

## Petrogenesis of lithium-rich pegmatites

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### Abstract

The experimentally determined liquidus of the system  $\text{NaAlSi}_3\text{O}_8(\text{Ab})\text{--SiO}_2(\text{Qz})\text{--LiAlSiO}_4(\text{Eu})\text{--H}_2\text{O}$  at 2 kbar  $P_{\text{H}_2\text{O}}$  has a eutectic near  $\text{Ab}_{34}\text{Qz}_{50}\text{Eu}_{16}$  weight percent at  $640^\circ \pm 10^\circ\text{C}$ . The field boundary of albite and quartz is depressed nearly  $100^\circ\text{C}$  from the  $\text{Ab}\text{--Qz}\text{--H}_2\text{O}$  sideline by saturation in Eu component; the field boundary between albite and lithium minerals varies little in  $\text{Li}_2\text{O}$  content ( $19 \pm 3$  percent Eu) between the eutectic and the  $\text{Ab}\text{--Eu}\text{--H}_2\text{O}$  sideline. Liquidus temperatures rise very steeply as Qz increases in the quartz field. The field boundaries indicate that pegmatite magma will crystallize feldspar and quartz and concentrate lithium in the remaining magma. Similar relations have been observed for the  $\text{Or}\text{--Qz}\text{--Eu}\text{--H}_2\text{O}$  system by Munoz (1971). Petalite will form if the field boundary is reached at high temperatures and low pressures; spodumene forms at lower temperatures and higher pressures.

The bulk compositions of natural homogeneous Li-rich pegmatites plot on a diagram for the system  $(\text{Or},\text{Ab})\text{--Qz}\text{--Eu}\text{--H}_2\text{O}$  in the thermal minimum or slightly toward  $(\text{Or},\text{Ab})$  from it. The geologic abundance and similarities of these bulk compositions together with the experimental data support a magmatic origin of homogeneous Li-rich pegmatites. Li-rich magma probably forms by partial melting of Li-bearing metasediments at temperatures  $75^\circ\text{C}$  or more below the minimum melting temperature at the same  $P_{\text{H}_2\text{O}}$  of the simplified "granite" system  $\text{KAlSi}_3\text{O}_8\text{--NaAlSi}_3\text{O}_8\text{--SiO}_2\text{--H}_2\text{O}$ . An origin by anatexis is most consistent with the irregular distribution of Li-rich pegmatites close to the sillimanite isograd but farthest of all pegmatite varieties from granites related to the same thermal event. The sparsity of Li-rich pegmatite bodies within related granites is also in accord with an anatectic origin: further heating in the source area would yield larger amounts of granitic rock and dilute the Li content to the normal  $<100$  ppm.

Magmatic differentiation adequately explains the sequence of zones in zoned pegmatites, including the abrupt appearance of lithium minerals in quantity and the observed limit on the abundance of lithium minerals in common natural bulk compositions. The occurrence of petalite or spodumene cannot be related to bulk composition, as all Li-pegmatite falls compositionally into the alkali feldspar-quartz-petalite volume. The high temperature-low pressure assemblage isochemically equivalent to zone 5 of Cameron *et al.* (1949) is perthite-plagioclase-petalite-quartz, and to zone 6 is plagioclase-petalite-quartz. These zones seem to be the last that can reasonably be interpreted to have originated from molten silicate magma.

Gases more siliceous than coexisting lithium aluminum silicate minerals were experimentally studied at  $75^\circ\text{C}$  and 2 kbar  $P_{\text{H}_2\text{O}}$ . Precipitation of the solids from such gases would yield compositions like those of silica-rich pegmatite zones. Compositions that could have formed from gas have quartz  $>$  feldspar. Eucryptite probably forms solely in the presence of such gases.

### Introduction

Geological mapping has proved the existence of regional compositional zoning of pegmatites adjacent to related granitic bodies (Mulligan, 1962, p. 420; Norton, 1975, p. 135–140). Li-rich pegmatites occur farthest from the granite, and constitute only one

percent at most of the mass or number of pegmatites present. The Li-rich pegmatites occur immediately adjacent to or in sillimanite-grade metamorphic rocks, but not within related granites. If Li-rich magma formed the Li-rich pegmatites, it could originate by anatexis of Li-bearing metasediments or by

very extensive differentiation of granitic magma. Deposition from gases emanating from the crystallizing magma has also been hypothesized. In this paper, geological evidence will be combined with data from experimental petrology to elucidate the processes involved in the petrogenesis of Li-rich pegmatite.

Pegmatites may be either homogeneous or internally zoned. The sequence of 11 mineral assemblages in zoned pegmatites reported by Cameron *et al.* (1949, p. 61) is still regarded as essentially correct. The minerals of these assemblages are generally named in decreasing order of the abundance of the minerals, and the sequence of the assemblages is from the contact with the country rock to the center or core of the pegmatite. Not all assemblages occur in all pegmatites or even in all pegmatite districts. Crystallization proceeded from the country rock contact inward because no outer assemblage cuts an inner assemblage, but inner assemblages do cut outer assemblages. The first four assemblages are feldspar-rich and differ from granite only in the ratio of one feldspar to another and in the abundance of muscovite. Where muscovite is abundant, potassic feldspar (perthite) is ordinarily absent or sparse. These first assemblages may be richer in  $Al_2O_3$  than many granites and may have reacted with country rock or lost alkalis to it, but the data are skimpy. Lithium minerals do not become a major component until assemblage 5, but persist through assemblages 5 to 8. The content of quartz increases in these assemblages, and quartz first becomes dominant in assemblage 7. The core commonly is almost entirely quartz.

The phase petrology of granitic magmas is reasonably well understood because of an extensive collection of geological and experimental evidence (reviewed in Luth, 1976). Granitic magma contains more normative feldspar components than normative quartz over the whole range of its probable composition. Silica (quartz) in the presence of steam always melts at a temperature hundreds of degrees higher than the melting temperature of the mixtures of feldspar components and silica found in granitic magma, which suggests that either the quartz core did not form from a magma or the magma contained components that were deposited elsewhere in the pegmatite, possibly in the mica-rich zones bordering the core. A thorough discussion of the complexities of the crystallization of hydrous pegmatitic magma, with emphasis on textural development, is given by Jahns and Burnham (1969). Subsolvus reactions are also common in pegmatites, and particular attention to this phenomenon in lithium-rich pegmatite was

given by Stewart (1960, p. 28) and Munoz (1971). A question specifically addressed in this paper will be whether or not lithium-rich zones are the last to have a composition that could have formed from a magma or are the first to form largely from gas.

Clearly the magma that formed each assemblage need not have the same bulk composition as the mass of crystals precipitated to form that particular zone. The crystals could have accumulated from a melt of much different composition, and not all the phases at a single place necessarily precipitated at the same time.

#### The composition of lithium-rich pegmatite and the distribution of lithium minerals in it

Numerous estimates of the bulk compositions of individual pegmatites have become available since the late 1940's. Estimates for simple granitic pegmatites are most numerous, and a few tens of estimates are for the bulk compositions of lithium-rich pegmatites, many of which are homogeneous. Only a few estimates are available for the bulk compositions of zoned pegmatites and for their individual zones. Estimates are reported in various terms, such as visual or measured modes, weighed mineral separates, or partial or complete chemical analyses. These different kinds of estimates are not easily compared. In several instances the tonnages and compositions of individual zones have been estimated to calculate the bulk compositions. Such estimates are of particular interest because they permit important portions of the process of differentiation to be discussed, although the reliability of the estimate tends to decrease as the structural complexity increases.

An estimate of the standard error of the estimate of the  $Li_2O$  content of homogeneous lithium-rich pegmatite can be obtained from the exemplary description of the very large Kings Mountain, NC, deposits given by Kesler (1961)<sup>1</sup>. Assays for  $Li_2O$  from 226 core samples, mostly 20 feet long, representative of many million tons of pegmatite are given in his Figure 6. A plot of these analyses shows a normal distribution and only slight skewness toward low values. The mean of the array is 1.53 weight percent  $Li_2O$ , and the standard deviation,  $\sigma$ , is 0.32 percent  $Li_2O$ . Kesler (1961, Table 3) also gave weighted average  $Li_2O$  contents for analyses from 14 cross sections. The mean of the data for these cross sections is 1.54 weight percent  $Li_2O$ , and  $\sigma = 0.15$  percent  $Li_2O$ , or

<sup>1</sup> The distributed reprint of this article contains additional material in Figs. 4 and 6.

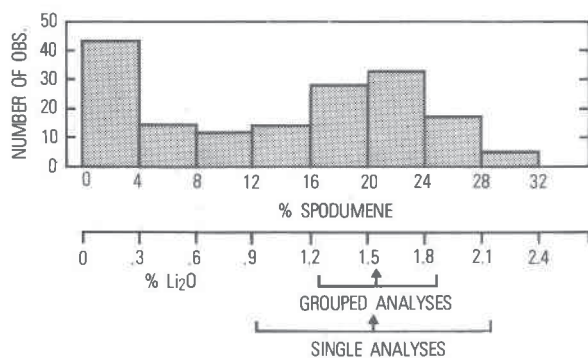


Fig. 1. Distribution of spodumene (weight percent) in 168 pegmatite samples from Kings Mountain (Lovering, 1958) compared to the mean and  $\pm$  two standard deviations of single analyses and grouped analyses from data given by Kesler (1961). The bimodal distribution indicates that most spodumene pegmatites contain 16 to 24 percent spodumene, and a second group of pegmatites contains little or no spodumene.

half the standard deviation for single analyses. Presumably the best approximation of the standard deviation would be that from the grouped analyses for the cross sections, and thus the 95 percent confidence limits ( $2\sigma$ ) for the  $\text{Li}_2\text{O}$  content of this pegmatite mass could be 1.23 and 1.85 percent  $\text{Li}_2\text{O}$ . Kesler reported the weighted average grade of all ore milled from 1954 to 1960 was 1.56 percent  $\text{Li}_2\text{O}$ .

Kesler (1961, Table 1) accounted for the distribution of  $\text{Li}_2\text{O}$  among the principal minerals; 97.6 weight percent of the  $\text{Li}_2\text{O}$  was present in spodumene, which had an average  $\text{Li}_2\text{O}$  content of 7.46 weight

percent as compared to the theoretical 8.04 percent. Using this information, which is rarely available, we can convert the standard deviation in  $\text{Li}_2\text{O}$  to that of spodumene, 4.2 percent spodumene in single samples, or 2.1 percent spodumene in grouped samples. Comparable data for other minerals no doubt would show standard deviations as large. The standard deviation to be attached to estimates less well founded can be larger still, a factor to remember in the comparisons among pegmatites below. The topic is also discussed by Norton and Page (1956) and Norton (1970).

Kesler (1961, Fig. 2 and p. 1066) reported that quartz monzonite pegmatites also occurred at Kings Mountain and that, where these pegmatites adjoin spodumene-rich pegmatite, their quartz and feldspars are coextensive and presumably are contemporaneous.

Modal data for 168 samples of homogeneous pegmatite in the Kings Mountain district gathered by W. R. Griffiths were used by T. G. Lovering (1958) as a geologic example of a bimodal distribution, Figure 1. By combining the above estimates of spodumene abundance and 95 percent confidence limits as shown by the figure, the existence of two types of homogeneous pegmatite is shown. One type has a considerable amount of spodumene ( $\sim 20$  percent), and the other has practically none. In addition to information concerning the reliability of various estimates of spodumene content, some explanation is apparently needed for the appearance of so much spodumene, just as is observed within zoned pegmatites. If spodumene pegmatite for economic or other reasons re-

Table 1. Modes of spodumene pegmatites rounded to nearest percent

Locality and Reference	Spodumene (wt. %)	Quartz (wt. %)	$\Sigma$ Alkali Feldspars (wt. %)	Muscovite (wt. %)	Total (wt. %)
Kings Mountain, NC Kesler (1961)	20	32	41	6	99
Kings Mountain, NC Browning, Clemmons, McVay (1961)	18	33	44	5	100
Val D'Or, Quebec Browning, Clemmons, McVay (1961)	21	41	32	6	100
Peg Claims, Maine Sundelius (1963)	22	27	44	7	100
Beardmore, Ontario Milne (1962)	20	30	45	5	100
Mateen Pegmatite, Hill City, SD Browning, Clemmons, McVay (1961)	16	38	36	8	98

Table 2. Modes\*, in percent, Etta pegmatite from Norton *et al.* (1964, Table 5)

Unit	Quartz	Albite	Perthite and microcline	Spodumene	Muscovite	Biotite	Tourmaline
Microcline-biotite pegmatite	10	--	70	--	2	15	3
Quartz-muscovite-albite pegmatite	60	15	2	3	20	--	<1
Perthite-quartz-spodumene pegmatite	25	10	50	10	5	--	--
Quartz-cleavelandite-spodumene pegmatite	35	35	1	25	3	--	--
Quartz-spodumene pegmatite	70	1	3	25	1	--	--
Quartz pegmatite	99	<1	--	<1	<1	--	<1

\* By visual estimates of surface exposures, supplemented by measurements of spodumene content.

quired a grade of about 35 percent to be minable, such a grade would be most unlikely to be attained over any considerable volume of rock in this district.

Estimates of the modes of representative homogeneous or nearly homogeneous Li-rich pegmatites from other areas are given in Table 1, along with the data for Kings Mountain. In general, these compositions also contain traces of other minerals, most notably 0.3-0.4 weight percent beryl. In view of the accuracy of such estimates, there are enough similarities to suggest that something akin to a eutectic composition is involved.

The quartz-cleavelandite-spodumene zone of a famous and structurally simple zoned lithium pegmatite, the Etta spodumene mine, SD, (Table 2; from Norton *et al.*, 1964, p. 316) is the only spodumene-bearing zone that approximates the composition of homogeneous Li-rich pegmatite. Inner zones are quartz-rich, and outer zones are rich in feldspar, mica, or quartz, and the course of magmatic differ-

entiation is not readily interpretable. The bulk compositions of such zoned pegmatites commonly contain half or less the Li<sub>2</sub>O content of the homogeneous Li-rich pegmatites, even though some zones have the same composition as homogeneous Li pegmatites.

Modal data can be utilized with chemical data for each mineral present to yield an estimated chemical composition. Table 3 shows that the calculated bulk compositions of homogeneous spodumene pegmatites and of some petalite pegmatites are similar. In most compositions Na<sub>2</sub>O > K<sub>2</sub>O. The exception in the table, Beardmore, may not be serious in view of the imprecision of such estimates. Li-rich pegmatite contains about 2 weight percent more Al<sub>2</sub>O<sub>3</sub> than Nockolds' (1954) average alkali granite and approximately the 2 weight percent less combined Na<sub>2</sub>O and K<sub>2</sub>O. The narrow range of Li<sub>2</sub>O contents is unlikely to be fortuitous. The appearance of spodumene rather than petalite seems not to be a function of composition, but the two minerals seem antithetic.

Table 3. Major chemical components of some Li-rich pegmatites

Component weight per cent	With Spodumene			With Petalite	
	Kings Mtn., NC Kesler, 1961	Peg Claims, ME Sundelius, 1963	Beardmore, Ont. Milne, 1962	Bikita, Rhod. Gallagher, 1962	Hirvikallio, Finl. Vesasalo, 1959, 2 averaged
SiO <sub>2</sub>	74.6	73.5	76.0	73	73.7
Al <sub>2</sub> O <sub>3</sub>	16.4	16.7	15.9	16	16.9
Na <sub>2</sub> O	3.3	3.4	2.9	4.5	3.1
K <sub>2</sub> O	2.4	2.6	3.3	2	2.9
Li <sub>2</sub> O	1.5	1.4	1.6	1.5	1.8
Σ 5 components	98.2	97.6	99.7	97.0	98.4



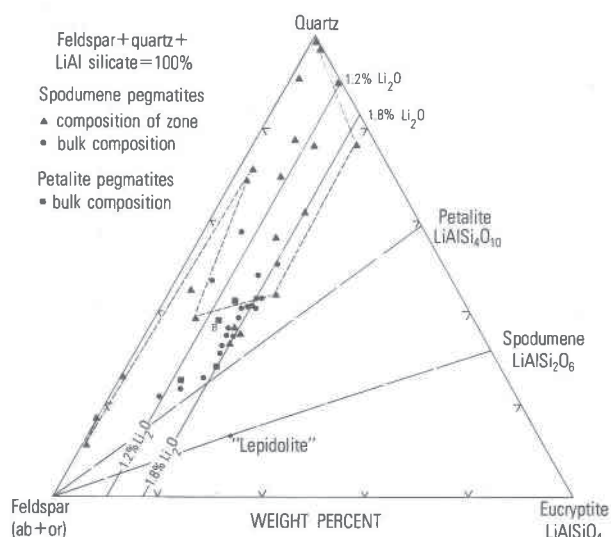


Fig. 2. A plot of the compositions of Li-rich pegmatites recalculated to 100 weight percent combined alkali feldspars, quartz, and eucryptite, ignoring mica and other minor amounts of minerals present. The bulk compositions of homogeneous spodumene pegmatites (Table 1 and other sources) are shown by dots. The bulk compositions of petalite pegmatites (Table 3 and other sources) are shown by squares, that for Bikita being marked with a 'B'. Crosses are used to mark the compositions of individual zones from zoned pegmatites, the suite from the Etta spodumene mine (Table 2) being connected by short dashes. The 95 percent confidence limits for  $\text{Li}_2\text{O}$  in grouped analyses of Kings Mountain spodumene pegmatites are shown by labeled lines. All Li-rich pegmatite compositions, whether homogeneous or not, fall in the triangle feldspar-quartz-petalite.

The modal and chemical information can be usefully compared (Fig. 2) by recalculation to 100 weight percent of combined feldspars, quartz, and a lithium-bearing end member, arbitrarily calculated as eucryptite,  $\text{LiAlSiO}_4$ . Mica has been ignored. Figure 2 shows that all bulk and zone compositions fall within the triangle feldspar-quartz-petalite, demonstrating again that the occurrence of petalite or spodumene is not controlled by compositional differences. Almost all *bulk* compositions contain more feldspar than quartz, but compositions of zones scatter widely, including some very silica-rich compositions which are the only virtually monomineralic zones found. Contours of  $\text{Li}_2\text{O}$  content will be parallel to the feldspar-quartz sideline because the Li content of feldspar and quartz is negligible. The 95 percent confidence limits established earlier for grouped samples of the homogeneous Kings Mountain pegmatite are shown, and almost all the bulk compositions for homogeneous

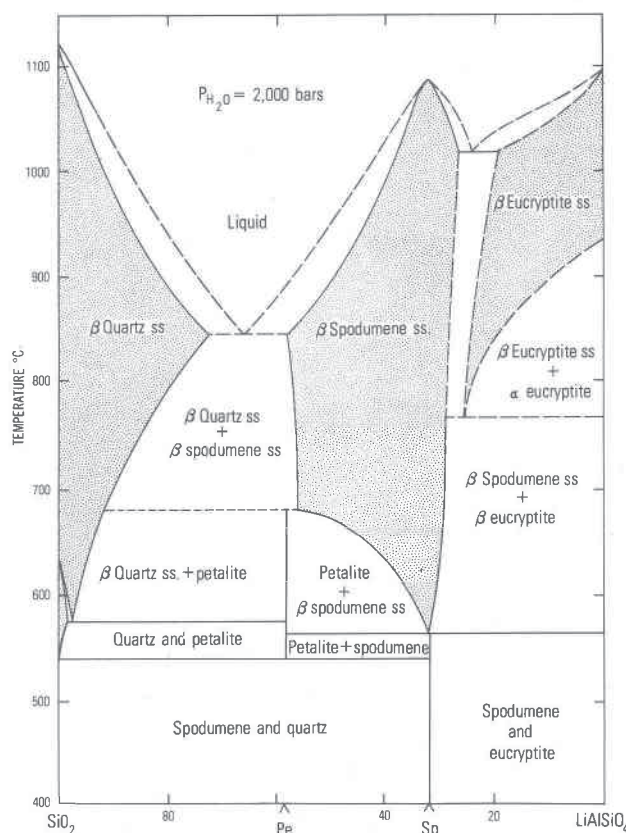


Fig. 3. Tentative  $T$ - $X$  phase diagram for the system Qz-Eu- $\text{H}_2\text{O}$  at 2 kbar  $P_{\text{H}_2\text{O}}$ . Only phase relations below  $840^\circ\text{C}$  have been investigated experimentally. All natural pegmatite compositions project onto this sideline between Qz and Pe compositions. Note the limited temperature interval for the stability of petalite.

pegmatites fall within these limits. Zones of several zoned pegmatites correspond in composition to homogeneous lithium-rich pegmatites, but many strongly zoned pegmatites contain very siliceous zones (commonly fracture fillings or small zones) that also contain lithium minerals. The sequence of inner zones in the Etta pegmatite shows both types of zones.

The foregoing chemical evidence can be summarized briefly before seeking explanations from experimental petrology:

1. Many Li-rich pegmatites have almost the same composition. They contain more feldspar than quartz and approximately 1.5 weight percent  $\text{Li}_2\text{O}$ .
2. The occurrence of particular lithium minerals is not controlled by differences of bulk composition, because all compositions fall in a narrow range within the triangle feldspar-quartz-petalite.
3. Some mechanism exists that can produce a bi-

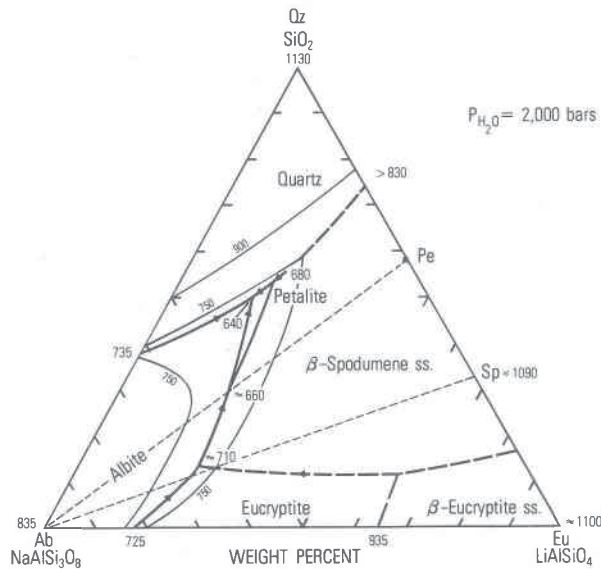


Fig. 4. Liquidus of the system Ab-Qz-Eu-H<sub>2</sub>O at  $P_{H_2O} = 2$  kbar. Temperature in °C.

modal distribution of compositions of homogeneous pegmatites such that a substantial amount of lithium mineral(s) appears where any is present, and yet the total amount that can be present is limited.

4. The sequence of zones from country rock inward appears to be from plagioclase-quartz-muscovite compositions through compositions with K-feldspars to lithium-rich compositions and finally to silica-rich compositions. The silica-rich compositions are distinctive, may contain lithium minerals, and must be accounted for.

5. Some internal zones in zoned pegmatites correspond to lithium-rich homogeneous pegmatite, but many zoned pegmatites contain silica-rich inner zones that lack equivalents among homogeneous pegmatites.

#### Experimental petrology

Because pegmatitic lithium minerals occur with quartz, alkali feldspars, micas, and little else, part of the system H<sub>2</sub>O-Li<sub>2</sub>O-K<sub>2</sub>O-Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> would describe such assemblages. However, simplifying assumptions are needed to make an experimental study practical. Sodic feldspar is almost twice as abundant as potassic feldspar in Li-rich pegmatites, and the selection of NaAlSi<sub>3</sub>O<sub>8</sub>(Ab) as the feldspar component avoids the complexity caused by the appearance of lithium mica (Munoz, 1971) and of leucite. The CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>(An) content of natural albite is 1 to 3 percent and has been ignored. SiO<sub>2</sub> (Qz) is taken as a

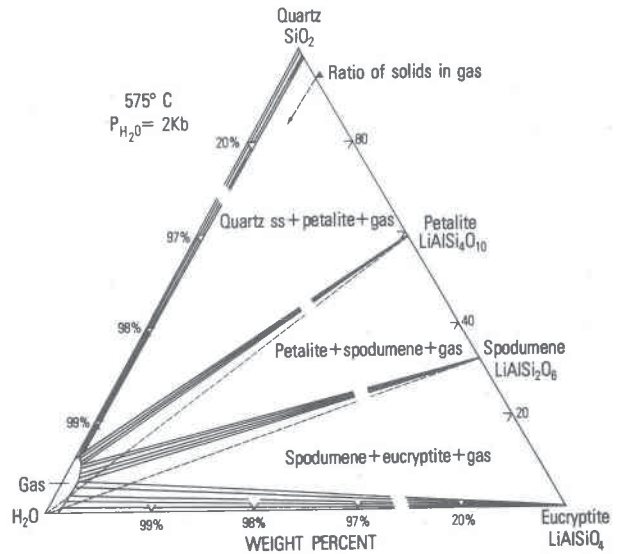


Fig. 5. Schematic representation of the compositions of the gases that coexist with lithium minerals or quartz at 575° and  $P_{H_2O} = 2$  kbar. The gases are more siliceous than the coexisting lithium minerals. For natural compositions that project to between quartz and petalite composition, the ratio of solids that could precipitate from the gas is shown. This composition is like that found in some complexly-zoned pegmatites (Fig. 2).

component along with LiAlSiO<sub>4</sub> (Eu) to describe the principal lithium minerals except lithium micas. Consideration of the excess Al<sub>2</sub>O<sub>3</sub> required to form muscovite is omitted to avoid anticipated complexities (Luth, 1976, p. 369-372). Shaw (1963) studied the four-phase curve K-feldspar-quartz-liquid-gas and determined that only small amounts of Al<sub>2</sub>O<sub>3</sub> (equivalent to about 3 percent muscovite) could be dissolved in the silicate liquid. This amount of Al<sub>2</sub>O<sub>3</sub> depressed the liquidus 20 to 30°C at 2 kbar (U. S. Geological Survey, 1961, p. 74).

Either higher pressures or the presence of Ab component causes greater solution of Al<sub>2</sub>O<sub>3</sub>. The pegmatites tabulated in Table 1 contain 5 to 8 weight percent muscovite. J. J. Norton (personal communication, 1978) found a median of 8 weight percent muscovite in pegmatitic Harney Peak granite, SD. Huang and Wyllie (1973, p. 3) produced a homogeneous melt from a sample of Harney Peak granite containing 13.8 weight percent muscovite (and plagioclase with An 5.1), and found that its solidus with excess H<sub>2</sub>O was identical within the limits of experimental error with that for the system Ab-Or-Qz-H<sub>2</sub>O.

Liquidus temperatures for the system Ab-Qz-Eu-H<sub>2</sub>O would also be lowered by the addition of

$\text{KAlSi}_3\text{O}_8$  (Or) component. Further depressions of 35–70°C are anticipated depending on the Or content, as estimated by comparison of the temperature of the four-phase assemblage albite–quartz–liquid–gas with the alkali feldspar–quartz–liquid–gas boundary curve in the system Or–Ab–Qz–H<sub>2</sub>O at constant H<sub>2</sub>O pressure (Tuttle and Bowen, 1958) and Ab:Or  $\approx$  2:1.

A constant H<sub>2</sub>O pressure of 2 kbar was chosen for convenience and because alkali feldspar in Li-rich pegmatites crystallizes as two separate minerals, implying substantial depression of liquidus temperatures by moderate to high H<sub>2</sub>O pressure. All experiments were performed at saturation with H<sub>2</sub>O, but this condition may not occur throughout crystallization in nature.

The Eu–Ab–H<sub>2</sub>O sideline was reported by Stewart (1960), along with a description of the reagents used in the present work, preparation of starting materials, and other experimental details. The albite synthesized did not show the same (131–131) separations as would have been expected for pure  $\text{NaAlSi}_3\text{O}_8$  under the same experimental conditions, as confirmed and extended by Edgar and Piotrowski (1967), so some difference in alkali content or Al:Si ratio apparently exists in the disordered synthetic feldspar that has not been found in natural low albite from Li-rich pegmatites.

The phase relations on the Qz–Eu–H<sub>2</sub>O sideline are complex and incompletely understood. The approximation given in Figure 3 represents current understanding, but metastability is notorious with some of these phases, and determination of the composition of the extensive high-temperature solid solutions is dependent on graphs to relate precise measurements of unit-cell parameters to composition. Graphs determined by B. J. Skinner, H. T. Evans, W. C. Phinney and me for 21 compositions were used to determine compositions (Skinner and Evans, 1960, and personal communications). A comprehensive study of phase relations for  $\text{LiAlSi}_2\text{O}_6$  given by Munoz (1969) is illustrative of the difficult synthesis of spodumene at low pressures experienced by everyone who has attempted to work with this system (Shternberg *et al.*, 1972; Edgar, 1968). The high-temperature phases have not yet been found in nature, however, and the discrepancies between the reported positions for the  $\alpha$ – $\beta$  spodumene transition are not critical. Although the reaction  $\text{LiAlSi}_4\text{O}_{10} = \text{LiAlSi}_2\text{O}_6 + 2\text{SiO}_2$  (petalite = spodumene + 2 quartz) has been reported at temperatures that differ by tens of degrees at 2 kbar by Stewart (1963) and Munoz (1971), this discrepancy is

not serious and may well reflect minor differences in composition (particularly of traces of  $\text{Fe}_2\text{O}_3$ ) of the starting materials or in length of runs. Experimental runs, thermodynamic calculations, and observed natural pseudomorphs of spodumene and quartz after petalite indicate that at low temperature and high pressure the assemblage spodumene plus quartz is more stable than petalite. An experimentally-determined *P*–*T* diagram for the Pe composition is given in Černý and Ferguson (1972, p. 673).

The four-phase point (Fig. 4) on the sideline Ab–Qz–H<sub>2</sub>O was redetermined to be at  $735 \pm 5^\circ\text{C}$  and Ab62Qz38 composition by using Schairer and Bowen's (1956, Table 2) glasses N, M, LM, K, and 162 by courtesy of J. F. Schairer. Two additional glasses were prepared by Schairer's methods at Ab60Qz40 and Ab65Qz35. The position of the four-phase point is at the same composition found by Tuttle and Bowen (1958, p. 53) but is at about 15°C lower temperature, a trivial difference.

Portions of the liquidus of the system Ab–Qz–Eu–H<sub>2</sub>O at 2 kbar (Fig. 4) were determined by using ten glasses of ternary composition. Stability fields for albite, quartz, petalite, eucryptite,  $\beta$ -spodumene solid solution, and  $\beta$ -eucryptite solid solution appear on the liquidus, but spodumene was not synthesized in the presence of silicate liquid. The liquidus is characterized by a eutectic near Ab34Qz50Eu16 at  $640^\circ \pm 10^\circ\text{C}$ . This composition falls in the triangle Ab–Qz–Pe and corresponds to Ab34Qz27.1Pe38.9, or Ab34Qz42.4Sp23.6. The field boundary between albite and lithium minerals falls steadily as Qz increases, from 725°C on the Ab–Eu sideline to about 715°C where it crosses the Ab–Sp join and 660°C where it crosses the Ab–Pe join, but the Li<sub>2</sub>O content varies little (Eu =  $19 \pm 3$  percent or Li<sub>2</sub>O =  $2.2 \pm 0.35$  weight percent). The liquidus at the Ab–Qz sideline is depressed nearly 100°C by saturation with lithium component, and the proportion of quartz to feldspar is increased by 60 percent. Liquidus temperatures rise very steeply as Qz increases in the quartz field.

The liquidus determined for the system Ab–Qz–Eu–H<sub>2</sub>O has many features in common with that deduced by Munoz (1971, p. 2078) for the system Or–Qz–Eu–H<sub>2</sub>O. The last liquids in both systems at 2 kbar disappear with the crystallization of alkali feldspar, petalite, and quartz. Munoz estimated the eutectic temperature in the potassic system to be between 600 and 625°C, only slightly lower than that found here for the sodic system. When both alkali feldspars are present the temperature will be further



depressed by 35°C or more, but according to Figure 3 of this work and Munoz' Figure 5, petalite is still the lithium mineral on the liquidus until temperatures below ~550°C are attained. Such low temperatures may not be reached by the liquidus at 2 kbar even if all of the additional  $\text{Al}_2\text{O}_3$ ,  $\text{BeO}$ , and other components known in nature are present. The field boundary in the presence of additional components may shift position, but no estimate can be made now of the amount.

The field boundary of the lithium-rich phases limits to about 2.2 weight percent the amount of  $\text{Li}_2\text{O}$  that can accumulate in a melt that begins to crystallize in the feldspar field and in that part of the quartz field where feldspar will begin to crystallize before lithium minerals. The limiting amount of  $\text{Li}_2\text{O}$  is somewhat greater than the amount of  $\text{Li}_2\text{O}$  present at the eutectic (1.85 percent  $\text{Li}_2\text{O}$ , 81.0 percent  $\text{SiO}_2$ ), because of the curvature of the field boundary. The limiting amount of  $\text{Li}_2\text{O}$  is equivalent to about 27 percent spodumene of theoretical composition, or 45 percent petalite. Comparison of the bulk compositions of homogeneous Li-rich pegmatite and of the zones of zoned Li-pegmatites to the liquidus results should contribute to understanding the petrogenesis of these compositions.

#### Petrogenetic significance of positions of pegmatite compositions on the liquidus

Comparison of Figures 2 and 4 reveals that the bulk compositions of Li-rich pegmatites are closely grouped in the region of minimum melting temperatures on the liquidus. This correspondence suggests that the compositions of homogeneous lithium pegmatites could have been magmas at the temperatures and pressures shown on the diagram. If crystallization starts from the feldspar-silica sideline, no lithium mineral will form until the field boundary is reached. Thus the liquidus diagram provides an explanation for the sequence of zones observed, for the abrupt appearance of lithium minerals in quantity from compositions near the field boundary when the field boundary is reached, and for the limit on the abundance of lithium minerals. The limit on the grade of spodumene (or petalite) in Li-rich pegmatite derived from its magmatic origin should be a useful concept for guiding development of and prospecting for lithium ores. The phase diagram for the Qz-Eu sideline and diagrams for the *P-T* stability of spodumene and petalite indicate that petalite pegmatites should be the high temperature-low pressure equivalents of spodumene pegmatites.

The liquidus diagram implies a more complex process than magmatic crystallization for the silica-rich zones, which would require very much higher temperatures to be completely molten than any of the zones which precede them in formation. The silica-rich zones are found only in complexly-zoned pegmatites, are small in volume relative to the whole pegmatite, and occur as inner zones or fracture fillings. It will be argued below that these compositions were deposited from gas (steam) that was in equilibrium with crystalline or partly crystalline assemblages.

#### Incongruent solubility in the gas phase

The composition of the  $\text{H}_2\text{O}$ -rich gaseous phase that coexists with lithium minerals, alkali feldspar, and quartz can be studied only with difficulty in conventional cold-seal pressure vessels, because the 20–50 mg of quenched fluid is difficult to analyze accurately for so many constituents. The method used in this study was to select an isothermal isobaric section at 575°C and 2 kbar, and attempt to determine phase boundaries in the system Eu-Qz- $\text{H}_2\text{O}$  by experiments on 6 compositions with which successively larger amounts of  $\text{H}_2\text{O}$  were equilibrated. Examination of the solid phases after the experiments indicated their compositions, and by difference the composition of the gas was qualitatively determined.

These experiments indicated the phase relations shown schematically in Figure 5. Equilibrium was not attained in all runs;  $\beta$ -spodumene was present in most runs rather than spodumene, though spodumene was synthesized in many runs. One or two eucryptite crystals were observed on the surfaces of some runs also containing petalite or quartz, suggesting metastable persistence after rapid initial leaching of the surface of the glass by steam. Figure 5 shows that as  $\text{H}_2\text{O}$  is added to glass of Pe composition and allowed to equilibrate, the following sequence of assemblages should be observed (all plus gases of different compositions): petalite, petalite plus spodumene, spodumene, spodumene plus eucryptite, eucryptite, and finally complete solution into the gas. The amount of petalite that can be dissolved in the gas at 575°C, 2 kbar was about 0.64 weight percent. Greater amounts of solids would probably be dissolved from compositions between petalite and quartz, which is the range of natural compositions. If the gas composition is held constant by buffering in the presence of both quartz and petalite, the solid precipitated from it would have a very silica-rich composition (Fig. 5). A composition (Qz59.5Eu40.5) slightly more siliceous than petalite (Qz58.9Eu41.1) with 31 percent



H<sub>2</sub>O yielded petalite and spodumene and no apparent quartz, proving the gas was very siliceous. The gas composition buffered by spodumene and quartz under conditions where petalite is not stable was not determined by my experiments. Edgar (1968, p. 223) reported that  $\beta$ -spodumene formed from spodumene was more siliceous than the LiAlSi<sub>2</sub>O<sub>6</sub> composition, indicating that the gas should be Li-rich, but where enough  $\beta$ -spodumene was obtained in my experiments for reliable estimates of composition from cell-edge measurements, it was always as siliceous or slightly less siliceous than the starting glass. The compositions of the solids precipitated from gases associated with alkali feldspars, micas, spodumene, and quartz are probably like those plotted in the Qz-rich part of Figure 2.

These experiments also suggest that subsolidus leaching from or exchange with earlier-formed assemblages containing spodumene or petalite provide a mechanism by which eucryptite can form in nature. This topic was reviewed by Stewart (1960, p. 28–29). Burt *et al.* (1977) postulated a stability field for the assemblage eucryptite plus quartz at low *P* and *T*. No bulk compositions of zones reported fall outside the triangle petalite–quartz–alkali feldspar, so magmatic crystallization seems to be incapable of producing eucryptite-bearing assemblages. Subsidiary recrystallization of alkali feldspars and spodumene or petalite with F-bearing steam can yield lepidolite, as determined experimentally by Munoz (1971). Lepidolite most commonly occurs in abundance in the innermost zones and involves the same gas phase discussed above.

Compositions that could have formed from gas can probably be distinguished from those that could have formed from magma by the ratio of quartz to feldspar. Where quartz exceeds feldspar, gas is much involved; however, feldspar-rich compositions could be from magmas. The association of gas with quartz > feldspar seems to accord with the textural criteria of Jahns and Burnham (1969), as demonstrated by Černý and Ferguson (1972, p. 674) for petalite-bearing intermediate zones of the Tanco pegmatite. Very large petalite-bearing pegmatites at Bikita, Rhodesia (Cooper, 1964), Varuträsk, Sweden (Quensel, 1956) and the Tanco pegmatite, Manitoba, were noted by Černý and Ferguson (1972, p. 676) to have potassium feldspar > albite in the petalite zones and to be enriched in quartz. The bulk composition of the Bikita pegmatite (Gallagher, 1962) seems not to be unusually rich in Qz (Fig. 2). The involvement of a gas phase probably causes both the enrichment of

quartz and of potassium feldspar. Orville (1960) and Norton (1970) conclusively showed the asymmetric distribution of potassium in pegmatites, and related it to gravitational forces such as would be involved when a gas and a silicate liquid are in contact with each other. The geologic occurrences of petalite in near-surface contact aureoles of granites in Devon, Elba, Japan, Wyoming, and elsewhere suggest that petalite components are readily transported in gases.

The alkali composition of the gas phase might be postulated to be responsible for the quartz-rich cores. However, according to Orville (1963), at 500–600°C and 2 kbar the ratio of Na<sup>+</sup> to K<sup>+</sup> in the gas that coexists with albite and microcline will be about 4:1 for a wide range of total alkali concentrations. According to Scavnicar and Sabatier (1957), in the same temperature interval if the ratio of Li<sup>+</sup> to (Na<sup>+</sup>+K<sup>+</sup>) were as high as 0.5, the sodium in albite or the potassium in microcline will be exchanged for Li<sup>+</sup>, and a siliceous  $\beta$ -spodumene (possibly with quartz) will result. Because no  $\beta$ -spodumene has been found even in the petalite pegmatites where appropriate temperatures are probable, it is likely that the Li<sup>+</sup> concentration did not exceed 0.5 (Na<sup>+</sup>+K<sup>+</sup>). Combination of these two results indicates that Na<sup>+</sup> > K<sup>+</sup> > Li<sup>+</sup> in the gas, and episodes of Li<sup>+</sup>-rich gases to cause quartz-rich cores are not probable, nor should they cause extensive Li-metasomatism outside pegmatites. The regions of lithium amphibole (holmquistite) in the contact rocks around some lithium pegmatites (Kesler, 1961; Heinrich, 1965) also contain potassium-bearing lithium micas and albite, an expected consequence from this analysis.

### Concluding discussion

The hypothesis that Li-rich pegmatites could have formed from a magma is sustained for both homogeneous pegmatites and for the feldspar-rich zones that contain spodumene or petalite in zoned pegmatites. The high temperature–low pressure isochemical equivalent of assemblage 5 of Cameron *et al.* (1949) is perthite–plagioclase–petalite–quartz, and of assemblage 6 is plagioclase–petalite–quartz. These zones seem to be the last that can reasonably be interpreted to have originated from molten silicate magma. The remaining zones, core, and fracture fillings require the participation of transport through a gas, or subsolidus recrystallization.

Fractional crystallization is a superficially attractive process to invoke for the generation of Li-rich magma. However, granites associated with lithium pegmatites typically contain less than 100 ppm Li

(Mulligan, 1973; J. J. Norton, personal communications 1948–1978), and even very perfect fractionation that would yield a typical Li-rich pegmatite containing ~7100 ppm Li (=1.53 weight percent Li<sub>2</sub>O) would require at least 70 times as much parental magma as pegmatite. Extreme mechanical problems arise in extracting such a small fraction of rest liquid. Alternate suggestions have been made (Norton, 1973, p. 369), and my present opinion is that anatexis is the hypothesis most consistent with geological and experimental evidence. As Li-rich pegmatite and related granites that have normal (<100 ppm Li) contents are associated in time and space, they most probably received lithium from the same source. Partial melting of Li-enriched metasediments would yield Li-rich magma at temperatures 75°C (or more) lower than those at which granitic magmas of minimum melting composition in the system Or–Ab–Qz–H<sub>2</sub>O could form. Continued heating would yield larger amounts of granitic magma and would dilute the lithium content. The irregular distribution of Li-rich pegmatite farthest of all pegmatite varieties from related granite and the sparsity of Li-rich pegmatites within related granites are in accord with an anatexis origin. Li-rich pegmatites occur near the sillimanite isograd in metamorphic rocks, indicating temperatures of >501°C at any pressure and greater than 625°C at 2 kbar (Holdaway, 1971), quite consistent with liquidus temperatures determined experimentally. Processes capable of producing concentration ratios of hundreds or thousands to one relative to granites seem to have operated to create valuable and geochemically unique deposits of Rb, Cs, Nb, Ta, and Sn in pegmatites, and magmatic differentiation processes alone seem not to suffice.

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