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HIGH-TEMPERATURE X-RAY INVESTIGATION OF SANIDINE – ANALBITE CRYSTALLINE SOLUTIONS: THERMAL EXPANSION, PHASE TRANSITIONS, AND VOLUMES OF MIXING

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ABSTRACT

Unit-cell parameters and volumes have been measured for an eleven-member sanidine – analbite series from room temperature to 950°C. Slopes dV/dT and, in turn, coefficients of thermal expansion, vary systematically with composition, as sodic members expand to a greater degree than potassic ones. Volumes of K–Na mixing (V_{ex}) reach maximum values in the sodic part of the compositional range at all temperatures, but decrease in magnitude by about 20% from room to elevated temperature, as the distribution of V_{ex} values also becomes increasingly symmetrical with respect to composition. Transformation from triclinic to monoclinic symmetry occurs above room temperature for the five most sodic samples. Transformation temperature is related linearly to the mole fraction of potassium in the feldspar.

Keywords: volumes of mixing, phase transitions, temperature, alkali feldspars, sanidine, analbite.

SOMMAIRE

Nous avons mesuré les paramètres réticulaires et les volumes de onze membres de la solution solide sanidine – analbite à partir de la température ambiante jusqu'à 950°C. Les pentes dV/dT et, à leur tour, les coefficients d'expansion thermique, varient systématiquement avec la composition, de telle sorte que les membres sodiques montrent une expansion plus importante que les membres potassiques. Les volumes de mélange K–Na (V_{ex}) atteignent un maximum dans la portion sodique du système peu importe la température, mais diminuent en importance de 20% en allant de température ambiante jusqu'à température élevée, et la distribution des valeurs V_{ex} devient progressivement plus symétrique par rapport à la composition. La transformation d'un feldspath alcalin triclinique à la symétrie monoclinique a lieu à une température supérieure à la température ambiante dans la cas des cinq compositions les plus sodiques. La température de transformation dépend de façon linéaire de la fraction molaire de potassium dans le feldspath.

(Traduit par la Rédaction)

Mots-clés: volumes de mélange, transitions de phase, température, feldspaths alcalins, sanidine, analbite.

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INTRODUCTION

An important issue in thermodynamics is whether mixing properties (Thompson 1967) measured near room temperature and pressure can be applied to elevated temperatures and pressures. Hovis & Graeme-Barber (1997) addressed this question for the volumes of K–Na mixing in microcline – low albite crystalline solutions, and Hovis & Navrotsky (1995) studied the same problem for enthalpies of K–Na mixing in sanidine – analbite. [The term "analbite" is retained to describe a dimensionally triclinic Na-feldspar having a topochemically monoclinic Al–Si distribution, in this case the same Al–Si distribution as the potassic end-member.] As part of this continuing work, the study has been extended to the volumes of mixing for sanidine – analbite feldspars. Since members of this solid solution series may undergo a triclinic – monoclinic inversion, a second important aspect of this research bears on phase transitions in this system as they relate to temperature and composition.

This study formed the basis for a series of undergraduate research experiences at Lafayette College, including one senior thesis (Brennan 1995) and several summer and semester-long projects. Contributors to those projects are coauthors of this paper.

METHODOLOGY

Crystalline solutions for this investigation were synthesized from a specimen of low albite from Amelia, Virginia, using disordering and ion-exchange techniques described previously (Hovis & Navrotsky 1995, Hovis 1986, 1988). These procedures produced an eleven-member ion-exchange series of highly disordered alkali feldspars, the same specimens studied calorimetrically by Hovis & Navrotsky (1995). Basic chemical and room-temperature unit-cell dimension data are reported in the publications cited. For convenience, the mole fraction $KAlSi_3O_8$ (N_{Or}) of each feldspar is included in Table 1.

It was the purpose of this study to investigate the thermal behavior of each feldspar. High-temperature X-ray powder-diffraction experiments were carried out at the University of Cambridge, U.K., utilizing the X-ray system described by Salje *et al.* (1993), shown in their Figure 2, in which focused monochromatic $CuK\alpha_1$ radiation is diffracted by the sample and collected by an Inel 4K–PSD position-sensitive detector. Samples were mixed with reagent-grade alcohol and deposited as a slurry onto a thin (0.2 mm) Pt strip that rested on a ceramic plate. During an experiment, the strip was heated in air and held at constant temperature with a Eurotherm controller. Temperatures were monitored by a Pt/Rh–Pt thermocouple welded to the base of the strip. The accuracy of measured temperatures was checked during independent experiments on quartz using unit-cell parameters of quartz and the alpha–beta quartz transition at 573°C. On this basis, we estimate that measured temperatures below 600°C could be too high by 20 to 30°C. This error seems to be approximately constant to higher temperatures based on the triclinic – monoclinic transition for analbite – monalbite, which from the current study occurs at 1021°C (sample 7001, $N_{Or} = 0.01$; see later discussion), about 40°C higher than the 980 and 979°C results, respectively, of Winter *et al.* (1979, based on their Amelia sample only) and Kroll *et al.* (1980).

Each sample was mixed with National Bureau of Standards silicon, standard reference material 640a, with a stated unit-cell dimension of 5.430825 Å. This served as the internal standard upon which 2θ was correlated with detector channel number. High-temperature cell-parameter data for silicon (Parrish 1953) were used to compute the positions of Si diffraction maxima as a function of temperature. Feldspar peaks were indexed first at room temperature from the data of Hovis (1986,

TABLE 1. UNIT-CELL VOLUMES FOR SANIDINE–ANALBITE AS A FUNCTION OF TEMPERATURE

SAMPLE NUMBER AND N_{Or}	TEMPERATURE (°C)	UNIT-CELL VOLUME (Å³)
7001	22	667.60 (35)
0.010	200	670.52 (32)
	375	674.79 (34)
	550	678.25 (51)
	750	682.61 (54)
	925	686.10 (52)
9101	22	673.53 (60)
0.075	200	676.16 (67)
	650	685.15 (58)
	800	687.92 (84)
	950	692.81 (95)
8001	22	679.05 (36)
0.140	100	679.81 (45)
	200	682.42 (53)
	300	684.77 (67)
	400	686.05 (92)
	500	689.34 (92)
	650	692.21 (37)
	800	694.14 (49)
	950	698.33 (47)
9102	22	685.54 (60)
0.215	125	685.99 (59)
	225	688.53 (54)
	250	690.64 (63)
	270	689.76 (40)
	290	690.97 (85)
	310	691.59 (87)
	330	688.79 (79)
	350	690.72 (77)
	400	692.84 (54)
	550	695.35 (48)
	700	697.81 (49)
	900	700.12 (55)
	1000	701.70 (50)
9103	22	692.06 (69)
0.290	100	693.22 (66)
	200	693.99 (55)
	350	697.80 (55)
	500	700.54 (56)
	650	702.90 (62)
	800	705.27 (79)
	950	706.39 (75)
9104	22	695.57 (42)
0.365	200	696.80 (72)
	350	700.48 (59)
	500	701.06 (53)
	650	703.81 (65)
	800	708.19 (78)
	950	711.36 (83)
8008	22	699.63 (78)
0.440	200	702.87 (40)
	350	704.30 (74)
	500	708.26 (58)
	650	710.74 (104)
	800	711.33 (63)
	950	714.81 (117)
9105	22	706.87 (32)
0.589	180	709.43 (31)
	340	711.29 (41)
	500	713.29 (39)
	650	717.91 (32)
	825	720.18 (43)
	950	722.17 (23)
8034	22	713.50 (21)
0.738	200	716.56 (34)
	350	719.25 (47)
	500	720.14 (37)
	650	722.20 (53)
	800	726.68 (53)
	950	729.20 (90)
9106	22	718.95 (10)
0.862	180	722.61 (40)
	340	723.87 (79)
	500	726.60 (38)
	650	728.40 (31)
	825	732.53 (57)
	950	734.36 (52)
7201	22	723.66 (32)
0.986	150	725.25 (33)
	300	727.09 (37)
	450	729.30 (30)
	600	730.61 (40)
	750	733.30 (40)
	1000	737.58 (47)

Uncertainties in final decimal places are given in brackets.

1989); this in part provided the basis for peak identification at higher temperatures. Feldspar unit-cell parameters were computed using LCLSQ (Burnham 1962).

It was only after our measurements had been completed that we became aware of data (Evain *et al.* 1993, Roux & Volfinger 1996) that show the nature of measurement errors associated with Inel X-ray systems. These studies indicate that the use of an internal standard whose peaks are spaced at wide intervals of 2θ, as is the case for silicon, is not sufficient to correct for the rather erratic pattern of peak-position errors inherent in Inel systems. After completion of our study, we checked the Inel system on which our data had been collected *via* separate experiments using $Na_2Ca_3Al_2F_{14}$ (Courbion & Ferey 1988), a cubic compound having a large number of diffraction maxima. These measurements confirmed an erratic pattern of errors similar in nature to those reported by Evain *et al.* (1993) and Roux & Volfinger (1996), yielding values of 2θ that were as much as 0.05° too high in the 0–40° and 80–110° ranges, and as much as 0.08° too low in the 40–80° range. Corrections to all data sets would have been prohibitive timewise, but we did make corrections to a single dataset, then calculated the resulting unit-cell dimensions from the revised values of 2θ. Although the corrections did make a difference, the resulting unit-cell dimensions were within two to three standard errors of uncorrected values, insufficient to change our conclusions, which depend mostly on the *relative* cell-parameter changes observed in all eleven samples over a wide range in temperature. Furthermore, uncertainties in the stated temperatures, in the high-temperature silicon data, and (especially) in the indexing of low-intensity high-2θ peaks, upon which the cell parameters calculated from Inel data are highly dependent, outweigh other smaller adjustments to the unit-cell data. Although the previous Guinier-based study (Hovis & Graeme-Barber 1997) produced data of seemingly higher accuracy and precision, the present study brings the advantage of an eleven-member (rather seven-member) series, which in part makes up for the loss in accuracy. Moreover, reported temperatures of the previous work also have a degree of uncertainty.

RESULTS AND INTERPRETATION

Volume – temperature relations

The unit-cell volumes resulting from this study are reported in Table 1 (complete unit-cell data may be

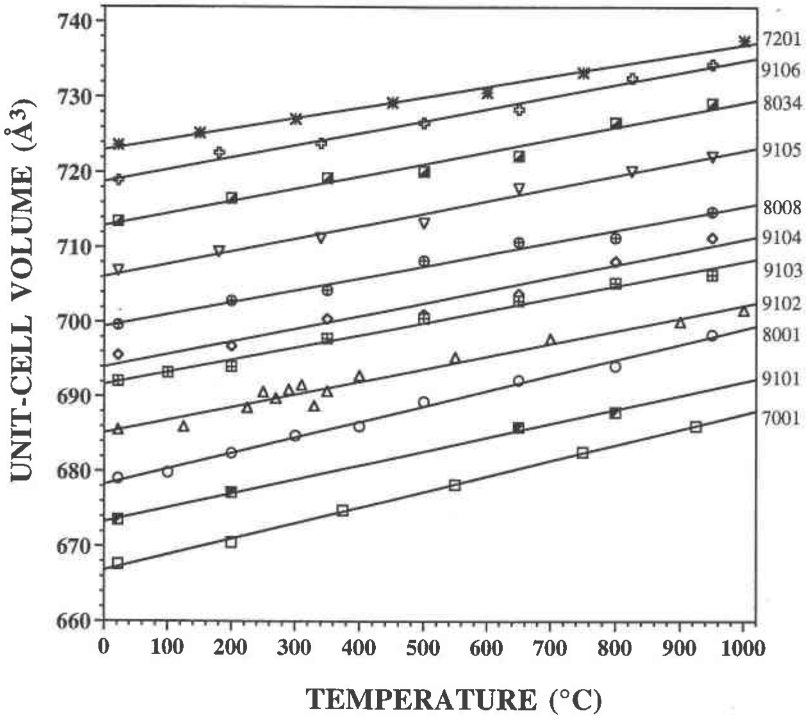

FIG. 1. Unit-cell volume as a function of temperature for each of the eleven feldspars studied during this investigation. Data are given in Table 1. Equations for the lines are given in Table 2.

TABLE 2. COEFFICIENTS OF THERMAL EXPANSION AND EQUATIONS RELATING UNIT-CELL VOLUME TO TEMPERATURE (°C) FOR SANIDINE – ANALBITE AND MICROCLINE – LOW ALBITE FELDSPARS

SANIDINE - ANALBITE SAMPLE NUMBER	N_{Or}	INTERCEPT AT 0 °C (Å^3)	SLOPE (Å^3/deg)	COEFFICIENT OF THERMAL EXPANSION $\alpha \times 10^6$ (deg^{-1})	MICROCLINE - LOW ALBITE SAMPLE NUMBER*	N_{Or}	COEFFICIENT OF THERMAL EXPANSION $\alpha \times 10^6$ (deg^{-1})
7001	0.010	666.83	0.0209	31.2	7010	0.010	30.7
9101	0.075	673.21	0.0192	28.5	8205	0.170	29.9
8001	0.140	678.24	0.0208	30.7	8429	0.334	29.2
9102	0.215	685.18	0.0171	24.9	8047	0.493	26.3
9103	0.290	691.64	0.0165	23.9	8204	0.655	21.7
9104	0.365	693.99	0.0171	24.6	8206	0.830	19.9
8008	0.440	699.44	0.0161	23.0	71104	0.997	18.6
9105	0.589	706.09	0.0169	23.9			
8034	0.738	712.94	0.0164	23.0			
9106	0.862	718.78	0.0161	22.4			
7201	0.986	723.02	0.0139	19.3			

Intercepts and slopes for members of the microcline - low albite series can be found in Table 2 of Hovis and Graeme-Barber (1997).

obtained from the first author or from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario, Canada K1A 0S2). In order to analyze the variation of volume with temperature, least-squares fits were made to the unit-cell-volume data of each feldspar (Fig. 1). [Note that unit-cell volume given in Å^3/unit-cell can be converted to molar volume either in cm^3/mol or J/bar-mol through division by 6.6419 or 66.418, respectively.] Statistical analyses of the data indicate that the best general model for volume–temperature behavior is linear. Coefficients for the resulting equations are given in Table 2.

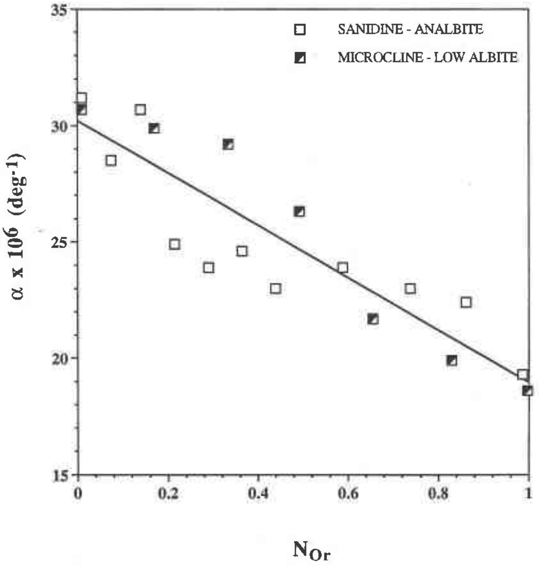

FIG. 2. Coefficients of thermal expansion (dV/dT divided by room-temperature volume) for sanidine – analbite and microcline – low albite feldspars, the latter based on data in Hovis & Graeme-Barber (1997). Values are given in Table 2. The linear least-squares fit to all data is expressed by Eq. 3.

The dV/dT slopes for the three most sodic feldspars, all of which maintain triclinic symmetry over most of the temperature range studied, are between 0.019 and 0.021 Å^3/°C. Feldspars having higher potassium contents and monoclinic symmetry over most or all of the temperatures studied give lower slopes, between 0.016 and 0.017 Å^3/°C; data for the most potassic feldspar produces a slope of 0.014 Å^3/°C. Clearly, the capability of sanidine – analbite feldspars to expand, which (as for K–Na substitution) takes place mostly along the *a* crystallographic axis, is dependent on composition, a result that coincides with observations for microcline – low albite (Hovis & Graeme-Barber 1997). This is shown well in Figure 2, where coefficients of thermal expansion (dV/dT for each series divided by room-temperature volume; see Table 2) are plotted against composition for both sanidine – analbite and microcline – low albite. Although the details of the variation are somewhat different for the two series, the general picture is clear.

The size of the ion occupying the alkali site and the feldspar framework together limit the degree to which a feldspar expands with increasing temperature. If the alkali site is occupied by the smaller sodium ion, the potential for expansion is relatively large. With increasing temperature, the greater volume occupied by the vibration of sodium mimics to a continually increasing degree occupancy of the alkali site by a larger ion. Occupancy of the site by potassium, however, clearly limits the rate expansion of a framework already stretched to an extent by the larger alkali ion.

Volumes of K–Na mixing

A principal aim of this project was to learn if volumes of K–Na mixing (V_{ex}) in sanidine – analbite change with temperature. In order to make this determination, equations in Table 2 were used to calculate the unit-cell volume of each feldspar at 22° (room T), 300°, 600°, and 900°C (Fig. 3). The resulting data for each temperature were analyzed as a function of composition. Third-order polynomial fits to the data were adopted, since statistics for these generally were better than for second-order regressions. Coefficients of the resulting relationships, including the equivalent Margules formulation (Thompson 1967) for each, are presented in Table 3.

The unit-cell volumes of K–Na mixing for sanidine – analbite crystalline solutions for room temperature reach maximum values of about 8 Å^3/unit cell in the Na-rich part of the compositional range (Fig. 4), a result similar to that obtained for microcline – low albite [Hovis & Graeme-Barber (1997); also see Figure 9 and the related discussion of Kroll *et al.* (1986)]. This observed asymmetry suits one's intuition that the substitution of K^+ in sodic feldspar would have a greater impact on excess volume than would the substitution of smaller Na^+ ions in potassium feldspar. From room temperature to 900°C, the maximum values of V_{ex} decrease in magnitude by about 20%, as the distribution of V_{ex} values also becomes increasingly more symmetrical with respect to composition. The latter result may not be surprising; indeed, as temperature increases, one might expect an expanded framework of highly vibrating tetrahedra to be relatively insensitive to the actual size of the cation occupying the alkali site and more sensitive to the "effective size" of the vibrating species.

TABLE 3. COEFFICIENTS TO EQUATIONS FOR UNIT-CELL VOLUME AS A FUNCTION OF COMPOSITION AT FOUR TEMPERATURES FOR THE SANIDINE–ANALBITE SOLID SOLUTION

TEMPERATURE (°C)	a_0 b_0	a_1 b_1	a_2 b_2	a_3 b_3
22	666.20	104.34	-78.83	32.58
22	666.20	58.08	46.26	13.68
300	672.19	96.93	-65.36	24.40
300	672.19	55.97	40.96	16.55
600	678.64	88.96	-50.84	15.59
600	678.64	53.71	35.25	19.66
900	685.09	80.97	-36.31	6.78
900	685.09	51.43	29.53	22.76

Equations have the form: V (Å^3/unit cell) = $a_0 + a_1 N_{Or} + a_2 N_{Or}^2 + a_3 N_{Or}^3$ and V (Å^3/unit cell) = $b_0 + b_1 N_{Or} + b_2 N_{Or} N_{Ab}^2 + b_3 N_{Ab} N_{Or}^2$, respectively.

Despite these observations, we cannot be certain that the present results represent a real departure from those

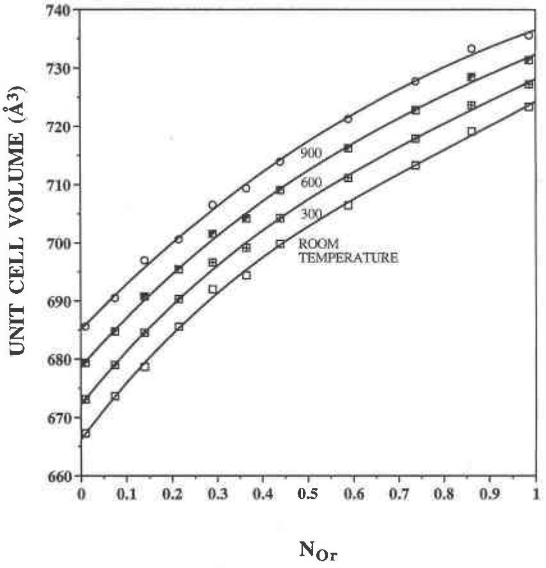

FIG. 3. Unit-cell volumes for eleven sanidine – analbite feldspars at four temperatures (°C). Values at each temperature are based on equations given in Table 2. Curves are based on third-order Taylor expansion series, whose coefficients are given in Table 3.

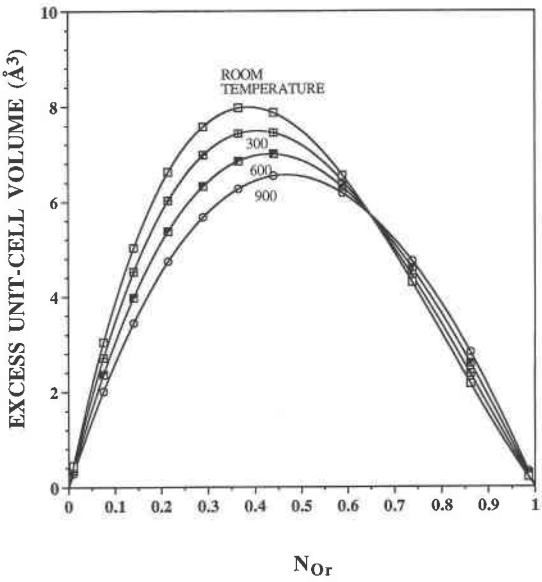

FIG. 4. Volumes of K–Na mixing for four temperatures based on data from Figure 3. Margules parameters are included in Table 3.

for microcline – low albite, for which Hovis & Graeme-Barber (1997) concluded that volumes of K–Na mixing did not vary significantly with temperature. Indeed, changes in V–N_{Or} curves are subtle relative to the magnitudes of uncertainty in unit-cell data based on refinement errors and temperature measurement. The two studies do agree in the asymmetry of V_{ex} over all temperatures. Both studies show maximum values of V_{ex} to be in the range 6.5 to 8.4 Å^3/unit-cell over all temperatures. Differences in interpretation may in part originate from the availability of data for eleven members (and closely spaced data for sodic compositions) for sanidine – analbite, which do potentially provide more detail than data for the seven members of microcline – low albite (Hovis & Graeme-Barber 1997). Moreover, as noted above, if the trends in V_{ex} with temperature for sanidine – analbite crystalline solutions are correct with regard to changes in magnitude and symmetry, those changes do make good physical sense.

Phase transitions

Based on the conversion of disordered albite to sanidine by ion exchange, it was previously established that sanidine – analbite samples of the present investigation possessed topochemically monoclinic Al–Si distributions (Hovis 1986). [Note the observation of Kroll *et al.* (1986, p. 4) that such evidence does not constitute proof in every case of a monoclinic Al–Si distribution.] All triclinic samples, therefore, had the potential for triclinic → monoclinic (T/M) inversion. A principal aim of this work was to determine how the temperature of the inversion ($T_{T/M}$) is related to composition.

A variety of crystallographic parameters can be used to characterize the departure of a crystal from monoclinic geometry. One of these is ϕ, the angle between *b* and *b**, which Donnay (1940) called obliquity. The cosine of this angle is related to the interaxial angles of the unit cell: $\cos\phi = \sin\alpha^* \sin\gamma$ [Thompson & Hovis (1978), also see Donnay (1940) and Gay (1956)]. In a dimensionally monoclinic feldspar, both α^* and γ are 90°, so $\cos\phi$ is 1 and $(1 - \cos\phi)$ is zero. In order to determine the temperatures of the triclinic–monoclinic transformation, then, we plotted values of $(1 - \cos\phi)$ against temperature for our five most sodic feldspars (Fig. 5). The resulting linear trends of $(1 - \cos\phi)$ with temperature were fit by least-squares techniques, then solved for the temperature at which $(1 - \cos\phi)$ attains a value of zero (see Table 4). Analysis of the five transformation temperatures as a function of composition gives the following (Fig. 6):

$$T_{T/M}\ (^\circ\mathrm{C}) = 1064\ (8) - 3317\ (45)\ N_{Or} \qquad (1)$$

(one standard deviation of the individual coefficients given in brackets) with a correlation coefficient (R^2) of 0.999.

It is a concern that there was no practical way of checking the accuracy of temperature measurement during each of our X-ray experiments. We noted earlier that the temperature of the analbite → monalbite inversion determined in the present study is about 40°C above

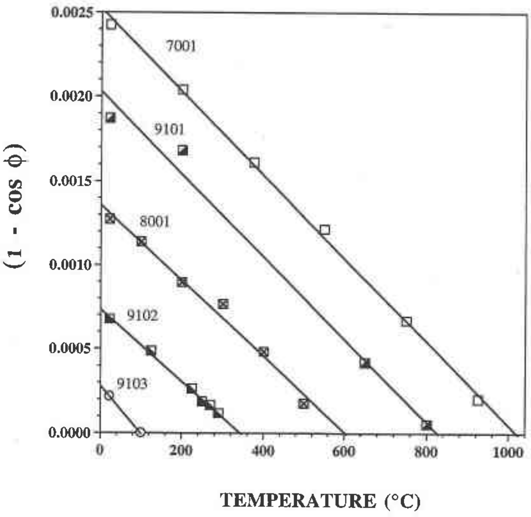

FIG. 5. Plots of $1 - \cos\phi$ ($= 1 - \sin\alpha^* \sin\gamma$) against temperature for the five most sodic feldspars. The triclinic–monoclinic transformation temperature for each feldspar is that at which $(1 - \cos\phi)$ attains a value of zero.

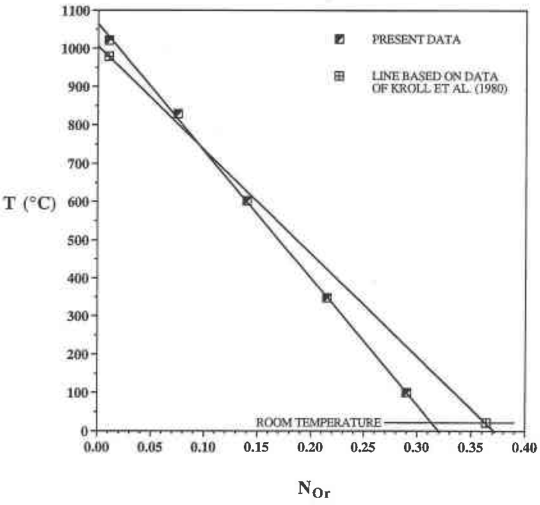

FIG. 6. Transformation temperatures for the five most sodic sanidine – analbite feldspars (Figs. 5, Table 4) plotted against temperature. The resulting line is expressed by Eq. 1. The second line is based on the data of Kroll *et al.* (1980), as explained in the text.

TABLE 4. TEMPERATURES OF TRANSFORMATION AND ROOM-TEMPERATURE DATA RELEVANT TO THE TRICLINIC–MONOCLINIC INVERSION

SAMPLE NUMBER	COMPOSITION (N_{Or})	TRANSFORMATION TEMPERATURE FROM HIGH-T DATA (°C)	ROOM-T α^* (deg)	ROOM-T γ (deg)	ROOM-T $(1 - \cos\phi)$
7001	0.010	1021	86.012	90.175	0.002426
9101	0.075	829	86.495	90.049	0.001871
8001	0.140	602	87.110	90.119	0.001274
9102	0.215	347	87.893	90.046	0.000676
9103	0.290	101	88.803	90.015	0.000218

Cos ϕ is defined in the text.

those reported by Winter *et al.* (1979) and Kroll *et al.* (1980). We also noted that separate measurements performed on quartz indicated that stated temperatures near 600°C may be too high by 20–30°C. Nevertheless, because our measurements were made at widely divergent times with different thermocouples, some more degraded than others, we cannot be confident that a single correction to all data would be appropriate.

As a check on the internal consistency of our T/M data, we utilized Eq. 1 to calculate a triclinic–monoclinic transformation *composition* for room temperature. Substituting a temperature of 22°C on the left side of the Eq. 1 results in a triclinic–monoclinic conversion composition (N_{Or}) of 0.314. For comparison, we also analyzed values of $(1 - \cos\phi)$ as a function of composition for *room temperature* Inel data on the five most sodic feldspars (Fig. 7). This yielded

$$(1 - \cos\phi) = 0.00246\,(6) - 0.0080\,(3)\,N_{Or} \qquad (2)$$

(correlation coefficient of 0.995). Substitution of a value of zero for $(1 - \cos\phi)$ in Eq. 2 results in a room-temperature transformation composition (N_{Or}) of 0.308, which constitutes reasonable convergence between the high-temperature and room-temperature Inel data. Further, these values are virtually identical to results based on room-temperature measurements made at Lafayette College (Fig. 7) using an entirely different X-ray system (Scintag DMS 2000 powder-diffraction system; Hovis & Navrotsky 1995). The data do indeed fit within the range of T/M compositions for various series of disordered feldspars from other laboratories [N_{Or} = 0.314 to 0.366; summary in Table 2 of Hovis (1980)], although they are at the low end of that range.

Our high-temperature data seem to disagree with the results of Kroll *et al.* (1980, their Fig. 8), who used their experimental data to develop an equation for $T_{T/M}$ as a function of both chemical composition and Al–Si equilibration temperature [$T_{equilib}$; also see Kroll (1984), especially his Fig. 9]. Eq. 1 of Kroll *et al.* (1980) predicts an analbite – monalbite $T_{T/M}$ of 979°C for our specimen 7001 (N_{Or} = 0.010, $T_{equilib}$ = 1052°C), 42°C below that found for the same sample based on the present data. Using Eq. 2 of Kroll *et al.* (1980), one can combine the latter data-point with a predicted room-temperature T/M composition (N_{Or}) of 0.364 to produce a second line on Figure 6, one that disagrees in slope with the present data. We cannot reconcile that line with the present data, because it predicts that temperatures around 600°C in the present work are too low (not too high as found from our quartz measurements) and also that our temperatures are in increasingly greater error as temperature decreases. Our intuition, on the other hand, is that if temperature errors do exist in all our data, they most likely decrease as room temperature is approached.

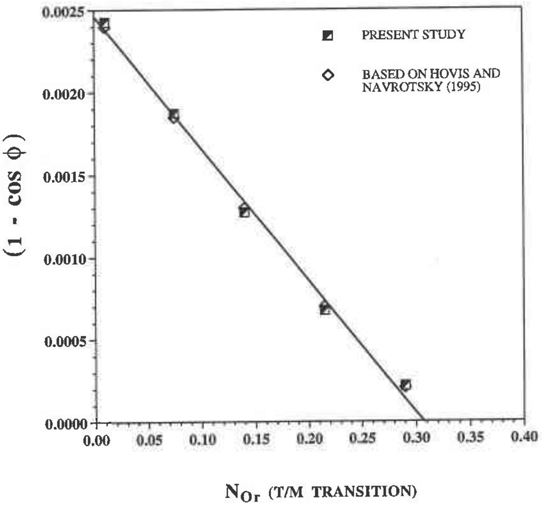

FIG. 7. Values of $(1 - \cos\phi)$ at room temperature for each of the five most sodic sanidine – analbite feldspars. The linear least-squares fit to the data gives a room-temperature triclinic–monoclinic inversion composition (N_{Or}) of 0.308. Results are compared to similar values of Hovis & Navrotsky (1995).

In short, we cannot account for the differences between our data and those of Kroll *et al.* (1980). Indeed, it is interesting to note the wide divergence in predicted temperatures for the analbite – monalbite $T_{T/M}$ [930° to 1054°C for $N_{Or} = 0$; see Table 2 of Hayward & Salje (1996)], as well as the wide range in room-temperature T/M compositions for disordered alkali feldspars (Table 2 of Hovis 1980). Could there be differences among the feldspar samples used in these studies that account for a portion of this disagreement? Perhaps the warning of Kroll *et al.* (1986, p. 4) is pertinent, that seemingly monoclinic feldspars may not be truly monoclinic.

DISCUSSION

The geometry of disordered alkali feldspars is affected similarly by K-for-Na substitution and the increase of temperature. Both of these cause unit-cell volume to increase linearly. Both result in linear trends of (1 – cos ϕ) and transitions from triclinic to monoclinic symmetry. These observations are consistent with previous ones by Hazen (1976) and Thompson & Hovis (1979) relative to the comparative effects of composition, temperature, and pressure on these framework silicates.

The previous study of volumes for microcline – low albite feldspars (Hovis & Graeme-Barber 1997) and the present one for topochemically monoclinic samples produce similar, even though not identical, results. Whether the progressive decrease of dV/dT slopes from sodic to potassic compositions is linear, curved, or stepwise is not certain (Fig. 2). It is clear, however, that occupancy of the alkali site by the larger potassium ion limits the potential for volume expansion with temperature. The collective data from both series produces a linear relationship (displayed in Fig. 2) that exhibits a decreasing coefficient of thermal expansion with increasing K content

$$\alpha\ (\mathrm{deg}^{-1}) = [30.2\ (7) - 11\ (1)\ N_{Or}] \times 10^{-6} \qquad (3)$$

(uncertainties in the last decimal place of the intercept and slope given in brackets, correlation coefficient = 0.820).

Maximum values for the volumes of K–Na mixing in sanidine – analbite crystalline solutions decrease by about 20% from room temperature to 900°C, as the distribution of V_{ex} values becomes increasingly symmetrical with respect to composition (Fig. 4). Both of these effects are consistent with a highly vibrating framework that is less sensitive at high than at low temperature to the entity that occupies the alkali site, and with vibrating Na ions that increasingly simulate the size of vibrating K as temperature increases. Even so, occupancy of the alkali site by potassium, as opposed to sodium, continues to make some difference to feldspar geometry even at high temperature. This is reflected well by the continued compositional asymmetry of V_{ex} values up to temperatures that approach those of melting.

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