

## Experimental study of lithium-rich granitic pegmatites: Part I. Petalite + albite + quartz equilibrium

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### ABSTRACT

Petalite is one of the major lithium aluminosilicate minerals occurring in Li-rich granitic pegmatites. Experiments have been carried out at a confining pressure of 1.5 kbar, and at 450 °C and 600 °C to study the equilibrium between petalite, albite, quartz, and the coexisting chloride solution. Very little Na or Li enter the structure of petalite or albite respectively. When petalite coexists with albite and quartz, the alkali composition of the fluid is buffered. The value of the Na/(Na + Li) ratio of the fluid has been determined to be  $0.520 \pm 0.020$  at 450 °C and  $0.545 \pm 0.015$  at 600 °C in the buffered medium. This indicates that temperature has only a very slight influence on the composition of the buffered solution under the given experimental conditions.

### INTRODUCTION

Li is one of the characteristic elements of granitic pegmatites, where it is concentrated to varying degrees. During magmatic fractionation, Li does not behave as a typical alkali element (Heier and Billings, 1970). It is incorporated only in negligible amounts into the octahedral sites of ferromagnesian minerals owing to its suitable ionic size (0.68 Å) but low charge. As the crystallochemical misfit prevents Li from entering the structure of felsic rock-forming minerals, its concentration in melt increases with crystallization, leading first to the maximum possible contents of Li in rock-forming phases (feldspars, micas), before it reaches the level sufficient to trigger the crystallization of Li minerals.

The most common independent Li minerals in lithium pegmatites are the major lithium aluminosilicates petalite,  $\text{LiAlSi}_4\text{O}_{10}$ ,  $\alpha$ -spodumene,  $\text{LiAlSi}_2\text{O}_6$ ,  $\alpha$ -eucryptite,  $\text{LiAlSiO}_4$ , a variety of lithian micas including lepidolite, the phosphates amblygonite-montebrazite,  $\text{LiAlPO}_4(\text{F},\text{OH})$ , and lithiophilite triphylite,  $\text{Li}(\text{MnFe})\text{PO}_4$ . As a group, the lithium aluminosilicates, spodumene, petalite, and eucryptite are the most abundant and most frequently encountered Li minerals in pegmatites. These three phases are valuable indicators of the conditions of crystallization in lithium pegmatites (Stewart, 1978; London and Burt, 1982a, 1982b, 1982c). Information on their stability relations is therefore important to the understanding of the petrogenesis of lithium pegmatites.

Ranked by Heinrich (1975) as the third most abundant Li mineral, petalite occurs principally as giant crystals in the inner parts of zoned pegmatites. It is most commonly associated with quartz and feldspars (Černý and Ferguson, 1972; Stewart, 1978; London and Burt, 1982a). Fresh crystals are vitreous, transparent to translucent, and colorless, white or grey. Spodumene and petalite crystallize directly from silicate magmas (London and Burt, 1982d;

London, 1986) whereas eucryptite would be a replacement mineral of secondary origin (Norton et al., 1962; London and Burt, 1982b, 1982c). Natural occurrences provide important qualitative information on the pressure-temperature stability field of petalite: thus petalite seems to be stable at high temperature and low pressure. At several localities, petalite has been replaced isochemically by intergrowths of spodumene and quartz (e.g., Černý and Ferguson, 1972; Rossovskii and Matrosov, 1974) or eucryptite and quartz (e.g., Hurlbut, 1962). These replacements frequently are pseudomorphic after petalite and presumably form with decreasing temperatures.

Many of the albite-rich pegmatite units are considered to be primary in origin. The formation of secondary albite by replacement (albitization) of pre-existing minerals of pegmatites is also a well documented and an important phenomenon in the hydrothermal stage. All three lithium aluminosilicates may be converted to albite in quartz-saturated, Na-rich environments (Burt et al., 1977; London and Burt, 1982c). So, albite is generally present in the pegmatitic system as an associated mineral, both in primary and secondary lithium pegmatite bodies.

In the light of these data, we have carried out experiments on the two systems, petalite-albite-quartz and spodumene-albite-quartz, in equilibrium with a (Na,Li) chloride solution, in order to investigate the field of Li-rich granitic pegmatites. The results of these experiments are presented in parts I and II (Lagache and Sebastian, 1991) of this study.

### PREVIOUS EXPERIMENTAL WORK

Stability relations among the lithium aluminosilicates, with or without quartz, have been thoroughly investigated by ceramists because of the fluxing properties and low thermal expansion of lithium aluminosilicate glasses and glass-ceramics (e.g., Hatch, 1943; Roy et al., 1950; Os-

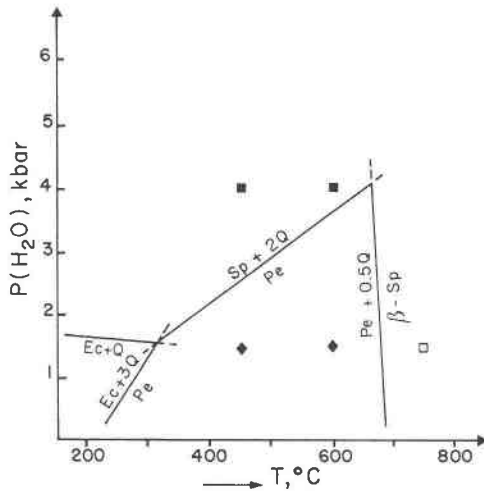


Fig. 1. Experimental pressure-temperature phase diagram for the system  $\text{LiAlSiO}_4\text{-SiO}_2\text{-H}_2\text{O}$  after London (1984). The diamonds show the pressure-temperature conditions of this study. The squares show the pressure-temperature conditions of the study on the spodumene + albite + quartz assemblage (Lagache and Sebastian, 1991). Ec = eucryptite; Pe = petalite; Q = quartz; Sp = spodumene.

tertag et al., 1968). Most of these experiments explained some important aspects of their stability relations, but were not related to the context of their occurrence in pegmatites. Hydrothermal phase equilibria experiments by Stewart (1963) provided the first geologically meaningful quantitative data on the stability field of petalite. Stewart's work confirmed that petalite is the high temperature, low pressure equivalent of the assemblage (spodumene + quartz) and that the isochemical replacement of petalite by (spodumene + quartz) is triggered by cooling at moderate pressures. The studies by Burt et al. (1977), London and Burt (1982b) and London (1984) in the system  $\text{LiAlSiO}_4\text{-SiO}_2\text{-H}_2\text{O}$  have furnished the pressure-temperature diagrams that are directly applicable to the petrogenesis of lithium pegmatites. The qualitative phase diagrams of London and Burt (1982c, Figs. 4 and 5), based on experimental phase equilibrium studies at moderate pressure and temperature explain the formation conditions of eucryptite or the metasomatic replacement of spodumene and petalite in the course of pegmatitic evolution. The experimental studies by London (1984) indicate that the stability field of petalite is bounded by  $\beta$ -spodumene at high temperature ( $>685^\circ\text{C}$ ), by  $\alpha$ -spodumene + quartz at moderate to high pressures and lower temperatures, and by eucryptite + quartz at low pressures and temperatures (Černý and London, 1983), as shown in Figure 1.

Until recently, lithium pegmatites were considered to crystallize from a granitic silicate melt coexisting with a concentrated saline fluid (Jahns and Burnham, 1969; Stewart, 1978; Černý et al., 1985). Norton et al. (1962) and Jahns (1982) attributed the origin of latest assemblages to the role of a supercritical fluid exsolved during the crystallization of the core of the pegmatite. Recent studies by London et al. (1988, 1989) on vapor undersaturated experiments with Macusani glass +  $\text{H}_2\text{O}$  suggest that the formation of pegmatite fabrics stems primarily from fractional crystallization in a volatile rich melt. A vapor phase does not appear to be necessary for the development of the primary features of pegmatites (fabrics and zonation). While an aqueous fluid is clearly present during solidus or subsolidus crystallization, there is little information on the chemical composition of this phase. London (1987) characterizes the late magmatic fluids by their high concentration of B, P, and F; Cl is relatively low. Until now, most of the experiments on rare-alkali elements systems have been performed with Cl-bearing fluids (Lagache and Sabatier, 1973; Lagache, 1984; Webster et al., 1989; Manier-Glavinaz et al., 1989; Sebastian and Lagache, 1990). In order to compare these results to this experimental study of Li-rich pegmatites, we have also carried out our experiments with a chloride solution.

Following Stewart (1978), lithium pegmatites occur at temperatures of  $>500^\circ\text{C}$  at any pressure or greater than  $625^\circ\text{C}$  at 2 kbar. Burnham and Nekvasil (1986) have shown that the lowest temperature of the liquidus of the  $\text{H}_2\text{O}$ -saturated natural pegmatite melt is at about  $660^\circ\text{C}$  and 2 kbar, which is in good agreement with the diagram from London et al. (1989). According to the above studies and to fluid inclusions and isotope studies (Bazarov and Motorina, 1969; Taylor et al., 1979; London, 1986) crystallization under quartz-saturated conditions is thought to occur at temperatures below  $660^\circ\text{C}$  and pressures below 4 or 5 kbar. In the case of this study on the petalite + albite + quartz assemblage, all the experiments have been performed at 1.5 kbar and at two different temperatures:  $450^\circ\text{C}$  and  $600^\circ\text{C}$ . The same temperatures and a pressure of 4 kbar have been chosen for the experimental study on the  $\alpha$ -spodumene + albite + quartz assemblage, and  $750^\circ\text{C}$  and 1.5 kbar for the  $\beta$ -spodumene + albite + quartz assemblage (Fig. 1).

The fluid is a Li-Na chloride solution (1M). Information is not available on the phase domains in the system  $\text{LiCl-NaCl-H}_2\text{O}$ , but under our experimental conditions, the system  $\text{NaCl-H}_2\text{O}$  is situated in the supercritical domain (Sourirajan and Kennedy, 1962). Weisbrod (personal communication) estimates that the  $\text{LiCl-H}_2\text{O}$  domain of immiscibility is at still lower temperature.

TABLE 1. Chemical composition of the petalite used

$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Li}_2\text{O}$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$	$\text{Rb}_2\text{O}$	$\text{MnO}$	Total
78.96	16.12	4.95	0.13	0.08	0.07	0.01	0.007	0.004	0.00	100.331

TABLE 2. Results of the experiments at 450 °C, 1.5 kbar

Number	Days	Reactants			Final bulk solid composition μmol/100 mg			Solution composition μmol/100 μL					
		mg	mol	μL	Na	Li	X	Na	Li	Y			
1	60	Pe	100	NaCl	1	13	Pe	1	323	0.003	26	74	0.26
				+									
2	60	Pe	100	LiCl	1	38	Pe	1	321	0.003	25	73	0.26
				+									
3	60	Pe	100	NaCl	1	50	Pe + Q + Ab	22	310	0.07	50	46	0.52
				+									
4	60	Pe	100	NaCl	1	100	Pe + Q + Ab	45	282	0.14	53	47	0.53
5	60	Pe	50	NaCl	1	100	Pe + Q + Ab	89	235	0.28	53	47	0.52
6	60	Pe + Q + Ab	50	LiCl	1	50	Pe + Q + Ab	104	205	0.34	54	50	0.52
7	60	Pe	50	NaCl	1	200	Pe + Q + Ab	166	153	0.52	54	47	0.53
8	60	Pe + Q + Ab	100	NaCl	1	50	Pe + Q + Ab	180	135	0.57	52	48	0.52
9	60	Pe + Q + Ab*	100	NaCl	1	50	Pe + Q + Ab	179	134	0.57	50	46	0.52
10	60	Ab + Q	100	LiCl	1	100	Pe + Q + Ab	175	45	0.80	50	51	0.50
11	60	Ab + Q	50	LiCl	1	100	Pe + Q + Ab	210	95	0.69	49	50	0.50
				+									
12	60	Ab + Q	100	LiCl	1	100	Pe + Q + Ab	312	6	0.98	54	47	0.53
				+									
13	60	Ab + Q	100	NaCl	1	100	Ab + Q	303	4	0.99	57	45	0.56
				+									
14	60	Pe + Q + Ab	50	NaCl	1	50	Ab + Q	303	4	0.99	61	40	0.60
				+									

Note: See text for explanations of results. Reactants: Pe = natural petalite; Q = quartz; Ab = albite gel, Ab\* = natural low albite. Final bulk solid composition: Pe = petalite, Q = quartz; Ab = high albite.

The equilibrium studied here is



Quartz is always present in the assemblage, and we assume that it is pure SiO<sub>2</sub>. Applying the laws of mass action at equilibrium, one finds that the ratio of activities

of Na<sup>+</sup> and Li<sup>+</sup> in solution is a function of the temperature, pressure, and composition of the solid phase.

#### EXPERIMENTAL PROCEDURE

The starting materials for mineral synthesis were natural colorless petalite (chemical composition is in Table

TABLE 3. Results of the experiments at 600 °C, 1.5 kbar

Number	Days	Reactants			Final bulk solid composition μmol/100 mg			Solution composition μmol/100 μL					
		mg	mol	μL	Na	Li	X	Na	Li	Y			
15	18	Pe	100	NaCl	1	13	Pe	1	324	0.003	26	72	0.27
				+									
16	18	Pe	50	LiCl	1	38	Pe	1	322	0.003	26	72	0.27
				+									
17	30	Pe	100	NaCl	1	25	Pe + Q + Ab	11	303	0.04	56	44	0.56
18	18	Pe	100	NaCl	1	50	Pe + Q + Ab	28	287	0.09	52	42	0.56
19	18	Pe	100	NaCl	1	100	Pe + Q + Ab	50	275	0.15	55	47	0.54
20	18	Pe	50	NaCl	1	100	Pe + Q + Ab	83	243	0.26	57	46	0.55
21	18	Pe + Q + Ab	50	LiCl	1	50	Pe + Q + Ab	102	217	0.32	54	44	0.55
22	30	Pe	50	NaCl	1	150	Pe + Q + Ab	120	185	0.39	53	44	0.55
23	18	Pe	50	NaCl	1	200	Pe + Q + Ab	186	157	0.54	55	46	0.54
24	18	Pe + Q + Ab	100	NaCl	1	50	Pe + Q + Ab	176	133	0.57	56	46	0.55
25	18	Pe + Q + Ab*	100	NaCl	1	50	Pe + Q + Ab	184	135	0.58	56	48	0.54
26	18	Ab + Q	50	LiCl	1	100	Pe + Q + Ab	202	110	0.65	56	48	0.54
27	18	Ab + Q	100	LiCl	1	100	Pe + Q + Ab	202	54	0.79	52	46	0.53
28	18	Pe + Q + Ab	50	NaCl	1	100	Pe + Q + Ab	255	64	0.80	56	46	0.55
29	30	Pe + Q + Ab	50	NaCl	1	150	Pe + Q + Ab	274	20	0.93	53	44	0.55
30	18	Ab + Q	100	NaCl	1	100	Pe + Q + Ab	326	6	0.98	52	47	0.53
				+									
31	18	Ab + Q	100	LiCl	1	100	Ab + Q	321	4	0.99	57	43	0.57
				+									
32	18	Pe + Q + Ab	50	NaCl	1	200	Ab + Q	328	5	0.99	61	38	0.61
				+									

Note: See text for explanations of results. Reactants: Pe = natural petalite; Q = quartz; Ab = albite gel; Ab\* = natural low albite. Final bulk solid composition: Pe = petalite; Q = quartz; Ab = high albite.

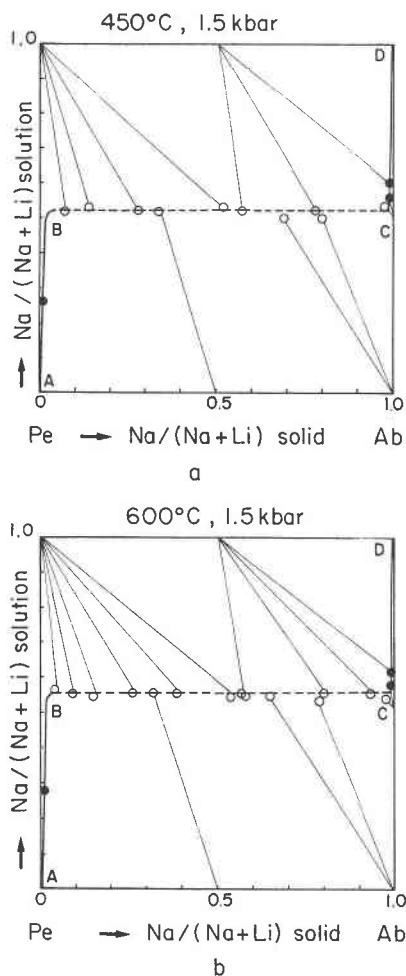


Fig. 2. Isotherm-isobar of distribution curves at 450 °C (a), and 600 °C (b). Slanting lines connect the starting assemblage and final assemblage for an individual experiment. The solid circles represent petalite (Pe) or albite (Ab) + quartz (Q) and empty circles represent (Pe + Q + Ab).

1) from Minas Gerais, Brazil and albite gel prepared by the classical gelling method (Hamilton and Henderson, 1968). The chemical composition of the gel was verified by wet chemical analysis. Petalite was finely powdered in an agate mortar. Varying amounts (50–100 mg) of petalite or a mechanical mixture of albite gel and natural quartz in stoichiometric proportions were weighed in Au tubes of 2.5 to 4 cm length and 4.4 mm diameter, to which varying volumes (25–200  $\mu\text{L}$ ) of alkali chloride solutions were added. Some experiments were conducted with a mixture of 1 mol of petalite, 1 mol of quartz, and 1 mol of albite. For the experiments near the petalite composition, a mixture of LiCl and NaCl in the ratio 3:1 was added and for those near the albite composition, a 1:1 mixture of LiCl and NaCl was added. This permits the amount of Na in petalite or Li in albite to be fixed, thereby retaining a measurable amount of Na or Li in solution

after the experiment. The tubes were welded at both ends and subjected to the required pressure and temperature in a Bridgman type pressure vessel. The vessel was entirely immersed in the furnace, preventing a temperature gradient over the capsules. Temperature was monitored and measured by external chromel-alumel thermocouples situated close by the charge. The thermocouples were calibrated against the melting point of Pb. The cumulative uncertainty due to regulation and measurement was estimated to be within  $\pm 1\% \pm 2^\circ\text{C}$ . The filling of the vessel with  $\text{H}_2\text{O}$  was calculated using PVT data from Kennedy (1950) and Burnham et al. (1969) in order to reach the required pressure. The pressure was not measured during the experiment. Its uncertainty is directly proportional to the uncertainty of the temperature.

The duration of the experiments was 18 or 30 d at 600 °C and 60 d at 450 °C. At the end of the experiment the pressure vessel was cooled in a compressed air blast. The tubes were opened and solid and aqueous phases were extracted using deionized  $\text{H}_2\text{O}$  and separated in a centrifuge. The solid phase was then dried and the solution was made up to a definite volume. Li was determined in both solid and solution by atomic absorption and Na by flame emission spectrophotometry. The precision obtained for both is better than 2% of the amount present. The chloride concentration was checked to verify that most of the solution had been recovered. The crystalline solid phases were identified by X-ray diffraction.

## RESULTS

The results are presented in Tables 2 and 3.  $X$  is the Na mole fraction of the total Li plus Na in the solid assemblage and  $Y$  is the Na mole fraction in solution. Calculations are made for solids in micromoles ( $\mu\text{mol}$ ) per 100 mg and for solutions in micromoles per 100  $\mu\text{L}$ . Graphical representation is shown by the classical isotherm-isobar distribution diagrams (Figs. 2a and 2b) in which the bulk composition of the solid assemblage is plotted against that of the solution and expressed by the  $\text{Na}/(\text{Na} + \text{Li})$  ratio, which varies from 0 to 1. The two sets of experiments conducted at 600 °C with different durations, led to similar compositions of solids and solutions, indicating that a steady state has been attained. Lines connecting the starting nonequilibrium assemblage and the final bulk assemblage show that equilibrium could be attained in the forward and reverse directions.

In Figures 2a and 2b the system is bivariate along AB and CD. Along AB, petalite is enriched in Na until point B where albite starts to crystallize. Point B is not strictly determined by the experiments. The composition  $X$  of petalite saturated in Na is situated between 0.003 and 0.07 at 450 °C and between 0.003 and 0.04 at 600 °C. In any case the value of the ratio  $\text{Na}/(\text{Na} + \text{Li})$  in petalite is very low. This result agrees with the chemical analysis of natural petalite (Černý and London, 1983). Along DC, albite is enriched in Li until point C where petalite starts to crystallize. At both temperatures the maximum of the

ratio Na/(Na + Li) in albite is  $0.015 \mp 0.005$ . Very little Li enters the structure of albite as already shown by Heier and Adams (1964) for natural samples.

The horizontal section BC represents a univariant system along which petalite saturated with Na, albite saturated with Li, and quartz coexist in equilibrium with the fluid. Along BC the three-phase assemblage buffers the solution composition (Y) which remains constant at  $Y = 0.545 \pm 0.015$  at 600 °C and  $Y = 0.520 \pm 0.020$  at 450 °C. These results show that in a buffered medium, the Na/Li ratio of the solution is only slightly larger at elevated temperature than at lower temperature.

Two experiments were conducted with natural low albite instead of albite gel as the reactant, and the results show that this does not change either the solid assemblage or the solution compositions. We must recall that in all the experiments starting with the albite gel, in hydrothermal conditions, albite always crystallizes with the high temperature structure (Wyart and Sabatier, 1956). A similar observation was reported previously in Sebastian and Lagache (1990).

### CONCLUSION

This study has permitted us to determine precisely the alkali composition of Na and Li in the Li-rich pegmatite medium. When petalite saturated with Na and albite saturated with Li are simultaneously present, together with quartz, the ratio Na/(Na + Li) of the coexisting chloride solution is buffered at a value which is very near 0.50, almost independent of the temperature.

The extremely restricted solid solution formation of sodium petalite and lithium albite agrees with the analytical results of natural petalite and albite samples.

In a following paper (Dujon et al., in preparation) we discuss the thermodynamic implication of these results together with those obtained on the two assemblages spodumene + albite + quartz and pollucite + albite + quartz.

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