

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 ($<44 \mu\text{m}$) silica gel in 2 N LiOH solution. As the pH of the solution falls, gelatinous silica coprecipitates with $\text{Al}(\text{OH})_3$, 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 $\text{Al}(\text{OH})_3$. 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 $\text{LiAlSi}_2\text{O}_6$ to $\text{Li}_4\text{AlSi}_2\text{O}_6$ 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 $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ 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

re carried out in gold capsules approximately 2 cms long x 0.1 g to 0.2 g of gel that had been dried at 105 °C in air dried over silica gel.

Run	Material	wt % H ₂ O	Temp °C	Pressure Bars	Dur D.
02	gel + Li ₂ CO ₃	50%	300	2000	
	" "	50%	300	1000	
02	" "	50%	310	1000	
	" "	leaked 25%	300	2000	
	" "	50%	300	2000	
	" "	50%	300	2000	
	" "	leaked	300	2500	
	" "	leaked	300	2000	
2	" "	50%	300	2000	
	" "	50%	300	2000	
	" "	leaked	300	2000	
	" "	50%	300	2500	
2	" "	50%	300	2000	
2	Kaolin + Li ₂ CO ₃	50%	300	2000	