Excess free energies of mixing of Sr,Ba-bearing binary feldspar solid solutions (experimental data)

A. R. KOTELNIKOV

Institute of Experimental Mineralogy Chernogolovka, Moscow distr., 142432, Russia

AND

I. V. CHERNYSHEVA

Vernadsky Institute of Geochemistry and Analytical Chemistry, Kosygin str., 19, 117975, Moscow, Russia

Abstract

The distribution of potassium and strontium, potassium and barium between feldspars and aqueous chloride solutions was studied at 700°C, 2 kbar and 800°C, 2 kbar respectively. The distribution of Sr and Ba between coexisting feldspar and chloride solutions is not ideal; Sr and Ba are enriched in feldspar relative to solution. In order to estimate the phase state of the chloride solutions, special experiments were conducted using the synthetic fluid-inclusion method in the systems $KCl-BaCl_2-H_2O$ and $KCl-SrCl_2-H_2O$ at 700–800°C, 2 kbar. It was shown that ($0.5M$ KCl+$0.5M$ $SrCl_2$) aqueous solution is homogeneous at 800°C, 2 kbar. The $0.25-0.5M$ $SrCl_2$ solutions are homogeneous at 700°C, 2 kbar. The ($0.5M$ KCl+$0.5M$ $BaCl_2$) solution is homogeneous at 700°C, 2 kbar and heterogeneous at 800°C, 2 kbar. Margules parameters for describing the excess energy of mixing of the (K,Sr)- and (K,Ba)-feldspar solid solutions were calculated. The integrated values of excess energy of mixing (G_{int}^{ex}) were estimated for the different binary feldspar solid solutions, and a correlation of G_{int}^{ex} with the crystallochemical parameter $\rho = (R_A-R_B)/D(Me-O)$ was observed. Feldspar solid solutions can be subdivided into three groups based on the relationship between G_{int}^{ex}, ρ and the stability of the solid solution.

KEYWORDS: (K,Sr) and (K,Ba) feldspar solid solutions, ion exchange equilibria, mixing properties.

Introduction

RECENT scientific studies have shown widespread isomorphic substitution between strontium, barium, sodium, potassium and calcium in natural as well as in synthetic feldspars (Bruno and Gazzoni, 1968; Gay and Roy, 1968; Sirazhiddinov et al., 1971, 1972; Nager, 1974; Bambauer et al., 1974; Schops, 1980; Viswanathan and Kielhorn, 1983; Bambauer et al., 1984; Brastad, 1985; Harneit, 1989; Viswanathan and Harneit, 1989; Pan and Fleet, 1991; Chernysheva et al., 1991). Strontium and barium distribution between feldspars and aqueous chloride solutions has been studied (Kotelnikov et al. 1987, Lagache and Dujon, 1987; Kotelnikov et al., 1989, 1990; Lagache and Catel, 1992; Kotelnikov et al., 1992, Lagache,

1993) in order to calculate excess free energies of mixing. It is now possible to find relationships between crystallochemical and energetic features of these solid solutions.

The ionic radii of the large cations in feldspar are: sodium (1.13 Å) calcium (1.07 Å) — for coordination number 7; potassium (1.55 Å), rubidium (1.63 Å) — for coordination number 9 (Shannon and Prewitt, 1969; Urusov, 1987). Chernysheva et al. (1991) have shown that ΔH_{mix} values for solid solutions of (Ca,Sr)-, (Ca,Ba)- and (Sr,Ba)-feldspars depend on the differences of ionic radii of the substituting elements.

The goal of this study is to examine the relationships between excess energies of mixing and crystallochemical properties of the binary

TABLE 1. Compositions of starting material (feldspars and glass)

Oxides or element	Chemical composition					
	1	2	3	4	5	6
Na_2O	0.15(20)	0.00	0.00	0.00	0.00	0.00
K_2O	17.13(33)	14.71(11)	12.11(19)	11.68(30)	7.20(23)	3.68(15)
SrO	–	2.17(39)	8.98(30)	–	–	–
BaO	–	–	–	12.65(24)	23.58(41)	32.84(34)
Al_2O_3	17.80(21)	19.81(22)	21.99(20)	21.05(40)	23.40(51)	25.30(34)
SiO_2	64.55(52)	62.44(71)	56.95(34)	54.50(82)	46.12(38)	38.69(71)
Total	99.63	99.13	100.03	99.88	100.30	100.51
Na	0.01	0.00	0.00	0.00	0.00	0.00
K	1.02	0.88	0.75	0.75	0.50	0.27
Sr	–	0.06	0.25	–	–	–
Ba	–	–	–	0.25	0.50	0.75
Al	0.97	1.09	1.25	1.25	1.49	1.73
Si	3.01	2.94	2.75	2.75	2.51	2.25
O	8.00	8.00	8.00	8.00	8.00	8.00
Ab	1.00	–	–	–	–	–
Ort	99.0	93.6	75.0	75.0	50.0	26.5
Sr-Fsp	–	6.4	25.0	–	–	–
Cn	–	–	–	25.0	50.0	73.5

(1) Enriched in potassium orthoclase ($Na_{0.01}K_{1.02}Al_{0.97}Si_{3.01}O_8$); (2) (K,Sr)-glass ($K_{0.88}Sr_{0.06}Al_{1.09}Si_{2.94}O_{0.8}$); (3) synthetic (K,Sr)-feldspar ($K_{0.75}Sr_{0.25}Al_{1.25}Si_{2.75}O_8$); (4–6) synthetic glass of the (K,Ba)-feldspars, (4) $K_{0.75}Ba_{0.25}Al_{1.25}Si_{2.74}O_8$, (5) $K_{0.5}Ba_{0.5}Al_{1.49}Si_{2.5}O_8$, (6) $K_{0.27}Ba_{0.75}Al_{1.73}Si_{2.25}O_8$.

Compositions were determined by electron microprobe analysis and recalculated to 8 oxygen atoms. Standard errors are given in parenthesis and refer to the last decimal place(s).

feldspar solid solutions. We have correlated the values of excess energies of mixing with the relative differences between ionic radii of the substituting elements and the parameter of adaptability of the substituting ion in the mineral (Iiyama, 1972) for Sr,Ba-bearing feldspars with heterovalent substitutions (systems: Na–Sr, K–Sr, K–Ba and others) and with isovalent substitutions (systems: Ca–Sr, Ca–Ba, Sr–Ba and others). The cation-exchange reaction data were used to calculate excess free energies of mixing.

Experimental procedure

Starting materials. The starting materials used were: (1) natural orthoclase enriched in potassium by treatment in KCl melt at 900°C (duration 3 days); (2) synthetic glass of (K,Sr)- and (K,Ba)-feldspar composition prepared by melting pure oxide mixtures in graphite crucibles at 1700°C; (3) a few samples of (K,Sr)-feldspars prepared hydrothermally from gel mixtures at 700°C and P=1 kbar (duration 10

days). Compositions of the starting materials are presented in Table 1. Experiments carried out under the same $P–T$ conditions with different starting materials have led to similar results (Table 3, 4). We used 0.25 M to 1.0 M (K,Sr)- and (K,Ba)-chloride solutions for the cation exchange experiments.

State of fluid. Fluid unmixing in the system NaCl–$BaCl_2$–H_2O at 800°C, 2 kbar was detected by Kotelnikov et al. (1990) by the method of synthetic fluid inclusion. It was demonstrated that the chloride solution separates into two phases at mole fraction of Ba in fluid X_{Ba} =Ba/(Ba+Na)>0.37. Immiscibility of water salt solutions (1 M KCl + 1 M $BaCl_2$) and (1 M NaCl + 1 M $BaCl_2$) at 600°C, 1.5 kbar and 750°C, 2 kbar was detected by Lagache (1993). We have no information about the state of fluid in the system KCl–$SrCl_2$–H_2O.

In order to examine the phase state of fluid in the system KCl–$BaCl_2$–H_2O and KCl–$SrCl_2$–H_2O, special experiments were conducted by the synthetic fluid inclusions method. The results of these experiments are presented in the Table 2(a,b).

TABLE 2a. Results of the experiments. The state of fluid phase in the system $KCl+BaCl_2+H_2O$ at 700, 800°C and 2 kbar

Initial chloride solution	Mole fraction of Ba[1]	Type of synthetic fluid inclusions[2]	State of fluid[3]
		700°C	
0.5M KCl	0.0	G + L	Hom
0.5M KCl+0.5MBaCl₂	0.25	G + L	Hom
0.5M KCl+0.5MBaCl₂	0.50	G + L	Hom
0.5M BaCl₂	1.0	G + L	Hom
		800°C	
0.25M BaCl₂	1.0	G + L, G + L + S	Het
0.5M BaCl₂	1.0	G + L, G + L + S	Het
0.75M BaCl₂	1.0	G + L, G + L + S	Het
1.0M BaCl₂	1.0	G + L, G + L + S	Het
0.5M KCl+0.5MBaCl₂	0.50	G + L, G + L + S	Het
0.5M KCl+0.5MBaCl₂	0.75	G + L, G + L + S	Het

[1] Mole fraction of Ba: $X_{Ba} = Ba/(Ba+K)$
[2] G – gaseous phase, L – liquid phase, S – solid phase
[3] Hom – homogeneous, Het – heterogeneous state of fluid

The KCl+BaCl₂ chloride solution. The wide spread field of fluid unmixing exists at 800°C, 2 kbar in 0.5 *M* chloride solutions. Even in 0.25 M BaCl₂ we have detected evidence of immiscibility. We may suppose that 0.5 *M* chloride solutions in the system KCl + BaCl₂ + H₂O separate at 800°C and 2 kbar into vapour and brine phases which correspond to (G + L) and (G + L + S) types of synthetic fluid inclusions (Table 2a). We have not found any evidence of immiscibility in the 0.5 *M* chloride solution at 700°C, 2 kbar — all synthetic fluid inclusions are present as (G + L) type.

The KCl + SrCl₂ chloride solution. A homogeneous fluid in the system KCl–SrCl₂ (*0.5M*

TABLE 2b. Results of the experiments. The state of fluid phase in the system KCl + SrCl₂ + H₂O at 700, 800°C and 2 kbar

Initial chloride solution	Mole fraction of Sr[1]	Type of synthetic fluid inclusions[2]	State of fluid[3]
		700°C	
0.25M SrCl₂	1.0	G + L	Hom
0.5M SrCl₂	1.0	G + L	Hom
		800°C	
0.5M KCl	0.0	G + L	Hom
0.5M KCl+0.5M SrCl₂	0.25	G + L	Hom
0.5M KCl+0.5M SrCl₂	0.50	G + L	Hom
0.5M KCl+0.5M SrCl₂	0.75	G + L	Hom

[1] Mole fraction of Sr: $X_{Sr} = Sr/(Sr+K)$
[2] G – gaseous phase, L – liquid phase, S – solid phase
[3] Hom – homogeneous, Het – heterogeneous state of fluid.

TABLE 3. Conditions and results of experiments on cation-exchange reactions between (K,Sr)-feldspars and chloride solutions (700°C; 2 kbar)

Run number	Starting materials			Run time (days)	Run products			$\ln K_D$
		X_{Sr}^{Fsp}	X_{Sr}^{fl}	M^1		X_{Sr}^{Fsp2}	X_{Sr}^{Fsp3}	X_{Sr}^{fl}	
4073	gl[4]	0.06	0.05	1.0	33	0.09(2) (0.095)[5]	–	0.022	1.55
4072	cr	0.25	0.04	1.0	33	0.20(3)	0.18	0.050	1.73
2882	cr	0.00	0.60	0.5	20	0.32(3)	0.32	0.065	2.23
4067	gl	0.06	0.40	1.0	33	0.38(4) (0.39)	0.38	0.090	2.21
2881	cr	0.00	0.80	0.5	20	0.43(3)	0.45	0.095	2.43
4068	gl	0.06	0.50	1.0	33	0.48(3)	0.49	0.120	2.44
4069	gl	0.06	0.60	1.0	33	0.62(3) (0.64)	0.66	0.144	3.08
3239	cr	0.00	0.90	0.5	21	0.76(3)	0.72	0.210	3.67
3221	cr	0.25	1.00	0.5	28	0.96(3)	0.95	0.650	4.72

[1] Molarity of aqueous chloride solutions.
[2] Standard errors are given in parenthesis and refer to the last decimal place.
[3] Composition estimated from $\overline{2}01$ peak position.
[4] Initial material: gl – glass; cr – crystal.
[5] Total compositions of (K,Sr)-feldspars estimated by microprobe analysis of the Li-metaborate glasses (runs 4073, 4067, 4069).

solution) exists at 800°C, 2 kbar. At 700°C, 2 kbar we studied the part of the system H_2O–$SrCl_2$ (0.25–0.5 M solutions), but found no evidence of fluid unmixing. We suppose that fluid in the system KCl–$SrCl_2$–H_2O (0.5–1.0 M chloride solution) is homogeneous at 700°C, 2 kbar because: (1) the binary systems KCl–H_2O and $SrCl_2$–H_2O are homogeneous at these conditions; (2) the ternary system KCl–$SrCl_2$–H_2O is homogeneous at 800°C and 2 kbar; (3) the fluid unmixing usually decreases with decreasing temperature; (4) no evidence of unmixing of fluid (1 M KCl + 1 M $SrCl_2$) was observed by Lagache (1990) at 750°C and 2 kbar.

Experimental. The charges (about 100 mg) with different starting compositions of aqueous chloride (250–300 μl) solutions were sealed in platinum capsules (diameter 0.5 cm). Cold seal vertical reactor devices were used for most of the experiments. The reactors were calibrated using an internal thermocouple (accuracy ± 3°C). Pressure was controlled by Bourdon tube gauges (uncertainty ± 50 bar). The experiments were performed at 700 and 800°C, 2 kbar. Run duration depended on the temperature and varied from 14 to 33 days. After the runs, reactants were quenched by compressed air and water-flow to freeze the cation distributions.

Measurement. The solid phase was separated from the solution for analysis by microprobe (solids) and by atomic absorption spectrometry (AAS) and

inductively coupled plasma (ICP) atomic emission spectrometry (solutions). The feldspar compositions were determined by electron microprobe 'Camebax' with energy-dispersive spectrometer 'Link 860/500' and WD-spectrometers. The accelerating voltage was 15–20 kV, and natural sanidine, albite, celestine and baryte were used as standards. These measurements were ZAF-corrected. The sizes of synthesized feldspar crystals were 20–30 μm. The number of microprobe analyses for each specimen was at least 15–20. The precision of the determination of each element is not worse than ± 2–5 rel.%, and precision of mole fraction calculation is accordingly 3.5 mol.%. For some runs the specimens were divided into two parts, one of which was studied in the usual way with microprobe. The second part was melted with lithium metaborate in a 1:3 ratio. The glass was also analysed by microprobe in order to determine the total composition of feldspar. As a rule, the composition of the feldspar grains coincided with the composition of the glass within the margins of error. Estimated uncertainty of the solution analyses is not worse than 3 rel.% (precision of mole fraction calculation is 3.0 mol.%).

X-ray powder diffraction was used for phase identification in order to examine what phases crystallized during the experiments. We have not detected any phase other than feldspar and quartz in run products. X-ray powder photographs of the

feldspar products using Guinier-Jagodzinski technique (Ge-monochromator: Cu-$K\alpha_1$ λ = 1.5405981 Å) were obtained and then scanned with an automatic densitometer system, GUFI (Dinnebier, 1989). Peak positions were corrected with an internal Si standard and could be determined to $\pm$ 0.01°(2θ). We have calculated unit cell parameters with the least squares algorithm of Burnham (1962, 1991).

The (K,Sr)-feldspar series. Lagache (1990) has shown that it is possible to determine the composition of (K,Sr)-feldspars from the peak position of the $\bar{2}01$ reflection. We have used this calibration curve to estimate the (K,Sr)-feldspar composition. Results are presented in Table 3.

The (K,Ba)-feldspar series. Harneit (1989) has synthesized (K,Ba)-feldspar solid solutions and has determined their unit cell parameters. We have used the compositional dependence of the beta angle and unit cell volume of Harneit (1989) to estimate feldspar composition (Table 4). Microprobe analysis of (K,Sr)- and (K,Ba)-feldspar solid solutions corresponded to the estimate obtained from the X-ray procedure.

Calculation of the excess energies of mixing. The ideal mixing model for fluids and a two parameter subregular Margules model for feldspar solid solutions were selected. For the cation exchange reaction:

$$2NaAlSi_3O_8 + CaCl_2 =$$
$$CaAl_2Si_2O_8 + 2NaCl + 4SiO_2 \quad (1)$$
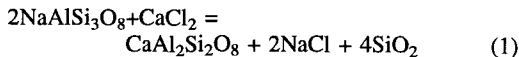
the equilibrium constant may be expressed as:

$$K = \frac{X_{An}f_{An}(X_{NaCl})^2(aSiO_2)^4}{(X_{Ab}f_{Ab})^2 X_{CaCl_2}} \quad (2)$$

$$RT\ln K = -\Delta G \quad (3)$$

We describe activity coefficients in the terms of the two-parameter. Margules model:

$$RT\ln f_{Ab} = \{(X_{An}^2)\}\,[W1+2(1-X_{An})(W2-W1)] \quad (4)$$

$$RT\ln f_{An} = \{(1-X_{An})^2\}\,[W2+2X_{An}(W1-W2)] \quad (5)$$

Using equations (3)–(5) we transformed expression (2) to:

$$RT\ln K = RT\ln K_D + (1-X_{An})^2$$
$$[W2+2X_{An}(W1-W2)]-2(X_{An}^2)$$
$$[W1+2(1-X_{An})(W2-W1)] \quad (6)$$

$$RT\ln K_D + (1-X_{An}^2)[W2+2X_{An}(W1-W2)]$$
$$-2(X_{An}^2)[W1+2(1-X_{An})(W2-W1)]+\Delta G=0 \quad (7)$$

Equation (7) was used to calculate Margules parameters by a least squares method. Average

Table 4 Conditions and results of experiments on cation-exchange reactions between (K,Ba)-feldspars and chloride solutions (800°C; 2 kbar)

Run number	Starting materials				Run time (days)	Run products		$\ln K_D$
		X_{Ba}^{Fsp}	X_{Ba}^{fl}	M^1		X_{Ba}^{Fsp}	X_{Ba}^{fl}	
i2820	cr[2]	0.00	1.00	0.25	15	0.32(3)[3] 0.29[4]	0.045	2.64
i2821	cr	0.00	0.25	0.25	15	0.06(2) 0.07[4]	0.004	2.82
i2822	cr	0.00	0.5	0.25	14	0.15(3)	0.010	3.01
i2823	cr	0.00	0.75	0.25	14	0.23(3)	0.020	2.92
3001	cr	0.00	1.00	0.5	30	0.59(4) (0.55)[5]	0.150	2.83
3002	gl	0.25	1.00	0.5	30	0.84(3)	0.360	3.62
3003	gl	0.50	1.00	0.5	30	0.94(4)	0.550	4.57
3004	gl	0.73	1.00	0.5	30	0.96(3) (0.95)[5]	0.730	4.09
3005	cr	0.00	0.50	0.5	30	0.37(3) (0.34)[5]	0.040	3.07

[1] Molarity of aqueous chloride solutions.
[2] Initial material: gl – glass; cr – crystal.
[3] Standard errors are given in parenthesis and refer to the last decimal place.
[4] (K,Ba)-feldspar composition determined from X-ray data.
[5] Total compositions of (K,Ba)-feldspars estimated by microprobe analysis of the Li-metaborate glasses (runs 3001, 3004, 3005).

errors for the Margules parameters were estimated by least squares method; they were not worse than 15 rel.% (for 95% confidence interval). For the feldspar solid solution with an immiscibility gap, Margules parameters were calculated using the compositions of coexisting phases (I and II) according to the following procedure: under equilibrium conditions:

$$\mu_{Ca}^{I} = \mu_{Ca}^{II} \qquad (8)$$

$$\mu_{Na}^{I} = \mu_{Na}^{II} \qquad (9)$$

$$\mu_{Ca}^{I} = \mu_{Ca}^{0} + RT\ln(a_{Ca}^{I}) \qquad (10)$$

$$\mu_{Ca}^{II} = \mu_{Ca}^{0} + RT\ln(a_{Ca}^{II}) \qquad (11)$$

$$\mu_{Na}^{I} = \mu_{Na}^{0} + RT\ln(a_{Na}^{I}) \qquad (12)$$

$$\mu_{Na}^{II} = \mu_{Na}^{0} + RT\ln(a_{Na}^{II}) \qquad (13)$$

From equation (8)–(13) we obtain the following expressions:

$$RT\ln(X_{Ca}^{I}) + RT\ln(f_{Ca}^{I}) = $$
$$RT\ln(X_{Ca}^{II}) + RT\ln(f_{Ca}^{II}) \qquad (14)$$

$$RT\ln(X_{Na}^{I}) + RT\ln(f_{Na}^{I}) = $$
$$RT\ln(X_{Na}^{II}) + RT\ln(f_{Na}^{II}) \qquad (15)$$

Using equations (4), (5) for the compositional dependence of the activity coefficients, we transformed expressions (14), (15) to:

$$RT\ln\left(\frac{X_{Ca}^{I}}{X_{Ca}^{II}}\right) = (1 - X_{Ca}^{II})^2[W2 + 2X_{Ca}^{II}(W1 - W2)]$$
$$- (1 - X_{Ca}^{I})^2[W2 + 2X_{Ca}^{I}(W1 - W2)] \qquad (16)$$

$$RT\ln\left(\frac{1 - X_{Ca}^{I}}{1 - X_{Ca}^{II}}\right) = (X_{Ca}^{II})^2[W1 + 2(1 - X_{Ca}^{II})(W2 - W1)]$$
$$- (X_{Ca}^{I})^2[W1 + 2(1 - X_{Ca}^{I})(W2 - W1)] \qquad (17)$$

We have calculated Margules parameters (W1, W2) by simultaneous solution of these equations (16–17).

Results

New experiments

(K,Sr)-feldspars. Lagache (1990) studied the cation exchange reaction between feldspar and aqueous chloride solutions at 600°C, 1.5 kbar and at 750°C, 2 kbar:

$$2KAlSi_3O_8 + SrCl_2 = $$
$$SrAl_2Si_2O_8 + 4SiO_2 + 2KCl \qquad (18)$$
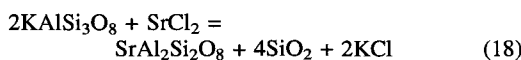
Monoclinic (K,Sr)-feldspar solid solutions were obtained (Lagache, 1990). We have studied the forward direction of the reaction (18) at 700°C, $P = 2$ kbar, since a cation exchange reaction in this direction is more rapid than in the opposite case (Orville, 1972). Experiments performed with different run durations (20 and 33 days) led to identical results; therefore it is assumed that 20 days is sufficient for the attainment of a steady state at 700°C, 2 kbar.

Lagache (1990) has not detected evidence of fluid unmixing in cation exchange studies between (K,Sr)-feldspars and chloride solutions at 750°C and $P = 2$ kbar. Our data on synthetic fluid inclusions have indicated a homogeneous state of fluid at 700°C, 2 kbar. The experiments, performed under the same conditions, starting with different chloride solution concentrations led to identical results (Table 3). All these facts confirm the ideality of the fluid phase at the run conditions.

The experimental results are presented in Table 3 and on Fig. 1. Strontium is enriched in feldspars relative to the coexisting solutions as well as at 750°C, 2 kbar, Lagache, (1990). The distribution coefficient (K_D) is calculated according to the equation:

$$K_D = \frac{X_{Sr}^{Fsp}(1 - X_{Sr}^{fl})^2}{(1 - X_{Sr}^{Fsp})X_{Sr}^{fl}} \qquad (19)$$

where X_{Sr}^{Fsp} = mole fraction of Sr in feldspar, and X_{Sr}^{fl} that of Sr in fluid. Strontium distribution between fluid and feldspar is not ideal. The $\ln K_D$ values show a quadratic dependence on the composition (Fig. 2):
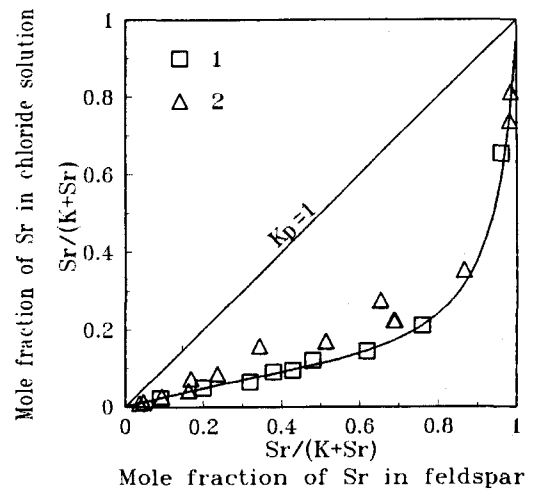

FIG. 1. Distribution of K and Sr between feldspar and aqueous chloride solution: (1) — our data at 700°C, 2 kbar; (2) — data of Lagache (1990) at 750°C, 2 kbar.

$$\ln K_D = 1.438 + 1.251 X_{Sr}^{Fsp} + 2.241 (X_{Sr}^{Fsp})^2$$

$$\text{(s.e.e.=0.15)} \qquad (20)$$

where s.e.e. is the standard error of estimation, s.e.e.= $(St_{\alpha,n})/\sqrt{n}$, with S as the standard deviation, $t_{\alpha,n}$ as the Student criterion (for 95% probability usually), and n as the number of experiments. The results of these calculations have shown that the excess free energy of mixing is described by the Margules two-parameter equation:

$$G_{mix}^{ex} = X_{Sr}^{Fsp}(1-X_{Sr}^{Fsp})[X_{Sr}^{Fsp}W1 + (1-X_{Sr}^{Fsp})W2]$$

$$(21)$$

where W1 = 11.1 kJ/mol, W2 = 8.5 kJ/mol. The Margules parameters calculated with data by Lagache (1990) are: W1=13.13, W2=8.39 kJ/mol (750°C, 2 kbar).

(K,Ba)-feldspars. Gay and Roy (1968) synthesized crystals of a continuous solid solution at 500−700°C and refined unit cell parameters of (K,Ba)-feldspars. Later, Harneit (1989) made more precise determination of the unit cell parameters of (K,Ba)-feldspars. Lagache (1993) studied the K,Ba partition between feldspars and aqueous chloride solutions at 600 and 750°C, 1.5 to 2.5 kbar. Immiscibility in 1 M (K,Ba)-chloride solution was demonstrated at 600°C, 1.5 kbar at 750°C, 2.0 kbar, and its influence on the K,Ba partition has been observed. We have observed fluid unmixing at 800°C, 2 kbar in 0.5 M (KCl+BaCl$_2$) and a homogeneous state of this

chloride solution at 700°C, 2 kbar. We studied the following cation exchange reaction under hydrothermal conditions at 800°C, 2 kbar:

$$2KAlSi_3O_8 + BaCl_2 =$$
$$BaAl_2Si_2O_8 + 4SiO_2 + 2KCl \qquad (22)$$
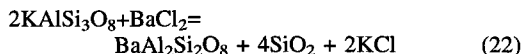
The run conditions and experimental results are presented in Table 4 and in Fig. 3. The shape of the isotherm of K,Ba-distribution does not indicate fluid immiscibility, in contrast with the data of Lagache (1993) at 750°C, 2 kbar. Our experiments were performed with 0.25–0.5 molar chloride solutions, instead of 1 M (KCl + BaCl$_2$) in the experiments of Lagache (1993), to avoid the fluid unmixing. Dujon and Lagache (1986, 1987) have shown that the exchange reactions occur mainly with the brine phase of the unmixed fluid. A low ratio k = (mass of the feldspar)/(mass of the solution)<0.2 led to reaction predominantly between the (K,Ba)-feldspar and the brine phase in our experiments. Possibly we have not detected the influence of the vapour phase on the compositions of coexisting feldspars and fluid. We have observed the same results for the system (Na,Ba)-feldspar–NaCl–BaCl$_2$–H$_2$O at 800°C, 2 kbar (Kotelnikov *et al.*, 1990).

Barium is enriched in the feldspars relative to the coexisting solution at 800°C. (K,Ba)-distribution between feldspar and solution is not ideal. The compositional dependence of the distribution coefficient ($\ln K_D$) is described by a cubic equation (Fig.4):
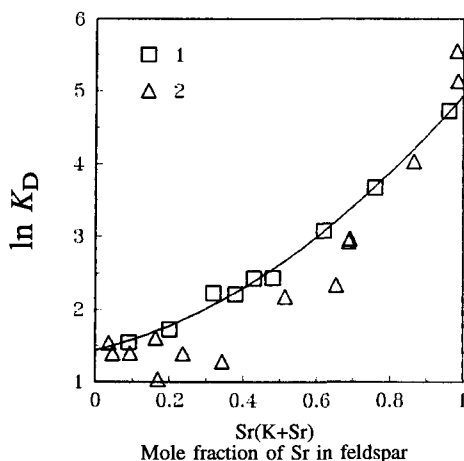

FIG. 2. Dependence of the Sr distribution coefficient ($\ln K_D$) on (K,Sr)-feldspar composition: (1) — our data at 700°C, 2 kbar; (2) — data of Lagache (1990) at750°C, 2 kbar.
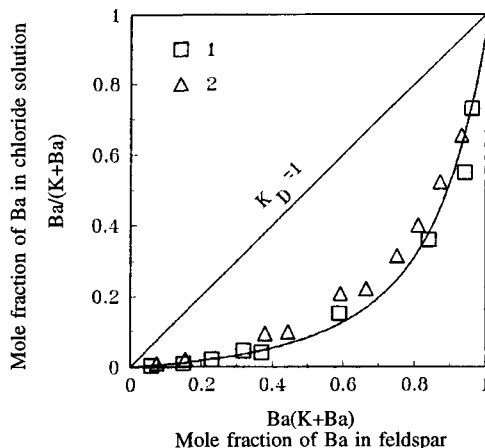
FIG. 3. Distribution of K and Ba between feldspar and aqueous chloride solution: (1) — our data at 800°C, 2 kbar; (2) — data of Lagache (1993) at 750°C, 2.5 kbar.

$$\ln K_D = 2.806 + 1.502X_{Ba}^{Fsp} - 6.115(X_{Ba}^{Fsp})^2$$
$$+ 6.528(X_{Ba}^{Fsp})^3 \qquad \text{(s.e.e.} = 0.32) \qquad (23)$$

From the data of Lagache (1993) $\ln K_D$ is described by a cubic equation also (Fig.4):

$$\ln K_D = 2.115 + 0.826X_{Ba}^{Fsp} - 2.032(X_{Ba}^{Fsp})^2$$
$$+ 2.973(X_{Ba}^{Fsp})^3 \qquad \text{(s.e.e.=0.12)} \qquad (24)$$

Evidence for the unmixing of fluid at 800°C and 2 kbar in our experiments was considered and Margules parameters for the (K,Ba)-feldspar solid solution were estimated from the data of Lagache (1993), using equation (24): Wl = 4.30 and W2 = 2.52 kJ/mol.

Published data

(Na,Sr)-feldspars. The existence of continuous solid solutions between $NaAlSi_3O_8$ and $SrAl_2Si_2O_8$ at 700–1100°C was shown by Schops (1980) and Bambauer *et al.* (1984). The transition from the triclinic albite structure to the monoclinic celsian structure takes place at at room temperature (Bambauer *et al.*, 1984). The cation exchange reaction between feldspar and aqueous chloride solution
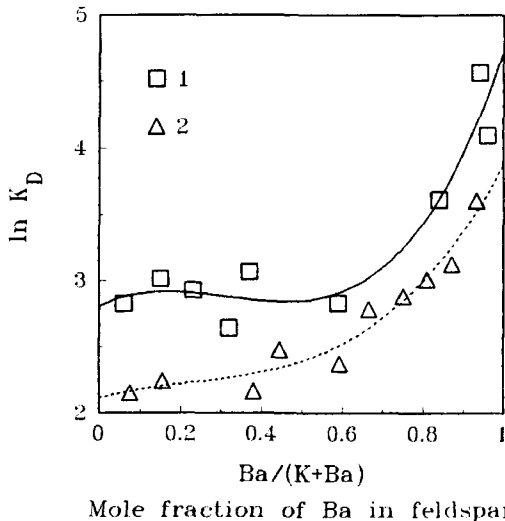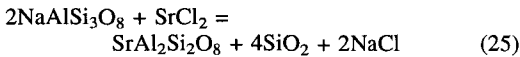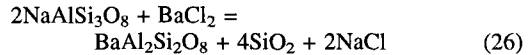
$$2NaAlSi_3O_8 + SrCl_2 =$$
$$SrAl_2Si_2O_8 + 4SiO_2 + 2NaCl \qquad (25)$$

was studied by Lagache and Dujon (1987) and Kotelnikov *et al.* (1987). Strontium is enriched in feldspar relative to solution at 600–800°C. Strontium distribution between fluid and feldspar is not ideal. There is no temperature dependence of the distribution coefficient ($\ln K_D$) (Fig. 5). We used all the experimental data (Lagache and Dujon, 1987; Kotelnikov *et al.*, 1987) to calculate the excess mixing energy parameters. Margules parameters calculated for the binary (Na,Sr)-feldspar solid solutions are: W1 = 11.79 and W2 = 0.89 kJ/mol (600–800°C, 1.5–2 kbar).

(Na,Ba)-feldspars. (Na,Ba)-feldspar solid solutions were studied by Rudert (1972), whose data indicated the existence of a large immiscibility field. Viswanathan and Harneit (1989) and Lagache and Catel (1992) observed immiscibility only near the albite end-member. The coexisting feldspar phases were detected up to 750°C (Lagache and Catel, 1992) and up to 850°C (Viswanathan and Harneit, 1989). The cation exchange reaction between feldspar and chloride solutions at 800°C, 2 kbar:

$$2NaAlSi_3O_8 + BaCl_2 =$$
$$BaAl_2Si_2O_8 + 4SiO_2 + 2NaCl \qquad (26)$$

was studied by Kotelnikov *et al.* (1990). Continuous solid solutions of (Na,Ba)-feldspars were synthesized and no evidence of unmixing was observed. We

FIG. 4. Dependence of the Ba distribution coefficient ($\ln K_D$) on (K,Ba)-feldspar composition: (1) — our data at 800°C, 2 kbar; (2) — data of Lagache (1993) at 750°C, 2.5 kbar.
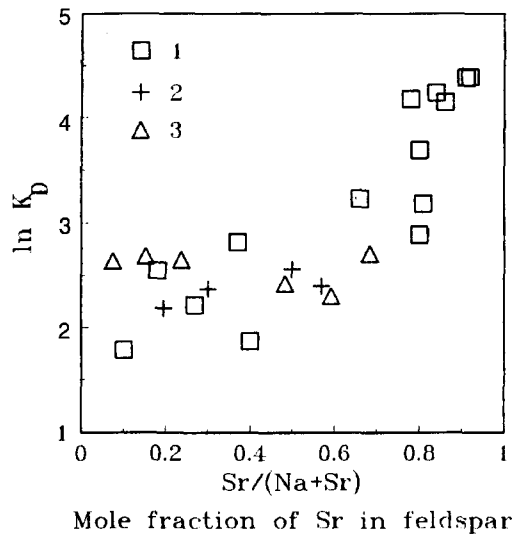

FIG. 5. Dependence of the Sr distribution coefficient ($\ln K_D$) on (Na,Sr)-feldspar composition: (1) — data of Kotelnikov *et al.* (1987) at 800°C, 2 kbar; (2) — data of Lagache and Dujon (1987) at 600°C, 1.5 kbar; (3) — data of Lagache and Dujon (1987) at 750°C, 2 kbar.

calculated Margules parameters using cation exchange data (Kotelnikov *et al.*, 1990): W1 = 12.55 and W2 = 16.51 kJ/mol.

(Ca,Sr)-feldspars. Solid solutions of (Ca,Sr)-feldspars have been studied by Nager *et al.* (1970), Sirazhiddinov *et al.* (1971), and Nager (1974). The (Ca,Sr)-feldspar solid solution has triclinic–monoclinic transition (from anorthite type to celsian type structure). McGuinn and Redfern (1993) have determined more precisely the position of the triclinic- monoclinic transition in (Ca,Sr)-feldspar solid solution; at room temperature it occurs at $Ca_{0.09}Sr_{0.91}Al_2Si_2O_8$ and the transition temperature increases with increasing of Ca-content. The distribution of Ca,Sr between feldspar and chloride solution was studied at 600, 750°C and P = 1.5, 2.0 kbar (Lagache and Dujon, 1987) and at 700°C, 1 kbar; 800–900°C, 2 kbar (Kotelnikov *et al.*, 1989) under hydrothermal conditions. At 950 and 1000°C the Ca,Sr distribution between feldspar and molten $CaCl_2$ + $SrCl_2$ was studied in (Kotelnikov *et al.*, 1989). The following cation exchange reaction was studied:

$$CaAl_2Si_2O_8 + SrCl_2 = SrAl_2Si_2O_8 + CaCl_2 \qquad (27)$$

The rates of forward and reverse reactions are approximately equal for feldspars with isovalent substitutions (Zyryanov, 1981). This allows equilibrium to be approached from both sides. The Ca,Sr distribution between feldspar is not ideal. With the available experimental data (Lagache and Dujon 1987; Kotelnikov *et al.*, 1989) it is possible to

calculate the effect of temperature on the Margules parameters:

$$W1 = W2 = 64.852 - 0.0473T(K)$$
$$(s.e.e. = 1.9 \text{ kJ/mol}) \qquad (28)$$

The temperature dependence of parameters W1 = W2 is shown in Fig. 6. From equation (28) values of the Margules parameters at 800°C are: W1 = W2 = 14.09 kJ/mol. Calculated from cation-exchange data at 800°C, the Margules parameters are: W1 = W2 = 15.97 kJ/mol.

(Ca,Ba)-feldspars. The difference between the ionic radii of Ca and Ba is too large (0.42 Å) to allow a homogeneous solid solution to form. Bambauer *et al.* (1974) reported limiting compositions for the miscibility gap at 1450°C (25 mol.% of anorthite in celsian) and at 1500°C (30 mol.% of anorthite in celsian). Later the immiscibility gap was determined at 1200–1450°C by Chernysheva *et al.* (1991). A sharp asymmetry is observed in the extent of solid solution — a relatively wide region of solid solution near celsian and a narrow range near anorthite. Thus, at 1350°C the compositions $Ca_{0.95}Ba_{0.05}Al_2Si_2O_8$ and $Ca_{0.2}Ba_{0.8}Al_2Si_2O_8$ coexist. We have studied the cation exchange reaction:

$$CaAl_2Si_2O_8 + BaCl_2 = BaAl_2Si_2O_8 + CaCl_2 \qquad (29)$$
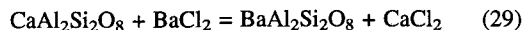
at 700, 900°C and 2 kbar. Our data are plotted along with others (Bambauer *et al.*, 1974; Chernysheva *et al.*, 1991) in Fig. 7. All experimental data and
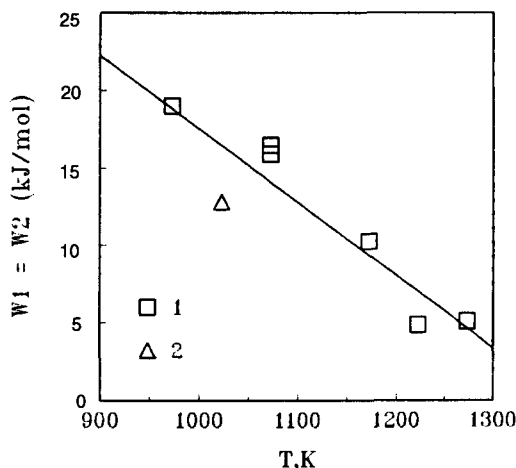

FIG. 6. The temperature dependence of the Margules parameters (W1 = W2) for (Ca,Sr)-feldspar solid solutions: (1) — data of Kotelnikov *et al.*, (1989); (2) — data of Lagache and Dujon (1987).
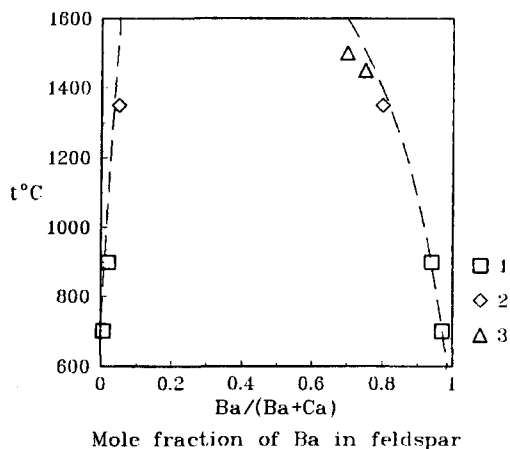
FIG. 7. The immiscibility gap of (Ca,Ba)-feldspar solid solution: (1) — our data; (2) — data of Chernysheva *et al.* (1991); (3) — data of Bambauer *et al.* (1974). Dotted lines calculated after Urusov (1977).

theoretical data were used to calculate Margules parameters from the solvus position. At 800°C W1 = 31.00, W2 = 41.02 kJ/mol.

(*Sr,Ba*)-*feldspar*. Feldspar solid solutions in this system were studied by Nager (1974) and later at 1300°C by Chernysheva *et al.* (1991) by the method of solid state reactions. Continuous solid solutions were observed at 1300°C. (Sr,Ba)-feldspars along with (Sr,Ba)-carbonates and aqueous chloride solutions were studied by Kotelnikov *et al.* (1992). Our data confirm the existence of continuous solid solutions in (Sr,Ba)-feldspars. However, the Sr,Ba distribution between feldspar and chloride solution is not ideal. The Margules parameters were calculated using cation-exchange equilibria data: W1 = W2 = 9.23 kJ/mol (800°C, 2 kbar).

Discussion

The calculated Margules parameters and the difference between ionic radii of substituting elements are presented in Table 5. We added to Table 5 data for (Na,Ca)-, (Na,K)- and (K,Ca)-

feldspar solid solutions. The calculated Margules parameters for plagioclases are consistent with all accessible experimental data given by Aranovich and Podlesskii (1989) and Perchuk *et al.* (1990). The data of Schliestedt and Johannes (l990) are also included in Table 5. For (Na,K)-feldspar (high albite-sanidine) we calculated W1 and W2 parameters based on cation-exchange reactions between alkaline feldspar solid solution and molten KCl + NaCl (Zyryanov, 1981). We estimated W1 and W2 parameters of (K,Ca)-feldspar based on the solvus position at different temperatures from data by Lagache (1988). The values of excess mixing energies at 650°C for (Na,Rb)- and (K,Rb)-feldspar solid solutions were estimated by Lagache (1984). We calculated the Margules parameters from these data (Table 5), and used integrated excess energy of mixing to compare energetic parameters of the different solid solutions (Kotelnikov *et al.*, 1990; Kotelnikov and Chernysheva, 1993):

$$G_{int}^{ex} = \int_0^1 (G_{int}^{ex}) dX \qquad (30)$$

TABLE 5. Crystallochemical and energetic parameters of the feldspar solid solutions

	ΔR^1 Å	$W1^2$ kJ/mol	W2 kJ/mol	ρ^3	$G_{int}^{ex\,4}$ kJ/mol	$T(°C)$	Reference
			Heterovalence type of isomorphic substitution				
K–Ca	0.48	29.11	24.01	0.163	4.43	750	Lagache, 1988
K–Sr	0.24	11.10	4.50	0.080	1.63	700	This work
K–Ba	0.08	4.30	2.52	0.027	0.60	750	Lagache, 1993
Na–Ca	0.06	11.31	1.43	0.021	1.06	800	Perchuk *et al.*, 1990
Na–Ca	0.06	6.59	1.51	0.021	0.67	700	Schliestedt and Johannes, 1990
Na–Sr	0.18	11.79	0.89	0.060	1.05	800	Lagache and Dujon, 1987; Kotelnikov *et al.*, 1987
Na–Ba	0.34	12.55	16.51	0.118	2.42	800	Kotelnikov *et al.*, 1990
			Isovalence type of isomorphic substitution				
Ca–Sr	0.25	15.97	15.97	0.099	2.66	800	Kotelnikov *et al.*, 1989
Ca–Ba	0.41	31.00	41.02	0.163	6.00	800	This work
Sr–Ba	0.16	9.23	9.23	0.064	1.54	800	Kotelnikov *et al.*, 1992
Na–K	0.42	12.62	19.54	0.146	2.68	800	Zyryanov, 1981
Na–Rb	0.51	26.19	39.47	0.177	5.47	650	Lagache, 1984
K–Rb	0.08	4.18	4.18	0.027	0.70	650	Lagache, 1984

[1] ΔR – absolute value of a difference between isomorphic cation radii: Na, Ca – coordination number 7; K, Rb, Sr, Ba coordination number 9.
[2] Margules excess energy parameters.
[3] Crystallochemical parameter (absolute value) $\rho = (R_A - R_B)/D(Me-O)$.
[4] Integrated excess energy of mixing $G_{int}^{ex} = \int_0^1 (G_{int}^{ex}) dX$.

where G_{int}^{ex} is the excess energy of mixing:

$$G_{int}^{ex} = X(1-X)[XW1+W2(1-X)] \qquad (31)$$

G_{int}^{ex} is a total value and does not depend on any symmetry of the excess free energy of mixing. Values of G_{int}^{ex} for different feldspar solid solutions are listed in Table 5. We consider the variations of the values of integrated excess energies of mixing with the crystallochemical parameter ρ (Iiyama, 1972):

$$\rho = (R_A-R_B)/D(Me-O) \qquad (32)$$

where R_A and R_B are the ionic radii of isomorphic elements, and $D(Me-O)$ is the average interatomic distance between the cation M and the surrounding oxygen atoms. The absolute values of the parameter ρ are presented in Table 5. The variation of the integrated excess free energies of the feldspar solid solutions with the parameter ρ is shown in Fig. 8. A clear-cut relationship between energetic and crystallochemical properties of feldspars is observed. As is seen from the diagram (Fig. 8) the feldspars may be subdivided into three groups: (1) Feldspar solid solutions with the same end-member structure type (Na,Ca-, K,Sr-, K,Ba-, K,Rb- and Sr,Ba-feldspars) — Field I. These feldspars have the smallest values of G_{int}^{ex}, 0.70–1.54 kJ/mol for absolute values of ρ = 0.02–0.064. They form continuous solid solutions at 700–800°C. (2) Feldspar solid solutions with different structure type for the end-members (Na,Sr-, Ca,Sr- and Na,K-feldspars) — Field II.

They are characterized by median values of G_{int}^{ex}, 1.06–2.68 kJ/mol and values of ρ = 0.06–0.10. They also form continuous solid solutions at 700–800°C), but the Na,K- and Ca,Sr-feldspars have miscibility gaps at lower temperatures (Zyryanov, 1981; Lagache and Dujon, 1987). (3) Feldspar solid solutions with different structure types for the end-members and fields of unmixing (Na,Ba-, K,Ca-, Na,Rb- and Ca,Ba-feldspars) — Field III. They are characterized by the largest values of G_{int}^{ex}, 2.42–6.00 kJ/mol, and values of ρ = 0.118–0.177.

The variation of the integrated excess free energies of mixing with the absolute values of the ρ-parameters is described by the equation:

$$G_{int}^{ex} = 0.442 + 21.373(\rho) - 202.703(\rho)^2 + 1424.98(\rho)^3 \qquad s.e.e. = 0.36 \quad (33)$$

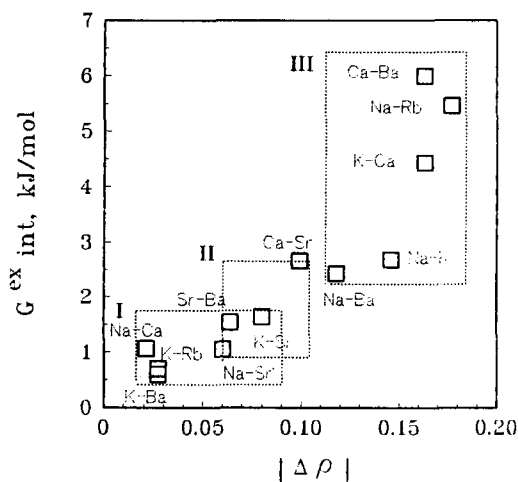This dependence may be used to estimate the energetic parameters for other tectosilicate solid solutions (Ca,Eu- ; Rb,Sr-feldspars).

FIG. 8. Dependence of the integrated excess mixing energies (G_{int}^{ex}) of the feldspar solid solutions on the absolute values of crystallochemical parameter $\rho = (R_A-R_B)/D(Me-O)$.

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