

A STUDY OF PLAGIOCLASE FELDSPARS IN LOW-GRADE
METAMORPHIC ROCKS FROM THE MADOC AREA OF
SOUTHEASTERN ONTARIO

A STUDY OF PLAGIOCLASE FELDSPARS
IN LOW-GRADE METAMORPHIC ROCKS
FROM THE MADOC AREA OF
SOUTHEASTERN ONTARIO

by

MICHAEL VINCENT WHITE

A Thesis

Submitted to the Faculty of Arts and Science
in Partial Fulfillment of the Requirements
for the Degree
Bachelor of Science

McMaster University

May, 1968

ABSTRACT

A brief description of a low grade regionally-metamorphosed region in the Madoc area in Southern Ontario is given. Plagioclase compositions from metamorphosed basic rocks of this region were studied with the intention of finding co-existing plagioclases in the region of peristerite solvus.

X-ray diffraction was found useful in determining the presence of two co-existing plagioclase feldspars. Two peaks occurred in the region of the $1\bar{3}1$ and 131 peaks if this was the case. Compositional determinations for albitic feldspars were found inaccurate as the angular separation ($\Delta 2\theta$) between the 131 and $1\bar{3}1$ peaks was apparently reduced indicating plagioclase composition less than An_0 . For anorthite rich feldspars the angular separation between 131 and $1\bar{3}1$ gave relatively accurate compositions.

The electron microprobe was used to determine the plagioclase compositions of samples from the Madoc area. Results compared well for anorthite rich feldspars determined by both X-ray diffraction and electron microprobe techniques.

Only one rock was found to contain two plagioclases related to a peristerite solvus. A zoned nature appears to

exist. Albite and oligoclase coexist, the oligoclase grading into andesine.

Also, albitic plagioclase is associated with epidote inclusions; a diffusion relationship probably existing between the two. With increased metamorphic grade, epidote disappears and the anorthite content of plagioclase increases.

ACKNOWLEDGEMENTS

Dr. H. P. Schwarcz suggested this study and gave freely of his knowledge throughout the work; his assistance is gratefully acknowledged. I wish to thank Mr. F. Tebay for his help in the X-ray diffraction analysis and Mr. H. Walker for his assistance in the use of the electron microprobe.

I also wish to thank my mother and Miss S. Schonfeld who spent valuable time in typing this thesis.

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
GEOLOGY	4
Location	4
Description	4
Discussion	11
X-RAY DIFFRACTION	14
X-ray Diffraction Analysis	16
Analytical Procedure	16
Preparation of Standards	17
Analytical Results	20
Discussion	25
REFRACTIVE INDEX DETERMINATIONS	28
ELECTRON MICROPROBE ANALYSIS	30
X-ray Optics	30
Analytical Procedure	30
Plagioclase Standards	32
Preparation of Polished Thin Sections	34
Calibration Curves	34
Analytical Results	34
Discussion of Probe Results	45
GENERAL DISCUSSION	48
BIBLIOGRAPHY	52

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
i	Map of Sample Location from Madoc Area	3
1	Positions of X-ray Diffraction Peaks Determined from A.S.T.M. Cards	15
2	Step Scan Graph for 90% Ab, 10% olig.	21
3	Step Scan Graph for 10% Ab, 90% olig.	22
4	Step Scan Graph for Sample VT II 14	23
5	Step Scan Graph for Sample WV-1	24
6	Calibration Curve for Plagioclase Standards (microprobe)	33
7	Electron Photo $K\alpha$ X-ray Photos; Strip Chart Record for Sample WV-1	36
8	Electron Photo $K\alpha$ X-ray Photos; Strip Chart Record for Sample WV-3	38
9	Electron Photo $K\alpha$ X-ray Photos; Strip Chart Record for Sample WV-3	39
10	Electron Photo $K\alpha$ X-ray Photos; Strip Chart Record for Sample WV-4	41
11	Electron Photo $K\alpha$ X-ray Photos; Strip Chart Record for Sample WV-7	43

LIST OF TABLES

		<u>Page</u>
TABLE 1	Petrographic Description of Samples from Madoc Area	6
TABLE 2	Analytical Results of X-ray Diffraction Analysis	19
TABLE 3	R.I., X-ray Diffraction and Electron Microprobe Compositional Determination	28
TABLE 4	Analysis of Samples from Madoc Area	35

INTRODUCTION

The purpose of this study was to examine the plagioclase feldspar present in the low grade metavolcanics of the Madoc area in Southern Ontario. Also, it was proposed to examine the efficiency of X-Ray diffraction methods in the determination of the composition and presence of two co-existing plagioclases together in the area of the peristerite solvus.

As laboratory investigation of the peristerite solvus has been rather unsatisfactory because of slow reaction rates, it has been suggested that metamorphic rocks might provide natural systems in which to observe the variations of plagioclase composition with varying temperatures and pressures.

Dewaard (1959) studying the metamorphics in the island of Timor and Lumbers (1966) studying rocks in the Madoc area both observe an absence of plagioclase composition between An5 and An20. This certainly suggests that the peristerite solvus has some significance in metamorphic reactions.

Crawford M. L. (1966) studying low grade regionally metamorphosed semi-pelitic schists claims that plagioclase compositions for rocks found below the almandine

isograd suggest a peristerite solvus approximately between composition An5 and An23. She suggests the top of the solvus lies slightly above the temperature expressed by the almandine isograd.

Generally, she observed albitic grains mantled by oligoclase. Above the almandine isograd plagioclase grains are zoned but the zoning is not systematically distributed around the grains.

The peristerite solvus determined by Crawford suggests a significant temperature range over which two plagioclases might be expected to occur.

Thus it was expected that by examining low grade rocks, containing significant amounts of plagioclase feldspar, over the range indicated by Crawford's peristerite solvus, two plagioclase feldspars would be found. The low grade metavolcanics of the Madoc area were thought to be suitable for this study.

It was proposed to examine the plagioclases using X-ray diffraction and electron microprobe techniques.

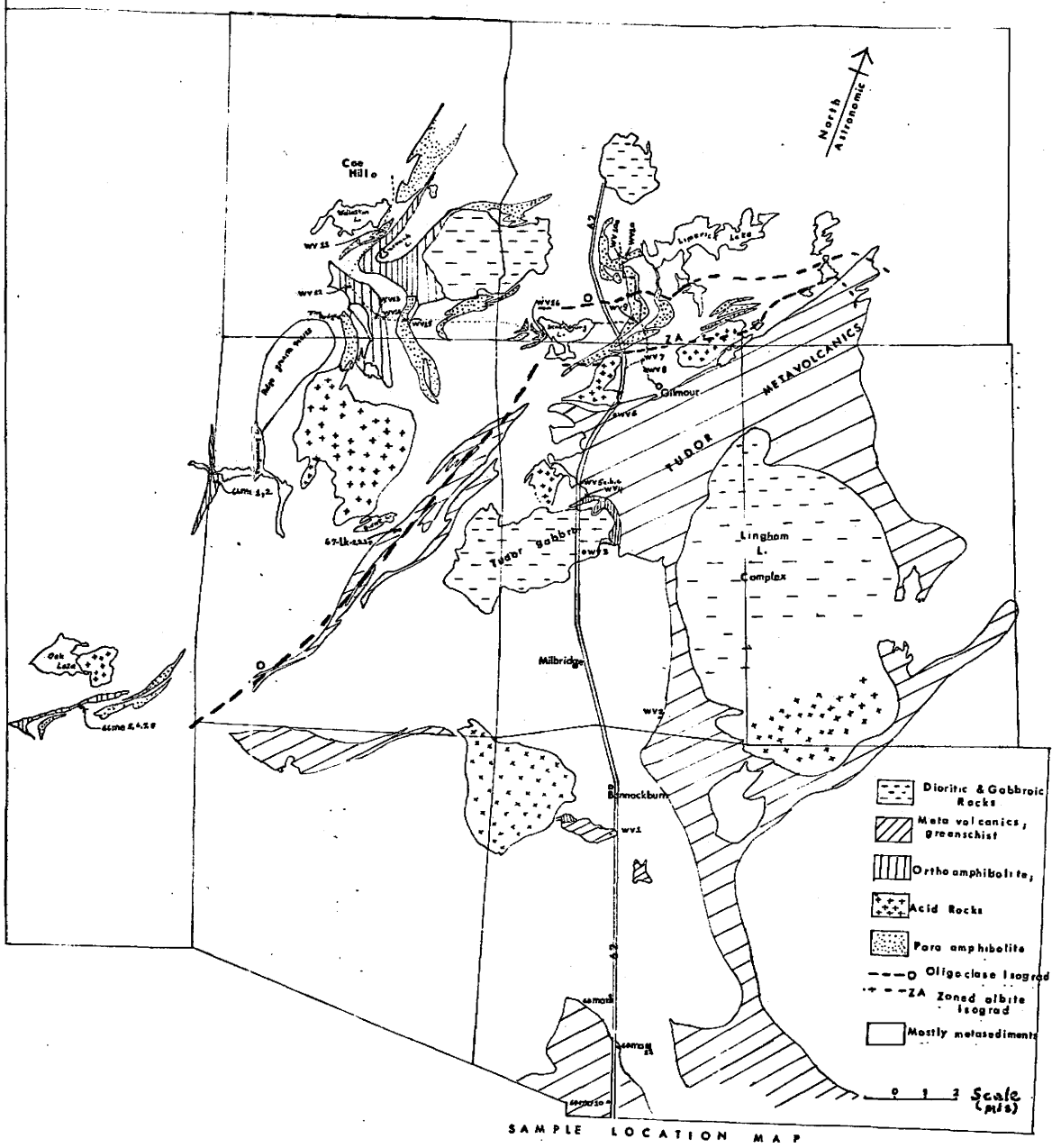


Fig. 1

GEOLOGY

Location

The area from which samples have been collected is indicated by the map (Fig. i). It lies generally to the north of Madoc and to the southwest of Bancroft, extending no further north than Coe Hill. (Note that not all of the samples collected from this area, indicated by sample points, were studied.)

Description

The geology of the area is described in the Ph.D. thesis by S. B. Lumbers (1967).

Generally, it is underlain by metavolcanic rocks, originally of basaltic and andesitic composition. These are represented by the Tudor metavolcanics, possibly the oldest rock outcropping in the area. Intruding these are plutonic rocks generally of dioritic composition. Overlying much of the area are younger sedimentary rocks.

The rocks in the area studied have generally been regionally metamorphosed to the greenschist facies, the grade increasing northwards and westwards. Contact metamorphism is associated with many of the plutons.

From geologic and geochronologic data, Lumbers concludes that much of the regional metamorphism preceded

plutonic activity which was accompanied by folding of the surficial rocks which are only slightly older than the oldest plutonic rocks.

Lumbers has constructed several isograds. The lower amphibolite facies is defined by the andesine isograd (first appearance of andesine) and the oligoclase isograd. Higher grade rocks are defined by a Sillimanite isograd.

A zoned albite isograd (first appearance of zoned albite) marks the division of upper and middle greenschist facies rocks. This isograd marks the disappearance of most of the primary microtextures in the rocks.

In the middle greenschist facies rocks unzoned albite is common (An 0-5). No plagioclase compositions in the range An5 to An20 were found. With increasing grade, zoned albites progressively increase to zoned oligoclase-andesine.

In all cases, above the zoned albite isograd the plagioclases were reversely zoned.

The above description appears to indicate that the area should be ideal for the study of two co-existing plagioclases in the region of the peristerite solvus. As the metavolcanics were thought likely to contain more plagioclase most of the samples studied were taken from these lithologic units.

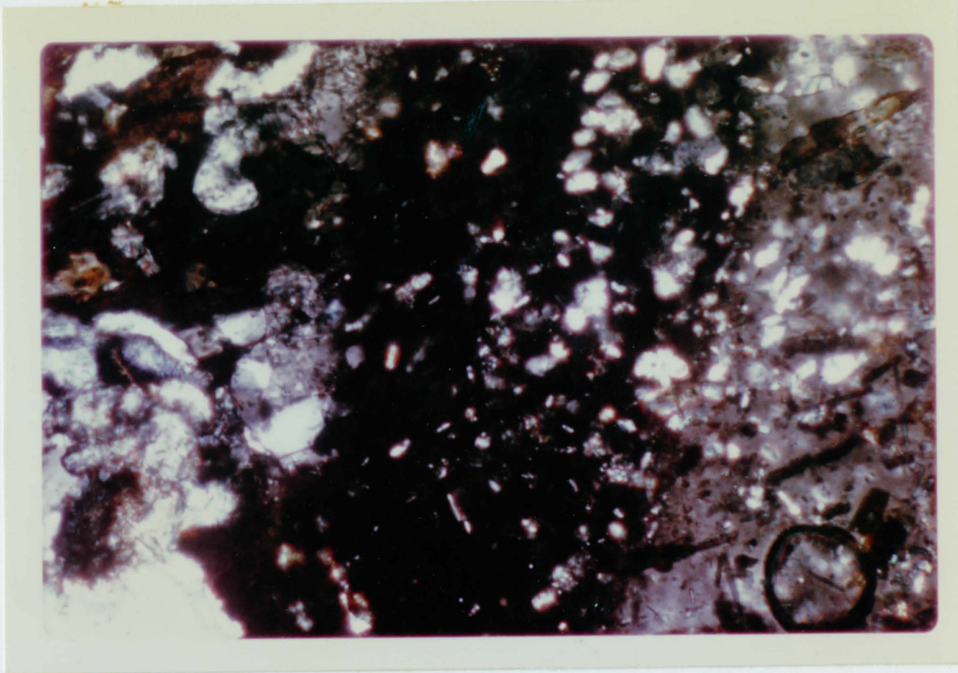
PETROGRAPHIC DESCRIPTION

TABLE 1

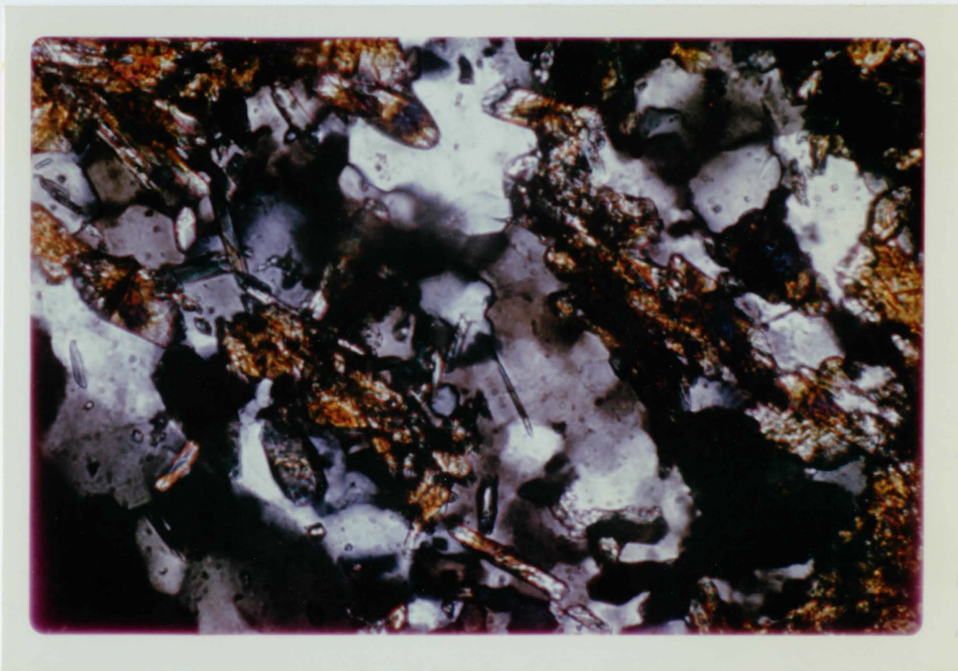
Sample	Minerals	Mode	Texture
WV-1	Plagioclase (Albite) Chlorite Biotite Epidote Calcite Apatite Quartz	~50% 25% 5% 12% 1% 1% ~5%	From Tudor Metavolcanics Albite porphyroblasts contain multiple inclusions consisting of epidote, sericite, chlorite and minor apatite. Groundmass consists of mostly fine-grained quartzo-feldspathic material with subparallel laths of chlorite and biotite and abundant epidote distributed through the rock.
WV-3	Plagioclase (Andesine) (Chlorite & relict hornblende) Epidote Magnetite Calcite	40-45% 35% 20% 5% 1%	From Tudor Metagabbro Large grains of plagioclase enclose relict hornblendes and chlorite. Only small amounts of hornblende are not altered to chlorite. Epidotization to an Fe rich epidote is extensive around the edges of the plagioclase and in patches within the grains. Where few epidote grains are present, heavily saussuritized plagioclase is present. Within the saussurite tiny Fe rich epidotes are observed under high magnification (1000X). These have the birefringence characteristic of zoisite.
WV-4	Quartz & Plagioclase (oligoclase) Quartz Chlorite Epidote Magnetite Calcite	10%? 15% 55% 18% 2% 1%	From Tudor Metavolcanics Plagioclase is of a fine-grained granular nature and is intermixed with quartz. Chlorite is abundant and has a faint orientation but mostly occurs throughout the rock in patches of varying dimensions.

TABLE 1 (cont'd)

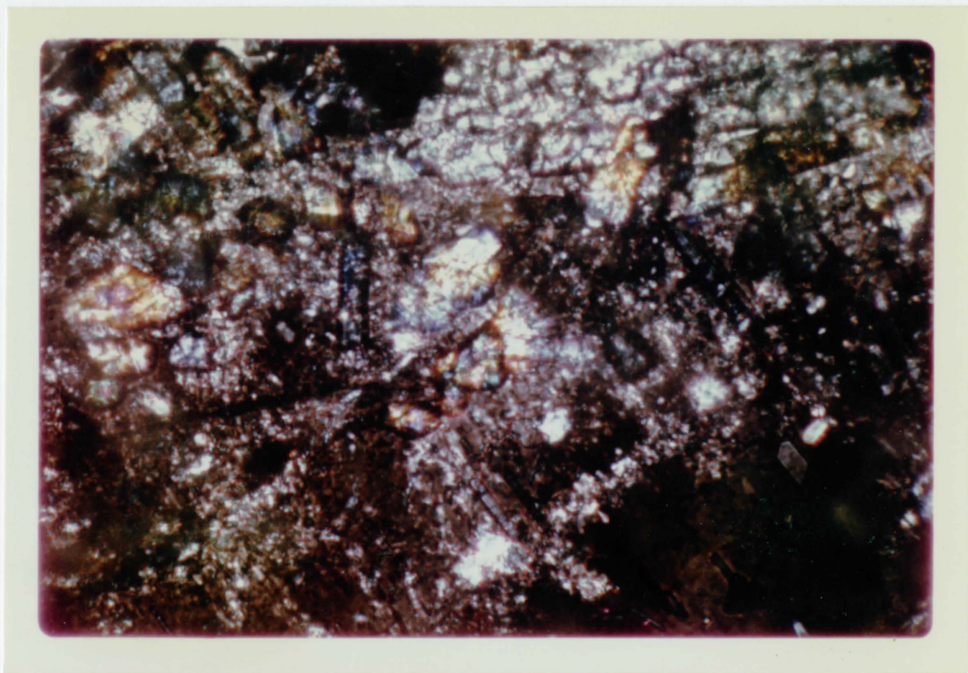
Sample	Minerals	Mode	Texture
WV-7	Plagioclase (oligoclase) Actinolite Chlorite Magnetite Quartz	50% 45% 4% 1% ?	The rock consists of equigranular patches of actinolite and plagioclase intermixed. Actinolite has a hornfelsic texture and the plagioclase has a granular texture. Faint twinning is observable in some of the granular plagioclase patches. Overall there is a tendency for the amphiboles and plagioclase to segregate. Some chlorite is associated with the actinolite.
WV-5b	Quartz Feldspar Scapolite Chlorite Biotite Epidote Muscovite Magnetite	70% 7% 5% 10% 2-3% 2%	From Tudor Metavolcanics The rock is extremely fine-grained so that the recrystallized mixture of quartz, feldspar and scapolite is relatively indistinguishable. Patches of epidote occur scattered randomly through the section but there is a tendency for the mafics to be segregated from the quartz and feldspar.
67 LK-1	Amphibole Chlorite Biotite Calcite Quartz- Feldspar Magnetite	5% 25% 10% 15% 45% 1%	Porphyroblasts of euhedral amphibole; anhedral biotite and large grains of calcite occur in a very fine-grained quartzofeldspathic matrix with subparallel grains of chlorite. Chlorite also occurs as large patches of interlocking grains.
67 LK-2	Amphibole Chlorite Biotite Calcite Quartz- Feldspar Magnetite	5% 25% 10% 15% 45% 1%	Large anhedral to subhedral porphyroblasts of actinolite occur in a very fine quartzofeldspathic matrix with subparallel laths of biotite. Minor chlorite occurs here and there and patches of recrystallized quartz of larger grain size are also present.



WV - 1 Magnification = 400×
Plagioclase with sericite and epidote
inclusions

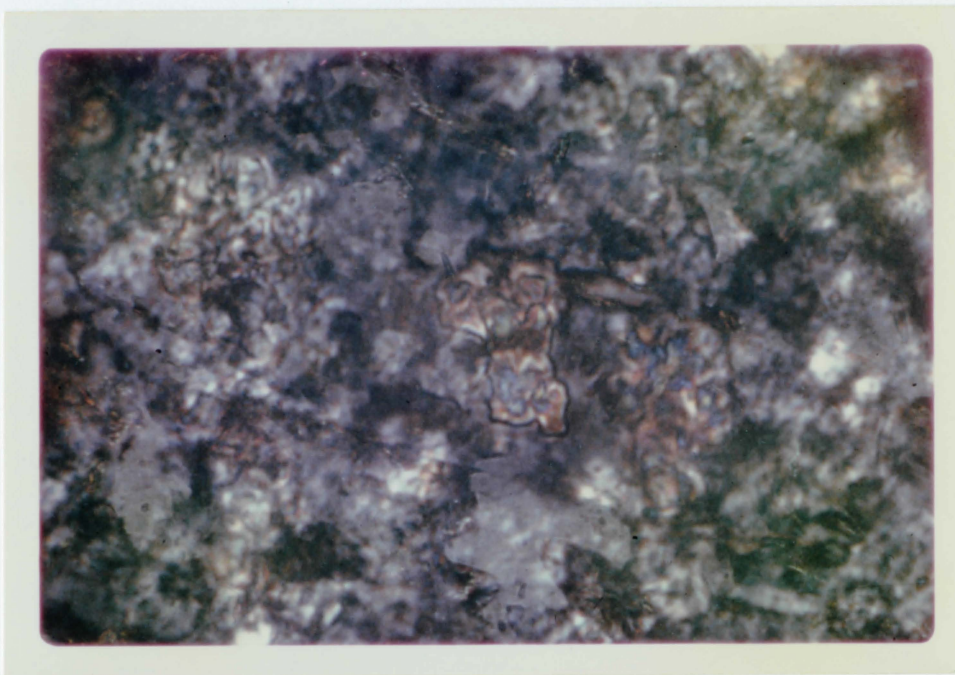


WV-7 Magnification = 400×
Plagioclase and Actinolite; note recrystallized
nature of feldspar



WV-3 Magnification = 600×

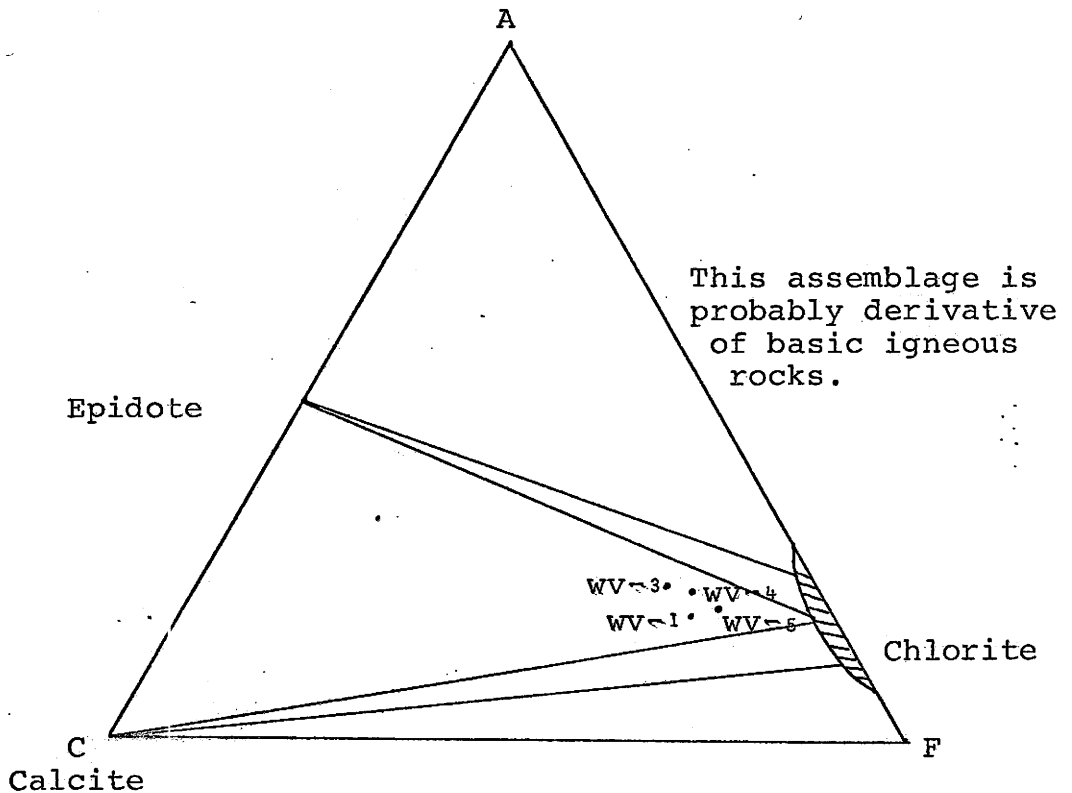
Epidote inclusions saussuritized plagioclase.



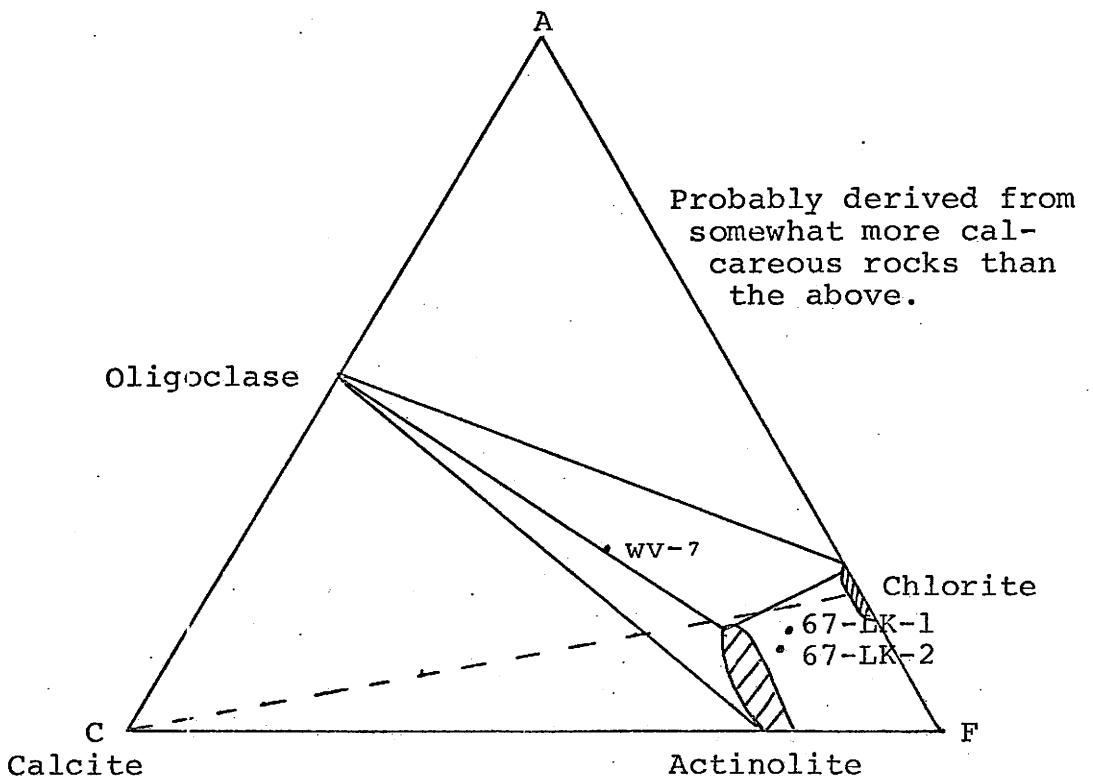
WV-3 Magnification = 1600×

Epidote forming in saussurite: bright white spots
are sericite.

* All photomicrographs taken under X-nicols



These represent rocks in the quartz-albite-epidote-biotite subfacies of the greenschist facies after Turner and Verhoogen.



Represents slightly higher grade, bordering the amphibolite facies.

DISCUSSION OF TEXTURAL RELATIONSHIPS

Modal analyses and descriptions of all the samples studied are given in Table 1. Samples WV-1 to WV-7 represent continuously increasing grade of metamorphism according to isograd relationships suggested by Lumbers.

WV-1, WV-3, WV-4, WV-5 (no feldspar compositions) fall within the lower middle Greenschist facies. WV-7 falls at the border of the zoned albite region (upper greenschist).

The albite porphyroblasts containing abundant inclusions are probably texturally relict of the original plagioclase. The mineral assemblage appears to indicate equilibrium for a rock of basic composition.

WV-3, WV-4, WV-5 are from the same general area and should represent the same grade, and hence mineral assemblages, as they all seem to be derived from basic igneous rocks. This is observed to be at least partially the case (i.e., they all contain chlorite and epidote). The plagioclases, however, are of widely differing composition. The plagioclase in WV-3 (a meta-gabbro or diorite) is very coarse grained and mainly of andesine composition showing good twins of the albite and Carlsbad laws. This specimen has evidently not entirely attained equilibrium at the same metamorphic grade as the adjoining amphibolites,

since it contains prominent textural relicts of its igneous protolith.

WV-4 contains fine grained plagioclase of an oligoclase composition (determined by X-ray and microprobe). WV-5 is similar in texture to WV-4 but no compositional determinations were made on the plagioclase. The difference in grain size and feldspar composition certainly suggests a difference in metamorphic grade. It therefore seems likely that since WV-3 and WV-4 are within close proximity that a contact metamorphic relationship exists between the two rocks.

Also, it was observed that much of the andesine in WV-3 was heavily altered to epidote. The rims of the grains were almost completely altered to epidote and epidote inclusions occurred within the grains. Much of the feldspar was also extremely cloudy due to alteration to a very fine-grained mineral of a relatively colourless to white colour (saussurite). Under extremely high power, this saussurite was observed to contain tiny grains of epidote optically determined to be Fe rich. Thus, a relationship is thought to exist between saussurite and the formation of epidote. WV-3 was the only rock in which saussuritic alteration was observed and it appears to be the lowest grade rock represented. Epidote-saussurite relationships can be seen in the photomicrographs.

WV-7 falls within the zoned albite region and is optically observed to be faintly zoned in a few areas. A definite recrystallized texture compared with the earlier rocks can be seen. Quartzo-feldspathic patches of very fine-grained nature are surrounded by mafics consisting mainly of actinolite.

It was expected that X-ray diffraction and electron microprobe techniques would clarify the feldspar compositions and relationships.

X-RAY DIFFRACTION

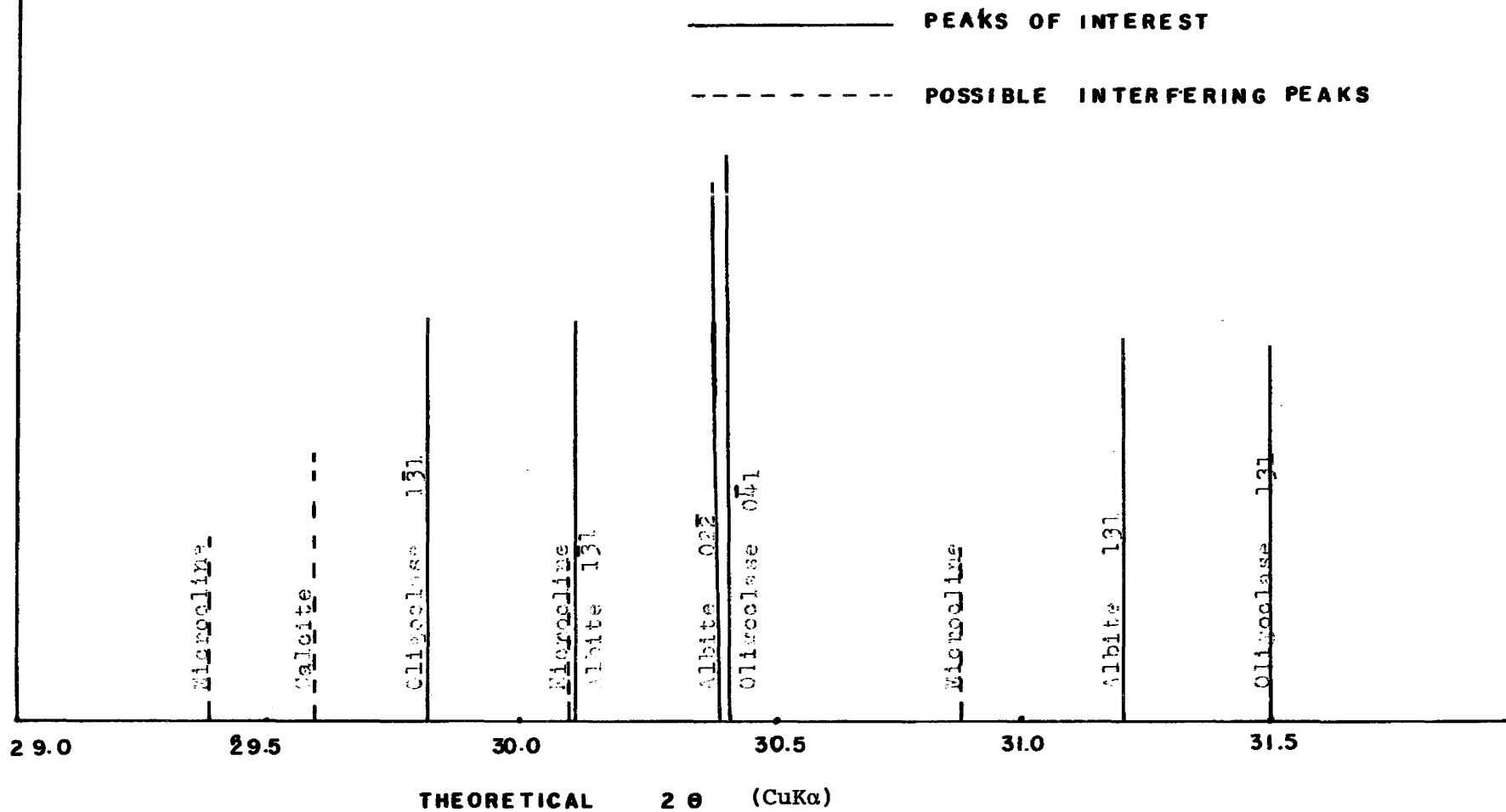
Standard studies of plagioclase feldspars by X-ray methods (Laves, 1954, Gay and Smith, 1955) show that single crystals of ordered plagioclase in the range An₂ to An₁₈ are unmixed into the phases with the compositions An₀₋₁ and An₂₅₋₂₈ (peristerites).

Smith and Yoder (1956) found that over the composition range An₀ to An₃₀, the angular separation ($\Delta 2\theta$) between the 131 and $\bar{1}\bar{3}1$ peaks was useful for determining the composition. They constructed curves plotting Mole percent Anorthite against the angular separation ($\Delta 2\theta$). These curves have been improved by Bambauer et al (1967) S.M.P.M.¹ p. 333-349.

The position and intensity of the X-ray diffraction lines show characteristic variations depending on the anorthite content and structural state. It is, therefore, reasonable to assume that the presence of two plagioclase feldspars in a rock could be determined by X-ray diffraction techniques. If this is the case, two peaks should occur within the vicinity of the 131 and $\bar{1}\bar{3}1$ peaks.

¹ Schweizerische Mineralogische und Petrographische Mitteilungen, 1967, Vol. 47.

FIG-1



Source of data A.S.T.M. cards

X-ray Diffraction Analysis

For all analyses here, a Phillips Geiger counter X-ray goniometer unit was used.

Analytical Procedure

CuK α radiation was used in all analyses. Preliminary measurements were taken from strip charts. This was found useful as a check for the presence of useful peaks and also to determine if various minerals were present, which had peaks in the vicinity of the plagioclase peaks of interest. Possible interfering peaks are shown in Fig. 1.

Quartz was used as an internal reference standard, and subsequent plagioclase peaks were corrected accordingly.

The $1\bar{3}1$ and $1\bar{3}1$ peaks for both albite and oligoclase were found useful in determining the presence of 2 plagioclases as the angular separation ($\Delta 2\theta$) between the respective $1\bar{3}1$ albite and $1\bar{3}1$ oligoclase peaks was found to be a maximum, though it was only of the order of $0.30^\circ 2\theta$. The intention of the operator was to find both albite and oligoclase peaks in this area.

In most cases, it was found that the peaks were of sufficiently low intensity that they were more or less obscured by the background. It was, therefore, found necessary to step scan across the peaks of interest (i.e., $1\bar{3}1$ peaks) to determine their exact nature. In step counting, a fixed count method was used. A count interval

of 1000 counts was used and the times required were recorded. As a substantial counting error was involved, it was found necessary to choose a scale factor, so that the time required for 1000 counts was in the order of 1-2 minutes. The error was then reduced to less than $\pm 4\%$. Counts were taken every $0.02^\circ 2\theta$ across the peak and three successive counts were taken so as to further reduce the possible error.

Graphs were prepared from the times obtained.

Time was plotted as the ordinate function and 2θ as the abscissa.

Preparation of Standards

Standards were prepared containing both albite and oligoclase and quartz as an internal reference. This was done in order to observe the behaviour of $1\bar{3}1$ and $1\bar{3}1$ peaks when two plagioclases were present in the sample.

Varying proportions of the feldspars were prepared and are as follows:

10% Albite	90% Oligoclase
50% "	50% "
90% "	10% "
100% "	0 "
0 "	100% "

These were mounted on glass slides for analysis according to the standard procedure.

Preparation of Standards (cont'd)

It was thought advisable to test this method on rocks from an area in which two plagioclases had been discovered. Rocks from southeast Vermont were used for this purpose. Crawford (1966) had discovered two plagioclases in low grade rocks of this area.

1. The samples were crushed and sieved to a 100-mesh fraction.
2. The dust was floated off leaving the coarser-grained fraction.
3. Magnetite was removed, using a hand magnet.
4. Quartz and feldspar was separated from the Fe rich mafics, using a Frantz magnetic separator.
5. Calcite was removed by washing in dilute HCl.
6. Powder was ground to extreme fineness and mounted on a glass slide for analysis.

It is important that all samples have the same thickness so that results are reproducible.

TABLE 2

Sample Standards	Plagioclase Present	$\Delta 2\theta$ (131- $\bar{1}\bar{3}1$)		Composition
		Ab	Olig.	
Pure Albite	Albite	1.1		An 2
Pure Oligoclase	Oligoclase	1.55		An 20
90% Ab. 10% Olig.	Albite Oligoclase	1.02 1.52	0.38	<An 0 An 19
10% Ab. 90% Olig.	Albite Oligoclase	1.05 1.62	0.29	<An 0 An 24
VT II 9A	Albite Oligoclase	1.00 1.50	0.35	<An 0 An 18
VT II 10	Peaks indistinct within background error.			
VT II 11	Very similar to VT II 10.			
VT II 12	Albite	1.08		An 0
VT II 14	Albite Oligoclase	0.95 1.46	0.35	<An 0 An 17
VT II 15	Oligoclase	1.45		An 17
WV-1	Albite Oligoclase	1.03 1.70	.36	<An 0 An 30
WV-4	Oligoclase	1.70		An 30

Analytical Results

Results are listed in Table 2. Results on six rocks from the area studied by Crawford (1966) are also included (VI II 9-15).

It was found that on analysis of pure albite and oligoclase standards, the respective $\Delta 2\theta(131-1\bar{3}1)$ values were in good agreement with values determined by Smith and Yoder (1956).

Figures showing the results for samples containing 2 feldspars are given (Fig. 4,5). Other samples contained only one feldspar and it was thought necessary to include figures for them.

Figs. 2 and 3 represent step scan analyses of 90% Albite + 10% Oligoclase and 10% Albite + 90% Oligoclase.

A.S.T.M. 2θ values predict a $\Delta 2\theta(1\bar{3}1 \text{ Ab} - 1\bar{3}1 \text{ Olig.})$ of $0.3^\circ 2\theta$. The value found in Fig. 2 was greater than the expected value.

The $1\bar{3}1$ Albite peak is observed to be only slightly higher than the $1\bar{3}1$ oligoclase peak though the respective proportions were considerably different. This indicates that the X-ray diffraction technique is more sensitive to oligoclase than to albite.

Fig. 3 shows a $\Delta 2\theta(1\bar{3}1 \text{ Ab} - 1\bar{3}1 \text{ Olig.})$ close to the A.S.T.M. determined $\Delta 2\theta$. The Albite peak here is quite small as would be expected. In all samples where two plagio-

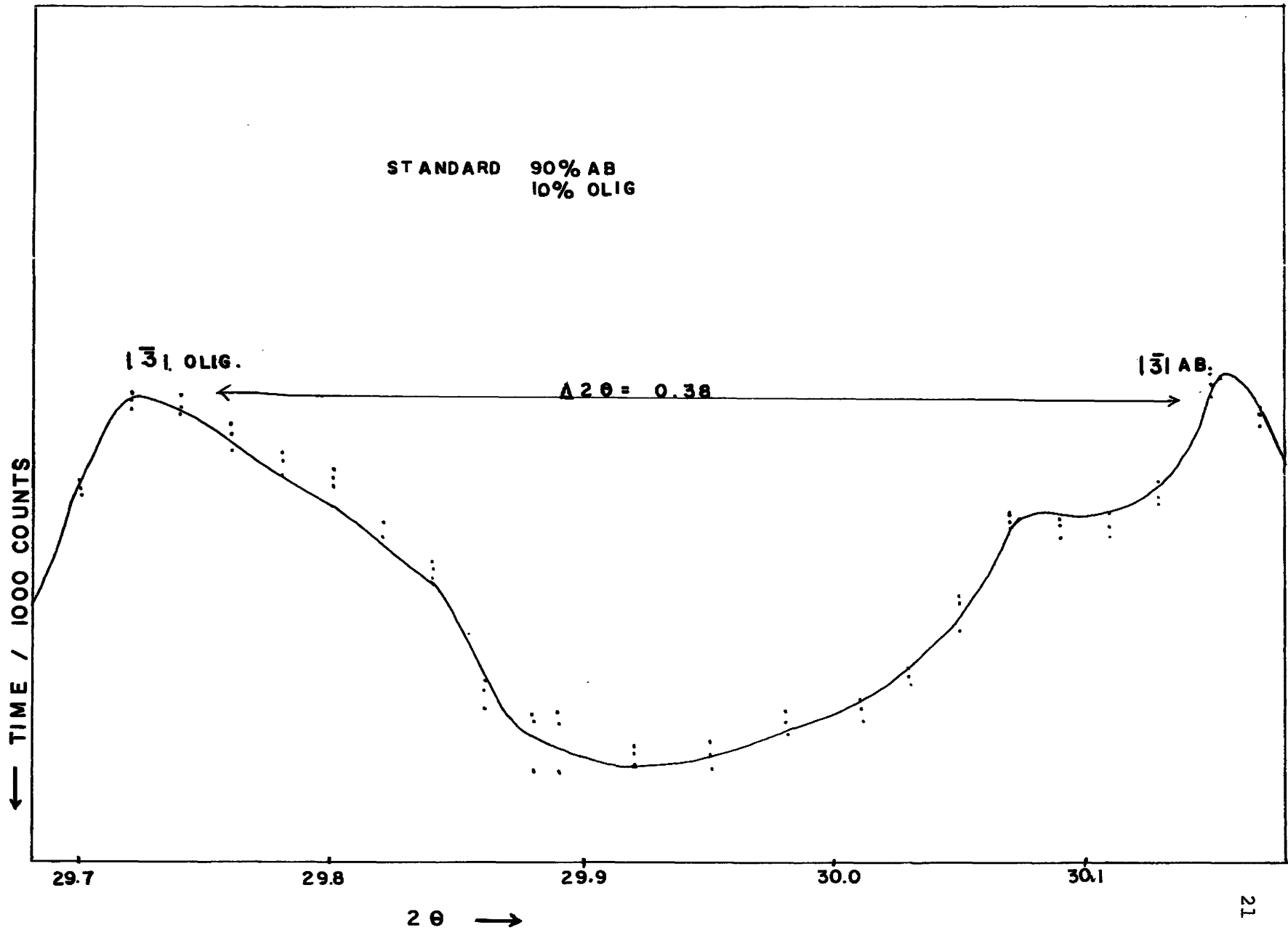


Fig. 2

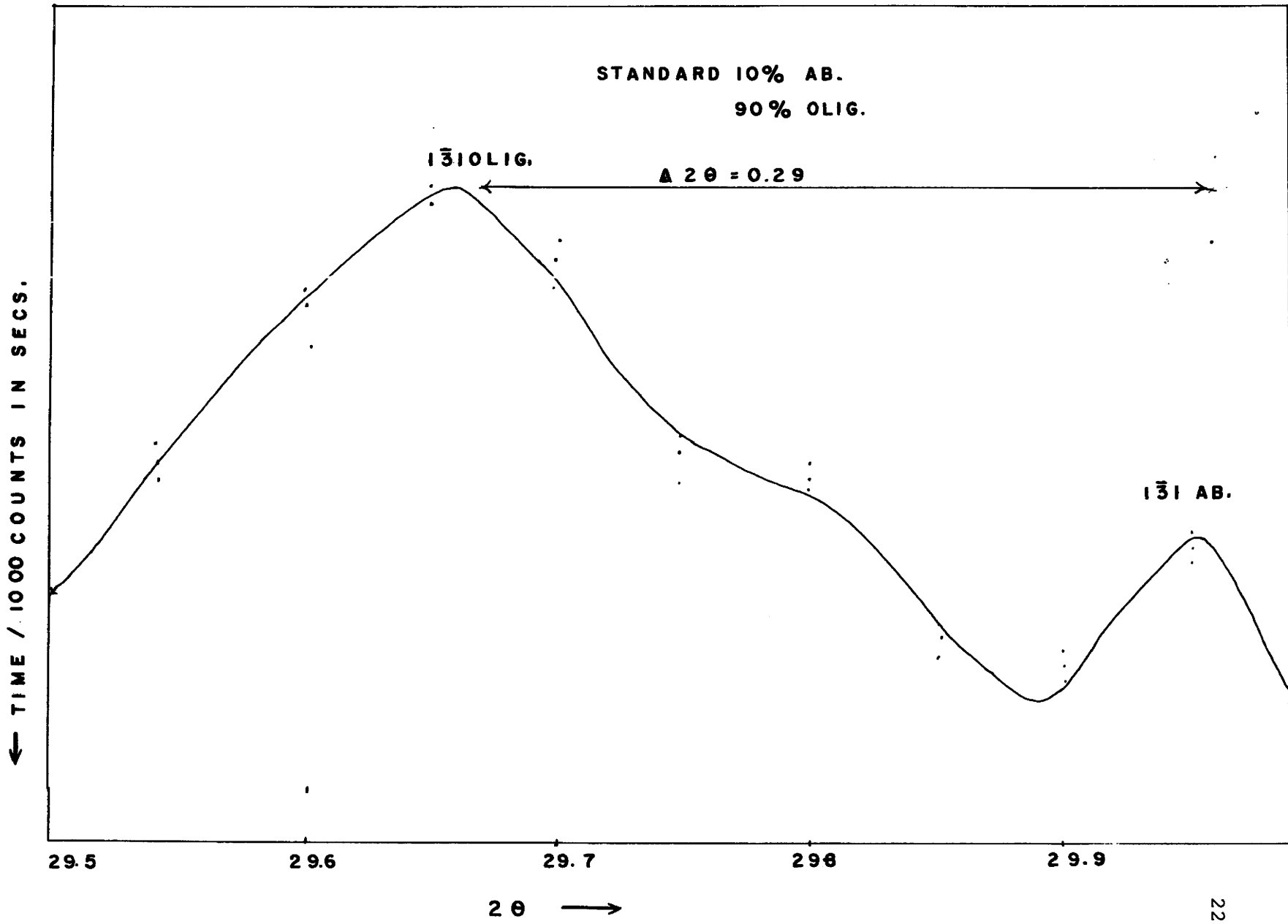


Fig. 3

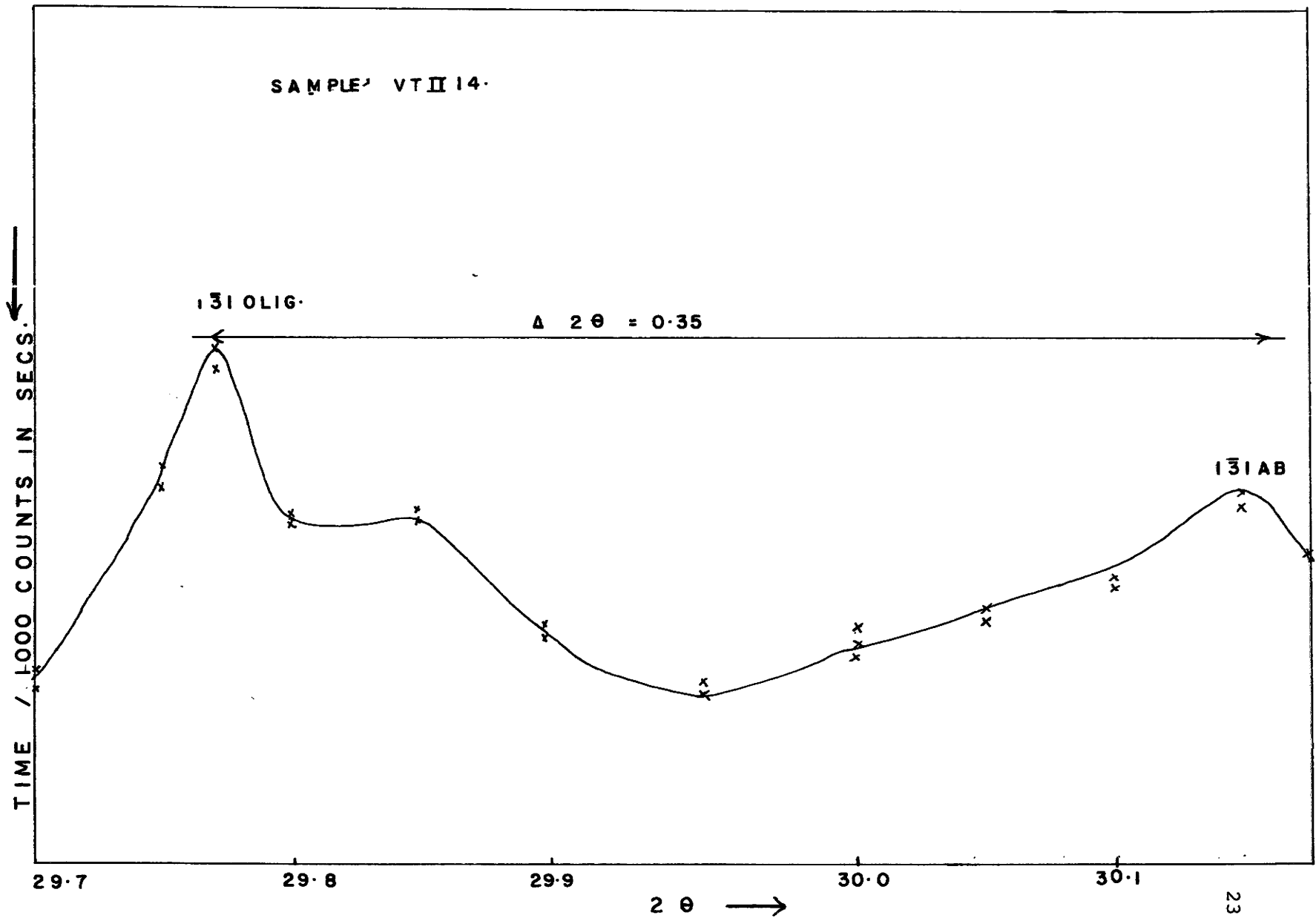


Fig. 4

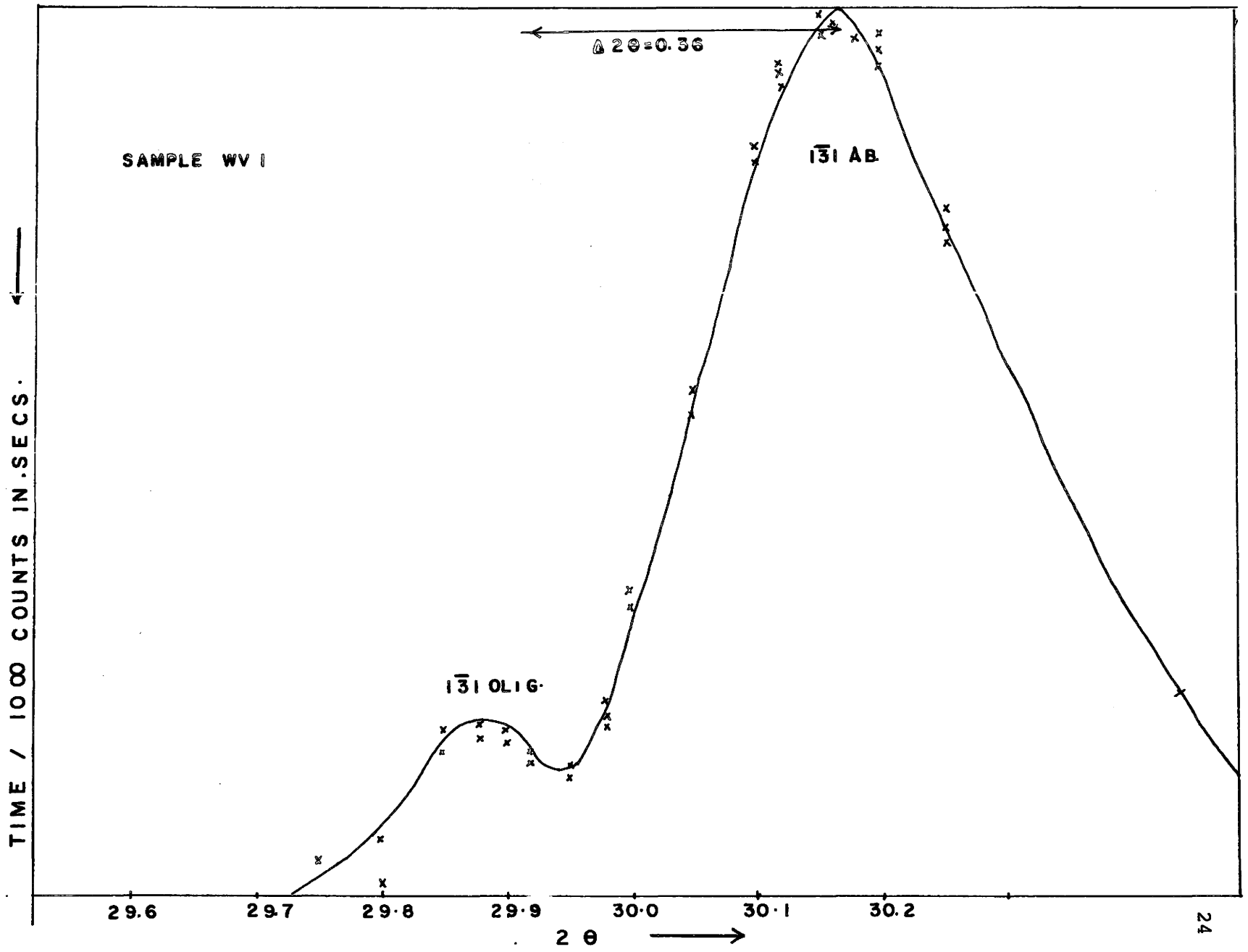


Fig. 5

classes were found, a broadening of the central peak between 131 and $1\bar{3}1$ peaks in the vicinity of $02\bar{2}$ albite and $0\bar{4}1$ oligoclase peaks was observed. An apparent reduction over pure albite in the $\Delta 2\theta(131-1\bar{3}1)$ for the albitic phase was also observed. These observations were expected to be helpful in determining the presence of two plagioclases in the rock samples analyzed.

In Vermont rocks examined (VT II 9A-15) only VT II 9A and 14 were thought to contain two plagioclases. These showed values less than $\Delta 2\theta$, found by Smith and Yoder and Bambauer for An0 in the $(131-1\bar{3}1)$ Ab peaks and a broadening of the central peak in the vicinity of the $02\bar{2}$ Ab and $0\bar{4}1$ Olig. peaks.

Fig. 4 represents Sample WV-1 from the Madoc area which, by comparing results, shows a smaller value of $\Delta 2\theta(131-1\bar{3}1)$ Albite. This was thought to contain two plagioclases but only a minor amount of oligoclase, because of the small size of the oligoclase $1\bar{3}1$ peak with respect to the albite peak.

Other samples, listed in Table 2, showed only one plagioclase.

Discussion

It would appear that X-ray diffraction is useful in some instances in the determination of the presence of

two plagioclase feldspars.

If two feldspars of different proportions of anorthite are present, one falling in the field of albite and one falling in the field of oligoclase, several marked characteristics appear (if substantial amounts of both feldspars are present) in respect to two peaks in close proximity to each other.

1. A broadening of the peak central to the 131 and $\bar{1}\bar{3}\bar{1}$ peaks for both structural states occurs. This is due to the merging of the $02\bar{2}$ Ab and the $0\bar{4}\bar{1}$ Olig. peaks, which are in very close proximity to each other.
2. A decrease in the angular separation $\Delta 2\theta(131-\bar{1}\bar{3}\bar{1})$ for a feldspar of albite composition. That is the $\Delta 2\theta$ is smaller than values determined by Smith and Yoder (1956) and Bambauer et al (1967) for a composition of An₀, which was around 1.08. Values for Albite compositions determined when two plagioclases were present were found in this study to go as low as 0.95, indicating an apparent anorthite composition considerably less than An₀.

Thus, it seems that X-ray diffraction under two-plagioclase conditions cannot be used to determine compositions of Albitic material though it seems fairly accurate for determining compositions of An rich feldspars.

Another difficulty arises from the fact that the technique is considerably more sensitive to oligoclases than to albites. Thus, if a low proportion of albitic feldspar is present, it is likely that it will not produce a detectable peak (i.e., it will be obscured by the background).

This method, therefore, seems unreliable if a low proportion of either feldspar is present (especially that of albitic composition). Also, compositional determinations are liable to be inaccurate.

REFRACTIVE INDEX DETERMINATIONS

Powders used in X-ray diffraction were immersed in index refraction oils. The oils were new and hence their accuracy was assumed to be reliable. An accuracy of 0.001 could be expected.

The double variation method was used, varying oils and the wave length of light using a monochromater.

Composition was then determined using the determination table in Winchell (1951) Part II, Fig. 174, p. 281.

R.I. determinations were used in order to check the results obtained by X-ray diffraction.

Compositions determined by R.I. methods are shown in Table 2 along with compositions determined by X-ray diffraction and electron microprobe.

TABLE 3

Sample	Plagioclase Composition (R.I.)	Name	Composition X-R-D	Composition (Probe)
VT II 9A	An 22-23	Albite Oligoclase	<An 0 An 19	-
VT II 10 VT II 11	No suitable grains found.			
VT II 12	An 4-5	Albite	An 0	-

TABLE 3 (cont'd)

Sample	Plagioclase Composition (R.I.)	Name	Composition	Composition Probe
VT II 14	a) An 4-5	Albite	<An 0	-
	b) An 20-22	Oligoclase	An 17	-
VT II 15	An 23-24	Oligoclase	An 17	-
WV-1	-	Albite	<An 0	An 0-3
		Oligoclase	An 30	-
WV-4		Oligoclase	An 30	An 27-30

ELECTRON MICROPROBE ANALYSIS

For analysis of polished thin sections, an MS-64 Acton Probe with four spectrometers was used.

A brief discussion of the pertinent features will be given here but for a detailed examination of probe elements and operation, the reader is referred to M.Sc. thesis by Haughton, D. R., McMaster University, "A Mineralogical Study of Scapolite" (1967).

X-ray Optics

The MS-64 Acton Probe has four spectrometers, each of which received X-rays from the specimen at a take-off angle of 18° . Two of these are flow proportional counters and two are sealed proportional counters. The window between the flow proportional counters and the evacuated chamber was collodion and the window between the sealed proportional counters and the chamber was beryllium.

Various types of crystals can be interchanged in the spectrometers depending on the element being examined.

Analytical Procedure

In the analysis of plagioclase, both sealed and flow proportional counters were used. Ca was analyzed on the sealed counters using the $10\bar{1}1$ reflection of quartz while

Al was examined on the flow counter using a mica crystal.

A beam intensity of 100 nanoamps, a specimen current of 50 nanoamps and an accelerating voltage of 15 KV was utilized in all analyses. A spot size of 1μ was also used.

In this study, $CaK\alpha$ intensities were used to determine the mole percentages of anorthite in the plagioclases and $AlK\alpha$ intensities as a check to distinguish between feldspars and non-aluminum-bearing mineral inclusions such as quartz and apatite and inclusions with a lower percentage of aluminum than feldspar such as epidote and various amphiboles.

In analyzing samples, 10-second spot counts were made and the 2-pen strip chart recorder was used, analyzing simultaneously for Ca and Al. The latter method was found suitable as a semiquantitative analysis was only required. For the standards a stationary spot was used, but during the analysis of polished thin sections, the stepping drive was used to move the specimen beneath the electron beam. This was found necessary as it was observed that the Ca content within the plagioclase was not homogeneous in all cases.

From the analysis of plagioclase standards, calibration curves for Ca were prepared plotting $I(\text{cps})$ as the ordinate function and percentage anorthite (An) as the

abscissa. I represents the intensity of CaK α radiation from a suitable end member. Because of drift in the machine with time, it was found necessary to check standards frequently. However, it was found that when drift was discovered, a minor correction of the window adjustment or alignment would correct this factor. Also, it was found necessary frequently to check the focus as drift in the intensities was observed if the beam was allowed to go out of focus.

All samples and standards analyzed were provided with a thin coat of carbon using an evaporator. All samples were coated together in order to provide an even thickness, and hence to reduce error which might result from thickness variation in the conducting carbon film.

Plagioclase Standards

Standards used were provided by courtesy of D. R. Haughton. These samples covered a 10 mole per cent interval from 0-100 mole % anorthite. Analysis for Ca and Al were carried out and calibration curves prepared. These were in all cases essentially linear.

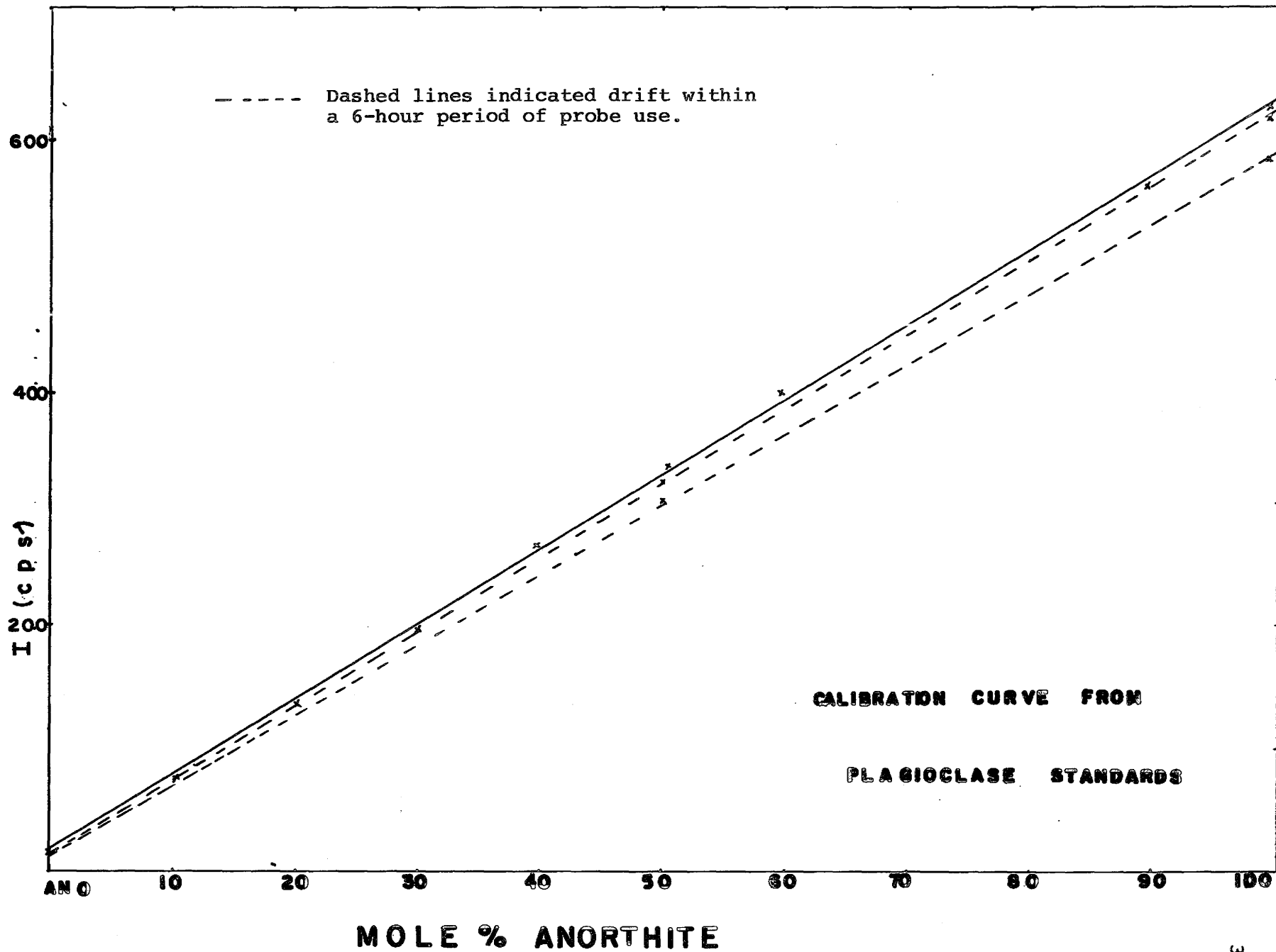


Fig. 6

Preparation of Polished Thin Sections

Polished thin sections were prepared for use on the microprobe by Rudolf Von Huene (Pasadena, California).

Epoxy cement was used as a mounting medium.

Beforehand, fresh specimens were cut to suitable dimensions on a diamond saw.

Procedures are outlined intensively by D. R. Haughton in the afore-mentioned thesis.

Calibration Curves

Fig. 6 represents a typical calibration curve for the plagioclase standards used. In all cases they represent essentially a linear relationship for Ca intensities. Dotted lines represent drift during a 6-hour period. This is the maximum amount expected if the machine is adjusted correctly. However, if frequent reference to standards is not made, it was found that variation could be much more substantial.

Analytical Results

The results from the analysis of samples from the Madoc area are given in Table 3.

WV-1 to WV-7 supposedly represent basic rocks of increasing metamorphic grade. However, petrological examination showed WV-3 to be somewhat extraneous.

Figures showing traces across feldspar grains and respective electron backscatter photographs and X-ray photographs for Ca and Al are given for each sample.

ANALYSIS OF SAMPLES FROM MADOC AREA

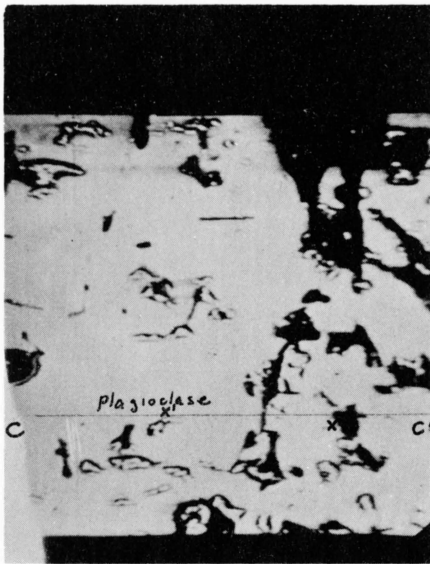
TABLE 4

Sample	Plagioclase Composition			
	Range	Average		
Fig. 7	WV-1	An 0- 3	An 1	Albite
Fig. 8-9	WV-3	An 2- 6 An 34-37	An 3 An 35	Albite Andesine
Fig. 10	WV-4	An 27-30	An 28	Oligoclase
Fig. 11	WV-7	An 25-33	An 26	Oligoclase

Wide range is due to andesine grains occurring at the edge of a few oligoclase grains (i.e., zoning effect).

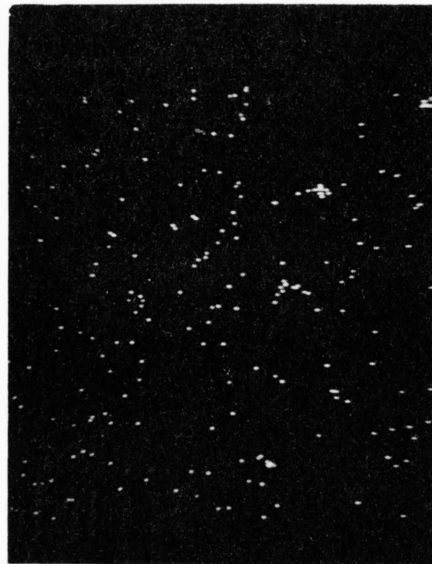
It should be noted that in part (c) of Figs. 7-11, the lower trace represents $AlK\alpha$ intensities. Separate channels were used and the Al trace is slightly ahead of the Ca trace. Al was run at a scale setting of 2×10^2 cps full scale while Ca was run at a setting of 1×10^2 cps. Also note that 0.124" on the strip chart is the equivalent of 10μ spectrometer travel.

The line of traverse indicated on the photos is indicated on the chart in part (c) of the figures. Parts (a), (b) and (d) of the figures are self-explanatory.



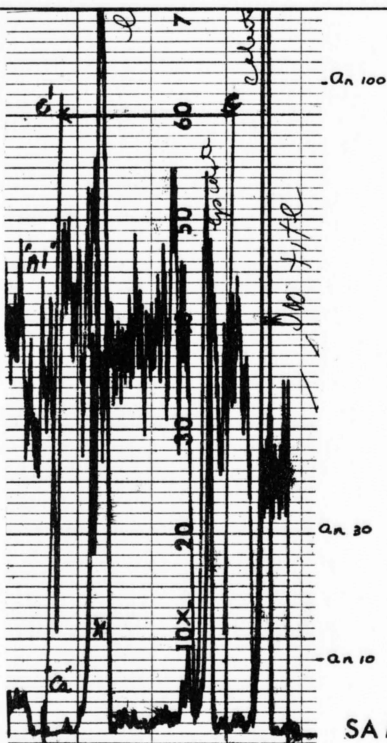
ELECTRON PHOTO

(a)



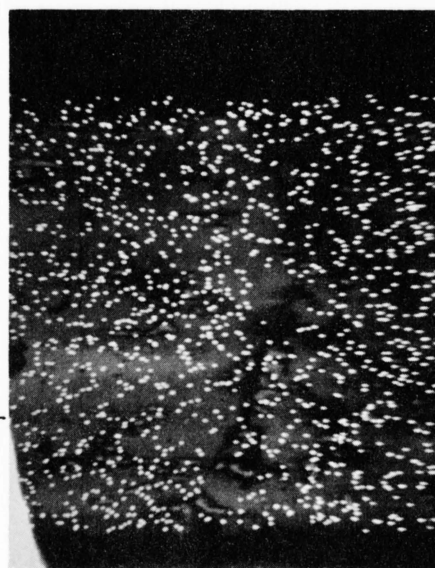
Ca K α X RAYS

(b)



(c)

SAMPLE



Al K α X RAYS

(d)

WV1

FIG. 7

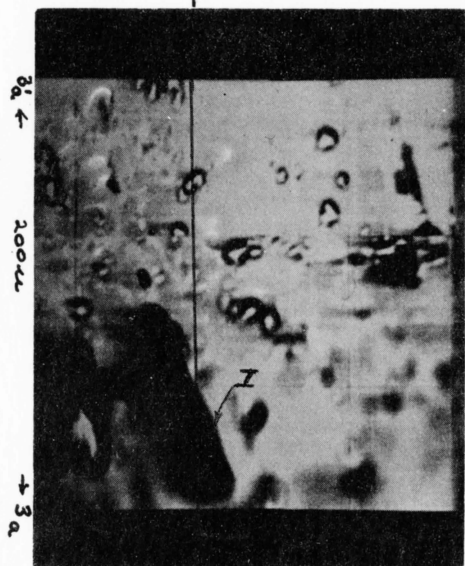
Sample WV-1

Fig. 7 represents results obtained from probe analysis of sample WV-1; C-C' represents a traverse across a plagioclase grain. C-C' represents approximately 100 μ . X and X' on Figs. 7(a) and (c) represents Ca rich inclusions which, as can be observed in 7(c), are high in calcium with respect to the plagioclase. As most of the Ca inclusions are either epidote or apatite (mainly the former) X, which has high Ca and has little variation from the plagioclase in Al content, was thought to be epidote. X', which as a high Ca peak and a negligible corresponding Al peak was thought to be apatite.

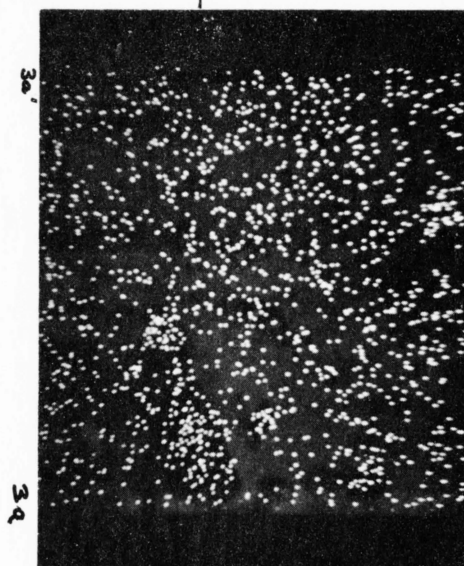
The distribution of Ca and Al can be seen in Figs. 7(b) and 7(d). Fig. 7(b) shows a low percentage of Anorthite in the plagioclase around small Ca rich inclusions represented by clusters of CaK α X-rays. These can be correlated to darker areas in 7(a). Fig. 7(d) shows the Al distribution to be relatively homogeneous.

Sample WV-3

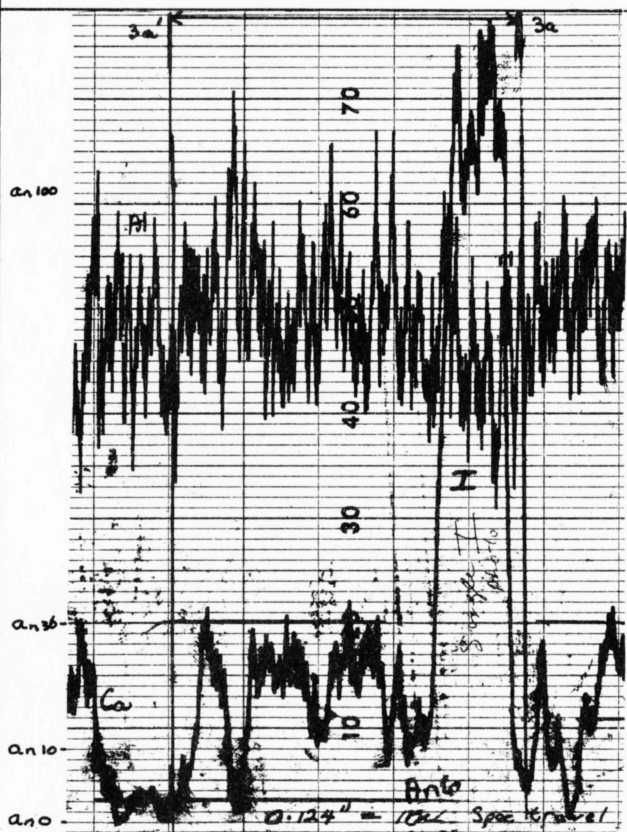
This sample is represented by Figs. 8-9. Two traverses 3a-3a' respectively are represented each equivalent of 200 μ . These traverses were taken within the same grain but similar results were obtained for other grains. As epidote inclusions were extensively replacing the plagioclase in places, an area relatively free from inclusions



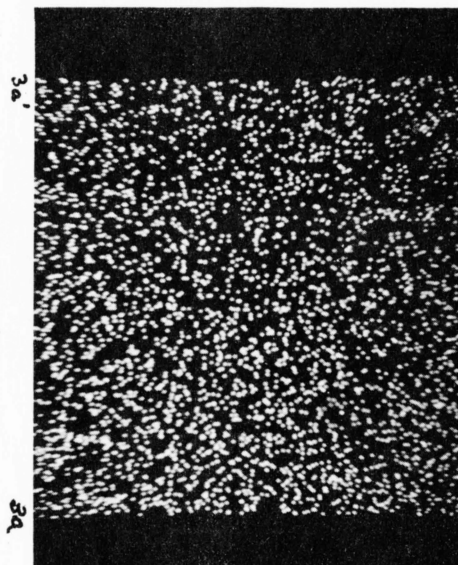
ELECTRON PHOTO (a)



Ca Kα X RAYS (b)



(c)



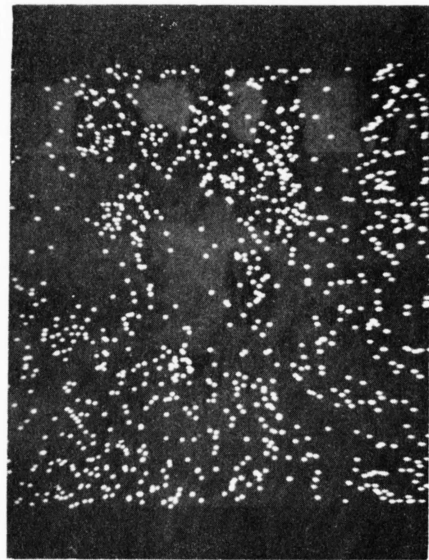
Al Kα X RAYS (d)

SAMPLE W V 3

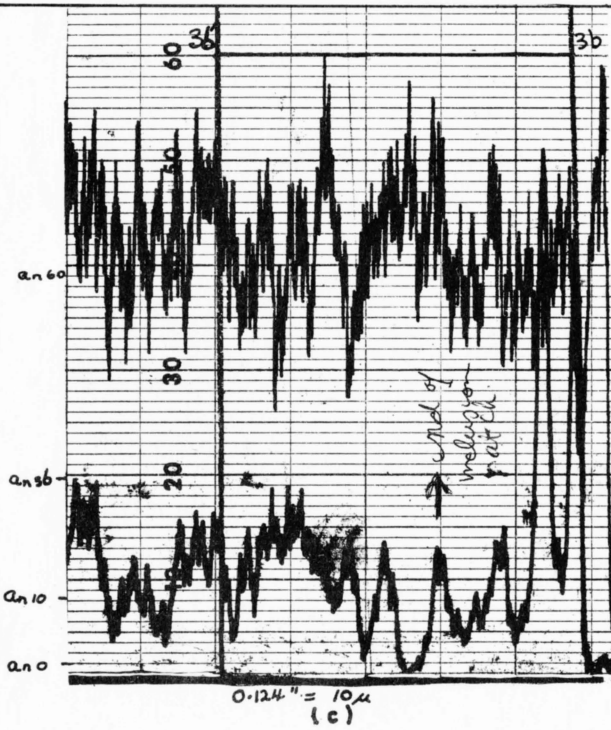
FIG. 8



ELECTRON PHOTO
(a)

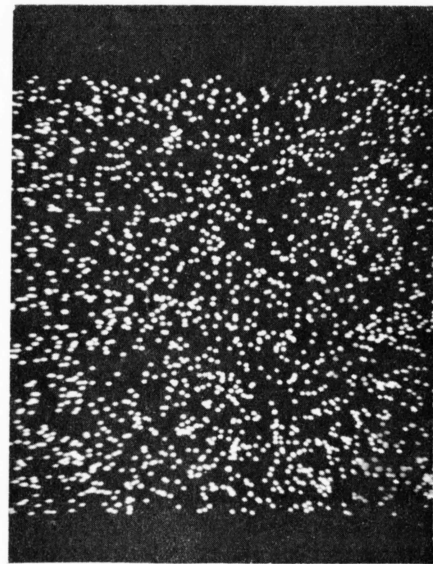


Ca K α X RAYS
(b)



SAMPLE

WV3

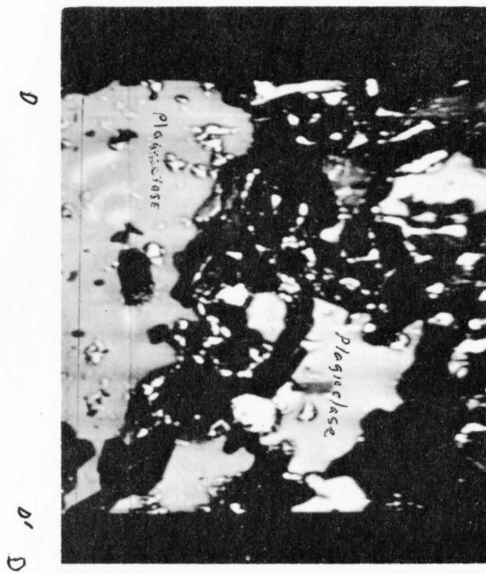


Al K α X RAYS (d)
FIG. 9

was chosen for the traverses.

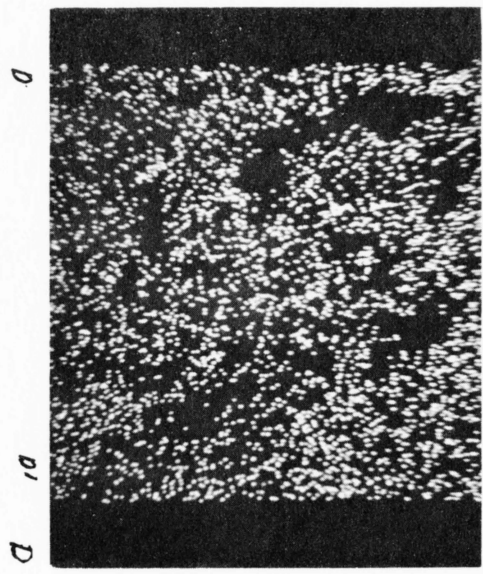
In Fig. 8(a) and (c), I represents an epidote inclusion. This is observed to be high in Ca and slightly lower in Al than the surrounding plagioclase. One particular feature is marked and that is the reduction in Anorthite content of the plagioclase in the vicinity of an inclusion of epidote the Ca content drops abruptly from an Andesine to an Albitic composition. Away from the inclusion the Anorthite content climbs back up to a maximum, but occasionally it is observed to be gradational from An25 up. The dimension of the surrounding albitic plagioclase zone, associated with the epidote inclusions, depends on the size of the inclusions. The same depletion of calcium content in the plagioclase associated with epidote inclusions is observed in Fig. 9 except that it is more marked, due to a greater proportion of inclusions at the start of the traverse. Also, in Fig. 9 the gradational increase in Ca above An25 is more marked.

In both Figs. 8 and 9 the CaK α X-ray photos show a distinct clustering of CaK α X-rays with adjacent areas of depletion. These correspond to inclusions of more albitic plagioclase in surrounding oligoclase. The corresponding AlK α X-ray photos show an essentially homogeneous Al distribution. Thus, two discrete feldspars appear to coexist, not gradational into one another. Not



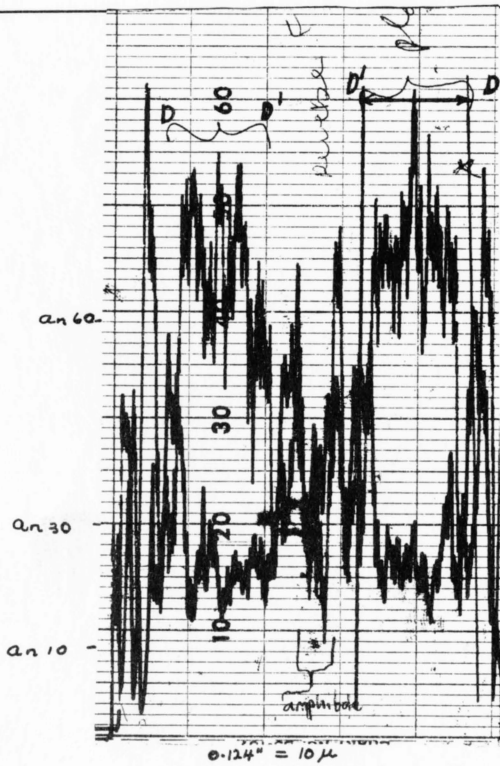
ELECTRON BACKSCATTER PHOTO

(a)



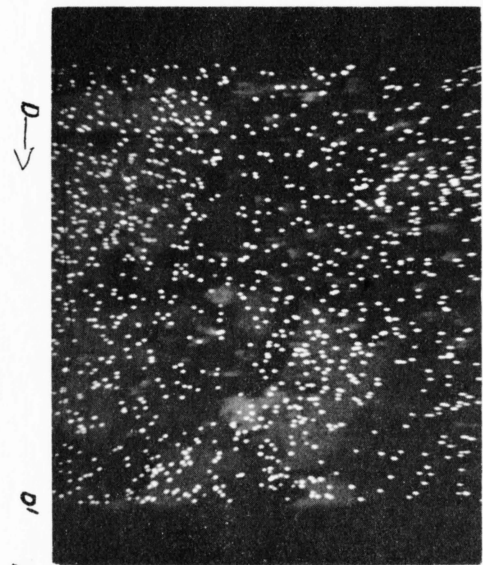
Ca Kα X RAYS

(b)



(c)

SAMPLE



Al Kα X RAYS

(d)

WV 4

FIG. 10

all these patches of albite appear to be associated with epidote although there may have been nearby epidote inclusions out of the plane of the thin section.

Sample WV-4

This sample is represented by Fig. 10. Traverse D-D' is equivalent to 80 μ . Because of the fine grain size longer traverses could not be made.

As can be observed, relatively few inclusions occur which are considerably richer in Ca than the surrounding plagioclase. In Fig. 10(d) feldspar is represented by lower calcium and high aluminum, while the surrounding material is high in calcium and low in aluminum. The surrounding Ca rich material is mainly epidote. There are also present Al poor calciferous amphiboles. However, all feldspar seemed to be relatively homogeneous (An₂₈).

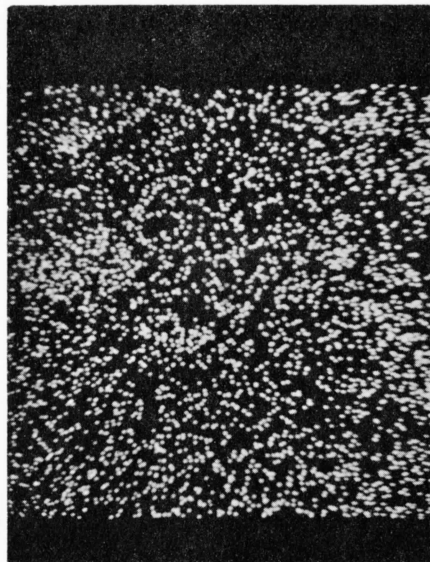
In Fig. 10(b) and 10(d) the Ca and Al distribution is shown. It will again be observed that the areas of high Ca and low Al correspond to dark areas in 10(a). The areas of no Ca, observed in 10(b), represent chlorite.

Sample WV-7

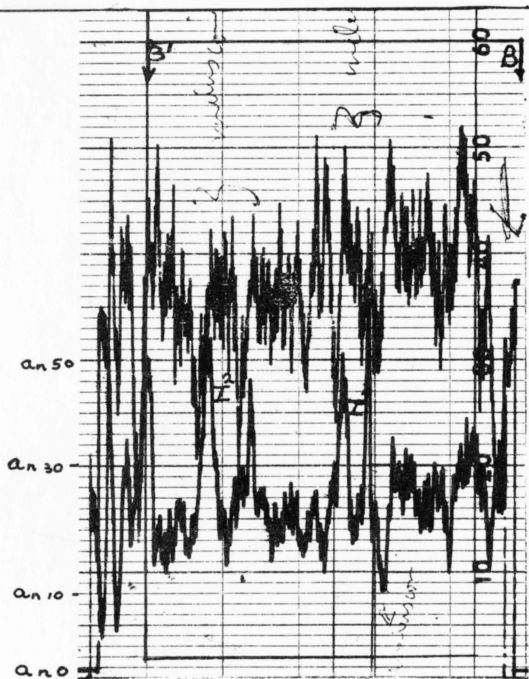
Fig. 11 represents this sample. A traverse B-B' was made which is shown in Fig. 11(a) and (c). Again, as in WV-4, less variation is observed in the Ca content of



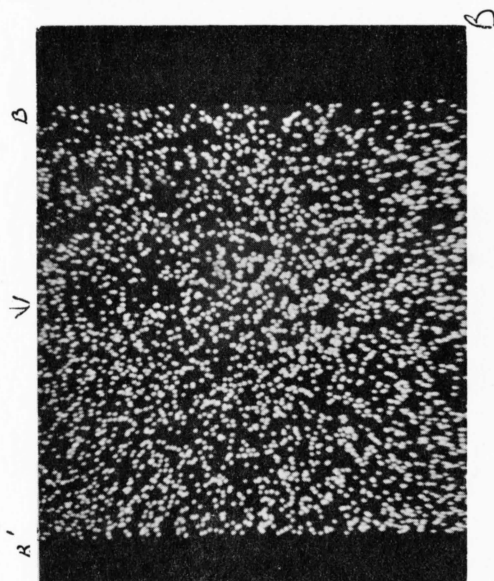
ELECTRON PHOTO
(a)



Ca Kα X RAYS
(b)



(c)



Al Kα X RAYS (d)

SAMPLE WV 7

FIG. II

plagioclase with respect to inclusions than in samples WV-1 and WV-3. The inclusions and surrounding material are dominantly actinolite. They are indicated by peaks of higher Ca and lower Al than in the plagioclase. The plagioclase is essentially homogeneous. A non-symmetrical zoning is observed in a few grains. Small andesine grains occasionally occur around the edge of the oligoclase grains. The majority of feldspar compositions is An₂₆, but some reach as high as An₃₃.

DISCUSSION OF PROBE RESULTS

It has been observed that there is an increase in the amount of Ca in the plagioclase and a relative decrease in the abundance of epidote with increasing metamorphic grade.

In one of the specimens (WV-3) two discrete plagioclases were found to coexist. Epidote consistently appears to have a spatial relationship with plagioclase of low anorthite content. Traverses across areas containing these inclusions indicate a high Ca content for the epidote and immediately dropping to compositions of An₀₋₃ around the inclusions. In some instances, away from the inclusions, the anorthite content of the plagioclase climbs sharply to about An₂₅, and above this there appears to be gradational increase to an andesine composition. The size of the areas altered to albite were observed to depend on the size and abundance of epidote inclusions. This suggests that Ca rich inclusions (mainly epidote) are a major factor in the formation of albite in low grade rocks.

WV-1, containing albite porphyroblasts and abundant inclusions is thought to have formed this way. Although only one feldspar was found in this sample by microprobe techniques, X-ray diffraction analysis indicated a small

amount of oligoclase was present in the rock. The fact that it was not observed by probe techniques may indicate an inhomogeneous distribution through the rock.

The exact mechanism of formation is not completely clear, but it seems likely that Ca ions migrate from the plagioclase structure to form the epidote inclusions. The presence of very small grains of epidote, which are Fe-rich (determined by optical means), suggests that the epidote is forming within the plagioclase structure probably nucleating about Fe^{+3} impurities which substitute for Al in the tetrahedral sites. Corlette and Ribbe (1966) observed as much as 0.34% Fe in andesine.

Thus, there is sufficient Fe to form the early (small) epidote inclusions. With increasing temperature, Fe would be available from outside the feldspar structure (Fe-bearing mafics, etc.).

If this is the case, epidote should be most abundant where the least diffusion is necessary, i.e., the edges of the feldspar grains. This is, in fact, observed to be the case.

Petrological examination indicates an association of minute grains with saussurite. However, probe traverses across saussuritized areas gave no variation in anorthite content from andesine (An₃₄) unless an epidote was present. The only constituent in epidote not included in the plagio-

class structure is H_2O and this is likely to have been readily available during low-grade metamorphism.

Arranging probed samples in order of increasing anorthite composition, a sequence WV-3 (albite + relict andesine), WV-1 (albite), WV-4 (oligoclase), WV-7 (oligoclase + minor non-symmetrical rims of andesine) is suggested.

GENERAL DISCUSSION

The main purpose of this study was a search for two plagioclase feldspars related to the peristerite solvus. With the possible exception of WV-3, these were not found. WV-1 shows two feldspars by X-ray diffraction methods, but two plagioclases do not intimately coexist as the peristerite solvus would require. This may indicate that the conditions under which two plagioclase compositions occur are not as extensive as Crawford (1967) suggests.

Crawford claims that oligoclase first appears as tiny grains along the margins of albite. This suggests a zoning effect with the amount of oligoclase depending on the amount of Ca which is diffusing into the albite structure which is then re-crystallized to oligoclase. Multiple tiny grains suggest that the plagioclases in WV-4 and WV-7 are re-crystallized. However, no albite remains within the structure. Indeed, within WV-7 some grains show minor thin non-symmetrical rims of small andesine grains. Lumbers (1967) reports finding reversely-zoned albites.

However, no plagioclases of a reversely-zoned albite nature were studied. It seems possible that the zoned albite region found by Lumbers corresponds to the zone of two plagioclases described by Crawford studying rocks from

New Zealand and southeast Vermont. The descriptions of the feldspars in the zoned albite region of Lumbers in the Madoc area and the occurrence of two feldspars discovered by Crawford are quite similar. This would then seem to suggest that two plagioclases separated by the peristerite solvus would occur over a narrow temperature range. Temperatures would be low enough to produce relatively slow reaction rates yet high enough to induce diffusion of Ca. As the metamorphic grade increases Ca would continue to migrate until all the albite is re-crystallized to oligoclase. This process would be continued as andesine starts to form rims on oligoclase. The latter process seems to have begun on a few grains in sample WV-7. It is, however, unlikely that at the temperature at which andesine is forming reaction rates would be still slow enough to permit any albite to remain unless the grains are large, which is unlikely at this stage of metamorphism.

If the above is the case, it would seem more meaningful to place the oligoclase isograd, defined by Lumbers, at the first appearance of oligoclase grains around the edges of albite grains. As Lumbers states himself, the oligoclase grains at the oligoclase isograd, become progressively rimmed by andesine. Thus, if isograds are to be defined by the first appearance of a mineral, it would seem more meaningful to substitute the zoned albite isograd

with the oligoclase isograd and the oligoclase by andesine isograds. If, as Lumbert seems to suggest, the oligoclase isograd is represented by the disappearance of albite, kinetic effects may be involved which could be partially dependent on grain size. Thus, if larger grains are present, the time for complete conversion of the feldspar to oligoclase may be more than for smaller grains. The coarse grain size in WV-3 may produce the non-equilibrium assemblage observed. Hence, two feldspars coexist because of slow reaction rates. Crawford's data seem to fit a zoning model better than her inferences of a peristerite solvus, oligoclase forming around albite as the metamorphic grade increases.

Data collected in this study indicates a gap in composition between An₃ and An₂₅ which is undoubtedly the effect of the presence of a peristerite solvus, but it seems that, due to kinetic effects, a zoned growth pattern will occur in the feldspars. It is unlikely that the shape of the peristerite solvus can be determined from data collected from such narrow range temperature defined by these plagioclases.

Overall, it appears likely that two processes are active in forming two plagioclases in the region of the peristerite solvus:

1. A downgrading of the feldspar forming albite and epidote. This is represented by WV-3 in which two compositions are separated by a gap between An3 and An25. Above An25 the composition gradationally increases until the composition of the original feldspar is attained.
2. An upgrading of the feldspar by the reverse process to the above. Oligoclase forms around the albite as the metamorphic grade increases producing non-symmetrical zoning. This is accompanied by the disappearance of epidote.

BIBLIOGRAPHY

- BAMBAUER, H. U., CORLETT, M., EBERHARD, E., VISWANATHAN, K.
(1967): Diagrams for the determination of plagioclases using X-ray powder methods. SMPM¹ 47/1, 333-349.
- BAMBAUER, H. U., CORLETT, M., EBERHARD, E., VISWANATHAN, K.
(1967): The lattice constants and related parameters of plagioclases (low). SMPM¹ 47/1, 351-364.
- CRAWFORD, M. L. (1966): Composition of plagioclase and associated minerals in some schists from Vermont and southwest New Zealand with inferences about the peristerite solvus. *Contribs. to Mineral. and Petrol.* 13, 269-294.
- DEER, W. A., HOWIE, R. A., ZUSSMAN, J. (1962): Rock forming minerals, vol. 5, Non-silicates, 371 p. London: Longmans, Green & Co. Ltd.
- DEWAARD, D. (1959): Anorthite content of plagioclase in basic and pelitic crystalline schists as related to metamorphic zoning in the Usu Massif, Timor. *Am. J. Sci.* 257, 553-562.
- GAY, P., SMITH, J. V. (1955): Phase relations in the plagioclase feldspars: composition range An₀ to An₇₀. *Acta Cryst.* 8, 64-65.

¹ Schweizerische Mineralogische und Petrographische Mitteilungen.

BIBLIOGRAPHY (cont'd)

- LAVES, F. (1954): The coexistence of two plagioclases in the oligoclase composition range. *J. Geol.* 62, 409-411.
- RIBBE, P. H. (1960): An X-ray and optical investigation of the peristerite plagioclases. *Amer. Min.* 45, 626-644.
- RIBBE, P. H., SMITH, J. V. (1966): X-ray emission microanalysis of rock forming minerals. IV Plagioclase Feldspars. *J. Geol.* 74, 217-233.
- SMITH, J. V. (1965): X-ray emission microanalysis of common rock forming minerals. I Experimental Techniques. *J. Geol.* 73, 830-864.
- SMITH, J. R., YODER, H. S. (1956): Variations in X-ray powder patterns of plagioclase feldspars. *Amer. Min.* 41, 632-647.
- TSUJI, S. (1967): Petrology of the Higo metamorphic complex in the Kosa-Hamamati area, Kumamoto Prefecture, Kyusyu, Japan. *Japanese Journal of Geol. and Geog.* vol. 38, 1.
- TURNER, F. J., VERHOOGEN, J. (1960): *Igneous and metamorphic petrology.* McGraw-Hill Co. Inc.
- WINCHELL A. N., WINCHELL, H. (1951): *Elements of optical mineralogy.* Part II Description of minerals.