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BURBANKITE FROM MONT ST. HILAIRE, QUEBEC

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ABSTRACT

Burbankite occurs as small colorless, yellow or pink, dihexagonal prismatic crystals embedded in analcime or natrolite in the miaroles and pegmatite dikes in nepheline syenite, Mont St. Hilaire, Quebec. It is commonly associated with microcline, aegirine and minor amounts of calcite, siderite and ancylite.

The space group symmetry of burbankite is $P6_3mc$ with $a = 10.514$ and $c = 6.520$Å. The mineral has a hardness of 4 and a distinct prismatic cleavage. It is optically uniaxial, $\omega_D = 1.616$ and $\epsilon_D = 1.597$.

Average electron microprobe analysis gave Na_2O 8.30; CaO 12.03; SrO 32.35; BaO 11.02; Ce_2O_3 2.12; Nd_2O_3 0.13; Dy_2O_3 0.08; Yb_2O_3 0.10; total 66.13%. Assuming the stoichiometric amount (33.17%) of CO_2 the analysis recalculates to $Na_{1.78}Ca_{1.42}Sr_{2.07}Ba_{0.48}RE_{0.10}(CO_3)_5$. With $Z = 2$, density (calc) = 3.50 g/cm³.

$Na_2Ca_2Sr_2(CO_3)_5$ with the burbankite structure was synthesized at 1.5 kb and 500°C, indicating that rare earth elements are not essential in burbankite. Ba-bearing burbankite was also synthesized but the extent of the Ba substitution is uncertain.

INTRODUCTION

Burbankite was first described by Pecora & Kerr (1953) as yellow hexagonal crystals intimately intergrown with ancylite in the carbonate veins of shonkinite at Bearpaw Mountains, Montana. It was later found as pink fibrous spheroidal aggregates in the lacustrine deposits of the Green River Formation, Wyoming (Milton & Fahey 1960), and as irregular veinlets and hexagonal crystals in calcite-dolomite veins in the Vuori-Järvi pluton, USSR (Borodin & Kapustin 1964). The chemical formula of burbankite was originally proposed by Pecora & Kerr (1953) as $Na_2(Ca,Sr,Ba,RE)_4(CO_3)_5$ where *RE* represents total rare earth elements. Recently, from their crystal structure analysis of burbankite, Voronkov & Shumyatskaya (1968) established the structural formula to be $A_3B_3(CO_3)_5$, where $A =$ Na, Ca and $B =$ Ca, Sr, Ba, *RE*. Povarennykh (1972, p. 611) assigned burbankite the ideal formula $(Na_2Ca)(Sr_2Ca)(CO_3)_5$ and noted that Ba may substitute for Sr up to 13.6 wt.% (approximately 0.5 atom per formula) and *RE* for Ca up to 15.1 wt.% (approximately 0.7 atom per formula).

The occurrence of burbankite at Mont St. Hilaire was first reported by Chao *et al.* (1967). Studies on this burbankite indicated that its composition is much closer to the ideal composition than burbankite from other localities.

OCCURRENCE

At Mont St. Hilaire burbankite occurs in small quantity as small, long-prismatic crystals embedded in analcime and natrolite in miaroles and pegmatite dikes in nepheline syenite. The burbankite is commonly associated with microcline, aegirine and minor amounts of calcite, siderite and ancylite. Some burbankite crystals are partly altered on the surfaces to ancylite. A few crystal molds of hexagonal prismatic habit similar to that of burbankite were noted. These hollow crystals are partly filled with minute crystals of ancylite and a reddish brown powdery material suggesting complete alteration and removal of the parental burbankite.

X-RAY CRYSTALLOGRAPHY AND PHYSICAL PROPERTIES

Eight single crystals were studied by precession and Weissenberg *x*-ray methods with Mo$K\alpha$ and Cu$K\alpha$ radiations respectively. The diffraction symmetry and systematic extinctions as shown by the *x*-ray photographs are consistent with those of the space groups $P\bar{6}2c$, $P6_3mc$ and $P6_3/mmc$. Although $P6_3/mmc$ was adopted by Pecora & Kerr (1953) and by Borodin & Kapustin (1964), piezoactivity study and crystal structure analysis by Voronkov & Shumyatskaya (1968) ascertained the correct space group to be $P6_3mc$.

The cell parameters obtained from single crystal photographs were refined by a least-squares method using powder diffraction data (Table 1). The indexing of the powder pattern was based on the observed and calculated *d*-values using single crystal photographs as a guide. The refined values are $a = 10.514(3)$ and

TABLE 1. *X*-RAY POWDER DIFFRACTION DATA OF BURBANKITE

	Burbankite Mont St. Hilaire			Synthetic $(Na_2Ca)(CaSr_2)(CO_3)_5$	
hkl	d_{calc}Å	d_{obs}Å	*I*	d_{obs}Å	*I*
100	9.105	9.103	2	9.086	2
101	5.301	5.276	5	5.238	5
110	5.257				
200	4.553	4.533	2	4.538	1
201	3.733	3.732	5	3.713	6
210	3.441	3.444	2	3.430	1
002	3.260	3.258	3	3.230	1
211	3.043	3.041	8	3.027	8
301	2.752	2.754	4	2.740	4
202	2.651	2.651	8	2.629	10
220	2.628	2.631	10	2.621	10
311	2.355	2.354	1	2.344	2
400	2.276	2.278	½	2.268	1
302	2.221	2.220	½	2.209	1
401	2.149	2.150	5	2.139	6
103	2.114	2.112	½	2.094	2
222	2.046	2.046	3	2.034	2
410	1.987	1.989	2	1.982	4
203	1.961	1.960	2	1.945	2
402	1.866	1.867	2	1.856	2
213	1.838	1.837	½		
322	1.759	1.756	3	1.748	4
412	1.697	1.698	½		
421	1.664	1.664	3	1.657	4
511	1.586	1.586	½	1.580	1
403	1.572	1.570	½	1.561	1
204	1.535	1.537	½		
422	1.522	1.520	½	1.513	2
431	1.459	1.460	½	1.453	2

CuKα radiation (λ=1.5418Å); Si standard, 114.6mm camera; synthetic $(Na_2Ca)(CaSr_2)(CO_3)_5$ grown at 1.5 kb, 500°C.

$c = 6.520(2)$Å, comparable to the values reported for burbankite from other localities (Table 2).

The colour of the St. Hilaire burbankite varies from colourless, pale yellow to pink. The mineral has a vitreous luster, a hardness of about 4 and a distinct prismatic cleavage. The crystals are dihexagonal prismatic with a shallow pyramidal termination. The prismatic faces are heavily striated parallel to *c*. The mineral effervesces strongly in dilute (10%) HCl.

The optical properties of the St. Hilaire burbankite measured in Na-light at 25°C on a spindle stage are given in Table 2 where they are compared with properties of burbankite from other localities. The St. Hilaire burbankite is characterized by low refractive indices that are comparable to the refractive indices of synthetic $Na_2Ca_2Sr_2(CO_3)_5$.

TABLE 2. CELL PARAMETERS AND OPTICAL PROPERTIES OF BURBANKITE

	1	2	3	4
a(Å)	10.514(3)	10.53(5)	10.41	10.477(2)
c(Å)	6.520(2)	6.47(2)	6.48	6.456(3)
ω	1.616(1)	1.627	1.632-1.635	1.615(1)
ε	1.597(1)	1.615	1.620-1.623	1.596(1)
ω-ε	0.019	0.012	0.012	0.019
Density (g cm^3)	3.50(calc)	3.50	3.54-3.58	3.25(calc)

1. Mont St. Hilaire, R.I. at 25°C, Na-light, spindle stage.
2. Montana (Pecora & Kerr 1953).
3. Vuori-Järvi pluton, USSR (Borodin & Kapustin 1964).
4. Synthetic $Na_2Ca_2Sr_2(CO_3)_5$. R.I. at 25°C, Na-light.

ELECTRON MICROPROBE ANALYSIS

The St. Hilaire burbankite was analysed using a Cambridge MK5 electron microprobe. A preliminary qualitative scan was first made to survey the elements present for the selection of standards. The standards used were pyroxene (for Ca), jadeite (Na), celestite (Sr), benitoite (Ba), bastnaesite (Ce,La,Sm,Pr), anorthite glass (Al), $NdAlO_3$ (Nd), $Dy_3Al_5O_{12}$ (Dy), $Yb_3Ga_5O_{12}$ (Yb) and metallic Nd and Gd. Analyses were made using a defocused beam at 15 kv accelerating voltage and a specimen current of about 50 nanoamps. The intensity data were processed by computer using the program written by Rucklidge & Gasparrini (1969). All grains analysed were first checked for identity by *x*-ray diffraction using a Gandolfi camera.

The averaged analysis of burbankite is given in Table 3. CO_2 was not analysed due to the small amount of material available. Assuming a stoichiometric amount of CO_2, the analysis was recalculated, on the basis of 5 oxygen atoms per formula (excluding CO_2), to

$(Na_{1.78}Ca_{1.07})(Ca_{0.35}Sr_{2.07}Ba_{0.48}RE_{0.10})(CO_3)_5$.

TABLE 3. CHEMICAL ANALYSES OF BURBANKITE

	1.	2.	3.
Na_2O	8.30	9.69	12.19
Al_2O_3	n.d.	0.25	-
CaO	12.03	13.46	9.81
SrO	32.35	19.42	9.96
BaO	11.02	13.56	14.60
Ce_2O_3	2.12	9.48	16.22
La_2O_3	n.d.		
Gd_2O_3	n.d.		
Nd_2O_3	0.13		
Sm_2O_3	n.d.		
Pr_2O_3	n.d.		
Y_2O_3	-		
Dy_2O_3	0.08	-	
Nb_2O_5	n.d.	-	
Yb_2O_3	0.10	-	
CO_2	(33.17)	32.55	32.14
K_2O	-	0.15	0.74
SiO_2	-	0.16	0.06
Fe_2O_3	-	0.03	0.10
MgO	-	0.14	-
P_2O_5	-	0.12	-
$H_2O\pm$	--	0.18	2.60
S	-	0.24	-
Total	(99.30)	99.31	98.42

1. Mont St. Hilaire, Quebec, Yellow crystal; CO_2 calculated.
2. Montana (Pecora and Kerr, 1953); analysis includes 4% impurity.
3. Vuori-Järvi pluton, USSR, (Borodin and Kapustin, 1964); analysis includes impurity.

With this analysis and assuming $Z = 2$, the calculated density, 3.50g/cm^3, is well within the range of values reported for burbankite from other localities (Table 2). The small deviation of the total of cations from the ideal number (6) is attributable, in part, to errors in the analysis of Na. It was noted that during the analysis, Na counts decreased with time, tending to give lower Na values.

The St. Hilaire mineral may be distinguished from burbankite from other localities by its high Sr and low total rare earth contents (Table 3). The association of low rare earth content and low refractive indices for the St. Hilaire burbankite falls in line with the observations by Borodin & Kapustin (1964) that the refractive indices of burbankite increase with increasing rare earth content.

Several crystals of burbankite, although optically clear, were shown by *x*-ray diffraction method to contain ancylite and carbocernaite. Electron microprobe analyses of these crystals consistently gave very high values of Ce_2O_3 and La_2O_3, up to a total of 46%.

SYNTHESES OF BURBANKITE

In order to determine whether the rare earth elements are essential in burbankite, an attempt was made to synthesize rare-earth-free burbankite. Stoichiometric starting materials were prepared from reagent-grade $CaCO_3$, Na_2CO_3, $BaCO_3$ and $SrCO_3$. The mixtures were finely ground to ensure homogeneity. For all the runs, about 70 mg of the mixture and 25 mg H_2O were sealed in a gold tube and treated hydrothermally at 1.5kb and 500°C for a week. The products were quenched, examined under a polarizing microscope and identified by *x*-ray powder diffraction. The starting compositions and their products are listed in Table 4. Most of the runs were repeated and in all cases identical results were obtained.

Of all the runs only $Na_2Ca_2Sr_2(CO_3)_5$ (run 1, Table 4) consistently yielded single-phase products that gave an *x*-ray powder pattern identical to that of natural burbankite (Table 1). Calcium-free and Sr-free runs (5 and 6, Table 4) yielded no burbankite. All other runs contained Ba and yielded burbankite plus benstonite with or without strontianite.

TABLE 4. HYDROTHERMAL SYNTHESIS OF BURBANKITE (500° ± 10°C, 1.5 kb, 7 days)

	Starting Composition (number of formula weights)				
Run	Na_2CO_3	$CaCO_3$	$SrCO_3$	$BaCO_3$	Products
1.	1	2	2	-	BB
2.	1	1	3	-	BB+St+Cc+Sc
3.	1	3	1	-	BB+Cc
4.	1	2.5	1.5	-	BB+Cc
5.	1	-	2	2	Wt+St+Sc
6.	1	2	-	2	Bc+Sc
7.	1	1.33	2	0.67	BB+St+Bs
8.	1	2	1.33	0.67	BB+Bs
9.	1	2	1.5	0.5	BB+Bs
10.	1	1.5	2	0.5	BB+St+Bs
11.	1	1	2	1	BB+St+Bs
12.	1	2	1	1	BB+Bs

BB burbankite; St strontianite; Cc calcite; Sc sodium carbonate hydrate; Wt witherite; Bs benstonite; Bc barytocalcite.

The crystals of synthetic $Na_2Ca_2Sr_2(CO_3)_5$ are small (0.03 x 0.01 x 0.01mm) prismatic, with shallow pyramidal terminations (Fig. 1) resembling the natural crystals. The refractive indices of the synthetic compound are comparable to those of the St. Hilaire burbankite, whereas the cell parameters are considerably smaller (Table 2). The compositions of the synthetic Ba-bearing burbankite (runs 7-12) are uncertain due to the presence of other phases. However, the larger cell parameters and the higher refractive indices of the Ba-bearing compounds in comparison with those of the $Na_2Ca_2Sr_2(CO_3)_5$ suggest that significant amounts of Ba must have been incorporated in the structure.

Despite the fact that rare earth elements may be present in natural burbankite up to 0.7 atom per formula, the results of this experiment suggest that they are not essential for burbankite. However, the results are inconclusive on the

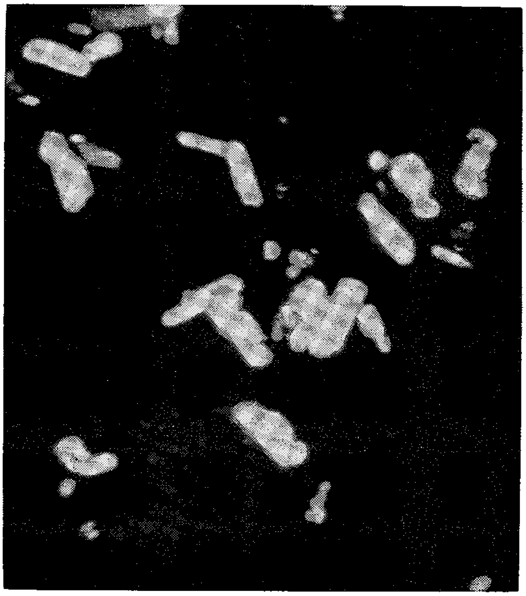

FIG. 1. Synthetic crystals of $Na_2Ca_2Sr_2(CO_3)_5$. Average length of crystals is approximately 0.03 mm.

extent of the Ba substitution in burbankite. The analyses of natural burbankite minerals suggest that the Ba substitution may be limited as the Ba content was never found to be greater than 0.5 atom per formula.

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