

Volumes of K-Na mixing for low albite–microcline crystalline solutions at elevated temperature: A test of regular solution thermodynamic models

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ABSTRACT

High-temperature volumes of K-Na mixing have been investigated for a seven-member low albite–microcline ion-exchange series by conducting X-ray powder diffraction measurements from room temperature to approximately 1000 °C using Guinier techniques. Volume expansion is a linear function of temperature for all series members and is due mainly to the lengthening of the *a* unit-cell axis, although some expansion of *b* and *c* occurs for relatively sodic members. The maximum expansion possible for each feldspar is determined both by chemistry and temperature, thus $\Delta V/\Delta T$ slopes are steepest for the sodic third of the series, then decrease abruptly for increasingly potassic feldspars. Volumes of K-Na mixing for this series are essentially constant with temperature, regardless of the mixing model utilized, and thus are adequately represented by regular solution thermodynamic models.

INTRODUCTION

It is a common practice in geology to apply certain types of thermodynamic data collected at one temperature and pressure, such as internal energies and volumes of mixing (E_{ex} and V_{ex} , respectively, using the terminology of Thompson 1967), to a wide range of temperatures and pressures. Indeed, standard “regular solution” models assume that these functions are independent of both temperature and pressure (see Thompson 1967, Eqs. 47, 49, and 69).

In recent work, we asked if enthalpies of K-Na mixing for disordered alkali feldspars are a function of temperature (Hovis and Navrotsky 1995). By making high-temperature (704 °C) lead borate solution calorimetric measurements on an analbite-sanidine solid-solution series, then comparing the resulting enthalpies of mixing with those from lower temperature (50 °C) hydrofluoric acid solution calorimetry (Hovis 1988), Hovis and Navrotsky (1995) determined that a regular solution model did indeed represent enthalpies of mixing well over a wide temperature range.

Here we ask the same question about volumes of mixing. We chose to study a low albite–maximum microcline solid-solution series. The volumetric properties of this mineral series at room temperature and pressure are well known from previous investigations (Hovis 1986, 1988; Kroll et al. 1986; Waldbaum and Robie 1971; Waldbaum and Thompson 1968). No phase transformations across the series confuse interpretation of the data, at either low or high temperature, so these minerals make excellent materials for volume analysis.

SAMPLE PREPARATION

A seven-member Na-K ion-exchange series ranging from low albite to microcline was prepared using the procedures described in Table 2 of Hovis (1986). Amelia low albite (sample 7001) was used as the Na end-member. A corresponding microcline (sample 71104) was produced by ion exchange of the albite powder (<325 mesh) in molten KCl at 840 °C for 16.5 h. Compositionally intermediate samples were made by combining powders of the low albite and microcline in the desired proportions, mixing and then compressing these powders in cylindrical platinum crucibles, and annealing them for various lengths of time (normally about 10 d) at 935 ± 10 °C (for details see Table 1 of Hovis 1986). Each sample was removed from the furnace approximately every 24 h, re-mixed in acetone (to randomize grains of various compositions), then repacked and reloaded for further annealing. The ion-exchange procedures had no detectable effect on the Al-Si distributions of the various samples, owing to the sluggish rates of Al-Si disordering at homogenization and ion-exchange temperatures (see discussion in Hovis 1986, p. 871).

Raw chemical data both for end-member feldspars and for intermediate compositions were obtained by atomic absorption spectroscopy and were reported in Table 3 of Hovis (1986). For convenience the mole fraction of KAlSi_3O_8 (N_{or}) for each feldspar is reported again in Table 1 of this paper.

X-RAY EQUIPMENT AND PROCEDURES

X-ray data were collected at room and elevated temperatures for each feldspar sample at the University of Cambridge, England. Measurements were made using a

TABLE 1. Unit-cell parameters

Sample	N_{or}	T (°C)	a (Å)	b (Å)	c (Å)	α (°)	α^* (°)	β (°)	γ (°)	Unit-cell volume (Å ³ /unit cell)	Molar volume (cm ³ / mol)	Molar volume (J/ bar-mol)
71104	0.997	22	8.5882(21)	12.9578(25)	7.2217(20)	90.622(19)	90.440(19)	115.948(14)	87.674(19)	722.02(39)	108.706	10.871
71104	0.997	205	8.6187(14)	12.9593(12)	7.2249(13)	90.675(12)	90.376(12)	115.919(9)	87.682(10)	725.18(25)	109.182	10.918
71104	0.997	357	8.6471(16)	12.9607(14)	7.2280(14)	90.708(13)	90.325(12)	115.905(9)	87.709(11)	728.06(28)	109.616	10.962
71104	0.997	510	8.6653(15)	12.9548(14)	7.2251(15)	90.734(14)	90.293(14)	115.863(10)	87.714(12)	729.24(28)	109.793	10.980
71104	0.997	664	8.6807(30)	12.9579(13)	7.2270(15)	90.740(13)	90.276(13)	115.841(10)	87.732(10)	731.05(32)	110.066	11.007
71104	0.997	816	8.7010(21)	12.9480(13)	7.2265(16)	90.719(12)	90.303(12)	115.841(11)	87.724(11)	732.14(35)	110.230	11.023
71104	0.997	969	8.7250(32)	12.9585(17)	7.2338(22)	90.724(16)	90.291(17)	115.780(17)	87.731(15)	735.88(52)	110.793	11.080
8206	0.830	22	8.5238(14)	12.9597(18)	7.2143(12)	90.769(14)	90.289(14)	115.933(11)	87.648(12)	716.07(26)	107.810	10.781
8206	0.830	154	8.5490(12)	12.9618(18)	7.2181(13)	90.749(12)	90.287(13)	115.918(9)	87.696(11)	718.81(25)	108.223	10.823
8206	0.830	303	8.5761(15)	12.9580(22)	7.2182(14)	90.779(16)	90.236(16)	115.890(10)	87.729(13)	721.07(27)	108.563	10.857
8206	0.830	453	8.5981(17)	12.9532(20)	7.2162(20)	90.758(17)	90.248(17)	115.852(13)	87.749(16)	722.53(37)	108.783	10.879
8206	0.830	602	8.6216(25)	12.9524(25)	7.2193(22)	90.800(17)	90.213(18)	115.856(16)	87.727(16)	724.89(46)	109.138	10.914
8206	0.830	751	8.6490(13)	12.9495(12)	7.2190(13)	90.790(10)	90.217(10)	115.798(9)	87.735(9)	727.38(23)	109.513	10.952
8206	0.830	900	8.6584(28)	12.9584(16)	7.2223(20)	90.824(14)	90.165(14)	115.761(16)	87.764(13)	728.73(45)	109.717	10.972
8204	0.655	22	8.4555(20)	12.9471(24)	7.2109(20)	91.066(22)	89.985(21)	115.898(14)	87.589(21)	709.51(40)	106.823	10.682
8204	0.655	146	8.4725(27)	12.9506(22)	7.2084(16)	91.011(18)	90.034(18)	115.932(13)	87.618(20)	710.68(41)	106.999	10.700
8204	0.655	266	8.4888(30)	12.9460(18)	7.2069(18)	90.992(20)	90.030(20)	115.891(14)	87.666(22)	711.92(45)	107.186	10.719
8204	0.655	386	8.5100(32)	12.9457(26)	7.2092(19)	90.954(21)	90.071(21)	115.907(15)	87.669(23)	713.82(48)	107.472	10.747
8204	0.655	506	8.5326(22)	12.9440(25)	7.2064(19)	90.984(20)	90.050(21)	115.867(14)	87.642(19)	715.57(41)	107.735	10.774
8204	0.655	626	8.5584(22)	12.9401(22)	7.2087(21)	90.963(18)	90.058(19)	115.849(15)	87.670(17)	717.86(43)	108.080	10.808
8204	0.655	746	8.5756(13)	12.9347(17)	7.2048(11)	90.919(14)	90.085(14)	115.772(9)	87.709(13)	719.11(24)	108.268	10.827
8204	0.655	866	8.6156(18)	12.9315(17)	7.2057(17)	90.855(15)	90.152(16)	115.779(14)	87.720(13)	722.33(37)	108.753	10.876
8204	0.655	986	8.6268(22)	12.9365(23)	7.2096(23)	90.797(20)	90.202(19)	115.795(17)	87.752(19)	723.86(47)	108.983	10.899
8047	0.493	22	8.3839(26)	12.9357(28)	7.2037(29)	91.523(24)	89.433(25)	116.017(18)	87.688(19)	701.48(49)	105.614	10.562
8047	0.493	144	8.4100(20)	12.9375(21)	7.2035(22)	91.394(19)	89.568(19)	116.023(14)	87.705(14)	703.73(37)	105.953	10.595
8047	0.493	289	8.4329(18)	12.9410(19)	7.2029(19)	91.308(16)	89.674(17)	115.966(12)	87.682(12)	706.12(33)	106.312	10.631
8047	0.493	425	8.4570(21)	12.9404(22)	7.1992(23)	91.188(19)	89.781(20)	115.956(14)	87.734(15)	707.82(40)	106.568	10.657
8047	0.493	569	8.4761(22)	12.9392(25)	7.1989(33)	91.159(22)	89.818(22)	115.889(17)	87.722(18)	709.73(51)	106.856	10.686
8047	0.493	709	8.5054(17)	12.9433(18)	7.2029(22)	91.068(15)	89.901(15)	115.829(11)	87.753(16)	713.18(37)	107.375	10.738
8047	0.493	849	8.5414(45)	12.9604(28)	7.2111(38)	91.055(24)	89.906(25)	115.849(26)	87.774(29)	717.85(77)	108.078	10.808
8429	0.334	22	8.3090(28)	12.8864(21)	7.1901(27)	92.541(27)	88.298(30)	116.173(21)	87.699(16)	690.07(57)	103.896	10.390
8429	0.334	179	8.3317(26)	12.9010(12)	7.1917(26)	92.227(18)	88.660(19)	116.032(19)	87.667(9)	693.83(56)	104.462	10.446
8429	0.334	334	8.3543(40)	12.9081(39)	7.1927(39)	92.035(28)	88.865(29)	116.089(29)	87.690(16)	695.91(84)	104.766	10.478
8429	0.334	490	8.3761(32)	12.9108(17)	7.1949(31)	91.892(22)	89.040(23)	116.001(23)	87.652(13)	698.64(67)	105.186	10.519
8429	0.334	639	8.4053(38)	12.9220(29)	7.1974(35)	91.700(35)	89.256(36)	115.975(27)	87.643(22)	702.11(74)	105.709	10.571
8429	0.334	790	8.4364(39)	12.9335(19)	7.2032(34)	91.618(24)	89.353(25)	115.884(26)	87.628(15)	706.46(76)	106.364	10.637
8429	0.334	941	8.4569(41)	12.9382(27)	7.2023(34)	91.484(32)	89.472(34)	115.886(26)	87.688(22)	708.38(73)	106.653	10.665
8205	0.170	22	8.2239(37)	12.8447(26)	7.1724(27)	93.507(23)	87.182(22)	116.350(19)	87.785(21)	677.60(58)	102.018	10.202
8205	0.170	150	8.2361(41)	12.8496(27)	7.1703(29)	93.373(24)	87.342(26)	116.317(21)	87.764(23)	678.94(68)	102.220	10.222
8205	0.170	306	8.2620(41)	12.8630(26)	7.1738(29)	93.158(24)	87.575(25)	116.232(21)	87.774(22)	682.74(67)	102.792	10.279
8205	0.170	451	8.2833(44)	12.8703(31)	7.1796(32)	92.919(28)	87.880(29)	116.148(23)	87.692(24)	686.05(70)	103.291	10.329
8205	0.170	609	8.3009(39)	12.8818(32)	7.1815(33)	92.719(33)	88.102(35)	116.077(23)	87.690(20)	688.82(72)	103.708	10.371
8205	0.170	752	8.3218(42)	12.8904(23)	7.1824(36)	92.549(28)	88.286(30)	116.074(25)	87.701(15)	691.19(82)	104.065	10.407
8205	0.170	901	8.3436(71)	12.9045(23)	7.1928(50)	92.428(37)	88.433(45)	115.986(39)	87.671(23)	695.32(1.29)	104.686	10.469
7010	0.010	22	8.1444(43)	12.7856(40)	7.1600(29)	94.245(36)	86.420(38)	116.602(24)	87.667(28)	664.79(67)	100.090	10.009
7010	0.010	170	8.1537(29)	12.7974(32)	7.1582(20)	94.202(24)	86.475(26)	116.478(16)	87.649(22)	666.76(46)	100.386	10.039
7010	0.010	315	8.1800(18)	12.8038(15)	7.1614(12)	94.029(13)	86.672(13)	116.369(10)	87.639(11)	670.31(27)	100.921	10.092
7010	0.010	459	8.1985(22)	12.8201(21)	7.1674(14)	93.911(18)	86.807(18)	116.344(12)	87.631(15)	673.47(33)	101.397	10.140
7010	0.010	603	8.2129(24)	12.8325(23)	7.1691(15)	93.834(22)	86.914(22)	116.246(13)	87.585(20)	676.09(35)	101.791	10.179
7010	0.010	747	8.2344(26)	12.8482(23)	7.1738(16)	93.680(22)	87.092(22)	116.223(14)	87.574(19)	679.37(39)	102.285	10.229
7010	0.010	892	8.2522(29)	12.8551(22)	7.1766(24)	93.499(21)	87.302(22)	116.156(17)	87.553(18)	681.98(50)	102.678	10.268

Note: Uncertainties in the last decimal places are given in brackets.

Huber 632 heating Guinier powder camera with a 4 mm fine-focus X-ray tube and a quartz monochromator for $\text{CuK}_{\alpha 1}$ radiation (de Dombal and Carpenter 1993). Temperatures were regulated by a Huber 633 controller linked to a chromel-alumel thermocouple positioned within a few millimeters of the sample. A temperature gradient between the sample and the controlling thermocouple made it necessary to check independently the temperature of the system. This was done with a Pt-Rh (13%) thermocouple attached to the sample holder and bent into place about 1 mm from the center of one face of the sample. Using this system, Redfern (1989) checked the

set temperatures against melting, sublimation, and phase-transition temperatures of known standards (discussion in de Dombal and Carpenter 1993). "True" temperatures are presented in Table 1. Temperature fluctuations of the furnace were generally within 2 °C of the given values. Additional experimental details for measurements like these are described in detail in the two references cited above.

Powder lines on the resulting films were read to within $0.01^\circ 2\theta$ on an Enraf-Nonius FR508V Guinier viewer. Corrections were made for film expansion and shrinkage. High-purity alumina, the line positions of which were calculated from the high-temperature unit-cell data of Par-

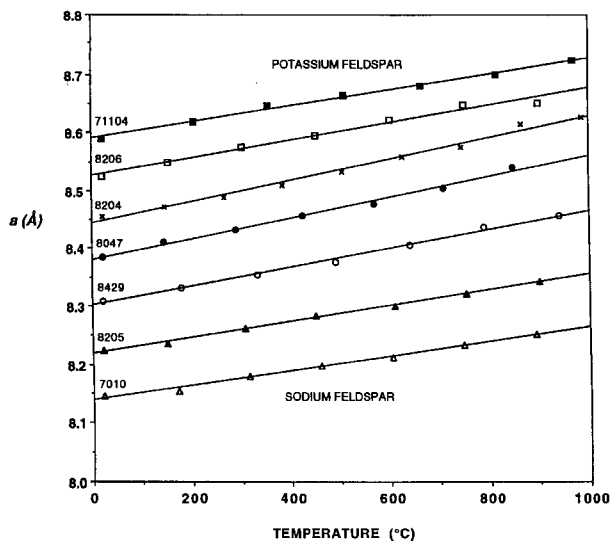


FIGURE 1. Plot of the a unit-cell dimension vs. temperature for the designated feldspars. Slopes of the lines are shown in Figure 2.

rish (1953), was mixed with each feldspar powder as an internal standard. Feldspar lattice parameters were calculated from the X-ray data using the least-squares program Cell written at Cambridge University. Computations were performed on a microVAX 2000.

RESULTS

Variation of individual unit-cell parameters with temperature

Unit-cell parameters and volumes at the various temperatures, and associated standard errors, are reported in Table 1. A few observations on individual unit-cell parameters are instructive because they relate to volumes.

Of the three unit-cell axes, only a increases for all feldspars throughout the temperature range of our experiments (Fig. 1). It is perhaps not surprising that the main parameter affected by composition (K/Na ratio), the a dimension, is also the one most affected by temperature. The behavior of a with temperature is clearly linear, but change of the $\Delta a/\Delta T$ slopes with composition is not constant. Slopes for potassic and sodic end-member feldspars are similar but less than those of feldspars with intermediate compositions (Fig. 2).

Variation of the b and c unit-cell dimensions with temperature is quite systematic. For potassic feldspars, already stretched to a large degree by K substitution, temperature has little or no effect. Conversely, increased temperature expands b and c by greater and greater amounts as Na increases. This is shown well on a plot of b vs. c over all temperatures (Fig. 3), where one sees clusters of data points that are limited in extent for the four most potassic feldspars, then increasingly spread out for the three most sodic series members. For feldspars in the potassic half of the compositional range, then, volume

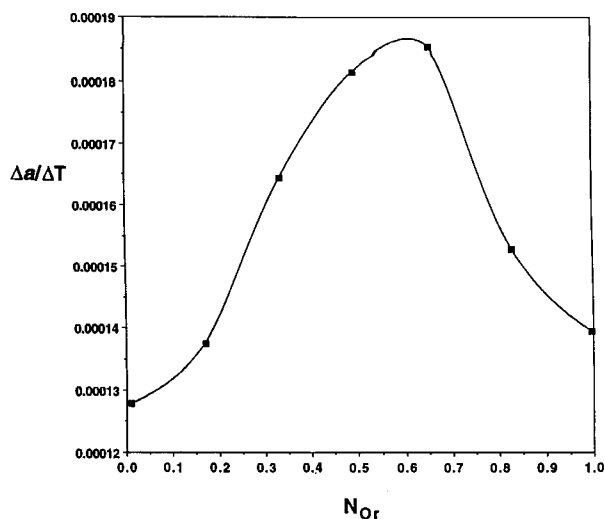


FIGURE 2. Slope of the a unit-cell dimension with temperature from Figure 1 plotted as a function of mole fraction KAISi_3O_8 (N_{Or}). The curve is interpolated and is not a least-squares fit.

expansion is accomplished almost solely by expansion of the a axis.

Of the interaxial angles, the variation in γ is almost exclusively related to Al-Si distribution, so γ changes little with either composition or temperature (for short-term heating experiments). Although β changes only to a small extent with either composition or temperature, α (or the reciprocal unit-cell angle α^*) is quite sensitive to composition, and this in large part must be associated with the same physical changes that are related to the triclinic-monoclinic displacive transformation that occurs as a function of K/Na ratio in topochemically monoclinic feldspar series (see discussion by Thompson et al. 1974). Thompson and Hovis (1978) showed that a plot of $\cot \alpha^*$ vs. composition separates various feldspar series well over all temperatures. For the feldspar samples in this study (Fig. 4) significant differences in $\cot \alpha^*$ are especially evident among members of the sodic part of the compositional range, regardless of temperature, and it is perhaps not fortuitous that significant contrasts in behavior begin near the compositional region where the displa-

TABLE 2. Coefficients for volume-temperature equations

Sample	a_0	a_1
71104	722.29	0.013409
8206	716.29	0.014266
8204	708.31	0.015347
8047	700.65	0.018418
8429	689.57	0.020157
8205	676.59	0.020225
7010	663.92	0.020375

Note: Equations have the form $V[\text{\AA}^3(\text{unit cell})] = a_0 + a_1 T$. Coefficients here are for unit-cell volumes but may be converted to molar volumes in cubic centimeters per mole or joules per bar-mole through division by 6.6419 or 66.418, respectively.

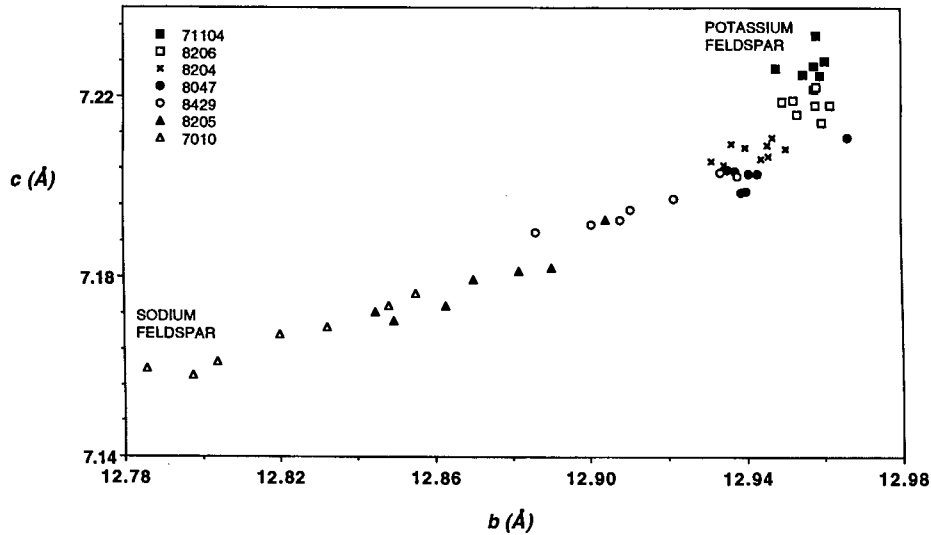


FIGURE 3. Plot of the b vs. c unit-cell dimensions of various feldspars. Values increase from lower left to upper right as temperature increases for each feldspar. Note that these parameters expand for sodic feldspars but are essentially constant with temperature for potassic feldspars.

cive transformation takes place at room temperature for the analbite-sanidine series ($N_{Or} = \sim 0.35$). So even though the triclinic Al-Si distribution of the feldspar samples prevents their conversion to monoclinic symmetry, dimensional changes do take place as a function of N_{Or} that are similar to those in topochemically monoclinic series. These differences also may be subtle factors in the contrasting expansion behavior of different feldspars.

Variation of volume with temperature

As with the individual parameters, unit-cell and molar volumes vary linearly with temperature. Least-squares fits for all series are presented in Figure 5 and Table 2; note that unit-cell volumes (\AA^3) can be converted to molar volumes in units of either cubic centimeters per mole or joules per bar-mole through division by 6.6419 or 66.418, respectively. Despite the rather odd variation of the $\Delta a/\Delta T$ slopes with composition, and the nonlinear behavior

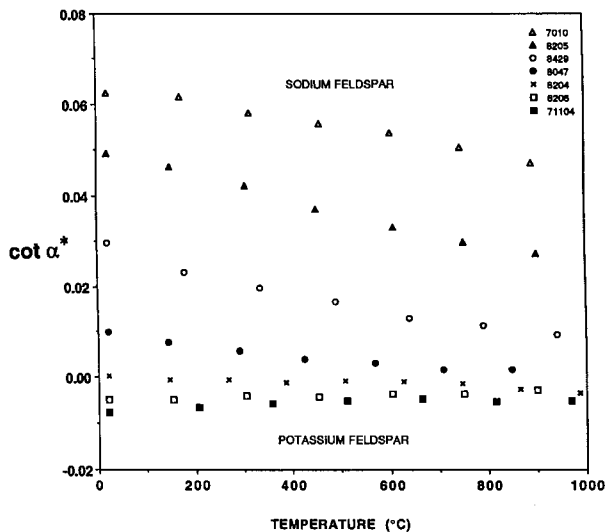


FIGURE 4. Plot of $\cot \alpha^*$ vs. temperature for all feldspars. Values for potassic feldspars are bunched and essentially constant with temperature. Sodic feldspars become more widely spaced, and values decrease with temperature.

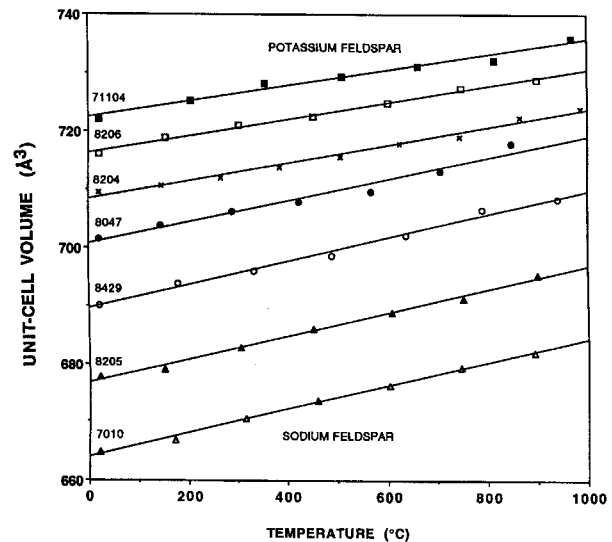


FIGURE 5. Unit-cell volume as a function of temperature for the designated feldspars. Slopes of the least-squares lines generally decrease with increasing K content. Equations for the lines are given in Table 2, and slopes are plotted in Figure 6.

TABLE 3. Unit-cell volumes (\AA^3) at various temperatures from equations given in Table 2

Sample	N_{Or}	22 °C	300 °C	600 °C	900 °C
71104	0.997	722.59	762.32	730.34	734.36
8206	0.830	716.61	720.57	724.85	729.13
8204	0.655	708.65	712.92	717.52	722.13
8047	0.493	701.56	706.05	710.89	715.73
8429	0.334	690.01	695.61	701.66	707.71
8205	0.170	677.03	682.66	688.72	694.79
7010	0.010	664.36	670.03	676.14	682.25

Note: Room-temperature values are raw and not derived from equations in Table 2. Coefficients here are for unit-cell volumes in cubic angstroms but may be converted to molar volume in cubic centimeters per mole or joules per bar-mole through division by 6.6419 or 66.418, respectively.

of $\Delta b/\Delta T$ and $\Delta c/\Delta T$ with composition, slopes of $\Delta V/\Delta T$ are quite systematic, steep for the three most sodic feldspars, then decreasing abruptly as K content increases (Fig. 6). Here again, K-for-Na substitution seems to account for a percentage of some maximum expansion that each feldspar can attain. Similar behavior is seen in end-member disordered feldspar analogs, analbite and sanidine (Hovis and others, unpublished data).

Volume of mixing as a function of temperature

We used equations given in Table 2 to calculate volumes at 300, 600, and 900 °C for each feldspar (see Table 3). With these isothermal data, volumes of K-Na mixing were then determined by fitting the data at each temperature (including room temperature) to Taylor expansion series of increasing order, in the manner described by Hovis (1988) for room-temperature data.

Although least-squares fits as high as fourth and fifth order were performed, these were not warranted generally by the resulting statistics. Room-temperature and 300 °C data were, in fact, best satisfied by equations of second order, whereas data at higher temperatures required fits of at least third order, on the basis of both standard deviations of fit (included in Table 4) and T tests to the individual coefficients. We shall, therefore, confine our discussion to second- and third-order volume expressions.

Quadratic and cubic fits to the unit-cell volumes of Table 3 are shown in Figures 7 and 8, respectively. Coefficients to the equations are given in Table 4. Statistical

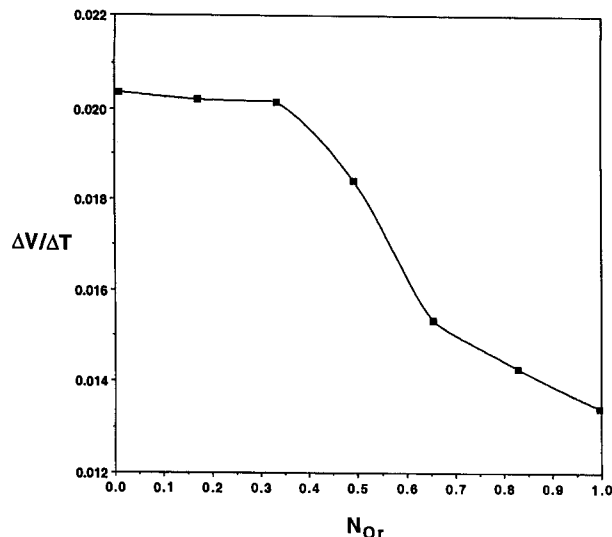


FIGURE 6. Slope of unit-cell volume as a function of temperature from Figure 5 plotted against composition. Note that the slope is high for the three most sodic feldspars, then falls off steeply with increasing K content.

distinctions between the fits are reflected by the standard deviations of fit; these also are included in Table 4.

The main objective of this study was to examine volumes of K-Na mixing as a function of temperature. Expressions for V_{cx} were derived from the coefficients in Table 4 following the method described by Thompson (1967) and Hovis (1988). The resulting curves, symmetric or asymmetric with respect to composition for second- vs. third-order expressions, are shown in Figures 9 and 10, respectively.

On the basis of a symmetric mixing model (Fig. 9), curves for the four temperatures are so similar that they appear as one. From such a model, one can make no claim of temperature dependence. The cubic fits to volume (Fig. 10), on the other hand, give slightly different results because maximum volumes of mixing are not constrained to occur at the midpoint of the compositional range. For these the maximum volumes of mixing increase in magnitude and shift to more sodic compositions

TABLE 4. Coefficients for volume-composition equations at various temperatures

Temperature and equation	a_0	a_1	a_2	a_3	Standard deviations of fit starting with second order	Best order of fit
22 °C, quadratic	663.14	91.400	-32.069		0.781, 0.902	2
22 °C, cubic	663.12	91.620	-32.652	0.387		
300 °C, quadratic	669.02	89.250	-32.194		0.712, 0.778	2
300 °C, cubic	668.79	93.255	-42.819	7.042		
600 °C, quadratic	675.35	86.958	-32.350		0.784, 0.733, 0.713, 0.159, 0.000	6
600 °C, cubic	674.89	95.035	-53.772	14.198		
900 °C, quadratic	681.69	84.678	-32.519		0.972, 0.786, 0.878	3
900 °C, cubic	681.00	96.825	-64.738	21.355		

Note: Equations have the form $V[\text{\AA}^3(\text{unit cell})] = a_0 + a_1N_{Or} + a_2N_{Or}^2 + a_3N_{Or}^3$. Coefficients here are for unit-cell volumes but may be converted to molar volumes in cubic centimeters per mole or joules per bar-mole through division of coefficients by 6.6419 or 66.418, respectively.

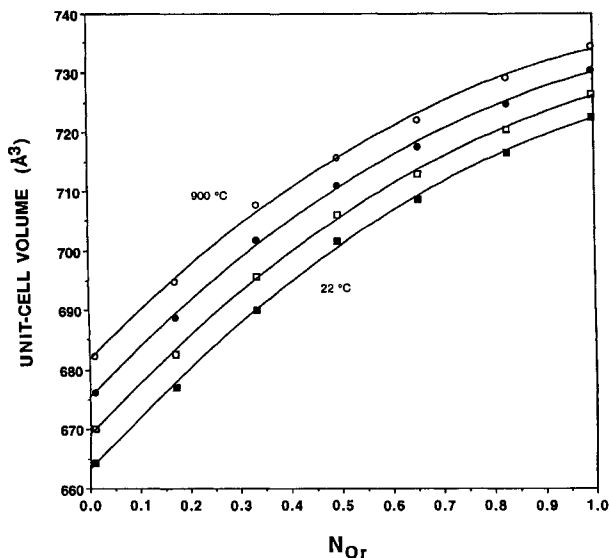


FIGURE 7. Unit-cell volumes for feldspars at temperatures of 22, 300, 600, and 900 °C derived from equations in Table 2 and given in Table 3. Curves represent quadratic fits to the data; coefficients to the equations are given in Table 4. A molar volume plot would have the same appearance.

with increasing temperature. As noted above, higher order fits (Fig. 11) do not change this analysis.

Despite the fact that second-order fits adequately represent the lower temperature data, we believe as a general model that fits no lower than third order should be utilized to represent the variation of volume with composition. This is consistent with extensive analysis of thirteen room-temperature data sets (Hovis 1988). Moreover,

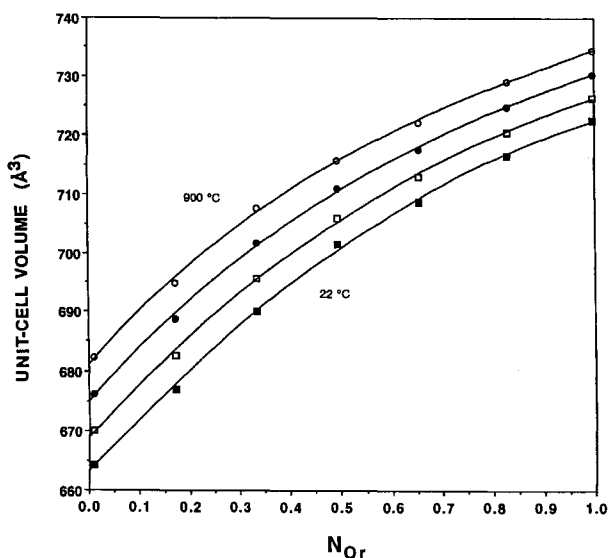


FIGURE 8. The same data as in Figure 7, but the curves shown are cubic. Equations are found in Table 4.

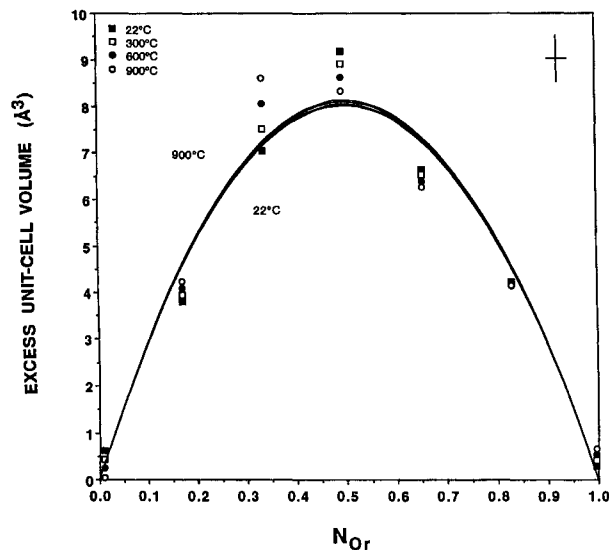


FIGURE 9. Unit-cell volumes of K-Na mixing derived from the quadratic curves in Figure 7. An average error bar is shown in the upper right corner. The appearance of excess molar volume curves would be identical.

asymmetric volumes of mixing would seem to make a reasonable model for a system in which the substituting ions (K-Na) are of very different sizes. Even with third-order fits, however, the shift in the asymmetry of excess volume is small, and the maximum value for V_{ex} increases in magnitude by $<1 \text{ \AA}^3$ between room temperature and 900 °C. Such a change is within the uncertainty of the volume determinations, especially when one considers

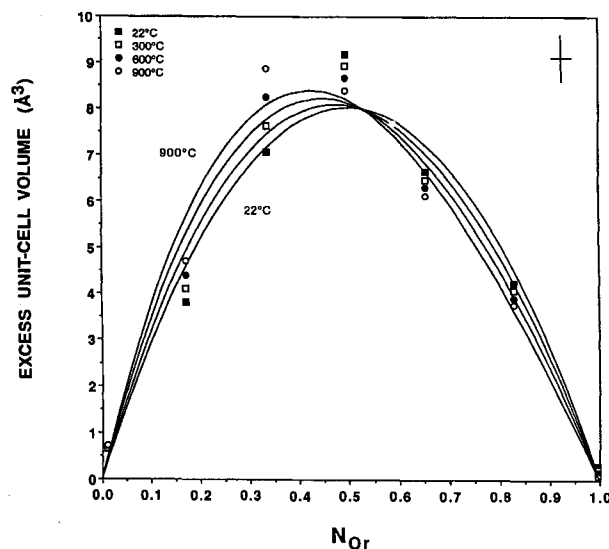


FIGURE 10. Unit-cell volumes of K-Na mixing derived from the cubic curves in Figure 8. An average error bar is shown in the upper right corner.

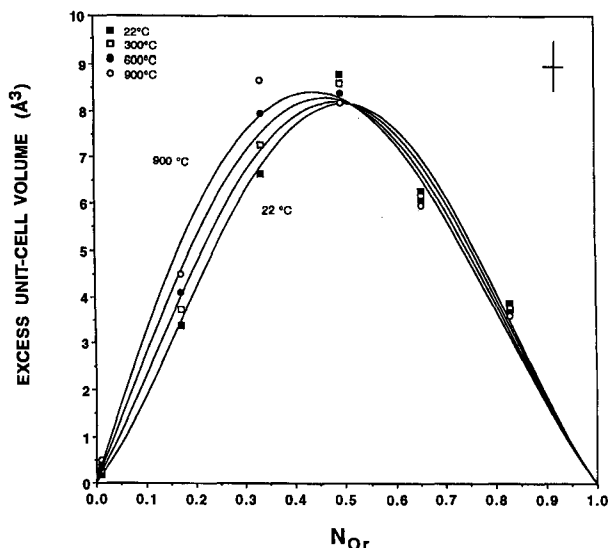


FIGURE 11. Unit-cell volumes of K-Na mixing derived from a fourth-order fit of volume as a function of composition. Note that these provide no improvement over the third-order model of Figure 10.

additional errors from the smoothing procedures represented by Figure 5. Moreover, these changes are too small to affect significantly thermodynamic calculations that would account for them.

On the basis of these measurements, it is our conclusion that volumes of K-Na mixing for low albite-microcline crystalline solutions can be taken as constant from room temperature to the highest temperatures of our experiments, and probably to the melting temperatures of these minerals. For volume, then, as with enthalpy (Hovis and Navrotsky 1995), mixing properties seem to be essentially constant above room temperature.

In this case, and possibly other cases in which phase transitions do not occur from low to high temperature, regular solution thermodynamic models appear to represent mixing behavior adequately, at least with regard to temperature. Thus, it is permissible to utilize room-temperature volumes of mixing (e.g., Hovis 1988; Kroll et al. 1986) in high-temperature applications. We would like to know if the same is true for pressure.

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