Staročeskéite, $Ag_{0.70}Pb_{1.60}(Bi_{1.35}Sb_{1.35})_{\Sigma2.70}S_6$, from Kutná Hora, Czech Republic, a new member of the lillianite homologous series

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ABSTRACT

A new mineral species, staročeskéite, ideally $Ag_{0.70}Pb_{1.60}(Bi_{1.35}Sb_{1.35})_{\Sigma2.70}S_6$, has been found at Kutná Hora ore district, Czech Republic. The mineral occurs in the late-stage Bi-mineralization associated with other lillianite homologues (gustavite, terrywallaceite, vikingite, treasurite, eskimoite and Bi-rich andorite-group minerals) and other bismuth sulfosalts (izoklakeite, cosalite and Bi-rich jamesonite) in quartz gangue. The mineral occurs as lath shaped crystals or anhedral grains up to 80 μm × 70 μm, growing together in aggregates up to 200 μm × 150 μm across. Staročeskéite is steel-grey in colour and has a metallic lustre, the calculated density is 6.185 g/cm^3. In reflected light staročeskéite is greyish white; bireflectance and pleochroism are weak with greyish tints. Anisotropy is weak to medium with grey to bluish grey rotation tints. Internal reflections were not observed. The empirical formula based on electron probe microanalyses and calculated on 11 apfu is: $(Ag_{0.68}Cu_{0.01})_{\Sigma0.69}(Pb_{1.56}Fe_{0.01}Cd_{0.01})_{\Sigma1.58}(Bi_{1.32}Sb_{1.37})_{\Sigma2.69}(S_{6.04}Se_{0.01})_{\Sigma6.05}$. The ideal formula is $Ag_{0.70}Pb_{1.60}(Bi_{1.35}Sb_{1.35})_{\Sigma2.70}S_6$, which requires Ag 7.22, Pb 31.70, Bi 26.97, Sb 15.72 and S 18.39 wt.%, total 100.00 wt.%. Staročeskéite is a member of the lillianite homologous series with $N = 4$. Unlike gustavite and terrywallaceite, staročeskéite, similarly to lillianite, is orthorhombic, space group *Cmcm*, with $a = 4.2539(8)$, $b = 13.3094(8)$, $c = 19.625(1)$ Å, $V = 1111.1(2)$ Å^3 and $Z = 4$. The structure of staročeskéite contains four sulfur sites and three metal sites: one pure Pb site and two mixed sites, $M1$ (0.52Bi + 0.356Ag + 0.124Sb) and $M2$ (0.601Sb + 0.259Pb + 0.14Bi). The mineral is characterized by the Bi:Sb ratio 1:1 (Bi/(Bi + Sb) = 0.50) and the $Ag^+ + Bi^{3+}$, $Sb^{3+} \leftrightarrow 2 Pb^{2+}$ substitution ($L\%$) equal to 70%. Thus the mineral lies between two series of the lillianite structures with $N = 4$, between the lillianite–gustavite series and the andorite series.

Introduction

Staročeskéite, ideally $Ag_{0.70}Pb_{1.60}(Bi_{1.35}Sb_{1.35})_{\Sigma2.70}S_6$, has been found at the Staročeské pásmo Lode of the Kutná Hora base-metal ore district, Czech Republic, during an extensive search for bismuth sulfosalts in the ore district. It is named after the type locality. The history of the mineral goes back

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to 2005, when first samples of bismuth mineralization from Kutná Hora ore district were measured using an electron probe microanalyser (EPMA), including compositions corresponding to staročeskéite. Then, the compositions were considered as an intermediate member between gustavite and andorite-group minerals. The Bi–Sb intermediate member posed an interesting challenge, so a fragment of a homogenous grain *ca.* 40 μm by 30 μm in size of the holotype sample ST 37 was extracted for single-crystal X-ray diffraction (SC-XRD) analysis. The structure

was solved and published in 2010 (Pažout and Dušek, 2010) but the phase was still not recognized by the authors as a new mineral species. Later on, after the description of the new mineral terrywallaceite from Huancavelica, Peru (Yang *et al*., 2013), which is also a Bi–Sb member of the lillianite homologous series, it became apparent that the mineral found in Kutná Hora is a new mineral species. Therefore, in 2015–2016 another large set of polished sections with Bi-mineralization from Kutná Hora was measured using EPMA and more samples with staročeskéite compositions were discovered. Subsequently, the proposal for a new mineral was submitted and the new mineral and its name were approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA 2016-101; Pažout and Sejkora, 2017). The holotype sample has been deposited in the mineralogical collections of the National Museum in Prague, Department of Mineralogy and Petrology, Cirkusová 1740, Praha 9, Czech Republic under the catalogue number P1P 30/2016.

Staročeskéite is a member of the lillianite homologous series of sulfosalts with $N = 4$. The structural and chemical features of the lillianite homologues have been described in detail by Makovicky and Karup-Møller (1977*a*,*b*), and Makovicky and Topa (2014). The pronounciation of the mineral name is best approximated as /ˈstarotʃeski:ait/ using the International Phonetic Alphabet. The acute accent ´ symbol indicates that the main stress is on the /sta/ syllable.

Occurrence

Staročeskéite was found in twenty-one different samples (~50 analytical points) in the material collected from medieval mine dumps of the Staročeské pásmo Lode (Old Bohemian Lode) of the Kutná Hora Ag–Pb–Zn ore district in 1999–2015. Therefore no information is available on their *in situ* position within individual vein structures. The GPS coordinates of the type occurrence are 49° 58.47882′ N, 15°16.15142′ E. The Kutná Hora Ag–Pb–Zn ore district (located 60 km east of Prague, Central Bohemia, Czech Republic) contains a hydrothermal vein type mineralization of Variscan age (Holub *et al*., 1982, Žák *et al*., 1996). It was one of the main European producers of silver in the 14th to 16th centuries, with hundreds of mines on twelve major lodes (Fig. 1). Each lode (also called pásmo in Czech or zug in German)

represents a hydrothermally altered zone of several hundred metres to about three kilometres long and dozens of metres wide, with the depth range between several hundred metres to 1 km, each consisting of several, usually parallel veins (Holub *et al*., 1982).

Geologically and mineralogically, two mineral assemblages are present in this ore district, one 'silver-rich' in the southern part of the ore district and one 'pyrite-rich' in the northern part (Malec and Pauliš, 1997). The Staročeské pásmo Lode belongs to the northern pyrite-rich lodes and it is the biggest lode of the Kutná Hora ore district, both in terms of the amount of extracted ore and the amount of extracted silver (~300–500 tons of Ag).

The silver-rich assemblage (southern part) consists mainly of miargyrite, pyrargyrite, freibergite, native silver, galena, pyrite, sphalerite, berthierite and Pb–Sb (–Ag) sulfosalts (boulangerite, jamesonite and owyheeite) in quartz–kutnohorite gangue. The pyrite-rich assemblage (northern part) comprises pyrite, arsenopyrite, sphalerite, Ag-bearing galena, pyrrhotite, marcasite, chalcopyrite, stannite, freibergite–tetrahedrite and Pb–Sb (–Ag) sulfosalts in quartz gangue without kutnohorite. Typical of the pyrite-rich assemblage is the presence of Bi and Sn (each from a different mineralization stage), completely absent in the former, Ag-rich assemblage. More than 150 mineral species are known from the Kutná Hora ore district (Malec and Pauliš, 1997; Pauliš, 1998; Pažout, 2017; Pažout *et al*., 2017).

The new mineral was found in quartz gangue in the rich Ag–Pb–Bi–Sb sulfosalt association (gustavite, terrywallaceite, vikingite, treasurite, eskimoite, erzwiesite, Bi-rich fizelyite and Bi-rich ramdohrite) accompanied by Ag- and Bi-bearing galena and Pb–Bi–Sb sulfosalts (izoklakeite, cosalite and Bi-rich jamesonite) (Figs 2 and 3). The new mineral forms late in the Bi sulfosalt paragenesis, following the usual sequence of crystallization from early Bi-rich to later Sb-rich phases: native Bi → galena$_{ss}$ → matildite → izoklakeite/cosalite → eskimoite/vikingite → gustavite → Sb-rich gustavite → terywallaceite/staročeskéite → Bi-rich andorite minerals → Bi-rich jamesonite (Pažout 2017; Pažout *et al.*, 2017). The origin of this Bi sulfosalt mineralization is related to the penetration of low-temperature fluids (~100–250°C) into tectonically opened fractures in older ore vein fillings (pyrite, arsenopyrite and stannite). Virtually no mobilization of elements from the earlier vein filling took place; hydrothermal fluids must have been relatively rich in Ag and Pb and
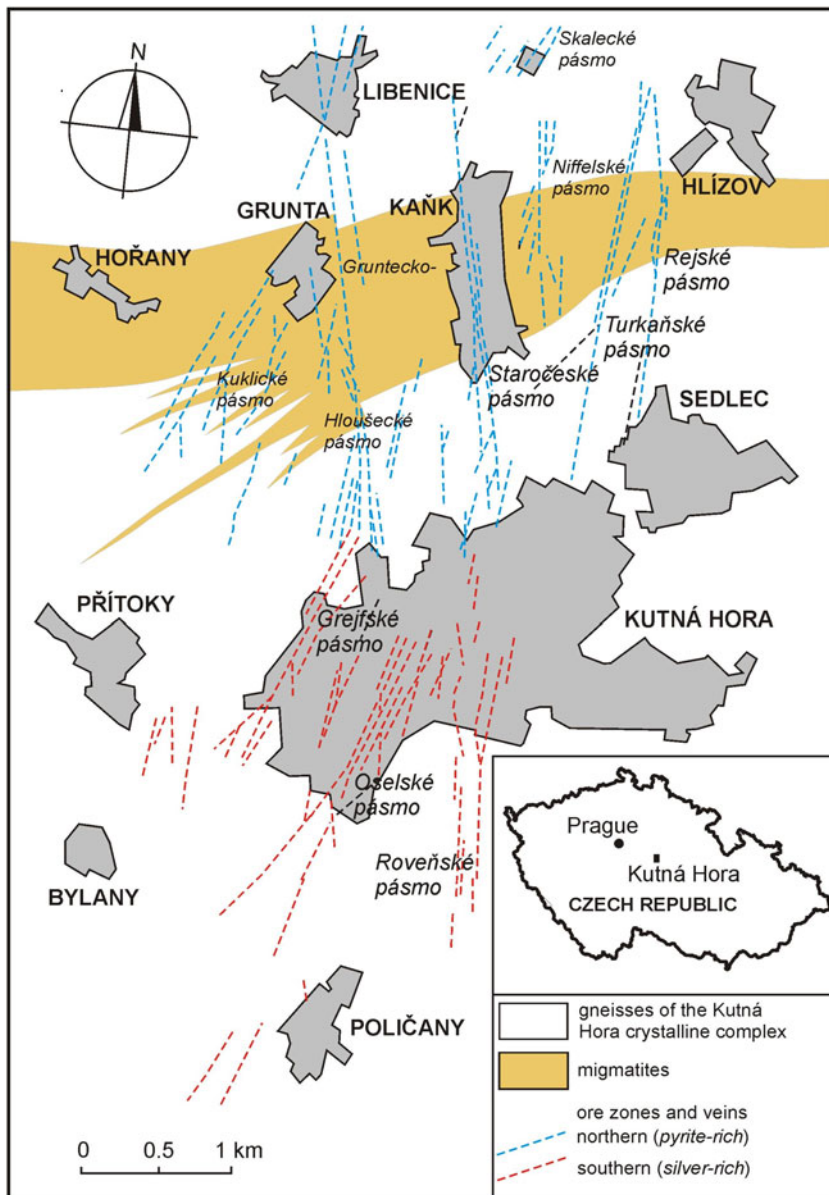
FIG. 1. Map of Kutná Hora ore district with major ore zones (lodes), after Malec and Pauliš (1997). Each lode ('pásmo' in Czech) consists of several veins.

simultaneously poor in Cu. A high Bi content was characteristic of the initial stage of the mineralization. Gradually, the Bi/Sb ratio decreased considerably with more Sb-rich minerals originating. At the final stage, Bi-rich Pb–Sb sulfosalts with lower Ag contents crystallized (Pažout *et al.*, 2017).

Physical and optical properties

The mineral occurs as lath-shaped crystals or anhedral grains up to 80 μm × 70 μm, growing together in aggregates up to 200 μm × 150 μm across (Figs 2 and 3). Staročeskéite is steel-grey in
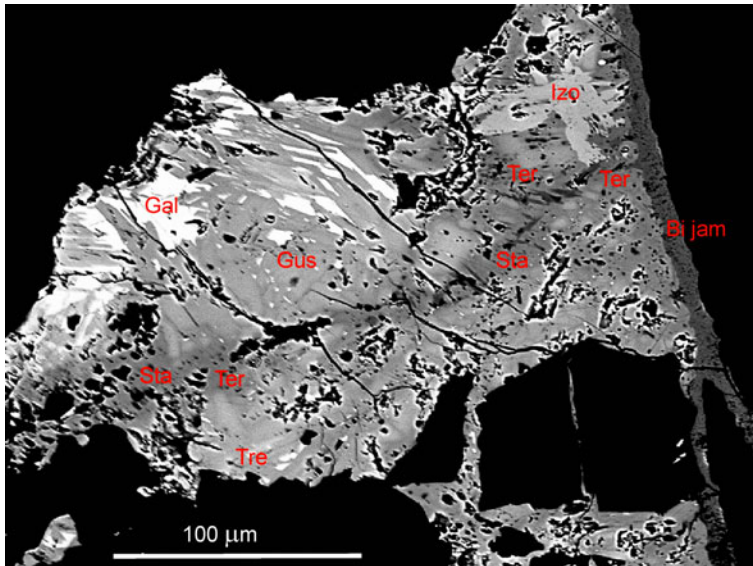
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FIG. 2. The association of Sb-rich Bi-sulfosalts and Bi-rich Sb-sulfosalts from the Kutná Hora ore district. The earliest (oldest) Ag- and Bi-bearing galena (Gal) is replaced by izoklakeite (Izo) and treasurite (Tre), followed by Sb-rich gustavite (Gus), terrywallaceite (Ter) and staročeskéite (Sta). The right rim of the grain is formed by latest Bi-rich jamesonite (Bi jam). Back-scattered electron (BSE) image of sample ST 4 F.

colour and has a metallic lustre, the calculated density is 6.185 g/cm^3. In reflected light staročeskéite is greyish white; bireflectance and pleochroism are weak with greyish tints. Anisotropy is weak to medium, with grey to bluish grey rotation tints. Internal reflections were

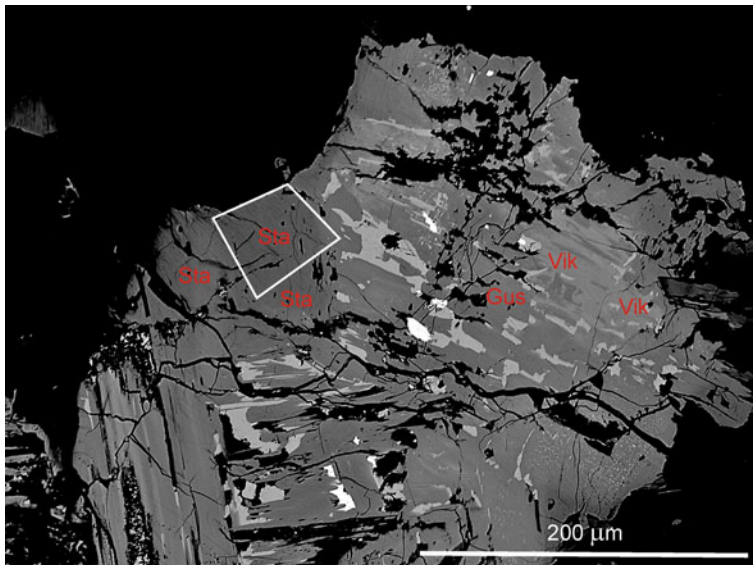

FIG. 3. Staročeskéite (Sta), gustavite (Gus) and vikingite (Vik), BSE image of holotype sample ST 37. Galena (white) is the earliest mineral. A fragment for SC-XRD analysis of staročeskéite was extracted from the area marked by white lines.

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TABLE 1. Reflectance values* for staročeskéite, plotted in Fig. 4.

$R_{min.}/R_{max.}$ (%)	λ (nm)	$R_{min.}/R_{max.}$ (%)	λ (nm)
39.3/41.6	400	37.4/39.2	560
39.7/41.7	420	37.1/38.9	580
39.6/41.6	440	**37.1/38.8**	**589**
39.2/41.0	460	37.0/38.7	600
39.0/40.8	**470**	36.8/38.5	620
38.7/40.5	480	36.8/38.4	640
38.4/40.2	500	**36.7/38.3**	**650**
38.0/39.8	520	36.7/38.4	660
37.7/39.5	540	36.6/38.3	680
37.6/39.4	**546**	36.5/38.1	700

*Obtained using WTiC standard in air, Zeiss 370; spectrophotometer MSP400 Tidas at Leica microscope, 50× objective.
Wavelengths required by the Commission on Ore Mineralogy are given in bold.

not observed. Reflectance percentages for the four wavelengths required by the Commission on Ore Mineralogy (R_{min} and R_{max}) for staročeskéite from Kutná Hora are: 39.0/40.8 (470 nm), 37.6/39.4 (546 nm), 37.1/38.8 (589 nm) and 36.7/38.3 (650 nm). A full reflectance dataset is given in Table 1 and Fig. 4.

Chemical composition

Chemical analyses of the holotype sample were performed using a JEOL JXA-8600 electron probe microanalyser in wavelength-dispersive spectroscopy (WDS) mode (25 kV and 35 nA) and a beam diameter of 5 μm. The following standards and X-ray lines were used: $CuFeS_2$ (Cu$K\alpha$ and Fe$K\alpha$), Ag (Ag$L\alpha$), PbS (Pb$L\alpha$), Bi_2S_3 (Bi$L\alpha$ and S$K\alpha$), Sb_2S_3 (Sb$L\alpha$), CdTe (Cd$L\beta$ and Te$L\alpha$), Bi_2Te_2S (Bi$L\alpha$ and Te$L\alpha$) and Bi_2Se_3 (Se$K\alpha$). Raw data were corrected with an online ZAF-4 procedure.

A second set of polished sections with staročeskéite was measured on a CAMECA SX 100 electron probe microanalyser at the National Museum, Prague in 2015. The analytical conditions were as follows: WDS mode, accelerating voltage of 25 kV, beam current of 20 nA, electron-beam diameter of 2 μm and standards: chalcopyrite (S$K\alpha$), Bi_2Se_3 (Bi$M\beta$), PbS (Pb$M\alpha$), Ag (Ag$L\alpha$), halite (Cl$K\alpha$), Sb_2S_3 (Sb$L\alpha$), CdTe (Cd$L\alpha$), HgTe (Hg$M\alpha$), pyrite (Fe$K\alpha$), Cu (Cu$K\alpha$), ZnS (Zn$K\alpha$), NiAs (As$L\alpha$) and PbSe (Se$L\beta$). Measured data were corrected using *PAP* software (Pouchou and Pichoir, 1985).

Analytical data for the holotype sample are given in Table 2. Its empirical formula (calculated on the basis of 11 atoms per formula unit) is: $(Ag_{0.68}Cu_{0.01})_{\Sigma0.69}(Pb_{1.56}Fe_{0.01}Cd_{0.01})_{\Sigma1.58}(Bi_{1.32}Sb_{1.37})_{\Sigma2.69}(S_{6.04}Se_{0.01})_{\Sigma6.05}$, corresponding to $N_{chem} = 3.94$,
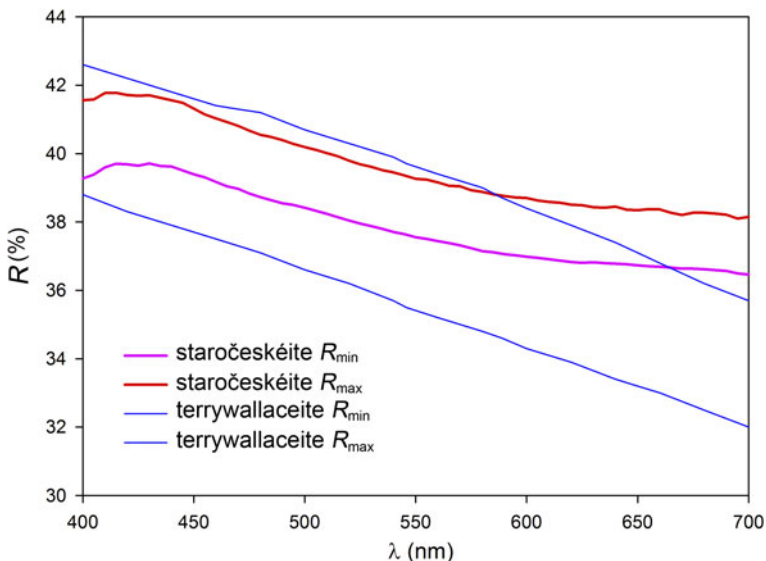

FIG. 4. Reflectivity curves for staročeskéite (this paper) and terrywallaceite (Yang *et al.*, 2013).

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TABLE 2. Chemical data (wt.%) for staročeskéite ($n = 5$). Holotype sample ST 37.

Constituent	Wt.%	Range	S.D.	Probe standard
Ag	7.02	6.61–7.51	0.29	Ag
Cu	0.05	0.04–0.07	0.01	$CuFeS_2$
Fe	0.05	0.04–0.05	0.002	$CuFeS_2$
Pb	31.09	29.67–31.82	0.78	PbS
Cd	0.10	0.07–0.12	0.02	CdTe
Bi	26.62	25.36–27.94	0.98	Bi_2S_3
Sb	16.01	14.74–16.69	0.68	Sb_2S_3
Se	0.07	0.03–0.09	0.02	Bi_2Se_3
S	18.66	18.29–18.82	0.19	Bi_2S_3
Total	99.67	99.42–99.91	0.21	

S.D. – standard deviation.

$Bi/(Bi + Sb) = 0.49$ and $L\% = 70.5$. An ideal formula, corresponding to: (1) 70% of the $Ag^+ + (Bi^{3+}, Sb^{3+}) \leftrightarrow 2\,Pb^{2+}$ substitution relative to the Ag-free ideal composition of lillianite $Pb_3Bi_2S_6$ and (2) the Bi:Sb ratio 1:1 (i.e. $Bi/(Bi + Sb) = 0.50$), can be written as $Ag_{0.70}Pb_{1.60}(Bi_{1.35}Sb_{1.35})_{\Sigma2.70}S_6$,

TABLE 3. Representative compositions of staročeskéite from Kutná Hora* ordered according to increasing $Bi/(Bi + Sb)$.

	1	2	3	4	5	6	7	8	9	10
Wt.%										
Ag	7.04	7.00	6.90	7.57	7.20	7.50	7.30	7.43	7.45	6.86
Cu	0.04	0.04	0.05	0.02	0.01	0.01	0.03	0.03	0.06	0.04
Pb	31.82	31.51	31.56	31.50	31.86	30.95	31.18	30.10	30.54	31.10
Fe	0.05	0.04	0.05	0.02	0.06	0.04	0.00	0.05	0.04	0.05
Cd	0.07	0.12	0.08	0.15	0.20	0.12	0.09	0.20	0.12	0.07
Bi	25.36	25.75	26.31	26.74	26.58	27.39	27.44	28.05	28.65	28.99
Sb	16.69	16.44	16.20	16.39	16.10	16.25	15.88	15.27	15.36	13.84
S	18.75	18.82	19.03	17.93	18.98	18.05	18.00	18.68	18.68	18.69
Se	0.09	0.07	0.05	0.00	0.10	0.03	0.00	0.07	0.06	0.00
Total	99.91	99.81	100.23	100.40	101.08	100.44	100.02	99.87	100.95	99.63
Coefficients of empirical formula based on 11 atoms per formula unit										
Ag	0.67	0.67	0.66	0.74	0.68	0.73	0.71	0.72	0.71	0.67
Cu	0.01	0.01	0.01	0.00	0.00	0.00	0.01	0.01	0.01	0.01
Pb	1.59	1.57	1.56	1.60	1.57	1.57	1.59	1.51	1.52	1.57
Fe	0.01	0.01	0.01	0.00	0.01	0.01	0.00	0.01	0.01	0.01
Cd	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.02	0.01	0.01
Bi	1.25	1.27	1.29	1.34	1.30	1.37	1.38	1.39	1.42	1.45
Sb	1.42	1.39	1.37	1.41	1.35	1.40	1.38	1.30	1.30	1.19
S	6.04	6.06	6.09	5.88	6.05	5.90	5.92	6.04	6.01	6.10
Se	0.01	0.01	0.01	0.00	0.01	0.00	0.00	0.01	0.01	0.00
N	3.98	3.96	3.92	4.07	4.02	3.98	3.97	4.02	3.99	3.98
$L\%$	69.20	69.50	69.50	70.97	68.96	72.17	71.44	72.47	72.80	69.10
x	0.68	0.68	0.67	0.73	0.70	0.72	0.70	0.73	0.72	0.68
$Bi/(Bi + Sb)$	0.47	0.48	0.49	0.49	0.49	0.50	0.50	0.52	0.52	0.55

*Samples: 1 – ST 37, 2 – ST 37, 3 – ST 55 gr1, 4 – ST 4 F, 5 – ST 90 A, 6 – ST 4 F, 7 – ST 4 F, 8 – ST 90 A, 9 – ST 42 C gr1, 10 – ST 70C.

N, $L\%$ and x values were calculated according to Makovicky and Karup-Møller (1977a) – see text.
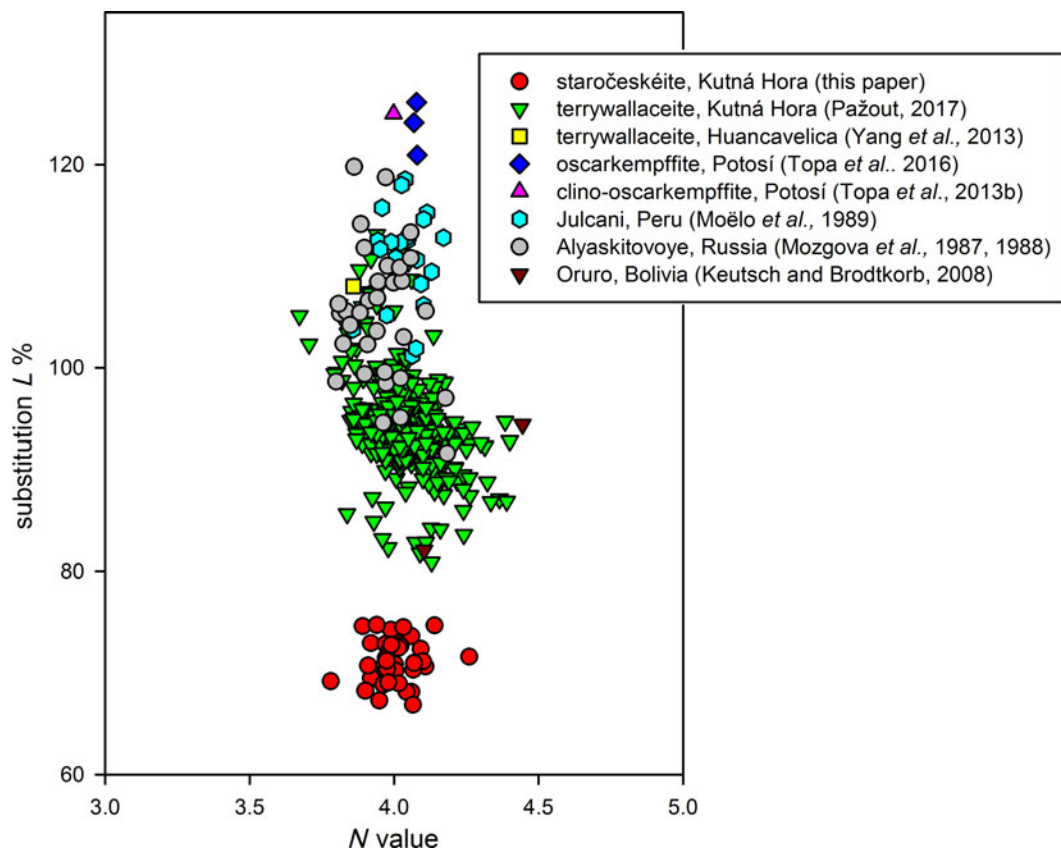
FIG. 5. The N_{chem} value *vs.* $Ag^+ + (Bi,Sb)^{3+} \leftrightarrow 2\ Pb^{2+}$ substitution ($L\%$) plot for lillianite homologues with $N = 4$ and distinct Bi/Sb substitution.

which requires Ag 7.22, Pb 31.70, Bi 26.97, Sb 15.72 and S 18.39 wt.%, total 100.00 wt.%.

Staročeskéite was found in 21 samples (∼50 analytical points), representative analyses are given in Table 3. It can be differentiated chemically from similar members of the lillianite homologous series on the basis of the Ag content $L\%$ and the Bi/(Bi + Sb) ratio (Figs 5 and 6).

Crystallography and crystal structure

X-ray diffraction data were collected at ambient temperature on the single-crystal diffractometer Gemini (Oxford Diffraction) with CCD area detector Atlas using monochromatic Mo*K*α radiation (λ = 0.71073 Å). A small fragment of the sample, 0.0442 mm × 0.0270 mm × 0.0214 mm in size, was used for collection of X-ray data at

ambient temperature. An orthorhombic cell was found with $a = 4.2539(8)$, $b = 13.3094(8)$ and $c = 19.6253(12)$ Å. Unlike a typical natural gustavite, images from data collection clearly showed a *C*-centred unit cell with no reflections breaking the cell centring. Also, no reflections were observed that would double the size of the short *a* parameter, as occurs in the unit cell of fizélyite and ramdohrite. Atomic coordinates, displacement parameters, selected interatomic distances, details of data collection and refinement and the structure description are given in Pažout and Dušek (2010). There are only three distinct cation sites, giving the stoichiometry $M3(M2)_2(M1)_2S_6$. Staročeskéite has *M*3 completely occupied by Pb, *M*2 dominated by trivalent cations with Sb >> Bi, and *M*1 occupied mainly by trivalent cations with Bi >> Sb, but also with substantial Ag^+ for charge balance.

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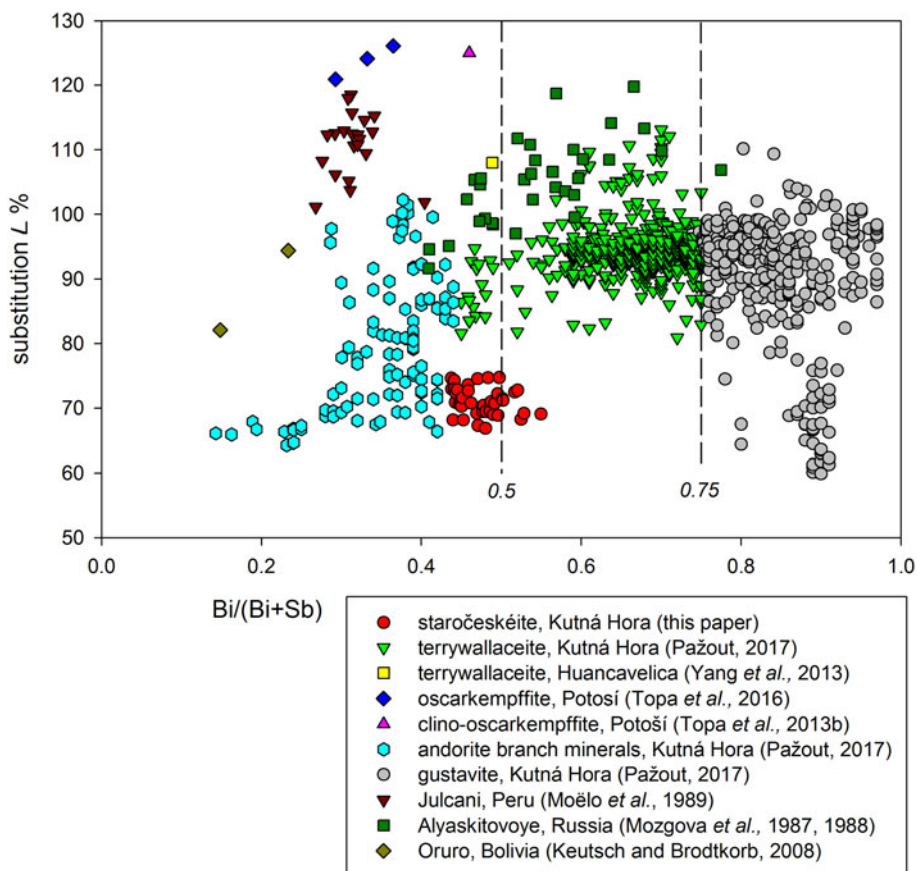
Fig. 6. The Bi/(Bi + Sb) (at.%) *vs.* $Ag^+ + (Bi, Sb)^{3+} \leftrightarrow 2\,Pb^{2+}$ substitution (L%) plot for lillianite homologues with $N = 4$ and distinct Bi/Sb substitution.

The structure of staročeskéite (Fig. 7), a natural Sb–Bi orthorhombic ^{4,4}L homologue of the lillianite homologous series, consists of one Pb site (*M*3) in trigonal prismatic coordination and two octahedral mixed sites *M*1 and *M*2 each consisting of three elements (Pažout and Dušek, 2010). The octahedral site *M*1 positioned at the margin of the diagonal chain of four octahedra is formed by a mixed site with the occupancy 52% Bi, 35.6% Ag and 12.4% Sb, the central octahedral site *M*2 is formed by one mixed site with the occupancy 60.1% Sb, 25.9% Pb and 14% of Bi. The final empirical formula is $Ag_{0.71}Pb_{1.52}Bi_{1.32}Sb_{1.45}S_6$, which is in a good agreement with the EPMA-established composition $Ag_{0.69}Pb_{1.56}(Bi_{1.32}Sb_{1.37})_{\Sigma2.69}(S_{6.04}Se_{0.01})_{\Sigma6.05}$. Cation charge of the final formula is 12.059 against anion charge 12.0. The final R_w was 5.08% for observed reflections. On the basis of site

occupancies, the formula of staročeskéite is ^{M3}Pb $^{M2}(Sb_{0.60}Pb_{0.26}Bi_{0.14})_{\Sigma2}$ $^{M1}(Bi_{0.52}Ag_{0.356}Sb_{0.124})_{\Sigma2}S_6$, which can be simplified to give $^{M3}Pb^{M2}Sb_2^{M2}$ $(AgBi)_{\Sigma2}S_6$, which has two different-valence cations in only one site, and hence is an end-member in the sense of Hawthorne (2002). The structures of gustavite (Pažout and Dušek, 2009) and staročeskéite were compared by Pažout and Dušek (2010).

To assess the composition boundaries within which the name staročeskéite applies we consider the following: for staročeskéite, *M*3 = Pb; *M*2 is mainly trivalent, Pb < (Sb + Bi) with Sb >> Bi; *M*1 is dominated by (Bi + Sb) + Ag with Bi > Sb. If we assume exclusively Pb in *M*3, allow up to 50% Pb in *M*2, and, given the absence of Pb in *M*1, set Ag ≥ 0.5 and Bi ≥ Sb conditions there, then limiting compositions for the name to be applicable are given in Table 4.
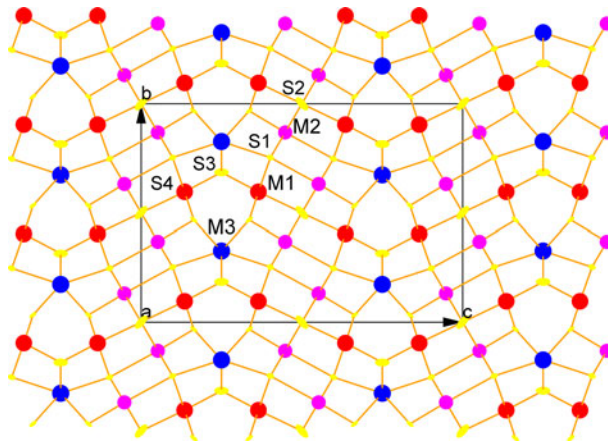
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FIG. 7. The crystal structure of staročeskéite. $M3$–Pb in bicapped trigonal prismatic coordination (CN 8), $M1$–Bi/Ag/Sb mixed site (Bi is major component), $M2$–Pb/Sb/Bi mixed site (Sb is a major component), both in octahedral coordination, S – sulfur atoms. Viewed along the a axis.

Thus the name staročeskéite would be valid for a lillianite structure with composition $Ag_xPb_{3-2x}Bi_ySb_{2+x-y}S_6$ in a two-dimensional composition space with the boundaries $\frac{1}{2} \leq x \leq 0.8$ and $1-\frac{1}{2}x \leq y \leq 2$, where the parameter x = Ag content = $L\%$ expressed as a fraction and y = total Bi content. The top range of the x parameter is assumed to be not more than 0.8 because for $x = 1$ the phase would chemically correspond to Bi-rich andorite-VI (with $L\% = 100$ and Bi/(Bi + Sb) = 0.19) or terrywallaceite (with $L\% = 100$ and Bi/(Bi + Sb) = 0.66), depending on the Sb content, and for $x = 0.9$ the phase would chemically correspond to Bi-rich andorite-IV (with $L\% = 90$ and Bi/(Bi + Sb) = 0.19) or terrywallaceite (with $L\% = 90$ and Bi/ (Bi + Sb) = 0.69). Thus it is evident that for staročeskéite to exist, there must be some Pb in $M2$ (because Pb just in $M3$ results in other clearly defined minerals). Therefore, from these empirical assumptions and tests of gustavite and terrywallaceite grains with various $L\%$ by single-crystal diffraction (Pažout 2017), it can be concluded that staročeskéite compositional limits

regarding the Ag + (Bi,Sb) = 2 Pb substitution are from $L\% = 50$ to $\sim L\% = 80$. Nevertheless, the ultimate answer to which phase is dealt with is given by SC-XRD.

Although it is possible to define an ideal end-member composition for staročeskéite as noted above, the solid-solution ranges of complex sulfosalts do not necessarily include such members, and several structurally related species with different observed solid-solution ranges may share the same end-member(s). Therefore, we prefer to define the composition range corresponding to the name 'staročeskéite' in terms of the parameter $L\%$ (Ag content) and Bi/(Bi + Sb) ratio. In addition, staročeskéite possesses a simple lillianite structure with no doubling of a repeat or other superstructure, and no distortion away from $Cmcm$ symmetry, in contrast to related species such as terrywallaceite and the andorite-group minerals.

For the purpose of this article only points with $L\%$ between 65 and 75 and the Bi/(Bi + Sb) = 0.44–0.55 were considered to represent staročeskéite. To check the validity of the 'maximum Sb' situation, grains

TABLE 4. Limiting compositions for the mineral staročeskéite.

	Minimum Pb ($M3$ + 0.2Pb in $M2$)	Maximum Pb ($M3$ + 0.5Pb in $M2$)
Maximum Sb for Bi	$Pb(Pb_{0.4}Sb_{1.6})(Ag_{0.8}Bi_{0.6}Sb_{0.6})S_6$	$Pb(PbSb)(Ag_{0.5}Bi_{0.75}Sb_{0.75})S_6$
All $^{M2}M^{3+}$= Sb, all $^{M1}M^{3+}$= Bi	$Pb(Pb_{0.4}Sb_{1.6})(Ag_{0.8}Bi_{1.2})S_6$	$Pb(PbSb)(Ag_{0.5}Bi_{1.5})S_6$
Minimum Sb for Bi	$Pb(Pb_{0.4}Bi_{0.8}Sb_{0.8})(Ag_{0.8}Bi_{1.2})S_6$	$Pb(PbBi_{0.5}Sb_{0.5})(Ag_{0.5}Bi_{1.5})S_6$

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with compositions corresponding to $L \approx 70\%$ and Bi/(Bi + Sb) between 0.35 and 0.43 should be extracted for single-crystal analysis and characterized structurally. Grains with these compositions were found in the Kutná Hora ore district in the Bi-sulfosalt mineralization and were interpreted as Bi-rich fizélyite if $L\%$ was between 64 and 70, and Bi-rich ramdohrite if $L\%$ was between 70 and 75 (Pažout, 2017). Even if the single-crystal data of the extracted fragments were not good enough to solve the structure, the data collection images should clearly show a C-centred cell with the 'short 4 Å' cell parameter of staročeskéite or a primitive P cell with the 'double 8 Å' cell parameter of fizélyite or ramdohrite. This direction will be exploited further in the future.

As already mentioned, the cell parameters given were refined from single-crystal data. The amount of material was not sufficient for experimentally obtained powder X-ray data. A theoretical pattern (Table 5) was calculated with *Jana2006* software (Petříček *et al.*, 2006) employing a wavelength corresponding to that of Cu$K\alpha_1$ radiation (λ = 1.540598 Å). Cell parameters, space group, atom positions, site-occupancy factors and isotropic displacement factors from the crystal-structure determination were used.

Relation to other species

Staročeskéite is a new member of the lillianite homologous series, class 3.1.1. of the Sulfosalt systematics (Moelo *et al.*, 2008). A comparison of selected data for lillianite $Pb_3Bi_2S_6$, terywallaceite

TABLE 5. Calculated powder XRD data for staročeskéite.

h	k	l	d (Å)	$I_{rel.}$ (%)	h	k	l	d (Å)	$I_{rel.}$ (%)
0	2	0	6.6463	0.3	0	6	6	1.8358	1.7
0	2	1	6.3018	1.6	0	4	9	1.8237	3.2
0	2	2	5.5078	5.8	2	2	5	1.8002	23.4
0	0	4	4.9059	0.7	2	4	0	1.7919	7.8
0	2	3	4.6631	0.9	2	4	1	1.7848	5.6
1	1	0	4.0526	5.8	1	3	9	1.7783	5.0
0	2	4	3.9495	12.7	1	5	7	1.7579	2.9
1	**1**	**2**	**3.7463**	**33.2**	1	7	0	1.7357	4.3
1	0	3	3.5685	0.2	1	7	1	1.7292	5.1
1	**1**	**3**	**3.4458**	**61.5**	2	2	6	1.7230	6.7
0	**2**	**5**	**3.3819**	**100.0**	1	7	2	1.7091	2.3
0	4	0	3.3285	22.1	0	4	10	1.6904	6.5
0	4	1	3.2807	17.5	0	8	1	1.6576	4.1
0	4	2	3.1530	2.5	0	8	2	1.6404	4.3
1	1	4	3.1258	6.0	2	0	8	1.6067	0.8
1	3	0	3.0707	1.5	1	7	5	1.5876	0.6
1	**3**	**1**	**3.0348**	**44.8**	1	5	9	1.5688	1.0
1	**3**	**2**	**2.9323**	**80.5**	2	6	1	1.5313	0.4
1	1	5	2.8204	1.7	1	1	12	1.5167	0.6
1	**3**	**3**	**2.7786**	**33.8**	0	0	13	1.5100	1.2
0	2	7	2.5830	4.1	2	6	3	1.4947	1.0
0	4	5	2.5371	0.5	1	7	7	1.4759	0.7
0	0	8	2.4532	2.3	2	6	4	1.4652	6.4
1	3	5	2.4186	1.2	2	0	10	1.4428	6.5
0	4	6	2.3334	0.8	2	5	7	1.4298	3.6
1	1	7	2.3053	14.3	3	0	1	1.4146	6.0
1	3	6	2.2402	1.3	3	1	2	1.3957	1.2
1	5	2	2.2009	0.6	2	6	6	1.3899	1.3
0	6	2	2.1639	0.9	2	4	9	1.3846	1.8
0	4	7	2.1433	3.4	3	1	3	1.3783	2.5
1	5	3	2.1335	14.5	1	7	9	1.3580	3.2
2	0	0	2.1272	29.0	1	3	13	1.3547	3.4

The strongest lines are given in bold.

TABLE 6. Comparative data for staročeskéite and related minerals[†].

	Staročeskéite	Lillianite	Gustavite	Terrywallaceite
Locality	Kutná Hora, Czech Republic	Vulcano, Italy	Rotgülden, Austria	Julcani, Peru
Reference	This paper	Pinto *et al*. (2006)	Topa and Makovicky (2011)	Yang *et al*. (2013)
Ideal composition	$Ag_{0.70}Pb_{1.60}(Bi_{1.35}Sb_{1.35})_{\Sigma2.70}S_6$	$Pb_3Bi_2S_6$	$AgPbBi_3Sb_6$	$AgPb(Sb,Bi)(Bi,Sb)_2S_6$
Empirical composition	$Ag_{0.69}Pb_{1.56}(Bi_{1.32}Sb_{1.37})_{\Sigma2.69}$ $(S_{6.04}Se_{0.01})_{\Sigma6.05}$	$Pb_{2.88}Bi_{2.12}(S_{5.67}Se_{0.33})_{\Sigma6.00}$	$Pb_{1.06}Ag_{0.95}Bi_{2.80}Sb_{0.20}S_{5.99}$	$Ag_{1.02}Pb_{0.87}(Sb_{1.53}Bi_{1.47})_{\Sigma3.00}$ $(S_{5.94}As_{0.06})_{\Sigma6.00}$
Space group	*Cmcm*	*Cmcm*	$P112_1/a$	$P112_1/a$
a/Å	4.2539(8)	4.1216(4)	8.2219(16) $= 2 \times 4.1110$	8.3870(4) $= 2 \times 4.1985$
b/Å	13.3094(8) $= 6.6547 \times 2$	13.567(1) $= 6.7835 \times 2$	7.0567(14) $= 6.7498 / \sin\gamma$	6.9764(4) $= 6.6528 / \sin\gamma$
c/Å	19.625(1) Å	20.655(2)	19.6905(39)	19.351(1)
β			106.961(3)	107.519(2)
V	1111.1(2)	1155.0(2)	1092.7(2)	1079.7(1)
Z	4	4	4	4
Strongest lines in the XRD powder pattern	3.746/33* 3.446/62 3.382/100 3.035/45 2.932/81	3.684/37* 3.528/100 3.422/71 3.014/42 2.922/59	3.652/35* 3.402/100 3.373/78 3.000/56 2.900/72	3.680/23** 3.369/100 3.010/33 2.911/58 2.080/26

* – data calculated from the structure; ** – measured powder XRD data.
†The space group and cell parameters of lillianite, gustavite and terrywallaceite are transformed into axial settings corresponding to staročeskéite.

$AgPb(Sb,Bi)(Bi,Sb)_2S_6$ and gustavite $AgPbBi_3S_6$ is given in Table 6. Structurally, staročeskéite has a unit cell and symmetry similar to those of lillianite. However, chemically, staročeskéite differs from lillianite by the $Bi/(Bi + Sb)$ ratio which is always close to 1 for lillianite and by the Ag content $L\%$ which is usually close to zero but can be between 0 and 50% for lillianite and 50 to 80% for staročeskéite. In fact, in the light of the research presented in this paper, 'lillianite' with $L\% > 50$ should be called staročeskéite if the most straight-forward definitions of compositional boundaries are defined (see above). While ideal gustavite is $PbBi_2(AgBi)S_6$, gustavite in Nature is chemically similar to lillianite with regard to $L\%$ as it can have a varying degree of $Ag^+ + (Bi^{3+}, Sb^{3+}) \leftrightarrow 2\ Pb^{2+}$ substitution. Verified gustavite is known only for $L\% = 85\%$ and above (D. Topa, *pers. comm.*) However, the first author of this paper detected by single-crystal diffraction the gustavite unit cell in a crystal fragment with $L\% = 70$ (Pažout, 2017). The $Bi/(Bi + Sb)$ ratio for gustavite is always above 0.75. In addition, structurally gustavite has the ordered monoclinic superstructure, as does terry-wallaceite. Terrywallaceite can have the same amount of Sb and Bi as in staročeskéite, but the $Ag^+ + Bi^{3+} \leftrightarrow 2\ Pb^{2+}$ substitution is between 85 and 110% and it has a monoclinic cell and symmetry similar to those of gustavite. There are uncertainties for the case of Bi-rich ramdohrite in the Kutná Hora ore district because of a very close substitution percentage and occasionally a very high Bi content, reaching up to $Bi/(Bi + Sb) = 0.42$. Bi-rich fizélyite from Kutná Hora shows a narrower limit of Bi for Sb substitution with $Bi/(Bi + Sb)$ between 0.16 and 0.38 (Pažout, 2017). However, both fizélyite and ramdohrite display $P2_1/n$ symmetry with a cell volume double that of staročeskéite.

Thus staročeskéite stands as a unique mineral both structurally and chemically, distinctly different from lillianite, gustavite, terrywallaceite and other known members of the lillianite homologous series. It is defined as a lillianite homologue with the following requirements: $N = 4$, L ($Ag^+ + Bi^{3+}$, $Sb^{3+} \leftrightarrow 2\ Pb^{2+}$ substitution) $\approx 70\%$ (with structurally derived limits of $L\%$ between 50 and 80), and $\sim$50 at.% of bismuth is replaced by antimony ($Bi/(Bi + Sb) \approx 0.5$), with structurally derived limits from $Bi/(Bi + Sb) \approx 0.3$ to 0.8.

More Bi–Sb and Sb–As mixed members are known in the oversubstituted end of the series ($L\% > 100$): arsenquatrandorite $Pb_{12.8}Ag_{17.6}Sb_{38.08}As_{11.52}S_{96}$ (And_{110} – Topa *et al.*, 2013c) and jasrouxite $Pb_4 Ag_{16}Sb_{24}As_{16}S_{72}$ ($And_{136.5}$ – Topa *et al.* 2013a);

and two Sb–Bi members oscarkempffite $Pb_4Ag_{10} Sb_{17}Bi_9S_{48}$ (And_{124}) and clino-oscarkempffite $Pb_6 Ag_{15}Sb_{21}Bi_{18}S_{72}$ (And_{125}). Oscarkempffite is characterized by the $Bi/(Bi + Sb)$ range between 0.29 and 0.37 (Topa *et al.*, 2016), clino-oscarkempffite has the $Bi/(Bi + Sb)$ ratio derived from the formula equal to 0.46 (Topa *et al.*, 2013b).

Notable occurrences of mixed Bi–Sb members with $N = 4$ (Sb-rich gustavite and Bi-rich andorite) were in the past described on the basis of the EPMA data from Alyaskitovoye deposit, Yakutia, Russia (Mozgova *et al.*, 1987, 1988), from Julcani, Peru (Moëlo *et al.*, 1989) and Oruro, Bolivia (Keutsch and Brodtkorb, 2008). The extraordinary extent of the Bi–Sb substitution in minerals of the lillianite homologous series was described recently from the Kutná Hora ore dictrict, Czech Republic (Pažout, 2017). Comparing the data from Kutná Hora with published data from the past (Figs 5 and 6) it is apparent that a mineral phase corresponding to staročeskéite has not been described before. Mineral phases from Alyaskitovoye deposit (Mozgova *et al.*, 1987, 1988) show $L\%$ between 94 and 114 and $Bi/(Bi + Sb) = 0.41$–0.70, and thus correspond mainly to terrywallaceite which is also supported by their diffraction data. Samples from Julcani (Moëlo *et al.*, 1989) with $L\% = 101$–118 and $Bi/(Bi + Sb) = 0.31$–0.40 correspond to Bi-rich andorite-VI (analyses with $L\% \approx 101$) or oscakempffite (analyses with $L\% \approx 118$). The majority of analyses show $L\%$ between 105 and 115 and precise identification of these minerals would be possible on the basis of structural characterization by single-crystal diffraction. Samples from Oruro (Keutsch and Brodtkorb, 2008) with $L\% = 94.4$ and $Bi/(Bi + Sb) = 0.23$ correspond to Bi-rich andorite-IV.

Acknowledgements

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