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GEOCHEMICAL ASPECTS OF THE MESOSTASIS OF SOME FRACTIONATED IGNEOUS ROCKS.

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ABSTRACT.

Many layered igneous rocks consist of two main parts: the cumulus (plus adcumulus and heteradcumulus) material and the pore material (or 'mesostasis') produced by the crystallisation of the trapped liquid which necessarily had the composition of the contemporary magma. Part One of this thesis is primarily concerned with the geochemistry of the mesostasis of some layered igneous cumulates.

In the past no workable method, has been developed for deducing the amount or composition of the mesostasis, for igneous cumulates in general. Wager (1963) established a method for the Skaergaard intrusion, East Greenland, by assuming that all the phosphorus in a rock of the Lower and Middle Zones (i.e. before the incoming of cumulus apatite) of the Layered Series existed in the mesostasis, so that the phosphorus content of any rock gave a relative measure of the amount of mesostasis. Furthermore, the phosphorus contents of the successive fractions of the Skaergaard magma were known from another approach and so it was possible to deduce the absolute amount of mesostasis. For most other layered intrusions the successive compositions of the fractionated magma are not known and the method cannot be applied to them. Knowledge about the geochemistry of the mesostasis (and hence the contemporary magma) would be most useful in straight comparative geochemical studies; in deducing fractionation trends; and in the determination of solid/liquid trace element partition coefficients, which in turn could be useful is considering the petrogenesis of certain other fractionated igneous rocks. Thus, an attempt has been made to produce a geochemical method for deducing the

amount of mesostasis in igneous cumulates. For this method, elements of contrasting geochemical behaviour are required: those that show a strong preference to remain in the residual liquid of a fractionating basic magma (the so called 'low-k elements') and those which tend to preferentially enter one of the cumulus phases (the 'high-k elements').

Two methods are considered: the first uses the existence of rhythmic layering and is applicable, without adaptation, only to adcumulates. The concentration of a high-k element in a rock can be related to the amount and composition of the mesostasis in that rock by the equation: $pM + (1 - p)C = T$, where p is the proportion of the mesostasis; M, C, and T are the concentrations of the high-k element in the mesostasis, the overall cumulus assemblage, and the whole rock respectively. If this rock is taken from a band of rhythmic layering then another rock can be taken close to the first one but with very different proportions of the minerals in the cumulus assemblage. An equation of the same form can be drawn up for this rock. It is shown that it is possible to find C and T by direct measurement for each rock. The equations can then be solved simultaneously for p and M by using the low-k element concentrations in the two rocks to establish the relative amounts of the mesostasis. A second method is also discussed whereby the amount and composition of the mesostasis might be determined by analysing rocks from along the strike of the layering provided there were a variation in the amount of mesostasis in the rocks. Error analyses of both methods are presented.

The main section of Part One is an investigation into the suitability of certain elements as indicators of the relative amounts of mesostasis in igneous cumulates. In a general discussion it is shown that As, Cs,

halogens, Hf, P, U, and Zr, are probably suitable low-k elements. The distribution of phosphorus in the minerals and rocks of the Skaergaard, Bushveld and Rhum igneous intrusions has been investigated using activation analysis. It is shown that in the Lower Zone of the Skaergaard intrusion most of the phosphorus resides in the mesostasis. The phosphorus content of the minerals from adcumulates is taken to be that of the cumulus phases and it is shown that the order of entry of phosphorus is: olivines (about 80 ppm.); felspars (about 50 ppm.); and clinopyroxenes (about 30 ppm.). Phosphorus concentrations of cumulus magnetite and ilmenite are low (about 9 and 20 ppm. respectively). However, the amounts of phosphorus in the minerals of mesocumulates or orthocumulates are generally more variable and much higher (e.g. in plagioclases up to 1,400 ppm. has been recorded) than those of adcumulates. These relatively high amounts are interpreted as arising from crystallisation of the trapped liquid to give zoning to the appropriate minerals which is enriched in phosphorus because of the ever increasing phosphorus concentrations of the remaining liquid as the trapped liquid fractionates. Compared to the Lower Zone rocks the amount of phosphorus in the cumulus minerals is small. Wager's method is critically reviewed in the light of these results.

The distribution of phosphorus in the Bushveld igneous intrusion (before the incoming of cumulus apatite) shows that many of the rock types are adcumulates as a large amount of the phosphorus in a rock can be accounted for by the amount in the minerals. The amount of phosphorus in the rocks does not show a steady increase with height as might have been expected. The values fluctuate between 9 and 200 ppm. until the horizon where cumulus apatite enters and the value rises to 14,000 ppm. The minerals tend to have slightly less

phosphorus than the Skaergaard cumulus minerals though the order of entry is the same: olivine (about 40 ppm.); felspar (about 35 ppm.); pyroxenes (about 20 ppm.). The Rhum rocks generally have very low phosphorus concentrations and of the units studied, those of 7, 8 and 9 appear to consist of adcumulates. The allivalite of unit 3 has considerably more phosphorus than the other units and this implies that it has more mesostasis. This confirms the work of Brown, (1956). The order of entry of phosphorus into the Rhum minerals is the same as those of the Skaergaard and Bushveld cumulus phases. This order is not the same as that found by Koritnig (1965) who analysed similar minerals for phosphorus from a variety of environments and found that most was in the olivines and least in the felspars. Some olivines from olivine nodules have phosphorus concentrations very similar to those from the layered intrusions.

Determinations of bromine in some Bushveld rocks show no coherence with the phosphorus values. An investigation into uranium, also considered to be a low-k element, has been carried out. It is shown that in the Skaergaard Lower Zone rocks there is a strong coherence between phosphorus and uranium irrespective of rock type. This implies that most of the uranium resides in the mesostasis and is confirmed by the fact that almost a negligible quantity of uranium is found in the cumulus minerals though a small amount is found in the clinopyroxenes. Like phosphorus, uranium shows a relative enrichment in those minerals which have partly crystallised from the trapped liquid. A similar coherence has been found between uranium and phosphorus in the Rhum rocks and similar amounts were found in the Rhum cumulus minerals as in the Skaergaard ones. However, little coherence was noted between these elements in the Bushveld rocks

and this is considered to be because of the complexities of the history of fractionation of the Bushveld magma. Amounts of uranium in the Bushveld minerals are much the same as for the cumulus minerals of the Skaergaard and Rhum intrusions.

Data on strontium (considered to be a high-k element) is presented for some of the Skaergaard and Rhum rocks and minerals. The content of the Skaergaard Lower Zone felspars indicate that the contemporary magma contained less than 480 ppm. Sr. The Rhum felspars are interesting in that those from the allivalites have significantly lower strontium contents than those from the peridotites in the two units studied.

The phosphorus, uranium and strontium data are used in applying the theoretical method to the Skaergaard Lower Zone and Rhum rocks. Determinations of specific gravities and modes of these rocks are presented. It is shown that application of the method to mesocumulates and orthocumulates is possible if mineralogical evidence is used as an aid in determining the proportions of the different minerals that make up the cumulus assemblage. It is concluded that there is much variation in the amount of the mesostasis of the rocks of the Skaergaard Lower Zone; that the amount of strontium in the contemporary magma was of the order of 340 ppm. and of phosphorus, 2,000 ppm. The results for the Rhum rocks show that some of them are adcumulates whilst others may be regarded as mesocumulates. The application and failings of the second method are briefly discussed.

The mineralogy of the rocks can be helpful in determining the relative proportions of the minerals in the cumulus assemblage. Zoning is particularly useful in this respect and in giving a lower limit to the amount of mesostasis in any rock. Some evidence of sintering of cumulus olivine

crystals in the Skaergaard and Rhum melanocratic rocks is shown. The mineralogy of the mesostasis in the Skaergaard Lower Zone rocks is briefly discussed.

In Part Two the determinative methods that have been developed and used are described. Phosphorus has been determined by activation analysis. The choice of final precipitate is discussed and magnesium ammonium phosphate decided upon. A previously published method using this precipitate has been tried but is shown to be inadequate for this work. Several adaptations to this method have been made and a full investigation into the suitability of the final precipitate is described in detail: this includes tests on self-absorption and stoichiometry. The method uses a colorimetric technique for determining the yield of the final precipitate.

A method for the determination of bromine using activation analysis is described and criticised. The 'delayed neutron' technique for uranium and thorium determination is summarised and new work on this method is described, especially an investigation into the effect of high gamma-ray fluxes on the neutron count rate. It is concluded that the method is suitable for uranium determination provided that the activated sample has a gamma activity below a certain level. Strontium has been determined by X-ray fluorescence using a direct method for the determination of the mass absorption coefficient.

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PREFACE.

L.R. Wager (1963) used the phosphorus content of the Skaergaard Lower Zone and Middle Zone rocks to give an indication of the amount of pore material that they contained, by making the assumption that the cumulus minerals were essentially free of phosphorus. The original intention in carrying out the research embodied in this thesis was to investigate in more detail the distribution of phosphorus in igneous cumulates; to see how much phosphorus is in the cumulus minerals and hence to apply Wager's method with more precision. It was also intended to investigate the variation in adcumulus growth with height in the Bushveld igneous complex, in much the same way as Wager had done for the Skaergaard intrusion. These intentions have been carried out and the results form the most important section (chapter three) of Part One of this thesis. However, the conclusions about the amount of pore material (or 'mesostasis') that could be obtained from such a study can only be qualitative, or at the best, semi-quantitative, for most igneous cumulates. Thus, attempts have been made to produce a method by which the actual amount and composition of the mesostasis in an igneous cumulate can be found. The attempts are presented in chapter two but as is shown by their application in chapter four they are not entirely satisfactory. However, they are the first attempts to establish a quantitative geochemical method for deducing the amount of mesostasis in igneous cumulates and their application has not been fruitless. Thus, the results of chapter three are also viewed in the light of these possible methods.

Part Two of this thesis describes the analytical methods that have been developed and used in this geochemical study.

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PART ONE

GEOCHEMISTRY

CHAPTER ONE.

Introduction and Previous Research.

A. Introduction.

In the classic memoir on the Skaergaard Intrusion of East Greenland, by Wager and Deer, the hypothesis was put forward, (1939, page 127): "that the material forming the rocks of the layered series can be divided into two parts" :-

1. The primary precipitate consisting of discrete crystals or small glomeroporphyritic groups which separated from the overlying magma and formed about 80 per cent. of the final rock.
2. The interprecipitate material, amounting to about 20 per cent. of the total rock, which crystallised from the magma surrounding the primary precipitate".

In Wager, Brown and Wadsworth (1960) the nomenclature of these different genetic parts of the rock was altered and strictly defined. The 'primary precipitate crystals' were renamed the 'cumulus crystals', and the 'interprecipitate material' changed to 'intercumulus material'. Other terms which described the particular nature of layered rocks were also introduced; terms such as orthocumulate, adcumulate, etc. (for these details reference to the paper, op. cit., should be made). Furthermore these authors revised the percentage figures for the cumulus and intercumulus parts as the previous ratio of 80:20 (assumed by Wager and Deer) was considered to be too high for most orthocumulates.

As well as defining these terms the authors discussed the subsequent history of the intercumulus liquid. This is considered to have crystallised into one or two generations of minerals by:

1. Growth of cumulus crystals while forming the top of the crystal pile - the, so called, process of adcumulus growth,

and/or

2. Crystallisation of the magma finally trapped between the cumulus (plus adcumulus) parts, to give a lower temperature material. This is called the pore material (Wager et al, 1960).*

There are two points about this work that are important to this thesis. The first is that all or part of the intercumulus liquid can be driven out by the process of adcumulus growth. The mechanism by which this can occur was introduced and discussed by Hess (1939). He considered that a diffusion mechanism can be operative by which a small temperature difference between the overlying magma and crystal mush allows a slight increment of mineral growth, with essentially the same composition as the cumulus phase, to occur. This small growth increment sets up a composition gradient between the intercumulus liquid and the magma. Diffusion of the appropriate ions restores the equilibrium and allows further precipitation of exactly the same mineral with the same composition to occur. Such a mechanism has been used to explain the

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* The term mesostasis, rather than pore material, is generally used in this thesis. This term is more embracing as it includes the products (if any) from reaction of the pore material with the cumulus parts; secondary alteration products of the pore material; etc. For fuller discussion see Appendix A.

formation of monomineralic layers. The formation of heteradcumulus minerals which are different from the cumulus ones is simply caused by suitable temperature (and/or pressure) conditions to allow rare nucleation within the crystal mush followed then by the mechanism described above.

The extent to which adcumulus growth can occur will be determined by the effectiveness of the diffusion process and this, in turn, will be closely related to the rate of accumulation of crystals on the floor of the intrusion. This rate undoubtedly fluctuated in many intrusions, (Hess 1960).

The second important aspect of the above reasoning is that when crystal accumulation is fast the intercumulus liquid is trapped and this liquid "will necessarily have had the over-all composition of the contemporary magma and thus the composition of the pore material must also be that of the contemporary magma". (Wager et al 1960, page 77). Many attempts have been made in the past to assess the proportion of the mesostasis and its composition, for such data might be invaluable in giving information about compositions, at various stages, of a fractionated magma (as opposed to the fractionation products), and rates of crystal settling.

It is the purpose of this thesis to attempt to produce theoretical analyses which may be used to deduce the amount and composition of the mesostasis of layered igneous rocks. A further purpose is to make a preliminary investigation into the application of the theoretical analyses.

B. Removal of the intercumulus liquid.

In the formation of certain layered rocks the initial stage was the accumulation of crystals to form a crystal/liquid mush on the chamber floor. It has been shown that adcumulus growth can push out all or part of the intercumulus liquid. The adcumulus and heteradcumulus crystals generally will not be zoned whereas the pore material most probably will be.

Wager et al (1960) stated that the exact way in which adcumulus growth occurs is not certain. Hess proposed the diffusion mechanism mentioned above, whilst Voll (1960) proposed a mechanism of crystal sintering to produce monomineralic layers. Voll states that if the interfacial tension between the crystals of the mineral is lower than the crystal/liquid interfacial tension then crystals will tend to coalesce and grow together. The manifestations of this 'sintering' process are triple intersections of 120° of the minerals and curved crystal boundaries. (See Chapter Five for further discussion and photographs). This mechanism of sintering pushed out the intercumulus liquid.

Whichever is the dominant factor in the formation of adcumulates makes little difference to the arguments presented later in this thesis, provided that the possibility of there being some trapped liquid is still present.

C. Nature of the trapped liquid.

The trapped liquid is considered to have had the composition of the

contemporary magma and so the pore material is also considered to have that same composition. If the trapped liquid reacts with the cumulus phases the composition of the resultant mesostasis will no longer be the same as that of the contemporary magma. (This point is discussed further in Chapter Two where it is shown that such reaction has little effect on the application of the method proposed for determining the composition of the contemporary magma). However, it is thought that such reaction was not common in the Rhum, Bushveld, and Skaergaard intrusions (Wager et al 1960), although Jackson (1961) discusses the manifestations of it in the Ultramafic Zone of the Stillwater Complex.

Adcumulus growth has been explained by a diffusion mechanism which is considered to be effectively stopped if a sufficiently thick accumulation of crystals above the layer in question is deposited. There is the possibility of an intermediate stage where certain small ions may be able to diffuse whilst others cannot because of the poor diffusing conditions to and from the overlying magma. The final trapped liquid will no longer have the composition of the contemporary magma. Whilst such a process cannot at the present be excluded it is not discussed further in this thesis.

Another process that can locally affect the nature of the trapped liquid is inter-pore diffusion. This is likely if the pores are connected but would not have much effect over a considerable distance (say one foot) as there is little reason for large compositional gradients to be set up. To reduce any effect of this process it is necessary to analyse a large specimen. The use of a large specimen is

also advocated because of the likelihood that the pore material will not be evenly distributed throughout the rock, especially in orthocumulates.

D. Previous methods of deducing the composition or amount of the mesostasis.

Wager and Deer (1939) noted that it was difficult to determine by microscopic examination whether material was cumulus or intercumulus. They observed, however, that phosphorus did not enter appreciably into the composition of any of the cumulus minerals of the lower layered rocks of the Skaergaard Intrusion upto the level at which apatite became a cumulus phase. They believed that most of the phosphorus existed in the 20% of intercumulus liquid (op.cit. p.227). They suggested, therefore, that the phosphorus contents of the rocks could throw light upon their relative amount of initial intercumulus liquid. (Note: at this time the existence of adcumulus growth was not recognised and so no distinction was made between intercumulus and pore material).

G.M. Brown (1956), working on a Rhum allivalite from Unit 3, found that the felspars were far more zoned than those from higher units, despite the cores being essentially constant in composition throughout the layered series. He therefore attributed the zoning to crystallisation of the trapped liquid. Brown attempted to find the composition of this trapped liquid by subtracting a suitable proportion of the composition of the cumulus crystals (based on those analysed from Unit 10) from the whole-rock analysis. From this calculation he found that an assumed 50% of trapped liquid gave a reasonable composition for the trapped basaltic magma.

L.R. Wager (1960) used a similar subtraction method for deducing the composition of the trapped liquid of a labradorite cumulate of LZa of the Skaergaard intrusion. If 68% of the rock was assumed to be of cumulus plagioclase then the liquid composition derived by subtraction of this composition from the total analysis, agreed closely with the liquid composition of the magma as determined from the size and successive rock compositions of the intrusion (see Wager and Deer 1939; Wager 1960). This, therefore, produces a figure of 32% for the pore material of this rock.

The subtraction method used by Brown and later by Wager requires certain assumptions to be made about the packing of the cumulus minerals or about the composition of the contemporary magma. By perforce, such a method cannot be very accurate. Wager (1960) writes: "The method of obtaining the composition of the trapped liquid by subtracting the presumed cumulus material is likely to be more valuable as a means of deciding on the make-up of a particular cumulate, assuming the composition of the contemporary magma obtained by the successive rock composition method, than as a means of obtaining the composition of a trapped liquid by assumptions about the nature of the cumulate".

In 1963, Wager again stressed the difficult or impossible nature of determining the amount of trapped liquid by a micrometric analysis, and he turned again to using chemical evidence as Wager and Deer (1939) had done. Taking the initial assumption that, before apatite becomes a cumulus phase, all the phosphorus in a rock of the Skaergaard Layered Series resides in the pore material, he was able to deduce how much

pore material there was in any rock by determining its total phosphorus content and comparing it to the phosphorus content of the magma at that stage, which was known from the successive rock composition method. This phosphorus method is discussed further in Chapter Three, and some of its failings and inaccuracies outlined. For most layered intrusions the successive compositions of the fractionated magma are not known and the above method is unworkable. A method is proposed in Chapter Two which overcomes these difficulties.

E. The geochemical significance of the mesostasis.

In many layered rocks the mesostasis contributes a significant part to the geochemical make-up. Even in an adcumulate with only 5% mesostasis the whole rock composition could be significantly different from the composition of the cumulus (plus adcumulus) parts. The value of whole rock analyses of layered intrusions will be much greater if the percentage of the mesostasis and its composition are known. Trace element analyses may be more valuable in comparative studies when full recognition is given to the geochemical importance of the mesostasis.

Certain inherent properties of the mesostasis (as pore material) can be stated:

1. The higher the percentage of mesostasis in any rock, all other things being equal, then the closer the whole rock analysis approaches that of the contemporary magma; i.e. the higher the percentage, the lower is the degree of fractionation.

2. The mesostasis consists, or potentially consists, of a lower temperature mineral assemblage than that of its host.

If the mesostasis (as pore material) is compositionally the same as the contemporary magma, then it will be possible, by determining the composition of the mesostasis from various crystallisation levels, to deduce the fractionation sequence of a magma. Furthermore it will be possible to deduce the partition coefficients for trace elements between the liquid and the various cumulus minerals. In turn, these data may be correlated with geochemical data from basalts with phenocrysts. Such evidence may help to elucidate fractionation trends of some basalt series.

By careful selection of material it may be possible to deduce the composition of the scoriaceous material in ejected blocks of plutonic aspect in volcanic regions, without separating the respective phases, by application of the theory outlined later, (for examples of such blocks see Lewis 1964; Baker 1966). It is also shown in later chapters that knowledge about the mesostasis can indicate much about the different stages of crystallisation of the minerals that make up mesocumulates, and heteradcumulates. It is also possible that if the theory outlined later can be applied to the whole of the Layered Series of the Skaergaard Intrusion then it will be possible to assess more accurately the extent, or composition, of the Hidden Zone.

CHAPTER TWO

Possible Methods for Deducing the Composition and Amount of the Mesostasis

A. Introduction

It has been shown in Chapter One that until now there has been no workable method for deducing the composition and amount of the mesostasis in layered igneous rocks. This chapter outlines theoretical analyses of possible new methods of which one is applied later in this thesis. This chapter is entirely confined to the presentation of the analyses and does not discuss the feasibility of their application.

The theory outlined demands the presence of elements of contrasting geochemical behaviour. These types of behaviour may be categorised into two groups as follows:

1. Elements which on fractional crystallisation of a basic magma show a strong preference to remain in the residual liquid phase and which do not enter appreciably any cumulus phase; i.e. the partition coefficients of these elements between all cumulus solid phases and the liquid phase should be very low. In this thesis these elements will be referred to as low-k elements.
2. Elements, of trace quantities, which on fractional crystallisation of a basic magma show a strong preference for entering one of the cumulus phases such that the solid-liquid partition coefficients for these elements are greater than 1 for that cumulus phase but very low for the other cumulus phases. The cumulus phase which the element (or elements) preferentially enters should be one which

shows large variations in its modal proportions from one rock horizon to the next; i.e. it should be a mineral whose presence or absence in any one layer is sensitive to the processes producing rhythmic layering in fractionated igneous rocks. These elements will be referred to as high-k elements.

B. Analysis of first method.

This method relies upon the presence of rhythmic layering (Wager and Deer, 1937 p.36-37) and upon the following two premises:

Premise 1: That the mesostasis, as pore material, has the same composition as that of the initial trapped liquid which necessarily had the composition of the contemporary magma.

Premise 2: That the concentration of elements in the contemporary magma did not change by a significant amount over small degrees of fractionation as the total amount of any such element concentrated in any one layer would be small compared to the total amount in the remaining magma. Such an approximation only holds whilst there was still much magma to be fractionated.

For any high-k element the following equation, relating the element's concentration in the whole rock to that in the constituent parts, may be drawn up:

$$pM + (1 - p)\,C = T \qquad (1).$$

where p is the volumetric proportion of the mesostasis; M, C and T are the absolute concentrations, in grams per unit volume, of the high-k element in the mesostasis; the total cumulus assemblage; and in the whole rock respectively.

p and K are unknown and before they can be found it is necessary to know C. The determination of C requires data both on the concentrations of the high-k element and the relative modal ratios to each other of the different minerals that make up the cumulus (plus adcumulus*) phase. The concentrations can readily be found by separating and analysing the minerals. The modal ratios are not always easily obtainable. In the case of adcumulates with little mesostasis there is no difficulty as the mode of the actual rock will clearly reflect the relative proportions of the different cumulus (plus adcumulus) minerals. In orthocumulates, however, the mode is unlikely to be so indicative though an assessment of the cumulus (plus adcumulus) mineral ratios can be made by excluding material that is obviously of the mesostasis. The value of C so determined would only be an approximation to the true value but nonetheless may prove to be satisfactory especially if the trapped liquid has crystallised to give, in part, minerals in roughly the same relative proportions as the similar cumulus (plus adcumulus) minerals.

Thus, the ensuing method for determining C is really only applicable to the case of adcumulates. Orthocumulates, however, need not be rejected out of hand as it is shown later that in practice it is possible to derive the value of C by jointly considering the mineralogy and chemistry of the rock and by some trial and error application of the theory. This practical aspect is discussed later, (Chapter Four).

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* 'adcumulus' and 'adcumulate' are taken to include 'heteradcumulus' and 'heteradcumulate' where appropriate.

The determination of C for adcumulates is best illustrated by an algebraic example:-

Let rock 'A' from a certain horizon in a layered igneous series contain three cumulus minerals in the relative ratios x:y:z, where y is small. A high-k element enters preferentially the mineral whose modal proportion is y to a concentration of E ppm., and taking a particular case where the element does not enter the other two minerals at all, then the concentration of the chosen element in the total cumulus assemblage is:-

$$\frac{y.f.E}{x + y + z} = C_A \qquad (2).$$

where f is a factor converting the concentration into weight per unit volume.

If 'A' is a rock from a rhythmically layered series then it is possible to select another rock 'B' from a layer above or below, but close to, 'A' which has very different relative ratios of the cumulus minerals. Let these relative ratios (of the same cumulus minerals as in 'A') be m:n:o; where (m + o) is much smaller than (x + z) and n is much greater than y. Thus, the concentration of the same high-k element in the total cumulus assemblage of 'B' will be:-

$$\frac{n.f.E}{m + n + o} = C_B \qquad (3).$$

and C_B is much greater than C_A.

Using the premises 1 and 2 and equation (1) above it is possible to draw up the simultaneous equations for rocks A and B as follows:

$$p_A M + (1 - p_A)C_A = T_A$$
$$p_B M + (1 - p_B)C_B = T_B \qquad (4).$$

where the subscripts refer to the rock A or B.

Then if M is eliminated from these equations (4):

$$\frac{p_A}{p_B} = \frac{T_A - C_A + C_A \cdot p_A}{T_B - C_B + C_B \cdot p_B} \qquad (5).$$

The ratio p_A / p_B can clearly be obtained directly from the ratio (W) of the whole rock concentrations of a low-k element, and so p_B can be replaced by p_A / W.

Thus,

$$W(T_B - C_B) + C_B \cdot p_A = T_A - C_A + C_A \cdot p_A \qquad (6).$$

and therefore:-

$$p_A = \frac{(T_A - C_A) - W(T_B - C_B)}{(C_B - C_A)} \qquad (7).$$

The solution to this equation gives the proportion of the mesostasis in the rock 'A'. Substitution back into the equations will give solutions for p_B and M. In the case where W = 1, the equation (7) simplifies to:

$$p_A = \frac{(T_A - T_B)}{(C_B - C_A)} + 1. \qquad (8).$$

It has here been assumed that low-k elements do not enter any cumulus phase. This is almost certainly not found in practice but provided the solid/liquid partition coefficient of the element is low

for all minerals involved then a simple correction can be made to the whole rock analysis by subtracting a suitable concentration based on the concentration of the low-k element in the cumulus phase. This point is discussed further in Chapters 3 and 4.

From the theory presented it should be possible to determine the percentage of the mesostasis in two adcumulates by analysing both of these rocks for a low-k and high-k element; and analysing, and ascertaining the relative proportions of, the minerals of the cumulus phase for a high-k element. Not only does this theory give a means of obtaining the proportion of the mesostasis but also its composition.

It is probably clear from the above that many elements may be used in applying these equations. The more elements that are used to solve the equations for two rocks then the more accurate will the results for the mesostasis be.

One of the assumptions that has been used is that the mesostasis represents the pore material. If, however, the trapped liquid reacted with the cumulus phases then the mesostasis no longer represents the pore material. This circumstance should not greatly affect the validity of the above theory as such reaction does not affect the concentrations of elements in the whole rock or in the cumulus plus adcumulus phases, but only changes slightly the modal proportions of the different minerals. Insofar as the reaction is generally of the kind olivine going to pyroxene or of one pyroxene going to another pyroxene then selection of a high-k element that does not enter these minerals, but enters (say) plagioclase only, will nullify any possible effect on the determined

concentrations C_A or C_B. Thus the results obtained will still give the initial amount of trapped liquid (p) and the concentration of the high-k element in this liquid (M).

In any case Wager et al (1960) considered that reaction of this kind was not common in the Bushveld, Rhum and Skaergaard intrusions, which are the ones studies for this thesis.

C. Error analysis of first method.

Errors may arise in:-

1. Determination of the relative ratios of the different cumulus minerals.
2. Low-k element concentration values.
3. High-k element concentration values.
4. Density determinations and corrections.

From equation (7) the following holds:-

$$\sigma^2_{p_A} = \left(\frac{\partial p_A}{\partial T_A}\right)^2 \sigma^2_{T_A} + \left(\frac{\partial p_A}{\partial C_A}\right)^2 \sigma^2_{C_A} + \left(\frac{\partial p_A}{\partial T_B}\right)^2 \sigma^2_{T_B}$$

$$+ \left(\frac{\partial p_A}{\partial C_B}\right)^2 \sigma^2_{C_B} + \left(\frac{\partial p_A}{\partial W}\right)^2 \sigma^2_{W} . \qquad (9).$$

where:-

$$\frac{\partial p_A}{\partial T_A} = \frac{1}{(C_B - C_A)} \qquad (10).$$

$$\frac{\partial p_A}{\partial C_A} = \frac{(C_A - C_B) + [(T_A - C_A) - W(T_B - C_B)]}{(C_B - C_A)^2}$$

$$= \frac{T_A - C_B - W(T_B - C_B)}{(C_B - C_A)^2} \qquad (11).$$

$$\frac{\partial p_A}{\partial T_B} = \frac{-W}{(C_B - C_A)} \qquad (12).$$

$$\frac{\partial p_A}{\partial C_B} = \frac{C_A - T_A + W(T_B - C_A)}{(C_B - C_A)^2} \qquad (13).$$

$$\frac{\partial p_A}{\partial W} = \frac{(C_B - T_B)}{(C_B - C_A)} \qquad (14).$$

Now $T_B \approx C_B \gg C_A \approx T_A$

Thus, term 1 on R.H.S. of equation (9) is $\ll \left(\frac{\sigma T_A}{T_A}\right)^2$.

From equation (11) $\partial p_A / \partial C_A$ is of the order of $-1/C_B$, thus term 2 of equation (9) is $\ll (\frac{\sigma C_A}{C_A})^2$.

From equation (12), as C_A is much less than C_B, $\partial p_A / \partial T_B$ is approximately $-W/C_B$, so that the third term is of the order of $(\frac{W \sigma T_B}{T_B})^2$.

The R.H.S. of equation (13) is of the order of W/C_B.

The R.H.S. of equation (14) is less than one and generally is expected to be a small number such that it is not greater than $1/W$. In suitable cases its value will be about 0.1.

Thus, the important contributors to the variance in p_A are terms 3 and 4 of the R.H.S. of equation (9), so that:-

$$\sigma^2_{p_A} = \left(\frac{W\sigma_{T_B}}{T_B}\right)^2 + \left(\frac{W\sigma_{C_B}}{C_B}\right)^2 \text{ which is less than } 2\left(\frac{W\sigma_{C_B}}{C_B}\right)^2 , \qquad (15).$$

since T_B is more directly, and therefore more accurately, determinable than C_B. Thus, the variance of C_B needs to be known so as to assess the contribution to equation (15).

From equation (3):

$$\frac{\sigma^2_{C_B}}{C_B^2} = \left(\frac{1}{C_B}\cdot\frac{\partial C_B}{\partial E}\right)^2\sigma^2_E + \left(\frac{1}{C_B}\cdot\frac{\partial C_B}{\partial n}\right)^2\sigma^2_n + \left(\frac{1}{C_B}\cdot\frac{\partial C_B}{\partial f}\right)^2\sigma^2_f . \qquad (16).$$

where:-

$$\frac{1}{C_B}\cdot\frac{\partial C_B}{\partial E} = \frac{n.f}{m+n+o}\cdot\frac{(m+n+o)}{n.f.E} = \frac{1}{E} . \qquad (17).$$

$$\frac{1}{C_B}\cdot\frac{\partial C_B}{\partial n} = \frac{(m+o).f.E}{(m+n+o)^2}\cdot\frac{(m+n+o)}{n.f.E} = \frac{m+o}{n(m+n+o)} \qquad (18).$$

$$\frac{1}{C_B}\cdot\frac{\partial C_B}{\partial f} = \frac{n.E}{(m+n+o)}\cdot\frac{(m+n+o)}{n.f.E} = \frac{1}{f} \qquad (19).$$

The R.H.S. of equation (18) can be written $1/n(1 + \frac{n}{m+o})$ and this is of the order of $1/2n$, so that the coefficient of the second term of the R.H.S. of equation (16) is substantially less than $(\sigma_n/n)^2$.

As the variance of f is probably small, the main contributor to the relative variance in C_B is the relative variance in E.

If we can assume the relative standard deviation of K to be about 5%, then the standard deviation for p_A, from equation (15), is about 0.03 if W has a value around $\frac{1}{2}$. Thus, if p_A is about 0.2, this gives a relative standard deviation in p_A of about 15%. As W climbs in value so does the standard deviation of p_A so that, from the point of view of errors, it is better if there is more mesostasis in the rock in which the high-k element is richest.

D. Analysis of second method.

Although this method is the second to be discussed it was originally the first to be devised as the intention at the outset was to develop a method which did not necessitate any knowledge about the modal proportions of the various minerals in the cumulus (plus adcumulus) phase. However, this method requires the use of further premises some of which may not always be realisable in practice. This method uses premises 1 and 2 of the first method and also the following:-

Premise 3: that in any one horizon of a layered, fractionated rock sequence the chemical compositions, and the relative modal proportions, of the minerals of the cumulus plus adcumulus phase can be considered to be constant over not too great a horizontal distance.

Premise 4: that the composition of the remaining magma does not differ horizontally and so neither does the composition of the pore material.

Premise 5: that the percentage of pore material may vary from rock to rock along any one horizontal plane. This variation could be brought about by differences in packing of the cumulus minerals and different degrees of adcumulus growth.

From premises 1 to 5 the following simultaneous equations may be drawn up for two rocks taken from one layer:

$$p_A.M + (1 - p_A)\, C_A = T_A$$

$$p_a.M + (1 - p_a)\, C_a = T_a \qquad (20).$$

where the symbols have the same meaning as earlier; A and a referring to the two rocks from the same horizon.

Also the following equations hold:

$$p_A = QR_A$$

$$p_a = QR_a \qquad (21).$$

where Q is a constant and R_A, R_a are the concentrations of a low-k element in the two rocks. Thus:

$$p_A = \frac{p_a.R_A}{R_a} \qquad (22).$$

Furthermore, from premise 3, $C_A = C_a = C$. The use of this premise and equations (21) and (22) allows M to be eliminated from equations (20) as follows:

$$\frac{T_A - (1 - p_a.R)C}{p_a.R} = \frac{T_a - (1 - p_a)C}{p_a} \qquad (23).$$

where R is the ratio R_A / R_a. Thus:-

$$C = \frac{T_A - T_a.R}{1 - R} \qquad (24).$$

Thus the concentration of an element in the cumulus plus adcumulus parts can be found by the above method without the need of analysing mineral separates and determination of modal proportions as was necessary in Method 1.

After C has been found there are two ways in which p_a, p_A, and M can be determined. A third rock from the same layer as A and a but with a different amount of mesostasis from either of them, allows a similar treatment as above to be applied except that three simultaneous equations of type (20) can be drawn up. If Q (equation (21)), M, and C are regarded as the three unknowns, then the three simultaneous equations are soluble. Thus, the presence of rhythmic layering is not a pre-requisite of this method. If, however, rhythmic layering is present then a similar treatment can be made on two rocks from an adjacent layer as was done for A and a above, and having found C_A and C_B, equation (7) of the first method can be applied to the two pairs of rocks, each pair consisting of a rock from each layer.

As in the first method, this method also requires the concentrations of the high-k and low-k elements to be expressed in volumetric units. One small advantage of this method is that reaction of the trapped liquid with the cumulus phases produces no change in the value of M and p as modes are not considered.

E. Error analysis of second method.

From equation (24)

$$\frac{\sigma_C^2}{C^2} = \left(\frac{1}{C}\frac{\partial C}{\partial T_A}\right)^2 \sigma_{T_A}^2 + \left(\frac{1}{C}\frac{\partial C}{\partial T_a}\right)^2 \sigma_{T_a}^2 + \left(\frac{1}{C}\frac{\partial C}{\partial R}\right)^2 \sigma_R^2. \qquad (25).$$

where:-

$$\frac{1}{C}\frac{\partial C}{\partial T_A} = \frac{1}{T_A - T_a R} \qquad (26).$$

$$\frac{1}{C}\frac{\partial C}{\partial T_a} = \frac{-R}{T_a R - T_A} \qquad (27).$$

$$\frac{1}{C}\frac{\partial C}{\partial R} = \frac{(T_A - T_a)}{(1 - R)(T_A - T_a R)} \qquad (28).$$

Thus, it is seen from equation (26) to (28) that the assessment of the standard deviation of C depends upon the values T_A, T_a, and R, so much that it is not possible to draw precise conclusions. If, however, the amount of mesostasis is small then $T_A \approx T_a$, and so the R.H.S. of equation (26) goes to $1/T_A(1-R)$, that of (27) goes to $-R/T_a(R-1)$, and that of (28) goes to $(1 - T_a/T_A)/(1-R)^2$. Provided that R is greater than, or equal to, 2 then the modulus of the R.H.S. of (26) is less than or equal to $1/T_A$, that of (27) is less than or equal to $2/T_a$, whilst that of (28) tends towards zero or a small number.

It is seen, therefore, that the second term of the R.H.S. of equation (25) contributes most to the relative variance in C.

Once an assessment of the standard deviation of C has been made, the error analysis for the first method - equations (9) to (15) - can be applied.

F. The use of partition coefficients.

One of the consequences of the successful application of the above theory is the possibility of deducing the partition coefficients of trace elements between the liquid and solid phases. McIntire (1963) reviewed partition coefficient theory and its applications to geological problems. Most of his paper is concerned with the distribution law of Henderson and Kracek (1927) which is:

$$D = \frac{\left(\frac{Tr}{Cr}\right)_S}{\left(\frac{Tr}{Cr}\right)_L} \qquad (29).$$

where $\left(\frac{Tr}{Cr}\right)_S$ refers to the ratio of microcomponent or 'tracer', Tr, to the macrocomponent or 'carrier', Cr, in the solid phase, and $\left(\frac{Tr}{Cr}\right)_L$ is the ratio in the liquid phase. This distribution law requires knowledge of the exact carrier for each tracer; for multicomponent systems, such as a magma, the required knowledge may not be available. Indeed in many cases there is serious doubt as to which elements camouflage other trace elements in silicate lattices; (an aspect of this is discussed in the section on phosphorus geochemistry). It seems safer, therefore, to use the Berthelot-Nerst distribution law which does not require knowledge of tracer-carrier relationships. This distribution law states (McIntyre op. cit.) that at equilibrium the ratio of the concentration of the trace component in the solid (C_S) to its concentration in the liquid (C_L) is a constant:

$$\frac{C_S}{C_L} = k. \qquad (30).$$

The constant k is called the partition coefficient of the trace element. Throughout this thesis this distribution law is the one that is used.

In the determination of the amount of mesostasis by the first method it is necessary to analyse the cumulus phases for a high-k element. It may be difficult to obtain accurate results for the concentrations if some of the trapped liquid has crystallised to give lower temperature fractionation products that are similar to the cumulus minerals which they envelope. The pore material often exists as zoned extensions to original cumulus and adcumulus parts and it is, therefore, essential to analyse unzoned specimens or just the cores of zoned specimens. In the case of adcumulates with little mesostasis there is no problem as zoning will be very slight. In orthocumulates, rock crushing and mineral separating processes are unlikely to completely remove the outer zones. These outer zones will be enriched or depleted in low-k and high-k elements respectively, compared with the cores, and could seriously interfere in the analyses. If, however, one can consider the entry of trace elements into silicate lattices as a solid solution process then the concentration of a trace element in a cumulus phase should be constant over a small degree of fractionation. Thus by taking a pure separate of an unzoned mineral from an adcumulate adjacent to the orthocumulate, the high-k element concentration could be found and substituted into the equations for the orthocumulate. It is in this respect that use is

made of the constancy of the partition coefficient over small fractionation increments. Similarly, it should only be necessary to analyse mineral separates from one of the two rocks used in the first method if both rocks contain the same cumulus and adcumulus minerals.

The partition coefficient is temperature and pressure dependent but is not a function of the concentration of a trace element whilst this behaves as a dilute solution. Thus two similar magmas with differences only in their respective trace element concentrations, which have fractionated under identical conditions would be expected, at similar fractionation stages, to have the same mineral/liquid partition coefficients.

Thus, the ascertainment of trace element partition coefficients between a specific mineral and the co-existent liquid phase from a variety of fractionated basic magmas should prove to be more useful in comparative studies than just trace element concentrations. Armed with partition coefficient data from layered intrusions it may be possible to elucidate fractionation trends of some basalt series.

CHAPTER THREE

Geochemistry of Phosphorus and some other Elements.

A. Suitability of elements.

In Chapter Two it was stated that the application of the theory there developed demanded the presence in layered rocks of elements which show contrasting geochemical behaviour: the so-called high-k and low-k elements. Other requirements are that the concentrations of these elements can be readily and accurately determined and that high-k elements should only be in trace quantities so that they obey the distribution law, though this latter requirement is not always needed.

The major elements, silicon, aluminium, oxygen, magnesium, iron, sodium, potassium, and calcium are not suitable as they generally enter more than one cumulus mineral. However, once the proportion of the mesostasis of any rock has been determined by using other elements, it is clearly a simple matter to determine the concentration of these elements in the mesostasis.

This section discusses briefly the suitability of minor and trace elements for use in the application of the theoretical analyses of Chapter Two for the case of basic layered rocks only, especially the lower, or earlier, fractionation products. The reason for this bias is that it was decided for the purposes of this thesis to test the theory on rocks of comparatively simple mineralogy that were well-documented. Thus, the Lower Zone of the Skaergaard intrusion, East Greenland (Wager and Deer 1939), and the layered ultrabasic rocks of Rhum (Brown 1956) were chosen. Some work has also been carried out on the Bushveld igneous complex.

Many minor and trace elements are unsuitable for the purposes of the theory generally for one of four reasons:

1. The elements enter both mafic and femic (with accessory) cumulus minerals. In this group are Au; Cd; In; Li; Sb; Ti.
2. They show a preference for entering the immiscible sulphide phase (Wager et al 1960). Included in this group are Ag(?); Cu; Mo(?); S; Se; Zn(?).
3. The elements are in very low concentrations and/or are difficult to analyse for. Be; B; C; Pb; Rb; Th; fall into this group.
4. There is at present insufficient information about the element's geochemistry to state whether they are really suitable or not: This group includes Ag; Hg; Lanthanides; Mo; Nb; Platinum metals; Re; Se; Sn; Ta; Tc; Te; Tl; W; Y; Zn.

The remaining suitable elements fall into two categories. Firstly those elements which show a strong preference to remain in the magma during fractional crystallisation, i.e. low-k elements. These elements are As; Cs; ~~Ba;~~ Halogens; P; Zr; Hf; and U. The halogens and phosphorus are unsuitable when cumulus apatite is present as they enter this mineral. Zirconium is found in early stage pyroxenes and cumulus apatite though it is generally concentrated in residual liquids and Brooks (1965) has suggested that this element could be used as a low-k element until the crystallisation of zircon.

The second category includes those elements which show a strong preference to enter only one of the main cumulus minerals: pyroxene;

olivine; or felspar, such that the partition coefficient C_S/C_L is high, i.e. high-k elements, see Chapter Two. Rhythmic layering in certain intrusions consists of olivine-pyroxene-rich bands alternating with felspar-rich bands, whilst in others the alternation is from pyroxene-rich to felspar-rich bands. Insofar as pyroxene is almost ubiquitous, this second category can be divided into three sub-groups consisting of those elements that:

1. preferentially enter olivine: Ni*
2. preferentially enter pyroxene (or pyroxene and olivine): Mn; Ge; Sc; Cr.
3. preferentially enter felspar: Ba; Ga; Sr.

The elements listed do not behave ideally but their preferences are distinct enough to be included in the above groups. In those cases where the rhythmic layering is from olivine to felspar-rich layers elements in sub-groups 1 and 3 will be the only suitable ones, whilst in pyroxene-rich and felspar-rich alternations those in 2 and 3 will be suitable. Many of these elements exist in basic magmas only in low concentrations or are depleted strongly during fractionation and in these cases activation analysis can be used.

For the purpose of this thesis it was decided to investigate the appropriate geochemical behaviour of phosphorus and uranium and make a

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*Although nickel is strongly concentrated in early fractionated olivines it also enters slightly into magnetite and ilmenite so that it may not in all cases be suitable.

preliminary investigation into the behaviour of bromine as low-k elements. Strontium was selected for study as a high-k element.

B. The geochemistry of phosphorus.

Although there is a lot of data available on the geochemistry of phosphorus in rocks, little is known about the distribution of the element in silicates as in these minerals it is present in only very low concentrations. The use of activation analysis has enabled the accurate determination of low concentrations of phosphorus. The analytical method that has been developed is described in Chapter 6.

i. The Skaergaard intrusion.

In their memoir on the Skaergaard intrusion of East Greenland, Wager and Deer (1939, p.227) stated ".... nor does P_2O_5 enter appreciably into the composition of any of the primary minerals. The P_2O_5 of the early layered rocks is believed to have existed only in the 20 per cent. of inter-precipitate magma and to have crystallised from it as rare, small, apatite crystals." This aspect of phosphorus geochemistry was used by Wager (1963) to show that the amount of trapped liquid in the rocks of the layered series decreased with height in the intrusion, and from this he drew the conclusion that the amount of adcumulus growth had increased with height until, at least, the stage where cumulus apatite entered. Furthermore, in earlier work (Wager, 1960) the amount of phosphorus in the successive residual liquids of the fractionating Skaergaard magma had been deduced; and hence from this information it was shown (Wager 1963 op. cit.) that the amount of pore liquid in any one rock could be calculated if the whole

rock phosphorus content was known.

The variation of phosphorus with height in the instrusion both for the whole rocks and for the successive liquids is reproduced in Figure 1. which is taken from Wager, 1963, which in turn uses the results of Curren (1959). In Figure 2. is shown the zonal classification of the Skaergaard intrusion which is based upon the incoming or outgoing of certain cumulus phases.

In this work described above, two assumptions were made:

a. That a negligible amount of phosphorus enters the cumulus and adcumulus* minerals prior to the formation of cumulus apatite (i.e. below UZb).

b. and, following from a, that the amount of phosphorus in a rock (below UZb) is a relative measure of the amount of pore material in that rock.

The accuracy of these assumptions becomes questionable when a rock such as EG.5109 (Figure 1.) is examined, as the value of its phosphorus content indicates that there is about 85% pore material in that specimen. This value is not compatible with the estimated maximum pore material of about 50 per cent. for any rock of the layered series (Wager et al. 1960) nor does the whole rock analysis of EG.5109 approach that of the contemporary magma as would be expected if 85 per cent of the rock consisted of pore material (Wager 1960, pp. 387-391). Thus, either the above assumptions

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*Hereafter, the terms 'adcumulus' and 'adcumulate' are taken to include 'heteradcumulus' and 'heteradcumulate' where appropriate.

FIGURE 1.

Phosphorus content vs. height.

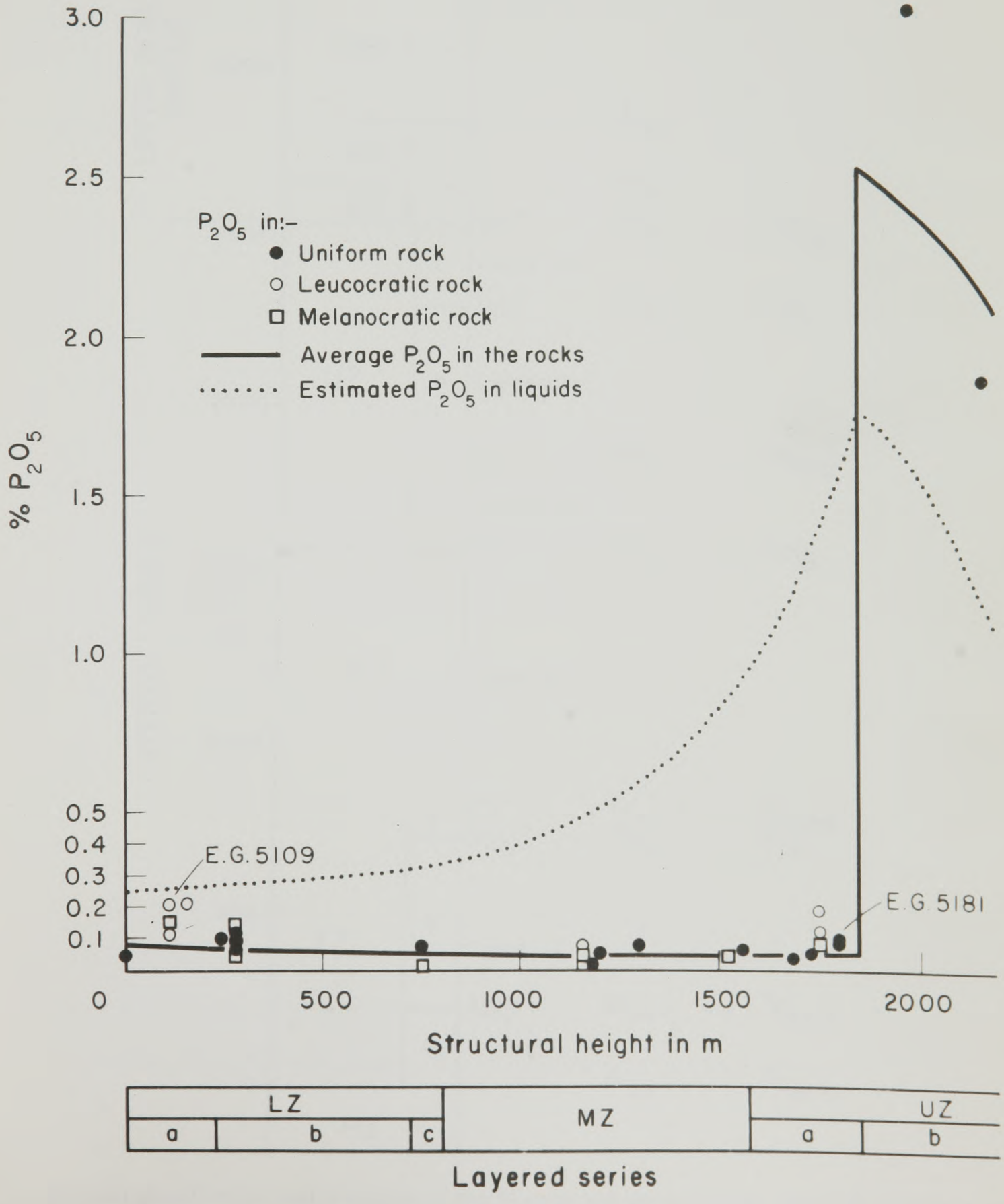
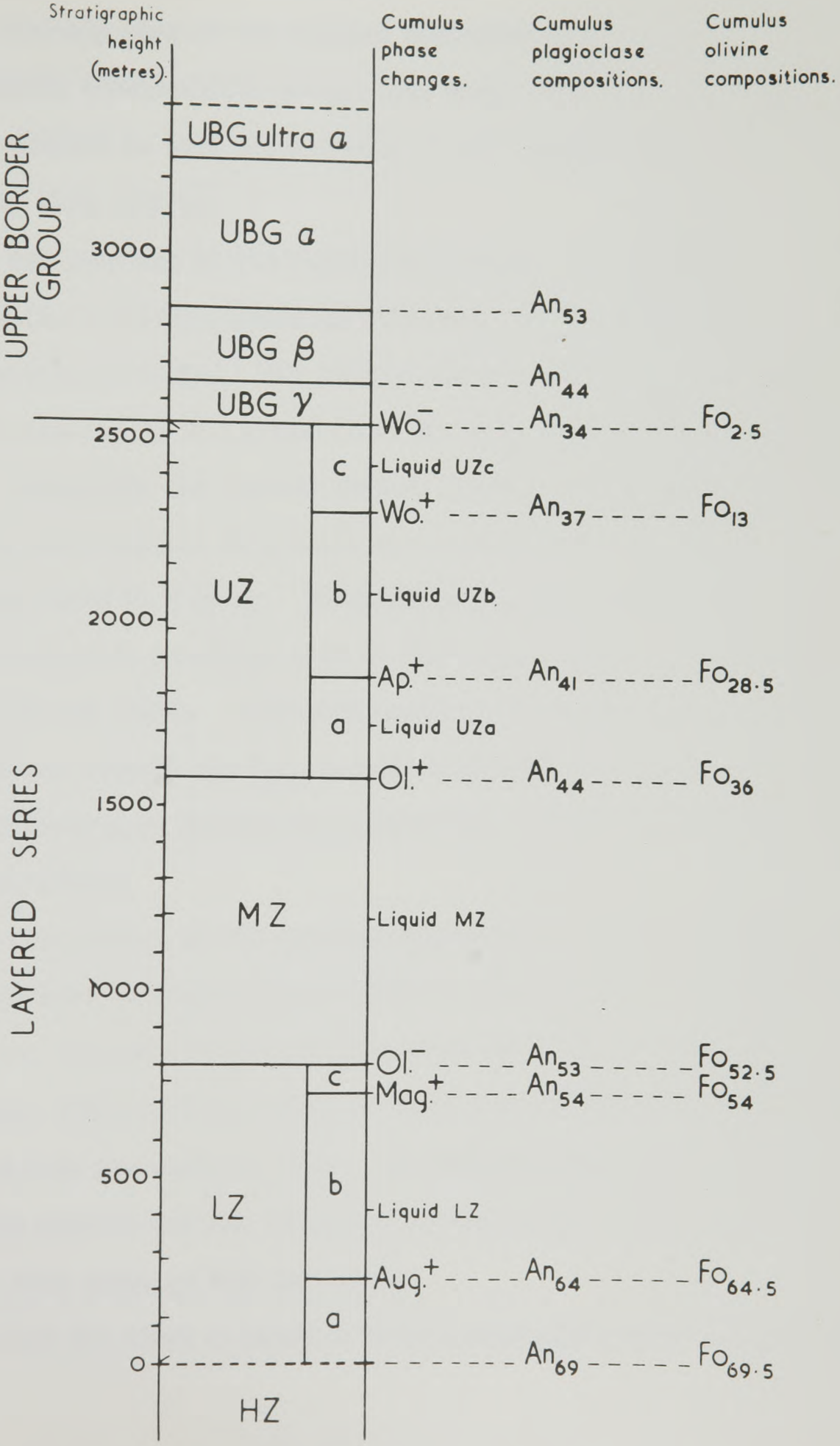


FIGURE 2.



Revised classification and thickness of the Skaergaard layered series and upper border group,

are not entirely true or the deduced compositions of the Skaergaard magma at successive fractionation stages (see Wager 1960) are inaccurate. It was thus decided to test the validity of the assumptions, and this is the subject of this section.

For the purposes of the ensuing discussion it is expedient to summarise the knowledge, prior to this work, of the distribution of phosphorus in the Skaergaard rocks. The chilled olivine gabbro contains 0.1 per cent P_2O_5 and this figure is assumed to be the P_2O_5 concentration of the initial magma. Throughout the layered series, average rocks contain about 0.05 per cent. P_2O_5 until apatite is present as a cumulus mineral (at UZb) when the percentage rises to 2 or 3. Below UZb there is generally more phosphorus in the leucocratic cumulates than in the melanocratic or average rocks (Wager 1960 and 1963). Published analyses of minerals from the layered series do not include any P_2O_5 results and there do not appear to be any published figures on phosphorus in minerals, excluding apatite, of the Skaergaard rocks.

The composition of the contemporary magma at various fractionation stages has been estimated (Wager 1960) to have been about 0.28 per cent. P_2O_5 at the time of formation of the Lower Zone (LZ); 0.50 per cent. at the Middle Zone (MZ); 1.25 per cent. at Upper Zone a (UZa); 1.35 per cent. at UZb; and 0.40 per cent. at UZc. The boundary UZa-b marks the incoming of cumulus apatite and the estimated concentration of P_2O_5 in the contemporary magma at this stage is 1.75 per cent.

To test the first assumption that a negligible amount of phosphorus

enters the cumulus and adcumulus minerals (except cumulus apatite), olivine pyroxene, felspar, and iron ore fractions were separated from selected rocks and analysed for phosphorus by activation analysis. For this work the purity of the separated mineral fractions needs to be high. However, if a cumulus phase contains inclusions then from the point of view of testing the above assumptions the cumulus mineral plus inclusions should be analysed. Thus, the results would not necessarily indicate the amount of phosphorus occupying lattice sites. The presence of inclusions was not noticed but their existence cannot be ruled out. Analysed olivines were free of enclosed iron ore as far as could be ascertained.

A more important aspect of analysing cumulus minerals for a low-k element is that there should be no pore material included in the sample. In the case of zoned minerals it is often impossible to remove completely the outer zones which originated, at least in part, from the trapped liquid. Thus, it is clearly advisable that the separated minerals should be adcumulates where the risk of contamination from the pore material is low. The minerals that are discussed below were taken from orthocumulates, mesocumulates, and adcumulates, and the effect of contamination from pore material is clearly shown.

The new analyses are presented in Table 1. If one can take Wager's assumptions as a working hypothesis then the phosphorus results can be discussed in the light of the phosphorus concentration of both the individual whole rocks and that of the contemporary magma. These figures are, therefore, included in Table 1 and from them are calculated pore material percentages

TABLE 1

Phosphorus in some Skaergaard minerals

EG ROCK No & TYPE	STRUC. HEIGHT & ZONE	WHOLE ROCK P_2O_5%	MAGMA P_2O_5% +	PORE LIQUID %	MINERAL	DETERMINATIONS P ppm. →	AVERAGE P ppm	P_2O_5 %
4312	1860 UZb	-	-	-	PYROXENE OLIVINE MAGNETITE	894; 731 298; 375 4,279; 3,763	812 336 4,020	0.186 0.077 0.92
5181	1800	0.094	1.5	6	PLAG (An40)	46.6; 44.5	45.5	0.010
Aver.	UZa				PYROXENE	29.4; 33.7; 30.3; 28.9	∠ 29.8 (\$ 2)	0.007
					MAGNETITE	9.0; 8.4	8.7	0.002
					ILMENITE	20.3; 21.5	20.9	0.005
5112	580	-	-	-	PLAG (An37)	53.4	53	0.012
Aver.	LZb							
4389	290	-	-	-	PLAG	110.4	110	0.025
Aver.	LZb							
5093	280	0.078	0.27	29	PLAG 1st frac	1,400	1,400	0.32
Leuco.	LZb				" 2nd "	269; 285	277	0.064
5086	280	0.12	0.27	44	PLAG	435; 327	381	0.087
Aver.	LZb				PYROX	32.0; 72.4	77.2	0.018
					OLIV. (Fa37)	77.3; 83.9	80.6	0.018
5109	110	0.21	0.25	84	PLAG	453; 648	550	0.126
Leuco	LZa				PYROX.	79.2; 73.3	76.2	0.018
5107	110	0.12	0.25	48	PLAG	1,130	1,130	0.26
Aver.	LZa	→						

* analyst: W.D. Curren (1959)

→ analyst: P. Henderson. (Results for EG 5107 whole rock agree with Curren's value 0.12)

\+ from Wager (1963)

∠ the relative standard deviation (~6%) for 5181 pyroxene is considerably less than SA 660 (see chapter 6). This may be because the pyroxene is comparatively more homogeneous.

(which are necessarily only tentative).

The plagioclases are, generally, highly enriched in phosphorus compared with the pyroxenes and olivines. However, most of the plagioclases studied are from orthocumulates or mesocumulates except for EG.5181 which can be considered to be an adcumulate*. All the felspars, except those of EG.5112 and EG.5181, show extensive zoning in thin section. Thus these high phosphorus concentrations can be interpreted as being due to the crystallisation of trapped liquid to form, in part, extensions to the cumulus plagioclase. With the progressive crystallisation of the trapped liquid the concentration of low-k elements in the remaining liquid fraction increased considerably so that, in turn, the crystallising material became even more enriched in these elements. Thus, the results for all the felspars, except for those of EG.5112 and EG.5181, have little significance except that they show that the mineral separates were not devoid of zoned material. This strong, somewhat random, zoning of the plagioclases could also account for the poor reproducibility shown by some of the replicates. For activation analysis only a small amount (100 mgm.) of mineral is required and in such an amount inhomogeneities could manifest themselves. The reproducibility of replicate analyses of material from adcumulates is far superior.

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*The boundary between adcumulates and mesocumulates was put at 5 per cent. (Wager et al., 1960) and so it might appear from Table 1, column 5 that EG.5181 is strictly a mesocumulate. However, as it is clear that some phosphorus is entering the cumulus phases the figure of 6 per cent. is probably too high. Furthermore, on microscopic examination the rock EG.5181 contrasts strongly with other rocks that are definitely mesocumulates in its absence of zoned minerals etc., so it seems justifiable to call it an adcumulate.

The case of EG.5093 is particularly interesting. When the rock was being crushed and ground to reduce it to fragments suitable for mineral separating, sifting for the appropriate grain size (-80 + 160 mesh) was made at various stages of the grinding process. It was thought that the first material to be reduced to -80 mesh (0.2 mm. diameter) would be relatively richer in the outer zones of plagioclase compared to later fractions, as the average smallest dimension of the crystals is about 1 mm. Thus, when about half of the specimen had been reduced to -80 mesh, the -80 + 160 mesh fraction was taken and put aside. The remaining coarse fraction was further reduced to give a second -80 + 160 mesh fraction. Mineral separation of the felspar was made on each of the two -80 + 160 mesh fractions, and the plagioclase from each was analysed for phosphorus. The results show that the first pure mineral separate is highly enriched in phosphorus compared with the second fraction, as was expected.

The concentration in plagioclase (An40) from EG.5181 (45.6 ppm.) is more significant as zoning of the plagioclase cannot be detected in thin section except against the rare mesostasis (Wager, 1963). This phosphorus concentration is, therefore, that in cumulus plagioclase of this fractionation stage. The concentration of phosphorus in the contemporary magma was about 1.5 per cent. P_2O_5 which gives a Cplag./Cliq. partition coefficient of about 0.007. It is unlikely that this partition coefficient remained constant during fractionation as there were changes in the plagioclase composition, temperature, and pressure, as well as the fact that the phosphorus concentration in the liquid UZa was so rich that the distribution law may not

have been obeyed. It is, therefore, difficult to predict the concentration of phosphorus in cumulus plagioclase of the Lower Zone. Phosphorus concentrations in rocks of the Lower Zone, analysed by Curren (1959) and other workers, imply that all those analysed are mesocumulates or orthocumulates, and it may not be possible to find a suitable adcumulate in the Lower Zone for the accurate determination of the concentration of phosphorus in cumulus plagioclase. However, a microscopic examination of some LZ rocks showed that EG.5112 (LZb) contained zoned plagioclase but that the zoning was not so extensive as EG.5109 etc. The plagioclase from EG.5112 (An57) contains about 50 ppm. phosphorus which puts an upper limit to the concentration in Lower Zone cumulus plagioclases.

The pyroxenes* show only a little zoning in the LZa rocks studied, and from this evidence, and some other given later, the pyroxenes are considered to be essentially a heteradcumulus phase at this fractionation stage.

The pyroxene from EG.5109 (LZa) has a similar concentration (76.2 ppm.) to that from EG.5086 (LZb). However, the phosphorus content is much lower in the pyroxene from the adcumulate EG.5181 and it might be possible that the LZ pyroxenes crystallised, in part, from the trapped liquid. The 5181 pyroxene is of the same order as that of Bushveld and Rhum clinopyroxenes, and gives a C pyrox./C liq. k value of about 0.004.

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*The main details of the pyroxenes can be found in Brown (1957) and Brown and Vincent (1963). They are predominantly Ca-rich (augite) though there are small amounts of co-existing Ca-poor pyroxenes which are unlikely to have been separated from the analysed Ca-rich material.

The rock EG.4312 is from a horizon just above that where apatite is found as a cumulus phase and presumably the pyroxene (and possibly the other minerals) is contaminated with apatite inclusions.

The olivine from EG.5086 shows no zoning and appears as a pure cumulus phase. Its phosphorus content is, therefore, taken as being that of cumulus olivine of the LZ. The olivine from EG.4312, like the pyroxene, may well be contaminated with cumulus apatite. The 5086 olivine gives a C oliv./C liq. k value at the LZb of about 0.07.

The results for ilmenite and magnetite from EG.5181 show that there is little phosphorus in these minerals, and that there is a preferential entry into ilmenite. The magnetite from EG.4312 appears to be contaminated with cumulus apatite (?).

It has been shown, therefore, that the first assumption used by Wager that the amount of phosphorus in the cumulus minerals is negligible, is not strictly correct, though the entry of phosphorus into cumulus minerals is of a low order. Nonetheless, these low concentrations make a significant contribution to whole rock phosphorus contents and may comprise most of the phosphorus in certain adcumulates. However, it would seem that the difference between the phosphorus concentration in the whole rock and that in the overall cumulus plus adcumulus phases could be a relative measure of the volume of pore material in that rock. With this proviso, the second assumption might appear to be valid. However, in the use of the assumption Wager (1960), Figure 1, made no allowance for the fact that the phosphorus content was measured in weight per unit weight rather than in

weight per unit volume. Leucocratic rocks have very different specific gravities from melanocratic rocks (e.g. 2.76; 3.89 respectively, Wager and Deer, 1939, p.85), whereas it is likely that the contained pore material has the same specific gravity in the two rock types if they are close to each other in the fractionation sequence. Thus, if the whole rock phosphorus content is going to be taken as a measure of the volume of pore material, it is essential that all concentrations are expressed in weight per unit volume. If this is taken into consideration, and also the fact that there is phosphorus in the cumulus minerals, the pore material in EG.5109 is found to be about 50 per cent. by volume, (assuming that the P_2O_5 content of the magma as given by Figure 1 is correct).

Further conclusions about the geochemistry of phosphorus in the Skaergaard intrusion are discussed in Chapter 4.

ii. The Bushveld igneous complex.

The state of present knowledge about the petrology, structure, age, etc. of the Bushveld igneous complex of the Central Transvaal, South Africa, is summarised by Hall (1932), Lombard (1935), Willemse (1964), Atkins (1965), and for fuller details these works should be consulted.

The igneous intrusion consists of a number of so-called 'Zones' of which the 'Marginal Zone' of the medium to fine grained gabbros is one. The estimated maximum thickness of this zone is 400 feet. The remaining zones are each superincumbent upon another zone, starting at the base with the 'Basal Zone' of 4,500', maximum thickness, which consists predominantly of adcumulates and heteradcumulates made up essentially of combinations of

bronzite, olivine, pyroxene, plagioclase, and chromite. Above the Basal Zone, starting with the 'Main Chromitite' seam comes the 'Critical Zone', about 2,800' thick and with much rhythmic layering. The rocks of this zone are cumulates with plggioclase, bronzite, and chromite present as cumulus phases, and also diopsidic augite towards the top.

The next 'Main Zone' makes up a large part of the intrusion as it is about 17,000' thick, delimited by the famous Merensky reef (a pyroxene cumulate layer containing exploitable platinum) at its base and by the incoming of cumulus magnetite at the top. The zone may be divided into two parts - the lowest few hundred feet which show good layering and consist of adcumulates, some with orthopyroxene clusters, followed by the rest of the zone of uniform cumulates of plagioclase, augite, and calcium poor pyroxene.

At the top of the intrusion is the 'Upper Zone', the lowest rocks of which are ferrogabbros. About 1,100 and 2,600 feet above the base of this zone, olivine and apatite respectively enter as cumulus phases. At about 2,500 feet above the base the rocks are essentially ferrodiorites, which grade upwards into granodiorites forming the highest rocks and to give an overall thickness to the zone of about 6,300 feet.

One of the original reasons for studying the distribution of phosphorus in layered intrusions was to see if the degree of adcumulus growth in the Bushveld intrusion changed with fractionation in a similar way to the Skaergaard intrusion. Very little was known about the variation of phosphorus content with height in the intrusion, or about the concentration in the separate minerals. Liebenberg (1960) published some data on

phosphorus in Bushveld rocks but much of it is presented only in graphical form, of phosphorus content against an adjusted Larsen function, from which it is difficult to extract the required information, especially as the relative heights of the rocks in the intrusion are not given.

Unlike the Skaergaard there are no data concerning the concentrations of phosphorus in the various stages of the fractionating magma, as there has, in the past, been no way of ascertaining such information. However, by analogy with the Skaergaard data it can be confidently said that the amount of phosphorus in the remaining magma would have increased with fractionation until apatite started to crystallise as a cumulus phase. The phosphorus results for the Bushveld can thus be viewed in this light. Furthermore, Atkins (1965) presented an analysis of a rock which he had collected from the intrusion and which he considered to be 'the best available representative of the Bushveld chilled gabbro'. The phosphorus concentration in this rock (SA.1087), along with results for other Bushveld rocks, is presented in Table 2. The concentration in SA.1087 (0.11 per cent. P_2O_5) is very similar to that of the Skaergaard chilled gabbro (0.10 per cent.) and in relation to it all the other Bushveld rocks are significantly poorer in phosphorus until apatite is present as a cumulus mineral.

The results in Table 2 show that the amount of phosphorus, and hence the amount of mesostasis, varies quite markedly from one horizon to the next (e.g. SA.722 and 730). It might be questioned whether this variation in phosphorus content is brought about by sudden changes in the whole rock

TABLE 2

Phosphorus in some Bushveld ~~minerals~~ rocks

ROCK No SA:	ZONE	STRUCTURAL HEIGHT IN ZONE (ft.)	DETERMINATIONS P ppm	MEAN ppm.	P_2O_5%	
1149	UZc	5,500	468; (444)	468	0.11	
940	UZc	5,300 (?)	8.9; 8.9	8.9	0.002	
1147 ≠≠	UZc	5,200	495; 570	532	0.12	
1131	UZc	4,360	14,720; 14,630	14,680	3.36	
1131*			14,570; 13,340	13,960	3.20	Apatite +
1123	UZb	2,000	309; 316	312	0.072	
1121	UZb	1,400	170; 179	174	0.040	
1112	MaZb	7,500	44.4; 46.4	45.4	0.010	
1110	MaZb	7,200	46.7; 48.5	47.6	0.011	
1102	MaZb	5,500	161; 164	162	0.037	
739 ≠≠	MaZb	4,300	65.0; 64.1	64.6	0.015	
1096	MaZb	4,180	142	142	0.032	
1095	MaZb	4,100	150; 118	134	0.031	
733	MaZa	3,000	45.1; 43.7	44.4	0.010	
732	MaZa	2,300	88.7; 99.2	94.0	0.022	
731	MaZa	1,100	81.1; 70.5	75.8	0.017	
730	MaZa	90	198.6; 192.2	195	0.045	
722	MaZa	0	27.0; 23.0; 32.4; 30.1; 33.2	29.1 ≠ (± 3.7)	0.007	
660	CZ	1,400	see chapter 6	49.0	0.011	
675	BZ	3,200	9.9; 10.6; 6.6	9.0	0.002	
678	BZ	2,320	24.8; 24.2	24.5	0.006	
681	BZ	1,800	46.3; 45.7	46.0	0.010	
682	BZ	980	8.5; 7.0; 12.1; 10.2	9.5	0.002	
685	BZ	100	29.5; 27.6; 29.3	28.8	0.007	
1087	Chill	-	471	471	0.108 ≠	

Analyst: P. Henderson.

* as 1131 but with very thin acid vein in rock.

≠≠ analysed by unadapted method, see chapter 6.

( ) SA 1149 analysis in which there was a slight loss of sample before processing.

≠ relative standard deviation about the same as SA 660, see chapter 6.

≠ previous analysis by H. Hegedus using colorimetry gave 0.12% P_2O_5 (Atkins 1965).

TABLE 3

Phosphorus in some Bushveld minerals

SAMPLE SA:	RESULTS P ppm	MEAN ppm.	P_2O_5%
940 Plag. (An40)	4.4; 4.7	4.6	0.001
1139 Olivine	235.1	235	0.05
1138 Ca-rich pyrox. ##	27.8; 26.4	27.1	0.006
740 Ca-rich pyrox. ##	18.9; 29.5	24.2	0.006
733 Plag. (An72)	34.4; 33.7	34.0	0.008
" Ca-rich pyrox.	18.7; 21.0	19.8	0.004
" Ca-poor pyrox.	23.4; 26.9	25.2	0.006
660 Plag. (An77)	38.7; 34.9	36.8	0.008
" Ca-rich pyrox.	19.4; 21.7	20.6	0.005
" Ca-poor pyrox.	15.1; 11.3; 10.6	12.3	0.003
681 Oliv. (Fo88)	38.1; 38.4	38.2	0.009

Analyst: P. Henderson.

analysed by unadapted method, see chapter 6.

TABLE 3A

Distribution of phosphorus in some Bushveld rocks

MINERAL	SA 600		SA 722		SA 733	
	MODE	P (ppm) Contribution	MODE	P (ppm) Contrib	MODE	P (ppm) Contrib
Plagioclase	64.7	23.8	36.5	12.4	57.1	19.4
Ca-rich Pyx	12.6	2.6	14.0	2.8	21.0	4.2
Ca-poor Pyx	22.7	2.8	49.5	9.0	21.9	5.5
Chromite	tr	n.d.	tr	n.d.	-	n.d.
Qtz.	tr	n.d.	tr	n.d.	tr	n.d.
P		28.2		24.2		29.1
Whole rock P	49.0		29.1		44.4	

tr = trace; n.d. = not determined.

Modes from Atkins (1965)

mineralogy from one horizon to the next. However, many rocks which show differing phosphorus contents have similar mineralogy, (see Appendix B for brief rock descriptions), and furthermore the phosphorus concentrations in all thecumulus minerals are spread over a fairly narrow range, see Table 3. In Table 3A modes for three of the rocks are given and the contribution of phosphorus in each mineral to the whole rock phosphorus content is calculated. The results show that these three rocks contain little pore material and are, therefore, adcumulates. By contrast the rock 730 (Table 2) contains a far greater amount of phosphorus and, therefore, more mesostasis. This strong variation in the content of the mesostasis means that the Bushveld rocks may well be suitable material on which to apply the theory presented in Chapter Two. As 660 and 733 are adcumulates, the results for phosphorus in the minerals represents that in the cumulus minerals.

In the felspars the phosphorus concentrations are very similar in the two rocks 733 and 660. The rock 940 and its separated felspar are very poor in phosphorus (about 9 and 5 ppm respectively) but because the rock is from a position far above the height where apatite becomes a cumulus phase it is difficult to assess the comparative richness in phosphorus of the magma at this stage. In comparison with those from the Skaergaard intrusion, the felspars of the Bushveld are poorer in phosphorus.

The concentrations in the Ca-rich pyroxenes are all of the same order. The slightly higher figure for 1138 could be attributed to contamination from apatite as this rock comes from the upper zone above the entry of cumulus apatite. It is difficult to see why the 733 Ca-poor pyroxene

(bronzite) should have more phosphorus than the similar 660 bronzite. In contrast to the Bushveld clinopyroxenes ($Ca_{43}Mg_{45}Fe_{12}$), the Skaergaard LZ clinopyroxenes ($Ca_{39}Mg_{42}Fe_{19}$) are about four times richer in phosphorus yet they are similar pyroxenes.

The above discussion shows that the amount of phosphorus in the Bushveld cumulus minerals, like the Skaergaard minerals, is of a low order. From these mineral results it has also been shown that the phosphorus contents of many Bushveld rocks cannot be accounted for solely on the phosphorus in the total cumulus phase and, therefore, some of these rocks contain a significant proportion of mesostasis.

It is worthy of note that the order of entry of phosphorus into minerals is: olivine, plagioclase, pyroxene, which is the same order as in the Skaergaard cumulus minerals.

iii. The layered ultrabasic rocks of Rhum.

The total area of ultrabasic rocks in the island of Rhum, Inner Hebrides, is about 12 square miles. The petrology and structure of a quarter of this area were described by Brown (1956), and it was from this described region that further collecting was made and rocks and minerals analysed for phosphorus and some other elements, (see later).

The Hallival-Askival area described by Brown (op.cit.) is a rhythmically layered sequence of ultrabasic material. The rhythmic layering consists of an olivine rich rock ('peridotite') grading upwards into a felspar rich rock ('allivalite'). Above the felspar rich rock the rhythm is abruptly

delimited by another peridotite. Fifteen such rhythmic patterns, or units, have been recognised by Brown (op.cit.) and they give a structural height to the intrusion of about 2,600 feet. It is thought (Brown, op.cit.) that the layering was formed by gravity accumulation of cumulus minerals with the subsequent development of adcumulus and heteradcumulus phases. The cumulus minerals are only olivine, plagioclase felspar, clinopyroxene, and 'chrome-spinel'. Cryptic variation has not been found throughout the sequence. The fifteen units are referred to by numbers starting at 1 for the lowest observable unit. Each unit can often be traced over considerable lateral distances, and although very similar to others, each unit exhibits its own characteristics, (for fuller details, see Brown op.cit.).

The concentration of phosphorus in the rocks and minerals appears to be very low from previous published work. Brown (op.cit.) found 0.02 per cent. P_2O_5 in an allivalite from unit 3 (5875) but only traces of phosphorus in higher units. In the fine-grained olivine gabbro (5781) and the marginal gabbro -intrusions associated with the layered sequence - he found 0.01 and 0.05 per cent. P_2O_5 respectively and in an analysis of an olivine, 0.01 per cent. P_2O_5 was recorded. The deductions made from unit 3 about the composition of the contemporary magma (see Chapter 1) gave a P_2O_5 content of about 0.04 per cent. to the magma. Wadsworth (1961) found 0.03 per cent. P_2O_5 in an olivine adcumulate from another region of the ultrabasic area.

In thin section the rocks from most units appear to contain only a small amount of pore material except in the case of unit 3 where the felspars show fairly strong zoning. The whole rock phosphorus results of units 3,

7, 8, and 9 in Table 4 confirm this observation. Results are also presented for the fine grained gabbro and these are in close agreement with the previous analysis by colorimetry (Brown op.cit.). The result for 5875 (unit 3 allivalite) is however, higher than previously recorded.

Zoning does occur in the felspars of both the peridotites and the allivalites of units 7 and 8. The zoning (Brown op.cit.) is normal and in the peridotites is from An_{83} to about An_{70} with a lower range in the allivalite of unit 7.

Minerals from units 7 and 8 have been separated and analysed for phosphorus by activation analysis and the results are presented in Table 5. The minerals were quite readily separated from the rocks of unit 8 and in all these cases (except the chrome spinel*) the purity of the analysed material is estimated to have been greater than 99 per cent. Hand picking was carried out after separation by the normal techniques. It was difficult to assess the purity of the chromites and it is thought to have been only about 90%. Minerals were far more difficult to separate in a pure state from the unit 7 rocks. The felspar fractions were greater than 99 per cent. pure; the 17120 pyroxene greater than 98 per cent. with chromite as the main contaminant; 17120 and 17122 olivines greater than 98 per cent. pure with a little iron ore held in pyroxene as contaminant. It was not possible to obtain a pure enough sample of pyroxene and olivine from 17123 and this may partly be due to the alteration of some of the mafic minerals.

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* referred to as chromite.

TABLE 4

Phosphorus in some Rhum rocks

ROCK No:	UNIT & TYPE	RESULTS P ppm	MEAN	P_2O_5%
17129	9. Allivalite	43.6; 50.8	47	0.011
17128	9. Allivalite	56.0; 59.5	58	0.013
17127	8. Allivalite	66.1; 48.2	57	0.013
17126	8. Peridotite	61.0;	61	0.014
17125	8. Peridotite	68.3; 56.7	62	0.014
17124	7. Allivalite	80.8; 108.0; 79.6	90	0.020
17123	7. Allivalite	85.9; 74.5; 50.5	70	0.016
17122	7. Peridotite	115.1; 129.7	122	0.028
17121	7. Peridotite	112.7; 92.2	102	0.024
17120	7. Peridotite	93.0; 108.0; 80.0	94	0.022
5875	3. Allivalite	189.1; 185.2	187	0.043
5781	Olivine Gabbro	(42.8); 50.3	50	0.012

Analyst: P. Henderson.

( ) indicates that there was a slight loss of sample after irradiation and before processing.

TABLE 5

Phosphorus in some Rhum minerals

SPECIMEN		RESULTS P ppm	MEAN ppm.	P_2O_5%
17127	Plagioclase:	31.8; 34.3	33.0	0.008
Unit 8	Pyroxene:	25.0; 30.9	28.0	0.006
Alliv.	Olivine:	40.9; 40.4	40.6	0.009
17126	Plag.:	45.5; 37.6	41.6	0.010
Unit 8	Pyrox.:	15.3; 16.0	15.6	0.004
Perid.	Oliv.:	26.9; 30.5	28.7	0.007
17125	Plag.:	27.0; 27.2	27.1	0.006
Unit 8	Pyrox.:	19.9; 23.9	21.9	0.005
Perid.	Oliv.:	36.9; 36.3	36.6	0.008
	"Chromite"	186.2	190	0.043
17123	Plag.:	42.5; 43.8	43.2	0.010
Unit 7				
Alliv.				
17122	Plag.:	121.3; 118.3	120	0.027
Unit 7	Oliv.:	72.1; 65.1	69	0.016
Perid.				
17120	Plag.:	78.9	79	0.018
Unit 7	Pyrox.:	25.5; 21.7	24	0.005
Perid.	Oliv.:	86.1	86	0.020

Analyst: P. Henderson.

The rocks from unit 8 contain less pore material than those of unit 7. For this reason and because of the discussion in the paragraph above, the results for the minerals from unit 8 are considered to be more reliable as true indicators of the amount of phosphorus in the cumulus phases.

The 17126 felspar shows more zoning than that of 17125 and this is reflected in the phosphorus results. Excluding the 17126 felspar the order of entry of phosphorus into these minerals is: olivine, felspar, pyroxene, as it was in the Skaergaard and Bushveld cumulus phases.

The plagioclase felspars of unit 7 show some zoning which accounts for the high phosphorus values of the 17120 and 17122 felspars. However, the felspar separated from the allivalite (17123) is most likely to have contained a lower proportion of zoned material and thus the results for this mineral approach that of the concentration in the pure cumulus phase.

It is clear that the chromite contains a greater amount of phosphorus than the magnetite of EG.5181 (Table 1). The chromite is considered to have been a cumulus phase and during mineral separation well-formed octahedra of the mineral were noted. It cannot be ruled out, however, that some of the chromite may be from crystallisation of some trapped liquid and further investigation into this point is needed. However, the rocks 17125 and 17127 contain less than 1 per cent. by volume of the chromite (see Chapter 4) and so for the purposes of the present discussion the contribution from 'cumulus' chromite to the whole rock phosphorus content can be ignored.

iv. Discussion on aspects of phosphorus geochemistry.

For basic igneous rocks and indeed for many rocks, there are innumberable whole rock analyses which include data on phosphorus. On the other hand information about the presence of the element in many of the minerals that make up basic rocks is wanting. Phosphorus is commonly present in all igneous rocks. Turekian and Wedepohl (1961) in a synthesis of data showed the average distribution of the element in igneous rocks to be: 220 ppm (0.05% P_2O_5) in ultrabasic rocks; 1100 (0.25) in basaltic rocks; 920 (0.21) in high-calcium granitic rocks; 600 (0.14) in low-calcium granitic rocks; and 800 ppm (0.18% P_2O_5) in syenites. In nearly all basic rocks the concentration is between 0.01 and 2 per cent. P_2O_5 and is generally between 0.01 and 1 per cent.

It has been shown in this work that the presence of phosphorus in certain basic igneous rocks is not necessarily dependent upon the presence of apatite and that some phosphorus is in the silicate minerals. The partition coefficient of phosphorus between the magma and the silicate minerals is extremely small and it has been shown that most of the element (in the absence of cumulus apatite) is concentrated in the residual liquid during magmatic fractionation.

There is a school of thought that expounds an origin for many basalts which involves a magma, at depth, undergoing fractional crystallisation in much the same way as that of the Skaergaard magma. If this is so, then these basalts can be viewed as being made up of cumulus phases (as xenocrysts) and residual 'magma', and provided cumulus apatite is absent,

those basalts containing proportionately more 'magma' should be richer in phosphorus. Muir et al. (1964) suggest that well-developed gabbroic intrusions should occur at quite moderate depths below the basalts forming the crust of the rift of the Mid-Atlantic ridge and it is interesting to note that dolerites from part of the rift zone contain normal plagioclase crystals (xenocrysts) of An_{70} but that in an interstitial residuum there are finer laths of the same mineral with much more sodic composition (down to An_{28}). An analysis of these differing plagioclases may show the more sodic ones to be far richer in suitable low-k elements.

Lewis (1964) in a study of plutonic blocks from the Soufriere Volcano, St. Vincent, was able to separate and analyse some interstitial scoriaceous material. It is interesting to note that this is quite rich in phosphorus, 0.16 and 0.18 per cent. P_2O_5. Lewis considers that these blocks represent cumulates fractionated from a basic magma, probably at depth. The blocks show evidence of adcumulus growth; the presence of heteradcumulus minerals; and a texture akin to harrisitic growth. The composition of the interstitial material is that of a silica saturated basalt.

It is interesting to note, in connection with the above discussion, that the phosphorus content of olivines from an ankaramite and from an olivine nodule from Jan Mayen, are similar to those of some olivines from layered intrusions. Two new analyses are given in Table 6, together with comparisons. Koritnig (1965) found from 50 to over 500 ppm phosphorus in four 'olivine' samples (types or localities not stated).

TABLE 6

Phosphorus in some olivines

Source	P ppm.
NJ 21 Ankaramite	43.8
Nordbukta olivine nodule	26.9
Rhum 17125	36.6
" 17126	28.7
" 17127	40.6
Skaergaard EG.5086	80.6
Bushveld SA.681	38.2

Analyst: P. Henderson.

Vincent (1950) presented analyses of an olivine tholeiite dyke rock from East Greenland and of its separated residual glassy phase. The P_2O_5 contents are respectively 0.54 and 0.98 per cent. Vincent (op.cit.) states that this enrichment in the glass is mainly due to tiny inclusions of apatite, but presumably these apatites originated in situ from the 'magma'. More recently, Wilkinson (1966) showed that the glass from an alkali-olivine basalt was enriched in P_2O_5 compared to the whole rock, (0.89 and 0.80 per cent. respectively). The mode of this rock was given as olivine 14; clinopyroxene 22; plagioclase 30; opaques 9; glass 22; others 3 volume per cent. Thus, if one substracts the proportion of phosphorus in the glass from the whole rock result, one finds the concentration of phosphorus in the host to be about 0.77 per cent. This host includes needles of apatite which may well have crystallised from the 'magma' in situ, so that its presence complicates the above discussion. In those rocks containing

apatite it would not be surprising if the late stage glassy residuum was poorer in phosphorus than the host and such is the case of a nepheline-basanite analysed by Wilkinson (op. cit.). Studies of this kind would be more significant in the case of low-k elements that do not tend to form their own important mineral phase as readily as does phosphorus (viz. apatite). In the tholeiite and basalt described above it is possible that besides the glassy phase there are two generations of minerals: the xenocrysts (not formed in situ) and the crystalline groundmass (formed in situ). This groundmass plus the glassy residuum would be equivalent in genetic nature to the mesostasis of rocks from layered intrusions (see Appendix A). Alternatively, all the crystalline products may have formed in situ.

The shortage of data on phosphorus in silicate minerals had been alluded to, and this situation is reflected in a statement by Landergren (1954):

> "The radius of Si^{4+} is 0.39 A and that of P^{5+} is 0.35 A. Consequently a diadochic replacement of Si by P can be expected. Mason and Berggren (1941) have found more than 4 per cent. P_2O_5 in a spessartite garnet where part of the SiO_4 groups are replaced by PO_4 groups. In a few cases a content of phosphorus has been reported in rock silicates and it seems reasonable that the replacement phosphorus-silica in silicate minerals may be a rather common phenomenon, as suggested by Mason and Berggren".

Koritnig (1965) attempted to rectify this deficiency and his paper

appears to be the only recent one to deal specifically with the entry of phosphorus into silicates. To be sure that the minerals analysed for phosphorus were free of apatite inclusions, the powdered material (mesh size ?) was shaken with cold 5N nitric acid for five hours. Colorimetric analyses was carried out and 140 determinations both on leached and unleached minerals are presented. The non-leachable phosphorus is considered by Koritnig to be that occupying lattice sites, (though he does not present any convincing evidence that this is so) and from the results he calculates the average amount of phosphorus in lattice sites of various minerals (e.g. determinations of phosphorus in three different plagioclase felspars yielded the results 5.5; 30; and 46 ppm. giving an average of 27 ppm). From these averages he goes on to show that generally only a small amount of the phosphorus in a variety of igneous and metamorphic rocks can be accounted for by the amount in the silicates. Furthermore, from these averages, Koritnig concludes that the more condensed an SiO_4-tetrahedral association is, then the less phosphorus is able to enter the lattice sites.

The Skaergaard, Bushveld and Rhum results presented in this section agree with Koritnig's general conclusion that only a small amount of phosphorus in an igneous rock is within the silicates. It is, of course, questionable whether the mineral results presented earlier are of phosphorus occupying lattice sites, but they do present a maximum for the possible amount in lattice positions of these minerals from their respective environments. It has been found in this work that the ease of entry of phosphorus is in the order: olivine, felspar, pyroxene, which does not

agree with Koritnig's conclusion, though it has not been found possible to suggest a reason for this.

In the case of the Skaergaard intrusion it has been established that phosphorus, prior to the incoming of cumulus apatite, strongly favoured the residual magma, and it is clear that for the other intrusions, Bushveld and Rhum, a similar behaviour has been observed. It can be concluded, therefore, that the suitability of phosphorus as a low-k element has been established for these rock types without cumulus apatite.

C. Some data on bromine.

It has been suggested in section A that bromine and the other halogens may be suitable as low-k elements in basic igneous rocks prior to the formation of apatite. It was hoped, therefore, that a study of this element in some suitable Bushveld rocks would show a strong correlation with phosphorus. An activation analytical method described by Filby (1964) was used but was found not to be very suitable for reasons discussed in Chapter 7. The concentrations of bromine in the Bushveld rocks were found to be of a low order and results of two bromine activation runs had to be rejected simply because the count rate from the bromine was too low. The situation was rectified in two later runs but it meant working with very active material (see Chapter 7) and the results still left something to be desired. The reproducibility was found to be considerably worse than Filby (op.cit.) obtained. (He obtained a standard deviation from four W.1 determinations of 0.051, the bromine value being 0.496 ppm.). Furthermore, the bromine results showed no correlation with phosphorus, and

TABLE 7

Bromine in certain rocks

SAMPLE	RESULTS Br. ppm.	MEAN ppm.	P ppm.
SA 733	1.2; 1.1	1.2	44
SA 731	0.33; 0.19	0.3	76
SA 722	0.9; 1.0	1.0	29
SA 678	0.1;	0.1	24
SA 682	0.2;	0.2	10
SA 685	0.17; 0.35	0.3	29
G.1	0.50; 0.32; 0.26	0.36*	

Analyst: P. Henderson.

* Filby (1964) obtained 0.484 ppm.

it was decided for these reasons and for those presented in Chapter 7 not to pursue the investigation further. This decision was also prompted by the establishment, at Aldermaston, of a rapid method for uranium determination, (see Chapter 8) and as uranium is known, with a little more certainty than in the case of bromine, to be a low-k element, the investigation was redirected toward this element.

However, some bromine results were obtained and these are presented in Table 7 along with the appropriate phosphorus results. Although the bromine results are not considered to be very reliable they serve to show the absence of any significant correlation with phosphorus, (see also Chapter 7).

D. The geochemistry of uranium.

It has been suggested by many workers that uranium behaves as a low-k element during the fractionation of a basic magma (Adams et al. 1959, Larsen and Phair, 1954, Hamilton, 1959). The purpose of the work for this thesis was to attempt to confirm this behaviour and in so doing to observe if the element is suitable for the present study. General discussions about the geochemical behaviour of uranium can be found in the references cited and will not be repeated here. Hamilton (1959 and 1960) discussed the distribution of uranium in the Skaergaard intrusion and found 0.2 ppm in the chilled olivine gabbro and a range from less than 0.1 to 0.45 ppm. in the Layered Series. In felspars and pyroxenes less than 0.1 ppm. was recorded. No systematic work has been made on the distribution of uranium

in the Bushveld and Rhum intrusions though in the case of the former occasional analyses are scattered throughout the literature.

i. The Lower Zone of the Skaergaard intrusion.

The LZ is considered to be made up essentially of mesocumulates and orthocumulates. As it has been shown that most of the phosphorus in these rocks resides in the mesostasis then a close coherence should be observed between phosphorus and uranium if the latter is a low-k element. New analyses on some LZ rocks have been made by the delayed neutron activation method of analysis (see Chapter 8) and these are presented in Table 8. It is immediately apparent that there is a wide variety of concentration values though they are within a limited range (0.05 to 0.66 ppm.). A plot of phosphorus against uranium content of these rocks, Figure 3, shows the expected coherence between these elements. The phosphorus data are taken from Curren (1959) and from the late Professor Wager's records.

Selected minerals were also analysed to observe (i) if uranium entered pure cumulus minerals to a significant extent and (ii) in the case of those minerals which are considered to have formed partly from the trapped liquid (on the basis of the phosphorus data), if the uranium concentrations indicate a similar genesis. The mineral results are presented in Table 9 and show that the pyroxenes from adcumulates (5181 and 5052) contain very low concentrations whilst the felspars contain a negligible amount compared to the whole rocks of the LZ. On the other hand, those minerals which have come from mesocumulates show higher uranium values which in turn show a strong correlation with the phosphorus contents. The case of the felspar

FIGURE 3

Uranium variation with phosporus in Skaergaard L Z. rocks.

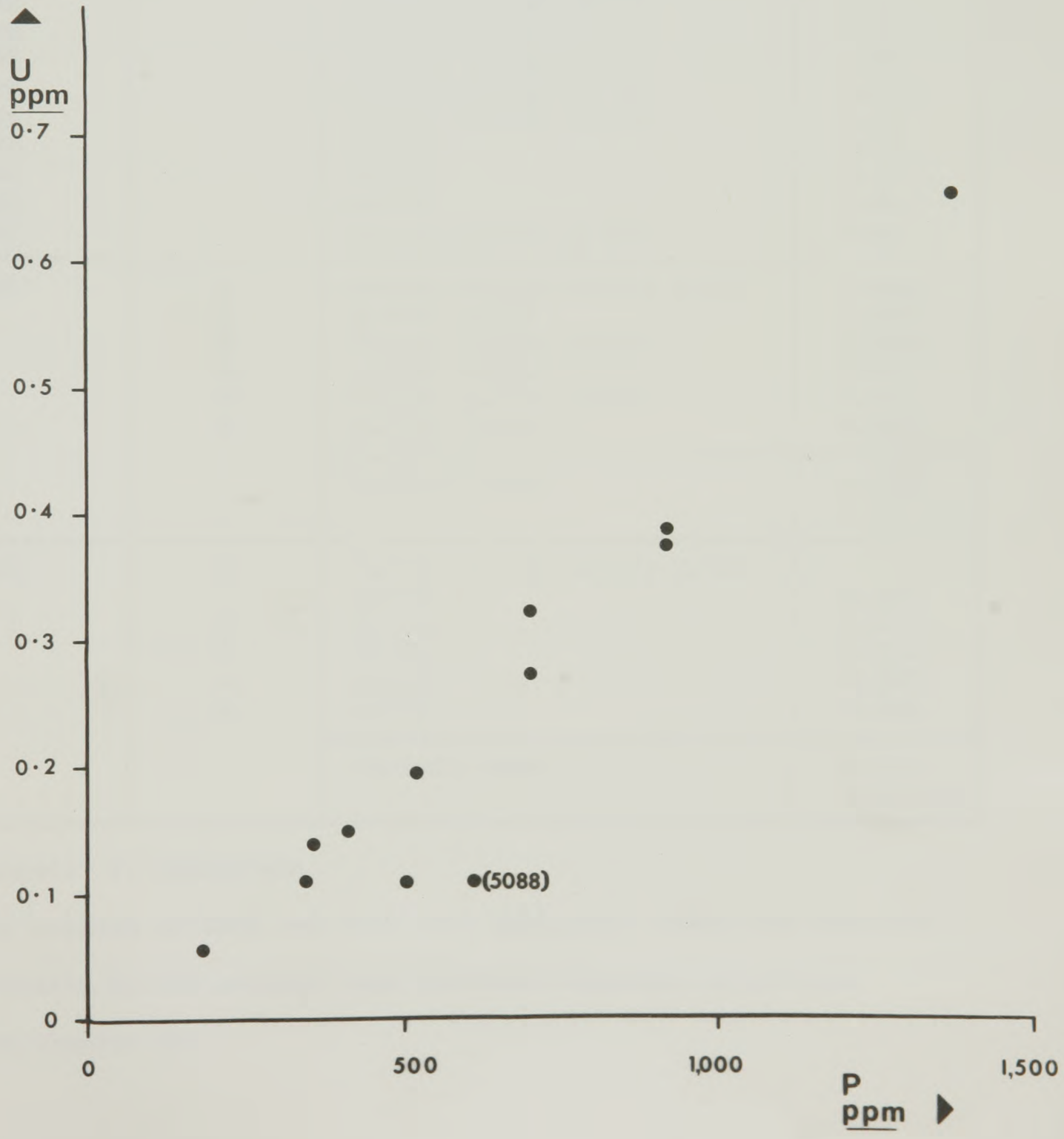


TABLE 8

Uranium in Skaergard Lower Zone rocks

ROCK No: EG:	SAMPLE	DETERMINATIONS ppm.	MEAN ppm.
5093		0.104; 0.115; 0.115	0.11
5092		0.054; 0.066; 0.049	0.06
5090		0.459; 0.471; 0.451	0.46
5089		0.313; 0.326; 0.340	0.33
5088		0.116; 0.103; 0.118	0.11
5086		0.107; 0.105; 0.119	0.11
5085		0.656	0.66
4532		0.154	0.15
5105		0.390	0.39
5107		0.184; 0.207; 0.198	0.20
5109*	1	0.254; 0.274; 0.254; 0.277	0.262
	2	0.298; 0.317	0.307
	3	0.292; 0.280; 0.267	0.280
	4	0.243; 0.323	0.283
	5	0.282; 0.278; 0.264	0.275
	6	0.244; 0.259	0.252
		Overall mean:	0.276 ± 0.017
5108*	1	0.150; 0.158; 0.167; 0.159	
		0.145	0.156
	2	0.125	0.125
	3	0.131	0.131
	4	0.158	0.158
	5	0.135	0.135
		Overall mean:	0.141 ± 0.014

Analyst: P. Henderson.

*Many samples of 5108 and 5109 were analysed. Thus, the standard deviation of the overall mean includes sampling variations, (see chapter 8).

TABLE 9

Uranium in some Skaergaard minerals

SPECIMEN No EG:	DETERMINATIONS: ppm.	MEAN ppm.
	FELSPARS	
5181	<0.030; 0.028; 0.024	<0.03
5052	<0.020; 0.011	<0.02
4389	0.057; 0.059	0.06
5093		
1st fraction	0.072	0.07
2nd "	0.015	0.02
5086	0.038; 0.054; 0.054	0.05
5109	0.048; 0.055; 0.063	0.06
5107	0.148; 0.128; 0.080; 0.141	0.13
	PYROXENES	
5181	0.059; 0.074; 0.069	0.06
5052	0.057; 0.058	0.06
5086	0.152; 0.180	0.17
	-160 mesh fraction	
5109	0.388	0.4

Analyst: P. Henderson.

fractions from 5093 is interesting as the ratio of the uranium concentrations in the two fractions is the same as that of phosphorus.

The relatively high concentration of uranium in the 5086 pyroxene confirms the deduction (see earlier) that some of this mineral formed from the trapped liquid. This fact is particularly important when it comes to applying the theory of Chapter 2 to these LZ orthocumulates and mesocumulates.

The -160 mesh fraction from the crushing of the rock 5109 for mineral separating was also analysed. It is considered likely, (Esson et al. 1965) that the finest fraction from the crushing of a rock for the purposes of mineral separation contains a relatively high proportion of the mesostasis material. The result for the rock 5109 shows that this fraction is enriched in uranium compared to the whole rock.

ii. The Bushveld intrusion.

Only a few analyses on Bushveld rocks and minerals have been made, Table 10. The minerals from the rocks 660 and 733 have very low concentrations and agree with the conclusion that these two rocks are adcumulates (see earlier). However, the whole rock values are far more difficult to interpret as there is little correlation between the phosphorus and uranium figures even when correction is made for the amount of phosphorus in the cumulus phases. Furthermore, some of the rocks contain a much higher concentration than the 'chilled gabbro' (0.07 ppm) which is surprising as these rocks are considered to be adcumulates and they are not very high

in the fractionation sequence. It is felt that this is because of the complexities inherent in the Bushveld intrusion rather than the complexities of the geochemistry of these elements. There is much evidence from published work which indicates that there was more than one influx of magma during the formation of the Bushveld fractionation sequence. Trace element studies may help to elucidate in more detail the history of crystallisation of this intrusion. This assumed complexity may also account for some of the lack of correlation between the bromine and phosphorus results of the Bushveld rocks.

It is interesting to note that the uranium concentrations in the pyroxenes are lower than the Skaergaard ones.

iii. The layered ultrabasic rocks of Rhum.

The results for the rocks and minerals of the Rhum intrusion, (see Table 11), confirm that these rocks are adcumulates with little pore material, except in the case of unit 3 where the rock 5875 contains a significantly higher amount of phosphorus. These results are entirely compatible with the phosphorus data (q.v.) and the work of Brown (1956).

iv. Conclusions.

It has been shown for the Lower Zone Skaergaard and Rhum intrusions that uranium behaves as a low-k element and that its distribution can be interpreted in much the same way as phosphorus. The very low concentrations of uranium in the overall cumulus phase* make this element perhaps even more

---

*excluding Skaergaard rocks very rich in pyroxene as the amount found in the adcumulus pyroxenes (0.06 ppm) would then be significant.

TABLE 10

Uranium in some Bushveld rocks and minerals

SAMPLE SA:		DETERMINATIONS ppm.	MEAN ppm.	P ppm.
1131*	Whole rock	0.136	0.14	14,000
733	Whole rock	0.023; 0.033	~ 0.03	44
732	Whole rock	0.217;	0.22	94
730	Whole rock	0.291;	0.29	195
660	Whole rock	0.088; 0.107; 0.108	0.10	49
1087	Whole rock	0.070; 0.073;	0.07	471
733	Felspar	0.022; 0.022; 0.026;		
		0.016	~ 0.02	
"	Ca-poor pyroxene	0.019; 0.017	~ 0.02	
660	Felspar	0.036; 0.028; 0.042;		
		0.021	~ 0.03	
"	Ca-rich pyroxene	0.034; 0.017; 0.045	~ 0.03	
"	Ca-poor pyroxene	0.040; 0.054; 0.040;		
		0.028; 0.036	~ 0.04	

Analyst: P. Henderson.

Those samples whose results are marked with an approximate sign had very low (i.e. less than three times background) neutron counts on determination.

TABLE 11

Uranium in some Rhum rocks and minerals

SAMPLE No.	DETERMINATIONS ppm.	MEAN ppm.
17127 Whole rock	0.020; 0.025; 0.025; 0.017; 0.029; 0.022	~ 0.02
17126 Whole rock	0.010; 0.011;	~ 0.01
17125 Whole rock	0.014; 0.009; 0.020; 0.024; 0.023; 0.025	~ 0.02
17123 Whole rock	0.019; 0.019; 0.019	~ 0.02
17122 Whole rock	0.034; 0.032	~ 0.03
17120 Whole rock	0.060; 0.042	~ 0.05
5875 Whole rock	0.051;	0.05
17127 Felspar	0.011; 0.014	~ 0.01
Pyroxene	0.039; 0.062; 0.046	~ 0.05
17125 Olivine	< 0.005	< 0.005
17123 Felspar	0.027; 0.023; 0.032; 0.017	~ 0.02

Analyst: P. Henderson.

Most of these results are only approximate as the samples contain such a small amount of uranium that they closely approached the sensitivity of the determinative method.

suitable for application in the theory of chapter 2 to the case of orthocumulates and mesocumulates, but its generally low concentration in basic magmas makes it a difficult element to analyse for in adcumulates even by activation analysis, and so in these rock types it is probably not so suitable as phosphorus. The results for the Bushveld intrusion indicate unknown complexities.

E. Aspects of strontium geochemistry.

The behaviour of strontium during the fractionation of a basic magma has been summarised by Turekian and Kulp (1956). It is fairly well-established that generally during fractionation the strontium concentration of the residual magma increases. It is also well-known that of the minerals generally crystallising from a basic magma, felspar and apatite are the ones that strontium enters to a significant degree: only small amounts being found in the pyroxenes and olivines. Carmichael and McDonald (1961) in a study of the geochemistry of some porphyritic pitchstones from the North Atlantic Tertiary province presented determinations of strontium in the felspar phenocrysts (xenocrysts?) and in the glasses and showed that for this element the felspar/glass partition coefficients ranged from 3.2 to 6.7.

Wager and Mitchell (1951) showed that the strontium content of the initial Skaergaard magma (based on the chilled olivine gabbro) was 350 ppm, and that the concentration steadily rose during fractionation so that the second liquid contained about 500 ppm. From then onwards the concentration decreased in the residual magma to 470 in the third liquid; 430 in the

fourth; 400 in the fifth; and 350 ppm. in the sixth liquid. A concentration of 1,000 ppm. was found in a LZ plagioclase whilst plagioclase, olivine, and pyroxene from the UZa contained 3,000; 100 (?); and 80 ppm. strontium respectively. From the data they had obtained, Wager and Mitchell (op. cit) deduced that the strontium plagioclase/liquid partition coefficients ranged from 2 to 6.

Loveridge et al. (1960) determined strontium in a number of UZ rocks and in the chilled olivine gabbro of the Skaergaard intrusion, by activation analysis. Hamilton (1963) published a few strontium analyses on some Skaergaard rocks (analysis by X-ray fluorescence and isotope dilution). Brooks (1965) presented a number of analyses (by XRF) of strontium in a variety of rocks and minerals including some of the Skaergaard intrusion.

There are no published strontium determinations on the rocks of the region of the Rhum intrusion under study.

Strontium has been determined in a number of rocks and minerals mainly in the hope that the data so obtained could be applied to the theory discussed in Chapter 2. Certain geochemical aspects, however, haveemerged from the results that necessitate some brief discussion. The results for the Skaergaard rocks and minerals are presented in Table 12, and those for Rhum in Table 13.

The felspars from the Skaergaard rocks 5107 and 5109 contain 482 and 449 ppm respectively. These results would indicate that the plagioclase/liquid partition coefficient (k) for strontium was less than 1, if the

TABLE 12

Strontium in some Skaergaard rocks and felspars

SAMPLE EG:	STRONTIUM ppm.	MEAN ppm.
5093	220.8; 221.3	221
5092	74.9;	75
5090	438.9; 432.1	436
5089	423.2; 425.9	425
5088	162.7	163
5086	184.8; 181.7	182*
5109	423.1; 426.6;	
	428.2; 420.0	424
5108	40.0; 40.1;	
	39.8; 40.3	40
5109 Plagioclase	476.4; 487.3	481
5107 Plagioclase	448.7	449

Analyst: P. Henderson.

* Brooks (1965) obtained 237 using an internal standard XRF method. Hamilton (1963) obtained 133 by isotope dilution. The average of these two is 185 !

TABLE 13

Strontium in some Rhum rocks and minerals

SAMPLE	UNIT	STRONTIUM ppm.	MEAN ppm.
17127	8 Alliv.	191.5; 192.4	192
17125	8 Perid.	70.7; 71.0	71
17123	7 Alliv.	202.4; 202.3; 200.5	202
17120	7 Perid.	88.8; 98.1	93
17127 Felspar	8 Alliv.	305.5; 301.2; 305.5	304
17125 Felspar	8 Perid.	437.7	438
17123 Felspar	7 Alliv.	300.8; 301.7; 302.4	302
17120 Felspar	7 Perid.	42.2; 420.7	420
17126 Pyroxene	8 Perid.	19.6; 19.7	20
17120 Pyroxene	7 Perid.	32.1; 31.8	32
17127 Olivine	8 Alliv.	<3	<3
17125 Olivine	8 Perid.	<3	<3

Analyst: P. Henderson.

the estimate by Wager and Mitchell (op.cit.) of the strontium content of the second liquid (500 ppm) is correct. However, Loveridge et al. (op.cit.) recorded a lower figure (267 ppm. by activation analysis) for the chilled olivine gabbro than Wager and Mitchell (by emission spectroscopy) had done (350 ppm), so it is possible that the figure of 500 ppm. is too high. As it is fairly well-established that the k value is greater than 1 under these conditions and it is also likely that strontium increased in the liquid throughout the formation of the Hidden Zone, the strontium content of the second liquid was probably somewhere between 270 and 480 ppm. The lower result for 5109 compared with 5107 felspar can be accounted for by the more extensive zoning in the former. The results for the Lower Zone rocks are used and discussed further in Chapter 4.

The Rhum felspar results are especially interesting. Felspars from the two allivalites both have a concentration of about 300 ppm., yet the poikilitic felspars from the peridotites contain over 400 ppm. This difference cannot be attributed to zoning in the allivalite felspars as this is not so extensive as to cause such a significant difference, especially as the plagioclase/liquid partition coefficient is probably not a large number. Clearly a more detailed investigation, with regard to trace element content, into the Rhum felspars is needed. The poikilitic felspars have strontium contents very similar to those of the Skaergaard LZ plagioclases.

Summary

The suitability of elements for the application of the theory presented

in chapter 2 has been discussed and it is concluded that only a few are suitable as high-k or low-k elements. An investigation into the distribution of phosphorus in three layered intrusions has shown the suitability of it as a low-k element, prior to the formation of cumulus apatite. The amount of phosphorus in the cumulus phases is of a low order compared to the Skaergaard LZ rocks. The fact that most of the phosphorus in many of the Rhum and Bushveld rocks can be accounted for by the amount in the constituent cumulus plus adcumulus phases shows that these rocks are mainly adcumulates, though unit 3 of Rhum is shown to have comparatively more mesostasis in the allivalite. The order of entry of phosphorus into the cumulus minerals in all three intrusions is: olivine, felspar, pyroxene. L.R. Wager's work on the distribution of phosphorus in the Skaergaard rocks is generally substantiated though some of the details have been altered.

In the Skaergaard Lower Zone rocks there is a strong coherence between uranium and phosphorus. The amount of uranium in the cumulus phases olivine, pyroxene, and felspar, is of a low order though a measurable amount is found in the pyroxenes. The situation is similar in the Rhum intrusion. In the Bushveld intrusion the expected coherence between phosphorus and bromine was not observed, nor was any coherence between phosphorus and uranium noted. More work into the geochemistry of this intrusion is clearly needed.

Some strontium determinations in a few Rhum and Skaergaard rocks show that if the Sr_{plag}/Sr_{liq} partition coefficient is greater than one, then the strontium content of the Skaergaard LZ contemporary magma was less than

500 ppm., and that of Rhum probably less than 300 ppm. The strontium contents of the felspars from the peridotites of Rhum are significantly higher than those from the allivalites in units 7 and 8.

CHAPTER FOUR

Attempts at Applying the Theoretical Method.

A. Introduction.

It has been shown in chapter 3 that phosphorus and uranium are suitable low-k elements and some data for the high-k element, strontium, have been presented. It is the purpose of this chapter to make a preliminary investigation into the application of the theory outlined in chapter 2 and for this the data presented earlier will be used. Certain parts of the theory also demand knowledge of the modes and specific gravities of the rocks. New determinations of these quantities for many rocks are presented in this chapter.

One of the requirements of the theory is that all concentrations should be in units of weight per unit volume. It has thus been necessary to convert the data presented into the appropriate units. To do this a standard specific gravity of 3 has been decided upon so that all converted concentrations are in weight per one-third c.c. The reason for this choice is that the specific gravity of the chilled olivine gabbro is close to 3 (2.98 and 2.95 recorded in Wager and Deer 1939), so that the results obtained, by the application of the theory, of the amount of any element in the magma can be directly correlated with the element's ppm. figure in the gabbro. Similarly, the magma probably had a density not far from 3 so that the results obtained are very close to their weight per unit weight values.

One of the assumptions of the theory was that the low-k element did not enter any of the cumulus (or adcumulus) minerals. It is clear from chapter 3 that such an ideal situation is unlikely to be encountered, though uranium and phosphorus are not far from the ideal. In cases where the low-k element does enter the cumulus phases slightly, a correction to the whole rock low-k element must be made. This will be difficult to do exactly, as the proportion of the mesostasis is, as yet, undetermined. However, provided the entry of the low-k element into the cumulus phases is very low compared to the whole rock, negligible error will be introduced by assuming that all the material, which is obviously not of the mesostasis, is cumulus. The actual low-k element correction can also be found by successive determinations of the proportion of the mesostasis, each time making more accurate corrections for the cumulus low-k element content. However, it is unlikely that such a method will be necessary except perhaps in some orthocumulates.

B. Application of the first method.

Equation (7) of chapter 2 is used:

$$p_A = \frac{(T_A - C_A) - W(T_B - C_B)}{(C_B - C_A)}$$

where p_A is the proportion of the mesostasis in rock A, T_A and T_B are the whole rock concentrations of the high-k element (in this case strontium), W is the ratio of the mesostasis in the two rocks A to B

derived from the corrected phosphorus and uranium whole rock concentrations. C_A and C_B are the concentrations of the high-k element in the overall cumulus phases as derived from knowledge of the concentration of the high-k element in each of the cumulus minerals and the relative proportions of the minerals that make up the total cumulus assemblage.

i. The Lower Zone, Skaergaard Intrusion.

The first method requires the presence of rhythmic layering. The frequent occurrence of rhythmic layering in the Lower Zone makes these rocks suitable from that point of view. However, most of the LZ rocks are mesocumulates or orthocumulates and it has already been stated that the application of the theory to such rocks is not straightforward. In these cases it is generally necessary to use mineralogical evidence as an aid in the determination of the relative proportions of the minerals that make up the total cumulus assemblage. These proportions, because of the nature of the evidence, cannot be very accurate but, provided the rocks are markedly leucocratic or melanocratic, they should be suitable for the application of the theory. Thus, mineralogical evidence and application of the theory must be used together to produce a self-consistent result.

Two sets of rocks have been studied, those from 110 metres in LZa and those at 280 metres in LZb. Data on the appropriate minerals are to be found in Table 14 which gives the specific gravities, the low-k and high-k elements concentrations both in ppm. and in the volumetric units,

TABLE 14

Data for the Lower Zone minerals

MINERAL	S.G.$_1$	Pppm.$_2$	Uppm.$_2$	Sr ppm$_2$	P vol$_3$	U vol$_3$	Sr vol$_3$
PLAG.	2.70	40	0.02	481	36	0.02	433
OLIVINE	3.69	81	Neglig	0	100	Neglig	0
PYROXENE	3.38	30	0.06	18	34	0.06	20

Sources 1. Specific gravities from Wager & Deer (1939) and Deer et al (1963).

2. Concentrations (ppm.) based on results from chapter 3. Sr concentrations in olivines and pyroxenes from Brooks (1965).

3. Concentrations converted to the volumetric units (see text).

TABLE 15

Data on the Skaergaard (LZ) rocks

ROCK	S.G.$_1$	P ppm$_2$	U ppm$_2$	Sr ppm$_2$	P vol$_3$	U vol$_3$	Sr vol$_3$
5108	3.48	a 655 b 349	0.141	40	a 759 b 405	0.164	46
5109	2.81	a 895 b 698	0.276	424	a 837 b 654	0.258	397
5086	3.18	506	0.111	183	536	0.118	194
5088	3.43	615	0.112	63	703	0.128	72
5089	2.75	722	0.326	425	662	0.299	390
5090	2.75	-	0.460	436	-	0.422	400
5092	3.35	188	0.056	75	210	0.062	84
5093	3.07	340	0.111	221	348	0.114	226

Sources: 1. Determined by P. Henderson, see Appendix D.

2. From chapter 3 and Curren (1959), a = activation analysis result
b = colorimetric result

3. Concentrations (ppm) converted to the volumetric units.

TABLE 16 A*

Further data on Skaergaard (LZ) rocks

ROCK		PLAG.	OLIV.	PYROX.	IRON ORE.	REM.	TOTALS	TOTAL P less cumulus P.
5108	1. MODES	8.1	69.4	20.2	0.8	1.5	100	-
MELAN	2. MESOSTASIS	Yes	No	67	Yes	Yes	16?	-
(110m)	3. P(cumulus) contrib to rock	-	69	3	-	-	72	a 687 b 333
	4. Sr contrib to cumulus	-	neg.	3	-	-	3	
5109	1	82.9	0.3	13.4	1.3	2.0	99.9	
LEUCO	2	10%?	Yes	9%?	Yes	Yes (inc qtz + apatite)	21%	
(110m)	3	26	-	1	-	-	27	a 310 b 627
	4	411	-	1	-	-	412	

* For description see text.

MODES: 5108 P. Henderson

5109 L.R. Wager

(see above). Table 15 presents the required data for the LZ rocks. Table 16 (A and B) is a compilation of data for each rock: the first row gives the mode in terms of the minerals: plagioclase, olivine, pyroxene, iron ore and remainder. The remainder includes such minerals as apatite, quartz, etc. which are obviously of the mesostasis. The second row gives the assumption (generally based on mineralogical evidence) on which minerals, or what proportions of the minerals, are of the mesostasis. The third row gives the phosphorus contribution to the whole rock that the assumed cumulus proportion makes. The fourth row states the amount of strontium that each mineral contributes to the total cumulus assemblage which is based upon the assumed proportions derived from the second row. The correction to the whole rock uranium content based upon the amount in the cumulus minerals is not given as it is considered that this correction is probably negligible, except in EG 5088 and 5093, as concentrations in the cumulus minerals are not known with sufficient accuracy, see chapter 3. Correction is made in the cases of 5088 and 5093 as these are pyroxene rich rocks.

EG. 5108 and 5109

On the basis of the mineralogy and texture, Wager (1960) considered the rock 5109 to be an orthocumulate, with plagioclase as the only cumulus mineral so that the pyroxene, ore, olivine, apatite, and quartz must have come from the trapped liquid. The plagioclase is zoned from about An66 to An55, and this is considered to be due to its crystallisation, in part, from the trapped liquid. The rock 5108 contains a significant amount of mesostasis, as apatite and some late stage minerals are present.

Furthermore, the plagioclase is poikilitic and zoned and most of it is likely to be of the mesostasis. In 5108 the olivine shows no zoning and appears as a pure cumulus phase but in 5109 the small amount of olivine is as skeletal poikilitic crystals and is more iron rich than the 5108 olivine, (Wager, op.cit.) In both of the rocks the iron ore exists as poikilitic patches and is unlikely to be a heteradcumulus phase especially as these rocks are about 600 metres below the horizon where cumulus magnetite enters.

Chemical evidence for the genesis of the different minerals is as follows: the 5109 felspar contains a relatively high amount of phosphorus which is interpreted as being due to crystallisation of some of the mineral from the trapped liquid, (see chapter 3). The phosphorus and uranium contents of the two rocks indicate that 5109 contains about one and a half times as much mesostasis as 5108 so it would be expected that 5108 would have less pyroxene than 5109 if in both rocks it crystallised from the trapped liquid. The fact that 5108 has more implies that some of this mineral is a heteradcumulus phase. An attempt was made to separate out the pyroxene from 5108 but it was closely associated with iron ore. An analysis of the contaminated pyroxene gave a phosphorus figure of about 300 ppm. which indicates that one or both of the minerals crystallised at least in part from the trapped liquid. Provided that all the felspar in 5108 is of the mesostasis it makes little difference to the total cumulus strontium figure how much pyroxene is heteradcumulus as the amount of strontium in the cumulus pyroxene and olivine is very small compared to the whole rock. Some workers (e.g. Esson et al, 1965) have presented

chemical evidence that the ore in the early LZ rocks is from the trapped liquid.

From the above discussion it would seem that in 5109, plagioclase is the only cumulus or adcumulus phase and that in 5108 all the olivine and about 9 per cent. from the pyroxene are cumulus and heteradcumulus phases respectively. Using these mineral proportions the high-k element values for C_{5109} and C_{5108} can be found. These values can then be used in the above equation. The other required data for the equation can be found in Tables 14, 15 and 16A. Both the phosphorus contents as recorded by colorimetry and by radio activation analysis are listed for these two rocks, though the average of the two phosphorus ratios and the ratio from the uranium values is taken for the value of W. The results obtained are p_{5109} = 34%, and p_{5108} = 21%. However, on this basis the strontium content of the magma obtained by substitution of these values does not agree in the two rocks. There is agreement in the strontium content if it is assumed (see also chapter 5) that some of the pyroxene is a heteradcumulus phase in 5109. The assumed proportions of the cumulus minerals are given in Table 16A and the results p_{5109} = 20% and p_{5108} = 13% with M (Sr) = 340 are obtained. (The figure for the content of strontium in the magma cannot be considered to be very accurate though it is probably of the right order).

The fact that the results obtained are in agreement with the assumptions and that the values are reasonable in the light of other petrological and geochemical work on the Skaergaard rocks in general, would imply that the initial assumptions are well founded.

TABLE 16B

		Plag.	Oliv	Pyr	Ore	Rem.	Total	P correct
5088	1 MODE	7.1	26.7	60.9	4.0	1.2	100	
MELAN	2 MESOSTASIS	Yes	No	Some?	Yes	Yes (+ apatite)	?	
(280m)	3 P CUMULUS CONTRIB.	-	27	21	-	-	48	655
	4 Sr. CONTRIB. TO CUMULUS	-	neglig	14	-	-	14	
5089	1	89.4	-	5.0	0.7	4.9	100	
LEUCO	2	Some	-	Yes	Yes	Yes (inc qtz + apatite)	?	
(280m)	3	30	-	-	-	-	30	632
	4	433	-	-	-	-	433	
5090	1	87.8	-	8.6	0.3	3.3	100	
LEUCO	2	Some?	-	Yes	Yes	Micropeg Yes	?	
(280m)	3	30	-	-	-	-	30	-
	4	433	-	-	-	-	433	
5092	1	17.1	50.3	27.7	4.5	0.4	100	
MELAN	2	6%?	No	Some?	Yes	Yes	10%	
(280m)	3	4	50	9	-	-	63	147
	4	54	Neg.	6	-	-	60	
5093	1	52.1	-	43.0	4.2	0.7	100	
LEUCO	2	15%?	-	No?	Yes	Yes	20%	
(280m)	3	13	-	15	-	-	28	322?
	4	200	-	11	-	-	211	

Modes: 5090; 5092; 5093; P. Henderson

5088; 5089; L.R. Wager.

The 280 metre rocks, MG. 5086 to 5093.

The six rocks studied all come from about the same horizon in the LZb. The rocks 5088 and 5090 are the most suitable of the six for application of the theory as it is relatively easy to assess the proportions of the minerals in the cumulus phase, (Table 16B). These three are dealt with first.

5089 and 5090 are inclusion-like masses in the Layered Series, 5089 being at least 40 yards across. They are unlike the hybrid inclusions (Wager and Deer 1939) and are considered to be non-laminated parts of the Layered Series, (Wager, personal communication). All of these rocks, except 5086, contain traces of apatite. 5089 and 5090 also contain quartz so that these two clearly have a high proportion of mesostasis.

5088 and 5090.

In 5088 the small amount of the poikilitic plagioclase is zoned and all of it is assumed to be of the mesostasis. No assumptions have to be made concerning the crystallisation of the pyroxene as it can be seen from the mode that changes in the assumed amount of heteradcumulus pyroxene have little effect on the strontium content of the total cumulus phase provided that all the plagioclase is of the mesostasis. In 5090, however, it seems reasonable to assume that the small amount of pyroxene is of the mesostasis. The plagioclase in this rock is much zoned and, together with the fact that micropegmatite is present, would imply that 5090 has a significant amount of mesostasis.

From the above discussion it is possible to find C_{5088} and C_{5090}, (see Table 16B). The ratio, W, is determined from the corrected uranium

values. The results obtained are p_{5088} = 16%, p_{5090} = 63% and M (Sr) about 370.

5088 and 5089.

As in 5090, the small amount of pyroxene in 5089 is assumed to be of the mesostasis. The corrected uranium values are used in the determination of W as the 5088 phosphorus result is probably anomalous (see Figure 3). The results are p_{5088} = 18%, p_{5089} = 49%, and M (Sr) about 340.

The other three rocks are not very suitable for the application of the theory as they contain three minerals that make up the total cumulus assemblage and thus, it is difficult to assess their relative proportions. However, as the discussion below shows, the application of the method is not fruitless. The results obtained and some of the assumptions that are made are necessarily tentative. Once the concentration of a low-k element in the magma is known accurately from more suitable rock types at the same horizon (as above) it is, of course, a simple matter to deduce the amount of pore material in the unsuitable rocks.

5088 and 5093.

Most of the pyroxene in 5093 appears to be cumulus from microscopic examination. The felspar is zoned and some must have originated from the trapped liquid. Furthermore, it has been shown earlier (chapter 3) that a substantial amount of the plagioclase is enriched in phosphorus and uranium compared to the whole rock. In view of the above one can assume that the pyroxene modal value of 43 per cent is not far from the actual amount of cumulus pyroxene present in the rock so that the limits for the proportion of cumulus felspar to pyroxene can be put at 0:43 and 52:43. A ratio of 28:43 or less produces a negative figure for the proportion of mesostasis

(using 5088 as the rock B in the equation) whilst a ratio of 45:43 or greater gives a very high and unlikely p figure to 5088. A ratio of 36:43 or less gives a result for p_{5093} that is so small that it is not consistent with the initial assumptions i.e. with this ratio there must be at least 20% mesostasis yet the determined value using this ratio is only 17%. It appears, therefore, that the felspar : pyroxene ratio lies somewhere between 36:43 and 45:43 but it is not possible to be more precise than this. However, a ratio of 37:43 gives a reasonable result of p_{5093} = 18% p_{5088} = 20% and M (Sr) = about 280.

It was attempted to derive the p_{5093} value using 5090 or 5089 as 'B' rocks but there was no ratio of felspar to pyroxene that gave a reasonable result that was consistent with the initial assumptions about the ratio. This failure is presumably due to inaccurate data or insufficient information concerning the assemblage of the cumulus plus adcumulus phase. The case of 5093 shows the difficulty of applying the theory to certain mesocumulates and orthocumulates though it also shows that some evaluation of cumulus mineral proportions can be made. Data on other high-k elements in the rocks could help to solve more precisely the equations and remove the discrepencies discussed above.

5089 and 5092.

Under the microscope the olivine and most of the pyroxene of 5092 appear as pure cumulus phases whilst the felspar is zoned and extends into the intercumulus parts. The rock contains little pore material (about 10 per cent.) on the basis of its phosphorus and uranium concentrations so that if one assumes there to be about 10% pore material with about 6

consisting of felspar and the rest as iron ore etc., one obtains the results $p_{5089} = 41\%$; $p_{5092} = 9\%$, which is not bad agreement. If 5090 is used as rock 'B' one obtains $p_{5090} = 53\%$ and $p_{5092} = 8\%$. These figures would seem to be of the right order but it is not possible to be more precise.

5086.

Certain aspects of the geochemistry of 5086 appear to be anomalous in comparison with other rocks of the Lower Zone by the rock having extraordinarily high concentrations of some elements, see Vincent and Crocket 1960; Esson et al 1965. It was hoped to be able to apply the equations to this rock in order to obtain the amount of mesostasis and to see if this could help in elucidating the reasons for such anomalies. However, the rock is an average one and it has not been found possible to deduce the proportions of the minerals in the cumulus phase with any precision. The phosphorus and uranium results imply that the rock has about 20 to 30 per cent. mesostasis.

Conclusions:

From the above results on the Skaergaard Lower Zone rocks, certain conclusions (some necessarily tentative) can be drawn:

1. That there is a wide variation in the amount of the mesostasis in the rocks of the Lower Zone.
2. That the inclusion-like masses at 280 metres appear to be local places where much contemporary magma was trapped.
3. That the strontium content of the contemporary magma was probably of the order of 340 ppm. (c.f. Wager and Mitchell's (1951) estimate of 500 ppm.

and the earlier discussion) so that C plag./C liquid partition coefficient is of the order of 1.4 at this fractionation stage.

4. The phosphorus content of the contemporary magma was of the order of 2,000 ppm. (c.f. Wager and Mitchell's estimate of 1,260 ppm.) and the uranium content was of the order of 1 ppm.

ii. The Rhum rocks.

The Rhum rocks are suitable insofar as there is much rhythmic layering present in the area studied. It is questionable whether the trace element content of the magma stayed the same during the deposition of each unit though for the present purposes this is assumed to be so. The rocks are also suitable in that they are adcumulates. The only disadvantage for the present study is the fact that the ~~strontium contents of the~~ felspars from the peridotite and allivalite of the same unit do not have the same strontium contents (see chapter 3). However, it seemed worthwhile to attempt te apply the method to these rocks and so the strontium content of the respective felspar was taken to be that in the cumulus felspar of that rock.

The data for the rocks and minerals are presented in Tables 17 and 18. The application of the method to the unit 8 rocks 17127 and 17125 gives the results P_{17127} = about 8%, P_{17125} = about 6%, and M (Sr) = about 190.

The unit 7 pair are less suitable as they are not fresh specimens and the ratio W is difficult to determine as the unit 7 mineral results for phosphorus are not very consistent. The unit 8 olivine phosphorus concentration has been used (see Table 17), with the selected unit 7

TABLE 17

Data on Rhum rocks and minerals

SAMPLE		S.G.$_1$	P ppm$_2$	Sr ppm$_3$	P. vol$_3$	Sr vol$_3$
17127 WR (unit 8) (Alliv)		2.94	57	192	56	188
17125 WR (8 Perid)		3.26	62	71	68	77
17123 WR (7 Alliv)		2.90	70	202	68	195
FELSPAR	Unit 8	2.73	33	438*	30	399*
	Unit 7	2.73	43	420*	39	382*
Sr Allivalites		-	-	303	-	276
PYROX	Unit 8	3.33	16	20	18	22
	Unit 7	3.33	16	32	18	36
OLIVINE		3.44	33	< 3	42	< 3

* for peridotite only.

Sources: 1 Specific gravity: rocks: determined by P. Henderson (see Appendix D)

minerals: taken from G.M. Brown (1956)

2 Values selected from chapter 3.

3 Converted from ppm values to weight per 1/3 cc. (see text)

TABLE 18

Data on the Rhum rocks

ROCK		PLAG.	OLIV.	PYROX.	'CHROMITE' ETC	TOTALS	PHOSPHORUS CORRECTED.
17127	1 MODE	67.5	27.0	4.9	0.6	100	-
Unit 8	2 P cumulus contribution	20.2	11.3	0.9	-	32	24
Alliv.	3 Sr contrib to cumulus	186	~ 1	1	-	188	-
17125	1	16.9	73.4	8.4	1.3	100	-
Unit 8	2	5.1	30.8	1.5	-	37	31
Perid.	3	67.6	~ 2	1.8	-	71	-
17123	1	73.8	18.8	6.8	0.5	99.9	-
Unit 7	2	28.8	16.9	1.2	-	47	27
Alliv.	3	204.0	~ 1	2.4	-	207	-
17120	1	26.2	60.6	10.8	2.4	100	-
Unit 7	2	10.4	25.4	1.9	-	49	49
Perid.	3	100	~ 1	4	-	105	-

Modes: P. Henderson.

felspar value in determining the correction to the whole rock phosphorus value. The W value so obtained is of about the same order as that indicated by the whole rock uranium results (see chapter 3). The results are $P_{17120} = 14\%$, $P_{17123} = 8\%$, and they indicate that these rocks may be regarded as mesocumulates, though these results cannot be considered to be very accurate. In the case of adcumulates a high-k element with a higher partition coefficient than strontium would be more suitable as it would be more sensitive to changes in the proportion of the mesostasis.

It is possible that the fine-scale layering found in some of the units may be more suitable material on which to apply the theory.

iii Other layered intrusions.

The application of the method to other layered intrusions should be feasible, especially the Bushveld and Stillwater intrusions (Hess 1960) where rhythmic layering is often well developed. The phosphorus results for the Bushveld have shown that there is a variation in the amount of the mesostasis and many of the rocks appear to be adcumulates and would, therefore, be suitable for the method. It is interesting to note that Jackson (1961) in a study of the ultramafic zone of the Stillwater Complex concluded that the 'trapped magma in the average chromitite apparently contained slightly larger amounts of iron and magnesium, and less aluminium, than the trapped magma in the average poikilitic harzburgite', (page 89). If this conclusion is correct then the application of the method to the Stillwater would not be possible insofar as the premise, that the trapped liquid represented the contemporary magma and would therefore not be expected to change significantly over small fractionation increments,

would be invalidated. However, Jackson, bases these conclusions on amounts of the mesostasis that are derived by a microscopic method and it is not claimed that this method is accurate. Furthermore in this work interstitial material is equated with 'trapped liquid' and this may not be accurate insofar as it ignores the reaction replacement material.

It may be possible, by suitable selection of material, to apply this method to certain ejected plutonic blocks such as those described by Lewis (1964). However, this has not been investigated.

C. Application of the second method.

The 'second' method is unlikely to find much application but it has been discussed because from it the 'first' method evolved. It is not likely that in layered intrusions the proportions of the various minerals that make up the cumulus plus adcumulus assemblage will be exactly the same along the strike of any one layer, which is required for this method. If they are then the possibility of there being significantly different amounts of mesostasis along the strike seems remote. There is also the difficulty of collecting material from along the strike of exactly the same horizon. This was attempted in the Rhum intrusion but it was found to be very difficult. Brown (1954, page 127) made two traverses a mile apart of unit 8 and recorded the modes of rocks at similar heights from the base of the unit, and showed that the agreement between the two traverses was good though the pyroxene percentage showed many fluctuations from one rock to the next. From the Rhum intrusion some rocks were collected along the strike to observe if there was any significant change in the amount of phosphorus concentration. 17125 is a peridotite of unit 8 and

was collected at a distance of about 20 feet laterally from 17126, but they both have closely similar phosphorus contents. A peridotite 17120 from unit 7 collected 260 feet laterally from 17122 does show a slightly lower amount of phosphorus (94 and 122 ppm respectively). Two rocks (17128-9) collected 700 feet apart from the unit 9 allivalite show a significant difference though it cannot be certain that they are both from the same horizon within the allivalite.

It is interesting to note that Cameron (1963) recorded a variation in the lithology of some pyroxenites along the strike of the Critical Zone of the Bushveld intrusion.

The second method may find application in those basalts with only one mineral present as phenocrysts which show variations in their distribution within the basalt. By selecting three rocks with different ratios of phenocrysts to groundmass; and analysing each for a high-k and low-k element it would be possible to deduce the concentration of the high-k element in the groundmass and in the phenocrysts without separation of material, (see chapter 3). In a similar way it may be possible to apply this method to the ejected plutonic blocks of the kind described by Lewis (1964) by careful selection of material.

D. Conclusions.

The application of the first method has been demonstrated both for mesocumulates and adcumulates, though the success has been limited. It has been shown that in the cases of orthocumulates and mesocumulates, the method is workable provided that mineralogical evidence is used. Although the method has severe limitations much can be deduced from its application to these rock types. In adcumulates the method may well be satisfactory

though a more suitable high-k element than strontium would be desirable as the strontium plagioclase/liquid partition coefficient does not appear to be a large number. An element with a high partition coefficient would be more suitable as its concentration in a rock would be more sensitive to changes in the proportion of the mesostasis.

The application of the second method is shown to be unfeasible in the case of layered intrusions though it may have some application in certain volcanic rocks.

CHAPTER FIVE

Aspects of Textures and Mineralogy

Part One of this thesis is primarily concerned with the geochemistry of the mesostasis of some fractionated igneous rocks and the mineralogical aspects where previously discussed have generally been incidental. However, certain aspects of the mineralogy have emerged in this study which it is felt deserve some comment though a rigorous treatment is outside the scope of this work.

A. Habit.

The habits of the various minerals that make up the Skaergaard and Rhum rocks have been well described, (Wager et al 1960), Brown 1956). It is noteworthy that in many of the Skaergaard LZ orthocumulates and mesocumulates some of the minerals that have crystallised from the trapped liquid exist as small poikilitic patches which are separated from each other by a few centimetres, see Plates 1 and 2. Such is the case of the olivine and iron ore in EG. 5109, (Wager, 1960).

It would appear, therefore, that after the trapped liquid had been sealed off from the overlying magma, interpore diffusion of elements in the trapped liquid could still occur, so that fractionation of the liquid was possible. It is interesting to note that Lewis (1964) in a study of some ejected plutonic blocks found that the contained scoriaceous, interstitial material (when it occupies about 10 per cent or more by volume) exists in pores that are continuously interconnected. The distance

between the patches may represent the maximum distance over which the diffusion occurred, or the patches may be the result of nucleation of minerals at random places. In some leucocratic rocks skeletal, poikilitic olivine patches are close to interstitial micropegmatite, (e.g. EG. 5109). As the trapped liquid crystallised it is to be expected that the inter-pore diffusion became more restricted.

Voll (1960) discussed the role that 'sintering' played in the removal of intercumulus liquid and in the formation of monomineralic layers. As has been mentioned in Chapter 1, 'sintering' of crystals occurs when the interfacial tension between them is less than the interfacial tension between the crystal and the liquid. Under these circumstances the crystals tend to coalesce together and expel the intercumulus liquid. The crystals can acquire an equilibrium shape, the manifestations of which are 120° grain boundaries at three grain junctions and curved crystal boundaries, by the diffusion of matter, (see Kretz 1966 for some theoretical discussion). In many of the Rhum and Skaergaard LZ melanocratic rocks the cumulus olivine crystals are often seen in clusters with the angles between grain boundaries at three-grain junctions close to 120°, and with curved crystal boundaries, see Plate 3.

Habit is only of limited use in the determination of the amount of the mesostasis by a microscopic examination. A maximum for the proportion of the mesostasis can be obtained by subtracting the proportion of the rock which is of unzoned, euhedral cumulus crystals, (see also Plate 4).

B. Zoning.

The extent (by volume) to which the felspars are zoned in the Skaergaard Lower Zone cumulates has been observed to be closely correlated with the concentration in the rock of low-k elements such as phosphorus. The separated, zoned felspars also have a relatively high concentration of low-k elements. This geochemical evidence supports the established idea that most of the normal zoning originated from the crystallisation of the trapped liquid. Although the volume of zoning is a function of the amount of trapped liquid, the range in zoning appears not to be. Unpublished and published (1960) work by L.R. Wager shows that in many of the leucocratic rocks of the Lower Zone the range in zoning is almost constant and involves a difference in the anorthite content of about 12 per cent., irrespective of the proportion of the mesostasis (provided it is present).

The importance of zoning especially in genetical considerations, has been stressed by Brown (1956). In the Skaergaard LZ rocks and in some of the Rhum allivalites, the zoning of the felspars, when present, is nearly always discontinuous with the core, see Plate 5. In many of the melanocratic layers, however, the zoning is patchy and continuous and most of the felspar must have crystallised from the trapped liquid, (for example EG 5088). The pyroxenes often show patchy zoning in the Skaergaard LZ rocks but in Rhum zoning of the pyroxenes is not common in the rocks studied (units 7 and 8) and so the mineral in these cases is taken to be mainly a heteradcumulus or an adcumulus phase. (See Plate 4).

The extent of zoning, therefore, is useful as an indication of the amount of mesostasis in a rock. A minimum figure for the amount of mesostasis can be obtained by measuring (microscopically) the volume of the zoned parts of the minerals where they are clearly differentiated from the cumulus (plus adcumulus) parts. Thus, with the upper limit for the mesostasis derived from the habit (see above), it will be possible to obtain the limits to the amount of mesostasis in certain rocks. In those cases where the volume of the zoning of the various minerals can be roughly determined, an assessment of the relative proportions of the minerals in the cumulus plus adcumulus parts can be made. The theory outlined in Chapter 2, could then be applied without difficulty to mesocumulates and orthocumulates. It is clear that further work in this field should give some fuitful results.

C. Mineralogy of the mesostasis.

By analogy with the overlying fractionation sequence of the MZ and UZ of the Skaergaard intrusion, and provided the physical conditions of crystallisation were the same, the trapped liquid of the LZ would be expected to have crystallised to about 60% felspar (less calcic than the cumulus plagioclase); 25% pyroxene (more iron rich); with the rest consisting of: iron-rich olivine; apatite; iron-ore; zircon; and micropegmatite. Although the physical conditions of crystallisation, especially with regard to pressure, of the trapped liquid are unlikely to have been the same as those of the Middle and Upper Zone cumulus minerals, none-the-less the observed mineralogy is closely similar to this expectation.

In many leucocratic rocks, containing a high proportion of mesostasis there is no olivine in the mesostasis presumably because it has been made over to pyroxene by reaction with excess silica.

If it can be assumed that the mineral assemblage of the mesostasis is the same in rocks that are close to one another in the fractionation sequence then it is possible to use this to elucidate the genesis of some of the minerals. A particular example is the pair of leucocratic rocks EG. 5109 (110 metres) and 5105 (135 metres) which both have a fairly high and similar P_2O_5 content of 0.21% (Curren 1959). 5105 consists of 92% felspar, about 4% pyroxene and 1% ore, with the rest being made up of quartz, apatite, and chlorite. 5109 is similar except that there is about 13% pyroxene and a lower felspar content (83%). Insofar as both rocks are considered to have a similar amount of mesostasis on the basis of their phosphorus concentrations then it would seem that at least 9% of the pyroxene in 5109 is a heteradcumulus phase. This conclusion does not agree with Wager (1960) who considered that all the pyroxene of 5109 was of the mesostasis, (see Chapter 4). This deductive process may be based on oversimplifications about the history of crystallisation of the trapped liquid. It is possible, for instance, that inter-pore diffusion of the trapped liquid in the early stages of trapping could have been over considerable distances.

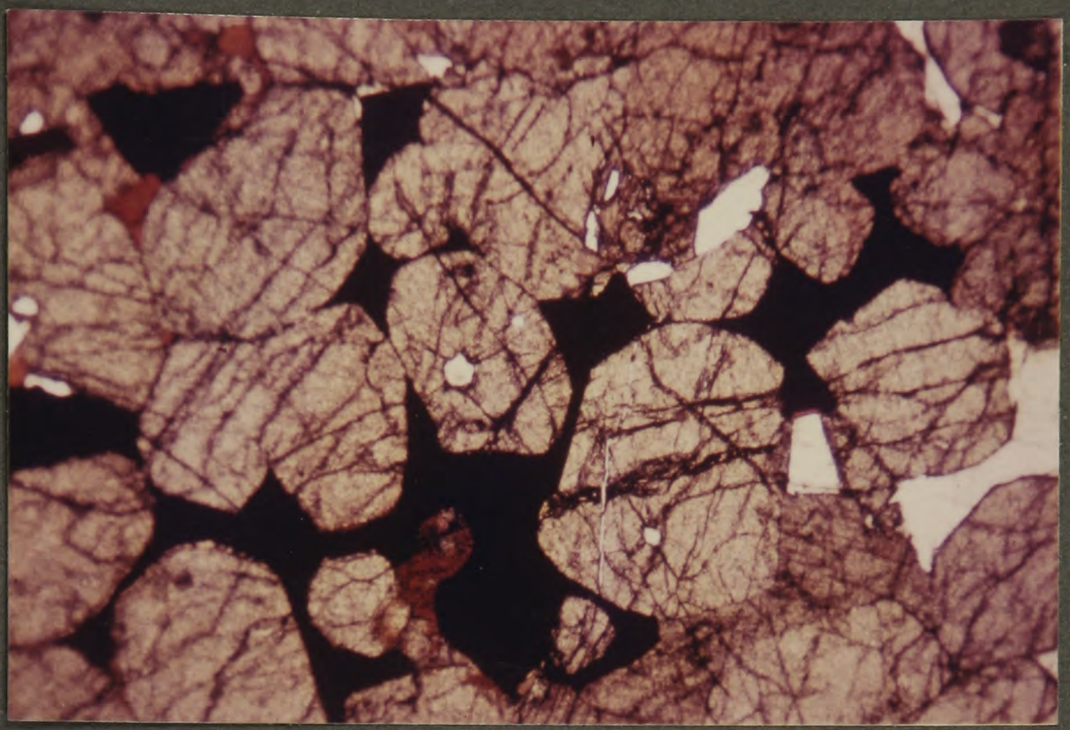
From the evidence of Chapter 4 and that above it appears that in the Lower Zone the trapped liquid gave very approximately: 60 - 65% felspar; 20% pyroxene; 5% quartz and micropegmatite; 5 - 10% iron ore; and small amounts of olivine, apatite, and zircon.

PLATE ONE

Photomicrograph of Skaergaard rock 5108 (from a melanocratic band at 110 metres LZa), showing cumulus olivine crystals surrounded by poikilitic iron-ore, and small amounts of poikilitic pyroxene and plagioclase felspar. Some biotite is also present. The felspar and iron-ore are considered to have crystallised from the trapped liquid. Plane polarised light; x 13.

PLATE TWO

Skaergaard rock 5109 (from a leucocratic band at 110 metres, LZa) showing the typical intercumulus habit of the pyroxene and iron-ore, which poikilitically surround the cumulus felspars. Plane polarised light; x 13.



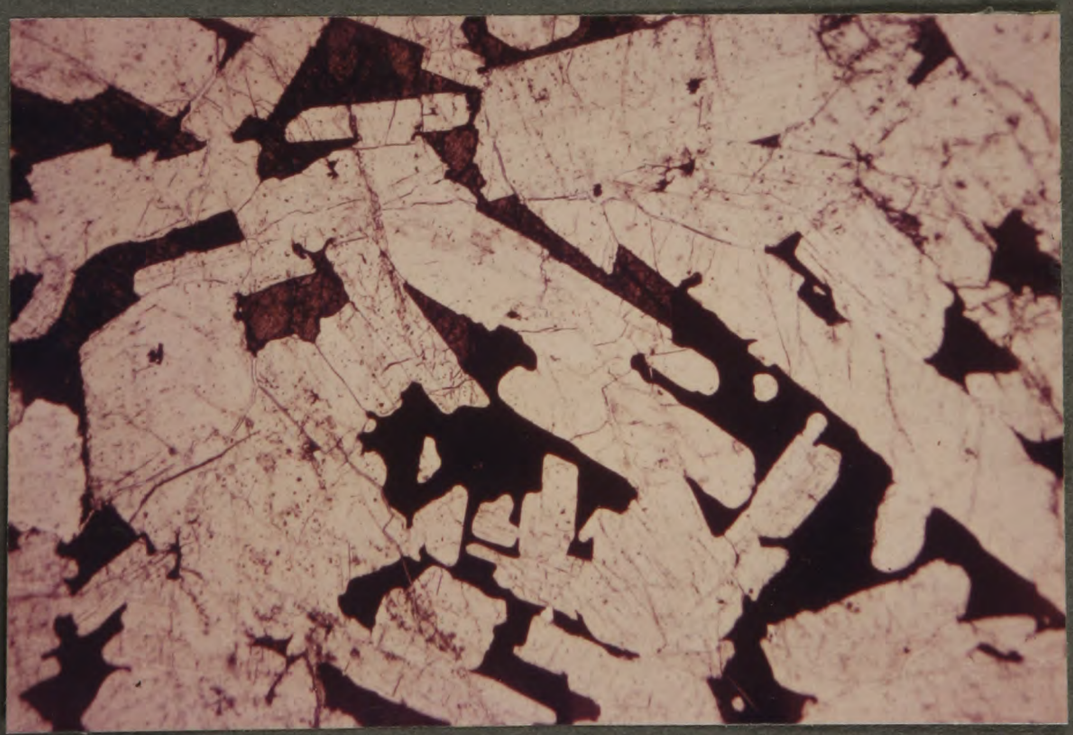
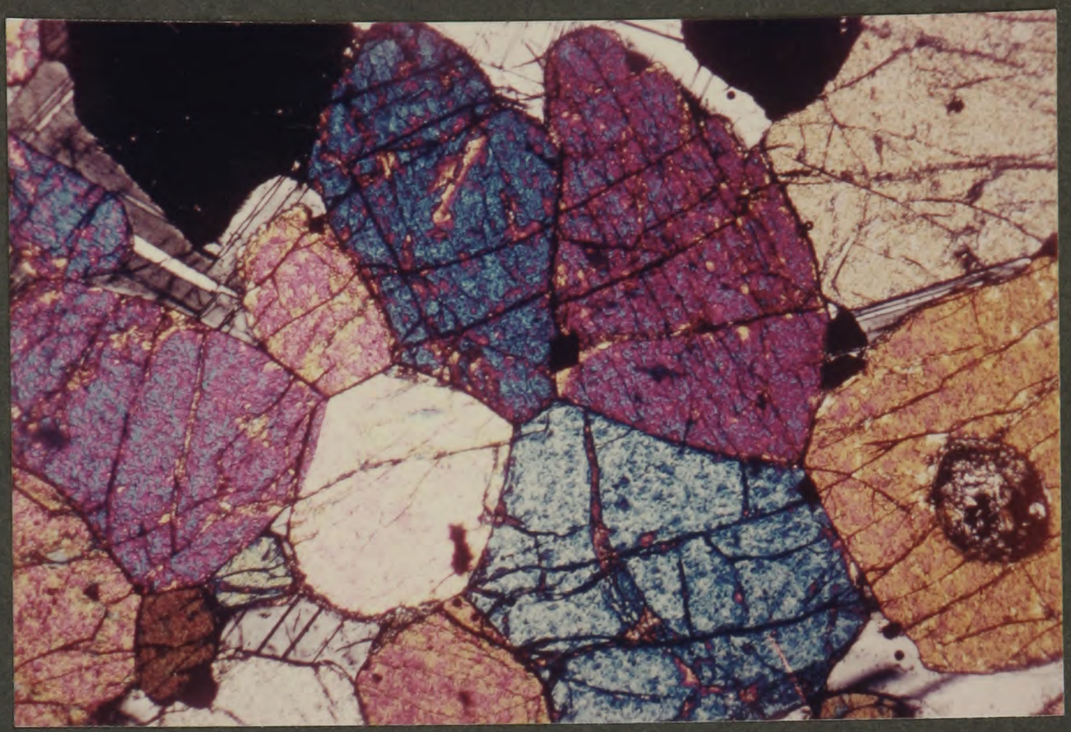


PLATE THREE

Rhum 17126, peridotite from unit 8, showing the habit of some of the cumulus olivines, particularly the 120° triple intersections at three grain junctions and the curved crystal boundaries. Poikilitic felspar, very slightly zoned, surrounds the olivine crystals. Some chromite is present. The black areas at the top of the photmicrograph are of olivine at extinction. Crossed nicols; x 33.

PLATE FOUR

Rhum 17128, allivalite from unit 8, showing poikilitic wisps of clinopyroxene around olivine (at extinction) and felspar. Some of the felspar is zoned. The pyroxene is considered to be essentially a heteradcumulus phase. Crossed nicols; x 33.



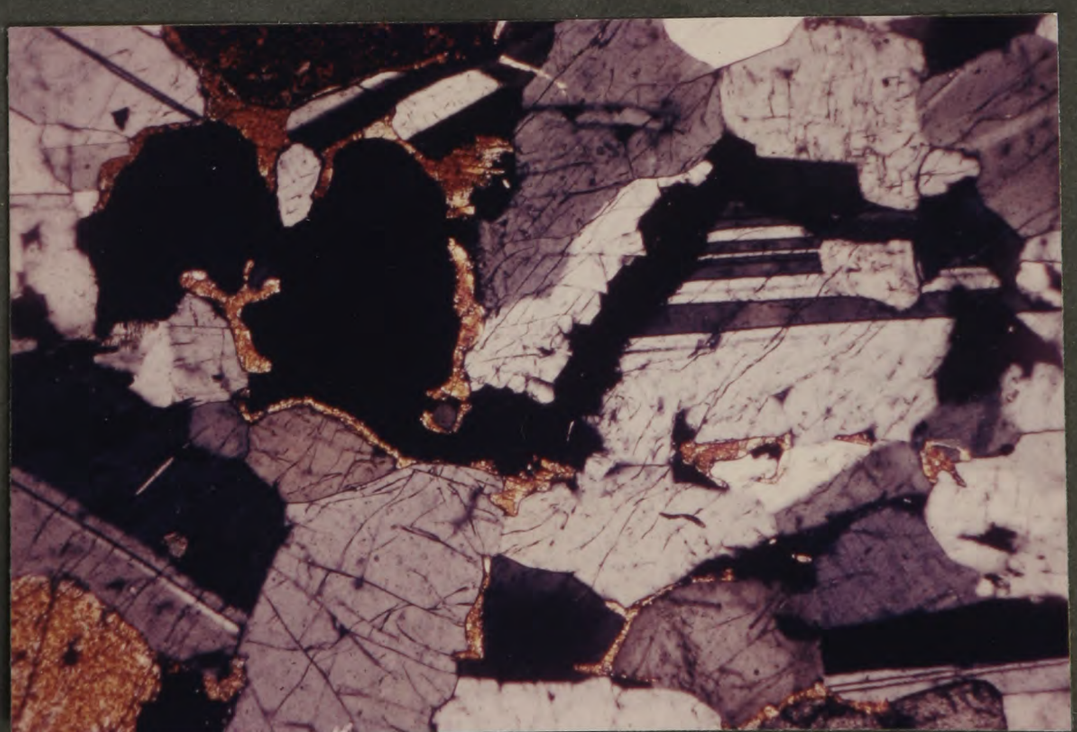
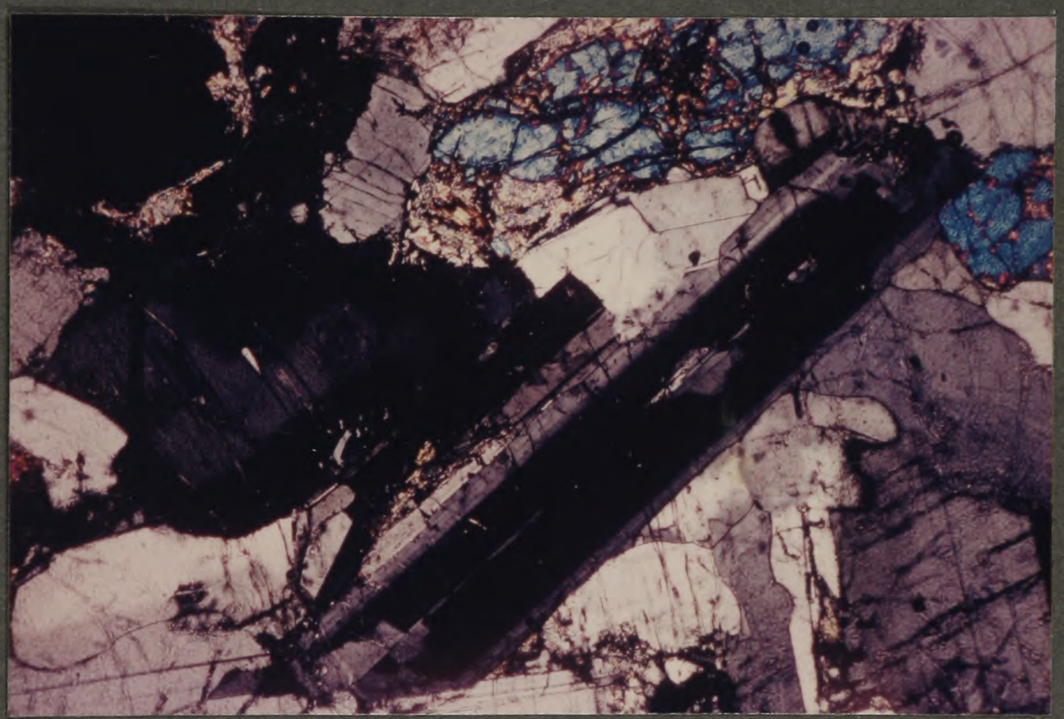


PLATE FIVE

Rhum 17123, allivalite from unit 7, showing discontinuous normal zoning of the plagioclase felspars, produced from the crystallisation of the trapped liquid. The olivine crystals at the top of the photomicrograph show alteration; top left: olivine at extinction. Crossed nicols; x 33.



PART TWO

ANALYTICAL CHEMISTRY.

CHAPTER SIX

Activation Analysis For Phosphorus

A. Introduction

The phosphorus content of layered igneous rocks varies enormously both from one rock type to another and from rocks in one horizon to similar ones in another horizon, for reasons given earlier. In some rocks (e.g. pyroxenites) where much adcumulus growth has occurred the phosphorus content may be only a matter of a few ppm. Similarly the phosphorus contents of many minerals are often low.

Colorimetric methods of determining phosphorus are generally far more sensitive than gravimetric or volumetric methods. However colorimetry is not*sensitive enough for some mineral analyses unless large quantities of the mineral are used, and this is not always possible. Furthermore, with low phosphorus concentrations the precision is generally not good and there is always the risk of interference from other elements present.

For the present work the following were required of the method for phosphorus determination:

1. High sensitivity
2. Good reproducibility
3. A straightforward and quick method of analysing large numbers of rocks and minerals for phosphorus only.

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* A recent paper by Djurkin et al (1966) claims a high sensitivity for colorimetric analysis of phosphorus.

The use of radioactivation analysis (Bowen and Gibbons 1963) satisfies these requirements and it was thus decided to use this technique.

In the past there have been many methods developed for the determination of phosphorus in a variety of materials (e.g. Curren 1959; Mullins & Leddicotte 1962) and it was initially hoped that existing methods of phosphorus determination could be satisfactorily applied to rock and mineral analysis. It was, therefore, decided to use the most common final precipitate in published methods, that of magnesium ammonium phosphate, $MgNH_4PO_4.6H_2O$, and the method proposed by Wayman (1964) was taken as a basis. Initial difficulties with this method were encountered and overcome as discussed below but it was not until ten irradiations of rock samples had been done that it was noticed that the reproducibility was not good enough. The method was thus fully investigated, tested and altered.

B. Nuclear reactions involved

On irradiation with thermal neutrons ^{31}P undergoes the following reaction: $^{31}P(n,\gamma)^{32}P$. The thermal neutron cross section of ^{31}P is 0.19 barns. ^{32}P decays by β^- emission to ^{32}S and has a half life of 14.3 days. The maximum energy of the β-particles is 1.707 MeV. ^{32}P does not decay by γ-ray emission.

Interfering reactions from other elements present in rocks are only:

$$^{32}S(n,\ p)^{32}P$$

and

$$^{35}Cl(n,\alpha)^{32}P$$

Both of these are fast neutron reactions.

W.D. Curren (1959) investigated interference from the sulphur reaction and found that provided the ratio of thermal to fast neutrons is high and that the S content is low (i.e. about 0.4 per cent) the interference is negligible. Under the irradiation conditions used the interference from the chlorine reaction is also negligible.

C. Choice of final precipitate

i. Ammonium Phosphomolybdate $(NH_4)_3PO_4.12MoO_3$. This compound has occasionally been used as a final weighing form (Mullins & Leddicotte 1962; Curren 1959). The advantages of using this compound are that it is readily reprecipitated after dissolving in ammonia and easily plated out, though not so well as magnesium ammonium phosphate. The disadvantages are that unless precipitation, washing and drying are carried out under the strictest conditions, the stoichiometry is open to doubt. (Even under rigid precipitation conditions it has been claimed that the stoichiometry is still not certain (Rieman and Beukenkamp 1961)). Furthermore this compound is hygroscopic.

ii. Magnesium Ammonium Phosphate $MgNH_4PO_4.6H_2O$. Like the ammonium phosphomolybdate this compound has been used extensively (e.g. Wayman 1964; Ricci 1964; Bowen and Gibbons 1963). It is easily prepared, reprecipitated and plated out. The disadvantage is that the precipitate does not have definite water of hydration. Drying at room temperature does not always remove superfluous water and drying at higher temperatures can remove some water of hydration. Curren (op. cit.) found self absorption but this was not found in the present

investigation (see later).

iii. Phosphomolybdic Anhydride. $MoO_3.P_2O_5$. This is prepared by heating ammonium phosphomolybdate to 450°C. Other than the inconvenience of heating large numbers of precipitates in an oven, this final weighing form also has the severe disadvantage that some phosphorus may be lost in the heating process, (Curren, op. cit).

iv. Magnesium Pyrophosphate $Mg_2P_2O_7$. This compound is more reliable as a final weighing form than magnesium ammonium phosphate. However the stoichiometry is not absolutely reliable (Rieman & Beukenkamp 1961) and it is an exceedingly difficult compound to plate out. Furthermore high temperature ignition (1100°C) is required in its preparation. Also, Curren (op. cit.) found severe self absorption.

v. Other Precipitates. (Rieman & Beukenkamp ibid). Uranyl pyrophosphate, bismuth phosphate, and oxine phosphomolybdate have been used for normal gravimetric phosphorus determination. They have not been generally used in activation analysis and were not considered for the present work.

Silver thallium phosphate (Ag_2TlPO_4) has been used by Khalil (private communication) as a final weighing form. This compound, in the method that he has developed, is produced from an initial ammonium phosphomolybdate precipitate. This method was tried (using inactive phosphorus) but the chemistry was found to be tedious and lengthy. It was, therefore, decided not to use this method, especially as it had not then yet been satisfactorily tested by Khalil himself.

Conclusions: Magnesium ammonium phosphate was decided upon for the final precipitate. The disadvantage of the uncertain amount of water of hydration was overcome as described later.

D. Phosphorus standard

Following after many previous workers, Analar diammonium hydrogen orthophosphate was used as a standard. Small quantities of a fine powder of the salt (kept in a desiccator) were irradiated in silica ampoules in each batch of rock or mineral irradiations. Three standards were generally used though in earlier runs up to five were used to check precision.

Self shielding: An experiment was carried out to confirm Curren's result, (op, cit.). Four ampoules containing different quantities of the standard were irradiated for two and a half days at pile factor 0.1. (i.e. 10^{10} neutrons per cm^2. per sec.)*.

The weights of standard were 3.7; 11.1; 26.7; 61.7; respectively and the specific counts observed were 98,217; 98,451; 102,740; 88,184; counts per minute respectively. This shows that slight self shielding occurs in the standard where about 60 mgms was packed into one ampoule. This result agrees with Curren's work except that the maximum amount of standard irradiated in this work was far greater than that used by Curren, who found no self shielding. It was, therefore, decided to use solid standards of less than 30 mgms weight per ampoule.

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* Unit pile factor is equal to 10^{11} neutrons. cm^{-2}. sec^{-1}.

Curren (op. cit.) proved that there was not significant self shielding in the rock powders, by irradiating different weights (range 50 - 200 mgms.) of each sample.

E. Standard preparation and opening

The standards of $(NH_4)_2HPO_4$ were weighed and sealed into silica ampoules. A K_2SO_4 standard, also in a silica ampoule, was generally included in with samples to monitor interference from the sulphur reaction. At pile factor 0.1 it was negligible.

The following method of opening the silica ampoules was devised: a mark was made at the constriction with a file. The solid material was tapped into the main body of the ampoule which was then inserted into a hole in a brass holder so that only the constriction and head of the ampoule projected from the holder. The holder was held on its side over a small beaker and the head of the ampoule knocked off with a slight tap from a pair of tongs. The head and main body of the ampoule fell directly into the beaker with no loss of standard.

Distilled water and a few drops of conc. nitric acid were added until the ampoule was well covered. The beaker was then heated until boiling occurred, cooled, reheated, and so on. By alternately boiling and cooling, water is driven out and drawn into the ampoule, and thereby dissolves and removes the standard into solution. This cycle was carried out about four times and the resultant solution, after cooling, was poured into a 250 ml. volumetric flask. The beaker was washed and the washings added to the flask. More water was added to the beaker and the above process repeated. The whole

process was repeated about seven times when it was then considered that all the standard had been transferred to the flask. The flask was then made upto the mark. Two 2ml. aliquots were taken, mixed with carrier, taken through part of the chemistry and finally counted and the yields determined.

F. Sample preparation

For preparation of rock powders and mineral separation methods used, see Appendix C.

Ampoule preparation: Generally 60 to 100 mgms of samples were placed in small polythene ampoules by means of a polythene funnel. The ampoules were sealed by heat at both ends. Polythene was used when the length of irradiation was three days or less, otherwise silica ampoules were used. The polythene ampoules, suitably marked for identification, were wrapped in aluminium foil and sent for irradiation in the normal aluminium cans.

Rock transference test: A small investigation was made to see how much rock powder was retained in a polythene ampoule after opening and tapping out the sample. The powder used was a rock sample at less than 400 mesh. The quantity remaining varied from 0.1 to a maximum of 0.5 mgms, irrespective of initial weight (all ampoules were the same size). All the material remaining could be removed by cutting off both ends of the ampoule and directing a jet of water through the ampoule. This was not always convenient as sodium peroxide/sodium hydroxide fusions were sometimes used. Provided the initial rock powder weight was greater than 50 mgms. the retention of these small amounts of powder would not cause significant error.

Ampoule opening: This was simply carried out by cutting the ampoule with a pair of scissors whilst holding the ampoule with tweezers. The powder could then be readily tapped into the fusion container. In the case of silica ampoules, the procedure as described for the standards was used, except that the holder was kept upright, the main body of the ampoule taken out from the holder after the head had been removed and then the powder tapped out.

G. Irradiation conditions used

Prepared samples and standards were sent to Harwell for irradiation in BEPO reactor.

In the choice of irradiation conditions for phosphorus analysis the following factors must be taken into account:-

a. The ratio of thermal to epi-thermal plus fast neutrons must be high so as to suppress the interfering sulphur reaction.

b. The duration of irradiation must be long enough to produce sufficient activity for accurate counting but not too long so that the counting is made inaccurate by large dead time corrections due to high activity. Furthermore, three days irradiation is about the most that polythene can take before it starts to break down; polythene ampoules are generally more convenient to work with than are silica ampoules.

c. The activity of the irradiated samples should not be so high that it is a health hazard to the worker if special

protection measures are not available.

For rock samples a pile factor of 0.1 or 0.2, for three days, was used as in this region of the reactor the ratio of thermal to epi-thermal plus fast neutrons is extremely high and, thus, these conditions comply with a. and c. above. However, when the phosphorus content of the samples was very low (less than 40 ppm.) the final count rate was not high (using the Tracerlab beta counter). Therefore, for mineral samples and rocks with expected, low phosphorus contents a pile factor of 1, for about three days, was found to be suitable. In the early stages of this work a pile factor of 12 was used for mineral analyses but the material in such cases was rather active to handle.

After irradiation the samples were allowed to cool down for two days, or more, before chemical separations were started.

H. Wayman 's method and adaptions of it

Wayman (1964) proposed a method for the simultaneous determination of sulphur and phosphorus in water by neutron activation analysis. This method was initially used in this work but it was found that many adaptions were needed. Thus, although Wayman 's method was used as a starting point the finally developed method is a new one.

In summary his method consists of an irradiation of the liquid samples, followed by an initial zirconium phosphate precipitation. The zirconium phosphate is dissolved in HF and then phosphomolybdate precipitated by the addition of a molybdate reagent. This precipitate

is dissolved in ammonia and finally a precipitate of magnesium ammonium phosphate ($MgNH_4PO_4.6H_2O$) is formed by the addition of a magnesia reagent. The final precipitate is washed and air dried on a filter paper disk, using a filter chimney, weighed and counted.

The various precipitates used by Wayman seem to be well chosen. The initial zirconium phosphate precipitate is fairly selective and, therefore, brings the activity of the material to be worked with down to a low level. Both the phosphomolybdate and magnesium ammonium phosphate precipitates are considered to be very selective and are regularly used for gravimetric determinations of phosphorus (see Vogel 1962; Rieman & Beukenkamp 1961). Whilst there is the possibility that some other metal phosphates may be precipitated with these precipitates, metals such as silver, arsenate etc. most of these are present in very small amounts in the rocks studied and many have short half lives or low cross sections. Wayman added citric acid before precipitating magnesium ammonium phosphate: this complexes Fe, Al, Ca, Ti, Mn, Zn, and Mo, so that these metals remain in solution, (Rieman and Beukenkamp, op. cit.)

The following investigations and adaptions were made:

a. Sample decomposition: At the outset HF decomposition of the sample in the presence of an accurately known amount of carrier solution, and c.HNO_3 (to bring all phosphorus to the same oxidation state) was used. However, the process is lengthy and any HF remaining prevents the precipitation of zirconium phosphate. Thus a sodium peroxide/sodium hydroxide fusion was used in later analyses and is discussed below.

b. Precipitation of Phosphomolybdate: Wayman's method is comprised of only three precipitations. The risk of active elements other than phosphorus in the final precipitate might thus be possible and in some cases this was found to be so. (See Section I). Hence the following extra steps were included to ensure radiochemical purity of the final precipitate.

i. The zirconium phosphate precipitate was washed with distilled water and then centrifuged. The washings were discarded. The zirconium phosphate precipitate is gel like and brings down other material and supernatant liquid which washing helps to remove.

ii. Before precipitating the phoshomolybdate, 2 mls. of a solution of holdback carriers was added. This solution contained Ba, Co, Cu, Fe, Mn, La, Rb, Sr, Sc, Zr, ions. The phosphomolybdate was re-precipitated twice more in the presence of holdback carriers and once without them.

The selection of these particular elements is based on the fact that the same elements if present in the irradiated samples form isotopes that decay by beta-ray emission. Some of them, such as strontium, have long half lives and it is necessary that they are absent from the final precipitate. Many isotopes, of elements not in this list, have short half lives (2 days or less) and provided

that at least a week has passed after irradiation and before counting the activity of the final precipitate, they are unlikely to have significant activity, should they be present in the final precipitate. Many elements (e.g. niobium) have isotopes with such long half lives that under the short duration of irradiation used in this work there is unlikely to be more than negligible activity from them if they contaminate the final precipitate.

It was also found that it was best not to heat the solution on a water bath to flocculate the phosphomolybdate precipitate as a temperature of above 50°C is conducive to the formation of molybdic acid. Instead the precipitates were given a few minutes to form at room temperature or at the temperature of the solution.

c. Precipitation of Magnesium Ammonium Phosphate: Wayman simply precipitated the final compound by first dissolving the phosphomolybdate in 1 ml. of NH_4OH and 2 mls. of a 50 per cent citric acid solution (to complex Mo) and then adding 10 mls. of a magnesia reagent (100 gms. $MgCl_2.6H_2O$ plus 10 drops HCl plus 100 mls. distilled water) whilst stirring. After this he added NH_4OH dropwise until the precipitate began to form whence he left it for three minutes with the subsequent addition of 4 mls. NH_4OH and finally allowed thirty minutes for complete precipitation.

This method proved to be very unsatisfactory as on addition of

NH_4OH, magnesium hydroxide was precipitated as well as magnesium ammonium phosphate. Furthermore, the precipitate sometimes took a long time to form and hence the dropwise addition of NH_4OH was inconvenient and its continuation often unnecessary as the pH was high. The first attempt to avoid the precipitation of $Mg(OH)_2$ was to add about 50 gms. NH_4Cl to the magnesia reagent so that the common ion effect would be brought into play. This prevented the formation of $Mg(OH)_2$ but did not remove the inconvenience of dropwise addition of ammonia solution. However, a solution to this problem was found in Rieman and Beukenkamp (1961) where it is said of the magnesium ammonium phosphate precipitation:

> "Careful control of pH is necessary. In order to exceed the solubility product of $MgNH_4PO_4.6H_2O$ the pH must be high enough to allow sufficient unprotonated phosphate PO_4^{-3}, and low enough to allow sufficient protonated ammonium NH_4^+. To permit the existence of as much as possible of both these ionic species in solution a pH of approximately 10.5 is needed. A lower or higher pH shifts the equilibrium in favour of the formation of HPO_4^{-2} and NH_3 respectively.
>
> Furthermore a lower pH permits the simultaneous precipitation of $MgHPO_4$ and a higher pH favours precipitation of $Mg_3(PO_4)_2$, $Mg(OH)_2$ and possibly $Mg_5(PO_4)_3OH$. A mixture of ammonia and ammonium

ions serves to buffer the solution at pH 10.5 in addition to acting as a reservoir of cations for the precipitate."

The magnesia reagent suggested by these authors was used. This consisted essentially of 400 gms. $MgCl_2.6H_2O$ and 300 gms. NH_4Cl dissolved in 1½ litres of water. For the details of preparation see later. 10 mls. of this reagent were used for each precipitation and 15N NH_4OH was added until the pH was about 10.5 as indicated by test papers. The solution was allowed to stand for an hour to give time for complete precipitation of magnesium ammonium phosphate.

For large number of precipitates the use of a filter chimney is inconvenient. Centrifuging with decantation was preferred and was used also after each washing of the precipitate. Plating out was done by means of a small pipette in the usual manner.

The next section describes a complete investigation into the suitability of the final precipitate as a weighing form, and here further changes were made.

I. Investigations of magnesium ammonium phosphate precipitate

a. Radiochemical Purity: In the early stages of using Wayman's method without extra precipitation steps, plots of the half life of the final precipitate gave a half life value close to 14.3 days only when the pile factor used had been 0.1 or 0.2. When the pile factor was 12 a long lived contaminant was sometimes recorded in the final precipitate. Plots were taken over seven half lives. After all the additional steps had been included as described above, the

half life was always found to be close to the value of 14.3 days. Absorption tests on the beta-particles showed there to be none with energies greater than those of the beta-particles from the standards.

These two tests indicate that the final precipitates were radiochemically pure and in later analyses this assumption was used, the tests not being made. Results for standard rocks such as Gl. and Wl. agree very favourably with the recommended values and this is a further indication that the precipitates must have been at least close to radiochemical purity.

b. Self absorption: Curren (1959) found self absorption of beta-particles in magnesium ammonium phosphate through he did not try a direct test on this. A direct test was, therefore, carried out. Six precipitates, containing active tracer, of approximate weights 7, 14, 40, 62, 68, and 125 mgms. were taken and counted. The relative amounts of phosphorus were determined after counting by colorimetry (see later) and the counts made specific in relation to an arbitrary colorimetric absorption value. All the specific activity results were identical (within experimental error) except for the precipitate of 125 mgms. which showed a count which was nearly 9 per cent lower, thus indicating some self absorption. It is difficult to see why Curren (op.cit.) should have found self absorption unless his precipitates still had superfluous water in them on weighing in which case the specific counts would be too low. This presence of superfluous water is likely and is discussed in the next section.

There is also the point that Curren was operating near the limit as he used specimens of about 90 mgms. weight.

In this work the final precipitate weight was kept below 70 mgms. (see later).

c. Stoichiometry of the precipitate: It was found after ten irradiations of rock samples that the reproducibility was not very good. Furthermore on some occasions the yield had been very close to or slightly more than 100 per cent and it was felt that an error lay in the final precipitate, especially as it was certain that the compound was radiochemically pure.

The first experiment to check the stoichiometry of the magnesium ammonium phosphate precipitate was to take five aliquots of a solution containing an accurately known amount of $(NH_4)_2HPO_4$. The precipitate was produced by adding the magnesia reagent (see above) and ammonia solution until the pH was about 10.5. The precipitates were allowed to form for forty five minutes and were then collected in previously weighed Gooch sintered glass crucibles, washed with 2 per cent NH_4OH solution; 50 percent alcohol; and finally by acetone. The crucibles were then placed in an oven at 25°C for a day and a half and then weighed. *See below. Weights ranged from 0.142 to 0.144 gms. compared with the theoretical yield of 0.129 gms. This experiment clearly shows that all the superfluous water had not been removed. The experiment was repeated but this time using a tracer of known activity.

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*N.B. Different workers suggest very different drying conditions (see; Duval 1963; Vogel 1962.)

The precipitates were plated out and treated to various drying conditions to see how the actual yield compared with the tracer yield.

To assess the specific activity of the tracer twelve aliquots were accurately pipetted into counting trays 1" by $\frac{3}{8}$" deep, and evaporated to dryness under a heating lamp. The activities were recorded by using the Tracerlab Omni-guard counter (see Appendix E). From the known specific activity the yield of the samples could be determined. Drying conditions ranging from room temperature to 35°C in an oven for two days were used but in none was good agreement found between actual and tracer yields. It was, therefore, decided to measure the amount of phosphorus in each tray by colorimetry (for the method see later). However agreement was still poor between yields obtained from colorimetry and those from tracer. Possible reasons for this seemed to be:

1. Self absorption of the beta particles by the precipitate.
2. Systematic errors in the colorimetry.
3. Incomplete homogenisation of nonactive and tracer phosphorus.
4. Plating errors.

A repeat of the self absorption experiment was made and it confirmed the previous findings.

No systematic errors in the colorimetry could be found.

The whole experiment was repeated a third time with extensive boiling of the carrier and tracer solutions with nitric acid before precipitation but still poor agreement was obtained.

The fourth possibility was then investigated and it was found that the error lay in the specific activity of the carrier. By drying the tracer in deep counting trays ($\frac{3}{8}$") there tended to be creep up the sides so that the activity was nearer the counter. The Tracerlab counter is very sensitive to such small changes in distance of the source (see graph in Appendix E) and so the count of the tracer was too high thus giving a low percentage yield for the precipitates. The experiment was repeated using very shallow trays for drying the tracer solution. Agreement between colorimetric and tracer yields was then found to be very good, there generally only being a difference in the second decimal place.

Colorimetric determination of the yield of the final precipitate has three significant advantages over weighing:

1. The carrier solution is accurately measured for its phosphorus content without further analysis, if it is used as the calibration solution.
2. The final precipitate need not be stoichiometric, nor absolutely free of inactive contaminants, (provided they do not interfere in the colorimetry).
3. There is no need to weigh the precipitates and counting trays.

The disadvantage is that the procedure of colorimetry for so many samples is tedious. However as the results by such a method are clearly reliable it was decided to use this method for yield determination.

It would be equally as suitable not to plate out the final precipitate but to redissolve it in 3NHCl and count the solution in a well-type beta-counter. After counting the solution could be accurately diluted and the yield determined by colorimetry as discussed below.

J. The developed method.

1. List of reagents

Sulphuric acid:	5 molar.
Nitric acid:	concentrated.
Hydrofluoric acid.	40%.
Ammonia:	880; 15 normal; and 1% solutions.
Zirconium nitrate solution:	30 gm. of $Zr(NO_3)_4$ dissolved in a litre of water, and then filtered.
Ammonium molybdate solution:	200 gm. of $(NH_4)_6MoO_{24}.4H_2O$ dissolved in 800 ml. of distilled water and 160 ml. 880 NH_4OH.
Citric acid solution:	50 gm. dissolved in 100 ml. of distilled water.
Magnesia reagent:	400 gm. of $MgCl_2.6H_2O$ and 300 gm. of NH_4Cl dissolved in 1.5 litres of warm distilled water. 15N NH_4OH added until the solution is just basic to litmus. The mixture is allowed to stand for an hour and filtered if necessary. 12N HCl is added to the filtrate until it is acid to litmus. The total volume is then about 2 litres.
Alcohol:	60%.
Holdback carrier solution:	solution containing about 2 mgm. per ml.

of salts of Ba, Co, Cu, Fe, Mn, La, Rb, Sr, Sc, Zr, ions.

Carrier solution: about 3 gm. of $(NH_4)_2HPO_4$ dissolved in 500 ml. of water. The phosphate need not be accurately weighed. This dilution gives a maximum weight of about 60 mgm. to the final precipitate.

Aerosol solution: 1%.

Reducing solution: a mixture of: 125 ml. 3N H_2SO_4; 38 ml. of an ammonium molybdate solution (5 gm. in 250 ml.); 60 ml. 0.01 M ascorbic acid. The resultant solution is diluted to 250 ml. (This solution should be made up immediately before use).

2. Procedure

All operations on the sample, before zirconium phosphate is precipitated, were made behind a lead brick screen which reduces considerably the activity reaching the worker. The irradiated sample was transferred from the ampoule to a nickel crucible. 5 ml. of carrier solution had previously been accurately added to the crucible and evaporated to dryness. About 2 gms. of A.R. sodium peroxide and 20 pellets of A.R. sodium hydroxide were added to the crucible which was then heated, with a lid on, at a temperature sufficient to fuse the contents. The temperature was then raised to red heat for ten minutes after which the contents were swirled round by holding the crucible with a

pair of tongs, and then allowed to cool. (This procedure completely fuses all of the samples dealt with in this work). The crucible and lid were transferred to a 250 ml. beaker, on a water bath, and 50 ml. of distilled water added to partially dissolve and disintegrate the fusion cake. When this process was completed the crucible and lid were removed and washed with distilled water; the washing being added to the beaker. About 20 to 50 ml. of 5M H_2SO_4 were added to help neutralise the hydroxide and then the solution was made acid by the addition of conc. HNO_3. The addition of 10 ml. of the zirconium nitrate solution precipitated zirconium phosphate. (The addition of the 5M H_2SO_4 appears to aid this precipitation but if too much is added the zirconium sulphate is formed which is soluble). Placing the beaker on a water bath for ten minutes helped to flocculate the precipitate.

The contents were then transferred to a test tube, centrifuged and decanted; the supernatant liquid discarded as active waste. The precipitate was then washed, centrifuged and decanted and the washings added to the waste. This precipitation brought the activity down to trace levels and it was then safe to work without a lead shield.

The $Zr_3(PO_4)_4$ precipitate was dissolved with 2 drops of HF solution and then diluted to about 10 ml. The contents were centrifuged again which brought down an insoluble fraction. The liquid was decanted into a clean tube and the solid residue discarded. Concentrated nitric acid, 2 drops of 1% aerosol

solution, 1 ml. of holdback carrier solution, and 5 ml. of the ammonium molybdate reagent were added to the solution in that order. The precipitate of ammonium phosphomolybdate was allowed to form for a few minutes before centrifuging and decanting off the supernatant liquid. The precipitate was dissolved in 1 ml. of ammonia, then holdback carriers, 3 ml. of molybdate reagent, aerosol and nitric acid were added to reprecipitate. The reprecipitation was repeated once more without holdback carriers and the precipitate finally washed in 10 ml. of distilled water.

The phosphomolybdate was then dissolved in 1 ml. of NH_4OH, 2 ml. of citric acid solution, and 10 ml. of the magnesia reagen t were added. The solution was brought to a pH of about 10.5, as indicated by test papers, by the addition of 15N NH_4OH. The precipitate is given two or more hours to form, with occasional stirring. Finally the precipitate was centrifuged and washed with 1% NH_4OH, 60% alcchol; and acetone; in that order. The magnesium ammonium phosphate precipitate was then slurried with acetone, plated out, and allowed to dry. It was then ready for counting.

The standards (see Section E) were mixed with carrier and brought to the boil for about 1 minute in the presence of conc. HNO_3. They were taken through one phosphomolybdate and one magnesium ammonium phosphate precipitation. They were plated out in the same way as the samples.

3. Counting

Samples and standards were counted in the same manner. In the early stages of this work counting was done by means of a shielded, end-window geiger counter connected to a scaler. The timing was done with a stop watch. In later runs the Tracerlab Omni-guard automatic, low background beta counter was used, which is described, along with a counting experiment, in Appendix E. Counting was normally continued until at least 10,000 counts per sample had been reached. The counts per minute were corrected for dead time and background (if significant). Yields of the samples were determined after they had been counted.

4. Yield determination

The yield of each sample was determined by a colorimetric method. The magnesium ammonium phosphate precipitate was dissolved in 3N HCl and the resultant solution, together with the washings, was quantitatively transferred to a 500 ml. volumetric flask, which was made upto the mark with distilled water. Two 5 ml. aliquots of this solution were pipetted out (using a Grade A pipette) and transferred to 50 ml. volumetric flasks*. 20 ml. of the reducing solution were added to each flask which was then made upto the mark with distilled water.

For a calibration curve, 5 ml. of the carrier solution were taken and accurately diluted to 500 ml.. 4 ml. (i.e. equivalent

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*These flasks contained conc. H_2SO_4 when they were not in use. They were thoroughly washed out with distilled water before use.

to 80% yield) 3 ml. (60%) and 2 ml. (40%) aliquots were taken and each added to a 50 ml. flask. This was done in duplicate. Reducing solution and distilled water were added to the flasks as for the samples. (This calibration procedure eliminates the necessity of accurately making up the carrier solution).

The flasks were allowed to stand overnight so that the "molybdenum blue" colour developed fully. (This colorimetric method has been well tried in the Department of Geology and was found to be most suitable for this work. For fuller details see Riley (1958) and Boltz (1958)). The optical density of each solution was measured on an Unicam SP 500 spectrophotometer at 827 mμ and with the solution held in 1 cm. cells. However, the optical density obtained by the above dilution procedure was too great to measure by normal methods and so the technique of differential spectrophotometry (Hiskey 1949) was used with the 40% yield solution as the reference. The 60% and 80% yield solutions were also measured in relation to the 40%. Thus it was possible to draw up a calibration curve of optical density against percentage yield, with 40% yield being taken as zero optical density. This curve was always a straight line. The average of the optical density values for each sample was taken, and from the calibration curve the yield was determined. Advantages of the colorimetric method of yield determination have been discussed in Section 1.

As many of the precipitates from early runs, whose yields had

been determined by weighing, had been thrown away, it was not possible to check the yields by colorimetry. Thus, the results from these runs were discarded (except for a few Bushveld results, see earlier) and the samples were re-analysed using the new method. In some cases the agreement between the old and new methods was not too bad, e.g. SA. 722: 29 and 32 ppm. respectively, but was not good in others e.g. 5875: 138 and 187 ppm respectively.

K. Speed; reproducibility, and sensitivity.

After sufficient practice in the developed method had been obtained, it was possible to pack up the samples for irradiation, analyse, count (using the automatic counter), determine the yields and calculate the results, in a total of about five working days for twelve samples and three standards, (i.e. generally six samples in duplicate). On previous occasions, especially when the method was still in the development stage, the total procedure took much longer. It must be pointed out that the use of an automatic counter can save almost a whole day's work per batch of irradiated samples.

The relative standard deviation for the standards was found to be generally about 2 per cent. (This was using pile factor 1). The relative standard deviation for the G.1. results is just under 13 per cent. and that for the Bushveld rock (SA. 660) samples is 14 per cent., see Table 19. It should be noted that the average values for G.1., and W.1., agree quite closely with the recommended values, though the results for T.1. are a little higher.
In appropriate parts of the thesis it is shown that, for

TABLE 19

Phosphorus (ppm) in some standard rocks

G.1.	W.1.	T.1.	SA 660
368.8	524.1	693.7	40.2
350.8	430.9	624.0	40.3
318.9	541.4	777.7	55.6
435.6	529.8	894.0	51.5
425.3			43.2
373.4			52.0
460.6			40.0
387.5			47.9
364.6			44.6
360.8			57.3
386.6			54.6
367.4			64.2
469.3			45.2
426.1			48.9
292.6			58.7
310.0			55.4
404.6			43.1
438.9			42.8
			46.1
Average: 386	519	747	49
Standard deviation: 49 (13%)	32 (6%)	98 (13%)	6.9 (14%)
% P_2O_5 0.088	0.109	0.171	0.012
Recommended P_2O_5 values 0.09*	0.14*	0.145**	

Analyst: P. Henderson

*Fleischer M; 1965

**Msusule tonalite pamphlet, 1961.

the same specimens, agreement between results obtained by this method and those from other methods is good.

The sensitivity of the method has been calculated from actual irradiations rather than producing a theoretical sensitivity. After irradiation at pile factor 1 for three days, and with an elapse of one week before counting, the activity of the standards was generally such that 100 c.p.m. was equivalent to 4×10^{-5} gm. phosphorus, (this was using the Tracerlab low background counter, which has an efficiency of about 30% under the conditions used). If one assumes a minimum count of 20 c.p.m. (this is over twenty times the background of the Tracerlab counter); a 100 per cent. yield; and 100 mgm. irradiated samples, then the sensitivity is about 1 ppm. of phosphorus. This was quite adequate for the present work.

The accuracy of activation analysis has been discussed in many analytical texts, see Jenkins and Smales (1956).

CHAPTER SEVEN

Activation Analysis for Bromine

A. The method of Filby

Filby (1964) proposed a method for the determination of bromine in rocks by neutron activation analysis. The method was used for this study but was found in certain respects to be unsatisfactory, as discussed below. Only four batches of samples were irradiated before it was decided to discontinue the investigation into bromine geochemistry and to study instead that or uranium, also a low-k element, as at this time a quick, reliable and straightforward method of analysis for this element was available, namely the 'delayed neutron' method, see Chapters 3 (c) and 8.

Full details of the method of bromine analysis can be found in Filby (1964). The reaction with which this method is concerned is $^{81}Br(n, \gamma)^{82}Br$. The thermal neutron cross section of ^{81}Br is 2.6 barns and the half life of ^{82}Br, which decays by beta and gamma-ray emission, is 35.9 hours. The other bromine isotopes produced from neutron irradiation of the stable ^{79}Br isotope are ^{80m}Br and ^{80}Br with half lives of 4.6 hours and 18 minutes respectively. The activity contributed from these species is effectively negligible if there is an elapse of about two days between the end of irradiation and counting. Interference produced by (n, p) and (n, α) reactions on krypton and rubidium isotopes in the samples is discussed by Filby (op. cit.) and is shown to be negligible. Interference from fission of ^{235}U is also insignificant.

The experimental procedure recommended by Filby involves the irradiation of 500 mg. of rock sample in an aluminium envelope in a thermal neutron flux of 2.5. 10^{12} $n.cm^{-2}.sec^{-1}$. for one week, followed by a cooling period of one day. The samples are then transferred from their envelopes into nickel crucibles and, in the presence of a known amount of bromide carrier, are decomposed by heating with sodium hydroxide. (Sodium hydroxide alone is used so as to avoid oxidation of bromide to bromine which may be lost by volatilisation). The fusion cake is dissolved in 50 ml. of water containing 10 ml. of iodine hold-back carrier (1 mg. of iodine per ml.), and the solution is neutralised with 5M sulphuric acid, with 10 ml. added to excess. The solution is cooled, transferred to a separating funnel to which are added 50 ml. carbon tetrachloride and a few drops of 0.5 M sodium nitrite solution, and the liberated iodine is extracted into the organic phase. The extract is discarded, and 30 ml. of carbon tetrachloride is added to the aqueous phase, followed by 0.1M potassium permanganate solution until the pink colour just persists. The bromine is extracted into the organic phase by shaking for one minute. The extract is filtered and the filtrate collected in a separating funnel to which water and 1 ml. of 1% hydrazine sulphate solution are added. The mixture is shaken until colourless; the aqueous phase is collected and a ferric hydroxide scavenge is carried out after which the solution is made just acid with 5M nitric acid and a slight excess of 5% silver nitrate added. The silver bromide precipitate is flocculated and collected by filtering in a sintered glass crucible. It is then

dried at 130°C for two hours. The precipitate is allowed to cool and as much as possible is accurately weighed into a counting vial.

The standards are prepared by drying 0.05 ml. of a bromide solution (0.5 mg. Br. per ml.) onto aluminium foil and they are irradiated in aluminium envelopes. (No self-shielding is observed in the standards prepared in this way). After irradiation and removal from the envelopes, they are dissolved in water. 1 ml. of 1% hydrazine sulphate solution and bromine carrier are added and the solution is made up to 1,000 ml. with water. 2ml. aliquots of this solution are counted directly.

The counting of the samples and standards was done by means of a scintillation counter and a single channel pulse-height analyser.

B. Application of the method

The method as described above was used with only minor modifications. Firstly it was found suitable to pack up the samples in polythene vials for irradiation, whilst the standards were contained in silica ampoules. Removal of the standard from the ampoule was carried out in a similar way to that described for the phosphorus standards (see Chapter 6 E). Secondly, insofar as Filby (op.cit.) found, that under the irradiation conditions he used, the method gave a sensitivity of about 0.001 ppm of bromine per gm. of sample and as it was thought that the bromine content of the samples might be about 0.1 ppm., smaller sample weights (about 100 mgm. compared with 500 mgm.) were irradiated at a relatively lower flux (pile factor 0.2) for three days. This was done in the first two runs so that

the activity of the samples was at a reasonable level to work with. Counting of these samples had to be done by determining the beta activity as the gamma-ray analyser was incapacitated at this time. The activities of the samples were so low that no meaningful results could be obtained. In the next two runs the highest available flux in BEPO reactor was used (i.e. 1.2×10^{12} $n.cm^{-2}.sec^{-1}$). with sample weights still at about 100 mgm. The counts from the samples were then found to be reasonable (by beta-counting) but were still not very good (i.e. about 100 counts per minute) and the results show poor reproducibility (see Chapter 3). The results may have been improved had gamma-ray analysis of the samples been carried out. However, the difficulty concerning the counting was not the main disadvantage in this work.

The irradiation conditions and the weights of the samples as recommended by Filby are such that one would have to process very active samples. The procedure outlined above does not contain a preliminary step which reduces the activity of the samples down to low levels. Indeed, the bromine step involves shaking the very active sample in a separating funnel for one minute. With the present equipment at the Oxford laboratory it is not convenient to do this except by hand. This feature is considered to be a significant disadvantage of the method.

Another feature is that in each of the last two runs it took two days to process six samples and the standards. With a half life of about 36 hours; low bromine concentrations in the samples; and one day for cooling, it would be impossible to increase the number

of samples per irradiation batch and hence the processing time, without significantly decreasing the sensitivity of the method.

There is finally the aspect of this work that the expected correlation between bromine and phosphorus was not found (see Chapter 3C). This and the above features made it appear that there was little purpose in continuing the investigation. (It was not realised until a lot later that the Bushveld rocks were probably not the most suitable ones to use in this preliminary work, see Chapter 3D).

CHAPTER EIGHT

Analysis for Uranium and Thorium

A. Introduction

Delayed neutron emission from the fission products of fissionable nuclides is the basis of the analytical technique used for the determination of uranium and thorium in some rock and mineral samples, (Dyer & Leddicotte, 1960; Hamilton, 1966). This analytical method is far quicker than normal activation analysis.

The establishment of the method for the purposes of the Department of Geology and Mineralogy, Oxford,* has been done by Dr. Gale with the help of Mr. A. Mackinnon and the present writer. Except for some aspects contributed from the work for this thesis, most of this development will be described elsewhere. The facilities and some of the equipment used were provided by A.W.R.E. at Aldermaston. In the early stages of the work some of the A.W.R.E. counting equipment was used, but later Dr. Gale set up the Department's own counting equipment so that only the irradiation facilities were required of A.W.R.E.

The technique of using delayed neutron emission for the determination of uranium and thorium has been described by Amiel (1962) and will be only briefly summarised here. When certain nuclei of atomic number greater than 89 are bombarded with neutrons they undergo fission to give products, some of which decay with neutron emission - to give the so called 'delayed neutrons'. The half-lives of these neutron emitters range from a fraction of a second to just

*Dr. E.I. Hamilton, formerly of the Department, initiated the work.

under one minute. U^{233} and U^{235} fission only when bombarded with slow neutrons, whilst fission of U^{238} and Th^{232} can only be caused by fast neutrons. Thus, it is possible to discriminate between uranium and thorium fission. When uranium is fissioned with a mixed neutron flux, the fission of U^{235} is still predominant. Amiel (op.cit.) discusses the optimal irradiation, delay, and counting times. He also discusses the effect of neutron generating impurities such as lithium, oxygen and beryllium and shows that provided the sample is not rich in lithium or beryllium, that irradiation is with thermal neutrons, and that there is a delay time of about 20 seconds before counting, there is no interference from these elements. With the conditions and materials used in this work the interference was considered to be negligible.

B. Experimental procedure

The Herald reactor and pneumatic transfer system ('rabbit system') at Aldermaston were used. Irradiation conditions consisted of a flux of about 5×10^{12} neutrons. cm^{-2}. sec^{-1}. with a thermal to fast neutron flux ratio of about 20.

3 to 6 gm. of sample (as powder, rock pieces, or mineral grains) were weighed into a polythene vial (about 1" by ½" diam.) which was then loaded by a suitable handling device into a rabbit and placed in the pneumatic tube. The rabbit was sent into the reactor and immediately on arrival at its destination an automatic timer was started. After precisely one minute the rabbit was automatically returned to the laboratory. The delay time of 25 seconds, from

the cessation of irradiation to the commencement of counting the sample, then followed during which the vial was transferred from the rabbit into the counter. Counting, automatically started by the timer, was taken over an exact period of one minute, after which the timer was available for another sequence. Polythene vials containing known amounts of uranium were irradiated and counted in the same way as the samples. (These standards were also used to detect any flux changes in the reactor during the course of a run).

To discriminate between uranium and thorium in the sample, the irradiation was repeated using a cadmium shield around the sample so that only fast neutrons caused any fission. The shield was in the form of a cadmium lined rabbit so that transference of the sample to the counter was straightforward. Insofar as some U^{238} as well as Th^{232} is fissioned by fast neutrons, the pure uranium standards were irradiated with and without cadmium shields in order to determine the ratio of uranium fissioned by slow (+fast) neutrons to that by only fast neutrons. Thus, for the cadmium shielded samples it was possible to correct the count for the interference from uranium (see below) and the adjusted count was related to the count from an irradiated thorium standard.

The counting equipment used consisted of eight $B^{10}F_3$ counters (six in the A.W.R.E. counter) set vertically in a block of paraffin wax (moderator) to form a ring of radius 11.5 cm. around a vertical central hole wherein the activated sample was placed. An EHT of about 3.4 kV was supplied to the counter assembly by a power supply, and the counts from the tubes were taken via a preamplifier, amplifier

and discriminator, to a fast scaler, (two scalers were used in practise so that any fault in either of them would be immediately noticed). The background count was determined and the sample and standard counts were accordingly corrected.

On the basis that the duration of irradiation, delay, and counting times are the same for standard and sample, and that background correction is made, the count from an irradiated sample can be related to the uranium and thorium contents as follows:

$$N = U.k_1 + Th.k_2$$

$$\boxed{N} = \frac{U.k_1}{R} + \frac{Th.k_2}{r}$$

where N and $\boxed{N}$ are the number of counts from the sample after an unshielded and shielded irradiation respectively.

U is the amount, in μg, of uranium in the sample.

Th is the amount (μg) of thorium in the sample.

k_1 is the number of counts per μg of uranium (obtained from the standard).

k_2 is the number of counts per μg of thorium.

R and r are the ratios of the counts after an unshielded to counts after a shielded irradiation of the uranium and thorium standards respectively.

These simultaneous equations can be re-arranged as follows:-

$$U = \frac{N/r - \boxed{N}}{k_1 (1/r - 1/R)}$$

$$Th = \frac{\boxed{N} - N/R}{k_2 (1/r - 1/R)}$$

Typical examples of values of k_1 for the old and new counters are about 430 and 400 counts respectively. For k_2 the values are

about 1.2 and 1.1. Values of R and r were generally about 44 and 1 respectively. The value of r was not always 1 as would be expected theoretically. It can be seen that the method is far more sensitive for uranium than for thorium determination.

The relative standard deviation of the results for uranium in a sample was found to be generally 5 per cent., (see also chapter 3). The samples studied for this thesis were analysed for thorium in order that an appropriate correction could be applied to the counts for the uranium determinations, see above. The thorium results are not included in this thesis as they are not very reliable because the counts from the irradiated, cadmium-shielded samples were generally very low, (often not much above background). The results for uranium in standard rocks (such as G.1.) analysed by this method are in good agreement with the recommended values, (Gale, in preparation).

C. Preparation of standards

One of the difficulties to be overcome in using the delayed neutron emission technique for the analysis of uranium is the establishment of reliable uranium standards. Thorium standards present no problem as the count rate (about 1 per μg of thorium) is so small that milligrams of a pure thorium salt can readily be weighed out and sealed into a polythene vial. On the other hand the count rate from uranium is much higher and only small quantities of uranium can be used so that the neutron activity is not too great for the counters to deal with. Furthermore, most laboratory salts or oxides of uranium are not of natural isotopic composition, and

it is not infrequent for reagent suppliers to make no comment about this fact on the bottle labels, as was often found out during the course of this work.

If it is absolutely certain that the uranium salt is stoichiometric and of natural isotopic composition then it is not too difficult to weigh out accurately a small quantity (few mgms.), to dissolve this in an appropriate weight of solvent, and then to transfer small aliquots of known weight into polythene vials, after which the solvent is evaporated off and the vial sealed.

In this work, to be sure that the uranium was of standard isotopic composition, the oxide, U_3O_8, was carefully prepared* from pitchblende. A small weight of the oxide was dissolved in nitric acid and the standards prepared in the above manner.

D. The gamma-ray effect

When certain samples were being analysed for uranium for the purposes of this thesis, it was noticed that they had extraordinarily high count rates. A particular case was that of the felspar separated from the Skaergaard rock 5109, which gave 1,700 counts per gram, yet the whole rock which consists of 83% (by volume) of felspar gave only 290 counts per gram. Furthermore, it was noted that the cadmium shielded irradiations of these samples produced a count rate which was so low that the count 'unshielded'/count 'shielded' ratio was far, far higher than the same ratio for the uranium standard. The only explanation at that time to account for such a phenomenon

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* by Dr. C.K. Brooks and Mr. A. Mackinnon.

was that there was some sort of enhancement to the count rate of samples which had been irradiated without cadmium shields. The same samples were irradiated and counted more than once during a day to see if the increased gamma activity of the samples affected the count rate, (Table 20). The results show no general increase, and little systematic variation of count with total duration of irradiation.

In an attempt to confirm that there was no gamma-ray interference, eight vials of the rock sample EG. 5109 were made up with their weights covering a wide range, see Table 21. The count rate shows a marked increase for irradiated samples heavier than about 2 gm. It thus appeared probable that in some way gamma-rays were interfering in the neutron count. Further experiments were made using a neutron source and observing the effect on the counts when a strong gamma source was brought into the proximity of the counters. A strong source greatly increased the neutron count, though when the gamma source was in the counter with no neutron emitter present, it made comparatively little difference to the background count. Gale and Mackinnon continued this work and found that of the elements present in rock samples, aluminium was the main contributor to the increased count rate through gamma-ray interference. This interference has been referred to, by the present investigators, as the 'gamma-ray effect'.

In the case of the Oxford counter, up to 1 gm. of irradiated aluminium metal (which is about a 200 millicurie source at the commencement of the counting period) in the counter made no difference to the background count and also did not interfere with the count

from a neutron source. Irradiated higher weights produced an increase in the background count and affected a neutron count. In the A.W.R.E. counter* the presence of only 0.15 gm. of irradiated aluminium quadrupled the background and interfered synergically with a neutron count. One of the main reasons why the Oxford counter is not so readily affected by a gamma source as the A.W.R.E. counter is the presence in the former of a cylindrical lead shield placed inside the ring of counters so that it is around the vertical central hole. This shielding considerably reduces the gamma activity reaching the neutron counters; it is not present in, nor can it be introduced into, the A.W.R.E. counter.

The weights of the rock and mineral samples were then taken in accordance with the 1 gm. maximum of aluminium.

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*some modifications have since been made to this counter.

TABLE 20

'Neutron count' variation with number of irradiations

		IRRADIATION		
SAMPLE	TYPE	FIRST	SECOND	THIRD
H 10	Felspar	2,837	1,376	1,583
H 11	Felspar	2,931	1,818	1,124
H 29	Felspar	8,043	5,013	4,779
H 36	Rock	3,067	2,760	2,536
H38	Felspar	3,727	2,738	2,955

TABLE 21

Variation of count with weight of sample, EG. 5109

No.	WEIGHT	COUNT	cnt/gm.
24	0.11834	13	110
25	0.18520	22	119
26	0.59679	80	134
28	1.09683	120	110
27	2.49817	525	210
2	3.25020	955	294
34	4.490	3,073	680

CHAPTER NINE

Determination of Strontium

The method of X-ray fluorescence was used for the determination of strontium in some rocks and minerals. The principles and fuller details of the method can be found from Liebhafsky et al 1960, and from Norrish and Chappell, in press. The experimental procedure is briefly described below. A new method for determining the mass absorption coefficient was recently introduced to the Department of Geology and Mineralogy, by B.W. Chappell (Norrish and Chappell, op. cit.) and many workers of the Department have since established the method in this laboratory.

A. Experimental procedure

The rock and mineral samples were ground down so as to pass a 400 mesh screen, either by a swing-mill (rocks) or by a small agate ball-mill (minerals). One drop of the binding agent, 'Mowiol', (Hahn-Weinheimer and Ackermann, 1962), was well mixed into about 2 gm. of the rock or mineral powder. The powder was then placed in the cylinder of a hydraulic press, followed by boric acid powder to act as a backing. The powder was pressed into a tablet by a 12 lb./in^2. pressure applied for thirty seconds. This procedure gives a tablet with one smooth surface to the sample which is backed with boric acid. In certain cases it was desired to have two surfaces for measuring as the powder was in short supply and, thus, it was not convenient to make up two separate tablets for duplicate determinations. In these cases about three drops of Mowiol was mixed with the powder which was then made into a tablet

as described above but without a boric acid backing. The two sample surfaces so produced are both suitable for determining the strontium content but the tablet is less robust and must be handled with care.

A Philips PW 1540 machine was used. Power for the X-ray tube (Mo target) was produced by a stabilized generator set at 54 kV and 18 mA. A LiF (100 cut) analysing crystal was used, though on one occasion a LiF 110 cut crystal was used instead. The counting and recording equipment consisted of a NaI scintillation counter connected through an amplifier and discriminator (which was set at the commencement of each day's work) to a scaler coupled with an automatic print out. The scintillation counter was operated at the low-voltage end of the plateau (about 800 volts) so that any voltage fluctuations would have a minimal effect on the count rate. The 2θ setting of the goniometer for the Sr K1 peak was found each day and the background settings were taken at suitable places symetrically either side of the peak setting (the background was assumed to be linear).

Samples were rotated during the counting so as to minimise the effect of any inhomogeneities that might have been present. Counting of the Sr peak for each sample was taken over 100 seconds and each of the two background positions over 60 seconds. A standard tablet (in this case a tablet of G1) was counted every fourth sample in

order to observe the stability of the electronics, peak 2θ setting etc. Only on one day was there any significant drift over the few hours that the machine was in use. Redeterminations were carried out on these samples.

Nine rocks whose strontium concentrations had been determined by isotope dilution, G.1, and W.1. were used as standards. The mass absorption coefficients of both the samples and the standards were determined (see below). The peak count was corrected for background. The corrected count is related to the amount of strontium in the sample as follows:

$$C.\mu_m = k.[Sr] \qquad (1)$$

where C is the corrected count, μ_m is the mass absorption coefficient of the sample for the appropriate strontium wavelength, k is a constant. k can be determined from the standards and substituted back into the equation to obtain the strontium concentrations of the samples. The average of the k values from the standards was taken.

B. Mass absorption coefficient

In passing through a specimen the X-rays are scattered and absorbed. The attenuation in intensity of a monochromatic beam of X-rays (of intensity I_o) when passed through a specimen of thickness x is related to the initial intensity as follows:

$$I = I_o.e^{-\mu.x} \qquad (2)$$

where I is the intensity of the emergent beam and μ is the linear absorption coefficient. It is found more convenient for this work

to express this equation in the form:

$$I = I_o.e^{(-\mu/\rho).\ x} \qquad (3)$$

where ρ is the density of the specimen, and μ/ρ is known as the mass absorption coefficient. This coefficient varies from rock to rock as it is dependent upon the chemical constitution. It is, thus, necessary to measure the coefficient, and there are a variety of ways of doing this (Norrish and Chappell, op.cit.). The one that has been used for this work is the direct determination of the absorption.

The technique is to press into a hole ($\frac{1}{2}$" diam.) of a Perspex die (1" by $1\frac{3}{4}$"), of known weight, a small amount of the sample powder, (100 to 500 mgms.), with the aid of a specially made press. The pressure (~ 700 lb/in^2) imposed by the press bonds the powder together into the form of a flat disc held in the hole of the Perspex holder. The holder with the sample is weighed so that the weight of the sample disc can be found and hence the mass per unit area determined.

The disc is used to determine the mass absorption coefficient as follows:

a 1% $SrCO_3$ tablet (diluted with boric acid) is placed in the machine and acts as a source for the appropriate wavelength. The peak 2θ, and discriminator settings are found and set. The intensity of the unattenuated beam is found by counting over a 100 second period. The Perspex die with the sample disc is then placed in a special

holder so that the sample is positioned between the analysing crystal and the scintillation counter such that the X-ray beam passes only through the sample disc. The diameter of the sample disc is the same as that of the X-ray beam. The relative intensity of the beam, now attenuated, is determined by counting over a 100 second period. (To ensure that the counts from either the attenuated or unattenuated beam were not so high that a large correction had to be made for the dead time of the scintillation counter, the X-ray tube was operated at a lower voltage and current (34 kV and 6mA). Counts were corrected for dead time of the scintillation counter (3 micro seconds) but the corrections were not large.

Once the relative intensities of the two beams have been measured and as the mass per unit area of the disc is known ($M/A = \rho x$) it is a simple matter to substitute these values into the equation (3) above and hence calculate the mass absorption coefficient at that wavelength of the sample. The results for the mass absorption coefficient agree fairly closely with calculated values (e.g. Skaergaard rock 5086: 13.7 by calculation; 14.6 by measurement) and results also agree quite well with those obtained by G. Glasby of the Department who used this method (e.g. sample BLM 15: 8.20 Glasby; 8.30 Henderson).

APPENDIX A.

The term 'mesostasis'

In gravitationally fractionated igneous rocks, the minerals may have three different types of genetic status, (Wager, Brown & Wadsworth 1960):

1. The cumulus phases.
2. The adcumulus extensions and/or heteradcumulus growths.
3. The final crystallized pore material from the trapped liquid.

Wager et al (1960, p.77) in their discussion on types of igneous cumulates said: "Any part of the intercumulus liquid which is eventually trapped by further accumulation of crystals is here distinquished as the trapped liquid. When this has crystallized it will be described as the pore material. The trapped liquid will necessarily have had the overall composition of the contemporary magma and thus the composition of the pore material must also be that of the contemporary magma". If this is the case then genetically (in this respect) the pore material is equivalent to the groundmass of a basalt with phenocrysts. If this genetic relationship holds then certain geochemical data (such as partition coefficients) may well be comparable for the two rock types and it is clear that such a relationship may well be of use in elucidating fractionation trends of some basalts. These points are discussed in the thesis and it is because the theory outlined covers a broader field than just that of the pore material of layered rocks that a more embracing term is required to cover pore material, groundmass etc.. Such a

requirement seems to be fulfilled by the term 'mesostasis'.

As can be seen from the quotation above, pore material is strictly defined but if, after trapping of the magma, reaction (however slight) occurs between it and the solid phases the resultant liquid will no longer have the strict composition of the contemporary magma. Reaction of this kind is not thought to be common (Wager, Brown and Wadsworth, ibid.) c.f. Jackson 1961) but such a contingency should be allowed for in the theoretical discussion of Chapter Two. If reaction occurs then the composition of the 'trapped liquid' (sensu lato) is the resultant composition after all reaction has finished. Thus the term pore material is not strictly applicable in this case whilst perhaps the term mesostasis is.

A further point is that secondary alteration or replacement (by percolating hydrous solutions) of the pore material may have occurred. The significance of the resultant composition may not be large within the context of this thesis but for the present this is beside the point. Here again the term pore material is inapplicable but 'mesostasis' seems suitable.

In view of this discussion it is proposed to use the term mesostasis instead of pore material, groundmass, etc. for the purposes of this thesis. The introduction of this word is in no way meant to replace terms such as pore material for specific purposes.

The term mesostasis has received different definitions in the literature. Five nomenclature reference works are quoted below:

"Gumbel. Same as basis, base, Zwischenklemmungemasse (Ger.). The interstitial material in hypocrystalline or cryptocrystalline rocks".

'A Descriptive Petrography of the Igneous Rocks'

by A. Johannsen. Volume 1. (2nd.edit.) 1939.

"A term applied to the ultimate interstitial material of a rock which consolidated in the final stage of solidification as a glass (e.g. in intersertal basalts), a single mineral (e.g. analcite in teschenite), or a eutectic (e.g. micropegmatite in granodolerite). (Holmes).

'Dictionary of Geological Terms'

by C.M. Rice, 1953.

"A term used by Gumbel for basis occurring in igneous rocks in such a small amount that only the interstices between early formed crystals are filled. At present the term includes all the final products of solidification in this manner, e.g. analcite in teshenite, micropegmatite in gabbro".

'Geological Nomenclature'

ed. by A.A.G. Schieferdecker, 1959.

Royal Geological & Mining Society of the Netherlands.

"1. The interstitial material between the larger mineral grains in a microcrystalline rock or a microcrystalline groundmass. Synonymous with Base or Basis. 2. Synonymous with Matrix or Groundmass as applied to igneous rocks".

'Glossary of Geology and Related Sciences'

The American Geological Institute. 2nd. edit. 1959.

"The last formed interstitial material of an igneous rock; glassy, cryptocrystalline, or microcrystalline".

'Dictionary of Geology'

by J. Challinor, 1961.

These definitions do not, amongst themselves, entirely agree. Challinor's is the simplest and is the one essentially used in this thesis except in the fact that the mesostasis can be of coarse grain. However, the above discussion should clarify the use of this term in this work.

APPENDIX B.

Sample Descriptions.

Skaergaard intrusion, East Greenland.

Specimens are housed in the L.R. Wager Collection, University Museum, Oxford. Each specimen number is prefixed by the letters EG.

4312. Average rock. Hortonolite ferrogabbro. UZb; 1860 metres. Apatite present as cumulus phase. Pukugaqryggen.

4389. Average lower olivine gabbro; LZb; 295 metres. Felspar, olivine and pyroxene as cumulus minerals. Possibly an orthocumulate. Uttentals Plateau W.

4532. Gabbro, slightly leucocratic; LZb; 240 metres? Plagioclase, olivine, pyroxene rock, some zoning of the plagioclase. Uttentals Plateau.

5052. Average rock. MZ; 825 metres. Plagioclase, magnetite, augite, cumulate. Kraemer's Island.

5085. Leucocratic rock. LZb; 275 metres. Inclusion like mass in LZb considered to be unlaminated Layered Series. Plagioclase zoned (An 63-50 approx.) Micropegmatite present. Uttentals Plateau.

5086. Average olivine gabbro. LZb; 280 metres. Orthocumulate or mesocumulate. Uttentals Plateau E.

5088. Melanocratic. LZb; 280 metres. 6" pyroxene rich band in gabbro. Uttentals Plateau.

5089. Leucocratic. LZb; 280 metres. Inclusion like mass probably unlaminated Layered Series. Micropegmatite present. Uttentals Plateau.

5090. Leucocratic. LZb; 280 metres. Associated with 5089 (q.v.). Plagioclase much zoned, (An61 - 48 approx.); micropegmatite present. Uttentals Plateau.

5092. Melanocratic. LZb; 280 metres. Olivine rich band; plagioclase zoned; augite grain clusters. Little mesostasis present. Uttentals Plateau.

5093. Leucocratic. LZb; 280 metres. Felspar rich, well laminated band just above 5092. Olivine absent? Mesocumulate. Uttentals Plateau.

5094. Leucocratic. LZb; 280 metres. Inclusion like mass 10' across. Plagioclase considerably zoned. Uttentals Plateau.

5105. Leucocratic. LZa; 150 metres. Felspathic band in gabbro; plagioclase zoned; micropegmatite present. Uttentals Plateau.

5107. Average. LZa; 110 metres. Olivine and plagioclase as cumulus minerals; augite intercumulus. Plagioclase zoned (An 66 - 55 approx.) Uttentals Plateau.

5108. Melanocratic. LZa; 110 metres. 6" melanocratic band in 5107. Olivine cumulus; the remainder intercumulus. Uttentals Plateau.

5109. Leucocratic. LZa; 110 metres. 24" band in 5107 horizon. Plagioclase cumulus and zoned (An 66 - 55 approx.); the remainder intercumulus. Uttentals Plateau.

5112. Average. LZb; 580 metres. Mesocumulate; some zoning of the plagioclase from An 57 but nowhere near so extensive as 5086, 5107, (q.v.) Isolated exposures along Sound.

5181. Average. Hortonolite ferrogabbro. UZa; 1800 metres. Adcumulate of olivine, plagioclase (An 40), ilmenite, magnetite, clinopyroxene.

Bushveld intrusion, South Africa.

Specimens are housed in the Department of Geology and Mineralogy. Each specimen number is prefixed with the letters SA.

660. Gabbro. 1,400 feet above CZ base. Poikilitic ortho- and clinopyroxene. Jagdlust Chrome mine.

675. Pyroxenite. 3,200 feet above base of BZ. Close to Jagdlust mine.

678. Harzburgite. 2,320 feet above base of BZ. Northern foot Lulu mountains.

681. Altered olivine rich rock. 1,800 feet above base of BZ. Close to Pyramids.

682. Pyroxenite. 980 feet above base of BZ. 200 yards from Basal Pyramids and beside Oliphant River.

685. Basal bronzitite. 100 feet above base of BZ. E. bank of Oliphants River.

722. Banded pyroxene-felspar cumulate of the Merensky Reef. (MaZa). Lulu Mountains.

730. Spotted anorthosite. 90 feet above Merensky Reef. MaZa. Northern foot Lulu mountains.

731. Gabbro. 1,100 feet above Merensky Reef. MaZa. Northern foot Lulu mountains.

732. Gabbro. 2,300 feet above Merensky Reef. MaZa. Lulu mountains.

733. Banded spotted gabbro. 3,000 feet above Merensky Reef. MaZa. Lulu mountains.

739. Gabbro. 4,300 feet above Merensky Reef. MaZb. Lulu mountains section.

740. Gabbro. as 739.

940. Anorthosite. 5,300 feet above base of UZc. Blood River section.

1087. Marginal 'chill'. 4½ miles East of the Klip River on road between Roossenekal and Lydenburg on western slopes of the Steenkampsberg ridge.

1095. Gabbro. 4,100 feet above Merensky Reef. MaZb. Exposures due west of Lydenburg.

1096. Gabbro close to 1095. [illegible]. 4,180 feet above Merensky Reef.

1102. Gabbro. About 5,500 feet above Merensky Reef. MaZb.

1110. Gabbro. 7,200 feet above Merensky Reef. MaZb. Below main magnetite band. Exposures due west of Lydenburg.

1112. Gabbro. 1,400 feet above base of Upper Zone. UZb.

1123. Gabbro. Just above Main Magnetite band. UZb.

1131. Diorite. 4,360 feet above base of UZ. UZc. Steelport River.

1131*. as 1131 but with thin acid vein.

1138. Ferrodiorite. 5,000 feet from base of UZ. UZc. Steelport River.

1139. Ferrodiorite. 5,200 feet above base of UZ. UZc. 250 yards north of Steelport River, farm Duikerkrans.

1147. Diorite. About 15 feet below upper contact with felsite. Hillside above Steelport River.

1149. Granodiorite. UZc. Close to upper contact. 2 miles north of Tauteshoogte, farm Duikerkrans.

Rhum intrusion, Inner Hebrides.

Specimens are housed in the Department of Geology and Mineralogy. Numbers are of the accession series.

5781. Fine grained olivine gabbro. Allt Mor na h'Uamha.

5875. Allivalite, unit 3. Scarp, east of Loch Coire nan Grund.

17120. Peridotite, unit 7. On hillside SW of Loch Coire nan Grund.

17121. As 17120. 160 feet along strike of layering from 17120.

17122. As 17120. 100 feet along strike from 17121. 260 feet from 17120.

17123. Allivalite, unit 7. On hillside SW of Loch Coire nan Grund.

17124. As 17123. Approximately 275 feet along strike of layering from 17123.

17125. Peridotite, unit 8. N.E. Slopes of Hallival.

17126. As 17125. 20 feet along strike of layering from 17125.

17127. Allivalite, unit 9. Northern flanks of Hallival.

17129. Allivalite, unit 9. North-eastern flanks of Hallival.

APPENDIX C.

Sample preparation.

Rock samples: These were prepared for analysis in the following manner: Bushveld samples: quite large rock pieces (about 300 to 800 gm.) were taken and all weathered surfaces removed on a diamond-chip impregnated wheel saw. Any contamination from the saw was removed by rubbing the rock surfaces with a coarse carborundum powder - water mixture on a rotating wheel. After this treatment the rock pieces were well washed with tap water and then distilled water and were allowed to dry. From this point clean rubber gloves were worn when handling the rock pieces. Each rock specimen was broken into smaller pieces, about one cubic inch each, by a hydraulic crusher and these were then reduced to a maximum particle size of less than a pea by a steel percussion mortar. The crushings were then reduced to less than 200 mesh by means of an agate swing mill.

Rhum specimens: these were treated in the same way as the Bushveld specimens except that the initial specimen was cut into at least three pieces so that rock slides could be made from planes in the rock that were mutually at right angles. These slides were used for the determination of the modes.

Mineral separation: The rock was crushed to pass through a 80 mesh cloth and the -80 +120 (in some cases the -120 +160) mesh fraction was collected by sieving, washed with distilled water and then acetone, and

dried. Removal of the iron ore was done by means of a hand magnet while a rough separation of magnetic and non-magnetic minerals was made on a 'Carpco' magnetic separator. Further separation was made by using a Frants isodynamic magnetic separator and it was possible to make quite clean separations from each other of the early Bushveld Ca-rich and Ca-poor pyroxenes; and of the Rhum olivines and pyroxenes. The felspar fractions were generally found to be pure enough after separation by the isodynamic separator for analysis without further treatment. The olivine and pyroxene fractions were purified by repeated treatment on the isodynamic separator and then followed by two (or three) purifications using the heavy liquid bromoform to separate out any felspar containing small iron ore inclusions. Final purification by hand picking was carried out on quantities sufficient for analysis.

Some separated Bushveld pyroxenes were kindly provided by Dr. F.B. Atkins and some of the Skaergaard minerals by Professor Wager.

APPENDIX D.

Determination of specific gravities.

The method consisted of weighing a small piece of the rock in air and then in water and from the results calculating the specific gravity in the normal manner. The details are as follows:

A small piece (50 to 100 gms.) of the rock was taken and any weathered or irregular surfaces were cut off. The piece was suspended by means of a piece of fine copper wire from the hook of a four place balance, and was then weighed in air. A small beaker containing distilled water was placed on a small, specially constructed wooden platform over the balance pan. The rock was submerged in the water and it was found suitable to remove any air bubbles from the smooth surfaces by slight shaking or by means of a pipette. The rock was then suspended and weighed in water. The wire on its own was weighed in air and in water (submerged by the correct amount) and the rock weights accordingly corrected, (though the weight of the wire, at about 0.04 gm., was effectively negligible).

The water was not held at constant temperature, though it is unlikely that it changed significantly. For the purposes of this work relative specific gravities of the rocks are all that is required and the method described is suitable for this. The absolute results are, however, probably not very accurate. It was found that determined specific gravities agreed closely with those obtained from calculation using the mode, (e.g. NG.5109:2.81 and 2.84 respectively).

APPENDIX E.

The Tracerlab Beta Counter.

Description: The Tracerlab Omni/Guard is an automatic low background beta counter. The counter itself consists of an inner detector which is an ultra-thin window gas flow counter, and a surrounding detector which is a gas flow, dome shaped counter sensitive to cosmic rays (see Figure 5). This surrounding detector is the 'guard' counter. Both counters are arranged in such a manner that radiation from the sample will only trigger the inner counter; while cosmic rays must pass through and trigger the guard counter before reaching the inner counter. The output of the two detectors is fed into an anti-coincidence circuit which rejects all pulses from the inner counter that are accompanied by simultaneous pulses from the guard counter, thus eliminating a great deal of the background due to cosmic radiation. The two counters are surrounded by extensive lead shielding. The imposed dead time of the sample counter is 100 μ sec.

Included with the machine is an automatic sample changer which can accommodate fifty samples. A specially designed sample elevator mechanism lifts the sample cup into the shield of the counter, placing it in a fixed position of about 0.75 mm. from the window of the sample counter. An automatic switching mechanism starts the counting which can be set to a range of preset times or counts. The counts and time are recorded on a scaler and at the end of the preset time or count period an automatic print out system records this information together with the sample number. The sample changer then brings the next sample into the position for counting.

Because of the close proximity of the planchets to the window of the counter, the counter is highly sensitive to small changes in distance of the sample from the counter, (see Figure 4). Thus, although the planchet is brought to a precise position by the sample changer, the active material in each planchet must be carefully positioned, e.g. any creep of an active precipitate up the sides of the planchet would greatly enhance the count of that precipitate.

Counting experiment: it was decided to investigate the effect on the background count of any empty planchet when other planchets containing active material were present in the automatic sample changer. The background of the empty planchet was less than 1 cpm. and this was not noticeably changed when a beta source (^{32}P, 1.7 MeV, normally with a count of about 4,800 cpm. when in the counter) was placed in the automatic sample changer in one of the positions immediately adjacent to the planchet being counted, (counts were taken over twenty minutes). However, when a ^{62}Co source (beta 2.9 MeV; gamma emitter of count about 4,500 when in counter), was in an adjacent position the background of the empty planchet rose to 19 cpm. When the active source was two planchet positions away in the automatic changer, the count of the empty planchet was 2 cpm. and when three positions away the background was the same as normal.

It is, therefore, essential, to have any strong source, such as discussed above, at least one planchet position away from any sample being counted, (N.B. this refers both to the left-right axis and the front-back axis of the automatic changer assembly).

FIGURE 4

Relative count rate vs. sample distance.

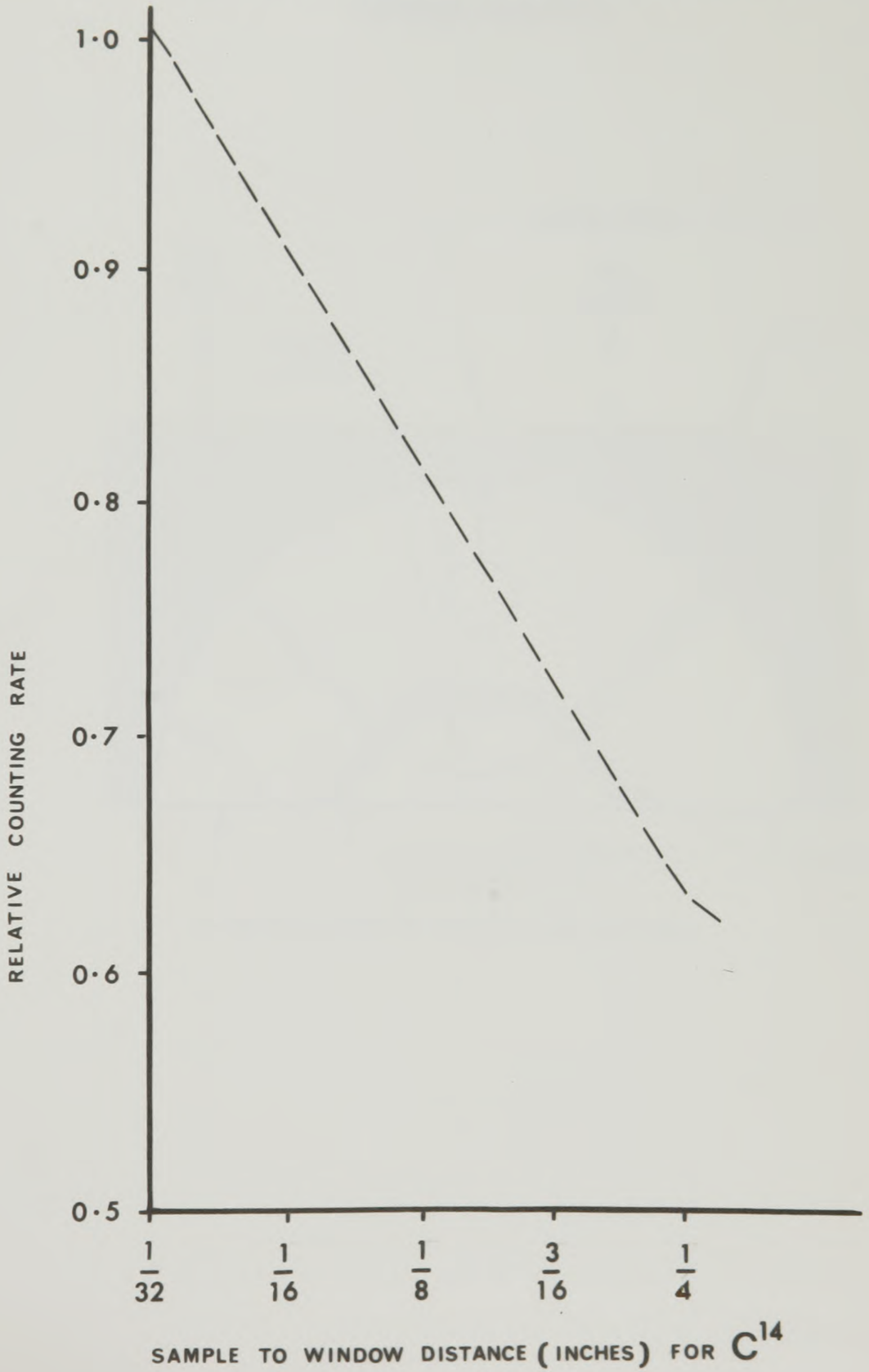
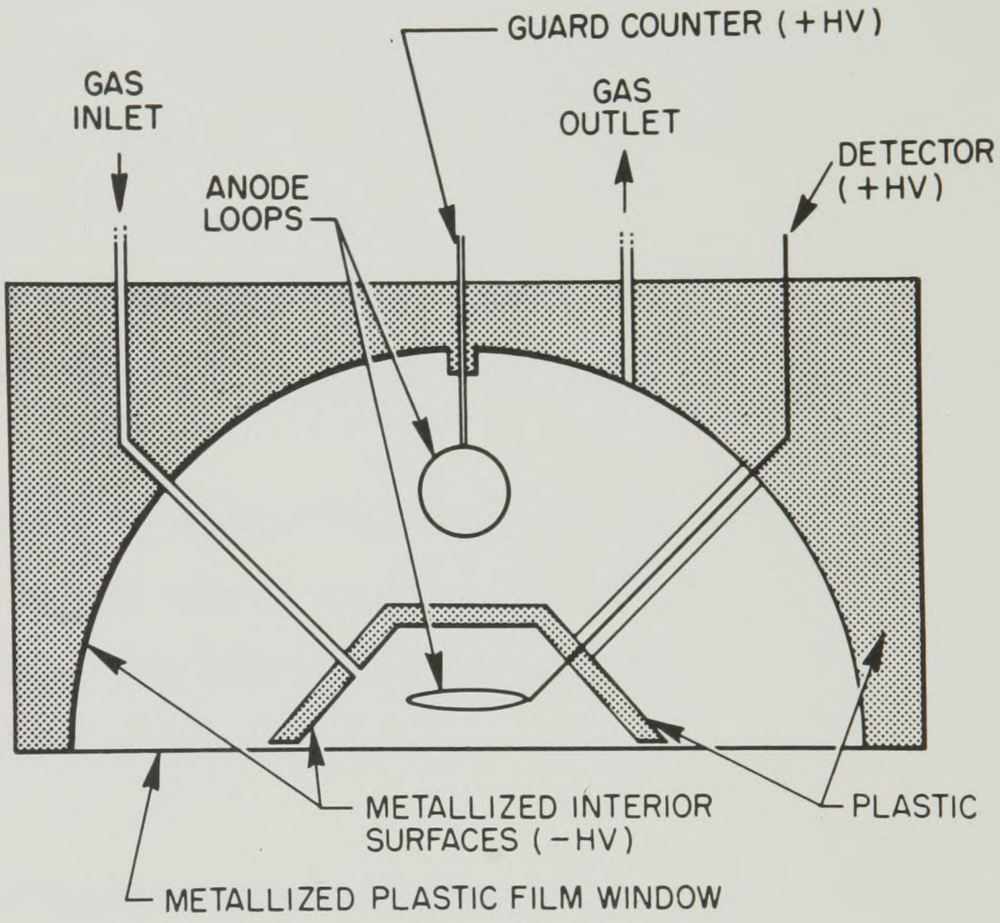


FIGURE 5.

Counter Assembly.



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