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THE CRYSTAL STRUCTURE OF ZIRCOPHYLLITE, $K_2NaFe^{2+}{}_7Zr_2(Si_4O_{12})_2O_2(OH)_4F$, AN ASTROPHYLLITE-SUPERGROUP MINERAL FROM MONT SAINT-HILAIRE, QUÉBEC, CANADA

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ABSTRACT

Here we report the crystal structure of zircophyllite, ideally $K_2NaFe^{2+}{}_7Zr_2(Si_4O_{12})_2O_2(OH)_4F$, from Mont Saint-Hilaire, Québec, Canada. This is the first determination of the crystal structure of zircophyllite, which was originally described by Kapustin (1972). Zircophyllite is a mineral of the astrophyllite group of the astrophyllite supergroup. Chemical analysis by electron microprobe gave SiO_2 31.89, Al_2O_3 1.54, Na_2O 1.91, K_2O 6.13, Rb_2O 0.19, Cs_2O 0.10, CaO 0.62, SrO 0.10, MgO 0.22, ZnO 0.48, FeO 17.60, MnO 17.19, TiO_2 4.48, ZrO_2 8.65, Nb_2O_5 2.07, F 1.36, $(H_2O)_{calc.}$ 2.53, sum 96.48 wt.%; H_2O was calculated from crystal-structure analysis. The empirical formula based on 31 (O + F) *pfu* is $(K_{1.85}Rb_{0.03}Cs_{0.01}Na_{0.05})_{\Sigma 1.94}(Na_{0.83}Ca_{0.16}Sr_{0.01})_{\Sigma 1}(Fe^{2+}{}_{3.48}Mn_{3.44}Zn_{0.08}Mg_{0.08})_{\Sigma 7.09}(Zr_{1.00}Ti_{0.80}Nb_{0.22})_{\Sigma 2.02}[(Si_{7.54}Al_{0.43})_{\Sigma 7.97}O_{24}]O_2[(OH)_{3.98}F_{0.02}]_{\Sigma 4}F$, $Z = 1$, $D_{calc.} = 3.365$ g/cm^3. Zircophyllite is triclinic, space group $P\bar{1}$, a 5.447(2), b 11.966(5), c 11.789(4) Å, α 112.95(1), β 94.688(6), γ 103.161(7)°, V 676.4(7) Å^3. The crystal structure has been refined from a twinned crystal to $R_1 = 3.79\%$ for 3657 unique ($F_o > 4\sigma F$) reflections. In the crystal structure of zircophyllite, the four $^{[4]}T$ sites, with $\langle T–O \rangle = 1.626$ Å, are occupied mainly by Si, with minor Al. The $^{[6]}D$ site is occupied by $Zr_{1.00}Ti_{0.78}Nb_{0.20}$, ideally Zr_2 *apfu*, with $\langle D–\varphi \rangle = 2.013$ Å ($\varphi = O$, F). The T_4O_{12} astrophyllite ribbons and D octahedra constitute the H (Heteropolyhedral) sheet. In the O (Octahedral) sheet, the four $^{[6]}M(1–4)$ sites, with $\langle M–\varphi \rangle = 2.173$ Å ($\varphi = O$, OH), are occupied by $(Fe^{2+}{}_{3.48}Mn_{3.44}Zn_{0.04}Mg_{0.04})$, ideally $Fe^{2+}{}_7$ *apfu*. The central O sheet and two H sheets form the HOH block, and adjacent HOH blocks link *via* a common anion ($X^P{}_D = F$) of two D octahedra. In the **I** (Intermediate) block between adjacent HOH blocks, the two interstitial cation sites, $^{[13]}A$ and $^{[10]}B$, are ideally occupied by K_2 and Na *apfu*, $\langle A–\varphi \rangle = 3.338$ Å and $\langle B–\varphi \rangle = 2.650$ Å ($\varphi = O$, F). Zircophyllite is a Zr-analogue of astrophyllite, $K_2NaFe^{2+}{}_7Ti_2(Si_4O_{12})_2O_2(OH)_4F$. Zircophyllite and astrophyllite are related by the substitution: $^DZr^{4+} \leftrightarrow {}^DTi^{4+}$.

Keywords: zircophyllite, astrophyllite group, astrophyllite supergroup, Mont Saint-Hilaire, Québec, Canada, electron microprobe analysis, crystal structure.

INTRODUCTION

Kapustin (1972, 1973) described zircophyllite from the Korgeredabin massif, Tuva, Russia. He called zircophyllite a *zirconium analogue of astrophyllite* and wrote its empirical formula as follows: $(K_{1.70}Na_{0.71}Ca_{0.24}Mn_{0.35})_{\Sigma 3}(Fe^{2+}{}_{3.57}Mn_{3.43})_{\Sigma 7}(Zr_{1.58}Nb_{0.25}Ti_{0.17})_{\Sigma 2}(Si_{7.76}Ti_{0.24})_{\Sigma 8}[O_{26.84}(OH)_{3.26}F_{0.90}]_{\Sigma 31}(H_2O)_{0.9}$, where the composition of the O sheet is $C_7 = (Fe^{2+}{}_{3.57}Mn_{3.43})_{\Sigma 7}$, *i.e.*, $Fe^{2+} > Mn$ and Fe^{2+} is the dominant cation in the O sheet. Following the original definition of zircophyllite, Sokolova *et al*. (2017b) placed zircophyllite in the astrophyllite group of the astrophyllite supergroup. Kapustin (1972, 1973) commented on the twinning of zircophyllite crystals and hence no possibility to do any goniometry work. The crystal structure of zircophyllite has not been studied until now because of pervasive twinning.

Here we report the crystal structure and chemical analysis for zircophyllite from Mont Saint-Hilaire, Québec, Canada. The zircophyllite sample used for this work is a part of sample #183Ц from the mineral collection of Anatoly Kasatkin, Moscow, Russia.

ASTROPHYLLITE SUPERGROUP

According to the new classification scheme, the astrophyllite supergroup is now divided into three groups: the astrophyllite group, the kupletskite group, and the devitoite group (Sokolova *et al*. 2017b).

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TABLE 1. IDEAL FORMULAE* AND UNIT-CELL PARAMETERS FOR THE ASTROPHYLLITE-SUPERGROUP MINERALS

Mineral	Ideal formula	*a* (Å) α (°)	*b* (Å) β (°)	*c* (Å) γ (°)	Space group	*Z*	Ref.
Astrophyllite group HOH blocks connect *via* D–X^P_D–D bridges, Fe^{2+} is dominant at C_7							
Astrophyllite	$K_2NaFe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4F$	5.3866 113.019	11.8821 94.578	11.6794 103.120	$P\bar{1}$	1	(1, 2)
Niobophyllite	$K_2NaFe^{2+}_7(Nb,Ti)(Si_4O_{12})_2O_2(OH)_4(O,F)$	5.4022 112.990	11.8844 94.588	11.6717 103.166	$P\bar{1}$	1	(3, 2)
Zircophyllite	$K_2NaFe^{2+}_7Zr_2(Si_4O_{12})_2O_2(OH)_4F$	5.447 112.950	11.966 94.688	11.789 103.161	$P\bar{1}$	1	(4, 5)
Tarbagataite	$(K\square)CaFe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_5$	5.3868 112.978	11.9141 94.641	11.7171 103.189	$P\bar{1}$	1	(6)
Nalivkinite	$Li_2NaFe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4F(H_2O)_2$	5.374 113.360	11.948 94.538	11.676 103.01	$P\bar{1}$	1	(7, 8)
Bulgakite	$Li_2(Ca,Na)Fe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4(O,F)$ $(H_2O)_2$	5.374 113.457	11.965 94.533	11.65 103.08	$P\bar{1}$	1	(8)
Kupletskite group HOH blocks connect *via* D–X^P_D–D bridges, Mn^{2+} is dominant at C_7							
Kupletskite-1*A*	$K_2NaMn_7Ti_2(Si_4O_{12})_2O_2(OH)_4F$	5.3784 112.964	11.9085 94.697	11.7236 103.112	$P\bar{1}$	1	(9, 10)
Kupletskite-2*M*	$K_2NaMn_7Ti_2(Si_4O_{12})_2O_2(OH)_4F$	5.4022	23.226 95.246	21.1782	$C2/c$	4	(10)
Niobokupletskite	$K_2NaMn_7(Nb,Ti)(Si_4O_{12})_2O_2(OH)_4(O,F)$	5.4303 112.927	11.924 94.750	11.747 103.175	$P\bar{1}$	1	(11)
Kupletskite-(Cs)	$Cs_2NaMn_7Ti_2(Si_4O_{12})_2O_2(OH)_4F$	5.3850 113.117	11.9350 94.614	11.7793 103.075	$P\bar{1}$	1	(12, 2)
Devitoite group HOH blocks do not connect *via* D–X^P_D–D bridges							
Devitoite	$Ba_6Fe^{2+}_7Fe^{3+}_2(Si_4O_{12})_2(PO_4)_2(CO_3)O_2(OH)_4$	5.3437 91.337	11.6726 96.757	14.680 103.233	$P\bar{1}$	1	(13)
Sveinbergeite	$(H_2O)_2[Ca(H_2O)](Fe^{2+}_6Fe^{3+})Ti_2(Si_4O_{12})_2O_2$ $OH)_4[OH(H_2O)]$	5.329 101.140	11.803 98.224	11.822 102.442	$P\bar{1}$	1	(14)
Lobanovite	$K_2Na(Fe^{2+}_4Mg_2Na)Ti_2(Si_4O_{12})_2O_2(OH)_4$	5.3327	23.1535 99.615	10.3775	$C2/m$	2	(15, 16)

* The ideal formula is of the form $A_{2p}B_rC_7D_2(T_4O_{12})_2IX^O_{D2}X^O_{A4}X^P_{Dn}W_{A2}$ (see text);
References (description of a new mineral, the latest work on the structure): (1) Weibye (1848); (2) Cámara *et al.* (2010); (3) Nickel *et al.* (1964); (4) Kapustin (1972, 1973); (5) Sokolova *et al.* (this work); (6) Stepanov *et al.* (2012); (7) Agakhanov *et al.* (2008); (8) Agakhanov *et al.* (2016); (9) Semenov (1956); (10) Piilonen *et al.* (2001); (11) Piilonen *et al.* (2000); (12) Yefimov *et al.* (1971); (13) Kampf *et al.* (2010); (14) Khomyakov *et al.* (2011); (15) Sokolova *et al.* (2017a); (16) Sokolova & Cámara (2008).

The HOH block is the main structural unit in all astrophyllite-supergroup structures; it consists of three H–O–H sheets where the T_4O_{12} astrophyllite ribbons occur in the H sheets. In each structure, HOH blocks alternate with **I** (Intermediate) blocks along [001]. The 12 minerals of the astrophyllite supergroup are divided into three groups based on: (1) the type of self-linkage of HOH blocks, *i.e.*, (a) HOH blocks link directly *via* D–X^P_D–D bridges, or (b) HOH blocks do not link directly; and (2) the dominant cation of the O sheet [the C group: C_7 *apfu* (atoms per formula unit)]. In the astrophyllite group, HOH blocks connect *via* D–X^P_D–D bridges, Fe^{2+} is dominant at C_7; in the kupletskite group, HOH blocks connect *via* D–X^P_D–D bridges, Mn^{2+} is dominant at C_7; in the devitoite group, HOH blocks do not connect *via* D–X^P_D–D bridges. The 12 minerals of the astrophyllite supergroup are listed in Table 1.

The general formula for the astrophyllite-supergroup minerals is of the form $A_{2p}B_rC_7D_2(T_4O_{12})_2IX^O_{D2}X^O_{A4}X^P_{Dn}W_{A2}$, where C [cations at the *M*(1–4) sites in the O sheet] = Fe^{2+}, Mn, Na, Mg, Zn, Fe^{3+}, Ca, Zr, Li; D (cations in the H sheets) = $^{[6,5]}Ti$, Nb, Zr, Sn^{4+}, $^{[5]}Fe^{3+}$, Mg, Al; T = Si, minor Al; $A_{2p}B_rIW_{A2}$ (**I** block) where p = 1, 2; r = 1, 2; A = K, Cs, Ba, H_2O, Li,

TABLE 2. CHEMICAL COMPOSITION AND UNIT FORMULA FOR ZIRCOPHYLLITE

	wt.%			*apfu*	
Constituent	This work[1]	Kapustin (1972)[2]		This work[1]	Kapustin (1972)[2]
Nb_2O_5	2.07	2.30	Si	7.54	7.76
ZrO_2	8.65	13.61	Al	0.43	0
TiO_2	4.48	2.30	Ti	0	0.24
SiO_2	31.89	32.64	ΣT	7.97	8.00
Al_2O_3	1.54	n.d.			
SrO	0.10	n.d.	Fe^{2+}	3.48	3.57
ZnO	0.48	0.23	Mn	3.44	3.43
FeO	17.60	18.06	Zn	0.08	0
MnO	17.19	18.83	Mg	0.08	0
CaO	0.62	0.94	ΣM	7.09	7.00
MgO	0.22	n.d.			
Rb_2O	0.19	n.d.	Zr	1.00	1.58
Cs_2O	0.10	0.93	Ti	0.80	0.17
K_2O	6.13	5.61	Nb	0.22	0.25
Na_2O	1.91	1.55	ΣD	2.02	2.00
H_2O	2.53*	3.20			
F	1.36	1.20	Na	0.83	0.71
F=O	–0.57	–0.49	Ca	0.16	0.24
Total	96.48	99.75	Sr	0.01	0
			Mn	0	0.35
			Σ*B*	1.00	1.30
			K	1.85	1.70
			Rb	0.03	0
			Cs	0.01	0
			Na	0.05	0
			ΣA	1.94	1.70
			ΣA+B	2.94	3.00
			F	1.02	0.90
			OH	3.98	3.26
			H_2O	0	0.90

[1] Locality: Mont Saint-Hilaire, Québec, Canada; formula unit calculated on 31 (O + F) *pfu*;

[2] Locality: Korgeredabin massif, Tuva, Russia; formula unit taken from Kapustin (1972);

n.d. = not detected;

* Calculated from crystal-structure analysis.

Rb, Pb^{2+}, Na, □; B = Na, Ca, Ba, H_2O, □; I represents the composition of the central part of the **I** block, excluding peripheral layers of the form $A_{2p}B_rW_{A2}$, *e.g.*, $(PO_4)_2(CO_3)$ (devitoite); anions: X^O = anions of the O sheet not bonded to Si; $X^O{}_D$ = anions at the common vertices of 3M and D polyhedra; $X^O{}_A$ = anions at the common vertices of 3M polyhedra; $X^P{}_D$ = apical anions of D cations at the periphery of the HOH block; $X^O{}_D$ = O; $X^O{}_A$ = OH, F; $X^P{}_D$ = F, O, OH, H_2O, □, where n = 0, 1, 2 for $(X^P{}_D)_n$; W_A = H_2O, □ (Sokolova *et al.* 2016b).

SAMPLE DESCRIPTION

We studied several grains from the zircophyllite sample which is a part of sample #183Ц (Ц – a cyrillic letter) from the mineral collection of Antoly Kasatkin, Moscow, Russia. This sample comes from the Poudrette Quarry, Mont Saint-Hilaire, Québec, Canada. We were told that the sample probably contains four minerals: zircophyllite, its Mn-analogue, kupletskite, and astrophyllite. We used SEM to determine the chemical composition of several grains; grain #9 gave the highest content of $Fe^{2+} > Mn$. A part of grain #9 was cut out and used as a crystal for the X-ray data collection and subsequent structure refinement; another part was analyzed by electron microprobe to accurately determine its chemical composition.

CHEMICAL COMPOSITION

Crystal #9 was analyzed with a Cameca SX-100 electron microprobe operating in wavelength-dispersive mode with an accelerating voltage of 15 kV, a specimen current of 20 nA, and a beam diameter of 10 μm. The following standards were used: Si, Ca: diopside; Na: albite; Al: andalusite; Nb: $Ba_2NaNb_5O_{15}$; Zr: zircon; Ti: titanite; Fe: fayalite; Mn: spessartine; Mg: forsterite; Zn: gahnite; Rb: $RbAlSi_2O_6$; Sr: $SrTiO_3$; Cs: pollucite; K: orthoclase; F: fluoro-riebeckite. The elements Pb, Rb, Sn, and Cl were sought but not detected. The data were reduced and corrected by the PAP method of Pouchou & Pichoir (1985). The H_2O was calculated from the results of the crystal-structure analysis on the basis of F + OH = 5 *apfu*. Table 2 gives the chemical composition of zircophyllite from Canada compared with the chemical analysis of the holotype material from Russia (Kapustin 1972, 1973). The empirical formula was calculated on the basis of 31 (O + F):

$$(K_{1.85}Rb_{0.03}Cs_{0.01}Na_{0.05})_{\Sigma 1.94}(Na_{0.83}Ca_{0.16}Sr_{0.01})_{\Sigma 1}$$
$$(Fe^{2+}{}_{3.48}Mn_{3.44}Zn_{0.08}Mg_{0.08})_{\Sigma 7.09}$$
$$(Zr_{1.00}Ti_{0.80}Nb_{0.22})_{\Sigma 2.02}\left[(Si_{7.54}Al_{0.43})_{\Sigma 7.97}O_{24}\right]O_2$$
$$\left[(OH)_{3.98}F_{0.02}\right]_{\Sigma 4}F, Z = 1, D_{\text{calc.}} = 3.365\ \text{g/cm}^3.$$

DATA COLLECTION AND STRUCTURE REFINEMENT

Single-crystal X-ray data for zircophyllite were collected using a Bruker APEX II ULTRA three-circle diffractometer equipped with a rotating-anode generator (Mo$K\alpha$), multilayer optics, and an APEX II 4K CCD detector. The intensities of 25294 reflections were measured from a twinned crystal of zircophyllite using 10 s per 0.3° frame. Unit-cell parameters were determined by least-squares refinement of reflections

TABLE 3. MISCELLANEOUS REFINEMENT DATA FOR ZIRCOPHYLLITE

a (Å)	5.447(2)
b	11.966(5)
c	11.789(4)
α (°)	112.95(1)
β	94.688(6)
γ	103.161(7)
V (Å^3)	676.4(7)
Space group	$P\bar{1}$
Z	1
Reflections ($I > 10\sigma I$)	7489
Absorption coefficient (mm^{-1})	5.00
F(000)	660.7
$D_{calc.}$ (g/cm^3)	3.365
Second component (%)*	15.8(6)
Crystal size (mm)	0.10 × 0.10 × 0.01
Radiation/monochromator	Mo$K\alpha$/graphite
2θ-range for data collection (°)	60.27
h	$-7 \leq h \leq 7$
k	$-16 \leq k \leq 15$
l	$0 \leq l \leq 16$
R(int) (%)	1.66
Reflections collected	25294
Independent reflections	4005
$F_o > 4\sigma F$	3657
Refinement method	Full-matrix least squares on F^2, fixed weights proportional to $1/\sigma F_o^2$
Final R(obs) (%)	
$F_o > 4\sigma F$	3.79
R_1	4.26
wR_2	10.72
Highest peak, deepest hole (e Å^{-3})	1.47, –1.23
Goodness of fit on F^2	1.080

* Structure refinement using HKLF5 dataset containing reflections that belong to the first component and overlap with reflections from the second component.

with $I > 10\sigma I$ and are given in Table 3, together with miscellaneous information on data collection and structure refinement. An absorption correction was done using the TWINABS program (Sheldrick 2008). CELL_NOW (Sheldrick 2004) was used to obtain an HKLF5 file. The crystal structure of zircophyllite was refined using the atom coordinates of bulgakite (Agakhanov *et al.* 2016) as a starting model, with the Bruker SHELXTL Version 5.1 system of programs (Sheldrick 2008). The refinement converged to R_1 = 3.79% based on 3657 unique reflections with ($F_o > 4\sigma F$), the twin ratio being 0.842(6):0.158(6). Scattering curves for neutral atoms were taken from the *International Tables for Crystallography* (Wilson 1992). Site-scattering values were refined for the *M*(1–4) sites with the scattering curve of Fe, *D* site (scattering curve of Zr), *A* site (scattering curve of K), *B* site (scattering curve of Na), and X^P_D site (scattering curve of F). For the final refinement, the D(donor)–H(1,2) distances were softly constrained to 0.98 Å where D = O atoms of OH groups at the $X^O_A(1,2)$ sites in the H sheet. Here and further on in the paper, we label cations and anions in accord with Sokolova *et al.* (2017b).

Final atom coordinates and displacement parameters are listed in Table 4, selected interatomic distances and framework angles are given in Table 5, refined site-scattering and assigned site-populations for selected cation and anion sites are listed in Table 6, bond-valence values for selected anions are presented in Table 7, and details of hydrogen bonding are given in Table 8. A list of observed and calculated structure factors and a Crystallography Information File (CIF) may be obtained from The Depository of Unpublished Data on the MAC website [document Zircophyllite CM54-5_10.3749/canmin.1600034].

STRUCTURE DESCRIPTION

Zircophyllite is isostructural with astrophyllite (Table 1). In the crystal structure of zircophyllite, the four *T* sites are occupied by Si and minor Al (Table 2). The T atoms are tetrahedrally coordinated by O atoms with <T–O> = 1.626 Å (Table 5). There is one Zr-dominant *D* site: it is occupied by $Zr_{1.00}Ti_{0.78}Nb_{0.20}$, ideally Zr_2 *apfu* (Table 6). The D atom is coordinated by five O atoms and an X^P_D anion (X^P_D = F), with <D–φ> 2.013 Å (φ = O, F). The <D–φ> distance of 2.013 Å is in accord with the larger ionic radii of $^{[6]}$Zr (0.72 Å, Shannon 1976) compared with (1) $^{[6]}$Ti (0.605 Å): <D–φ> 1.965 Å in bulgakite where D = Ti (Agakhanov *et al.* 2016) and (2) $^{[6]}$Nb (0.64 Å): <D–φ> 1.982 Å in niobokupletskite where D = (Nb,Ti), Nb > Ti (Piilonen *et al.* 2000).

There are four *M* sites octahedrally coordinated by O atoms and OH groups at the $X^O_A(1,2)$ sites, Tables 5–8, with <M–φ> = 2.173 Å (φ = O, OH). These four *M* sites give ($Fe^{2+}_{3.48}Mn_{3.44}Zn_{0.04}Mg_{0.04}$), ideally Fe^{2+}_7 *apfu*. As in most astrophyllite-supergroup structures, the sizes of M octahedra follow the pattern <M(1)–φ> > <M(2)–φ> > <M(3)–φ> > <M(4)–φ> due to the different linkages of M octahedra and the polyhedra of the H sheets (Sokolova 2012). The T tetrahedra share vertices to form the T_4O_{12} (ideally Si_4O_{12}) astrophyllite ribbon along [100]. Astrophyllite ribbons and D octahedra share common vertices to

TABLE 4. ATOM COORDINATES AND DISPLACEMENT PARAMETERS (Å^2) FOR ZIRCOPHYLLITE

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
M(1)	0.85048(9)	0.20620(5)	0.48125(5)	0.0086(3)	0.0087(3)	0.0160(3)	0.0063(2)	0.00423(18)	0.0032(2)	0.01044(18)
M(2)	0.28029(10)	0.06836(5)	0.48968(5)	0.0094(3)	0.0097(3)	0.0165(3)	0.0075(2)	0.0052(2)	0.0042(2)	0.01076(19)
M(3)	0.42296(10)	0.35246(5)	0.48586(6)	0.0099(3)	0.0105(3)	0.0178(3)	0.0081(2)	0.0052(2)	0.0044(2)	0.01160(19)
M(4)	0	½	½	0.0089(4)	0.0084(4)	0.0156(4)	0.0065(3)	0.0026(3)	0.0026(3)	0.0105(2)
D	0.07892(7)	0.08691(4)	0.19808(3)	0.00763(18)	0.0098(2)	0.01351(19)	0.00562(16)	0.00288(12)	0.00308(15)	0.00993(12)
T(1)	0.67949(19)	0.27442(9)	0.23196(9)	0.0105(4)	0.0077(4)	0.0114(4)	0.0049(3)	0.0020(3)	0.0015(3)	0.0098(2)
T(2)	0.8128(2)	0.54750(10)	0.25398(10)	0.0147(5)	0.0085(4)	0.0143(5)	0.0066(4)	0.0037(4)	0.0033(4)	0.0119(2)
T(3)	0.37623(19)	0.67382(10)	0.25606(9)	0.0130(4)	0.0080(4)	0.0140(4)	0.0069(4)	0.0028(3)	0.0028(4)	0.0109(2)
T(4)	0.50577(19)	0.92973(9)	0.23637(9)	0.0120(4)	0.0073(4)	0.0114(4)	0.0055(3)	0.0032(3)	0.0029(3)	0.0096(2)
A	0.1384(4)	0.27352(15)	0.99546(16)	0.0853(13)	0.0463(9)	0.0360(7)	0.0162(7)	0.0063(7)	0.0112(9)	0.0579(6)
B	½	0	0	0.0134(7)	0.0066(6)	0.0039(6)	0.0017(5)	0.0010(4)	0.0023(5)	0.0083(4)
O(1)	0.7261(5)	0.3182(3)	0.3835(3)	0.0116(12)	0.0115(12)	0.0113(11)	0.0055(10)	0.0029(9)	0.0025(10)	0.0113(5)
O(2)	0.1279(5)	0.3916(3)	0.5935(2)	0.0124(12)	0.0107(12)	0.0125(12)	0.0058(10)	0.0030(9)	0.0031(10)	0.0116(5)
O(3)	0.5617(5)	0.2576(3)	0.5891(2)	0.0126(11)	0.0101(12)	0.0147(11)	0.0056(10)	0.0040(9)	0.0037(10)	0.0122(5)
O(4)	0.5720(5)	0.0138(3)	0.3881(2)	0.0118(11)	0.0093(12)	0.0118(11)	0.0041(10)	0.0032(9)	0.0028(10)	0.0111(5)
O(5)	0.0700(7)	0.5912(4)	0.2018(3)	0.0254(17)	0.036(2)	0.0195(15)	0.0082(14)	0.0060(13)	–0.0056(14)	0.0305(8)
O(6)	0.2541(8)	0.0424(4)	0.8273(3)	0.0315(19)	0.049(2)	0.0205(16)	–0.0016(16)	0.0130(14)	–0.0197(18)	0.0439(12)
O(7)	0.4293(7)	0.4146(4)	0.7981(3)	0.038(2)	0.038(2)	0.0213(16)	0.0105(15)	0.0021(14)	0.0249(17)	0.0307(8)
O(8)	0.1310(9)	0.8051(5)	0.8319(3)	0.073(3)	0.064(3)	0.0204(16)	0.0203(18)	0.0221(18)	0.062(3)	0.0433(12)
O(9)	0.2666(9)	0.9551(4)	0.1719(4)	0.060(3)	0.044(2)	0.0228(17)	–0.0019(16)	–0.0118(17)	0.043(2)	0.0434(12)
O(10)	0.2671(9)	0.6057(3)	0.8048(3)	0.068(3)	0.0120(14)	0.0173(14)	0.0078(12)	0.0049(15)	0.0057(16)	0.0333(9)
O(11)	0.5721(9)	0.2214(3)	0.8011(3)	0.070(3)	0.0097(14)	0.0187(15)	0.0070(12)	0.0041(16)	0.0041(15)	0.0341(9)
O(12)	0.3897(7)	0.1928(5)	0.1673(3)	0.0251(18)	0.063(3)	0.0221(17)	0.0209(18)	–0.0068(14)	–0.0235(18)	0.0427(11)
X^{O}_{D}	0.1478(5)	0.1635(3)	0.3774(2)	0.0119(11)	0.0154(13)	0.0171(11)	0.0070(11)	0.0042(9)	0.0050(11)	0.0145(5)
$X^{O}_{A}(1)$	0.2985(5)	0.4638(3)	0.4028(3)	0.0137(13)	0.0146(13)	0.0167(13)	0.0076(11)	0.0044(10)	0.0044(10)	0.0145(5)
$X^{O}_{A}(2)$	0.9886(5)	0.1160(3)	0.5919(3)	0.0144(12)	0.0125(12)	0.0148(12)	0.0057(10)	0.0041(10)	0.0047(10)	0.0137(5)
X^{P}_{D}	0	0	0	0.0208(15)	0.0191(16)	0.0152(13)	0.0060(14)	0.0030(11)	0.0063(14)	0.0187(6)
H(1)	0.243(10)	0.414(4)	0.3121(13)	0.01739*						
H(2)	1.036(10)	0.178(4)	0.6802(17)	0.01643*						

* U_{iso}

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR ZIRCOPHYLLITE

M(1)–(X^{O}_{D})a	2.144(3)	M(2)–X^{O}_{A}(2)b	2.119(3)	M(3)–X^{O}_{A}(1)	2.125(3)
M(1)–O(3)	2.151(3)	M(2)–O(4)	2.135(3)	M(3)–O(1)	2.144(3)
M(1)–X^{O}_{A}(2)	2.177(3)	M(2)–X^{O}_{A}(2)c	2.140(3)	M(3)–O(2)	2.150(3)
M(1)–O(2)a	2.194(3)	M(2)–O(3)	2.215(3)	M(3)–O(3)	2.158(3)
M(1)–O(4)	2.230(3)	M(2)–X^{O}_{D}	2.227(3)	M(3)–X^{O}_{A}(1)d	2.182(3)
M(1)–O(1)	2.253(3)	M(2)–O(4)c	2.229(4)	M(3)–X^{O}_{D}	2.210(3)
<M(1)–φ>	2.192	<M(2)–φ>	2.178	<M(3)–φ>	2.162
M(4)–X^{O}_{A}(1) ×2	2.093(3)	T(1)–O(12)	1.596(4)	T(2)–O(10)d	1.620(3)
M(4)–O(1)b ×2	2.168(3)	T(1)–O(8)d	1.598(4)	T(2)–O(2)d	1.627(3)
M(4)–O(2) ×2	2.187(3)	T(1)–O(10)d	1.627(3)	T(2)–O(5)a	1.635(3)
<M(4)–φ>	2.149	T(1)–O(1)	1.633(3)	T(2)–O(7)d	1.637(3)
		<T(1)–O>	1.614	<T(2)–O>	1.630
T(3)–O(11)d	1.623(3)	T(4)–O(6)d	1.595(4)	T(1)d–O(10)–T(2)d	143.3(2)
T(3)–O(3)d	1.651(3)	T(4)–O(9)	1.602(4)	T(2)b–O(5)–T(3)	139.6(2)
T(3)–O(7)d	1.656(4)	T(4)–O(11)d	1.625(3)	T(2)d–O(7)–T(3)d	139.7(2)
T(3)–O(5)	1.658(4)	T(4)–O(4)e	1.633(3)	T(3)d–O(11)–T(4)d	143.6(1)
<T(3)–O>	1.647	<T(4)–O>	1.614	<T–O–T>	141.4
D–X^{O}_{D}	1.911(3)	A–O(8)k	2.921(5)	B–O(12) ×2	2.617(5)
D–O(9)g	2.009(4)	A–O(9)h	2.928(5)	B–O(6)c ×2	2.620(5)
D–O(6)f	2.011(4)	A–O(12)l	2.931(5)	B–O(9)g ×2	2.640(5)
D–O(8)h	2.016(4)	A–O(6)	2.949(5)	B–O(8)d ×2	2.648(5)
D–O(12)	2.021(4)	A–(X^{P}_{D})l	3.210(2)	B–X^{P}_{D} ×2	2.7235(9)
D–X^{P}_{D}	2.1113(9)	A–O(11)	3.415(5)	<B–φ>	2.650
<D–φ>	2.013	A–O(11)b	3.465(5)		
		A–O(10)m	3.477(5)		
		A–O(10)k	3.487(5)		
		A–O(5)h	3.557(4)		
		A–O(7)	3.637(4)		
		A–O(7)m	3.657(4)		
		A–O(5)l	3.754(4)		
		<A–φ>	3.338		

* φ = O, OH, F. Operators for generating equivalent atoms: a: *x*+1, *y*, *z*; b: *x*–1, *y*, *z*; c: –*x*+1, –*y*, –*z*+1; d: –*x*+1, –*y*+1, –*z*+1; e: *x*, *y*+1, *z*; f: –*x*, –*y*, –*z*+1; g: *x*, *y*–1, *z*; h: –*x*, –*y*+1, –*z*+1; k: –*x*, –*y*+1, –*z*+2; ; l: *x*, *y*, *z*+1; m: –*x*+1, –*y*+1, –*z*+2.

TABLE 6. REFINED SITE-SCATTERING VALUES AND ASSIGNED SITE-POPULATIONS FOR ZIRCOPHYLLITE

Site*	Refined site-scattering (*epfu*)	Site population (*apfu*)	Calculated site-scattering (*epfu*)	<X–φ>$_{obs.}$** (Å)	Ideal composition (*apfu*)
Cations					
M(1)	49.4(2)			2.192	
M(2)	49.9(2)	3.48 Fe^{2+} + 3.44 Mn +		2.178	
M(3)	50.5(2)	+ 0.04 Zn + 0.04 Mg		2.162	
M(4)	25.4(1)			2.149	
Σ*M*	175.2	3.48 Fe^{2+} + 3.44 Mn + 0.04 Zn + 0.04 Mg	178.16		Fe^{2+}_{7}
D	66.9(2)	1.00 Zr + 0.78 Ti + 0.22 Nb	66.18	2.013	Zr_2
$^{[13]}A$	37.2(2)	1.85 K + 0.03 Rb + 0.01 Cs + 0.05 Na + 0.06 □	37.36	3.338	K_2
$^{[10]}B$	15.6(1)	0.83 Na + 0.16 Ca + 0.01 Sr	12.71	2.650	Na
Anions					
$^{[3]}X^{O}_{A}$(1,2)		3.98 OH + 0.02 F			$(OH)_4$
X^{P}_{D}		1.00 F			F

* coordination number is given for non-[6]-coordinated sites;

** X = cation, φ = O, OH, F.

TABLE 7. HYDROGEN BONDING IN ZIRCOPHYLLITE

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	∠DHA (°)
X^O_A(1)–H(1)···O(8)a	0.98(1)	2.73(4)	3.472(6)	133(4)
X^O_A(1)–H(1)···O(12)	0.98(1)	2.87(4)	3.523(6)	125(4)
X^O_A(2)–H(2)···O(6)b	0.98(1)	3.13(5)	3.522(6)	106(3)
X^O_A(2)–H(2)···O(9)c	0.98(1)	3.12(5)	3.515(6)	106(3)

a: –*x*, –*y*+1, –*z*+1; b: *x*+1, *y*, *z*; c: –*x*+1, –*y*+1, –*z*+1.

form an H sheet. M(1–4) octahedra share common edges to form a trioctahedral O sheet. Two H and one O sheets form an HOH block identical to that in astrophyllite (Fig. 1). In the zircophyllite structure, HOH blocks connect *via* D–X^P_D–D bridges as in other astrophyllite-group minerals (Table 1). In the **I** (Intermediate) block between adjacent HOH blocks, the two interstitial cation sites, $^{[13]}A$ and $^{[10]}B$, are ideally occupied by K_2 and Na *apfu*, $<A–\varphi> = 3.338$ Å and $<B–\varphi> = 2.650$ Å (φ = O, F) (Tables 5, 6).

In the crystal structure of zircophyllite, there are 31 anions per formula unit. The 12 O atoms which coordinate Si atoms sum to O_{24} *apfu*. The X^O_D site is occupied by an O atom (Table 8) which coordinates 3M and D polyhedra (Table 5) and the X^O_D site ideally gives O_2 *apfu*. The OH groups at the X^O_A(1,2) sites are involved in weak hydrogen bonding (Table 7). The X^O_A(1,2) sites ideally give $(OH)_4$ *pfu*. The X^P_D site is occupied by F, giving F *apfu*.

We write the ideal formula of zircophyllite in the form $A_2BC_7D_2(T_4O_{12})_2X^O_{D2}X^O_{A4}X^P_D$ as follows: $K_2NaFe^{2+}_7Zr_2(Si_4O_{12})_2O_2(OH)_4F$, $Z = 1$. Zircophyllite and astrophyllite are related by the substitution $^{D}Zr^{4+} \leftrightarrow {}^{D}Ti^{4+}$.

SUMMARY

The crystal structure and chemical composition have been determined for zircophyllite, ideally $K_2NaFe^{2+}_7Zr_2(Si_4O_{12})_2O_2(OH)_4F$, from Mont Saint-Hilaire, Québec, Canada. This is the first determination of the crystal structure of zircophyllite.

Zircophyllite is a Zr-analogue of astrophyllite, $K_2NaFe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4F$. Zircophyllite and astrophyllite are related by the substitution $^{D}Zr^{4+} \leftrightarrow {}^{D}Ti^{4+}$.

Zircophyllite is a mineral of the astrophyllite group of the astrophyllite supergroup (Sokolova *et al.* 2017b).

Mont Saint-Hilaire, Québec, Canada is the second occurrence of zircophyllite. Zircophyllite was originally described by Kapustin (1972) from the Korgeredabin massif, Tuva, Russia.

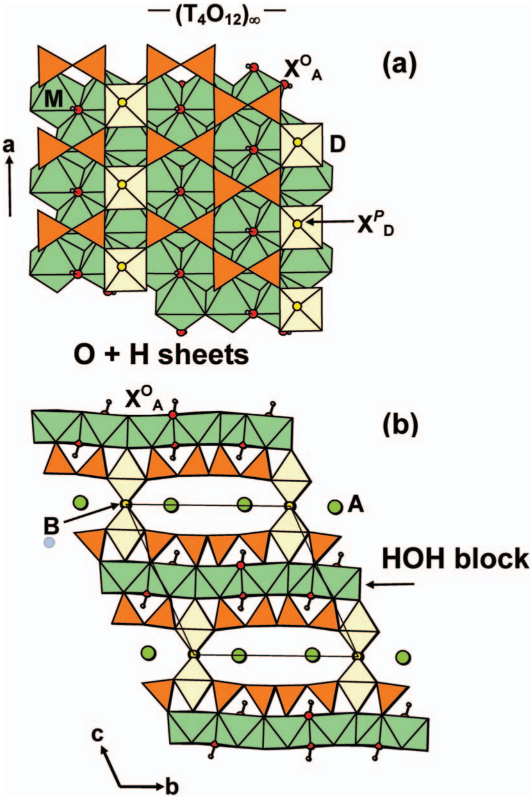

FIG. 1. The crystal structure of zircophyllite: (a) O and H sheets; (b) general view of the structure. The Fe^{2+}-dominant and Zr-dominant octahedra are green and yellow, respectively; Si tetrahedra are orange; K and Na atoms at *A* and *B* sites are shown as large green and medium navy blue spheres (that are hidden behind the yellow spheres of F); F atoms [X^P_D site] and O atoms of OH groups [X^O_A sites] are shown as small yellow and red spheres, respectively; H atoms of OH groups are shown as small grey spheres, O–H bonds are shown as black lines; the unit cell is shown with thin black lines.

TABLE 8. SELECTED BOND-VALENCE VALUES* FOR ZIRCOPHYLLITE

Atom**	M(1–4)	D	A	B	Σ
X^O_D	0.94	0.94			1.88
X^O_A(1)	1.11				1.11
X^O_A(2)	1.07				1.07
X^P_D		$0.45^{\times2\rightarrow}$	$0.07^{\times2\rightarrow}$	$0.08^{\times2\rightarrow}$	1.20

* Bond-valence parameters (*vu*) are from Brown (1981) and Brown & Altermatt (1985) for Zr-F; ** M = (Fe^{2+},Mn); D = (Zr,Ti); A = K; B = Na; X^O_D = O; X^O_A(1,2) = OH; X^P_D = F.

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