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# Thermochemistry of the alkali feldspars: Calorimetric study of the entropy relations in the low albite – low microcline series

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**Abstract**

New heat capacity data obtained on twelve samples of the low albite – low microcline series are presented. They were measured by relaxation and differential scanning calorimetry between 5 and 773 K. Two series, differing in their starting materials, were investigated, both of which were prepared via molten salt and solid-solid ion-exchange techniques in previous studies. The heat capacity of both series deviates positively from the ideal behaviour leading to positive excess vibrational entropies of mixing, which can be described by a Margules mixing model yielding $W^S_{AbOr}$ = 8.60 and $W^S_{OrAb}$ = 9.28 J mol$^{-1}$ K$^{-1}$. The heat capacity and the vibrational entropy obtained on these Al,Si ordered samples are compared with those described in the literature for disordered samples. The solvi of the Al,Si ordered and disordered alkali feldspar systems were calculated from the calorimetric data and compared to experimentally determined solvi. Large deviations are detected for the ordered system, whereas consistent results are found for the disordered system, provided Na,K clustering is taken into account.

Keywords: Low-temperature heat capacity; $NaAlSi_3O_8$; $KAlSi_3O_8$; enthalpy; mixing model; miscibility gap.

## Introduction

The heat capacity ($C_P$) of a solid solution has often been found to deviate from that of a mechanical mixture (ideal mixing) at low temperatures (~100 K) giving rise to excess vibrational entropies. Al,Si disordered alkali feldspars are characterised by positive excess vibrational entropies of up to 2.5 J $mol^{-1}$ $K^{-1}$ (Haselton et al. 1983). In high structural state plagioclases, positive excess vibrational entropies of up to 2.8 J $mol^{-1}$ $K^{-1}$ were measured by Benisek et al. (2009), whereas an almost ideal vibrational behaviour was found for the low structural state plagioclases at 298.15 K (Benisek et al. 2013). The K – Ca feldspar binary, although derived from high structural state plagioclases, is also characterised by a more or less ideal vibrational entropy-composition relation (Benisek et al. 2010a). On the other hand, strongly positive vibrational entropy behaviour has been found in ternary series of high structural state feldspars (Benisek et al. 2010b). Although the origin of these excess vibrational entropies is the heat capacity behaviour at low temperatures, it has a strong influence on the stability of crystalline solutions at high temperatures, as worked out by Benisek et al. (2010c) for the ternary Na–K–Ca feldspar system.

In an attempt to explain the source of the excess vibrational entropy, first principles studies proposed a “bond stiffness versus bond length” interpretation (Van de Walle and Ceder 2002, Burton and van de Walle 2006). The latter study compared the MgO – CaO and NaCl – KCl solid solutions and found a similar size mismatch but different excess vibrational behaviour, which was attributed to different bond stiffness relations. The Na – Cl bonds were significantly softened with increasing K content producing the positive excess vibrational entropy. Benisek and Dachs (2011, 2012) presented a relationship that allows to assess the excess vibrational entropy of a binary solid solution. It is based on the idea that the elastically

stiffer end member forces the softer one to fit to its size. Accordingly, the excess vibrational entropy was related to the difference between the end member volumes ($\Delta V$) and to the difference between the end member bulk moduli ($\Delta K$). The maximum deviation from ideal behaviour ($\Delta_{max}S^{exc}$) can be obtained from the relation:

$$\Delta_{max}S^{exc} = (\Delta V + m\,\Delta K)\,f, \quad (1)$$

where m and f are fit parameters. $\Delta V$ is defined to be positive, whereas $\Delta K$ may be positive or negative depending on which end member (larger or smaller) is elastically stiffer (i.e., $\Delta V = V_A - V_B$ and $\Delta K = K_A - K_B$, where end member A is larger than B). The authors found that strongly negative $\Delta K$ values are connected with negative excess vibrational entropies, whereas positive $\Delta K$ values correlate with positive ones. Equation (1) could be successfully applied to different classes of materials, i.e., silicate solid solutions, binary alloys, and the NaCl – KCl binary (Benisek and Dachs 2011, 2012, 2013).

The alkali feldspars constitute a binary system consisting of the end members $NaAlSi_3O_8$ (Ab) and $KAlSi_3O_8$ (Or). They represent a thoroughly investigated mineral group, for which many structural, calorimetric and phase equilibrium data have been obtained. The calorimetric data set, however, lacks information on the behaviour of the vibrational entropy across the Al,Si ordered system. This information is provided in this contribution to calculate the solvus and to compare it to the experimentally determined solvus. Due to the sluggish Al,Si (dis)ordering kinetics, the Al,Si ordering states of the samples that delineate the experimental solvi are not in equilibrium with temperature. Thus, solvi determined from Al,Si disordered and ordered samples are metastable with respect to their Al,Si distribution whereas calculation of the equilibrium solvus would require knowledge of the temperature variation of the state of the Al,Si order. An equilibrium solvus was estimated by Brown and Parsons (1984)

by interpolating data from Smith and Parsons (1974), Müller (1971) and Bachinski and Müller (1971). In this paper, we calculate solvi for both the Al,Si disordered and ordered alkali feldspar systems from calorimetric data and compare these to experimentally determined ones.

Experimentally determined solvus data incorporate in principle three quantities, i.e., the excess enthalpy, the excess configurational entropy and the excess vibrational entropy. The calorimetrically determined solvus, on the other hand, is usually based on the assumption of a fully disordered Na,K distribution free of excess configurational entropy contributions. Comparing these solvi delivers, therefore, information on the configurational entropy referring to the question whether Na and K are in fact fully disordered or do they posses short-range ordering (clustering). For the disordered alkali feldspar system, Hovis et al. (1991) performed already such a comparison. To achieve agreement between calorimetric data and the experimentally determined solvus, the authors reduced the calorimetrically measured positive excess entropy of mixing by introducing effects of Na,K short-range ordering as deduced from NMR measurements by Phillips et al. (1988).

## Experimental methods

### Alkali feldspars

The investigated alkali feldspars were prepared via molten salt and solid-solid ion-exchange techniques (for details see for example Orville 1967). Seven samples ($X_{Or}$ = 0.01, 0.17, 0.33, 0.49, 0.66, 0.83, 1) had already been investigated by X-ray diffraction and solution calorimetry in the study of Hovis (1988). For this series, low albite from Amelia Courthouse, Virginia, was used as parent material. The Amelia albite is a pegmatitic cleavelandite described in Waldbaum and Robie (1971) and

Sinkankas (1968). From the Amelia albite, a low microcline was prepared by ion-exchange in molten KCl, for which we use the terminology "K-derivative of the Amelia albite". Mixtures of the end members were then homogenised at elevated temperatures producing solid solution samples. The synthesis histories are given in detail by Hovis (1986) and are briefly summarised in Table 1. Five samples ($X_{Or}$ = 0, 0.3, 0.55, 0.75, 1) had been prepared by Kroll et al. (1986) using low albite (from a metamorphic pegmatite from Cazadero, California) and a transformation-twinned low microcline (perthitic amazonite from Prilep, Macedonia). The Prilep microcline was first treated in molten KCl to produce pure low microcline. Solid solutions were then obtained by homogenising mixtures of Cazadero albite and K-exchanged Prilep microcline. The samples were characterised by X-ray diffraction in Kroll et al. (1986). For preparation details of these samples see Table 1 and in more detail their study.

Relaxation calorimetry

The low temperature heat capacity was measured with a relaxation calorimeter (Physical Properties Measurements System (PPMS); Quantum Design®) between 5 and 300 K using a measuring technique which is described, e.g., by Dachs and Bertoldi (2005), Benisek et al. (2010b), Dachs et al. (2010), and Dachs and Benisek (2011). The sample powder (~10 mg) was put into an Al cup (~8 mg) made from an Al-foil. It was pressed to a cylindrical pellet (0.5 mm thickness, 5 mm in diameter), the Al-foil surrounding the sample powder. The pellet was then attached to the sample platform. From each sample up to three pellets were prepared and measured.

Differential scanning calorimetry

The heat capacity at higher temperatures was measured with a differential scanning calorimeter from Perkin Elmer (Diamond DSC®). The method used in this study is

given elsewhere (e.g., Benisek et al. 2009, 2010a, Dachs and Benisek 2011, Benisek et al. 2012). Most measurements were performed between 273 and 773 K (some were performed up to only 373 K) on samples weighing approximately 25 mg. Each sample was prepared in up to three different pans, each of which was measured three times.

Evaluation of the heat capacity data

At room temperature, our DSC method provides $C_P$ mean values of high accuracy (deviating less than 0.6% from the "true" values, Dachs and Benisek 2011). On the other hand, the PPMS data collected from powder samples systematically deviate from the "true" values up to 2% (Dachs and Bertolid 2005). The relative deviation, however, was nearly constant over the whole temperature range, when considering a single PPMS run. This behaviour enables a correction where all PPMS heat capacity values are multiplied by a constant factor, thereby yielding a smooth link to the DSC data (Dachs and Benisek 2011). Such correction enables an improved accuracy of the PPMS data as demonstrated on different oxide and silicate samples by Dachs and Benisek (2011). It was also applied successfully in various solid solution studies (Benisek et al. 2009, 2010a, 2010b, 2013), thereby reducing the scatter of the entropy data. The correction procedure was applied in a statistical way forming all possible combinations of the different PPMS and DSC data series, which resulted in up to nine PPMS data series, from which the means and standard deviations were calculated.

Calculation of the solvus

At a given equilibrium temperature and pressure, two alkali feldspars AF1 and AF2, separated by the miscibility gap, have the same chemical potential for both

components, Ab and Or ($\mu_{Ab}^{AF1} = \mu_{Ab}^{AF2}$ and $\mu_{Or}^{AF1} = \mu_{Or}^{AF2}$). Using experimentally determined mixing parameters and solving the two equations simultaneously, the common tangent to the Gibbs free energy of mixing function is found. The calculations for this paper used a Mathematica® routine, which searched the compositions of the coexisting alkali feldspars numerically. In order to investigate the uncertainties of the solvus, a Monte Carlo method was used. $10^4$ sets of mixing parameters were generated which were normally distributed about the experimentally determined values according to the respective standard deviations. Using these parameter sets, $10^4$ solvi were calculated from which the standard deviation of the solvus temperature at a given mole fraction could be obtained.

## Results and discussion

### Heat capacity of the alkali feldspars

The heat capacities of the investigated samples are available as electronic supplementary materials from the homepage of this journal. The excess heat capacity of mixing ($\Delta C_p^{exc}$) for the alkali feldspars is defined as

$$\Delta C_p^{exc} = C_p^{alk\ feldspar} - (C_p^{Ab} X_{Ab} + C_p^{Or} X_{Or}). \quad (2)$$

An example is given for an intermediate composition in Figure 1. In the low temperature region, $\Delta C_p^{exc}$ of all Al,Si ordered samples is positive reaching a maximum of 1.2 J mol$^{-1}$ K$^{-1}$ at ~85 K. At ~300 K, the data of the ordered $Ab_{51}Or_{49}$ sample suggest a negative peak (-0.7 J mol$^{-1}$ K$^{-1}$) which, however, may not be significant (1 s.d.$^{(300K)} \approx$ 0.4 J mol$^{-1}$ K$^{-1}$). The results of Haselton et al. (1983) obtained on a sample with a similar composition, $Ab_{55}Or_{45}$, but with a disordered Al,Si distribution, are added in Figure 1 for comparison. Both samples show similar excess heat capacity behaviour. The disordered sample, however, has no negative peak at ~300 K and has its maximum positive peak at a slightly lower temperature (~70 K).

Vibrational entropy of the alkali feldspars

The vibrational entropy at 298.15 K

$$S^{298.15} - S^{0} = \int_{0}^{298.15} \left( C_P^{\text{alk feldsp}} / T \right) \partial T \qquad (3)$$

of the low albite – low microcline series is shown in Figure 2 and listed in Table 2. Jointly fitting all data to an asymmetric Margules mixing model resulted in interaction parameters $W^S_{\text{AbOr}}$ = 8.60 and $W^S_{\text{OrAb}}$ = 9.28 J mol$^{-1}$ K$^{-1}$, showing only a small asymmetric behaviour. At 400 K, the excess vibrational entropy is slightly smaller than that at 298.15 K, the difference being less than one standard deviation.

If samples prepared from Amelia albite ($X_{\text{Or}}$ = 0.01, 0.17, 0.33, 0.49, 0.66, 0.83, 1) are considered separately from those prepared from Cazadero albite and Prilep microcline ($X_{\text{Or}}$ = 0, 0.30, 0.55, 0.75 and 1), a slightly different behaviour arises. In the Ab-rich region, the Amelia albite series shows slightly larger entropy values (Fig. 2), although the deviation from the Cazadero albite – Prilep microcline series lies within uncertainties. However, because the Amelia albite series has enthalpy values that are significantly different from other low albite – low microcline series (see below), the vibrational entropy values were fitted separately. Because of the low number of data and the very small asymmetry, a symmetric Margules mixing model was used. For the Amelia albite series, the separate fitting procedure resulted in $W^S$ = 8.7 $\pm$ 1.1 J mol$^{-1}$ K$^{-1}$, while the Cazadero albite – Prilep microcline series has slightly higher excess entropy values yielding $W^S$ = 9.1 $\pm$ 1.4 J mol$^{-1}$ K$^{-1}$.

The vibrational entropy results from this study are similar to those obtained on samples with a disordered Al,Si distribution (Haselton et al. 1983), as seen in Fig. 2. Compared to the samples of the Amelia albite series the disordered samples have lower entropy values in the Ab-rich region, but agree well with those of the Cazadero

albite – Prilep microcline series. The disordered series has a maximum excess vibrational entropy $\Delta_{max}S^{exc}$ = 2.5 J mol$^{-1}$ K$^{-1}$. In the ordered series the mean value of $\Delta_{max}S^{exc}$ is slightly smaller (2.3 J mol$^{-1}$ K$^{-1}$, this study). Thus, the entropic Na – K mixing behaviour does not depend significantly on the state of Al,Si order which is in contrast to the enthalpic mixing behaviour. In the analbite – sanidine series the maximum excess enthalpy, $\Delta_{max}H^{exc}$, amounts to 5.0 kJ mol$^{-1}$, whereas in the low albite – low microcline series, $\Delta_{max}H^{exc}$ is distinctly larger, 8.0 kJ mol$^{-1}$ (Hovis 1988). Additionally, the asymmetry of $\Delta H^{exc}$ increases with Al,Si ordering. The disordered series is almost symmetric, whereas the ordered series has its maximum at $X_{Or}$ = 0.37.

Studies on liquid binary alloys (e.g., Kubaschewski and Alcock 1979, Witusiewicz and Sommer 2000), on alkali halide, metallic and some oxide systems (Urusov et al. 2007, 2008) found a correlation between excess enthalpy and excess entropy of mixing. The data of the ordered and disordered Ab – Or series do not support this correlation. The excess vibrational entropy of mixing is, however, in accordance with a relationship recently published by Benisek and Dachs (2011, 2012), which estimates the maximum value of the excess vibrational entropy based on the differences between end member volumes and bulk moduli, as noted above.

The difference of the bulk modulus between low albite and low microcline ($\Delta K$ = 5.3 GPa, Downs et al. 1994, Allan and Angel 1997) is smaller than between analbite and sanidine ($\Delta K$ = 7.7 GPa, Curetti et al. 2011, Angel 1994). On the other hand, low albite and low microcline have a larger difference in their molar volumes ($\Delta V$ = 0.884 J bar$^{-1}$, Kroll and Ribbe 1983) compared to analbite and sanidine ($\Delta V$ = 0.858 J bar$^{-1}$, Kroll and Ribbe 1983). Using equation (1) with m = 0.0109 and f = 2.505 (Benisek and Dachs 2012), the estimated maximum excess vibrational

232 entropies are the same in both series, i.e., $\Delta_{max}S^{exc}$ = 2.4 J mol$^{-1}$ K$^{-1}$, which is in good
233 agreement with the experimental results. The positive excess vibrational entropy may
234 be explained by large Na – O bond lengths in samples with intermediate
235 compositions owing to the presence of the elastically stiffer and larger K – O
236 polyhedra. This effect decreases strongly the stiffness of the Na – O bonds and, in
237 consequence, the frequency of the Na – O vibrations, which are then excited at lower
238 temperatures giving rise to positive excess heat capacities of mixing. The large
239 increase of the Na – O bond lengths with the Na – K substitution is consistent with
240 results from $^{23}$Na NMR investigation of samples of the Al,Si ordered alkali feldspar
241 series (Phillips et al. 1988).
242
243 Excess enthalpy of mixing
244 To calculate the solvus of the Ab – Or system, the excess enthalpy and volume of
245 mixing have to be known in addition to the excess entropy of mixing. In Figure 3, the
246 enthalpy of solution in hydrofluoric acid for three different alkali feldspar series is
247 plotted as a function of composition. Two different Al,Si ordered series can be
248 compared, i.e., the one of Hovis (1988) (see Table 1 for preparation details) and the
249 one of Waldbaum and Robie (1971). The latter series was also prepared by the
250 molten salt and solid-solid ion-exchange techniques. However, Waldbaum and Robie
251 (1971) used Amelia microcline as parent material, a sample twinned due to the
252 diffusive Al,Si ordering transformation, whereas Hovis (1988) investigated samples
253 prepared from Amelia albite – a sample free of transformation twinning. Their
254 investigations yielded significantly different enthalpy values (Fig. 3). The results of
255 Hovis (1988) show larger enthalpy values with a maximum deviation from ideal
256 behaviour of $\Delta_{max}H^{exc}$ = 8.0 kJ mol$^{-1}$ at $X_{Or}$ = 0.37, whereas Waldbaum and Robie
257 (1971) measured a maximum deviation of $\Delta_{max}H^{exc}$ = 7.5 kJ mol$^{-1}$ at $X_{Or}$ = 0.43. The

258 excess behaviour measured by Waldbaum and Robie (1971) is thus smaller and
259 more symmetric compared to Hovis (1988). Waldbaum and Robie (1971) also
260 investigated two samples ($X_{Or}$ = 0 and 1), which were prepared from Amelia albite.
261 For these samples, excellent agreement (Fig. 3) can be found with the results of
262 Hovis (1988), also based on Amelia albite. The different results for the Al,Si ordered
263 series visible in Figure 3 are, thus, due to the use of different parent materials for
264 preparing the solid solution series. In Figure 3, the enthalpies of solution for the
265 analbite – sanidine series are also shown, which are characterised by larger values,
266 but a smaller maximum deviation from ideal behaviour ($\Delta_{max}H^{exc}$ = 5.0 kJ mol$^{-1}$).

267 Cation mixing due to formation of a solid solution produces local structural
268 distortions and in consequence strain energies (e.g., Christian 1975, Greenwood
269 1979), which is true for cation disordering as well. These strain energies should be
270 reflected in changes of the enthalpy. To discuss the enthalpic data of the alkali
271 feldspars (Fig. 3), let us first consider the Na end member as an example: Analbite
272 has the largest negative enthalpy of solution value followed by the Amelia albite and
273 then by the Na-derivative of the Amelia microcline. Considering their enthalpies of
274 formation, the opposite is true, i.e., analbite has the less negative value followed by
275 the other two. The relationship between enthalpy of solution and formation is
276 sketched in Figure 4 for these Na-feldspars. The sum of all bond energies is thus
277 smallest in analbite. This is certainly due to the bond energies being lowered by the
278 strain energies present in the disordered structure. The situation for the Amelia albite
279 and the Na-derivative of the Amelia microcline is somewhat surprising. Although the
280 Na-derivative of the Amelia microcline is characterised by transformation twinning
281 and hence by strain energies due to twin walls, the enthalpy of formation has the
282 largest negative value, i.e., the sum of all bond energies is largest. The Amelia albite
283 is obviously characterised by larger structural strain. This behaviour may be

284 explained by a higher defect concentration. Amelia albite is a cleavelandite – a
285 feldspar variety with curved or warped plates.

286 The same considerations are true for the K-feldspars (Fig. 3). The structural
287 heterogeneities caused by Na – K mixing also produce local elastic strain and
288 consequently positive deviations from ideal enthalpic behaviour. The excess enthalpy
289 of mixing is largest in the ordered series with Amelia albite as parent material, slightly
290 lower in the other ordered series prepared from Amelia microcline, and smallest in
291 the disordered series. The smaller excess enthalpy in the disordered series may be
292 explained by the fact that the structure is "held open" due to the Al,Si disorder so that
293 the local elastic strain due to Na – K mixing is less effective.

294

295 The low albite – low microcline solvus

296 The solvus for the Ab – Or system with an ordered Al,Si distribution was calculated
297 using two different thermodynamic data sets, one derived from the Amelia albite
298 series (ordered feldspar data set 1, Table 3), the other derived from the Amelia
299 microcline series for the enthalpy and the Cazadero albite – Prilep microcline series
300 for the entropy and volume (ordered feldspar data set 2, Table 3). The configurational
301 entropy was calculated using the one-site mixing model, which assumes Na,K to be
302 fully disordered.

303 When calculating the ordered feldspar solvus using data set 1, a critical
304 temperatures of 1510 ± 110°C is obtained, while the data set 2 results in $T_{crit}$ = 990 ±
305 100°C (Fig. 5). The difference arises mainly from the different enthalpic data
306 (previous chapter). Experimentally determined solvi (Bachinski and Müller 1971,
307 Delbove 1975) yielded $T_{crit}$ ~ 886°C. The solvus calculated from data set 1 ($T_{crit}$ =
308 1510 °C) is in clear conflict with these data and with the temperature of 1000°C,
309 which proved to be sufficiently high in order to prepare homogeneous intermediate

compositions ($0.2 \leq X_{Or} \leq 0.6$) (Kroll et al. 1986). The reason for the discrepancy is not clear. A possible explanation could be that the samples used for data set 1, which were prepared from Amelia albite posses a higher density of imperfections than do the samples for data set 2. The additional configurational entropy is not considered in the solvus calculation, but would lower the solvus when incorporated into the calculation. In contrast, the solvus of data set 2 is in agreement with both the homogenisation temperature of 1000°C and the experimentally determined solvus, provided the uncertainties are taken into account (Fig. 5).

If our solvus calculations would incorporate a configurational entropy model that includes Na,K clustering, which was found in ordered alkali feldspars homogenised at 930°C (Phillips et al. 1988), the solvus calculated from data set 2 would become clearly larger than the solvus of Bachinski and Müller (1971). On the other hand, results from older solvus studies (e.g., Spencer 1937, Goldsmith and Laves 1961) indicate critical temperatures higher than 1000°C, which may then become comparable with the calculated solvus using data set 2 when incorporating Na,K clustering. The effect of clustering on the solvus is discussed below.

The analbite – sanidine solvus

To calculate the solvus of the disordered system, the data of Hovis (1988) and Haselton et al. (1983) were used. They were measured on alkali feldspar series, which were prepared from Al,Si disordered Amelia albite (Table 3). Defects, which may exist in the Al,Si ordered samples, are expected to be annihilated during the Al,Si disordering procedure (e.g., 1052°C, 710 hours, for producing analbite from low albite, Hovis 1977). The resulting solvus has a critical temperature of 490 ± 25°C, which is lower than indicated by the experimentally determined solvus (e.g., Goldsmith and Newton 1974, Smith and Parsons 1974, Parsons 1978, Lagache and

336 Weisbrod 1977). The difference in the critical temperatures is ~160°C as seen from
337 Figure 6. If, however, the configurational entropy resulting from the Na,K distribution
338 is decreased in the Ab-rich compositional region by a maximum of 1.0 J $mol^{-1}$ $K^{-1}$, as
339 shown in Fig. 7, good agreement between calculation and experiment is obtained
340 (Fig. 6). Such a decrease can be generated assuming Na,K clustering/ordering to be
341 present. Phillips et al. (1988) investigated Al,Si ordered alkali feldspars homogenised
342 at 930°C. Their $^{23}Na$ NMR spectra especially of Ab-rich samples indicate that the
343 Na,K environment of a Na atom is skewed toward a relative enrichment of Na atoms
344 (Phillips et al., 1988), which we will term “short-range clustering”. Such clustering
345 above the solvus was also found in many metallic systems (e.g., Rudman and
346 Averbach 1954, Sakakibara et al. 1994). A similar behaviour is also to be expected in
347 disordered alkali feldspar samples close to the solvus. The solvus calculated from the
348 calorimetric data without considering short-range clustering (*solid line* in Fig. 6) thus
349 represents a hypothetical solvus with the two coexisting alkali feldspars being fully
350 disordered with respect to Na,K. Accordingly, a homogenous $Ab_{60}Or_{40}$ crystal for
351 example would be stable at 500°C only if its Na,K distribution were fully disordered.
352 However, Na,K short-range clustering present in such a crystal decreases the
353 configurational entropy which destabilises the solid solution raising the solvus to the
354 experimentally observed temperatures. Investigation on the NaCl – KCl crystalline
355 solution (Benisek and Dachs, 2013) shows that a similar amount of short-range
356 clustering (~0.5 J $mol^{-1}$ $K^{-1}$ in the Na-rich compositional region) has to be assumed to
357 obtain agreement between the calorimetrically determined solvus and the one
358 bracketed by Na – K exchange experiments.
359 The excess enthalpy and the excess vibrational entropy of mixing were
360 measured on Al,Si disordered samples, whose Na,K short-range clustering is to be
361 expected to be less pronounced (homogenised at 930°C) than in samples used to

experimentally determine the solvus (at T < 650°C). The excess vibrational entropy decreases slightly with an increase of the Na,K clustering, as found from DFT lattice dynamics calculations (Benisek and Dachs, in preparation). The excess enthalpy, too, is to be expected to be smaller in samples with a more pronounced clustering. A full description of the solvus samples would need, therefore, not only a reduction of the configurational entropy due to Na,K clustering, as done here, but also the effect of this reduction on the excess enthalpy and vibrational entropy.

The solvus samples in Fig. 5 and 6 represent alkali feldspars whose Na,K distribution is equilibrated, which is, however, not the case concerning their Al,Si distribution. The samples that have been used to determine the disordered alkali feldspar solvus have a larger degree of Al,Si disorder than required by the solvus temperatures. The Al,Si distribution of the samples of the ordered alkali feldspar solvus, on the other hand, is relatively too ordered, especially at the critical temperature. As mentioned above, an equilibrium solvus was estimated by Brown and Parsons (1984) by interpolating data from experimental solvi with different Al,Si order (Smith and Parsons 1974, Müller 1971, Bachinski and Müller 1971).

## Implications

The investigation of the entropic behaviour of the Al,Si ordered and disordered alkali feldspars confirms a model describing the nature of the excess entropy of mixing that can be applied not only in geosciences, but also in other fields like metallurgy.

The mixing properties of binary systems are often extracted from solvus data, which were experimentally determined (e.g., Green 1970, Powell 1974, Hovis et al. 1991, Holland and Powell 2003). Such mixing models, however, are only valid with respect to the solvus samples from which they were derived. In case of Al,Si

disordered alkali feldspars, the mixing parameters so derived are not suitable to model the high temperature activity-composition behaviour above the solvus. The equilibrium amount of Na,K short-range clustering present in samples held at temperatures close to the solvus is expected to be larger than in samples held at higher temperatures. The effect of this short-range clustering on the configurational entropy is, therefore, smaller in equilibrated high-temperature samples than in the metastable solvus samples. Many petrologic problems involve disordered alkali feldspars, for which the activity composition relations need to be known at high temperatures (~900°C, e.g., thermometry including ternary feldspars, melting of alkali feldspar). For such alkali feldspars, we present mixing parameters in Table 3. They agree within uncertainties with those incorporated into the ternary feldspar mixing model of Benisek et al. (2010c) and their Excel spreadsheet for calculating two-feldspar temperatures and are valid at high temperatures. For a comprehensive thermodynamic description of alkali feldspars at lower temperatures, the effects of Na,K short-range clustering and Al,Si ordering need to be considered. Whereas Al,Si ordering could be modelled by applying e.g., the symmetric formalism of Holland and Powell (1996), future studies on Na,K short-range clustering in alkali feldspars could be done using drop calorimetry in order to quantify the energetics of this effect. In the case of the Cu – Zn system, where ordering processes occur at lower temperatures than in the alkali feldspars, the energetic effects were successfully studied by DSC-methods (Benisek et al, submitted).

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570

571 **Figure Captions**

572 Fig. 1: Excess heat capacity of mixing ($\Delta C_p^{exc}$) of samples with intermediate
573 compositions ($Ab_{\sim 50}Or_{\sim 50}$). *Closed symbols*: ordered Al,Si distribution (this work),
574 *open symbols*: disordered Al,Si distribution (Haselton et al. 1983). Error bars
575 represent 1 s.d.

576

577 Fig. 2: Vibrational entropy at $T$ = 298.15 K ($S^{298.15} - S^0$) as a function of composition.
578 *Closed circles:* alkali feldspars prepared from Amelia albite, *closed squares:* alkali
579 feldspars prepared from Cazadero albite + Prilep microcline. The data were jointly
580 fitted to a Margules mixing model yielding $W^S_{AbOr}$ = 8.60 and $W^S_{OrAb}$ = 9.28 J $mol^{-1}$ $K^{-1}$
581 . Data of the analbite – sanidine series from Haselton et al. (1983) (*open triangles*)
582 are added for comparison. Error bars represent 1 e.s.d.

583

584 Fig. 3: Enthalpies of solution in hydrofluoric acid for the Ab – Or series. *Solid circles*:
585 data from Waldbaum and Robie (1971) obtained on samples prepared from Amelia
586 microcline and thus characterised by cross-hatched microcline twinning
587 (transformation twinning). *Open triangles*: data from Hovis (1988) for samples
588 prepared from Amelia albite. *Open circles*: data from Waldbaum and Robie (1971) for
589 pure and K-exchanged Amelia albite. *Open diamonds*: data from Hovis (1988) for the
590 analbite – sanidine series.

591

592 Fig. 4: A sketch of the relationship between enthalpies of solution and formation,
593 respectively, demonstrated for different Na-feldspars (not to scale). The numbers
594 represent the enthalpy changes (kJ $mol^{-1}$), when Na-feldspar is dissolved in
595 hydrofluoric acid at 50°C (Hovis 1988, Waldbaum and Robie 1971) and lead borate

596 solvent at 700°C, respectively (Newton et al. 1980, Carpenter et al. 1985, Hovis and
597 Navrotsky 1995, Benisek et al. 2003).
598
599 Fig. 5: Calculated solvi at 1 bar for the Al,Si ordered alkali feldspar system. The solvi
600 are compared with the phase equilibrium experiments of Bachinski and Müller (1971)
601 (*open diamonds*) and Delbove (1975) (*closed diamonds*). The calculations used two
602 different thermodynamic data sets. The data set of ordered feldspar 1 (Table 3) is
603 given by the upper *solid curve*, that of ordered feldspar 2 (Table 3) by the lower solid
604 curve. A Monte Carlo method was used to investigate the uncertainty of the
605 calculated solvi which is represented by the dashed lines (1 s.e.d.). Liquidus and
606 solidus curves are not shown.
607
608 Fig. 6: Solvi at 1 kbar for the Al,Si disordered alkali feldspar system. *Solid curve:*
609 Calculated solvus with uncertainties (dashed lines) based on calorimetric data from
610 Hovis (1988) and Haselton et al. (1983); the interaction parameters used are listed in
611 Table 3. *Dash-dotted curve*: same interaction parameters, however, accounting for
612 Na,K short-range clustering as shown in Fig. 7. Phase equilibrium experiments are
613 taken from Smith and Parsons (1974) and Parsons (1978) (*arrows*), and from
614 Lagache and Weisbrod (1977) (*bars with dots*). They are consistent with high
615 pressure solvus data (9 -15 kbar) from Goldsmith and Newton (1974), when the
616 volumetric mixing parameters of e.g., Kroll et al. (1986), Hovis (1988), or Hovis et al.
617 (1991) are used.
618
619 Fig. 7: Configurational entropy ($S^{cfg}$) in the alkali feldspar series. *Solid line*: One site
620 mixing model (= disordered Na,K distribution). *Broken line*: Reduction due to Na,K

621 short-range clustering in the Ab-rich region, described with a Margules mixing model

622 using $W_{OrAb}$ = -7, $W_{AbOr}$ = 0 J $mol^{-1}$ $K^{-1}$.

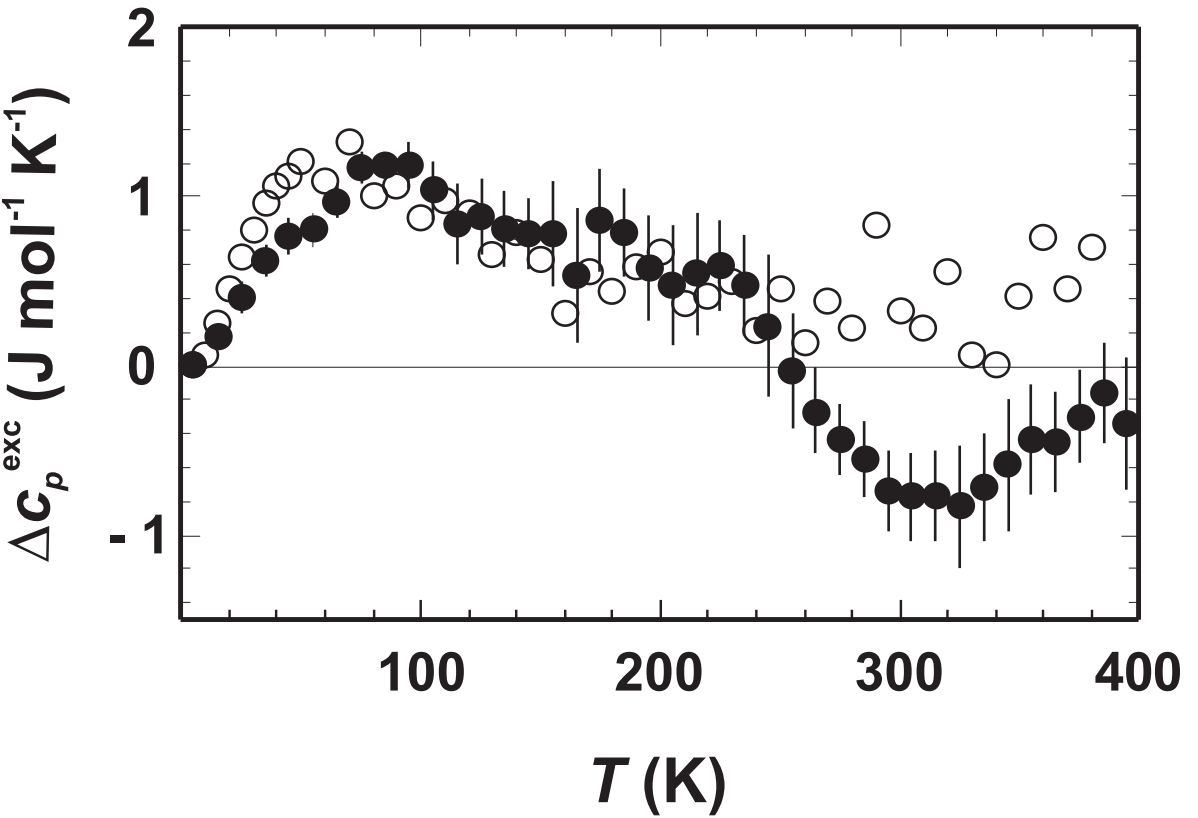


Fig. 1

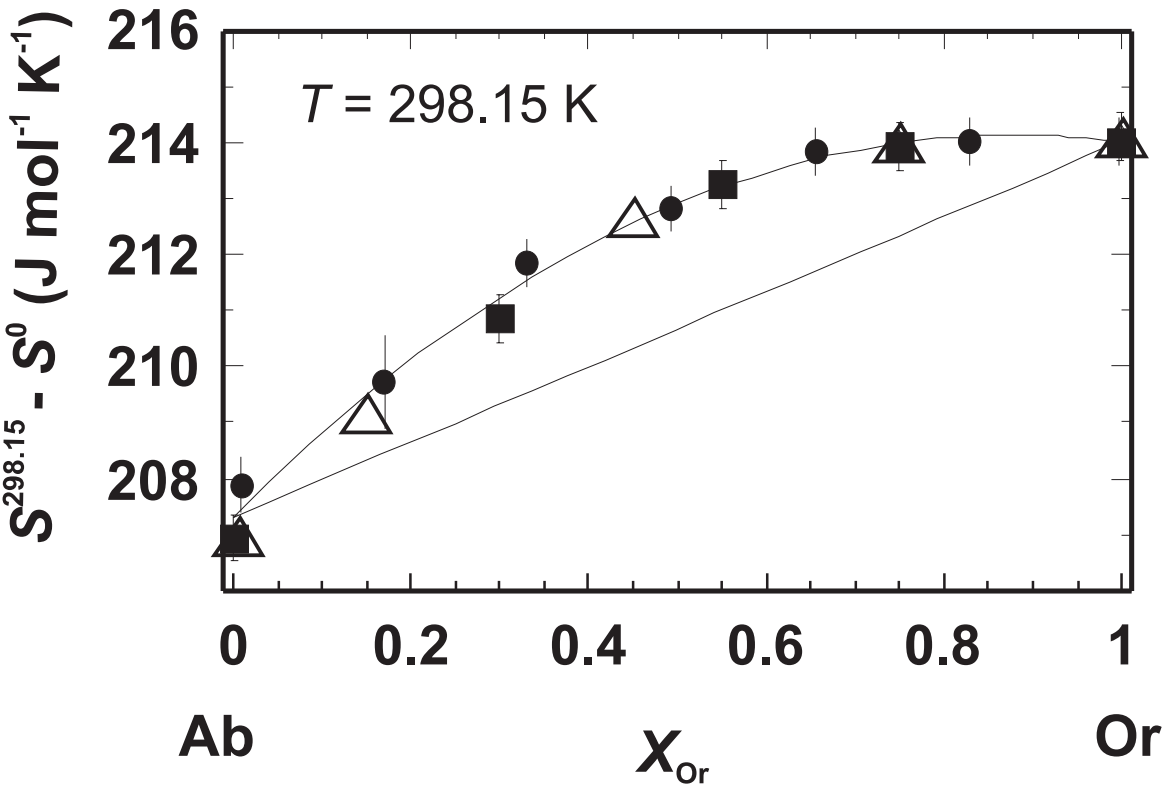
T = 298.15 K
216
214
212
210
208
S298.15 - S0 (J mol-1 K-1)
0
0.2
0.4
0.6
0.8
1
Ab
XOr
Or

Fig. 2

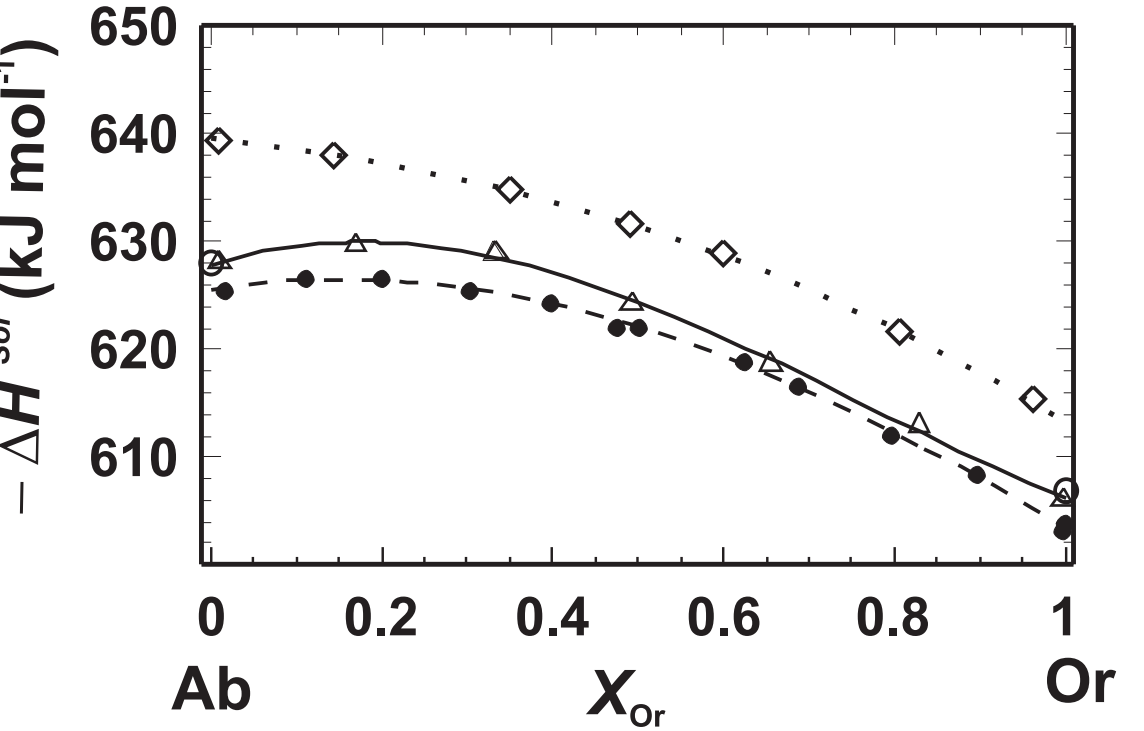


Fig. 3

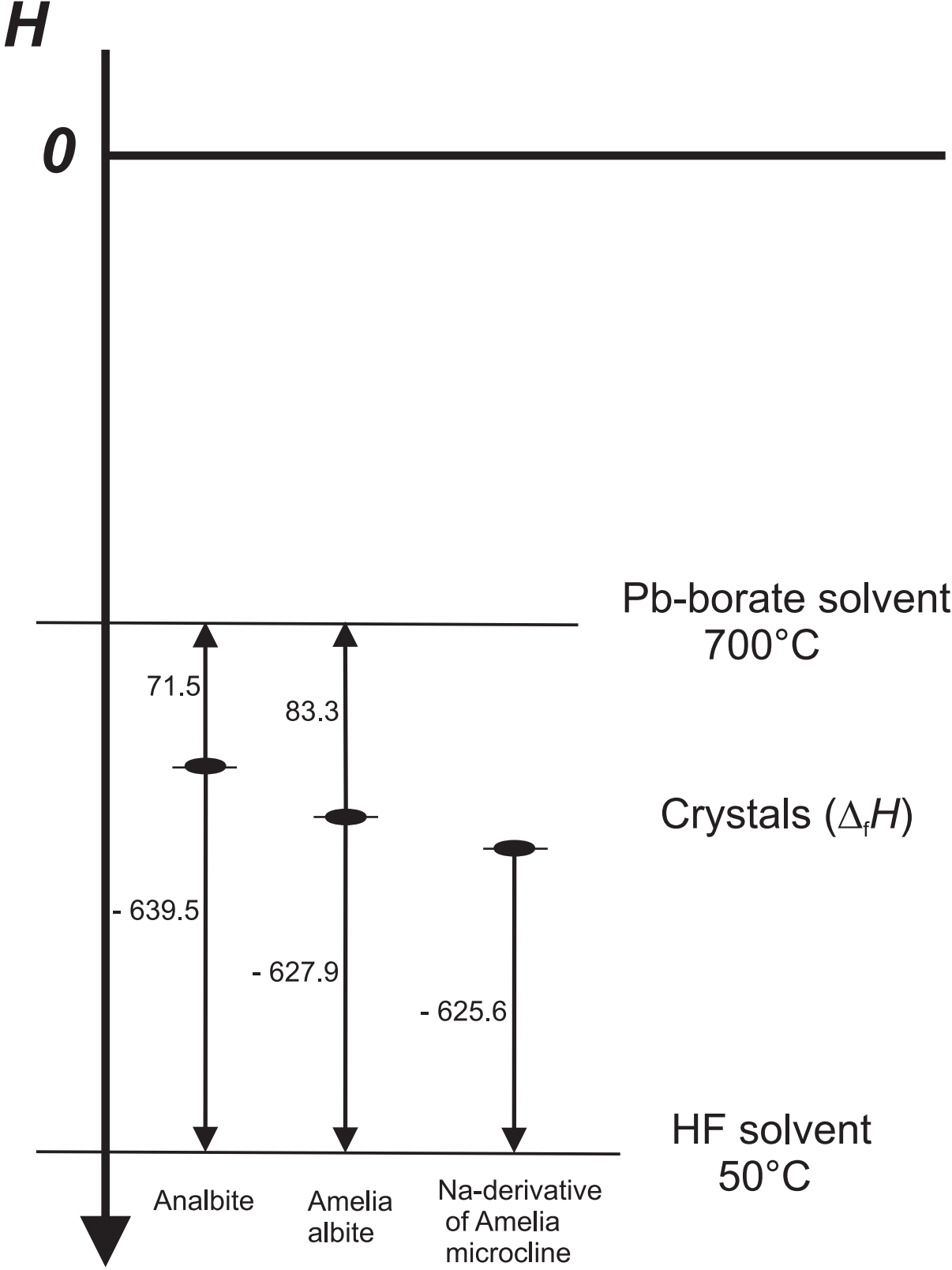
H
0
Pb-borate solvent
700°C
71.5
83.3
Crystals ($\Delta_f H$)
- 639.5
- 627.9
- 625.6
HF solvent
50°C
Analbite
Amelia albite
Na-derivative of Amelia microcline

Fig. 4

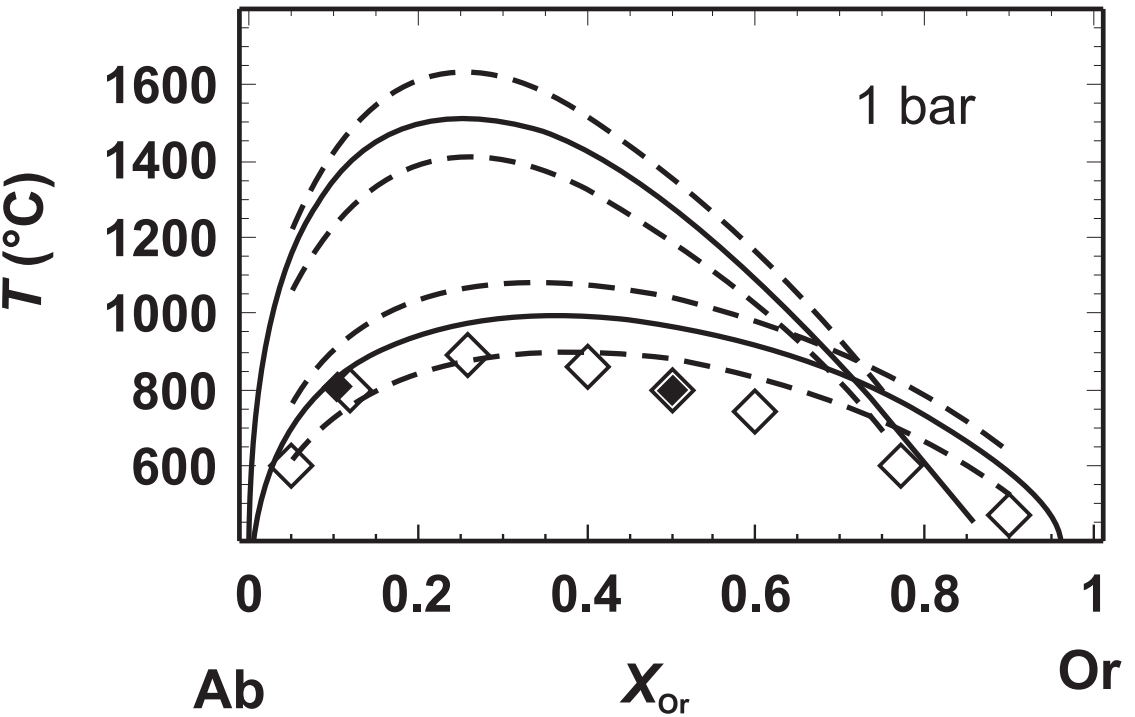


Fig. 5

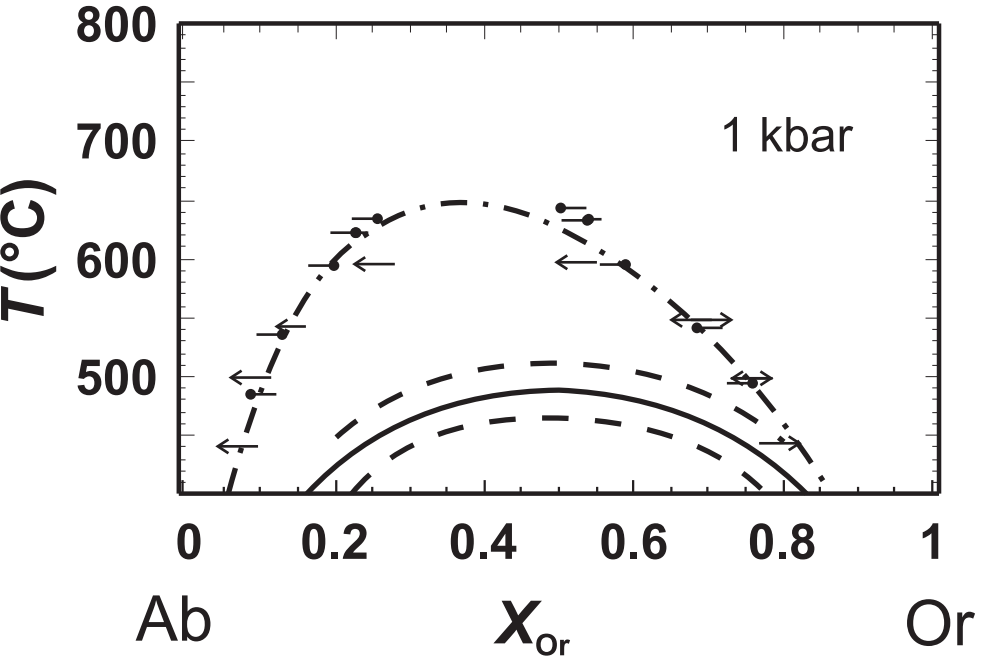


Fig. 6

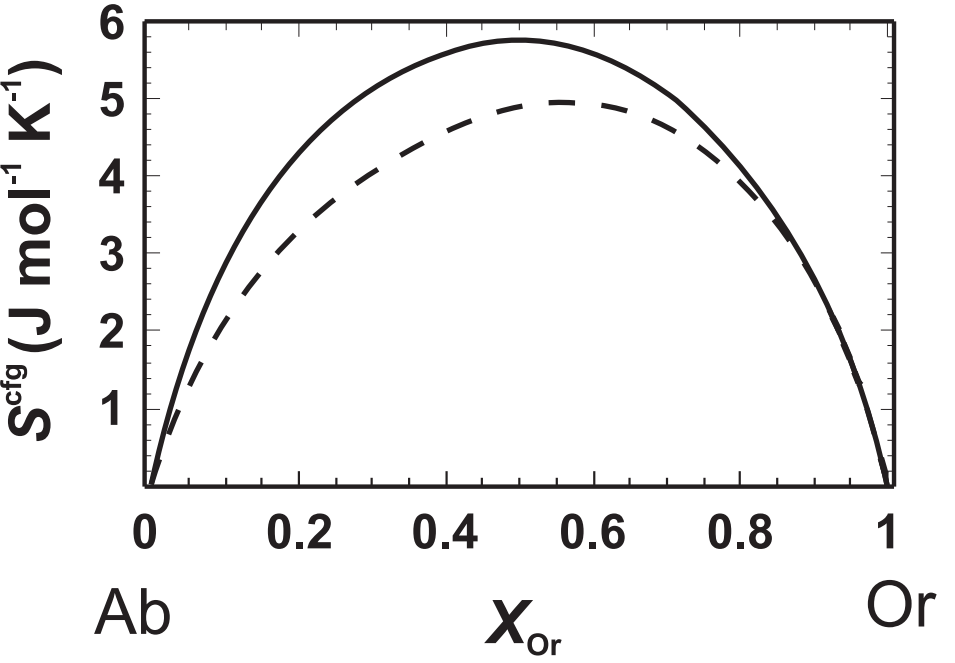


Fig. 7

Table 1 Provenance, preparation and characterisation of the two investigated ordered alkali feldspar series.

| | Amelia albite series [1)] | Cazadero albite – Prilep microcline series [2)] |
|---|---|---|
| Parent material | Amelia albite (Virginia) | Cazadero albite (California) + Prilep microcline (Macedonia) |
| Preparation of microcline | K-exchange of Amelia albite in molten KCl at 815°C to produce low microcline | K-exchange of Prilep microcline in molten KCl at 850°C to convert it into pure low microcline |
| Preparation of solid solution samples | Mechanical mixtures of Amelia albite and its K-derivative were homogenised at ~ 930°C/120h | Mechanical mixtures of Cazadero albite and K end member of Prilep microcline were homogenised at 800-1000 °C / 40-80 h |
| X-ray characterisation | Hovis (1988) | Kroll et al. (1986) |
| Transformation twinning | Not present | Present in the original Prilep microcline grains, not present in the original Cazadero albite grains |

[1)] Prepared by Hovis (1986).

[2)] Prepared by Kroll et al. (1986).

For more synthesis details, see their studies.

Table 2 Vibrational entropy at $T$ = 298.15 K ($S^{298.15}$-$S^0$) determined in this study. The standard deviations given in parentheses refer to the last digit. The sample names are the same as in the original studies of Hovis (1988) and Kroll et al. (1986).

| Samples | Or content (mol%) | $S^{298.15}$-$S^0$ (J mol$^{-1}$ K$^{-1}$) |
|---|---|---|
| Amelia albite series | | |
| 7010 | 0.99 | 207.9 (5) |
| 8205 | 16.95 | 209.7 (8) |
| 8207 | 33.11 | 211.8 (4) |
| 8047 | 49.26 | 212.8 (4) |
| 8204 | 65.53 | 213.9 (4) |
| 8206 | 82.95 | 214.0 (4) |
| 71104 | 99.72 | 214.0 (4) |
| Cazadero albite – Prilep microcline series | | |
| 7199o | 0.2 | 206.9 (4) |
| 7320u | 30.0 | 210.9 (4) |
| 7326m | 55.0 | 213.2 (4) |
| 7370u | 75.0 | 213.9 (4) |
| 7155m | 99.9 | 214.1 (4) |

Table 3 Margules mixing parameters and equations used to calculate the activities of Ab and Or components. The sources and the parent materials are also listed.

| Ordered feldspar data set 1 | AbOr | OrAb | Ref. | Parent material/transformation twinning |
|---|---|---|---|---|
| $W^H$ (J mol$^{-1}$) | 12426 ± 1757 | 46652 ± 1841 | Hovis (1988) | Amelia albite/no |
| $W^S$ (J mol$^{-1}$ K$^{-1}$) | 8.7 ± 1.1 | 8.7 ± 1.1 | This study | Amelia albite/no |
| $W^V$ (J mol$^{-1}$ bar$^{-1}$) | 0.619 ± 0.113 | 0.385 ± 0.117 | Hovis (1988) | Amelia albite/no |
| Ordered feldspar data set 2 | | | | |
| $W^H$ (J mol$^{-1}$) | 25899 ± 1715 | 35104 ± 2092 | Waldbaum & Robie (1971) | Amelia microcline/yes |
| $W^S$ (J mol$^{-1}$ K$^{-1}$) | 9.1 ± 1.4 | 9.1 ± 1.4 | This study | Cazadero albite/no + Prilep microcline/yes |
| $W^V$ (J mol$^{-1}$ bar$^{-1}$) | 0.389 ± 0.025 | 0.063 ± 0.038 | Kroll et a. (1986) | Cazadero albite/no + Prilep microcline/yes |
| Disordered feldspar series | | | | |
| $W^H$ (J mol$^{-1}$) | 20083 ± 879 | 20083 ± 879 | Hovis (1988) | Amelia albite/no |
| $W^S$ (J mol$^{-1}$ K$^{-1}$) | 10.3 ± 0.3 | 10.3 ± 0.3 | Haselton et al. (1983) | Amelia albite/no |
| $W^V$ (J mol$^{-1}$ bar$^{-1}$) | 0.301 ± 0.059 | 0.510 ± 0.050 | Hovis (1988) | Amelia albite/no |

| | |
|---|---|
| Asymmetric Margules model | $\Delta\Phi^{mix} = (1-X_K)^2 X_K W^{\Phi}_{NaK} + (1-X_K) X_K^2 W^{\Phi}_{KNa}$ ($\Phi$ = H, S, and V) |
| Mixing parameter | $W^G = W^H - T W^S + P W^V$ |
| Activity coefficient Ab | $R T \ln \gamma_{Ab} = X_{Or}^2 [W^G_{AbOr} + 2 (W^G_{OrAb} - W^G_{AbOr}) (1-X_{Or})]$ |
| Activity coefficient Or | $R T \ln \gamma_{Or} = (1 - X_{Or})^2 [W^G_{OrAb} + 2 (W^G_{AbOr} - W^G_{OrAb}) X_{Or}]$ |
| Ideal activity | $a_i^{id} = X_i$ i = Ab, Or |
| Activity | $a_i = a_i^{id} \gamma_I$ i = Ab, Or |