

*The mineralogy of the potassium–barium feldspar series  
III: Subsolidus relationships*

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*Summary.* Further data are presented on the properties of natural and synthetic members of this series. Cell constants have been determined for over 50 specimens across the composition range; the activation energy for a low–high transformation in an intermediate hyalophane has been evaluated as  $101.5 \pm 5.0$  kcal/mole; additional single crystal studies have revealed complexities not previously reported.

Although there remain many detailed problems to be resolved, the present studies allow some suggestions concerning the nature of the relationships within the series. Problems of nomenclature and subsolidus relations are discussed together with some structural implications.

THE mineralogically rare but structurally interesting potassium–barium feldspar series has not previously been systematically studied. The earlier papers in this series (Roy, 1965*a*; Roy, 1967) together with other publications by the present authors (Gay, 1965; Roy, 1965*b*) have reported on the properties of a collection of natural specimens and hydrothermally synthesized materials ranging over the whole composition field. Further data are added in the present paper to complete the observations necessary for a general survey of the field. Whilst this description of the mineralogy of the series is of intrinsic interest, it can lead to an understanding of subsolidus relations and their structural foundations. The results that have been obtained in these studies are probably as complete both in detail and range as can be expected for some time. They show that there are many problems still to be resolved, but, nevertheless, they do permit some preliminary discussion of the subsolidus relations in the series. This discussion, together with some speculation about structural implications and suggestions for nomenclature, is set out in this paper.

*The determination of cell constants*

In the series running between  $\text{KAlSi}_3\text{O}_8$  and  $\text{BaAl}_2\text{Si}_2\text{O}_8$  the essential substitution is of (BaAl) for (KSi) in the feldspar framework. Such

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substitution might of itself be expected to lead to dimensional and angular changes in the monoclinic cell over the series, but as in other feldspars there will also be the possibility of high, low, and intermediate structural states occurring at each composition. Moreover it has been known for some time (Gay, 1956) that barium-rich feldspars, like those rich in divalent calcium, show a doubled  $14 \text{ \AA}$   $c$ -axis. The cell constants for over 50 natural, heat treated, and synthetic specimens used in the present studies have been determined to provide data for initial structural discussion.

Diffraction traces are sufficiently similar over the whole series to allow the unambiguous indexing of most reflections with spacings down to about  $2 \text{ \AA}$  (see Table 3, Frondel, Ito, and Hendricks, 1966) though there are some marked intensity changes that can be confusing. This indexing is carried out for all specimens in terms of the  $14 \text{ \AA}$   $c$ -axis body-centred monoclinic cell of the barium-rich members (the type  $(b)$  reflections that denote the doubled  $c$ -axis are not observed on any diffraction record, and can only be seen in single-crystal examination). The traces were made from smear mounts containing an internal standard of transistor-grade silicon using  $\text{Cu-K}\alpha$  radiation. Some records were obtained from a Philips diffraction meter, whilst others came from a rebuilt Berthold instrument; there was no significant difference in traces from the same specimen using both instruments. Every specimen was recorded four times; the line positions were measured for each trace and averaged interplanar spacings obtained. The lattice constants were then calculated by a least-squares method using a digital computer (Smith, 1956; Kelsey, 1964).

The values obtained for the cell edges,  $\beta$ -angle, and volume for natural and heat-treated specimens are set out in table I, which also gives a brief description of the origin of specimens and analytical data; similar determinations for the synthetic specimens described by Roy (1967) are listed in table II. As might be expected the values show a much more regular variation over the series for the synthetic materials than for the natural specimens; for the latter there are often uncertainties and variations in the minor elements of their chemical constitution in addition to insufficiently detailed information on their geological history. Nevertheless, there appear to be certain underlying trends. For natural specimens the cell volume increases by about  $35 \text{ \AA}^3$  when the substitution ( $\text{BaAl}$ ) for ( $\text{KSi}$ ) is complete; this is achieved by an increase of about  $0.1 \text{ \AA}$  in the  $a$ -axis length, an increase of about  $0.05 \text{ \AA}$  in the  $b$ -axis length, little or no change in the  $c$ -axis, and a decrease of almost

TABLE I. Cell constants for natural and heat-treated specimens. The accuracy of the dimensional data varies from specimen to specimen depending on the quality of the diffractometer records, etc. The average accuracy for the cell edges is  $\pm 0.006 \text{ \AA}$ , with that for the  $\beta$  angle  $\pm 0.08^\circ$ , with a corresponding value for the volume. The value for the  $c$ -dimension is given for all specimens in terms of the doubled cell of celtsian. Celsius contents in wt %

No.	Cn %	a	b	c	$\beta$	V	No.	Cn %	a	b	c	$\beta$	V
10 (80199)	2.2	8.562	13.011	14.405	116.03°	1441.28 Å <sup>3</sup>	195867	45.3	8.557	13.040	14.400	115.69	1447.0
G	3.2	8.571	13.020	14.386	116.00	1443.12			(8.556)	(13.045)	(14.378)	(115.63)	(1446.8)
S. 61	10.2	(8.575)	(13.014)	(14.403)	(115.95)	(1445.24)	100446/3	59.1	8.598	13.048	14.412	115.64	1457.62
g11156	11.5	(8.574)	(13.019)	(14.373)	(115.92)	(1443.03)	G. 1	59.2	8.619	13.047	14.415	115.39	1464.40
F.F.	12.2	8.565	13.018	14.407	115.88	1445.25	5081	63.2	8.621	13.044	14.405	115.30	1464.50
g21009	13.8	8.601	13.005	14.412	116.01	1447.61	Kascite	65.2	8.598	13.047	14.404	115.45	1459.02
F. 15	22.6	8.539	13.003	14.422	115.97	1439.86	STR5/15	84.8	8.628	(13.091)	14.403	115.28	1472.62
g11130	25.0	8.570	13.003	14.405	115.89	1444.10	5081 A	85.0	8.624	(13.075)	(14.410)	(115.24)	(1470.29)
280560	29.5	8.593	13.008	14.396	115.86	1448.03	10062	91.9	8.634	13.043	14.417	115.22	1467.04
I00446/1	36.8	8.560	13.016	14.407	115.68	1446.60	STR 4	94.0	8.629	13.051	14.428	115.09	1471.47
B.M. 84765	37.5	(8.566)	(13.012)	(14.371)	(115.73)	(1442.84)	331038	97.2	8.632	13.045	14.416	115.09	1470.18
F. 54	38.4	8.594	13.023	14.400	115.77	1453.80	100978	97.7	8.638	13.059	14.408	115.19	1470.80
B.M. 31980	42.1	(8.578)	(13.023)	(14.361)	(115.74)	(1445.1)	B.M. 1958,		(8.634)	(13.054)	(14.412)	(115.12)	(1470.70)
I00446/2	42.5	8.564	13.026	14.404	115.69	1453.00	284	97.8	8.627	13.042	14.405	115.08	1467.95
B.M. 1959,	43.3	8.602	13.052	14.410	115.70	1447.81	102264	98.9	8.641	13.053	14.411	115.19	1470.85
359					115.82	1456.25			(8.631)	(13.050)	(14.412)	(115.14)	(1469.50)
					115.69	1451.72							

*Key to Table I*

- 10(80199) Barium-orthoclase. Nodo-tamagawa, Iwaté Prefecture, Japan. Contains BaO 1.60, CaO nil, K<sub>2</sub>O 14.19, Na<sub>2</sub>O 1.52. Analyst J. H. Scoon. Probe determination shows lower BaO content (0.90 BaO). Gay (1965); Roy (1965a).
- G Sanidine with barium, probably from basaltic tuff. Eifel, Switzerland. Spencer (1937); has 2.46 wt % Na<sub>2</sub>O.
- S. 61 Hyalophane with manganese minerals. Taguchi manganese mine Sidara, Japan. Contains BaO 4.15, CaO nil, K<sub>2</sub>O 12.61, Na<sub>2</sub>O 1.40. Analyst J. H. Scoon. Gay (1965). Values in parentheses determined after heating for 72 hours at 1200° C.
- g11156 Hyalophane, manganese deposits. Jakobsberg, Värmland, Sweden. Probe determination of Ba and K only. Gay (1965); Roy (1965a).
- F.F. Hyalophane, from silicate skarn. Franklin Furnace, New Jersey, U.S.A. Reddish brown material, probably similar to that described by Bauer and Palache (1926) with 3.50 wt % Na<sub>2</sub>O. Roy (1965a).
- g21009 Hyalophane. Långban, Sweden. SiO<sub>2</sub> 59.76, Al<sub>2</sub>O<sub>3</sub> 19.79, BaO 5.64, CaO 0.84, Na<sub>2</sub>O 2.41, K<sub>2</sub>O 11.13, H<sub>2</sub>O 0.31, with MgO 0.06, Fe<sub>2</sub>O<sub>3</sub> 0.75. Analyst R. Blix. Gay (1965).
- F. 15 Hyalophane, from silicate skarn. Franklin Furnace, New Jersey, U.S.A. No. 1 analysis of Frondel, Ito, and Hendricks (1966).
- g11130 Hyalophane. Sjögruvan, Västmanland, Sweden. SiO<sub>2</sub> 53.07, Al<sub>2</sub>O<sub>3</sub> 20.31, MnO 1.60, BaO 12.34, CaO 0.34, Na<sub>2</sub>O 0.95, K<sub>2</sub>O 10.33, H<sub>2</sub>O 0.18. Analyst N. Sahlborn. Probe analysis shows lower BaO content (10–11 % BaO). Gay (1965).
- 280560 Hyalophane. Nya Zealand, Långban, Sweden. SiO<sub>2</sub> 51.89, Al<sub>2</sub>O<sub>3</sub> 22.01, MnO 0.46, BaO 12.06, CaO 2.49, Na<sub>2</sub>O 1.64, K<sub>2</sub>O 9.05, H<sub>2</sub>O 0.11. Analyst R. Blix. Gay (1965); Roy (1965a). Values in parentheses determined after heating for 72 hours at 1380° C.
- 100446/1 Hyalophane, occurring as small bodies in manganese rock containing yoshimurite, biotite, and hypersthene. Taguchi manganese mine, Sidara, Japan. Fraction of zoned specimen, contains BaO 15.02, Na<sub>2</sub>O 0.41, K<sub>2</sub>O 9.26. Analyst J. H. Scoon. Provisional optical data given in Roy (1965a); revised and fuller optical data in Roy (1965b).
- B.M. 84765 Hyalophane. Binnenthal, Valais, Switzerland. Probe determination of Ba and K only. Gay (1965); Roy (1965a). Values in parentheses determined after heating for 24 hours at 1200° C.
- F. 54 Hyalophane, from silicate skarn. Franklin Furnace, New Jersey, U.S.A. No. 2 analysis of Frondel, Ito, and Hendricks (1966).
- B.M. 31990 Hyalophane. Binnenthal, Valais, Switzerland. Probe determination of Ba and K only. Gay (1965); Roy (1965a).
- 100446/2 Hyalophane, occurring as small bodies in manganese rock containing yoshimurite, biotite, and hypersthene. Probe determination of Ba only. See notes on optics and locality under 100446/1.
- B.M. 1959, 359 Hyalophane. Bosnia, Yugoslavia. Probe determination of Ba and K only. Gay (1965); Roy (1965a).

- 195867 Hyalophane. Busovaca, Bosnia, Yugoslavia.  $\text{SiO}_2$  49.54,  $\text{Al}_2\text{O}_3$  23.14,  $\text{BaO}$  19.01,  $\text{CaO}$  0.19,  $\text{Na}_2\text{O}$  1.65,  $\text{K}_2\text{O}$  6.37 with  $\text{MgO}$  0.04,  $\text{Fe}_2\text{O}_3$  0.11. Analyst J. H. Scoon. Probe analysis shows lower  $\text{BaO}$  content (18.5 %  $\text{BaO}$ ). Listed as 195367 in Gay (1965); Roy (1965a). Values in parentheses determined after heating for 24 hours at 1300° C.
- 100446/3 Hyalophane, occurring as small bodies in manganese rock containing yoshimurite, biotite and hypersthene. Taguchi manganese mine, Sidara, Japan. Probe determination of Ba only. See notes on optical properties for 100446/1.
- G. 1 Celsian, from silicate skarn. Franklin Furnace, New Jersey, U.S.A. No. 3 analysis of Frondel, Ito, and Hendricks (1966).
- 5081 Calciocelsian, occurring as lenses and streaks in acid gneiss. Broken Hill, New South Wales, Australia. Table 4 of Segnit (1946). Unusually high calcium content (4.0 wt %).
- Kasoite Kasoite, from manganese deposit. Kaso mine, Totiki Prefecture, Japan. Analysis in Yosimura (1936, 1939) is unusual, with marked deficiency in silica (38.48 wt %). Present probe re-determination shows  $\text{SiO}_2$  44.2,  $\text{Al}_2\text{O}_3$  21.9,  $\text{BaO}$  26.6,  $\text{K}_2\text{O}$  5.4, showing a more normal feldspar constitution. Gay (1965); Roy (1965a).
- STR5/15 Celsian, manganese deposits. Jakobsberg, Sweden. Listed as STR 5 in Gay (1965). Values in parentheses determined after heating for 72 hours at 1400° C.
- 5081 A Celsian, occurring as lenses and streaks in acid gneiss. Broken Hill, New South Wales, Australia. Table 1 of Segnit (1946). Probe analysis shows lower  $\text{BaO}$  content (34.72 %  $\text{BaO}$ ). Gay (1965); listed as 5081 in Roy (1965a).
- 10062 Celsian, manganese deposits. Jakobsberg, Sweden. Vermaas (1953). Probe determination gives  $\text{BaO}$  37.55 wt %;  $\text{K}_2\text{O}$  1.02 wt %. Roy (1965a).
- STR 4 Celsian, manganese deposits. Jakobsberg, Sweden. Probe determination of Ba and K only. Gay (1965); Roy (1965a).
- 331038 Celsian, manganese deposits. Jakobsberg, Sweden. Probe determination of Ba and K only. Gay (1965); Roy (1965a).
- 100978 Celsian, with quartz, wollastonite and taramellite. Big Creek, Fresno Co., California, U.S.A.  $\text{SiO}_2$  31.91,  $\text{Al}_2\text{O}_3$  25.70,  $\text{BaO}$  39.97,  $\text{CaO}$  0.78,  $\text{Na}_2\text{O}$  0.10,  $\text{K}_2\text{O}$  0.27 with  $\text{Fe}_2\text{O}_3$  0.33,  $\text{MnO}$  0.02,  $\text{MgO}$  0.05, and  $\text{CO}_2$  1.05. Analyst J. H. Scoon. Listed as 1920 in Gay (1965); Roy (1965a). Values in parentheses determined after heating for 24 hours at 1560° C.
- B.M. 1958, 284 Celsian, in cavities in granular rock veined with Fe and Mn oxides. Benallt Mine, Caernarvonshire, Wales. Spencer (1942). Probe determination gives slightly higher  $\text{BaO}$  (39.93 wt %). Listed as B.M. 1958, 24 in Gay (1965).
- 102264 Celsian, occurring as small glass-clear crystals, in a massive granular rock with pyrite, taramellite, pyrrhotite, quartz, and wollastonite. Mount Patterson Quadrangle, Fresno Co., California, U.S.A. Probe determination of Ba only. Values in parentheses determined after heating for 24 hours at 1560° C.

*References for table I*

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$1^\circ$  in the  $\beta$ -angle. For synthetic specimens there is again an increase in volume up to a value for pure celsian close to that for natural specimens though the total change of the series ( $25 \text{ \AA}^3$ ) is a little smaller; as before the  $a$ - and  $b$ -axes increase, though only by about half the changes noted for natural specimens, the  $c$ -axis increases by approximately  $0.05 \text{ \AA}$  to about the same value as the natural materials, whilst the decrease in  $\beta$ -angle is very similar to that recorded for the natural specimens. Indeed above 65 to 70 wt % Cn there is little significant difference between the natural and synthetic samples. Such dimensional variations cannot arise directly from substitution alone, and, as in other feldspar series, they must be due to more subtle modifications in the feldspar framework consequent upon the substitution and the thermal history of the specimen.

It is worthwhile to examine in more detail two of the changes described generally above. Fig. 1 shows the values of  $c$  and  $\beta$  plotted against wt % Cn for all specimens (the values for the synthetic materials are averaged for the two hydrothermal syntheses). For both parameters the synthetic specimens show a relatively smooth continuous variation (broken line, fig. 1). In contrast, the variation for the natural specimens is more erratic and  $c$ -axis lengths have a much greater spread, though it is clear that they cluster around a mean value that is probably little changed over the series. The scatter of  $\beta$ -angles of natural materials is much more limited and they follow the variation for synthetic specimens quite well. For the moment we will assume that the variations for the synthetic materials can be said to characterize the high structural state and those for the natural specimens the low structural state. This is in accord with the conclusion that there is a low-high transformation up to about 65 to 70 wt % Cn, with no distinction for more barium-rich compositions, as already suggested by Gay (1965) and Roy (1967).

TABLE II. Cell constants for hydrothermally synthesized specimens. At each composition the first line (*a*) is for material synthesized at 700° C, the second (*b*) for material synthesized at 500° C; both at  $P_{H_2O}$  2000 bars, by the methods described in Roy (1967). The accuracy of the dimensional data varies from specimen to specimen, depending on the quality of the diffractometer records, etc. The average accuracy for the cell edges is  $\pm 0.006 \text{ \AA}$ , and for  $\beta \pm 0.05^\circ$ , with a corresponding value for the volume. The *c*-dimension is given for all specimens in terms of the doubled cell of celsian

Cn (wt %)	<i>a</i> ( $\text{\AA}$ )	<i>b</i> ( $\text{\AA}$ )	<i>c</i> ( $\text{\AA}$ )	$\beta$	$V(\text{\AA}^3)$	Cn (wt %)	<i>a</i> ( $\text{\AA}$ )	<i>b</i> ( $\text{\AA}$ )	<i>c</i> ( $\text{\AA}$ )	$\beta$	$V(\text{\AA}^3)$
0	( <i>a</i> )	8.606	13.020	14.347	116.04°	60	8.612	13.050	14.395	115.47°	1460.7
	( <i>b</i> )	8.608	13.025	14.362	116.09		8.616	13.056	14.392	115.53	1460.9
10	( <i>a</i> )	8.603	13.026	14.367	116.02	65	8.610	13.055	14.399	115.45	1461.5
	( <i>b</i> )	8.611	13.037	14.368	116.04		8.614	13.049	14.393	115.35	1462.1
20	( <i>a</i> )	8.607	13.032	14.382	115.86	70	8.617	13.055	14.394	115.43	1462.3
	( <i>b</i> )	8.607	13.041	14.374	115.94		8.621	13.050	14.401	115.26	1465.3
30	( <i>a</i> )	8.619	13.038	14.392	115.75	80	8.623	13.054	14.405	115.28	1466.2
	( <i>b</i> )	8.607	13.037	14.385	115.79		8.629	13.049	14.400	115.18	1467.4
40	( <i>a</i> )	8.609	13.048	14.394	115.72	90	8.627	13.051	14.399	115.21	1466.2
	( <i>b</i> )	8.613	13.050	14.387	115.69		8.641	13.047	14.406	115.13	1470.5
50	( <i>a</i> )	8.616	13.049	14.398	115.66	100	8.642	13.040	14.399	115.22	1469.0
	( <i>b</i> )	8.616	13.051	14.391	115.65						

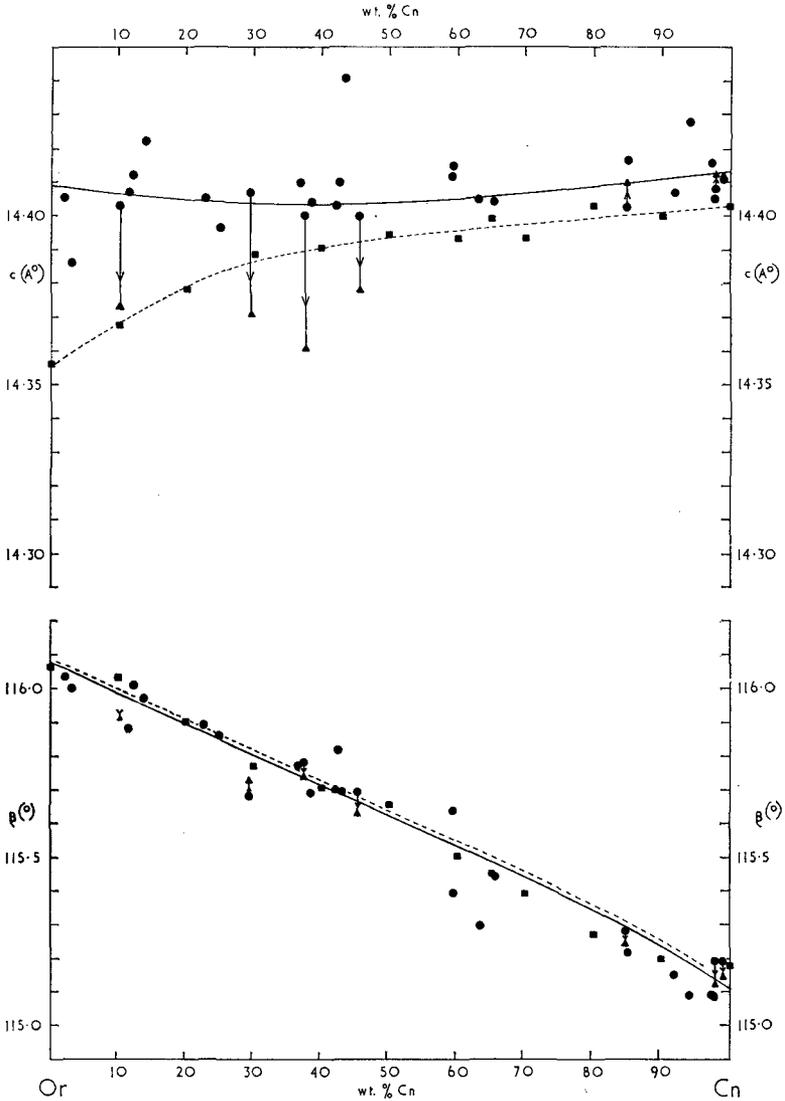


FIG. 1. Values of  $c(\text{\AA})$  and  $\beta$  plotted against wt % Cn. ● denotes values from natural specimens, ■ values from synthetic specimens, and ▲ values from heat treated natural specimens.

In the first instance, one may hope to relate this transformation and the orthoclase-sanidine change with which it must merge at the  $\text{KAlSi}_3\text{O}_8$  end of the series; there is a correlation between the observed increase in  $c$ -axis length and invariance of  $\beta$  in orthoclase-sanidine dimensions and similar dimensional changes for a fixed composition in the potassium-barium feldspar. Structurally the orthoclase-sanidine transformation is well characterized and involves Si-Al order-disorder arrangements (Cole *et al.*, 1949; Jones and Taylor, 1961). It may reasonably be expected that similar structural rearrangements can proceed within the potassium-barium feldspars, and evidence from a kinetic study of hyalophane described in the next section gives further support.

Nevertheless there are certain aspects of the present work that suggest that there may be complexities in this relatively straightforward picture. Apart from the single-crystal studies to be described later, the values of the cell constants obtained from heat-treated natural specimens are sometimes anomalous. For example, whilst the  $\beta$ -values are substantially unchanged by heating, there can be marked changes in the  $c$ -dimensions. At the barium-rich end of the series such changes are very small, but within the range of the proposed low-high transformation,  $c$ -axis values can decrease significantly below those recorded for synthetic specimens (see fig. 1). These could perhaps be taken to imply that the hydrothermally synthesized specimens are not in the ultimate high structural state, or at least that the structural rearrangements in the transformation proceed through intermediate stages. We shall return to this problem in the discussion of the subsolidus relations later.

#### *The kinetics of the low-high transformation in a hyalophane*

A general account of the methods that have been used in kinetic studies of feldspar polymorphic changes has been given in Gay (1961). In the present work the activation energy of the low-high transformation proposed for potassium-rich members has been obtained from experiments on a hyalophane B.M. 84765, 37.5 wt % Cn.

These experiments involve the determination of the rate of change of optic axial angle<sup>1</sup> in single crystals at different temperatures under dry conditions using the spindle stage described by Roy (1965c).

<sup>1</sup> In the description that follows the symbol  $2V'$  (not  $2V$ ) is used to indicate the optic axial angle for a heat treated specimen; this distinction is necessary since the values of  $2V'$  were always determined in a liquid whose refractive index matched  $\beta$  of the unheated material.

A moderately large crystal of the specimen was selected and its optic axial angle ( $2V_0 = 78.2 \pm 0.5^\circ$ ) determined accurately; this crystal was then broken into a number of fragments for use in isothermal experiments after checking  $2V_0$ . Preliminary experiments established that the most suitable temperature range was from 960 to 1100° C. Each fragment was then heated for increasing periods of time at a fixed temperature in a vertical tube furnace, in which the temperature was maintained to  $\pm 5^\circ$  C by an Ether 'Transistrol' controller and continuously monitored by a thermocouple close to the crystal. At given intervals of time at a fixed temperature the crystal was air-quenched and  $2V'$  determined; heating of a given fragment continued until a limiting value  $2V'_\infty$  was reached for each temperature. The values recorded at four temperatures are given in table III, in which the temperature dependence of the transformation rate is clearly demonstrated; extrapolation from the variation of  $2V_0 - 2V'_\infty$  with temperature suggests that  $2V_0$  will be unchanged even on prolonged heating below 800° C.

It is found that such results can be fitted well to a simple second-order rate law so that

$$kt(2V_0 - 2V'_\infty) = (2V_0 - 2V') / (2V' - 2V'_\infty),$$

where  $t$  is the time of heating, and  $k$ , the rate constant. This relation allows the derivation of the rate constant at each temperature ( $T$ , °K), and so provides the points for the Arrhenius plot shown in fig. 2. With such limited data it would be unwise to analyse the detailed nature of the transformation, though the slope permits the estimation of the activation energy for the low-high transformation in this hyalophane as  $101.5 \pm 5.0$  kcal/mole.

Values of the activation energies for polymorphic changes in feldspars are very limited at present. McConnell and McKie (1960) obtained a value of about 60 kcal/mole for the albite-high-albite transition under hydrothermal conditions; later the same authors (McKie and McConnell, 1963) showed that the activation energy for the same transformation under dry conditions was increased to about 74 kcal/mole, though an analysis of the data of Schneider (1957) on the kinetics of this change leads to a value ( $\sim 96 \pm 11$  kcal/mole) more in accord with that found in the present work. It has been suggested above that Si-Al rearrangements are responsible for the low-high change in the hyalophanes, and in albites this structural cause is well established; the Si-O bond energy is about 90 kcal/mole. The discrepancy with the results of McConnell

TABLE III. Change of optic axial angle with duration of heating at certain temperatures, B.M. 84765

Temp.	Time of heating (hours)	960° C			1060° C			Temp.	Time of heating (hours)	1100° C				
		2V'	2V <sub>0</sub> -2V'	2V <sub>∞</sub>	2V'	2V <sub>0</sub> -2V'	2V <sub>∞</sub>			2V'	2V <sub>0</sub> -2V'	2V <sub>∞</sub>		
960° C	6	75.1°	3.1°	71.4°	1060° C	1	76.3°	1.9°	69.9°	1100° C	1	76.3°	1.9°	69.9°
	12	73.6	4.6			3	73.2	5.0			3	73.2	5.0	
	21	72.1	6.1			5	71.4	6.8			5	71.4	6.8	
	48	72.7	5.5			10	69.8	8.4			10	69.8	8.4	
	120	71.5	6.7			20	69.5	8.7			20	69.5	8.7	
	240	71.3	6.9		48	70.3	7.9		48	70.3	7.9			
1060° C	1	71.6	6.6	66.9	1100° C	0.25	69.1	9.1	66.8	1100° C	0.25	69.1	9.1	66.8
	3	68.8	9.4			0.75	67.8	10.4			0.75	67.8	10.4	
	4	67.9	10.3			1.50	66.9	11.3			1.50	66.9	11.3	
	7	67.0	11.2			4.50	66.6	11.6			4.50	66.6	11.6	
	10	66.9	11.3			10.00	67.0	11.2			10.00	67.0	11.2	

and McKie could be ascribed to the differing experimental conditions; certainly they used powdered specimens for which the smaller grain size will have an effect upon transformation rate, whereas Schneider examined single crystals, as in the present work. Whatever the reasons for the spread of energies so far determined, the result from the present

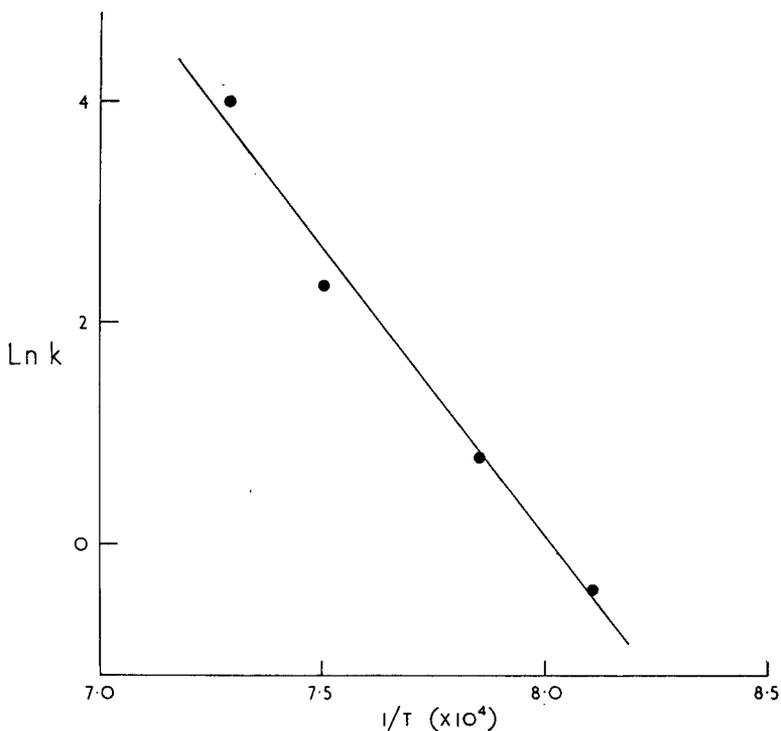


FIG. 2. Arrhenius plot,  $\ln k$  vs.  $1/T$  (in  $^{\circ}\text{K}$ ), for hyalophane B.M. 84765, 37.5 wt % Cn.

work is generally in accord with the suggestion that some kind of Si-Al order-disorder relations can be found in the potassium-rich members of this feldspar series.

#### *Single crystal X-ray studies*

All but a few of the natural specimens listed in table I have been examined using conventional oscillation-camera techniques; for some materials it proved impossible to find single crystals of sufficient size

and quality to obtain suitable diffraction patterns. It was not possible to examine any of the synthetic materials by X-ray methods due to their finely crystalline nature, but studies using electron diffraction methods have already been reported (Roy, 1965*b*, 1967). Particular attention has been paid to the observation of the type (*b*) reflections characteristic of the body-centred cell, and to features of the diffraction patterns that can suggest structural inhomogeneities not detectable by other methods.

In the work mentioned above Roy found that the type (*b*) maxima were not observed for synthetic specimens containing up to 65 wt % Cn; specimens containing 70 wt % Cn or more all showed the presence of such reflections. For natural specimens the results are similar, although the compositional range of the cell change cannot be so sharply defined. There is no doubt that type (*b*) reflections are not observed on potassium-rich members up to and including 100446/3 (59.1 wt % Cn) and G.1 (59.2 wt % Cn); it is extremely unlikely that they occur for the material kasoite (65.2 wt % Cn), though the quality of the diffraction patterns from this specimen is very poor. They have been detected for 5081 (63.2 wt % Cn), and for all specimens more barium-rich than STR 5/15 (84.8 wt % Cn). In all specimens the weak (*b*) reflections have similar relative intensities, which are also comparable as far as can be judged to those observed on the electron diffraction plates of the synthetic materials, although this comparison of the results of electron and X-ray diffraction cannot be completely reliable. Specimen 5081 is rather unusual, being described as a calcio-celsian and containing about 4.0 wt % CaO; if it is assumed that the divalent ions should be taken together, its composition is about 83 wt % (Cn+An) and is equivalent to more usual natural celsians showing the (*b*) reflections. Apart from the uncertainty in the compositional gap between 65 and 80 to 85 wt % Cn, it seems that the cell types for natural and synthetic specimens of a given composition are identical.

Within the composition range of the 14 Å *c*-axis cell, the general properties (optics, cell constants, density) show little convincing evidence for any low-high transformation; nevertheless the analogies between  $\text{CaAl}_2\text{Si}_2\text{O}_8$  and  $\text{BaAl}_2\text{Si}_2\text{O}_8$  outlined in Gay (1965) suggest possibilities that can only satisfactorily be pursued by single crystal work. These experiments entail the examination of the type (*b*) reflections from a crystal quenched after heating at very high temperatures to see whether there is any change in relative intensities or sharpness; such an examination is difficult both because of the technical

problems and because of the weakness of the original reflections. The authors have tried to carry out such experiments using natural celsians heated at temperatures between 1400° C and 1600° C; they believe that for two specimens (STR 5/15 and 102264) extended heating (1 to 3 days) at 1500 to 1600° C has perceptibly weakened the (*b*) reflections, and that these reflections are probably weakened under similar conditions for another specimen (100978). There is no indication that the maxima are less well defined after heating, but it is possible that any intensity change is easier to effect the greater the potassium content. This evidence for a structural change must at present be regarded as provisional, but it has not yet been possible to promote the transformation further by extended heating or by even higher temperatures due to technical difficulties.

Over the composition field of the 7 Å *c*-axis cell, all previous observations have pointed to a low-high structural change; the change is not easily apparent on the single-crystal patterns for it affects only slightly the relative intensities and positions of type (*a*) reflections. But the single-crystal studies of the low natural specimens reveal complexities so far unsuspected. It has been observed that deviations from monoclinic symmetry can be detected for some potassium-rich hyalophanes; these deviations can involve discrepancies in the intensities of related reflections and small but significant departures in the angles  $\alpha^*$  and  $\gamma^*$  from 90° (these deviations were first brought to our attention by Dr. J. B. Jones, private communication). A preliminary examination of a range of natural specimens suggests that such symmetry degeneration (towards triclinic maximum microcline) becomes more apparent with increasing potassium content, though the composition at which it occurs is somewhat uncertain; it seems likely the change is in the region containing the specimens F.15, g11130, and 280560, though extensive single-crystal studies would be necessary to define this more closely. Moreover, some hyalophanes show traces of the complex diffraction effects often described for alkali feldspars (see, for example, MacKenzie and Smith, 1955); such effects have also been observed by Dr. J. B. Jones and Dr. C. J. E. Kempster (private communication). It has not proved possible to systematically characterize these effects in hyalophanes for in addition to being very poorly developed, they vary from specimen to specimen and from crystal to crystal for the same specimen. It is the present authors' experience that such effects are confined to the potassium-rich members of the series that they have been able to examine, up to about 12 wt % Cn; some crystals

show partial inversion of a single component as described for adularia by McConnell (1965), some show traces of unmixing with the development of another monoclinic or a twinned triclinic form (and can be homogenized by heating), whilst others apparently have no complications of this kind. With the present scarcity of specimens, we can only note the existence of such complexities; some speculations as to their origin are set out in the next section.

### *Discussion*

Most feldspar studies have been concerned with members within the ternary field  $\text{NaAlSi}_3\text{O}_8$ - $\text{KAlSi}_3\text{O}_8$ - $\text{CaAl}_2\text{Si}_2\text{O}_8$ ; natural feldspars normally considered within this system commonly show additional cationic substitution. Although such substitution is widespread and involves many different cations, only Ba seems to achieve the status of a major constituent under natural conditions; the rarity of Ba-rich feldspars seems to be due more to the restricted occurrence of suitable paragenetic conditions than to any fundamental difficulties in accommodating Ba ions into the essential feldspar framework structure. To this extent one should perhaps regard natural feldspars within a quaternary system involving  $\text{BaAl}_2\text{Si}_2\text{O}_8$ ; there is, for example, no obvious structural reason why the substitution of Ba and Ca should not take place freely. The limitations of natural environments restrict the regions of this system that can be studied (e.g. Ba-plagioclases and Ca-celsians are very restricted in composition and exceedingly rare); experimental investigations of synthetic feldspars have almost always neglected barium. The comparatively few natural Ba-rich feldspars that have been described are regarded as members of the binary system  $\text{KAlSi}_3\text{O}_8$ - $\text{BaAl}_2\text{Si}_2\text{O}_8$ , an acceptable viewpoint from the available data though even some of these specimens indicate its over-simplicity. There is some analytical evidence that the Na-content can increase to significant amounts for the more K-rich members (see for example, Table 22, Deer, Howie, and Zussman, 1963), so that they could well be considered as part of a ternary system; although no systematic trend can be discerned in Ca-content, there are a few analyses showing rather high concentrations of this element, particularly for some Ba-rich materials.

Bearing in mind its place as part of a quaternary feldspar system it is now possible to discuss relations within the  $\text{KAlSi}_3\text{O}_8$ - $\text{BaAl}_2\text{Si}_2\text{O}_8$  binary system after clarifying the descriptive nomenclature employed in the series. The common descriptive terms include celsian (usually restricted to members with at least 80 to 90 % Cn) and hyalophane

(usually used for the more K-rich specimens though the relationship to celsians is ill-defined), with barium-orthoclase, barium-sanidine, and calcio-celsian applied to particular materials. It is convenient for the present discussion to use terms which, as far as possible, have a structural significance. Thus 'celsian' is used to describe all homogeneous members with a 14 Å *c*-axis; if necessary the nature of the celsian can be specified by the prefix high, low, etc. Any other homogeneous members with more than 15 % Cn and a 7 Å *c*-axis are described as 'hyalophanes'; again prefixes (which may include monoclinic and triclinic) may be added to define the nature of the hyalophane. The lower limit of the hyalophanes has been chosen to take account of those K-rich members of the series that may be homogeneous or unmixed to a greater or lesser degree; for the present it is suggested provisionally that these specimens shall be called 'barian orthoclases' to which can be added a perthitic classification if it becomes relevant. It is clear that this nomenclature may need revision particularly with regard to the relations of barian orthoclase and hyalophane in the light of future work, but it provides a suitable basis for the present discussions.

The high-temperature relationships across the series just below the solidus are considered first, though it should be emphasized that the liquidus–solidus temperatures for intermediate members are unknown. There is evidence that incongruent melting of  $\text{KAlSi}_3\text{O}_8$  to leucite extends into barian orthoclases and possibly hyalophanes (see Gay, 1965), but the limits of this field are unknown as is even the form of the liquidus–solidus. In the subsolidus, the present work suggests the existence of a solid solution with a hyalophane structure from pure K-feldspar up to at least 65 to 70 wt % Cn; it seems certain that such high hyalophanes are monoclinic over their entire range. Moreover the experiments on celsians heated to very high temperatures indicate that the 14 Å *c*-axis structure is likely to be converted into the 7 Å *c*-axis high hyalophane modification when some potassium is present. The field for a high celsian is very restricted, and its boundary has been set tentatively at 90 wt % Cn, so that the high hyalophane solid solutions extend across the series to this composition. It seems unlikely that the synthetic feldspars from 70 to 100 wt % Cn that show a celsian structure are representative of the high forms, probably due to the hydrothermal conditions of their formation in relation to the high melting temperatures (above 1600° C) of the barium-rich members.

The relations for the low structural state across the series are more complex. From pure Ba-feldspar, low celsian extends to 80 wt % Cn,

but there is a gap in the compositions of natural specimens from this point to about 65 wt % Cn. Earlier estimates of the K-rich limit of this compositional gap were set at about 40 wt % Cn by Yosimura (1939), and about 55 wt % Cn by Vermaas (1953), who attached some significance to its existence. Certainly it embraces the region of the structural change from hyalophanes to celsians, and Roy (1965*a*) has shown this is to be associated with discontinuity in optic orientation and other physical properties. It is doubtful whether of itself the hyalophane-celsian structural modification can be associated with any compositional discontinuity for similar structural changes occur in synthetic specimens over the restricted range from 65 to 70 wt % Cn. For the present it seems likely that the compositional gap for natural specimens is fortuitous. At compositions about 60 wt % Cn, the feldspars are low hyalophanes with monoclinic symmetry, though with increasing K-content there are indications of low hyalophanes with triclinic symmetry. The present studies are insufficiently detailed to locate the monoclinic-triclinic hyalophane change with any certainty, though it is reasonable for the moment to set it at about 25 wt % Cn; from here to the limit of the barian orthoclases at 10 to 15 wt % Cn, the departure from monoclinic symmetry is likely to increase. The behaviour of the barian orthoclases is complex, due probably to the existence of specimens that must be considered within a ternary field. At low temperatures  $\text{KAlSi}_3\text{O}_8$  (triclinic microcline) seems to have a limited range of homogeneous solid solution. The unmixing solvus of the alkali feldspars is well established and it is reasonable to expect this to extend into the ternary field to give unmixing under low-temperature conditions into a triclinic hyalophane and an alkali feldspar of the microcline type containing little or no barium; the degree of unmixing and the nature of the exsolved components would depend on the composition of the homogeneous feldspar and the character of the crystallization process. Such an explanation is purely speculative but it would account for the varieties of micro-perthitic and homogeneous crystals that have been observed in this composition field.

Diagrammatic representation of the proposed subsolidus relations in the  $\text{KAlSi}_3\text{O}_8$ - $\text{BaAl}_2\text{Si}_2\text{O}_8$  series is shown in fig. 3. Whilst some aspects of this diagram must be regarded as provisional, it is in general accord with the experimental data of the present and previous work; until more specimens become available there can be little hope of a more detailed description. Some comment is necessary at this point as to the character of the hydrothermally synthesized specimens of Roy (1967).

In the discussion above it has been suggested that at least at the Ba-feldspar end of the diagram these are in an intermediate or possibly low structural state. Heating experiments on natural specimens (see fig. 1) imply that even down to about 30 wt % Cn these synthetic materials deviate from the highest structural state.

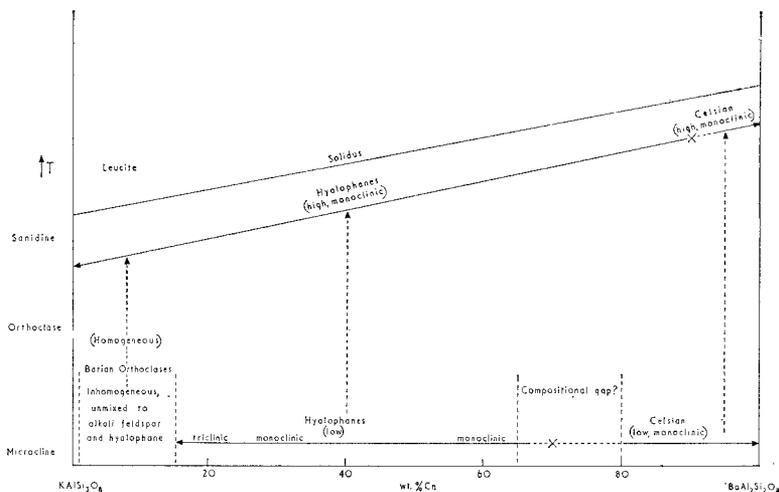


FIG. 3. Schematic representation of subsolidus relations in the feldspar system  $KAlSi_3O_8$ - $BaAl_2Si_2O_8$ .

From a structural viewpoint the end members  $KAlSi_3O_8$  and  $BaAl_2Si_2O_8$  are fairly well characterized. The variations of Si-Al order-disorder associated with the maximum microcline-orthoclase-sanidine changes have been established, whilst the Si-Al ordering scheme of the 14 Å c-axis celsian structure has been determined. It is clear that the low-high transition, which exists over most of the series, must be associated with the promotion of disordered Si-Al relationships. For nearly pure celsians it is possible that complete randomization is unattainable so that a structural position analogous to a stage in the body-centred anorthite  $\rightleftharpoons$  high-albite change in the plagioclases is reached. In the low hyalophanes, the replacement of Ba by K changes the ordering scheme towards that associated with the triclinic symmetry of a maximum microcline. On purely structural grounds the complications of the barian orthoclases are difficult to foresee. The relation to the alkali feldspars through a ternary field has already been pointed

out and it is perhaps relevant to draw attention to the analogy with the peristeritic unmixing in the plagioclases where, close to  $\text{NaAlSi}_3\text{O}_8$ , substitution of divalent Ca produces inhomogeneous crystals.

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