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SOME ASPECTS OF THE RECOVERY OF LITHIUM FROM SPODUMENE

G. D. White
T. N. McVay

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G. D. White
T. N. McVay, Consultant

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CONTENTS

Summary 1

Introduction 1

Occurrence and Mineralogy of Spodumene 2

Procedure and Equipment 3

Experimental Results and Discussions 3

- Determination of Firing Range 3
- Leached β-Spodumene 5
- Spodumene-CaO Reactions 6
- Thermal Effects of Spodumene-CaO Reactions 8
- Comparison of Spodumene from Different Locations in North America 9

Acknowledgments 11

SOME ASPECTS OF THE RECOVERY OF LITHIUM FROM SPODUMENE

G. D. White T. N. McVay, Consultant

SUMMARY

The mineral spodumene, $LiAlSi_2O_6$, is the chief source of lithium in North America. There are two ways of recovering the lithium: (1) the ore is calcined in order to convert the naturally occurring α-spodumene to β-spodumene, the calcined ore is acid-roasted with sulfuric acid, and then the soluble lithium sulfate formed in the roast is leached out; or (2) the spodumene is calcined with calcium carbonate, the calcined material is leached out, and the lithium is recovered as the soluble hydroxide. As an aid to solving some of the problems associated with these recovery processes, an investigation was launched, with the objectives of determining (1) the firing range for maximum lithium recovery in the acid-roast process, (2) some of the properties of the leached spodumene in the acid-roast process, (3) the reaction products of the calcining operation in the calcium carbonate process, and (4) the thermal effects of the calcining operation in the calcium carbonate process. Also, spodumenes from different geographical locations in North America were compared to determine whether there were any differences in their chemical composition or crystal structure.

The general procedure included the concentration of the spodumene by heavy-liquid separation, preparation of samples, heat treatment, which included either a simple firing in a resistance-heated furnace or differential thermal analysis firings, and phase identification by x-ray diffraction or petrographic microscope.

Data taken from calcining experiments in which the time at temperature was controlled and from pyrometric cone firings of spodumene-feldspar mixtures indicated a minimum temperature for complete inversion of the spodumene of between 1000 and 1050°C and a minimum temperature for glass formation, which lowers lithium recovery, of approximately 1175°C.

X-ray diffraction data indicated the leached β-spodumene to be a slightly different crystalline compound from β-spodumene. Data obtained also indicated that in basic slurry the β-spodumene resorbs part of the lithium, thus preventing complete lithium recovery.

Compositions of spodumene and calcium carbonate similar to the composition used in the commercial recovery process produced, when fired, reaction products which could have been predicted from the CaO-Al_2O_3-SiO_2 phase equilibrium diagram even though equilibrium was not attained. On the basis of leaching experiments the indications were that the lithium oxide had reacted with aluminum oxide to form soluble $LiAlO_2$.

In the calcining of the spodumene–calcium carbonate commercial composition, the proximity of the temperature ranges, as determined by differential thermal analysis, for the decomposition of calcium carbonate, which requires the input of a large quantity of heat, and for the formation of dicalcium silicate, which gives off a large amount of heat, would cause temperature control in the calcining operation to be very difficult.

INTRODUCTION

The mineral spodumene is the chief source of lithium in North America. It has the ideal formula $Li_2O{\cdot}Al_2O_3{\cdot}4SiO_2$ or $LiAlSi_2O_6$. The lithium is extracted chemically after the ore is calcined for conversion of the naturally occurring α-spodumene to the β-spodumene. It was of interest to investigate some of the problems associated with the lithium production processes.

Two patented processes are used for recovery of the lithium. One is an acid leach process in which the crude ore is calcined to convert the spodumene to the beta form. The inversion is accompanied by severe decrepitation, which leaves the spodumene very finely pulverized and thus facilitates the removal of the lithium. The calcined ore is heated with H_2SO_4 to approximately 250°C, and then water and $CaCO_3$ are added. The soluble $Li_2SO_4{\cdot}H_2O$ formed in the acid roast is decanted with the supernatant liquid.

The recovery of lithium in the acid-roast process was lower than had been expected; it was thought that improper calcining of the raw ore was partly responsible for the low recovery. Determination of the firing range of the crude spodumene ore which allows maximum lithium recovery was one of the objectives of this investigation. A study

was also made of the acid roast and subsequent leaching operation to determine whether lithium was being retained in the residue.

In the second process, limestone and spodumene concentrates are mixed and calcined. The spodumene again inverts accompanied by decrepitation, the $CaCO_3$ is decomposed, and, ideally, part of the resulting CaO reacts with the SiO_2 in the spodumene to form $2CaO{\cdot}SiO_2$ or $3CaO{\cdot}SiO_2$ and the Al_2O_3 reacts with the Li_2O to form $LiAlO_2$. The calcined material is leached with water, LiOH coming off in solution. Since knowledge of reaction products actually obtained in the calcining was desirable for maximum recovery of lithium, a study of the reaction of CaO and spodumene was included in the investigation at ORNL. Differential thermal analyses on CaO-spodumene mixtures were made for obtaining information on the energy relations during the heating cycle needed for controlling temperature during the calcining operation.

In addition to these investigations with direct application, a comparison on the basis of mineralogy, thermal behavior, and composition of spodumenes from five different locations in North America is presented in the report.

General procedure for the investigations could be divided into sample preparation, heat treatment, and phase identification. Concentrated samples of the spodumenes were prepared by heavy-liquid separation. The various compositions for determinations were heated in electric resistance furnaces. Phase identifications were made with a polarizing microscope and a Geiger counter x-ray diffractometer. Differential thermal and thermogravimetric analysis curves were used to obtain information on thermal effects and behavior.

OCCURRENCE AND MINERALOGY OF SPODUMENE

Spodumene occurs in pegmatites associated with quartz, feldspar, and mica and, sometimes, rarer minerals such as cassiterite and monazite. Since a pegmatite was the final part of a magma to solidify, the spodumene crystallized under very high pressure in the presence of gases, particularly water vapor. This probably accounts for the coarse crystalline nature of the spodumene and the other minerals in pegmatites.

Geographically, spodumene occurs in deposits of commercial value in North Carolina, South Dakota, and Quebec. It also is found in Maine, Massachusetts, Connecticut, and California.

Structurally, as determined by Warren and Biscoe,[1] spodumene is a chain silicate, the silica being present in the form of tetrahedra. Each silicon atom is surrounded by four oxygen atoms, which are situated at the corners of a tetrahedron. Two of the oxygens of each tetrahedron are shared, one with each of the two adjacent tetrahedra, thereby forming infinite chains. The silica chains are parallel, with the vertices of the tetrahedra pointing alternately in opposite directions. In the two directions normal to their lengths the chains are held together by oxygen-cation bonds, the cations being Li^+ and Al^{+++}. Both the Li^+ and the Al^{+++} have 8-fold coordination.

In *Dana's Textbook of Mineralogy*[2] spodumene is classed in the monoclinic section of the pyroxene group of minerals. Optically, it is biaxial and positive. The optic plane is parallel to 010 with an optic angle of 54 to 69 deg. The indices of refraction according to Winchell[3] lie between 1.65 and 1.68. The deeply colored varieties show strong pleochroism.

Hand specimens are described[2] as varying in color from greenish white to an emerald green. They are brittle, with a hardness of 7 on Mohs' scale, and have an uneven to subconchoidal fracture. Cleavage is parallel to the 110 and 100 faces.

On heating, spodumene inverts from the naturally occurring alpha form to the beta form. The inversion is accompanied by a large decrease in density, which accounts for the severe decrepitation. Winchell[3] gives the densities for the alpha and beta forms as 3.14 g/cc and 2.41 g/cc, respectively. The reported temperature of inversion, determined in air at atmospheric pressure, varies, the lowest being 690°C and the highest, 950°C. With these conditions the inversion is irreversible. Roy, Roy, and Osborn,[4] who conducted hydrothermal experiments, concluded that the inversion is reversible at 500°C and 10,000 psi in the presence of water; crystals of β-spodumene grown under these conditions were ditetragonal dipyramids approximately 0.1 mm in length and

[1] B. E. Warren and J. Biscoe, *Z. Krist.* 80, 391 (1931).

[2] W. E. Ford (ed.), *Dana's Textbook of Mineralogy*, 4th ed., Wiley, New York, 1932.

[3] N. H. Winchell and A. N. Winchell, *Elements of Optical Mineralogy, Part II, Description of Minerals*, 4th ed., Wiley, New York, 1951.

[4] R. Roy, D. M. Roy, and E. F. Osborn, *J. Am. Ceram. Soc.* 33, 152–159 (1950).

were uniaxial positive with $O = 1.516$ to 1.518 and $E = 1.522$ to 1.523.

PROCEDURE AND EQUIPMENT

A heavy-liquid technique was used to concentrate the spodumene samples. Even the large, apparently pure, crystals of spodumene contained quartz and feldspar inclusions; therefore it was necessary for the samples to be concentrated. Concentration was accomplished by the crystals or specimens being crushed and then sized with sieves in order for a −100 +325 mesh fraction to be obtained. The required fraction was agitated in a separatory funnel with acetylene tetrabromide, which has a specific gravity of 2.94. The quartz and feldspar float, but the spodumene sinks and can be drained at the bottom of the funnel. By repeating this procedure, a sample of better than 98% spodumene was obtained. A cleaner separation was impossible because of the interlocking of the quartz and feldspar with the spodumene even in the small grains. The concentrates were washed with benzene to remove the acetylene tetrabromide.

The samples were fired in Nichrome or Globar furnaces, depending upon the maximum temperature desired. The temperature was controlled only at maximum temperature. During firing, samples were contained in either porcelain or platinum, again depending on temperature of firing. Some of the compositions began to melt at as low as 1100°C; platinum was used to contain these samples.

Phases were identified by means of x-ray diffraction and by use of a petrographic microscope. Samples for x-ray identification were ground to pass a 325-mesh sieve and were packed into plastic sample holders. X-ray diffraction patterns were obtained at a scanning rate of 1 deg/min on a Geiger counter x-ray diffractometer with filtered copper K radiation. Identifying interplanar spacings were taken from the ASTM card file or were established by an x-ray diffraction pattern taken of a pure sample. Standard powdered-sample petrographic methods were used. Optical data used for the various phases were taken from various sources.[3–6]

[5]E. S. Larsen and H. Berman, "The Microscopic Determination of the Non-Opaque Minerals," *U.S. Geol. Survey Bull.* 848, 2d ed. (1934).

[6]A. N. Winchell, *The Microscopic Character of Artificial Inorganic Solid Substances or Artificial Minerals*, 2d ed., Wiley, New York, 1931.

When possible, samples to be run on the differential thermal analysis apparatus were sized to −100 +325 mesh. The samples were contained in platinum cups during the runs. The apparatus used is similar to the differential thermal and thermogravimetric apparatus designed at the National Bureau of Standards in Washington, D.C. The differential couple current is recorded on the vertical or y axis of an X-Y recorder, and the temperature is recorded on the horizontal or x axis. Platinum–platinum–10% rhodium couples are used for both measurements. Aluminum oxide is used as an inert standard in which one leg of the differential couple is embedded; a second cup of aluminum oxide is used to contain the couple for measuring temperature. The continuous weight-recording device, a modified analytical balance, is kept in balance electrically by means of a solenoid and magnet. The operation is made automatic by reflection of a beam of light from the balance beam into a dual phototube in a bridge circuit and amplification of the output of the bridge to provide current in the solenoid. Recording the voltage drop across a resistor in series with the solenoid gives a linear weight scale which can be made to read directly in milligrams.

EXPERIMENTAL RESULTS AND DISCUSSIONS

Determination of Firing Range

Concentrated samples of α-spodumene from the deposit at Kings Mountain, North Carolina, were fired in porcelain crucibles, inserted in a platinum-wound furnace, at five temperatures between 900 and 1050°C and held at temperature for varying periods. The rate of temperature rise was approximately 200°C per hour for all samples. After the samples were fired, they were examined by x-ray diffraction and with a petrographic microscope for determination of the degree of inversion.

Artificial mixtures of β-spodumene and microcline, a potash feldspar, were prepared for fusion tests. Concentrated α-spodumene from Kings Mountain was fired for 1 hr at 1050°C to convert all of the α-spodumene to the beta form. The microcline, which was furnished by the United States Bureau of Mines station at University, Alabama, was prepared by flotation from selected crystals of microcline from the crude Kings Mountain ore. The concentrated material contained approximately 30% quartz. The β-spodumene and microcline were mixed in compositions

varying from 0 to 100% β-spodumene and from 100 to 0% microcline at increments of 10%. The mixtures were formed into pyrometric cones, with dextrin used as a binder. The cones were prefired at 800°C and then set in cone plaques for the fusion test. Temperature rise during the test was 4°C per minute beginning at 800°C. The temperature at which the tip of the cone touched the plaque after deformation due to fusion was taken as the deformation point.

The temperature, time at temperature, and results of the time-temperature tests for the inversion of α-spodumene are given in Table 1.

The deformation temperatures for the β-spodumene–microcline preparations and the ratio in which they were used are given below:

β-Spodumene (%)	Microcline (%)	Cone Deformation Temperature (°C)
90	10	1330
80	20	1310
70	30	1280
60	40	1225
50	50	1225
40	60	1185
30	70	1175
20	80	1175
10	90	1210
0	100	1280

These temperatures cannot be considered as melting temperatures; they are the temperatures at which enough liquid phase is present for the cones to deform to such an extent that their tips touch the plaque. Except for the preparations made up of 100% spodumene or microcline, the compositions do not have true melting points but have, instead, a range of temperatures where liquid and solid exist in equilibrium.

The ideal firing range of the crude Kings Mountain ore for best lithium recovery by means of an acid leach process would be between the minimum temperature for complete spodumene inversion and the minimum temperature for glass formation. In leaching tests run by the Fundamental Study Group of the Y-12 Development Department, it was found that lithium recovery decreased with the formation of glass in the calcined crude ore. This would indicate that lithium is one of the components of the glass. In the cone deformation test the compositions with 70 and 80% microcline had the lowest deformation temperature, 1175°C. At this temperature, however, a considerable amount of glass had already formed; therefore, the temperature at which glass first began to form must be somewhat lower.

Minimum temperature for complete inversion of the Kings Mountain concentrated spodumene held at temperature for 1 hr or less was between 1000 and 1050°C, as shown in Table 1. A differential thermal analysis tracing on a synthetic mixture which approximated the composition of the crude ore indicated that the presence of microcline had no appreciable effect on the temperature or rate of inversion of the spodumene. Thus the data indicate that the firing range of spodumene which

Table 1. Time and Temperature Data for Spodumene Inversion

Temperature (°C)	Time at Temperature (hr)	Results
800	240	No β-spodumene
850	240	Trace of β-spodumene
900	24	Not completely inverted
	3	Beginning to invert
950	24	Completely inverted
	3	Trace of α-spodumene
1000	1	Not completely inverted
	3	Completely inverted
1030	Furnace shut down when temperature was reached	Small amount not inverted
1050	Furnace shut down when temperature was reached	Completely inverted

would allow best recovery is between 1000 and 1175°C. Such a small firing range would be difficult, if not impossible, to maintain in a rotary kiln.

Leached β-Spodumene Properties

A concentrated sample of α-spodumene was converted to β-spodumene by heating for 1 hr at 1050°C. Concentrated sulfuric acid was added to the β-spodumene in a ratio of 3 cc of acid to 5 g of spodumene. The mixture was heated at 250°C for 1 hr and was then leached with water. The leaching consisted in the acid-roasted material being agitated with water and filtered, and the filtered material being washed several times with water. A sample of the leached material was heated at 95°C in a weak LiOH solution. Differential thermal analysis curves and x-ray diffraction tracings were obtained for the β-spodumene, leached β-spodumene, and leached β-spodumene which had been reactivated by the LiOH treatment. In addition, x-ray diffraction tracings were taken on the leached β-spodumene which had been reactivated and heated to 1080°C and on the leached β-spodumene which had been heated to 1070°C.

Leaching experiments done by the Fundamental Study Group of the Y-12 Development Department indicated that, if the pH of the leaching slurry in the acid-roast process is not maintained on the acid side, the lithium will be resorbed partially and will go out with the tailings. The experiments reported here were done to determine what happens to the lithium in the process.

In Table 2 the interplanar spacings and relative intensities are listed for β-spodumene, leached β-spodumene, leached β-spodumene which had been treated with LiOH solution, and leached β-spodumene reactivated by the LiOH treatment and then heated to 1100°C. Figure 1 shows differential thermal analysis tracings for leached

Table 2. Interplanar Spacings and Relative Intensities for β-Spodumene and the Leached and LiOH-Treated Samples

β-Spodumene		Leached β-Spodumene		Leached Reactivated β-Spodumene		Leached Reactivated β-Spodumene Heated to 1100°C	
d (Å)	I/I_1	d (Å)	I/I_1	d (Å)	I/I_1	d (Å)	I/I_1
4.68	16	4.54	11	4.60	16	4.58	8
4.51	30	3.83	7	4.50	11	4.11	5
3.91	42	3.69	50	3.90	44	3.87	21
3.85	21	3.47	100	3.72	20	3.47	75
3.48	100	3.15	36	3.47	100	3.15	9
3.16	23	2.49	7	3.15	35	2.89	4
2.648	6	2.31	6	2.344	4	2.699	4
2.299	10	2.26	5	2.301	12	2.553	6
2.259	16	2.17	13	2.259	10	2.287	5
2.111	7	2.11	5	2.181	8	2.211	5
1.940	10	1.90	13	2.115	12	2.132	3
1.885	66	1.88	21	2.095	7	2.104	4
1.740	6	1.69	5	1.937	12	1.926	5
1.698	4	1.66	4	1.886	40	1.874	11
1.650	10	1.65	5	1.831	5	1.642	4
1.544	3	1.58	4	1.694	5	1.530	5
1.481	3	1.57	3	1.658	10	1.447	4
1.415	16	1.49	7	1.645	9		
		1.43	7	1.537	7		
		1.41	4	1.432	9		
				1.406	7		
				1.385	8		

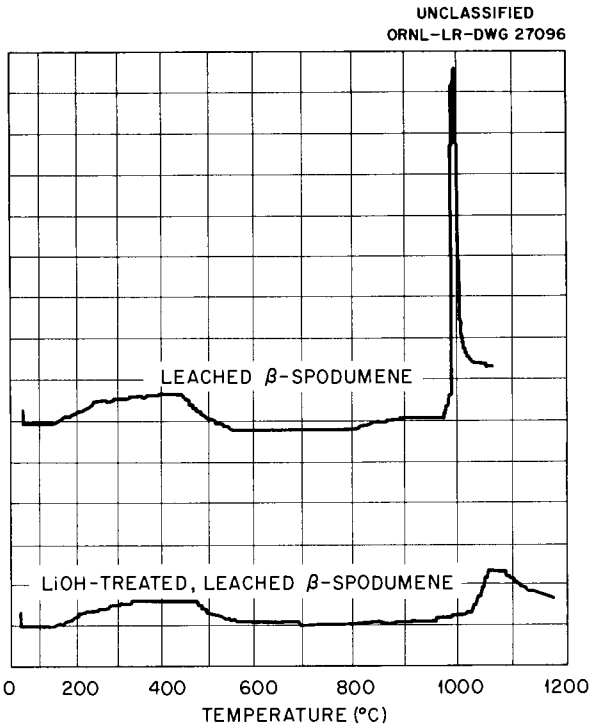

Fig. 1. Differential Thermal Analysis Curves for Leached β-Spodumene and Leached β-Spodumene Treated with LiOH.

β-spodumene and leached β-spodumene which had been treated with LiOH.

These data indicate that a definite change in crystal structure takes place during leaching of the β-spodumene but that, by treating with LiOH under proper conditions, the leached β-spodumene can be reconverted, partially, to a form very similar to the β-spodumene. Although the x-ray diffraction patterns for β-spodumene and leached β-spodumene are similar in having a few common interplanar spacings, there are significant differences in the larger interplanar spacings. In addition, heating of the β-spodumene and of the leached β-spodumene to approximately 1100°C produced entirely different results: the β-spodumene was unchanged, whereas the leached material formed mullite, $3Al_2O_3 \cdot 2SiO_2$, and cristobalite, a high-temperature modification of quartz.

When the leached material was compared with the material which had been leached and treated with LiOH, marked differences between them were revealed, also. The treated material produced an x-ray diffraction pattern with reflections similar to those for β-spodumene as well as to those for the leached structure. Again, more striking differences were apparent in the samples that were heated to approximately 1100°C. As stated above, the leached β-spodumene forms mullite and cristobalite when heated to this temperature, whereas the LiOH-treated material after being heated produced an x-ray pattern which did not contain the reflections characteristic of the heated leached form but did show reflections characteristic of the β-spodumene.

These changes in β-spodumene as a result of leaching and subsequent treatment with LiOH solution suggest an ion exchange in which hydrogen ions replace lithium ions in acid solution and lithium ions, in turn, replace hydrogen ions in basic solutions. Evidently the original lattice sites of the lithium ion in the β-spodumene are filled by the hydrogen ions. This theory is supported somewhat by the fact that some of the interplanar spacings shifted to smaller values when the β-spodumene was given the leaching treatment. Differential thermal analysis, however, does not produce an endothermic effect in the region between 150 and 600°C, where water would be expected to be driven off, but instead shows an exothermic effect. Efforts to index the different structures involved in the changes discussed above were unsuccessful; therefore definite knowledge of unit cell or lattice parameters was not obtained.

Spodumene-CaO Reactions

Concentrated α-spodumene and $CaCO_3$ were mixed in various proportions and pressed into small pellets. The pellets were set on platinum foil and fired for 2 hr each at 100°C intervals from 900 to 1300°C. Mixtures fired consisted of 1 part α-spodumene to 4 parts $CaCO_3$, 2 parts $CaCO_3$, and 1 part $CaCO_3$, respectively. The fired specimens were crushed and put through a 325-mesh sieve. They were examined with a petrographic microscope and by x-ray diffraction for phase determination.

Table 3 lists the reaction products of the mixtures at the various temperatures. All the samples, when they did not melt, contained either CaO or $Ca(OH)_2$ or a combination of the two. The presence or absence of $Ca(OH)_2$ was probably a function of the amount of exposure to air before examination. In none of the samples was spodumene present at 1100°C or above. Gehlenite, $2CaO \cdot Al_2O_3 \cdot SiO_2$, was formed only at 900 and 1000°C in the 4:1

Table 3. Reaction Products of α-Spodumene–$CaCO_3$ Mixtures Fired at Temperatures from 900 to 1300°C for 2 hr

Temperature (°C)	Composition (Parts by Weight)		
	4:1 Mixture	2:1 Mixture	1:1 Mixture
900	β-Spodumene	β-Spodumene	β-Spodumene
	CaO	CaO	CaO
	$Ca(OH)_2$	$Ca(OH)_2$	$Ca(OH)_2$
	$2CaO \cdot Al_2O_3 \cdot SiO_2$	$2CaO \cdot Al_2O_3 \cdot SiO_2$	β-$CaO \cdot SiO_2$
1000	β-Spodumene	β-Spodumene	β-Spodumene
	CaO	CaO	$Ca(OH)_2$
	$2CaO \cdot Al_2O_3 \cdot SiO_2$	$Ca(OH)_2$	β-$CaO \cdot SiO_2$
		$2CaO \cdot Al_2O_3 \cdot SiO_2$	
1100	CaO	$Ca(OH)_2$	Glass
	β-$2CaO \cdot SiO_2$	β-$2CaO \cdot SiO_2$	
		γ-$2CaO \cdot SiO_2$	
		$2CaO \cdot Al_2O_3 \cdot SiO_2$	
1200	CaO	CaO	Glass
	β-$2CaO \cdot SiO_2$	β-$2CaO \cdot SiO_2$	
	γ-$2CaO \cdot SiO_2$	γ-$2CaO \cdot SiO_2$	
		$2CaO \cdot Al_2O_3 \cdot SiO_2$	
1300	CaO	Glass	Glass
	β-$2CaO \cdot SiO_2$		
	γ-$2CaO \cdot SiO_2$		
	$3CaO \cdot SiO_2$		

$CaCO_3$-spodumene mixture. In the 2:1 $CaCO_3$-spodumene mixture, however, gehlenite was formed at all temperatures below the melting point. This behavior can be explained on the basis of the equilibrium phase relations in the CaO-Al_2O_3-SiO_2 system. On the phase diagram the composition of the 2:1 sample lies within the primary phase region for $2CaO \cdot SiO_2$ near the boundary with gehlenite. At 1100 and 1200°C, equilibrium would be more nearly attained; however, the presence of CaO in the composition at these temperatures indicates nonequilibrium. In the 4:1 samples the composition lies near an invariant point where the primary phase regions for CaO, $2CaO \cdot SiO_2$, and $3CaO \cdot SiO_2$ meet. The phases present in the 1300°C sample of the 4:1 composition are the equilibrium phases indicated in the phase diagram when a sample of this composition is cooled from the melting temperature. Samples of the 4:1 composition fired at 1100 and 1200°C contained none of the $3CaO \cdot SiO_2$, indicating that these samples were further from equilibrium than was the sample fired at 1300°C. The $2CaO \cdot Al_2O_3 \cdot SiO_2$ was absent at 1100°C and above as the reaction of the composition approached equilibrium.

Preparations of the 1:1 $CaCO_3$-spodumene mixture fired at 900 and 1000°C contained small amounts of $CaO \cdot SiO_2$ in addition to the CaO and

$Ca(OH)_2$. The CaO-Al_2O_3-SiO_2 composition of these preparations lies within the $CaO{\cdot}SiO_2$ primary phase region of the equilibrium diagram for the system; therefore the reaction products observed are those expected at nonequilibrium.

The samples of 1:1 composition melted at 1100°C and above, indicating a fusing temperature between 1000 and 1100°C. This composition lies near a eutectic in the CaO-Al_2O_3-SiO_2 phase diagram which melts at 1265°C and consists of $2CaO{\cdot}SiO_2$, $3CaO{\cdot}2SiO_2$, and $2CaO{\cdot}Al_2O_3{\cdot}SiO_2$. In addition, the composition contains about 6 wt % Li_2O. The 200°C difference between the fusion points illustrates the very strong fluxing action of Li_2O in aluminum silicate compositions. In the 4:1 and 2:1 compositions the Li_2O likewise must have had some effect on the reactions even though it was present in smaller quantity.

In none of the compositions was a phase containing Li_2O detected. The Li_2O was thought to have reacted with the Al_2O_3 to form $LiAlO_2$; however, none of the samples contained an amount of this compound detectable either by x-ray diffraction or petrographic microscope. To provide some indication of what was happening to the Li_2O, a series of leaching experiments were done. The three spodumene-$CaCO_3$ compositions were prepared and then fired at 1050°C overnight. Each sample was then leached with water and the filtrate analyzed for lithium, aluminum, and calcium. Since filtrates from each of the compositions contained aluminum in addition to the lithium and calcium, there is strong indication that the lithium actually does react with the aluminum to form the soluble $LiAlO_2$.

Lithium compounds are very poor diffractors of x rays; consequently, the absence of diffraction peaks for the lithium compound was expected. Observation of such a compound, even in very small amounts, should have been possible, however, with the petrographic microscope. A lithium compound was not observed; therefore the compound must have been present as very fine crystallites, probably on the surfaces of the other crystalline phases.

Thermal Effects of Spodumene-CaO Reactions

Differential thermal analysis curves were obtained on CaO–β-spodumene, CaO–α-spodumene, and $CaCO_3$–α-spodumene mixtures. The CaO was prepared by heating cp grade $CaCO_3$ at 1000°C; the product was then stored in a desiccator until it was to be used. The spodumene used was concentrated −100 +325 mesh material. The β-spodumene was prepared by heating the concentrate at 1050°C for 30 min. The calcined product was examined petrographically to ensure complete conversion.

The differential thermal analysis curves for the three mixtures are shown in Fig. 2. The endothermic effect between 400 and 500°C shown on the curve for the CaO–β-spodumene mixture probably was associated with the expulsion of water from calcium hydroxide. The strongly exothermic reaction indicated on the same curve

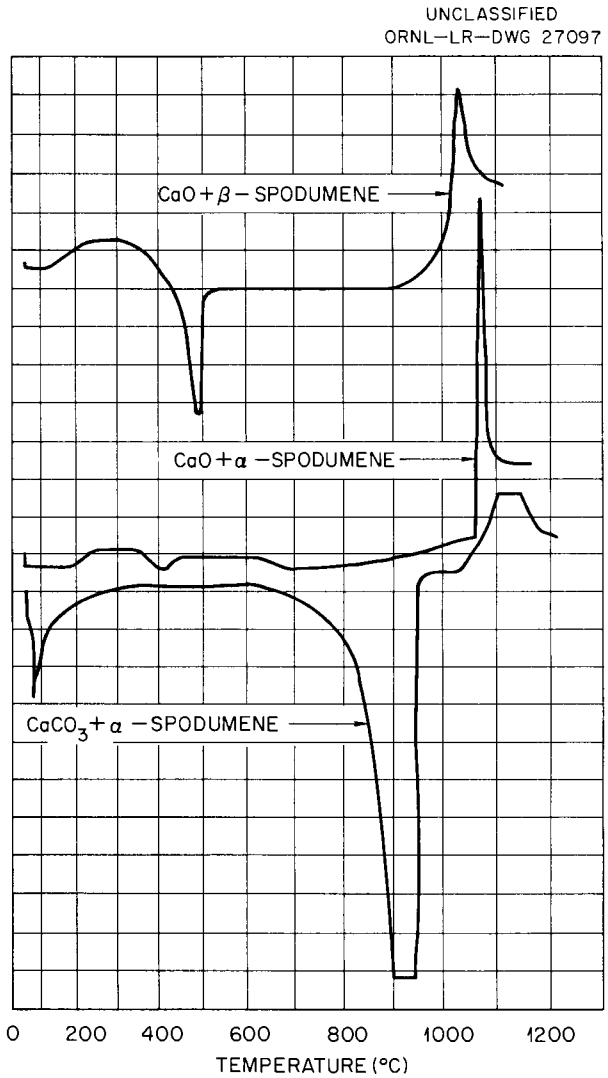

Fig. 2. Differential Thermal Analysis Curves for $CaCO_3$-Spodumene and CaO-Spodumene Mixtures.

between 920 and 1060°C was associated with the formation of dicalcium silicate. Similar thermal effects are shown on the curve for CaO–α-spodumene, except that the initial portion of the exothermic heat effect has been cancelled by the endothermic effect associated with the inversion of α-spodumene.

The thermal analysis curve for $CaCO_3$–α-spodumene illustrates the difficulty of temperature control which arises in the commercial calcination of this mixture. Decomposition of the $CaCO_3$ is strongly endothermic, as shown on the curve in Fig. 2 between 700 and 950°C. The inversion of the α-spodumene and the formation of dicalcium silicate start simultaneously and produce a leveling of the curve from 950 to 1040°C.

Inversion of α-spodumene is complete at 1040°C, but a large amount of heat continues to be given off by the formation of dicalcium silicate. The proximity of the temperature ranges for the decomposition of $CaCO_3$, which requires the input of a large quantity of heat, and for the formation of dicalcium silicate, which produces a large amount of heat, causes temperature control in the calcining operation to be very difficult.

Comparison of Spodumenes from Different Locations in North America

A comparison was made of large crystals of spodumene from North Carolina, South Dakota, Maine, and Quebec, concentrated by the method described in "Procedure and Equipment." Samples of the concentrated spodumene were chemically analyzed for lithium, aluminum, silicon, and iron by the Analytical Chemistry Division of Oak Ridge National Laboratory and spectrographically analyzed by the Spectrographic and Special Samples Laboratory, Technical Division, Y-12.

The chemical analyses and the molecular ratios of $Li_2O:Al_2O_3:SiO_2$ for the spodumenes are given in Table 4. The interlocked impurities observed with the microscope and the impurities revealed by chemical analyses showed correlation to a marked degree. The larger excesses of Al_2O_3 and SiO_2 over the theoretical amounts in the spodumene formula, $Li_2O_3 \cdot Al_2O_3 \cdot 4SiO_2$, are present in the Quebec and North Carolina samples. This reflects on the degree of separation obtainable rather than upon the actual chemical composition of the spodumene. There is nothing in the analyses to indicate any significant differences in chemical composition.

It was of interest that the auxiliary feldspar in the Lithium Corporation of America crude ore contained 1.5% rubidium. This figure was obtained by spectrographic analysis on a hand-picked crystal of the potash feldspar, called "microcline." This would suggest that there is more rubidium in the earth's crust than has normally been reported, because in wet chemistry analyses the rubidium would come out with the potassium and be reported as such.

The interplanar spacings and relative intensities for the various spodumenes are listed in Table 5. At the higher angles the deviation from the interplanar spacing values given was less than 0.05 Å; therefore only the one set of values is given for all five samples. There are large variations in the

Table 4. Chemical Analyses and Molecular Ratios of $Li_2O \cdot Al_2O_3 \cdot SiO_2$ for Six Spodumenes

Source of Sample	Composition (wt %)				Molecular Ratios		
	Li	Al	Si	Fe	Li_2O	Al_2O_3	SiO_2
Quebec	3.30	13.5	29.4	0.90	1	1.05	4.45
South Dakota	3.47	13.8	29.9		1	1.02	4.24
Maine	3.50	14.1	29.5	0.23	1	1.03	4.17
Kings Mountain, N. C.*							
Lincolnton	3.41	13.7	29.9		1	1.03	4.32
Foote Mineral Company	3.10	13.1	29.5		1	1.17	4.68
Lithium Corporotion of America	3.30	14.0	29.2		1	1.08	4.27

*Different mines in the Kings Mountain, N. C., spodumene district.

relative intensities of the reflections among the different spodumenes; however, there is good correlation between the samples with respect to strong-vs-strong and weak-vs-weak reflections. At first, the variations in relative intensities among the samples were thought to be significant. Tests were run to show whether the relative intensities would vary from sample to sample of the same spodumene. A sample was loaded into the holder, an x-ray diffraction tracing taken, the holder then dumped and reloaded, a second tracing taken, etc. This procedure was repeated four times, and the tracings obtained were compared for the variation in reflection intensities. The comparison indicated a strong tendency of the powders to orient preferentially. This is not surprising in view of the two perfect cleavages of the crystalline spodumene. The x-ray data indicate that the different spodumenes examined are identical crystalline minerals with no solid solution detectable.

All the spodumenes had the same optical properties when examined on the petrographic microscope. A large difference in the degree of interlocking between spodumene and quartz and/or feldspar could be detected with the microscope.

Table 5. X-Ray Diffraction Data for α-Spodumene

Interplanar Spacing, d (Å)	Relative Intensity, I/I_1				
	North Carolina		South Dakota	Maine	Quebec
	L.C.A.*	Foote**			
6.07	54	38	71	45	72
4.43	20	20	39	16	26
4.34	7	13	10	10	15
4.19	57	56	76	88	100
3.44	16	20	16	14	13
3.33	7	11	18	3	5
3.18	16	18	27	17	23
3.04	10	5	18	9	21
2.91	59	55	63	60	90
2.854	6	9	8	9	15
2.790	100	100	100	100	100
2.666	17	20	20	17	28
2.450	14	11	14	10	15
2.350	9	11	14	16	15
2.220	6	5	14	5	13
2.144	6	5	8	3	5
2.108	6	7	8	10	13
2.059	10	18	14	12	26
2.032	11	7	12	9	15
1.928	9	11	16	10	23
1.864	16	36	20	22	31
1.846	4	7	6	9	10
1.737	7	9	14	9	10
1.647	6	5	14	9	10
1.566	24	25	37	26	26
1.523	23	7	43	19	36
1.459	10	11	16	14	13
1.398	6	9	8	14	23
1.330	9	16	16	17	10

*Lithium Corporation of America, North Carolina spodumene from Kings Mountain.

**Foote Mineral Company, North Carolina spodumene from Kings Mountain.

The spodumene from Maine was the purest, with very little interlocking or inclusions. The trace amount of impurity present was in the form of discrete grains. The spodumenes from Quebec and North Carolina, however, had considerable interlocking of the impurity with the spodumene; interlocking in the South Dakota spodumene was not present to such an extent.

Differential thermal analysis curves for spodumenes from Maine, South Dakota, Quebec, and North Carolina (Lithium Corporation of America mine) are shown in Fig. 3. These curves indicate that the alpha-to-beta inversion occurs in a range of temperatures around 1000°C. The inversion is endothermic. Conceivably, there is correlation between the temperature range of the inversion of the various spodumenes and the degree of interlocking of the impurities. The range of inversion is highest for the Maine spodumene and lowest for the Quebec. The presence of the interlocked impurity either lowers the temperature of inversion or affects the thermal conductivity of the sample to such an extent that the heat effect is picked up by the couple faster.

Summarizing, it appears that the differences observed in the spodumenes from different localities in North America were a function of the degree of interlocking between the spodumene and the impurities. There is nothing in the data which indicates any definite differences in chemical composition or crystal structure.

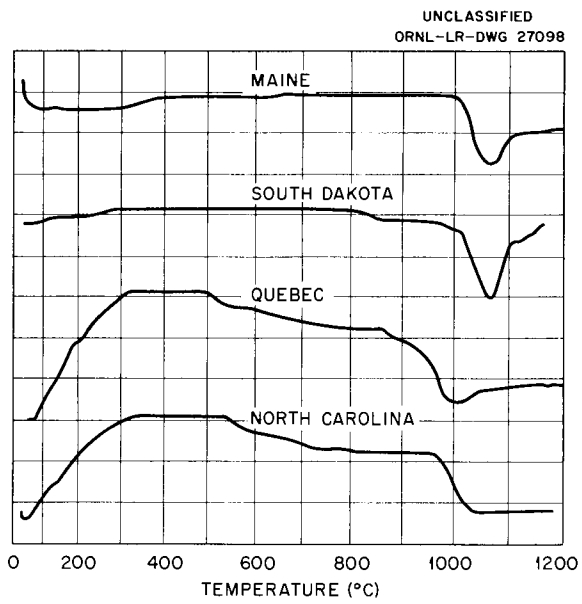

Fig. 3. Typical Differential Thermal Analysis Curves for Spodumene.

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