

BIKITAITE,  $\text{LiAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ , A NEW MINERAL FROM SOUTHERN RHODESIA\*CORNELIUS S. HURLBUT, JR., *Harvard University, Cambridge, Massachusetts.*

## ABSTRACT

Bikitaite,  $\text{LiAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$  is a new mineral from the lithium-rich pegmatites at Bakita, Southern Rhodesia. It occurs as a late mineral interstitial to granular eucryptite. No crystals were observed. X-ray study yields: monoclinic;  $a_0=8.63 \text{ \AA}$ ,  $b_0=4.95$ ,  $c_0=7.64$ ,  $\beta=114^\circ 34'$  ( $a_0:b_0:c_0=1.743:1:1.543$ ); space group,  $P2_1/m$ . Colorless to white. Specific gravity 2.34 (meas.) 2.29 (cal. for two formula-units per cell). Hardness 6. Optically biaxial (-);  $n_X=1.510$ ,  $n_Y=0.521$ ,  $n_Z=1.523$ ,  $2V=45^\circ$ ,  $r < v$ ,  $Z=b$ ,  $X \wedge c=28^\circ$ . Analysis gives:  $\text{SiO}_2$  55.79,  $\text{Al}_2\text{O}_3$  26.68,  $\text{Fe}_2\text{O}_3$  0.07,  $\text{Li}_2\text{O}$  6.51,  $\text{Na}_2\text{O}$  0.10,  $\text{K}_2\text{O}$  0.17,  $\text{MgO}$  0.33,  $\text{H}_2\text{O}$  9.82, Total 99.47. The strongest x-ray powder lines are: 4.19  $\text{\AA}$ , (10), 3.48 (10), 3.40 (10), 7.84 (8). The name *bikitaite*, is from the locality, Bikita.

## INTRODUCTION

The pegmatites of Bikita are located about forty miles east of Fort Victoria, Southern Rhodesia. Since the finding of cassiterite there nearly fifty years ago, they have been known as the "Bikita tinfield." From that time, the area has been a small tin producer, mostly from eluvial deposits. Shortly after the discovery of tin, tantalum was found at Bikita but little attention paid to it until World War II created a demand for the element. At present both metals are being mined on a small scale. The tantalum minerals, according to Macgregor (1946), are tantalite, simpsonite, microlite and an abnormal manganese tantalate.

The geology of the Bikita area has been mapped by Tyndale-Biscoe (1952). His map shows scattered pegmatites extending over a distance of two and one-half miles in a north-south direction. The major dike with N-S strike and easterly dip is approximately one mile long and lies in the southern part of the area, and at present is being actively mined for lithium. Development to date has shown this pegmatite to contain one of the world's great concentrations of lithium. Spodumene and amblygonite are both present but the chief lithium minerals are petalite and lepidolite, which are found in hundreds of thousands of tons. The southern half of this body is mined by Bikita Minerals, Ltd., with lepidolite the principal ore mineral. In the northern half George H. Nolan, Ltd., is mining mainly petalite.

## OCCURRENCE

In 1955 the writer collected specimens of eucryptite from the Nolan property. Some of the eucryptite was in coarse crystals, others in fine-

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grained granular aggregates, associated with granular quartz. Present in the granular material was an unidentified mineral in extremely limited amount. In a specimen recently received from Mr. George Nolan this unknown mineral, although not abundant, was in sufficient amount to separate for study. It proved to be a new mineral and is named *bikitaite* from the locality.

It is almost certain that a paragenetic study of the Bikita pegmatites would be most rewarding. This at present is impossible with the limited number of specimens at hand, but age relations of some of the minerals are known. Tyndale-Biscoe (1952) states, "It is probably very difficult to obtain pure samples of petalite for analysis as it always contains relics of feldspar which it probably replaces." Eucryptite appears to replace the petalite. Bikitaite is still later for it is found in small fractures within the eucryptite and fills interstices between quartz and eucryptite grains (Fig. 1). Quartz makes up about one-fourth and eucryptite three-fourths of the aggregate.

#### PHYSICAL AND OPTICAL PROPERTIES

Bikitaite is colorless and transparent in the small grains available. No cleavage was observed on the fragment used for single crystal work. When crushed material is observed microscopically, most of the grains

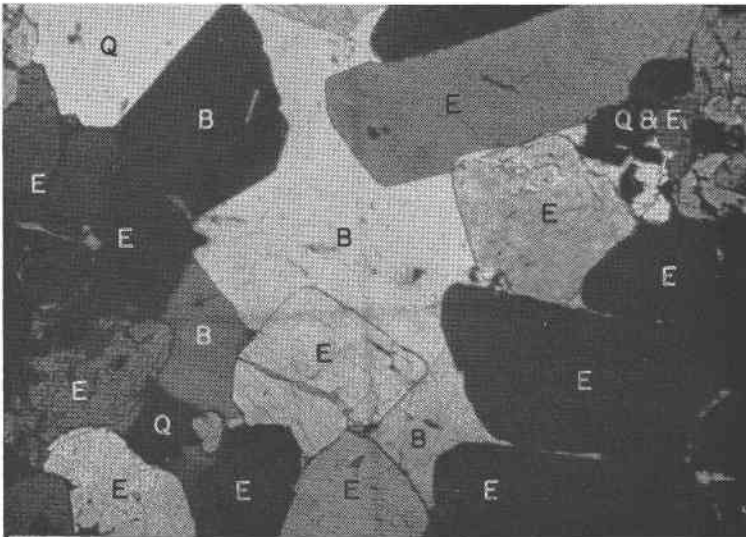


FIG. 1. Photomicrograph showing bikitaite interstitial to eucryptite and quartz. Crossed nicols. Photograph covers area of thin section  $3 \times 2.25$  mm. E-eucryptite. Q-quartz. B-bikitaite.

appear randomly oriented indicating the lack of a pronounced cleavage. However, a few show parallel extinction with positive elongation. Two different orientations are observed in these grains. In one orientation the X direction is essentially across the length and in the other the Y direction. It can be concluded, therefore, that there is poor {001} and {100} cleavage. The hardness is 6. Specific gravity measured by suspension in bromoform is  $2.34 \pm 0.04$  (calculated 2.29). The grains used for suspension were so small that it was difficult to tell when the density of the mineral was exactly matched with the density of the liquid; hence the uncertainty in the measured specific gravity. The streak is white. There is no fluorescence in either short- or long-wave ultraviolet radiation. This is in contrast to the eucryptite with which bikitaite is associated and which fluoresces pink to red. The optical properties are given in Table 1.

TABLE 1. OPTICAL PROPERTIES OF BIKITAITE

	n <sub>Na</sub>	
X $\wedge$ c = 28°	1.510 ± 0.001	opt. (-)
Y	1.521 ± 0.001	2V = 45°
Z = b	1.523 ± 0.001	r < v

## CHEMICAL COMPOSITION

As stated previously, bikitaite occurs in small amounts interstitial to quartz and eucryptite grains and as fracture fillings in eucryptite. To obtain material for chemical analysis it was necessary to crush the specimen to minus 150 mesh to liberate bikitaite from the eucryptite and quartz. A separation was then made in bromoform. About 40 grams of the specimen were used to obtain 400 milligrams of bikitaite.

The chemical analysis is given in Table 2 together with the contents of the unit cell. Using the measured specific gravity, 2.34 and cell volume,  $296.8 \text{ \AA}^3$ , the molecular weight of the cell contents was determined as,  $M = 418$ . This value multiplied by the atomic ratios give the cell contents as:  $(\text{Li, Na, K, Mg})_{1.89}\text{Al}_{2.20}\text{Si}_{3.90}\text{O}_{12.05} \cdot 2.3\text{H}_2\text{O}$ . This can be considered essentially as  $2(\text{LiAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O})$  which is equivalent to spodumene plus water. An excess of alumina and a deficiency of silica over the stoichiometric proportions indicates that some alumina may be substituting for silica in four-fold coordination. The presence of  $\text{Mg}^{++}$  substituting for  $\text{Li}^+$  makes at least a partial valence compensation for the substitution of  $\text{Al}^{+3}$  for  $\text{Si}^{+4}$ .

Bikitaite is apparently the first natural hydrated lithium aluminum silicate to be described, although several have been produced in the laboratory. In 1894 Thegutt obtained  $\text{LiAlSiO}_4 \cdot \text{H}_2\text{O}$  by heating a mixture of kaliophilite, lithium chloride, carbonate and water. In recent years

considerable work has been done on the synthesis of lithium aluminum silicates, notably by Hatch (1943), Winkler (1947), Roy and Osborn (1949) and Barrer and White (1951). Of these, however, only Barrer and White reported hydrated compounds. They synthesized two hydrated lithium aluminum silicates:  $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2 \cdot 5\text{H}_2\text{O}$  with ion exchange properties similar to zeolites. Neither of these compounds corresponds to bikitaite in  $x$ -ray powder data.

A differential thermal analysis of bikitaite showed two endothermic reactions, one beginning at  $190^\circ \text{C}$ . and ending at  $475^\circ \text{C}$ . and the other

TABLE 2. CHEMICAL ANALYSIS AND UNIT CELL CONTENTS OF BIKITAITE

	Weight per cent		Molecular ratios	Atomic ratios	Atoms per unit cell	Theoretical cell contents
	1	2				
$\text{SiO}_2$	55.79	56.13	.9338	(Si) .9338	3.90	4
$\text{Al}_2\text{O}_3$	26.68	26.84	.2633	(Al) .5266	2.20	2
$\text{Fe}_2\text{O}_3$	0.07	—				
$\text{Li}_2\text{O}$	6.51	6.55	.2192	(Li) .4384	1.83	2
$\text{Na}_2\text{O}$	0.10	0.10	.0016	(Na) .0032	0.01	
$\text{K}_2\text{O}$	0.17	0.17	.0018	(K) .0036	0.02	
$\text{MgO}$	0.33	0.33	.0082	(Mg) .0082	0.03	
$\text{H}_2\text{O}$	9.82	9.88	.5489	(H)1.0978	4.59	2
	99.47	100.00				

1. Jun Ito, *analyst*, 1957.

2. Recalculated to 100 per cent after deducting  $\text{Fe}_2\text{O}_3$ .

beginning at  $750^\circ \text{C}$ . and ending at about  $900^\circ \text{C}$ . The first reaction is interpreted as due to loss of water and the nearly  $300^\circ \text{C}$ . interval over which it is given off indicates it is zeolitic type. The  $d$  spacings as shown by an  $x$ -ray powder photograph of bikitaite after being heated to  $500^\circ \text{C}$ . are the same as given by the mineral before heating. This also indicates that water is nonessential. The loss of water lowers the refractive index to an average value of 1.485. Apparently water is not again taken up for holding the mineral in an atmosphere saturated with water vapor or immersing it in water does not raise the refractive index. The second endothermic reaction is the result of inversion to  $\beta$ -spodumene. After heating to  $900^\circ \text{C}$ ., bikitaite gives an  $x$ -ray powder photograph identical to that of  $\beta$ -spodumene taken on material supplied by R. A. Hatch and described by him (1943). The  $\beta$ -spodumene produced by heating bikitaite is an extremely fine aggregate of birefringent crystals with an average refractive index of 1.520. For  $\beta$ -spodumene Hatch gives  $n\text{O} = 1.518\text{--}1.519$ ,  $n\text{E} 1.523\text{--}1.524$ .

## X-RAY STUDY

No crystals of bikitaite are available for morphological study. In fact it was difficult to obtain a crystal fragment large enough to manipulate for single crystal x-ray work. To do this a portion of the eucryptite-bikitaite specimen was coarsely crushed (minus 50-plus 100 mesh), separated in bromoform, and the grains of the material of lesser density examined optically. A grain 0.25 millimeters in maximum dimension and free from eucryptite and quartz was thus selected. Two orientations were effected by the precession method enabling rotation and Wiessenberg photographs to be taken about the  $b$  and  $c$  axes. From these photographs the data in Table 3 were determined.

TABLE 3. UNIT CELL DATA FOR BIKITAITE

Crystal class	Monoclinic prismatic $2/m$
Unit cell dimensions	$a_0$ 8.63, $b_0$ 4.95, $c_0$ 7.64 Å, $\beta=114^\circ34'$ .
Axial ratios	$a_0:b_0:c_0=1.743:1:1.543$
Cell volume	296.8 Å <sup>3</sup>
Space group	$P2_1/m$ .
Formula units per cell	2

The only space group extinctions found were on the 0-level photographs for  $(0k0)$  with  $k=2n$ . The space group is thus  $P2_1/m$ .

The  $d$  spacings of a powder photograph taken with copper radiation are given in Table 4. The intensities of the various lines were obtained by means of a diffractometer.

TABLE 4. X-RAY POWDER SPACING FOR BIKITAITE  
Copper Radiation, Nickel Filter

I	$d$	I	$d$	I	$d$
8	9.21	10	3.40	2	1.900
6	8.04	7	3.29	2	1.895
8	7.84	8	3.22	1	1.855
6	6.95	4	3.08	1	1.615
4	6.84	2	2.93	1	1.610
3	4.39	1	2.87	1	1.565
6	4.30	1	2.79	1	1.535
10	4.19	4	2.53	2	1.465
3	4.08	3	2.52	2	1.432
1	4.03	4	2.475	2	1.350
1	3.91	1	2.320	1	1.345
2	3.82	1	2.045		
10	3.48	1	1.96		

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