STUDIES ON THE X-RAY DIFFRACTION, ANALYSIS AND GEOCHEMISTRY OF PLAGIOCLASE FROM THE MT. DAVIES IGNEOUS INTRUSION.

J. D. Kleeman, B.Sc.

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Geology Department,
Adelaide University.

Table

Figures

Abstract

In a two-fold study of twelve plagioclases from the Mt. Davies intrusion an X-ray determinative curve was calibrated and the chemistry of major elements and trace elements Sr and Ba was studied to illustrate the differentiation of the intrusion.

The calibration is successful, and further, a break in slope points to lattice changes in the plagioclase series at about An_{78} .

Differentiation by fractional crystallization is well illustrated by the changes in the chemistry of the plagioclases. The major element distribution is appraised in the light of modern knowledge of the plagioclase crystallography.

Strontium is found to exist almost exclusively in the plagioclase mineral phase of the rocks. The Sr content of the plagioclases increases with decreasing An content, towards the "top" of the intrusion. A discussion of these results in terms of magma concentrations and lattice changes is given.

The Barium content of plagioclase shows a similar trend.

Introduction

A preliminary examination of samples collected in 1963 by Nesbitt and Kleeman (A.W.) revealed a variation in plagioclase content. Accordingly a more detailed traverse was made over the critical southern side of the Mt. Davies body.

The purpose of the study is two fold : to calibrate a method for determining the Anorthite content of the plagioclase by X-ray diffraction, and to investigate the chemistry of the plagioclases to further illustrate the differentiation of the body.

A parameter T is obtained by the X-ra y diffraction of powder preparations and the measurement of the resulting lines of reinforcement.

$$T\ (^{o}2\theta) = 2\theta(131 - 1\bar{3}1) - 2\theta(1\bar{3}1 - 220)$$

It is dependent on changes in γ^*. Previous work is reported by Smith, J.R. and Yoder (1956), Smith, J.V. and Gay (1958) and Jackson, (1961). Calibration is achieved by chemically analysing the samples chosen.

The differentiation of the body will be reflected in the composition of the plagioclases, both in major constituents and trace elements. It was decided to study the trace element Strontium in both plagioclase and whole rock samples, and to make a preliminary investigation of the Barium distribution.

Twelve samples were selected to provide a range of values of T as well as a reasonably spaced traverse over the body.

A location map is provided for both the samples and the area. An excellent "one mile" sheet (i.e. 1" = 1 mile) is available, published by the Geological Survey of S.A., Department of Mines, under the name "Davies".

A synthetic plagioclase (Frit) was prepared to serve as a standard for some analytical techniques as well as to investigate its behaviour in X-ray diffraction when crystallized.

Experimental and Analytical Techniques.

1. Frit synthesis

The Frit (synthetic plagioclase) was prepared in a very similar manner to the method used by Shaw (1963).

Twenty grams of Frit were made up to the following formula :

	wt. %
SiO_2	49.14
Al_2O_3	32.72
CaO	15.34
Na_2O	2.82

The composition is 75.2 % An (atomic ratio).

These quantities were obtained from various starting materials :

SiO_2 : "Ludox" : an ammonia stabilized colloidal solution. Standardized by standard gravimetric technique to contain 36.30 g SiO_2 / 100 mls.

Al_2O_3 : from pure Al - foil, converted to a nitrate solution with nitric acid.

CaO : pure $CaCO_3$ is converted to nitrate solution.

Na_2O : from $NaNO_3$

The solutions are mixed in a platinum bowl in the order : Ludox, 30 mls conc HNO_3 to preserve the acidity, then $NaNO_3$, $Al(NO_3)_3$ and $Ca(NO_3)_2$.
Mixing is thorough.

Careful dehydration over a steam bath to a gel is followed by heating in an oven at 110^o to a solid. The heating is increased slowly to a final temperature of about 700^o for an hour.

After this all the water has been removed and the nitrates converted to oxides, leaving the appropriate composition.

(Most of these samples were already separated (in all) by R. Gandhi & crushed by AMK & S K Yong)

2. Sample Preparation

The rock specimens for mineral separation were crushed usihg a fly press with stainless steel plates. Minus twelve mesh size was reduced to -120# +200# with a manually operated stainless steel pounder and plates.

These powders were separated with a "Franz" electrodynamic magnetic separator. Very clean plagioclase fractions were obtained by this method requiring no further manipulation other than washing.

Nevertheless, the powders were inspected with a binocular microscope to ensure purity.

3. Chemical Analysis

(a) Calcium

Approximately 50 mg. of each plagioclase was digested using HF and $HClO_4$ and made up into a final 100 ml. volumetric solution (the HF having been evaporated off). These were titrated with E.D.T.A.

Aliquots of 2 ml. were mixed with Triethanolamine (5 ml.) to suppress Aluminium by complexing it, NaOH (3 ml.) to adjust the pH, and 10 ml. of distilled water to make up to a suitable volume for the titrator.

Titrations were performed with an "Eel" titrator. End-points of the indicator Acid Alizarin Black were detected by the passage of a beam of light through the solution. An appropriate filter was used to accentuate the intensity differences which were recorded from a phosoelectric cell on a galvanometer.

The titration value is graphically determined from this information.

The E.D.T.A. was standardized against an artificial Ca^{++} standard solution and the method checked against "Crystal Bay Plagioclase", a laboratory standard. An additional check is furnished by the Frit.

Blanks were made to cover all the operations of digestion and volumetry, using precisely the same quantities of acid and the same set of apparatus.

A calibration graph was constructed for fluorescent X-ray analysis, and this graph was used to analyse the three samples not analysed with E.D.T.A.

Methods of sample preparation for X-ray fluorescence are described in section 3(c).

The Kα peak was used for all counting. The peak was excited with X-rays from a Molybdenum tube run at 50 kV and 18 mA. Molybdenum X-rays were collimated and analysed with a LiF crystal and detected with a flow proportional counter. 400,000 counts were accumulated on the peak and about 1,000 counts on the background.

A standard Philips vacuum-path spectrograph was used. High voltage supply is by Ekco and the discrimination, amplification and counting electronics of Philips construction.

(b) Alkali Analysis - Na_2O and K_2O

The volumetric solutions prepared for CaO analysis proved quite inaccurate for alkali work. Results were systematically high and blanks of an order too large to be tolerated.

Difficulties were overcome by using H_2SO_4 instead of $HClO_4$ and avoiding all contact with glassware, except for the volumetric vessels, and quickly transferring solutions from the glass vessels to plastic storage bottles.

Approximately 25 to 40 mg. was taken up in a final 250 ml. volumetric solution.

The duplicate blanks demonstrated that contamination for materials and technique had been reduced to a very acceptable level.

Analysis of the solutions was performed using a flame photometer ("Eel").

(c) Trace Element Analysis by X-ray Spectrography.

As well as the twelve plagioclases, four whole rock samples were prepared for X-ray fluorescent analysis. Seven other mounts were already in existence, having been made by Yong (Hons. 1964). "Crystal Bay Plagioclase" and the Frit were also included for the CaO work.

(i) Sample Preparation

Two grams of the -120# +200# powders were ground under acetone

for about 1½ - 2 hours in an automatic mullite mortar ("Fischer Mill").

After this time the grain size was at least 95% below 17 μ and the largest pieces were rarely greater than 40 μ.

About 1.6 g. of this powder were pressed into a flat mount supported by boracic acid powder. Pressure applied was about 3 tons.

The "pellet" is circular and a cross section across a diameter is shown in the diagram below. (Fig. 2.)

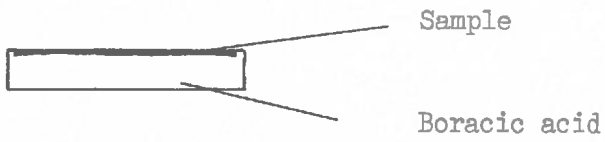


FIG. 2. Pressed pellets

The actual thickness of the sample in the mount is not known exactly, except that a simple experiment using different amounts of a given sample powder showed that the quantity used is more than adequate, even for the short wavelength determinations.

(ii) Matrix correction

Matrix corrections were made for Strontium and Barium.

The Mass Absorption coefficient for Sr was measured directly by the attenuation of an X-ray beam of the appropriate wavelength by a pressed mount of accurately known mass and area.

That of Barium was calculated from the composition. The mass absorption coefficient for the whole compound is the total of the coefficients of all the other elements present, due to the following relation :

$$\mu m = \frac{\text{wt. } \%_1}{100} \mu m_1 + \frac{\text{wt. } \%_2}{100} \mu m_2 + \text{etc.}$$

For a brief discussion of the theory of these matrix corrections see Appendix I.

A matrix correction was not necessary for Calcium, since the only

element with a very close absorption edge is Potassium and the quantity of potassium is always so low that it could be ignored in this regard.

It could be said that the matrix was very uniform in the plagioclases for Sr and Ba. However, the results show that this is not so.

(iii) Strontium Analysis

Strontium was determined in both plagioclase and whole rock samples by comparison with W1. A value for W1 (Sr) was obtained by comparison with G1, which was better established.

(iv) Barium

Barium was determined in one sample (A251/300) against G1 and this sample was then used as the counting standard.

The concentration of Ba in G1 is 1250 p.p.m. and in the plagioclases more of the order of 100 p.p.m., and the use of a sample of matrix close to that of the unknown material was considered to give better internal precision.

Due to poor resolution it was necessary to develop an alternative method to that generally used in this laboratory. The $L\alpha_1$ peak had previously been used, but is could not be resolved from a very close Ti peak.

The $L\beta_1$ was used. Although another Ti peak is close, the separation and resolution are good. This is illustrated in Fig. 5. It is a trace over G1.

The Ti peak is close enough to affect the peak height at the Ba wavelength. The contribution at the Ba wavelength was expected to be non-linear and therefore an experiment was performed to arrive at a correction.

Six grams of acid washed pure quartz were ground up for 2 hours in the automatic mortar and divided into three parts. To each part was added some spect. pure TiO_2, namely, 0.0003 g., 0.0017 g., and 0.0083 g. respectively.

The three parts are mixed with the TiO_2? under exactly the same conditions. Precise and thorough mixing was not attempted apart from reducing the TiO_2 to the required grain size and giving a relatively even

distribution. The exact quantities of TiO_2 present are not significant, only the counting rate.

It is noted that three samples have thus been prepared with varying amounts of Ti present but with exactly the same Ba content.

The three samples were then counted at the Ti peak position, Ba peak position and the background. The results and interpretation follow in "Results".

Contamination by the automatic mortar was investigated by grinding a split -100# portion of acid washed quartz. The two splits were ground

(i) by hand in a high purity mortar,

(ii) the automatic mortar.

No difference in the Ba content could be detected.

(v) Counting Details

Table 1 Counting details for X-ray fluorescent analysis

	Analysing Crystal	X-ray tube	Vacuum	Counter	EMT	Pulse Discrimination
Ca	LiF	Mo 50Kv 18mA	Yes	Flow proportional	1650v	10 - 34 v
Sr	LiF	Mo 50Kv 18mA	No	Scintillation	800v	10 - 34 v
Ba	LiF	Cr 44Kv 20mA	Yes	Flow proportional	1600v	7 - 31 v

	Peak	Angle ^{o} 2θ		No. of counts	
		Peak	Background	Peak	Background
Ca	K∝	113	115.2	400,000	1,200
Sr	K∝	24.97	24.27 + 25.67	40,000	40,000
Ba	L_{β_1}	79.18	80.2	4,000	4,000

4. X-ray diffraction

X-ray powder diffraction was performed on powder smears of the very fine powders. The smears were prepared by hand as an acetone slurry on a quartz plate, (cut at a suitable orientation to exclude interfering lines).

Eight oscillations were made over the range $28^{o}2\theta$ to $32^{o}2\theta$. The smears were remade after each four oscillations to offset any preferred orientation due to the cleavage of the plagioclase. The very fine grain size made this ritual possibly redundant. Care was taken to take an equal number of ascending and descending oscillations to counter any inaccuracies in the geometry of the instrument.

A Philips "10-9" generator and a "1050" goniometer were used. The pulses from the Gieger counter are discriminated and amplified with Ecko electronics and recorded on a Honeywell chart recorder.

The Peak identification is illustrated in Fig. 3. The peaks were determined at 2/3 peak height and the differences measured to two decimal places.

5. Frit Crystallization

The Frit was crystallized under anhydrous conditions. In one run the powder was held at $1300^{o}C$ in an electric furnace for 7 days (i.e. below the solidus). (Run I)

Secondly the powder was melted at $1550^{o}C$ and then the temperature dropped to 1300^{o} and kept there for 14 hours. Part was removed for study and the rest was held at 1300^{o} for an additional 7 days.

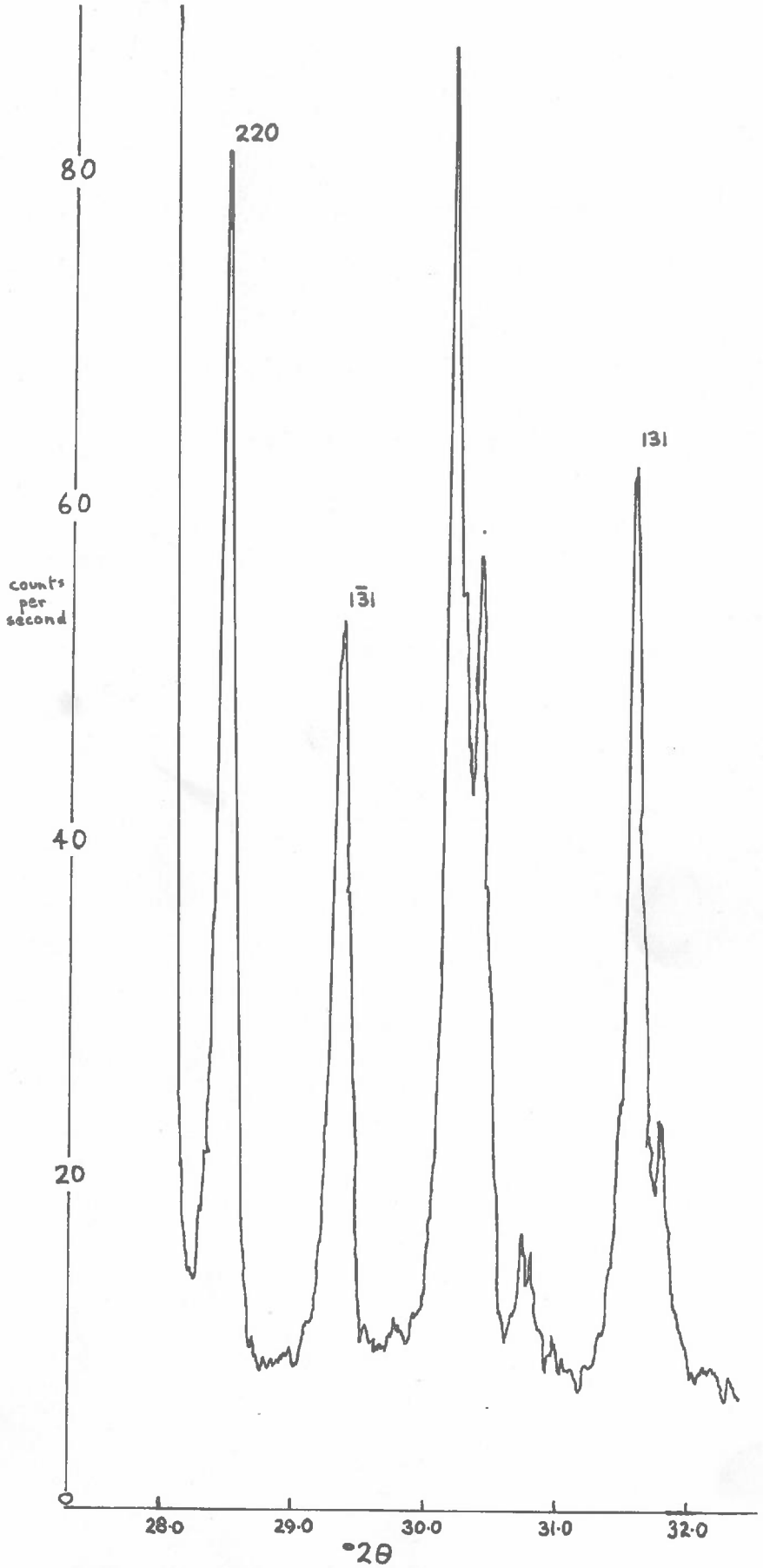


FIG 3. Peak Identification in X-ray powder diffraction.

Results

1. Calcium

(a) E.D.T.A. analyses. (wt. %)

Table 2 Calcium analysis by E.D.T.A. titration

	RUN I	RUN II	Other values
C.B.*	14.40 14.59	14.35 14.23	Lab. value 14.3% CaO A.M.D.L. 14.3% CaO
Frit	15.34 15.27	- -	made up to 15.34% CaO
118B≠	17.35 17.36 17.24	17.25 17.22 -	A.M.D.L. 17.5% CaO (whole rock)
117G	17.45	n.a.	
K1	16.86	16.50	
116B	15.61	15.69	
284	15.27	15.09	
294B	14.21	14.07	
296	13.45	13.42	
300	13.04	13.11	
K32	13.02	12.75	

* C.B. = Crystal Bay Plagioclase

≠ these sample numbers are abbreviated, the full numbers appear on the locality map.

The duplicate blanks gave almost insignificant titres which could scarcely be distinguished from the titre given by a distilled water blank. In view of this a blank correction was deemed unnecessary and was therefore not made.

A statistical analysis of these two runs by the method of analysing the variation of the differences in the results for each sample indicates

that the differences between them are larger than would be expected if they are due to random or chance errors. A perusal of the Table 2 above shows that the variation is due to larger than tolerable errors in two pairs of analyses.

These differences may be attributed to inexperience with the method in the first run. We look to the X-ray spectrography to provide extra information.

(b) Spectrography.

Table 3 shows the results of counting for Calcium in two runs (A + B).

Calcium by X-ray fluorescent spectrography

	RUN A c.p.s.	RUN B c.p.s.	AVERAGE c.p.s.	Final Recommended Value- %CaO
C.B.	10,6000	10,6000	10,6000	14.3 **
Frit	11,346	11,360	11,350	15.3 *
118B	12,850	12,970	12,910	17.3 *
117G	13,013	12,990	13,000	17.43
105	12,179	12,486	12,486	16,54
K1	12,273	-	12,273	16.50
160	11,936	12,166	12,050	16.20
163	11,338	11,377	11,360	15.30
166B	11,660	11,694	11,668	15.69
284	11,193	-	11,190	15.09
294B	10,431	-	10,430	14.07
296	10,050	9,890	9,970	13.43
300	9,700	9,670	9,680	13.11
K32	9,550	9,510	9,530	12.88

** All values standardized to compare with 10,600 c.p.s. on Crystal Bay Plagioclase

* Standards

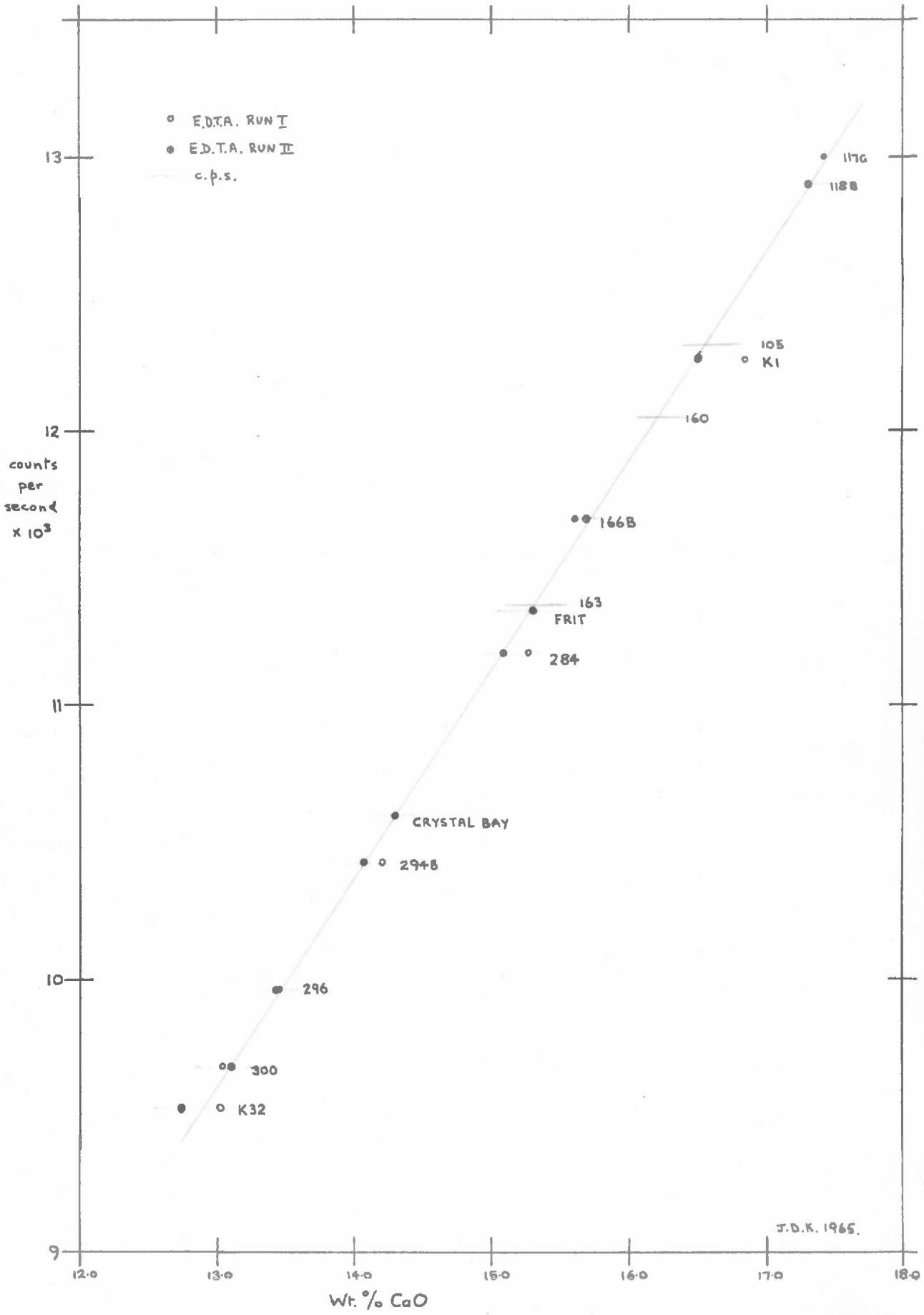


Fig. 4 Calibration curve for the Xray fluorescent analysis of Calcium.

Please note :- The number of decimal places here may seem superfluous, but they reflect the belief that the appraisal of the significance of values should be left until the last operation has been performed with them.

The result is an excellent calibration curve.* It is used to analyse the CaO in those specimens not analysed with E.D.T.A., and to arbitrate between those titrations which seem to be irreconcilable and therefore not to be averaged.

* See Fig. 4.

2. Na - K

Table 4 Alkali Analyses

	Na_2O (wt.%)	K_2O (wt. %)
Crystal Bay	3.22	0.18
Frit	2.93	0.006
118B	1.58, 1.56	0.036, 0.035
117G	1.49, 1.52	0.032, 0.036
105	1.96, 1.98	0.041, 0.042
K1	1.95	0.05
160	2.17	0.08
163	2.74, 2.71	0.145, 0.143
166B	2.41	0.097
284	2.76	0.15
294B	3.36	0.214
296	3.70	0.255
300	3.80	0.33
K32	4.03	0.30

Here again in many places more accuracy is portrayed than is really significant. It is felt that to cut the number of figures back at this stage would be unwise, considering the calculations to be performed with them.

The reasonable reproducability of the duplicates is an indication of good precision. The (duplicate) blanks registered very low readings on the flame photometer, and were almost identical. This fact gave confidence of acceptable accuracy for the analyses.

Independent checks on the accuracy of the method are furnished by analyses of the whole rock of 118B (Anorthosite with 2% Pyroxene) and Crystal Bay performed by the Australian Mineral Development Laboratories.

		J.D.K. 1965	A.M.D.L.
Crystal Bay	Na	3.22	3.15
	K	0.18	0.17
118B (whole rock)	Na	1.57	1.48 * 1.51 **
	K	0.04	0.07

* actual analysis

** corrected for 2% pyroxene

3. Diffractometry.

The results are presented as a mean, and standard deviation ~~and relative standard deviation~~ of the eight oscillations.

Table 5 X-ray powder diffraction. (I)

Sample	Mean	Standard Deviation
118B	1.355 °1e	± 0.013
117G	1.375	0.019
105	1.305	0.013
	1.309	0.012
K1	1.286	0.018
160	1.262	0.008
	1.263	0.005
163	1.168	0.027
166B	1.230	0.018
	1.216	0.011
284	1.146	0.015
294B	1.026	0.025
296	0.908	0.025
300	0.875	0.020
K32	0.843	0.018
	0.839	0.013
Crystal Bay	1.150	--

The reproducability can be estimated from the duplicate determinations presented.

Results of the diffraction of the products from the dry crystallization are tabled below. A more detailed report of these crystallizations appears in a later section.

Table 6. Diffraction of Frit crystals. (I)

RUN I		1-12
RUN II	(a)	1.28
	(b)	1.30

4. Strontium

(a) Mass absorption coefficients

Table 7. Strontium mass absorption coefficients.

Sample	μm Plagioclase	μm whole rock
118B	9.92, 9.85	(Anorthosite)
117G	9.79	11.1 *
105	9.77	10.9 *
K1	9.74	10.7 *
160	9.72	10.7 *
163	9.52	11.8 *
166B	9.64	10.6 *
284	9.47	10.9
294B	9.26	11.8
296	9.13	11.4
300	9.09	11.6
K32	9.02	12.0 *

* These values for the whole rock powders are taken from Yong (1964), since no more powder was available.

(b) Analysis

The standard G1 is a well known laboratory and interlaboratory standard for this work. Values of 8.63 for the mass absorption coefficient

and 257 p.p.m. for the Sr concentration were used.

W1 is analysed against this, and the following values obtained using um 13.1 .

nett c.p.s.		p.p.m. Sr		average
G1	W1			
775.3	389.7	196.1	- - -	195 p.p.m. Sr
796.0	397.1	194.6		

Table 8. Strontium Analyses. (p.p.m.)

	in Plagioclase	in Whole rock	Whole rock (YONG)
	p.p.m.	p.p.m.	p.p.m.
118B (i) *	286	(Anorthosite)	n.a.
118B (ii)	283	-	-
117G	245	105	96
105	281	175	158
K1	270	177	163
160	295	207	188
163	323	171	159
166B	323	224	205
284	313	226	n.a.
294B	362	190	n.a.
296	401	233	n.a.
300	374	199	n.a.
K32	412	223	190

* These are duplicate "pressed pellets"

n.a. = not analysed

A systematic difference is noticed at once between the values determined in this study and those by YONG (1964). The reason is simply

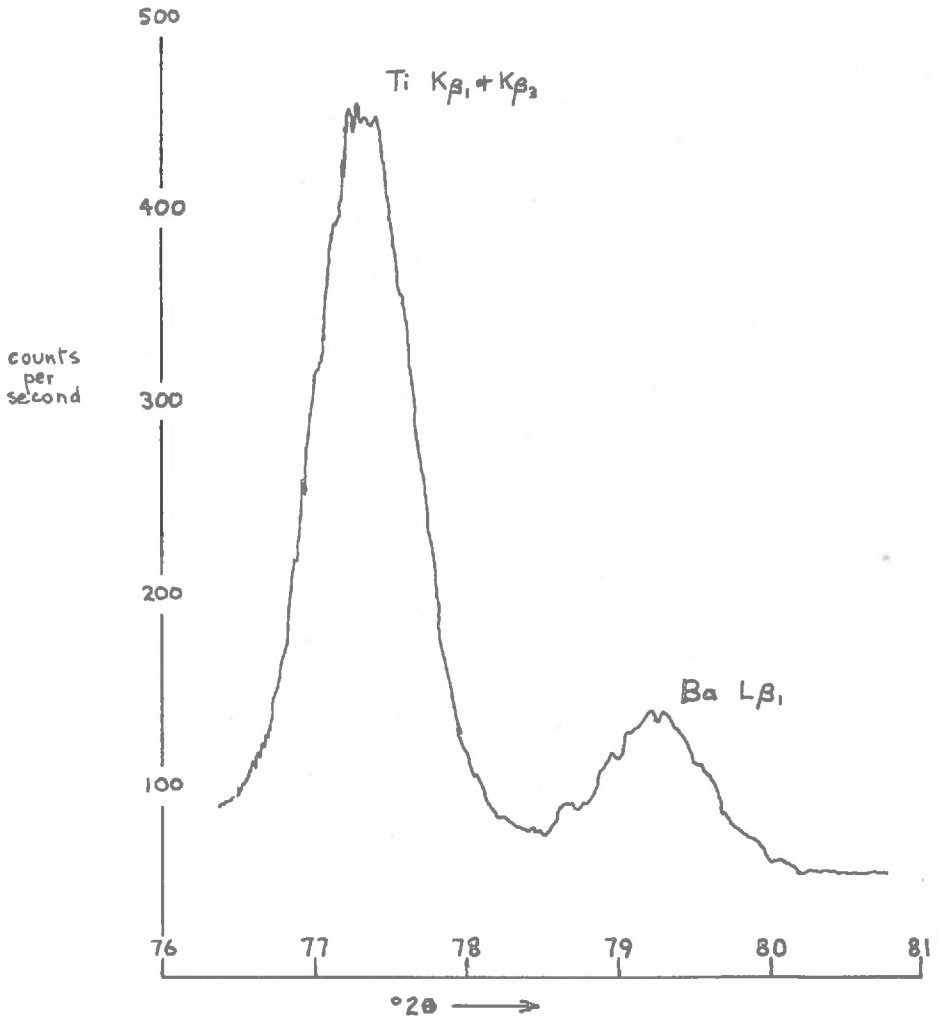


Fig.5. Peak positions in Barium analysis

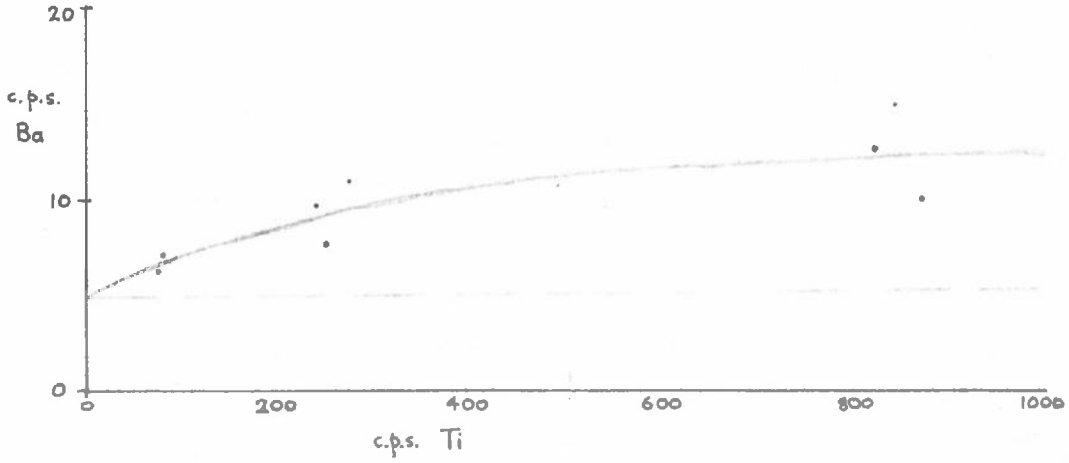


Fig 6 Correction for Ti presence in Ba fluorescent analysis

Taken from the "Davies" Geological Sheet, Department of Mines, S.A. 1964

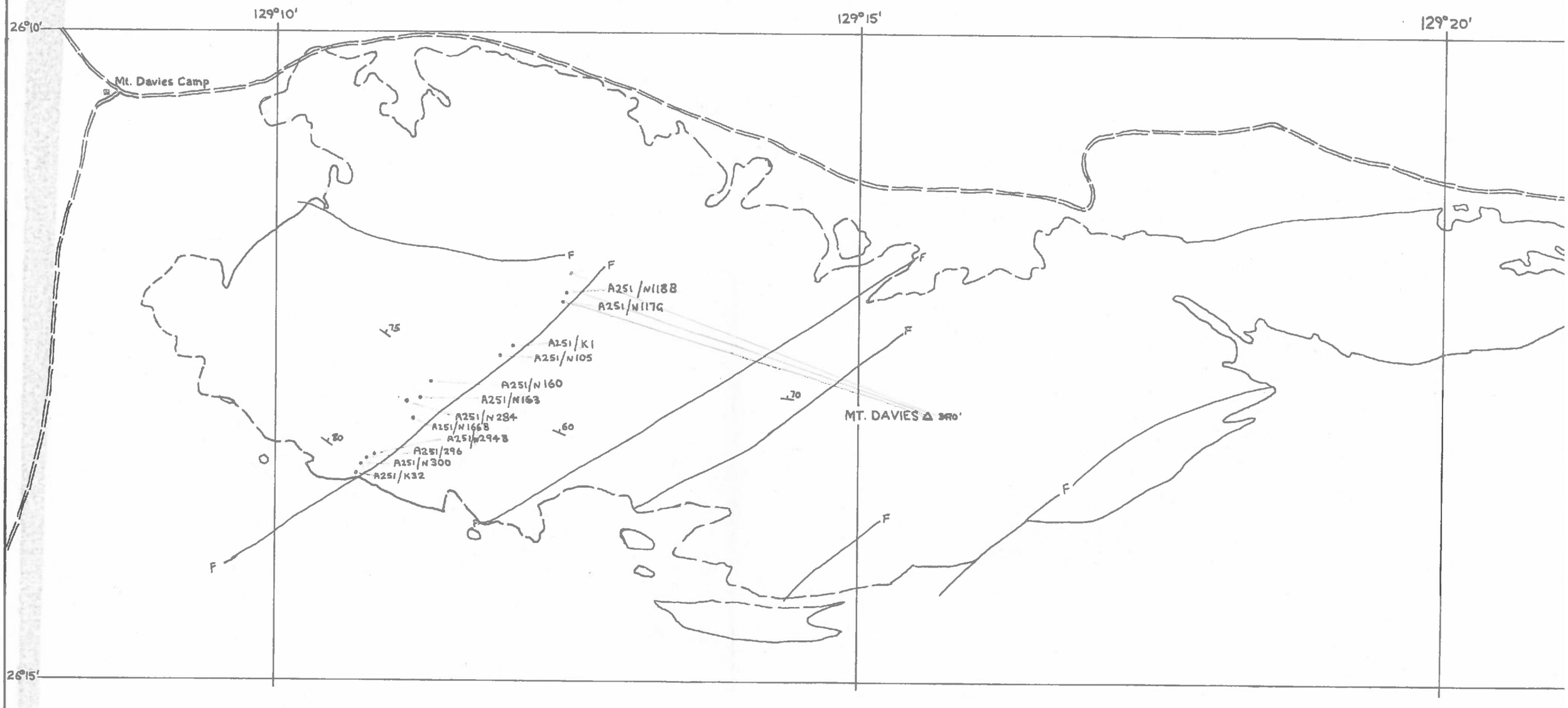


Fig 1 SAMPLE LOCALITY MAP

ONE MILE

Layering

Fault

Road

Boundary with country rock

Boundary with alluvium

that a different value for the standard, W1, was used in the calculations. The results are quite reconcilable, therefore.

5. Barium

(a) Correction for Ti

The results are graphed in Fig. 6. The spread of the values may at first seem very high, but the nett counting rates are quite low, and machine drift will therefore cause large relative errors.

The relationship is of the form :

$y = c - f(x)$ where $y \equiv$ nett c.p.s. Ba

$x \equiv$ nett c.p.s. Ti

When x = 0 we have the counting rate of Ba when there is no Ti present.

If an origin is made (dotted line in Fig.6.), the correction is the distance from this secondary origin to the curve and will be the correction for that nett rate for Ti.

It is applied by subtracting from the nett counting rate of Ba.

(b) Analyses

All mass absorption coefficients are calculated.

Table 9. Barium Analysis

(i) Standardizing A251/N300 against G1.

Sample	um	nett Ti c.p.s.	nett Ba c.p.s.	corrected	p.p.m. Ba
G1	169	550	108	102	1250
300	181	79	15.1	13.7	180

(ii) The remaining samples are then counted against A251/N300

These data must be regarded as strictly qualitative. Due to the low counting rates, a ny machine drift causes large variations.

Sample	um	nett Ti c.p.s.	nett Ba c.p.s.	corrected	p.p.m. Ba
118B	191	60	8.7	7.7	80
117G	192	46	7.1	6.5	70
105	189	223	9.8	6.3	65
K1	189	55	7.4	6.4	65
160	188	80	7·5	6·3	65
163	186	90	12.9	11.2	120
166B	187	78	14.8	13.5	140
284	185	96	10·9	9·2	90
294B	183	94	16·2	14·5	145
296	181	84	15.6	14.0	140
300	181	100	20	18.0	180
K32	180	96	21.1	19.2	190

6. Frit Crystallization

Both runs produced crystalline material with respect to X-ray diffraction.

Run I did not give crystals visible under the normal petrological microscope, but the products from Run IIa and IIb were both obviously crystalline and twinning (probably albite twins) was developed. Photographs of these twins are presented in the plate. (Plate 1.)

Values of T are recorded in Section 3 of these results. (p. 14.)

Table 10. Results Summary

Sample	CaO	Na_2O	K_2O	Sr	Ba	An	Ab	Or *	SrF	T
	wt. %	wt.%	wt.%	p.p.m.	p.p.m.	%	%	%	%	$^{o}2\theta$
118B	17.3	1.57	0.04	285	80	85.8	14.0	0.21	0.09	1.355
117G	17.4	1.50	0.03	245	70	86.4	13.4	0.20	0.09	1.375
105	16.5	1.97	0.04	281	65	82.1	17.7	0.25	0.10	1.31
K1	16.5	1.95	0.05	270	65	82.1	17.5	0.30	0.10	1.29
160	16.2	2.17	0.08	295	65	80.1	19.4	0.46	0.11	1.26
163	15.3	2.72	0.14	323	120	75.1	24.1	0.84	0.12	1.17
166B	15.7	2.41	0.10	323	140	77.8	21.6	0.57	0.12	1.225
284	15.1	2.76	0.15	313	95	74.4	24.8	0.88	0.12	1.15
294B	14.1	3.36	0.21	362	145	69.0	29.8	1.25	0.13	1.03
296	13.4	3.70	0.26	401	140	65.5	32.7	1.49	0.15	0.91
300	13.1	3.80	0.33	374	180	64.3	33.8	1.94	0.14	0.88
K32	12.9	4.03	0.30	412	190	62.8	35.5	1.74	0.15	0.84

* Here again it is realized that the order of accuracy shown is better than can be claimed.

% An, Ab and Or in Atomic ratios, also SrF.

i.e. % An = Atomic ratio $\left(\frac{Ca + Sr}{Ca + Sr + Na + K} \right) \times 100\ \%$

% Ab = Atomic ratio $\left(\frac{Na}{Ca + Sr + Na + K} \right) \times 100\ \%$

% Or = Atomic ratio $\left(\frac{K}{Ca + Sr + Na + K} \right) \times 100\ \%$

Discussion of the Results

A. The crystallography of the plagioclases - X-ray powder diffraction.

Interesting problems are revealed by the powder diffraction results. These are presented in Fig. 7 as T plotted against the atomic ratio % An. ("Atomic ratio" is preferable as a term to "Mole fraction" because it is a more rigorous term in concept.)

The graph also shows a regression line for twelve samples determined by Jackson (1961) from plagioclases from a very similar environment, viz. the Stillwater Complex. Not only is the trend of points in the present work not concurrent with that line, but this study has revealed a change or discontinuity. There is a distinct change in slope between samples 163 and 166B.

These observations are due to one or a combination of factors. Changes in composition, thermal history, structural state and crystallography may be influencing variables.

It is perhaps unfair to compare too critically the difference in the points of the graph with Jackson's regression line. For example, it may be that potassium has no real bearing on the parameter T (or an influence not understood), while it does influence the ~~ordinate~~ abcissa determined by the calculation of the atomic ratio.

The first conclusion therefore is that the trends in T reported for other bodies of very similar type are not exactly the same as the determinations performed on the Mt. Davies intrusion. The comment is made that it is not surprising that the parameter should have to be recalibrated for a different body.

A second conclusion is that the calibration is successful, although the non linearity over the range studied reduces the accuracy of those regions. Some checking would be desirable before attaching too much certainty to determinations made with the curve on plagioclases from different bodies in the igneous complex. This is because while all other influencing factors would be equal, the K content may vary. As before, this affects the atomic

ratio, but may not affect Δ . The inaccuracies thus introduced may not exceed 1 or 2 % An, anyway, so the difficulty is one of degree.

The Thermal history of the plagioclases is considered to be a fixed quantity in this study. Modern studies (Megaw, 1962) have shown that annealing to the low temperature structural state is rapid. These feldspars would have to be held at somewhere a little below 1150° for a relatively short time to allow complete changeover to the low temperature state. A large body such as this would provide these conditions.

Δ is dependent on changes in γ^*. Therefore changes in it must be related to a changing crystallography with composition,(having already decided to consider only the low temperature form).

Smith and Gay (1958) suggested a change in lattice type from body centred to primitive at about An_{80-90}.

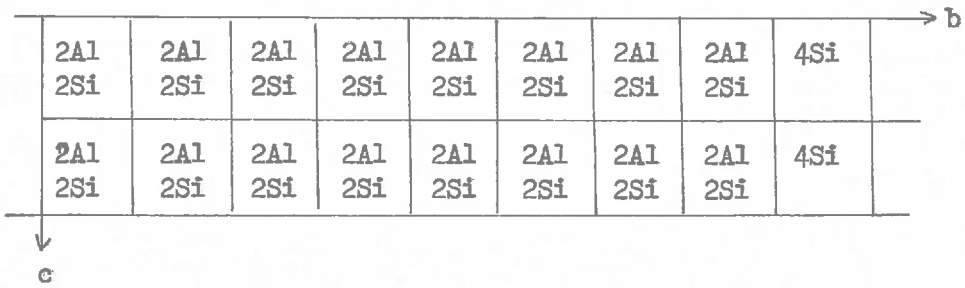
Brilliant theoretical work by Megaw (1960) has predicted some significant changes in the lattice at An_{78}. Work by her and many others, summarized by Taylor (in the press) has shown that there is a gradual transition from primitive Anorthite between An_{80-90} as shown by the increasing diffuseness of "c" type reflections in single crystal oscillation photographs. New sharp reflections of "e" and "f" types are found at about An_{77} .

This represents a discontinuous change to a new framework type called the Low Intermediate Plagioclase. The model of this lattice derives an ideal plagioclase unit cell defined along slightly different axes by edges a_o , $9b_o$, $2c_o$. That is, there are 18 subcells of dimensions a_o , b_o , c_o , ~~(Megaw, 1960)~~. These subcells are very similar to the four subcells in the anorthite type lattice. The composition An_{78} provides exactly the right ratio of Si and Al for this lattice type.

Distribution of the silicon and aluminium is not as fully ordered amongst the subcells as in the primitive Anorthite structure.

It is best to imagine the 18 subcells as 4 unit cells, each with 4 subcells, placed end to end, giving perfect alternation of Si and Al in the 8 pairs of subcells. Two of the cells have been modified slightly to allow 2 subcells containing no Al to add to them without too much strain.

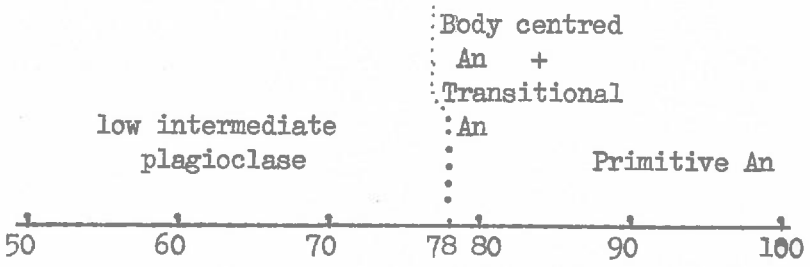
i.e.



The low intermediate plagioclase structure.

Sodium going into the lattice is thought to prefer the Si rich cells. Since the sizes of Na and Ca are practically the same, the reason will be due to the different electronegativity due to different charges. This will be explained in the section following this one. (p.23)

From these considerations, one would expect γ^* to change as the lattice changes the size of its unit cell and axis direction. The structural states resulting purely from compositional variations are :



We expect with decreasing Anorthite content a gradual, though possibly not regular, change as the transitional Anorthite structure accomodates its varying composition.

At An 78 we expect a decisive change, as the ideal intermediate plagioclase is established. With decreasing anorthite from here we expect a regular variation of Γ with composition, due to more orderly changes. Somewhere between An 78 and An 50 another change in slope is expected as two more Si rich subcells are formed. Fig. 1. of Smith and Gay (1958) shows some unusual happenings at just this range of composition, which may be due to this effect.

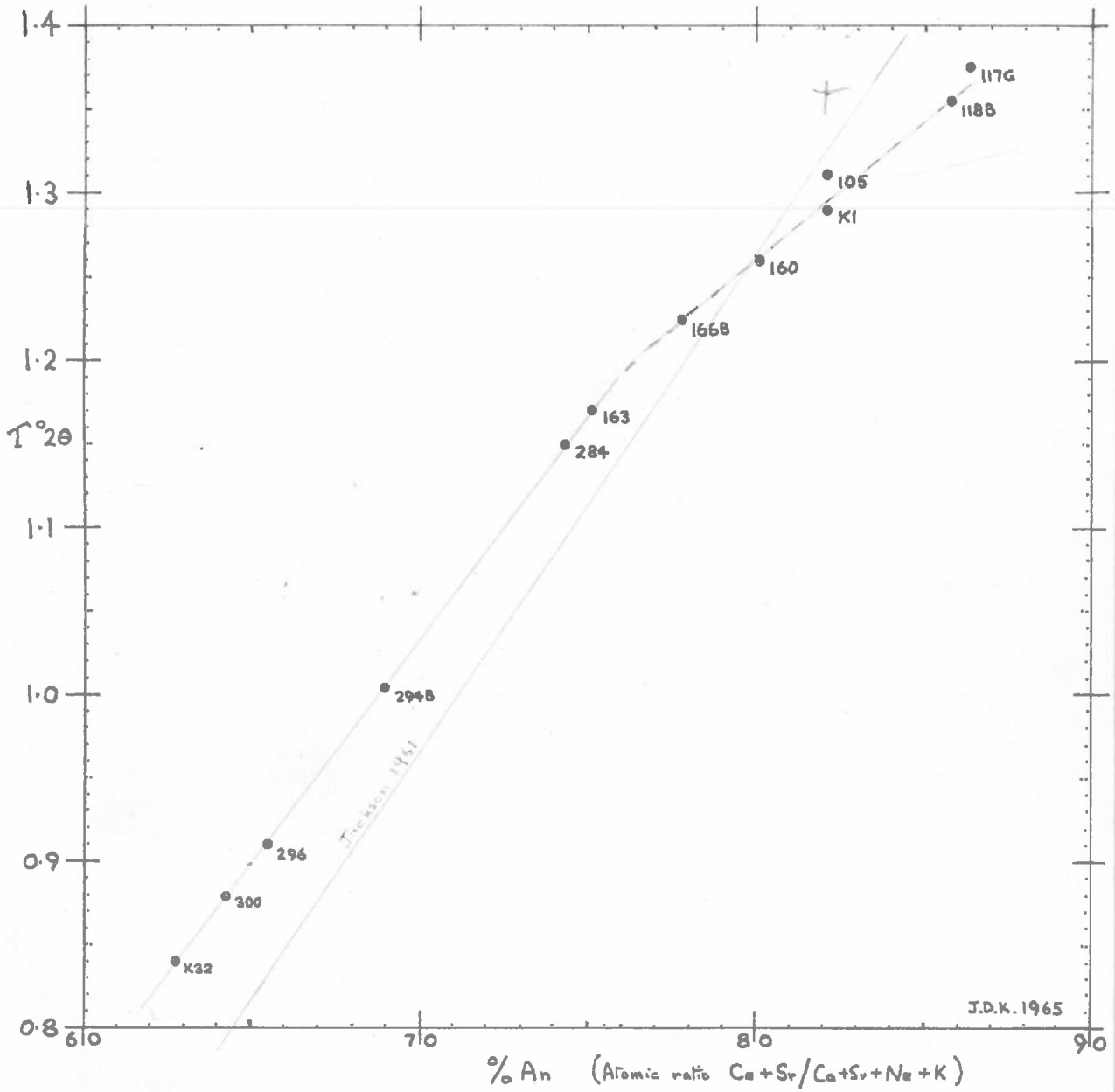


Fig 7. Plagioclase determination by X-ray powder diffraction

The graphical presentation of T against An content in the present study reveals that these predictions are substantiated in the range studied. T changes regularly with composition up to about An_{77}, where there is a definite break in slope, and above this composition the variation is not so regular.

B. The chemistry of the Plagioclase, with special reference to the differentiation of the body.

The differentiation of basic magmas has been made classical by Wager and Deer (1939) on the Skaergaand body. The Stillwater complex (Hess, 1956) and Bushveld (Willemse, J.) have also been accurately documented. The principles are reviewed by Mason (1958).

Very similar results are obtained in this study. The ensuing discussion of the implications of the results may not be entirely factual, since we are only now beginning to look at the plagioclase lattice in more detail.

The postulate, which is already evident from the results, is that the South side of the Mt. Davies intrusion is the last fraction to crystallize. We imply from this that since we have other evidence from layering, crystal settling and flow structures that the differentiation is by a convecting chamber, and the south side was once the top.

Please refer to the locality map (Fig. 1.) for the field relationships of the various samples.

A rock crystallizing from a liquid is composed of several phases. These forming minerals are in equilibrium not only with the parent liquid, but also with each other. Therefore while much can be deduced from a study of the plagioclases alone, it must be remembered that the other phases present may influence the compositions.

Crystal lattices forming by crystallization will strive to produce the most stable, most ordered structure. Generally a compromise is made due to the composition of the magma.

1. The Anorthite - Albite trends.

The most stable, most ordered plagioclase is the primitive Anorthite. The Si and Al occupy positions in near perfect alternation and the high electronegativity of Ca^{++} permits a collapsed structure which is very stable. The tendency is for it to form therefore.

A compromise is made however, because there are other cations present in the liquid of suitable size and charge, especially sodium. When the concentration relative to calcium is large enough, its presence cannot be ignored by the lattice. The easiest path is then the admittance of sodium to the lattice in increasing amounts.

The results is a plagioclase with always a ratio of Ca/Na greater than that of the liquid, but as in the course of crystallization this ratio is reduced in the liquid because of the discrimination against sodium so the plagioclase crystallizing is more albitic.

Sodium is almost certain to go into the Si-rich subcells when the composition of the low intermediate plagioclase structure is formed, and at more anorthitic compositions into the Si-rich domains in the lattice referred to by Megaw (1962).

This association of Na with the more Si-rich parts of the lattice is due to the attempt to retain as much contraction as possible. Na^{+}, having lower electronegativity is probably preferred to Ca^{++} in these positions because it has less tendency to distort the Si-O polarization, which is quite strong and very stable.

2. Potassium.

It is well reported that the potassium content of plagioclase shows a rise with increasing albite. For example J.R. Smith (1956) working on material from the Stillwater, Skaergaard and Bushveld bodies.

Sen (1959) reported a similar relationship, and also noted that more K is accomodated at higher temperatures.

In this study we are dealing with a small temperature change and in any case the more K-rich plagioclases are the later forming (lower temperature) ones, so the effect is not in the direction required. It is there-

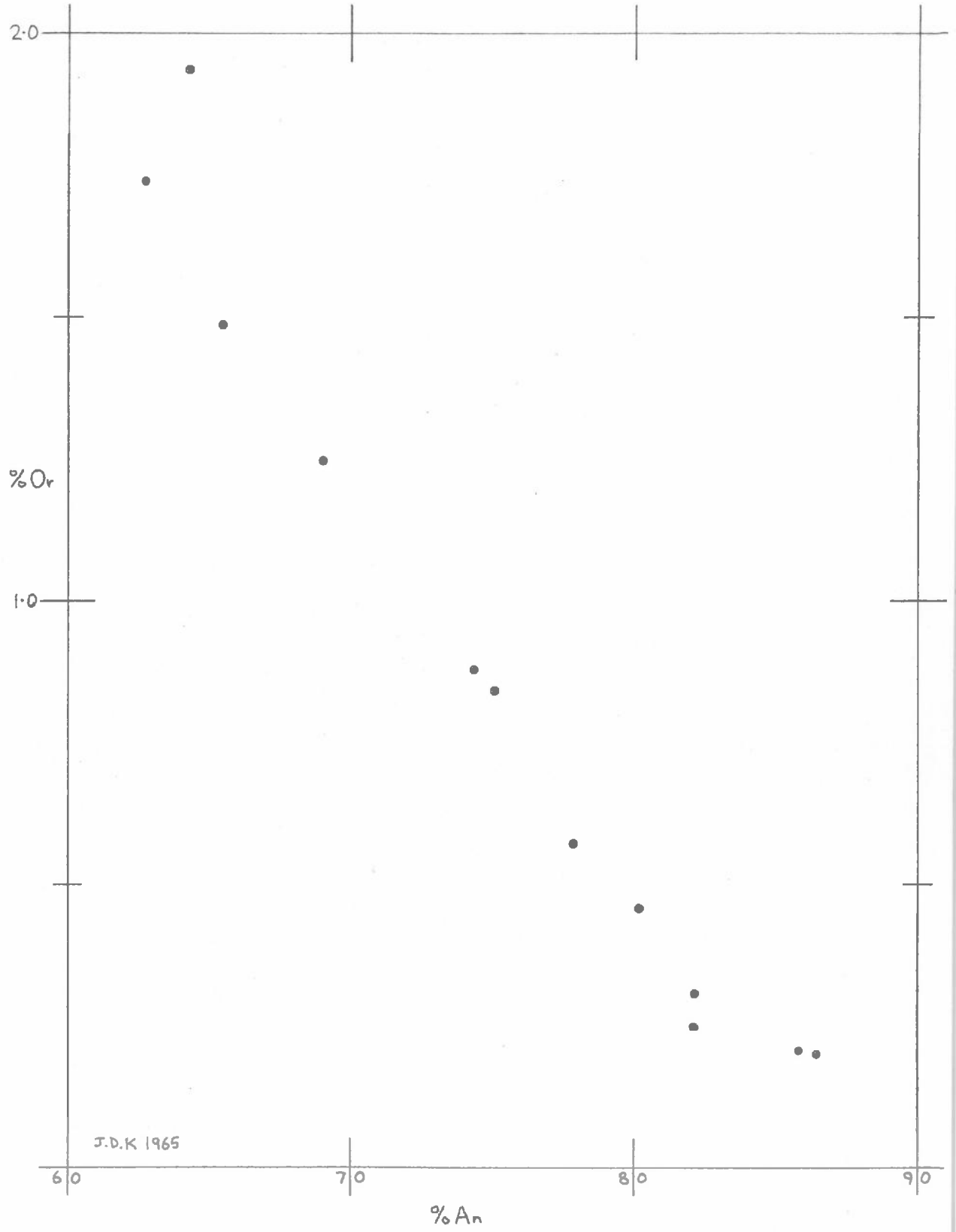


FIG. 8. % Or (Atomic ratio) v. % An (Atomic ratio) in the plagioclase.

fore possible to ignore temperature differences.

The Or content of the plagioclases is presented, plotted against the An content, in Fig. 8. There is a steady increase in Or with increasing Ab. The reason for this relationship is a combination of the changing lattice type and the changing concentration of K in the liquid. This reinforcing of the two controls explains why the K content changes by almost 10 x , while the corresponding increase in Na is only $2\frac{1}{2}$ x .

Primitive and Transitional Anorthite have quite collapsed lattices. The size and low charge of K^+ results in it being discriminated against, increasing its concentration in the liquid in the course of crystallization.

As more albitic plagioclase forms as fractional crystallization proceeds, K is much more easily accepted by the lattice. It seems certain that it goes into Na positions in the Si-rich subcells previously described. Its lower electronegativity, due to larger size, results in even less pull on the electrons of oxygen, allowing an even more polarized Si-O bond, with a consequent increase in the stability of the lattice at that point.

Since the number of silicon rich subcells increases with increasing albite, it follows that an increase in K should be observed.

Presumably there is a maximum amount that can be accepted by the plagioclase lattice for a given set of thermal conditions before modal Or is formed.

It is interesting to note the presence of a very small amount of modal biotite in A251/N300 and almost 1% in A251/K32. The biotite may have formed to use up the K not taken by the plagioclase, or it could have competed for it. The plagioclase K32 shows slightly less K than 300, so the latter case may be operative. The late formation of biotite, which is generally the case, supports the former, however.

3. Strontium.

Trace element concentrations of Sr are found in both the whole rocks and the plagioclases in them.

The rock forming by crystallization from a magma is an assemblage of minerals, and therefore the incorporation of trace elements will be

determined by the requirements or tolerances of the individual minerals. The data from Table 8, is processed in this light.

From a consideration of the other minerals present, the hypothesis is made that all the Sr is present in the plagioclase.

A fair test of this hypothesis would be to calculate, using the whole rock analyses, a figure for the Sr concentration in the plagioclase. The normative plagioclase content is used. (Norms calculated by A.W. Kleeman)

Table 11. Strontium calculations.

	Sr whole rock p.p.m.	Normative Plagioclase	Sr calculated in plagioclase p.p.m.	Actual Sr in plagioclase p.p.m.
118B	(Anorthosite)	98	[illegible]	285
117G	105	45	232	245
105	175	63	278	281
K1	177	67	263	270
160	207	72	288	295
163	171	56	305	323
166B	224	70	320	323
284	226	73	312	313
294B	190	60	318	362
296	233	63	369	401
300	199	58	340	374
K32	223	57	391	412

In most cases the plagioclase has actually more Sr than we would expect from these calculations. A modal analysis is to be undertaken to check the normative calculations. Yong (1964) found that 118C, an olivine pyroxenite, contained only 15 p.p.m. Sr., with similar values for another pyroxenite studied.

The indications are very strongly in support of the hypothesis, and one would be very confident in asserting that the Sr is almost entirely in the plagioclase.

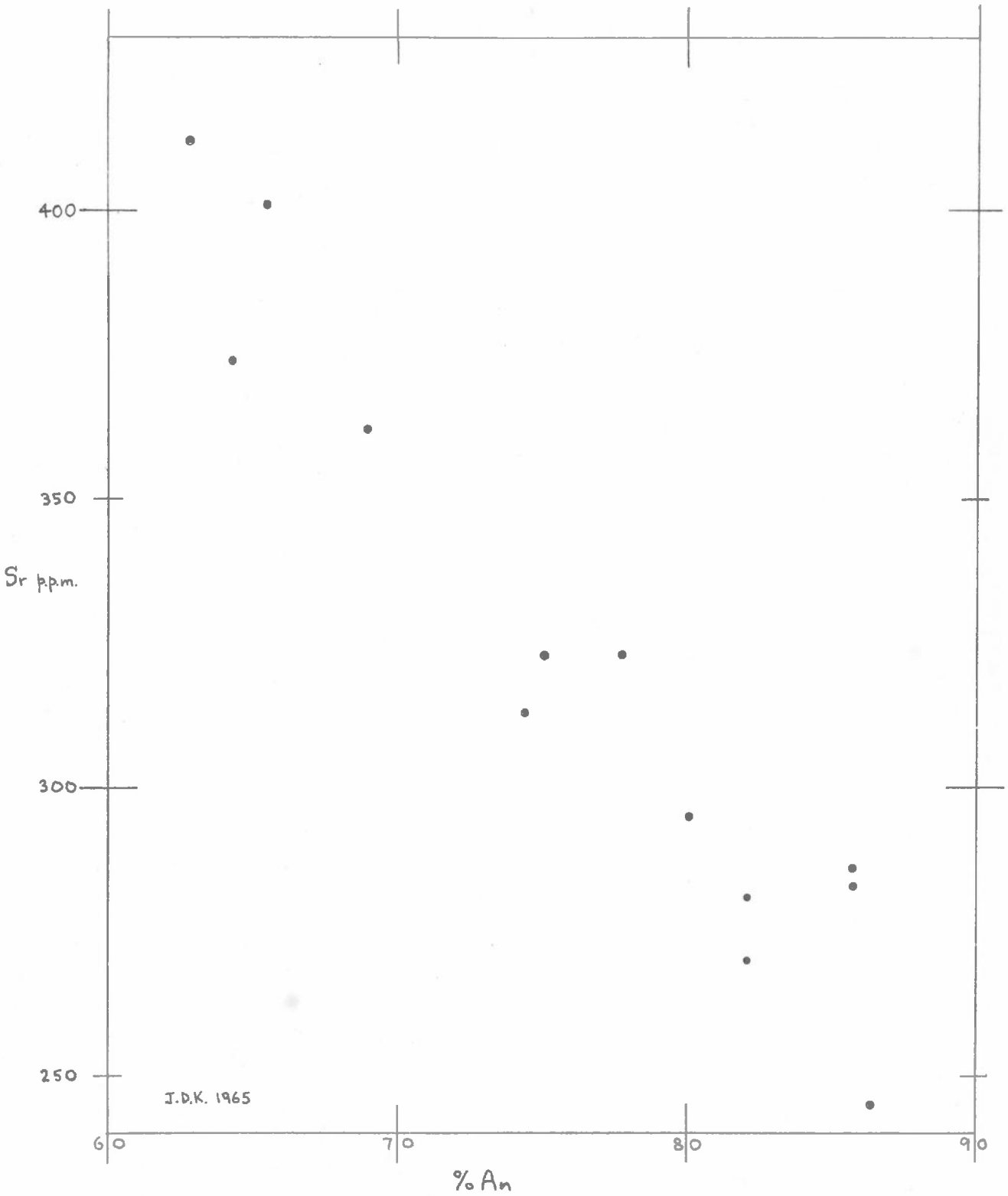


FIG 9. Sr content of plagioclase v. Anorthite content

The graph in Fig. 9. reveals a definite, though unsteady, relationship with the composition of the plagioclase, which may be variously interpreted.

Wager and Mitchell have found the same trend of concentration of Sr in the plagioclase as crystallization proceeds.

Explanation of this phenomenom is generally made by calling the entry of Sr into the plagioclase as one of "admittance".

Sr^{++} has an atomic radius within 15% of Ca^{++} and is thought to occupy Ca positions in the lattice. However, because it is larger than Ca, it will be at a disadvantage, so that it will not compete as successfully against Ca for lattice positions. The concentration of Sr in the liquid remaining will therefore rise gradually and this increasing concentration with respect to Ca will cause more to be admitted to the plagioclase forming.

One serious objection to this explana tion lies in the fact that there is no evidence that the concentration of Sr in the residual liquid did ever rise significantly. The whole rock analyses for the "top" of the intrusion show scarcely more Sr than those for rocks near the ultrabasic, "bottom" layers.

This is not to say that Wager and Mitchell's explanation is at fault, far from it. The concentrations involved in the Skaergaard magma are much higher than at Mt. Davies, and therefore would have played a much more important part in the equilibrium. Certainly the concentration of Sr relative to Ca is important, for the lattice in the Skaergaard plagioclases takes up to 5,000 p.p.m. Sr .

With a much smaller Sr/Ca ratio in the Davies magma we expect that any discrimination against Sr will make only small changes in the concentration of Sr in the residual liquid anyway.

It may then be that the control is largely due to changes in the feldspar with changing composition.

Turekian and Kulp (1956) find that the Sr content of plagioclases in granites increases with increasing Ca, and for basic rocks the opposite is found (as in the present study.). Granites have plagioclases of low An content while the basic bodies have higher An content. Somewhere in the series there must be a plagioclase lattice with the maximum admittance of Sr. Wager and Mitchell found the maximum Sr content in plagioclases of An_{40} composition.

This leads to the conclusion that the controlling factor is very largely due to changes in the crystal lattice structure.

The preceding evidence also suggests strongly that Sr is in Ca positions, since at very low Ca content its presence is proportional in concentration to Ca. This trend does not continue above about An_{40} because the lattice becomes increasingly more collapsed as calcium becomes the dominant cation present. When this happens there is increasing discrimination against the larger Sr^{++} cation.

Naturally the magam concentration of Sr would increase during fractionation because of this, but it is considered to be very much a by-product of the crystallographic changes, and will not be very effective unless overall concentrations are high.

4. Barium

The results are strictly qualitative, but the trend is unmistakenly towards increasing Barium with decreasing Anorthite content.

The position of Barium in the lattice is not very well known. Wager and Mitchell attributed the dominant reason for a similar trend in the Skaergaard plagioclases to the large size of Ba^{++} . This causes it to be left out of the lattice to some extent and concentrated in the remaining liquid as a result. Due to its increasing concentration it will be forced into the lattice of the later forming plagioclases.

There is no real evidence to suggest that the Mt. Davies plagioclases are also under this sort of control, however if the effect of concentration is sensitive enough it will be a reasonable explanation.

Conclusions

1. The most efficient means of chemically analysing the cations of plagioclase is by X-ray fluorescent spectrography for CaO (based on standards established by E.D.T.A. titration) and by analysing the alkalis, Na_2O and K_2O, with the flame photometer.
2. Calibrations for Γ against An content for other bodies are not directly applicable to the plagioclases from the Mt. Davies intrusion.
3. The calibration is successful for this body, although non linearity of part of the range reduces accuracy in that section. Below An_{76} a precision of $\pm$ 1% An is within the limits of measurement of Γ. Above this composition the uncertainty of the graph position reduces the accuracy, but not the order of precision available.
4. Γ changes regularly with composition from An_{63} to about An_{76}, where there is a definite break in slope. This may be a reflection of changes in the plagioclase unit cell structure with composition, Γ being dependent on γ^*.
5. The composition of the plagioclases reflect the differentiation by fractional crystallization of the Mt. Davies intrusion. The differentiation proceeds southwards.
6. Potassium in the plagioclases increases with increasing albite. This is attributed mainly to the control of the changing lattice.
7. Strontium appears to go exclusively into the plagioclase mineral phase.
8. The Sr content increases with decreasing An. The trend is related to both lattice change and increase in magma concentration, the former being the dominant character.
9. Barium exhibits a similar change. The cause is probably due to changes in magma concentration which are brought about by geochemical processes.

Acknowledgements

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Appendix I

This supplement considers only the basic theory of the two methods of obtaining corrections for the absorbence of the photons emitted by the element in question by the matrix containing it. A detailed discussion of the methematical theory is not the prerogative of the author.

Much of the development of the first method in particular is due to the work of Dr. K. Norrish, who has not published on the matter yet.

A brief account of the assumptions and theory is written by Koch and MacGillavry (1962).

The linear absorption of monochromatic X-rays passing through an isotropic material is given by

$$I = I_0 e^{-\mu l}$$

where I_0 = incident intensity
I = emergent intensity
l = length of path (cm.)
μ = linear absorption coefficient

.... providing (1) the incident X-rays are strictly monochromatic
(2) the incident X-rays are parallel
(3) the material is homogeneous (where applicable)
(4) the material has plane-parallel surfaces, normal to the beam
(5) the beam cross section is less than the area of cross section of the sample
(6) the number of photons is not appreciable altered

In practice these conditions are quite easily met, to a quite reasonable degree, using a pressed mount of the powder in question. Using a method of direct measurement of this beam attenuation at the appropriate wavelength, the relationship is best rewritten as the Mass Absorption Coefficient.

$$I = I_0 e^{-\mu/p \cdot pl}$$

pl = mass/sq. cm.
μ/p = Mass Absorption Coeff. (called μ_m)

I_0 becomes the unattenuated beam of the same area of cross section (fixed by the use of a stop)

I is the attenuated beam (i.e. with sample in place)

from this $\ln \frac{I_o}{I} = \mu_m \cdot pl$

then $\mu_m = \frac{\ln \frac{I_o}{I}}{pl}$

It has been found that to a good approximation, a value for Mass absorption coefficient is abstained from the addition of those of the elements composing the matrix. This is possible because the mass absorption is approximately independent of the physical state of the material.

$\mu_m = \sum_i mi \, \mu mi$

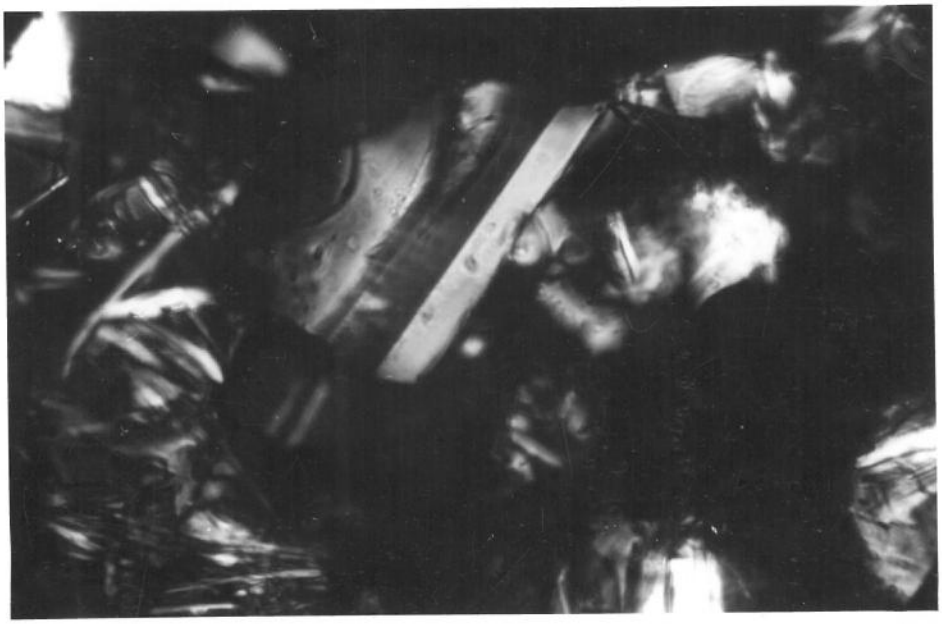
mi = mass fraction of element i $= \frac{wt.\%}{100}$

μ_{mi} = mass absorption coefficient of element i

This method of calculation does have drawbacks if an analysis is not available, however for plagioclases good estimates could be made from only the cation analyses, the other elements being approximated.

It is necessary for Barium because of the soft wavelength involved.

PLATE I



Photomicrograph of Frit Crystals (x250)