, données optiques.

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INTRODUCTION

Mcauslanite, ideally $\text{HFe}_3\text{Al}_2(\text{PO}_4)_4\text{F}\cdot 18\text{H}_2\text{O}$, is a new mineral species encountered during routine X-ray powder-diffraction characterization of minerals from the greisen-hosted East Kemptville tin deposit (lat. $44^\circ 06' \text{N}$, long. $65^\circ 41' \text{W}$), Yarmouth County, southwestern Nova Scotia. This deposit, North America's only producing primary tin mine, is owned by East Kemptville Tin Corporation and is currently managed by Rio Algom Limited. The property was held previously by Shell Canada Resources Ltd. The mine is located within the fluorine- and phosphate-rich Davis Lake granitic complex, beneath an irregular inflection in the contact between granite and metasedimentary host-rocks. Cassiterite is the principal tin mineral and occurs in a stockwork of greisen-bordered zones and massive quartz-topaz greisen. The geology of the deposit is further documented by Richardson *et al.* (1982) and

Richardson (1983, 1988a, b). Mcauslanite is the first new mineral reported from this area, but other known phosphates include fluorapatite, triplite (Mandarino *et al.* 1984), childrenite-eosphorite, phosphophyllite and vivianite. This description is based on material from the four known mcauslanite clusters.

Mcauslanite is named in honor of Dr. David A. McAuslan (1943–), formerly Eastern Exploration manager for Shell Canada Resources Ltd. Between 1977 and 1982, his guidance and encouragement were instrumental in the initial discovery and subsequent development of the East Kemptville deposit. The new mineral species and mineral name were approved by the Commission on New Minerals and Mineral Names, I.M.A. Only one hand specimen containing mcauslanite clusters is known. It contains several milligrams of the mineral and is part of the Systematic Reference Collection of the National Mineral Collection at the Geological Survey of Canada, Ottawa, Ontario (catalog number NMC64806). One grain of mcauslanite and an X-ray powder-diffraction pattern are entered in the mineral collection at the Department of Earth Sciences, Carleton University (catalogue number CU4427).

PHYSICAL AND OPTICAL PROPERTIES

Mcauslanite occurs on open joints or fracture surfaces in sericitized leucomonzogranite as clear, yellowish white, transparent, vitreous blades and translucent silky fibres that do not exceed 1 mm in length and 0.2 mm in width. The largest cluster of radiating crystals measures up to 4 mm across. The mineral has a white streak, a hardness of 3.5, is nonfluorescent and brittle, shows good cleavage parallel to $\{001\}$, and does not effervesce in dilute HCl. Individuals blades are terminated by the forms $\{010\}$ major, $\{100\}$ minor and $\{001\}$ very minor. The (010) face also shows a twin suture. Suspension of mcauslanite in heavy liquids gave a measured density of $2.22(2) \text{ g/cm}^3$. The density calculated using the ideal formula is 2.17 g/cm^3 .

Optical measurements were made on a spindle stage using sodium light (λ 589 nm). Mcauslanite is biaxial negative, α 1.522(1), β 1.531(1), γ 1.534(1); $2V_{\text{meas}}$ is $55(5)^\circ$, close to $2V_{\text{calc}}$ 59.7° . There is no pleochroism, absorption or dispersion. The orientation of the indicatrix is $X:b = 17^\circ$ in β obtuse, $Y:c = 18^\circ$ in α obtuse and $Z:a = 14^\circ$ in γ obtuse.

X-RAY CRYSTALLOGRAPHY

Two transparent blades of mcauslanite, one mounted parallel to and the other perpendicular to the axis of elongation $\{001\}$, were examined by precession single-crystal techniques using Zr-filtered

TABLE 1. X-RAY POWDER DATA FOR MCAUSLANITE

test.	d λ_{meas}	d λ_{calc}	hkl	test.	d λ_{meas}	d λ_{calc}	hkl
90	10.6	10.57	010	5	2.307	2.309	$\bar{4}2\bar{1}$
85	9.53	9.53	100	10	2.266	2.267	$3\bar{1}\bar{2}$
5	8.51	8.53	$\bar{1}10$			2.227	$1\bar{2}\bar{3}$
70	6.55	6.55	001	10	2.222	2.226	041
3	5.88	5.83	$10\bar{1}$			2.218	05 $\bar{1}$
25	5.41	5.39	$\bar{1}20$			2.188	$\bar{1}32$
		4.93	011	10	2.184	2.183	003
100	4.96	4.91	$02\bar{1}$			2.175	03 $\bar{3}$
20	4.77	4.76	200			2.142	$33\bar{1}$
3	4.28	4.27	$\bar{2}20$	15	2.140	2.140	$\bar{1}3\bar{3}$
5	4.10	4.11	120	3	2.113	2.114	$3\bar{3}\bar{1}$
20	3.77	3.77	$\bar{1}21$	1	2.087	2.087	$\bar{3}30$
20	3.68	3.70	$\bar{1}30$			2.062	$\bar{1}13$
3	3.61	3.66	$\bar{1}3\bar{1}$			2.060	103
5	3.52	3.61	021	5	2.056	2.060	330
35	3.436	3.52	030			2.054	240
10	3.347	3.437	$0\bar{1}\bar{2}$			2.010	$23\bar{3}$
10	3.265	3.345	$\bar{3}10$			2.008	$42\bar{1}$
10	3.201	3.261	$2\bar{3}\bar{1}$	5	2.008	2.006	$\bar{1}4\bar{3}$
20	3.175	3.201	$\bar{3}20$			2.004	$52\bar{0}$
3	3.126	3.176	300			1.989	222
3	2.960	3.126	$\bar{1}2\bar{2}$	3	1.988	1.988	$\bar{3}10$
10	2.916	2.960	102			1.954	420
10		2.915	202	5	1.947	1.943	$\bar{3}03$
10		2.889	012			1.939	150
55		2.873	$03\bar{2}$	5	1.934	1.939	$\bar{1}31$
45		2.812	2809			1.929	$14\bar{3}$
3		2.785	$\bar{1}40$	2	1.919	1.919	$\bar{1}6\bar{1}$
3		2.723	$\bar{3}\bar{3}\bar{1}$	10	1.880	1.879	$\bar{1}42$
3		2.647	040	10	1.851	1.852	$\bar{2}60$
5		2.603	222			1.831	023
15		2.511	$2\bar{3}\bar{2}$	10	1.829	1.828	$\bar{2}62$
5		2.482	$\bar{3}31$			1.827	$2\bar{5}\bar{1}$
1		2.421	230			1.800	402
10		2.419	$\bar{3}40$	10	1.798	1.798	$\bar{3}60$
		2.406	$\bar{3}4\bar{1}$			1.794	$34\bar{2}$
			$\bar{3}12$				
			$\bar{4}11$				

- 114.6 mm Gandolfi camera, Co radiation, Fe filter (λ Co $K\alpha = 1.79021 \text{ \AA}$)
 - intensities estimated visually
 - indexed on a 10.055, b 11.568, c 6.888 \AA , α 105.84°, β 93.66°, γ 106.47°

Mo radiation. The levels collected were $h01$ – $h31$, $0k1$ – $3k1$ and $hk0$ – $hk2$. The symmetry is triclinic, and measurements of zero-level precession films gave d_{100} 9.48, d_{010} 10.54, d_{001} 6.51 Å, α^* 72.33°, β^* 81.17° and γ^* 71.67°. Possible space-groups are $P1(1)$ or $P\bar{1}(2)$ (diffraction aspect P^*). Twinning by 180° rotation about a^* was observed on $h0l$ precession photographs. A fully indexed X-ray powder-diffraction pattern is given in Table 1. Based on 21 powder lines between 3.77 and 1.851 Å for which unambiguous indexing was possible, the refined reduced unit-cell parameters are a 10.055(5), b 11.568(5), c 6.888(5) Å, α 105.84(6)°, β 93.66(6)°, γ 106.47(5)°, V 730.43(1.81) Å³, $Z = 1$ and $a:b:c = 0.8692:1:0.5954$.

CHEMICAL COMPOSITION

The electron-microprobe data (Table 2, column 1) for all elements with an atomic number greater than 8 were obtained using an ARL-SEMQ electron microprobe using maricite (Na,Fe), montgomeryite (Ca,Mg,Al,P), fluorapatite (F) and manganite (Mn) as standards. Analyses were done at 15 kV and a specimen current of 0.025 μ A measured on brass. The data were corrected using standard Bence-Albee factors (Bence & Albee 1968).

H₂O contents were determined by TG-EGA on two samples using a Mettler Thermoanalyzer and an integrated mass spectrometer. One sample, weighing 1.6 mg, was purified by hand-picking, and the other, weighing 1.4 mg, was purified in methylene iodide – acetone density columns. Larger samples could not be used owing to the restricted amount of material available. Both samples were subjected to 98% relative humidity prior to weighing, and were then placed under high vacuum for several hours at 30°C. This treatment gave an averaged loss of 21 wt.%. A further loss averaging 13 wt.% was noted from 30 to 450°C, with H₂O pressure maxima between 110 and 160°C. Minor HF (<1 wt.%) also evolved from 300 to 400°C. Water contents totalled 34 and 35 wt.%, respectively, for the two samples.

The decomposition of mcauslanite was characterized by the evolution of substantial amounts of water at relatively low temperatures. At higher temperatures, the loss of water slowed gradually. This feature suggests that an appreciable amount of water may be of an interlayer or zeolitic nature. There was insufficient material to determine whether the anhydrous product is capable of rehydration.

Results of the electron-microprobe analysis (Table 2, column 1) sum to 84.8 wt.%. With the addition of the water content determined by TG-EGA analysis, the raw data sum to 117.6 wt.%. We ascribe this anomalous result to the loss of loosely held H₂O under vacuum during carbon coating and electron-microprobe analysis. This loss results in a

TABLE 2. CHEMICAL COMPOSITION OF MCAUSLANITE

	1.	2.	3.
FeO (wt.%)	23.0	18.1	22.78
MnO	6.3	5.0	-
Al ₂ O ₃	14.1	11.1	10.78
P ₂ O ₅	38.6	30.5	30.02
H ₂ O	-	34	35.25
F	2.8	2.2	2.01
Sum	84.8	100.9	100.85
-O=F		0.9	0.85
Total		100.0	100.00

1. Primary electron-microprobe data

2. Electron-microprobe data normalized to 100 wt.%

with 34 wt.% H₂O. Analytical formula is H_{1.02}

(Fe²⁺_{2.40} Mn_{0.57})_{23.07} Al_{2.08} (PO₄)_{4.10} F_{1.10} · 17.49H₂O.

Numbers of cations based on 35 O+F anions per unit cell.

3. Ideal composition of HFe²⁺₃Al₂(PO₄)₄ F · 18H₂O.

corresponding increase in the determined proportions of the major elements (wt. % oxides). Accordingly, the microprobe data given in column 2 of Table 2 have been normalized to 100 wt.%, assuming an average of 34 wt.% H₂O.

Depending on the oxidation state of iron, these data can be interpreted as either (Fe²⁺,Mn)₂(Al,Fe³⁺)₃(PO₄)₄F · 18H₂O or H(Fe²⁺,Mn)₃Al₂(PO₄)₄F · 18H₂O based on 35 (O+F) anions per unit cell. The extreme scarcity of material precluded a good titration for Fe²⁺, but microchemical tests indicate that Fe²⁺ is dominant, with only minor concentrations of Fe³⁺. The association of several Fe²⁺-bearing phosphate minerals in the deposit (triplite, vivianite, phosphophyllite and childrenite-eosphorite) supports this assumption. Because a weak positive reaction for Fe³⁺ could have been caused by surface alteration, and because Al is close to the stoichiometric value (2.08 atoms per 4.10 P), we have chosen to present the ideal formula as HFe²⁺₃Al₂(PO₄)₄F · 18H₂O based on the combined and recalculated electron-microprobe and TG-EGA results (Table 2, column 2). The ideal values for the end member are listed in column 3, Table 2. The analyzed material is thus a manganous mcauslanite.

Using Gladstone-Dale constants from Mandarino (1976, 1979) and the normalized proportions of oxides (Table 2, column 2), a K_C value of 0.2375 was obtained. K_P calculated using the averaged indices of refraction and the measured density is 0.2384. Thus, $1 - (K_P/K_C)$ is -0.0034, indicating superior compatibility between the physical and chemical data (Mandarino 1981). Recalculation using the calculated density of 2.17 g/cm³ resulted in excellent compatibility.

OCCURRENCE

Transition-metal phosphate minerals occur in various geological settings including complex pegmatites, hydrothermal vein sequences and greisens, and as a fracture-filling in phosphatic ironstone. Genetic interrelationships among the first three styles of mineralization are documented schematically by Strong (1981). Volatile- and metal-dominated magmatic fluid regimes are similar. Within the East Kemptville deposit, a complex group of hydrothermal veins and fractures cross-cut leucomonzogranite and greisen (Richardson *et al.* 1982, Richardson 1988a, b). Several types of veins are distinguishable on the basis of mineralogy, associated alteration and cross-cutting relationships.

Apatite is present as a primary magmatic accessory mineral in the leucomonzogranite. The hydrothermal phosphate-bearing veins cross-cut cassiterite-topaz greisen and do not have alteration envelopes. Colorless quartz-, sulfide-, phosphate- and fluorite-bearing veins are divided into three suites. The oldest suite contains quartz, fluorite, sphalerite, pyrite, pyrrhotite, chalcopyrite and very minor galena. The second oldest contains quartz, sulfides, fluorite, abundant cream-pink triplite (Mandarino *et al.* 1984) and rare crystals of green apatite. Both types of veins are common throughout the deposit. The third group of veins, which is the youngest and the least common, contains only quartz, triplite and rare apatite. This group of veins is cross-cut in turn by *en échelon* "ribbed" veins, 1 to 50 cm long by 1 cm wide, that contain 2-mm-wide bands of colorless quartz, albite, rare apatite and triplite. Apatite occurs also as small (1 to 2 mm) subhedral, green crystals.

Mcauslanite, vivianite, phosphophyllite and childrenite-eosphorite occur as part of a complex assemblage of carbonate-group, phosphate-group and zeolite-group supergene minerals. These supergene phosphates do not obviously replace primary magmatic or hydrothermal phosphates, but occur as open-space fillings within joints and shear zones near the erosional surface. Tabular crystals and sheared plates of vivianite are common. Mcauslanite, phosphophyllite and childrenite-eosphorite are rare; to date, only one occurrence of each is known from the deposit. The supergene phosphate minerals are located near the southern roof-pendant, a part of the deposit that contains many phosphate-bearing hydrothermal veins. Much of the rock that had been exposed at the surface in this locality is now mined out, but additional samples of mcauslanite, phosphophyllite and childrenite-eosphorite may be obtained when the pit is expanded.

At East Kemptville, both granite and greisen are poor in Ca(Sr), Ba and Li, and are rich in F and Fe; thus, compositional variation is restricted in the phosphate mineral suite. Triplite is the most abun-

dant species, apatite is much less common, and triphylite and triploidite are not present. Vivianite is the most abundant supergene mineral; mcauslanite, phosphophyllite and childrenite-eosphorite are very rare.

DISCUSSION

The predominance of ferrous iron in the hydrothermal mineral triplite and supergene minerals vivianite, mcauslanite and childrenite-eosphorite indicates that Fe^{2+} was the dominant valence-state of iron for a significant period of time at East Kemptville (*i.e.*, during the transition from hydrothermal to meteoric water; Richardson 1988a). As Fe^{2+} -bearing phosphates are susceptible to oxidation (Fransolet *et al.* 1986), it seems reasonable to assume that the $f\text{O}_2$ also was low during that interval. At present, vivianite is blue in color, not green, indicating that more oxidizing conditions have commenced.

Below 250–300°C, primary phosphate minerals will be altered to vivianite or ludlamite when placed in contact with an aqueous phase (Moore & Molin-Case 1974). The lack of alteration and absence of open space in quartz-triplite veins suggest that these veins closed above this temperature range. The supergene phosphate minerals vivianite, phosphophyllite, childrenite-eosphorite and mcauslanite probably crystallized below 250–300°C. The 21 wt.% loss at 30°C and further 13 wt.% loss between 30 and 450°C, as determined by TG-EG analysis of mcauslanite, supports such an assumption.

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