

## POUDRETTEITE, $\text{KNa}_2\text{B}_3\text{Si}_{12}\text{O}_{30}$ , A NEW MEMBER OF THE OSUMILITE GROUP FROM MONT SAINT-HILAIRE, QUEBEC, AND ITS CRYSTAL STRUCTURE

JOEL D. GRICE, T. SCOTT ERCIT AND JERRY VAN VELTHUIZEN

Mineral Sciences Division, National Museum of Natural Sciences, Ottawa, Ontario K1A 0M8

PETE J. DUNN

Department of Mineral Sciences, Smithsonian Institution, Washington, D.C. 20560, U.S.A.

### ABSTRACT

Poudretteite is a new mineral species from the Poudrette quarry, Mont Saint-Hilaire, Quebec. It occurs in a marble xenolith included in nepheline syenite, associated with pectolite, apophyllite, quartz and minor aegirine. It forms clear, colorless to very pale pink, equidimensional, subhedral prisms up to 5 mm. It is brittle,  $H$  about 5, with a splintery fracture;  $D_{\text{meas.}}$  2.51(1)  $\text{g/cm}^3$ ,  $D_{\text{calc.}}$  2.53  $\text{g/cm}^3$ . Uniaxial positive,  $\omega$  1.516(1),  $\epsilon$  1.532(1). It is hexagonal, space group  $P6/mcc$ ,  $a$  10.239(1),  $c$  13.485(3) Å and  $Z=2$ . The strongest ten X-ray-diffraction lines in the powder pattern [ $d$  in Å( $hkl$ )] are: 6.74(30)(002), 5.13 (100)(110), 4.07(30)(112), 3.70(30)(202), 3.369(30)(004), 3.253(100)(211), 2.956(40)(300), 2.815(60)(114), 2.686(50)(213,204) and 2.013(30)(321). An analysis by electron microprobe gave:  $\text{SiO}_2$  77.7,  $\text{B}_2\text{O}_3$  11.4,  $\text{K}_2\text{O}$  5.2,  $\text{Na}_2\text{O}$  6.2, sum 100.5 wt.%, which yields the empirical formula  $\text{K}_{1.00}(\text{Na}_{1.87}\text{K}_{0.04})_{\Sigma 1.91}\text{B}_{3.05}\text{Si}_{12.14}\text{O}_{30}$ . The structure, which is isotopic with that of osumilite, was refined to  $R=3.0\%$ , and is ordered with K in a [12]-co-ordinated C-site, Na in octahedrally co-ordinated A site, B in tetrahedrally co-ordinated T2 site, Si in tetrahedrally co-ordinated T1 site, and the B site is vacant.

**Keywords:** poudretteite, new mineral species, osumilite group, Mont Saint-Hilaire, borosilicate, structure refinement.

### SOMMAIRE

On a découvert la poudretteite, nouvelle espèce minérale, dans la carrière Poudrette, au mont Saint-Hilaire (Québec). On la retrouve dans une enclave de marbre dans la syénite néphélinique, associée à pectolite, apophyllite, quartz, et aegirine en traces. Les prismes hypidiomorphes, équidimensionnels, transparents, et incolores à rose pâle atteignent 5 mm. Elle est cassante, de dureté environ 5, et montre une cassure en écailles. Densité 2.51(1) (mesurée), 2.53 (calculée). Les cristaux sont uniaxiaux positifs,  $\omega$  1.516(1),  $\epsilon$  1.532(1). Symétrie hexagonale, groupe spatial  $P6/mcc$ ,  $a$  10.239(1),  $c$  13.485(3) Å,  $Z=2$ . Les dix raies les plus importantes du cliché de poudre [ $d$  en Å ( $hkl$ )] sont: 6.74(30)(002), 5.13(100)(110), 4.07(30)(112), 3.70(30)(202), 3.369(30)(004), 3.253(100)(211), 2.956(40)(300), 2.815(60)(114), 2.686(50)(213,204), et 2.013(30)(321). L'analyse à la microsonde électronique a donné (% en poids):  $\text{SiO}_2$  77.7,  $\text{B}_2\text{O}_3$  11.4,  $\text{K}_2\text{O}$  5.2,  $\text{Na}_2\text{O}$  6.2, total 100.5, d'où la formule empirique  $\text{K}_{1.00}(\text{Na}_{1.87}\text{K}_{0.04})_{\Sigma 1.91}\text{B}_{3.05}\text{Si}_{12.14}\text{O}_{30}$ . La structure, affinée à un résidu  $R$  de 3%, est isotypique de celle de l'osumilite. Elle est ordonnée; le potassium occupe la

position C à coordinance XII, le sodium, la position A à une coordinance VI, le bore, la position T2 à coordinance IV, le silicium, la position T1 à coordinance IV, et la position B est vacante.

**Mots-clés:** poudretteite, nouvelle espèce minérale, groupe de l'osumilite, mont Saint-Hilaire, borosilicate, affinement de la structure.

### INTRODUCTION

The optical and physical properties of members of the osumilite group are similar to those of common minerals such as quartz and cordierite; for this reason, they are probably generally overlooked. However, it is becoming more evident that the group is quite widespread in occurrence. In an ongoing study of the mineralogy of the Mont Saint-Hilaire alkaline complex, two members of the osumilite group have been identified: milarite and the new species *poudretteite* (pronounced: PÜ-DRETÏT).

There are presently thirteen mineral species in the osumilite group; these occur in a variety of geological environments. Merrihueite, roedderite and yagiite are found in meteorites. Eifelite, osumilite and osumilite-(Mg) are associated with volcanic rocks or high-temperature contact-metamorphic aureoles. The remainder of the group, armenite, brannockite, darapiosite, milarite, poudretteite (present study), sogdianite and sugilite, are found in alkali-rich rocks such as syenites, alkalic granites and calcite veins. This diversity in chemistry and geological environment make the group interesting.

Grew (1982) described osumilite as an important rock-forming mineral. Hemingway *et al.* (1984) have studied its thermodynamic properties. Structure refinements of several of the species have been performed, and Černý *et al.* (1980) described the crystal chemistry of milarite in detail.

Poudretteite is named in honor of the Poudrette family, which operates the Carrière R. Poudrette, Mont Saint-Hilaire, Rouville Co., Quebec. The name and mineral description have been approved by the I.M.A. Commission on New Minerals and Mineral Names. The type material comes from this quarry; it comprises cotypes NMNS #51743 and NMNS

#51791, deposited in the National Museum of Natural Sciences, Ottawa, and a cotype at the Smithsonian Institution, Washington, D.C. (NMNH #163776). To date, seven crystals are known, each a few millimetres in size.

### OCCURRENCE

There is extensive literature on the mineralogy and geology of the alkali gabbro – syenite complex at Mont Saint-Hilaire, one of the ten Monteregian Hills. This virtually linear series of monadnocks rises above the platform of the Saint Lawrence Lowlands between Oka and Megantic. The recent field-trip guidebook of Mandarino *et al.* (1986) contains a description of the geology and mineralogy of Mont Saint-Hilaire and a comprehensive list of references.

The study specimens were collected from the quarry in the mid 1960s by M. Jacques Bradley. Poudretteite occurs in the marble xenoliths within the nepheline syenite breccia, associated with pectolite and apophyllite, and with minor aegirine. Milarite was found in this assemblage as well, but not as a direct associate of poudretteite.

### PHYSICAL AND OPTICAL PROPERTIES

Poudretteite resembles anhedral quartz, and it can be confused with associated apophyllite. It is colorless to very pale pink and transparent with a vitreous lustre; it has a white streak, and shows no fluorescence with either LW or SW ultraviolet light. Crystals are roughly equant, deeply etched, barrel-shaped prisms measuring up to 5 mm. Poudretteite is relatively hard (Mohs hardness ~5), brittle, with

no apparent cleavage; it has a splintery to conchoidal fracture. The density, measured with a Berman balance and temperature-corrected, is 2.51(1) g/cm<sup>3</sup>, which agrees well with the calculated density of 2.53 g/cm<sup>3</sup>.

Poudretteite is uniaxial positive, with indices of refraction  $\omega$  1.516(1) and  $\epsilon$  1.532(1), measured with sodium light (gel-filtered,  $\lambda$  589.9 nm). The mineral displays sharp extinctions and a sharp uniaxial figure with no biaxial distortions, as are observed in many specimens of milarite.

### CHEMICAL COMPOSITION

Specimen NMNH #163776 was analyzed with an ARL-SEMQ microprobe with operating conditions of 15 kV, sample current 25 nA (measured on brass) and a focused beam. The following standards were used: volcanic glass (Si), microcline (K), and synthetic plagioclase, An<sub>40</sub> (Na). Specimen NMNS #51791 was analyzed for boron with a JEOL 733 microprobe operating at 5 kV, 100 nA (measured on a Faraday cup), 40 s collection time, using lead stearate as the analyzing crystal and a defocused beam (40  $\mu$ m). Synthetic Ni<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> was used as a standard for B. Poudretteite is very stable under the electron beam; cathodoluminescence was not observed. Beryllium and lithium were sought but not detected by ICP and AA, respectively.

The chemical analytical data are: SiO<sub>2</sub> 77.7, B<sub>2</sub>O<sub>3</sub> 11.4, BeO 0.0, Li<sub>2</sub>O 0.0, K<sub>2</sub>O 5.2, Na<sub>2</sub>O 6.2, sum 100.5 wt.%. Based on 30 oxygen atoms, this gives the empirical formula K<sub>1.00</sub>(Na<sub>1.87</sub>K<sub>0.04</sub>)<sub>Σ1.91</sub>B<sub>3.05</sub>Si<sub>12.14</sub>O<sub>30</sub>. This is very close to the ideal formula KNa<sub>2</sub>B<sub>3</sub>Si<sub>12</sub>O<sub>30</sub>, which would have the corresponding chemical content: SiO<sub>2</sub> 77.15, B<sub>2</sub>O<sub>3</sub> 11.18, K<sub>2</sub>O 5.04, Na<sub>2</sub>O 6.63%.

In the structure analysis of poudretteite, the site-occupancy factor of boron was refined. It converged to an occupancy of 94(2)% with the boron scattering curve. This indicates that within the 3 $\sigma$  experimental limits of precision, this atomic site is fully occupied by boron, which compares well with the electron-microprobe results. Grice *et al.* (1986) advocated this method as a reliable chemical analytical technique for boron in the description of moydite, (Ca,REE)[B(OH)<sub>4</sub>]CO<sub>3</sub>.

### X-RAY CRYSTALLOGRAPHY

X-ray precession photographs show poudretteite to be hexagonal with possible space-groups *P6/mcc* or *P6cc*. Results of the crystal-structure refinement, presented below, establish the space group as *P6/mcc*. The unit-cell parameters were refined from X-ray powder-diffraction data obtained with a 114.6-mm-diameter Debye-Scherrer camera with CuK $\alpha$  (Ni-filtered) radiation (Table 1). The refined

TABLE 1. POUDETTEITE: X-RAY-DIFFRACTION DATA

hkl	dcalc	dobs	Iobs	hkl	dcalc	dobs	Iobs
100	8.87	8.90	2	324	1.742	1.740	<1
002	6.74	6.74	3	008	1.686	1.682	3
102	5.37	5.38	<1	414	1.678	1.682	3
110	5.12	5.13	10	421	1.563	1.662	3
200	4.43	4.43	<1	316	1.659	1.627	<1
112	4.08	4.07	3	422	1.626	1.600	1
202	3.70	3.70	3	118	1.601	1.572	<1
004	3.371	3.369	3	415	1.572	1.522	<1
211	3.252	3.253	10	334	1.522	1.522	3
104	3.157	3.154	2	326	1.506	1.506	<1
300	2.956	2.956	4	218	1.506	1.465	2
114	2.816	2.815	6	308	1.464	1.423	3
213	2.687	2.686	5	425	1.423	1.407	<1
204	2.684	2.557	1	228	1.408	1.389	<1
220	2.560	2.462	2	522	1.389	1.371	2
310	2.459	2.421	<1	515	1.371	1.353	2
311	2.419	2.389	2	523	1.354	1.345	<1
222	2.393	2.310	<1	604	1.353	1.345	2
214	2.377	2.223	<1	611	1.345	1.306	1
312	2.310	2.157	1	524	1.308	1.306	1
304	2.222	2.157	<1	11,10	1.304	1.280	2
313	2.157	2.059	<1	613	1.295	1.255	<1
116	2.058	2.013	3	440	1.280	1.224	2
321	2.011	1.988	2	530	1.267	1.224	2
314	1.987	1.936	<1	700	1.267	1.198	1
410	1.935	1.912	<1	614	1.255	1.224	2
411	1.915	1.858	3	621	1.224	1.210	2
216	1.867	1.818	<1	622	1.210	1.198	1
412	1.850	1.790	4	338	1.199	1.187	1
323	1.853	1.773	2	444	1.197	1.186	1
315	1.817	1.773	2	428	1.188	1.186	1
306	1.789	1.773	2	623	1.186	1.186	1
500	1.773	1.773	2				

Ni-filtered CuK $\alpha$  radiation; cell dimensions a 10.239(1), c 13.485(3) Å.

unit-cell parameters and volume are:  $a$  10.239(1),  $c$  13.485(3) Å and  $V$  1224.3(4) Å<sup>3</sup>;  $Z=2$ .

### REFINEMENT OF THE CRYSTAL STRUCTURE

#### Experimental

A crystal fragment chosen from the type material (NMNS #51743) was ground to an ellipsoid measuring  $0.30 \times 0.30 \times 0.45$  mm. This crystal gives a distinct uniaxial interference-figure and sharp, single diffraction-maxima on precession photographs. Intensity data were collected on a fully automated Nicolet *R3m* four-circle diffractometer using the method of Grice & Ercit (1986). The data relevant to the structure refinement are given in Table 2.

#### Structure refinement

For the structure refinement of poudretteite, the atomic co-ordinates of milarite (Černý *et al.* 1980) were used. Refinement of positional and isotropic thermal parameters gave residual indices  $R=5.5\%$  and  $R_w=6.4\%$ . When the thermal parameters were refined anisotropically, the residual index dropped to 3.0%, and with the weighting scheme incorporating an isotropic, primary-extinction correction,  $R_w=3.3\%$ . The final positional parameters and equivalent isotropic temperature-factors are given in Table 3, and the anisotropic temperature-factor coefficients are given in Table 4. Bond lengths and angles are given in Table 5. The observed and calculated structure-factors have been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada K1A 0S2.

### DISCUSSION

The discovery of the new mineral species *poudretteite* leads to a new series of possible boron-bearing species within the osumilite group, of general structural formula  $^{IX}B^{XII}C^{VI}A_2^{IV}(T2)_3^{IV}(T1)_{12}O_{30}$ . Boron, a difficult element to analyze for, particularly in low concentrations or when only small amounts of sample are available, probably eludes many researchers. Perhaps some of the chemical analytical problems encountered to date in analyzing osumilite-group minerals are a result of unanalyzed boron. For example, as little as 1.7 wt. % B gives rise to 1.5 atoms (on the basis of 30 oxygen atoms) in the ideal formula of osumilite, which would make it the dominant tetrahedrally co-ordinated element in the T2 site.

Boron in the T2 site has a characteristically short B-O bond distance (1.473 Å) as compared to the same site in milarite (Be-O 1.643 Å (Černý *et al.* 1980), osumilite, Al-O 1.762 Å (Brown & Gibbs 1969), synthetic magnesian merrihueite, Mg-O 1.955 Å (Khan *et al.* 1972) and sugilite, Li-O 1.971 Å

TABLE 2. POUDRETTEITE: STRUCTURE-REFINEMENT DATA

Ideal Formula:	$KNa_2B_5Si_{12}O_{30}$	$a$ (Å):	10.253(1)
Space Group:	$P6/mmc$	$c$ (Å):	13.503(4)
Z:	2	$V$ (Å <sup>3</sup> ):	1229.4(4)
Rad/Mon:	Mo/graphite	No. of $F_o$ :	784
$\mu$ :	9.8 cm	No. of $F_o > 2.5\sigma(F_o)$ :	638
Min. transmission:	0.630	Final $R$ (obs.):	3.0%
Max. transmission:	0.706	Final $R_w$ (obs.):	4.3%
$R = \Sigma( F_o  -  F_c ) / \Sigma F_o $			
$R_w = \Sigma w( F_o  -  F_c )^2 / \Sigma w F_o ^2, w = \sigma^{-2}(F_o)$			

TABLE 3. POUDRETTEITE: POSITIONAL AND THERMAL PARAMETERS

SITE	x	y	z	$U(eq) \times 10^4 \text{ \AA}^2$
K (C)	0	0	1/4	177(4)
Na (A)	1/3	2/3	1/4	148(5)
B (T2)	0	1/2	1/4	80(12)
Si (T1)	0.06952(6)	0.33761(6)	0.11333(4)	65(2)
O1	0.0821(3)	0.3921(3)	0	142(9)
O2	0.1892(2)	0.2820(2)	0.1333(1)	133(6)
O3	0.1004(2)	0.4710(2)	0.1873(1)	92(5)

TABLE 4. POUDRETTEITE: ANISOTROPIC TEMPERATURE-FACTORS ( $\times 10^4 \text{ \AA}^2$ )

Site	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	$U(eq)$
K (C)	164(5)	164(5)	205(8)	0	0	82(2)	177(4)
Na (A)	105(6)	105(6)	235(11)	0	0	52(3)	148(5)
B (T2)	93(18)	91(13)	70(16)	0	0	47(9)	80(12)
Si (T1)	62(3)	74(3)	60(3)	-5(2)	2(2)	36(2)	65(2)
O1	225(12)	156(11)	54(9)	0	0	103(10)	142(9)
O2	110(7)	156(8)	165(8)	-33(7)	-17(6)	91(6)	133(6)
O3	97(6)	104(7)	77(7)	-29(5)	12(5)	51(6)	92(5)

TABLE 5. POUDRETTEITE: SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°)

		K (C-site) polyhedron		
K-O2	3.000(1) X12			
		Na (A-site) octahedron		
Na-O3	2.378(1) X6		03-Na-O3 X6	108.0(0)
03-03	3.247(3) X3			
03-03	2.346(3) X3		03-Na-03 X3	86.1(11)
03-03	3.849(3) X6		03-Na-03 X3	59.1(11)
	mean			90.3
		B (T2-site) tetrahedron		
B-03	1.473(2) X4		03-B-03 X2	109.8(1)
03-03	2.411(4) X2		03-B-03 X2	113.1(1)
03-03	2.458(3) X2		03-B-03 X2	105.5(1)
03-03	2.346(3) X2		mean	109.4
	mean			
	2.405			
		Si (T1-site) tetrahedron		
S1-O1	1.612(1)		01-S1-O2	109.8(1)
S1-O2	1.613(2)		01-S1-O2	110.5(1)
S1-O2	1.621(2)		01-S1-O3	110.5(1)
S1-O3	1.593(2)		02-S1-O2	104.3(1)
	mean		02-S1-O3	109.8(1)
	1.610		02-S1-O3	111.8(1)
01-O2	2.638(3)		mean	109.4
01-O2	2.656(2)			
01-O3	2.633(2)			
02-O2	2.553(3)			
02-O3	2.622(3)			
03-O2	2.662(2)			
	mean			
	2.627			

(Kato & Miura 1976). This tight tetrahedron has a mean O–O distance of 2.405 Å. The BO<sub>4</sub> tetrahedron shares one short edge (O–O distance of 2.346 Å) with the Na octahedron, which distorts it considerably.

The *B* crystallographic site is normally at least partly filled in many osumilite-group minerals by Na or H<sub>2</sub>O (or both). Černý *et al.* (1980) observed that “natural milarites with uniaxial optics seem to be confined to compositions with high alkali, Be and H<sub>2</sub>O contents”, which would require the *B* site to be almost fully occupied. However, poufretteite has a vacant *B* site, yet is still uniaxial. Thus the reason for uniaxial *versus* biaxial character in this mineral group still requires further investigation.

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#### REFERENCES

- BROWN, G.E. & GIBBS, G.V. (1969): Refinement of the crystal structure of osumilite. *Amer. Mineral.* **54**, 101-116.
- ČERNÝ, P., HAWTHORNE, F.C. & JAROSEWICH, E. (1980): Crystal chemistry of milarite. *Can. Mineral.* **18**, 41-57.
- GREW, E.S. (1982): Osumilite in the sapphirine–quartz terrane of Enderby Land, Antarctica: implications for osumilite petrogenesis in the granulite facies. *Amer. Mineral.* **67**, 762-787.
- GRICE, J.D. & ERCIT, T.S. (1986): The crystal structure of moydite. *Can. Mineral.* **24**, 675-678.
- \_\_\_\_\_, VAN VELTHUIZEN, J.V., DUNN, P.J., NEWBURY, D.E., ETZ, E.S. & NIELSEN, C.H. (1986): Moydite, (Y,REE)[B(OH)<sub>4</sub>](CO<sub>3</sub>), a new mineral species from the Evans Lou pegmatite, Quebec. *Can. Mineral.* **24**, 665-674.
- HEMINGWAY, B.S., ROBIE, R.A., KITTRICK, J.A., GREW, E.S., NELEN, J.A. & LONDON, D. (1984): The heat capacities of osumilite from 298.15 to 1000 K, the thermodynamic properties of two natural chlorites to 500 K, and the thermodynamic properties of petalite to 1800 K. *Amer. Mineral.* **69**, 701-710.
- KATO, T. & MIURA, Y. (1976): Crystal structure of sugilite. *Mineral. J.* **8**, 184-192.
- KHAN, A.A., BAUR, W.H. & FORBES, W.C. (1972): Synthetic magnesian merrihueite, dipotassium pentamagnesium dodecasilicate: a tetrahedral magnesian silicate framework crystal structure. *Acta Cryst.* **B28**, 267-272.
- MANDARINO, J.A., CHAO, G.Y., GAULT, R.A. & HERD, R.K. (1986): Mineralogy and petrology of Mont St-Hilaire, Quebec. *Geol. Assoc. Can., Mineral. Assoc. Can., Can. Geophys. Union, Field Trip Guidebook* **9A**.

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