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Experimental study of Li-rich granitic pegmatites: Part II. Spodumene + albite + quartz equilibrium

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ABSTRACT

Spodumene is one of the principal sources of Li and the most important Li mineral in pegmatites. Experiments have been carried out at 450 °C and 600 °C at 4 kbar and 750 °C at 1.5 kbar to study the equilibrium between spodumene, albite, quartz, and the coexisting hydrothermal chloride solution. Solid-solution formation in spodumene as well as in albite is very much restricted. When spodumene coexists with albite and quartz, the alkali composition of the fluid is buffered. The value of the ratio Na/(Na + Li) of the fluid has been determined to be 0.550 ± 0.020 at 450 °C, and 0.485 ± 0.025 at 600 °C, conditions at which the stable form of spodumene is α spodumene. At 750 °C, 1.5 kbar, the stable form is the high-temperature polymorph β spodumene. In the presence of an excess of quartz, the assemblage albite + β spodumene partially melts from Ab30-Sp70 to Ab75-Sp25. The value of the ratio Na/(Na + Li) in the fluid buffered by coexisting albite and spodumene, with or without melt, is constant and has been determined to be 0.510 ± 0.020 at 750 °C.

INTRODUCTION

Spodumene is the most abundant Li mineral in pegmatites and is considered to be primary when formed during the pegmatitic period of crystallization. A second generation of spodumene that crystallized during a later pneumatolytic period of mineralization is also known. Primary spodumene is found in a variety of occurrences: (1) as phenocrysts in poorly zoned pegmatites, (2) as a constituent of one or more zones, principally intermediate zones and cores, (3) rarely, as constituents in replacement units, and (4) as fillings in vugs (Heinrich, 1975; London and Burt, 1982b). In cores it has been found as giant crystals (e.g., 2 m thick and 13 m long at the Etta mine, South Dakota). It occurs in some aplites and has been reported in a few gneisses (Deer et al., 1978). Spodumene is commonly associated with quartz, feldspar, micas, and minor accessory minerals such as beryl in granitic pegmatites (Gabriel et al., 1942). Spodumene can have high Fe^{3+} contents, since its pyroxene structure can accommodate up to 1.6 wt% of Fe_2O_3 (Heinrich, 1975). The substitution of small amounts of Fe^{3+} for Al^{3+} markedly increases the stability of spodumene (Appleman and Stewart, 1968). Secondary spodumene produced by the breakdown of petalite is relatively pure (Quensel, 1938; Černý and Ferguson, 1972; Chang, 1974).

There are three polymorphs of the compound $LiAlSi_2O_6$, α spodumene being the only naturally occurring low-temperature stable form with a monoclinic pyroxene structure. At high temperature, $LiAlSi_2O_6$ can exist in the form of two stuffed derivatives of silica. Beta spodumene is a high-temperature tetragonal form, isostructural with the silica polymorph keatite (Li and Peacor, 1968a; Clarke and Spink, 1969). Gamma spodumene has hexagonal symmetry and is isostructural with β quartz (Li and Peacor, 1968b; Ioffe and Zonn, 1970). The polymorphic transformations among the α, β, and γ forms are reconstructive. Beta spodumene and γ spodumene are absent in nature; however, virgilite, which is a solid solution between γ spodumene and β quartz, has been found in the Macusani volcanic glass, Peru (French et al., 1978; London, 1987; London et al., 1989). The absence of β spodumene in nature indicates that the temperature must have remained below the transition temperature of α to β [550–630 °C, at pressures of approximately 0.35 to 3.1 kbar, as determined by Edgar (1968)]. Stewart (1978), London and Burt (1982a), and London (1984) place the limit of the decomposition of petalite to β spodumene at a temperature around 680 °C and pressure below 4 kbar. The transition of α to β is monotropic, and Edgar (1968) found that, at atmospheric pressure, the inversion temperature is between 530 and 550 °C.

Alpha spodumene has proved difficult to form synthetically (Barrer and White, 1951; Drysdale, 1975; Graham, 1975; Isaacs and Roy, 1958; Munoz, 1969; Roy and Osborn, 1949; Roy et al., 1950) but is very common in nature and has been reported in many pegmatite deposits without the presence of either petalite or eucryptite (Munoz, 1971; Stewart, 1978). The α spodumene structure is very dense (specific gravity = 3.2) with Al in sixfold coordination. Synthesis under geologically realistic conditions requires nucleation and growth of this dense phase, where these processes are slow. Several lower density phases (specific gravity = 2.4) like β spodumene, petalite, α and β eucryptite, each with Al in fourfold coordination, can easily grow metastably (Drysdale, 1975). The proposed instability of α spodumene at low pressures

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TABLE 1. Chemical composition of spodumene

% SiO_2	% Al_2O_3	% Li_2O	% Na_2O	% K_2O	% Fe_2O_3	% CaO	% MgO	% Rb_2O	% MnO	Total
65.75	26.44	7.43	0.34	0.06	0.29	0.02	0.02	0.005	0.02	100.375

(Shternberg et al., 1972; Edgar, 1968; London, 1984) precludes its crystallization in shallow, low-pressure environments.

In a previous paper (Sebastian and Lagache, 1991), we have reviewed the experimental work conducted so far on the stability fields of lithium aluminosilicates and presented new experimental results on the petalite + albite + quartz equilibrium. This work deals with similar experimental studies on the spodumene + albite + quartz equilibrium to determine the composition of Na and Li in the hydrothermal fluid that is in equilibrium with this assemblage. This work has been undertaken in order to understand the whole system, including (Na-Li) aluminosilicates and coexisting hydrothermal fluids at temperatures ranging from 450 to 750 °C and pressures of 1.5 kbar and 4 kbar.

Estimates of the conditions of fluid-inclusion entrapment generally place the formation of primary spodumene in the range of 500 to 600 °C and 3 to 5 kbar (Bazarov and Motorina, 1969; Taylor et al., 1979; London, 1986). According to Sheshulin (from Heinrich, 1975), the homogenization temperatures of the fluid inclusions were 500 to 650 °C for the primary spodumene and 290 to 390 °C for the secondary spodumene. We have carried out our experiments on α spodumene at 450 and 600 °C and 4 kbar. Experiments on β spodumene have been performed at 750 °C and 1.5 kbar.

As in the previous studies (Sebastian and Lagache, 1990, 1991), the hydrothermal fluid is a chloride solution, even though the most important anions in such pegmatitic systems are considered to be B, F, and P (London et al., 1989). Further studies will be necessary to reproduce a bulk composition compatible with natural observations (London, 1987).

The equilibrium studied here is $LiAlSi_2O_6 + SiO_2 + Na^+ \leftrightharpoons NaAlSi_3O_8 + Li^+$. The principle is similar to the one discussed earlier for petalite (Sebastian and Lagache, 1991), i.e., at equilibrium, the ratio of activities of Na^+ and Li^+ in solution is a function of the temperature, pressure, and composition of the solid phase.

EXPERIMENTAL PROCEDURE

Starting material

Gels of spodumene and albite were prepared by the classical gelling method (Hamilton and Henderson, 1968). The chemical composition of the gels was verified by wet chemical analysis. From the pure spodumene gel at 450 or 600 °C and 4 kbar, petalite and α eucryptite crystallized instead of α spodumene. However, at 600 °C and 4 kbar, when starting with a mixture of spodumene gel, quartz, and NaCl solution, it was possible to crystallize α spodumene, albite, and quartz.

Because of these difficulties of crystallization, natural α spodumene from Minas Gerais, Brazil, was used in the experiments. Its composition is given in Table 1. The natural spodumene was finely powdered in an agate mortar. Varying amounts of a mechanical mixture of the powdered spodumene and natural quartz or albite gel were weighed in Au tubes to which varying volumes of alkali chloride solutions (1 *M*) were added. The tubes were welded at both ends. Some experiments were performed with a mixture of 1 mol of natural spodumene, 1 mol of albite gel, and quartz. For the experiments from the albite end-member, 2 mg of natural spodumene were added to the albite gel as nuclei to facilitate the reverse reaction. Natural low albite was used in some experiments instead of albite gel.

Experimental procedure

The experiments at 750 °C, 1.5 kbar, were conducted in a Bridgman-type pressure vessel, which was partially filled with H_2O in order to reach the required pressure (see Sebastian and Lagache, 1991). The experiments at 450 and 600 °C, 4 kbar, were performed in a modified Bridgman-type pressure vessel. The required H_2O pressure was maintained within the pressure vessel by externally applying pressure using a pump connected to a Bourdon-tube pressure gauge. The temperature was maintained within ±2 °C by chromelalumel thermocouples.

The duration of the experiments was 30 or 80 d at 450 °C, 12 or 18 d at 600 °C, and 18 d at 750 °C. The analytical procedure and the precision of the results are the same as in the previous paper on the petalite + albite equilibrium (Sebastian and Lagache, 1991).

RESULTS

The results are presented in Tables 2, 3, and 4. X is the mole fraction of Na in the bulk solid assemblage, excluding quartz, and Y is the mole fraction of Na in the solution. Graphical representation is shown by the classical isotherm-isobar distribution diagrams (Fig. 1a–1c) in which the composition of the solid is plotted against that of the solution and expressed as the ratio Na/(Na + Li), which varies from 0 to 1. Calculations are made for solids in micromoles (μM) for 100 mg and for solutions in micromoles per 100 microliters (μL).

Two sets of experiments conducted for different durations at 450 and 600 °C, 4 kbar, led to similar compositions of solutions and solids, indicating that a steady state was attained. In all of the experiments, the duration of the experiments was sufficient to obtain equilibrium in the forward and reverse directions, as shown by the con-

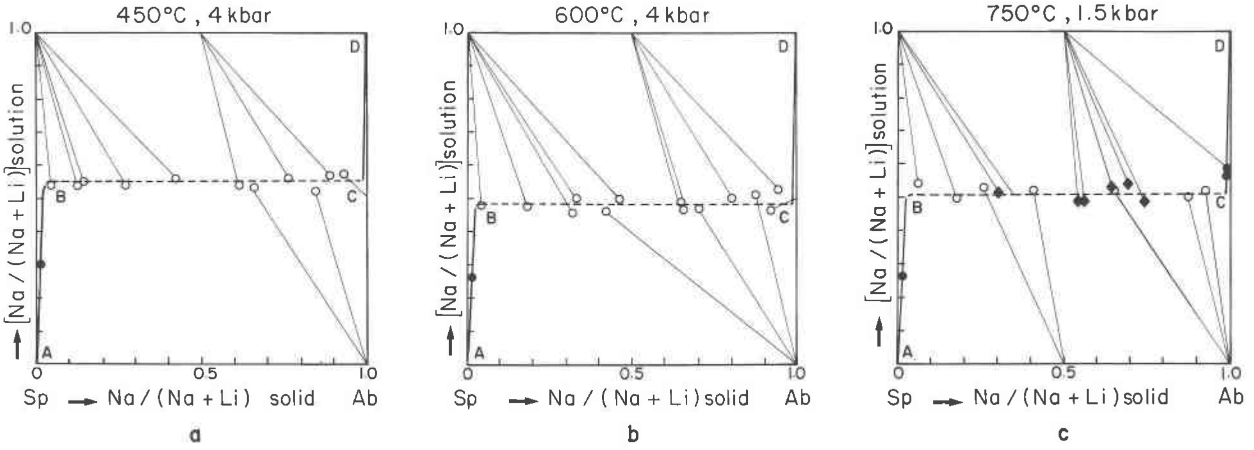

Fig. 1. Isothermal, isobaric distribution curves at 450 °C (**a**), 600 °C (**b**), and 750 °C (**c**). Slanting lines connect the starting assemblage and final assemblage for an individual experiment. The solid circles represent Sp + Q or Ab and empty circles represent (Sp + Q + Ab). The diamonds represent the partially molten final assemblage.

necting lines between the initial nonequilibrium assemblages and the final equilibrium assemblages (Fig. 1a–1c).

In Figure 1, the system is bivariant along AB and CD. There is only restricted solid solution along AB and CD. In both α and β spodumene, the ratio Na/(Na + Li) never exceeds 0.01, irrespective of the different structural forms. In albite, the maximum ratio Li/(Na + Li) is also approximately 0.01, as in earlier studies (Sebastian and Lagache, 1991). The compositions of the solid solutions were not directly determined but were estimated by the position of points B and C. The horizontal section of the isotherm BC represents a univariant system, along which spodumene saturated with Na, albite saturated with Li, and quartz coexist in equilibrium with the fluid. Along BC, the composition of the mechanical mixture of the solid phases (X) varies, and the trimineral assemblage buffers the solution composition (Y) which remains constant. The Y values vary between 450 and 600 °C: $Y = 0.550 \pm 0.020$ at 450 °C, 4 kbar and $Y = 0.485 \pm 0.025$ at 600 °C, 4 kbar. The solutions are more sodic at 450 °C than at 600 °C.

DISCUSSION

The albite that crystallizes in the experiments performed with gels and the albite that crystallizes from the transformation of spodumene + quartz is always of the high-temperature form (Sebastian and Lagache, 1990 and 1991). Experiments performed with natural low albite instead of gels led to comparable results at all three temperatures; however, the superimposition of the XRD peaks of albite and spodumene did not permit identification of the structural form of the albite at the end of the exper-

TABLE 2. Results of experiments at 450 °C, 4 kbar

Reactants							Final bulk solid composition μM/100 mg				Solution composition μM/100 μL		
Number	Days	Solid	mg	Solution	M	μL		Na	Li	X	Na	Li	Y
33	80	Sp + Q	100	NaCl + LiCl	1 1	13 38	Sp + Q	3	368	0.01	28	66	0.30
34	80	Sp + Q	100	NaCl	1	25	Sp + Q + Ab	14	361	0.04	52	44	0.54
35	80	Sp + Q	50	NaCl	1	50	Sp + Q + Ab	47	331	0.14	54	44	0.55
36	30	Sp + Q	50	NaCl	1	50	Sp + Q + Ab	42	286	0.13	54	44	0.55
37	80	Sp + Q	50	NaCl	1	100	Sp + Q + Ab	90	250	0.27	50	42	0.54
38	80	Sp + Q	50	NaCl	1	200	Sp + Q + Ab	155	217	0.42	55	43	0.56
39	80	Sp + Q + Ab	50	NaCl	1	50	Sp + Q + Ab	215	137	0.61	50	42	0.54
40	30	Sp + Q + Ab*	50	NaCl	1	50	Sp + Q + Ab	228	146	0.61	52	44	0.54
41	80	Ab + 2mgSp	50	LiCl	1	100	Sp + Q + Ab	260	135	0.66	50	44	0.53
42	80	Sp + Q + Ab	50	NaCl	1	100	Sp + Q + Ab	272	80	0.77	56	42	0.57
43	80	Ab + 2mgSp	50	LiCl	1	50	Sp + Q + Ab	311	56	0.85	52	48	0.52
44	80	Sp + Q + Ab	50	NaCl	1	200	Sp + Q + Ab	330	41	0.89	55	41	0.57
45	80	Ab + 2mgSp	50	NaCl + LiCl	1 1	25 25	Sp + Q + Ab	316	23	0.93	57	43	0.57

Note: Reactants: Sp = natural α spodumene, Q = quartz, Ab = albite gel, Ab* = natural low albite. Final bulk solid composition: Sp = α spodumene, Q = quartz, Ab = high albite.

Table 3. Results of experiments at 600 °C, 4 kbar

Reactants							Final bulk solid composition μM/100 mg				Solution composition μM/100 μL		
Number	Days	Solid	mg	Solution	*M*	μL		Na	Li	*X*	Na	Li	*Y*
46	18	Sp + Q	100	NaCl + LiCl	1 1	13 38	Sp + Q	4	366	0.01	24	70	0.26
47	18	Sp + Q	100	NaCl	1	25	Sp + Q + Ab	16	354	0.04	50	54	0.48
48	18	Sp** + Q	50	NaCl	1	50	Sp + Q + Ab	56	290	0.16	44	52	0.46
49	12	Sp + Q	50	NaCl	1	50	Sp + Q + Ab	51	241	0.18	48	52	0.48
50	18	Sp** + Q	50	NaCl	1	100	Sp + Q + Ab	113	240	0.32	45	52	0.46
51	12	Sp + Q	50	NaCl	1	100	Sp + Q + Ab	110	225	0.33	48	48	0.50
52	18	Ab + 2mgSp	50	LiCl	1	200	Sp + Q + Ab	160	218	0.42	44	52	0.46
53	18	Sp + Q	50	NaCl	1	200	Sp + Q + Ab	183	216	0.46	47	47	0.50
54	12	Sp + Q + Ab*	50	NaCl	1	50	Sp + Q + Ab	233	128	0.65	46	48	0.49
55	18	Sp + Q + Ab	50	NaCl	1	50	Sp + Q + Ab	225	115	0.66	45	50	0.47
56	18	Ab + 2mgSp	50	LiCl	1	100	Sp + Q + Ab	265	110	0.70	45	50	0.47
57	12	Sp + Q + Ab	50	NaCl	1	100	Sp + Q + Ab	240	60	0.80	48	48	0.50
58	12	Ab + 2mgSp	50	LiCl	1	50	Sp + Q + Ab	326	51	0.87	51	49	0.51
59	18	Ab + 2mgSp	50	NaCl + LiCl	1 1	25 25	Sp + Q + Ab	268	22	0.92	45	50	0.47
60	18	Sp + Q + Ab	50	NaCl	1	200	Sp + Q + Ab	245	15	0.94	53	47	0.53

Note: Reactants: Sp = natural α spodumene, Sp** = spodumene gel, Q = quartz, Ab = albite gel, Ab* = natural low albite. Final bulk solid composition: Sp = α spodumene, Q = quartz, Ab = high albite.

iment. The two experiments performed with spodumene gel also led to chemical equilibria similar to those obtained with natural spodumene.

At 750 °C, 1.5 kbar, the natural α spodumene inverts to the β form. In the reverse reactions with albite and LiCl solution, β spodumene is formed, which confirms that the reaction is monotropic, as observed by Edgar (1968). The *Y* value is 0.510 ± 0.020. In the experiments where no melting appears, we observe that there is a deficiency of quartz in the product assemblage by comparing the relative intensities of diffraction peaks for quartz in the starting assemblage and in the product assemblage. The studies on phase-equilibrium relations at high temperature in the system $LiAlSiO_4$-SiO_2 (Hatch, 1943; Skinner and Evans, 1960; Munoz, 1969; Stewart, 1978; London, 1984) have shown that β spodumene forms a series of solid solutions with keatite, a high-temperature polymorph of silica. The deficiency of quartz in the product assemblage may be explained by the presence of highly siliceous β spodumene-keatite solid solution.

At 750 °C, 1.5 kbar, when quartz is present in the starting assemblage, melting is observed from XRD patterns

Table 4. Results of experiments at 750 °C, 1.5 kbar

Reactants							Final bulk solid composition μM/100 mg				Solution composition μM/100 μL		
Number	Days	Solid	mg	Solution	*M*	μL		Na	Li	*X*	Na	Li	*Y*
61	18	Sp + Q	100	NaCl + LiCl	1 1	13 38	βSp + Q	2	344	0.01	25	70	0.26
62	18	Sp + Q	100	NaCl	1	50	βSp + Q + Ab	23	313	0.07	50	42	0.54
63	18	Sp + 2Q	50	NaCl	1	50	βSp + Q + Ab	55	260	0.18	50	51	0.50
64	18	Sp + Ab	50	LiCl	1	100	βSp + Q	112	316	0.26	52	46	0.53
65	18	Sp + Q	50	NaCl	1	100	βSp + Ab + M	97	231	0.30	46	44	0.51
66	18	Sp + 2Q	50	NaCl	1	100	βSp + Ab + M	107	200	0.35	47	47	0.50
67	18	Sp + Ab	50	LiCl	1	50	βSp + Ab	177	255	0.41	52	48	0.52
68	18	Sp + Q + Ab	100	NaCl	1	50	βSp + Ab + M	163	128	0.56	44	46	0.49
69	18	Sp + Q + Ab*	100	NaCl	1	50	βSp + Ab + M	127	103	0.55	46	48	0.49
70	18	Sp + 2Q + Ab	50	NaCl	1	50	βSp + Ab + M	210	120	0.64	50	45	0.53
71	18	Ab	50	LiCl	1	100	βSp + Ab	258	141	0.65	50	47	0.52
72	18	Sp + 2Q + Ab	50	NaCl	1	100	βSp + Ab + M	163	74	0.69	50	42	0.54
73	18	Sp + Q + Ab	50	NaCl	1	100	βSp + Ab + M	178	63	0.74	45	51	0.49
74	18	Ab	50	LiCl	1	50	βSp + Ab	320	45	0.88	47	48	0.50
75	18	Ab	100	LiCl	1	50	βSp + Ab	325	24	0.93	54	50	0.52
76	18	Sp + Q + Ab	50	NaCl	1	200	Ab	340	5	0.99	58	40	0.59
77	18	Ab	100	NaCl + LiCl	1 1	25 25	Ab	350	5	0.99	57	43	0.57

Note: Reactants: Sp = natural α spodumene, Q = quartz, Ab = albite gel, Ab* = natural low albite. Final bulk solid composition: βSp = β spodumene, Q = quartz, Ab = high albite, M = melt.

where $0.30 < Na/(Na + Li) < 0.75$ in the bulk (solid + melt). For compositions with Na/(Na + Li) equal to 0.55, the assemblage is almost completely molten. This is in good agreement with the liquidus diagram of the system albite-eucryptite-quartz determined by Stewart (1978). This phenomenon is not observed in experiments without quartz in the starting assemblages, where there are 41% and 65 mol% of albite in the final product assemblages.

We can assume that the melt present during the experiments contains approximately 4–5% dissolved H_2O (London et al., 1988). This corresponds to a maximum of 10% of the fluid present in experiments 68 and 69, 5% in experiment 70, and 2.5% in experiments 72 and 73, if all the final product assemblages are supposed to be melt. The amount of solution is then reduced, and its concentration is enhanced. It has been shown many times (Orville, 1963; Lagache, 1984) that homovalent exchanges between minerals and solution are independent of the molality of the solution. In that particular case, we can also estimate that the solubility of H_2O in the melt does not affect the chemical equilibrium between the solid phase and the fluid.

It is remarkable that the ratio $Y = Li/(Li + Na)$ in the solution is the same whether melt is present or not, and even when the bulk final assemblage is a melt. From experimental results (Carron and Lagache, 1980; London et al., 1988; Webster et al., 1989), we know that there is little or no significant vapor-melt fractionation for alkali elements at 750 °C. When the bulk solid assemblage is entirely molten, its composition is approximately that of the fluid, and the ratio Na/Li is near unity in the fluid and in the melt.

CONCLUSION

As we had already seen for the petalite + albite assemblage, the composition of the solution in equilibrium with the assemblage spodumene (saturated with Na) + albite (saturated with Li) + quartz is not very much affected by a change in the temperature. The Na/Li ratio is always near unity, as in the case of petalite. Although the influence of temperature is small, it is opposite that of the petalite + albite equilibrium: the solution is richer in Na for the petalite + albite equilibrium at higher temperatures, where it is richer in Li for the spodumene + albite equilibrium. We discuss these results in a forthcoming paper (Dujon et al., in preparation).

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