

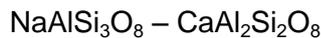
## Research project P20210-N10 funded by FWF

### Improvement of two-feldspar thermometry

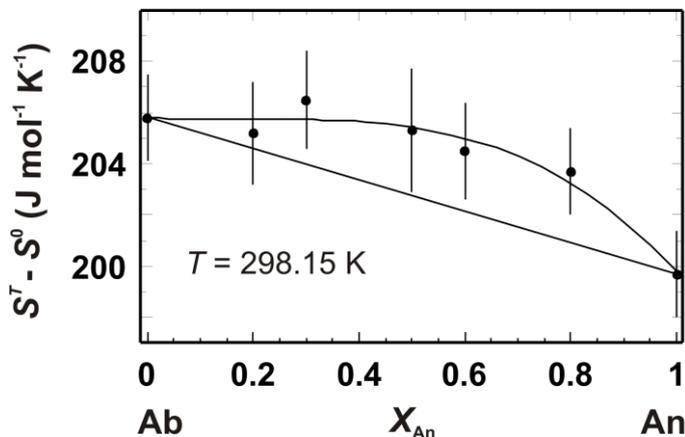
<b>Status</b>	finished
<b>Project leader</b>	Edgar Dachs
<b>Investigator</b>	Artur Benisek

The scientific results obtained during the course of this project may be classified into three different objects. 1) Results that are related to the heat capacity and entropy of feldspar solid solutions, 2) to feldspar petrology, and 3) to the physical nature of the excess entropy.

#### 1) Results on the heat capacity and entropy of feldspar solid solutions



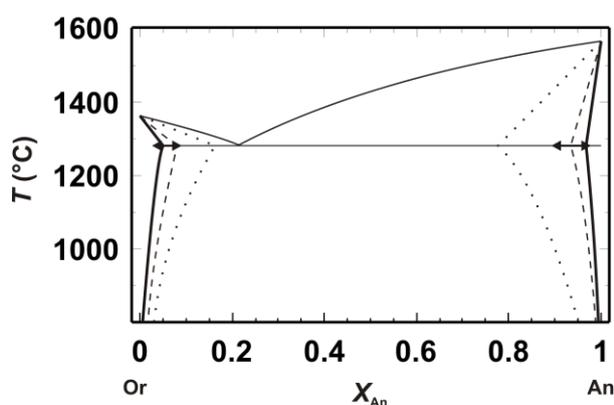
Seven samples of the disordered  $\text{NaAlSi}_3\text{O}_8 - \text{CaAl}_2\text{Si}_2\text{O}_8$  feldspar binary (high plagioclase) have been investigated, showing that this solid solution is characterised by positive excess heat capacities, i.e., the heat capacity-composition behaviour deviate from that of a mechanical mixture. The observed excess heat capacities produce excess vibrational entropies ( $\Delta S_{\text{vib}}^{\text{ex}}$ ) amounting to a maximum value of  $\Delta S_{\text{vib}}^{\text{ex}} = 2.8 \text{ J mol}^{-1} \text{ K}^{-1}$  at  $\text{CaAl}_2\text{Si}_2\text{O}_8$ -rich compositions and  $T = 298.15 \text{ K}$  ([Benisek et al., 2009](#)).



**Fig. 1:** Vibrational entropy of the plagioclase solid solution at  $T = 298.15 \text{ K}$ . Curve represents a two-parameter Margules model with  $W_{\text{AbAn}}^{\text{Svib}} = 16.4$  and  $W_{\text{AnAb}}^{\text{Svib}} = 4.7 \text{ J mol}^{-1} \text{ K}^{-1}$ . Straight line represents a mechanical mixture. Error bars denote one standard deviation.

## KAlSi<sub>3</sub>O<sub>8</sub> – CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>

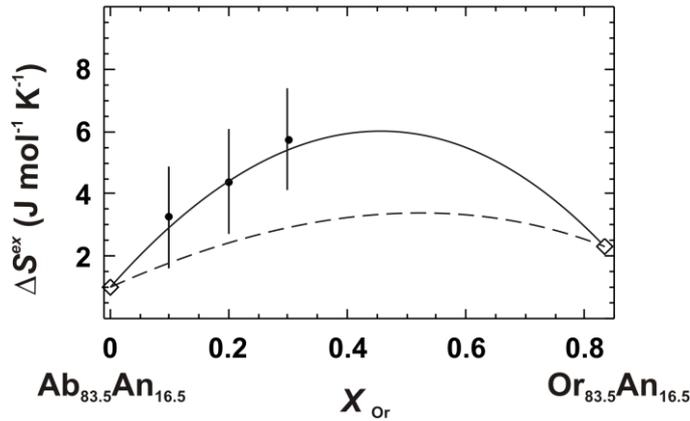
The vibrational entropy of disordered KAlSi<sub>3</sub>O<sub>8</sub> – CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> feldspars, however, behaves almost ideal. At  $T = 800$  K, the entropy data scatter around that of a mechanical mixture. In combination with the calorimetrically determined heat of mixing (large deviation from ideal mixing, Benisek et al., 2003), the solvus of this binary could be calculated. Mixing models for this binary, which had been extracted from compositional data of phase equilibrium experiments, show a smaller solvus compared to the new results (Fig. 2). The results are published by [Benisek et al. \(2010\)](#).



**Fig. 2:** Phase diagram for the (K,Ca)-feldspar binary at  $P = 11.3$  kbar. *Solid solvus:* Mixing model from our calorimetric data is compared to models based on phase equilibrium experiments, *dashed:* Elkins and Grove (1990), *dotted:* Fuhrman and Lindsley (1988). Arrows represent the compositional range of the experimental data from Nekvasil and Carroll (1993). Eutectic system calculated using the thermodynamic data from Holland and Powell (1998), updated in Thermocalc 3.2.

## Ternary feldspars

The heat capacity of the ternary feldspar samples deviate strongly from ideal behaviour producing positive excess vibrational entropies that amount to a maximum value of  $\Delta S_{\text{vib}}^{\text{ex}} = 5.8 \text{ J mol}^{-1} \text{ K}^{-1}$  at  $T = 298.15$  K. Modelling the ternary feldspars, these excess values can be described by a ternary entropic Margules parameter of  $W_{\text{AbOrAn}}^{\text{S}} = 93.9 \text{ J mol}^{-1} \text{ K}^{-1}$  (Fig. 3). The results are published by [Benisek et al. \(2010\)](#).

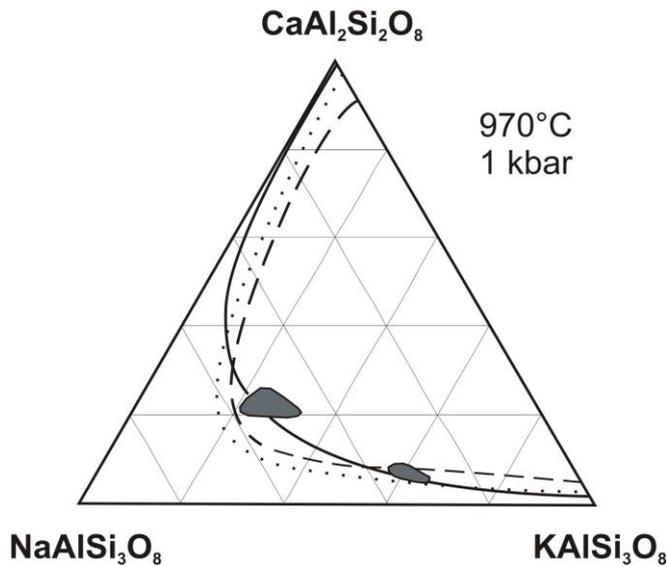


**Fig. 3:** Excess entropy of mixing at  $T = 298.15$  K for the ternary series with  $X_{An} = 0.165$ . Solid lines represent the excess entropy of mixing using a ternary asymmetric Margules mixing model with  $W^S_{AbOrAn} = 93.9$  J mol<sup>-1</sup> K<sup>-1</sup>. Dashed lines represent  $\Delta S^{ex}$  with  $W^S_{AbOrAn} = 0$  J mol<sup>-1</sup> K<sup>-1</sup>, *i.e.*, only the non-ideal contributions from the binaries are considered. Solid symbols with error bars are the data from this study with one standard deviation. Open diamonds represent binary values.

## 2) Results related to feldspar petrology

### Formulation and application of a new mixing model

The entropy values calorimetrically determined in the course of this project allowed a formulation of a ternary feldspar-mixing model, which is based exclusively on calorimetric and volumetric data. Comparison with existing mixing models, which are based on phase-equilibrium experiments (e.g., Fuhrman and Lindsley, 1988; Elkins and Grove, 1990; Benisek et al., 2004) reveals distinct differences. The incorporation of K into Ca-rich plagioclase and of Ca into K-rich alkali feldspar is more strongly limited by our calorimetry-based model, whereas the stability field of Na-rich feldspars is broadened. The new mixing model describes natural feldspars more reliably than phase-equilibrium based mixing models. This could be shown by applying the models on feldspars from natural rocks, whose compositions allow the deduction of the shape of the ternary solvus. In Figure 4, the bulk compositions of perthites from the Klokken syenogabbro, South Greenland (Parsons and Brown, 1983) are shown. Based on melting experiments and petrological findings, they should lie on the  $\sim 970^\circ\text{C}/1\text{kbar}$  isotherm (Parsons and Brown, 1983). In that figure, the isotherm calculated with our new mixing model is compared to phase equilibrium based mixing models demonstrating the improvement through our new model. The results derived on natural feldspar assemblages are published by [Benisek et al. \(2010\)](#).



**Fig. 4:** Compositions of the feldspars from the Klokken syenogabbro, South Greenland. The 970°C/1kbar isotherm of this study (*solid line*) is compared to those resulting from phase equilibrium experiments (*dashed curve*: Fuhrman and Lindsley, 1988; *dotted curve*: Elkins and Grove, 1990).

### 3) Results on the physical nature of the excess entropy of mixing

In the course of this project, we could bring some light into the physical nature of the excess heat capacity and excess vibrational entropy of mixing. The model is based on considerations how the bond lengths of the substituted and substituent cation are changed across a binary. Let us assume a solid solution AC – BC with different bond lengths and different elasticity of the A-C and B-C polyhedra. We may expect that the elastically stiffer polyhedron impose its size on the elastically softer one. Considering the size and the elasticity of the polyhedra involved in the substitution, we distinguished three different cases:

- B-C polyhedron is larger and elastically stiffer. Cation A will find itself in a strongly enlarged structure. The amount of A – C distance increase is more pronounced than B – C distance decrease. The mean frequency of the vibrations is decreased because of the net increase of the mean bond length (Badger, 1934). Decreasing frequencies increase the probability of exciting a vibration. Hence, larger heat capacities at a given temperature are generated, which produces positive excess heat capacities and vibrational entropies of mixing.
- B-C polyhedron is again larger but elastically softer. In this case, the amount of bond length increase may be similar to that of bond length decrease or even smaller. Their effect on the vibrational entropy tends to be compensated or results in even negative excess entropies.
- In cases where the elasticity of the A-C and B-C polyhedron is similar but the sizes are different, the amount of bond length increase is also larger than bond length decrease. This follows from the typical asymmetric dependence of the potential energy on the interatomic distance energetically favouring elongated bond lengths,

when compared to compressed bond lengths. In consequence, positive excess entropies are produced in such cases.

For simplification, the elasticity of the polyhedra was represented by the bulk moduli of the end-members. Doing so, the excess entropy of already measured silicate solid solutions could be related to the difference in end-member volumes and end-member bulk moduli ([Benisek and Dachs, 2011](#)). In a further study, the entropic behaviour of metallic alloys is included into this relationship yielding consistency with the analysed silicates ([Benisek and Dachs, 2012](#)).