



Solvus reversals and related thermodynamic mixing properties of nepheline-kalsilite crystalline solutions having elevated excess silicon

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Minerals in the nepheline-kalsilite system vary compositionally both in Na:K ratio and in silicon content. Solvus experiments have been conducted at room pressure between 500° and 1050°C on crystalline solutions of composition $(\text{K,Na})_{0.875}\text{Al}_{0.875}[\text{Si}_{1.125}\text{O}_4]$, having 0.125 excess Si (plus an equivalent number of vacancies \square in the alkali sites) per 4 oxygen ions. Reversed phase equilibria, approaching the solvus both from the "inside out" and "outside in", were achieved throughout this temperature range. These highly silicic feldspathoids produced a solvus with a critical temperature of 961°C, contrasted with critical temperatures of 1108°C for a nearly stoichiometric series (0.017 excess Si per 4 oxygens) and 1265°C for a series based on a natural nepheline specimen (from Monte Somma) containing intermediate Si content (0.052 excess Si per 4 oxygens) but also a small amount of Ca that caused vacancies to vary systematically across the series via $[\text{Ca} = 2(\text{Na,K})$ exchange (Hovis and Crelling, 2000). The solvus for the highly silicic specimens also is compositionally narrower than for the previous series, fitting inside both the other solvi (ibid). Although the 304°C difference in critical temperature among the series is impressive for what seem to be relatively small differences in Si content, this correlates well with large energetic differences in end-member enthalpies for specimens having various Si contents (Hovis and Roux, 1993 and 1999). However, the lack of a pattern in these

results relative to excess Si suggests that something in addition to Si content is needed to explain the data.

We also have collected solution calorimetric data for this high-Si nepheline-kalsilite series in 20.1 weight percent hydrofluoric acid at 50°C under isoperibolic conditions. The heats of solution demonstrate that enthalpies of K-Na mixing for solvus compositions are lower in magnitude than for either of the other series, but also that such excess occurs over a shorter compositional range than for previously studied series (Hovis and Roux, 1993 and 1999). The calorimetric data, therefore, correlate well with solvus data. Hovis (1997) demonstrated for feldspars that the substitution of a third component (An) in a binary (Ab-Or) solid-solution series lessens binary mixing effects by effectively "shortening" compositional variation across the series. This is a possible explanation for present data as well, in which the presence of vacancies in alkali sites lessens the span, and thus the effect, of K-Na substitution. The fact that specimens based on Monte Somma nepheline display a higher critical temperature and greater enthalpies of mixing than the other series, despite intermediate excess Si content, may be related to $[\text{Ca} = 2(\text{Na},\text{K})]$ ion exchange and systematic variation in the number of vacancies across that series.

Given the significant energetic effects of $(\text{K},\text{Na})\text{Al} = [\text{Si}]$ and $2(\text{Na},\text{K}) = [\text{Ca}]$ substitutions in nepheline-kalsilite crystalline solutions, one wonders how significant such effects might be in other solid solution series where $\text{Al} = \text{Si}$ substitution takes place, or in which coupled substitutions create structural vacancies.

References:

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