A first attempt at a determination of felspars by activation analysis.

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Summary.—Small crystals (2 mg.) of plagioclase and potassium felspar were irradiated for four weeks in an atomic pile. Subsequent analysis of the radiation showed that this is a possible method for the determination of the sodium and potassium content, and it should be possible to develop the method further in this direction. It has not proved a suitable method for the determination of calcium.

THE felspars, like so many silicates, have variable compositions When dealing with such material, it is seldom satisfactory to relate optical measurements, made on single grains or crystals, to chemical analyses which have been made on bulk material. This paper describes an attempt to develop an alternative method of analysis, a so-called activation analysis, which can be carried out on a very small amount of material—2 or 3 milligrams. It has, moreover, the advantage of being a non-destructive method, and the analysis can be repeated on the same material. It should be noted that these results are from the first experiments, and that fully satisfactory methods of mounting, handling, and measuring have yet to be developed. The material selected was not made up of 'ideal' crystals but was a fair cross-section of the sort of material that a geologist might like to have analysed. The results have proved sufficiently encouraging to justify a brief report on progress.

Method.

The crystals used were in section, 100μ thick. Each was mounted individually on aluminium foil with the minimum possible quantity of a dilute solution of Canada balsam; the foil was then folded over, envelope fashion, to prevent damage to the crystal during transit. Reference material packed in the same can comprised small, flat cleavage rhombs of calcite (mounted in the same way as the felspar crystals), sodium and potassium carbonate (sealed in a silica tube), and blank samples of foil plus Canada balsam. The whole was irradiated for one month in the Harwell atomic pile, at the highest flux available.

When the can was returned, the calcite and felspar crystals were removed from the aluminium foil and remounted. A solution of the carbonate mixture was evaporated on a mounting disk to give a film of comparable thickness: the concentration of the solution was determined by means of a flame photometer.

The sodium and potassium radiations were measured over the first 40 hours. Aluminium filters were used to discriminate between the different types of radiation; the principles on which the measurements were based are as follows:

Sodium has an exceptionally high activation cross-section, rivalled by few common elements other than the rare-earth metals. It yields a radioactive isotope, Na^{24}, which has very hard and abundant γ-rays (2·76 MeV[1] and 1·38 MeV) together with a moderately hard β-ray (1·39 MeV).

Potassium has a moderately high activation cross-section, and gives an isotope having an exceptionally hard β-radiation (3·58 MeV max.), with a few γ-rays. This β-radiation is equalled only by Mn^{56} and Ga^{72}. Consequently, filters capable of discriminating between the very hard (3·58) and medium energy (1·39) β-rays and between β-rays and γ-rays, can give very good discrimination between sodium and potassium. If measurements are made at widely separated intervals an additional check is available from a consideration of the half-life period. The only element capable of seriously interfering here is gallium.

The *calcium* radiation is much weaker (β 0·25 MeV) and longer-lived: the half-life is 150 days. In addition, the activation cross-section is very low. Two tests are available. Firstly, as no γ-rays are emitted, a filter just thick enough to cut off the Ca^{45} β-ray should pass no radiation at all; any radiation getting through must be due to other elements. Some estimate of the hardness of this radiation can be made by inserting the original filters (used in the Na/K determinations), and the residual radiation, not transmitted by the other filter (that opaque to Ca^{45} β-rays), can be calculated. Secondly, the residual radiation, as measured above, can be determined from time to time, and its rate of decay plotted. This should correspond with the 150-day half-life of Ca^{45}.

The results shown are from two separate irradiations, the same methods being employed in both. It was found that the radiation

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[1] Mega-electron-volts.

transmitted by a filter opaque to Ca^{45} β-rays often decayed rapidly. In the crystals investigated the decay was complex, and no assignment of element or elements was made. Unfortunately, when dealing with a long half-life element, it is difficult to maintain sufficiently stable counting conditions over an adequately long period to obtain a good half-life determination. It is generally preferable to follow the decay for at least two half-lives, which is clearly impracticable for calcium. The calcium results were divided into two classes. In the first the penetrating component was of relatively small proportions, and the curve after correction for it corresponded reasonably well with the half-life of Ca^{45}. In the second group the penetrating component was the major long-lived activity, and the residual activity, after correcting for it, still showed a rapid decay. Clearly no value for the calcium content could be deduced under these circumstances.

Sodium and potassium determinations.

Plagioclase felspars. In table I results obtained from the activation analyses and from the refractive index measurements are compared. Refractive index readings were made, after irradiation, on the crystal or part of a crystal which showed the greatest birefringence. These readings appear in the table as α' and γ', except in those cases where the optic figure showed that β had in fact been measured. If the crystal is ideally orientated (giving α and γ) the composition values obtained from the two indices will be equal: in less favourable cases a composition range of up to 6 % An is recorded.

Each value is the mean of three determinations (Na light: the probable error is 0·001 or less). The refractive index—composition graph of K. Chudoba[1] has been used to determine composition, but where the values given by the revised graph of F. Chayes[2] are different, these are included too.

Three plagioclases were examined:

The bytownite in a leuco-norite from the Bushveld Complex is clear, without visible inclusions, and with sharp, broad twin boundaries. Single crystals are not large enough for separate irradiation, but since the rock is largely made up of plagioclase, it was possible to select a small unit of 4 or 5 crystals free of other minerals. Earlier[3] universal-stage measurements made on the plagioclase from this rock had shown

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[1] The determination of the feldspars in thin section. London, 1933 [M.A. 5–386].

[2] Amer. Journ. Sci., 1952, Bowen vol., p. 85 [M.A. 12–134].

[3] O. Bradley, Min. Mag., 1953, vol. 30, p. 223 [M.A. 12–291].

it to be a homogeneous low-temperature bytownite, with Ab 20–30 %. The present investigation confirmed that this was a homogeneous felspar, and the consistently low potassium value is worth noting. The albite content (12–18 %) given by the activation analysis is always lower than that given by refractive index determinations (17–32 %).

TABLE I. Activation analysis of sodium and potassium in plagioclase felspars.

Material.	Spec. no.	Wt. in mg.	Activation analysis. % K.	% Na.	% Or.	% Ab.	Refr. ind.	% Ab. A.	B.
Bytownite in leuco-norite. Bushveld complex.	1	1·25	0·075	1·55	0·5	18	α' 1·565 γ' 1′575	22·5 22·5	27·5 27·5
	2	1·3	0·10	1·41	0·7	16	α' 1·570 γ' 1·576	12·5 19	17 25
	3	1·2	0·01	1·30	0·1	15	α' 1·568 γ' 1·576	17 19	21 25
	4	0·9	0·13	1·35	0·9	15	α' 1·566 γ' 1·572	22 28	26 32
	39	2·2	0·18	1·10	1·3	12	not suitable		
Oligoclase from pegmatite. Locality unknown.	45	1·9	2·4	5·45	17	62	α' 1·537 γ' 1·543	82 86	
	46	2·0	0·9	4·73	6	54	α' 1·537 γ' 1·542	81 88	 93
	47	1·5	1·67	5·08	12	58	not suitable		
	48	1·5	0·5	5·38	3·5	61	α' 1·537 γ' 1·543	82 86	 87
Andesine in olivine-gabbro. Stonehead, Aberdeen.	63	1·85	1·67	4·25	11	49	β' 1·560 γ' 1·562	43·5 44·9	45
	64	1·30	0·96	2·6	9	30	β' 1·560 β'' 1·562	43·5 40	45 43
	65	0·9	2·2	3·75	16	43	not suitable		

A. Ab values from the refractive index - -plagioclase composition graph of Chudoba.
B. Ab values from the revised refractive index—-plagioclase composition graph of Chayes.

The pegmatitic oligoclase was unfortunately an unlocalized specimen, but it is included because in other respects it was very suitable for analysis. The fragments examined were parts of large single crystals and contained only a very small amount of sub-microscopic inclusions. The sodium values are fairly consistent, the potassium ones much less so—although this is not unexpected when dealing with pegmatitic material. As with the Bushveld crystals, the activation analysis values for Ab content are markedly lower than those obtained from refractive indices. This seems to be due to some factor in the analysis as yet imperfectly understood. On the other hand, it is perhaps worth noting that F. Chayes,[1] discussing recent chemical analyses given by R. C.

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[1] Amer. Journ. Sci., 1954, vol. 252, p. 172 [M.A. 12–368].

Emmons and others, suggests that inclusions of quartz, potassium felspar, and mica would tend to raise the refractive index of plagioclase, whereas potassium felspar or excess SiO_2 in solid solution would probably lower it. Where unexplained discrepancies do occur in these American results, the Ab value obtained from the refractive index is usually higher than that given by chemical analysis—although the difference, of course, is much less than that found with the activation analysis.

The third plagioclase examined was an andesine from an olivine-gabbro, Stonehead, Aberdeen. This rock is really too fine-grained and complex to be satisfactorily analysed by this technique; it was included because a number of optical measurements had already been made on the plagioclase.[1] It proved rather difficult to obtain a large enough sample of felspar without including other minerals, and the crystals finally selected proved to be complex and zoned, with poorly defined twinning: the analysis results suggest that they are, in part, perthitic. Earlier optical work on this plagioclase gave an albite composition of about 50 % which agrees fairly well with two out of the three activation analyses. The plagioclase crystals include small apatites; the phosphorus in these is undoubtedly responsible, in part, for the unsatisfactory calcium analyses described later.

Potassium felspars. Only literature analyses of other specimens from the same locality were available for these felspars, and they could not, of course, be checked by optical measurements. However, these analyses provide a general guide to the composition, which is all that is required in this early stage of investigation. Two potassium felspars were examined, and the results are summarized in table II.

The first felspar was an adularia from St. Gotthard, Switzerland. This material is microscopically clear and appears homogeneous, except for a limited amount of parallel intergrowths. The activation analysis gives a consistent and satisfactory value for the potassium content; the sodium values, although more variable, are still not improbable.

Secondly, an amazonite from Mursinsk, Urals, was examined. This microcline is crowded with unidentifiable sub-microscopic inclusions. The samples used are largely single crystal fragments, but it proved difficult to obtain these sufficiently homogeneous. In one case (no. 58) some small plagioclase lamellae are included; in a second (no. 55) a fragment of quartz. The sodium and potassium values for this mineral are variable but agree tolerably well with the recorded analysis. The reason for the high potassium value of no. 58 is not known but when

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[1] O. Bradley, loc. cit.

TABLE II. Activation analysis of sodium and potassium in potassium-rich felspars.

Material.	Spec. no.	Wt. in mg.	Activation analysis			
			% K.	% Na.	% Or.	% Ab.
Adularia,* St. Gotthard, Switzerland.	59	3·5	10·9	0·8	77	9
	60	2·6	11·0	1·32	77	15
	61	3·05	10·9	1·08	77	12
Amazonite,† Mursinsk, Urals.	55	1·5	8·4	0·92	70	10
	56	1·3	12·5	0·61	89	7
	57	0·85	11·4	0·57	81	6·5
	58	0·8	16·3	2·2	115	25

* Literature analysis has K 11·6 %, Na 0·75, Ca 0·96 % (Dana, System of mineralogy, 6th edn, 1892, p. 319); this gives orthoclase 82·5 %, albite 8·5 %, anorthite 6·6 %.

† Literature analysis has K 11·55 %, Na 1·23 %, Ca 0 % (Dana, loc. cit., p. 323); this gives orthoclase 82·0 %, albite 14·2 %.

the weight of the crystal is only 0·8 mg. small errors in weighing can invalidate the whole analysis. Samples weighing 2–3 mg. should be used whenever the nature of the material permits it.

Calcium determinations.

These values are the least reliable part of the analysis; there are a number of elements that may be present as impurities in the crystals, and which are capable of interfering with the relatively weak calcium radiation. It appears likely that accurate determinations can only be made on a nearly pure plagioclase.

Figs. 1 and 2 show a selection of the decay curves obtained. In all cases the filtered and unfiltered decay curves are shown. The difference between these two curves, the residual radiation, should correspond to the 150-day half-life of Ca^{45}—if no interfering radiation is present. Three different samples of calcite (Iceland spar) were used as control material; in each case the hard radiation formed an insignificantly small part of the total, and can be neglected. The blank experiments with Canada balsam showed that some radioactivity can be induced in this material, but that this is not important when only a small amount is used for mounting. The blank experiment used about ten times as much balsam. Moreover, the early activity shown on the graph is due to the aluminium foil which adheres to the balsam but not to the crystals, and can therefore be ignored.

Three of the five felspars investigated had more or less suitable decay curves, but the calcium values, quoted in table III, should be treated

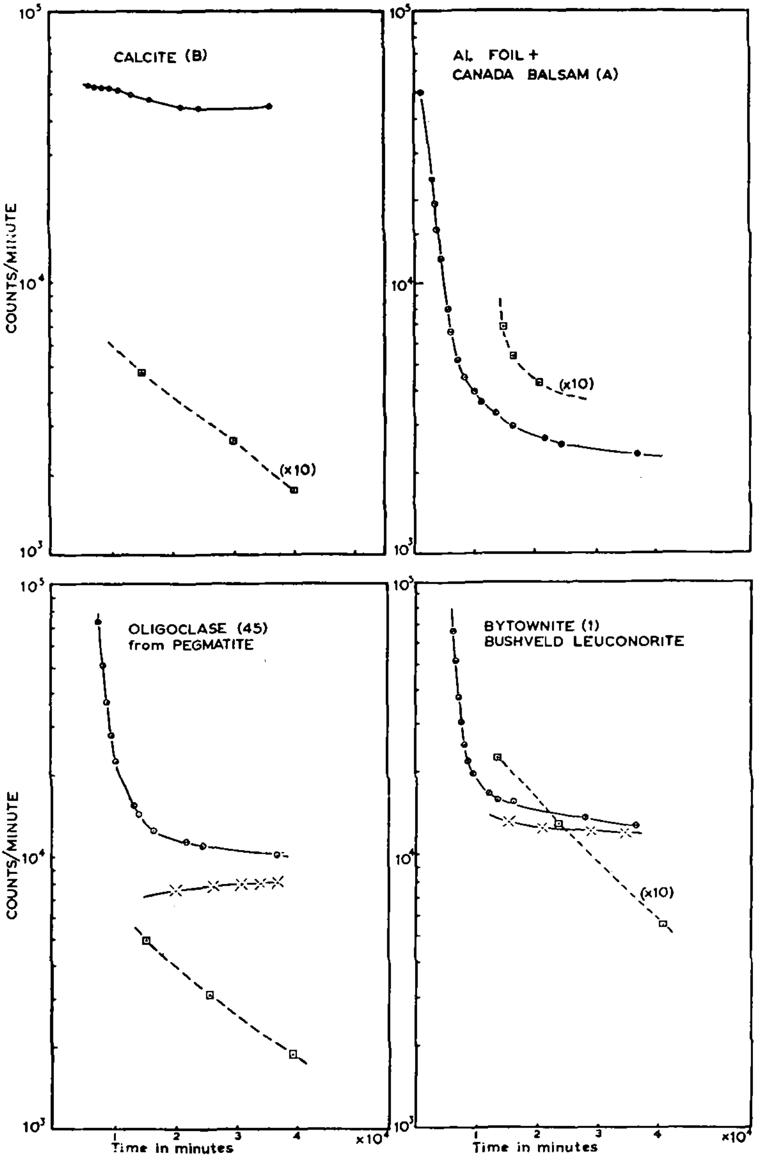

FIG. 1. Decay curves from first activation. —⊙— unfiltered radiation; —⊡— filtered radiation; - -×— soft β-component.

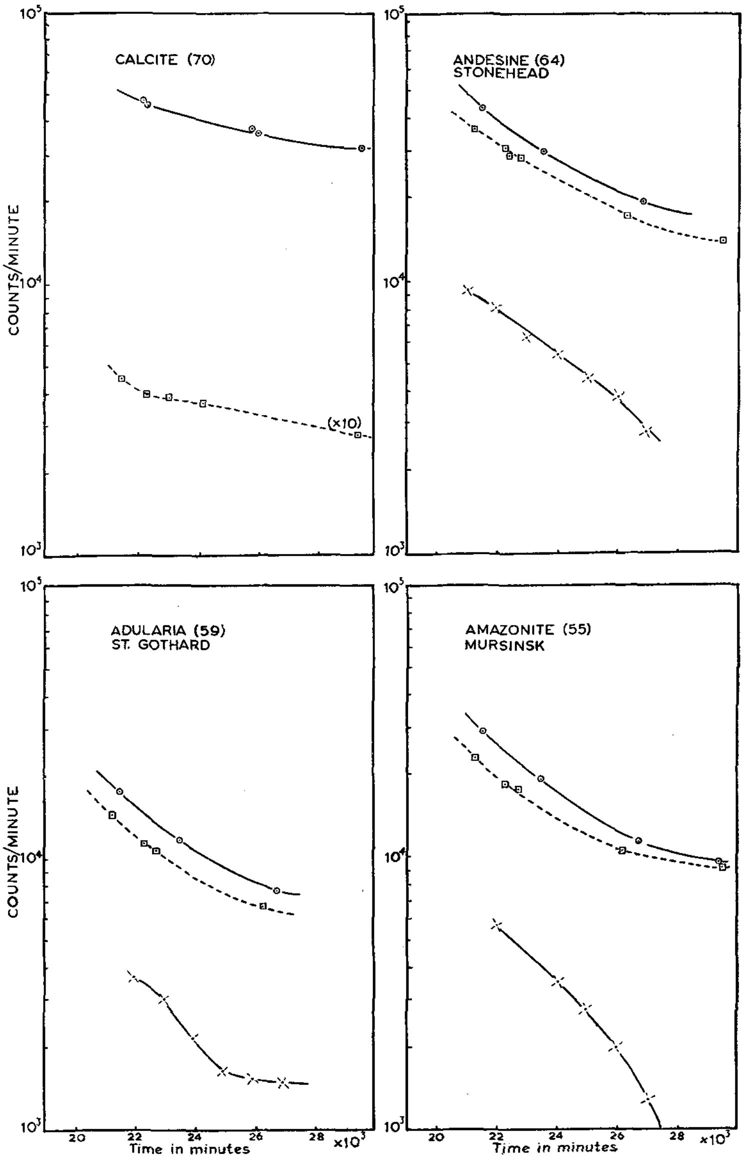

Fig. 2. Decay curves from second activation. —⊙— unfiltered radiation; —⊡— filtered radiation; —×— soft β-component.

with some reserve. All values for Ca were taken at 25,000 minutes. The Bushveld bytownite gives satisfactory results, at least in three out of four cases; the St. Gotthard adularia is once again surprisingly homogeneous; and the pegmatitic oligoclase is still very variable. It is perhaps significant in this latter case that high Ca values are linked with high K values, suggesting that the impurity complicating the calcium decay curve is associated with the potassium. The andesines from Stonehead cannot be estimated because the interfering radiations are too complex, while in the example shown of the Mursinsk amazonite (fig. 2) the induced radioactivity is not due to calcium at all.

Finally, as a matter of interest, the sum of all the felspars is given in the last column of table III. It appears that when the Na, K, and Ca present are recalculated in terms of the felspar molecules, there is in most cases excess silica, or alumina, or both (see, for example, R. C. Emmons (loc. cit.), and more particularly E. D. Belyankina).[1] If the two quoted analyses of potassium felspar are recalculated in this way, both have excess silica and alumina; the adularia has 89 % felspar, the amazonite 96 %.

TABLE III. Activation analysis of calcium in suitable felspars.

Material.	Spec. no.	% Ca.	% An.	% Or.*	% Ab.*	'Total felspar' %†
Bytownite in Bushveld leuco-norite.	1	10·8	79	0·5	18	98
	2	11·5	80	0·7	16	97
	3	14·3	99	0·1	15	115
	4	12·1	84	0·9	15	100
Oligoclase from pegmatite. Locality unknown.	45	5·5	39	17	62	118
	46	3·1	22	6	54	82
	47	5·9	41	12	58	111
	48	2·9	20	3·5	61	85
Adularia, St. Gotthard, Switzerland.	59	2·0	14	77	9	100
	60	2·2	15	77	15	107
	61	2·1	14·5	77	12	103·5

* From tables I and II.

† That is, the sum of the An, Or, and Ab calculated from the percentages of Ca, K, and Na found.

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[1] Е. Д. Белянкина, Труды Инст. Геол. Наук, Акад. Наук СССР [Trans. Inst. Geol. Sci., Acad. Sci. USSR], 1953, no. 147, Petrogr. Ser. no. 43, p. 185 [M.A. 12-417].