An X-ray powder method for the estimation of (K, Ba) feldspars

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Summary. Examination of previous physical methods of estimating the barium-content of these feldspars showed that they are generally unsatisfactory. A new variation diagram is constructed correlating BaO content and values of d_{132} determined from diffractometer records. It is estimated that the BaO content of these feldspars can normally be determined to about 2–3 % by using this diagram.

Some of the problems of the mineralogy of the series are reviewed in the light of the experimental results, in particular the effect of polymorphic changes on the variation diagram. Some experimental evidence of the effect of different structural states upon the value of d_{132} is obtained, and the limitations imposed upon the method by the existence of such states are discussed.

Introduction

FELDSPARS with appreciable barium contents are thought to form a series from potassium to barium feldspar. Barium-orthoclases, hyalophanes, and celsians are regarded as members of this series, and despite their rarity, their relationships within the series are of some interest, particularly in the light of recent work on the sub-solidus relations in the commoner alkali and plagioclase feldspar series. From time to time individual members of the series have been described, but a systematic study of the series as a whole seems to have been neglected. With this objective, the author began to form a collection of potassium-barium feldspars some years ago. Whilst this collection is still rather limited, enough specimens are available over the series to allow a preliminary survey of the mineralogy to be made. These results will be presented elsewhere, and the present paper is restricted to the attempts to determine and classify the specimens by X-ray powder methods.

The rarity of the specimens often meant that they were available only in minute quantities; they were described as hyalophane, celsians, etc., and usually nothing more about their constitution (in particular the Ba-content) was known. Conventional analytical procedures cannot be used, and the optical properties of the series are so imperfectly known that the few variation diagrams that have been proposed can only be regarded as speculative (see the comments of Segnit (1946)). Vermaas

(1953) suggested an X-ray powder method for the determination of the composition of hyalophanes, and it was an examination of this method, in the hope that it would prove suitable for the available specimens, that led to the work to be described.

Previous X-ray powder work

Vermaas (1953) studied eight members of the series, together with various adularias and sanidines to be used as the potassium-rich end members. For each specimen, he measured 2θ values using standard X-ray powder photographic techniques. From these 2θ tables, four variation diagrams were constructed, in each of which the difference in 2θ between a selected pair of lines was plotted against the wt. % $BaAl_2Si_2O_8$ determined either chemically or spectroscopically. The four plots are very similar and the same general conclusions apply to all of them.

For hyalophanes from pure potassium feldspar (Cn_0) to Cn_{37} (i.e. 15·2 % BaO wt.), these line separations vary linearly with composition. The extrapolation of the linear relationship to Cn_0 passes very near to the recorded separation values of the adularias, and so adularia, rather than sanidine, is to be regarded as to potassium end-member of the series. Vermaas records that for more barium-rich specimens there are marked changes in relative intensities, and that the line separations for the four specimens examined are not systematically related to composition or to each other. Nevertheless he suggests that there is some kind of discontinuity and that there are two distinct series Cn_0–$Cn_{40}\pm$ and $Cn_{45}\pm$–Cn_{100}; the unsystematic line separations observed for specimens in the latter series are attributed to an abnormally high replacement of Al^{3+} by Fe^{3+}, and other possible cation replacements in some of his specimens. He claims that, using a combination of the variation diagrams, the composition of hyalophanes can be determined to ±5 % Cn (or about 2 % BaO wt.).

Since the quantities of most of the specimens available in the present work allowed the preparation of smear diffractometer mounts, this method seemed to present a possible way of determining unknown materials, particularly hyalophanes. It was thought advisable to index the diagnostic peaks arbitrarily chosen by Vermaas, and this revealed that his determinative peaks were multiple maxima, and hence rather unreliable. Further, both calculation of 2θ values from the cell dimensions of a celsian (Newnham and Megaw, 1960) and measurement of diffractometer records showed that the 2θ values given by Vermaas

(stated to be correct to $0 \cdot 03°$) were always too large; even for a single well-resolved peak, the discrepancy could be as much as $\frac{1}{3}°$ (2θ).

In the light of these facts, it was decided to attempt to draw up a new variation diagram for use in the present work, and the remainder of this paper is concerned with the preparation of such a diagram, and discussion of its significance.

Experimental procedures

(a) *Specimens.* A number of specimens over the series were used in the construction of the diagram. Full details of these specimens will be given elsewhere; they will be referred to here by reference numbers and general localities only. For some of these specimens full chemical analyses were possible, but for others the quantities were such that only their BaO content was determined with the electron beam micro-analysis probe by Dr. J. V. P. Long. Available analyses show that there can be replacement of potassium and barium by sodium and calcium respectively, and aluminium by iron, but it would have been a complex task to undertake quantitative investigation of all elements present by the probe technique. Whilst it is apparent that such replacements will have some effect upon the positions and intensities of lines upon a powder record, it is probable that they will be secondary to the main changes occurring over the series. In the present work there was no course other than to neglect them, and to classify the various specimens within the series in terms of their weight percentage of BaO.

(b) *X-ray examination.* For each specimen four records from a smear mount with a silicon internal standard from $12°$ (2θ) to $40°$ (2θ) were obtained using a rebuilt Berthold diffractometer with CuKα radiation. This low-angle range avoids, as far as possible, overlap of lines in a complex pattern and allows unambiguous indexing of peaks. Each of the records was carefully measured, and the average line positions determined for each specimen. Although the accuracy of such measurements depends on many factors, not least the quality of the trace, it would appear that the values obtained are, at the worst, reliable to $\pm 0 \cdot 01°$ (2θ), and often the accuracy is rather higher.

(c) *Interpretation of the records.* Over the whole series, indexing was carried out in terms of the 14 Å c-axis body-centred monoclinic cell of celsian (Gay, 1956). If the usual nomenclature for such feldspars is used, the barium-rich members of the series should show both type (*a*) and (*b*) reflections, whereas the more potassium-rich specimens still have a monoclinic cell but show only type (*a*). For celsians, the type (*b*)

reflections are very weak, and they have not been observed on any diffractometer record. All indices assigned to recorded maxima are therefore of type (a) with $h+k$ even, l even.

TABLE I. Indexed powder pattern of a celsian

Celsian, Jakobsberg, Sweden (Vermaas, 1953)		Celsian, Jakobsberg, Sweden STR 4		
2θ	Intensity*	2θ	Intensity	(hkl)
13·98	50	13·565	48	$\begin{cases} 002 \\ 020 \end{cases}$
		15·068	10	$\bar{1}12$
19·59	50	19·241	32	022
		22·171	7	112
		22·756	17	200
23·75	50	23·396	54	130
		24·537	31	$\bar{1}32$
		25·041	45	$\bar{2}22$
26·06	100	25·631	100	$\bar{1}14$
26·97	117	26·594	100	220
		27·157	46	$\bar{2}04$
27·73	117	27·319	59	$\begin{cases} 004 \\ 040 \end{cases}$
29·94	133	29·541	95	132
31·00	67	30·657	47	$\begin{cases} 024 \\ 042 \end{cases}$
32·64	83	32·272	50	$\bar{1}34$
		34·431	21	$\bar{3}14$
35·06	167	34·716	77	$\begin{cases} 114 \\ \bar{2}42 \end{cases}$
		35·154	10	310
		35·934	2	240
37·42	50	37·090	13	$\bar{1}52$
		37·559	5	$\bar{3}32$
38·96	50	38·615	14	$\bar{1}16$
		39·570	7 $\Big\}$	$\begin{cases} \bar{3}34 \\ 134 \\ 330 \\ \bar{2}\bar{2}6 \end{cases}$
39·93	17	39·641	7	
		39·981	7	

* These intensities have been scaled to equivalence with those estimated in the present work.

An indexed pattern for a celsian is compared with photographic measurements given by Vermaas (1953) for a very similar specimen in table I. It is clear that in the photographic work many lines were not recorded or not resolved, and that there are serious discrepancies in the 2θ values for single peaks. Lack of resolution may account for some of the differences in relative intensities, although the use of unfiltered radiation must also add to the inaccuracy of the photographic estimates.

The table includes two unresolved line groups ($31 \cdot 00°$ (2θ) and $35 \cdot 06°$ (2θ)) used by Vermaas in the construction of variation diagrams.

From a table drawn up for all specimens, it was possible to follow the shifts in line position for the indexed maxima. Full details of all the diffraction patterns which were used in a study of cell volumes will be published elsewhere, but attention must be drawn to marked changes in relative intensities for some peaks over the series. These can result in the virtual (or complete) disappearance of some lines of the celsian patterns for more potassium-rich members, and vice versa.

Construction of the variation diagram

Ideally for the construction of this diagram, the well-resolved peak(s) chosen should show reasonable intensities for all specimens, and appreciable change in spacing over the series; it is often convenient for them to be as close as possible to a peak of a common standard material. Examination of the table of 2θ values for these feldspars reveals that there are few low-angle maxima which are at all satisfactory. For example, the ($\bar{2}02$) peak[1] extensively used for the determination of homogeneous alkali feldspars, although present for the potassium-rich hyalophanes, is of insignificant or zero intensity for many of the barium-rich specimens. On the other hand, the line group (220), ($\bar{2}04$), (004), and (040) at $26\frac{1}{2}$–$27\frac{1}{2}°$ (2θ), although a dominating feature of every record, is not sufficiently well resolved over the whole series. The most suitable reflection appears to be (132) at $29\frac{1}{2}$–$30°$ (2θ), and it was decided to construct the diagram in terms of its absolute position measured relative to the (111) peak of the silicon standard at $28 \cdot 466°$ (2θ). Table II (a) shows 2θ (132) together with the corresponding values of d_{132} for all specimens arranged in order of the estimated BaO wt. % (pure $BaAl_2Si_2O_8$ contains $40 \cdot 8$ % BaO wt.)

In fig. 1, d_{132} is plotted against BaO content, and the variation in this spacing over the series is reasonably systematic. The exact form of this variation remains indeterminate, and a reasonable curve has been drawn through the points. If the assessment of the accuracy of line position is reliable, then the values of d_{132} should be correct to about $0 \cdot 001$ Å. The accuracy of the estimated BaO contents is not so easy to assess, particularly for those specimens for which a few grains have been examined by the micro-analysis probe method. Comparative measurements on materials which had been chemically analysed confirm that the

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[1] ($\bar{2}02$) are the indices of this reflection for a 14 Å c-axis cell; in alkali feldspar work, with only 7 Å c-axis cells, the same maximum is indexed as ($\bar{2}01$).

TABLE II. (a) Values of 2θ (132), d_{132}, and BaO content; (b) Values of 2θ (132), d_{132}, for heat-treated specimens. The heat treatment is given in parentheses, e.g. (3–1400) indicates heating for 3 days at 1400° C

Specimen and locality	(a)			(b)	
	BaO wt. %	2θ (132) (°)	d_{132} Å	2θ (132) (°)	d_{132} Å
1920. Fresno Co., California	40·0	29·536	$3·024_3$		
BM 1958, 24. Benallt Mine, Rhiw, Wales	38·9	29·551	$3·022_8$		
331038. Jakobsberg, Värmland, Sweden	38·0	29·541	$3·023_7$		
STR 4. Jakobsberg, Värmland, Sweden	36·9	29·541	$3·023_6$		
5081A. The Piggery, Broken Hill, N.S.W., Australia	35·8	29·573	3.020_5		
STR 5. Jakobsberg, Värmland, Sweden	34·6	29·543	$3·023_9$	29·551 (3–1400)	$3·022_8$
Kaso. Kaso mine, Japan	25·5	29·641	$3·013_7$		
195367. Bosnia, Yugoslavia	19·0	29·751	$3·002_9$	29·699 (3–1400)	$3·008_0$
BM 31990. Binnenthal, Valais, Switzerland	15·7	29·743	$3·003_7$		
BM 1959, 359. Bosnia, Yugoslavia	15·7	29·749	$3·003_8$		
BM 84765. Binnenthal, Valais, Switzerland	15·1	29·786	$2·999_5$		
g 11130. Sjögruvan, Västmanland, Sweden	12·3	29·789	$2·999_2$		
280560. Nya Zealand, Långban, Sweden	12·1	29·754	$3·002_6$	29·656 (3–1380)	$3·010_9$
F. F. Franklin Furnace, New Jersey, U.S.A.	11·5	29·821	$2·996_0$		
g 21009. Långban, Sweden	5·6	29·849	$2·993_3$		
g 11156. Jakobsberg, Värmland, Sweden	4·7	29·829	$2·995_2$		
S. 61. Taguchi mine, Sidaru, Japan	4·2	29·853	$2·992_9$	29·801 (3–1200*)	$2·998_0$
10 (80199). Nodo Tamagawo mine, Iwate Prefecture, Japan	1·6	29·873	$2·990_9$		
Md. Antisirabey, Madagascar	0·0	29·881	$2·990_1$		

* At slightly higher temperatures, the specimen melts incongruently to give leucite.

probe results agree with the chemical analysis to within about ±5 % of the BaO content. Further, with the limited data no account can be taken of the effect on d_{132} of any substitution by sodium, calcium, or other cations.
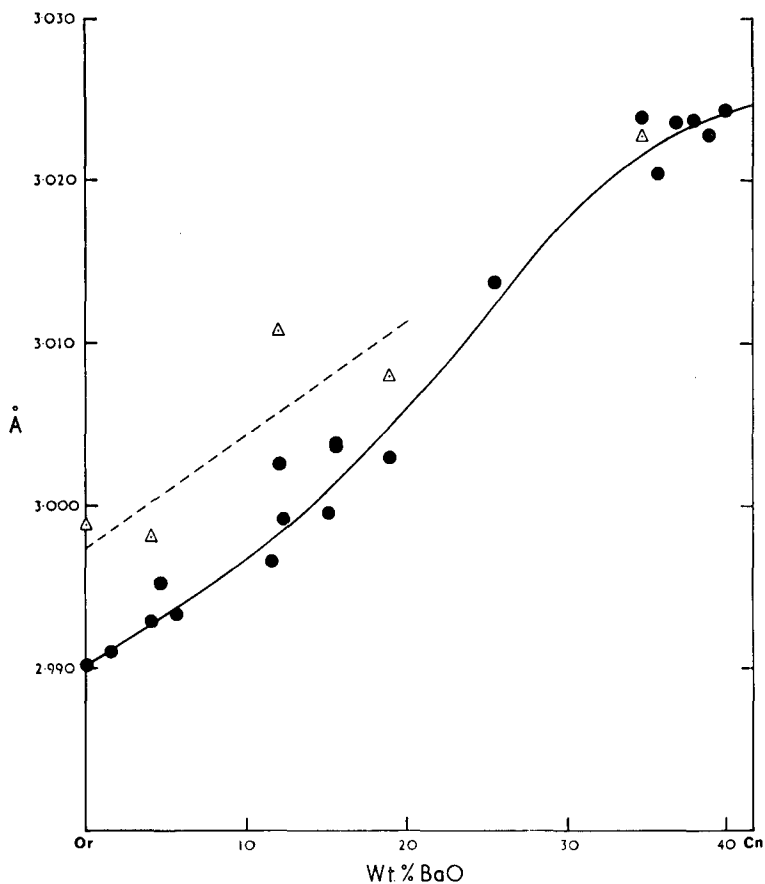
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Fɪɢ. 1. Variation diagram of d_{132} (Å) against BaO content of the feldspar. Points shown (●) are from natural specimens; points shown (△) are from heat-treated specimens. The full curve has been drawn for the natural specimens, while the dotted curve has been drawn for the heat-treated specimens.

Discussion

If the present form of the variation diagrams were correct, determination of the value of d_{132} would give the barium content of the feldspar to about $\frac{1}{2}$–1 % BaO wt. In view of the uncertainties in the data already mentioned, a fairer estimate of accuracy might be thought of as 2–3 % BaO wt.

The present results throw no light on the possibility of a discontinuity in the solid solution series as suggested by Vermaas (1953) from his

X-ray work and by Yosimura (1939) when examining optical properties. Indeed it could be argued that the present more extensive survey, if allowance is made for all possible errors, shows an effectively continuous linear spacing change with barium content, and provides better evidence for continuity of structural change within the series than either of the previous authors have given for discontinuity. However, resolution of this problem and that of the possible existence of a miscibility gap must await the results of a more detailed survey of the series by optical and more sensitive X-ray methods both upon natural and synthetic specimens.

The utility of the d_{132} diagram must also be considered with regard to any polymorphic changes which these feldspars show, for studies on other feldspar series indicate that it is not usually possible to determine either composition or structural state from a diagram of one physical parameter. It is generally accepted that $KAlSi_3O_8$ can exist in a range of structural states from triclinic microclines with maximum obliquity through intermediate microclines to monoclinic orthoclase and sanidines with increasing temperature. Since no feldspar containing an appreciable amount of barium has been shown to be triclinic, d_{132} for a monoclinic orthoclase was used as the end point in the diagram; but to take account of different structural states, d_{132} for a high sanidine must also be plotted. At the other end of the series, there is at present no direct evidence of any polymorphism in $BaAl_2Si_2O_8$, but one may consider possible changes by comparison with the Ca-analogue, anorthite. Primitive and body-centred anorthite structures exist, and the primitive form may be converted into the body-centred form by heat treatment; in turn the body-centred form may be changed into an albite-like structure at high temperatures. In celsians, there has been no evidence for a primitive 14 Å c-axis structure, and it seems likely that the only type of transformation feasible will be one in which the 14 Å c-axis is destroyed. In the plagioclases, this is associated with the randomization of an ordered Si–Al distribution, and very severe heating conditions are necessary to promote it. It is to be expected that it will be more difficult to destroy Si–Al order in celsians, if it is possible at all for the more Ba-rich specimens. This is confirmed by single-crystal X-ray work, to be described elsewhere, which has shown that a 14 Å c-axis structure remains in barium-rich specimens (> 35 % BaO wt.) even after extended heating at temperatures up to $1500°$ C. Considering the effect upon the d_{132} variation diagram, we should expect therefore that a number of different structural states will be detectable for potassium-

rich specimens, but that the spread in d_{132} values at a fixed composition will decrease with increasing barium content to become negligible as pure celsian is approached.

From what is known of the geological environments of the specimens used in the construction of the diagram, there is no reason to expect them to deviate significantly from a low structural state. It was decided to attempt a general confirmation of the expected effect of differing structural states on d_{132} by heat treatment of some specimens. The limited amounts of specimens severely restricts the selection of material for heat treatment, so that the data recorded in table II (b) are very

TABLE III. Relative intensities of the line group (220), ($\bar{2}04$), (004), and (040) after varying heat treatment of a hyalophane specimen, 195367; three peaks A, B, C, are observed at angles of 26·892, 27·208 and 27·491 (°2θ) respectively for the unheated specimen

	Peak heights		
Heat treatment	A	B	C
Unheated	105	70	120
3 days; 1000° C	135	75	110
3 days; 1100° C	140	80	105
3 days; 1200° C	135	70	90
3 days; 1300° C	110	65	70
3 days; 1400° C	115	65	70

sparse. The very tentative curve drawn in fig. 1 for these experiments can only be regarded as giving a general indication of the spread of d_{132} values with varying structural states. Nevertheless the evidence generally supports the conclusion of the preceding paragraph. It is also found that heat treatment can cause marked changes in the relative intensities of certain lines. For example, the effect of successive heat treatments upon the intensities of the line group (220), ($\bar{2}04$), (004), and (040) for a hyalophane is given in table III. As far as the limited evidence allows, it appears that similar changes with structural state hold for all potassium-rich hyalophanes. For the low-temperature natural specimens, relative intensities change with composition, and it seems that heating such potassium-rich specimens has the same effect upon them as an increase in barium-content; this is in accord with the change in d_{132} with structural state.

We must conclude that, whilst ambiguities in the interpretation of a value of d_{132} are unlikely to be important if the BaO content of the feldspar exceeds about 15 % BaO, they can occur for more potassium-rich specimens. If the field or other evidence strongly supports the

presumption of a low structural state, the composition may be esti-
mated; if the composition is known, the variation diagram can roughly
assess the structural state.

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