```
ORTHOCLASE


LOCALITY:  BENSON MINES, ST. LAWRENCE COUNTY, NEW YORK
DONOR:     D.B.STEWART;  DECEMBER 1970
REFERENCE: (1)D.B.STEWART AND T.L.WRIGHT  BULL.SOC.FR.MINERAL.
              CRISTALLOGR., 1974, 97,P367
           (2)FOLAND,K.A.,1974,GEOCHIMICA ET COSMOCHIMICA ACTA,
              VOL.38,PP. 151 TO 166
                                     ELEM.
OXIDE REF(1)       REF(2)            WT. %
NA20 =00.36(WC)*--00.007(FP) ----00.27
AL203=19.24(WC)                      10.18
SI02 =63.42(WC)                      29.64
K20  =15.34(WC)*--15.21 (FP) ----12.74
CA0  =00.08(WC)                      00.06
P205 =00.49(WC)                      00.21
FE203=00.11(WC)                      00.08
SR0  =00.02(WC)                      00.02
BA0  =00.62(WC)                      00.56
H20+ =00.02
H20- =00.02
TOTAL=99.72

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Bull. Soc. fr. Minéral. Cristallogr.
(1974), 97, 356-377.

Al/Si order and symmetry of natural alkali feldspars, and the relationship of strained cell parameters to bulk composition

by David B. Stewart and Thomas L. Wright,
U. S. Geological Survey, Reston, Virginia 22092.

Abstract. — The method proposed by Stewart and Ribbe (1969) to deduce the Al/Si ordering scheme of alkali feldspar has been tested using precise cell parameters from known crystal structures and from alkali feldspars used in cation exchange, heating, and thermochemical experiments. All of the basic assumptions of the Stewart-Ribbe model have been sustained, although small changes are necessary in cell parameters for the low albite and high sanidine end members.

The *b*-*c* and α^*-γ^* plots are revised and used to characterize Al/Si distributions of 98 alkali feldspars, mostly from previously studied collections, whose cell parameters have been newly determined. The *b*-*c* plot is contoured for *a*, using data from many homogeneous feldspars. The index of strain Δa, is defined as $a_{observed}$ minus $a_{estimated}$, where $a_{estimated}$ is derived from the *b*-*c* plot, with $\Delta a > 0.05$ Å arbitrarily reset as the « threshold » for strained feldspars. Cell parameters of 138 potassic feldspars, together with our new data, are used to define for natural feldspars the interrelations of Al/Si distribution and symetry to geologic occurrence and thermal history. These data are also used to discuss the related processes of alkali exsolution, polymorphism, and development of strain in natural feldspars. A suite of 139 potassic feldspars from a single geologic area studied by Guidotti, Herd, and Tuttle (1973) is also interpreted to yield details of the ordering process and symmetry change between orthoclase and microcline.

We conclude that maximum microcline, orthoclase with 0.8 ± 0.1 Al in T_1 sites, and low sanidine with 0.58 ± 0.05 Al in T_1 sites are abundant because they form in especially common thermal regimes in nature, *not* because they represent energetically preferred ordering configurations. Orthoclase is stable from 750° C to at least as low as 625° C (sillimanite-grade metamorphic rocks and quartz monzonite or adamellite plutons) and apparently is a primary crystallization product because more highly disordered feldspar has not been found in these environments. Assuming maximum microcline to be stable below 375° ± 50° C, and low sanidine to be stable between 800°-900° C, the equilibrium Al/Si distributions in potassic feldspars vary nonlinearly with temperature, resembling those for sodic feldspars. Furthermore, the equilibrium amount of Al in T_1 sites may nearly correspond in potassium and sodium feldspars formed at the same temperature. The equilibration rate is much faster for sodic feldspars, and even the slow cooling of thousands of cubic kilometers of metamorphic rocks may be inadequate for potassic feldspars to attain equilibrium Al/Si distributions.

Potassic feldspars whose T_1 sites contain 0.95 to 0.70 of the total Al may be either monoclinic or triclinic by X-ray powder diffraction methods. The monoclinic structure with orthogonal transverse wawes described by McConnell in 1971 seems able to accommodate as much as 0.92 Al in T_1 sites. Only triclinic potassic feldspars contain more than 0.95 Al in T_1 sites, and no triclinic potassic feldspar contains less than 0.70 Al in T_1 sites.

Ordering of Al/Si in monoclinic alkali feldspar is continuous ; the geologic evidence from assemblages obtained both by heating and by cooling is most satisfactorily interpreted by hypothesizing a discontinuous transformation between monoclinic orthoclase and triclinic microcline. The symmetry change does *not* occur at one particular value of Al in T_1 sites. Many paths for the ordering of intermediate microcline are followed in nature ; thus we were unable to deduce a stability field for intermediate microcline.

Strained feldspars, which are common in nature, make up about one-third of the samples studied by us. They occur as perthitic composites, and although the unit cell volumes of the coexisting phases are consistent with their respective compositions, the other cell parameters, particularly the cell edges, are significantly different from homogeneous feldspars in which Ab + Or components exceed 95 percent. The amount of strain in the potassic phase is greatest for perthites with sodic bulk composition, and our data suggest a linear dependence of strain on Ab content of the bulk perthite. Individual phases in cryptoperthites show substantially more strain than those in microperthites, but the maximum amount of strain possible is nearly independent of the Al/Si order or the symmetry of either phase. The amount of strain depends only qualitatively on size of

TABLE III.

Analyses of alkali feldspars.

Sample Descriptions.

MP3 and P63-1--Orthoclase-microcline intergrowths from aegirine-orthoclase-nepheline pegmatites, Rocky Boy stock, Bearpaw Mountains, Mont.

USNM 113188--Perthite, Harris farm mica mine, Oliver, Goochland County, Va.

64Ahr35--Anorthoclase from Nunivak Island, Alaska. Collected by J.M. Hoare.

Benson--Orthoclase from Benson mine, St. Lawrence County, N.Y. Collected by D.R. Wones.

	MP3-Or	MP3-Mi	MP3-Or	MP3-Mi	P63-1 Or	P63-1 Mi	USNM 113188	64Ahr35	Benson
SiO_2	64.34	64.27	64.7	63.8	64.2	64.6	64.58	66.06	63.42
TiO_2	0.02	0.02					0.00	0.02	0.00
Al_2O_3	18.26	18.13	18.1	18.9	18.2	18.4	19.20	20.42	19.24
Fe_2O_3	}0.64	0.58	}0.62	}0.27	}0.56	}0.56	0.17	}0.23	0.11
FeO		0.05							
MgO	0.00	0.00	0.09	0.05	0.03	0.00	0.00	0.02	0.00
SrO							0.21	0.45	0.02
BaO		0.22					0.83	0.14	0.62
CaO	0.00	0.00	0.04	0.10	0.08	0.02	0.11	0.79	0.08
Na_2O	1.03	0.83	1.0	0.70	1.0	0.94	1.87	8.24	0.36
K_2O	15.14	15.60	15.5	15.9	15.8	15.7	13.31	3.50	15.34
H_2O^+		0.11					0.06	.02	0.02
H_2O^-	0.00	0.00					0.02		0.02
Total	99.43	99.86*	100.05	99.72	99.87	100.22	100.36	99.89	99.72**
Number of atoms on the basis of 8 oxygen atoms									
Si	2.986	2.987	2.990	2.962	2.995	2.982	2.967	2.937	2.941
Ti	0.001	0.001						0.001	P=0.024
Al	0.999	0.993	0.986	1.034	0.995	1.001	1.039	1.070	1.052
Fe	0.022	0.020	0.022	0.009	0.019	0.019	0.006	0.008	.004
Σ	4.008	4.001	3.998	4.005	4.009	4.002	4.012	4.016	4.021
Mg			0.006	0.003	0.002			0.001	
Sr							0.006	0.012	.001
Ba		0.004					0.015	0.002	.011
Ca			0.002	0.005	0.004	0.001	0.006	0.038	.004
Na	0.093	0.075	0.089	0.063	0.090	0.084	0.167	0.710	.032
K	0.897	0.925	0.914	0.942	0.936	0.924	0.780	0.199	.908
Σ	0.990	1.004	1.011	1.013	1.032	1.009	0.974	0.962	.956

* includes 0.05 SO_3 ** includes 0.49 P_2O_5; pycnometric sp gr 2.564(2).

Analysts	(1)	(1)	(2)	(2)	(2)	(2)	(3)	(3)	(3)

(1) E.L. Munson, U.S. Geological Survey, Denver, under direction of L.C. Peck.

(2) Paul Elmore, Sam Botts, Gillison Chloe, Lowell Artis, H. Smith U.S. Geological Survey, Denver.

(3) J.J. Fahey, U.S. Geological Survey, Washington.

Semiquantitative spectrographic analyses by Helen W. Worthing, U.S. Geological Survey, Washington, D.C. Results are reported to the nearest number in the series 1, 0.7, 0.5, 0.3, 0.2, 0.15, and 0.1, etc., which represent approximate midpoints of interval data on a geometric scale. The assigned interval for semiquantitative results will include the quantitative value about 30% of the time.

P63-1 Or: Mn=0.0015%, Ag=0.02%, Ba=0.07%, Cr=0.0003%, Cu=0.003%, Ga=0.002%, Ni=0.001%, Pb=0.003%, Sn=0.007%, Sr=0.03%, V=0.0007%, Zr=0.015%.

P63-1 Mi: Mn=0.002%, Ag=0.03%, B=0.005%, Ba=0.2%, Be=0.0002%, Cr=0.0003%, Cu=0.005%, Ga=0.002%, Ni=0.003%, Pb=0.01%, Sn=0.015%, Sr=0.02%, V=0.0007%.

MP3-Or: Mn=0.0007%, Ag=0.03%, Ba=0.15%, Cr=0.0005%, Cu=0.005%, Ga=0.002%, Ni=0.001%, Sn=0.002%, Sr=0.02%, V=0.0007%.

MP3-Mi: Mn=0.003%, Ag=0.03%, B=0.005%, Ba=0.1%, Be=0.0002%, Cr=0.0002%, Cu=0.005%, Ga=0.002%, Ni=0.001%, Pb=0.005%, Sn=0.003%, Sr=0.02%, V=0.0007%.

USNM 113188: Mn=0.00007%, Ag=0.00005%, B < 0.003%, Cr=0.0003%, Cu=0.0002%, Ga=0.001%, Ni=0.0005%, Pb=0.05%.

Benson: Mn=0.0007%, Ag=0.0001%, B=0.003%, Cr=0.0005%, Cu=0.002%, Ga=0.0007%, Ni=0.0003%, Pb=0.003%.

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Ar^{40} diffusion in homogeneous orthoclase and an interpretation of Ar diffusion in K-feldspars

K. A. Foland

Department of Geological Sciences and Materials Research Laboratory,
Brown University, Providence, Rhode Island 02912, U.S.A.*

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Abstract—Ar^{40} diffusion in a natural, non-perthitic orthoclase has been studied in isothermal heating experiments between 500° and 800°C under both vacuum and hydrothermal (2 kbar) conditions. The sample is a one-phase K-feldspar without detectable chemical of structural inhomogeneities as verified by heating experiments, chemical and microprobe analyses, and cell refinements. The orthoclase does not disorder detectably and is stable for the duration of the heating interval. Diffusion coefficients were calculated using an isotropic model for spherical grains. Agreement of diffusion coefficients obtained on grain-sizes which differed by a factor of four indicate that the effective dimension for Ar^{40} diffusion is the actual particle size. A series of experiments at 700°C show that Ar^{40} loss may be described by the ideal spherical model and that the diffusion coefficient does not change with time. The Arrhenius relation is obeyed with a single activation energy and the diffusion coefficients are described by: $D = (0{\cdot}00982) \exp - (43800/RT)$. Agreement of experiments conducted under vacuum and hydrothermally (up to 2 kbar) indicate that pressure and H_2O do not significantly affect Ar^{40} loss. Relatively small amounts of alkali exchange between the feldspar and hydrothermal salt solutions do not affect the loss behavior.

The simple behavior obtained for this orthoclase is attributed to the use of a simple technique within the region of sample stability and to the homogeneous nature of the feldspar. Effects due to sample instability and to the use of perthites are discussed. The new data are compared to those for homogeneous feldspars showing that the orthoclase gives diffusion coefficients which are as low as those for sanidine. It is suggested that perthitization of feldspars in nature may reduce the effective grain size for diffusion and thereby allow diffusional loss of Ar^{40} at relatively low temperatures.

INTRODUCTION

K-FELDSPARS, particularly the low temperature forms, microcline and orthoclase, are well known for yielding K–Ar ages which are low when compared to ages of coexisting minerals. While the low feldspar age phenomenon has been recognized for a number of years (WETHERILL *et al.*, 1955; WASSERBURG *et al.*, 1956; and others), the reason for it has not been established conclusively. The low ages are usually attributed to Ar^{40} loss.

Numerous studies on Ar diffusion in feldspars may be found in the literature. Published laboratory measurements of K-feldspar diffusion coefficients range over nearly 7 orders of magnitude at the same temperature. The results of detailed study on one homogeneous orthoclase are reported here along with an attempt to clarify the argon diffusion status.

Since MUSSETT (1969) has reviewed the subject of Ar diffusion in minerals, an extensive review is not necessary. Two points, with regard to past work and to any future work, are emphasized here. Much of the variability found in Ar diffusion data probably results from the factors of minerals stability and suitability.

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* Present address: Department of Geology, University of Pennsylvania, Philadelphia, Pennsylvania 19174, U.S.A.

A prime requirement is that the mineral remain stable for the duration of the experiment. This stability applies to size and shape of the mineral as well as its structure and major element chemistry. Transport effects other than volume diffusion will be minimized only if this condition is satisfied. Perhaps the most notable violation of this condition has been in diffusion studies on hydrous minerals where the samples were heated in an anhydrous environment. However, stability considerations are also important in the study of feldspars. It is well known that at high temperatures alkali feldspars will disorder with respect to Al–Si tetrahedral distribution. The K-feldspar triclinic to monoclinic structural change is a relatively slow reaction, but it may occur rapidly at temperatures in excess of 1000°C. It is also well known that perthites will homogenize at high temperatures. As shown by ORVILLE (1967), a K-feldspar–Na-feldspar intergrowth will readily homogenize at 900°C. As summarized by MUSSETT (1969), there seems little doubt that these effects have significantly affected the measurement of the true Ar^{40} diffusional behavior in feldspar. Depending on the nature of the sample and of the experiment, disordering and homogenization may result in anomalous behavior at temperatures in excess of 900°C. The magnitude of these effects at lower temperatures is difficult to estimate.

Secondly, a mineral sample chosen for study must be selected with care and be described as fully as possible. Since feldspars show great variability in nature, sample selection is of special significance. For example, the distinction between microcline and microcline perthite is an important one, as the Ar loss behavior may be different for each. Perthites might be expected to show complicated behavior since they can suffer the effects of homogenization and since the location of Ar^{40} (as to the phase or even the phase boundary) is uncertain. Perthites cannot be regarded as one-phase samples. The vast majority of previous feldspar, Ar diffusion studies have been conducted on natural samples which were perthitic. Again depending on the nature of the sample and of the experiment, perthitic samples will probably yield varied and complicated behavior. These considerations cast serious doubt on the interpretations of many argon diffusion studies.

In the present study, a one-phase feldspar was chosen in order to obtain the simplest diffusional behavior. The use of a homogeneous orthoclase should yield data on the true Ar^{40} behavior in a low temperature K-feldspar. The method used was isothermal heating, which is probably the simplest and most direct way to measure Ar^{40} diffusional behavior.

ORTHOCLASE SAMPLE

Use of a natural, untreated sample is necessary because it should contain the decay products in those sites where they would normally be found, and, therefore, would more nearly reflect diffusion processes in nature. The sample used in this study is an orthoclase from a pegmatite at the Benson Mines near Star Lake, New York in the Adirondack Mountains. It has a K–Ar age of 850 m.y.

The sample derives from a hand specimen which contained small amounts of green amphibole and iron oxide. The specimen was carefully ground by hand, since hard grinding can cause Ar loss (DALRYMPLE and LANPHERE, 1969), and purified (sample purity > 99·9 per cent) by magnetic separation. Purified feldspar was sized by repeated sieving and the sizes were then determined by measurement under the microscope. The three size fractions used were those with average diameters of 125 ± 6, 232 ± 10, and 480 ± 17 μm ($2\bar{\sigma}$).

The Benson Mines orthoclase is clear and colorless with well-developed cleavage. Optical examination shows no alteration, zoning, or twinning. No extraneous phases, including a separate plagioclase phase, can be seen in either grain mounts or X-ray diffraction powder patterns. Since small amounts of other phases could be present and not show up on a powder pattern, a sample was heated (950°C for 3 days) to test for homogeneity. Measurements of the compositionally dependent ($\bar{2}01$) orthoclase reflection against a standard (101) $KBrO_3$ peak showed no change. Therefore, no more than 1 per cent albite could be present as a separate phase. As a further check, electron microprobe analysis was performed and showed no variations within a single grain, between different grains of the same size fraction, between different size fractions or on a scale of a few microns. The evidence indicates that the Benson Mines orthoclase is a homogeneous, one-phase (i.e. non-perthitic) feldspar.

The sample corresponds to Or_{94} and has a low concentration of Ca (Table 1). In analyzing different aliquots, the only significant variations observed are approximately 5 per cent in Sr concentration for five analyses of two size fractions. These may reflect slight Sr inhomogeneities but may also be partly or wholly analytical. No difference between different size fractions is seen in chemical, argon or microprobe analyses. The constancy of Ar^{40} concentration between different fractions (see Table 4) is worth noting since some authors have found differences for feldspar samples. The Ar^{40} value in Table 1 is actually the average for values obtained using different Ar^{38} spike sets.

Table 1. Benson Mines orthoclase used for this study

$K = 3{,}230{\cdot}0 \pm 21{\cdot}0\ \mu moles/g$ (fp)
$Na = 213{\cdot}0 \pm 6{\cdot}0\ \mu moles/g$ (fp)
$Rb = 5{\cdot}12 \pm 0{\cdot}04\ \mu moles/g$ (id)
$Sr = 4{\cdot}24 \pm 0{\cdot}16\ \mu moles/g$ (id)
$Ca = 3{\cdot}2 \pm 0{\cdot}8\ \mu moles/g$ (aa)
$Ar^{40} = 2{\cdot}40 \pm 0{\cdot}02 \times 10^{-8}$ g-atom/g (id)
$(K/Rb) = 631{\cdot}0$ $(K/Sr) = 761{\cdot}0$
$(K/Na) = 15{\cdot}15\ (Or_{93{\cdot}8})$ $(Sr^{87}/Sr^{86}) = 0{\cdot}766$
Microprobe analysis (wt. fraction):
$SiO_2 = 0{\cdot}6456$
$Al_2O_3 = 0{\cdot}1957$
$K_2O = 0{\cdot}1564$
$Na_2O = 0{\cdot}00758$
$K_{0{\cdot}915}\,Na_{0{\cdot}067}\,Al_{1{\cdot}06}\,Si_{2{\cdot}96}\,O_8$
$CaO = 0$
$FeO = 0{\cdot}0005$

id = isotope dilution; fp = flame photometry;
aa = atomic absorption.

Cell refinement data for the Benson Mines orthoclase is given in Table 2. Unit-cell parameters were obtained by the procedures of WRIGHT and STEWART (1968) and the least squares cell refinement program developed by EVANS *et al.* (1963). Reflections were indexed on the monoclinic cell using the 2 c/m systematic extinctions. Data in Table 2 are for samples taken from widely separated portions of the original specimen (A–E), samples after purification and sizing (127 μm, 232 μm), and samples of run products (54, 47). Lack of significant variation between the samples in Table 2 demonstrates that: (1) at the level of measurement, the original specimen was homogeneous in structural state. Homogeneity with respect to Or content is shown by a constant value for the ($\bar{2}01$) reflection; (2) the orthoclase did not change structural state during the course of hydrothermal treatment. That is, the feldspar did not significantly disorder with respect to Si and Al. In the *b–c* plot of Fig. 1, disordering would be shown by displacement, approximately along the *a* contour, toward high sanidine. Runs 54 (750°C for 4 weeks) and 47 (800°C for 10 days) were selected because they represent the highest temperatures and

Table 2. Unit-cell parameters of selected samples (see text for explanation of sample notation). Numbers in parentheses indicate one sigma standard deviations in the last place

Sample	No. reflections used	a (Å)	b (Å)	c (Å)	β	V (Å^3)	Std. error (°2θ)
A	13	8·563(6)	12·985(5)	7·197(2)	115° 54·(3)′	719·9(5)	0·0220
B	12	8·562(5)	12·984(4)	7·192(2)	115° 57·(3)′	719·0(5)	0·0185
C	12	8·569(4)	12·984(4)	7·195(2)	116° 0·(2)′	719·5(4)	0·0151
D	12	8·567(6)	12·978(4)	7·194(2)	116° 3·(3)′	718·6(5)	0·0181
E	11	8·565(4)	12·984(3)	7·197(2)	115° 59·(2)′	719·4(4)	0·0145
127 μm	17	8·566(2)	12·991(2)	7·199(1)	116° 1·(1)′	719·9(2)	0·0101
232 μm	15	8·567(3)	12·992(3)	7·202(3)	116° 3·(2)′	720·3(3)	0·0139
232 μm	13	8·574(3)	12·990(3)	7·198(2)	116° 4·(2)′	720·2(3)	0·0124
54	15	8·574(3)	12·992(3)	7·200(2)	116° 2·(1)′	720·6(3)	0·0132
47	13	8·575(2)	12·993(2)	7·197(1)	116° 1·(1)′	720·3(2)	0·0079

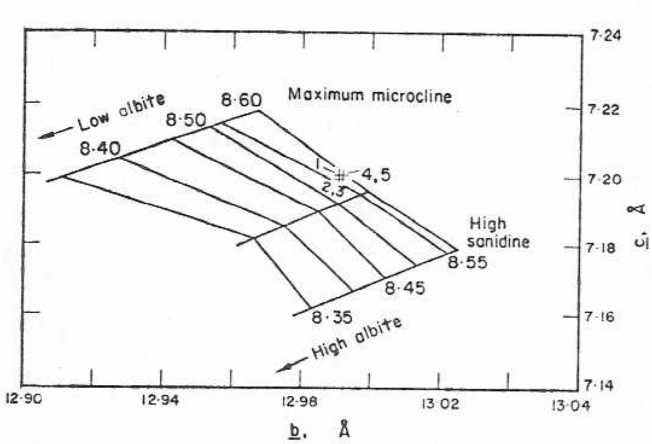

Fig. 1. *b–c* plot (after WRIGHT and STEWART, 1968). Specimen numbers refer to data in Table 2, according to the following: 1 = 127 μm; 2,3 = 232 μm; 4 = 47; and, 5 = 54.

longest times. If disordering were significant, then it would have been evidenced in these samples.

After hydrothermal and vacuum heating experiments, X-ray analysis showed no change in either the position or character of the reflections; optical examination showed the feldspar to be identical with the starting material. Grains still had sharp outlines and no overgrowths were observed. Some mechanical crushing occurred in runs with fluid/solid ratios less than about 1/4 and such conditions were avoided in runs used to determine diffusion parameters.

In summary, the Benson Mines orthoclase sample is a homogeneous, non-perthitic feldspar (Or_{94}) without significant structural or chemical inhomogeneities. The sample was stable for the duration of the experiment.

EXPERIMENTAL METHOD

The general method used in this study was simple isothermal heating. The amount of Ar^{40} lost during the heating interval is determined as the difference between initial Ar^{40} content and