The mineralogy of the potassium–barium feldspar series. II. Studies on hydrothermally synthesized members

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Summary. Members of the $KAlSi_3O_8$–$BaAl_2Si_2O_8$ feldspar series have been synthesized by hydrothermal methods. Although the products are too finely crystalline for complete detailed study, some X-ray and optical measurements have been made, together with some electron-diffraction observations.

The results presented confirm the existence of high structural states over the greater part of the series, and suggest that a simple solid-solution series is formed between the end-members at high temperatures.

EQUILIBRIUM studies on the binary system $KAlSi_3O_8$–$BaAl_2Si_2O_8$ have not been previously undertaken, although some results on the end-members have been reported in studies of the alkali feldspars and of ternary systems involving barium. Experimental work involving $KAlSi_3O_8$ is well known (see Deer, Howie, and Zussman, vol. 4, 1963), but materials of the composition $BaAl_2Si_2O_8$ have not been so extensively investigated. The first synthesis of celsian was attempted by Fouqué and Michel-Lévy (1880) who produced minute crystals unsuitable for detailed study. Dittler (1911) was able to establish the biaxial character of synthetic celsian, though Ginsberg (1915) cooled a melt of oxides of celsian composition and obtained optically positive uniaxial crystals. Eskola (1922) showed that potassium and barium feldspars could form solid solutions, and prepared celsian crystals of about 0·55 mm length by using a barium vanadate flux; he also pointed out that the melting temperature of celsian seemed to be far above 1700° C. Yoshiki and Matsumoto (1951) produced mica-like crystals of a hexagonal form of celsian by electro-fusing kaolinite and barium carbonate; subsequently Davis and Tuttle (1952) synthesized hexagonal celsian from the appropriate oxide mixture. These latter authors showed that a transformation from hexagonal to monoclinic celsian takes place after prolonged heating, whilst von Planz and Müller-Hesse (1963) demonstrated that hexagonal celsian can exist in both high and low forms. Sorrell (1962) attempted to substitute potassium by barium, strontium, and lead, and synthesized celsian by this method. More recently Seki and Kennedy (1964) have synthesized celsian from an appropriate oxide mixture of cymrite, $BaAlSi_3O_8(OH)$, composition under hydrothermal conditions.

There has, however, been little or no systematic work on the intermediate members of the K–Ba feldspar series, and consequently there has been no comparative study of the properties of natural and synthetic specimens within the series. The present paper describes the preparation of such synthetic specimens, and gives some account of their properties.

Experimental procedures. The method of preparation of the initial charges is straightforward, although it must be undertaken most carefully, especially as the silicate mixture contains potassium. Essentially the procedure is similar to that described by Roy (1956) and Hamilton and MacKenzie (1960). Preliminary analyses of the source materials were carried out to estimate the percentage yield as oxides and the loss of K_2O at experimental temperatures. Charges with the compositions of the end-members of the series were prepared using carbonates of potassium and barium ('analar' grade) as sources of K_2O and BaO; pure aluminium powder provided the source of Al_2O_3, while ethyl orthosilicate ($(C_2H_5)_4SiO_4$) was used to obtain SiO_2. Mixtures of oxides appropriate to $KAlSi_3O_8$ were crushed repeatedly in an agate mortar, suspended in distilled water and evaporated to dryness on a steam bath until optical and X-ray examination showed that they were uniformly amorphous; the loss of weight on ignition for orthoclase was found to be 1·8 % and for celsian 1·3 %. Intermediate compositions were prepared at intervals of 10 % (wt.) celsian by mixing the appropriate amounts of the two end members;[1] each of these preparations was finally crushed and mixed in a ball mill for one hour.

Crystallization of these charges from dry melts is found to be very slow, and to require very high temperatures (~1700° C) for barium-rich specimens; however it is found to proceed quite rapidly under hydrothermal conditions with 2000 bars H_2O pressure at temperatures in the 500° to 700° C range, and the present work was carried out in this way. Standard cold-seal pressure vessels (Tuttle, 1949) were used, and all runs were quenched by immersion of these vessels in cold water. The temperature of the gold capsule containing the charge and water was

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[1] In the first paper of this series (Roy, 1965) the term 'mole per cent' was inadvertently substituted for 'weight per cent'. In all the diagrams and in the text of that paper, 'weight per cent' should be substituted for 'mole per cent'.

determined by a thermocouple in a well at the end of the bomb; the temperature difference (~10° C) was determined in separate experiments in which the thermocouple was placed in the position of the capsule. During experiments the temperature was accurately determined against the ice-point by inserting a Pt : 13 %Rh,Pt thermocouple into a groove in the bomb; it was monitored continuously and controlled to within ±5° C by an Ether 'Transistrol'.

Results. Hydrothermal runs of 7 days duration were carried out at temperatures of 500° C and 700° C and with the possible exception of potassium-rich specimens there was little difference in the properties of the products of a given composition at either temperature. Unfortunately these conditions do not produce crystals large enough for detailed optical and X-ray work; even when the duration of the experimental runs was increased to 21 days the products were still too finely crystalline for such techniques.

Optical examination shows that the crystalline product was usually very homogeneous, though some glasses of intermediate composition show the possible existence of minute quantities of a second, metastable phase; it was not possible to pursue the study of this phase, and its insignificant quantity could not have affected the composition of the synthetic feldspar crystals. The mean refractive index of crystalline material synthesized at 700° C under 2000 bars H_2O pressure for 7 days was determined at a constant temperature (21±1° C); the results are given in table I, and were plotted across the series in fig. 6 of an earlier paper (Roy, 1965).

Diffractometer traces of each product were obtained using a Philips instrument. These showed the characteristic peaks of K–Ba feldspar; no additional peaks were detected, even for specimens that had been suspected of showing minute quantities of a metastable phase in optical examination. The traces were indexed in the low angle region (up to 50° 2θ for Cu-$K\alpha$ radiation), details of the patterns and the cell constants derived from them will be given in another paper (Gay and Roy, in preparation). For the present, attention will be fixed upon the interplanar spacing d_{132}, for which a variation diagram has already been constructed for natural specimens. This spacing was measured for all synthetic specimens, and the values are given in table I. Fig. 1 shows a variation diagram constructed from these values. The values are considered to be correct to at least ±0·001 Å.

Single-crystal X-ray studies of natural K–Ba feldspars have shown that there is a significant structural change between about 50 % and

80 % Cn, associated with distinctive changes in properties. This is manifested by the appearance of type (*b*) reflections indicating a 14 Å *c*-axis structure in the more barium-rich specimens; such reflections are too weak to be detected on diffractometer records. It was decided to examine the occurrence, if any, of these reflections for synthetic specimens by using selected-area electron-diffraction methods with an E.M. 6 electron microscope fitted with a variable diaphragm; specimens were mounted from an alcohol suspension on a carbon film supported on a standard electron-microscope grid. For specimens containing 70 % Cn or more, careful examinations of the plates showed that type (*b*) maxima are present for synthetic specimens; as far as can be judged, corresponding maxima are as sharp and of much the same intensities as on the X-ray diffraction patterns of barium-rich natural specimens. To delineate their occurrence a little more closely, a new specimen of 65 % (wt.) Cn was prepared; this did not show the subsidiary maxima.

TABLE I. Mean refractive indices and interplanar spacings d_{132} for feldspars synthesized hydrothermally

Composition (wt. %)	Synthesized at 700° C, 2000 bars H_2O, 7 days		Synthesized at 500° C, 2000 bars H_2O, 7 days
	n	d_{132}	d_{132}
$Cn_0\,Or_{100}$	1·515	$2{\cdot}993_3$ Å	$2{\cdot}995_3$ Å
$Cn_{10}Or_{90}$	1·527	$2{\cdot}996_7$	$2{\cdot}998_6$
$Cn_{20}Or_{80}$	1·535	$3{\cdot}002_9$	$3{\cdot}000_7$
$Cn_{30}Or_{70}$	1·544	$3{\cdot}006_1$	$3{\cdot}004_2$
$Cn_{40}Or_{60}$	1·549	$3{\cdot}008_1$	$3{\cdot}008_4$
$Cn_{50}Or_{50}$	1·557	$3{\cdot}010_3$	$3{\cdot}009_5$
$Cn_{60}Or_{40}$	1·563	$3{\cdot}013_9$	$3{\cdot}013_4$
$Cn_{65}Or_{35}$	1·567	$3{\cdot}014_9$	—
$Cn_{70}Or_{30}$	1·568	$3{\cdot}016_6$	$3{\cdot}015_3$
$Cn_{80}Or_{20}$	1·575	$3{\cdot}019_7$	$3{\cdot}020_0$
$Cn_{90}Or_{10}$	1·584	$3{\cdot}021_6$	$3{\cdot}021_6$
$Cn_{100}Or_0$	1·589	$3{\cdot}023_7$	$3{\cdot}021_7$
	±0·002		

Discussion. The earlier work suggested the existence of a high K–Ba feldspar series, at least for all but the most barium-rich members. Gay (1965) showed that significant changes in d_{132} spacings were produced when many natural specimens were severely heat-treated, an observation that has been independently confirmed by additional experiments in the present work. The values of d_{132} for synthetic specimens are significantly different from those for unheated natural specimens up to 60 % Cn (fig. 1), and more in accord with those from heated materials.

It may be questioned whether the crystalline material produced hydrothermally in the present study represents the ultimate high structural state, though, judging from synthetic work on other feldspars and from the similarities in properties between synthetic and severely heat treated

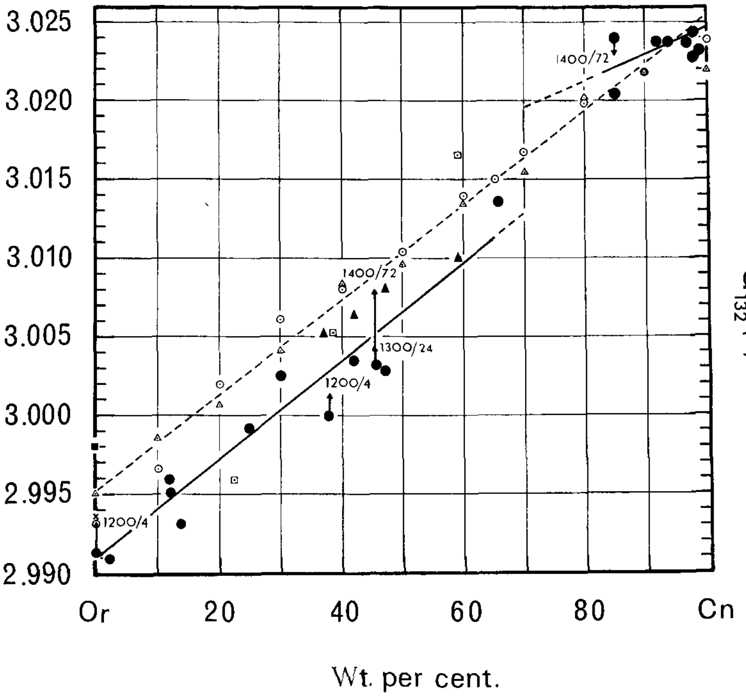

Fig. 1. Variation diagram for d_{132} (Å) against celsian content. The broken line represents the variation for members synthesized at 700° C (⊙) and 500° C (△) under 2000 bars H_2O pressure for 7 days. The solid lines (●, ▲) represent the variations for unheated natural specimens (● specimens from various localities; ▲ different density fractions of a zoned specimen from Taguchi manganese mine, Japan). The arrows indicate the change in d_{132} due to heating at various temperature and time conditions (e.g. 1400/72 represents heating at 1400° C for 72 hours etc.). ⊡ specimens from Franklin, New Jersey, U.S.A. Discrepancy probably due to An content. × heat-treated natural orthoclase (Cole *et al.*, 1949); ■ synthetic orthoclase (Donnay and Donnay, 1952).

materials, it seems probable that the synthetic materials do not depart appreciably from this condition. For the more barium-rich specimens, there is some ambiguity. The measured properties of natural, heated, and synthetic materials are not sufficiently different to allow the certain distinctions of low and high structural states to be made. There is some evidence that extended heating of natural specimens at high temperatures (~1500° C) can promote some changes in the intensities of type (*b*) reflections, so indicating a structural change to be associated with a high form of celsian; this will be discussed in a later paper (Gay and Roy, in preparation). For the present it may be noted that these reflections are to be found on the electron-diffraction patterns of the barium-rich synthetic specimens, so that it may well be that these materials are in an intermediate, or even low, structural state.

With this reservation in mind, the variations in properties for the synthetic feldspars are those expected from the classic solid solution series; they vary continuously in a linear manner across the series (broken line, fig. 1), and there are no inflexions or discontinuities of the kind suggested for natural specimens. The occurrence of a miscibility gap, which has been suggested for natural (low structural state) K–Ba feldspars, is eliminated for synthetic (high or intermediate structural state). It is thought that this gap occurs in the region 50–80 % Cn, but it is clear that there is no evidence for its existence at higher temperatures. The present work seems to suggest that the structural change from 7 Å to 14 Å *c*-axis cells occurs over a small composition interval (between 65 and 70 % Cn) with no intervening structural conditions.

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