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Unit-cell dimensions and molar volumes for a sanidine–analbite ion-exchange series

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Abstract

Unit-cell parameters and molar volumes have been determined for seven members of a sanidine–analbite ion-exchange series by least-squares refinements of X-ray powder diffraction data. The quadratic least-squares fit to the molar volume data yields:

$$\bar{V}\,(\text{cal/bar}) = 2.3982 + 0.2064\,N_{\text{Or}} + 0.0862\,N_{\text{Or}}N_{\text{Ab}}$$

where N_{Or} and N_{Ab} represent mole fractions of $KAlSi_3O_8$ and $NaAlSi_3O_8$, respectively. Excess molar volume of K–Na mixing may be expressed as:

$$\bar{V}_{ex}\ (\text{cal/bar}) = W_V N_{\text{Or}} N_{\text{Ab}} = 0.0862\,N_{\text{Or}}N_{\text{Ab}}$$

The Margules parameter for molar volume, W_V, for this sanidine–analbite ion-exchange series agrees well not only with W_V values determined for several other (hydrothermally synthesized) sanidine–analbite series, but also with those for other alkali feldspar series. Thus, volumes of K–Na mixing in the alkali feldspars are insensitive to Al–Si order–disorder.

Mole fractions of Al in the T_1 and T_2 tetrahedral sites for all members of the series are 0.271 and 0.229, respectively, based on b and c unit-cell dimensions, making this series somewhat more disordered than those synthesized hydrothermally by others.

Introduction

A new alkali feldspar ion-exchange series has been synthesized and represents the most disordered feldspar series, with respect to Al–Si distribution, studied until now. The method of synthesis makes it likely that all members of this series of feldspars possess essentially the same degree of Al–Si order.

The three sanidine–analbite series whose unit-cell parameters and volumes have been reported previously (Donnay and Donnay, 1952; Orville, 1967; Wright and Stewart, 1968; Luth and Querol-Suñé, 1970) were hydrothermally-synthesized series (Table 1), and for this reason were not true ion-exchange series. However, because the synthesis experiments were short-term relative to the time it takes for the Al–Si distribution of a feldspar to equilibrate with its environment (see experiments of MacKenzie, 1957; also Martin, 1969), these feldspar series have relatively disordered Al–Si distributions which are probably nearly constant for each series. Had synthesis times been long, this probably would not be the case, since the Na/K ratio in the starting material affects not only the kinetics of Al–Si redistribution (Spencer, 1937; Martin, 1969; and others) in the feldspar, but also the actual equilibrium distribution among the tetrahedral sites.

In the present investigation the unit-cell parameters and molar volumes of the new ion-exchange series were measured, using X-ray powder diffraction data. The paper that follows (Hovis and Waldbaum, 1977) presents the results of solution calorimetric experiments on the same feldspar series.

Methods of synthesis

All of the analbite–sanidine crystalline solutions were synthesized starting with Amelia low-albite (Rutherford Mine, Amelia County, Virginia), with the following procedures:

(1) Analbite: Fragments of Amelia low-albite about 1 cm across were annealed in a covered platinum crucible at 1052°C, 1 atm, for 710 hours.

(2) Sanidine: Part of the analbite sample was ground to −325 mesh, then was ion-exchanged in several batches in molten KCl at 817° to 825°C for 25 to 38 hours. The resulting sanidine samples were elutriated in distilled water, then acetone, to remove

Table 1. Synthesis procedures used to prepare various sanidine-analbite series

Investigator(s)	Synthesis Procedures	Starting Materials
Donnay and Donnay, 1952	Hydrothermal crystallization, 700° and 800°C, 0.98 kbar, 1 to 9 days	glasses
Orville, 1967	Hydrothermal crystallization, 800°C, 1 kbar, 5 to 7 days	glasses
Luth and Querol-Suñé, 1970	Hydrothermal crystallization, 800°C, 0.5 kbar, ? days	dehydrated gels
This investigation	1. Anneal low albite, 1052°C, 1 atm, 710 hours	Amelia low albite
	2. Ion-exchange the resulting analbite in molten KCl, 817 to 825°C, 1 atm, 25 to 38 hours, to produce sanidine.	analbite
	3. Alkali homogenization of mechanical mixtures, 940°C, 1 atm, 6 to 7 days	analbite-sanidine mechanical mixtures

the finest grain sizes for the heat-of-solution experiments; this was done for the analbite and the compositionally intermediate crystalline solutions, as well.

(3) Crystalline solutions of intermediate compositions: Powders of analbite and sanidine were mixed ultrasonically in acetone in various proportions to create different feldspar mechanical mixtures. After drying, each mixed powder was packed tightly in a gold crucible under 500 psi (in most cases) to promote as much grain-to-grain contact as possible. To homogenize the alkali ions the samples were then annealed at 940°C for 153–155 hours in a silicon carbide furnace which had never been used for fused salt studies, a procedure necessary to minimize the possibility of external alkali contamination. Details concerning synthesis of individual samples are given in Table 2. This method is analogous to that used by Waldbaum and Robie (1971, p. 390; also Hafner and Laves, 1957) to produce intermediate members of their triclinic feldspar series, except that their samples were based on a potassic end-member (microcline), not a sodic one.

All members of the ion-exchange series produced by the procedures outlined above should have the same Al–Si distribution. Ion-exchange in molten KCl, as well as alkali homogenization procedures, probably had no effect on the Al–Si distribution of the analbite from which all series members were prepared, because the molten-salt ion-exchange (825°C) and alkali homogenization (940°C) were carried out at temperatures significantly *less,* and for periods much shorter, than that at which the analbite was produced (1052°C). Thus, any *change* in Al–Si distribution should have involved ordering (not disordering), which has been shown by several investigators (*e.g.,* MacKenzie, 1957; Martin, 1969) to proceed extremely slowly, even under hydrothermal conditions. The resultant feldspars, therefore, truly belong to an ion-exchange series.

Compositions of the feldspars

Major and minor element analyses of Amelia low-albite have been given by Waldbaum and Robie (1971, Tables 2 and 3). Their data confirm the high chemical purity of this material. Substitutions of elements outside the $(K,Na)AlSi_3O_8$ system are minor.

The effect of K–Na ion exchange on minor-element chemistry was not checked. However, as minor elements were not present in large amounts in the starting material, the changes that might have taken place during exchange should have been very small and most likely involved only monovalent cations. Waldbaum (1966, p. 51) has shown that rubidium, the major "impurity" in Amelia low albite, is largely unaffected by ion exchange in KCl.

During the calorimetric investigation on these

Table 2. Details of synthesis histories of feldspars with intermediate (K–Na) compositions.

Feldspar	Annealing Temperature (°C)	Annealing Time (hrs.)	*Packing Pressure (psi)
7044	915, 939	58.5, 94.5	500
7057	940	155	500
7058	940	155	750
7059	940	153	500
7060	940	153	500

* Pressure under which the mechanical mixture of feldspars was packed in the gold crucible.

Table 3. Chemical analyses (for K and Na) of the feldspars

Feldspar	K*	Na*	Calculated N_{Or}	Average † Calculated N_{Or}
7015	.155**	8.82**	.0102	
7015	1.18	58.2	.0118	.0114
7015	5.676	269.5	.0122	
7059	2.21**	7.10**	.1547	
7059	27.0	90.1	.1498	
7059	32.1	104.3	.1532	.1521
7059	55.4	183.6	.1507	
7057	106.9	106.5	.3711	
7057	5.34**	5.00**	.3857	.3711
7057	68.8	73.0	.3565	
7044	63.8	34.2	.5231	
7044	7.14**	4.04**	.5096	.5091
7044	105.2	63.2	.4946	
7058	162.0	60.8	.6104	
7058	8.62**	2.96**	.6313	.6183
7058	171.0	63.4	.6133	
7060	163.0	16.22	.8553	
7060	92.3	10.36	.8397	
7060	11.30**	1.478**	.8180	.8358
7060	295.0	35.5	.8301	
7036	64.0	1.20	.9691	.9691

Analyses were done by flame photometry (Geochron, Inc.) using a Beckman DU spectrophotometer. Aliquots of actual calorimetric solutions in which feldspars had been dissolved were evaporated to dryness, then converted to dilute sulfate solutions for analysis.

* Given in ppm unless stated otherwise; actual numbers are arbitrary, only relative moles of K/(K+Na) is significant. Numbers of significant figures are as given by the analyst.

** Given in weight % K or Na.

† Each number in this column represents an average of all analyses listed for each feldspar in the previous column.

feldspars (Hovis and Waldbaum, 1976 and 1977), many of the hydrofluoric acid solutions in which the crystalline solutions were dissolved were analyzed for potassium and sodium by flame photometric techniques. These data are given in Table 3 and constitute the major source of information on the K/(K + Na) ratios in the feldspars.

Homogeneity of alkali ions in the feldspar crystalline solutions

The synthesis of feldspar crystalline solutions by the method described above resulted in samples which had X-ray diffraction patterns with sharp, well-defined, narrow peaks. Within the detection limits of this analytical technique the feldspars are homogeneous. However, electron microprobe analyses of the feldspar samples (by M. Kastner, personal communication) indicated some degree of inhomogeneity in the samples. For three of the samples (7059, 7044, and 7058) the spread in composition was ±3.5 mole percent Or. For sample 7060 the spread was ±2.5 percent. Only for sample 7057 was inhomogeneity serious, with a spread of ±11 percent.

Methods used in X-ray investigation

Unit-cell dimensions and molar volumes (Table 4) were determined by least-squares refinement of X-ray powder diffraction data, using the digital computer program LCLSQ of Burnham (1962); uncertainties reported in Table 4 are least-squares standard errors as defined by Burnham. Forward and reverse X-ray scans were made over a 20° to 60° 2θ range at ¼°/minute (chart speed ½ inch/minute) with a Philips X-ray goniometer using Cu$K\alpha$ radiation. Data for each feldspar were collected for at least three such scans. The feldspars were mixed with semi-conductor grade silicon as an internal standard; the silicon was assumed to have a unit-cell dimension of 5.43054 A (25°C; Parrish, 1960) and the calculated positions of the (111), (220), and (311) peaks were 28.443° and 28.515°, 47.304° and 47.428°, and 56.123° and 56.275° for $K\alpha_1$ and $K\alpha_2$ copper wavelengths (taken to be 1.54051 A and 1.54433 A), respectively.

Peaks for sanidine and analbite were indexed following Borg and Smith (1969, p. 667–668 and 635–636). Peaks for crystalline solutions of intermediate compositions were indexed by first running a preliminary refinement for each based on the positions of peaks which could be identified unambiguously, then calculating the theoretical positions of *all* peaks based on cell parameters of the preliminary refinement. After the latter operation, final refinements were performed, using 2θ data for additional peaks which were indexed based on the calculated positions. This method proved to be very satisfactory, not only in unambiguously identifying certain peaks, but also in greatly improving (lowering) the standard errors of the refinements due to the use of relatively high-angle data.

Unit-cell dimensions

Unit-cell data are given in Table 4 and shown in Figure 1. Least-squares fits to four of the cell parameters are given below:

$$a(\text{A}) = 8.1553(\pm.0015) + 0.4567(\pm.0025)N_{\text{Or}} \quad (1)$$

$$b(\text{A}) = 12.8687(\pm.0019) + 0.3705(\pm.0090)N_{\text{Or}} - 0.2109(\pm.0085)N_{\text{Or}}^2 \quad (2)$$

$$c(\text{A}) = 7.1114(\pm.0014) + 0.1448(\pm.0065)N_{\text{Or}} - 0.0804(\pm.0065)N_{\text{Or}}^2 \quad (3)$$

Table 4. Unit-cell dimensions and molar volumes of sanidine–analbite crystalline solutions

Feldspar, Refinement No.	N_{Or}	Lines*	Data Points**	a(Å)	b(Å)	c(Å)	α (deg)	β (deg)	γ (deg)	V(Å³)	$\bar{V}$(cal/bar)	Z †
7015, R1506	.0114	21	53	8.1617 .0017	12.8731 .0012	7.1118 .0015	93.479 .012	116.450 .011	90.211 .012	667.36 .33	2.4015 .0012	---
7059, R1505	.1521	25	100	8.2267 .0014	12.9174 .0011	7.1320 .0009	92.605 .011	116.387 .007	90.177 .012	678.01 .20	2.4398 .0007	---
7057, R1504 ††	.3711	24	59	8.3169 .0026	12.9822 .0017	7.1550 .0022	89.947 .028	116.160 .020	90.011 .020	693.40 .49	2.4952 .0018	---
7057, R1503 ††	.3711	24	59	8.3174 .0025	12.9839 .0015	7.1576 .0016	90.0	116.164 .016	90.0	693.77 .41	2.4965 .0015	---
7044, R1502	.5091	24	56	8.3929 .0016	12.9999 .0013	7.1653 .0008	90.0	116.104 .010	90.0	702.04 .23	2.5263 .0008	---
7058, R1501	.6183	17	47	8.4368 .0015	13.0155 .0013	7.1660 .0009	90.0	116.020 .010	90.0	707.14 .23	2.5446 .0008	0.077
7060, R1500	.8358	29	92	8.5334 .0011	13.0295 .0009	7.1752 .0007	90.0	115.992 .007	90.0	717.09 .16	2.5804 .0006	0.079
7036, R1223	.9691	29	78	8.6013 .0013	13.0312 .0013	7.1783 .0009	90.0	115.992 .009	90.0	723.21 .22	2.6025 .0008	0.091

* Number of lines used in each refinement.

** Total number of data points used in each refinement (for all scans).

† Calculated from equation (3) of Hovis (1974). This equation is not valid for the more sodic members of the series and should be used only for feldspars where N_{Or} is more than 0.55.

†† Two sets of results are presented for sample 7057, the first based on a triclinic model, the second on a monoclinic model.

$$\beta(\text{deg}) = 116.490(\pm.014) - 1.058(\pm.065)N_{Or} + 0.550(\pm.065)N_{Or}^2 \quad (4)$$

where N_{Or} is mole fraction of $KAlSi_3O_8$. Standard errors of fit for these equations are ±0.0047 A, ±0.0041 A, ±0.0030 A, and ±0.003°, respectively. Fits were not performed for the α and γ unit-cell parameters, since only two of the seven feldspars are triclinic. These regression equations are based on data for both monoclinic and triclinic feldspars. Though discontinuities in the data may occur as a function of the monoclinic–triclinic inversion (Waldbaum and Thompson, 1968; Vogel *et al.*, 1973), there were not enough data to justify fitting the monoclinic and triclinic regions separately. Application of the Gauss criterion (Worthing and Geffner, 1943) to the fits for *a* and *b* indicated that the best fits for these parameters are first and second order, respectively, as indicated by equations (1) and (2). The same criterion applied to the fits for *c* and β indicated that the best fits are *third* and *fourth* order, respectively, for these parameters. However, because of the possibility of discontinuities in the data due to the monoclinic–triclinic transition, and since there are data for only seven feldspars, the higher-order fits are thought not to be justified, and second-order fits only are given for these parameters [equations (3) and (4)].

Composition of the monoclinic–triclinic transition

With only two feldspars in the triclinic part of the alkali feldspar composition range, no attempt was made to estimate the transition composition. The refinement of unit-cell parameters for feldspar 7057 (at $N_{Or} = 0.3711$) indicated a statistically better fit to the X-ray data for a monoclinic model than for a triclinic one. However, the K–Na inhomogeneity in this sample makes this result ambiguous. Orville (1967) and Luth and Querol-Suñé (1970) both estimate the transition composition to be at values of N_{Or} somewhat higher than 0.37.

Al–Si distribution and symmetry of the feldspars

Thompson *et al.* (1974, p. 219–220) have discussed the distribution of Al and Si in triclinic and monoclinic alkali feldspars. Alkali feldspars which have monoclinic symmetry or which have a topochemically monoclinic Al–Si distribution, even though they may have triclinic lattices (such as analbite; Laves, 1952), require only one ordering parameter,

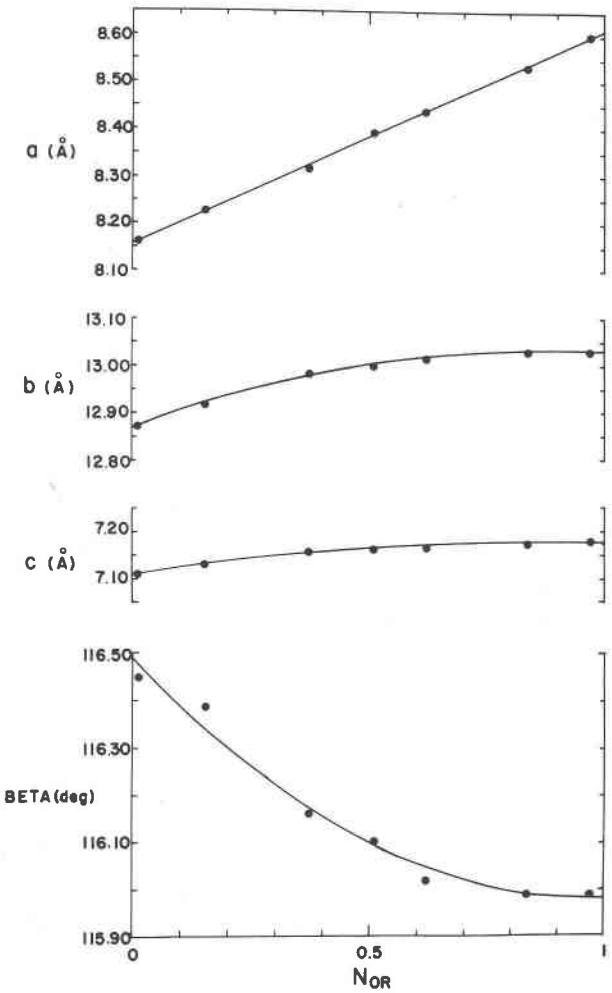

Fig. 1. *a*, *b*, *c*, and β unit-cell dimensions of sanidine–analbite crystalline solutions plotted against composition. For *a*, *b*, and *c* the size of the data points is about ten times the standard error of the refined values, for β about twice the standard error. Curves correspond to equations (1), (2), (3), and (4).

such as Z [$= 2(N_{Al(T1)} - N_{Al(T2)})$] (Thompson, 1969, 1970), to characterize their Al–Si distributions.

In the present investigation, the albite (sample 7015) synthesized by long-term heating of low albite is thought to have a topochemically monoclinic Al–Si distribution, because (1) the temperature at which it was annealed (1052°C, 710 hours) should have been sufficient to produce such a distribution (Kroll and Bambauer, 1971; Thompson *et al.*, 1974), and (2) ion-exchange in KCl produced a monoclinic potassium feldspar (see data for sanidine 7036), not a triclinic one. This is possible only if the feldspar has a topochemically monoclinic (or very nearly so) Al–Si distribution. All feldspars of the present series may be assumed to have the same Al–Si distribution as sample 7015.

A Z-value for all members of the present series may be estimated by substituting values of the *b* and *c* unit-cell dimensions of its *potassic* members into equation (3) of Hovis (1974). These data are included in Table 4. The *average* Z-value for the three most potassic feldspars is 0.082, which corresponds to tetrahedral site occupancies of $N_{Al(T1)} = 0.271$ and $N_{Al(T2)} = 0.229$ (for nomenclature see Thompson, 1969).

In relative terms the Al–Si distribution in feldspars of the present investigation is more disordered than those in the series of Donnay and Donnay (1952; also see Wright and Stewart, 1968), Orville (1967), and Luth and Querol-Suñé (1970), as is apparent in a plot of *b vs. c* (Fig. 2), where data for the series of Orville (1967) are taken as representative of those for all three of the series. Members of the present series have relatively higher *b* and lower *c* values than do corresponding members of the other series, indicating greater disordering in the present feldspars (see Stewart and Ribbe, 1969; Stewart and Wright, 1974). The present series may be more disordered because of the higher temperature (1052°C) at which the analbite starting material was prepared relative to the synthesis temperature (800°C) of the hydrothermally produced series.

Molar volumes

Quadratic (Fig. 3) and cubic least-squares fits of the molar volume data in Table 4 may be expressed as:

$$\bar{V}\,(\text{cal/bar}) = 2.3982\,(\pm.0009) + 0.2064\,(\pm.0011)N_{Or} + 0.0862\,(\pm.0040)N_{Or}N_{Ab} \qquad (5)$$

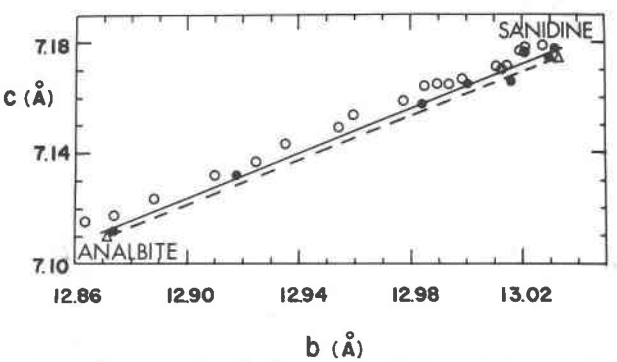

Fig. 2. *b vs. c* unit-cell dimensions of the sanidine–analbite crystalline solutions (closed circles) relative to those for Orville's series (1967; open circles) and the "ideal end-members" of Stewart and Wright (1974; triangles). Solid line represents a linear least-squares fit of *c* as a function of *b* for the present series. Dashed line connects values for Stewart and Wright (1974) end-members.

and

$$\bar{V}\,(\text{cal/bar}) = 2.3970\,(\pm.0011) + 0.2093\,(\pm.0018)N_{Or} + 0.064\,(\pm.011)N_{Ab}N_{Or}^2 + 0.107\,(\pm.011)N_{Or}N_{Ab}^2 \quad (6)$$

(To convert the molar volume of either equation to units of joules/bar, multiply the coefficients by 4.184. To convert to A^3/unit cell, divide by 0.0035985.) Standard errors for the fits are ±0.0019 and ±0.0018 cal/bar, respectively. Strict application of the Gauss criterion (Worthing and Geffner, 1943) suggests that the cubic formulation is the better of the two fits. However, considering that the standard errors for the individual volume determinations (Table 4) are high relative to the standard errors of fit, that there are only seven data points, and that the cubic fit does not greatly improve the standard error, only the quadratic fit can be justified for this series of feldspars.

The Margules parameters for molar volume based on quadratic fits (W_V, following the notation of Thompson, 1967) and on cubic fits ($W_{V,Or}$ and $W_{V,Ab}$) of molar volume data of all previously studied sanidine–analbite series may be compared with those of the present series (Table 5). The agreement of W_V values for all series is excellent. For four of the five data sets W_V values agree to within 0.003 cal/bar. For cubic fits, however, $W_{V,Or}$ and $W_{V,Ab}$ values vary considerably from one series to another. Not only are the values for $W_{V,Or}$ and $W_{V,Ab}$ different among the various series, but there is disagreement as to which one is larger. This is further justification for use of a quadratic fit to alkali feldspar molar volume data at this time.

Based on a quadratic fit to the molar volume data, the excess volume of mixing (Fig. 4) for the present feldspar series is expressed as:

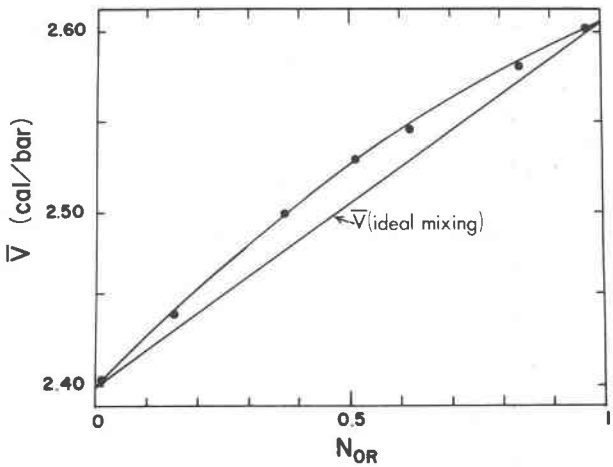

Fig. 3. Quadratic fit of molar volume data for sanidine–analbite crystalline solutions. The size of the data points is about four times the standard errors of the volume determinations. The cubic fit is nearly indistinguishable from the quadratic curve shown here.

$$\bar{V}_{ex}(\text{cal/bar}) = 0.0862\,(\pm.0040)\,N_{Or}N_{Ab} \quad (7)$$

At $N_{Or} = 0.50$, $\bar{V}_{ex}$ is 0.022 cal/bar.

Excess molar volume parameters as functions of Al–Si distribution in alkali feldspars

Molar volume data are available for two microcline-low albite series (Waldbaum, 1966; Waldbaum and Robie, 1971; Orville, 1967). W_V values for both of these series are slightly higher (0.110 and 0.123 cal/bar, respectively, Waldbaum and Thompson, 1968) than for any of the sanidine–analbite series reported in Table 3. However, a recent reinvestiga-

Table 5. Margules volume parameters based on least-squares fits of molar volume data for several sanidine–analbite series

Investigator(s)*	No. of Data Points	W_V (cal/bar; quadratic fit)	$W_{V,Or}$ (cal/bar; cubic fit)	$W_{V,Ab}$ (cal/bar; cubic fit)
Donnay and Donnay, 1952	12	.088 ±.002	.051 ±.003	.128 ±.004
Wright and Stewart, 1968 (Donnay and Donnay data)	9	.086 ±.003	.078 ±.008	.095 ±.008
Orville, 1967	20	.089 ±.002	.072 ±.003	.107 ±.003
Luth and Querol-Suñé, 1970	29	.102 ±.001	.162 ±.002	.051 ±.002
This investigation	7	.086 ±.004	.107 ±.011	.064 ±.011

*Data for the first three papers are taken in part from Waldbaum and Thompson, 1968.

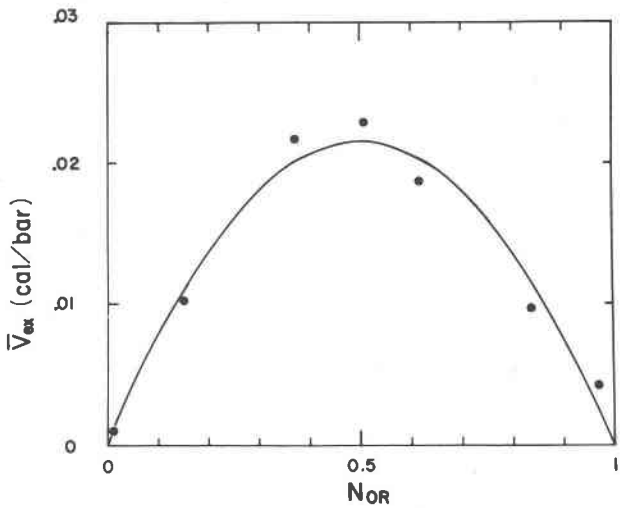

Fig. 4. Excess molar volume of K–Na mixing plotted against composition for sanidine–analbite crystalline solutions. Curve corresponds to equation (7). Data points are relative to the line for "mechanical mixtures" based on equation (5) and Fig. 3.

tion of the Waldbaum and Robie series (Hovis and Peckins, in preparation) indicates a lower W_V of 0.078 cal/bar. Thus, it seems doubtful at present that Al–Si distribution has any measurable effect on molar volume mixing properties for the alkali feldspars. If there is an effect, it is quite small.

Conclusions

The thermodynamic non-ideal behavior of the alkali feldspars is well established. One segment of the information needed to thermodynamically characterize alkali feldspars, molar volume data, is now nearly complete for data collected at room temperature. Molar volumes for all alkali feldspar series behave non-ideally, deviating positively from linearity as a function of K/(K + Na) ratio. That is, the volumes of homogeneous alkali feldspars with intermediate K/(K + Na) ratios are greater than those of chemically equivalent mechanical mixtures of end-member feldspars. This positive deviation from ideality corresponds to positive values for the Margules volume parameters.

Symmetrical (quadratic) least-squares fits to molar volume data as a function of K/(K + Na) ratio may be better, in general, than cubic fits. If so, this indicates that the departure from ideality (that is, the *volume of mixing*) is about the same when a potassium ion substitutes for a sodium ion in a sodic feldspar as it is when a sodium ion substitutes for a potassium ion in a potassic feldspar.

Though absolute values of molar volumes increase slightly with Al–Si disordering, the volumes of K–Na *mixing* are relatively insensitive to Al–Si distribution in alkali feldspars. Because Al–Si order–disorder has a very small effect on molar volume (Orville, 1967; Stewart and Ribbe, 1969; Hovis, 1971 and 1974), it is the K/(K + Na) ratio which has the major influence on the molar volumes of these feldspars. The three-dimensional tetrahedral network behaves as a framework which either expands (with the substitution of K for Na) or contracts (with the substitution of Na for K) as ions occupying the "*M*" crystallographic sites among the tetrahedra are changed, but the distribution of Al and Si ions within the different types of tetrahedra is relatively unimportant in terms of volume properties.

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References

Borg, I. Y. and D. K. Smith (1969) Calculated X-ray powder patterns for silicate minerals. *Geol. Soc. Am. Mem. 122.*

Burnham, C. W. (1962) Lattice constant refinement. *Carnegie Inst. Wash. Year Book, 61,* 132–135.

Donnay, G. and J. D. H. Donnay (1952) The symmetry change in the high-temperature alkali feldspar series. *Am. J. Sci. 250A,* 115–132.

Hafner, S. and F. Laves (1957) Ordnung/Unordung und ultrarot-Absorption. II. Variation der Lage und Intensitat einiger Absorptionen von Feldspaten. Zur Struktur von Orthoklas und Adular. *Z. Kristallogr., 109,* 204–225.

Hovis, G. L. (1971) *Thermodynamic Properties of Monoclinic Potassium Feldspars.* Ph.D. dissertation, Harvard University, Cambridge, Massachusetts.

—— (1974) A solution calorimetric and X-ray investigation of Al–Si distribution in monoclinic potassium feldspars. *In* Mac-

Kenzie, W. S., and J. Zussman, eds., *The Feldspars,* 114–144. University of Manchester Press, Manchester, England.

——— and D. R. Waldbaum (1976) Enthalpy and volume of K–Na mixing for a sanidine–analbite ion-exchange series (abstr.) *Trans. Am. Geophys. Union (EOS) 57,* 340–341.

——— and ——— (1977) A solution calorimetric investigation of K–Na mixing in a sanidine–analbite ion-exchange series. *Am. Mineral., 62,* 680–686.

Kroll, H., and H. U. Bambauer (1971) The displacive transformation of (K,Na,Ca)-feldspars. *Neues Jahrb. Mineral. Monatsh. 1971,* 413–416.

Laves, F. (1952) Phase relations of the alkali feldspars. *J. Geol., 60,* 436–450.

Luth, W. C. and F. Querol-Suñé (1970) An alkali feldspar series. *Contrib. Mineral. Petrol. 25,* 25–40.

MacKenzie, W. S. (1957) The crystalline modifications of $NaAlSi_3O_8$. *Am. J. Sci., 255,* 481–516.

Martin, R. F. (1969) The hydrothermal synthesis of low albite. *Contrib. Mineral. Petrol. 23,* 323–339.

Orville, P. M. (1967) Unit-cell parameters of the microcline-low albite and sanidine-high albite solid solution series. *Am. Mineral., 52,* 55–86.

Parrish W. (1960) Results of the I.U.Cr. precision lattice project. *Acta Crystallogr., 13,* 838–850.

Spencer, E. (1937) The potash–soda feldspars. I. Thermal stability. *Mineral. Mag., 24,* 453–494.

Stewart, D. B. and P. H. Ribbe (1969) Structural explanation for variations in cell parameters of alkali feldspars with Al/Si ordering. *Am. J. Sci., 267 A,* 444–462.

——— and T. L. Wright (1974) Al/Si order and symmetry of natural alkali feldspars, and the relationship of strained cell parameters to bulk composition. *Bull. Soc. fr. Minéral. Cristallogr., 97,* 356–377.

Thompson, J. B. (1967) Thermodynamic properties of simple solutions. In P. H. Abelson, Ed., *Researchers in Geochemistry, Vol. 2,* 340–361. John Wiley and Sons, Inc., New York.

——— (1969) Chemical reactions in crystals. *Am. Mineral., 54,* 341–375.

——— (1970) Chemical reactions in crystals: corrections and clarification. *Am. Mineral., 55,* 528–532.

——— D. R. Waldbaum and G. L. Hovis (1974) Thermodynamic properties related to ordering in end-member alkali feldspars. In W. S. MacKenzie and J. Zussman, Eds., *The Feldspars,* 218–248. University of Manchester Press, Manchester, England.

Vogel, T. A., R. Ehrlich and W. C. Luth (1973) Non-linear variation of cell parameters with composition in alkali feldspar series. *Am. Mineral., 58,* 905–908.

Waldbaum, D. R. (1966) *Calorimetric Investigation of the Alkali Feldspars.* Ph.D. dissertation, Harvard University, Cambridge, Massachusetts.

——— and R. A. Robie (1971) Calorimetric investigation of Na–K mixing and polymorphism in the alkali feldspars. *Z. Kristallogr., 134,* 381–420.

——— and J. B. Thompson, Jr. (1968) Mixing properties of sanidine crystalline solutions. II. Calculations based on volume data. *Am. Mineral., 53,* 2000–2017.

Worthing, A. G. and J. Geffner (1943) *Treatment of Experimental Data.* John Wiley and Sons, Inc., New York.

Wright, T. L. and D. B. Stewart (1968) X-ray and optical study of alkali feldspar. I. Determination of composition and structural state from refined unit-cell parameters and 2*V*. *Am. Mineral., 53,* 38–87.

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