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Borocookeite, a new member of the chlorite group from the Malkhan gem tourmaline deposit, Central Transbaikalia, Russia

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ABSTRACT

Borocookeite, ideally $Li_{1+3x}Al_{4-x}(BSi_3)O_{10}(OH,F)_8$ (where "x" varies in the range 0.00–0.33 apfu), in which $^{[4]}Al$ is replaced by B relative to cookeite, occurs as a late-stage pocket mineral in the Sosedka and Mokhovaya pegmatite veins, Malkhan gem tourmaline deposit, Chikoy district, Chita oblast, Russia. Borocookeite proper, as well as boron-rich cookeite, is light grey with a pinkish or yellow hue and occurs as a dense, massive crypto-flaky aggregate or thin crusts and snow-like coatings on crystals of quartz, tourmaline, and feldspars from miarolitic cavities. Fragments of elbaite, danburite, and albite are included in the borocookeite mass. In some pockets, the coating is composed of borocookeite and boron-rich muscovite (or boromuscovite) which are not distinguishable visually. Chemical analysis yields (wt%): SiO_2 34.19, TiO_2 0.02, Al_2O_3 41.77, FeO 0.06, MnO 0.07, MgO 0.04, CaO 0.08, Na_2O 0.01, $K_2O < 0.01$, Li_2O 4.65, Rb_2O 0.004, Cs_2O 0.005, B_2O_3 4.06, BeO 0.05, H_2O^+ 14.17, H_2O^- 0.11, F 1.22, –O = F 0.51, total 100.00. The empirical formula calculated on the basis of 28 positive charges is: $Li_{1.61}Al_{3.80}(Al_{0.44}B_{0.60}Be_{0.01}Si_{2.95})_{\Sigma 4.00}O_{10}[F_{0.33}(OH)_{7.81}]_{\Sigma 8.14}$. The unit-cell parameters, calculated from X-ray powder diffraction data, are $a = 5.110(4)$, $b = 8.856(3)$, $c = 14.080(6)$ Å, $\beta = 96.93°(4)$ these values are smaller than those for cookeite. $D_{calc} = 2.69(1)$ g/cm^3. The mineral has a Mohs hardness of 3, light pinkish-grey streak, greasy luster, perfect (001) cleavage, and no parting or fracture. Optical properties (for white light): $\alpha = 1.574$, $\beta = 1.580$, $\gamma = 1.591$ (all ± 0.002), $2V_{calc} = 72°$, dispersion not determined. The optical sign and the angle of the optical axis were not measured because of the small size and strong curvature of the mineral flakes.

Borocookeite, as well as other boron-rich phyllosilicate minerals, crystallized from evolved residual solutions in miarolitic cavities at temperatures not less 265–240 °C. The ratio of activities of K, Li, B, F, and H_2O in the mineral-forming fluids of isolated evolving pockets determined whether borocookeite or boromuscovite formed separately or together.

INTRODUCTION

Boron-rich layer silicates are very scarce in nature. Early in the past century A. Lacroix described the only known occurrence of manandonite (commonly erroneously referred to as belonging to the chlorite group) in pegmatites in Madagascar (Lacroix 1912, 1922). Boron-containing cookeites occur in pegmatites at the Muiane deposit in Mozambique (Sahama et al. 1968) at and Radkovice in the Czech Republic (Černý et al. 1971). Boromuscovite was discovered in the Little Three pegmatite, California (Foord et al. 1989, 1991) and at Řečice in the Czech Republic (Liang et al. 1995). During an investigation of the miarolitic pegmatites of Transbaikalia and Pamirs, the authors collected numerous samples of boron-bearing mica and chlorite (Zagorsky et al. 1998). The boron-rich chlorites from pegmatites of the Malkhan deposit were later found to contain the new mineral species borocookeite. The name and the status of this mineral (00-013) were approved by the IMA Commission on New Minerals and Mineral Names (CNMMN). The type material (no. 2522/1) was subsequently deposited at the Fersman Mineralogical Museum of the Russian Academy of Science, Moscow.

FORMS AND CONDITIONS OF BOROCOOKEITE OCCURRENCE

The Malkhan pegmatite field represents the largest source of gem- and specimen-quality tourmaline in Russia. The deposit is located in the Krasny Chikoy area of the Chita region in Russia. The geology, mineralogy, and geochemistry of the pegmatite field are described in detail by Zagorsky and Peretyazhko (1992) and Zagorsky et al. (1999). The boron-rich micas and chlorites occur in many gem tourmaline-bearing pegmatite bodies in the district. However, true borocookeite occurs only in the Sosedka and Mokhovaya pegmatite veins. The type sample was collected from the Sosedka pegmatite. This vein is a steeply dipping lens-like pegmatite body, about 100 m long and up to 60 m thick, in metamorphosed diorite. Its external zones, 4–17 m thick, consist of schorl-bearing quartz-oligoclase pegmatite with coarse graphic texture. The internal

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zone has a complex structure consisting predominantly of coarse graphic to pegmatitic K-feldspar alternating with blocky K-feldspar and, in places, quartz. The K-feldspar is often albitized in fractures. In some places, the quartz-albite (and associated spessartine) rocks have a granitic texture. The albite is sometimes sugar-like in texture. Blocky K-feldspar encloses the majority of the visible miarolitic cavities, which are lined with lepidolite-albite assemblages containing differently colored tourmaline. There are also sites of a loose porous aggregate composed of thick-tabular albite crystals with small crystals of dark brown elbaite and rare danburite in numerous small vugs (so-called "steam leaching zones").

Borocookeite was found in pockets where it is associated with elbaite, lepidolite, danburite, boron-rich muscovite, laumontite, quartz, and albite. The mineral forms massive, nearly monomineralic aggregates, or thin (0.5–2 mm) crusts and snow-like coatings on the other minerals. Figures 1 and 2 show samples of borocookeite and B-rich cookeite (0.60 and 0.48 apfu tetrahedral B^{3+}, respectively) recovered from loose pocket-filling material. The first sample is a dense, somewhat greasy, crypto- to fine-grained chlorite aggregate containing numerous crystals of pink elbaite, multicolored tourmaline up to 5 cm long, and segregations of pale violet flaky lepidolite, 1 cm in diameter (Fig. 1). The tourmaline crystals, as a rule, have smooth surfaces with vertical striations on the prism edges. The smaller crystals have good terminations. In addition, most of the chlorite contains small (up to 1.5 mm) segregations of semi-transparent, colorless, corroded albite and short columnar (up to 1 mm long) crystals of danburite. The size of the borocookeite flakes ranges from <0.01 mm to 0.15 mm. The flakes are bent, elongated, or, in places, wedge-like in shape with rough (unfaceted) edges.

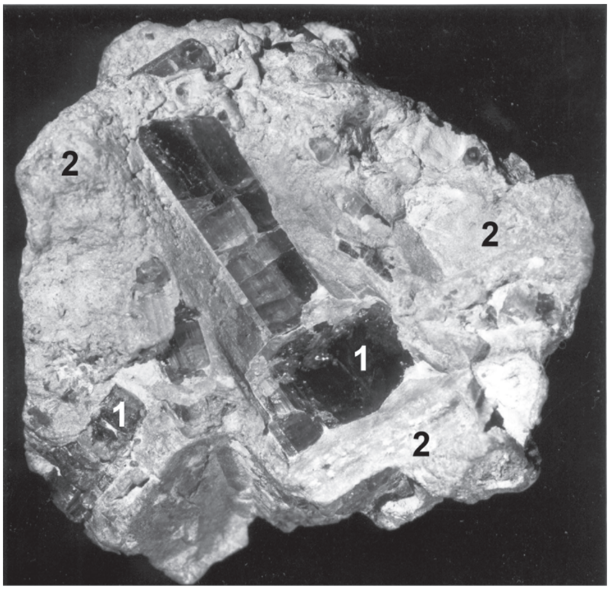

FIGURE 1. Multicolored tourmaline crystals (1) in fine-flaky aggregate of borocookeite (2). Sample MLX-2705, Sosedka mine. The sample size is 5 × 5 cm.

The second sample is from a 2 mm thick crust on a 2 cm long crystal of elbaite. The crust has a zonal structure (Fig. 2). The external zone of the crust represents a dense fine-flaky aggregate of boron-rich cookeite with a minor amount of quartz. The internal zone is porous and consists of a weakly consolidated chlorite aggregate containing an admixture of well-formed crystals of transparent colorless quartz, white laumontite, and fragile, plate-like separations of an unidentified dark brown amorphous substance. X-ray diffraction patterns of the amorphous material, annealed at 800 °C in air, show no recrystallization. Microprobe analysis indicates that this substance contains the following components (average of three analyses in wt%): SiO_2 45.74, TiO_2 0.25, Al_2O_3 34.25, FeO 5.33, MgO 0.85, MnO 0.02, CaO 0.28, K_2O 1.04, Na_2O 0.14, Cr_2O_3 0.04, NiO 0.04, total 87.98.

PHYSICAL PROPERTIES

Borocookeite is light-grey with a pinkish or yellowish hue. The mineral has a greasy luster, a light pinkish-grey streak, and Mohs hardness of 3. It is not transparent or elastic, but has perfect (001) cleavage. Parting and fracture were not observed. The density measured by suspension in a water-Klerichi liquid mixture is 2.62(1) g/cm^3, D_{calc} = 2.69(1) g/cm^3. The 0.07–0.08 g/cm^3 difference between the calculated and measured values probably results from air trapped in the fine-grained masses of borocookeite. Using a Ur-2.0 device the following bands are distinguished in infrared absorption spectra of the mineral for the range 200–4000 cm^{-1}: 485, 535, 665, 770, 795, 950, 1100, 1550, 3580, and 3700 cm^{-1}.

OPTICAL PROPERTIES

The optical properties of borocookeite were determined for the white variety. The mineral is colorless, without pleochroism. Dispersion was not established. The principal indices of refraction are as follows: $\alpha = 1.574(2)$, $\beta = 1.580$ (1.576–1.582), $\gamma = 1.591(2)$. The latter parameter coincides with the elongation of the mineral flakes. The optical sign and the angle of the optical axis were not measured because of the very small size and curvature of the mineral flakes. The $2V$, calculated by analogy with optically positive cookeite, is 57–86° (72° average).

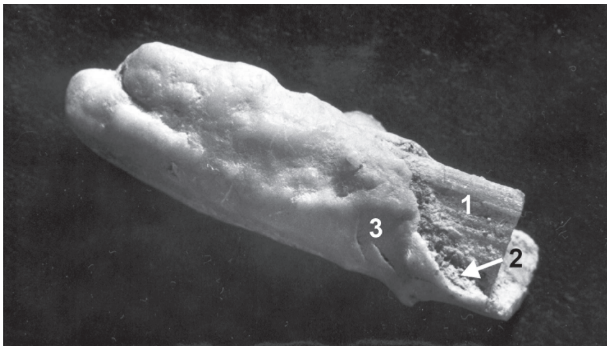

FIGURE 2. Zoned coating of boron-rich chlorite on an elbaite crystal. Sample MP-175-3, Mokhovaya mine. The sample length is 2 cm. 1 = Elbaite; 2 and 3 = inner porous (2) and outer dense (3) coating zones.

CHEMISTRY

Borocookeite was analyzed by a variety of methods, and in some instances, in duplicate. The analytical results by wet chemistry (B_2O_3, BeO, H_2O, F), flame photometry (Li_2O, Rb_2O, Cs_2O) and electron microprobe (SiO_2, TiO_2, Al_2O_3, FeO, MnO, MgO, CaO, K_2O, Na_2O) are shown in Table 1. As determined from the X-ray data, the material studied by wet chemistry and flame photometry contains insignificant (about 2 wt%) quartz admixture. The presence of quartz explains the 1.91 wt% difference in SiO_2 content between wet chemical and electron microprobe analyses. Therefore, the data on the composition of borocookeite were recalculated to 100% after deduction of admixed quartz.

The composition of borocookeite is close to the theoretical composition of boron lithium chlorite $LiAl_4(BSi_3)O_{10}(OH)_{8,}$ but differs in increased lithium and decreased boron contents (Table 1). Borocookeite contains up to 1.22 wt% F and 4.06 wt% B_2O_3. The associated lepidolite contains only 0.13 wt% B_2O_3, which is 3 times lower than in lepidolite from the pegmatite at Řečice, Czech Republic, which contains tourmaline, hambergite, and boromuscovite in pockets (Novak et al. 1999). The boron-rich cookeites contain elevated BeO (0.05–1.06 wt%), which exceeds by 50 to 1000 times the content of this element in boromuscovite (Foord et al. 1991). However, the concentrations of Rb and Cs in boron-rich chlorite is 1–2 times lower than in boron-bearing mica, in which Rb predominates over Cs, whereas the chlorite samples show opposite ratios (Zagorsky et al. 1998). The sum of the oxides of K, Na, Ca, Mg, Fe, and Mn in borocookeite and other boron-rich chlorites does not exceed 0.25 wt%. Ba, Pb, Cu, Zn (20–30 ppm), Ge, Bi, Nb (3–6 ppm) and Ag (0.1ppm) were measured in borocookeite by optical spectral analysis.

X-RAY AND ELECTRON DIFFRACTION AND UNIT-CELL DATA

The borocookeite material was not suitable for single-crystal study because of its small size and the curvature of the mineral flakes. The powder diffraction data for borocookeite (Table 2) were obtained with a DRON-3 diffractometer using Cu$K\alpha$ radiation. The patterns correspond closely to the 14 Å chlorite structure. According to the distribution of the 20*l* and $\overline{2}0l$ re-

TABLE 1. Chemical composition (wt%) and unit-cell data for borocookeite, boron-bearing cookeite, manandonite, and lepidolite

	1	2	3	4	5	6	7
SiO_2	34.19	35.09	34.72	34.15	35.62	23.02	54.69
TiO_2	0.02	0.04	0.02	n.d.			0.01
Al_2O_3	41.77	39.98	43.56	46.35	40.31	47.85	20.38
Fe_2O_3			0.20	0.09		0.36	
FeO	0.06	0.04					0.10
MnO	0.07	0.03	0.10			0.02	0.21
MgO	0.04	0.02	0.83	tr.		0.03	0.02
CaO	0.08	0.05	0.58	0.16		0.07	0.05
Na_2O	0.01	n.d.	0.07	0.10		0.13	0.19
K_2O	n.d	0.06		tr.			10.87
Li_2O	4.65	5.64	2.28	3.18	2.95	5.38	6.60
Rb_2O	0.004	0.0015					0.62
Cs_2O	0.005	0.0035					0.67
B_2O_3	4.06	3.19	1.66	0.38	6.88	7.71	0.13
BeO	0.05	0.05		1.06			
H_2O^+	14.17	15,28	14.21	14.06	14.24	15.40*	0.80*
H_2O^-	0.11	0.31	1.70	0.42			
F	1.22	0.83		0.35			7.80
$-O{=}F_2$	0.51	0.35		0.15			3.28
Total	100.00	100.27	99.93	100.15	100.00	99.97	99.86
$^{[4]}B^{3+}$	0.60	0.48	0.26	0.06	1.00	1.15	
a_0, Å	5.110(4)	5.120(4)	5.137(5)	5.16(2)		5.057(4)	
$b_?$, Å	8.859(3)	8.856(3)	8.890(6)	8.92(2)		8.765(7)	
$c_?$, Å	14.069(6)	14.080(6)	14.145(13)	14.21(6)		13.767(9)	
β	96.93(4)°	97.05(4)°	96.78(7)°	97°15¢(10¢)			
V, Å^3	632.2	633.6		648.8		610.3	

Notes: Empirical structural formulas for chlorites calculated on the basis of 28 positive charges, and for lepidolite on the basis of 22 positive charges:

1 = $Li_{1.61}Ca_{0.01}Al_{3.80}$ $(Al_{0.44}B_{0.60}Be_{0.01}Si_{2.95})_{\Sigma 4.00}O_{10}(F_{0.33}OH_{7.67})_{\Sigma 8.00}$; $(OH)_{exp} = 8.14$; borocookeite, sample MLX-2705, Sosedka mine, Malkhan deposit.

2 = $Li_{1.98}K_{0.01}Al_{3.65}(Al_{0.45}B_{0.48}Be_{0.01}Si_{3.06})_{\Sigma 4.00}O_{10}(F_{0.23}OH_{7.77})_{\Sigma 8.00}$; $(OH)_{exp} = 8.87$; boron-rich cookeite, sample MP-175-3, Mokhovaya mine, Malkhan deposit (Zagorsky et al. 1998).

3 = $Li_{0.82}Na_{0.01}Ca_{0.06}Mn_{0.01}Mg_{0.11}Fe^{3+}_{0.01}Al_{3.90}$ $(Al_{0.66}B_{0.26}Si_{3.08})_{\Sigma 4.00}O_{10}$ $(OH)_8$; $(OH)_{exp} = 8.42$; boron-rich cookeites: Radkovice, Czech Republic. Recalculated analysis after deduction of lepidolite admixture. Mineral contains (wt%) 0.051 GeO_2, 0.011 Ga_2O_3, 0.016 Cr_2O_3, and 0.036 NiO (Černý et al. 1971)

4 = $Li_{1.12}Na_{0.02}Ca_{0.02}Al_{4.02}$ $(Al_{0.74}B_{0.06}Be_{0.22}Si_{2.98})_{\Sigma 4.00}O_{10}(F_{0.10}OH_{7.90})_{\Sigma 8.00}$; $(OH)_{exp} = 8.18$; boron-bearing cookeites Muiane, Mozambique (Sahama et al. 1968).

5 = $LiAl_4\,(BSi_3)O_{10}(OH)_8$; theoretical composition of boron-lithium chlorite (Fleischer 1987).

6 = $Li_{1.87}Na_{0.02}Ca_{0.01}Fe^{3+}_{0.02}Al_{4.01}$ $(Al_{0.86}B_{1.15}Si_{1.99})_{\Sigma 4.00}O_{10}\,(OH)_8$; $(OH)_{exp} = 8{,}87$; manandonite, Sahatany valley, Madagascar (Ranorosoa et al. 1989).

7 = $(K_{0.92}Na_{0.02}Rb_{0.03}Cs_{0.02})_{\Sigma 0.99}$ $(Li_{1.75}Fe^{2+}_{0.01}Mn_{0.01}Al_{1.21})_{\Sigma 2.98}$ $(Al_{0.37}B_{0.02}Si_{3.61})_{\Sigma 4.00}O_{10}(F_{1.63}OH_{0.37})_{\Sigma 2.00}$; $(OH)_{exp} = 0.35$; lepidolite in association with borocookeite, sample MLX-2705, Sosedka mine, Malkhan deposit.

$^{[4]}B^{3+}$ = boron unit-cell content at the tetrahedral site. n.d. = not detected. tr. = traces. $(OH)_{exp}$ = experimental concentration of OH.

* H_2O_{total}.

TABLE 2. X-ray powder diffraction data for borocookeite, boron-bearing cookeite, and manandonite

borocookeite MLX-2705				boron-bearing cookeite (Sahama et al. 1968)			manandonite (Ranorosoa et al. 1989)		
hkl	d_{obs}	d_{calc}	*I*	*hkl*	*d*	*I*	*hkl*	*d*	*I*
001	14.1	13.96	10	001	14.03	17	–	–	–
002	7.05	6.99	50	002	7.03	29	002	6.92	100
003	4.71	4.66	70	003	4.70	100	–	–	–
–	–		–	020,110	4.44	6	110	4.362	25
–	–		–	–	–	–	111	4.158	10
004	3.512	3.493	100	004	3.52	87	004	3.447	80
005	2.807	2.794	20	005	2.816	47	–	–	–
200	2.545	2.542	5	200	2.555	7	–	–	–
$\bar{2}02$	2.491	2.487	8	$\bar{2}02$	2.503	10	131,201	2.489	15
006	2.332	2.328	14	006	2.347	11	132,202	2.376	35
202	2.304	2.300	16	202	2.315	9	–	–	–
–	–		–	–	–	–	133,203	2.214	5
007	2.001	1.996	7	007	2.013	18	134,204	2.039	10
–	–		–	$\bar{2}05$	1.990	2	–	–	–
204	1.946	1.946	17	204	1.959	4	–	–	–
–	–		–	–	–	–	135,205	1.863	15
008	1.746	1.746	5	008	1.761	7	008	1.720	<5
206	1.620	1.622	10	206	1.634	3	136,206	1.698	5
–	–		–	009	1.566	2	–	–	–
$\bar{2}08$	1.527	1.528	5	–	–	–	–	–	–
–	–		–	–	–	–	137,207	1.552	3
060	1.476	1.476	7	060	1.486	3	330,060	1.461	10
00.10	1.396	1.397	5	00.10	1.410	6	138,208	1.424	10

flections, the strongest reflections 202, 204, and 206 being especially indicative, the structure is composed of units Ia (Bailey 1975) or 0330(3) (Zvyagin et al. 1979), which are characteristic of cookeite (Vrublevskaya et al. 1975). The 20*l* reflections coincide with $\bar{1}.3.l + 1$ and the $\bar{2}0l$ reflections coincide with 1.3.*l*-1. These reflections were resolved in electron diffraction patterns of cookeite with perfect structure studied previously by Vrublevskaya et al. (1975). The unit-cell parameters of borocookeite, calculated from powder diffraction data, are as follows: a = 5.110(4), b = 8.856(3), c = 14.080(6) Å, β = 96.93(4)°.

The borocookeite sample was studied by electron diffraction as well. The device used was an electronograph EMR-102, operating at 100 kV, and the tilt angle was 60 degrees. The texture patterns, where the three-dimensional set of hk*l* reflections is distributed two-dimensionally over a sequence of *hk* ellipses, displayed a semi-random chlorite structure (reflections with $k = 3n$ being sharp and distinct, the others forming continuous ellipses of scattering). The intensities of reflections with $k = 3n$ (especially 20*l* and $\bar{2}0l$; 13*l* and $\bar{1}3l$ of the second ellipse) are the same as for the perfect cookeite described in Vrublevskaya et al. (1975). Weak reflections indicated layer stacking type Ia, as reported by Bailey (1975), or t0s6s6t06, according to Zvyagin et al. (1979). The reflection positions define a pseudo-monoclinic unit cell with a = 5.114(2), b = 8.858(3), c = 14.14(2) Å, β = 96.92(5)°, which is in good agreement with the X-ray powder data. The texture electron diffraction and X-ray powder data are therefore consistent with the idea that the borocookeite belongs to the pseudo $C2/m$ space group as a degeneration of $C1$. In this case, B^{3+} and Al^{3+} may be allocated independently of Si^{4+} in the tetrahedral site, where B^{3+} dominates over Al^{3+}.

DISCUSSION

The boron-rich aluminosilicates are considered to be rare minerals. Occurrences of layered boro-aluminosilicates, i.e., manandonite and boromuscovite, are very rare (Lacroix 1912, 1922; Ranorosoa et al. 1989; Foord et al. 1991; Liang et al. 1995; Zagorsky et al. 1998; Novak et al. 1999). Therefore, the material described here is of interest with respect to the role of isomorphism of boron in aluminosilicates and phyllosilicates in particular.

Previously, it was believed that boron and aluminum, while differing in their effective radius and ionization potential, do not make up a true isomorphous couple. Their joint presence in aluminosilicates is due to the so-called endocrypty phenomena alone (Fersman 1933; Gorbov 1976). The term "endocrypty" describes the situation where one of the elements cannot form its own mineral but is dissipated in the crystal structure of a mineral containing another element with similar crystallochemical properties (i.e., one of the endmember components is hypothetical). Recently, the experimental and theoretical aspects of the difference between proper isomorphism and endocrypty phenomena have been discussed in detail (Tauson 1999). An important argument in favor of endocrypty for the couple boron-aluminum is the absence of natural isomorphous mixtures intermediate in composition between borosilicates and their aluminosilicate analogues, e.g., mineral pairs like anorthite-danburite ($CaAl_2Si_2O_8$-$CaB_2Si_2O_8$), albite-reedmergnerite ($NaAlSi_3O_8$-$NaBSi_3O_8$), and K-feldspar and its synthetic boron analogue ($KAlSi_3O_8$-$KBSi_3O_8$). However, we recently determined intermediate compositions in the mineral pair muscovite-boromuscovite [$(KAl_2(AlSi_3)O_{10}(OH,F)_2$-$(KAl_2(BSi_3)O_{10}(OH,F)_2$] (Zagorsky et al. 1998).

In lithium chlorites, as in the majority of natural and synthetic boron-rich silicates, e.g., reedmergnerite (Milton et al. 1960), boromuscovite (Foord et al. 1991), synthetic phlogopite and biotite (Noda et al. 1944; Eugster and Wright 1960; Stubican and Roy 1962), B^{3+} enters the tetrahedral site in place of Al^{3+}, rather than Si^{4+}, in spite of a closer proximity of the ionic radii of boron to silicon than to aluminum. In chlorites of the Malkhan field, the amount of B^{3+} replacing tetrahedral Al^{3+}

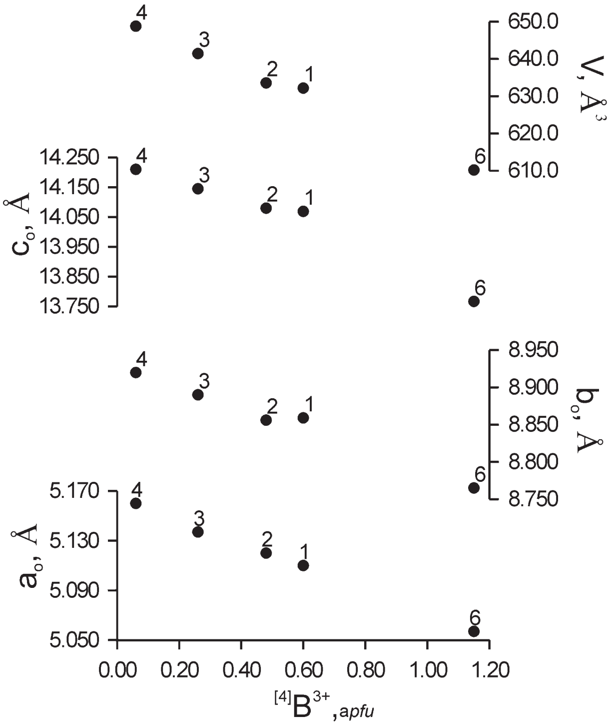

FIGURE 3. Unit-cell dimensions vs. boron contents in tetrahedra of borocookeite, boron-bearing cookeites, and manandonite. The numbers correspond to the sample numbers in Table 1.

reaches 0.48–0.60 apfu which is at least twice that reported for lithium chlorites from the Muiane and Radkovice pegmatites (Sahama et al. 1968; Černý et al. 1971) where the amount of B^{3+} replacing tetrahedral Al^{3+} is 0.06–0.26 apfu. The available set of boron-bearing chlorite samples indicates the presence of a natural isomorphous series in cookeite -borocookeite, at least within the range of contents 0.00–0.60 apfu $^{[4]}B^{3+}$. The entry of boron into the tetrahedral position of lithium chlorites results in a regular change of parameters *a*, *b*, and *c* (Fig. 3). Thus, the entry of boron into layered aluminosilicates is not limited to endocrypty phenomena only.

A different ratio of tetrahedral cations is observed in manandonite, which had an uncertain chemical formula and mineralogical status for a long time (Bailey 1975). Based on the chemical data of Lacroix (1912, 1922), Strunz (1957) proposed the formula $LiAl_2[(OH)_2/AlBSi_2O_{10}]\cdot Al_2(OH)_6$ which does not balance electrostatically. Frank-Kamenetsky (1960) and Caillére et al. (1982) classified manandonite as dioctahedral and di-trioctahedral chlorite, respectively. Hawthorne and Černý (1982), as well as London and Burt (1982), considered manandonite to be boron-rich cookeite. This appears to be the reason why Fleischer (1987) presented the formula $LiAl_4(BSi_3)O_{10}(OH)_8$ for manandonite which is not in agreement with the chemical composition of the mineral. Finally, Ranorosoa et al. (1989) and Zheng and Bailey (1995) restudied manandonite from the same locality originally described by Lacroix (1912) and showed clearly that it is isostructural with an amesite-like mineral and belongs to the 7 Å serpentine-kaolinite group, but not the 14 Å cookeite group. Additionally, manandonite was shown to differ from cookeite in its thermal behavior and infrared spectrum. From chemical composition and crystallographic properties, Ranorosoa et al. (1989) proposed the ideal formula $Li_2Al_4(AlBSi_2)O_{10}(OH)_8$ for manandonite, i.e., with B^{3+} predominantly entering the tetrahedral Si^{4+} site, instead of replacing Al^{3+}, whereas in cookeite-borocookeite B^{3+} substitutes for tetrahedral Al^{3+}. The entry of boron in place of silicon in manandonite causes a change of the elementary cell parameters in the same proportions as in boron-bearing cookeites and borocookeite (Fig. 3). It appears that a necessary condition for manandonite formation may be significant undersaturation of silicon relative to alumina in boron-rich solutions.

In principle, the idealized formula of borocookeite would have been similar to that erroneously given to manandonite previously, $LiAl_4(BSi_3)O_{10}(OH)_8$ (Fleisher 1987). However, in practically all known boron-rich chlorites, the amount of octahedral Li exceeds 1 apfu, because of the substitution $3Li^+ \rightarrow Al^{3+}$, quite independent of the tetrahedral B^{3+} content. In particular, the above described borocookeite and boron-rich cookeite of the Malkhan deposit contain 1.61 and 1.98 apfu Li^+, respectively (Table 1). The $3Li^+ \rightarrow Al^{3+}$ isomorphous scheme for lithium chlorites was substantiated previously (Černý 1970). In this connection, the formula $Li_{1+3x}Al_{4-x}(BSi_3)O_{10}(OH)_8$ (where $x = 0.00–0.33$ is the amount of octahedral Al^{3+}, which is replaced by Li^+ according to the substitution $3Li^+ \rightarrow Al^{3+}$) is undoubtedly more correct for borocookeite. Thus the ideal formula for borocookeite is $Li_{1+3x}Al_{4-x}(BSi_3)O_{10}(OH)_8$. Borocookeite is distinguished from cookeite by high boron (> 0.5 apfu at the tetrahedral site) and smaller unit cell parameters. It differs from manandonite in both composition and structure.

The place of boron-rich chlorites and micas in the genetic scheme of pegmatite formation is such that they crystallize from residual boron-rich solutions in miarolitic cavities during the final stage of the pegmatite-forming process. Thermobarogeochemical data show that the concentrations of boric acid in mineral-forming solutions at the post-magmatic stage of boromuscovite- and borocookeite-bearing pegmatite formation reach 27 wt% (Peretyazhko et al. 1999, 2000; Smirnov et al. 2000). The stability fields of boron-bearing micas and chlorites undoubtedly overlap. This is proved by the similar and quite particular features of their aggregates, association with the same minerals, and above all, their coupled presence in chlorite-muscovite aggregates containing 5.71 wt% B_2O_3 (Zagorsky et al. 1998). However, in most cases they occur separately. Which of the two boron-bearing minerals, chlorite or muscovite, is formed in each case, most probably depends on the ratio of activities of K, Li, B, F, and water in the residual solutions of autonomously evolving miarolitic cavities. Even in neighboring miarolitic cavities in the same pegmatite body, mineral compositions in the drusy complex and loose pocket filling material drastically differ, and ratios of the above-mentioned components do not remain constant (Zagorsky and Peretyazhko 1992; Zagorsky et al. 1999). According to geological and experimental data, as well as thermodynamic calculations, cookeite is stable within the range of temperatures from 250 to 480 °C and pressures from less than 0.5 to over 5

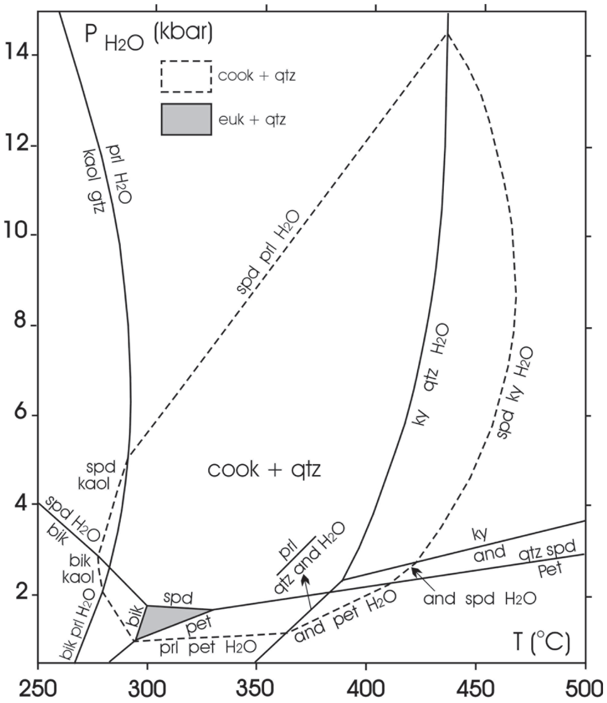

FIGURE 4. Phase relations under quartz- and water-saturated conditions in the Li_2O-Al_2O_3-SiO_2-H_2O system (Vidal and Goffie 1991); and = andaluzite, bik = bikitaite, cook = cookeite, euc = eucriptite, kaol = kaolinite, ky = kyanite, pet = petalite, prl = pyrophyllite, qtz = quartz, spd = spodumene.

kbar (Rijks and van der Veen 1972; Vidal and Goffe 1991). From the *P-T* phase diagram for the SiO_2- and H_2O-saturated Li_2O-Al_2O_3-SiO_2-H_2O system (Fig. 4), it is evident that increasing pressure from 0.5 to 3 kbar expands the temperature range of cookeite stability from 295–365 °C to 275–435 °C (Vidal and Goffe 1991). In the same system with boric acid, the temperature range will be somewhat different, but it can be inferred that the effect of pressure on the temperature of mineral stability will remain the same. As a result of the "autoclave effect", the pressure in different miarolitic cavities of the same body, and in pockets from different bodies in particular, can be noticeably different. In some instances, pressure values can exceed external pressure, which causes pocket rupture (Foord et al. 1989; Zagorsky and Peretyazhko 1992; Zagorsky et al. 1999). From thermodynamic modeling, the boric acid concentrations in the mineral-forming solutions may affect fluid pressure in miarolitic cavities significantly (Peretyazhko and Zagorsky 2002). The effect of fluid pressure may explain why, in some cases, the boron-bearing cookeites begin crystallizing from solutions jointly with elbaite, whereas in others they develop only as lower temperature, late, snow-like coatings on tourmaline, smoky quartz, and other minerals of the drusy complex within pockets.

The temperatures of homogenization of primary fluid inclusions in pink tourmaline, with its crystals either enclosed in the massive aggregate of borocookeite or covered with a coating of borocookeite, range from 305 to 265 °C (Zagorsky et al. 1998). In the Sosedka vein, the homogenization temperature of primary fluid inclusions in smoky quartz with a coating of boron-rich muscovite and boron-rich cookeite is 390 °C, and in a later generation of transparent colorless quartz with hair-like syngenetic separations of fine-flaky mica it is 265–240 °C. The boron-rich micas and chlorites in pockets precede in time only the formation of zeolites, e.g., stilbite and laumontite. The occurrence and textural relationships with other minerals provide evidence for their formation by crystallization from solutions, rather than the result of metasomatic replacement of tourmaline, as was assumed for manandonite (Lacroix 1912). First, the boron-rich micas and chlorites form crusts and coatings not only on tourmaline, from which they could derive boron, but also on feldspar, quartz, and lepidolite, and secondly, crystals of tourmaline covered with such crusts retain their mirror-smooth faces, and normally do not show any signs of replacement.

It is suggested that in tourmaline-rich miarolitic pegmatites the boron-rich micas and chlorites are more widespread than commonly believed. However, boromuscovite proper and borocookeite in particular, represent rare minerals.

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