The Canadian Mineralogist
Vol. 43, pp. 965-972 (2005)

PAUTOVITE, $CsFe_2S_3$, A NEW MINERAL SPECIES FROM THE LOVOZERO ALKALINE COMPLEX, KOLA PENINSULA, RUSSIA

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ABSTRACT

Pautovite, the cesium-dominant analogue of rasvumite and picotpaulite, is a new mineral species found in the Palitra peralkaline pegmatite, Kedykverpakhk Mountain, Lovozero alkaline complex, Kola Peninsula, Russia. It is associated with belovite-(Ce), villiaumite, aegirine, ussingite, natrosilite, microcline, sodalite, potassicarfvedsonite, sérandite, nordite-(Ce), ferronordite-(Ce), bornemanite, vuonnemite, lomonosovite, vitusite-(Ce), phosinaite-(Ce), barytolamprophyllite, mangan-neptunite, manaksite, chkalovite, kapustinite, kazakovite, steenstrupine-(Ce), thorosteenstrupine, bario-olgite, nalipoite, sphalerite, löllingite, wurtzite, bartonite, chlorbartonite, and zakharovite, among others. Pautovite occurs in a hydrothermal assemblage as crudely prismatic to acicular crystals up to 120 μm long and up to 15 μm thick, typically forming subparallel overgrowths on belovite-(Ce). Twinning was not observed. Pautovite is opaque, dark steel-grey with a strong metallic luster, becoming dull black on exposure to moist air. It is flexible. Cleavage is perfect on {110}, and the fracture is splintery. D(calc.) equals 3.85(1) g/cm^3. The density and hardness could not be measured, and the streak could not be observed because of the minute size of the crystals. In reflected light, pautovite is strongly bireflectant, with distinct pleochroism from greyish white to grey with a slight pinkish tint. The anisotropy is strong in pale brownish tints. No internal reflections were observed. Reflectance values (λ in nm: R_1, R_2, in %); measured in air (SiC standard) are: 470: 14.0, 24.6; 546: 14.7, 23.5; 589: 15.2, 24.6; 650: 16.0, 27.1; values are presented for the interval 400–700 nm. A chemical analysis by electron microprobe gave: K 0.21, Rb 1.31, Cs 36.12, Tl 0.50, Fe 33.80, S 28.85, total 100.79 wt.%. The empirical formula, based on a sum of six atoms, is $(Cs_{0.91}Rb_{0.05}K_{0.02}Tl_{0.01})_{\Sigma 0.99}Fe_{2.02}S_{2.99}$. The idealized formula is $CsFe_2S_3$, which requires: Cs 39.00, Fe 32.78, S 28.22 wt.%. Pautovite is orthorhombic, *Cmcm* (by analogy with other representatives of the rasvumite structure-type, including synthetic $CsFe_2S_3$). Unit-cell dimensions: *a* 9.477(4), *b* 11.245(4), *c* 5.485(2) Å, *V* 584.5(6) Å^3, $Z = 4$. The strongest lines of the X-ray powder diagram [*d* in Å (*I*)(*hkl*)] are: 4.69(30)(200), 4.28(20)(111), 2.981(100)(221), 2.723(40)(002), 2.003(30)(312,151,421), 1.910(60)(042, 060), 1.785(30)(402), and 1.565(40)(313). The name honors Leonid A. Pautov (b. 1958), in recognition of his studies of minerals by physical methods. Both the mineral and its name have been approved by the IMA Commission on New Minerals and Mineral Names (IMA no. 2004–005).

Keywords: pautovite, new mineral species, rasvumite, picotpaulite, cesium, rubidium, thallium, alkali sulfide, peralkaline pegmatite, Lovozero complex, Kola Peninsula, Russia.

SOMMAIRE

Nous décrivons ici la pautovite, l'analogue à dominance de césium de la rasvumite et la picotpaulite, nouvelle espèce minérale découverte dans la pegmatite hyperalcaline de Palitra, mont Kedykverpakhk, complexe alcalin de Lovozero, péninsule de Kola, en Russie. Elle est associée à bélovite-(Ce), villiaumite, aegyrine, ussingite, natrosilite, microcline, sodalite, potassicarfvedsonite, sérandite, nordite-(Ce), ferronordite-(Ce), bornemanite, vuonnemite, lomonosovite, vitusite-(Ce), phosinaïte-(Ce), barytolamprophyllite, mangan-neptunite, manaksite, chkalovite, kapustinite, kazakovite, steenstrupine-(Ce), thorosteenstrupine, bario-olgite,

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nalipoïte, sphalerite, löllingite, wurtzite, bartonite, chlorbartonite, et zakharovite, parmi d'autres. La pautovite se présente dans un assemblage hydrothermal sous forme de cristaux *grosso modo* prismatiques à aciculaires atteignant 120 μm en longueur et 15 μm en largeur, typiquement en surcroissances subparallèles sur la bélovite-(Ce). Nous ne voyons aucun signe de macles. La pautovite est opaque, gris acier foncé, avec un éclat métallique prononcé, devenant noir mât en présence de l'air humide. Les cristaux sont flexibles. Le clivage est parfait sur {110}, et la fracture est en esquilles. D(calc.) est égal à 3.85(1) g/cm^3. Nous n'avons pû mesurer la densité et la dureté, ou observer la rayure, à cause de la taille infime des cristaux. En lumière réfléchie, la pautovite est fortement biréflectante, avec un pléochroïsme distinct allant de blanc grisâtre à gris avec teinte légèrement rosâtre. L'anisotropie est forte en teintes brunâtres pâles. Aucune réflexion interne est évidente. Les valeurs de la réflectance (λ en nm: R_1, R_2, en %) mesurées dans l'air (étalon SiC) sont: 470: 14.0, 24.6; 546: 14.7, 23.5; 589: 15.2, 24.6; 650: 16.0, 27.1; nous présentons les valeurs mesurées sur l'intervalle 400–700 nm. Une analyse chimique réalisée avec une microsonde électronique a donné: K 0.21, Rb 1.31, Cs 36.12, Tl 0.50, Fe 33.80, S 28.85, pour un total de 100.79% (poids). La formule empirique, fondée sur un total de six atomes, serait $(Cs_{0.91}Rb_{0.05}K_{0.02}Tl_{0.01})_{\Sigma 0.99}Fe_{2.02}S_{2.99}$. La formule idéalisée est $CsFe_2S_3$, ce qui requiert: Cs 39.00, Fe 32.78, S 28.22%. La pautovite est orthorhombique, *Cmcm* (par analogie avec d'autres phases adoptant le structure de la rasvumite, y inclus le $CsFe_2S_3$ synthétique). Les dimensions de la maille élémentaire sont: *a* 9.477(4), *b* 11.245(4), *c* 5.485(2) Å, *V* 584.5(6) Å^3, *Z* = 4. Les raies les plus intenses du spectre de diffraction X (méthode des poudres) [*d* en Å (*I*)(*hkl*)] sont: 4.69(30)(200), 4.28(20)(111), 2.981(100)(221), 2.723(40)(002), 2.003(30)(312,151,421), 1.910(60)(042, 060), 1.785(30)(402), et 1.565(40)(313). Le nom honore Leonid A. Pautov (b. 1958), et reconnait ainsi ses contributions à la minéralogie, surtout dans l'étude des minéraux par méthodes physiques. La nouvelle espèce et son nom ont été approuvés par la Commission des Nouveaux Minéraux et des Noms de Minéraux de l'IMA (#2004–005).

(Traduit par la Rédaction)

Mots-clés: pautovite, nouvelle espèce minérale, rasvumite, picotpaulite, césium, rubidium, thallium, sulfure alcalin, pegmatite hyperalcaline, complexe de Lovozero, péninsule de Kola, Russie.

INTRODUCTION

Cesium typically is a lithophile element, found in oxygen-based compounds in nature. The major concentrations of cesium and about half of the fifteen known cesium minerals, including pollucite that forms large deposits, are found in lithium-enriched granitic pegmatites. Cesium mineralization is uncommon in alkaline complexes. The only exception is found in the Darai-Pioz alkaline massif, in the Alai Range, in Tajikistan, in which the unusual quartz-bearing agpaitic pegmatites are abnormally enriched by B, Li and Cs. Three cesium minerals were discovered there: kupletskite-(Cs) (Efimov *et al.* 1971), telyushenkoite (Agakhanov *et al.* 2003), and zeravshanite (Pautov *et al.* 2004); several potentially new species are currently under study. In other alkaline massifs, minerals of cesium *sensu stricto* were unknown until now, but several Cs-bearing minerals were reported. The highest cesium content in oxygen-bearing minerals of alkaline complexes (other than Darai-Pioz) was reported in the zeolite-like beryllosilicate leifite, $(Na,K,Cs,Rb)Na_6[Be_2Al_3Si_{15}O_{39}F_2]$: 1.4 wt.% Cs_2O in a sample from the Ilímaussaq complex, South Greenland (Petersen *et al.* 1994), and 0.9 wt. % Cs_2O in a sample from the Khibiny complex, Kola Peninsula (Menshikov *et al.* 1999).

Recently, significant concentrations of cesium and rubidium were found in sulfide minerals with the structural type of rasvumite, KFe_2S_3 (with Cs and Rb substituting for K), formed in a peralkaline environment. A sample of rasvumite enriched in Cs (1.6–2.9 wt.% or 0.03–0.06 atoms per formula unit, *apfu*) and Rb (6.5–7.4 wt.% or 0.20–0.22 *apfu*) was found in sodalite syenite at Mont Saint-Hilaire, Quebec, Canada (Chakhmouradian *et al.* 2001). In this paper, we describe a new mineral species with the ideal composition, $CsFe_2S_3$, the cesium-dominant analogue of rasvumite and picotpaulite, $TlFe_2S_3$. The new species was discovered in a hyperagpaitic pegmatite at the well-known Lovozero alkaline complex, Kola Peninsula, Russia. We have named it *pautovite* (in Cyrillic: паутовит) in honor of Leonid Anatol'evich Pautov (b. 1958) (in Cyrillic: Леонид Анатольевич Паутов), an outstanding Russian mineralogist, affiliated with the Fersman Mineralogical Museum of Russian Academy of Sciences, Moscow, in recognition of his significant contributions to the study of minerals by physical methods, the mineralogy of alkaline pegmatites and the mineralogy of cesium. Both the mineral and the mineral name have been approved by the IMA Commission on New Minerals and Mineral Names (IMA no. 2004–005). The holotype specimen is deposited at the Fersman Mineralogical Museum of Russian Academy of Sciences, Moscow (registration record no. 3168/1).

OCCURRENCE AND GENERAL APPEARANCE

The Lovozero agpaitic complex is one of the world's largest alkaline massifs; it hosts huge deposits of Nb, Ta and the rare-earth elements. Magmatic loparite, the main ore mineral, has been mined for many years. The Lovozero complex is famous for its mineralogical wealth (Vlasov *et al.* 1966, Khomyakov 1995, Pekov 2000), with 390 mineral species recognized so far, including 93 first discovered there. The mineral diversity is connected with numerous peralkaline pegmatites, including hydrothermal assemblages developed at the expense of the primary minerals.

Pautovite was found in the Palitra (in English, *Palette*) pegmatite, discovered in the summer of 2002 during underground mining operations in the northern part of Kedykverpakhk Mountain, in the northwestern part of the Lovozero complex. It is the largest known "dry" hyperagpaitic pegmatite in the Lovozero complex, in which the typical late-stage, low-temperature hydrothermal activity is barely developed. This resulted in the formation of remarkably fresh anhydrous and H_2O-deficient ultra-alkaline minerals, rarely found elsewhere. To date, 46 minerals were found in the Palitra pegmatite including four new species: kapustinite (Pekov *et al.* 2003a), bario-olgite (Pekov *et al.* 2004a), potassicarfvedsonite (Pekov *et al.* 2004b) and pautovite.

The Palitra is a thick lens-shaped pegmatite with a length of 7 m and a maximum thickness of more than 1.5 m, within complex layered urtite – foyaite – lujavrite rocks. It has two distinct zones: a thin, upper nepheline-rich zone (up to 12 cm thick) immediately below the upper contact, and a lower zone (more than two thirds of the thickness) consisting of aegirine, eudialyte and microcline. The most striking feature of the pegmatite is the abundance of fibrous aegirine spherulites, up to 30 cm in diameter in the lower zone, with large crystals of microcline and eudialyte segregations, with smaller concentrations of nepheline, sodalite, lorenzenite, lamprophyllite and villiaumite in the interstices of the microcline crystals and aegirine spherulites. Within this zone are numerous nests consisting of hyperalkaline minerals such as sodalite, analcime, ussingite, villiaumite and natrosilite and smaller amounts of lomonosovite, manaksite, potassicarfvedsonite, vuonnemite, sérandite, sphalerite, steenstrupine-(Ce) and kapustinite. Other rare accessory minerals present in these nests are: nordite-(Ce), ferronordite-(Ce), vitusite-(Ce), phosinaite-(Ce), belovite-(Ce), kazakovite, barytolamprophyllite, bornemanite, mangan-neptunite, zakharovite, chkalovite, revdite, thorosteenstrupine, bario-olgite, nalipoite, löllingite, galena, wurtzite, bartonite, chlorbartonite, troilite, pautovite and molybdenite.

Pautovite is one of the rarest minerals of the Palitra pegmatite, present only in minute quantities in the hydrothermal assemblage, typically as an overgrowth on needle-shaped to hair-like crystals of belovite-(Ce). The dark crystals of pautovite are visible, in spite of their minute size, on the surface of white "cotton-like" belovite-(Ce) (Fig. 1). Some pautovite crystals were observed on ussingite, microcline, nordite-(Ce) and bornemanite, and as inclusions in massive, late-stage villiaumite in cavities.

Pautovite occurs as crudely prismatic to acicular crystals (Figs. 2a, b) up to 120 μm long and up to 5 μm (rarely up to 15 μm) thick. Twinning was not observed. The crystals are generally slightly curved and split. By analogy with rasvumite, an elongation of the crystals in the direction [001] can be inferred. Crystals are usually found as isolated individuals, and clusters are rarely observed; pautovite typically forms subparallel (epitactic?) overgrowths on earlier-formed belovite-(Ce) (Fig. 2b).

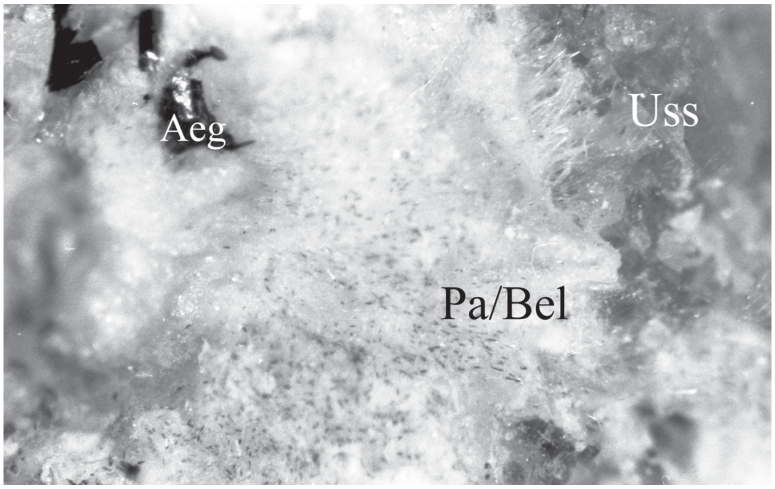

FIG. 1. Numerous small dark prismatic crystals of pautovite on the surface of an aggregate consisting of white hair-like belovite-(Ce) crystals (Pa/Bel). Associated minerals are earlier-formed ussingite (Uss) and aegirine (Aeg). The field of view covers 2 × 1.2 mm.

PHYSICAL AND OPTICAL PROPERTIES

Megascopically, pautovite is opaque, dark steel-grey with a very strong metallic luster, but in moist air, it becomes dull black. The mineral is soft (Mohs hardness probably <2), the cleavage is perfect on {110}, by analogy with rasvumite. The fracture is splintery, and crystals are easily split into flexible needles. The calculated density is 3.85(1) g/cm^3. The density and hardness could not be measured, and the streak could not be observed because of the minute size of the crystals.

In plane-polarized reflected light, pautovite in the section is greyish white and strongly bireflectant nearly parallel to elongation. It is distinctly pleochroic from greyish white to grey with slightly pinkish tint. Anisotropy (polars crossed) is strong with parallel extinction, and colors vary from dark grey to hardly noticeable pale brownish grey. On the section perpendicular to the crystal elongation (probably {001}), pautovite is isotropic. No internal reflections were observed.

The reflectance measurements were made with a MSPH–10 microspectrophotometer (LOMO, Russia) relative to a SiC reflectance standard (Zeiss, 545). The objectives used for observations in air had magnifying powers of ×40. A constant effective numerical aperture was obtained by adjustment of the aperture diaphragm of the illuminator. The bandwidth of the grating monochromator was set to 12 nm, and intensity data were collected at an interval of 20 nm from 400 to 700 nm. The diameter of the spot was 2.5 μm. The measurements were carried out in air on a strongly anisotropic section nearly parallel to the crystal elongation. Table 1 shows the reflectance and color values for pautovite, rasvumite and picotpaulite. In its optical properties, including the configuration of the reflectance spectra and color values, pautovite is close to rasvumite and picotpaulite (Tables 1, 2, Fig. 3). The reflectance spectra of pautovite for both R_1 and R_2 vibration directions resemble to those of rasvumite (Fig. 3). The R_1 curve of picotpaulite differs from curves of pautovite and rasvumite. The most probable explanation for this finding is the different orientation of the section of the picotpaulite crystal studied.

Color values for pautovite and picotpaulite were calculated using a MicroMin computer program (Boldyreva *et al.* 2002) based on the weighted ordinate method, from sixteen readings of reflectance at 20 nm intervals from 400 to 700 nm. The Commission Internationale de l'Eclairage (CIE) spectral tristimulus values were used, but weighted for this shorter spectral range. In the case of incomplete reflectance spectra for picotpaulite, the MicroMin extrapolates values in gaps to calculate color values. Color values were obtained relative to the CIE recommended illuminants C and A, with color temperatures of 6774 and 2856 K, respectively. Color values for both illuminants (Table 1) show insignificant differences in hue (dominant wavelength, λ_d) for pautovite and rasvumite. Similarly, the differences in saturation of hues (excitation purity, P_e in %) are small and confirm cream-like and pinkish tints of these minerals in plane-polarized reflected light.

CHEMICAL COMPOSITION

The chemical composition of pautovite was studied with an electron microprobe. Analyses were carried out

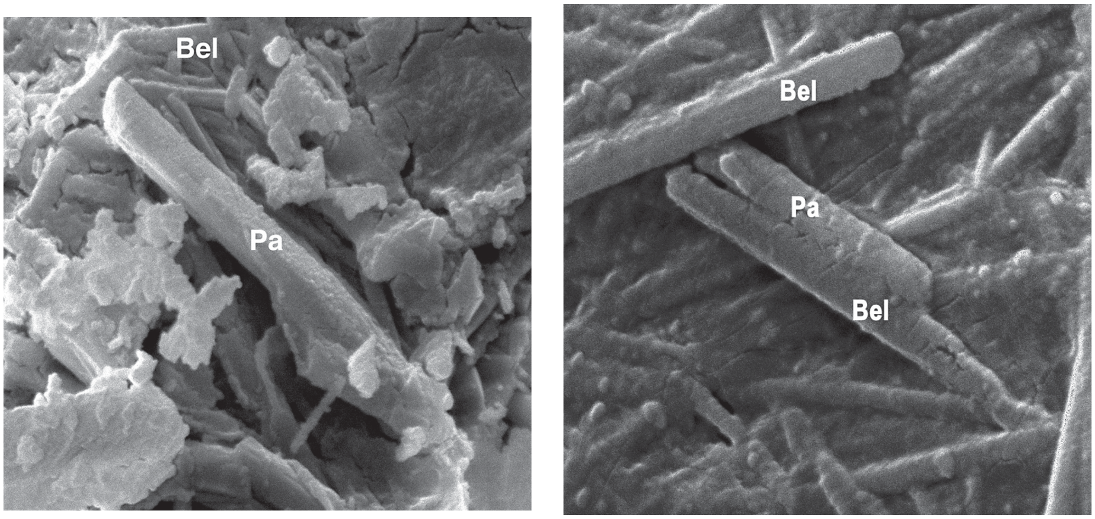

FIG. 2. Crystals of pautovite (Pa) on belovite-(Ce) (Bel): (a) crystal on the surface of a belovite-(Ce) aggregate; (b) epitactic (?) overgrowth. SEM photo. The width of the field of view is: a) 30 μm; b) 20 μm.

using both energy-dispersion (EDS) and wavelength-dispersion (WDS) methods. The best results were obtained using the EDS mode (JXA 50 instrument equipped with a modified LINK 640 spectrometer operating at 20 kV and 2 nA estimated beam current; beam area: 2–3 μm) because of a low beam current. It was used to minimize damage to the mineral, which is unstable under the electron beam. The WDS mode (Camebax SX 50 microprobe) was used mainly for the detection of Tl because of significant overlap of the most intense *M*α line of Tl (the only available analytical line where Tl content is low) by very intense *K*α line of S in the energy-dispersion spectrum. We used microcline (K), $Rb_5Nb_{11}O_{30}$ (Rb), $CsTb(PO_3)_4$ (Cs), $TlAsS_2$ (Tl), FeS_2 (Fe, S) as standards. Counting periods for the EDS: from 90 to 200 seconds for different measurements.

The average values of 16 analyses (wt.%, ranges in parentheses) are: K 0.21 (0.15–0.25), Rb 1.31 (1.0–1.8), Cs 36.12 (35.3–36.8), Tl 0.50 (0.4–0.9), Fe 33.80 (33.1–34.1), S 28.85 (28.6–29.2), total 100.79. The contents of Na, Ca, Sr, Ba, Pb, Ag, Mg, Mn, Co, Ni, Cu, Zn, Se, Te and Cl were found to be below the detection limits.

The empirical formula based on the sum of 6 atoms is $(Cs_{0.91}Rb_{0.05}K_{0.02}Tl_{0.01})_{\Sigma 0.99}Fe_{2.02}S_{2.99}$. The idealized formula of pautovite is $CsFe_2S_3$ (Z = 4), which requires: Cs 39.00, Fe 32.78, S 28.22, total 100.00 wt.%.

X-RAY CRYSTALLOGRAPHY

Single-crystal diffraction study of pautovite was not carried out because of the minute size and poor quality of the crystals. The X-ray powder diagram given in Table 3 was obtained on powder pellet sample using an RKU 114.6 mm camera and Mn-filtered Fe*K*α radiation. The data obtained are similar to those of rasvumite, picotpaulite and synthetic $CsFe_2S_3$ (Table 2), all orthorhombic phases. The unit-cell dimensions of pautovite calculated from the powder data are: *a* 9.477(4), *b* 11.245(4), *c* 5.485(2) Å, *V* 584.5(6) Å^3. A decrease in the interplanar spacings and unit-cell dimensions of pautovite in comparison with synthetic $CsFe_2S_3$ is apparently caused by the isomorphous replacement of part of the Cs by Rb, Tl and K. It is not excluded that so important a difference can be also caused by a measurement error.

TABLE 1. REFLECTANCE DATA AND COLOR VALUES IN AIR FOR PAUTOVITE, RASVUMITE AND PICOTPAULITE

	Pautovite[1]		Rasvumite[2]		Picotpaulite[3]	
λ, nm	R_1	R_2	R_1	R_2	R_1	R_2
400	13.2	23.9	16.7	30.1		
420	13.5	24.2	16.9	30.5	24.5	30.3
440	13.65	24.65	17.1	30.75	25.5	31.9
460	13.85	24.8	17.3	30.25	25.8	32.4
470 (COM)	**13.95**	**24.6**	**17.4**	**29.9**	**25.6**	**32.2**
480	14.0	24.4	17.5	29.6	25.4	32.0
500	14.15	23.9	17.65	29.35	24.6	31.3
520	14.45	23.5	17.9	29.35	24.3	31.0
540	14.6	23.3	18.1	29.4	24.2	31.0
546 (COM)	**14.65**	**23.45**	**18.2**	**29.5**	**24.25**	**31.1**
560	14.8	23.8	18.5	29.8	24.4	31.4
580	15.0	24.3	19.0	30.3	24.6	32.2
589 (COM)	**15.15**	**24.55**	**19.3**	**30.6**	**24.85**	**32.6**
600	15.3	24.9	19.6	31.0	25.2	33.1
620	15.7	25.6	20.1	31.7	25.7	33.8
640	16.0	26.6	20.6	32.5	26.5	34.7
650 (COM)	**16.0**	**27.05**	**20.7**	**32.9**	**26.9**	**35.15**
660	16.0	27.5	20.8	33.2	27.3	35.6
680	16.05	28.0	20.9	33.6	28.2	36.6
700	16.1	28.4	21.0	33.8	29.2	37.6
CIE Color values: Illuminant C (6774 K)						
x	0.320	0.314	0.323	0.315	0.312	0.316
y	0.324	0.312	0.324	0.314	0.311	0.315
Y, %	14.8	24.2	18.6	30.1	24.7	31.9
$λ_d$	582	*c*505	585	*c*498	*c*592	*c*494
P_e, %	4.8	2.6	5.5	1.9	2.2	1.7
CIE Color values: Illuminant A (2856 K)						
x	0.457	0.455	0.460	0.454	0.451	0.455
y	0.408	0.402	0.408	0.404	0.403	0.403
Y, %	15.0	24.4	18.9	30.4	24.9	32.2
$λ_d$	591	*c*510	593	*c*505	*c*525	*c*505
P_e, %	7.3	3.2	8.8	2.3	2.4	2.8

[1] this work; [2] Criddle & Stanley (1993); [3] Picot & Johan (1977): only the reflectance data. *c*: complementary.

TABLE 2. COMPARATIVE DATA OF PAUTOVITE, RASVUMITE, PICOTPAULITE AND SYNTHETIC $CsFe_2S_3$

Mineral	Pautovite[1]	Rasvumite[2]	Picotpaulite[3]	*Synthetic*[4]
Formula	$CsFe_2S_3$	KFe_2S_3	$TlFe_2S_3$	$CsFe_2S_3$
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Cmcm*	*Cmcm*	*Cmcm*	*Cmcm*
a, Å	9.477	9.049	9.04*	9.5193
b, Å	11.245	11.019	10.72	11.5826
c, Å	5.485	5.431	5.40*	5.4820
V, Å^3	584.5	541.5	523	604.44
Z	4	4	4	4
Powder data (*hkl*: *I* – *d*, Å)	Observed	Observed	Observed	Calc. from the structural data
110	10 – 7.16	100 – 6.993		13 – 7.354
020	10 – 5.57	67 – 5.509	50 – 5.40	16 – 5.791
200	30 – 4.69	8 – 4.524	50 – 4.53	9 – 4.760
111	20 – 4.28	6 – 4.289	90 – 4.26	39 – 4.395
021	10 – 3.82	2 – 3.868	70 – 3.80	13 – 3.981
220		6 – 3.497	40 – 3.46	19 – 3.677
130	10 – 3.45	10 – 3.403	70 – 3.33	57 – 3.578
221	100 – 2.981	29 – 2.940	100 – 2.912	100 – 3.054
131	10 – 2.860	4 – 2.884		4 – 2.996
002	40 – 2.723		40 – 2.706	6 – 2.741
311	15 – 2.629		50 – 2.556	16 – 2.672
112	10 – 2.548	6 – 2.531	50 – 2.513	17 – 2.568
Habit	prismatic to acicular	prismatic to acicular	lamellar to acicular	acicular
Bireflectance	strong	strong	strong	
Anisotropy	strong, in pale brownish tints	strong, in pale cream and gray-violet tints	strong, in gray-violet tints	

References: [1] this work, [2] Sokolova *et al.* (1970), Czamanske *et al.* (1979), Clark & Brown (1980), [3] Johan *et al.* (1970), Balić-Žunić *et al.* (in prep.), [4] Mitchell *et al.* (2004). * The setting given by Johan *et al.* (1970) is: *a* 5.40, *b* 10.72, *c* 9.04 Å.

The stoichiometry, X-ray powder diagram, unit-cell dimensions, crystal morphology, physical properties and optical data of pautovite, including its reflectance spectra, clearly show a very close relationship with those of rasvumite, KFe_2S_3, and picotpaulite, $TlFe_2S_3$ (Table 2). The rasvumite structure-type is stable over wide ranges of composition. It is found in chalcogenides and halides with general formula AB_2X_3: rasvumite (Clark & Brown 1980), picotpaulite (Balić-Žunić *et al.*, in prep.), and synthetic $CsFe_2S_3$, $RbFe_2S_3$, KFe_2S_3 (Mitchell *et al.* 2004), $BaFe_2S_3$ (Hong & Steinfink 1972), $CsFe_2Se_3$, $RbFe_2Se_3$, $CsFe_2Te_3$, $RbFe_2Te_3$ (Klepp *et al.* 1996), and $CsCu_2Cl_3$ (Brink *et al.* 1954). As was shown from results of Rietveld refinements, synthetic KFe_2S_3, $RbFe_2S_3$ and $CsFe_2S_3$ form a continuous solid-solution; in particular, compounds $(Cs_{0.5}Rb_{0.5})Fe_2S_3$, $(Rb_{0.5}K_{0.5})Fe_2S_3$ and $(Cs_{0.5}K_{0.5})Fe_2S_3$ adopt the same structure and crystallize in space group *Cmcm* (Mitchell *et al.* 2004). We may infer that pautovite is a representative of this structure type, the natural analogue of synthetic $CsFe_2S_3$.

DISCUSSION

The discovery of (Cs,Rb)-bearing rasvumite (Chakhmouradian *et al.* 2001) and especially of pautovite, one of the natural compounds of Cs most enriched in this element, shows a new aspect of the geochemistry of cesium and rubidium in ultra-alkaline derivatives of agpaitic nepheline syenite complexes, especially of the hypersodic variety, such as Lovozero and Mont Saint-Hilaire. These elements are closely related to the exotic potassium sulfide type of mineralization. Both Cs and Rb show a close affinity to the rasvumite structure-type. In the Palitra pegmatite, the potassium iron sulfides bartonite and chlorbartonite, both deficient in Rb and Cs (below their detection limit with the electron microprobe), are closely associated with pautovite. Apparently, this affinity is caused by the different size of the coordination polyhedra occupied by the alkali metal atoms in sulfides. For example, the interatomic distance <K–S> is 3.41–3.70 (mean 3.52) Å in rasvumite (Clark & Brown 1980), 3.12–3.47 (mean 3.37) Å in bartonite (Evans & Clark 1981), and 3.13–3.46 (mean 3.36) Å in djerfisherite (Dmitrieva & Ilyukhin 1975). For this reason, the large Cs and Rb atoms may show a preference for the rasvumite-type structure.

It is known that the relative affinity of metals for sulfur, in each subgroup of the periodic table, increases with atomic number (*i.e.*, with an increase of atomic and ionic radius). This is caused by the tendency for the bonding of the largest cations with the S atom, which is significantly larger than the O atom. For example, the equilibria in the reactions: $BaO + ZnS \rightarrow BaS + ZnO$ and $Rb_2O + K_2S \rightarrow Rb_2S + K_2O$ are shifted to the right (Urusov 1975). This pattern can explain the "chalcophile" behavior of rubidium and especially cesium under reducing conditions (natrosilite and villiaumite in the Palitra pegmatite contain abundant gas inclusions in which carbon monoxide and hydrocarbons strongly prevail over carbon dioxide).

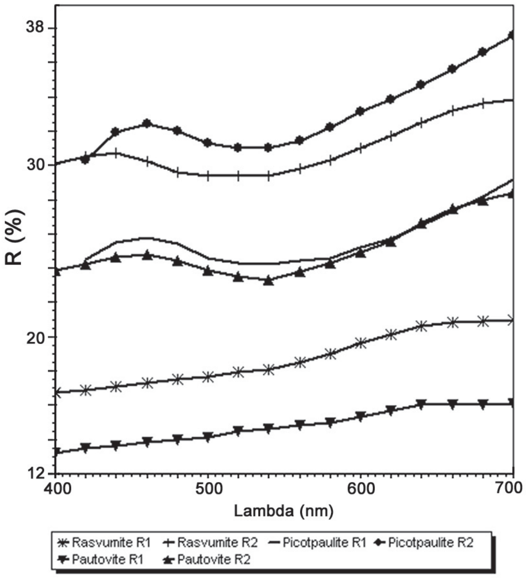

FIG. 3. The reflectance spectra in air for pautovite, rasvumite and picotpaulite.

TABLE 3. X-RAY POWDER DATA FOR PAUTOVITE

I	d_{obs}, Å	d_{calc}, Å	*hkl**
10	7.16	7.247	110
10	5.57	5.622	020
30	4.69	4.738	200
20	4.28	4.373	111
10	3.82	3.926	021
10	3.45	3.486	130
100	2.981	3.023	221
10	2.860	2.942, 2.811	131, 040
40	2.723	2.743	002
15	2.629	2.660	311
10	2.548	2.565, 2.502	112, 041
5	2.368	2.374, 2.369	202, 400
10	2.230	2.212	241
30	2.003	2.037, 2.032, 2.028	312, 151, 421
60	1.910	1.963, 1.874	042, 060
20	1.862	1.869, 1.832	510, 350
30	1.785	1.793	402
10	1.712	1.720, 1.711	441, 152
5	1.650	1.661, 1.632	261, 223
40	1.565	1.567	313
20	1.514	1.522, 1.512	171, 442
5	1.472	1.471, 1.465	262, 621
20	1.279	1.287, 1.282, 1.276	443, 224, 134
10	1.256	1.263, 1.250	263, 314

* The *hkl* indices were selected taking into account the intensities calculated from the structural data for synthetic $CsFe_2S_3$ given in Mitchell *et al.* (2004).

A good example of the "chalcophile" behaviour of niobium, another typically lithophile element, in highly alkaline natural systems under reducing conditions is the occurrence of edgarite, $FeNb_3S_6$, in the neighboring Khibiny alkaline complex and closely related to the Lovozero complex (Barkov *et al.* 2000).

Pautovite is not only the first cesium mineral at the Lovozero complex, but also the most thallium-enriched phase (0.5 wt.% Tl) there. This is the second case where significant amounts of Cs and Tl have been found in a natural sulfide; isomorphism of these elements was discovered in galkhaite, $(Cs,Tl)(Hg,Cu,Zn)_6(As,Sb)_4S_{12}$, from hydrothermal deposits of mercury (Chen & Szymański 1981, 1982).

The crystal-chemical and geochemical relationship of Tl^+ and K^+ is well known, and sulfide minerals demonstrate it especially clearly. In addition to rasvumite-type phases (Table 2), other series of K and Tl chalcogenide minerals exist. Their members have the same stoichiometry and symmetry and close unit-cell dimensions, which leads to an inference of their structural identity: murunskite, $K_2Cu_3FeS_4$ – thalcusite, $Tl_2Cu_3FeS_4$ – bukovite, $Tl_2(Cu,Fe)_4Se_4$ (Makovicky *et al.* 1980, Evstigneeva *et al.* 2003); djerfisherite, $K_6Na_{0-1}(Fe,Cu,Ni)_{24}S_{26}Cl$ – thalfenisite, $Tl_6(Fe,Ni,Cu)_{25}S_{26}Cl$ (Rudashevskiy *et al.* 1979).

Solid solutions of thallium and potassium sulfides are typical of peralkaline complexes. Chalcothallite, $Tl_2(Cu,Fe)_6SbS_4$, from Ilímaussaq contains 0.8 wt.% K (Makovicky *et al.* 1980). About 0.4 wt.% K was detected in thalcusite from Ilímaussaq (Kovalenker *et al.* 1978) and up to 2.3 wt.% K in thalcusite from the Murun alkaline complex, Siberia, Russia (atom ratio: K/Tl = 0.45). For Murun, murunskite with 3.44 wt.% Tl was reported; a murunskite – thalcusite solid-solution series was inferred (Dobrovol'skaya *et al.* 1982, Konev *et al.* 1996). Thallium-for-potassium solid solution was also found in sulfides of K from peralkaline pegmatites of Khibiny [up to 0.2 wt.% Tl in rasvumite: Lisitsin *et al.* (2002); about 0.2 wt.% Tl in djerfisherite: our data] and Lovozero (up to 0.3 wt.% in bartonite: Pekov *et al.* 2003b). Thus, potassium and cesium sulfides seem the best concentrators of thallium in alkaline complexes.

The above-mentioned findings illustrate the very similar behavior of K, Rb, Cs and Tl if late sulfide mineralization forms in peralkaline complexes. The existence of the continuous solid-solution rasvumite – hypothetic mineral $RbFe_2S_3$ – pautovite – picotpaulite can be expected in nature.

ACKNOWLEDGEMENTS

We are grateful to I.A. Bryzgalov for his assistance in the determination of Tl concentration by electron microprobe, R.H. Mitchell and A.R. Chakhmouradian for kindly providing information on synthetic alkali thioferrates before publication, and T. Balić-Žunić for kindly providing unpublished data on picotpaulite, helpful discussion and comments. We thank L. Horváth, who improved the English in our manuscript, referees A.Yu. Barkov and T. Balić-Žunić, and Robert F. Martin for valuable comments. The work was in part supported by the Grant No. 1087–2003–5 of the Fundamental Science School Program of the Russian Academy of Sciences and by the Grant No. 04–05–64118 of the Russian Scientific Foundation.

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Received July 26, 2004, revised manuscript accepted March 20, 2005.