Thermodynamic mixing properties of Rb-K feldspars

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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 (ΔH_ex) for this series are positive, with maximum values skewed toward Rb-rich compositions. However, the magnitudes of ΔH_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 ΔV 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 K₀.₈₇Na₀.₁₃AlSi₃O₈ (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 Rb₀.₀₂Na₀.₀₈K₀.₉₉AlSi₃O₈, measured via ICP-MS by Matthew Gorring (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...