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# Experimental study of Li-rich granitic pegmatites: Part III. Thermodynamic implications of the experiments in the Na-Li-Cs system: Consequences for the properties of solutes

SAINT-CLAIR DUJON, MARTINE LAGACHE, ANSOM SEBASTIAN
Laboratoire de Géologie, Ecole normale supérieure, URA 1316, 24, rue Lhomond, Paris 75231, France

## ABSTRACT

Previous experimental studies in the systems albite-petalite-pollucite-quartz-$H_2O$ or albite-spodumene-pollucite-quartz-$H_2O$, both with NaCl, LiCl, and CsCl in solution, have shown that the minerals form restricted solid solutions and that the composition of the fluid is buffered by the coexisting mineral assemblages. New experiments on the assemblage petalite + pollucite + quartz + chloride solution confirm the internal consistency of the experiments in the whole system of albite-petalite-pollucite-quartz fluid at 450 and 600 °C, 1.5 kbar. The variation in the composition of the fluids with temperature allows us to calculate the difference in entropy terms for the solutes in the fluid: NaCl, LiCl, CsCl. Comparisons among the experiments show that (1) pressure has no influence upon the properties of the fluids, (2) there is no measurable effect of mixing entropies in the fluid, and (3) the standard Gibbs energy of formation of the aqueous species, which is certainly related to the hydration of the species, changes with temperature, in a different way for the different species.

## INTRODUCTION AND PREVIOUS WORK

In the late stage of crystallization of granitic pegmatites, the growth of the rare alkali minerals petalite, spodumene, and pollucite indicates high concentrations of Li and Cs in the system. In previous papers (Sebastian and Lagache, 1990, 1991; Lagache and Sebastian, 1991) we have presented experiments on the partitioning of Li, Na, and Cs among these typical rare alkali pegmatitic minerals, albite, and a coexisting alkali-chloride aqueous solution.

The reactions studied were the following:

$$\underset{\text{petalite}}{LiAlSi_4O_{10}} + NaCl \rightleftharpoons \underset{\text{albite}}{NaAlSi_3O_8} + \underset{\text{quartz}}{SiO_2} + LiCl \quad (1)$$

$$\underset{\alpha\text{ spodumene}}{LiAlSi_2O_6} + \underset{\text{quartz}}{SiO_2} + NaCl \rightleftharpoons \underset{\text{albite}}{NaAlSi_3O_8} + LiCl \quad (2)$$

$$\underset{\text{pollucite}}{CsAlSi_2O_6} + \underset{\text{quartz}}{SiO_2} + NaCl \rightleftharpoons \underset{\text{albite}}{NaAlSi_3O_8} + CsCl. \quad (3)$$

The experimental results discussed in the earlier papers have already shown that the minerals contain very limited solid solutions except for Na in pollucite, in which the maximum value of the atomic proportion Na/(Na + Cs) reaches 0.2 at 600 °C, 1.5 kbar in the presence of albite. At equilibrium, for each reaction, the assemblage of the three minerals involved buffers the binary aqueous chloride solution. The compositions of these buffered fluids were determined by the experiments and are presented in Table 1, together with the experimental conditions. They are given by the ratio $Y_i = i/(i + j)$, where $i$ is the molar concentration of the alkali chloride in the first member of each reaction, and $j$ is the molar concentration of the alkali chloride in the second member.

## PETALITE-POLLUCITE-QUARTZ-FLUID: Li-Cs EXCHANGE

In 1846, Breithaupt (Fairbanks, 1928) described two minerals constantly associated in the cavities of the granite from the isle of Elba. He named them castorite ($LiAlSi_4O_{10}$) and pollucite ($CsAlSi_2O_6$) after the names of the Dioscuri Castor and Pollux, twins famous in Greek mythology for their inseparable companionship. Castorite is now called petalite. Since this time, this two-mineral assemblage has been found in many pegmatite bodies. In the famous Tanco pegmatite, where the two minerals occur, a low-pressure regime tends to produce this assemblage (Černý and Ferguson, 1972).

### New experiments

In this paper, we present new experimental results on the binary exchange Cs-Li in the assemblage pollucite + petalite + quartz + aqueous chloride solution.

The reaction studied is

$$\underset{\text{petalite}}{LiAlSi_4O_{10}} + CsCl \rightleftharpoons \underset{\text{pollucite}}{CsAlSi_2O_6} + \underset{\text{quartz}}{2SiO_2} + LiCl. \quad (4)$$

Two sets of experiments were performed: six experiments at 450 °C, 1.5 kbar and 16 experiments at 600 °C, 1.5 kbar. The experimental procedure is the same as described in the previous papers (Sebastian and Lagache,

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**TABLE 1.** Ratio of the molar concentrations of the elements *i* and *j* in the buffered fluid at 450 and 600 °C for Reactions 1, 2, 3, and 4

| Reaction | Temperature °C | $P_{H_2O}$ kbar | $Y_i = i/(i + j)$ |
|---|---|---|---|
| 1 | 450 | 1.5 | 0.520 ± 0.020 |
| 1 | 600 | 1.5 | 0.545 ± 0.015 |
| 2 | 450 | 4 | 0.550 ± 0.025 |
| 2 | 600 | 4 | 0.485 ± 0.025 |
| 3 | 450 | 1.5 | 0.910 ± 0.010 |
| 3 | 600 | 1.5 | 0.820 ± 0.010 |
| 4 | 450 | 1.5 | 0.120 ± 0.020 |
| 4 | 600 | 1.5 | 0.220 ± 0.020 |

1991; Lagache and Sebastian, 1991). The reactants are natural petalite and quartz, pollucite gel, and 1-molar chloride solution.

The results are presented in Tables 2 and 3. $X$ is the mole fraction Cs/(Cs + Li) in the bulk solid assemblage, and $Y$ is the mole fraction Cs/(Cs + Li) in the solution. A graphical representation by the classical isotherm-isobar distribution diagram is given in Figure 1.

As in previous studies, the results show that the fluid composition is buffered at equilibrium by quartz, petalite, and pollucite. The experimental values of $Y$ in the buffered solutions are equal to 0.120 ± 0.020 at 450 °C and to 0.220 ± 0.020 at 600 °C. These results are also reported in Table 1.

The maximum amount of substitution in minerals was not determined but is constrained by the limits of the plateau of constant solution composition (buffered solution) in Figure 1. At 600 °C the substitution is very restricted in both minerals. As solid solution gaps increase when $T$ decreases, the substitution must be even more restricted at 450 °C, although we did not perform the entire set of experiments at this temperature.

### Comparison with previous work

The results of these new experiments could have been predicted. Reactions 1 and 3 are two limiting binary systems of the ternary system Na-Cs-Li (albite–quartz–petalite–pollucite–aqueous chloride solution), which has not been directly studied. The study of Reactions 1 and 3 has shown that solid solutions of Li and Cs in albite and of Na in petalite and pollucite are restricted. The more the atomic numbers of two alkali elements are different, the more difficult the solid substitution. Thus we would expect solid solutions of Cs in petalite and of Li in pollucite to be limited.

Under these conditions, the whole mineral assemblage of the ternary system buffers a ternary aqueous solution whose composition is entirely determined. Knowing the compositions of the buffered solutions in Reactions 1 and 3, it is then possible to calculate Cs/(Cs + Li) in the solution of the Reaction 4. These calculated values are 0.10 at 450 °C and 0.21 at 600 °C, both at a confining pressure of 1.5 kbar. Both are within the error limits of the experimentally determined values. This indicates that all the experiments are internally consistent.

## DETERMINATION OF THE FLUID PROPERTIES FROM THE THERMODYNAMICS OF THE REACTIONS

We will emphasize the partial molar entropies of the fluid species. For a given fluid system, the standard properties are constant at given temperature and pressure and are independent of the solid minerals.

Interpretation of the experimental studies will allow us to determine: (1) if there is an influence of pressure on fluid properties, (2) if the different solutes interact one with each other, which would result in a measurable thermodynamic function of mixing, (3) how the calculated values of the thermodynamic functions fit with the experimental variations of the fluid composition, (4) what the relationships are between the thermodynamic functions and the atomic size of the solutes, and (5) what can be deduced from the thermodynamic function about the variation of hydration of the aqueous species as temperature increases.

### Method

In the fluid phase, the partial molar entropy $\overline{S}$ and the ratio of concentrations $Y_{ij}$ are related by

$$\overline{S}_i - \overline{S}_j = (\overline{S}_i^0 - \overline{S}_j^0) + (\overline{S}_i^{\mathrm{ex}} - \overline{S}_j^{\mathrm{ex}}) - \mathrm{R}\frac{\partial[T\ln(Y_i/Y_j)]}{\partial T}. \tag{5}$$

The variable $i$ is the alkali chloride solute in the first member of the reaction: NaCl for the Reactions 1 to 3 and CsCl for Reaction 4. The variable $j$ is the alkali chloride solute in the second member. These solutes are treated as perfectly mobile in Korzhinskii's conventions (1957).

The quantities $S_i$ and $S_j$ are the partial molar entropies

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

| | | Reactants | | | | | Final bulk solid composition µmol/100 mg | | | | Solution composition µmol/100 µL | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Number | Days | | mg | | M | µL | | Cs | Li | $X$ | Cs | Li | $Y$ |
| 78 | 65 | Pe | 50 | CsCl | 1 | 75 | Po + Q + Pe | 88 | 187 | 0.32 | 11 | 81 | 0.11 |
| 79 | 65 | Po + Pe | 100 | CsCl | 1 | 50 | Po + Q + Pe | 172 | 112 | 0.60 | 14 | 84 | 0.14 |
| 80 | 65 | Po + Pe | 50 | CsCl | 1 | 50 | Po + Q + Pe | 197 | 69 | 0.74 | 12 | 90 | 0.12 |
| 81 | 65 | Po + Pe | 50 | CsCl | 1 | 100 | Po + Q + Pe | 241 | 10 | 0.96 | 12 | 88 | 0.12 |
| 82 | 65 | Po + 2Q | 100 | LiCl | 1 | 50 | Po + Q + Pe | 212 | 10 | 0.95 | 10 | 86 | 0.10 |
| 83 | 65 | Po + 2Q | 50 | LiCl | 1 | 50 | Po + Q + Pe | 188 | 15 | 0.97 | 12 | 87 | 0.12 |

*Note:* Reactants: Pe = natural petalite, Po = pollucite gel, Q = quartz. Final bulk solid composition: Pe = petalite, Po = pollucite, Q = quartz.

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

| | | Reactants | | | | | Final bulk solid composition µmol/100 mg | | | | Solution composition µmol/100 µL | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Number | Days | | mg | | M | µL | | Cs | Li | $X$ | Cs | Li | $Y$ |
| 84 | 35 | Pe | 200 | CsCl | 1 | 25 | Pe + Po + Q | 9 | 310 | 0.03 | 20 | 75 | 0.21 |
| 85 | 35 | Pe | 100 | CsCl | 1 | 25 | Pe + Po + Q | 18 | 303 | 0.06 | 22 | 74 | 0.23 |
| 86 | 35 | Pe | 100 | CsCl | 1 | 50 | Pe + Po + Q | 35 | 284 | 0.11 | 22 | 76 | 0.22 |
| 87 | 35 | Pe | 100 | CsCl | 1 | 100 | Pe + Po + Q | 66 | 233 | 0.22 | 24 | 76 | 0.24 |
| 88 | 35 | Po + 2Q | 50 | LiCl | 1 | 200 | Pe + Po + Q | 69 | 169 | 0.29 | 20 | 70 | 0.22 |
| 89 | 35 | Pe | 100 | CsCl | 1 | 150 | Pe + Po + Q | 94 | 181 | 0.34 | 24 | 76 | 0.24 |
| 90 | 35 | Pe | 50 | CsCl | 1 | 100 | Pe + Po + Q | 110 | 155 | 0.42 | 22 | 75 | 0.23 |
| 91 | 35 | Pe + Po | 100 | CsCl | 1 | 25 | Pe + Po + Q | 150 | 126 | 0.54 | 18 | 72 | 0.20 |
| 92 | 35 | Pe + Po | 100 | CsCl | 1 | 50 | Pe + Po + Q | 164 | 121 | 0.58 | 22 | 72 | 0.23 |
| 93 | 35 | Po + 2Q | 50 | LiCl | 1 | 100 | Pe + Po + Q | 177 | 58 | 0.75 | 20 | 74 | 0.21 |
| 94 | 35 | Pe + Po | 50 | CsCl | 1 | 75 | Pe + Po + Q | 250 | 68 | 0.79 | 18 | 72 | 0.20 |
| 95 | 35 | Po + 2Q | 100 | LiCl | 1 | 100 | Pe + Po + Q | 188 | 30 | 0.86 | 22 | 78 | 0.22 |
| 96 | 35 | Pe + Po | 50 | CsCl | 1 | 100 | Pe + Po + Q | 229 | 26 | 0.90 | 20 | 75 | 0.21 |
| 97 | 35 | Po + 2Q | 100 | LiCl | 1 | 25 | Pe + Po + Q | 208 | 10 | 0.95 | 20 | 74 | 0.21 |
| 98 | 35 | Pe + Po | 50 | CsCl | 1 | 150 | Po + Q | 261 | 8 | 0.97 | 38 | 75 | 0.41 |
| 99 | 35 | Pe + Po | 50 | CsCl | 1 | 300 | Po + Q | 265 | 4 | 0.99 | 65 | 30 | 0.68 |

*Note:* Reactants: Pe = natural petalite, Po = pollucite gel, Q = quartz. Final bulk solid composition: Pe = petalite, Po = pollucite, Q = quartz.

of the alkali chlorides $i$ and $j$ in the fluid. The quantities $S_i^0$ and $S_j^0$ are the standard partial molar entropies at the pressure and temperature of the experiments. With a chosen standard state and for a specific fluid system, pressure, and temperature, they are constant.

The quantities $\overline{S}_i^{ex}$ and $\overline{S}_j^{ex}$ are the excess partial molar entropies of mixing of the species $i$ and $j$ at the same conditions. In addition to the above parameters, $\overline{S}^{ex}$ is dependent also on the concentrations of the species $i$ and $j$.

These concentrations are expressed by the molar ratio $Y_i/Y_j = i/j$. This ratio varies only slightly in our experiments between 450 °C and 600 °C for the same pressure, and it is probable that this slight variation does not affect the $\overline{S}^{ex}$ values.

At equilibrium and for a given pressure, we can write for Reactions 1 to 4:

$$dG = n_i d\mu_i - n_j d\mu_j - \Delta S_s dT = 0. \tag{6}$$

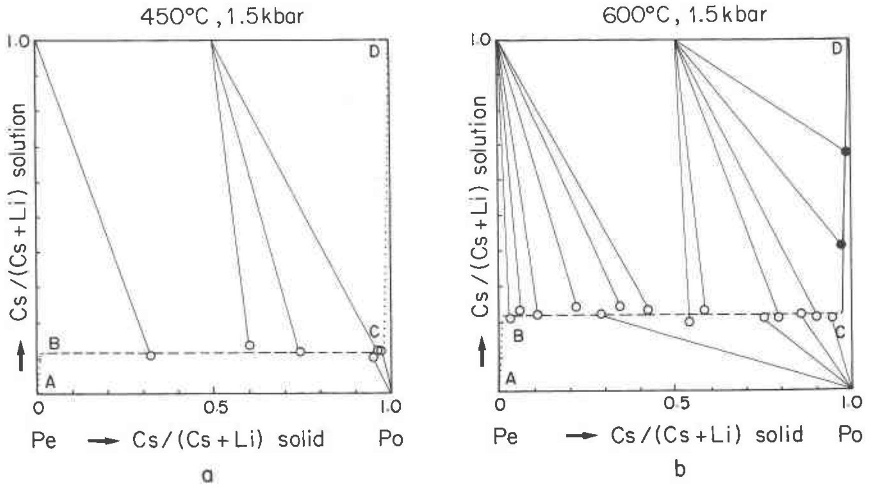
The quantity $G$ is the Gibbs free energy of the system. The quantities $\mu_i$ and $\mu_j$ are the chemical potentials of the alkali species in aqueous solution. The coefficients $n_i$ and $n_j$ are the stoichiometric coefficients of the reactant $i$ and of the product $j$. The quantity $\Delta S_s$ is the overall variation of entropy of the solid phases, which are considered to be perfectly inert.

By partial differentiation of Equation 6 with respect to temperature, we can write

$$n_iS_i - n_jS_j = \Delta S_s. \tag{7}$$

Since $S_i - S_j = \partial(\mu_i - \mu_j)/\partial T$, Reactions 1 to 4 are represented in a $(\mu_i - \mu_j)$ vs. $T$ diagram by straight lines, the slopes of which are negatives of the overall variations in entropy of the solid phases.

**Numerical calculations.** With sets of experiments at 450 and 600 °C, 1.5 kbar for the Reactions 1 to 4, it is possible



a

b

Fig. 1. An isothermal isobaric projection showing distribution curves at 450 °C (**a**) and 600 °C (**b**), 1.5 kbar. Slanting lines connect the starting and final assemblages for each experiment. The solid circles represent pollucite + quartz, and empty circles represent pollucite + petalite + quartz. Dotted lines correspond to assemblages that have not been experimentally determined.

**TABLE 4.** Molar entropy values ($\overline{S}_s$) of the minerals involved in the reactions studied at 298 K

| Mineral | $\overline{S}_s$ (J/mol·K) |
|---|---|
| Petalite | 232.6 (London, 1984) |
| α spodumene | 129.3 (Robie et al., 1978) |
| Pollucite | 207.2 (Bennington et al., 1983) |
| High albite | 226.4 (Robie et al., 1978) |
| Quartz | 41.5 (Robie et al., 1978) |

**TABLE 5.** Calculated thermodynamic functions

| Reaction | $\Delta\overline{S}_s$ | $R\frac{\partial[T\ln(Y_i/Y_j)]}{\partial T}$ | $(\overline{S}^0+\overline{S}^{ex})_i-(\overline{S}^0+\overline{S}^{ex})_j$ |
|---|---|---|---|
| 1 | +32.3 | +5.5 ± 6.1 | +37.8 ± 6.1 |
| 2 | +50.6 | −11.0 ± 8.1 | +39.6 ± 8.1 |
| 3 | −28.7 | −19.5 ± 8.2 | −48.2 ± 8.2 |
| 4 | +61.0 | +19.0 ± 13.3 | +80.0 ± 13.3 |

*Note:* First column: reaction involved. Second column: variation in the overall entropy of the solids at 525 °C. Third column: variation between 450 and 600 °C in the term related to the concentration of the fluid (calculated from the experimental results). Fourth column: difference in characteristic entropy terms of the fluid. All values are in J/mol·K.

to determine $(\overline{S}^0 + \overline{S}^{ex})_i - (\overline{S}^0 + \overline{S}^{ex})_j$ in the fluid at the intermediate temperature 525 °C.

According to Equation 7 we will substitute $\Delta\overline{S}_s$ for $\overline{S}_i - \overline{S}_j$ in Equation 5, calculated from molar entropies of the minerals given in the literature (Table 4). As $n_i = n_j = 1$, we can write

$$\Delta\overline{S}_s = (\overline{S}_i^0 - \overline{S}_j^0) + (\overline{S}_i^{ex} - \overline{S}_j^{ex}) - R\frac{\partial[T\ln(Y_i/Y_j)]}{\partial T}. \qquad (8)$$

The quantity $R\partial[T\ln(Y_i/Y_j)]/\partial T$ has been calculated from the experimental results at 450 and 600 °C from the variations of $Y_{ij}$ with temperature, assuming a linear variation between the two experimental points. The concentrations of the species $i$ and $j$ are molar concentrations.

The sum of $\Delta\overline{S}_s$ and $R\partial[T\ln(Y_i/Y_j)]/\partial T$, from Equation 5 gives $(\overline{S}^0 + \overline{S}^{ex})_i - (\overline{S}^0 + \overline{S}^{ex})_j$. The three sets of values for each of the four reactions are given in Table 5.

**Discussion on the values of the entropies of the solids.** In our experiments, there are only restricted solid solutions, so we have taken the values of the molar entropies of formation of the pure end-member minerals. These values are given at 298 K in Table 4, after various authors. The changes of these values between the temperature of the experiments and 298 K depend upon the values of $C_P$, the specific heats of the minerals. To maintain uniformity, we used the same fitting law of variation of $C_P$ with the absolute temperature $T$ for all experiments:

$$C_P = k_0 + k_1T^{-0.5} + k_2T^{-2} + k_3T^{-3}.$$

Coefficients $k_0$ to $k_3$ for quartz and high albite are taken from Berman (1988). For α spodumene and petalite, they are taken from Vidal and Goffé (1991). These authors fitted the data of α spodumene from Robie et al. (1978) and calculated the $k$ parameters for petalite, assuming that these values were the sum of the $C_P$ functions of their oxide constituents. The values of $C_P$ resulting from their calculation did not differ by more than 1.2% from those measured by Hemingway et al. (1984). These last authors gave a fitting law of $C_P$ with temperature that is different from the one given above; for this reason, we prefer Vidal and Goffé's law. For pollucite, the value of entropy at 298 K (Table 4), is known but there are no data for $C_P$. Fortunately, this mineral has the same structure as leucite, with which it forms complete solid solution (Martin and Lagache, 1975). Thus we have taken the $C_P$ value for leucite as a first approximation for that of pollucite. The fitted $k$ parameters for leucite are (Berman, personal communication) $k_0 = +271.13965$, $k_1 = -944.133$, $k_2 = -7\,857\,238$, $k_3 = +959\,202\,560$.

With these data, we have calculated for each reaction the difference of $\Delta\overline{S}_s$, the overall partial molar entropy variation of the solids, between 798 K (the temperature of interest) and 298 K. This variation (in J/mol·K) is equal to −3.4 for Reaction 1, to −5.0 for Reaction 2, to −6.4 for Reaction 3, and to 3.0 for Reaction 4. Knowing $\Delta\overline{S}_s$ at 298 K from Table 4, we can then calculate $\Delta\overline{S}_s$ at 798 K (Table 5).

## Results

**Influence of pressure on the properties of the fluids.** This influence can be determined by comparing Reactions 1 and 2, which involve Na-Li exchange. In both reactions, the species in the fluid phase are the same, i.e., NaCl and LiCl.

Reaction 1 was performed at 1.5 kbar, 450 and 600 °C, allowing us to calculate $(\overline{S}^0 + \overline{S}^{ex})_{NaCl} - (\overline{S}^0 + \overline{S}^{ex})_{LiCl}$ at the intermediate temperature of 525 °C at 1.5 kbar (Table 5). Reaction 2 was performed at 4 kbar, 450 and 600 °C, allowing us to calculate $(\overline{S}^0 + \overline{S}^{ex})_{NaCl} - (\overline{S}^0 + \overline{S}^{ex})_{LiCl}$ at the intermediate temperature of 525 °C at 4 kbar (Table 5). The two values of $(\overline{S}^0 + \overline{S}^{ex})_{NaCl} - (\overline{S}^0 + \overline{S}^{ex})_{LiCl}$, at the same temperature but at different pressures, overlap broadly within the error range. This indicates that there is no detectable influence of pressure between 1.5 and 4 kbar on this entropy term for the concentrations determined in the NaCl-LiCl system. The value of this entropy term is estimated to be 39 J/mol·K at 525 °C.

**Interaction between the different solute species.** This interaction can be determined by the comparison of Reactions 1, 3, and 4. If we suppose that $\overline{S}^{ex}$ is negligible, the $\overline{S}^0_{CsCl} - \overline{S}^0_{LiCl}$ value for Reaction 4 is obtained by the difference between $\overline{S}^0_{NaCl} - \overline{S}^0_{LiCl}$ for Reaction 1 and $\overline{S}^0_{NaCl} - \overline{S}^0_{CsCl}$ for Reaction 3. This difference (86.0 ± 14.3 J/mol·K) overlaps the value 80.0 ± 13.3 J/mol·K determined for Reaction 4. When the reaction takes place, the entropy variation of the solids is thus mainly accommodated by the variation in the standard entropy of the fluids. There is no measurable interaction among the solutes in the ternary system NaCl-LiCl-CsCl in solution: $\overline{S}^{ex}$ can actually be disregarded.

**Variation of fluid composition with temperature.** A classical representation of the variation of the system with temperature is a $(\mu_i - \mu_j)$ vs. $T$ diagram (London and Burt, 1982). In the petalite-albite system (Sebastian and Lagache, 1991), the ratio of concentrations of the species NaCl and LiCl increases with temperature even though $(\mu_{NaCl} - \mu_{LiCl})$ decreases. In contrast, in the spodumene-albite system (Lagache and Sebastian, 1991), the ratio of concentrations decreases with temperature as does $(\mu_{NaCl} - \mu_{LiCl})$.

This apparent discrepancy can be explained by the fact that the molar entropy of petalite is higher than that of spodumene. Thus, $\Delta\overline{S}_s$ is higher in the spodumene-albite system. In Equation 8, the term dependent on the fluid concentration is the difference between $\Delta\overline{S}_s$ and $\overline{S}^0_i - \overline{S}^0_j$, which is the same in the two systems. This term is positive in the petalite-albite system and negative in the spodumene-albite system.

**Relation between thermodynamic properties and atomic numbers of alkali chloride solutes.** This relation is set up by comparison of Reactions 1 and 3. As seen above, $\overline{S}^{ex}$ can be disregarded. Thus, the differences of standard entropy of the fluid species from Table 5 are $\overline{S}^0_{NaCl} - \overline{S}^0_{CsCl} = 41.8 \pm 8.2$ J/mol·K (determined in Reaction 3) and $\overline{S}^0_{LiCl} - \overline{S}^0_{NaCl} = 37.8 \pm 6.1$ J/mol·K (determined in Reaction 1). The values of these two entropy terms overlap: the entropy term decreases from Li to Na as much as from Na to Cs. This variation of $\overline{S}^0$ can be related to the variation of the atomic number of the alkali element, on which the ionic size strongly depends.

**Information on variation with temperature of hydration of aqueous species in the fluid.** The free energy of formation of the aqueous species in the fluid is related to the bond energies between the species and the surrounding $H_2O$ molecules. Brimhall and Crerar (1987) state that hydration of ions in solution becomes relatively less important as temperature increases to near-magmatic conditions because of the effect of increasing temperature on the dielectric constant of $H_2O$. Under our experimental conditions, species are associated and are not ionic (Helgeson, 1969). Thus, they are much less polar than the ionic ones, but even with a weak polarity, they must be hydrated at low temperature. The decrease of the dielectric constant of the $H_2O$ must induce a decrease of hydration. The bond energies between hydrated species and $H_2O$ molecules must then decrease.

As the entropy is the negative of the derivative of the free energy with respect to temperature, the results of the present paper indicate that the standard Gibbs free energy of formation decreases in a different way for the different species when temperature increases. It is interesting to note that $Li^+$ is the most hydrated alkali ion at low temperature (Brimhall and Crerar, 1987) and that the standard entropy of LiCl is the higher (this work). For a better understanding of the relation between $G$ and the hydration, it is necessary to have information on the different terms of the energy of hydration of the associated species (solvation, collapse of the solvent).

## CONCLUSION

The new experiments performed on the system petalite–pollucite–quartz–aqueous chloride solution are consistent with previous work. Using the results of the present work and of previous studies (Sebastian and Lagache, 1990, 1991; Lagache and Sebastian, 1991), we have calculated the differences between the standard entropies of the aqueous chloride species LiCl-NaCl, NaCl-CsCl, and LiCl-CsCl. The determination of these constants leads to several conclusions: (1) When temperature increases between 450 and 600 °C, the entropy, i.e., the change with temperature of the Gibbs free energy of formation of aqueous species in the fluid, is different for the different alkali chloride species. (2) Standard entropies of the solutes vary according to the atomic size of the elements. (3) There is no measurable influence of pressure on the properties of the NaCl-LiCl solution and no measurable mixing energy between the solutes. (4) In a $(\mu_i - \mu_j)$ vs. $T$ diagram, the slope of the univariant line corresponding to the reaction may not be deduced from the variation in the concentration of the fluid with temperature.

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