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Burbankite from the Green River Formation, Wyoming

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Abstract

The rare earth-bearing carbonate, burbankite, occurs in thin microcrystalline coatings and veinlets with mckelveyite–ewaldite at the base of the Wilkins Peak member of the Green River Formation in Sweetwater County, Wyoming. Fragments yield excellent powder patterns from which the hexagonal cell dimensions have been determined to be *a* 10.451(3), *c* 6.510(2) Å, very close to those of burbankite from Mont St. Hilaire, Quebec. The Wyoming burbankite is heavily contaminated with organic matter which can be removed by moderate heating. The decomposition temperature in air of this burbankite is near 600° C; the products of decomposition have been partly identified. The morphology has been examined by scanning electron microscopy, which shows that the prismatic habit of even the smallest crystallites is similar to the habit of megascopic burbankite from some other localities. Microprobe analysis shows that the Wyoming burbankite is extremely rare-earth rich and approaches the upper limit of rare-earth content imposed by stoichiometry. Calculated sigma values for burbankites from several localities show a fairly restricted range of variation at high atomic percentages of Ce, La, and Pr.

Introduction

Burbankite was first recognized in veins in shonkinite in Montana (Pecora and Kerr, 1953). Other occurrences in igneous associations have been reported from an "altered alkaline rock, probably melteigite" in the Zeerust District, Transvaal (Verwoerd, 1963), from the Vuori-Järvi pluton USSR (Borodin and Kapustin, 1964) and in nepheline syenite at Mont St. Hilaire, Quebec (Chen and Chao, 1974).

In contrast to its occurrence in or with igneous alkaline rocks, burbankite in the Eocene Green River Formation is an authigenic mineral in sediments formed in a highly sodic lacustrine environment. This occurrence of burbankite was first reported by Milton and Eugster (1959, p. 136) who stated: "*Burbankite* is associated with nahcolite in Utah and with trona in Wyoming, occurring in pinkish fibrous spheroidal aggregates of microscopic size. It is not known whether its strontium and rare-earth contents are essential or whether the phase $Na_2CO_3 \cdot 4CaCO_3$ exists." This question has been answered in part by Chen and Chao (1974, p. 344) who synthesized a burbankite-like phase of composition $Na_2Ca_2Sr_2(CO_3)_5$. However, from the determination of the structure by Voronkov and Shumyatskaya (1968) it is known that the cations occupy only two structurally distinct positions.

Milton and Fahey (1960) listed burbankite among carbonate minerals of the Green River Formation but made no statement as to its abundance. Milton *et al.* (1965, p. 608) stated that "Mckelveyite and burbankite are both probably fairly widespread minerals in the Wyoming Green River Formation; burbankite is also known from many Green River localities in Utah." Milton (1971, p. 58 and 60) listed burbankite among the authigenic minerals of the Green River Formation with abundance 5, defined as "local and never abundant," and stated that "burbankite is fairly widespread though always in microscopic quantity."

Material

This study is based on material received from Professor Charles Milton. In a letter from Dr. J. D. Love to Professor Milton, dated May 1, 1974, the source is identified as follows: ". . . sample LW-869 . . . is a 'core biscuit" from a depth of 1,784 feet in J. M.

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Perkins No. 3 core hole, SW ¼ sec. 8, T. 17 N., R. 107 W., Sweetwater County, Wyoming." This is in "zone 1" of the uraniferous phosphatic zones described by Love (1964, table 2 and p. 24) and is at the very base of the Wilkins Peak member of the Green River Formation. The locality is also recorded by Milton *et al.* (1963) in their Figure 5, which shows "the location . . . of the four known occurrences of mckelveyite," the depth being given as 1,786 feet, rather than 1,784 feet. All four locations are in the Wilkins Peak member of the Green River Formation. In the same paper the association of burbankite with mckelveyite is reported (Milton *et al.*, p. 608–610, Table 8 and Fig. 8), but there is no statement as to the particular locality or localities where the association was recognized.

The core fragments furnished to us are composed of a soft, very fine-grained, pale gray rock. Scattered about in this are patches of isolated crystals of pyrite, nahcolite, and mckelveyite that can be recognized megascopically, in places in contact with each other. The nahcolite occurs in clear, cleavable crystals, up to a centimeter or more in dimension. Both mckelveyite and pyrite may be embedded in such nahcolite.

Dolomite is the principal constituent of the fine-grained matrix. Other constituents, in approximate order of abundance, are oligoclase, microcline, muscovite, quartz, and trona. However, the rock shows a faint banding or bedding, best seen in some of the thin sections. Abrupt changes in the mineral composition may occur, and dolomite is entirely lacking in some bands.

The burbankite

Burbankite is less abundant than any of the minerals mentioned thus far. Though present in each of the five core pieces, it was found in only two of five thin sections. In the present study it was first recorded as "microbotryoidal crusts" seen in the cavities adjoining mckelveyite and in places extending into the matrix. Figure 1 shows such an occurrence as seen in thin section. These crusts or seams of burbankite are at most a few tenths of a millimeter thick. Bits of such material are easily freed from the associated minerals. Under a binocular microscope they appear to have a velvety texture, and the color is yellow to dark brown, often varying markedly within a small fragment. Many bits of crust are almost colorless in their outer parts. About a dozen bits of crust were examined by X-ray diffraction. Each yielded a pure smooth powder pattern of uncontaminated burbankite with little or no evidence of orientation, even though the extinction sweeping across adjoining sheaves within crustal bits or as seen in thin section suggests orientation of fibers in bundles. Clearly, the groups of fibers within a bit of crust are so small and so distorted that the orientation is effectively random.

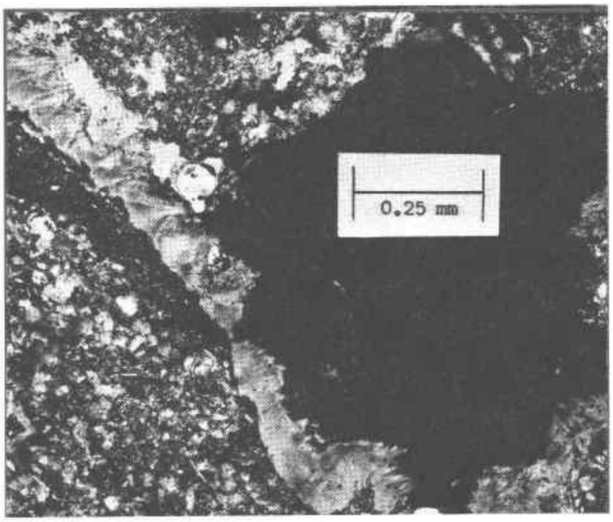

FIG. 1. Thin section in polarized light. Burbankite forms a microbotryoidal crust about 0.1 thick on one side of a crystal of mckelveyite and extends into the adjoining sediment which is composed larely of dolomite with some quartz and muscovite, all in the size range 0.03 to 0.01 mm or less.

It seems probable that burbankite was one of the last minerals to form in the location from which our material came. The burbankite is never enclosed in any of the associated minerals, and the thin crusts of it do not have other minerals implanted on them.

Untreated bits of burbankite microbotryoidal crust have an apparent density of 2.95(5) as determined by suspension (Bloss, 1961, p. 63–64), the indicated uncertainty being partly attributable to variation between bits. Heated fragments have a density close to 3.36. It seems certain from the morphology and the loss of weight on heating that the low density of untreated burbankite is attributable to the presence of organic matter. The slightly low value of the density of the heated material which has lost the organic matter, relative to the calculated value, 3.47, or the values reported for other burbankites, 3.50–3.58, may be due to voids in the finest recesses between the fibers not filled by the suspending liquid.

The hardness of burbankite has been reported to be in the range 3.5 (Montana) to 5 (Karelia). Due to the extreme fragility of the burbankite aggregates from the Green River Formation, they are easily crushed when touched with a needle and give the impression of being much softer than the megascopic crystals.

Powder patterns of Wyoming burbankite, made from untreated or heated fragments closely match previously published (Pecora and Kerr, 1953, Chen and Chao, 1974) patterns. The cell dimensions of Wyoming burbankite were found to be *a* 10.541(3), *c* 6.510(2) Å, close to those reported by Chen and Chao (1974), *a* 10.547(9) and *c* 6.502(6) Å.

Upon heating, the minute yellow-brown aggregates of burbankite lose their color but are otherwise unchanged, as shown by optical and X-ray examination of heated bits. This loss of color was considered to be due to the destruction or removal of organic matter, usually referred to as kerogen, included between the fibers of burbankite though not optically recognizable as a separate phase. Heating a lot of over one hundred tiny bits with aggregate weight of 1.51 mg in air to 355° C for 15 hours resulted in a weight loss of 7.3 ± 1.3 percent. Further heating at the same temperature for 20 hours and at 390° for 18 hours produced no further weight loss.

The Wyoming burbankite yields an unchanged powder pattern after heatings up to 515° C. After 24 hours at 615° C it was fully converted to a mixture of new phases. The principal phases recognized were $(Sr,Ba)CO_3$, corresponding to a slightly barian strontianite, and BaO. A trace of $CaCO_3$ (calcite) is represented by its strongest line only. A DTA curve of the Karelian burbankite, published by Borodin and Kapustin (1964), shows "decomposition peaks at 670 and 730°." It is possible that burbankite persists to such high temperatures upon rapid heating during differential thermal analysis and that these peaks are attributable to burbankite breakdown. The difference between our results and those of the Russian authors may be attributed to the slow rate of breakdown of burbankite and to the difference in procedures.

Chemistry

Analytical procedure

Approximately one dozen fragments of the Wyoming material were mounted in epoxy and polished for examination with an ARL eight-channel scanning electron micro-quantometer/analyzer. The electron probe was operated at an accelerating voltage of 15 kV. An optimum sample current of 0.05μA was achieved by maximizing the count to background ratio on sodium just below the point at which the count rate began to decline sharply over an interval of 20 seconds when totalled every 2 seconds. Care was taken to insure that the defocused beam did not rest on the area to be analyzed until counting was about to commence. Using this method, the total number of counts on sodium was reproducible and consistent.

Of the dozen or so fragments, five were chosen which gave the most consistent count rates. Standards employed were pirssonite (for Na and Ca), strontium anorthite (for Sr), burbankite from the Montana locality (for Ba and Y), rare-earth standards #1 and #2 containing rare-earths in anorthite glass (for Ce, La, Pr, Nd, and Sm),[2] and thalenite (for Gd). The counts were corrected for dead-time, drift, background, fluorescence, absorption, and atomic number effects using program Process written by R. Powell and C. Bacon. Absorption, fluorescence, and atomic-number effects were corrected simultaneously by the method of Bence and Albee (1968) using the calculated alpha factors of Albee and Ray (1970), and measured values where available.

Initial attempts to use burbankite from the Montana locality as a standard for sodium proved unsatisfactory. Repeated analyses using albite and pirssonite as sodium standards yielded consistently low values for the Montana material, although all other elements were accurately reproduced using the stand-

TABLE 1. Microprobe analysis of burbankite from the Green River Formation, Wyoming

	1 original sample	2 recalculated to 100%	3 no. of moles	4 atoms based on 5 oxygens
Na_2O	10.47	11.79	.1902	2.498 Na
SrO	15.61	17.57	.1696	1.114 Sr
BaO	5.73	6.45	.0421	0.276 Ba
CaO	8.00	9.01	.1607	1.055 Ca
Ce_2O_3	8.65	9.74	.0297	0.390 Ce
Y_2O_3	0.19	0.21	.0011	0.014 Y
La_2O_3	3.73	4.20	.0129	0.169 La
Pr_2O_3	1.57	1.77	.0054	0.071 Pr
Nd_2O_3	4.60	5.18	.0154	0.202 Nd
Sm_2O_3	0.55	0.62	.0018	0.024 Sm
(CO_2)	(29.73)	(33.47)	(.7605)	
Total	(88.83)			
impurities				
SiO_2	0.25			
Al_2O_3	0.30			
FeO	0.03			
Total	(89.41)			

Gd not detected

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[2] Prepared by Dan Weill, University of Oregon

ards as listed. As a result, the Montana material was abandoned as a sodium standard and pirssonite was adoped instead.

Results

The averaged analysis of 75 points is shown in Table 1. It seems probable that the low total is caused by the presence of "kerogen." Up to 8.7 percent of included organic material has been reported in mckelveyite from the same locality (Milton *et al.*, 1965). Leucosphenites from elsewhere in the Green River Formation have also been found to contain organic matter (Pabst and Milton, 1972).

Optical examination showed that the fragments were inhomogenous, having irregularly distributed dark and light brown regions. As previously discussed, heating the fragments produced a marked color change and a weight loss of approximately 7.3 percent. Powder patterns run after each heating showed that the burbankite remained unaltered during the course of the heating. A comparison of SEM photographs of heated and unheated fragments suggests that the organic material has been adsorbed at the surfaces of the individual crystals. Considering the variation in appearance between fragments, it is reasonable to assume that the organic matter is not evenly distributed. It is likely that "kerogen" concentrations are higher in the larger, darker pieces selected for microprobe analysis than in some of the fragments chosen for heating.

TABLE 2. Analyses of burbankites from several localities

	Wyoming	Mount St. Hilaire[1]	Montana[2]	U.S.S.R.[3]	U.S.S.R.[4]
Na_2O	11.79	8.30	10.17	12.19	11.44
SrO	17.57	32.35	19.70	9.96	12.86
BaO	6.45	11.02	14.02	14.60	11.62
CaO	9.01	12.03	13.68	9.81	10.86
Ce_2O_3	9.47	2.12	4.65	8.34	8.18
Y_2O_3	0.21	-	0.10	0.26	0.00
La_2O_3	4.20	n.d.	2.34	4.24	4.73
Pr_2O_3	1.77	n.d.	0.37	0.64	0.53
Nd_2O_3	5.18	0.13	1.40	2.45	1.61
Sm_2O_3	0.62	n.d.	0.10	0.17	0.06
Gd_2O_3	0.0	n.d.	0.08	0.12	0.01
Dy_2O_3	-	0.08	-	-	-
Yb_2O_3	-	0.10	-	-	-
CO_2	(33.47)	(33.17)	33.39	32.14	34.30
K_2O	-			0.74	0.99
Al_2O_3	(0.3)			0.00	1.05
SiO_2	(0.25)			0.06	0.19
Fe_2O_3	(0.03)			0.10	0.48
MgO	-			0.00	0.35
$H_2O^{\pm}$	-			2.60	0.97
S	-			-	-
Total RE_2O_3	21.72	2.33	9.48	16.22	15.12
Total	100.0	99.30	100.0	98.42	100.23

[1] microprobe analysis, Chen and Chao, 1974

[2] Na_2O and K_2O by flame photometer, REE's by spectrograph, Pecora and Kerr, 1953

[3] Karelia, USSR, REE's by x-ray spec., Borodin and Kapustin, 1962

[4] Karelia, USSR, REE's by x-ray spec., Borodin and Kapustin, 1962

TABLE 3. Rare-earths in burbankite, mckelveyite, and ewaldite from the Green River Formation, Wyoming

	Burbankite[1]	McKelveyite[2]	Ewaldite[3]
Ce_2O_3	9.74	0.16	-
Y_2O_3	0.21	7.7	4.76
La_2O_3	4.20	0.09	0.05
Pr_2O_3	1.77	0.05	-
Nd_2O_3	5.18	0.26	-
Sm_2O_3	0.62	0.34	0.03
Eu_2O_3	-	0.19	0.07
Gd_2O_3	0.0	1.18	0.65
Tb_2O_3	-	0.38	-
Dy_2O_3	-	1.00	0.50
Ho_2O_3	-	0.28	0.12
Er_2O_3	-	0.95	0.81
Tm_2O_3	-	0.12	-
Yb_2O_3	-	0.61	0.65
Lu_2O_3	-	0.08	0.05

[1] electron microprobe, this paper

[2] spectrograph, Milton et al. (1965)

[3] spectograph, recalculated from total $(Y,Ln)_2O_3$, Donnay and Donnay (1970)

When the analysis is recast to 100 percent, the resulting formula is close to ideal: $(Na_{5.0}Ca_{.62})(Ca_{1.48}Sr_{2.22}Ba_{.56}REE_{1.74})(CO_3)_{10}$ It would therefore appear that the presence of an additional component, rather than the absence of some component in the burbankite is causing low totals.

The slight deficiency of cations is due, in part, to counting errors on sodium, since some drop in sample current was always noted during the 20-second counting interval. A probe analysis on the Mont St. Hilaire material (Chen and Chao, 1974) shows an almost identical deficiency, suggesting that vacancies on the sodium site may also be in part responsible.

TABLE 4. Σ calculations for burbankite

	Atomic %			
	Wyoming	Montana	U.S.S.R.	U.S.S.R
La	3.58	2.00	3.62	4.03
Ce	8.09	3.97	7.12	6.98
Pr	1.51	0.32	0.55	0.45
Nd	4.44	1.20	2.10	1.38
Sm	0.53	0.09	0.15	0.05
Gd	0.00	0.07	0.10	0.01
Y	0.17	0.08	0.20	0.00
Total	18.32	7.73	13.84	12.90
	Atomic % Recast to 100% Total			
La	19.54	25.87	26.16	31.24
Ce	44.16	51.63	51.45	54.11
Pr	8.24	4.14	3.97	3.49
Nd	24.24	15.52	15.17	10.70
Sm	2.89	1.16	1.08	0.39
Gd	0.00	0.91	0.72	0.08
Y	0.93	1.03	1.45	0.00
Σ=La+Ce+Pr	71.94	81.37	81.58	88.84

Rare-earth concentrations

The distinguishing feature of burbankites from the Wyoming locality is a concentration of rare-earths exceeding that from any previously reported locality (see Table 2). A comparison of rare-earth concentrations between burbankite and its associated minerals ewaldite and mckelveyite in the Green River Formation shows that the cerium and yttrium rare-earths are strongly partitioned—the former concentrating in the burbankite and the latter in the other two minerals (Table 3). As pointed out by Milton *et al.* (1965), this partitioning must be due to differences in the crystal-chemical character of the three minerals and not to the geochemical environment, since all three formed under identical geochemical conditions.

Murata *et al.* (1957) have defined the quantity Σ as the sum of the atomic percentages of La, Ce, and Pr, and have used it as an index of comparison for all cerium rare-earth-bearing minerals. They have found that the cerium rare-earth minerals can be categorized into two groups; those which show a large variation in Σ (monazite, cerite, and allanite), and those which show a restricted range of variation at high concentrations (bastnaesite). Table 4 gives the results of Σ calculations on burbankites from four of the reported localities. These values are consistent with those of other minerals from alkaline environments, and are among the highest Σ values thus far reported. Burbankite appears to belong to the bastnaesite type of cerium rare-earth minerals, since these calculated sigmas are high and fairly restricted in range when compared to Σ values of monazite, cerite, and allanite. While other minerals have shown higher sigmas, bastnaesite and burbankite are the only two which are consistently high. These two minerals are therefore among the most cerium rare-earth rich of all the rare-earth-bearing minerals thus far investigated. The concentration of rare-earths in the Wyoming burbankite approaches the upper limits set by stoichiometry in the burbankite structure (Voronkov and Shumyatskaya, 1968).

It should be noted that while the total rare-earth content in the Wyoming material is higher than in

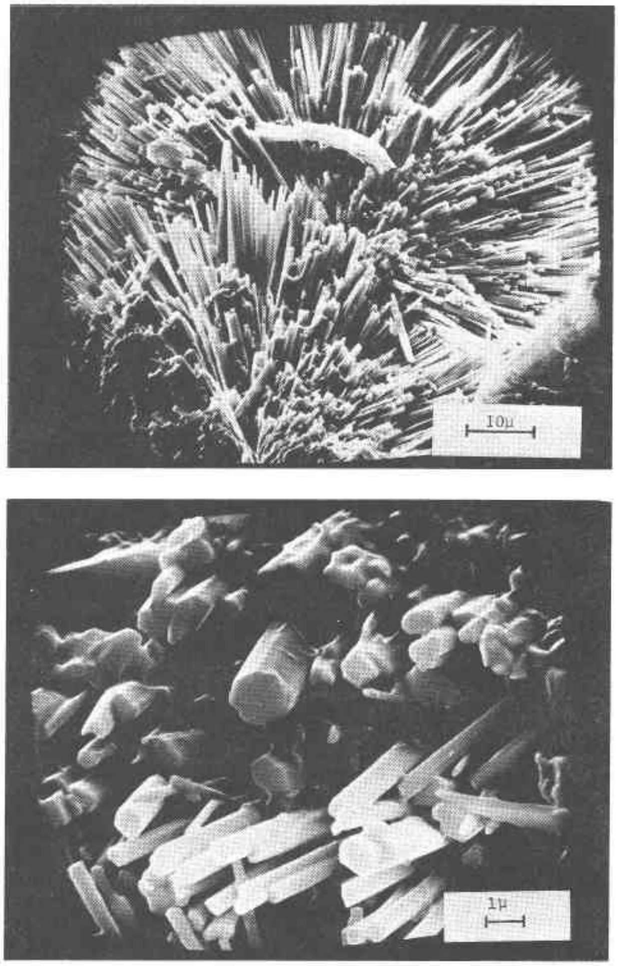

FIG. 2, A AND B. SEM micrographs of microbotryoidal crusts. Crystals occur in bundles of radiating fibers which clearly show hexagonal morphology. Terminations are usually simple pedions.

other burbankites, its Σ value is significantly lower. This is due to the relative enrichment of neodymium and samarium in comparison to the sum of La, Ce, and Pr.

Morphology

SEM photographs show that the burbankite occurs in bundles of elongated hexagonal prisms which usually terminate in simple pedions (Fig. 2, a and b). The morphology of the Wyoming material is essentially identical to that reported from both the Soviet Union and the Mont St. Hilaire localities. However, the vertical striations parallel to *c* reported in those studies were not seen on any of the Wyoming material examined.

Acknowledments

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