

## Hydrofluoric acid solution calorimetric investigation of the effects of anorthite component on enthalpies of K-Na mixing in feldspars

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### ABSTRACT

Enthalpies of solution have been measured at 50 °C in 20.1 wt% hydrofluoric acid under isoperibolic conditions for a nine-member K-Na ion-exchange series based on a disordered oligoclase specimen containing 23.1 mol% anorthite (An) component. The series displays positive enthalpies of K-Na mixing, but magnitudes are substantially reduced relative to An-free analogs. Volumes of K-Na mixing for the series are similarly reduced; the asymmetry of these with respect to composition is the opposite of that for alkali feldspars. Lower magnitudes of the mixing properties are probably related to the shortened compositional range of this series, relative to normal alkali-feldspar series, and to a 23% An structural background against which the energetic effects of K-for-Na substitution are dampened.

### INTRODUCTION

Most minerals are not simple binary solutions, yet knowledge of the thermodynamic mixing properties of minerals is confined primarily to binary systems. If thermodynamic data are to be used to predict phase equilibria in natural systems, it is essential to know the effects of third and fourth components on thermodynamic mixing behavior. For enthalpy, third-component effects on binary mixing properties have been systematically investigated on few systems (Hovis and Roux 1993).

The binary mixing properties of alkali feldspars have been studied extensively. Currently there are reliable data for enthalpies of K-Na mixing (Hovis 1988), volumes of K-Na mixing (Waldbaum and Thompson 1968; Waldbaum and Robie 1971; Hovis 1986; Kroll et al. 1986; Hovis and Navrotsky 1995), and entropies of K-Na mixing (Hovis et al. 1991). From these same studies we also know the effects of Al-Si distribution on enthalpies and volumes. Additionally, we have been able to estimate the effects of short-range order (Hovis et al. 1991; Haselton et al. 1983; Hovis and Navrotsky 1995) on the thermodynamic behavior of these minerals. Lastly, we have studied the effects of temperature on both enthalpies (Hovis and Navrotsky 1995) and volumes of mixing (Hovis and Graeme-Barber, 1997). Because of this solid foundation of data, feldspars are excellent for the study of the thermodynamic effects of additional chemical components.

Most naturally occurring feldspars are at least ternary solutions, so it is a natural extension of work on alkali (K, Na) feldspars to quantify the effects of anorthite component on thermodynamic mixing properties. As an initial step in investigating the  $\text{KAlSi}_3\text{O}_8$  (Or)– $\text{NaAlSi}_3\text{O}_8$  (Ab)– $\text{CaAl}_2\text{Si}_2\text{O}_8$  (An) ternary system, therefore, we synthesized a K-Na series of feldspars having moderate An content and studied their volumes and enthalpies of mixing.

### STARTING MATERIAL

The starting material for the present investigation was oligoclase 80165, a colorless translucent specimen from the Hawk Mica Mine, Bakersville, North Carolina. The specimen was obtained from the United States National Museum (Smithsonian Institution). Data provided by the USNM gave a composition of  $\text{Ab}_{73.4}\text{Or}_{13.5}\text{An}_{23.1}$  on the basis of spectrochemical analyses made by Dr. Tren Haselton at the United States Geological Survey. The same specimen was also analyzed by Kracek and Neuvonen (1952; technique not described), who gave a composition of  $\text{Ab}_{73.1}\text{Or}_{13.7}\text{An}_{23.2}$ . We too measured the composition on the basis of two partial atomic absorption spectrometric analyses for CaO,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$  performed at the Pennsylvania State University. The average of these nearly identical analyses matched the Haselton result, so we adopted that as the oligoclase composition.

From this oligoclase specimen we synthesized a disordered nine-member K-Na ion-exchange series. The primary purpose of this paper, then, is to report on the volumes and enthalpies of K-Na mixing determined for this series and to compare these results with similar data for An-poor alkali feldspars (Hovis 1986, 1988).

### SAMPLE PREPARATION

Because the state of Al-Si order is known to affect thermodynamic mixing properties (Hovis 1986, 1988), reliable comparison of the mixing properties of an oligoclase-based series with those of an An-free feldspar series requires that the two series have similar Al-Si distributions. In the present case this was complicated because the parent materials had different values of Al:Si and could not possibly attain the same Al-Si distribution, and because the parent materials had formed under different geologic conditions and represented different degrees of

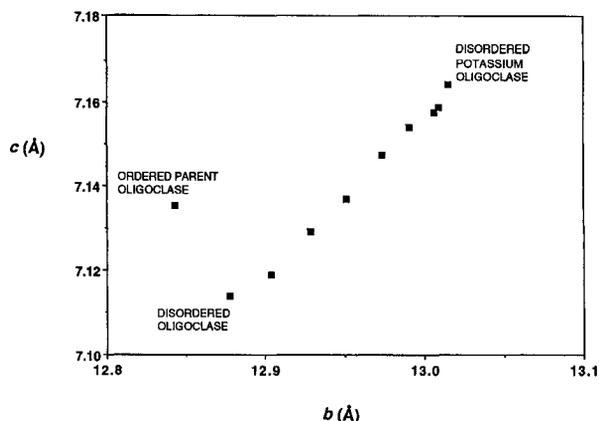


FIGURE 1. Plot of the  $b$  vs.  $c$  unit-cell dimensions for members of the ion-exchange series.

Al-Si disorder. It seemed reasonable that the most valid comparison of K-Na mixing properties would be provided by a disordered oligoclase series, the properties of which could be compared with those of disordered alkali feldspars, namely the sanidine-analbite series of Hovis (1986, 1988).

Parent oligoclase 80165 was disordered through annealing at  $1131 (\pm 1)^\circ\text{C}$  in a Deltech Model DT-31 furnace for 518.5 h, resulting in specimen 8714. Although we were not successful in producing a perfect monoclinic Al-Si distribution, the resulting feldspar did achieve a high degree of disorder, as discussed in detail in the next section. Furthermore, the  $b$  unit-cell dimension of specimen 8714 significantly increased relative to that of the 80165 parent material, and the  $c$  dimension decreased as a result of disordering (Fig. 1), in exactly the same way that the unit-cell dimensions of alkali feldspars change with disorder (Stewart and Ribbe 1969).

From the disordered parent material a corresponding "pure potassium oligoclase" (i.e., Na-free) was produced by double ion exchange in molten KCl. That is, oligoclase 8714 was first K exchanged in molten KCl at  $808 (\pm 4)^\circ\text{C}$  for 23.0 h in a Lindberg Model 51844 box furnace; the exchange was performed in platinumware using a large excess of salt over feldspar. The feldspar was separated by dissolution of the quenched salt in distilled water, then dried and reexchanged in fresh KCl for an additional 21.7 h at  $805 (\pm 4)^\circ\text{C}$ , again with a large excess of salt over feldspar.

Feldspars of intermediate composition were made by combining powders of the parent material (8714) and the corresponding potassium oligoclase (8817) in desired proportions. These mixtures were placed in cylindrical platinum crucibles, compressed, and annealed for various durations at elevated temperatures. Powders were normally removed from the furnace every 24 h, remixed in acetone to randomize grains of various compositions, and then repacked and reloaded for further annealing. This same procedure has been successful in homogenizing K and Na in alkali feldspars (Hovis 1986), as reflected in

TABLE 1. Synthesis histories of disordered oligoclase samples

Feldspar	$N_{or}$	Synthesis history
8714	0.035	D, 80165, 1131, 21.6 (8714).
8818	0.127	H, 8714 + 8817, 845, 18.3 (8818).
8848	0.217	H, 8714 + 8817, 845, 18.3 (8819); H, 8819, 884, 5.25 (8844); H, 8844, 931, 5.04 (8848).
8903	0.308	H, 8714 + 8817, 845, 18.3 (8820); H, 8820, 884, 5.25 (8845); H, 8845, 931, 5.04 (8849); H, 8849, 935, 4.45 (8903).
8911	0.399	H, 8714 + 8817, 750, 18.1 (8835); H, 8835, 793, 24.0 (8840); H, 8840, 842, 5.46 (8851); H, 8851, 860, 10.0 (8854); H, 8854, 901, 5.71 (8911).
8904	0.491	H, 8714 + 8817, 750, 18.1 (8836); H, 8836, 793, 24.0 (8841); H, 8841, 842, 5.46 (8852); H, 8852, 860, 10.1 (8855); H, 8855, 860, 4.45 (8904).
8837	0.581	H, 8714 + 8817, 750, 18.1 (8837).
8838	0.672	H, 8714 + 8817, 750, 18.1 (8838).
8817	0.769	I, 8714, 1.0, 808, 0.96 (8816); I, 8816, 1.0, 805, 0.90 (8817).

Note: I = molten chloride ion-exchange experiment, H = dry homogenization experiment, and D = disordering experiment. For ion-exchange experiments, the number after the "I" identifies the plagioclase sample used as the starting material, followed by the composition of the salt (given by the mole fraction of KCl in the salt), the temperature ( $^\circ\text{C}$ ), and the duration of the run (d). The bracketed number at the end is that of the resulting feldspar. For homogenization and disordering experiments, the "H" or "D" is followed by the identification number of the starting plagioclase sample, the temperature ( $^\circ\text{C}$ ), the duration of the run (d), and the identity of the resulting series member.

the current study by the sharp  $\bar{2}01$  X-ray peaks of the resulting specimens. Synthesis conditions for various specimens are given in Table 1. Compositions reported in Table 2 reflect carefully weighed proportions of the two end-members.

#### SAMPLE CHARACTERIZATION

Unit-cell dimensions were determined from data collected on an automated Scintag DMS 2000 X-ray powder diffraction system. We used National Bureau of Standards 640a Si, with a stated unit-cell dimension of  $5.430825 \text{ \AA}$ , as an internal standard in all spectra. Burnham's (1962) LCLSQ program was utilized to calculate unit-cell dimensions from the feldspar data. The resulting parameters are given in Table 2. A plot of the  $b$  vs.  $c$  unit-cell dimensions of the resulting feldspars (Fig. 1) shows a trend similar to those seen in analogous diagrams for the alkali feldspars (Kroll and Ribbe 1983; Hovis 1986). The plot also reflects the change in state of order from the original parent oligoclase (80165) to its disordered equivalent (8714).

We also plotted the quantity  $(1 - \cos \phi)$  (see Thompson and Hovis 1978) as a function of composition in Figure 2. This function, where  $\cos \phi = \sin \gamma \sin \alpha^*$ , is zero for a dimensionally monoclinic feldspar. Figure 2 illustrates that  $(1 - \cos \phi)$  values for the three most potassic members of the series come close to, but do not quite reach, zero (note also the non- $90^\circ$  values for  $\alpha$  and  $\gamma$  in Table 2). The lack of perfect monoclinic symmetry is also indicated by the failure of certain "split" X-ray peaks

TABLE 2. Unit-cell parameters

Feldspar	$N_{Or}$	$a/a^*$	$b/b^*$	$c/c^*$	$\alpha/\alpha^*$	$\beta/\beta^*$	$\gamma/\gamma^*$	Unit-cell volume ( $\text{\AA}^3$ )	Molar volume ( $\text{cm}^3$ )	Molar volume (J/bar)
80165	0.035	8.1682(13)	12.8431(14)	7.1354(9)	93.794(14)	116.449(10)	89.043(13)	668.66(11)	100.69(2)	10.067(2)
		0.136751(20)	0.078042(9)	0.156867(16)	86.239(13)	63.556(10)	89.181(12)			
8714	0.035	8.1649(12)	12.8814(12)	7.1113(7)	93.377(11)	116.321(9)	90.275(11)	668.83(10)	100.71(2)	10.070(2)
		0.136724(21)	0.077813(7)	0.157251(13)	86.096(10)	63.612(9)	88.020(10)			
8818	0.127	8.2067(13)	12.9021(17)	7.1209(9)	93.086(15)	116.297(13)	90.171(14)	674.67(13)	101.59(2)	10.158(2)
		0.135978(23)	0.077655(11)	0.156941(18)	86.472(15)	63.652(13)	88.282(14)			
8848	0.217	8.2433(25)	12.9296(27)	7.1285(13)	92.585(23)	116.242(17)	90.179(22)	680.54(21)	102.48(3)	10.246(3)
		0.135296(45)	0.077447(17)	0.156612(22)	87.030(22)	63.720(18)	88.525(21)			
8903	0.308	8.2784(24)	12.9487(23)	7.1371(15)	92.090(24)	116.177(19)	90.088(24)	686.00(20)	103.30(3)	10.329(3)
		0.134627(35)	0.077294(14)	0.156260(35)	87.628(21)	63.801(19)	88.874(21)			
8911	0.399	8.3278(42)	12.9734(24)	7.1453(16)	91.429(27)	116.087(26)	90.024(22)	693.07(29)	104.36(4)	10.435(4)
		0.133710(60)	0.077111(14)	0.155887(26)	88.397(26)	63.904(26)	89.273(20)			
8904	0.491	8.3574(19)	12.9927(20)	7.1543(14)	90.951(22)	116.035(17)	89.961(21)	697.90(18)	105.09(3)	10.508(3)
		0.133171(30)	0.076979(12)	0.155588(21)	88.961(20)	63.962(17)	89.579(18)			
8837	0.581	8.4105(27)	13.0034(23)	7.1583(15)	90.452(23)	115.954(21)	89.866(25)	703.89(22)	105.99(3)	10.598(3)
		0.132237(36)	0.076905(14)	0.155372(23)	89.562(20)	64.046(21)	89.929(22)			
8838	0.672	8.4340(22)	13.0097(24)	7.1610(14)	90.321(25)	115.915(19)	89.899(24)	706.71(20)	106.42(3)	10.640(3)
		0.131823(30)	0.076867(14)	0.155259(27)	89.692(22)	64.086(19)	89.956(21)			
8817	0.769	8.4578(21)	13.0186(21)	7.1653(13)	90.245(24)	115.919(22)	89.902(22)	709.60(19)	106.85(3)	10.684(3)
		0.131457(31)	0.076814(12)	0.155170(38)	89.775(21)	64.081(22)	89.990(19)			

Note: Uncertainties in the final decimal places are shown in brackets.

(e.g., 131-131 and 132-132) to close fully for the same three feldspar samples.

The degree of disorder of our samples can be estimated using the method of Kroll (1983; see also Viswanathan 1971). From equation V in his Table 1, after correction of  $\gamma$  for  $N_{Or}$  content, we calculated the difference in the mole fractions of Al in the T1o and T1m tetrahedral sites for sample 8714 to be 0.05 (the value would be zero for a topochemically monoclinic Al-Si distribution). A similar calculation for the original ordered parent oligoclase, also after correction for  $N_{Or}$  content, gave a difference of 0.59. Clearly, the annealing of parent feldspar 80165 was successful in producing a highly disordered product in

8714, even though the sample did not attain a monoclinic Al-Si distribution. Al-Si reordering is known not to occur in alkali feldspars for the relatively low temperatures and short durations of our K exchange and homogenization experiments (e.g., Waldbaum and Robie 1971), so it is reasonable to assume that all members of the ion-exchange series have the same Al-Si distribution.

$N_{Or}$  contents for individual members of this series can be estimated from either the  $a$  unit-cell dimension or the 201 X-ray diffraction maximum, both of which vary substantially with K/Na. Coefficients for determinative equations are reported in Table 3.

It is important to recognize that the K-Na ion-exchange series synthesized in this investigation is limited in its compositional variation relative to a normal alkali-feldspar series. Because the K-exchange experiments did not remove An component from the feldspar samples, all members of the present series have a constant An content of 23.1 mol%. Even the most K-rich sample (with zero Na), therefore, contains only 76.9 mol% Or, not 100% as would be the case for an alkali-feldspar end-member. Thus, one would not expect the differences in unit-cell dimensions, nor indeed in other properties, between Na and K ends of the series to be as great as those for an alkali-feldspar series.

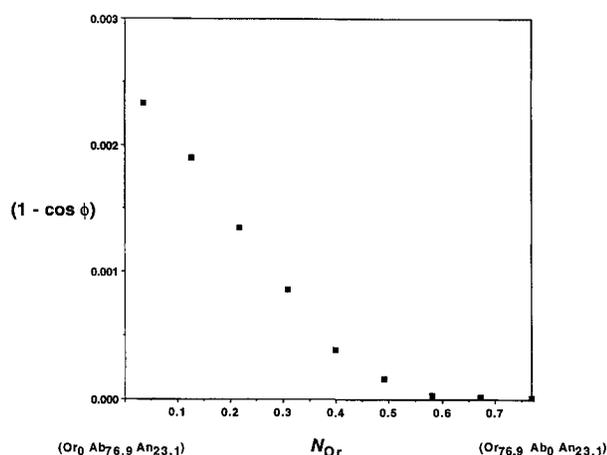


FIGURE 2. Plot of  $(1 - \cos \phi)$ , defined in the text, vs. composition ( $N_{Or}$  = mole fraction  $\text{KAlSi}_3\text{O}_8$ ) for members of the ion-exchange series. The three most potassic members display non-zero values for feldspars that are nearly, but not exactly, monoclinic.

TABLE 3. Determinative equations for  $N_{Or}$ 

	$x_0$	$x_1$	For $N_{Or}$
$a$	-18.434	2.2624	<0.58
$a$	-32.850	3.9748	>0.58
201	21.192	-0.96267	<0.58
201	38.889	-1.7905	>0.58

Note: Equations have the form  $N_{Or} = x_0 + x_1Q$ , where  $Q$  is either the value for  $a$  or 201. Correlation coefficients for all least-squares fits are 0.997 or higher.

### CALORIMETRIC PROCEDURES

Each feldspar sample was dissolved in 910.1 g (approximately one liter) of 20.1 wt% hydrofluoric acid at 50 °C under isoperibolic conditions using an internal sample container (Waldbaum and Robie 1970). Either one or two dissolutions were performed in a single acid solution. Multiple experiments in the same solution violate the rule of strict stoichiometry (Hovis 1974), but no effect on the data was observed within the precision of our experiments. This is probably due to the high dilution of dissolved ions in the acid solution, as most experiments used only 0.25 g of sample, and none utilized more than 0.31 g.

In connection with sample synthesis, specimens were ground to pass through a 325-mesh sieve and then elutriated in deionized water to remove the finest grain sizes. These grain sizes are well above those that would affect calorimetric data (Nitkiewicz et al. 1983; Roux and Hovis, 1996).

General principles and procedures of acid-solution calorimetry have been discussed by Robie and Hemingway (1972). Solution calorimetric measurements during the present investigation were made on an automated data-acquisition system previously described by Hovis and Roux (1993), except that a more sensitive digital voltmeter (Hewlett Packard Model 3458A), one able to read voltages to two additional significant figures, was used instead of the HP Model 3456A for voltage measurements. Calorimetric samples were weighed on a new Mettler AT-201 electronic balance, which improved weighing accuracy. Both of these changes are reflected in the improved precision of the calorimetric data, relative to precision that was already very high (e.g., Hovis and Roux 1993). Experiments conducted in our present reaction vessel produced slightly higher absolute values for enthalpies of solution than those in the model used for earlier work on feldspars (Hovis 1988) because of a slightly different superheating correction for the latter (see discussion by Hovis and Roux 1993). On the basis of calibration experiments using Fisher A-581 reagent-grade aluminum hydroxide, enthalpies of solution for present experiments were multiplied by a factor of 0.9980. This has only a small effect on the calorimetric data and in no way affects conclusions.

### MATHEMATICAL TREATMENT OF DATA

The correct mathematical treatment of both volumetric and calorimetric data is important. From the failure of  $(1 - \cos \phi)$  values to reach zero (Fig. 2), it is evident that this series does not undergo a true phase transition as a function of composition; therefore, it can be treated as a single continuous series. Nevertheless, the series does mimic such a phase transition, as values of  $(1 - \cos \phi)$  change steeply, and in fact linearly, near the sodic end of the series and then level off to near-zero values for the three most potassic members. Furthermore, two segments of the series have different trends on plots of both  $a$  (Fig. 3) and volume (Fig. 4B) vs. composition, with a break in

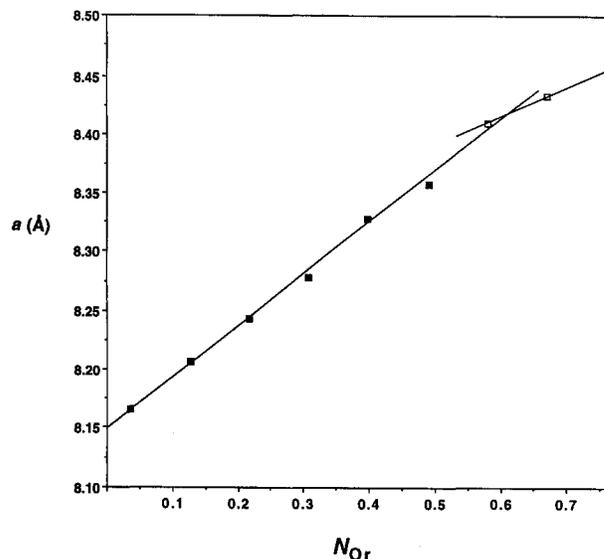


FIGURE 3. Plot of the  $a$  unit-cell dimension vs. composition. Note that the series can be analyzed as consisting of two linear segments.

slope in both cases occurring near the composition of feldspar 8837 ( $N_{Or} = 0.581$ ). We show below that enthalpies of mixing display a double maximum, and that the minimum between these could indeed be related to a phase change near the potassic end of the series. Because we cannot demonstrate that there is a phase change along the series, we treat the series as continuous, but note in various places the consequences of treating the series as two separate entities.

### VOLUMES OF K-NA MIXING

Molar and unit-cell volumes for all feldspar samples are included in Table 2. When treated as a continuous series, the best least-squares fit to the data is third order (Fig. 4A):

$$V [\text{J}/(\text{bar}\cdot\text{mol})] = 10.044 + 0.774 N_{Or} + 0.918 N_{Or}^2 - 1.10 N_{Or}^3 \quad (1)$$

with a standard error of  $\pm 0.008$  J/(bar·mol) and a correlation coefficient of 0.999. This equation, of course, is valid only for compositions up to the pure-K end-member at  $N_{Or} = 0.769$ . These molar volumes can be converted to other units (cubic centimeters per mole) or to unit-cell volumes (cubic angstroms) through multiplication of all coefficients on the right side of Equation 1 by 9.9998 or 66.418, respectively.

Corresponding molar volumes of mixing (Fig. 5) are expressed as

$$V_{ex} [\text{J}/(\text{bar}\cdot\text{mol})] = -0.058 N_{Or} + 0.918 N_{Or}^2 - 1.10 N_{Or}^3 \quad (2)$$

again valid for  $N_{Or}$  values up to 0.769. The asymmetry of the volumes of mixing is the reverse of that in alkali

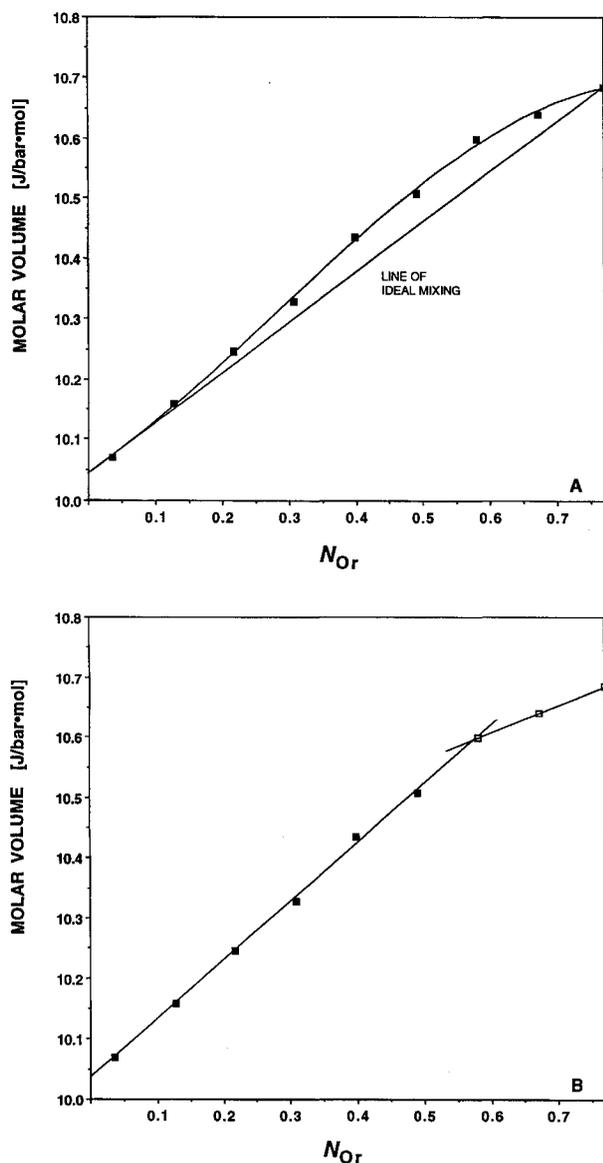


FIGURE 4. (A) Analysis of molar volume as a single continuous series. The least-squares curve through the data corresponds to Equation 1. (B) Plot of molar volume vs. composition. Note that the series can be divided into two linear segments. Open symbols are for nearly monoclinic members.

feldspars, with a larger departure from ideality at potassic compositions. The reason for this is not clear, but it is accounted for by the same effect that changes the trend in  $V-N_{Or}$  relations near the potassic end of the series.

The maximum magnitudes for  $V_{ex}$  are only about one-half those of disordered alkali feldspars (Hovis and Navrotsky 1995). Indeed, one might expect lower magnitudes for a series that has a "shortened" compositional span, in this case only 77% that of a normal alkali-feldspar series.

If treated as two separate series, volumes for the tri-

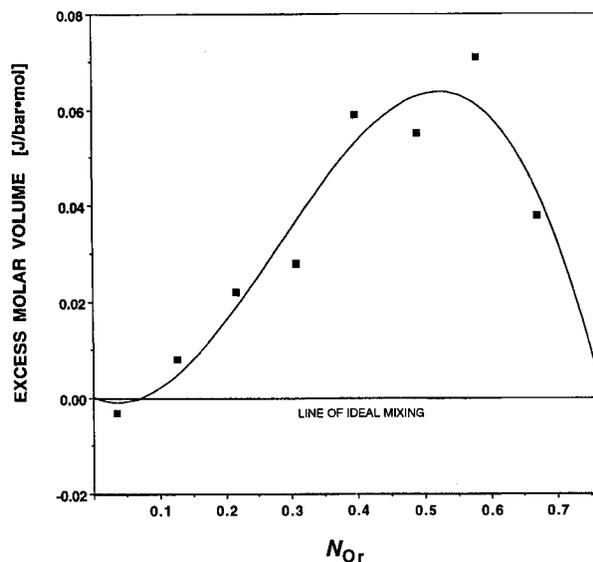


FIGURE 5. Volumes of mixing derived from the volume analysis of Figure 4A. The curve corresponds to Equation 2.

clinic and near-monoclinic regions each behave linearly with composition (Fig. 4B); for such an analysis volumes of mixing are nonexistent. Equations for these lines are

$$V \text{ [J/(bar·mol)]} = 10.035 + 0.971 N_{Or} \quad (3)$$

for the seven most sodic compositions, with a standard error of fit of  $\pm 0.006$  J/(bar·mol) and a correlation coefficient of 0.999, and

$$V \text{ [J/(bar·mol)]} = 10.332 + 0.457 N_{Or} \quad (4)$$

for the three most potassic compositions, with a standard error of  $\pm 0.0003$  J/(bar·mol) and a correlation coefficient of 1.000. Note that the volume of feldspar 8837 was used in both fits.

### CALORIMETRIC RESULTS

Calorimetric data are given in Table 4 and presented in Figure 6. The precision of the data is high; differences between the maximum and minimum heats of solution (i.e., the spread in values) at individual compositions ranges from just 0.05% to 0.24% of the enthalpies of solution and averages 0.14% for the nine series members. This level of precision is excellent considering the small sample weights per experiment. Small samples not only are prone to higher weighing errors, on a percentage basis, but they generate smaller temperature changes during dissolution, producing greater uncertainties in the  $\Delta T$  related to dissolution, and thereby greater uncertainties in the heats of solution. That this double effect was overcome attests to improvements in our calorimetric system noted earlier, namely the addition of a more sensitive voltmeter and a better balance for weighing samples.

### Enthalpy of disorder

The average difference in the enthalpies of solution of specimen 80165 and its disordered equivalent (8714) is

TABLE 4. Calorimetric data

Sample	Expt.	Composi- tion ( $N_{Or}$ )	Sample weight (g)	T change during dissolution (°C)	Calorimeter heat capacity I (J/°C)	Calorimeter heat capacity II (J/°C)	Mean solution T (°C)	Gram formula weight (g/mol)	Negative enthalpy of solution I (kJ/mol)	Negative enthalpy of solution II (kJ/mol)
80165	659	0.035	0.25591	0.164499	3877.31	3874.64	50.011	266.4811	664.160	663.704
80165	662	0.035	0.27662	0.177293	3875.97	3872.92	50.007	266.4811	661.997	661.474
80165	685	0.035	0.25592	0.164245	3874.84	3874.64	50.020	266.4811	662.704	662.633
80165	686	0.035	0.25388	0.163528	3870.66	3871.92	50.025	266.4811	664.398	664.578*
8714	641	0.035	0.30584	0.199373	3875.81	3876.52	50.036	266.4811	673.289	673.411
8714	643	0.035	0.26528	0.173199	3875.35	3874.55	50.006	266.4811	674.247	674.105
8714	671	0.035	0.25603	0.167411	3870.28	3870.12	49.994	266.4811	674.394	674.331*
8714	676	0.035	0.25261	0.164711	3874.43	3874.30	50.014	266.4811	673.222	673.160
8818	646	0.127	0.25507	0.165318	3879.40	3877.90	50.007	267.9618	673.745	673.490
8818	672	0.127	0.24921	0.161683	3874.09	3873.17	49.988	267.9618	673.524	673.348
8818	682	0.127	0.25329	0.164334	3873.55	3872.92	50.023	267.9618	673.448	673.302
8848	644	0.217	0.27000	0.173355	3876.39	3875.93	50.010	269.4184	670.545	670.465
8848	673	0.217	0.25298	0.162771	3870.45	3870.79	49.992	269.4184	670.930	670.992*
8848	678	0.217	0.24993	0.160457	3875.60	3873.51	50.005	269.4184	670.356	669.992
8903	648	0.308	0.25489	0.162555	3875.93	3875.68	50.006	270.8749	669.566	669.519
8903	674	0.308	0.25082	0.159892	3874.68	3873.21	50.007	270.8749	669.084	668.817
8903	683	0.308	0.25093	0.160083	3871.20	3871.20	50.019	270.8749	668.992	668.950*
8911	645	0.399	0.25448	0.160730	3877.44	3876.39	50.004	272.3427	666.967	666.783
8911	666	0.399	0.25079	0.158454	3874.80	3874.30	50.043	272.3427	666.762	666.637
8911	684	0.399	0.24919	0.157556	3874.80	3874.43	50.021	272.3427	667.243	667.135
8904	649	0.491	0.25441	0.159689	3876.73	3875.22	50.007	273.8251	666.130	665.867
8904	670	0.491	0.25098	0.157266	3874.93	3873.13	49.992	273.8251	664.863	664.557
8904	679	0.491	0.24694	0.155101	3871.20	3870.79	50.006	273.8251	665.796	665.725*
8837	675	0.581	0.25175	0.156875	3870.91	3870.70	50.009	275.2719	663.988	663.955*
8837	680	0.581	0.24835	0.154539	3874.51	3874.55	50.012	275.2719	663.691	663.662
8838	650	0.672	0.25596	0.157994	3876.85	3875.10	50.002	276.7446	662.256	661.955
8838	669	0.672	0.25214	0.155509	3874.47	3872.00	49.996	276.7446	661.310	660.888
8838	681	0.672	0.25081	0.155090	3870.41	3870.66	50.013	276.7446	662.348	662.356*
8817	642	0.769	0.30804	0.188000	3876.64	3874.22	50.026	278.3075	658.461	658.047
8817	667	0.769	0.25104	0.153143	3875.10	3872.79	49.993	278.3075	657.896	657.511
8817	677	0.769	0.25177	0.153893	3871.79	3871.87	50.006	278.3075	658.649	658.662*

\* Using acid of preceding experiment.

10.6 ± 1.7 kJ/mol. This value is less than that of 12.0 ± 2.0 kJ/mol (Hovis 1988, Eq. 7) for the transition of perfectly ordered low albite to fully disordered analbite. Although these values are within the combined uncertainties of each other, the difference between them is probably real. Unlike analbite, sample 8714 does not have a true monoclinic Al-Si distribution, nor does the degree of disorder associated with the 10.6 kJ/mol change in enthalpy represent the difference between a perfectly ordered and a fully disordered state (see discussion of site populations under Sample Characterization). Furthermore, one would expect a lower enthalpy of disorder in oligoclase than in albite because its higher Al:Si should combine with Al avoidance to quantitatively limit the degree of disorder that is possible relative to that in albite.

#### Enthalpies of K-Na mixing

Perusal of the calorimetric data (Fig. 6) suggests a linear relationship between heat of solution and composition; in fact, such a fit produces a good correlation coefficient of 0.979. However, we believe that there are several valid reasons for considering higher order fits to the data. First, a linear fit fails to intersect data at four compositions, including the end-members, and data for the latter both lie below such a line, possibly implying a concave downward relationship and positive enthalpies of mixing. Second, volumes for this series clearly display

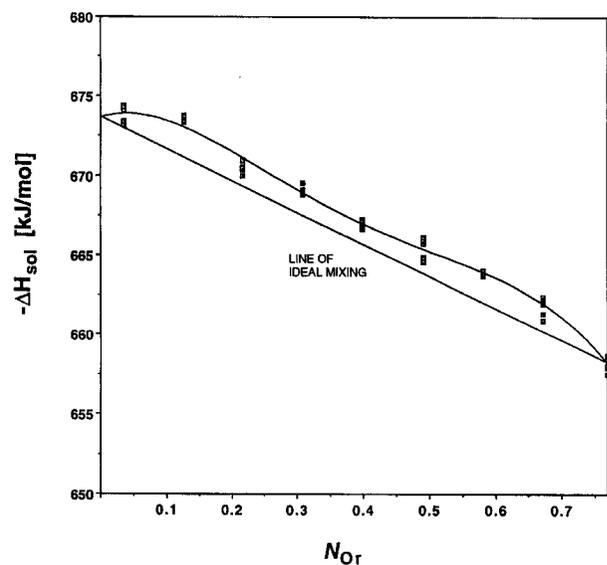


FIGURE 6. Negative enthalpies of solution vs. composition. Data are given in Table 4. The fourth-order curve corresponds to Equation 5.

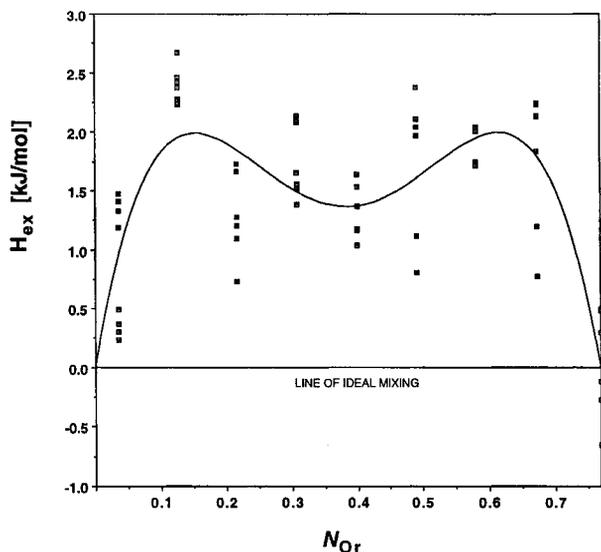


FIGURE 7. Enthalpies of K-Na mixing resulting from analysis of the calorimetric data given in Figure 6. The curve corresponds to Equation 6.

positive excess quantities associated with K-Na substitution. Third, positive volumes and enthalpies are clearly associated with K-Na mixing in alkali-feldspar systems (Hovis 1988). For these reasons, we believe it is likely that the oligoclase-based series of this investigation does indeed possess positive (obviously small) excess enthalpies.

As the order of fit to the calorimetric data is increased, correlation coefficients improve. A second-order fit produces a concave downward relationship and small posi-

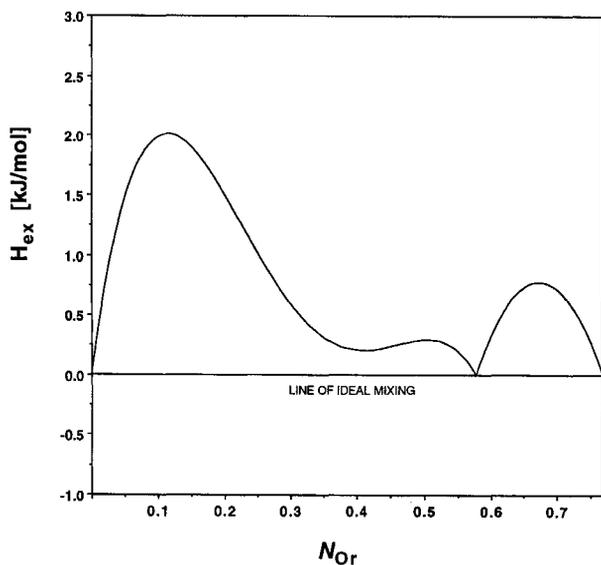


FIGURE 8. Enthalpies of K-Na mixing resulting from analysis of the calorimetric data as two separate series, with an intermediate end-member at  $N_{Or} = 0.578$ .

tive heats of mixing. However, data near the sodic end of the series, especially at  $N_{Or} = 0.127$ , are missed badly by the resulting curve. That factor and the very high precision of data for the three calorimetric experiments at the latter composition (note the data in Table 4) convinced us to consider higher order expressions. It is not until a fourth-order equation is used that data near the sodic end of the series are well represented. We accept this as the best representation of the data but recognize that alternate interpretations are nearly as reasonable. The resulting relationship, stated here as the negative of the enthalpies of solution ( $-H_{sol}$ ) so that the mixing coefficients reflect the positive enthalpies of mixing shown in Figure 6, is

$$-H_{sol} \text{ (kJ/mol)} = 673.63 + 12.24 N_{Or} - 173.64 N_{Or}^2 + 342.30 N_{Or}^3 - 222.62 N_{Or}^4 \quad (5)$$

valid for  $N_{Or}$  values from zero to 0.769, with a correlation coefficient of 0.991 and a standard error of  $\pm 0.50$  kJ/mol.

The enthalpies of K-Na mixing ( $H_{ex}$ ) derived from Equation 5 are expressed as

$$H_{ex} \text{ (kJ/mol)} = 32.34 N_{Or} - 173.64 N_{Or}^2 + 342.30 N_{Or}^3 - 222.62 N_{Or}^4 \quad (6)$$

The fourth-order fit to the calorimetric data produces a curve (Fig. 7) having a double maximum for the enthalpies of mixing, one that is symmetric about the compositional center of the ion-exchange series. This is a mathematical consequence of such a fit and in this case has no physical basis that relates to the minerals themselves. We had no desire, however, to utilize a fifth-order fit for a mineral series with only nine members; furthermore, the latter produced a mixing curve quite similar to that in Figure 7.

If the oligoclase ion-exchange series is treated as two separate entities, the results in detail are different. Using calorimetric data for sample 8837 for both parts of the compositional range, we fitted the enthalpies of solution for the seven most sodic members of the series as a fourth-order polynomial, and for the three most potassic members of the series as a second-order polynomial. Such a treatment produced the enthalpies of K-Na mixing shown in Figure 8, with a compositionally intermediate end-member (determined by the intersection of the two heat-of-solution curves) located at a  $N_{Or}$  value of 0.578. In this case maximum enthalpies of mixing are reduced for the potassic part of the series but are maximized at about the same magnitude and the same composition for the sodic part of the series, relative to those shown in Figure 7.

#### INTERPRETATION OF RESULTS

Regardless of the model or order of fit used to represent the new data reported here, it is clear that the presence of An component in feldspars substantially reduces excess properties associated with K-Na mixing. Maximum volumes of mixing are reduced by one-half. Maximum enthalpies of mixing reach values of 5 kJ/mol for disordered An-free feldspars (Hovis 1988; Hovis and Na-

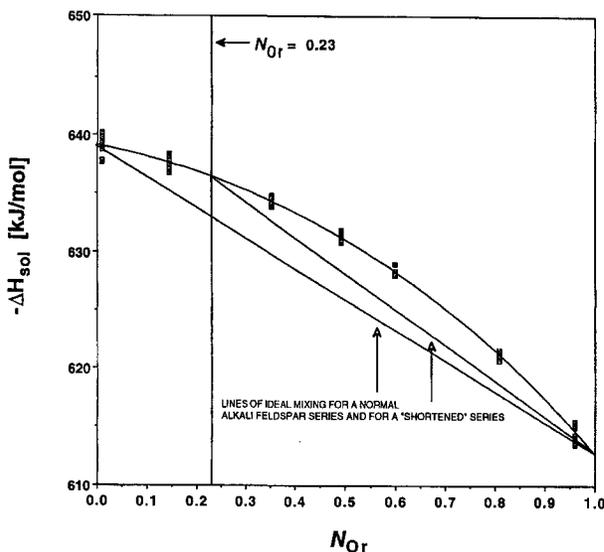


FIGURE 9. Calorimetric data from Hovis (1988) for disordered alkali feldspars. This diagram illustrates that heats of K-Na mixing are substantially reduced if data at the sodic end of the series, up to  $N_{Or} = 0.23$ , are eliminated.

vrotsky 1995) but are reduced to 2 kJ/mol for oligoclase. The physical reason for these effects is uncertain. The presence of Ca in 23% of the alkali sites perhaps provides an average occupancy for the alkali site against which the strain effects of K-for-Na substitution are substantially dampened; there are simply fewer alkali positions in which a large  $K^+$  ion is situated near a smaller  $Na^+$  or  $Ca^{+2}$  ion.

In alkali-feldspar series with near-zero An, it is instructive to note the shapes of the heat-of-solution curves (see Hovis 1988, Fig. 2). Enthalpies of solution behave more linearly at the potassic ends of most series, which would seem to imply that the substitution of Na into a pure potassium feldspar is close to ideal. The enthalpic effects of K substitution into pure sodium feldspars, however, are somewhat different. As the feldspar becomes more potassic, the energy associated with K-for-Na substitution decreases, causing the heats of solution to become curved with composition. If we eliminate the most sodic 23% of the data for such a series, mixing effects are significantly diminished (Fig. 9). In the present study it appears that CaAl mimics the effect of NaSi at the sodic end of an alkali-feldspar series. Thus, one could imagine that the most curved part of the heat-of-solution curve, from 0 to 23% An, was inaccessible during the present study.

The reason for the double maximum in the heat-of-mixing curve for this series, if it is real, is unclear. We can only surmise that it is related to the near attainment of monoclinic symmetry in the compositional region near  $N_{Or} = 0.5-0.6$ . There may be another phase transition that would account for this behavior, perhaps related to the distribution of K-Na-Ca, but detailed analysis of X-ray powder diffraction data did not reveal such a transition.

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## REFERENCES CITED

- Burnham, C.W. (1962) Lattice constant refinement. Carnegie Institution of Washington, Yearbook, 61, 132-135.
- Haselton, H.T., Jr., Hovis, G.L., Hemingway, B.S., and Robie, R.A. (1983) Calorimetric investigation of the excess entropy of mixing in analbite-sanidine solutions: Lack of evidence for Na,K short-range order and implications for two-feldspar thermometry. *American Mineralogist*, 68, 398-413.
- Hovis, G.L. (1974) A solution calorimetric and X-ray investigation of Al-Si distribution in monoclinic potassium feldspars. In W.S. MacKenzie and J. Zussman, Eds., *The feldspars*, p. 114-144. University of Manchester Press, Manchester, U.K.
- Hovis, G.L. (1986) Behavior of alkali feldspars: Crystallographic properties and characterization of composition and Al-Si distribution. *American Mineralogist*, 71, 869-890.
- Hovis, G.L. (1988) Enthalpies and volumes related to K-Na mixing and Al-Si order/disorder in alkali feldspars. *Journal of Petrology*, 29, 731-763.
- Hovis, G.L., Delbove, F., and Roll Bose, M. (1991) Gibbs energies and entropies of K-Na mixing for alkali feldspars from phase equilibrium data: Implications for feldspar solvi and short-range order. *American Mineralogist*, 76, 913-927.
- Hovis, G.L., and Roux, J. (1993) Thermodynamic mixing properties of nepheline-kalsilite crystalline solutions. *American Journal of Science*, 293, 1108-1127.
- Hovis, G.L., and Navrotsky, A. (1995) Enthalpies of mixing for disordered alkali feldspars at high temperature: A test of regular solution thermodynamic models and a comparison of hydrofluoric acid and lead borate solution calorimetric techniques. *American Mineralogist*, 80, 280-284.
- Hovis, G.L., and Graeme-Barber, A. (1997) Volumes of K-Na mixing for low albite-microcline crystalline solutions at elevated temperature: A test of regular solution thermodynamic models. *American Mineralogist*, 82, 159-165.
- Kracek, F.C., and Neuvonen, K.J. (1952) Thermochemistry of plagioclase and alkali feldspars. *American Journal of Science*, 250A (Bowen Volume), 293-318.
- Kroll, H. (1983) Lattice parameters and determinative methods for plagioclase and ternary feldspars. In *Mineralogical Society of America Reviews in Mineralogy*, 2, 101-119.
- Kroll, H., and Ribbe, P.H. (1983) Lattice parameters, composition and Al, Si order in alkali feldspars. In *Mineralogical Society of America Reviews in Mineralogy*, 2, 57-99.
- Kroll, H., Schmiemann, I., and von Cölln, G. (1986) Feldspar solid solutions. *American Mineralogist*, 71, 1-16.
- Nitkiewicz, A.M., Kerrick, D.M., and Hemingway, B.S. (1983) The effect of particle size on the enthalpy of solution of quartz: Implications for phase equilibria and solution calorimetry. *Geological Society of America Abstracts with Programs*, 15, 653.
- Robie, R.A., and Hemingway, B.S. (1972) Calorimeters for heat of solution and low-temperature heat capacity measurements. United States Geological Survey Professional Paper 755, 32 p.
- Roux, J., and Hovis, G.L. (1996) Thermodynamic mixing models for muscovite-paragonite solutions based on solution calorimetric and phase equilibrium data. *Journal of Petrology*, 37, 1241-1254.
- Stewart, D.B., and Ribbe, P.H. (1969) Structural explanation for variations in cell parameters of alkali feldspar with Al/Si ordering. *American Journal of Science*, 267A, 444-462.
- Thompson, J.B., Jr., and Hovis, G.L. (1978) Triclinic feldspars: Angular relations and the representation of feldspar series. *American Mineralogist*, 63, 981-990.
- Viswanathan, K. (1971) A new X-ray method to determine the anorthite

- content and structural state of plagioclases. *Contributions to Mineralogy and Petrology*, 30, 332–335.
- Waldbaum, D.R., and Thompson, J.B., Jr. (1968) Mixing properties of sanidine crystalline solutions: II. Calculations based on volume data. *American Mineralogist*, 53, 2000–2017.
- Waldbaum, D.R., and Robie, R.A. (1970) An internal sample container for hydrofluoric acid solution calorimetry. *Journal of Geology*, 78, 736–741.
- Waldbaum, D.R., and Robie, R.A. (1971) Calorimetric investigation of Na-K mixing and polymorphism in the alkali feldspars. *Zeitschrift für Kristallographie*, 134, 381–420.

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