

Theoretical studies of the alteration of spodumene, petalite, eucryptite and pollucite in granitic pegmatites: exchange reactions with alkali feldspars

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Abstract. The ratios Na/Li, K/Li, Na/Cs and K/Cs have been calculated for exchange equilibria among the Li and Cs silicates spodumene, petalite, eucryptite, and pollucite, and the alkali feldspars albite and K-feldspar plus quartz, in pure water and in chloride solutions at temperatures from 100° to 700°C and pressures from 0.5 to 4 kbar, using available thermodynamic data for minerals and the modified HKF equation of state for aqueous species. For exchange equilibria between Li-bearing aluminosilicates and the alkali feldspars, the activities of the alkali metals in solution under most of the conditions investigated follow the order $Li > Na > K$, and Na/Li and K/Li decrease with decreasing temperature. For exchange equilibria between pollucite and the alkali feldspars the order is $Na > K > Cs$ in solution; Na/Cs and K/Cs increase strongly with decreasing temperature. The absolute values of these alkali metal ratios are in good agreement with the few available experimental data. The effect of chloride ion pairing on the calculated ratios is slight and does not consistently improve agreement between theory and experiment. These results suggest that the alteration of eucryptite, petalite or spodumene to albite and/or K-feldspar should be a normal consequence of the closed system evolution of rare element pegmatites upon cooling, in agreement with the ubiquity of such phenomena worldwide. On the other hand, alteration of pollucite to albite or K-feldspar upon cooling is only likely to occur if external fluids, with very high Na/Cs and/or K/Cs ratios, gain access to the pegmatite. Owing to the heterogeneity of rare element pegmatites, the fluid need not be external to the entire pegmatite, but could be simply external to the particular zone containing pollucite. Fluids in equilibrium with typical subsolidus rare metal pegmatite assemblages will invariably have high Li contents, thus explaining the common occurrence of Li-metasomatic halos about pegmatites. These same fluids are predicted to have relatively low Cs contents, in apparent agreement with the lesser

role of Cs relative to Li in metasomatic halos. However, preferential formation of complexes of the alkali metals with fluoride, borate or aluminosilicate components potentially could alter the calculated alkali metal behaviors.

Introduction

It is fairly widely accepted that much of the primary mineralogy and most of the primary textures of Li- and Cs-bearing granitic pegmatites are magmatic in origin (Jahns and Burnham, 1969; Cerny 1975; Cerny and Simpson 1978; Stewart 1978; Burnham and Nekvasil 1986; London et al. 1989). With the exception of London et al. (1989), these authors envisaged that crystallization occurred in the presence of an aqueous vapor, and concluded that such a vapor was essential to produce the observed textures. London et al. (1989) have recently challenged this conclusion by showing that all of the primary textures can be produced by non-equilibrium fractional crystallization of a volatile-rich melt in the absence of a separate aqueous vapor phase. Whether or not the characteristic primary textures require the intervention of an aqueous phase, it is nevertheless clear that aqueous fluids evolve from the parent magma at some, perhaps quite late, stage (London 1986a), and do ultimately play a role in the subsolidus evolution of rare element pegmatites. The most convincing evidence of this is the widespread occurrence of Li- and Cs-enriched metasomatic halos (commonly manifested by the appearance of holmquistite and/or Li- and Cs-bearing micas) in the rocks hosting such pegmatites (Heinrich 1965; London 1986b; Shearer et al. 1986; Morgan and London 1987; Shearer and Papike 1988). Furthermore, Stewart (1978) cites experimental and field observations suggesting that up to 0.64 wt% petalite can be dissolved in an aqueous vapor at 575°C and 2 kbar. Additional support for subsolidus involvement of hydrothermal (here hydrothermal simply refers to any high-temperature aqueous fluid, whether derived internally or externally relative

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to the pegmatite) solutions in pegmatite evolution comes from the nearly ubiquitous alteration of primary spodumene, petalite and pollucite to a variety of secondary phases or phase assemblages including albite, muscovite, K-feldspar, kaolinite, montmorillonite, eucryptite, lepidolite, cookeite (cf Cerny 1972; Cerny and Ferguson 1972; Cerny and Simpson 1978; London and Burt 1982a,b; Foord et al. 1986; Whitworth and Rankin 1989). A deeper understanding of the thermodynamics of these secondary processes is required in order to determine quantitatively the chemical evolution of the aqueous fluids responsible for both the internal alteration of the primary pegmatite minerals and the development of exomorphic halos (potentially important in exploration) in the wall-rocks.

London and Burt (1982b) provided the chemographic framework for a thermodynamic analysis of pegmatite alteration, but did not quantify their schematic phase diagrams owing to the paucity of thermochemical data at that time. Gordiyenko et al. (1988) carried out limited theoretical calculations on phase relationships between spodumene, albite, K-feldspar, and muscovite at 400 °C and 1 kbar. There have also been some experimental studies addressing the relative partitioning of Li, Cs, K and Na among aqueous fluids, melts and solid phases (Volfinger 1970, 1976; Lagache and Sabatier 1973; Carron and Lagache 1980; Dujon et al. 1991; Lagache and Sebastian 1991; Sebastian and Lagache 1990, 1991), but the range of pressures and temperatures covered by these studies is somewhat limited. Recently published thermochemical data for Li and Cs silicates (Bennington et al. 1983; Hemingway et al. 1984), and improvements that have been made to the Helgeson-Kirkham-Flowers (HKF) equation of state for aqueous species at elevated temperatures and pressures (Tanger and Helgeson 1988; Shock and Helgeson 1988), permit quantification of the phase relationships identified by London and Burt (1982a) and estimation of fluid-mineral partitioning of Li and Cs relative to Na and K.

In this paper we determine equilibrium constants for exchange reactions between the alkali feldspars, albite and K-feldspar, and the Li and Cs silicates, spodumene, petalite, eucryptite, and pollucite, and use these data to evaluate stability relationships among these phases in terms of the activity ratios Na/Li, K/Li, Na/Cs and K/Cs. The major finding of the study is that the alteration of eucryptite, petalite or spodumene to albite and/or K-feldspar is a normal consequence of closed-system pegmatite evolution, whereas alteration of pollucite to alkali feldspar implies infiltration of the pegmatite by an external fluid with very high Na/Cs and K/Cs ratios. The study also predicts that saline aqueous fluids in equilibrium with typical rare element pegmatites will have high Li and low Cs contents, relative to Na and K. Our hope, in presenting these results, is to provide a theoretical framework that will be of help in interpreting the cause of subsolidus alteration phenomena in rare element pegmatites.

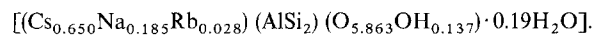
Methodology

We have performed our phase equilibrium calculations for temperatures from 100 ° to 700 °C and pressures from 0.5 to 5 kbar, the

probable maximum range of conditions for subsolidus alteration of most rare element pegmatites. In view of the common occurrence of saline fluid inclusions in these pegmatites (London 1986a; Thomas and Spooner 1988; Whitworth and Rankin 1989; Channer and Spooner 1992), we have also examined the effects of elevated concentrations of Cl ions in the aqueous phase on the cation ratios. The reactions that have been investigated in this study are listed in Table 1 and the thermochemical data for the mineral phases involved in these reactions are listed in Table 2.

The $\Delta H_{f,298}$, S_{298}° and V values for the Li minerals were taken from London (1984) in order to ensure consistency with his experimental P - T diagram showing the stability relationships among these minerals. The heat capacity data for these minerals are not reported by London (1984) and were therefore taken from Robie et al. (1978) in the case of spodumene and eucryptite, and from Hemingway et al. (1984) in the case of petalite. The P - T boundaries calculated using these data agree within experimental error with those shown by London (1984) and are internally consistent with the thermodynamic data base of Robie et al. (1978).

To our knowledge there are no thermodynamic data for end-member pollucite. We have therefore employed the $\Delta G_{f,298}$, $\Delta H_{f,298}$ and S_{298}° values for pollucite derived from experimental data of Bennington et al. (1983) for a natural phase having a composition of:



We have not attempted to make any correction to $\Delta G_{f,298}$ of this impure pollucite. In the absence of heat capacity data above 674 K, we have, following the recommendation of Dujon et al. (1991), used the heat capacity function for leucite given in Robie et al. (1978). The molar volume of pollucite was calculated from crystallographic data reported by Cerny (1974).

Thermodynamic data for quartz, albite and K-feldspar were taken from Helgeson et al. (1978). These data were employed because they are consistent with a wide variety of experimental phase equilibrium determinations and because the free energy data for K-feldspar in Helgeson et al. (1978) take into account the change in the state of ordering of this mineral as a function of temperature. However, the Helgeson et al. (1978) data-base does not contain the Li- or Cs-bearing minerals of interest here and Hemingway et al. (1982) have suggested that the 25 °C enthalpy data of Helgeson et al. (1978) for all aluminum-bearing phases (with the exception of gibbsite) differ by approximately 6485 J relative to those of Robie et al. (1978). Therefore, in an attempt to make the feldspar data from Helgeson et al. (1978) consistent with the thermodynamic data of Robie and coworkers for the aluminum-bearing phases, spodumene, petalite, eucryptite and pollucite, we systematically subtracted 6485 J from the free energies of albite and K-feldspar given by Helgeson et al. (1978). Recently, Sverjensky et al. (1991) have suggested that the free energies of albite and K-feldspar (as well as muscovite and paragonite) given by Helgeson (1978) require addi-

Table 1. Reactions investigated in this study

Reaction No.	Reaction
(1)	$\text{euc} + \text{Na}^+ + 2\text{qtz} = \text{alb} + \text{Li}^+$
(2)	$\text{euc} + \text{K}^+ + 2\text{qtz} = \text{ksp} + \text{Li}^+$
(3)	$\text{spd} + \text{qtz} + \text{Na}^+ = \text{alb} + \text{Li}^+$
(4)	$\text{spd} + \text{qtz} + \text{K}^+ = \text{ksp} + \text{Li}^+$
(5)	$\text{pet} + \text{Na}^+ = \text{qtz} + \text{alb} + \text{Li}^+$
(6)	$\text{pet} + \text{K}^+ = \text{qtz} + \text{ksp} + \text{Li}^+$
(7)	$\text{pol} + \text{qtz} + \text{Na}^+ = \text{alb} + \text{Cs}^+$
(8)	$\text{pol} + \text{qtz} + \text{K}^+ = \text{ksp} + \text{Cs}^+$
(9)	$\text{euc} + 3\text{qtz} = \text{pet}$
(10)	$\text{pet} = \text{spd} + \text{qtz}$
(11)	$2 \text{alb} + 2 \text{Li}^+ = \text{euc} + \text{pet} + 2\text{Na}^+$
(12)	$2 \text{alb} + 2 \text{Li}^+ = \text{spd} + \text{pet} + 2\text{Na}^+$
(13)	$2 \text{ksp} + 2 \text{Li}^+ = \text{euc} + \text{pet} + 2\text{K}^+$
(14)	$2 \text{ksp} + 2 \text{Li}^+ = \text{spd} + \text{pet} + 2\text{K}^+$

Table 2. Thermodynamic data for the mineral phases employed in the study

Phase (Abbrev.)	Formula	$\Delta G_{f,298}$ (cal/mol)	$\Delta H_{f,298}$ (cal/mol)	S°_{298} (cal/K-mol)	V (cal/bar)	a	b (10^3)	c (10^6)	d (10^2)	e (10^5)
Eucryptite (euc)	LiAlSiO ₄	-484196	-512440 ^a	21.7 ^a	1.1465 ^a	59.0 ^c	0	0	-4.92	-3.08
Petalite (pet)	LiAlSi ₄ O ₁₀	-1097551	-1163528 ^a	55.59 ^a	3.0688 ^a	209.4 ^c	-49.7	1.27	-25.55	9.64
Pollucite (pol)	CsAlSi ₂ O ₆	-697873 ^c	-740564 ^c	49.53 ^c	2.3 ^f	35.5 ^d	32.1	0	0	-5.17
Spodumene (spd)	LiAlSi ₂ O ₆	-688520	-729804 ^a	31.36 ^a	1.395 ^a	100.7 ^c	-5.74	0	-11.42	4.57
Albite (alb)	NaAlSi ₃ O ₈ (low)	-886310 ^b	-939680 ^b	49.51 ^b	2.391 ^b	61.7 ^b	13.9	0	0	15.01
		(high)	-884510 ^b	-937050 ^b	52.30 ^b	2.399 ^b	61.7 ^b	13.9	0	0
K-spar (ksp)	KAlSi ₃ O ₈	-895370 ^b	-949190 ^b	51.13 ^b	2.603 ^b	76.6 ^b	4.3	0	0	29.95
Quartz (qtz)	SiO ₂	-204646 ^b	-217650 ^b	9.88 ^b	0.542 ^b	11.2 ^b	8.2	0	0	-2.70

^aLondon (1984); ^bHelgeson et al. (1978); ^cRobie et al. (1978); ^dApproximated by the heat capacity parameters for leucite given by Robie et al. (1978); ^eBennington et al. (1983); ^fCerny (1974)

Note: the heat capacity equation corresponds to: $C_p = a + bT + cT^2 + dT^{1/2} + eT^2$

tional adjustments on the order of several hundred joules in order to be consistent with the experimentally determined phase equilibria of Hemley (1959), Hemley and Jones (1964) and Montoya and Hemley (1975) for the system Na₂O-K₂O-Al₂O₃-SiO₂-H₂O and the phases K-feldspar, muscovite, albite, paragonite, kaolinite and pyrophyllite. Because the suggested corrections are applied to all K- and Na-bearing phases in the Helgeson et al. (1978) data-base, the resulting free energies remain consistent with the experimental phase equilibrium constraints employed by Helgeson et al. (1978). We have therefore made the adjustments suggested by Sverjensky et al. (1991) to the free energies of albite and K-feldspar given in Helgeson (1978). Note that the adjustments suggested by Hemingway et al. (1982) and Sverjensky et al. (1991) are further justified in that the total correction applied is well within the experimental error quoted by Robie et al. (1978) for the calorimetrically derived free energies for these minerals. Finally, it should be noted that the thermodynamic data employed for albite correspond with those for the structural type (high or low) with the lower $\Delta G_{f,T,P}$ at each pressure and temperature.

The data discussed above and the data and equations of state for aqueous alkali metal ions from Tanger and Helgeson (1988) and Shock and Helgeson (1988) were used to calculate equilibrium constants (K) for the reactions listed in Table 1, and thus the activity ratios Na/Li, Na/Cs, K/Li and K/Cs, assuming that all minerals were in their standard state (i.e. the pure endmember phases at pressure and temperature). These calculated log K values were then used to construct log activity-temperature phase diagrams.

The assumption of negligible solid solution among the minerals involved in the reactions in Table 1 is well justified. Experimental studies by Sebastian and Lagache (1991), Lagache and Sebastian (1991), and Dujon et al. (1991) show that there is negligible substitution of Na in petalite or spodumene, and of Li in coexisting albite, at temperatures corresponding with those of the present study. It would, likewise, be expected that little K would substitute for Li in spodumene or petalite (or Li in K-feldspar), given the substantial differences in ionic radii of Li⁺ ($r = 0.68 \text{ \AA}$) and K⁺ ($r = 1.33 \text{ \AA}$). This expectation is confirmed by the experimental results of Volfinger (1970), which show that the Li/K ratio in sanidine at 600 °C and 1 kbar remains below 0.1 even as the solution Li/K ratio increases up to saturation with respect to spodumene. We are not aware of any data on the extent of substitution of K or Na for Li in eucryptite, but it is also likely to be small. Thus, the assumption that all minerals are in their standard states is reasonable for the Li-, Na- and K-bearing minerals involved in the reactions in Table 1. Experimental studies by Lagache and Sabatier (1973), Volfinger (1976), Carron and Lagache (1980) and Sebastian and Lagache (1990) suggest that the degree of substitution of Cs into albite and K-feldspar is very small, even at temperatures as high as 800 °C. However, the study by Sebastian and Lagache (1990), and data on natural pollucites (Cerny 1974), do suggest that Na readily enters into the pollucite structure, forming a nearly complete solid solution series between pollucite and analcime (the actual substitution being

Na⁺ + H₂O for Cs⁺; Cerny 1974). Therefore, for reactions in Table 1 involving pollucite, the assumption of negligible solid solution is made only as a first approximation. Further refinements of these calculations must await determination of the thermodynamics of mixing of pollucite and analcime.

Results

The results of the calculations discussed above are presented as plots of log activity ratios vs temperature for each simple exchange reaction (i.e. involving only one rare metal phase) in Table 1 at pressures of 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 kbar in Figs. 1 and 2. In the discussion that follows, where necessary and for convenience, we will use the symbol A to denote either Na or K.

The eucryptite-albite exchange reaction (reaction 1 and Fig. 1a) is characterized by an overall trend of increasing Na/Li with increasing temperature. The eucryptite-K-feldspar exchange reaction (reaction 2 and Fig. 1b) also shows a trend of increasing activity ratios (K/Li), but the absolute activity ratios are significantly lower than those for reaction (1). In both reactions (1) and (2) there is a crossover of A/Li ratio with changing temperature and pressure, i.e. at lower temperatures the A/Li ratios increase with increasing pressure, whereas the reverse is the case at higher temperatures. The temperature of crossover in both reactions is approximately 250 °C.

Exchange between spodumene and albite (reaction 3 and Fig. 1c), and spodumene and K-feldspar (reaction 4 and Fig. 1d), is also characterized by trends of increasing Na/Li ratios with increasing temperature. As in reactions (1) and (2) there is a crossover of A/Li ratio with changing temperature and pressure, although at much higher temperature, 550 ° and 450 °C, respectively. The K/Li ratio of reaction (4) is, likewise, much higher than the Na/Li ratio for reaction (3) at the same pressure and temperatures.

Reactions involving exchange between petalite and albite or K-feldspar (reactions 5, 6 and Fig. 2a, b) both display trends of increasing A/Li with increasing temperature, although the absolute A/Li ratio is much higher in the reaction involving albite (reaction 5). However, there is no indication of the type of crossover that was described above for the exchange reactions involving eucryptite and spodumene.

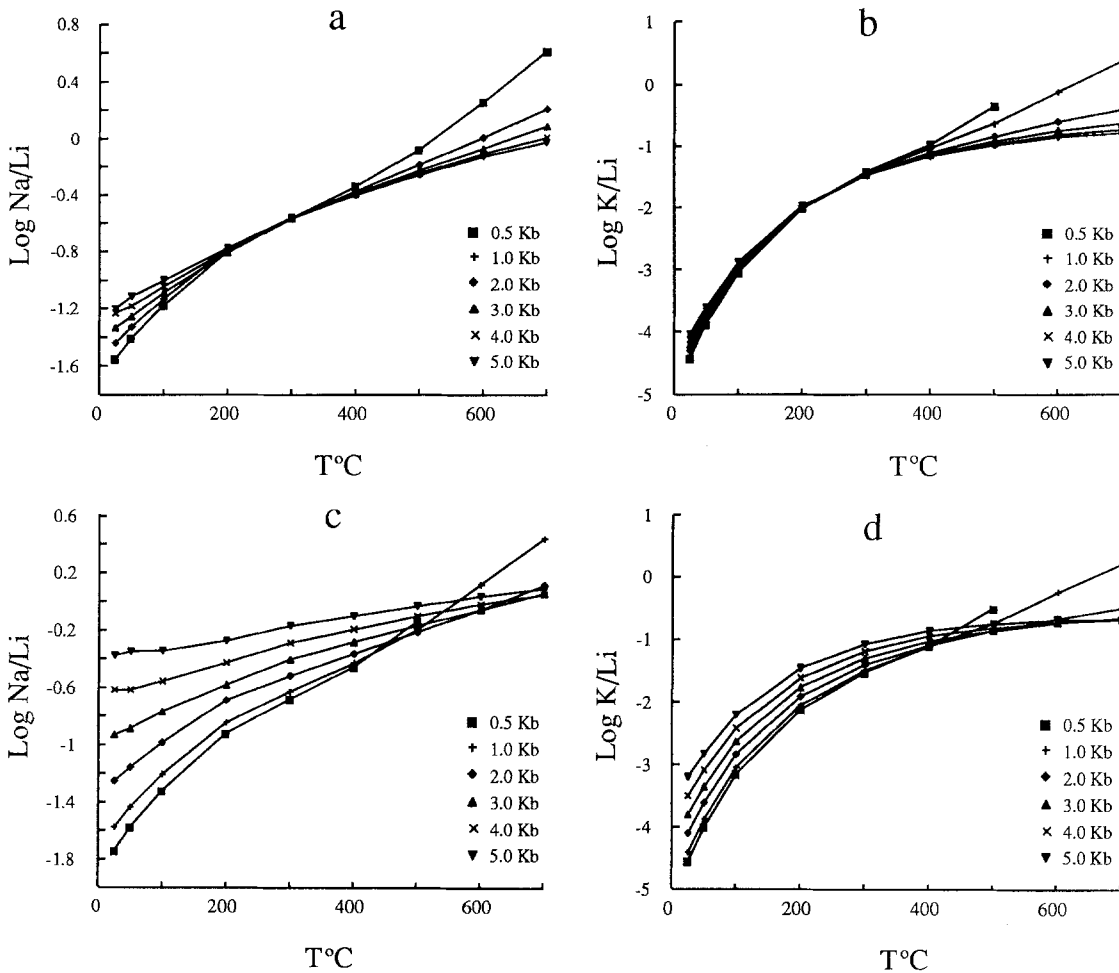


Fig. 1a-d. Calculated alkali metal activity ratios as a function of temperature and pressure: **a** Na/Li for albite-eucryptite exchange (reaction 1, Table 1); **b** K/Li for K-feldspar-eucryptite exchange

(reaction 2, Table 1); **c** Na/Li for albite-spodumene exchange (reaction 3, Table 1); **d** K/Li for K-feldspar-spodumene exchange (reaction 4, Table 1)

Exchange reactions between pollucite and albite or K-feldspar exhibit somewhat different behavior from the corresponding reactions involving Li-bearing minerals (reactions 7, 8, Fig. 2c, d). Firstly, the A/Cs ratio is much higher than the A/Li ratio in the latter reactions. Secondly, whereas the ratio A/Li generally increases with increasing temperature, the reverse is true for A/Cs. However, similar to the Li-exchange reactions, the ratio Na/Cs is consistently higher than the K/Cs ratio. In both the pollucite-albite and pollucite-K-feldspar exchange reactions, the A/Cs ratio decreases with increasing pressure. The apparently different behavior of Cs and Li is not so surprising. Quite consistently the smaller ion of the two involved in each exchange reaction is more strongly partitioned into the vapor phase as temperature decreases. That is, the overall preference for the hydrothermal fluid at low temperature follows the order $\text{Li} > \text{Na} > \text{K} > \text{Cs}$, which is the same order as that of the ionic radii.

The above discussion does not take into account the fact that the Li-bearing minerals are not necessarily stable over the complete range of temperature and pressure for which the exchange reactions have been investigated. We have therefore constructed temperature-activity (A/Li) diagrams to show the stability fields of assemblages involving these minerals, albite or K-feldspar, and quartz.

Quartz was included in the assemblage because it is an essential mineral in virtually all rare metal granitic pegmatites and it serves to fix the activity of silica in the calculations. The diagrams were constructed using data for the simple exchange reactions presented above (reaction 1-6), the equilibrium temperatures for the solid-solid reactions involving spodumene, quartz, eucryptite and petalite, and linear combinations (reactions 9-14) of the simple exchange reactions as required by chemographic analysis (cf. London and Burt, 1982b).

It can be seen from London (1984) that the stability of eucryptite, in the presence of quartz, is constrained by breakdown reactions to petalite or spodumene. As a result, exchange reactions (1) and (2) are applicable only at pressure and temperature conditions below 1.8 kbar and 300 °C. The equilibrium boundaries of these reactions, as a function of log activity ratio (A/Li) and temperature, are presented in Fig. 3a and 4a for a pressure of 1 kbar. In the case of reaction (1) the boundary extends from log activity (Na/Li) of approximately -1.2 to -0.7 , and in reaction (2) from log activity (K/Li) of approximately -3.0 to -1.8 , between 100° - 250 °C at 1 kbar.

We can also see from Figs. 3a and 4a that the exchange reactions (5) and (6) are only applicable at temperatures above 250 °C at 1 kbar. At higher pressures these reac-

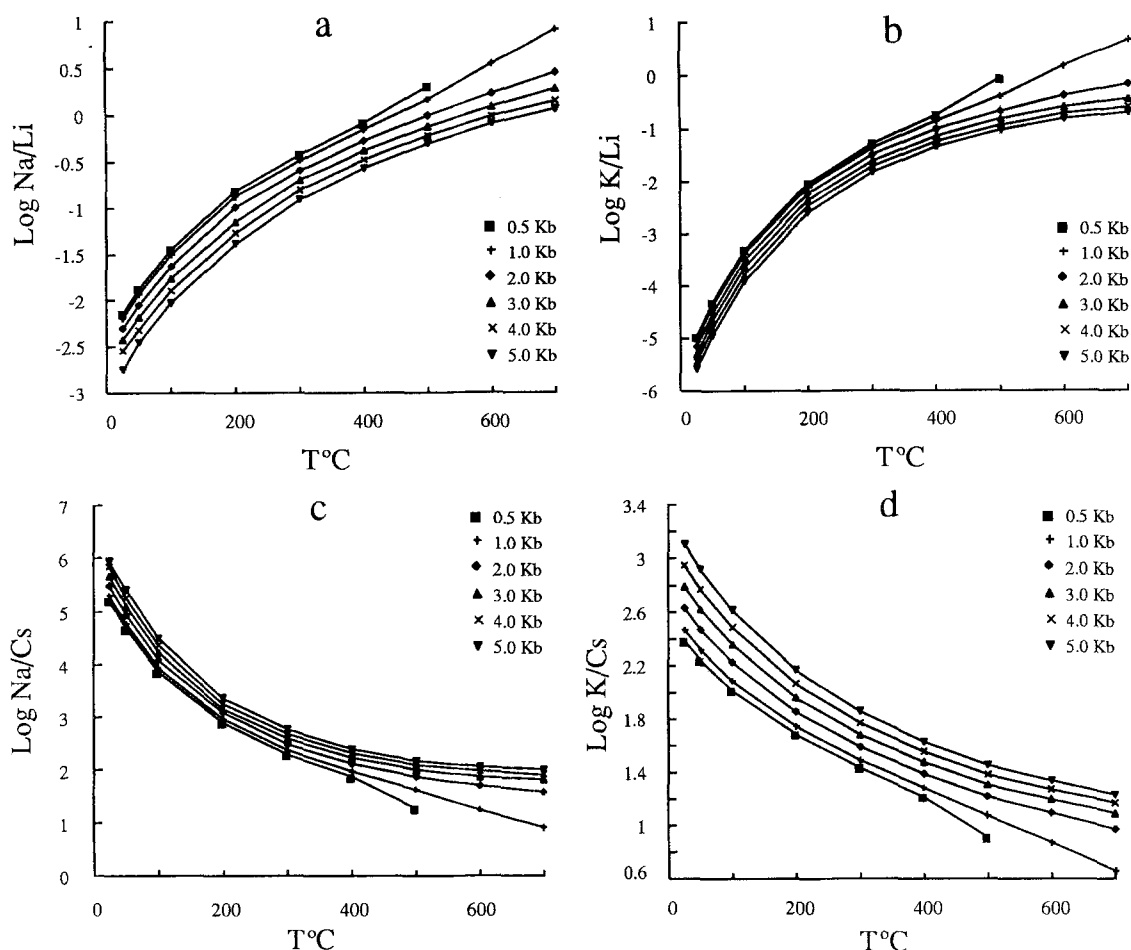


Fig. 2a-d. Calculated alkali metal activity ratios as a function of temperature and pressure: a Na/Li for albite-petalite exchange (reaction 5, Table 1); K/Li for K-feldspar-petalite exchange (reaction

6, Table 1); c Na/Cs for albite-pollucite exchange (reaction 7, Table 1); d K/Cs for K-feldspar-pollucite exchange (reaction 8, Table 1)

tions are limited to even higher temperature conditions. Thus, for example, at 4 kbar, they are limited to temperatures above 600 °C (Figs. 3c, 4c). At lower temperatures, spodumene and quartz are stable relative to petalite. The log activity (Na/Li) for reaction (5) ranges from approximately -0.70 at 250 °C to 0.8 at 700 °C at 1 kbar. The log activity ratio (Na/Li) decreases at higher pressures, and at 4 kbar is 0.20 at 700 °C. The corresponding ratio for reaction (6) at 1 kbar ranges from about -1.8 to 0.0 between 250 °C and 550 °C. At 4 kbar and 700 °C it is about -0.80 . Note that some of the exchange reactions may be further limited by melting at high temperatures and high water pressures.

Spodumene is stable only at pressures above 1.7 kbar, the pressure for the invariant assemblage quartz + petalite + spodumene + eucryptite (London 1984). The thermal stability of spodumene + quartz is limited by its breakdown to petalite, which ranges from 310 °C at 1.7 kbar to 675 °C at 4.2 kbar (London 1984). At higher temperatures and pressures spodumene + quartz break down to virgilite (cf. London 1984) or melt. Reactions (3) and (4) are thus constrained to temperatures below 350 °C at 2 kbar, and below 600 °C at 4 kbar. The log activity ratio (Na/Li) for (3) ranges from -0.95 (2 kbar) to -0.6 (4 kbar) at 100 °C and -0.4 (2 kbar) at 350 °C to 0.0 (4 kbar) at 600 °C. That of K/Li for (4) ranges from -2.8 (2 kbar) to -2.4

(4 kbar) at 100 °C and -1.2 (2 kbar) at 350 °C to -0.70 at 600 °C.

Discussion

Before attempting to apply our results to some geological problems, it is instructive to compare our calculated activity ratios with the few experimentally determined concentration ratios in the literature. In order to make this comparison, the activity coefficients of the aqueous alkali cations need to be known or estimated. For simplicity, we make the reasonable assumption that these activity coefficients approximately cancel when activity ratios are taken.

Sebastian and Lagache (1991) experimentally determined the ratio $\text{Na}/(\text{Na} + \text{Li})$ of a hydrothermal chloride solution in equilibrium, with petalite + albite + quartz at 1.5 kbar and 450 ° and 600 °C. Lagache and Sebastian (1991) conducted a similar set of experiments at 4 kbars using spodumene instead of petalite. Finally, Sebastian and Lagache (1990) measured the $\text{Na}/(\text{Na} + \text{Cs})$ ratio of aqueous chloride-bearing solutions in equilibrium with pollucite + albite + quartz at 1.5 kbar. We compare our calculated ratios with these experimental values in Table 3.

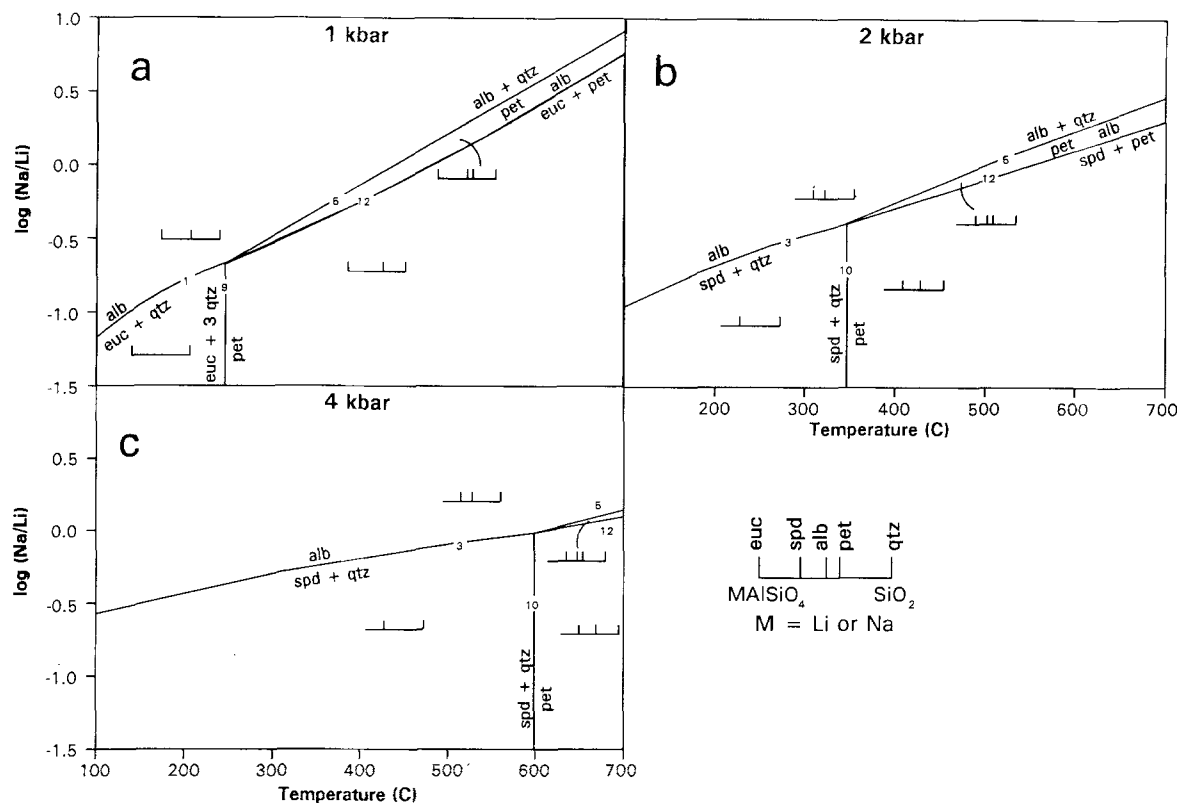


Fig. 3a-c. Log activity (Na/Li) vs temperature diagram at **a** 1 kbar; **b** 2 kbar; and **c** 4 kbar showing equilibria among albite, quartz, spodumene, eucryptite and petalite. Note that exchange equilibria involving nepheline are not shown on this diagram owing to the fact

that nepheline is rare in the types of pegmatites under discussion. Where eucryptite is not stable, the compositional input is shown open to the left for emphasis

Given the assumptions made in the calculations, the agreement with experimental values is very good. Furthermore, in the case of the petalite reaction, both the calculated and experimental Na/(Na + Li) values increase with temperature, and in the case of the pollucite reaction, both experimental and theoretical results show Na/(Na + Cs) decreasing with temperature. The trends for the spodumene reaction predicted by theory and indicated by experiment are not in perfect agreement, although the absolute measured and calculated values of the Na/(Na + Li) ratios are relatively close.

Despite the good agreement between experimental and calculated values, it may be possible further to improve the latter by making provisions in the model for the following: (1) alkali metal-chloride ion-pairs; (2) activity coefficient effects in the aqueous solution; and (3) solid solution between Na- and Cs-/Li-bearing phases.

At the present time, reliable dissociation constants for the alkali metal-chloride ion-pairs are only available for a limited range of the pressure-temperature conditions considered in this study. However, the effect of including alkali ion pairing with chloride on our calculated values can be partially assessed using the alkali metal-chloride ion-pair dissociation constants retrieved by Oelkers and Helgeson (1988). These constants are all quite similar at a given temperature and pressure (Oelkers and Helgeson 1988) and therefore will tend to cancel in our calculations. The effect of including them in our model is thus predicted to be small. Comparisons of calculated Na/(Na + Li) and Na/(Cs + Li) ratios, corrected for alkali metal-chloride

ion-pairing, with the measured values are presented in Table 3. It is evident from this table that the corrections are small and do not consistently improve the agreement between calculated and experimental values. However, although chloride-ion pairing does not significantly affect the alkali metal ratios, the absolute concentrations of all the alkalis will necessarily increase with increasing chloride (or any other anion for that matter) content of the fluid owing to the requirement that electroneutrality be maintained.

Current models for predicting activity coefficients of species in hydrothermal solutions suffer from relatively large uncertainties (Brimhall and Crerar 1987), but, because activity ratios are being employed in our study, it is reasonable to expect that the activity coefficients will largely cancel. We therefore conclude that including them will not significantly improve the accuracy nor the precision of our calculations.

Finally, as mentioned above, no meaningful improvement in our calculated alkali metal ratios is likely to result from taking into account the very minor solid solution effects for reactions involving Li-aluminosilicates. However, it is possible that the absolute calculated ratios for reactions involving pollucite will change significantly when thermodynamic data for solid solutions of this mineral become available. Nevertheless, the calculated trends with respect to temperature are probably valid.

The close agreement of our calculated alkali metal ratios with the few experimental data available, and the fact that further improvements to our thermodynamic

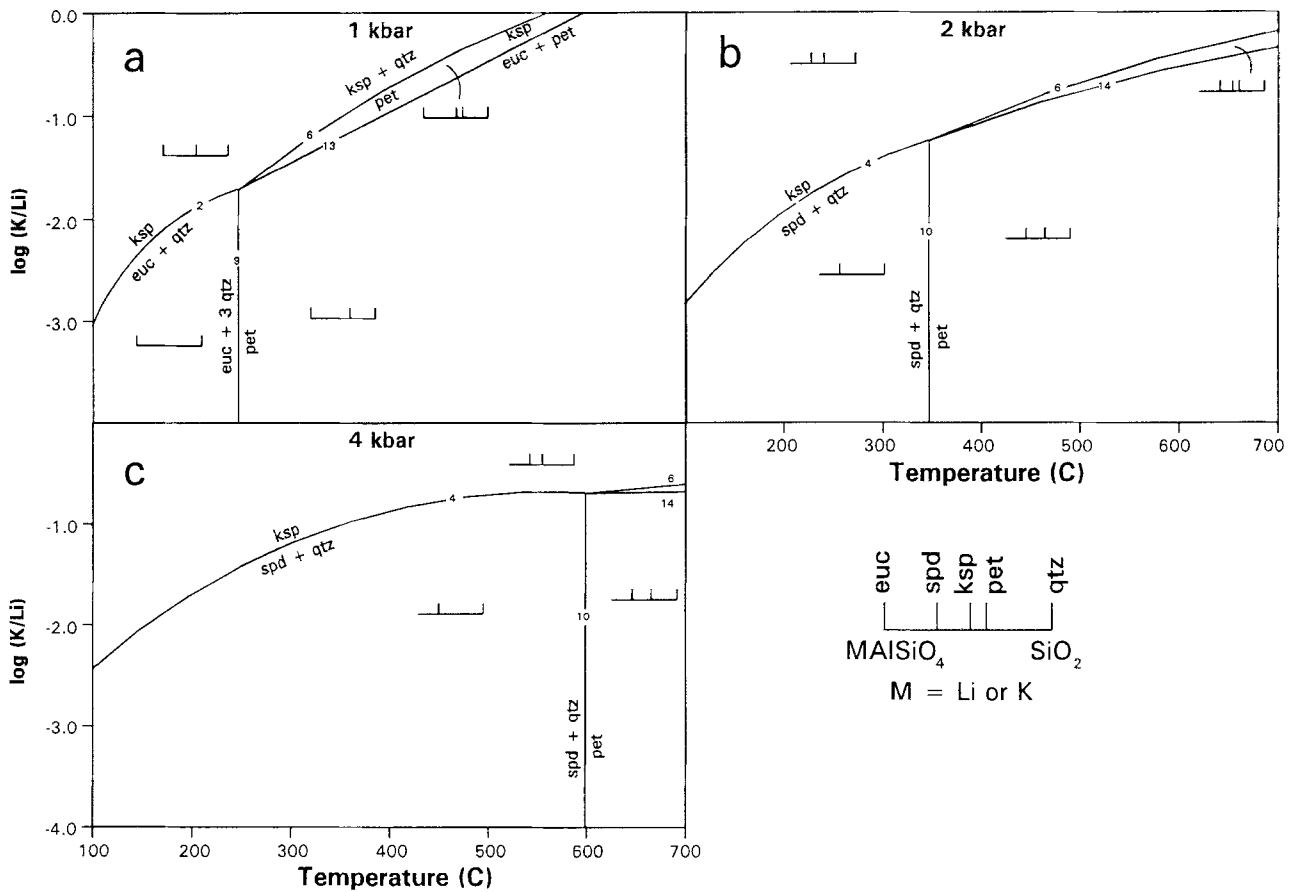


Fig. 4a-c. Log activity (K/Li) vs temperature at a 1 kbar; b 2 kbar; and c 4 kbar showing equilibria among K-feldspar, quartz, spodumene, eucryptite and petalite. Note that exchange equilibria involving leucite are not shown on this diagram owing to the fact that leucite is

rare in the types of pegmatites under discussion. Where eucryptite is not stable, the compositional input is shown open to the left for emphasis

model are likely to result in minimal changes to the overall trends in these ratios, suggests that we may apply our model calculations with some confidence to subsolidus alteration phenomena in natural pegmatites.

Geological application

One of the most striking aspects of the calculated Na/Li and K/Li ratios is that, under most temperature and pressure conditions of this study, Li predominates over Na and K in aqueous solutions in equilibrium with Li-aluminosilicates, alkali feldspars and quartz. Furthermore, Li becomes increasingly predominant with decreasing temperature. This suggests that if such a fluid were to escape from the pegmatite into the wall rocks, it would contain substantial Li, which would then be available to form Li-metasomatic halos. For example, at 4 kbar and 500°C, a solution containing 2 molal total alkali in equilibrium with quartz + K-feldspar + albite + spodumene is predicted to have the following concentration distribution: 1.03 molal Li, 0.82 molal Na and 0.15 molal K, or Na/Li and K/Li ratios of 0.79 and 0.15, respectively. Channer and Spooner (1992) have recently reported ion chromatographic analyses of leachates from fluid inclusions in the Tanco Pegmatite. These analyses yield low K/Li ratios in reasonable agreement with the

predicted ratios. The agreement is less satisfactory for the Na/Li ratio; the measured values in the fluid inclusions being consistently greater than unity and higher than the calculated values. The significance of this finding is presently unclear.

Assuming equilibrium is maintained with the pegmatite assemblage during cooling, the Li content of any aqueous fluid would increase dramatically with decreasing temperature. This suggests that Li-metasomatic halos may be more likely to form at a relatively late stage of pegmatite evolution, which is in agreement with geological observations (D. London, personal communication, 1990). That Na/Li and K/Li ratios generally increase with temperature is also consistent with the fact that albite and K-feldspar are almost invariably observed to replace Li-aluminosilicates rather than the other way around, and that such replacement appears to be a normal consequence of pegmatite evolution (London and Burt 1982b). Assuming that the pegmatite system is a closed one, the total amount of Li contained in the fluid and in the minerals should be constant. As temperature decreases, more and more Li will go into solution at the expense of the Li-aluminosilicate, and eventually albite and/or K-feldspar will completely replace the Li-bearing mineral.

The behavior of the Na/Cs and K/Cs ratios in fluids in equilibrium with pollucite + albite + K-feldspar +

Table 3. Comparison of experimental and calculated alkali metal ratios $\{Na/(Na + X)\}$ where X = Li or Cs

T (°C)	P (kbar)	Reaction ^a	Calculated ^b	Calculated ^c	Measured
450	4	3	0.42	—	0.55 ± 0.02^d
600	4	3	0.49	—	0.49 ± 0.03^d
450	1.5	5	0.46	0.59	0.52 ± 0.02^e
600	1.5	5	0.71	0.71	0.55 ± 0.02^e
450	1.5	7	0.99	0.98	0.89^f
600	1.5	7	0.96	0.98	0.78^f

^aReaction numbers keyed to Table 1; ^bCalculated neglecting chloride ion-pairing; ^cCalculated taking chloride ion-pairing into account;

^dLagache and Sebastian (1991); ^eSebastian and Lagache (1991); ^fSebastian and Lagache (1990)

quartz contrasts with that of the analogous ratios involving Li. First of all, under all conditions investigated in this study, Cs is a minor component of the fluid compared with Na, K and Li. This finding and the lesser abundance of Cs in general in pegmatites may explain the less prominent role of Cs, compared to Li, in metasomatic halos around rare metal pegmatites. Secondly, the equilibrium Na/Cs and K/Cs ratios increase with decreasing temperature. Applying reasoning analogous to that used in the case of the Li equilibria, it is difficult to envisage pollucite being replaced by either albite or K-feldspar in a closed pegmatite system with decreasing temperature. However, partial alteration of pollucite to both albite and K-feldspar does occur at the Tanco Pegmatite, Manitoba and elsewhere (Cerny and Simpson 1978). Such alteration would appear to be possible only if fluids external to the pegmatite, with extremely high Na/Cs and K/Cs ratios, enter the system. Indeed, Cerny and Simpson (1978) called upon an external source of fluids in order to explain the spatial distribution and zonation of alteration of the pollucite body at Tanco. It should be pointed out that the pollucite-altering fluids need not be external to the pegmatite as a whole, but might also come from other Cs-poor zones in a heterogeneous rare metal pegmatite.

Leachate analyses of fluid inclusions in quartz from Tanco (Channer and Spooner 1982) yield Na/Cs ratios in broad agreement with our calculated ratios. However, the K/Cs ratios are generally less than one, in contrast to our calculated values. Additional leachate data of this type from a variety of rare metal pegmatites, or better, direct analyses of individual fluid inclusions are clearly required before the meaning of this discrepancy can be understood.

We have dealt with relatively simple fluid compositions in this paper. Recent fluid inclusion (London 1986a) and experimental (London et al. 1989) studies have shown that magmatic fluids existing during early stages of pegmatite formation may be complex borosilicate melts charged with volatiles. Our calculations, based on simple aqueous fluids, may not be directly applicable to this stage of pegmatite evolution, owing to the possible existence of alkali borate (London 1986a) or alkali aluminosilicate complexes (Burnham and Nekvasil 1986). There is some evidence that such complexes may exhibit different stability behavior depending on the alkali metal (London 1986a; Burnham and Nekvasil 1986), and the ratios of total activities of the alkali metals in complicated solution may exhibit different trends from those calculated here. However, although relatively few attempts have been made to characterize the temperature and other physico-chemical characteristics of the fluids specifically respons-

ible for subsolidus alteration processes in rare element pegmatites, several studies have suggested the eventual evolution of a predominantly aqueous, chloride-bearing fluid as pegmatite evolution proceeds and borosilicate and aluminosilicate components are lost to crystallizing phases (London 1986a; Whitworth and Rankin 1989; Thomas and Spooner 1988). The theoretical calculations of this paper are directly applicable to these later subsolidus fluids.

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Note added in proof

An additional check on the accuracy of our calculations can be made by comparing our results for the K/Na ratio for an aqueous fluid in equilibrium with albite + K-feldspar with direct experimental measurements reported in the literature. From our calculations at 1 kbar we obtain K/Na ratios of 0.133, 0.204, 0.280 and 0.43 at 300°, 400°, 500° and 600 °C, respectively. Lagache and Weisbrod (1977) measured K/Na to be 0.083, 0.139, 0.200 and

0.264 at the same temperatures, essentially constant over the pressure range 0.2 to 2 kbar. In a similar set of experiments, Orville (1963) measured K/Na to be 0.227 at 500 °C and 0.302 at 600 °C and 2 kbar. Both experimental and theoretical results suggest a rather weak pressure dependence. The agreement between experiment and theory is excellent, especially considering that our theoretical calculations do not take into account the significant solid solution that occurs between albite and K-feldspar.