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THE CRYSTAL STRUCTURES OF NIOBOPHYLLITE, KUPLETSKITE-(Cs) AND Sn-RICH ASTROPHYLLITE: REVISIONS TO THE CRYSTAL CHEMISTRY OF THE ASTROPHYLLITE-GROUP MINERALS

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ABSTRACT

The crystal structures of niobophyllite, $K_2\,Na\,Fe^{2+}{}_7\,(NbTi)\,(Si_4O_{12})_2\,O_2\,(OH)_4\,O$, kupletskite-(Cs), $Cs_2\,Na\,Mn_7\,Ti_2\,(Si_4O_{12})_2\,O_2\,(OH)_4\,F$, and Sn-rich astrophyllite, $K_2\,Na\,Fe^{2+}{}_7\,Ti_2\,(Si_4O_{12})_2\,O_2\,(OH)_4\,F$, all members of the astrophyllite group, have been refined in space group $P\bar{1}$ to R_1 values 5.96, 3.33 and 3.53% for 3576, 3490 and 3791 observed $[F_o > 4\sigma F]$ unique reflections measured with Mo$K\alpha$ radiation on a Bruker AXS diffractometer with a CCD SMART APEX detector. The crystal structures of all three minerals are topologically identical to that of triclinic astrophyllite. The crystals used in the collection of the X-ray intensity data were analyzed by electron microprobe, $Fe^{3+} : (Fe^{2+} + Fe^{3+})$ ratios were measured by Mössbauer spectroscopy, and Li was determined by laser-ablation – inductively coupled plasma – mass spectrometry (LA–ICP–MS). The empirical formulae were calculated on an anion basis, (O + OH + F) = 31 *apfu*: niobophyllite, $(K_{1.79}\,Cs_{0.03})_{\Sigma 1.82}\,Na_{1.01}\,(Fe^{2+}{}_{4.02}\,Mn_{1.98}\,Fe^{3+}{}_{0.55})_{\Sigma 6.55}\,(Nb_{1.46}Ti_{0.55}Ta_{0.01})_{\Sigma 2.02}\,[(Si_{7.77}\,Al_{0.20})_{\Sigma 7.97}O_{24}]\,O_{2.73}\,[(OH)_{4.13}F_{0.13}]_{\Sigma 4.26}$; kupletskite-(Cs), $(Cs_{1.42}K_{0.36}Ca_{0.08}Pb_{0.06}Na_{0.05}Sr_{0.02})_{\Sigma 1.99}\,(Na_{0.73}Ca_{0.27})_{\Sigma 1}\,(Mn_{3.74}\,Fe^{2+}{}_{1.82}Li_{0.68}Zn_{0.50}Fe^{3+}{}_{0.13}Mg_{0.11})_{\Sigma 6.99}\,(Ti_{1.54}Nb_{0.45}Zr_{0.02})_{\Sigma 2.01}\,[(Si_{7.90}Al_{0.05})_{\Sigma 7.95}O_{24}]\,O_{2.03}\,[(OH)_{4.26}F_{0.71}]_{\Sigma 4.97}$; Sn-rich astrophyllite, $(K_{1.70}Ca_{0.04}Cs_{0.03}Pb_{0.01})_{\Sigma 1.78}\,(Na_{0.96}Ca_{0.04})_{\Sigma 1}\,(Fe^{2+}{}_{6.18}Mn_{0.45}Fe^{3+}{}_{0.26}Ca_{0.09}Zn_{0.02})_{\Sigma 7}\,(Ti_{0.74}Sn_{0.62}Nb_{0.44}Zr_{0.16}Ta_{0.02}Mg_{0.02})_{\Sigma 2.00}\,[(Si_{7.75}\,Al_{0.16})_{\Sigma 7.91}O_{24}]\,O_2\,[(OH)_{4.356}F_{0.65}]_{\Sigma 5.00}$; Z = 1. In Sn-rich astrophyllite, Sn^{4+} replaces Ti^{4+} at the *D* site, and there is a corresponding expansion of the D octahedron: $\langle D\text{–}\varphi \rangle = 1.979$ Å, where φ represents O, F, OH. The discovery of Sn-rich astrophyllite indicates that there is potential for a new species in the astrophyllite group with Sn^{4+} as the dominant cation at the *D* site. We have identified three distinct *A* sites, *A*(1), *A*(2) and *A*(3) with coordinations [13], [5] and [13], respectively, that are separated by ≤1.2 Å such that locally adjacent sites cannot both be occupied. We suggest the possibility of Ca occupying the *B* site *via* the substitution ${}^{B}Ca^{2+} + {}^{A}\square \rightarrow {}^{B}Na^{+} + {}^{A}K^{+}$ and producing a potential new mineral of the astrophyllite group. The general formula of the astrophyllite-group minerals should be written as $A_2\,B\,C_7\,D_2\,(T_4O_{12})_2\,O_2\,(OH)_4\,X_{0-1}$

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as this (i) preserves the correct formula of the silicate radical in the structure, and (ii) identifies the $\mathrm{O_2}$ anion component of the structure as not bonded to Si.

Keywords: niobophyllite, kupletskite-(Cs), Sn-rich astrophyllite, astrophyllite group, crystal structure, electron-microprobe analysis, Mössbauer spectroscopy.

SOMMAIRE

Nous avons affiné la structure cristalline de niobophyllite, $\mathrm{K_2\,Na\,Fe^{2+}{}_7\,(NbTi)\,(Si_4O_{12})_2\,O_2\,(OH)_4\,O}$, kupletskite-(Cs), $\mathrm{Cs_2\,Na\,Mn_7\,Ti_2\,(Si_4O_{12})_2\,O_2\,(OH)_4\,F}$, et astrophyllite riche en étain, $\mathrm{K_2\,Na\,Fe^{2+}{}_7\,Ti_2\,(Si_4O_{12})_2\,O_2\,(OH)_4\,F}$, tous membres du groupe de l'astrophyllite, dans le groupe spatial $P\overline{1}$ jusqu'à un résidu R_1 de 5.96, 3.33 et 3.53%. Ces affinements sont fondés sur 3576, 3490 et 3791 réflexions uniques observées $[F_o > 4\sigma F]$ mesurées en rayonnement Mo$K\alpha$ avec un diffractomètre Bruker AXS muni d'un détecteur CCD SMART APEX. Ces trois structures sont topologiquement identiques à celle de l'astrophyllite triclinique. Les cristaux utilisés pour le prélèvement des données en diffraction X ont par la suite été analysés avec une microsonde électronique, les rapports $\mathrm{Fe^{3+} : (Fe^{2+} + Fe^{3+})}$ ont été établis par spectroscopie de Mössbauer, et la teneur en Li a été mesurée par plasma inductif couplé avec spectrométrie de masse et ablation au laser (LA–ICP–MS). Les formules empiriques ont été calculées sur une base de 31 anions O + OH + F par unité formulaire: niobophyllite, $\mathrm{(K_{1.79}\,Cs_{0.03})_{\Sigma 1.82}\,Na_{1.01}\,(Fe^{2+}{}_{4.02}Mn_{1.98}Fe^{3+}{}_{0.55})_{\Sigma 6.55}\,(Nb_{1.46}Ti_{0.55}Ta_{0.01})_{\Sigma 2.02}\,[(Si_{7.77}\,Al_{0.20})_{\Sigma 7.97}O_{24}]\,O_{2.73}\,[(OH)_{4.13}F_{0.13}]_{\Sigma 4.26}}$; kupletskite-(Cs), $\mathrm{(Cs_{1.42}K_{0.36}Ca_{0.08}Pb_{0.06}Na_{0.05}Sr_{0.02})_{\Sigma 1.99}\,(Na_{0.73}Ca_{0.27})_{\Sigma 1}\,(Mn_{3.74}Fe^{2+}{}_{1.82}Li_{0.68}Zn_{0.50}Fe^{3+}{}_{0.13}Mg_{0.11})_{\Sigma 6.99}\,(Ti_{1.54}Nb_{0.45}Zr_{0.02})_{\Sigma 2.01}\,[(Si_{7.90}\,Al_{0.05})_{\Sigma 7.95}\,O_{24}]\,O_{2.03}\,[(OH)_{4.26}\,F_{0.71}]_{\Sigma 4.97}}$; astrophyllite riche en Sn, $\mathrm{(K_{1.70}Ca_{0.04}\,Cs_{0.03}Pb_{0.01})_{\Sigma 1.78}\,(Na_{0.96}Ca_{0.04})_{\Sigma 1}\,(Fe^{2+}{}_{6.18}Mn_{0.45}Fe^{3+}{}_{0.26}Ca_{0.09}Zn_{0.02})_{\Sigma 7}\,(Ti_{0.74}\,Sn_{0.62}Nb_{0.44}Zr_{0.16}Ta_{0.02}Mg_{0.02})_{\Sigma 2.00}\,[(Si_{7.75}\,Al_{0.16})_{\Sigma 7.91}O_{24}]\,O_2\,[(OH)_{4.356}F_{0.65}]_{\Sigma 5.00}}$; $Z = 1$. Dans l'astrophyllite enrichie en étain, $\mathrm{Sn^{4+}}$ remplace $\mathrm{Ti^{4+}}$ au site *D*, et l'octaèdre D s'en trouve gonflé: $\langle \mathrm{D}–\varphi \rangle = 1.979$ Å, où φ représente O, F, OH. La découverte de l'astrophyllite ainsi enrichie en Sn montre qu'il pourrait y avoir d'autres espèces à découvrir ayant une prédominance de $\mathrm{Sn^{4+}}$ au site *D*. Nous avons identifié trois sites *A* distincts, *A*(1), *A*(2) et *A*(3), en coordinences [13], [5] et [13], respectivement; ceux-ci sont séparés par ≤1.2 Å, de sorte que deux sites adjacents ne pourraient pas être occupés simultanément. Nous proposons comme possibilité l'incorporation du Ca au site *B via* la substitution ${}^{B}\mathrm{Ca^{2+}} + {}^{A}\square \rightarrow {}^{B}\mathrm{Na^{+}} + {}^{A}\mathrm{K^{+}}$, ce qui créerait un nouveau membre du groupe de l'astrophyllite. La formule des minéraux de ce groupe devrait s'écrire $\mathrm{A_2\,B\,C_7\,D_2\,(T_4O_{12})_2\,O_2\,(OH)_4\,X_{0–1}}$; cette version démontre la formule correcte du radical silicaté dans la structure, et montre que la composante anionique $\mathrm{O_2}$ dans la structure n'est pas liée au Si.

(Traduit par la Rédaction)

Mots-clés: niobophyllite, kupletskite-(Cs), astrophyllite riche en Sn, groupe de l'astrophyllite, structure cristalline, analyses avec microsonde électronique, spectroscopie de Mössbauer.

INTRODUCTION

The astrophyllite-group minerals are alkali titanosilicates; they are divided into two main subgroups on the basis of the dominance of $\mathrm{Fe^{2+}}$ (astrophyllite, Weibye 1848) or $\mathrm{Mn^{2+}}$ (kupletskite, Semenov 1956) at the octahedrally coordinated sites in the structure. There has been extensive work on the structure and composition of the astrophyllite-group minerals. Piilonen *et al.* (2003a, b) reviewed previous work, presented a considerable amount of data (crystal-structure refinements, electron-microprobe analyses and Mössbauer spectra), and generalized the crystal chemistry of the astrophyllite-group minerals. They wrote the general formula as $\mathrm{A_2\,B\,C_7\,D_2\,T_8\,O_{26}\,(OH)_4\,X_{0–1}}$, where A = ${}^{[10]–[13]}$(K, Rb, Cs, Na, $\mathrm{H_3O^+}$, $\mathrm{H_2O}$ or $\square$), B = ${}^{[10]}$(Na or Ca); C = ${}^{[6]}$($\mathrm{Fe^{2+}}$, Mn, $\mathrm{Fe^{3+}}$, Na, Mg or Zn); D = ${}^{[6]}$(Ti, Nb, Zr); T = Si, Al and X = F, OH, O, $\square$. In accord with the general formula, Piilonen *et al.* (2003a) revised formulae for astrophyllite, $\mathrm{K_2\,Na\,(Fe^{2+},Mn)_7\,Ti_2\,Si_8\,O_{26}\,(OH)_4\,F}$, magnesiumastrophyllite, $\mathrm{K_2\,Na\,[Na\,(Fe^{2+},Mn)_4\,Mg_2]\,Ti_2\,Si_8\,O_{26}\,(OH)_4}\,\square$, niobophyllite, $\mathrm{K_2\,Na\,(Fe^{2+},Mn)_7\,(Nb,Ti)_2\,Si_8\,O_{26}\,(OH)_4\,(F,O)}$, kupletskite, $\mathrm{K_2\,Na\,(Mn,Fe^{2+})_7\,(Ti,Nb)_2\,Si_8\,O_{26}\,(OH)_4\,F}$, kupletskite-(Cs), $\mathrm{(Cs,K)_2\,Na\,(Mn,Fe,Li)_7\,(Ti,Nb)_2\,Si_8\,O_{26}\,(OH)_4\,F}$, niobokupletskite, $\mathrm{K_2\,Na\,(Mn,Zn,Fe^{2+})_7\,(Nb,Zr,Ti)_2\,Si_8\,O_{26}\,(OH)_4\,(O,F)}$ [the latter formula was taken unchanged from Piilonen *et al.* (2000)], and zircophyllite, $\mathrm{K_2\,(Na,Ca)\,(Mn,\,Fe^{2+})_7\,(Zr,Nb)_2\,Si_8\,O_{26}\,(OH)_4\,F}$. Piilonen *et al.* (2003a) listed niobophyllite, kupletskite-(Cs) and zircophyllite as minerals lacking structure data. Recent work on the crystal chemistry of the astrophyllite group includes crystal-structure refinement of a Zn-rich astrophyllite (Piilonen *et al.* 2004), re-investigation of the crystal structure of magnesiumastrophyllite (Sokolova & Cámara 2008), and description and crystal structure of a new lithium-dominant member, nalivkinite, ideally $\mathrm{Li_2\,Na\,Fe^{2+}{}_7\,Ti_2\,[Si_8\,O_{24}]\,O_2\,(OH)_4\,F}$ (Agakhanov *et al.* 2008, Uvarova *et al.* 2008).

This work is a continuation of our interest in the crystal chemistry of the astrophyllite-group minerals. A natural next step is structural work on the three minerals lacking structure data, niobophyllite, kupletskite-(Cs) and zircophyllite. We were unable to obtain any sample of zircophyllite. The sample of kupletskite-(Cs) was kindly provided by Adriana and Renato Pagano, Milan, Italy, from their mineral collection (Collezione Mineralogica, sample 5621B). This sample of kupletskite-(Cs) came from the type locality, the moraine of the Dara-i-Pioz glacier, Tien–Shan mountains, northern Tajikistan (Yefimov *et al*. 1971). We started with two niobophyllite samples: (1) a holotype sample of niobophyllite from Seal Lake, Labrador (Nickel *et al*. 1964) obtained from the Royal Ontario Museum, sample M26148, and (2) a sample of *niobophyllite* from the Zomba–Malosa pegmatite, Monte Malosa, Zomba, Malawi, from the mineral collection of Adriana and Renato Pagano (sample 8714). The *niobophyllite* from Malawi, described as such by Guastoni *et al*. (2003), turned out to be Sn-rich astrophyllite. In this paper, we present the crystal-structure, Mössbauer and electron-microprobe data for niobophyllite, kupletskite-(Cs) and Sn-rich astrophyllite, and revise some aspects of the crystal chemistry of the astrophyllite group.

CHEMICAL COMPOSITION

Mössbauer spectroscopy

Mössbauer spectra for these minerals were collected at room temperature (RT) using a ^{57}Co(Rh) point source. A single crystal (size ~300 μm) was used for the collection of the Sn-rich astrophyllite spectrum, and powdered absorbers containing ~2 mg Fe/cm^2 were used for kupletskite-(Cs) and niobophyllite. The spectrometer was calibrated using the spectrum of α-Fe at RT. The spectra were fitted to a model having two generalized sites, one for Fe^{2+} (with two Gaussian components) and the other for Fe^{3+} (with one Gaussian component), using a Voigt-based quadrupole splitting distribution (QSD) analysis. The fitted spectra are shown in Figure 1, together with the QSD curves for Fe^{2+}; selected hyperfine parameters are listed in Table 1. The Mössbauer parameters and the QSD curves for Fe^{2+} will be discussed in detail in a separate paper. Assuming equal recoil-free fractions for Fe^{2+} and Fe^{3+}, the Fe^{3+}:Fe$_{tot}$ ratio is 0.12(2), 0.07(2) and 0.04(2) for niobophyllite, kupletskite-(Cs) and Sn-rich astrophyllite, respectively. The ratio of the spectral areas of the low-velocity peak to the high-velocity peak (A–/A+) was allowed to vary for the Fe^{2+} site, whereas it was constrained to be equal to unity for the minor Fe^{3+} peaks because of the presence of a small residual texture effect.

Electron-microprobe analysis

The crystals used for collection of the X-ray intensity data were mounted on a Perspex disc, ground, polished, carbon-coated and analyzed with a Cameca SX 100 electron microprobe operating in wavelength-dispersion mode with an accelerating voltage of 15 kV, a specimen current of 20 nA, a beam size of 10 μm, and count times on peak and background of 20 and 10 s, respectively. The following standards were used for *K* and *L* X-ray lines: Si, Ca: diopside, Al: andalusite, Na: albite, K: orthoclase, F: fluororiebeckite, Mg: forsterite, Ti: titanite, Mn: spessartine, Fe: fayalite, Zn: gahnite, Nb: $Ba_2NaNb_5O_{15}$, Ta: $MnNb_2TaO_9$, Sn: SnO_2, Cs: pollucite, Zr: zircon, Pb: PbTe, Sr: $SrTiO_3$, Rb: $RbAlSi_2O_6$, Ba: barite, Ce: $CePO_4$, La: $LaPO_4$, and Nd: $NdPO_4$. The data were reduced and corrected with the PAP method of Pouchou & Pichoir (1985). The amount of H_2O was calculated from the structure refinement (see discussion below). For kupletskite-(Cs) and Sn-rich astrophyllite, OH + F = 5 *apfu* (atoms per formula unit). For niobophyllite, OH + F = {5 – [O$^{2–}$ (= 0.5 Nb)]} *apfu*. The single crystal of kupletskite-(Cs) was analyzed by laser ablation – inductively coupled plasma – mass spectrometry (LA–ICP–MS) and gave 0.69 wt. % Li_2O. The empirical formulae were calculated on an anion basis of (O + OH + F) = 31 *apfu*: niobophyllite, $(K_{1.79}\,Cs_{0.03})_{\Sigma 1.82}\,Na_{1.01}\,(Fe^{2+}_{4.02}Mn_{1.98}\,Fe^{3+}_{0.55})_{\Sigma 6.55}\,(Nb_{1.46}Ti_{0.55}Ta_{0.01})_{\Sigma 2.02}\,(Si_{7.77}Al_{0.20})_{\Sigma 7.97}\,O_{24}]\,O_{2.73}\,[(OH)_{4.13}F_{0.13}]_{\Sigma 4.26}$; kupletskite-(Cs), $(Cs_{1.42}\,K_{0.36}Ca_{0.08}Pb_{0.06}Na_{0.05}\,Sr_{0.02})_{\Sigma 1.99}\,(Na_{0.73}Ca_{0.27})_{\Sigma 1}\,(Mn_{3.74}\,Fe^{2+}_{1.82}Li_{0.68}Zn_{0.50}Fe^{3+}_{0.13}Mg_{0.11})_{\Sigma 6.99}\,(Ti_{1.54}\,Nb_{0.45}Zr_{0.02})_{\Sigma 2.01}\,(Si_{7.90}\,Al_{0.05})_{\Sigma 7.95}\,O_{24}]\,O_{2.03}\,[(OH)_{4.26}F_{0.71}]_{\Sigma 4.97}$; Sn-rich astrophyllite, $(K_{1.70}Ca_{0.04}\,Cs_{0.03}Pb_{0.01})_{\Sigma 1.78}\,(Na_{0.96}Ca_{0.04})_{\Sigma 1}\,(Fe^{2+}_{6.18}Mn_{0.45}Fe^{3+}_{0.26}\,Ca_{0.09}Zn_{0.02})_{\Sigma 7}\,(Ti_{0.74}Sn_{0.62}Nb_{0.44}Zr_{0.16}Ta_{0.02}Mg_{0.02})_{\Sigma 2.00}\,(Si_{7.75}\,Al_{0.16})_{\Sigma 7.91}\,O_{24}]\,O_2\,[(OH)_{4.356}F_{0.65}]_{\Sigma 5.00}$, Z = 1 (Table 2).

CRYSTAL STRUCTURE

X-ray data collection and structure refinement

X-ray diffraction data were collected with a Bruker AXS diffractometer equipped with a SMART APEX

TABLE 1. MÖSSBAUER PARAMETERS FOR ASTROPHYLLITE-GROUP MINERALS

	δ_0 mm/s	δ_1	Δ mm/s	σ_Δ mm/s	A %	Γ mm/s
			niobophyllite			
Fe^{2+} : 1	1.25(3)	-0.04(1)	2.43(6)	0.27(5)	91(18)	0.15(2)
Fe^{2+} : 2			1.9(1)	0.1(1)	9(18)	
Fe^{3+}	0.33(9)	0*	0.8(2)	0.4(1)	12(2)	
			kupletskite-(Cs)			
Fe^{2+} : 1	1.30(3)	-0.06(1)	2.40(4)	0.33(5)	89(8)	0.14(3)
Fe^{2+} : 2			1.7(1)	0.07(2)	11(8)	
Fe^{3+}	0.36(4)	0*	0.7(1)	0.1(1)	7(2)	
			Sn-rich astrophyllite			
Fe^{2+} : 1	1.23(3)	-0.03(1)	2.81(8)	0.1(1)	25(21)	0.12(2)
Fe^{2+} : 2			2.49(9)	0.27(6)	75(21)	
Fe^{3+}	0.3(1)	0*	0.7(3)	0.2*	4(2)	

The center shift (CS) is linearly correlated to the quadrupole splitting (Δ): CS = $\delta_0 + \delta_1 \Delta$. σ_Δ is the Gaussian width of the QSD component, A is the relative area, and Γ is the absorber Lorentzian linewidth of the elemental doublet of the QSD. * Fixed parameter.

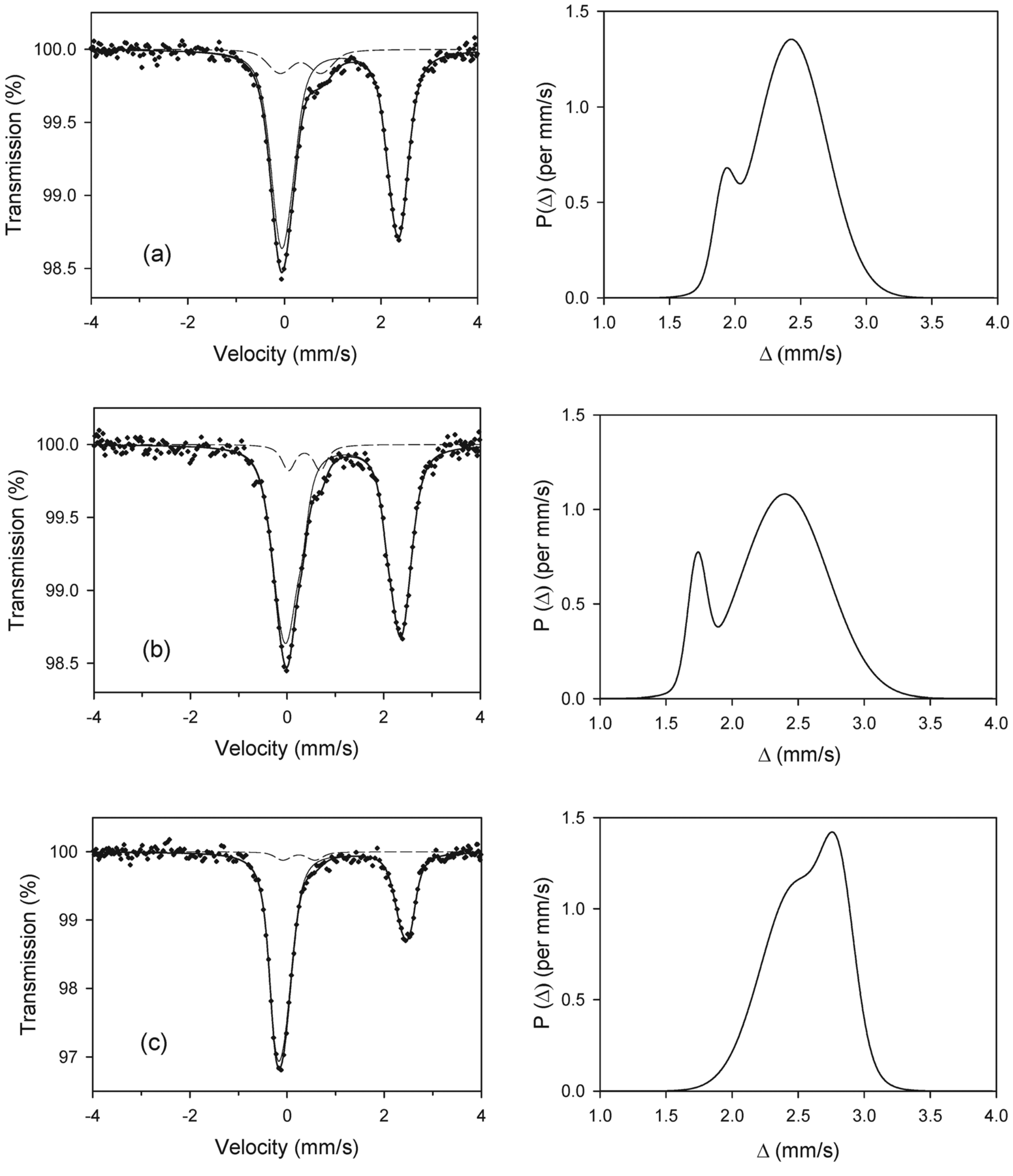

FIG. 1. Room-temperature Mossbauer spectra and profiles of Voigt-based quadrupole-splitting distributions (QSD) for Fe^{2+} in (a) niobophyllite, (b) kupletskite-(Cs), and (c) Sn-rich astrophyllite.

CCD detector (Mo$K\alpha$ radiation). The intensities of ~10000–15000 reflections with $-7 < h < 7$, $-16 < k < 15$, $-16 < l < 16$ were collected to 60°2θ using 0.2° frame and integration time of 60 s for niobophyllite, 5 s for kupletskite-(Cs) and 15 s for Sn-rich astrophyllite. The refined unit-cell parameters were obtained from reflections with $I > 10\sigma I$ (4422 for niobophyllite, 7244 for kupletskite-(Cs) and 9986 for Sn-rich astrophyllite). An empirical absorption correction (SADABS, Sheldrick 1998) was applied for niobophyllite and Sn-rich astrophyllite. Crystals of kupletskite-(Cs) were found to be twinned (twin law $|\bar{1}\ 0\ 0,\ 1\ 0\ 1,\ -0.43\ 0\ -0.854|$): both components of the twin were integrated and, after correcting for absorption using TWINABS v1.02 (Bruker Nonius ®), only non-overlapping reflections corresponding to the highest-volume component (80:20) were used for the refinement. Using atom coordinates from Piilonen *et al.* (2000), the crystal structures of niobophyllite, kupletskite-(Cs) and Sn-rich astrophyllite were refined to R_1 values of 3.33–5.96% and Go*F* values of 1.064–1.231 with the Bruker SHELXTL version 5.1 system of programs (Sheldrick 1997). For kupletskite-(Cs) and Sn-rich astrophyllite, we observed a splitting of the *A* site into two and three sites, respectively, separated by short distances. For further refinement, displacement parameters for *A*(1,2) and *A*(1,2,3) sites in kupletskite-(Cs) and Sn-rich astrophyllite were constrained to be equal. Site-scattering values were refined (1) in all structures for the *M* (scattering curve of Fe) and *B* sites (scattering curve of Na); (2) for the *D* site, with scattering curves of Nb, Ti and Sn for niobophyllite, kupletskite-(Cs) and Sn-rich astrophyllite, respectively; (3) niobophyllite: for the *A* site (scattering curve of K); kupletskite-(Cs): for the *A*(1) and *A*(2) sites (scattering curves of K and Cs); Sn-rich astrophyllite: for the *A*(1), *A*(2) and *A*(3) sites (scattering curves of K, K and Cs). Hydrogen atoms were included at the final stages of refinement, and both H positions were softly constrained by setting the O–H distances equal to 0.98 Å. Details of data collection and structure refinement are given in Table 3, final atom parameters are given in Table 4, selected interatomic distances

TABLE 2. CHEMICAL COMPOSITION (wt.%) AND UNIT FORMULAE (*apfu*) OF ASTROPHYLLITE-GROUP MINERALS

	niobophyllite				kupletskite-(Cs)				Sn-rich astrophyllite		
	Nickel *et al.* (1964)[1]	This work[2]			Yefimov *et al.* (1971)[3]	This work[2]			This work[2]		
	wt%	wt%		*apfu*	wt%	wt%		*apfu*	wt%		*apfu*
Nb_2O_5	14.76	14.14	Si	7.77	4.95	4.02	Si	7.90	4.11	Si	7.75
Ta_2O_5	0.52	0.20	Al	0.20	0.06	n.d.	Al	0.05	0.27	Al	0.16
TiO_2	2.94	3.21	ΣT	7.97	8.28	8.33	ΣT	7.95	4.17	ΣT	7.91
ZrO_2	n.d.	n.d.			1.01	0.14			1.37		
SnO_2	n.a.	n.d	Nb	1.46	n.a.	n.d.	Ti^{4+}	1.54	6.55	Ti	0.74
SiO_2	33.40	33.98	Ti	0.55	33.00	32.03	Nb	0.45	32.64	Sn	0.62
Al_2O_3	0.89	0.73	Ta	0.01	0.52	0.17	Zr	0.02	0.56	Nb	0.44
REE oxides	1.50[4]	n.d.	ΣD	2.02	n.a.	n.a.	ΣD	2.01	n.d.	Zr	0.16
Fe_2O_3	23.74	3.21[5]			3.05	0.74[5]			1.44[5]	Ta	0.02
FeO	0.00	21.00			10.00	8.82			31.13	Mg	0.02
MnO	9.83	10.24			19.66	17.91			2.23	ΣD	2.00
MgO	0.16	n.d			n.a.	0.29			0.05		
ZnO	n.a.	n.d	Fe^{2+}	4.02	n.a.	2.74	Mn	3.74	0.13	Fe^{2+}	6.18
PbO	n.a.	n.d	Mn	1.98	n.a..	0.83	Fe^{2+}	1.82	0.21	Mn	0.45
BaO	n.d.	n.d	Fe^{3+}	0.55	n.d.	n.d.	Li	0.68	n.d.	Fe^{3+}	0.26
SrO	n.a.	n.d	ΣC	6.55	n.d.	0.11	Zn	0.50	n.d.	Ca	0.09
CaO	0.72	n.d.			0.35	1.33	Fe^{3+}	0.14	0.65	Zn	0.02
Na_2O	2.49	2.28			2.46	1.63	Mg	0.11	2.09	ΣC	7.00
K_2O	5.51	6.12			1.15	1.13	ΣC	6.99	5.62		
Li_2O	n.a.	n.a.			0.46	0.69			n.a.		
Rb_2O	n.a.	n.d.	K	1.79	0.18	n.d.	Cs	1.42	n.d.	K	1.70
Cs_2O	n.a.	0.34	Cs	0.03	11.60	13.55	K	0.36	0.25	Ca	0.04
H_2O	3.64	2.71[6]	ΣA	1.82	1.47	2.55[6]	Ca	0.08	2.75[6]	Cs	0.03
F	0.46	0.18			1.26	0.91	Pb	0.06	0.87	Pb	0.01
O=F	–0.19	–0.08			–0.54	–0.38	Na	0.05	–0.37	ΣA	1.78
Total	100.37	98.26			98.92	96.85	Sr	0.02	96.72		
							ΣA	1.99			
			Na	1.01			Na	0.73		Na	0.96
			ΣB	1.01			Ca	0.27		Ca	0.04
							ΣB	1.00		ΣB	1.00
			OH	4.13			OH	4.26		OH	4.35
			F	0.13			F	0.71		F	0.65
			$\Sigma\varphi^-$	4.26			$\Sigma\varphi^-$	4.97		$\Sigma\varphi^-$	5.00

n.d.: not detected; n.a.: not analyzed. [1] Wet chemical analysis. [2] Electron-microprobe analysis. [3] Wet chemical analysis and flame photometry for alkali cations. [4] A qualitative spectroscopic analysis indicates mainly Ce_2O_3 and La_2O_3. [5] Fe^{3+}/Fe_{tot} determined by Mössbauer spectroscopy. [6] Calculated from structure refinement (see discussion in the text).

in Table 5, refined site-scattering values and assigned populations for selected cation sites are given in Table 6, positional disorder at the *A* site is presented in Table 7, details of hydrogen bonding in Table 8, and bond-valence values for selected anions in Table 9. A table of structure factors may be obtained from the Depository of Unpublished Data on the MAC website [document Astrophyllite group CM48_1].

Topology of the structure

The crystal structures of niobophyllite, kupletskite-(Cs) and Sn-rich astrophyllite are topologically identical to that of astrophyllite (Piilonen *et al.* 2003b). The M(1), M(2), M(3) and M(4) octahedra (C-group atoms) share edges to form a sheet of close-packed octahedra (*O*) of ideal composition C_7O_{14}. The characteristic feature of the astrophyllite structure is the (Si_4O_{12}) ribbon [a branched silicate chain in the terminology of Liebau (1985)] that extends along [100]. These (Si_4O_{12}) ribbons share common vertices with D octahedra to form the heteropolyhedral (H) sheet. In the crystal structure of astrophyllite-group minerals, the O sheet and two H sheets form an HOH block of composition $C_7\,D_2\,(Si_4\,O_{12})_2\,O_2\,(OH)_4\,X_{0-1}$. Along [001], these HOH blocks connect *via* common X anions of D octahedra and interstitial cations at the *A* and *B* sites (Fig. 2a).

TABLE 3. MISCELLANEOUS STRUCTURE-REFINEMENT DATA FOR ASTROPHYLLITE-GROUP MINERALS

	niobophyllite	kupletskite-(Cs)	Sn-rich astrophyllite
a (Å)	5.4022(6)	5.3850(3)	5.3866(4)
b	11.8844(6)	11.9350(5)	11.8821(7)
c	11.6717(6)	11.7793(6)	11.6794(8)
α (°)	112.990(1)	113.117(1)	113.019(2)
β	94.588(1)	94.614(1)	94.578(2)
γ	103.166(1)	103.075(1)	103.120(3)
V ($Å^3$)	659.7(1)	666.0(1)	658.1(3)
Space group		$P\bar{1}$	
Z		1	
Absorption coeff. (mm^{-1})	4.99	6.78	5.71
F(000)	651.4	686.5	665
$D_{calc.}$ (g/cm^3)	3.396	3.609	3.482
Crystal size (mm)	0.01 × 0.06 × 0.08	0.07 × 0.20 × 0.25	0.025 × 0.3 × 0.46
Radiation/filter	MoKα/graphite		
2θ upper limit for data collection (°)		60.00	
R(int) (%)	3.08	3.74	3.26
Reflections collected	10350	11070	14996
Independent reflections	3858	3883	3852
$F_o > 4\sigma F$	3576	3490	3791
Refinement method	Full-matrix least squares on F^2, fixed weights proportional to $1/\sigma F_o^2$		
Goodness of fit on F^2	1.231	1.069	1.064
Final $R_{(obs)}$ (%) [$F_o > 4\sigma F$]	5.96	3.33	3.53
R indices (%) (all data)	$R_1 = 6.52$ $wR_2 = 12.99$	$R_1 = 3.72$ $wR_2 = 8.58$	$R_1 = 3.47$ $wR_2 = 9.00$

Cation sites

Site populations were assigned on the basis of the refined site-scattering values (Table 6), the chemical formulae (Table 2) derived from electron-microprobe analysis, and the Mössbauer results (Table 1), and the observed mean bond-lengths (Table 5).

The D site: This site is usually occupied by the high-charge cations Ti^{4+} and Nb (Piilonen *et al.* 2003b), and in Sn-rich astrophyllite, we expect Sn^{4+} to occupy this site. The higher refined site-scattering value for this site in Sn-rich astrophyllite relative to the values in niobophyllite and kupletskite-(Cs) (Table 6) shows that this is the case. Moreover, the radius of Sn^{4+} (0.69 Å, Shannon 1976) is significantly larger than that of Ti^{4+} (0.605 Å) and Nb (0.64 Å), and this difference is reflected in the <D–O> distance, 1.979 Å, in Sn-rich astrophyllite relative to those in niobophyllite and kupletskite-(Cs) (Table 5). The ideal compositions of the *D* site are (NbTi) (niobophyllite) and Ti_2 *apfu* [kupletskite-(Cs) and Sn-rich astrophyllite].

The A and B sites: In the structure of the astrophyllite-group minerals, there are two interstitial sites, the K-dominant *A* site and the Na-dominant *B* site. The *B* site is [10]-coordinated with a <B–φ> distance of 2.633–2.645 Å, where φ represents O, F, OH (Table 5). In accord with previous work summarized in Piilonen *et al.* (2003b), we assigned mainly Na and less Ca to fill this site in accord with the refined site-scattering values (Table 6).

The stereochemistry of the *A* site is more complicated. The cavity in which the *A* site occurs is surrounded by 13 anions with a <A–φ> distance of ~3.3 Å. It is mainly occupied by K (*e.g.*, astrophyllite, kupletskite, Piilonen *et al.* 2003a, b), rarely Cs [*e.g.*, kupletskite-(Cs), Yefimov *et al.* 1971], Li (nalivkinite, Uvarova *et al.* 2008), and Na and Rb in minor amounts (*e.g.*, kupletskite-1*A*, Christiansen *et al.* 1998; niobokupletskite, Piilonen *et al.* 2000) (Table 7). The details of the coordination depend on the constituent cation(s). Christiansen *et al.* (1998) and Piilonen *et al.* (2003b) described the splitting of the *A* site into two sites, a [12–13]-coordinated site and a [5]-(or [13]) coordinated site, within the *A* cavity, denoted *A*(1a) and *A*(1b) by Piilonen *et al.* (2003b) . These two sites are separated by <1 Å, and hence cannot both be occupied at the local scale [*i.e.*, occupancy of one site precludes occupancy of the locally adjacent site]. Here, we have identified one *A* site in niobophyllite (Fig. 2b), the splitting of the *A* site into two sites in kupletskite-(Cs) (Fig. 2c), and the presence of three sites in Sn-rich astrophyllite (Fig. 2d) (Table 6). The nomenclature *A*(1a) and *A*(1b) seems needlessly complicated, and we have renamed these sites *A*(1) and *A*(2), the latter being invariably [5]-coordinated, and we have added the *A*(3) site. Therefore, there are *A*(1) and *A*(2) sites in kupletskite-(Cs), and *A*(1), *A*(2) and *A*(3) sites in Sn-rich astrophyllite (Tables 5, 6; Figs. 2c, d). The occupancies of the *A* sites are

TABLE 4. COORDINATES AND DISPLACEMENT FACTORS OF ATOMS IN ASTROPHYLLITE-GROUP MINERALS

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
					niobophyllite					
M(1)	0.85126(17)	0.20540(9)	0.47941(9)	0.0076(4)	0.0102(5)	0.0117(5)	0.0054(4)	0.0028(3)	0.0025(3)	0.0095(3)
M(2)	0.27875(15)	0.06798(8)	0.48781(8)	0.0091(4)	0.0111(4)	0.0128(4)	0.0072(3)	0.0040(3)	0.0042(3)	0.0099(3)
M(3)	0.42066(15)	0.35128(8)	0.48479(8)	0.0086(4)	0.0101(4)	0.0144(4)	0.0060(3)	0.0042(3)	0.0039(3)	0.0104(3)
M(4)	0	½	½	0.0071(5)	0.0067(5)	0.0125(6)	0.0030(4)	0.0013(4)	0.0016(4)	0.0092(3)
D	0.07425(10)	0.08160(5)	0.18633(7)	0.0036(2)	0.0078(3)	0.0153(4)	0.0068(2)	0.00271(19)	0.00257(18)	0.00805(19)
T(1)	0.6786(3)	0.27391(14)	0.23318(14)	0.0102(6)	0.0069(6)	0.0094(7)	0.0040(5)	0.0020(5)	0.0021(5)	0.0087(3)
T(2)	0.8148(3)	0.54744(15)	0.25427(15)	0.0160(7)	0.0090(7)	0.0117(7)	0.0043(6)	0.0021(6)	0.0027(6)	0.0124(3)
T(3)	0.3796(3)	0.67519(15)	0.25707(15)	0.0146(7)	0.0090(7)	0.0125(7)	0.0062(6)	0.0014(5)	0.0025(5)	0.0117(3)
T(4)	0.5066(3)	0.93104(14)	0.23737(14)	0.0106(6)	0.0070(6)	0.0082(6)	0.0047(5)	0.0022(5)	0.0020(5)	0.0082(3)
A	0.1382(5)	0.2762(2)	0.99610(19)	0.0845(19)	0.0497(14)	0.0269(10)	0.0132(9)	0.0062(10)	0.0121(12)	0.0562(9)
B	½	0	0	0.033(2)	0.021(2)	0.014(2)	0.0054(15)	0.0019(15)	0.0063(17)	0.0234(13)
O(1)	0.7254(7)	0.3194(4)	0.3853(4)	0.0088(16)	0.0098(17)	0.0091(17)	0.0024(14)	0.0026(13)	0.0029(14)	0.0097(7)
O(2)	0.1462(7)	0.1597(4)	0.3687(4)	0.0130(18)	0.0148(19)	0.0108(18)	0.0046(15)	0.0029(14)	0.0046(15)	0.0130(8)
O(3)	0.1275(8)	0.3912(4)	0.5935(4)	0.0116(17)	0.0097(17)	0.0117(18)	0.0038(14)	0.0025(14)	0.0017(14)	0.0115(7)
O(4) OH	0.2995(8)	0.4639(4)	0.4027(4)	0.0140(18)	0.0158(19)	0.0126(19)	0.0057(16)	0.0049(15)	0.0071(16)	0.0136(8)
O(5) OH	0.9912(8)	0.1169(4)	0.5916(4)	0.0150(19)	0.017(2)	0.0095(18)	0.0046(16)	0.0045(14)	0.0076(16)	0.0135(8)
O(6)	0.5581(8)	0.2569(4)	0.5893(4)	0.0120(18)	0.0132(18)	0.0141(19)	0.0065(16)	0.0031(15)	0.0040(15)	0.0128(8)
O(7)	0.5719(7)	0.0141(4)	0.3899(4)	0.0094(17)	0.0143(18)	0.0102(17)	0.0060(15)	0.0021(13)	0.0053(14)	0.0107(7)
O(8)	0.0739(10)	0.5905(5)	0.2012(4)	0.023(2)	0.032(3)	0.016(2)	0.007(2)	0.0033(18)	-0.006(2)	0.0273(11)
O(9)	0.2475(12)	0.0423(6)	0.8249(5)	0.036(3)	0.052(4)	0.017(2)	-0.007(2)	0.012(2)	-0.033(3)	0.050(2)
O(10)	0.4275(10)	0.4137(5)	0.7999(5)	0.034(3)	0.031(3)	0.019(2)	0.006(2)	0.002(2)	0.021(2)	0.0272(11)
O(11)	0.1276(14)	0.8053(7)	0.8289(5)	0.089(5)	0.073(4)	0.012(2)	0.016(3)	0.019(3)	0.075(4)	0.048(2)
O(12)	0.2661(14)	0.9570(6)	0.1731(5)	0.068(4)	0.057(4)	0.018(3)	-0.005(2)	-0.014(3)	0.057(4)	0.049(2)
O(13)	0.2675(11)	0.6063(4)	0.8062(4)	0.056(3)	0.0058(19)	0.015(2)	0.0046(16)	0.003(2)	0.002(2)	0.0269(11)
O(14)	0.5742(12)	0.2219(4)	0.8023(5)	0.056(3)	0.011(2)	0.017(2)	0.0083(18)	0.002(2)	0.003(2)	0.0287(12)
O(15)	0.3848(11)	0.1939(7)	0.1700(5)	0.030(3)	0.068(4)	0.015(2)	0.019(3)	-0.007(2)	-0.034(3)	0.0468(19)
X	0	0	0	0.008(2)	0.013(3)	0.014(3)	0.005(2)	0.0036(19)	0.004(2)	0.0112(10)
H(1)	0.269(14)	0.422(6)	0.3098(11)	0.01627(0)*						
H(2)	1.021(14)	0.155(7)	0.6844(11)	0.01620(0)*						
					kupletskite-(Cs)					
M(1)	0.84929(10)	0.20464(5)	0.47646(5)	0.0113(3)	0.0089(3)	0.0103(3)	0.0041(2)	0.00273(19)	0.0035(2)	0.01001(19)
M(2)	0.27839(8)	0.06637(4)	0.48642(4)	0.0112(3)	0.0101(3)	0.0130(3)	0.00530(19)	0.00345(17)	0.00345(19)	0.01114(16)
M(3)	0.42056(9)	0.35069(4)	0.48188(5)	0.0122(3)	0.0113(3)	0.0131(3)	0.0071(2)	0.00477(18)	0.00527(19)	0.01106(18)
M(4)	0	½	½	0.0102(3)	0.0087(3)	0.0121(3)	0.0052(2)	0.0023(2)	0.0030(2)	0.0100(2)
D	0.07679(7)	0.08356(4)	0.19345(4)	0.0055(2)	0.0068(2)	0.0149(2)	0.00570(16)	0.00273(15)	0.00232(14)	0.00853(13)
T(1)	0.67902(14)	0.27225(7)	0.23299(7)	0.0092(3)	0.0080(3)	0.0088(4)	0.0041(3)	0.0016(3)	0.0023(3)	0.00851(17)
T(2)	0.81517(14)	0.54765(7)	0.25821(7)	0.0087(3)	0.0061(3)	0.0087(4)	0.0033(3)	0.0017(3)	0.0021(3)	0.00777(17)
T(3)	0.38069(14)	0.67665(7)	0.26053(7)	0.0085(3)	0.0063(3)	0.0079(3)	0.0035(3)	0.0017(3)	0.0020(3)	0.00738(17)
T(4)	0.50596(14)	0.93100(7)	0.23615(7)	0.0093(3)	0.0059(3)	0.0085(4)	0.0033(3)	0.0010(3)	0.0016(3)	0.00792(17)
A(1)	0.15101(6)	0.29883(3)	0.99834(3)	0.02442(17)	0.02230(16)	0.01744(16)	0.00796(12)	0.00333(11)	0.00580(12)	0.02171(10)
A(2)	0.1123(5)	0.2182(2)	0.9976(2)	0.02442(17)	0.02230(16)	0.01744(16)	0.00796(12)	0.00333(11)	0.00580(12)	0.02171(10)
B	½	0	0	0.0233(8)	0.0092(7)	0.0068(6)	0.0025(5)	0.0018(5)	0.0034(5)	0.0137(4)
O(1)	0.7270(4)	0.3183(2)	0.3834(2)	0.0131(10)	0.0141(10)	0.0085(10)	0.0056(8)	0.0011(7)	0.0024(8)	0.0119(4)
O(2)	0.1444(4)	0.1570(2)	0.3658(2)	0.0149(10)	0.0124(10)	0.0056(9)	0.0022(8)	0.0016(7)	0.0054(8)	0.0113(4)
O(3)	0.1271(4)	0.3910(2)	0.5910(2)	0.0111(10)	0.0099(10)	0.0109(11)	0.0041(8)	0.0016(8)	0.0030(8)	0.0107(4)
O(4) OH	0.2968(5)	0.4631(2)	0.3999(2)	0.0149(11)	0.0140(11)	0.0150(11)	0.0070(9)	0.0038(9)	0.0043(9)	0.0142(5)
O(5) OH	0.9914(4)	0.1187(2)	0.5926(2)	0.0149(10)	0.0141(11)	0.0127(11)	0.0068(9)	0.0018(8)	0.0049(9)	0.0134(5)
O(6)	0.5564(4)	0.2565(2)	0.5881(2)	0.0113(10)	0.0095(10)	0.0083(10)	0.0031(8)	0.0007(8)	0.0023(8)	0.0101(4)
O(7)	0.5734(4)	0.0133(2)	0.3873(2)	0.0124(10)	0.0109(10)	0.0090(10)	0.0031(8)	0.0004(7)	0.0035(8)	0.0112(4)
O(8)	0.0757(4)	0.59098(18)	0.20490(19)	0.0099(9)	0.0142(9)	0.0121(9)	0.0048(8)	0.0023(7)	0.0012(7)	0.0127(4)
O(9)	0.2503(4)	0.0424(2)	0.8292(2)	0.0162(10)	0.0173(10)	0.0149(10)	0.0036(8)	0.0057(8)	-0.0027(8)	0.0183(4)
O(10)	0.4265(4)	0.41291(18)	0.79553(18)	0.0128(9)	0.0130(9)	0.0120(9)	0.0043(8)	0.0013(7)	0.0068(7)	0.0124(4)
O(11)	0.1269(4)	0.8071(2)	0.8309(2)	0.0253(11)	0.0234(11)	0.0152(10)	0.0105(9)	0.0088(8)	0.0190(9)	0.0180(4)
O(12)	0.2628(4)	0.9549(2)	0.1711(2)	0.0212(11)	0.0153(10)	0.0167(10)	0.0030(8)	-0.0019(8)	0.0108(8)	0.0183(4)
O(13)	0.2676(4)	0.60582(18)	0.80379(19)	0.0214(10)	0.0075(9)	0.0140(10)	0.0050(8)	0.0023(8)	0.0025(8)	0.0145(4)
O(14)	0.5727(4)	0.22182(18)	0.8003(2)	0.0235(11)	0.0085(9)	0.0127(10)	0.0050(8)	0.0028(8)	0.0038(8)	0.0149(4)
O(15)	0.3854(4)	0.1897(2)	0.1680(2)	0.0145(10)	0.0203(10)	0.0142(10)	0.0093(9)	-0.0006(8)	-0.0045(8)	0.0176(4)
X	0	0	0	0.0236(13)	0.0192(12)	0.0138(12)	0.0060(10)	0.0030(10)	0.0062(10)	0.0192(5)
H(1)	0.251(7)	0.416(3)	0.3082(10)	0.01707(0)*						
H(2)	1.026(7)	0.159(3)	0.6852(10)	0.01613(0)*						

TABLE 4 (cont'd). COORDINATES AND DISPLACEMENT FACTORS OF ATOMS IN ASTROPHYLLITE-GROUP MINERALS

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
					Sn-rich astrophyllite					
M(1)	0.85153(8)	0.20561(4)	0.48017(4)	0.0085(2)	0.0094(2)	0.0137(2)	0.00565(17)	0.00274(15)	0.00237(15)	0.01028(15)
M(2)	0.27930(8)	0.06826(4)	0.48837(4)	0.0086(2)	0.0100(2)	0.0145(2)	0.00627(17)	0.00336(15)	0.00287(15)	0.01055(15)
M(3)	0.42088(8)	0.35112(4)	0.48492(4)	0.0088(2)	0.0102(2)	0.0149(2)	0.00684(17)	0.00371(15)	0.00338(15)	0.01056(15)
M(4)	0	½	½	0.0078(3)	0.0085(3)	0.0131(3)	0.0050(2)	0.0018(2)	0.0020(2)	0.0097(2)
D	0.07685(5)	0.08531(3)	0.19385(3)	0.00726(14)	0.01041(15)	0.01796(16)	0.00766(11)	0.00314(10)	0.00281(10)	0.01122(10)
T(1)	0.67803(16)	0.27365(8)	0.23323(8)	0.012(4)	0.0090(4)	0.0111(4)	0.0047(3)	0.0017(3)	0.0021(3)	0.01092(17)
T(2)	0.81369(16)	0.54764(8)	0.25524(8)	0.0106(3)	0.0092(4)	0.0115(4)	0.0047(3)	0.0015(3)	0.0021(3)	0.01047(17)
T(3)	0.37723(15)	0.67597(8)	0.25782(8)	0.0099(3)	0.0090(3)	0.0117(4)	0.0055(3)	0.0019(3)	0.0023(3)	0.00990(17)
T(4)	0.50748(16)	0.93258(8)	0.23834(8)	0.0123(4)	0.0092(4)	0.0110(4)	0.0046(3)	0.0019(3)	0.0023(3)	0.01083(17)
A(1)	0.1342(5)	0.26893(17)	0.99484(16)	0.0971(13)	0.0268(9)	0.0225(5)	0.0097(8)	0.0030(6)	0.0065(12)	0.0515(5)
A(2)	0.113(5)	0.2204(18)	0.9959(17)	0.0971(13)	0.0268(9)	0.0225(5)	0.0097(8)	0.0030(6)	0.0065(12)	0.0515(5)
A(3)	0.154(6)	0.3074(17)	-0.001(2)	0.0971(13)	0.0268(9)	0.0225(5)	0.0097(8)	0.0030(6)	0.0065(12)	0.0515(5)
B	½	0	0	0.0268(11)	0.0163(9)	0.0086(9)	0.0033(7)	0.0014(7)	0.0042(7)	0.0183(6)
O(1)	0.7271(4)	0.3182(2)	0.3858(2)	0.0110(9)	0.0118(9)	0.0010(9)	0.0042(8)	0.0016(7)	0.0024(7)	0.0112(4)
O(2)	0.1468(4)	0.1637(2)	0.3771(2)	0.0111(9)	0.0117(10)	0.0167(10)	0.0065(8)	0.0029(8)	0.0032(8)	0.0130(4)
O(3)	0.1259(4)	0.3906(2)	0.5921(2)	0.0112(9)	0.0106(9)	0.0109(9)	0.0045(8)	0.0020(7)	0.0025(7)	0.0110(4)
O(4) OH	0.3015(4)	0.4635(2)	0.4020(2)	0.0131(10)	0.0127(10)	0.0142(10)	0.0060(8)	0.0031(8)	0.0035(8)	0.0132(4)
O(5) OH	0.9886(4)	0.1157(2)	0.5912(2)	0.0134(10)	0.0131(10)	0.0144(10)	0.0056(8)	0.0023(8)	0.0032(8)	0.0138(4)
O(6)	0.5628(4)	0.2564(2)	0.5881(2)	0.0120(9)	0.0109(9)	0.0100(9)	0.0040(8)	0.0017(7)	0.0025(7)	0.0112(4)
O(7)	0.5750(4)	0.0163(2)	0.3909(2)	0.0119(9)	0.0117(9)	0.0092(9)	0.0039(8)	0.0024(7)	0.0036(8)	0.0110(4)
O(8)	0.0736(5)	0.5911(3)	0.2018(2)	0.0138(11)	0.0294(13)	0.0170(11)	0.0078(10)	0.0038(9)	-0.0008(10)	0.0219(5)
O(9)	0.2483(7)	0.0423(4)	0.8256(3)	0.0441(19)	0.059(2)	0.0201(14)	-0.0098(14)	0.0183(14)	-0.0373(18)	0.0583(14)
O(10)	0.4270(5)	0.4118(3)	0.7969(2)	0.0218(12)	0.0294(14)	0.0181(12)	0.0083(10)	0.0023(9)	0.0154(11)	0.0223(5)
O(11)	0.1286(10)	0.8049(4)	0.8306(3)	0.105(3)	0.086(3)	0.0202(14)	0.0267(17)	0.0283(18)	0.087(3)	0.0570(13)
O(12)	0.2670(9)	0.9573(4)	0.1737(3)	0.085(3)	0.057(2)	0.0209(14)	-0.0085(14)	-0.0205(16)	0.060(2)	0.0571(14)
O(13)	0.2697(7)	0.6056(2)	0.8041(3)	0.064(2)	0.0093(11)	0.0145(11)	0.0053(9)	0.0022(12)	0.0021(12)	0.0311(7)
O(14)	0.5745(7)	0.2195(3)	0.7998(3)	0.068(2)	0.0099(11)	0.0156(12)	0.0067(9)	0.0026(13)	0.0024(12)	0.0327(7)
O(15)	0.3857(7)	0.1941(4)	0.1692(3)	0.0347(17)	0.084(3)	0.0188(14)	0.0248(17)	-0.0114(12)	-0.0413(18)	0.0564(13)
X	0	0	0	0.0199(13)	0.0210(14)	0.0164(13)	0.0071(11)	0.0030(10)	0.0053(11)	0.0195(6)
H(1)	0.252(8)	0.419(4)	0.3094(10)	0.01587(0)*						
H(2)	1.035(9)	0.157(4)	0.6837(10)	0.01654(0)*						

* U_{iso} = 1.5 U_{eq} of O(donor).

summarized in Table 7. Results of previous work show that the [13]-coordinated *A*(1) site is occupied mainly by K and ☐ (vacancy), the [5]-coordinated *A*(2) site is occupied by Li as a dominant constituent in nalivkinite, and the [13]-coordinated *A*(3) site is occupied by ☐ (vacancy) and K in niobokupletskite. Here the site populations were assigned according to this pattern of distribution. The refined site-scattering values at the *A*(1), *A*(2) and *A*(3) sites are given in Table 6. For niobophyllite, the sum of the alkali and alkaline-earth cations remaining after assignment of cations to the *B* site is assigned to the *A* site, and the effective scattering of these cations (46.7 *epfu*) is close to the refined site-scattering (49.8 *epfu*). For kupletskite-(Cs), the sum of the alkali and alkaline-earth constituents in the formula is 3.67 *apfu* (Table 2). As the sum of the constituents of the *A* and *B* sites cannot exceed 3 *apfu*, at least 0.67 *apfu* alkali and alkaline-earth cations must be assigned to other sites in the structure. The refined site-scattering value at the *A* site indicates that Cs dominates this site. We assume that K, Sr and Pb also occur at this site to give an effective scattering of 92.8 *epfu* compared with the refined value of 87.6 *epfu*. For Sn-rich astrophyllite, the *A*(1) and *A*(2,3) sites are dominated by K and vacancy (Table 6). The ideal compositions of the *A* site are K_2 (niobophyllite and Sn-rich astrophyllite) and Cs_2 *apfu* [kupletskite-(Cs)].

The M sites: In Sn-rich astrophyllite, the sum of the medium-sized divalent (Fe^{2+}, Mn^{2+}) and trivalent (Fe^{3+}) cations is 6.89 *apfu*, indicating that the *M*(1–4) sites are filled with Fe^{2+}, Mn^{2+} and Fe^{3+}, except possibly for a small amount of an additional component (0.11 *pfu*, 0.09 Ca and 0.02 Zn according to the formula, Table 2). This observation is in accord with the refined site-scattering values at the *M*(1–4) sites (Table 6). In astrophyllite-group minerals, the size of the M polyhedra follows the pattern M(1) > M(2) > M(3) > M(4) (Piilonen *et al.* 2003b). In Sn-rich astrophyllite, <M–φ> distances vary from 2.158 [M(1)] to 2.133 Å [M(4)], and we assign more Mn^{2+} (r = 0.83 Å) to the *M*(1) and *M*(2) sites and Fe^{3+} (r = 0.645 Å) to the *M*(3) and *M*(4) sites, Fe^{2+} being the dominant cation at all four *M* sites (Table 6). The *M*(1–4) sites give $Fe^{2+}_{6.18}Mn_{0.45}Fe^{3+}_{0.26}Ca_{0.09}Zn_{0.02}$ (total charge 14.26^+), which is in good agreement with ideal composition Fe^{2+}_7 *pfu* (charge 14^+).

In niobophyllite and kupletskite-(Cs), the sum of the medium-sized divalent and trivalent cations is << 7 *apfu*, suggesting (1) vacancies at the *M* sites (partial

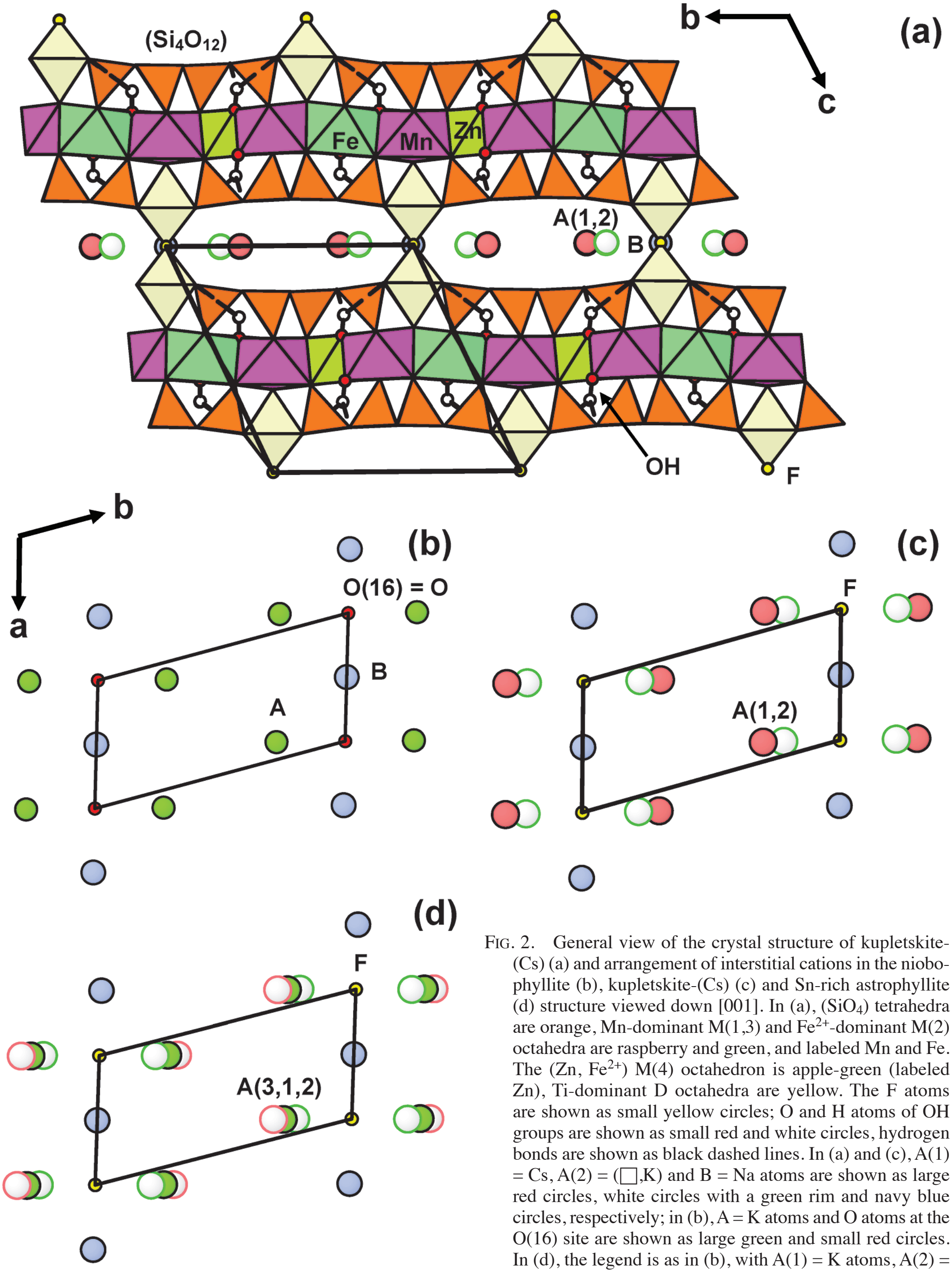

FIG. 2. General view of the crystal structure of kupletskite-(Cs) (a) and arrangement of interstitial cations in the niobophyllite (b), kupletskite-(Cs) (c) and Sn-rich astrophyllite (d) structure viewed down [001]. In (a), (SiO_4) tetrahedra are orange, Mn-dominant M(1,3) and Fe^{2+}-dominant M(2) octahedra are raspberry and green, and labeled Mn and Fe. The (Zn, Fe^{2+}) M(4) octahedron is apple-green (labeled Zn), Ti-dominant D octahedra are yellow. The F atoms are shown as small yellow circles; O and H atoms of OH groups are shown as small red and white circles, hydrogen bonds are shown as black dashed lines. In (a) and (c), A(1) = Cs, A(2) = (□,K) and B = Na atoms are shown as large red circles, white circles with a green rim and navy blue circles, respectively; in (b), A = K atoms and O atoms at the O(16) site are shown as large green and small red circles. In (d), the legend is as in (b), with A(1) = K atoms, A(2) = (□,K) and A(3) = (□,Cs) atoms are shown as large green circles, white circles with a green rim, and white circles with a red rim, respectively.

TABLE 5. SELECTED INTERATOMIC DISTANCE (Å) AND ANGLES (°) IN ASTROPHYLLITE-GROUP MINERALS

	niobophyllite	kupletskite -(Cs)	Sn-rich astrophyllite
M(1)–O(5)	2.162(4)	2.190(2)	2.157(2)
M(1)–O(2)a	2.163(4)	2.170(2)	2.104(2)
M(1)–O(6)	2.164(4)	2.176(2)	2.126(2)
M(1)–O(3)a	2.182(4)	2.195(2)	2.166(2)
M(1)–O(7)	2.206(4)	2.203(2)	2.182(2)
M(1)–O(1)	2.229(4)	2.221(2)	2.213(2)
<M(1)–φ>	2.184	2.193	2.158
M(2)–O(5)b	2.093(4)	2.116(2)	2.094(2)
M(2)–O(7)	2.099(4)	2.112(2)	2.098(2)
M(2)–O(5)c	2.132(4)	2.138(2)	2.119(2)
M(2)–O(6)	2.194(4)	2.205(2)	2.195(2)
M(2)–O(7)c	2.214(4)	2.240(2)	2.214(2)
M(2)–O(2)	2.239(4)	2.259(2)	2.204(2)
<M(2)–φ>	2.162	2.178	2.154
M(3)–O(4)	2.107(4)	2.121(2)	2.107(2)
M(3)–O(1)	2.109(4)	2.113(2)	2.111(2)
M(3)–O(3)	2.130(4)	2.137(2)	2.123(2)
M(3)–O(6)	2.145(4)	2.166(2)	2.147(2)
M(3)–O(4)d	2.182(4)	2.212(2)	2.179(2)
M(3)–O(2)	2.224(4)	2.250(2)	2.178(2)
<M(3)–φ>	2.150	2.167	2.141
M(4)–O(4)	2.079(4) ×2	2.086(2) ×2	2.089(2) ×2
M(4)–O(1)b	2.141(4) ×2	2.155(2) ×2	2.144(2) ×2
M(4)–O(3)	2.174(4) ×2	2.166(2) ×2	2.165(2) ×2
<M(4)–φ>	2.131	2.136	2.133
D–O(2)	1.925(4)	1.833(2)	1.935(2)
D–O(12)e	1.959(5)	1.963(2)	1.971(2)
D–O(11)f	1.963(5)	1.969(2)	1.976(2)
D–O(9)g	1.963(5)	1.961(2)	1.970(2)
D–O(15)	1.965(5)	1.970(2)	1.978(2)
D–X	1.9644(7)	2.0580(5)	2.0469(3)
<D–φ>	1.957	1.959	1.979
T(1)–O(11)d	1.595(5)	1.603(2)	1.592(3)
T(1)–O(15)	1.595(5)	1.602(2)	1.586(3)
T(1)–O(1)	1.620(4)	1.614(2)	1.628(2)
T(1)–O(13)d	1.633(5)	1.647(2)	1.628(3)
<T(1)–O>	1.611	1.617	1.609
T(2)–O(3)d	1.607(4)	1.604(2)	1.612(2)
T(2)–O(13)d	1.614(5)	1.617(2)	1.610(2)
T(2)–O(8)a	1.632(5)	1.643(2)	1.637(3)
T(2)–O(10)d	1.643(5)	1.641(2)	1.635(3)
<T(2)–O>	1.624	1.626	1.624
T(3)–O(14)d	1.609(5)	1.618(2)	1.612(3)
T(3)–O(6)d	1.621(4)	1.611(2)	1.627(2)
T(3)–O(10)d	1.646(5)	1.648(2)	1.641(3)
T(3)–O(8)	1.650(5)	1.647(2)	1.639(3)
<T(3)–O>	1.632	1.631	1.630
T(4)–O(9)d	1.593(5)	1.607(2)	1.591(3)
T(4)–O(12)	1.598(5)	1.601(2)	1.588(3)
T(4)–O(7)h	1.624(4)	1.621(2)	1.626(2)
T(4)–O(14)d	1.630(5)	1.642(2)	1.623(3)
<T(4)–O>	1.611	1.618	1.607

	niobophyllite	kupletskite -(Cs)	Sn-rich astrophyllite
T(2)b–O(8)–T(3)	139.0(3)	138.7(1)	138.7(2)
T(2)d–O(10)–T(3)d	138.2(3)	138.4(1)	139.7(2)
T(1)d–O(13)–T(2)d	142.0(3)	142.2(1)	143.1(2)
T(3)d–O(14)–T(4)d	142.2(3)	142.7(2)	143.5(2)
<T–O–T>	140.4	140.5	141.3
A(1)–O(11)j	2.925(7)	3.084(2)	2.868(5)
A(1)–O(15)i	2.926(7)	3.109(2)	2.880(5)
A(1)–O(12)f	2.937(8)	3.099(2)	2.884(5)
A(1)–O(9)	2.944(8)	3.122(2)	2.884(5)
A(1)–X	3.215(2)	3.4836(3)	3.138(2)
A(1)–O(14)	3.389(6)	3.400(2)	3.407(4)
A(1)–O(14)b	3.417(6)	3.441(2)	3.417(4)
A(1)–O(13)j	3.430(6)	3.425(2)	3.467(4)
A(1)–O(13)k	3.440(6)	3.415(2)	3.455(4)
A(1)–O(8)f	3.519(6)	3.418(2)	3.566(3)
A(1)–O(10)	3.562(6)	3.460(2)	3.626(3)
A(1)–O(10)k	3.615(6)	3.452(2)	3.700(3)
A(1)–O(8)i	3.680(6)	3.519(2)	3.749(3)
<A(1)–φ>	3.308	3.341	3.311
A(2)–O(11)j		2.560(3)	2.57(2)
A(2)–O(9)		2.562(3)	2.49(2)
A(2)–O(12)f		2.557(3)	2.58(2)
A(2)–O(15)i		2.568(3)	2.49(2)
A(2)–Xi		2.558(3)	2.48(2)
<A(2)–φ>		2.559	2.52
A(3)–O(11)f			3.12(2)
A(3)–O(15)			3.13(2)
A(3)–O(12)l			3.19(2)
A(3)–O(9)m			3.19(2)
A(3)–O(8)l			3.30(2)
A(3)–O(10)m			3.36(2)
A(3)–O(10)d			3.38(2)
A(3)–O(13)d			3.40(3)
A(3)–O(13)f			3.41(3)
A(3)–O(14)m			3.41(3)
A(3)–O(14)n			3.42(3)
A(3)–O(8)			3.43(2)
A(3)–X			3.56(2)
<A(3)–φ>			3.33
A(1)–A(2)		0.934(3)	0.57(2)
A(1)–A(3)l			0.43(2)
A(2)–A(3)			1.12(2)
B–O(12)e	2.619(8) ×2	2.634(2) ×2	2.620(6) ×2
B–O(15)	2.629(8) ×2	2.594(2) ×2	2.625(6) ×2
B–O(9)c	2.638(8) ×2	2.605(2) ×2	2.626(6) ×2
B–O(11)d	2.650(8) ×2	2.640(2) ×2	2.639(6) ×2
B–X	2.7011(1) ×2	2.6925(1) ×2	2.6933(2) ×2
<B–φ>	2.645	2.633	2.641

φ: unspecified anion: O, OH, F; O(4) and O(5): O atoms of OH groups; A(1) = A for niobophyllite.
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* + 1, –*z* + 1; g: –*x*, –*y*, –*z* + 1; h: *x*, *y* + 1, *z*; i: *x*, *y*, *z* + 1; j: –*x*, –*y* + 1, –*z* + 2; k: –*x* + 1, –*y* + 1, –*z* + 2; l: –*x*, –*y* + 1, –*z*; m: *x*, *y*, *z* – 1; n: *x*–1, *y*, *z*–1.

TABLE 6. REFINED SITE-SCATTERING (*epfu*) AND ASSIGNED SITE-POPULATIONS (*apfu*) FOR ASTROPHYLLITE-GROUP MINERALS

Site	Refined site-scattering	Site population	Calculated site-scattering	$\langle X\text{–}\varphi\rangle_{calc}$* (Å)	$\langle X\text{–}\varphi\rangle_{obs}$ (Å)
		niobophyllite			
M(1)	44.0(3)	1.0 Mn + 0.73 Fe^{2+} + 0.27 □	44.0	2.174	2.184
M(2)	50.5(3)	1.46 Fe^{2+} + 0.50 Mn + 0.04 □	50.5	2.151	2.162
M(3)	49.4(3)	1.33 Fe^{2+} + 0.28 Mn + 0.25 Fe^{3+} + 0.14 □	48.1	2.135	2.150
M(4)	25.5(2)	0.50 Fe^{2+} + 0.30 Fe^{3+} + 0.20 Mn	25.8	2.115	2.131
D	68.2(3)	1.46 Nb + 0.53 Ti + 0.01 Ta	72.3	1.998	1.957
$^{[13]}A$	39.3(4)	1.79 K + 0.03 Cs + 0.18 □	35.7		3.308
$^{[10]}B$	10.5(2)	1.0 Na	11.0	2.654	2.645
		kupletskite-(Cs)			
M(1)	42.9(2)	1.68 Mn + 0.32 Li	43.0	2.194	2.193
M(2)	49.1(2)	1.15 Fe^{2+} + 0.76 Mn + 0.09 Li	49.2	2.163	2.178
M(3)	46.5(2)	1.30 Mn + 0.35 Fe^{2+} + 0.14 Fe^{3+} + 0.20 Li + 0.01 □	45.8	2.162	2.167
M(4)	25.19(9)	0.50 Zn + 0.32 Fe^{2+} + 0.11 Mg + 0.07 Li	24.85	2.117	2.136
D	52.3(1)	1.54 Ti + 0.46 Nb	52.7	1.968	1.959
$^{[13]}A(1)$	76.7(2)	1.42 Cs + 0.11 K + 0.47 □	80.2		3.344
$^{[5]}A(2)$	10.94(8)	1.54 □ + 0.25 K + 0.08 Ca + 0.06 Pb + 0.05 Na + 0.02 Sr	12.58		2.559
$^{[10]}B$	13.39(8)	0.73 Na + 0.27 Ca	13.4	2.622	2.633
		Sn-rich astrophyllite			
M(1)	50.6(2)	1.77 Fe^{2+} + 0.17 Mn + 0.06 Ca	51.5	2.166	2.158
M(2)	50.8(2)	1.77 Fe^{2+} + 0.20 Mn + 0.03 Ca	51.6	2.153	2.154
M(3)	50.9(2)	1.76 Fe^{2+} + 0.16 Fe^{3+} + 0.08 Mn	51.9	2.136	2.141
M(4)	25.5(1)	0.88 Fe^{2+} + 0.10 Fe^{3+} + 0.02 Zn	26.1	2.130	2.133
D	70.2(2)	0.74 Ti + 0.62 Sn + 0.44 Nb + 0.16 Zr + 0.02 Ta + 0.02 Mg	73.4	2.005	1.979
$^{[13]}A(1)$	29.9(3)	1.57 K + 0.43 □	29.9		3.311
$^{[5]}A(2)$	2.8(2)	1.89 □ + 0.06 K + 0.04 Ca + 0.01 Pb	2.8		2.52
$^{[13]}A(3)$	2.8(2)	1.90 □ + 0.07 K + 0.03 Cs	3.0		3.33
$^{[10]}B$	11.4(1)	0.96 Na + 0.04 Ca	11.4	2.635	2.641

* Calculated by summing constituent ionic radii; values from Shannon (1976). φ: unspecified anion: O, OH, F. Coordination numbers are shown for non-octahedral sites.

TABLE 7. POSITIONAL DISORDER OF THE *A* SITE IN THE ASTROPHYLLITE-GROUP MINERALS

Mineral	Composition of the *A* site (*apfu*)			CN*			<A – φ>** (Å)			A–A (Å)***	Ref.
	A(1)	*A*(2)	*A*(3)	*A*(1)	*A*(2)	*A*(3)	*A*(1)	*A*(2)	*A*(3)		
kupletskite-(Cs)	$Cs_{1.42}K_{0.11}\square_{0.47}$	$\square_{1.54}K_{0.25}Ca_{0.08}Pb_{0.06}Na_{0.05}Sr_{0.02}$		13	5	–	3.341	2.559		$0.934^{1\text{-}2}$	(1)
Sn-rich astrophyllite	$K_{1.57}\square_{0.43}$	$\square_{1.89}K_{0.06}Ca_{0.04}Pb_{0.01}$	$\square_{1.90}K_{0.07}Cs_{0.03}$	13	5	13	3.311	2.52	3.33	$0.57^{1\text{-}2}$ $0.43^{1\text{-}3}$ $1.12^{2\text{-}3}$	(1)
kupletskite-1*A*	$K_{1.77}\square_{0.23}$	$\square_{1.77}K_{0.23}$		13†	5	–	3.265	2.407		$0.92^{1\text{-}2}$	(2)
kupletskite-1*A*	$K_{1.74}\square_{0.26}$	$\square_{1.74}Na_{0.26}$		12	5	–	3.270	2.380		$0.85^{1\text{-}2}$	(3)
kupletskite-1*A*	$K_{1.89}\square_{0.11}$	$\square_{1.86}Na_{0.14}$		13†	5	–	3.33	2.40		$0.86^{1\text{-}2}$	(4)
nalivkinite	$K_{0.75}Li_{0.14}Cs_{0.09}Na_{0.02}\square_{1.00}$	$Li_{1.00}\square_{1.00}$		13	5	–	3.310	2.28		$1.28^{1\text{-}2}$	(5)
niobokupletskite	$K_{0.96}Rb_{0.13}\square_{0.91}$		$\square_{1.18}K_{0.82}$	13	–	13	3.32		3.32	$0.37^{1\text{-}3}$	(6)

* coordination number; ** φ – O,F; A(1,3) – φ ≤ 3.8 Å; *** $0.934^{1\text{-}2}$ indicates that A(1) – A(2) = 0.934 Å; † CN for the A(1) site was revised and changed from 12 to 13. References: (1) this work, (2) Piilonen *et al.* (2001, sample RUS9), (3) Piilonen *et al.* (2003b, sample NOR17), (4) Christiansen *et al.* (1998), (5) Uvarova *et al.* (2008), (6) Piilonen *et al.* (2000).

dioctahedral character), or (2) incorporation of additional cations at the *M* sites. In this regard, Piilonen *et al.* (2003b) assigned sufficient Na to the *M*(1) site in astrophyllite-group minerals to bring the cation sum to 7 *apfu* at the *M*(1–4) sites. Moreover, Na is the sole occupant of the *M*(1) site in magnesiumastrophyllite (Sokolova & Cámara 2008).

In niobophyllite, the sum of the dominant type of M cations (Fe^{2+}, Mn^{2+} and Fe^{3+}) is 6.55 *apfu*. The total refined site-scattering at the *A* and *B* sites is 49.8 *e*, and the total effective scattering of the alkali cations (K, Cs and Na) is 46.7 *e*. Hence there is no excess of alkali cations that we can assign to the *M* sites, and the difference between the total number of *M* sites and the sum of the small divalent and trivalent cations must represent a true vacancy component, 0.45 □. The total refined site-scattering at the *M* sites in niobophyllite is 169.4 *epfu*, and the total effective scattering of Fe^{2+}, Mn^{2+} and Fe^{3+} is 168.4 *epfu*, in accord with the previous conclusion that there is no excess of alkali cations to assign to the *M* sites. Hence the site populations were assigned in accord with the range in <M–φ> distances for the M polyhedra: M(1), 2.184 – M(4), 2.131 Å: significant Mn was assigned to the *M*(1,2) sites, and all Fe^{3+} to the *M*(3,4) sites according to the refined site-scattering values (Table 6). In niobophyllite, Mn is dominant at the one *M*(1) site, and Fe^{2+} is dominant at the three sites *M*(2,3,4). The four *M* sites give $Fe^{2+}_{4.02}Mn_{1.98}Fe^{3+}_{0.55}\square_{0.45}$ (charge 13.62^+) or ideally Fe^{2+}_7 *pfu* (charge 14^+).

In kupletskite-(Cs), the sum of dominant M cations (Fe^{2+}, Mn^{2+}, Fe^{3+}, Mg and Zn) is 6.31 *apfu*. The difference between this sum and the total available at the *M* sites, 7 – 6.31 = 0.69 *pfu*, is essentially equal

TABLE 8. HYDROGEN BONDING IN ASTROPHYLLITE-GROUP MINERALS

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	∠DHA (°)
		niobophyllite		
O(4)OH-H(1)...O(11)a	0.98(1)	2.81(7)	3.427(8)	122(5)
O(4)OH-H(1)...O(15)	0.98(1)	2.81(6)	3.457(8)	124(5)
O(5)OH-H(2)...O(9)b	0.98(1)	2.85(7)	3.459(9)	121(5)
O(5)OH-H(2)...O(12)c	0.98(1)	2.86(6)	3.491(9)	123(5)
		kupletskite-(Cs)		
O(4)OH-H(1)...O(11)a	0.98(1)	2.74(3)	3.433(3)	128(3)
O(4)OH-H(1)...O(15)	0.98(1)	2.85(3)	3.501(3)	125(3)
O(5)OH-H(2)...O(9)b	0.99(1)	2.92(3)	3.533(3)	121(2)
O(5)OH-H(2)...O(12)c	0.99(1)	2.90(3)	3.519(3)	122(3)
		Sn-rich astrophyllite		
O(4)OH-H(1)...O(11)a	0.98(1)	2.75(4)	3.432(5)	127(3)
O(4)OH-H(1)...O(15)	0.98(1)	2.82(4)	3.448)(5	122(3)
O(5)OH-H(2)...O(9)b	0.98(1)	2.85(4)	3.468(5)	122(3)
O(5)OH-H(2)...O(12)c	0.98(1)	2.91(4)	3.481(6)	118(3)

a: $-x, -y + 1, -z + 1$; b: $x + 1, y, z$; c: $-x + 1, -y + 1, -z + 1$.

TABLE 9. BOND-VALENCE* TABLE FOR MONOVALENT ANIONS, OH AND F IN ASTROPHYLLITE-GROUP MINERALS

	M(1)	M(2)	M(3)	M(4)	D	A(1)	A(2)	B	H(1)	H(2)	Σ
					niobophyllite						
O(4)			0.36 0.30	0.33					0.97		1.96
O(5)	0.30	0.39 0.35								0.98	2.02
X**					$0.80^{\times 2}$→	$0.02^{\times 2}$→		$0.12^{\times 2}$→			1.88
					kupletskite-(Cs)						
O(4)			0.38 0.31	0.35					0.97		2.01
O(5)	0.30	0.37 0.35								0.98	2.00
X**					$0.42^{\times 2}$→	$0.05^{\times 2}$→	$0.03^{\times 2}$→	$0.10^{\times 2}$→			1.20
					Sn-rich astrophyllite						
O(4)			0.38 0.31	0.39					0.97		2.05
O(5)	0.29	0.34 0.32								0.98	1.93
X**					$0.49^{\times 2}$→	$0.06^{\times 2}$→	$0.01^{\times 2}$→	$0.05^{\times 2}$→			1.22

* bond-valence parameters (*vu*) from Brown (1981) and Brown & Altermatt (1985).

** X = $O_{0.73}F_{0.13}OH_{0.13}$ (niobophyllite), $F_{0.71}OH_{0.29}$ [kupletskiite-(Cs)] and $F_{0.65}OH_{0.35}$ (Sn-rich astrophyllite). The bond valence incident at X calculated with cation–oxygen parameters for niobophyllite and cation–fluorine parameters for kupletskiite-(Cs) and Sn-rich astrophyllite.

to the excess of alkali cations, 0.67 *apfu*, that cannot be accommodated at the *A* and *B* sites. This excess of alkali cations is due to 0.68 *apfu* Li (Table 2), and we assign all Li (r = 0.76 Å) to the *M* sites of the *O* sheet. Consider first the *M*(1) site. The refined site-scattering, 42.9 *epfu* (Table 6), is compatible with a site population of 1.68 Mn + 0.32 Li, and the large <*M*(1)–φ> distance, 2.193 Å, is in accord with the dominance of Mn (r = 0.83 Å) at this site. This leaves 0.36 Li *pfu* to be assigned to the *M*(2–4) sites. The refined site-scattering values, 49.1, 46.5 and 25.2 *epfu*, respectively, indicate that *M*(3) contains the largest amount of a scattering species of low scattering-power, *i.e.*, Li. In accord with findings of Piilonen *et al.* (2004), we assign all 0.50 Zn *apfu* to the *M*(4) site. For the *M*(2–4) sites, the assigned site-occupancies show good correlations between refined and calculated site-scattering and observed and calculated mean bond-lengths (Table 6). The *M*(1–4) sites give $Mn_{3.74}Fe^{2+}_{1.82}Li_{0.68}Zn_{0.50}Fe^{3+}_{0.14}Mg_{0.11}\square_{0.01}$ (total charge 13.44$^+$), which is in good agreement with the ideal composition Mn_7 *pfu* (charge 14$^+$).

We write an ideal cation component, $A_2\,B\,C_7\,D_2$, of the structure for the niobophyllite, kupletskite-(Cs) and Sn-rich astrophyllite as follows: $K_2\,Na\,Fe^{2+}_7\,(NbTi)$, $Cs_2\,Na\,Mn_7\,Ti_2$ and $K_2\,Na\,Fe^{2+}_7\,Ti_2$, respectively.

Hydrogen bonding

Details of hydrogen bonding are given in Table 8. Weak hydrogen bonds occur between OH groups of the O sheet, central atoms O(4) and O(5), and O atoms, which are common anions for D octahedra and (SiO_4) tetrahedra, O(9,11,12,15) (see Fig. 2a). Each H atom is involved in a bifurcated hydrogen bond. The H…O distances in niobophyllite, kupletskite-(Cs) and Sn-rich astrophyllite are 2.74–2.92 Å, and ∠DHA varies from 118 to 128°.

Anion consideration

In niobophyllite, kupletskite-(Cs) and Sn-rich astrophyllite, there are twelve sites, O(1), O(3), O(6–15), occupied by O atoms which belong to (SiO_4) tetrahedra and give 24 O atoms *pfu*. Those 24 O atoms correspond to two astrophyllite (Si_4O_{12}) ribbons. There is one site, O(2), which receives bond valence from three M octahedra and a D octahedron, giving O_2 *pfu*. There are two sites, O(4) and O(5), which are occupied by OH groups (see discussion above). Bond valence incident at each of these two sites (including contribution from an H atom) sums to 1.96–2.05 and 2.02–1.93 *vu* (valence unit) (Table 9). The two O(4) and O(5) sites give $(OH)_4$ *pfu*. There is one *X* site that can be occupied by F, OH, O and $\square$ (Piilonen *et al.* 2003a, b). In niobophyllite, the *X* site is [6]-coordinated; it receives bond valence from two D, two A(1) and two B cations. In niobophyllite, the bond valence incident at the *X* site is 1.88 *vu* (Table 9), and it reflects the composition of the *X* site, $O_{0.74}F_{0.13}OH_{0.13}$, ideally O *apfu*. The amount of O^{2-} atoms at the *X* site correlates with the content of Nb at the *D* site, 0.73 *apfu*. Therefore, we write the anion part of the niobophyllite structure as $(Si_4O_{12})_2\,O_2\,(OH)_4\,O$. In kupletskite-(Cs) and Sn-rich astrophyllite, the X atom is [6]-coordinated; it receives bond valence from two D, two A(1) [or alternatively two A(2)] and two B cations, 1.20 and 1.22 *vu*, respectively (Table 9). In kupletskite-(Cs) and Sn-rich astrophyllite, the composition of the *X* site is $F_{0.71}OH_{0.29}$ and $F_{0.65}OH_{0.35}$, ideally $F_{1.00}$ *apfu*. For kupletskite-(Cs) and Sn-rich astrophyllite, we write the anion part of the structure as $(Si_4O_{12})_2\,O_2\,(OH)_4\,F$.

DISCUSSION

Chemical formulae

Niobophyllite, kupletskite-(Cs) and Sn-rich astrophyllite: We write their ideal chemical formulae as the sum of the cation and anion parts: niobophyllite, $K_2\,Na\,Fe^{2+}_7\,(NbTi)\,(Si_4O_{12})_2\,O_2\,(OH)_4\,O$, kupletskite-(Cs), $Cs_2\,Na\,Mn_7\,Ti_2\,(Si_4O_{12})_2\,O_2\,(OH)_4\,F$, and Sn-rich astrophyllite, $K_2\,Na\,Fe^{2+}_7\,Ti_2\,(Si_4O_{12})_2\,O_2\,(OH)_4\,F$. Compare our formulae with those revised by (Piilonen *et al.* 2003a) for niobophyllite, $K_2\,Na\,(Fe^{2+},Mn)_7\,(Nb,Ti)_2\,Si_8\,O_{26}\,(OH)_4\,(F,O)$; kupletskite-(Cs), $(Cs,K)_2\,Na\,(Mn,Fe,Li)_7\,(Ti,Nb)_2\,Si_8\,O_{26}\,(OH)_4\,F$ and astrophyllite, $K_2\,Na\,(Fe^{2+},Mn)_7\,Ti_2\,Si_8\,O_{26}\,(OH)_4\,F$. Our formulae for kupletskite-(Cs) and Sn-rich astrophyllite (= astrophyllite) are compatible with those of Piilonen *et al.* (2003a). Based on the structural data, X in the formula for niobophyllite is given as O (= $O_{0.74}F_{0.13}OH_{0.13}$, see above). Revised ideal formulae and unit-cell parameters for astrophyllite-group minerals are given in Table 10.

Zircophyllite: Zircophyllite is the only astrophyllite-group mineral that lacks structural characterization. Kapustin (1973) carried out a chemical analysis of zircophyllite, and we calculated its empirical formula unit based on 31 (O+OH+F) anions (the content of H_2O was changed from 3.20 to 2.70 wt.% to achieve OH + F = 5 *apfu*): $K_{1.66}\,(Na_{0.70}\,Ca_{0.23})_{\Sigma 0.93}\,(Fe^{2+}_{3.51}Mn_{3.71}Zr_{0.26})_{\Sigma 7.48}\,(Zr_{1.28}Ti_{0.40}Nb_{0.24}Hf_{0.08})_{\Sigma 2.00}\,(Si_{7.59}O_{24})\,O_2\,(OH_{4.19}F_{0.88})_{\Sigma 5.07}$. This empirical formula tells us that Si is low, 7.59 instead of 8 *apfu*, and there is an excess of C cations, 7.48 instead of the maximum allowed, 7 *apfu*. Therefore, it is not possible to write a simplified or ideal formula, or to revise it with any confidence. Zircophyllite was originally described as an Fe^{2+}-dominant mineral (Kapustin 1973). Piilonen *et al.* (2003a) listed it as a Mn^{2+}-dominant mineral and gave a revised chemical formula: $K_2\,(Na,Ca)\,(Mn,\,Fe^{2+})_7\,(Zr,Nb)_2\,Si_8\,O_{26}\,(OH)_4\,F$. Although in the empirical formula, Mn – Fe^{2+} = 0.20 *apfu* (see above), the excess of 0.48 *apfu* for the C cations makes the evaluation of zircophyllite as a Fe^{2+}- or Mn-dominant mineral problematic.

The astrophyllite-ribbon component: There is one conceptual difference concerning presentation of the

TABLE 10. IDEAL FORMULAE AND UNIT-CELL PARAMETERS FOR THE ASTROPHYLLITE-GROUP MINERALS*

Mineral	A_2	B	C_7	D_2	$(Si_4O_{12})_2$	O_2	$(OH)_4$	X	*a* (Å) α (°)	*b* (Å) β (°)	*c* (Å) γ (°)	Space group	*Z*	Ref.
astrophyllite	K_2	Na	Fe^{2+}_7	Ti_2	$(Si_4O_{12})_2$	O_2	$(OH)_4$	F	5.3754 113.133	11.8970 94.638	11.6634 103.081	$P\bar{1}$	1	(1)
magnesium-astrophyllite	K_2	Na	$(Fe^{2+}_4Mg_2Na)$	Ti_2	$(Si_4O_{12})_2$	O_2	$(OH)_4$	□	5.3327	23.1535 99.615	10.3775	*C*2/*m*	2	(2)
nalivkinite	Li_2	Na	Fe^{2+}_7	Ti_2	$(Si_4O_{12})_2$	O_2	$(OH)_4$	F	5.3745 113.325	11.930 94.524	11.651 103.080	$P\bar{1}$	1	(3)
niobophyllite	K_2	Na	Fe^{2+}_7	(NbTi)	$(Si_4O_{12})_2$	O_2	$(OH)_4$	O	5.4022 112.990	11.8844 94.588	11.6717 103.166	$P\bar{1}$		(4)
Sn-rich astrophyllite**	K_2	Na	Fe^{2+}_7	Ti_2	$(Si_4O_{12})_2$	O_2	$(OH)_4$	F	5.3866 113.019	11.8821 94.578	11.6794 103.120	$P\bar{1}$	1	(4)
kupletskite-1*A*	K_2	Na	Mn_7	Ti_2	$(Si_4O_{12})_2$	O_2	$(OH)_4$	F	5.3784 112.964	11.9085 94.697	11.7236 103.112	$P\bar{1}$	1	(5)
kupletskite-2*M*	K_2	Na	Mn_7	Ti_2	$(Si_4O_{12})_2$	O_2	$(OH)_4$	F	5.4022	23.226 95.246	21.1782	*C*2/*c*	4	(6)
niobokupletskite	K_2	Na	Mn_7	(NbTi)	$(Si_4O_{12})_2$	O_2	$(OH)_4$	O	5.4303 112.927	11.924 94.750	11.747 103.175	$P\bar{1}$	1	(7)
kupletskite-(Cs)	Cs_2	Na	Mn_7	Ti_2	$(Si_4O_{12})_2$	O_2	$(OH)_4$	F	5.3850 113.117	11.9350 94.614	11.7793 103.075	$P\bar{1}$	1	(8)

* Zircophyllite is not included (see discussion in text); ** $D_2 = Ti^{4+}_{0.74}\mathbf{Sn^{4+}}_{0.62}Nb_{0.44}Zr_{0.16}Ta_{0.22}$.
References (the latest and the first references on structure are the first and second entries in the numbered list of references, respectively): (1) Piilonen *et al.* (2003b, sample RUS8), Woodrow (1967) and Peng & Ma (1963), model; (2) Sokolova & Cámara (2008), Shi *et al.* (1998); (3) Uvarova *et al.* (2008); (4) this work; (5) Piilonen *et al.* (2003b, sample NOR17), Peng & Ma (1964); (6) Piilonen *et al.* (2001, sample RUS9); (7) Piilonen *et al.* (2000); (8) this work.

Si–O radical: $(Si_4O_{12})_2$ (this work) *versus* $Si_8\,O_{26}$ [Piilonen *et al.* (2003a)]. We write the astrophyllite-ribbon component of the formula as $(Si_4O_{12})_2$ in order to emphasize that (1) the translational repeat fragment of the ribbon has the formula (Si_4O_{12}); (2) there are two ribbons (corresponding to two H sheets) attached to the central O sheet; (3) the O_2 anions do not link to Si, and this information should be preserved in the chemical formula by writing them separately from the silicate radical: $(Si_4O_{12})_2O_2$. In the first publication on the crystal structure of astrophyllite, Peng & Ma (1963) wrote the astrophyllite-ribbon component as $[Si_4O_{12}]_2$. In his discussion of common features for micas, astrophyllite-group minerals and Ti disilicates of the bafertisite group, Belov (1976) also gave the astrophyllite-ribbon formula as $[Si_4O_{12}]$. We propose to maintain the original crystal-chemical form of the astrophyllite group and write all formulae with the component $(Si_4O_{12})_2O_2$.

A-site disorder and potential new species in the astrophyllite group

Table 7 gives details of the *A*-site disorder in minerals of the astrophyllite group. To summarize, the interstitial *A* site can occur as a single site or may be split into two or three sites separated by short distances and hence partly occupied. The [13–12]-coordinated *A*(1) site is occupied mainly by K and □ (vacancy) as dominant constituents, and Li, Rb and Na in minor amounts. The [5]-coordinated *A*(2) site is occupied by Li as a dominant constituent, and K, Na, Ca, Pb and Sr as minor constituents. The [13]-coordinated *A*(3) site is occupied by □ (vacancy) and K as major constituents, and Cs as a minor constituent. The presence of vacancy at all three sites makes it possible to predict potential compositions that are currently unknown. For example, the Na-dominant *B* site commonly hosts minor Ca (Piilonen *et al.* 2003b). The ions Ca^{2+} and Na^+ have a similar size [$^{[10]}r$ = 1.29 (Na) and 1.23 Å (Ca)], suggesting that a Ca-dominant astrophyllite-group mineral is possible. Excess positive charge at the *B* site can be compensated by vacancy at the *A* site: $^{B}Ca^{2+} + {}^{A}\square \rightarrow {}^{B}Na^{+} + {}^{A}K^{+}$, leading to $(K\,\square)\,Ca\,Fe^{2+}_7\,Ti_2\,(Si_4O_{12})_2\,O_2\,(OH)_4\,F$. Note that Sokolova & Cámara (2008) proposed another potential new composition, ideally $K_2\,Ca\,(Fe_4\,Mg_2\,Na)\,Ti_2\,(Si_4O_{12})_2\,O_2\,(OH)_4\,F$, with the topology of the magnesiumastrophyllite structure and related to magnesiumastrophyllite by the substitution $^{B}Na^{+} + {}^{X}\square \rightarrow {}^{B}Ca^{2+} + {}^{X}F^{-}$.

SUMMARY

Three minerals of the astrophyllite group, niobophyllite, $K_2\,Na\,Fe^{2+}_7\,(NbTi)\,(Si_4O_{12})_2\,O_2\,(OH)_4\,O$, kupletskite-(Cs), $Cs_2\,Na\,Mn_7\,Ti_2\,(Si_4O_{12})_2\,O_2\,(OH)_4\,F$, and Sn-rich astrophyllite, $K_2\,Na\,Fe^{2+}_7\,Ti_2\,(Si_4O_{12})_2$

O_2 $(OH)_4$ F, have been structurally and chemically characterized.

(1) We suggest that the general formula of the astrophyllite-group minerals be written as A_2 B C_7 D_2 $(T_4O_{12})_2$ O_2 $(OH)_4$ X_{0-1} as this (i) preserves the correct formula of the silicate radical in the structure, and (ii) identifies the O_2 anion component of the structure as not bonded to Si.

(2) The discovery of Sn-rich astrophyllite tells us that there is potential for a new mineral species of the astrophyllite group where Sn^{4+} is a dominant cation at the *D* site.

(3) We have identified three distinct *A* sites, *A*(1), *A*(2) and *A*(3) with coordinations [13], [5] and [12–13], respectively, that are separated by ≤1.28 Å such that locally adjacent sites cannot both be occupied.

(4) We suggest the possibility of Ca occupying the *B* site via the substitution ${}^{B}Ca^{2+} + {}^{A}\square \rightarrow {}^{B}Na^{+} + {}^{A}K^{+}$, producing a potential new mineral species.

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THE CRYSTAL STRUCTURES OF NIOBOPHYLLITE, KUPLETSKITE-(Cs) AND Sn-RICH ASTROPHYLLITE: REVISIONS TO THE CRYSTAL CHEMISTRY OF THE ASTROPHYLLITE-GROUP MINERALS: ERRATUM

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In the above article [*Can. Mineral.* **48** (2010), 1-16], the four bond-lengths reported in Table 5 for the *A*(2) site of the Sn-rich astrophyllite and the *A*(2)–Xi bond-length of kupletskite-(Cs) are incorrect. We report here the correct values:

In Table 6, in the <*A*–ϕ>** (Å) column, <*A*(2)–ϕ> = 2.57 for Sn-rich astrophyllite. In Table 7, in the <*A*–ϕ>$_{obs}$** (Å) column, <*A*(2)–ϕ>$_{obs}$ = 2.57 for Sn-rich astrophyllite. In the *A*–*A* (Å)*** column, *A*(2)–*A*(3) = 0.99 for Sn-rich astrophyllite.

We apologize to readers. We thank Robert T. Downs, University of Arizona, who compiles and maintains The American Mineralogist Crystal Structure Database, for calling our attention to the inconsistencies in these tables.

	Kupletskite-(Cs)	Sn-rich astrophyllite
A(2) – O(11)j	2.560(3) Å	2.57(2) Å
A(2) – O(9)	2.562(3)	2.57(2)
A(2) – O(12)f	2.557(3)	2.59(2)
A(2) – O(15)i	2.568(3)	2.57(2)
A(2) – Xi	2.549(3)	2.57(2)
<A(2) – φ>	2.559	2.57
A(2) – A(3)		0.99(2)

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