Thermodynamic mixing properties of Rb-K feldspars

GUY L. HOVIS1,* AND JACQUES ROUX2

1Department of Geology and Environmental Geosciences, Lafayette College, Easton, Pennsylvania 18042, U.S.A.
2Physique des Minéraux et des Magmas, IPGP, 4 Place Jussieu, 75252 Paris cedex 05, France

ABSTRACT

Hydrofluoric acid solution calorimetric measurements conducted at 50 °C on a series of Al-Si ordered Rb-K feldspars reveal that the enthalpies Rb-K mixing ($H_{\text{ex}}$) for this series are positive, with maximum values skewed toward Rb-rich compositions. However, the magnitudes of $H_{\text{ex}}$ are greatly reduced relative to those for Na-K feldspars, as are the positive volumes of Rb-K mixing observed for this series. Both observations can be explained by the substitution of two ions that are relatively similar in size. The difficulty in synthesizing Rb-rich sanidine via Rb-exchange of K-sanidine, contrasted with the ability to synthesize rubicline from K-microcline by such exchange, together with a vanishingly small $\Delta V$ between ordered rubicline and disordered Rb-sanidine suggest that the volume of Rb-feldspar is close to the limit to which the feldspar structure can be expanded at 1 bar.

Keywords: Rb-K feldspars, solution calorimetric data, thermodynamics, mixing properties

INTRODUCTION

To understand and document mineral processes at a fundamental level, it is informative to measure the energies that are housed in various forms within minerals. Among these are energies associated with chemical bonding. Moreover, energy changes that are the result of chemical substitution across solid-solution series relate to mineral stability. Such data bring with them the question of whether there are so-called mixing or excess thermodynamic energies associated with the particular substitution of interest. These excess properties are important not only because they relate to the thermodynamic stability of intermediate members of mineral series, but also because they provide an energy based explanation for phenomena such as exsolution.

A long-term interest of this laboratory has been the measurement of thermodynamic data, including the excess properties, of feldspars (e.g., Haselton et al. 1983; Hovis 1986, 1988, 1997; Hovis and Graeme-Barber 1997; Hovis and Navrotsky 1995; Hovis et al. 1991, 2003; Thompson and Hovis 1979), feldspathoids (Hovis and Roux 1993, 1999; Hovis and Crelling 2000; Hovis et al. 2002), micas (Roux and Hovis 1996), and glasses (Hovis 1984; Hovis et al. 2004; Richet et al. 2004, 2006). In addition to thermodynamic characterization of these materials, there also is the desire to understand the origins of these properties.

It is common for K-Na substitution in various mineral systems to produce positive enthalpies and/or volumes of K-Na mixing; this is exemplified by data for the low albite-microcline, analbite-sanidine, nepheline-kalsilite, paragonite-muscovite, and K-Na silicate glass systems (ibid). With the relatively recent discovery of Rb-rich feldspars (Teertstra et al. 1998), which in essence form a K-Rb feldspar system, it became an interesting question to ask what mixing properties, if any, such feldspars might possess and how such properties would compare with those of more common K-Na feldspars. Those issues are the focus of the present study.

SYNTHESIS AND CHARACTERIZATION OF MATERIALS

Because natural Rb-rich feldspars are limited in availability and quantity, and bring with them unwanted impurities, synthetic specimens were utilized for this study. McMillan et al. (1980) and Kovalskii and Kotelnikov (2002) have described the preparation of Al-Si ordered Rb-rich feldspar specimens. It has been noted that direct Rb-for-Na ion exchange in alkali feldspar synthesis is not successful. If one is to employ ion-exchange techniques, it is necessary to begin with a K-rich specimen. Prior to the current study, this already had been accomplished by K-exchange of powdered Amelia low albite in molten KCl at 840 °C as described in Hovis (1986). Two exchange experiments over a total period of 66 h were utilized to remove virtually all Na from the albite, which resulted in microcline 71104 of composition $K_{0.00}Na_{0.00}AlSi_{3}O_{8}$ (Hovis 1986). Specimen 71104 then underwent initial Rb-exchange at 852 °C over 216 h in molten RbCl. A second Rb-exchange experiment was performed over 370 h at the same temperature after the initial feldspar powder was removed from the Pt crucible, separated from chloride via RbCl dissolution in deionized water, dried, and returned to the oven in a fresh batch of RbCl. The rather long times for the RbCl experiments were necessitated by sluggish Rb-for-K exchange; however, these experiments did successfully produce a high-Rb sample (0405) with composition $Rb_{0.97}K_{0.03}Na_{0.03}AlSi_{3}O_{8}$, measured via ICP-MS by Matthew Gorrin (personal communication) of Montclair State University, New Jersey.

Samples having intermediate Rb:K ratios were produced by thoroughly mixing powders of 0405 rubicline (the designated name for ordered Rb-rich feldspar; Teertstra et al. 1998) and 71104 microcline in the desired molar ratios. Each mixture was placed in a Pt crucible, tamped down with a bent spatula, and
annealed in a 1 atm furnace. In all cases crucibles were removed from the furnace every 24 to 48 h, the powders mixed with a spatula and tamped down, then replaced in the furnace. Synthesis times and temperatures are included in Table 1.

For samples of intermediate composition Rb-K exchange between grains was slow. X-ray diffraction (XRD) data were utilized to check the progress of chemical “homogenization” by monitoring the convergence of K- and Rb-versions of hkl-equivalent peaks into single peaks. In all, a total of eight intermediate compositions were made. Compositions of the latter were computed utilizing measured weights of the 71104 and 0405 powders in conjunction with known compositions for these end-members.

A sample of Rb-sanidine was needed to compare the thermodynamic properties of rubicline with those of its disordered equivalent. However, no natural occurrence of such a mineral has been described. Several attempts were made to synthesize Rb-sanidine by disordering rubicline 0405, but these experiments resulted in partial breakdown of the sample. On the other hand, hydrothermal synthesis of Rb-sanidine using the gelling technique described by Hamilton and Henderson (1968) was successful. The resulting sample, ScOc, produced a clearly identified feldspar powder XRD pattern.

### X-RAY POWDER DIFFRACTION AND SOLUTION CALORIMETRIC TECHNIQUES

#### Unit-cell measurement

Powder XRD data were collected at Lafayette College utilizing a Scintag DMS 2000 automated diffractometer. Scans were made from 15 to 70° 2θ at 0.25°/min utilizing filtered Cu radiation and a solid-state detector. CuKα peaks were mathematically stripped using Scintag software. Diffraction maxima were located using Scintag’s Peakfinder program. Peaks for rubicline were indexed using the rubicline unit-cell parameters of Kovalski and Koteckih (2002), then calculating peak positions from the Miller indices for microcline; partial data also are given by McMillan et al. (1980). For intermediate compositions, diffraction maxima were tracked across the series. The identity of Miller indices for the X-ray peaks of sample ScOc Rb-sanidine were based in part on earlier work by Henderson (1978) and also through calculation using Miller indices for sanidine peaks in conjunction with Rb-sanidine unit-cell parameters (Henderson 1978). Unit-cell dimensions for all samples were calculated with the program of Holland and Redfern (1997) from manually corrected Kα data, employing NBS standard reference silicon 640a having a stated unit-cell dimension of 5.430826 Å.

#### Solution calorimetry

The calorimetric system used to measure enthalpies of solution has been described in Hovis and Roux (1993) and Hovis et al. (1998). The latter paper demonstrates that this system enables the measurement of precise enthalpies of solution from samples as small as 10 mg. For the present study, sample availability did not necessitate the use of sample weights below 43 mg. Each sample was dissolved in 910.1 g (about 1 L) of 20.1 wt% hydrofluoric acid (HF) at 50 °C under isoperibolic conditions (i.e., the temperature of the water bath surrounding the calorimeter is held constant) utilizing an internal sample container (Waldbaum and Robie 1970). Either one or two dissolution experiments were performed in each liter of acid. As in previous studies, multiple runs in the same solution had no detectable effect on the data due to the high dilution of dissolved ions in the acid. Because these samples dissolved rapidly, the calorimetric experiments were conducted on powders, but not ultrafine material. This avoided the possibility of heat effects associated with extremely small grain sizes (Nikitewicz et al. 1983).

### RESULTS

#### Unit-cell data

Unit-cell data for the 10 members of the rubicline-microcline series are given in Table 1, which also includes data for Rb-sanidine ScOc. Figures 1 through 5 display variation of the unit-cell parameters compared with similar data for low albite-microcline crystalline solutions. As is true of the latter, the a unit-cell dimension is the most sensitive parameter to composition and over much of its range is nearly a linear function of Rb/K ratio. Because of curvature near the Rb-rich end of the series, however, a cubic fit to the data is given (Table 2). Similarly, if Rb content is determined as a function of a, the mole fraction of Rb (N_Rb) in a K-Rb feldspar can be calculated as:

$$N_{Rb} = -10743.116 + 3707.8795a - 426.984a^2 + 16.406a^3. \quad (1)$$

#### Table 1. Synthesis conditions and unit-cell dimensions for Rb-K feldspars

<table>
<thead>
<tr>
<th>Sample</th>
<th>α₀</th>
<th>β₀</th>
<th>γ₀</th>
<th>Temperature (°C)</th>
<th>Time at temperature (h)</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>α (°)</th>
<th>β (°)</th>
<th>γ (°)</th>
<th>Unit-cell volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ScOc*</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>NA</td>
<td>NA</td>
<td>8.849(2)</td>
<td>13.046(3)</td>
<td>7.194(1)</td>
<td>90</td>
<td>116.33(2)</td>
<td>90</td>
<td>744.3(2)</td>
</tr>
<tr>
<td>0405*</td>
<td>0.970</td>
<td>0.020</td>
<td>0.010</td>
<td>810 ± 5/840 ± 5</td>
<td>36/16.5</td>
<td>8.835(2)</td>
<td>12.962(2)</td>
<td>7.231(2)</td>
<td>90.52(2)</td>
<td>116.20(2)</td>
<td>87.97(2)</td>
<td>744.7(2)</td>
</tr>
<tr>
<td>0525</td>
<td>0.872</td>
<td>0.119</td>
<td>0.009</td>
<td>825 ± 2</td>
<td>245.0</td>
<td>8.816(1)</td>
<td>12.965(2)</td>
<td>7.248(1)</td>
<td>90.53(1)</td>
<td>116.15(1)</td>
<td>87.98(1)</td>
<td>743.1(1)</td>
</tr>
<tr>
<td>0524</td>
<td>0.773</td>
<td>0.219</td>
<td>0.007</td>
<td>825 ± 2</td>
<td>245.0</td>
<td>8.793(1)</td>
<td>12.965(1)</td>
<td>7.244(1)</td>
<td>90.54(1)</td>
<td>116.12(1)</td>
<td>87.94(1)</td>
<td>741.0(1)</td>
</tr>
<tr>
<td>0529</td>
<td>0.750</td>
<td>0.242</td>
<td>0.008</td>
<td>827 ± 2</td>
<td>146.0</td>
<td>8.792(1)</td>
<td>12.966(1)</td>
<td>7.245(1)</td>
<td>90.53(1)</td>
<td>116.11(1)</td>
<td>87.94(1)</td>
<td>741.1(1)</td>
</tr>
<tr>
<td>0512</td>
<td>0.675</td>
<td>0.317</td>
<td>0.008</td>
<td>851 ± 2</td>
<td>146.0</td>
<td>8.768(1)</td>
<td>12.966(1)</td>
<td>7.242(1)</td>
<td>90.55(1)</td>
<td>116.10(1)</td>
<td>87.90(1)</td>
<td>738.8(1)</td>
</tr>
<tr>
<td>0510</td>
<td>0.527</td>
<td>0.466</td>
<td>0.007</td>
<td>827 ± 2</td>
<td>138.5</td>
<td>8.728(1)</td>
<td>12.968(2)</td>
<td>7.236(1)</td>
<td>90.62(1)</td>
<td>116.08(1)</td>
<td>87.85(1)</td>
<td>735.3(1)</td>
</tr>
<tr>
<td>0513</td>
<td>0.352</td>
<td>0.642</td>
<td>0.006</td>
<td>757 ± 3/777 ± 3</td>
<td>183.0/134.4</td>
<td>8.686(1)</td>
<td>12.970(2)</td>
<td>7.234(1)</td>
<td>90.61(1)</td>
<td>116.03(1)</td>
<td>87.77(1)</td>
<td>731.8(1)</td>
</tr>
<tr>
<td>0523</td>
<td>0.235</td>
<td>0.761</td>
<td>0.005</td>
<td>825 ± 2</td>
<td>222.0</td>
<td>8.653(1)</td>
<td>12.969(1)</td>
<td>7.234(1)</td>
<td>90.62(1)</td>
<td>115.99(1)</td>
<td>87.73(1)</td>
<td>728.7(1)</td>
</tr>
<tr>
<td>0522</td>
<td>0.119</td>
<td>0.877</td>
<td>0.004</td>
<td>825 ± 2</td>
<td>222.0</td>
<td>8.623(1)</td>
<td>12.972(2)</td>
<td>7.237(1)</td>
<td>90.63(1)</td>
<td>115.98(1)</td>
<td>87.70(1)</td>
<td>726.0(1)</td>
</tr>
<tr>
<td>71104</td>
<td>0.000</td>
<td>0.997</td>
<td>0.003</td>
<td>852 ± 2/870 ± 2</td>
<td>216.0/370.3</td>
<td>8.590(1)</td>
<td>12.965(1)</td>
<td>7.235(1)</td>
<td>90.55(1)</td>
<td>116.05(1)</td>
<td>87.85(1)</td>
<td>735.3(1)</td>
</tr>
</tbody>
</table>

*ScOc synthesized hydrothermally as explained in the text. Samples 0405 and 71104 from ion-exchange experiments in molten RbCl and KCl, respectively; other samples synthesized via “homogenization” of 0405 and 71104 powders, as described in the text.
Hovis and Roux: Thermodynamic Mixing Properties of Rb-K Feldspars

Figure 2. Variation of the $b$ unit-cell dimension with mole fraction Rb for Al-Si ordered K-Rb feldspars. Comparative data also are given for ScOc Rb-sanidine and microcline-low albite crystalline solutions (Hovis 1986).

Figure 3. Variation of the $c$ unit-cell dimension with mole fraction Rb for Al-Si ordered K-Rb feldspars. Comparative data also are given for ScOc Rb-sanidine and microcline-low albite crystalline solutions (Hovis 1986).

Table 2. Equations for cell-parameter and volume variation with composition

<table>
<thead>
<tr>
<th>Unit-cell parameter or volume</th>
<th>Constant term</th>
<th>$N_{Rb}$ term</th>
<th>$N_{Na}$ term</th>
<th>$N_{Al}$ term</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>8.5905</td>
<td>0.23533</td>
<td>0.056067</td>
<td>-0.060677</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>12.966</td>
<td>0.030575</td>
<td>-0.068207</td>
<td>0.033778</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>722.400</td>
<td>0.02170</td>
<td>0.006983</td>
<td>NA</td>
</tr>
<tr>
<td>$\alpha$ (°)</td>
<td>90.634</td>
<td>0.010464</td>
<td>-0.43184</td>
<td>0.31247</td>
</tr>
<tr>
<td>$\beta$ (°)</td>
<td>115.950</td>
<td>0.014696</td>
<td>-0.12366</td>
<td>0.16707</td>
</tr>
<tr>
<td>$\gamma$ (°)</td>
<td>87.633</td>
<td>0.46653</td>
<td>-0.10126</td>
<td>NA</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>722.82</td>
<td>25.482</td>
<td>-0.82960</td>
<td>-2.0928</td>
</tr>
</tbody>
</table>

Notes: $N_{Rb}$ is mole fraction RbAlSi$_3$O$_8$. NA = not applicable.

Equations that represent compositional relations for all unit-cell dimensions are given in Table 2. Except for $\gamma$, none of the unit-cell dimensions vary to as great a degree in the K-Rb as in K-Na feldspar system (e.g., Hovis 1986). This is to be expected,
given the relative ionic radii for 8-coordination among Rb$^{+}$ (1.61 Å), K$^{+}$ (1.51 Å), and Na$^{+}$ (1.18 Å) (Shannon 1976), with Rb-K having a considerably smaller size contrast than K-Na. This size contrast is reflected as well by the end-member unit-cell volumes (rubicline 745.0 Å$^3$, microcline 721.4 Å$^3$, and low albite 663.2 Å$^3$), for which differences are 24 Å$^3$ between Rb and K end-members and 58 Å$^3$ between K and Na end-members.

The unit-cell volumes of K-Rb feldspars shown in Figure 6 are not quite a linear function of composition, but they come close to this, again most likely due to size similarity of K$^{+}$ and Rb$^{+}$. The least-squares equation for volume data is included in Table 2. Volumes of K-Rb mixing, or excess volumes ($V_{ex}$), can be calculated by subtracting volumes along the line of ideal mixing ($V_{ID} = 722.82 + 22.560 N_{Rb}$) from the volume equation, resulting in:

$$V_{ex} (\text{Å}^3) = 2.922 N_{Rb} - 0.82960 N_{Rb}^2 - 2.0928 N_{Rb}^3.$$  \hfill (2)

Excess unit-cell volumes (Fig. 6) are small in magnitude in comparison with those of the microcline-low albite system, reaching a maximum of just 1.0 Å$^3$ at $N_{Rb} = 0.56$. This too can be attributed to the similar sizes of K$^{+}$ and Rb$^{+}$.

Solution calorimetric data

The enthalpies of solution for all rubicline-microcline samples, as well as Rb-sanidine ScOc, are recorded in Table 3. A plot of the negatives of these enthalpies ($-H_{sol}$) is shown in Figure 7, which also includes comparative data for microcline-low albite system, as well as K-sanidine and anabite. The negatives of the heats of solution are plotted because a concave-down relationship then directly reflects the positive enthalpies of mixing ($H_{mix}$) of a curve that stands above the “line of ideal mixing” that connects end-member heats of solution.

For the microcline-rubicline series, one can see that the enthalpies of solution for K-rich samples are linear (or nearly so) with composition, whereas data for Rb-rich samples deviate from a continuation of the latter trend. It is a challenge to model this behavior. Either of two choices is possible, one in which data for the K-rich and Rb-rich parts of the system are treated separately (data at the K-rich end of the series portrayed as linear), the other in which all data are included in a single expression. The latter has been chosen, as a continuous equation makes data analysis for the system straightforward in phase-equilibrium calculations that are based on continuous relationships for other parameters such as entropy and volume. The choice of a continuous fourth-order polynomial (Fig. 7) brings with it the appearance of slight non-linear behavior near the K-end of the series that is unjustified by the data. However, the departure of data from linearity is small, and the equation does represent non-linear data at the Rb-rich end of the series well:

$$H_{sol} = 722.82 + 22.560 N_{Rb} - 0.82960 N_{Rb}^2 - 2.0928 N_{Rb}^3.$$  \hfill (59)

Excess unit-cell volumes (Fig. 6) are small in magnitude in comparison with those of the microcline-low albite system, reaching a maximum of just 1.0 Å$^3$ at $N_{Rb} = 0.56$. This too can be attributed to the similar sizes of K$^{+}$ and Rb$^{+}$.

Solution calorimetric data

The enthalpies of solution for all rubicline-microcline samples, as well as Rb-sanidine ScOc, are recorded in Table 3. A plot of the negatives of these enthalpies ($-H_{sol}$) is shown in Figure 7, which also includes comparative data for microcline-low albite system, as well as K-sanidine and anabite. The negatives of the heats of solution are plotted because a concave-down relationship then directly reflects the positive enthalpies of mixing ($H_{mix}$) of a curve that stands above the “line of ideal mixing” that connects end-member heats of solution.

For the microcline-rubicline series, one can see that the enthalpies of solution for K-rich samples are linear (or nearly so) with composition, whereas data for Rb-rich samples deviate from a continuation of the latter trend. It is a challenge to model this behavior. Either of two choices is possible, one in which data for the K-rich and Rb-rich parts of the system are treated separately (data at the K-rich end of the series portrayed as linear), the other in which all data are included in a single expression. The latter has been chosen, as a continuous equation makes data analysis for the system straightforward in phase-equilibrium calculations that are based on continuous relationships for other parameters such as entropy and volume. The choice of a continuous fourth-order polynomial (Fig. 7) brings with it the appearance of slight non-linear behavior near the K-end of the series that is unjustified by the data. However, the departure of data from linearity is small, and the equation does represent non-linear data at the Rb-rich end of the series well:

$$H_{sol} = 722.82 + 22.560 N_{Rb} - 0.82960 N_{Rb}^2 - 2.0928 N_{Rb}^3.$$  \hfill (59)

Excess unit-cell volumes (Fig. 6) are small in magnitude in comparison with those of the microcline-low albite system, reaching a maximum of just 1.0 Å$^3$ at $N_{Rb} = 0.56$. This too can be attributed to the similar sizes of K$^{+}$ and Rb$^{+}$.

Solution calorimetric data

The enthalpies of solution for all rubicline-microcline samples, as well as Rb-sanidine ScOc, are recorded in Table 3. A plot of the negatives of these enthalpies ($-H_{sol}$) is shown in Figure 7, which also includes comparative data for microcline-low albite system, as well as K-sanidine and anabite. The negatives of the heats of solution are plotted because a concave-down relationship then directly reflects the positive enthalpies of mixing ($H_{mix}$) of a curve that stands above the “line of ideal mixing” that connects end-member heats of solution.

For the microcline-rubicline series, one can see that the enthalpies of solution for K-rich samples are linear (or nearly so) with composition, whereas data for Rb-rich samples deviate from a continuation of the latter trend. It is a challenge to model this behavior. Either of two choices is possible, one in which data for the K-rich and Rb-rich parts of the system are treated separately (data at the K-rich end of the series portrayed as linear), the other in which all data are included in a single expression. The latter has been chosen, as a continuous equation makes data analysis for the system straightforward in phase-equilibrium calculations that are based on continuous relationships for other parameters such as entropy and volume. The choice of a continuous fourth-order polynomial (Fig. 7) brings with it the appearance of slight non-linear behavior near the K-end of the series that is unjustified by the data. However, the departure of data from linearity is small, and the equation does represent non-linear data at the Rb-rich end of the series well:

$$H_{sol} = 722.82 + 22.560 N_{Rb} - 0.82960 N_{Rb}^2 - 2.0928 N_{Rb}^3.$$  \hfill (59)

Excess unit-cell volumes (Fig. 6) are small in magnitude in comparison with those of the microcline-low albite system, reaching a maximum of just 1.0 Å$^3$ at $N_{Rb} = 0.56$. This too can be attributed to the similar sizes of K$^{+}$ and Rb$^{+}$.

Solution calorimetric data

The enthalpies of solution for all rubicline-microcline samples, as well as Rb-sanidine ScOc, are recorded in Table 3. A plot of the negatives of these enthalpies ($-H_{sol}$) is shown in Figure 7, which also includes comparative data for microcline-low albite system, as well as K-sanidine and anabite. The negatives of the heats of solution are plotted because a concave-down relationship then directly reflects the positive enthalpies of mixing ($H_{mix}$) of a curve that stands above the “line of ideal mixing” that connects end-member heats of solution.

For the microcline-rubicline series, one can see that the enthalpies of solution for K-rich samples are linear (or nearly so) with composition, whereas data for Rb-rich samples deviate from a continuation of the latter trend. It is a challenge to model this behavior. Either of two choices is possible, one in which data for the K-rich and Rb-rich parts of the system are treated separately (data at the K-rich end of the series portrayed as linear), the other in which all data are included in a single expression. The latter has been chosen, as a continuous equation makes data analysis for the system straightforward in phase-equilibrium calculations that are based on continuous relationships for other parameters such as entropy and volume. The choice of a continuous fourth-order polynomial (Fig. 7) brings with it the appearance of slight non-linear behavior near the K-end of the series that is unjustified by the data. However, the departure of data from linearity is small, and the equation does represent non-linear data at the Rb-rich end of the series well:

$$H_{sol} = 722.82 + 22.560 N_{Rb} - 0.82960 N_{Rb}^2 - 2.0928 N_{Rb}^3.$$  \hfill (59)

Excess unit-cell volumes (Fig. 6) are small in magnitude in comparison with those of the microcline-low albite system, reaching a maximum of just 1.0 Å$^3$ at $N_{Rb} = 0.56$. This too can be attributed to the similar sizes of K$^{+}$ and Rb$^{+}$.

Solution calorimetric data

The enthalpies of solution for all rubicline-microcline samples, as well as Rb-sanidine ScOc, are recorded in Table 3. A plot of the negatives of these enthalpies ($-H_{sol}$) is shown in Figure 7, which also includes comparative data for microcline-low albite system, as well as K-sanidine and anabite. The negatives of the heats of solution are plotted because a concave-down relationship then directly reflects the positive enthalpies of mixing ($H_{mix}$) of a curve that stands above the “line of ideal mixing” that connects end-member heats of solution.

For the microcline-rubicline series, one can see that the enthalpies of solution for K-rich samples are linear (or nearly so) with composition, whereas data for Rb-rich samples deviate from a continuation of the latter trend. It is a challenge to model this behavior. Either of two choices is possible, one in which data for the K-rich and Rb-rich parts of the system are treated separately (data at the K-rich end of the series portrayed as linear), the other in which all data are included in a single expression. The latter has been chosen, as a continuous equation makes data analysis for the system straightforward in phase-equilibrium calculations that are based on continuous relationships for other parameters such as entropy and volume. The choice of a continuous fourth-order polynomial (Fig. 7) brings with it the appearance of slight non-linear behavior near the K-end of the series that is unjustified by the data. However, the departure of data from linearity is small, and the equation does represent non-linear data at the Rb-rich end of the series well:
\[-H_{\text{ex}}^N (\text{kJ/mol}) = 605.73 + 16.922 N_{Ru} - 113.64 N_{Ru}^2 - 284.09 N_{Ru}^3. \tag{3}\]

Note that Equation 3 is for the negative of the actual heats of solution to match the relationships seen in Figure 7.

Enthalpies of mixing ($H_{\text{ex}}$) for this series can be derived from Equation 3 by subtracting the ideal-mixing line \[-H_{\text{ex}}^N (\text{kJ/mol}) = 605.73 - 3.498 N_{Ru}\] from the heats of solution. This yields:

$$H_{\text{ex}} (\text{kJ/mol}) = 20.420 N_{Ru} - 113.64 N_{Ru}^2 + 215.31 N_{Ru}^3 - 122.09 N_{Ru}^4. \tag{4}$$

Values of $H_{\text{ex}}$ reach a maximum of 3.85 kJ/mol at a $N_{Ru}$ value of 0.81. This amounts to about half the maximum $H_{\text{ex}}$ achieved by the K-Na series (Fig. 7).

**DISCUSSION AND CONCLUDING REMARKS**

An interesting feature of the volume relationships is that the unit-cell volumes of end-member rubicline (745.0 ± 0.1 Å$^3$) and ScOc Rb-sanidine (744.3 ± 0.2 Å$^3$) are about equal. This similarity differs from what one might expect by comparison with the volume increase related to Al-Si disorder in the cases of microcline (721.4 Å$^3$)-sanidine (724.6 Å$^3$) (Hovis and Navrotsky 1995) and low albite (663.2 Å$^3$)-analbite (666.4 Å$^3$) (e.g., Hovis 1986), as derived from the equations for the K-Rb and K-Na series shown in Figure 6 and also Figure 2 of Hovis and Navrotsky (1995). The latter volume differences due to Al-Si disorder might be small, but they are statistically significant. This is not the case for Rb-feldspar. It is possible that the difference in Rb-end-member behavior is related to differences in synthesis techniques and parent materials as the ion-exchanged rubicline was made from what originally was Amelia low albite, whereas the hydrothermally produced Rb-sanidine made from a gel. However, given the additional observation that 0405 rubicline began to break down during attempted disordering experiments, one can infer that the rubicline structure is so stretched by Rb substitution that disorder can make little difference to its volume. This also is pertinent to the observation from Kovalskii (personal communication), confirmed by this laboratory, that it is impossible to synthesize compositions close to the Rb-sanidine end-member through RbCl-exchange of disordered K-sanidine. The most Rb-rich sample produced by such a technique has a maximum $N_{Ru}$ content of 0.5 to 0.6, contrasted with 0.97 $N_{Ru}$ for sample 0405 of the present study; this is similar to the results of Kovalskii and Kotelnikov (2002).

One can see from Figure 7 that the departure from ideality for microcline-rubicline enthalpies of solution is much less than that for microcline-low albite. This mimics the relationships for excess volume and is probably explained by the relatively similar sizes of the Rb$^+$ and K$^+$. Although the distinction in volume between rubicline and Rb-sanidine is nearly undetectable, such is not the case for enthalpy. Thus, bond energies are affected by Al-Si order-disorder even if volumes are not. Note that the enthalpy change associated with Al-Si disorder (6.6 kJ/mol) in Rb-feldspar is positive and easily detected. This compares well with similar relationships for microcline-sanidine (7.2 kJ/mol) and low albite-analbite (11.7 kJ/mol), both of which are shown in Figure 7.

In conclusion, it seems that the substitution of ions of similar size in the alkali site of Rb-K-Na feldspars greatly reduces both the volumes and enthalpies of mixing in these minerals. In his paper on the discovery of Rb-feldspar, Teertstra et al. (1998) noted that the described natural rubicline forms in structural coherence with host microcline, and moreover that rubicline was “formed by exsolution from a (K, Na, Rb)-enriched precursor, followed possibly by fluid-induced modification.” This conclusion implies that the K-Rb feldspar system has a solvus. Given the very low values of $H_{\text{ex}}$ at 50 °C, and the fact that a solvus requires substantial positive excess Gibbs free energies of mixing ($G_{\text{ex}}$, where $G_{\text{ex}} = H_{\text{ex}} - TS_{\text{ex}}$ and $S_{\text{ex}}$ represents excess entropy), the presence of a solvus at crustal pressures would require either that values of $H_{\text{ex}}$ increase with temperature or that entropies of mixing ($S_{\text{ex}}$) are negative and quantitatively significant. The former can be true only if the heat capacities of series members are such that $H_{\text{ex}}$ increases with increased temperature. Given the relatively similar sizes of K$^+$ and Rb$^+$, this seems unlikely. Moreover, Haselton et al. (1983) found that excess enthalpies in the K-Na feldspar system did not change substantially above room temperature, which was further supported by the data of Hovis and Navrotsky (1995) who saw no evidence for increased $H_{\text{ex}}$ with temperature in the sanidine-analbite system. These observations suggest that rubicline having an Al:Si ratio of 1:3 would not form directly by exsolution. Teertstra et al. (1998) also suggested, however, that excess Si may play a role in the stability of rubicline, given excess Si in a portion of his rubicline samples accompanied by a local association with quartz. This could be the case; indeed, Hovis and Roux (1999, 1993) have found that excess Si substitution has large energetic consequences in the nepheline-kalsilite system. Perhaps also, as suggested by Teertstra et al. (1998), fluid alteration did play a role in rubicline genesis.

**ACKNOWLEDGMENTS**

This research was supported by the Earth Sciences Division of the National Science Foundation via grant EAR-0408829. We are grateful to Andrey Kovalskii (Institute of Experimental Mineralogy, Chernogolovka, Moscow Region, Russia) for sharing his thoughts on the synthesis of Rb-feldspar. Many thanks to Matthew Goring (Montclair State University, Montclair, New Jersey), who chemically analyzed rubicline 0405. We appreciate the helpful reviews of an anonymous reviewer and of Associate Editor Matthias Gottschalk. Thanks to Joyce Hovis for help with proofreading.

**REFERENCES CITED**


— (1997) Hydrofluoric acid solution calorimetric investigation of the effect