

The determination of the orthoclase content of homogenized alkali feldspars using the $\bar{2}01$ X-ray method

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SUMMARY. Forty-three natural alkali feldspars have been homogenized and used to correlate $d_{\bar{2}01}$ with wt % K_2O . The regression of Or on $d_{\bar{2}01}$ is $Or \text{ (wt \%)} = 465.5 d_{\bar{2}01} (\text{\AA}) - 1877.5$, and is comparable to that obtained on an exchanged orthoclase (Wright, 1968). A deviation from the Orville (1963, 1967) determinative line for synthetic sanidine-albite is greatest at the high potassium end of the series. The discrepancy is not caused by failure to homogenize or incomplete disorder. The presence of cations other than potassium and sodium, or cation deficiency, or both cannot be discounted as a cause.

AN X-ray method for estimating the orthoclase content of synthetic alkali feldspars was introduced by Bowen and Tuttle (1950) as a means of obtaining the composition of phases produced in their hydrothermal experiments on the granite system. Since that time the method has been extensively used for similar purposes (e.g. Thompson and MacKenzie, 1967) and also for petrological investigations in natural rock systems (e.g. Wright, 1964, 1968; Parsons, 1965).

The method depends mainly on the change of the a cell dimension with changing composition, this variation being detected by the change of $d_{\bar{2}01}$. From a mineralogical viewpoint it would obviously be preferable to obtain direct values of all lattice parameters as was done by Orville (1967) and by Wright and Stewart (1968). However, we believe that the effort involved in obtaining a direct value for the a cell dimension is not warranted for routine petrological work, since there are other factors which probably produce larger errors in the estimated Or content.

The original calibration line of Bowen and Tuttle (1950) was based on synthetic feldspars and used olivine, calibrated against quartz, as an internal standard. Orville (1963) revised the determinative line using potassium bromate as an internal standard since minerals are, in some cases, unsuitable for this purpose. In this investigation potassium bromate has also been used since its 101 reflection is conveniently situated on the low-angle side of pure orthoclase feldspar. Determinative lines also exist for the natural system microcline-low-albite (Orville, 1960, 1967) and also for orthoclase-intermediate-albite (Wright and Stewart, 1968; Wright, 1968) but no curve has been published for natural feldspars in the sanidine-high-albite series.² Although it is now

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² All determinative curves based on synthetic materials represent the high-sanidine-high-albite series. Natural potassium-rich high-sanidines are rare, whilst sodic varieties are more common. With the exception of the anorthoclases, lack of resolution in the composite 040 002 peak (Jones, 1966) indicates that the majority of our specimens are in an intermediate structural state. This is probably true for most potassium-rich specimens homogenized for routine petrological determinations.

a routine petrological technique, it has been criticized by some writers (for example, Coombs, 1954) because non-homogeneous natural alkali feldspars have been observed with larger 201 spacings than the Or_{100} of Bowen and Tuttle (1950). Smith (1961) suggested the discrepancy could be explained in terms of strain due to exsolved perthite lamellae.

Method of study. The feldspars used were separated by conventional techniques and their purities checked in refractive index liquids. Potassium was measured flame photometrically on six specimens analysed in other laboratories (Table I), and as a test of precision, 5–8 replicate determinations were made on four specimens; the standard error of the mean ranged from 0.024 to 0.06 % K_2O .

TABLE I. *Comparative K_2O values on some standardized samples*

	This paper	Comparative values	
NBS 70	12.56	12.58	National Bureau of Standards
17263	11.46 ^a	11.46	Average of 7 determinations by different analysts using flame photometer or X-ray spectrograph.
21978	2.96	3.01	Wilkinson (1962)
G 1	5.51	5.45	Fleischer and Stevens (1962)
		5.52	Ingamells and Suhr (1963)
		5.48	Fleischer (1969)
NBS 99	0.40	0.41	National Bureau of Standards
21988	7.09	7.06	Emeleus and Smith (1959)

The method used in the determination of potassium is subject to error in the case of feldspars containing high quantities of rubidium. This is caused by the proximity of the analytical line of potassium and a strong emission line of rubidium. The interference can be effectively eliminated by narrow band-pass filters or high resolution monochromators. For the sample 17263 the rubidium content was known and a correction made by adding the required amounts of rubidium to the standard solutions. The K_2O value (11.46) was close to that (11.52) obtained using a combined narrow band-pass filter and monochromator (J. Cooper, pers. comm.).

The available data (Heier, 1962; Deer, Howie, and Zussman, 1963) suggest that the rubidium content of non-pegmatite alkali feldspars is generally less than 1000 ppm. Only five of the samples of table II are known to be from pegmatites (nos. 142, 16949, 21990, 17263, and 2785) and since a rubidium content of 2000 ppm only produces an apparent increase of approximately 0.15 % K_2O if not allowed for, the errors introduced are likely to be insignificant.

X-ray diffraction measurements were made only on samples heated until the 002, 040, 220 composite reflection of plagioclase had disappeared (1050 °C for 48 hours or more). Feldspars more potassic than Or_{40} were not measured unless the 130 and 131 peaks were sharp. This does not ensure complete Al–Si disorder but the effect on d_{201} will be small since the change in a from Spencer C to Spencer C sanidinized

(Cole, Sörum, and Kennard, 1949) is only 0.002 Å, corresponding to an error of approximately 0.4 % Or. We discuss this aspect in more detail later.

The difference between $2\theta_{101}$ of KBrO_3 and $2\theta_{201}$ of the feldspar was determined from four to eight oscillations on the diffractometer. Conditions were: 0.1 mm receiving slit, $\frac{1}{4}^\circ$ /minute scanning rate, 40 mm/degree chart drive.¹

The precision of the diffractometer measurements was checked by eight separate determinations on a single feldspar powder. After each series of six oscillations the smear mount was remade. The distance, in millimetres, between the centres of the feldspar and bromate peaks was measured at $\frac{2}{3}$ peak height and converted to degrees. This gave a standard deviation of $0.003^\circ 2\theta$ Cu- $K\alpha$ for the precision of measurement on a single sample. Two traces on a 15-mg sample of synthetic Or_{100} supplied by Dr. P. Orville yielded values of 4.2345 and 4.2336. Orville (1967) reports a calculated value for $2\theta_{201}$ of 4.234.

Results. Chemical and diffraction measurements are summarized in table II, and fig. 1 shows the data in relation to the determinative line of Orville (1967). The regression equation for the Or_{0-100} range is $Y = 465.5x - 1877.5$ (S.E.E. 2.3 % Or)² whereas a straight line fit of Orville's (1967) data is $Y = 489.19x - 1972.5$ (S.E.E. 1.2 % Or) ($Y = \text{wt \% Or}$, $x = d_{201}$ Å).

The data given in table II and fig. 1 show the greatest deviation from the values proposed by Orville (1967) and Bowen and Tuttle (1950) at the high-potassium end of the series. A similar trend is apparent in fig. 2 of Parsons (1968). The difference in slope of the two lines is outside both the precision and 'relative' accuracy.

The results of the above regression analysis on the data of Orville (1967) show that in synthetic systems much lower standard errors of estimate can be expected (see also Wright, 1968). No significant improvement in the S.E.E. is made by using the data of Orville in the separate ranges Or_{75-100} and Or_{0-75} , so there is no statistical basis for the break in slope in the determinative line as suggested by Orville (1963). However, Orville does state that these lines were fitted through the end-member compositions, since several determinations had been made on them, and consequently they were more reliable.

Discussion

Fig. 1 shows an obvious discrepancy between the determinative line of Orville (1963, 1967), and the regression of wt % Or on d_{201} calculated from our data. A similar discrepancy is apparent in the results of Wright and Stewart (1968) and Wright (1968). Full discussion of the reasons for this discrepancy is awaiting further analytical data. However, there are several possible explanations, which we shall discuss briefly since some may be eliminated using our present limited data.

¹ This nominal chart drive was in fact determined as 40.13 mm/degree based on a recalibration of the Honeywell recorder against silicon. Using this corrected value for the chart drive, and standardizing against silicon, a value for $2\theta_{101}$ KBrO_3 of $20.230^\circ = 4.3985$ Å was obtained (Cu- $K\alpha = 1.5418$ Å). Orville (1963) recommended $20.205^\circ 2\theta$, but on recalibration against fluorite has since suggested a value of 20.212° for Cu- $K\alpha_1$ radiation (Orville, 1967).

² This determinative line is close to that suggested by Wright (1968), who used an exchanged orthoclase. Wright does not comment on the discrepancy between natural and synthetic materials.

TABLE II. d_{201} and K_2O (wt %) for specimens used in the investigation

No.	Locality	% K_2O	% Or	d_{201}
142	Amelia, U.S.A.	0.25	1.47	4.0320
16949	Sitting Bull, U.S.A.	1.16	6.85	4.0431
21978	Spring Mt., N.S.W.	2.96	17.49	4.0724*
21979	Erebus, Antarctica	2.97	17.55	4.0688
1794	Erebus, Antarctica	3.24	19.14	4.0711
1793	Pantellaria	3.39	20.03	4.0715
21980	Mt. Anakie, Victoria	3.51	20.74	4.0795†
21981	Mt. Franklin, Victoria	3.96	23.40	4.0812
18106	Tanganyika	4.00	23.64	4.0842
21982	Texas	5.45	32.20	4.1040‡
21983	Texas	5.49	32.44	4.1046‡
21984	Texas	5.52	32.62	4.1052‡
21985	Texas	5.67	33.50	4.1072‡
14137	Mayor Is., New Zealand	5.75	33.98	4.1028
21986	Texas	6.08	35.93	4.1130‡
21987	Texas	6.27	37.05	4.1164‡
21988	Slieve Gullion	7.09	41.90	4.1232§
21989	South Greenland	7.32	43.26	4.1187
11346	Drachenfels, Germany	9.35	56.32	4.1582
2785	Wirrega, S. Australia	9.56	56.49	4.1585
21990	Giant's Head, S.A.	9.74	57.56	4.1600¶
1397	Ceylon	11.44	67.61	4.1785
17263	Boolcoomatta, S.A.	11.46	67.72	4.1742¶
22785	Boolcoomatta, S.A.	11.95	70.62	4.1818¶
292	No locality	12.13	71.68	4.1900
21991	No locality	12.87	76.06	4.1975**
21992	Reedy Creek, S.A.	13.28	78.48	4.2107
21993	Port Cygnet, Tasmania	13.40	79.19	4.1997**
21994	Reedy Creek, S.A.	13.91	82.20	4.2133
21995	Black Hill, S.A.	13.92	82.26	4.2165
21996	Nairne	14.07	83.15	4.2172
21997	St. Gotthard, Switzerland	14.31	84.57	4.2143**
21998	No locality	14.53	85.87	4.2112**
21999	Nairne, S.A.	14.72	86.99	4.2203
22000	Ceylon	14.81	87.52	4.2219
22001	South Australia	15.02	88.76	4.2210
22002	Broken Hill, N.S.W.	15.14	89.47	4.2200
22003	No locality	15.21	89.89	4.2240**
1242	Arkansas, U.S.A.	15.36	90.77	4.2330
22004	South Australia	15.57	92.01	4.2232
297	St. Gotthard, Switzerland	15.60	92.19	4.2268
22005	St. Gotthard, Switzerland	15.61	92.25	4.2282**
22006	Tyrol	15.71	92.84	4.2267**

* J. F. G. Wilkinson, 1962.

† Australian Museum, Sydney.

‡ M. F. Carman, University of Houston, Texas.

§ C. H. Emeleus and J. V. Smith, 1959 (specimen G31).

|| R. W. Nesbitt, 1961. Ph.D. Thesis, University of Durham (GGU23409).

¶ Minor triclinic component present, but d_{201} should be appropriate for dominant monoclinic component.

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Failure to achieve complete disorder. The maximum difference between the calibration lines microcline–low-albite and sanidine–high-albite is about 4 % Or (Orville, 1967). The sanidine–high-albite line has higher d_{201} values than the microcline–low-albite at the Or-rich and Ab-rich ends, but intersects and has lower values in the centre of the compositional range (Orville, 1967, fig. 9). Hence further heating of the natural materials would, in most cases, increase d_{201} causing an even greater discrepancy.

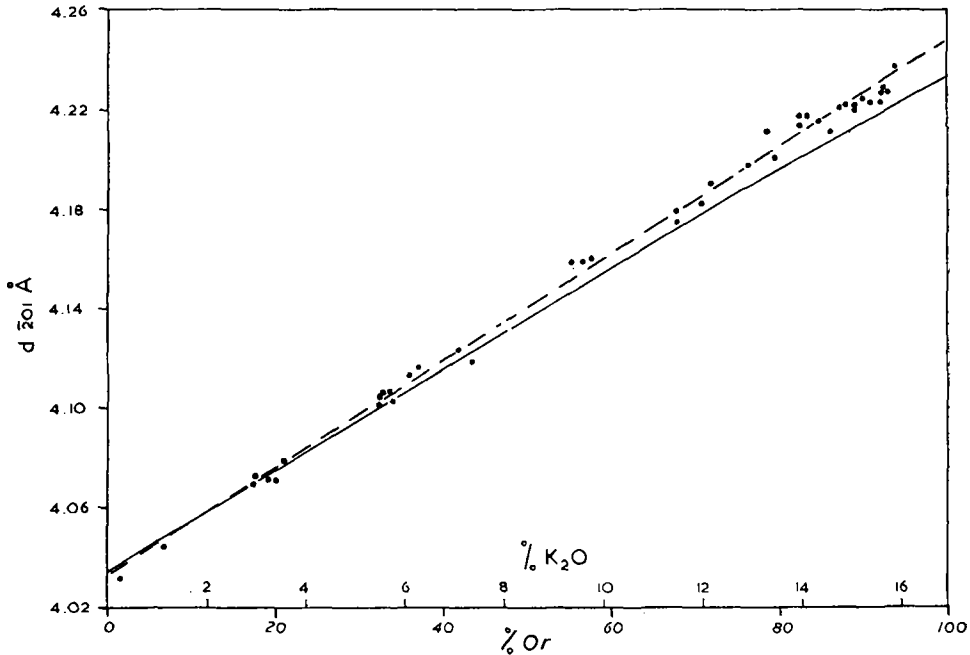


FIG. 1. Plot of d_{201} against wt % K_2O . Equivalent percentage Or shown on the abscissa obtained by multiplying % K_2O by 5.91. The dashed line is the regression curve $Or \% = 465.5 d_{201} - 1877.5$. The solid line is that of Orville (1967) for synthetic alkali feldspars converted from 2θ ($201-101$ $KBrO_3$) to d_{201} Å.

Furthermore, as was pointed out earlier, failure to achieve complete disorder produces only a minor error (about 0.002 Å) when dealing with natural material with sharp 130 peaks.

Incomplete homogenization has been suggested by Parsons (1968) as an explanation of the discrepancy of the natural feldspars. This is difficult to quantitatively evaluate because of the lack of criteria. However, MacKenzie (1954) on the basis of mixing two feldspars together and observing the intensity of the 002, 040, and 220 reflection, suggested that 2 % of exsolved albite could easily be detected in a powder pattern of potash feldspar. If this is the case then the total absence of this reflection in all of the material listed in table II suggests that the amount of albite remaining as a single phase is insignificant.

As a further check, two anomalous specimens (1242 and 297) were fused and

recrystallized at 600 °C at 2Kb P_{H_2O} for three weeks. The cell dimension refinement programme of Evans, Appleman, and Handwerker (1963) was used to obtain full cell-dimensions for both the natural and hydrothermally recrystallized specimens. The recrystallization resulted in an increase of 0.005 ± 0.002 Å in the fitted values for d_{201} for both specimens. Hence, complete homogenization and disorder produced by recrystallization shifts these two aberrant values even further from the sanidine-high-albite line.

Potassium contamination during heating. All the alkali determinations were carried out on unheated samples, so that if any addition of potassium took place in the vapour phase during heating (Brown, 1967) a d spacing larger than that appropriate to the determined K_2O content would result. One sample was analysed both before and after heating for five days at 1000 °C. The variation in the results was within the precision of the method used so that it seems unlikely that potassium transfer is affecting d spacing values. In addition the furnaces used are wound on alumina tubes, not mullite. As mentioned earlier, the presence of rubidium would affect the analytical result. However, large amounts of the element would tend to move the point towards the synthetic line, because K_2O is overestimated.

The presence of other cations in the feldspar structure would modify, to varying degrees, the cell dimensions of the mineral. Kempe (1966), for example, has suggested that calcium makes significant differences in the d_{201} of sodic alkali feldspars, thus disputing the conclusions of Carmichael and MacKenzie (1964). Our data are insufficient to comment further in the case of calcium, but analysis of many of the high-potassium feldspars that are discrepant on fig. 1 shows that they contain appreciable quantities of barium (up to 2.2 % Ba). The data in Deer, Howie, and Zussman (1963) also indicate that the barium content may be appreciable.

It is significant that the discrepancy between the determinative lines occurs at the high-potassium end, since barium has a greater geochemical affinity for potassium than for sodium. This element has an ionic radius similar to potassium and therefore will influence the cell size in a comparable manner. The tendency of the divalent charge to contract the feldspar is obviously more than offset by the compensating substitution of aluminium for silicon since celsian has a slightly larger a cell dimension than sanidine. It has been pointed out by Taylor (1965) that barium atoms can replace, at random, up to at least one-third the potassium atoms without major changes in the structure taking place.

A further possibility is the presence of iron substituting for aluminium in the tetrahedral group. This too would have the effect of expanding the feldspar lattice, as shown by the data of Wones and Appleman (1963), hence giving a larger d_{201} value than that expected from the orthoclase content.

Finally the question of *cation deficiencies* in the feldspar structure cannot yet be discounted. Luth and Tuttle (1966) have discussed this problem in detail and Carman and Tuttle (1967) have presented some preliminary results to support the concept of non-stoichiometry in the alkali feldspars. If the feldspars are deficient in cations it is probable that the structure would be expanded, producing a result similar to that seen in fig. 1.

In this connection, preliminary experiments were carried out by synthesizing a feldspar of composition $K_{0.95}Al_{0.95}Si_{3.05}O_8$ and measuring its d_{201} . The method of Shaw (1963) was used for synthesis and a check chemical analysis yielded 15.86 % K_2O compared with a theoretical content of 16.17 %. No phase, other than sanidine, was detected either optically or with an electron probe. The d_{201} value is $4.2374 \pm 0.007 \text{ \AA}$ which may be compared with Orville's value of 4.234 \AA for Or_{100} . Values predicted by Orville's curve and the new one presented here are 4.221 and 4.234 \AA respectively for a feldspar with 15.86 % K_2O .

Whilst the question of cation substitution requires further analytical data, it is unlikely that such an approach will ever convincingly demonstrate deficiencies. The synthesis of cation-deficient feldspars would appear to be more fruitful.

Conclusion

The data presented shows that the 201 spacings measured on homogenized natural potassium-rich alkali feldspars do not correlate well with those measured on synthetic samples with identical K_2O values. Barium is expected to have an effect similar to potassium on 201 spacings and since quite high concentrations have been found in some potassium-rich feldspars it is suggested that compositions of natural feldspars determined by the 201 method and using Orville's (1967) determinative line should be quoted in terms of $(Or+Cs)$. Alternatively, a better approximation to the Or content is given by the data on natural materials.

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