THE AMERICAN MINERALOGIST, VOL. 56, SEPTEMBER–OCTOBER, 1971

A SYNTHESIS OF BIKITAITE

D. J. DRYSDALE, *Division of Mineralogy, CSIRO*
Wembley, Western Australia

ABSTRACT

Bikitaite has been synthesized from gels in the Li_2O-Al_2O_3-SiO_2-H_2O system at 2 kbar P_{H_2O}, at temperatures between 300 and 350°C.

INTRODUCTION

Bikitaite, $LiAlSi_2O_6.H_2O$, is a rare mineral of lithium pegmatites. Hurlbut (1957) first described it in association with fine grained granular aggregates of eucryptite and quartz in a lithium pegmatite at Bikita (Rhodesia). The eucryptite appears to replace petalite, and bikitaite is still later, for it is found in small fractures within the eucryptite and fills interstices between quartz and eucryptite grains. Petalite and lepidolite are the chief lithium minerals in this part of the dyke, but spodumene and amblygonite are also present. Good crystals of bikitaite associated with quartz and eucryptite were described from this locality by Hurlbut (1958). The only other recorded occurrence is in a largely unzoned, spodumene rich, pegmatite at King's Mountain, N. Carolina (Leavens, Hurlbut, and Nelen, 1968) where bikitaite and eucryptite occur as bladed single crystals intergrown with quartz, albite apatite, and fairfieldite in small veins in the pegmatite.

Appleman (1960) showed bikitaite has a zeolite structure. Phinney and Stewart (1961) found that natural bikitaite decomposed at 390°C under 1 to 4 kbar P_{H_2O} to eucryptite+petalite, but noted that β eucryptite and β spodumene solid solutions readily formed metastably. The only reported synthesis of bikitaite is by Hoss and Roy (1960) from lithium exchanged gmelinite at 250°C under 1kbar water pressure.

EXPERIMENTAL

The experiments described below synthesized bikitaite at temperatures between 300° and 350°C, with P_{H_2O} from 1 to 2.5 kbar, all within the stability field found for natural bikitaite by Phinney and Stewart (1961).

All the synthesis have been made in sealed gold capsules approximately 2 cms long×5 mm bore, in externally heated, cold seal test tube pressure vessels. Temperatures were measured at thermocouple wells in the vessels beside the charges and are considered accurate to ±10°C; pressures were measured on Bourdon gauges rated accurate to ±50 bars. In all runs the vessels were brought up to pressure cold, then heated to run temperature in about twenty minutes. Quenching by air blast cooled the vessels to below 100°C in less than one minute. All phase identifications were made by X-ray diffraction.

A variety of starting materials were used, as it seemed desirable to approach equilibrium along as many routes as possible in view of the importance of metastability effects noted by Phinney and Stewart (1961). However, at the low temperatures of the experiments

glasses, chemical mixes, and kaolin based materials reacted very slowly and were prone to form non-equilibrium assemblages. Their use was soon abandoned, and gels were used for most runs.

Some gels were made by the organic silicate nitrate method of Roy (1956). Others were made by dropwise addition of aluminium nitrate solution to a clear solution of lithium silicate prepared by dissolving finely ground (<44 μm) silica gel in 2 N LiOH solution. As the pH of the solution falls, gelatinous silica coprecipitates with $Al(OH)_3$, and when sufficient nitrate solution has been added to give the desired Al:Si ratio the suspension is made alkaline with a slight excess of ammonia to ensure precipitation of all the Al as $Al(OH)_3$. Excess ammonia is removed on a steam bath, and the gel is filtered off and washed free of lithium and ammonium salts on a Buchner funnel. (The gel at this stage can be dried to a crumbly white powder amorphous to X-rays.) The gel is then re-dispersed in a solution of LiOH or Li_2CO_3 containing sufficient Li to produce the desired Li:Al:Si ratio, and the suspension evaporated to dryness, forming a very finely divided lithium aluminium silicate gel. This was dried in air at 105°C. Compositions were checked by analysis of several of the gels. Bulk compositions were prepared in the range $LiAlSi_2O_6$ to $Li_4AlSi_2O_6$ with constant Al_2O_3 to SiO_2 ratio of 1:4, and in addition one run (480) used a bulk composition corresponding to that of the quartz+spodumene zone in the Tin Mountain pegmatite, Black Hills, South Dakota, U.S.A. (Staatz, Page, Norton, and Wilmarth, 1963).

Results

Runs yielding bikitaite are listed in Table 1.
(Runs noted here are only some of an extensive series carried out during a broader investigation of relationships in spodumene and petalite bearing pegmatites, and relate only to the bikitaite part of this work.) A few charges that should have formed bikitaite did not, suggesting non-equilibrium effects, and runs at 350°C formed much β spodumene in the bikitaite stability field.

None of the gels prepared by Roy's (1956) method yielded bikitaite. Other gels prepared by the method described above but using LiF or Li_2SiO_3 to adjust the lithium content failed to react satisfactorily in the bikitaite temperature stability field.

More alkaline gels, with LiOH, formed another zeolite, Barrer and White's (1951) Species A (Table 2). It is likely that LiOH is more soluble at high temperature and pressure than Li_2CO_3, resulting in higher lithium activity as well as increased alkalinity.

At 400°C a variety of anhydrous lithium aluminosilicates appear—β spodumene, α eucryptite, and petalite, depending on bulk composition of the charge. Many of these are, on the evidence of Phinney and Stewart (1961), nonequilibrium assemblages.

Discussion

The bikitaite synthesis at low temperatures in the Li_2O-Al_2O_3-SiO_2-H_2O system when CO_3^{2-} containing solutions are present accords with its occurrence as a replacement or very late stage hydrothermal mineral

TABLE 1

Syntheses of Bikitaite

All runs were carried out in gold capsules approximately 2 cms long x 5 mm bore, containing 0.1 g to 0.2 g of gel that had been dried at 105 °C in air for several days and stored over silica gel.

Run No.	Bulk Composition	Material	wt % H_2O	Temp °C	Pressure Bars	Duration Days	Product
373	Li_2O Al_2O_3 $4SiO_2$	gel + Li_2CO_3	50%	300	2000	12	Bikitaite
248	" " "	" "	50%	300	1000	6	"
246	$2Li_2O$ Al_2O_3 $4SiO_2$	" "	50%	310	1000	12	"
286	" " "	" "	leaked 25%	300	2000	10	Bikitaite + trace zeolite A
267	" " "	" "	50%	300	2000	14	Bikitaite + trace zeolite A
318	" " "	" "	50%	300	2000	30	Bikitaite + trace zeolite A
309	" " "	" "	leaked	300	2500	28	Bikitaite
287	" " "	" "	leaked	300	2000	28	Bikitaite
273	$3Li_2O$ Al_2O_3 $4SiO_2$	" "	50%	300	2000	3	Bikitaite
307	" " "	" "	50%	300	2000	14	Bikitaite
316	" " "	" "	leaked	300	2000	30	Bikitaite
311	" " "	" "	50%	300	2500	33	Bikitaite + zeolite A
317	$4Li_2O$ Al_2O_3 $4SiO_2$	" "	50%	300	2000	30	Bikitaite
331	$2Li_2O$ Al_2O_3 $4SiO_2$	Kaolin + Li_2CO_3	50%	300	2000	5	Bikitaite

TABLE 1.—*Continued*

Run No.	Bulk Composition	Material	wt % H_2O	Temp °C	Pressure Bars	Duration Days	Product
320	$2Li_2O\ Al_2O_3\ 4SiO_2$	Kaolin + Li_2CO_3		300	2000	6	Bikitaite
312	" " "	gel + Li_2CO_3	leaked	300	2500	30	Bikitaite
480	Tin Mt quartz + spodumene assemblage	" "	50%	300	2000	7	Bikitaite + quartz
247	$2Li_2O\ Al_2O_3\ 4SiO_2$	gel + Li_2CO_3	50%	300	1000	6	Zeolite A + bikitaite
333	$2Li_2O\ Al_2O_3\ 4SiO_2$	Kaolin + Li_2CO_3	50%	350	2000	5	β Spodumene + bikitaite
340	$Li_2O\ Al_2O_3\ 4SiO_2$	" "	50%	350	2000	5	β Spodumene + bikitaite
338	$2Li_2O\ Al_2O_3\ 4SiO_2$	" "	50%	350	2000	5	β Spodumene + bikitaite
258	$2Li_2O\ Al_2O_3\ 4SiO_2$	gel + Li_2CO_3	50%	350	2000	5	β Spodumene + eucryptite + bikitaite

Other runs at 350° yielded β spodumene, sometimes with eucryptite, petalite and zeolite A.

TABLE 2

Synthesis of zeolite species A

Run No.	Bulk Composition	Material	wt % H_2O	Temp °C	Pressure Bars	Duration Days	Product
275	$2Li_2O\ Al_2O_3\ 4SiO_2$	gel + LiOH	10	300	2000	12	zeolite A
274	$2Li_2O\ Al_2O_3\ 4SiO_2$	" "	46	300	2000	11	" "
242	$Li_2O\ Al_2O_3\ 4SiO_2$	" "	10	300	1000	4	" "
243	$Li_2O\ Al_2O_3\ 4SiO_2$	" "	open	300	1000	4	" "
244	$Li_2O\ Al_2O_3\ 4SiO_2$	" "	50	300	1000	6	" "
276	$Li_2O\ Al_2O_3\ 4SiO_2$	" "	50	300	2000	12	" "
277	$Li_2O\ Al_2O_3\ 4SiO_2$	" "	10	300	2000	8	" "
288	$2Li_2O\ Al_2O_3\ 4SiO_2$	gel + Li_2CO_3	leaked	300	2000	30	zeolite A + quartz
257	$2Li_2O\ Al_2O_3\ 4SiO_2$	" "	50	350	1000		β spodumene + zeolite A
332	$2Li_2O\ Al_2O_3\ 4SiO_2$	Kaolin + LiOH	50	300	2000	5	zeolite A + quartz
457	$1Li_2O\ Al_2O_3\ 4SiO_2$	Organic + LiOH	50	300	2000	8	β spodumene + zeolite A

at Bikita and King's Mountain. One cannot be certain that CO_2 or CO_3^{2-} are essential to the formation of bikitaite as in some capsules that leaked bikitaite was formed although the concentration of these components may have been considerably decreased. On the other hand, as noted above, gels with LiF and Li_2SiO_3 added, but without carbonate, failed to produce bikitaite. The production of quartz+bikitaite assemblages from quartz+spodumene core bulk compositions perhaps sets a lower limit to the pressure-temperature field for formation of quartz+spodumene cores. The syntheses reported raise difficulties for Brotzen's (1959) view that presence of CO_3^{2-} keeps silica in a non-crystalline gel form down to 270°C, so explaining the low temperature of crystallization of quartz cores. As Phinney and Stewart (1961) observe, natural spodumene remains unaffected at the pressure and temperature at which bikitaite decomposes, and they suggest that bikitaite is less stable than spodumene under almost all natural pegmatite conditions. On the other hand spodumene has not been reproducibly synthesized hydrothermally and the stability of this mineral plus water relative to bikitaite must still be regarded as uncertain.

References

Appleman, D. E. (1960) The crystal structure of bikitaite, $LiAlSi_2O_6 \cdot H_2O$ [abstr.]: *Acta Crystallogr.* **13,** 1002.

Barrer, R. M., and E. A. D. White (1951) The hydrothermal chemistry of silicates. Part I. Synthetic lithium aluminosilicates. *J. Chem. Soc.* (London) **1951,** 1561–1571.

Brotzen, O. (1959) Outline of mineralization in zoned granitic pegmatites. A qualitative and comparative study. *Geol. Fören. Stockh. Förh.* **81,** 1–98.

Hoss, H., and R. Roy (1960) Zeolite studies III. On natural phillipsite, gismondite, harmotome, chabazite, and gmelinite. *Beitr. Miner. Petrogr.* **7,** 389–408.

Hurlbut, C. S. (1957) Bikitaite, $LiAlSi_2O_6 \cdot H_2O$, a new mineral from Southern Rhodesia. *Amer. Mineral.* **42,** 792–797.

——— (1958) Additional data on bikitaite. *Amer. Mineral.* **43,** 768–770.

Leavens, P. B., C. S. Hurlbut, and J. A. Nelen (1968) Eucryptite and bikitaite from King's Mountain, North Carolina. *Amer. Mineral.* **53,** 1202–1207.

Phinney, W. A., and D. B. Stewart (1960) Some physical properties of bikitaite and its dehydration and decomposition products. *U. S. Geol. Surv. Prof. Pap.* **424,** D353–357.

Roy, R. (1956) Aids in hydrothermal experimentation II. Methods of making mixes for both "dry" and "wet" phase equilibrium studies. *J. Amer. Ceram. Soc.* **39,** 145–6.

Staatz, M. H., L. R. Page, J. J. Norton, and V. R. Wilmarth (1963) Exploration for beryllium at the Helan Beryl, Elkhorn, and Tin Mountain pegmatites, Custer County, South Dakota. *U. S. Geol. Surv. Prof. Pap.* **297-C.**

Manuscript received, November 5, 1970; accepted for publication, March 27, 1971.