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## GENETIC MINERALOGY OF THE BURBANKITE GROUP

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The burbankite group consists of six mineral species with general formula  $A_3B_3(\text{CO}_3)_5$  where  $A = \text{Na} > \text{Ca}$ ,  $\text{REE}^{3+}$ ,  $\square$ ;  $B = \text{Sr}$ ,  $\text{Ca}$ ,  $\text{Ba}$ ,  $\text{REE}^{3+}$ ,  $\text{Na}$ : burbankite, khanneshite, calcioburbankite, remondite-(Ce), remondite-(La), and petersenite-(Ce). The burbankite structural type (space group  $P6_3mc$ ) is exclusively stable for chemical composition variations: khanneshite, calcioburbankite, remondite hexagonal analogue, and burbankite are isostructural and form the system of continuous solid solutions. All chemical compositions (94 analyses) of the burbankite group minerals can be described within the isomorphous system with end members:  $(\text{Na}_2\text{Ca})\text{M}^{2+}_3(\text{CO}_3)_5$  and  $\text{Na}_3(\text{REE}_2\text{Na})(\text{CO}_3)_5$ , where  $\text{M}^{2+} = \text{Sr}$ ,  $\text{Ba}$ ,  $\text{Ca}$ . There are three genetic types of the burbankite mineralization: 1) in carbonatites where the minerals with the "most averaged" chemical composition and increased contents of Ba and Ca are formed; 2) in alkaline hydrothermalites where the range of chemical compositions of the burbankite-like phases is extremely wide; 3) in pectolite metasomatites where burbankite is strongly REE-depleted. In carbonatites the burbankite group minerals are early phases formed under high-temperature conditions, whereas in nepheline syenite massifs they are formed during hydrothermal stages under low temperatures, which is due to different regime of  $\text{CO}_2$ . Under alkalinity decrease the burbankite group minerals are replaced by a whole series of secondary minerals, among which the alkali-free carbonates of REE, Sr, Ba, and Ca prevail.

5 tables, 3 figures, 50 references.

The burbankite group consists of six mineral species with general formula  $A_3B_3(\text{CO}_3)_5$  where  $A = \text{Na} > \text{Ca}$ ,  $\text{REE}^{3+}$ ,  $\square$ ;  $B = \text{Sr}$ ,  $\text{Ca}$ ,  $\text{Ba}$ ,  $\text{REE}^{3+}$ ,  $\text{Na}$ : burbankite  $(\text{Na}, \text{Ca}, \square)_3(\text{Sr}, \text{REE}, \text{Ba}, \text{Ca})_3(\text{CO}_3)_5$ , khanneshite  $(\text{Na}, \text{Ca})_3(\text{Ba}, \text{Sr}, \text{REE}, \text{Ca})_3(\text{CO}_3)_5$ , calcioburbankite  $(\text{Na}, \text{Ca}, \text{REE})_3(\text{Ca}, \text{REE}, \text{Sr})_3(\text{CO}_3)_5$ , remondite-(Ce)  $\text{Na}_3(\text{Ce}, \text{Ca}, \text{Na}, \text{Sr})_3(\text{CO}_3)_5$ , remondite-(La)  $\text{Na}_3(\text{La}, \text{Ce}, \text{Ca})_3(\text{CO}_3)_5$ , and petersenite-(Ce)  $(\text{Na}, \text{Ca})_4(\text{Ce}, \text{La}, \text{Sr})_2(\text{CO}_3)_5$ . The first three minerals are hexagonal (space group  $P6_3mc$ ), and others are pseudohexagonal monoclinic (sp. gr.  $P2_1$ ,  $\gamma = 119.8 - 120.5^\circ$ ).

In the crystal structures of hexagonal members of this group there are two independent cationic sites —  $A$  (Na и Ca) and  $B$  (REE, Sr, Ba и Ca), and three types of carbonate groups with different orientations. Ten-vertex  $B$ -polyhedra connected to  $\text{CO}_3$ -groups by vertices form the layers of six-member rings parallel (001). Eight-vertex  $A$ -polyhedra form infinite zigzag columns where neighboring polyhedra are contacted by planes (Voronkov, Shumyatskaya, 1968; Effenberger *et al.*, 1985; Belovitskaya *et al.*, 2000, 2001, 2002). The crystal structure of remondite is quite similar to that of burbankite (Ginderow, 1989). In the crystal structure of petersenite atoms of Na occupy with order two  $B$ -polyhedra out of six, which results to doubling of  $a$ -parameter (Grice *et al.*, 1994).

Burbankite group carbonates form hexagonal prismatic crystals but occur more often as irregular grains and their aggregates. These minerals are transparent, without cleavage, have vitreous up to greasy luster and light

colours: yellow, green, pale-brown, pink. Frequently colorless and white, less often red, orange and gray varieties occur.

Burbankite is a widespread mineral, whereas other members of the group are rare. In one of types of «rare-earth carbonatites» (Khibiny, Vuoriyarvi, Gornoe Ozero *etc.*) burbankite and its alteration products will form huge accumulations, being the main potentially industrial component and easily enriched complex ore of REE, Sr, and Ba.

In spite of a semi-centennial history of research, significant number of the publications, and extensive geography of finds, generalizing papers on the burbankite group minerals are absent. We have attempted to systematize earlier published materials and having supplemented them with comparable volume of new data to show the connection of chemical composition and structural features of these minerals with conditions of their formation. We have studied 32 samples from eight alkaline complexes — Khibiny, Lovozero (Kola Peninsula), Vuoriyarvi (Northern Kareliya), Vishnevye Gory (Southern Urals), Gornoe Ozero, Murun (East Siberia), Mont Saint-Hilaire (Quebec, Canada), and Khanneshin (Afghanistan).

The cation composition of the minerals (Tables 1–3) was studied by electronmicroprobe method. All analyses including reference data were calculated on charge sum equal 10.00, i.e. equivalent  $(\text{CO}_3)_5$ .  $B$ -site was filled up to 3.00 atoms per formula unit (apfu) by atoms of Sr, Ba, REE, Th, K, in case of their deficiency

by atoms of Ca, and then atoms of Na was added. After that the rest of Na and Ca atoms was placed in A-site. If the A-cations sum appeared less 3.00, the missing value was attributed to vacancy according to the crystallochemical data (Effenberger *et al.*, 1985; Belovitskaya *et al.*, 2000). At calculation the atomic mass of Ce is conditionally taken for old analyses where the rare-earth elements were determined as a sum. The cation composition of the burbankite group minerals widely varies (Fig. 1, 2). In A-sites, sodium always prevails (1.3–3 *apfu*), but sometimes amounts of calcium is also essential (up to 1.25 *apfu*). The cation composition is more diverse in B-sites where atoms of Sr, Ba, Ce, La, and Ca can dominate.

We make the X-ray powder studies for 11 samples (Table 4) including five species with different chemical composition, which crystal structures was refined by Rietveld method: 1) REE-depleted burbankite (an. 92), its X-ray diffraction pattern contains distinct doublets; 2) burbankite with «typical» composition (an. 64) and nonsplit peaks on X-ray spectrum; 3) khanneshite (an. 21); 4) calcioburbankite (an. 12); 5) the mineral with chemical composition of remondite-(Ce) (an. 79), but according to its X-ray powder diagram identical to representatives of the burbankite structural type.

Burbankite group minerals form complex isomorphous system with end members: REE-free phases  $(\text{Na}_2\text{Ca})\text{M}^{2+}_3(\text{CO}_3)_5$  where  $\text{M}^{2+} = \text{Sr, Ba, Ca}$  and petersenite  $\text{Na}_3(\text{REE}_2\text{Na})(\text{CO}_3)_5$ , without divalent cations. All chemical compositions of the minerals are situated in interval between these two points forming extended field — Fig 1, and 2a, b. In spite of two structural transitions: from hexagonal members to monoclinic remondite and then to petersenite, essential mixable intermissions in this system aren't determined. These structural transitions are concerned to the second type, i.e. they are realized gradually, without break of chemical bonds.

### Occurrences and formation conditions

Generalizing an available material, it was possible to distinguish three main genetic types of burbankite mineralization. Each of them is connected to alkaline rocks. The largest burbankite concentrations occur in carbonatites. This genetic type is studied better than others. In alkaline hydrothermalites the widest variations of chemical compositions and, accordingly, the greatest species variety are observed at relatively small amounts. We have distinguished the third genetic type, accumulations of REE-depleted burbankite, connected to specif-

ic pectolite metasomatites of Khibiny and Murun massifs. In each case the minerals are characterized by individual features of cation ratios (Fig. 1). Burbankite from soda-bearing sedimentary Green River Formation (USA) is in association with the majority of the same minerals as in carbonatites and alkaline hydrothermalites (Fitzpatrick, Pabst, 1977) and, probably, has low-temperature hydrothermal origin.

Occurrences of the burbankite group minerals with known chemical composition are briefly described in Table 5. They are grouped for genetic types. Localities connected to rocks enclosing carbonatites and also with products of hydrothermal activity in carbonatites are conditionally referred to carbonatite type. The finds made in late parageneses of pegmatite from nepheline syenite complex are referred to alkaline hydrothermalites.

Thus, burbankite group minerals are formed in alkali-carbonate systems connected to geological objects of different types. The temperature range these minerals crystallize in is extremely wide.

A number of massifs contain carbonatites where the burbankite group minerals are the main concentrators of strontium, barium, and rare-earth elements. Here burbankite and its analogs crystallize on early carbonatite formation stages under high temperatures (not below 500°C). That confirmed by the signs of joint growth with essential minerals of carbonatite rocks, the presence of the burbankite group minerals in primary inclusions, and the replacement of these minerals by products of later hydrothermal stages.

In alkaline hydrothermalites the burbankite group minerals are the late formations forming at essentially lower temperatures. Their crystals in cavities are frequently observed together with zeolites and hydrous soda minerals. Formation temperatures for these associations can be estimated as 100–250°C.

The difference in time of crystallization are first of all connected to different regime of carbon dioxide. The excess of  $\text{CO}_2$  is present in carbonatite formation systems, and already at early stages burbankite and its analogs appear under sufficient activity of sodium. In nepheline syenite massifs, with which the burbankite-bearing hydrothermalites are in general connected, increase of potential of  $\text{CO}_2$  and, accordingly, the development of carbonate mineralization take place mainly on a final stage of evolution

### Typochemism and structural typomorphism

The wide variations of cation composition make the burbankite group minerals very informative in genetic relation.

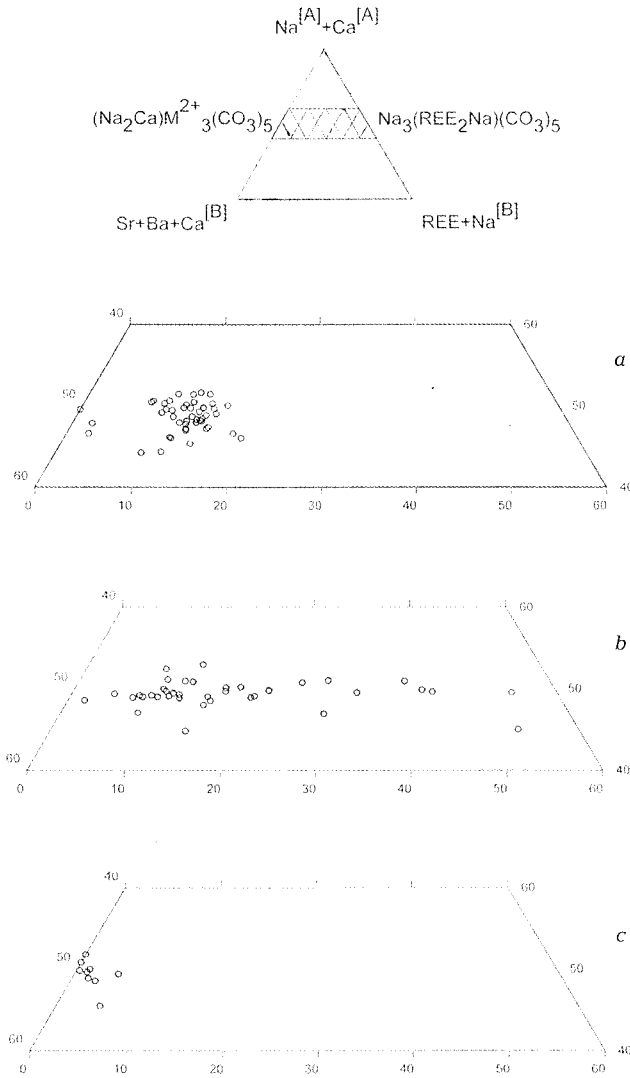


FIG. 1. Cation ratios in the burbankite group minerals: a — from carbonatites, b — from alkaline hydrothermalites, c — from pectolite metasomatites

In the system with end members  $(\text{Na}_2\text{Ca})\text{M}^{2+}_3(\text{CO}_3)_5$  and  $\text{Na}_3(\text{REE}_2\text{Na})(\text{CO}_3)_5$  (Fig. 1) samples from carbonatites occupy intermediate position making compact field. As a rule in the B-sites of these minerals atoms of Sr, rarely Ca and Ba prevail (Fig. 2a). Only in one sample from Vuoriayrvi domination of rare-earth elements is noted. The phases with «maximum averaged» chemical composition, often with comparable amounts of Sr (usually 0.7–1.5 *apfu*), Ba (on average 0.4–1.0 *apfu*), Ca (as a rule in B-site 0.3–1.0 *apfu*), and REE (usually 0.5–0.8 *apfu*), are typical for carbonatite complexes. Exactly in carbonatites the highest contents of barium for minerals of this group are fixed, and only here khanneshite is known (Khanneshin, Khibiny, Afrika-

nda, Kovdor). Usually 0.3–0.7 *apfu* of calcium are present in A-sites (Table 1). «Averaged» chemical composition of these minerals from early carbonatite associations (Fig. 1) and high content of barium, the largest cation (Fig. 2a), is explained by high-temperature conditions of crystallization. High concentration of a certain cation as well as considerable depletion of it is not typical for the samples from carbonatites. The ratios of rare-earth elements in burbankite-like phases from carbonatites are sufficiently stable and in general typical for most other minerals from alkaline rocks:  $\text{Ce} > \text{La} > \text{Nd}$ . The increase of content of strontium from early generations to late ones is characteristic for the burbankite group minerals from carbonatites: burbankite





Table 1. Chemical composition of burbankite group minerals from carbonatites (end)

Constituents	Burbankite						
	Afri-kanda	Kalkfeld	Shaxio- ngdong	Chipman Lake			
	An. 41	an. 42	an. 43	an. 44	an. 45	an. 46	an. 47
	wt %						
Na <sub>2</sub> O	7.47	10.6	13.1	6.03	7.38	7.20	6.70
K <sub>2</sub> O	-	-	-	-	-	-	-
CaO	8.24	3.6	5.5	14.52	21.09	15.01	13.53
SrO	16.82	25.6	26.7	29.49	29.12	30.44	28.63
BaO	20.17	5.5	5.2	4.88	4.06	1.85	3.37
ΣREE <sub>2</sub> O <sub>3</sub>	n.d.	n.d.	n.d.	12.53	n.d.	n.d.	n.d.
Y <sub>2</sub> O <sub>3</sub>	-	-	-	n.d.	0.47	0.71	0.45
La <sub>2</sub> O <sub>3</sub>	6.10	7.0	6.2	-"	0.76	0.54	4.34
Ce <sub>2</sub> O <sub>3</sub>	5.92	9.0	8.8	-"	1.20	0.77	5.80
Pr <sub>2</sub> O <sub>3</sub>	0.93	-	-	-"	0.18	0.15	0.60
Nd <sub>2</sub> O <sub>3</sub>	0.70	1.5	2.1	-"	0.21	0.26	1.64
Sm <sub>2</sub> O <sub>3</sub>	-	-	-	-"	0.15	0.07	0.00
(CO <sub>2</sub> )	n.d.	(29.8)	(33.3)	32.58	n.d.	n.d.	n.d.
Sum	66.35	92.6	100.9	100.03	65.06*	60.54*	65.19*
	Formula						
Na <sup>[A]</sup>	1.76	2.51	2.79	1.24	1.43	1.62	1.37
Ca <sup>[A]</sup>	0.82	0.35	0.26	1.14	1.22	1.13	1.02
Σ[A]	2.57	2.86	3.05	2.38	2.62	2.75	2.39
K <sup>[B]</sup>	-	-	-	-	-	-	-
Ca <sup>[B]</sup>	0.25	0.13	0.39	0.51	1.03	0.75	0.52
Sr <sup>[B]</sup>	1.18	1.82	1.70	1.81	1.68	2.05	1.75
Ba <sup>[B]</sup>	0.96	0.26	0.22	0.20	0.16	0.08	0.14
ΣM <sup>2+</sup> [B]	2.39	2.21	2.31	2.52	2.87	2.88	2.41
Y <sup>[B]</sup>	-	-	-	n.d.	0.03	0.04	0.02
La <sup>[B]</sup>	0.27	0.32	0.25	-"	0.03	0.02	0.17
Ce <sup>[B]</sup>	0.26	0.40	0.36	-"	0.04	0.04	0.22
Pr <sup>[B]</sup>	0.04	-	-	-"	0.01	0.01	0.02
Nd <sup>[B]</sup>	0.03	0.07	0.08	-"	0.01	0.01	0.16
Sm <sup>[B]</sup>	-	-	-	-"	0.01	-	-
ΣREE <sup>[B]</sup>	0.61	0.79	0.69	0.48	0.13	0.12	0.59
Σ[B]	3.00	3.00	3.00	3.00	3.00	3.00	3.00
(CO <sub>3</sub> )	5.00	5.00	5.00	5.00	5.00	5.00	5.00

## Note.

1, 2 — samples №№ 65111 and 65105 accordingly from collection of Fersman Mineralogical Museum RAS; 3, 4 (Borodin, Kapustin, 1962); 5–7, 10 — samples from V.V. Subbotin collection; 8, 9 (Subbotin *et al.*, 1999); 11 (Kukharensko *et al.*, 1965); 12, 13 (Subbotin *et al.*, 1999); 14 — sample № 65503 from collection of Fersman Mineralogical Museum RAS; 15 (Zdorik, 1966); 16 — sample from A.P. Khomyakov collection (Pekov *et al.*, 1998); 17, 18 — sample № 81605 from collection of Fersman Mineralogical Museum RAS (Pekov *et al.*, 1998); 19, 20 (Eremenko, Vel'ko, 1982); 21, 22 (Pekov *et al.*, 1998); 24 (Tikhonenkova, 1974); 25 (Tikhonenkova *et al.*, 1977); 26 (Mineralogy..., 1978); 27 (Dudkin *et al.*, 1981); 28 (Zaitsev *et al.*, 1990); 29, 30 (Zaitsev *et al.*, 1997); 31, 32 (Zaitsev *et al.*, 1998); 33 (Zhabin *et al.*, 1971); 34 (Pozharitskaya, Samoilov, 1972); 35, 36 (Ivanyuk *et al.*, 2002); 37–40 (Zaitsev, Chakhmouradian, 2002); 41 (Zaitsev, Chakhmouradian, 2002); 42, 43 (Buhn *et al.*, 1999); 44 (Shi Li, Tong Wang, 1993); 45–47 (Platt, Woolley, 1990); №№ 1, 2, 5–7, 10, 14, 23 — data of present research.

\* — The sum of analysis also contains (wt %): 3 — 0.35 MgO, 1.05 Al<sub>2</sub>O<sub>3</sub>, 0.48 Fe<sub>2</sub>O<sub>3</sub>, 0.19 SiO<sub>2</sub>, 0.97 H<sub>2</sub>O; 4 — 0.10 Fe<sub>2</sub>O<sub>3</sub>, 0.06 SiO<sub>2</sub>, 2.60 H<sub>2</sub>O; 11 — 0.03 Al<sub>2</sub>O<sub>3</sub>, 0.22 Fe<sub>2</sub>O<sub>3</sub>, 0.10 SiO<sub>2</sub>, 0.25 H<sub>2</sub>O; 15 — 0.14 MgO, 0.41 Al<sub>2</sub>O<sub>3</sub>, 0.24 Fe<sub>2</sub>O<sub>3</sub>, 0.16 SiO<sub>2</sub>, 0.023 H<sub>2</sub>O, 0.03 F; 19 — 1.59 H<sub>2</sub>O; 20 — 1.32 H<sub>2</sub>O; 25 — 0.93 Fe<sub>2</sub>O<sub>3</sub>; 26 — 0.10 MgO, 0.20 Al<sub>2</sub>O<sub>3</sub>, 0.10 Fe<sub>2</sub>O<sub>3</sub>, 0.22 SiO<sub>2</sub>, 1.37 H<sub>2</sub>O; 28 — 0.02 MgO, 0.07 MnO, 0.44 FeO, 0.20 SiO<sub>2</sub>, 0.85 H<sub>2</sub>O, 0.04 F, 0.02 -O=F<sub>2</sub>; 32 — 0.16 ThO<sub>2</sub>, 0.20 Gd<sub>2</sub>O<sub>3</sub> (0.01 apfu); 33 — 0.05 MnO, 0.37 Fe<sub>2</sub>O<sub>3</sub>, 1.76 H<sub>2</sub>O, 0.20 F, 0.08 -O=F<sub>2</sub>; 34 — 0.93 Al<sub>2</sub>O<sub>3</sub>, 0.23 Fe<sub>2</sub>O<sub>3</sub>, 1.81 H<sub>2</sub>O; 36 — 0.12 TiO<sub>2</sub>; 45 — 0.25 FeO, 0.15 MnO, 0.04 MgO; 46 — 0.53 FeO, 0.13 MnO, 2.88 MgO; 47 — 0.13 FeO, n.d. — constituent was not determined, dash — the amount of constituent is below detection limit. \*\* — The mineral was described as «burbankite», but according to chemical composition, corresponds to calcioburbankite.

replaces khanneshite in Khibiny (Pekov *et al.*, 1998) and calcioburbankite in Vuoriayrvi (Subbotin *et al.*, 1999), the high-strontian burbankite was found in the late association in Kovdor (Ivanyuk *et al.*, 2002).

In alkaline hydrothermalites all this group members are known except khanneshite. Here the range of their chemical composition is extremely wide (Fig. 1): from strongly REE-depleted burbankite (an. 73) to petersenite. Essential predominance of strontium (usually 1.6–2.3 apfu) over other B-cations (Fig. 2b) is observed in burbankite from alkaline hydrothermalites almost of all geological objects. High content of barium in burbankite-like phases is not typical for this genetic type (rarely more than 0.6 apfu), which is explained by that with temperature decrease the tendency of very large Ba<sup>2+</sup> to isolation intensifies, and it will form own phases practically without strontium: zeolites, BaTi-silicates, BaREE-fluorcarbonates, and others. Almost all finds of high-sodium members of the burbankite group are made in alkaline hydrothermalites. The maximum contents of sodium are reached here, which is a necessary condition for origin of remondite and petersenite. The specimens of the burbankite group in alkaline hydrothermalites are characterized by increased part of strontium and a little one of neodymium in spectrum of REE.

Burbankite from pectolite metasomatites approaches in its chemical composition to REE-free end member (Na<sub>2</sub>Ca)M<sup>2+</sup><sub>3</sub>(CO<sub>3</sub>)<sub>5</sub> (Fig. 1). It is strongly Sr-enriched (usually 2.1–2.5 apfu, Table 3). All samples from both Khibiny and Murun are characterized by predominance of lanthanum over cerium together with insignificant contents of praseodymium and neodymium.

The widest prevalence of burbankite forming very large accumulations among other members of the group is evidence of maximum stability of this structural type exactly under predominance of strontium in B-site. Also that can be confirmed by sharply Sr-enriched chemical compositions of burbankite from alkaline hydrothermalites. Here crystallization proceeds from water solutions under sufficiently low-temperature conditions, consequently, the fractionating of similar in properties chemical elements is accomplished by the best way, and affinity of different structural types to certain components is realized as much as possible. In high-alkaline hydrothermal systems the separation of strontium from more widespread calcium, which caused by the crystallochemical reasons, is clear demonstrated by stable paragenesis of high-strontian burbankite with shortite Na<sub>2</sub>Ca<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub> almost non-containing strontium. Location of calcium in A-site, than in B-site is more typical for burbankite-like phases from low-



