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LONDONITE FROM THE URALS, AND NEW ASPECTS OF THE CRYSTAL CHEMISTRY OF THE RHODIZITE–LONDONITE SERIES

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Abstract

Three old specimens, collected in the 19th century and now deposited in Fersman Mineralogical Museum, Moscow, are labeled as rhodizite from the Sarapulka, Shaitanka (both cotype localities) and Alabashka granitic pegmatite fields, Central Urals, Russia. All are Cs-dominant (Cs > K) and must now be considered londonite. The crystal structure of londonite from Sarapulka was solved from single-crystal data collected at 193 K and refined to $R = 0.0203$. The mineral is cubic, space group $P\bar{4}3m$, a 7.3149(7) Å. Its structure is based on a microporous quasi-framework formed by clusters of four edge-sharing AlO_6 octahedra linked by BO_4 and BeO_4 tetrahedra. Both Cs^+ and K^+ are ordered in the cages of the quasi-framework. The very short Cs–K distance, 0.51(3) Å, prevents simultaneous occupancy of these positions in the same cage. The Be and K atoms are also separated by an unallowable short distance of 2.76(3) Å, and thus their contents are coupled. The solid-solution system between rhodizite (K-dominant), londonite (Cs-dominant) and the hypothetical K- and Cs-free analogue, $(\square,H_2O)\{Al_4[Be_4B_{12}O_{28}]\}$, is complicated, with numerous coupled heterovalent substitutions. Taking into consideration chemical, structural and IR data, it can be presented as: $(\boldsymbol{A},\square,H_2O)_1(\mathbf{Al},Li)_4(\mathbf{Be},Li,Al,\square)_4(\mathbf{B},Be)_{12}[\mathbf{O}_{28-x}(OH,F)_x]$, where $\boldsymbol{A}$ = **K**, **Cs** and $x < 1$; the species-defining elements are marked in bold. The rhodizite–londonite series is structurally related to pharmacosiderite- and sodalite-type

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compounds. The association of pharmacosiderite-type [Al_4O_4] clusters and a sodalite-type [$B_{12}O_{24}$] framework results in the formation of an original complex, [$Al_4O_4B_{12}O_{24}$], in rhodizite and londonite.

Keywords: londonite, rhodizite, cesium, microporous berylloborate, crystal structure, pharmacosiderite structure-type, sodalite structure-type, infrared spectrum, granitic pegmatite, Urals, Russia, Madagascar.

SOMMAIRE

Ce travail porte sur trois échantillons prélevés au dix-neuvième siècle et déposés dans la collection permanente du musée minéralogique Fersman, à Moscou; on les avait catalogué *rhodizite*, provenant des champs de pegmatites granitiques de Sarapulka, Shaitanka (localités cotypes) et Alabashka dans les Ourales Centrales, en Russie. Dans les trois cas, le césium prédomine (Cs > K), et ces échantillons doivent dorénavant être considérés *londonite*. Nous avons résolu la structure de la londonite de Sarapulka au moyen de données prélevées sur monocristal à 193 K, et nous l'avons affiné jusqu'à un résidu *R* de 0.0203. Le minéral est cubique, groupe spatial $P\bar{4}3m$, *a* 7.3149(7) Å. Sa structure ressemble à une trame microporeuse formée de groupes de quatre octaèdres AlO_6 à arêtes partagées, auxquels sont rattachés des tétraèdres BO_4 et BeO_4. Les ions Cs^+ et K^+ sont ordonnés dans des cages de la quasi-charpente. La distance très courte séparant Cs et K, 0.51(3) Å, empêche l'occupation simultanée deux deux positions dans une seule cage. Les atomes Be et K sont aussi séparés par une distance trop courte, 2.76(3) Å, et leurs taux d'occupation sont donc couplés. La solution solide impliquant rhodizite (K prédominant), londonite (Cs prédominant) et un analogue hypothétique dépourvu de K et de Cs, ($\square$,H_2O){Al_4[$Be_4B_{12}O_{28}$]}, est compliquée, avec plusieurs schémas de substitution couplée. A la lumière de considérations chimiques, structurales et des spectres infrarouges, on peut exprimer la solution solide par la formule $(\boldsymbol{A},\square,H_2O)_1(\mathbf{Al},Li)_4(\mathbf{Be},Li,Al,\square)_4(\mathbf{B},Be)_{12}[\mathbf{O}_{28-x}(OH,F)_x]$, dans laquelle $\boldsymbol{A}$ = **K**, **Cs**, et $x < 1$; les éléments définissant les espèces figurent en caractères gras. La série rhodizite–londonite montrerait des points structuraux communs avec les composés de types pharmacosidérite et sodalite. L'association de groupements [Al_4O_4] rappelant la pharmacosidérite à une charpente [$B_{12}O_{24}$] typique de la sodalite mène à la formation d'une module original, [$Al_4O_4B_{12}O_{24}$], dans la rhodizite et la londonite.

(Traduit par la Rédaction)

Mots-clés: londonite, rhodizite, césium, béryllloborate microporeux, structure cristalline, structure de type pharmacosidérite, structure de type sodalite, spectre infrarouge, pegmatite granitique, Ourales, Russie, Madagascar.

INTRODUCTION

Rhodizite and londonite are aluminum berylloborates with large alkali cations. They represent a unique structure-type and form a continuous solid-solution series. In modern mineralogical nomenclature, the K-dominant mineral of the series is named rhodizite, whereas londonite is considered its Cs-dominant analogue. Nickel & Nichols (2009) gave idealized end-member formulae $KBe_4Al_4(B_{11}Be)O_{28}$ and $CsBe_5Al_4B_{11}O_{28}$ for rhodizite and londonite, respectively.

Rhodizite was first described 175 years ago by the famous German mineralogist Gustav Rose from two granitic pegmatites in the Central Urals, Russia, without quantitative chemical data (Rose 1834, 1835, 1836, 1842). The only known chemical analysis of rhodizite from the Urals was performed by Damour (1882) and was incomplete: Be and Li were missed, and the alkali metals (K, Rb, Cs) were not separated. Damour (1882) presented the last publication containing any original data on rhodizite from the Urals, which turns out to be an extremely rare mineral in this region.

In the first years of 20th century, rhodizite was found in Madagascar, where it is a relatively common mineral of many rare-element granitic pegmatites. All reliable quantitative data on rhodizite have been obtained from specimens from different localities in Madagascar. Both K- and Cs-dominant samples have been found in Madagascar pegmatites. Until recently, they were described in the literature only under the name *rhodizite*. In 2001, Simmons *et al*. proposed to restrict the name *rhodizite* to the K-dominant member of the series. Its Cs-dominant analogue was described as a new mineral species, londonite, from three pegmatites located in different parts of Madagascar (Simmons *et al*. 2001).

Thus, the precise chemical composition of rhodizite–londonite series minerals from the Urals remains unclear to date. In spite of numerous attempts undertaken by many mineralogists (including the senior author of this paper) and mineral collectors, no new reliable finds of rhodizite-like minerals in the Urals have been made. Such material only is available from old collections.

In the present work, we have studied specimens from three pegmatites of the central Urals, including both cotype localities of rhodizite. These specimens were collected in the 19th century and are now deposited in the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow. All these specimens turned out to be the Cs-dominant mineral, *i.e.*, they should be considered to be londonite according to the IMA-accepted nomenclature.

BACKGROUND INFORMATION

Minerals of the rhodizite–londonite series not only contain Cs, Rb, K, Li, Be and B in significant and variable amounts (Table 1), but they are also characterized by complex schemes of heterovalent substitutions involving B, Be, Li, Al, O and OH. These features make the determination of a complete chemical composition difficult. It remains complicated even for modern methods and impedes understanding of many important details of the crystal chemistry of these minerals. In particular, their formulae underwent a long evolution, which probably still is not complete.

Rhodizite was first described from the granitic pegmatites located close to the villages of Sarapulka and Shaitanka in the Central Urals (Rose 1834). The cotype localities are two pits where pink tourmaline was mined, namely Ministerskaya Yama (Minister's Hole) Pit near Sarapulka, Murzinka district, and Mor's Pits near Shaitanka, Rezh district (Pekov 1998). In the publications on rhodizite by Rose (1834, 1835, 1836, 1842), only chemical tests were described, leading to the conclusion that the samples studied represent a new lithium–boron mineral related to boracite.

TABLE 1. CHEMICAL COMPOSITIONS OF LONDONITE AND RHODIZITE: THIS WORK

Sample Locality	FMM-32135 Sarapulka, Urals		FMM-10325 Shaitanka, Urals		FMM-24685 Alabashka, Urals		Mad-1805 Sahatany, Madagascar	
Li_2O wt%	0.28		0.24		0.23		0.09	
Na_2O	0.03		0.02		0.02		0.08	
K_2O	0.95		0.89		1.01		3.84	
Rb_2O	0.21		0.17		0.20		1.14	
Cs_2O	11.21		11.51		10.47		1.86	
CaO	0.01		0.02		b.d.l.		0.01	
MgO	0.01		0.02		b.d.l.		0.01	
MnO	0.01		0.02		0.18		b.d.l.	
BeO	14.33		14.79		13.47		10.82	
B_2O_3	46.53		47.11		48.10		49.59	
Al_2O_3	25.68		25.83		25.44		27.20	
F	0.03		0.10		0.12		0.14	
$-O=F_2$	-0.01		-0.04		-0.05		-0.06	
Total	99.27		100.68		99.19		94.72	
Na *apfu*	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02
K	0.17	0.17	0.15	0.15	0.18	0.18	0.67	0.66
Rb	0.02	0.02	0.01	0.01	0.02	0.02	0.10	0.10
Cs	0.66	0.65	0.66	0.65	0.61	0.61	0.11	0.11
ΣA	***0.86***	***0.85***	***0.83***	***0.82***	***0.82***	***0.82***	***0.90***	***0.89***
Li	0.15	0.15	0.13	0.13	0.13	0.13	0.05	0.05
Be	4.72	4.67	4.81	4.76	4.41	4.38	3.53	3.49
B	11.02	10.90	11.00	10.88	11.30	11.23	11.62	11.50
Al	4.15	4.11	4.12	4.08	4.08	4.06	4.35	4.30
Mn	0.00	0.00	0.00	0.00	0.02	0.02	0	0
ΣM	***20.04***	***19.83***	***20.06***	***19.85***	***19.94***	***19.82***	***19.55***	***19.34***
ΣM+A	***20.90***	***20.68***	***20.89***	***20.67***	***20.76***	***20.64***	***20.45***	***20.23***
O	27.99	27.37	27.96	27.35	27.95	27.62	27.94	27.32
F	0.01	0.01	0.04	0.04	0.05	0.05	0.06	0.06
OH(calc.)	0	0.62	0	0.61	0	0.33	0	0.62

Note: b.d.l.: below detection limit; *A*: large cations: Na, K, Rb, Cs; *M*: Li, Be, B, Al, Mn. Each formula is calculated in two alternative variants: left column: based on $(O,F)_{28}$; right column: based on Σ*M*+*A* = 20.00 minus number of K *apfu*, according to the structural data (see text), showing that the Be–K distance is short and that Be and K cannot occupy adjacent sites. In the second variant, the deficiency of positive charge is compensated by partial substitution of O^{2-} by $(OH,F)^-$.

Damour (1882) carried out a chemical analysis of rhodizite from the Urals and published the following data: Na_2O 1.62, $(K_2O+Rb_2O+Cs_2O)$ 12.00, CaO 0.74, MgO 0.82, Fe_2O_3 1.93, Al_2O_3 41.40, B_2O_3 33.93, loss on ignition (LOI) 2.96, total 95.40 wt.%.

The first data on rhodizite from Madagascar were presented by Lacroix (1910). The first analysis of Madagascar rhodizite was performed by Pisani on a sample (with some spodumene impurity) from the Antandrokomby pegmatite, Manandona valley, Betafo Department, and gave: Li_2O 7.30, Na_2O 3.30, $(K_2O+Rb_2O+Cs_2O)$ 5.90, BeO 10.10, Al_2O_3 30.50, B_2O_3 40.60, SiO_2 1.36, LOI 0.45, total 99.51 wt.% (Lacroix 1910).

Duparc *et al.* (1911) analyzed rhodizite from the Manjaka pegmatite, Sahatany valley, Betafo Department, Madagascar, and obtained the following data: Li_2O 0.68, Na_2O 1.78, K_2O 1.41, Rb_2O 2.29, Cs_2O 3.47, MgO 0.11, Al_2O_3 27.40, B_2O_3 [43.33: by difference], SiO_2 3.18, LOI 1.42, total [100.00] wt.%. He proposed the formula $(Li,K,Cs,Rb,Na,H)_4Al_6Be_7B_{14}O_{39}$. This was the first analysis of rhodizite in which all of the alkali cations were reported separately; however, in view of the high Na and Si contents, we can suppose that the sample was probably contaminated with a Na-bearing silicate.

Subsequently, Lacroix (1922) described rhodizite from some other localities of Madagascar and proposed another formula: $(Cs,Rb,K,Na,H)_8Al_6Be_4B_{12}O_{35}$. It remains unclear why he reported this sequence of alkali cations.

The formula proposed by Strunz (1938) for rhodizite, $NaKLi_4Al_4Be_3B_{10}O_{27}$, was in use for many years. It was clearly derived from Pisani's results, with 7.30 wt.% Li_2O, as published by Lacroix (1910).

All of analyses discussed above were incomplete or performed on impure samples (or both). The first correct analysis of a mineral of this series was published by Frondel & Ito (1965); see column #1 in Table 2. This sample from Manjaka has Cs > K. Similar data were obtained for a sample from the same locality by Eremenko *et al.* (1988); see column #3 in Table 2.

The first determination of the structure of a mineral of this series was undertaken by Buerger & Taxer (1966) on a Cs-dominant crystal from Manjaka, a part of the sample studied by Frondel & Ito (1965). The idealized formula $CsAl_4Be_4B_{12}O_{28}$ obtained from the structural studies required cesium to be neutral in order to maintain charge balance (Buerger & Taxer 1966). Simultaneously, electron spin resonance and magnetic susceptibility measurements made by Donnay *et al.* (1966) showed that cesium in the mineral is present in its monovalent state. These authors postulated

TABLE 2. PREVIOUSLY PUBLISHED CHEMICAL COMPOSITIONS OF LONDONITE (1, 3-5) AND RHODIZITE (2, 6) FROM MADAGASCAR

No.	1		2		3		4	5	6
Locality	Manjaka		Ambatofinandrahana		Manjaka		Antandrokomby	Antsongombato	Andasy
Li_2O wt.%			0.03		0.10		0.04	0.06	0.03
Na_2O	0.12		0.06		0.36		0.11	0.43	0.19
K_2O	1.79		2.77		1.57		2.21	2.12	5.03
Rb_2O	1.83		0.73		1.38		1.04	1.48	0.51
Cs_2O	7.54		6.4		6.74		8.37	7.32	1.70
CaO			0.18		0.10		0.14	b.d.l.	0.04
MgO			0.01		0.07		b.d.l.	b.d.l.	b.d.l.
MnO							0.05	b.d.l.	0.03
BeO	12.20		14.3		14.56		(15.49)	(15.57)	(16.21)
B_2O_3	46.82		50.2		46.74		(47.39)	(47.66)	(49.60)
Al_2O_3	24.41		25.8		25.60		25.10	25.28	26.35
Fe_2O_3	0.12		0.10				0.06	b.d.l.	0.02
SiO_2	0.45						0.07	b.d.l.	0.08
Total	99.91*		101.0*		99.48*		100.07	99.92	99.79
Na *apfu*	0.03	0.03	0.02	0.02	0.10	0.10	0.03	0.11	0.05
K	0.32	0.32	0.46	0.45	0.27	0.27	0.38	0.36	0.82
Rb	0.17	0.17	0.06	0.06	0.12	0.12	0.09	0.13	0.04
Cs	0.46	0.46	0.36	0.35	0.39	0.39	0.48	0.42	0.09
Ca			0.02	0.02	0.01	0.01	0.02	-	0.01
ΣA	***0.98***	***0.98***	***0.92***	***0.90***	***0.89***	***0.89***	***1.00***	***1.02***	***1.01***
Li			0.02	0.02	0.05	0.05	0.02	0.03	0.02
Be	4.16	4.135	4.51	4.43	4.78	4.72	(5.00)	(5.00)	(5.00)
B	11.48	11.41	11.36	11.17	11.02	10.88	(10.99)	(11.00)	(10.99)
Al	4.09	4.065	3.99	3.92	4.12	4.07	3.98	3.98	3.99
Mg			0.00	0.00	0.01	0.01	-	-	-
Mn							0.01	-	0.00
Fe^{3+}	0.01	0.01	0.01	0.01			0.01	-	0.00
Si	0.06	0.06					0.01	-	0.01
ΣM	***19.80***	***19.68***	***19.89***	***19.55***	***19.98***	***19.73***	***(20.02)***	***(20.01)***	***(20.01)***
ΣM+A	***20.78***	***20.66***	***20.81***	***20.45***	***20.87***	***20.62***	***(21.02)***	***(21.03)***	***(21.02)***
O	28	27.945	28	27.10	28	27.26	28	28	28
OH(calc.)	0	0.055	0	0.90	0	0.74			
Reference	Frondel & Ito (1965)		Pring *et al.* (1986)		Eremenko *et al.* (1988)		Simmons *et al.* (2001)		

Note: b.d.l.: below detection limit; empty cell indicates no data; *A*: large cations: Na, K, Rb, Cs, Ca; *M*: Li, Be, B, Al, Mg, Mn, Fe, Si; * totals also include (wt.%): 1: Sn 0.1, H_2O^+ 4.10, H_2O^- 0.43; 2: H_2O^+ 0.32, CO_2 0.15; 3: loss on ignition 2.09. H_2O and CO_2 were not used for calculations of formulae. In columns 4–6, BeO and B_2O_3 contents were calculated from the assumption of 5 *apfu* Be and 11 *apfu* (B + Si); the sums Σ*M* and Σ*M+A* for these samples given in parentheses were obtained using calculated values for Be and B.

For columns 1-3, in which B and Be were determined directly, formulae are calculated in two alternative variants; left column: based on O_{28}; right column: based on Σ*M+A* = 20.00 minus number of K *apfu*, according to the structural data (see text) showing that the Be–K distance is short and that Be and K cannot occupy adjacent sites. In the second variant, the deficiency of positive charge is compensated by partial substitution of O^{2-} by OH^-.

disordered boron vacancies and two hydroxyl groups randomly distributed in the structure and proposed the alternative formula $CsAl_4Be_4B_{11}O_{26}(OH)_2$ (Donnay *et al.* 1967). In their comments on these data, Taxer & Buerger (1967) noted that "perhaps the loss of ignition… may have been due to loss of… possibly boron and alkali".

The +1 valence state of cesium in Cs-rich rhodizite has been confirmed by magic angle spinning nuclear magnetic resonance (Pring *et al.* 1986). An interpretation of the MAS–NMR ^{9}Be spectrum indicated that the beryllium is present in chemically equivalent sites. The structure refinement, carried out on a K-dominant sample (#2 in Table 2) from the Ambatofinandrahana district, Madagascar, confirmed by the chemical data, gave the formula: $(K,Cs)_{0.9}Al_4Be_{4.5}B_{11.35}O_{28}$ (Pring *et al.* 1986). These authors published detailed description of the crystal chemistry of rhodizite, and the above formula, idealized with whole-number coefficients, is now accepted for this mineral species. They also found a random distribution of alkali cations in the structure and noted: "with the total alkali content per cell close to unity, the alkali, boron and beryllium contents are balanced to achieve charge neutrality and minimize the number of vacant sites within the structure" (Pring *et al*. 1986). Below, we show that this statement is only partly confirmed in the crystal structure of londonite from the Urals, in which the Cs and K cations are distributed between symmetrically distinct sites.

Simmons *et al*. (2001) described the Cs-dominant member of the series as the new mineral species *londonite* and gave a review of occurrences of rhodizite and londonite in Madagascar, where these minerals are found in many rare-element pegmatites. The chemical data given by these authors (columns 4–6 in Table 2) show significant variability in the ratios of large alkali cations, especially the K:Cs ratio, in minerals of the rhodizite–londonite series from Madagascar.

SAMPLE DESCRIPTION

We studied three specimens from the Central Urals, labeled rhodizite, which are deposited in the Fersman Mineralogical Museum (FMM). They are spectacular specimens belonging to three historical collections acquired by the Museum the early 20th century. This circumstance made it impossible to extract much material for study. All three specimens were collected in the 19th century. The sample numbers used here are those used in the systematic (main) collection of the Museum.

Sample FMM–32135

This sample is from the collection of Prince Petr Arkad'evich Kochubey, amassed by him in the interval 1840s–1880s and acquired by the Museum from his son in 1913. This collection was considered one of the best private mineral collections at that time, not only in Russia but also in Western Europe. The locality is given on the original label as "Murzinka", but the specimen is very typical of the Ministerskaya Yama Pit, Sarapulka pegmatite field (near Sarapulka village), Murzinka district as well, and there is no doubt that it is from this locality. Crystals of tourmaline (with a core of black schorl and a rim of crimson elbaite) from Ministerskaya Yama form unusual, for pegmatites of the Urals, radial balls and bunches, which were very famous and popular in the mineral collections of the 19th century. In this specimen, londonite ("rhodizite") forms colorless, transparent well-shaped crystals up to 9 mm across bounded by {110} (rhombic dodecahedron) and subordinate {111} (octahedron) faces. They occur on the surface of a bunch of multicolored tourmaline crystals and are associated with microcline.

Sample FMM–10325

This sample is from the collection of mining engineer Vladimir Aleksandrovich Jossa, which was acquired by the Museum in 1918. The specimen is from Mor's Pits, Shaitanka pegmatite field (near Shaitanka village, later renamed Oktyabr'skoe), Rezh district. Londonite ("rhodizite") occurs as colorless, transparent, well-formed rhombic-dodecahedral crystals up to 2 mm on potassium feldspar and pink elbaite, from a miarolitic cavity in the pegmatite.

Sample FMM–24685

This sample is from the collection of mining engineer Il'ya Nikolaevich Kryzhanovsky, which was acquired by the Museum in 1912. The specimen is from the Mokrusha pegmatite, Alabashka pegmatite field, Murzinka district. Londonite ("rhodizite") occurs as colorless, transparent, perfect crystals up to 2 mm, formed by {110} and subordinate {111} faces, on microcline, from a miarolitic cavity in the pegmatite. No reliable data have been published on "rhodizite" from this locality. However, the matrix of this specimen is very typical for the Mokrusha pegmatite, and there is no reason to suspect that the label is incorrect.

For comparative purposes, we analyzed a typical crystal of rhodizite from Madagascar. This specimen (Mad–1805) is from the Sahatany pegmatite field (exact locality unknown), Betafo Department. Rhodizite forms yellowish semitransparent well-shaped, octahedral crystals with subordinate {110} faces, up to 1 cm in a massive aggregate of K-rich feldspar, albite and grey quartz.

Londonite from all three localities in the Urals shows orange fluorescence in ultraviolet light, bright under shortwave (245 nm) and weak under longwave (330 nm) radiation. Numerous specimens of rhodizite and londonite from different pegmatites of Madagascar that we examined show no fluorescence under ultraviolet illumination.

CHEMICAL COMPOSITION

The chemical composition of our samples (Table 1) was studied by electron-microprobe analysis and inductively coupled plasma – optical emission spectroscopy (ICP–OES).

The contents of B, F and the metals, except Be and Li, were determined with a Camebax SX 100 electron microprobe using wavelength-dispersion spectroscopic (WDS) mode, an operating voltage of 15 kV and a beam current of 30 nA. The electron beam was rastered over an area of 5×5 μm^2. We used, as standards: jadeite (Na), orthoclase (K, Al), augite (Ca, Mg), rhodonite (Mn), $Rb_2Nb_4O_{11}$ (Rb), $Cs_2Nb_4O_{11}$ (Cs), BN ceramics (B), and MgF_2 (F). The values given for these elements in Table 1 are the averaged results of six point-analyses each.

The Be and Li contents were determined by ICP–OES on microsamples (small grains: <1 mg each) without weighing. The samples were dissolved in concentrated HF mixed with 34% HNO_3 using an autoclave. After evaporation, and repeated eliminations of residual HF with HNO_3, a dry residuum was dissolved in 2% HNO_3 and analyzed using a Varian VISTA Pro instrument. The contents of Be, Li and Al were determined in relative units, and the averaged Al content, obtained by electron microprobe, was used to calculate the Be and Li contents. This procedure was checked with several standard samples with known Be and Li contents, and gave precise and accurate results.

The formulae (Tables 1, 2) were calculated in two alternative ways: the first is based on $(O,F)_{28}$, and the second based on the sum of "tetrahedrally coordinated cations" = 20.00 *apfu* minus an amount corresponding to the number of K *apfu* in accordance with the structural data, which indicate that Be and K cannot occupy adjacent sites simultaneously. In the second variant, the deficiency of positive charge may be compensated by partial replacement of O^{2-} by $(OH,F)^{-}$.

The samples studied from all three Urals localities are chemically similar (Table 1). They are characterized by the dominance of Cs over the other large alkali cations, K and Rb, *i.e.*, they correspond to londonite. The content of Li is low: 0.2–0.3 wt.% Li_2O. The sample from Madagascar is Cs-bearing rhodizite: K > Cs. It also differs from londonite from the Urals by higher contents of B and Rb and a significantly lower Be concentration. Concentrations of other elements with atomic numbers higher than 9 (F), except those listed in Table 1, are below the detection limits. The samples were checked for Sc, Fe and Si using the electron microprobe in WDS mode and for other elements in the EDS mode.

Note that londonite from the Urals is more Cs-rich (10.5–11.5 wt. % Cs_2O) than londonite from Madagascar (maximum 8.4 wt. % Cs_2O: Table 2).

INFRARED SPECTROSCOPY

Samples for IR spectroscopy were prepared as follows: about 1 mg of powdered mineral was mixed with 150–200 mg of anhydrous KBr, pelletized, and analyzed using a Specord 75 IR spectrophotometer. The IR spectrum of a pure KBr disk was subtracted from the overall spectrum. Polystyrene and gaseous NH_3 were used as frequency standards; the precision of the frequency measurement is ±1 cm^{-1}. For shoulders (in contrast to peaks), positions of inflection points were determined.

The IR absorption spectra of rhodizite from Madagascar (Mad–1805) and londonite from Madagascar (Ambalabe pegmatite, Betafo Department) and from the Urals (FMM–10325) are similar (Fig. 1). The most significant difference observed is in the intensities of the bands below 600 cm^{-1}, which are related mainly to bending vibrations of the framework, but also can involve low-force-strength extra-framework cations and H_2O molecules generating resonance modes. The range 875–1200 cm^{-1} corresponds to the frequencies of B–O stretching vibrations in BO_4 tetrahedra (Plyusnina 1977).

Unlike beryllosilicates and beryllophosphates, the berylloborates rhodizite and londonite do not show strong distinct bands of stretching vibrations of BeO_4 tetrahedra in the range 700–800 cm^{-1}. Instead, an indistinct band or shoulders are observed near the short-wave border of this range, indicating that Be–O bonds are involved in mixed-mode vibrations of the berylloborate framework. Similarly, the range 600–700 cm^{-1} (intermediate between the ranges of Al–O and Be–O stretching vibrations, respectively 500–600 and 700–800 cm^{-1}) may correspond to mixed modes involving both Al–O and Be–O bonds.

Both samples of londonite show weak bands of H_2O molecules, but the positions of the bands of H–O–H bending vibrations (at 1595 cm^{-1} for Uralian londonite and at 1625 cm^{-1} for the sample from Madagascar) indicate that the character of H_2O in these samples is different. The presence of OH groups in both samples is probable. The IR spectrum of rhodizite does not contain detectable bands in the range 1500–1700 cm^{-1}. At higher concentrations of the mineral in the KBr disk, the same sample of rhodizite shows distinct wide bands in the range of O–H stretching vibrations (2900–3600 cm^{-1}), but does not display bands corresponding to H–O–H bending vibrations. The most probable cause of this phenomenon is the presence of OH groups but not H_2O molecules in the rhodizite sample studied.

X-RAY CRYSTALLOGRAPHY AND CRYSTAL-STRUCTURE REFINEMENT

The single crystal used for the structural study was extracted from sample FMM–32135 (Sarapulka). The determination of the unit-cell parameters and data collection were performed on an IPDS–II area-detector system at 193 K using Mo$K\alpha$ radiation and graphite monochromator. The intensities were corrected for Lorentz and polarization effects, and a numerical absorption correction was applied. The crystallographic characteristics of londonite and the experimental conditions of data collection and refinement are reported in Table 3. All calculations were performed with the SHELX family of programs (Sheldrick 1997a, b). Atomic scattering factors and anomalous dispersion corrections were taken from the International Tables for Crystallography (Prince 2004). The crystal structure was solved by direct methods in space group $P\bar{4}3m$ and refined in an anisotropic approximation against F^2 data to residuals wR_2 = 0.0435 (for all 254 reflections), R = 0.0203 [for 247 reflections with $I > 2\sigma(I)$]. Note that the K atoms with a small occupancy next to Cs atoms were refined isotropically. Table 4 presents the final results for the atom positions and equivalent displacement parameters. Characteristic distances and angles are given in Table

5. A bond-valence calculation was performed using the algorithm and parameters given by Brown & Altermatt (1985), taking into account the occupancy factors for the cation positions (Table 6). A table of structure factors is available from the Depository of Unpublished Data on the MAC website [document Londonite CM48_241].

THE STRUCTURE OF LONDONITE AND COUPLED SUBSTITUTIONS IN THE RHODIZITE–LONDONITE SERIES

The general structure of londonite is based on an incomplete array of cubic close-packed oxygen atoms, as described by Buerger & Taxer (1966) and Taxer & Buerger (1967). Some of the octahedral voids inside a defective close-packing of oxygen atoms (28 atoms instead of 32 possible in the unit cell) are occupied by Al^{3+} cations. The Al–O bonds in the octahedra are divided according to symmetry into two groups, but they have very similar values, Al–O2 = 1.903(1) and Al–O1 = 1.907(1) Å. The B and Be atoms are ordered at two different positions with tetrahedral coordination (Fig. 2). A remarkable feature is a triple unit that consists of one [BeO_4] and two [BO_4] tetrahedra that share one common O3 vertex. Four edge-sharing AlO_6 octahedra form clusters that are linked by BO_4 and BeO_4 tetrahedra in a microporous quasi-framework with cages located at the cell centers (Fig. 3). The cage (formed by three crossed channels parallel to three coordinate directions of the cubic unit-cell), surrounded by 12 O atoms, can be considered to result from an absence of four oxygen atoms in the ideal cubic close-packing (Buerger & Taxer 1966, Taxer & Buerger 1967). The large alkali cations Cs^+ and K^+ occupy distinct positions in these cages, and both are coordinated by 12 oxygen atoms (Fig. 4).

Pring *et al.* (1986) assigned 0.5 beryllium atoms to the 12*h* sites occupied by 11.35 boron atoms. Our refinement also showed a small shortfall of boron in tetrahedra, made up by 10% of beryllium [$B_{10.80}Be_{1.20}$]; the occupancy factor for beryllium terahedra is equal to 3.64(3). Thus we assume some substitution of B by Be (up to 1 *apfu* Be) at the 12*h* sites, which is confirmed by the chemical composition (Table 1).

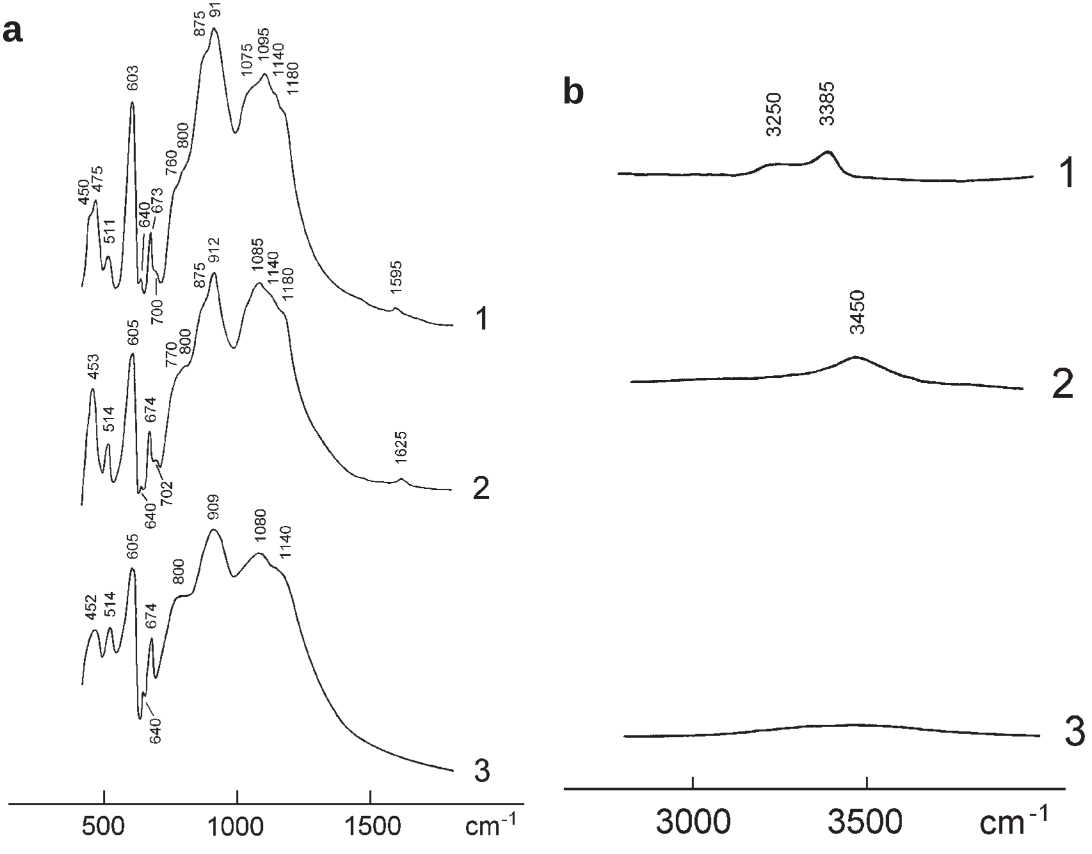


FIG. 1. Infrared spectra of londonite from Shaitanka, Urals (1), and Ambalabe, Madagascar (2), and rhodizite from Sahatany, Madagascar (3). Two ranges contain absorption bands: a) region of 400–1700 cm^{-1}, b) region of 2800–3800 cm^{-1}.

The structural formula of londonite derived from this model is $Cs_{0.55}K_{0.33}\{Al_4[Be_{3.64}(B_{10.80}Be_{1.20})O_{27}(OH,F)]\}$. One hydroxyl group together with an insignificant amount of F^- found with the electron microprobe (Table 1) is necessary to achieve charge balance. The occurrence of a small amount of hydroxyl is confirmed by IR spectroscopy data for rhodizite, as discussed above.

We found that Cs and K are ordered in londonite from the Urals, in contrast to their random distribution reported by Pring *et al.* (1986) for Cs-rich rhodizite from Madagascar. In the structure of londonite from the Urals, Cs^+ cations occupy the 1*b* special positions, where all alkali cations were placed in earlier studies (Taxer & Buerger 1967, Pring *et al.* 1986). The Cs is surrounded by 12 atoms of oxygen, with Cs–O distances of 3.245(1) Å (Table 5). The coordination sphere around the K^+ ions is also formed by 12 anions, but the location of the potassium on the less symmetrical 4*e* site leads to a situation when three oxygen atoms form shorter bonds, 2.82(3) Å; three others are at distance of 3.20(3) Å from K, and six more O are at distances of 3.49(4) Å (Table 5). Thus, the K^+ cations are moved toward the cage walls compared to the position of Cs^+ cation at the cage center. The very short interatomic Cs–K distances, 0.51(3) Å, prevent the simultaneous occupancy of these positions in the same cage. Our refinement shows

TABLE 3. LONDONITE FROM THE CENTRAL URALS (FMM–32135): CRYSTAL DATA AND DETAILS CONCERNING THECOLLECTION AND REFINEMENT OF X-RAY DATA

Crystal data	
Formula	$Cs_{0.55}K_{0.33}\{Al_4[B_{10.80}Be_{4.84}O_{27}(OH)]\}$
Absorption μ (mm^{-1})	1.840
Space group	$P\bar{4}3m$, $Z = 1$
Lattice constants	
a (Å)	7.3149(7)
V ($Å^3$)	391.40(6)
Density calculated ($g{\cdot}cm^{-3}$)	3.408
Crystal size (mm)	0.10 × 0.10 × 0.10
Data collection	
Diffractometer	IPDS area detector system (Stoe)
Radiation	Mo*K*α, graphite monochromator
Temperature (K)	193(2)
Scanning mode	Φ = 0–200.4°, δΦ = 1.2°, 3 min/rec
Measurement range	max θ 29.9°
Reflections (total)	4529
R_{int}	0.0535
Rs	0.0158
Refinement	
Reflections ($I > 2\sigma(I)$] unique, observed	254, 247
Parameters	33
Absorption correction	numerical
T_{max}, T_{min}	0.630, 0.519
Residuals	
R (observedreflections)	0.0203
R, wR_2 (all reflections)	0.0433, 0.0435
Goodness of fit *S*	1.211
Flack parameter	–0.04(3)
δρ (max), (min) ($e/Å^3$)	0.324, –0.236

TABLE 4. LONDONITE FROM THE CENTRAL URALS (FMM–32135): COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS OF ATOMS

	Wyckoff position	Occu-pancy	*x*/*a*	*y*/*b*	*z*/*c*	*U*
Cs	1*b*	0.553(14)	0.5	0.5	0.5	0.0146(8)
K	4*e*	0.332(10)	0.460(3)	0.460	0.460	0.0146(6)
Al	4*e*	4	0.85964(8)	0.85964	0.85964	0.0032(3)
B	12*h*	10.80(8)	0.5	0.7482(3)	0.0	0.0029(6)
Be'	12*h*	1.20(8)	0.5	0.7482(3)	0.0	0.0029(6)
Be	4*e*	3.64(3)	0.2415(4)	0.7585	0.7585	0.0050(15)
O1	4*e*	4	0.1185(2)	0. 8815	0.8815	0.0040(5)
O2	12*i*	12	0.5995(2)	0.86343(13)	0.86343	0.0033(3)
O3	12*i*	12	0.36488(13)	0.63512	0.9004(2)	0.0040(3)

Note: these coordinates are moved at ½½½ compared to data by Pring *et al.* (1986).

TABLE 5. LONDONITE FROM THE CENTRAL URALS (FMM–32135): INTERATOMIC DISTANCES (Å) AND SELECTED ANGLES (°)

Al octahedron		B tetrahedron		Be tetrahedron	
Al – O2	1.904(1) × 3	B – O3	1.480(1) × 2	Be – O1	1.557(5)
O1	1.907(1) × 3	O2	1.496(1) × 2	O3	1.645(2) × 3
Cs polyhedron		K polyhedron			
Cs – O3	3.245(1) × 12	K – O3	2.82(3) × 3		
		O3'	3.20(3) × 3		
		O3"	3.49(4) × 6		
∠O3–B–O3	112.1(1)				
∠O3–B–O2	108.6(7)	∠O3–Be–O3	113.0(1)	∠B–O2–B	121.1(1)
∠O3–B–O2'	108.1(7)	∠O1–Be–O3	105.6(1)	∠B–O3–B	120.3(1)
∠O2–B–O2	111.4(1)			∠B–O3–Be	111.7(1)

TABLE 6. LONDONITE FROM THE CENTRAL URALS (FMM–32135): BOND-VALENCE DATA

atom	Al	B(Be)	Be	Cs	K	Σ
O1	$0.501^{\rightarrow3\downarrow3}$		$0.564^{\downarrow2}$			2.067
O2	$0.506^{\rightarrow3}$	$0.714^{\rightarrow2\downarrow2}$				1.934
O3		$0.748^{\rightarrow2\downarrow2}$	$0.445^{\downarrow2}$	$0.060^{\rightarrow12}$	$0.051^{\downarrow3}$, $0.018^{\rightarrow3}$, $0.008^{\downarrow6}$	2.078
Σ	3.021	2.924	2.018	0.720	0.255	

Note: The symbols ↓n and →n indicate the multiplication of the corresponding contributions in the columns and rows owing to symmetry. The valence summations are expressed in valence units (*vu*).

TABLE 7. POSSIBLE COUPLED SUBSTITUTIONS IN THE SOLID-SOLUTION SYSTEM INVOLVING THE THREE END-MEMBERS RHODIZITE (1–4), LONDONITE (5–11) AND A HYPOTHETICAL Cs- AND K-FREE ANALOGUE (12)

	large cations		octahedra		tetrahedra	oxygen
	Wyckoff positions					
	4*e*	1*b*	4*e*	4*e*	12*h*	4*e* + 12*i*
1)	**K**		$\mathbf{Al}_4$	$\mathbf{Be}_2\mathrm{Al}$	$\mathbf{B}_{12}$	$\mathbf{O}_{28}$
2)	**K**		$\mathbf{Al}_4$	$\mathbf{Be}_3$	$\mathbf{B}_{12}$	$\mathbf{O}_{27}$(OH,F)
3)	**K**		$\mathbf{Al}_4$	$\mathbf{Be}_2\mathrm{Al}$	$\mathbf{B}_{11}\mathrm{Be}$	$\mathbf{O}_{27}$(OH,F)
4)	**K**		$\mathbf{Al}_{3.5}\mathrm{Li}_{0.5}$	$\mathbf{Be}_2\mathrm{Al}$	$\mathbf{B}_{12}$	$\mathbf{O}_{27}$(OH,F)
5)		**Cs**	$\mathbf{Al}_4$	$\mathbf{Be}_4$	$\mathbf{B}_{11}\mathrm{Be}$	$\mathbf{O}_{28}$
6)		**Cs**	$\mathbf{Al}_4$	$\mathbf{Be}_3\mathbf{Li}$	$\mathbf{B}_{12}$	$\mathbf{O}_{28}$
7)		**Cs**	$\mathbf{Al}_{3.5}\mathrm{Li}_{0.5}$	$\mathbf{Be}_4$	$\mathbf{B}_{12}$	$\mathbf{O}_{27}$(OH,F)
8)		**Cs**	$\mathbf{Al}_4$	$\mathbf{Be}_3\mathbf{Li}$	$\mathbf{B}_{11}\mathrm{Be}$	$\mathbf{O}_{27}$(OH,F)
9)		**Cs**	$\mathbf{Al}_{3.5}\mathrm{Li}_{0.5}$	$\mathbf{Be}_4$	$\mathbf{B}_{11}\mathrm{Be}$	$\mathbf{O}_{27}$(OH,F)
10)		**Cs**	$\mathbf{Al}_{3.5}\mathrm{Li}_{0.5}$	$\mathbf{Be}_3\mathbf{Li}$	$\mathbf{B}_{12}$	$\mathbf{O}_{27}$(OH,F)
11)		**Cs**	$\mathbf{Al}_{3.5}\mathrm{Li}_{0.5}$	$\mathbf{Be}_3\mathrm{Al}$	$\mathbf{B}_{11}\mathrm{Be}$	$\mathbf{O}_{28}$
12)			$\mathbf{Al}_4$	$\mathbf{Be}_4$	$\mathbf{B}_{12}$	$\mathbf{O}_{28}$

Note: only the compositions with no more than 1 (OH,F) *pfu* are given. The species-defining constituents are marked in bold. For case No. 12, the presence of H_2O as the species-defining constituent in the sites of large cations is not excluded.

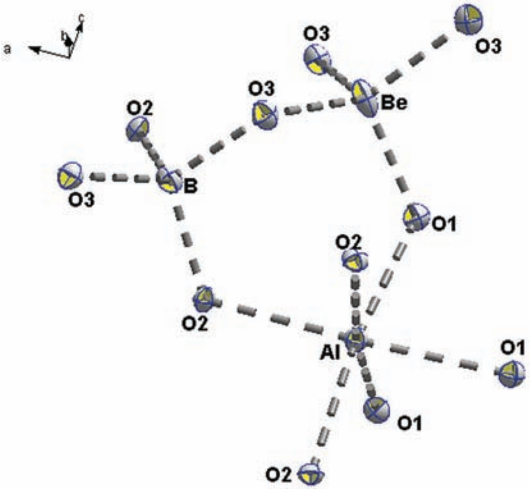


FIG. 2. The main structural elements of londonite. Displacement ellipsoids are drawn at the 90% probability level.

that the alkali atoms are distributed statistically in the following ratios: $Cs_{0.55}K_{0.33}\square_{0.1}$ (average, ignoring minor impurities). This confirms the results of chemical analyses (Tables 1, 2) and the structural data by Pring *et al.* (1986), which showed the total of the alkalis (except Li) in minerals of the rhodizite–londonite series to be usually less than 1 *apfu*. Some discrepancy in the Cs:K ratio between the microprobe data and crystal-structure refinement in sample FMM–32135 could be explained by 1) slight chemical heterogeneity of the sample, and 2) some mobility of potassium under the electron beam during the analysis.

It is important to note that the proportion of vacancies at the Be position is correlated with the amount of K. In addition to the complementary occupancy of K and Cs, Be and K are also separated by an unusually short distance, 2.76(3) Å, preventing their simultaneous occupancy. The capacity of these minerals for K is strongly coupled with the Be content in the 4*e* position, and is variable. The crystal structure of londonite and evidently that of rhodizite are stabilized by vacancy defects at these Be positions. The bond-valence calculation (Table 6) shows that bond strengths for oxygen atoms that participate in the coordination of beryllium (O1 and O3) and the alkali cations (O3) are nearly equal to 2. Therefore, significant changes in the Be content would infringe upon the structure's stability. Thus, the deficiency of large alkali cations from 1 *apfu* in rhodizite and londonite, as found by Pring *et al.* (1986) and Eremenko *et al.* (1988) (Table 2) and confirmed in this research, is not accidental.

The small amount of Li, and of Al in excess of 4 *apfu*, is not possible to determine in the X-ray crystal-structure analysis. It is possible that Li substitutes for Al in AlO_6 octahedra or for Be at the 4*e* positions (the latter assignment is like that found in the Li-rich variety

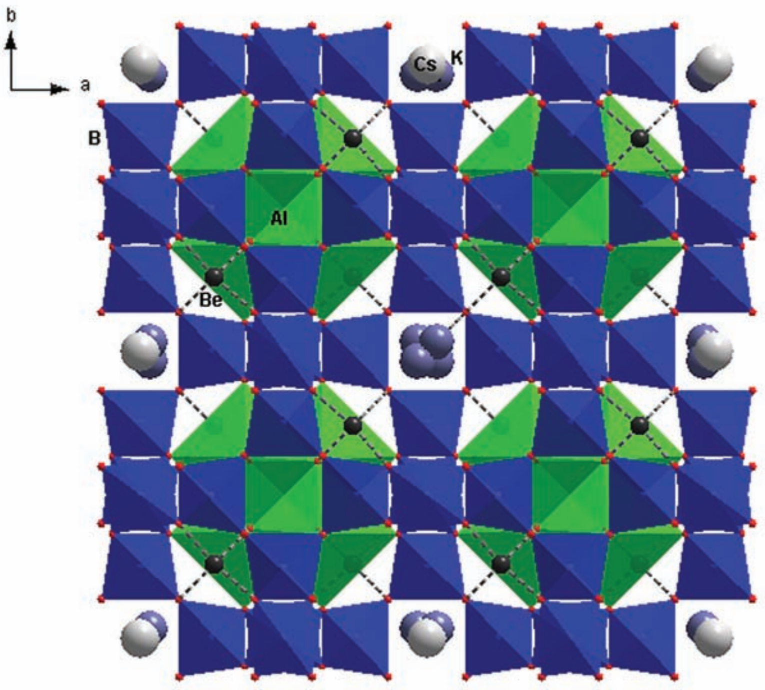


FIG. 3. The crystal structure of londonite from the Central Urals in *x–y* projection.

of beryl “vorobyevite” associated with londonite in the pegmatites of the Urals: Yakubovich *et al*. 2009) whereas surplus Al substitutes for Be at the 4*e* positions.

From the known and proposed types of substitutions, we can derive possible schemes for solid solution in the rhodizite–londonite series. All of the sites, both cationic and anionic, can be involved in schemes of substitution that are mainly heterovalent. Three of the sites, namely Be and *A* (K, Cs) sites, may be partially vacant. An ideal rhodizite-type quasi-framework is electroneutral: $\{Al_4[Be_4B_{12}O_{28}]\}^0$. It may be possible that a mineral corresponding to the idealized formula $\{Al_4[Be_4B_{12}O_{28}]\}$, or $(H_2O)\{Al_4[Be_4B_{12}O_{28}]\}$, could occur (taking into consideration H_2O molecules detected in londonite by IR spectroscopy) in spite of some violation in the bond-valence sums for the O1 and O3 atoms.

The solid-solution system with three end-members, namely rhodizite (A^+ = K), londonite (A^+ = Cs) and the hypothetical A^+-free end-member can formally be subdivided in two branches: potassian, with a corresponding deficiency at the 4*e* (Be) tetrahedral position, and cesian, ideally with full occupancy of this position. The simplest cases, with no more than two components per site, are listed in Table 7. The rhodizite–londonite solid-solution system could be presented as: $(\boldsymbol{A}, \square, H_2O)_1(\mathbf{Al}, Li)_4(\mathbf{Be}, Li, Al, \square)_4(\mathbf{B}, Be)_{12}[\mathbf{O}_{28-x}(OH,F)_x]$ or, in its simplified

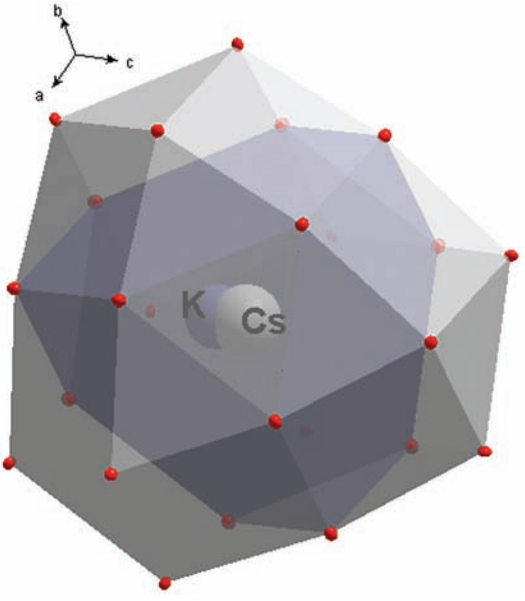


FIG. 4. The coordination of Cs and K by oxygen atoms in the structure of londonite.

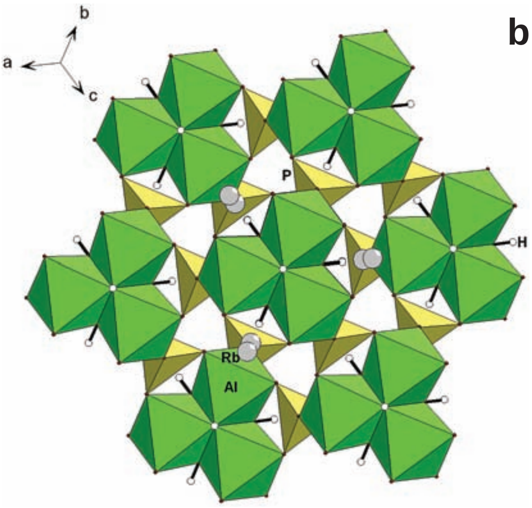
form, $(\boldsymbol{A},\square,H_2O)_1\mathbf{Al}_4(\mathbf{Be},\square)_4(\mathbf{B},Be)_{12}[\mathbf{O}_{28-x}(OH)_x]$, where $\boldsymbol{A}$ = **K**, **Cs** and $x < 1$; the species-defining elements are marked in bold. From the chemical data (Tables 1, 2), a "generalized" formula describing all of the chemical variations is: $[K_{0.15-0.8}Cs_{0.1-0.7}(\square,H_2O)_{0.0-0.15}]_{\Sigma 1}(Al_{3.85-4.0}Li_{0.0-0.15})_{\Sigma 4}(Be_{2.9-3.85}Li_{0.0-0.15}Al_{0.0-0.35}\square_{0.15-0.8})_{\Sigma 4}(B_{10.9-11.6}Be_{0.4-1.1})_{\Sigma 12}[O_{28-x}(OH,F)_x]$.

We do not discuss a role of Rb in the minerals of the rhodizite–londonite series, in spite of its significant presence in some samples from Madagascar (Table 2), because we do not know its position in the crystal structure; our samples are Rb-poor. It is not excluded that in future this solid-solution system will be extended to include a Rb-dominant member.

The substitution of Be for B at the 12*h* sites is the most important mechanism to charge-balance the Cs content in these minerals. Therefore, we consider the end-member formula of londonite to be $Cs\,Al_4(B_{11}Be)Be_4O_{28}$, in agreement with the conclusions of Simmons *et al.* (2001). The end-member formula of rhodizite is more problematic. Bearing in mind the competing occupancies between K and Be, and between K and Cs, we can suppose the end-member formula to be $KAl_4B_{12}(Be_3\square)O_{27}(OH)$. However, this requires verification through further study of rhodizite.

COMPARATIVE CRYSTAL CHEMISTRY

Interesting structural relationships have been revealed by comparing the structure type of rhodizite–londonite with that of pharmacosiderite, $K\{Fe_4(OH)_4[AsO_4]_3\}\bullet nH_2O$. The unit-cell parameter *a* of rhodizite and londonite, in the range 7.315–7.321 Å (Taxer & Buerger 1967, Pring *et al.* 1986, Simmons *et al.* 2001, Table 3), is close to the unit-cell parameter of the synthetic aluminophosphate $\{[Rb_{1.94}(H_2O,OH)_{3.84}](H_2O)_{0.1}\}\{Al_4(OH)_4[PO_4]_3\}$ (a = 7.493 Å), a representative of the pharmacosiderite structure-type, that has the same space-group, $P\bar{4}3m$ (Yakubovich *et al.* 2008). Clusters consisting of four Al octahedra with a similar configuration are an important part of the structures of rhodizite, londonite (Fig. 2), and this pharmacosiderite-type compound (Fig. 5). The most significant difference occurs in the nature of their polymerization to form a three-dimensional (3D) microporous quasi-framework. In structures of the pharmacosiderite type, this connection is done through isolated tetrahedra TO_4 (T = As, P,



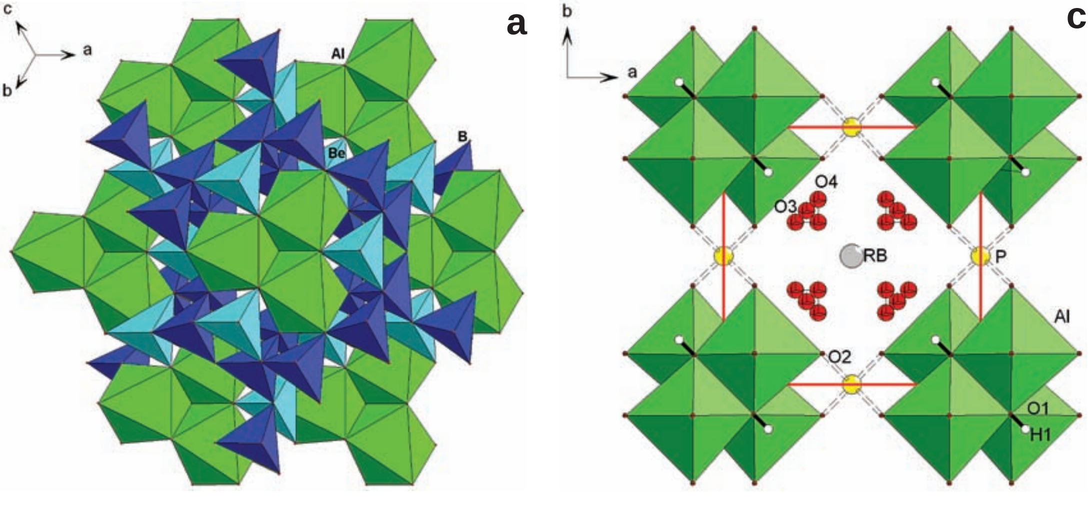


FIG. 5. Crystal structures of londonite (a) and pharmacosiderite-type Rb aluminophosphate (b, c): a, b) along [111], c) along [001].

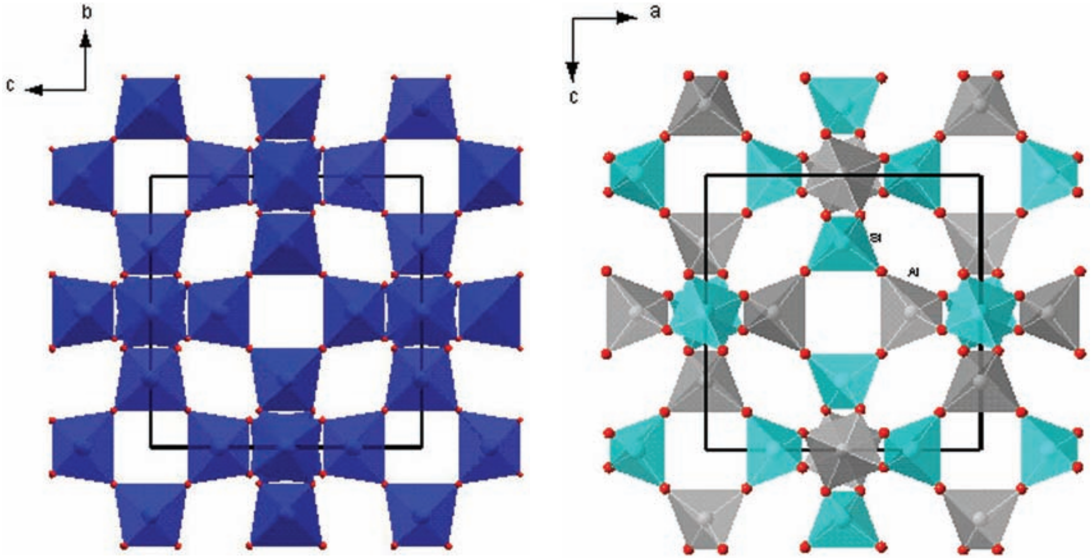


FIG. 6. Subframework of tetrahedra $[B_{12}O_{24}]_{\infty\infty\infty}$ in londonite (a) and framework of tetrahedra $[Al_6Si_6O_{24}]_{\infty\infty\infty}$ in sodalite (b).

S, *etc*.), which share all oxygen vertices with clusters built of four octahedra, whereas the corresponding AlO_6 clusters in rhodizite–londonite are incorporated into a framework composed of B- and Be-centered tetrahedra (Fig. 5). The more complex quasi-framework in the rhodizite–londonite structure-type results in a decrease in the size of the enclosed cages, which can involve less then one large cation *pfu*, whereas up to four cations and several H_2O molecules can be incorporated into the broad channels and cages of pharmacosiderite-type compounds.

Another remarkable feature of the rhodizite–londonite structure involves the subframework of BO_4 tetrahedra. This $[B_{12}O_{24}]_{\infty\infty\infty}$ subframework is topologically identical to the $[Al_6Si_6O_{24}]_{\infty\infty\infty}$ framework in sodalite, $Na_8[Al_6Si_6O_{24}]Cl_2$ (Fig. 6). Thus, the rhodizite–londonite structure may be considered formally to be built from clusters of four octahedra sharing edges (elements of the pharmacosiderite structure), and a sodalite-type framework of tetrahedra. The association of these two essential structural fragments, $[M_4O_4]$ and $[T_{12}O_{24}]$ (M: octahedron, T: tetrahedron), that have been found in the pharmacosiderite and sodalite structures, results in the formation of an original complex, $[Al_4O_4B_{12}O_{24}]^{8-}$ in londonite. The Be^{2+} and alkali cations fill the interstices and compensate for its anionic charge. This interpretation treats Be, Cs and K as guest (but necessary) components in the composition of rhodizite–londonite. Thus, vacancy defects at the Be, Cs and K positions in rhodizite–londonite are consistent with its structural "genealogy".

DOES RHODIZITE *SENSU STRICTO* OCCURS IN THE URALS?

All the specimens of "rhodizite" from the Urals studied in the present work show Cs to be dominant over K. Therefore, these specimens, including those from both cotype localities of rhodizite, correspond to londonite. A reasonable question arises: what mineral was studied and named rhodizite by Gustav Rose? We did not investigate the type material but can suppose, based on the first descriptions of rhodizite (Rose 1834, 1835, 1836, 1842), that the specimens that we studied are very similar to the rhodizite of Rose.

Indirect evidence that the original rhodizite is Cs-dominant is its density 3.416 g/cm^3 measured on a sample of 0.386 g and published by Rose (1842). Such a high value of density is not possible for a potassium-dominant member of the series.

However, we do not propose to change the accepted nomenclature and rename londonite, a Cs-dominant member of the series, to rhodizite [or to "rhodizite-(Cs)" with renaming of present-day rhodizite to "rhodizite-(K)"]. In our opinion, this would be reasonable if the type material of rhodizite from the Gustav Rose collection (if it is still preserved) clearly shows Cs > K. For the moment, we consider that the mineral that we studied from the Urals is londonite.

Does rhodizite *sensu stricto* (*i.e*., in the modern sense of this term), exist in pegmatites in the Urals? In spite of the data obtained in the present work, this possibility is not excluded: we know that some pegmatites in Madagascar contain both rhodizite and londonite.

In several Madagascar pegmatites, zoned crystals with Cs-dominant outer parts and both K- and Cs-dominant areas in a core are known. Generally, the content of Cs in minerals of the rhodizite–londonite series increases from simple to geochemically more-evolved pegmatites of Madagascar and from their earlier to later mineral assemblages (Simmons *et al*. 2001). Londonite in the pegmatites of the Urals was found only in late associations, typically in miarolitic cavities, on elbaite and K-feldspar. It seems possible that rhodizite, with K > Cs, will be found in earlier assemblages from minerals of pegmatites in the Urals.

In Madagascar, minerals of the rhodizite–londonite series occur in mica-free (or mica-poor) pegmatites (Simmons *et al*. 2001). Taking into account the significant abundance of these berylloborates, they can be considered, together with the associated Cs-rich beryl, as important concentrators of cesium in rare-element granitic pegmatites of this type. In pegmatites of the Urals, londonite was found in minute amounts together with Cs-enriched beryl ("vorobyevite") in mica-poor assemblages. Micas, because of their strong affinity for Cs, probably are detrimental to the stability of londonite.

Thus, minerals of the rhodizite–londonite series can be considered as indicators of a specific type of rare-element granitic pegmatites. In such pegmatites, Cs is especially closely connected with light elements, Li, Be and B. The minerals that contain these elements together, namely silicates of the beryl group like "vorobyevite", a Be,Li-disordered variety of beryl, $(Cs,Na)_x(Be_{3-x}Li_x)Al_2Si_6O_{18}\bullet nH_2O$, and the Be,Li-ordered species pezzottaite, $Cs(Be_2Li)Al_2Si_6O_{18}$ (Yakubovich *et al*. 2009), and berylloborates of the rhodizite–londonite series, become geochemically important (in some cases even the main) concentrators of cesium in these pegmatitic systems.

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